Presentation of a laboratory for the synthesis and study of special oxides and melt-grown crystalline materials

About special devices such as a mirror furnace, tube furnace, thermogravimetric analyzer and SQUID magnetometer, special constructions and concepts such as pressing dies and the preparation of rods, facilities such as gas supply, examples of materials preparation, and related topics

Report

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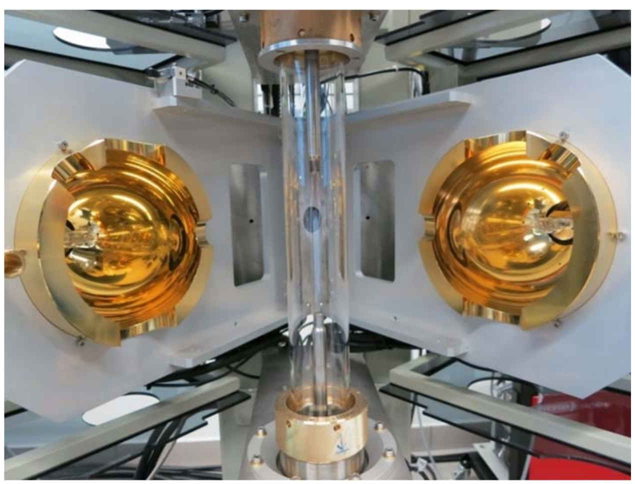

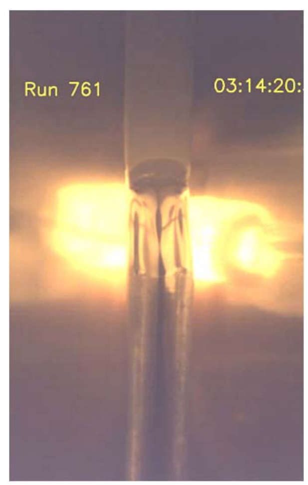

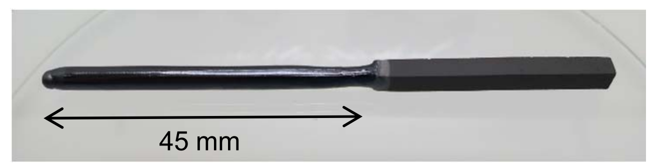

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Content overview 1 / 5

Content overview 2 / 5

- **Part 2 - 4:** Sample holders made of yttria stabilized zirconia
- **Part 2 - 5:** Zirconia-related oxides as technical ceramics: Overview and examples
- **Part 2 - 6:** An improved suspension and centering for the feed rod
- **Part 2 - 7:** Freely swinging sample holders for the feed rod
- **Part 2 - 8:** Advantages and potential disadvantages of the design of the rods and sample holders

- **Part 3:** Presentation of associated devices and technical facilities like turbo pumping station, gas supply, oxygen analyzer for argon, suction for exhaust gas lines, compressed air, and cooling water unit
- **Part 4:** Examples of melt-grown oxides prepared by the Cyberstar mirror furnace

Content overview 3 / 5

- **Part 5:** Preparation of rectangular feed and seed rods by special pressing dies made of ceramics or glass, a laboratory press, and sintering
- **Part 6:** Presentation of various FRIATEC components made of high temperature ceramics
- **Part 7:** Presentation of the Linn High Therm chamber furnace
- **Part 8:** Presentation of the GERO tube furnace
- **Part 9:** Preparation of oxide powder mixtures: Starting materials, analytical balance, and special mortars and pestles
- **Part 10:** Presentation of a Zeiss optical microscope and examples of pictures
- **Part 11:** Presentation of miscellaneous equipment

Content overview 4 / 5

- **Part 12:** Thermogravimetry
  - **Part 12 - 1:** What is thermogravimetry and sketch of its technical implementation
  - **Part 12 - 2:** Presentation of the NETZSCH thermogravimetric analyzer
  - **Part 12 - 3:** Examples of thermogravimetric measurements and results
- **Part 13:** Measuring magnetic properties of samples by a SQUID magnetometer
  - **Part 13 - 1:** Sketch of principle
  - **Part 13 - 2:** SQUID magnetometer Quantum Design MPMS3 at the Department of Materials of the ETH Zurich
  - **Part 13 - 3:** Mounting a sample within a straw
  - **Part 13 - 4:** Another SQUID magnetometers

Content overview 5 / 5

- **Appendix 1:** Presentation of the GERO mirror furnace which was used from 1999 – 2007 at the Institute of Physics of the University of Augsburg (Germany)

  Examples and pictures of melt-grown crystalline oxides

- **Appendix 2:** Presentation of the IBM mirror furnace which was used from 1989 – 1992 at the IBM Zurich Research Laboratory (Switzerland)

  Examples and pictures of melt-grown crystalline oxides

- **Appendix 3:** Another and very special floating zone melting furnaces

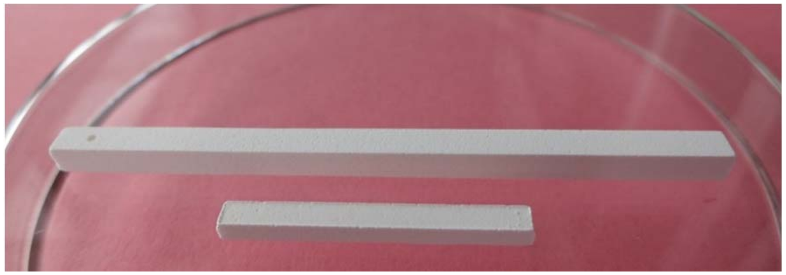
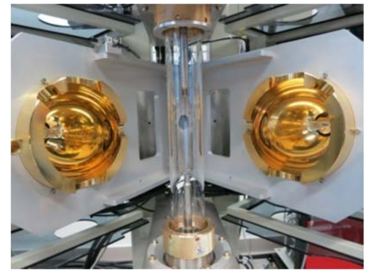
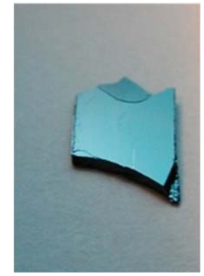
- **Appendix 4:** Pictures of melt-grown oxides from a NEC mirror furnace brochure

- **Appendix 5:** Examples of crystal structures: Layered perovskite-related oxides

- **Appendix 6:** Some aspects about (raw) materials on earth

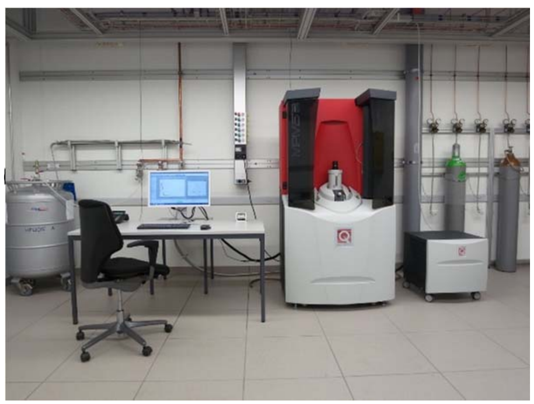
- **Appendix 7:** The Periodic Table of the Chemical Elements

Preface 1 / 3

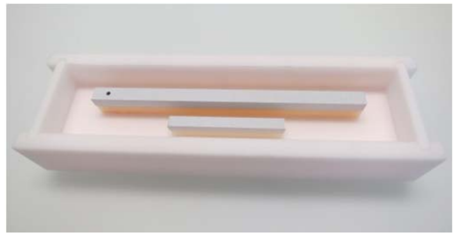





This slide set presents a laboratory for the synthesis and study of special oxides and melt-grown crystalline materials, and associated topics. The laboratory was established from 2011 to 2013 at the Department of Materials of the ETH Zurich (Switzerland) and extended in 2015 by a so-called SQUID magnetometer.

Scientific motivation and research topic of this lab: Synthesis of complex oxides and study of their physical and structural properties, especially searching for new superconductors and materials which are simultaneously ferroelectric and magnetic



Preface 2 / 3



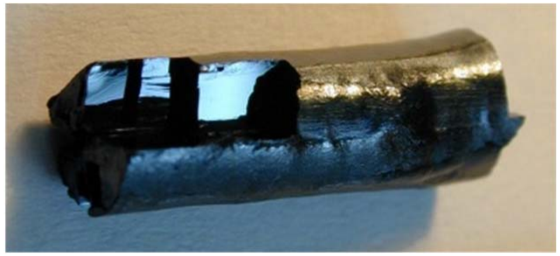
This slide set presents mainly devices, equipment, facilities, components, technical and engineering issues, examples of materials preparation, and pictures of various melt-grown crystalline oxides. Further related presentations and papers:

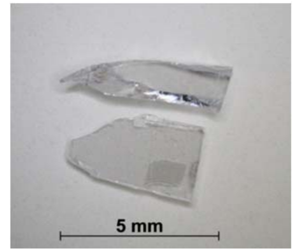
Presentation about oxides of the type $A_nB_nO_{3n+2}$ (file size about 11 MB pdf):
www.theory.mat.ethz.ch/lab/presentation2.pdf

Article about special oxides (3 MB pdf), published in Progress in Solid State Chemistry 36 (2008) 253 - 387: www.theory.mat.ethz.ch/lab/article2008.pdf

Presentation with videos about the melt-grown synthesis and structural and physical properties of $A_nB_nO_{3n+2}$ type materials and other perovskite-related layered oxides (Power Point Show, file type ppsx, file size 80 MB):
www.theory.mat.ethz.ch/lab/presentation3.ppsx

Preface 3 / 3

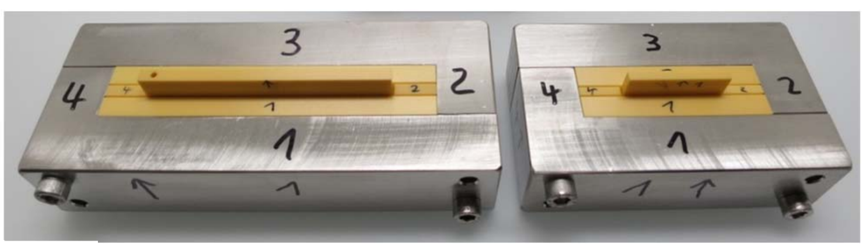




The materials which are presented in this slide set can be divided into two groups:

Special oxides such as $La_6Ti_4Fe_2O_{20}$ or $Sr_5Nb_5O_{17}$ which represent the research topic

Special construction materials such as the glass-ceramic composite material Macor, technical ceramics like alumina or yttria stabilized zirconia, and platinum-rhodium alloys. These construction materials were used to produce special components such as sample holders and pressing dies



Setting up and operating a lab for the synthesis and study of special oxides

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Part 1 / 7

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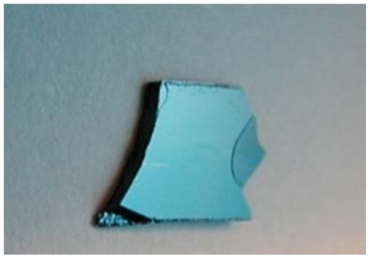
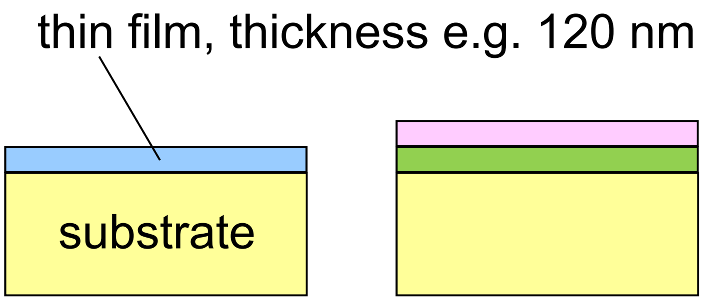
Introduction

Manifestations of solid matter, oxides, and an example of a materials preparation process

Examples of manifestations of solid matter such as oxides




Crystals



Thin films and heterostructures

Powder

Polycrystalline parts made of powder which was pressed or molded, sintered, and, if necessary, machined

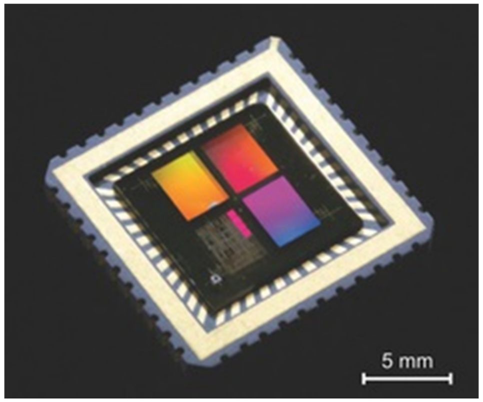
The comprehensive world of oxides 1 / 2

Oxides display a huge variety of chemical compositions, crystal structures, and physical and chemical properties. They can be prepared and processed in various ways. Oxides are extensively studied in fundamental and applied research and are used in various areas of technology. Here just a few examples of physical properties and chemical compositions:

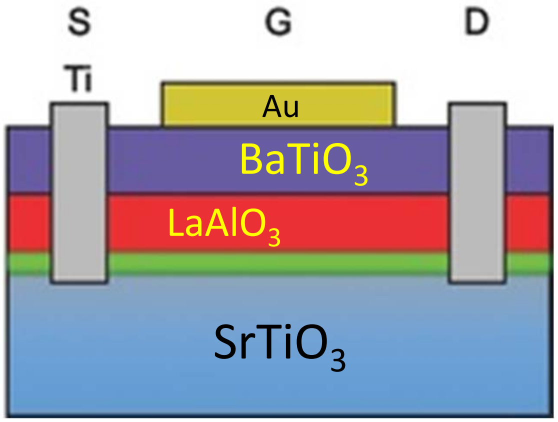
- Insulators such as ZnO , $MgAl_2O_4$ and $SrLaGaO_4$
- Ferroelectrics such as $BaTiO_3$ and $Sr_2Nb_2O_7$
- Multiferroics such as $BiFeO_3$ and $YMnO_3$ - both (anti)ferroelectric and (anti)ferromagnetic
- Ferromagnets or ferrimagnets such as CrO_2 , Fe_2O_3 , and $BaFe_{12}O_{19}$
- Metallic conductors such as RuO_2 , $LaNiO_3$ and $BaCa_{0.6}La_{0.4}Nb_2O_7$
- High-T_c superconductors such as $YBa_2Cu_3O_{7-\delta}$ ($T_c \approx 90$ K for $\delta \approx 0.07$) and $Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8.3}$ ($T_c = 138$ K)
- Technical ceramics such as alumina (Al_2O_3) and yttria stabilized zirconia ($Zr_{1-y}Y_yO_{2-0.5y}$)
- Formation of a conducting interface between two insulators like $SrTiO_3$ and $LaAlO_3$

The comprehensive world of oxides 2 / 2

Oxide electronics / Integrated circuits from functional oxides [1,2]



This chip comprises more than 700 000 field effect transistors (FETs) which are made of oxides



Sketch of the design of one field effect transistor (FET). The green region is a conducting interface

Thanks to J. Mannhart from the Max Planck Institute for Solid State Research in Stuttgart (Germany) for his talk about oxide electronics on 4 September 2014 at the ETH Zurich !

[1] R. Jany et al., Advanced Materials Interfaces 1 (2014) 1300031

[2] J. Mannhart, Jahrbuch 2014 / 2015, Oxidelektronik, Max-Planck-Institut für Festkörperforschung, Stuttgart

An example of a materials preparation process

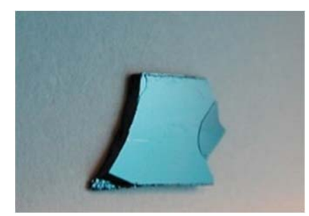
$Ca_2BaNb_3O_{10}$?

$EuTaO_3$?

It starts always with an idea about a (new or apriori hypothetical) oxide material which is specified by a certain

- chemical composition $A_wB_yO_x$
  such as $La_6Ti_4Fe_2O_{20}$ or $Sr_5Nb_5O_{17}$
- crystal structure

A = alkaline earth, alkali and / or rare earth element(s)
B = transition metal element(s)
O = oxygen



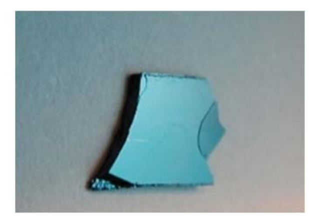
An example of a materials preparation process

$YMn_{0.95}O_{2.93}$?

$PrGd_3Ti_4O_{14}$?

Try to synthesize the devised oxide material in a single phase and polycrystalline or crystalline form via a chemical solid state reaction at elevated temperatures or a solidification from the melt, and study its structural and physical properties

The following pages describe an example of a materials preparation process which consists of 10 steps, namely the synthesis of crystalline oxides via a solidification from the melt



An example of a materials preparation process – Step 1 / 10

Devise a chemical composition such as

$La_6Ti_4Fe_2O_{20}$ – Example A

This represents an example of a material which can be prepared under air

$Sr_5Nb_5O_{17}$ – Example B

This represents an example of so-called reduced materials which require a preparation under a (nearly) oxygen-free atmosphere such as argon.

This implies a much more elaborate synthesis procedure when compared with example A.

In many cases the structural and physical properties of reduced materials depend strongly on their oxygen content. Therefore it is desirable that the synthesis procedure allows a precise control of the oxygen content.

In many cases the oxygen content of reduced materials such as $Sr_5Nb_5O_{17}$ can be determined by thermogravimetric analysis (see part 12). For the sake of process control it is desirable to measure the oxygen content of the powder, polycrystalline sintered rods, and crystalline material obtained in step 7, 9 and 10, respectively.

An example of a materials preparation process – Step 2 / 10

Select appropriate starting materials from commercially available powders such as oxides La_2O_3 , TiO_2 , Fe_2O_3 or Nb_2O_5 , carbonates like $SrCO_3$, or metals such as Nb

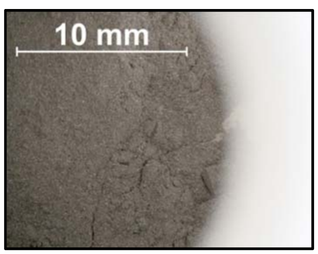
Examples of commercially available starting materials:

Fe_2O_3 powder

WO_3 powder

$SrCO_3$ powder

Nd_2O_3 powder



Nb powder

Storage of starting materials in an alumina crucible in a desiccator

Mn_2O_3 powder in this example

An example of a materials preparation process – Step 3 / 10

Calculate appropriate amounts (mass or weight) of the selected starting materials so that they correspond to the desired chemical composition

$La_6Ti_4Fe_2O_{20}$ – Example A

La_2O_3	3,757 g
TiO_2	1,225 g
Fe_2O_3	0,612 g

We have assumed the following reaction:

$3\ La_2O_3 + 4\ TiO_2 + Fe_2O_3 \rightarrow La_6Ti_4Fe_2O_{20}$

The valences of the La, Ti, and Fe ions in the starting materials and $La_6Ti_4Fe_2O_{20}$ remain unchanged: La^{3+}, Ti^{4+} and Fe^{3+}

In general: Oxygen is considered as O^{2-} and the chemical formulas of oxides correspond to charge neutrality

$Sr_5Nb_5O_{17} = SrNbO_{3.4}$ – Example B

$SrCO_3$	3,691 g
Nb_2O_5	3,176 g
Nb	0,102 g

The Nb powder represents a so-called reduced component which is not used in the following steps 4 – 6 but only in step 7

We have assumed the following reaction:

$SrCO_3 + 0.48\ Nb_2O_5 + 0.04\ Nb \rightarrow SrNbO_{3.4} + CO_2\uparrow$

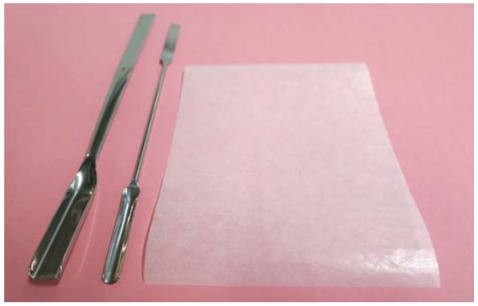
($SrCO_3 + 0.48\ Nb_2O_5$): under air (step 6)

($0.48\ Nb_2O_5 + 0.04\ Nb$): under argon (step 9 and 10)

The Sr valence 2+ remains unchanged but the Nb valences change from 5+ (Nb_2O_5) and 0 (Nb) into a mixed valence state 4+ / 5+ with an average value 4.8+ in $SrNbO_{3.4}$

An example of a materials preparation process – Step 4 and 5 / 10

4 Weighing the calculated amounts of the starting materials (powder) by an analytical balance



Spatula and weighing paper

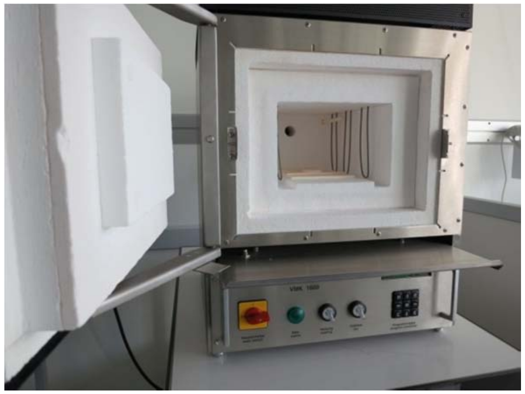
5 Grinding or mixing the weighed amounts of the starting materials by a mortar and pestle

The analytical balance and mortars and pestles are presented in more detail in part 9

An example of a materials preparation process – Step 6 / 10

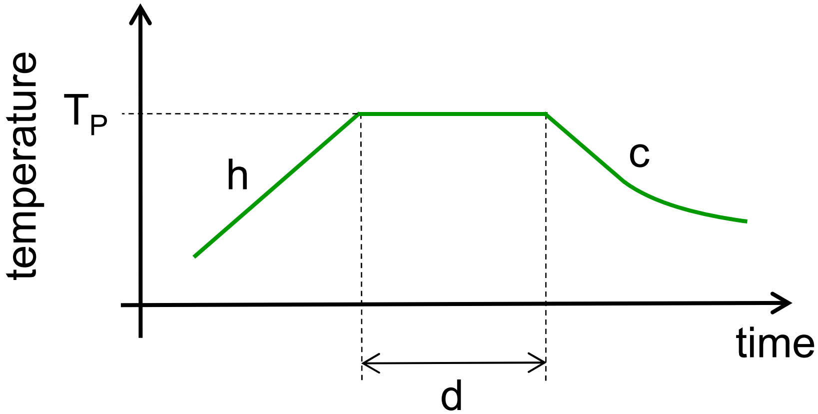
Pre-reaction of the grinded powder mixture at an appropriate high temperature T_P in air

The grinded powder mixture is filled into an alumina crucible which is put into a laboratory chamber furnace which is presented in more detail in part 7



During the pre-reaction several processes may happen:

- Formation of a new oxide / new oxides by chemical solid state reactions which are triggered by elevated temperatures
- Loss of CO_2 if carbonates such as $SrCO_3$ are part of the powder mixture
- Sintering
- Change of grain sizes



h heating-up
d dwell time, for example 4 h
c cooling down

An appropriate pre-reaction temperature T_P depends on the chemical composition, typical values are $600 \leq T_P \leq 1300$ °C

An example of a materials preparation process – Step 7 / 10

Example A

The devised material such as $La_6Ti_4Fe_2O_{20}$ implies in the following steps a preparation under air

↓

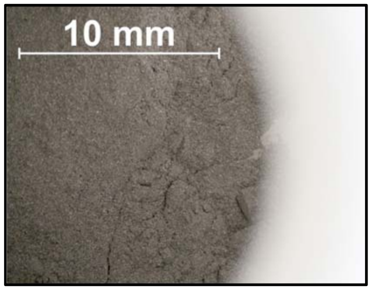
Grinding or mixing the pre-reacted powder mixture by a mortar and pestle

Example B

The devised material such as $Sr_5Nb_5O_{17}$ implies in the following steps a preparation under an (nearly) oxygen-free atmosphere such as argon

↓

Weighing of another starting material such as Nb powder and adding it to the pre-reacted powder mixture



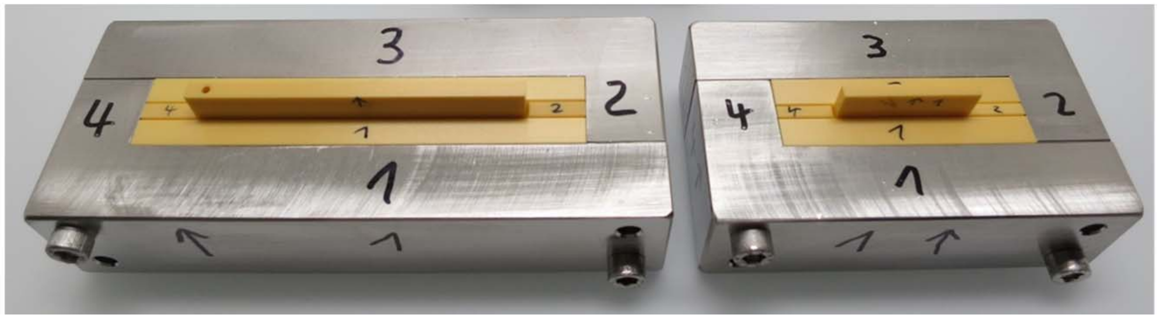
Nb powder

↓

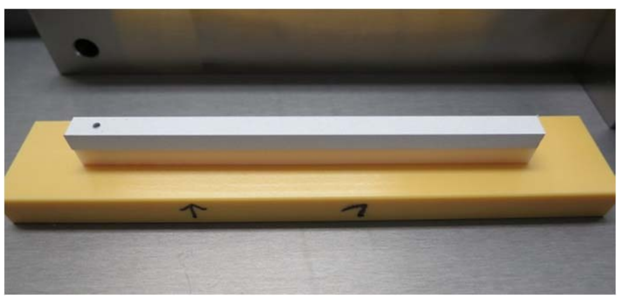
Grinding or mixing the pre-reacted and modified powder mixture by a mortar and pestle. The oxygen content *w* of the resulting composition $Sr_5Nb_5O_w$ can be checked or measured by thermogravimetry (see part 12)

An example of a materials preparation process – Step 8 / 10

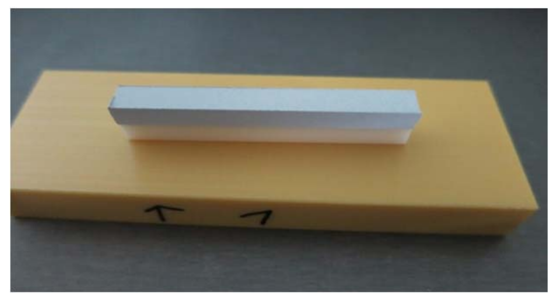
By means of special pressing dies and a press the powder from step 7 is pressed into the form of two rectangular rods, a long rod and a short rod. Such rods are required for step 10.



Special pressing dies



Powder pressed into the form of a 85 mm long rod



Powder pressed into the form of a 35 mm long rod

The pressing dies and the preparation of the rods are presented in more detail in part 5

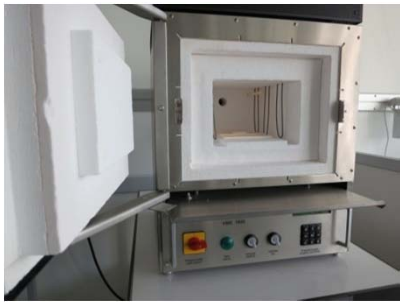
An example of a materials preparation process – Step 8 and 9 / 10

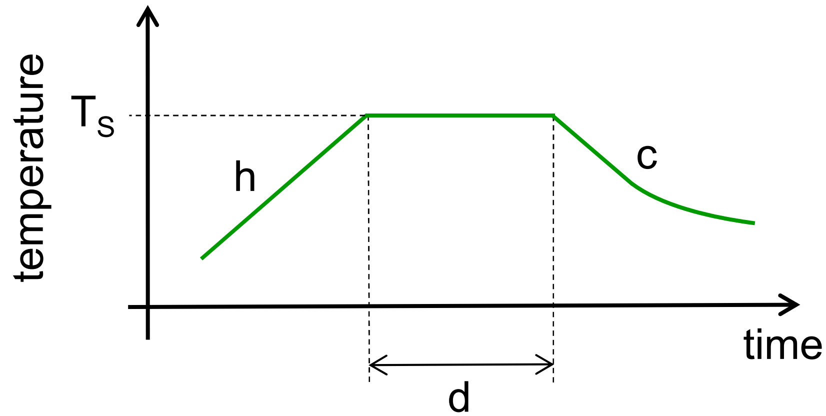
The pressed rods shown on the previous page are mechanically not stable. If they are touched in a not very careful way, then they become damaged or destroyed. However, for step 10 they are needed in a mechanically stable form so that they can be handled in a normal way. Therefore they are heated to an appropriate high temperature under a suitable atmosphere which results in sintering and further chemical solid state reactions

An example of a materials preparation process – Step 9 / 10

Example A – Sintering of the rods in a chamber furnace under air, e.g. for $La_6Ti_4Fe_2O_{20}$

Example B – Sintering of the rods in a tube furnace under argon, e.g. for $Sr_5Nb_5O_{17}$

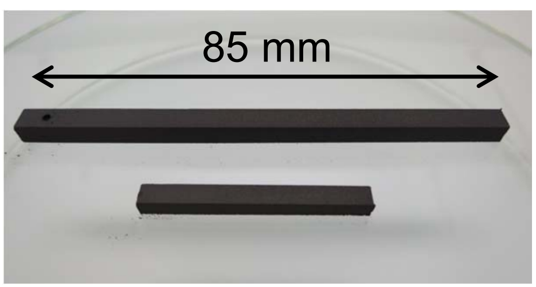

Chamber furnace




Tube furnace

h heating-up
d dwell time, for example 4 h
c cooling down

An appropriate sintering temperature T_S depends on the chemical composition, typical values are $700 \leq T_P \leq 1400$ °C

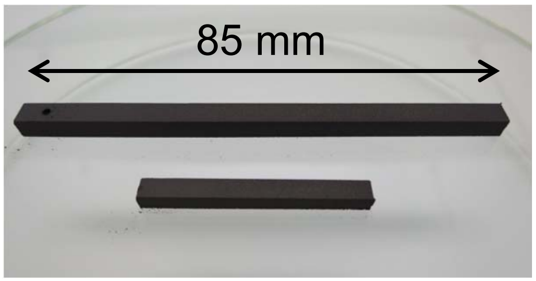


Example of polycrystalline sintered rods which are mechanically stable. In case of example B with a composition such as $Sr_5Nb_5O_w$ the oxygen content *w* of a rod can be checked or measured by thermogravimetry (see part 12). For that a small piece can be cut from a rod

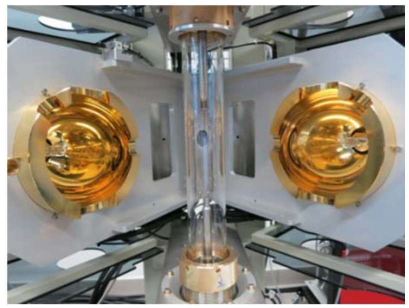
The chamber and tube furnace are presented in more detail in part 7 and 8

An example of a materials preparation process – Step 10 / 10

Try to synthesize the desired oxide material in a crystalline form via a solidification from the melt by processing the polycrystalline sintered rods from step 9 in a mirror furnace under an appropriate atmosphere such as air or argon. How that works is described in part 1, 2 and 4 and also in the appendix 1 and 2.



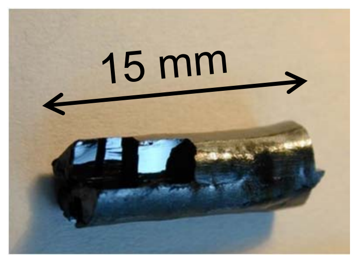
Example of polycrystalline sintered rods


Mirror furnace

Example of a whole as-grown sample which did crystallize from the melt

Example of crystalline pieces obtained by crushing the as-grown sample

$La_6Ti_4Fe_2O_{20}$



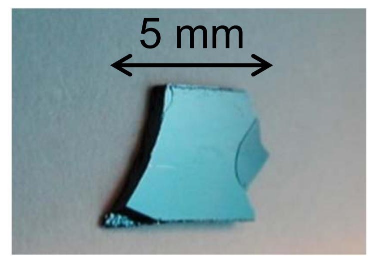


Plate-like crystal

$Sr_5Nb_5O_{17}$

$Sr_5Nb_5O_x$ is an example of a crystalline material whose oxygen content x can be checked or measured by thermogravimetry (see part 12)

Progress in Solid State Chemistry 29 (2001) 1 and 36 (2008) 253 • Melt-grown samples prepared at the University of Augsburg • Photo of $La_6Ti_4Fe_2O_{20}$ taken at the ETH Zurich

An example of a materials preparation process

The samples shown on the previous page can be used to study their structural and physical properties by techniques such as powder x-ray diffraction, single crystal x-ray diffraction, magnetic measurements, resistivity measurements, and / or optical spectroscopy.

The examples $Sr_5Nb_5O_{17}$ and $La_6Ti_4Fe_2O_{20}$ are mentioned because they are related to the main research topics of the new laboratory. Both examples belong to oxides of the type $A_nB_nO_{3n+2} = ABO_x$ which might have a potential to create new superconductors and / or novel materials which are simultaneously ferroelectric and ferromagnetic.

Progress in Solid State Chemistry 29 (2001) 1 and 36 (2008) 253 • Physical Review B 70 (2004) 245123
Journal of Physics: Condensed Matter 25 (2013) 076003

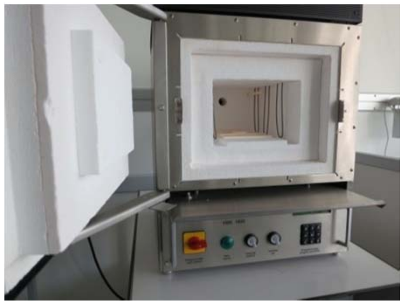
Note: In many cases the devised or desired material cannot be synthesized (in a single phase form) by the described preparation process because

- it requires other synthesis conditions which are possibly not yet known
- it does not exist in bulk form but maybe it can be prepared in form of thin films
- it does not exist / it cannot be synthesized at all

Brief furnace overview

Overview about various types of furnaces and their purpose of use

They are presented in more detail in part 2, 4, 7, 8, and in the appendix

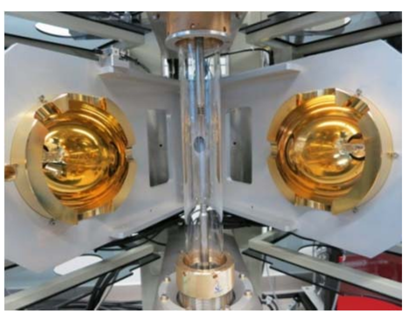


Non-gas-tight laboratory chamber furnace

For removing moisture of starting materials, pre-reactions, calcination, sintering or synthesis of polycrystalline materials in air

Gas-tight tube furnace

For preparation or sintering of polycrystalline materials under various non-air atmospheres such as oxygen, argon, argon plus hydrogen, or vacuum



Gas-tight mirror furnace / floating zone melting furnace

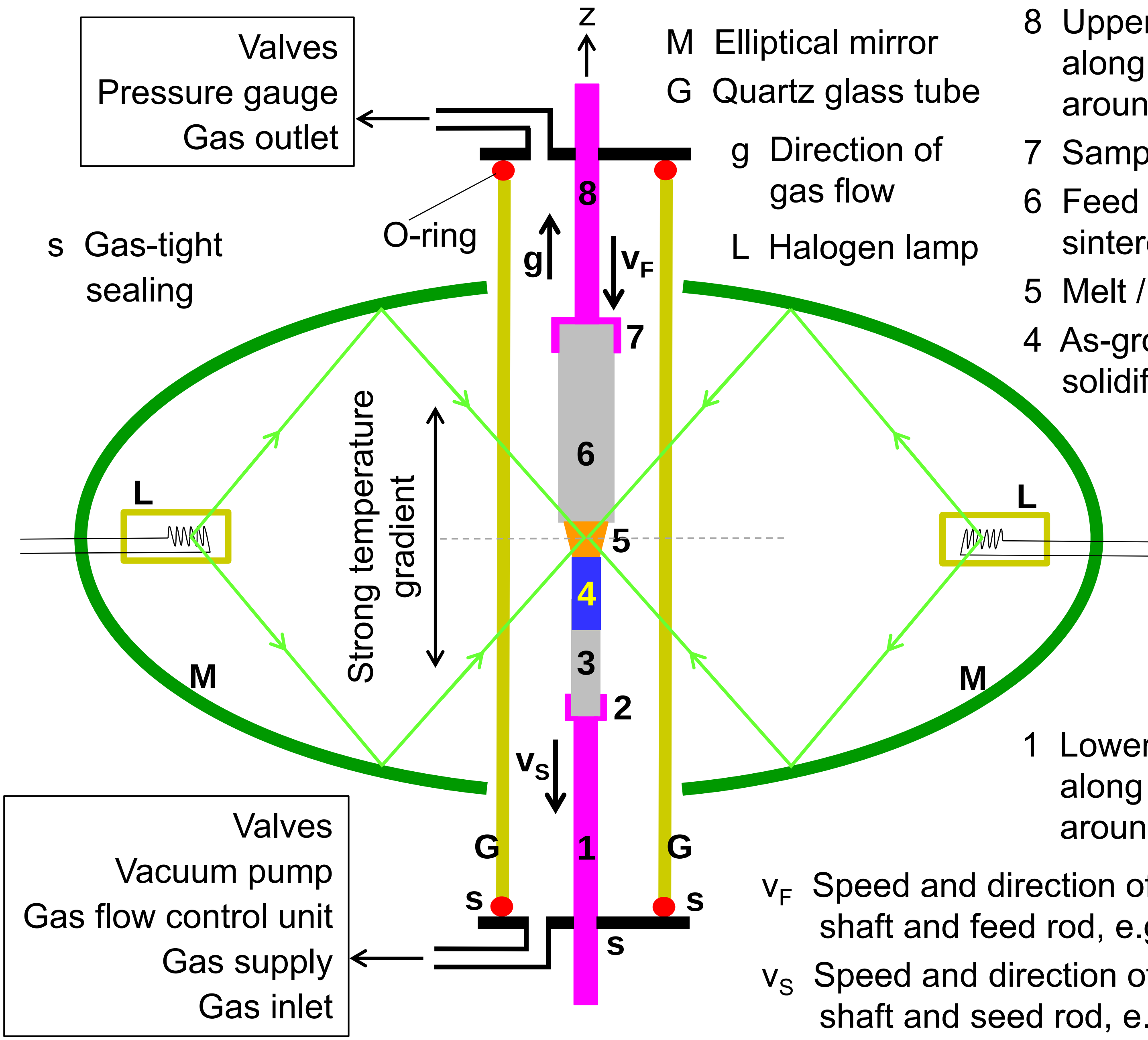
For synthesis of crystalline oxides via a solidification from the melt under various atmospheres like oxygen, air, argon, argon plus hydrogen or vacuum

Part 1

Synthesis of melt-grown oxides by a mirror furnace:

Sketch of principle and sketch of a run of the so-called floating zone melting process

Synthesis of melt-grown oxides by a mirror furnace - Sketch of principle



M Elliptical mirror
G Quartz glass tube
g Direction of gas flow
L Halogen lamp

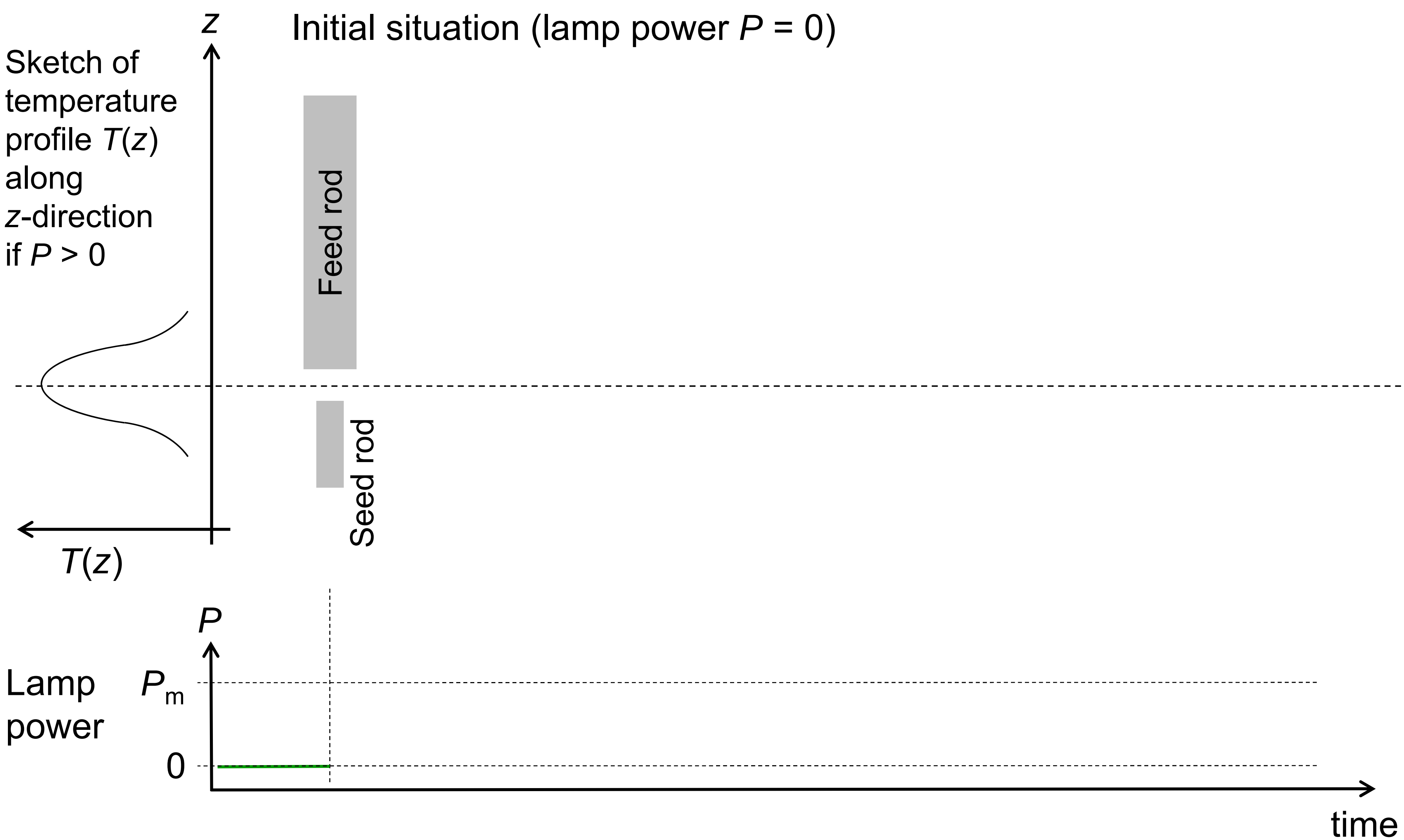
8 Upper shaft - Can be moved along z-direction and rotated around z-axis
7 Sample holder for feed rod
6 Feed rod (polycrystalline sintered rod)
5 Melt / Molten zone
4 As-grown crystalline material solidified from the melt

3 Seed rod (polycrystalline sintered rod or crystal)
2 Sample holder for seed rod

1 Lower shaft - Can be moved along z-direction and rotated around z-axis

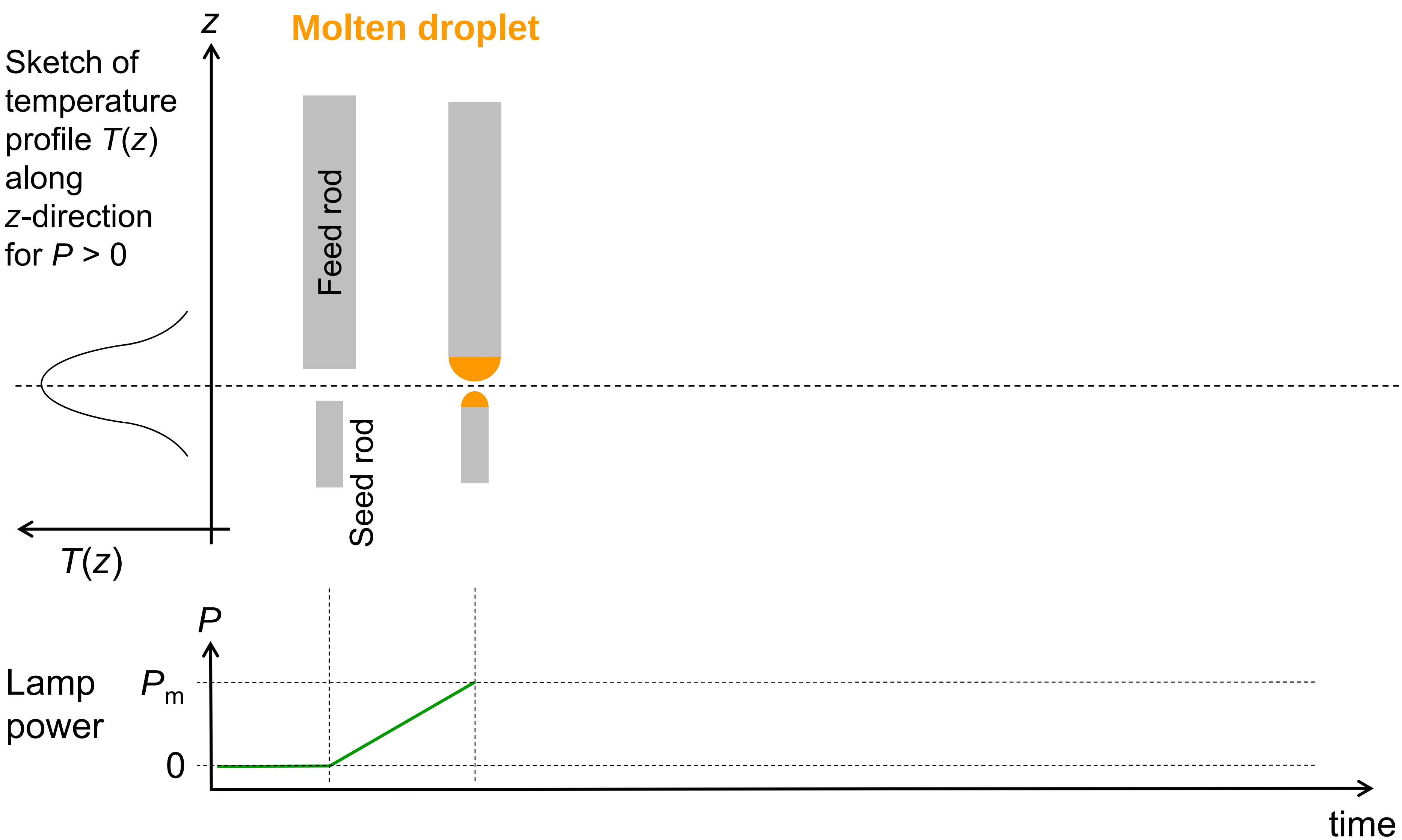
v_F Speed and direction of motion of upper shaft and feed rod, e.g. 15 mm / h
v_S Speed and direction of motion of lower shaft and seed rod, e.g. 10 mm / h

Synthesis of melt-grown oxides by a mirror furnace - Sketch 0 / 9 of a run



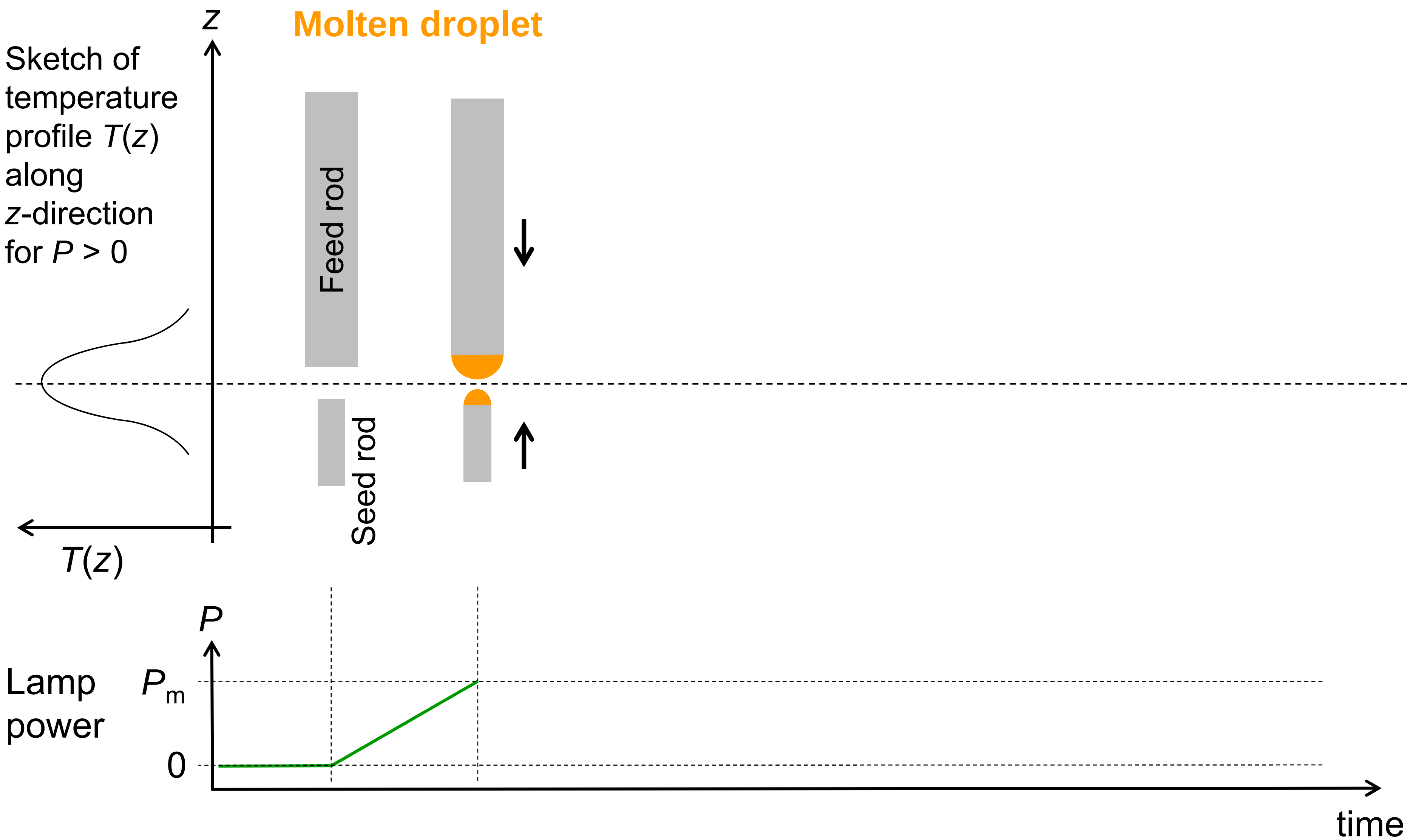
P_m = Lamp power which is required to melt the material

Synthesis of melt-grown oxides by a mirror furnace - Sketch 1/9 of a run



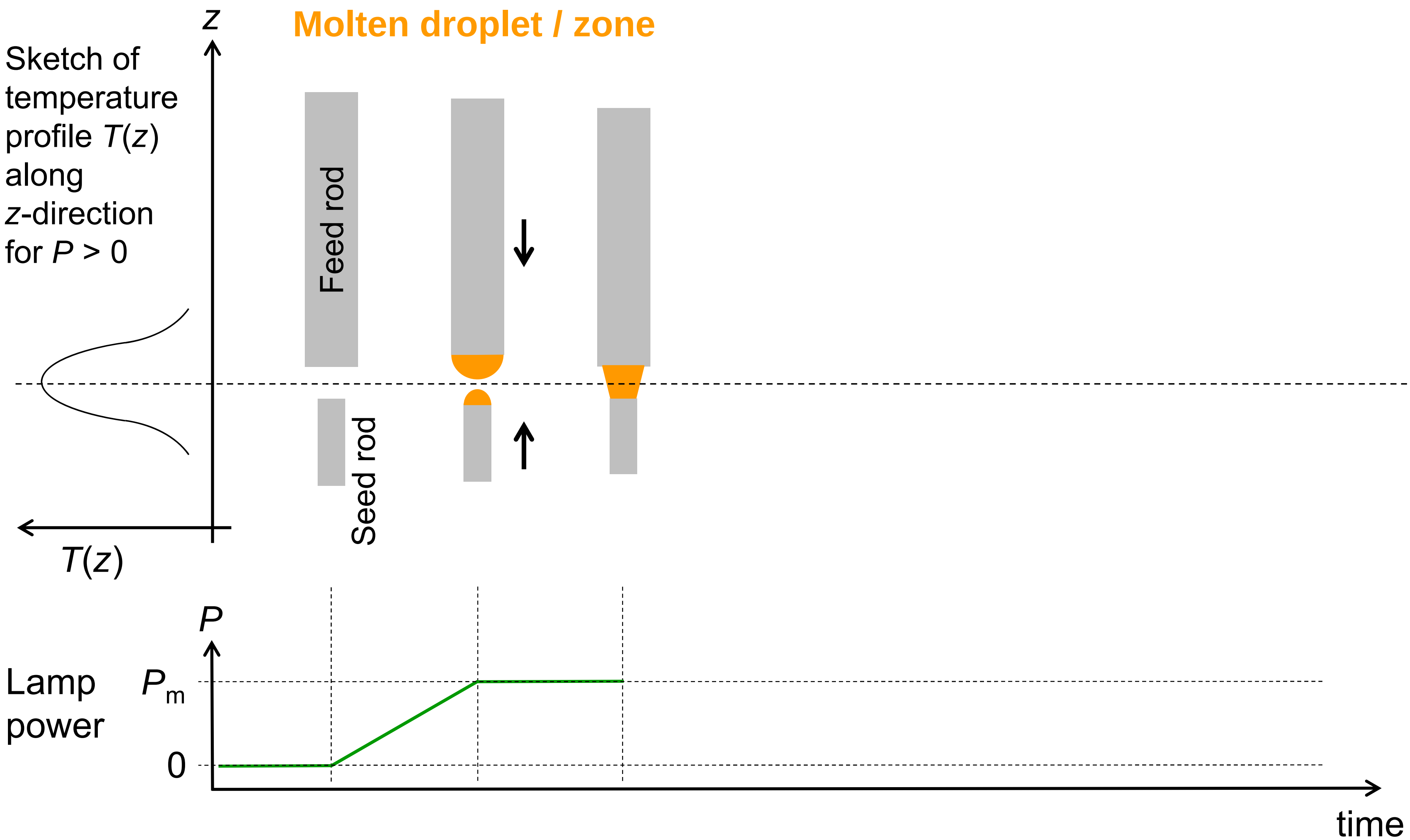
P_m = Lamp power which is required to melt the material

Synthesis of melt-grown oxides by a mirror furnace - Sketch 2 / 9 of a run



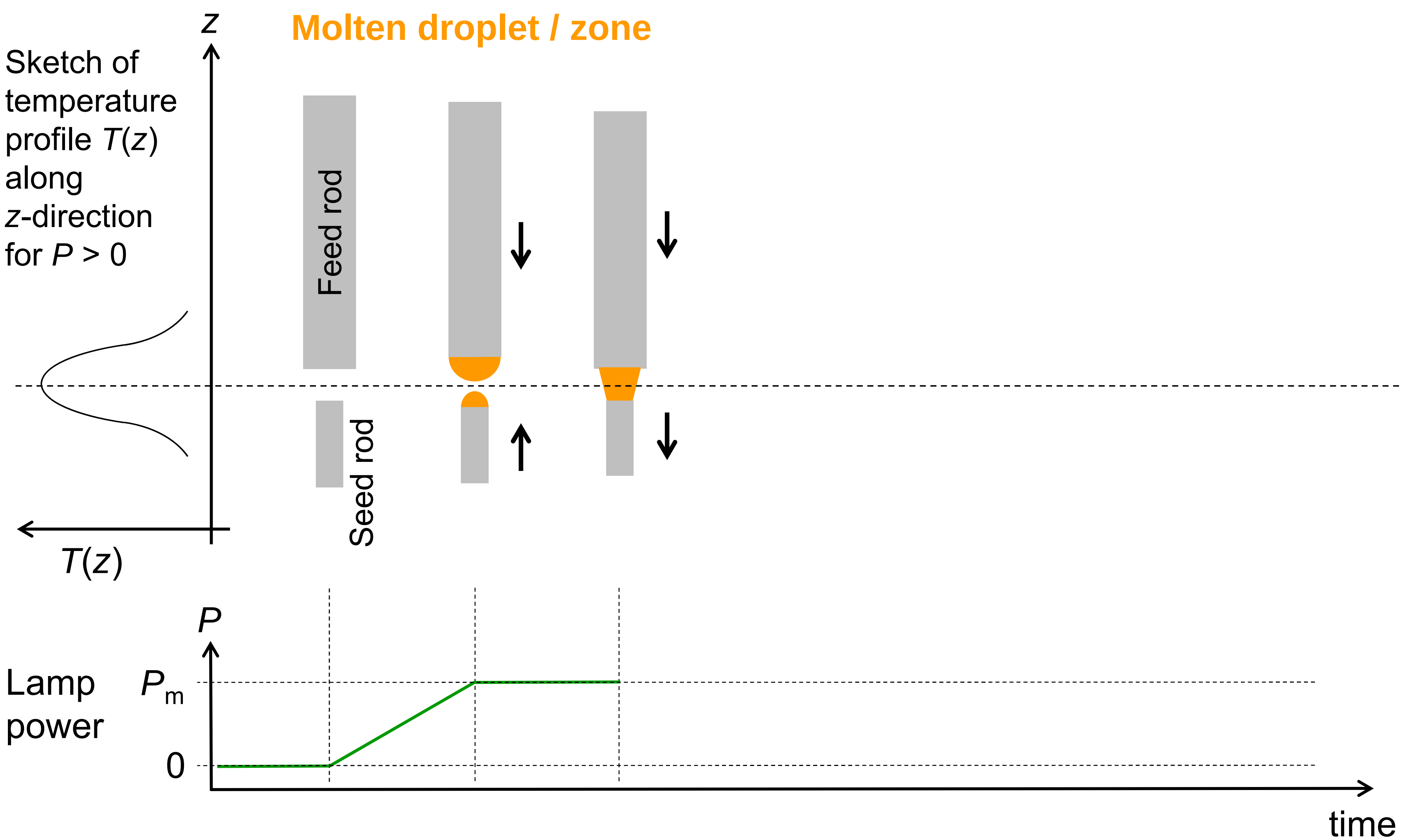
P_m = Lamp power which is required to melt the material

Synthesis of melt-grown oxides by a mirror furnace - Sketch 3 / 9 of a run



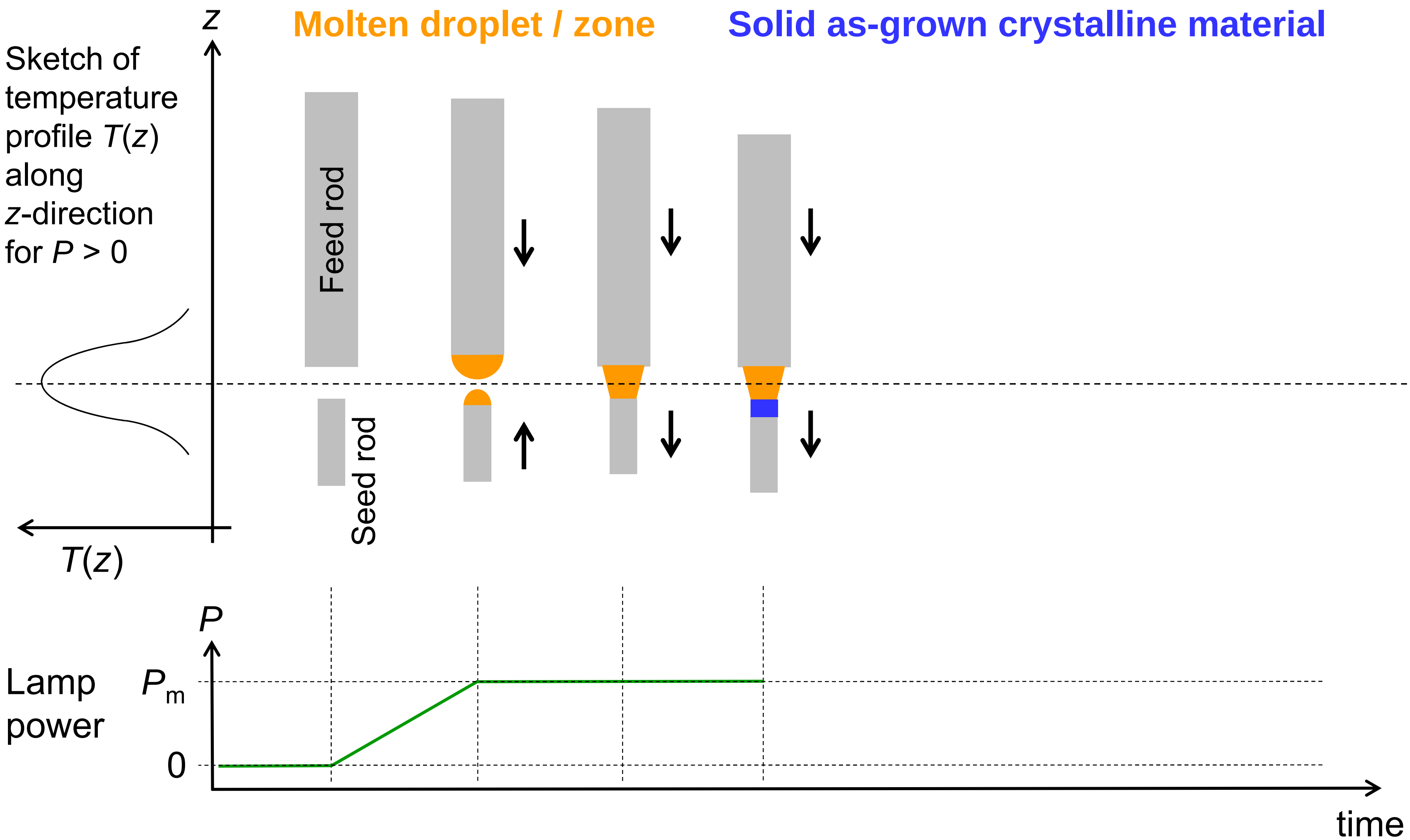
P_m = Lamp power which is required to melt the material

Synthesis of melt-grown oxides by a mirror furnace - Sketch 4 / 9 of a run



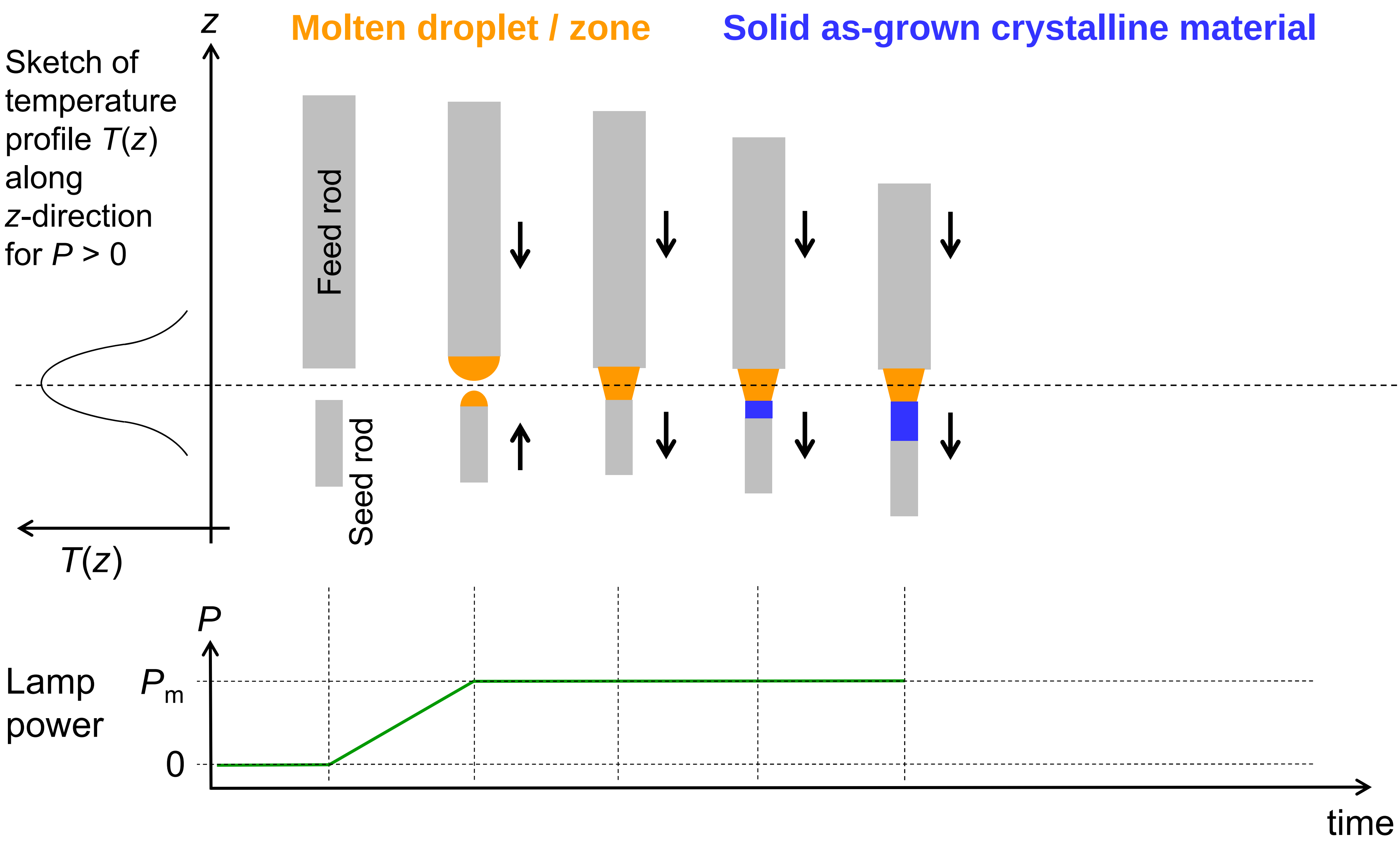
P_m = Lamp power which is required to melt the material

Synthesis of melt-grown oxides by a mirror furnace - Sketch 5 / 9 of a run



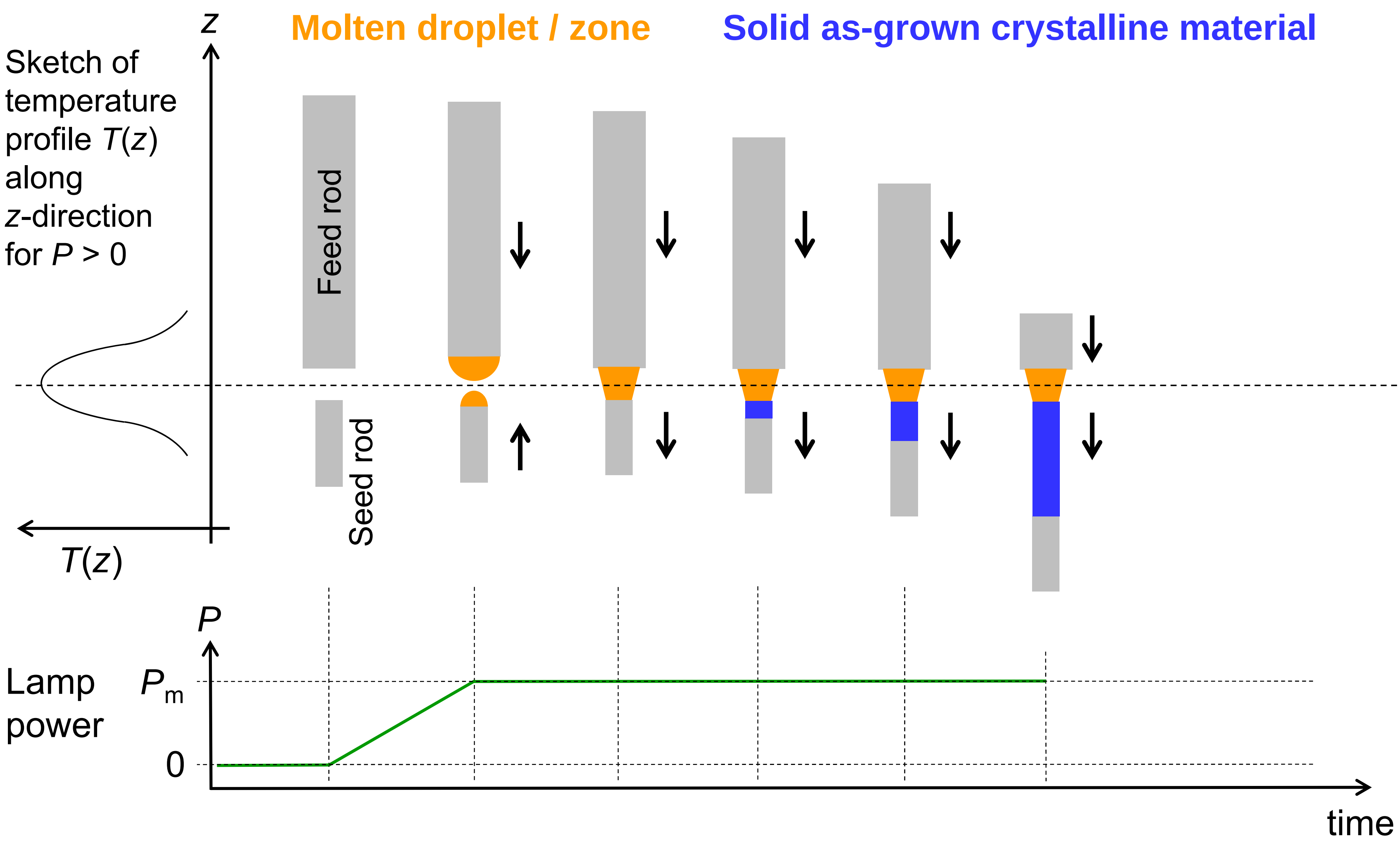
P_m = Lamp power which is required to melt the material

Synthesis of melt-grown oxides by a mirror furnace - Sketch 6 / 9 of a run



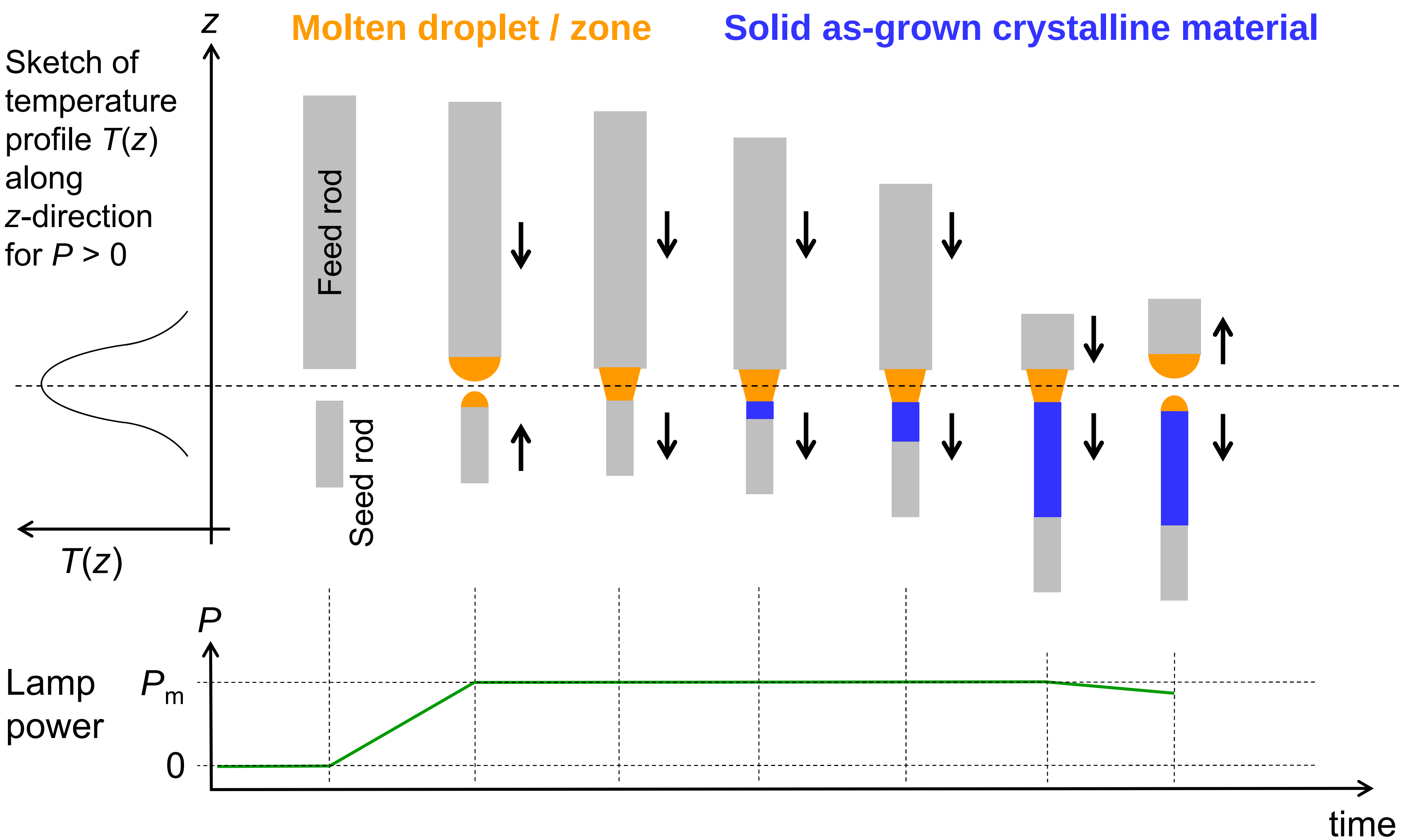
P_m = Lamp power which is required to melt the material

Synthesis of melt-grown oxides by a mirror furnace - Sketch 7 / 9 of a run



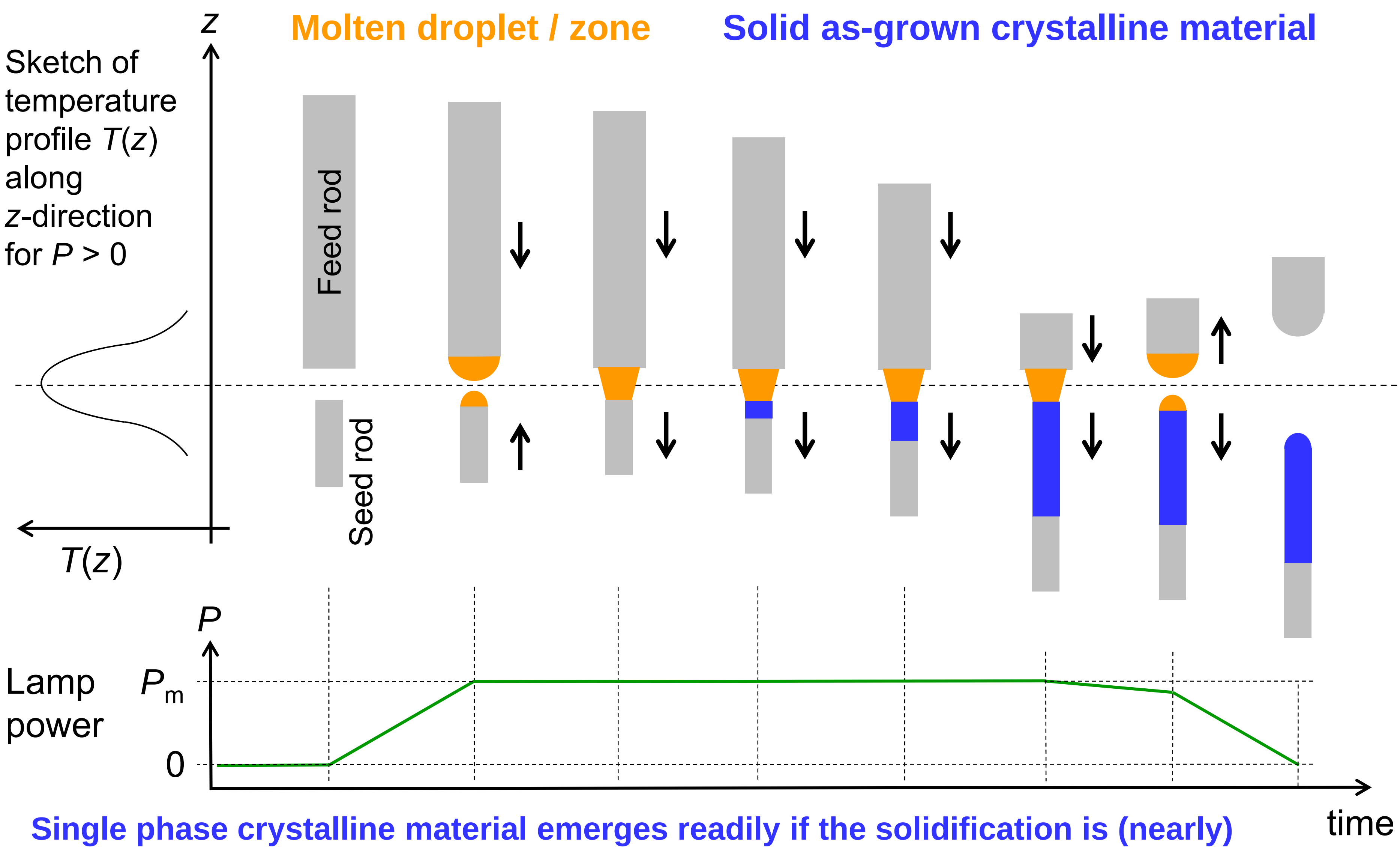
P_m = Lamp power which is required to melt the material

Synthesis of melt-grown oxides by a mirror furnace - Sketch 8 / 9 of a run



P_m = Lamp power which is required to melt the material

Synthesis of melt-grown oxides by a mirror furnace - Sketch 9 / 9 of a run



Single phase crystalline material emerges readily if the solidification is (nearly) congruent, i.e. if the melt and the solidified material have (nearly) the same chemical composition. If this is true depends on the chemical composition and is often not known or predictable, especially for unexplored chemical compositions

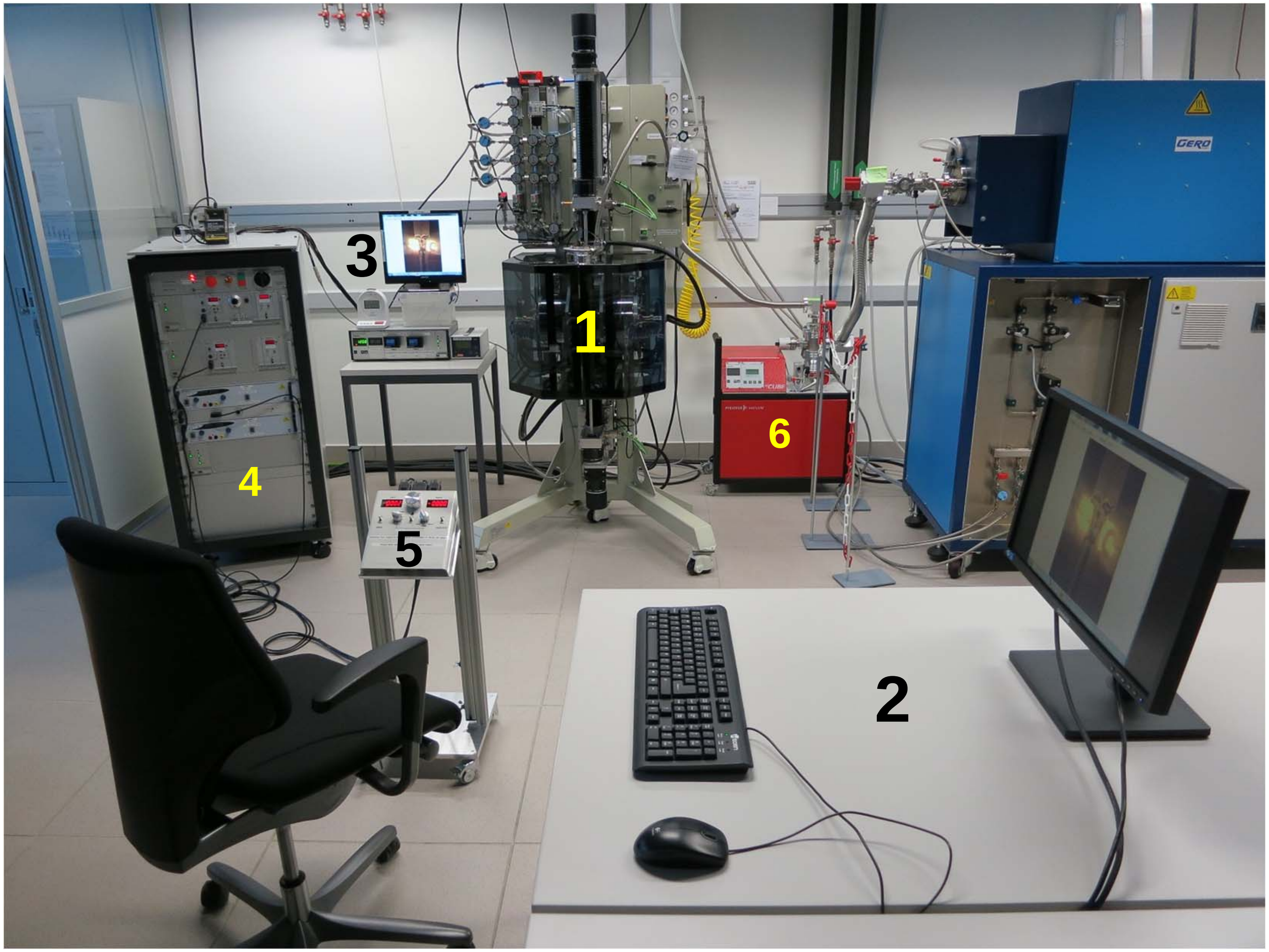
Part 2

Presentation of the
Cyberstar mirror furnace
and the design of
feed rods, seed rods
and sample holders

Part 2 - 1

The Cyberstar mirror furnace

Cyberstar mirror furnace



1 Mirror furnace

2 Monitor and keyboard of the video recording and processing system which is equipped with the software HIRIS from R&D Vision

3 Second monitor

4 Control cabinet

5 Movable control unit for lamp power and fast motion of seed and feed rod

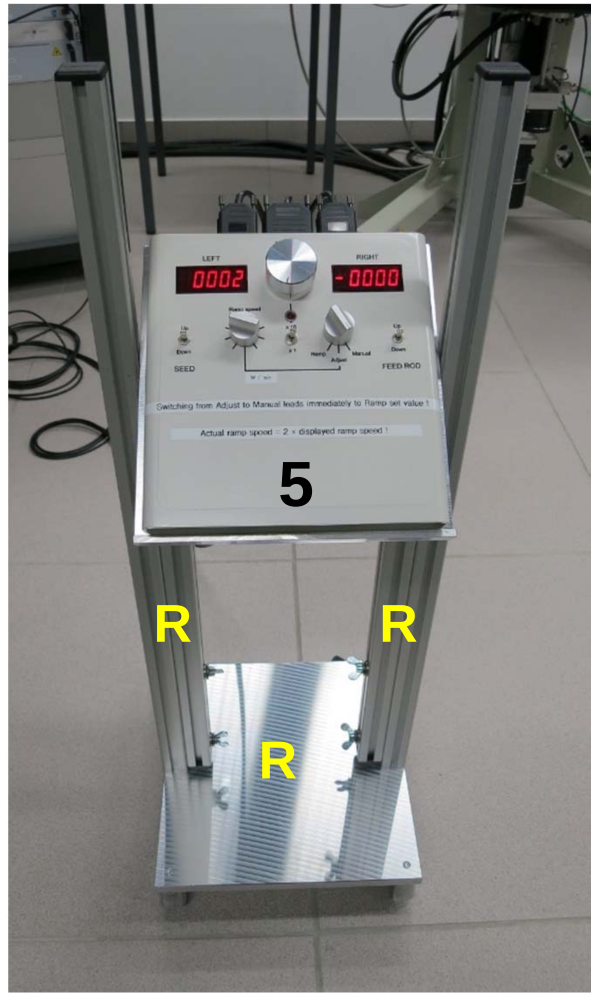
6 Turbo pumping station

Picture taken at the ETH Zurich in March 2016

Not visible in this picture: Computer of the video system, gas bottles, cooling water unit

Cyberstar mirror furnace – Some control units

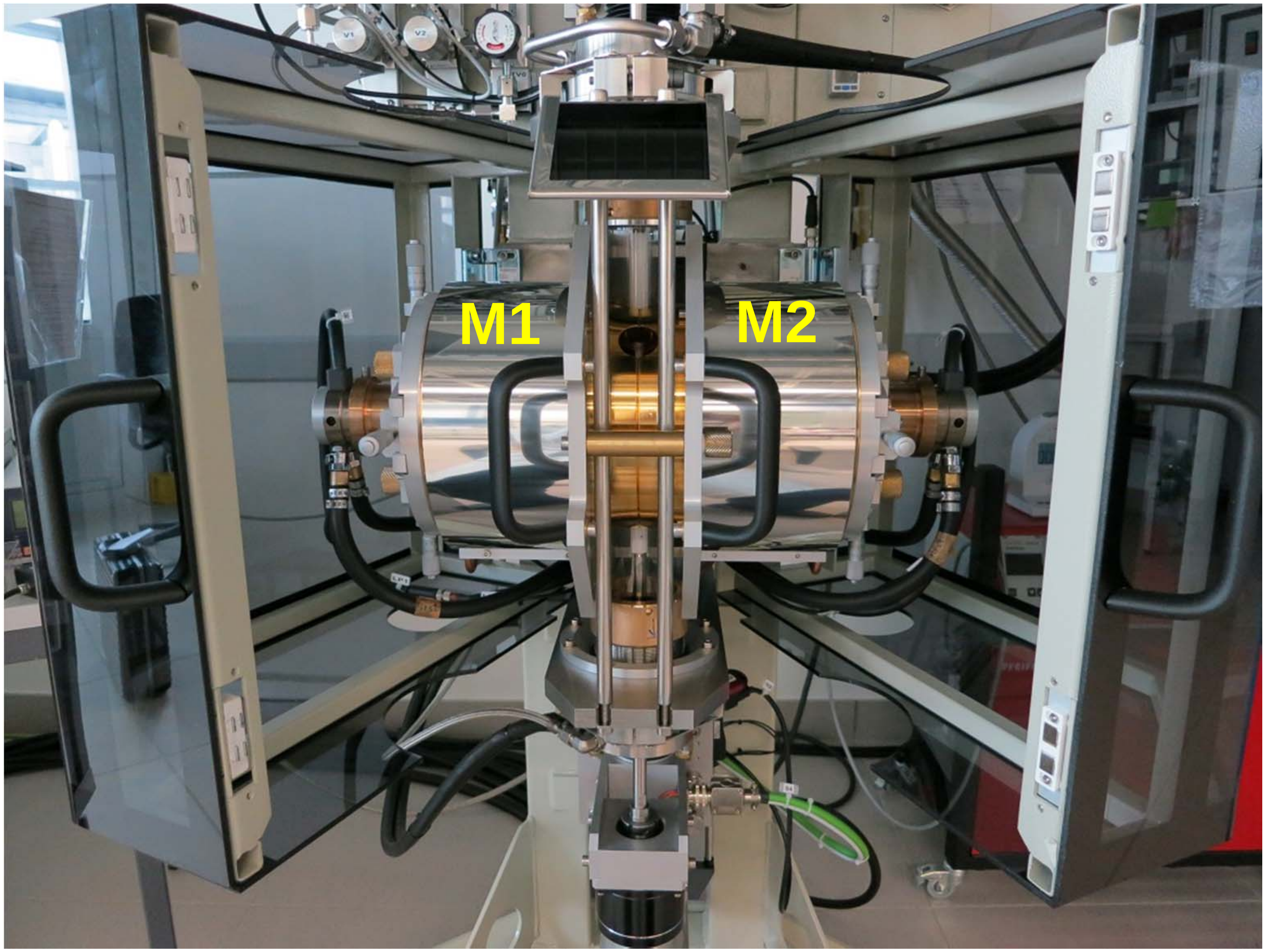
Control cabinet



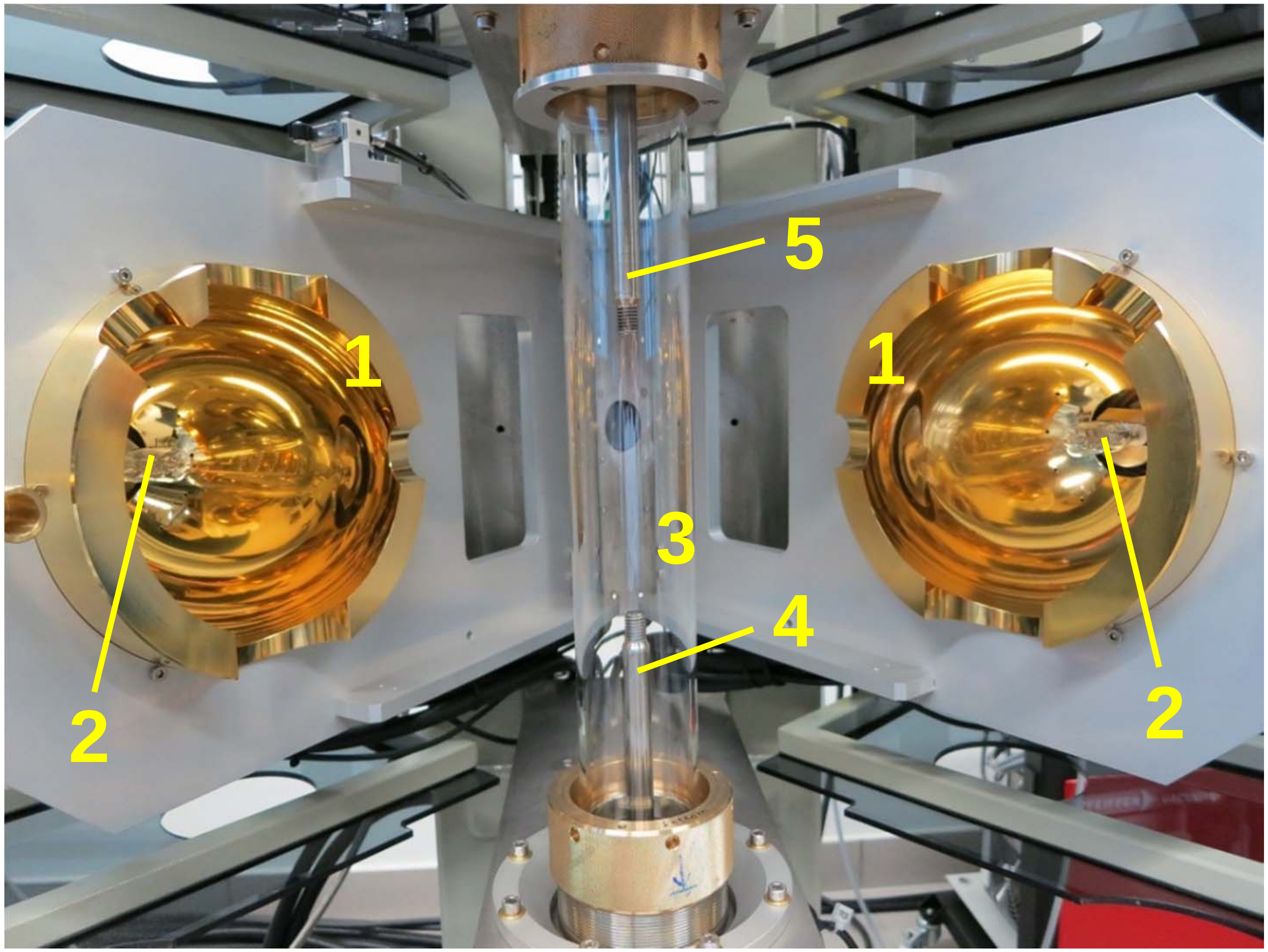
Control unit (5) for lamp power and fast motion of rods. It allows with one rotary button the simultaneous adjustment of the lamp power so that both lamps have always the same power

Movable rack (R) made by C. Roth and M. Elsener from the metal workshop of the Department of Materials of the ETH Zurich

Cyberstar mirror furnace – Casing open and mirrors M1 and M2 locked



Cyberstar mirror furnace – Mirrors unlocked – Not loaded with rods



1 Elliptical and gold-coated mirror

2 Lamp
P_{max} = 1000 W

3 Quartz glass tube

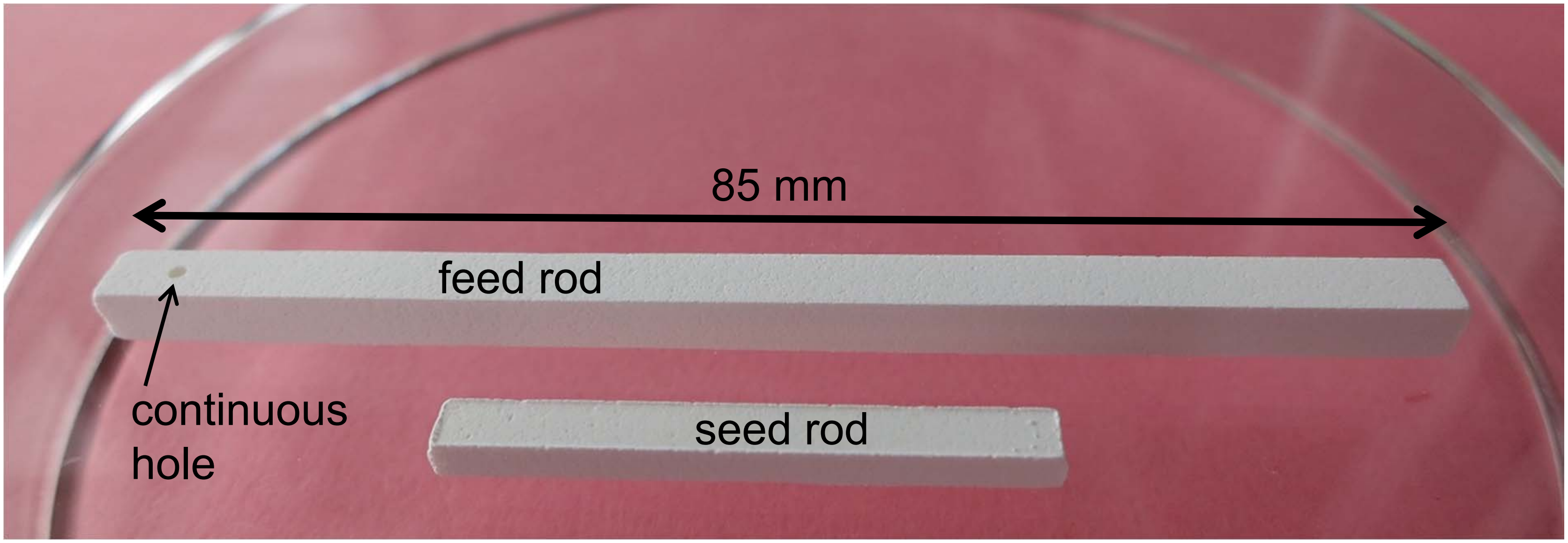
4 Lower shaft

5 Upper shaft

Mirrors and lamps are cooled by cooling water and a flow of compressed air

- Mirrors focus radiation from lamps into a small volume. If a material is located at that volume, then it can be molten if the lamp power is high enough
- Heating-up and melting of a material takes mainly place by its infrared absorption
- Mirrors are gold-coated because that enhances their infrared reflectivity

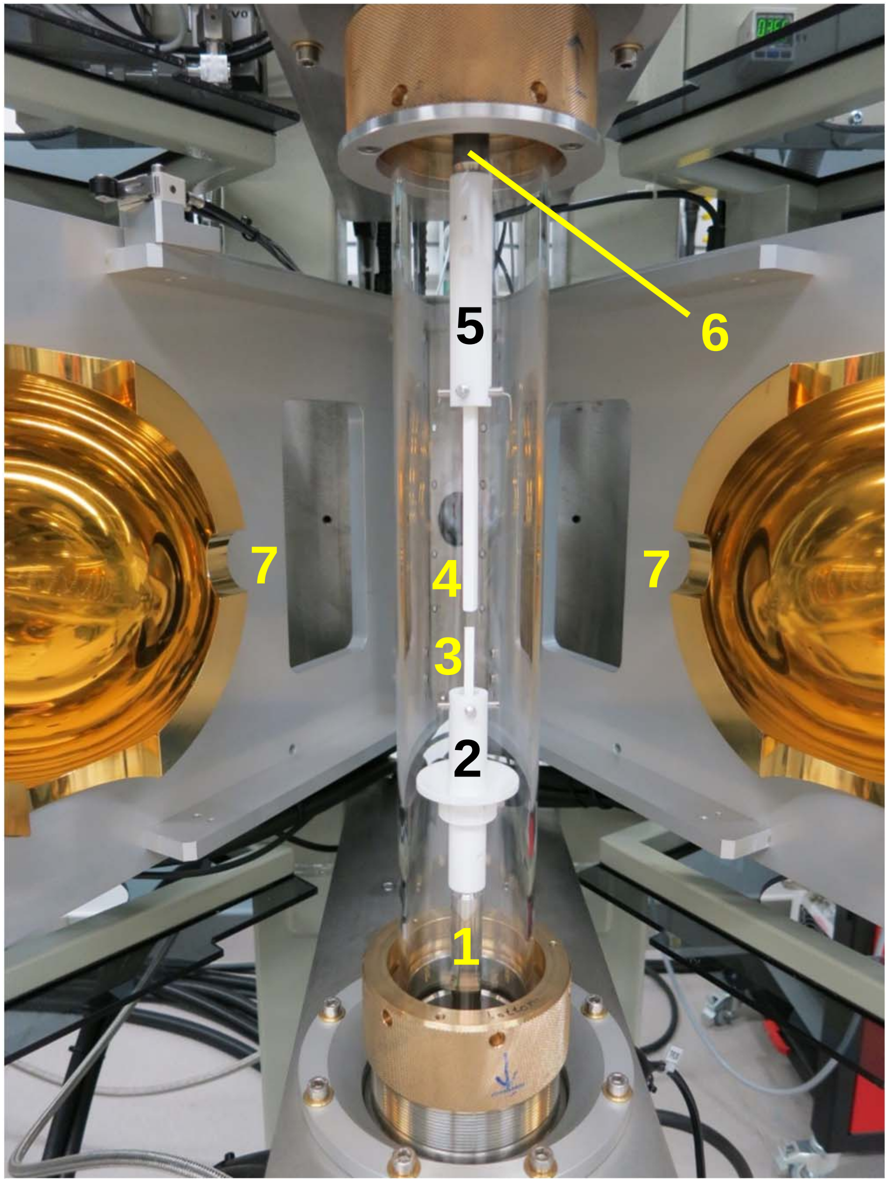
Synthesis of crystalline materials by a mirror furnace requires desired chemical composition in form of two rods



Example of polycrystalline sintered rods with same chemical composition such as $La_2Ti_2O_7$

Fixation of the rods at the lower and upper shaft by special sample holders ...

Cyberstar mirror furnace – Loaded with seed rod and feed rod



7 Recess in the mirror for observation by a video camera

6 Upper shaft

5 Sample holder for the feed rod

4 Feed rod

3 Seed rod

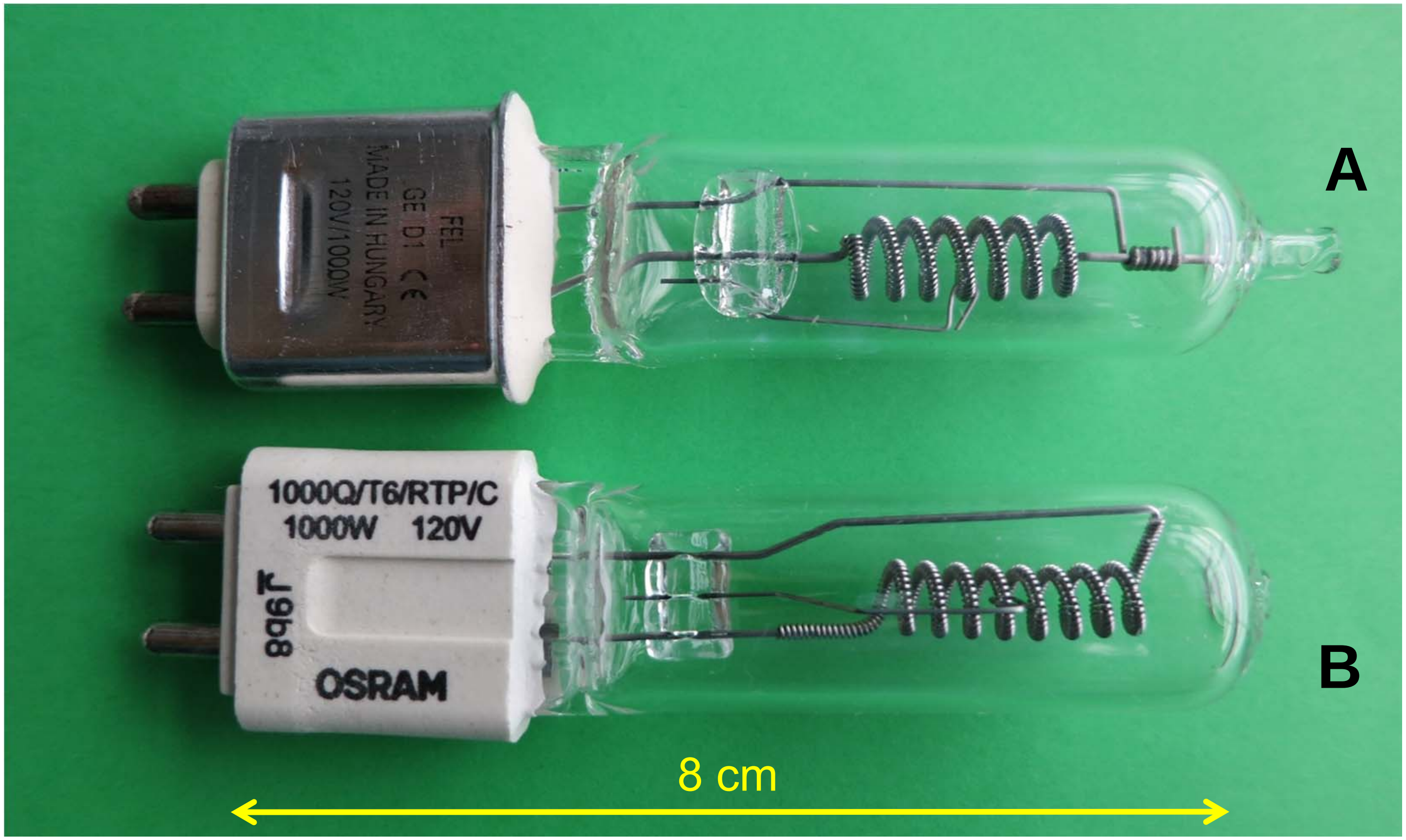
2 Sample holder for the seed rod

1 Lower shaft

The lower and upper shaft, and thus the seed and feed rod, can be rotated and vertically moved by electric direct drives

Cyberstar mirror furnace – Lamps

Slightly different types of bulbs of the same design (120 V, 1000 W, base type G 9.5)

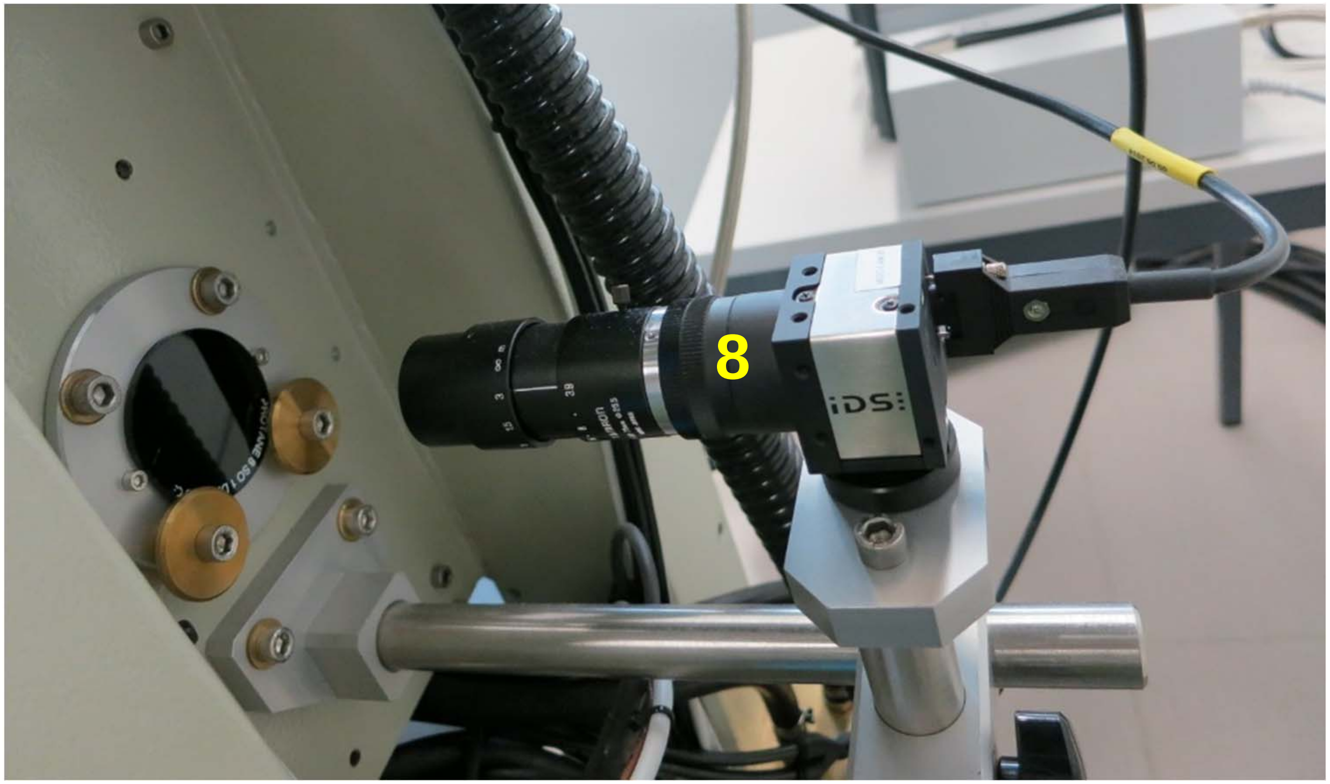


A Halogen bulb from GE (General Electric): FEL, 120 V, 1000 W, base G 9.5

B Halogen bulb from Osram: 1000Q / T6 / RTP / C, 120 V, 1000 W, base G 9.5

So far type A bulbs are used in our Cyberstar mirror furnace. Type A bulbs were also used in the GERO and IBM mirror furnace, see appendix 1 and 2

Cyberstar mirror furnace – Video camera at the rear side



Digital video camera (8) at the rear side

Synthesis of melt-grown oxides by the Cyberstar mirror furnace

Example of a snap shot [1] or real time video [2] of a floating zone melting process

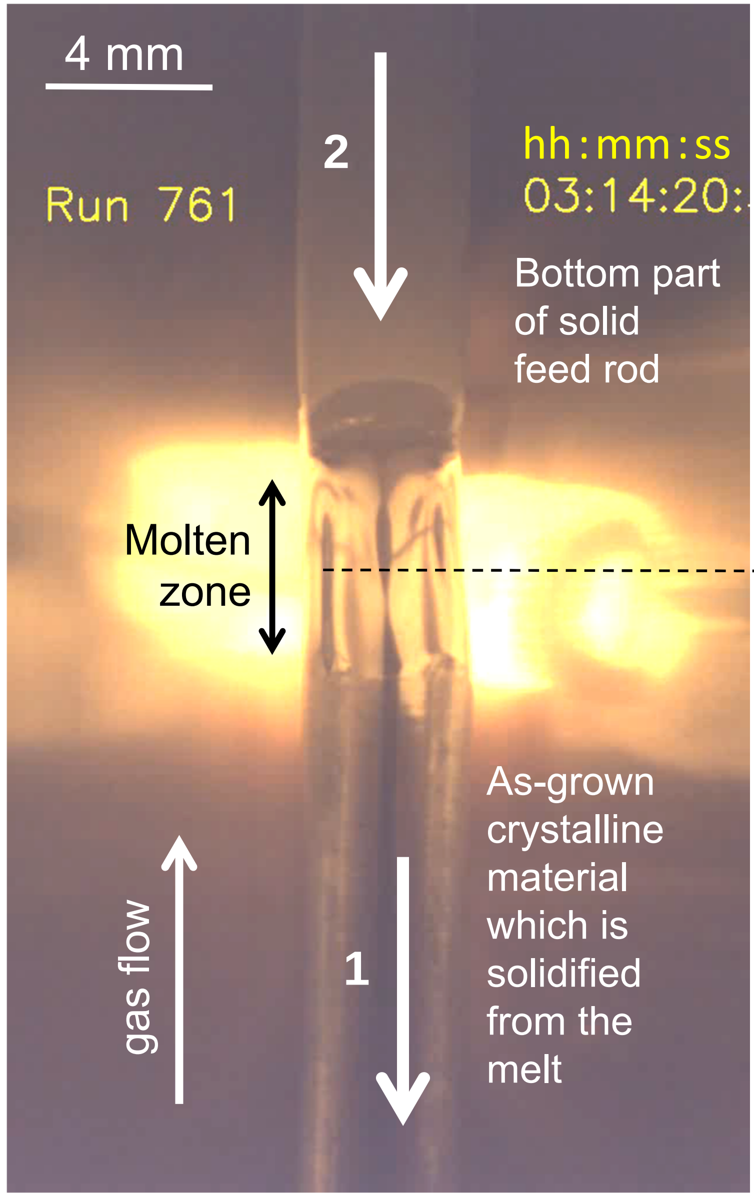
[1] pdf type or [2] ppsx type of this presentation, see page 2

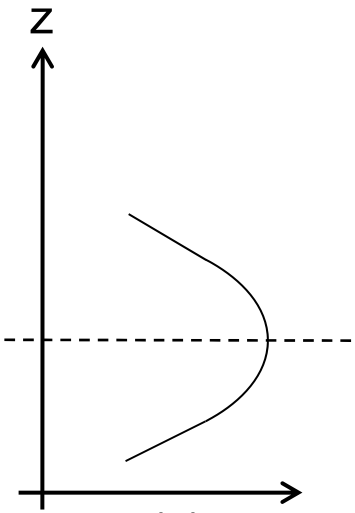
The polycrystalline feed rod is converted via the melt into a crystalline material which is created by a solidification from the melt

2 Slow downwards motion of the feed rod, e.g. 10 mm / h

1 Slow downward motion of the seed rod, e.g. 8 mm / h

The crystalline material grows onto the upper part of the seed rod which is not visible in this image. The seed rod is located below the bottom boundary of this picture

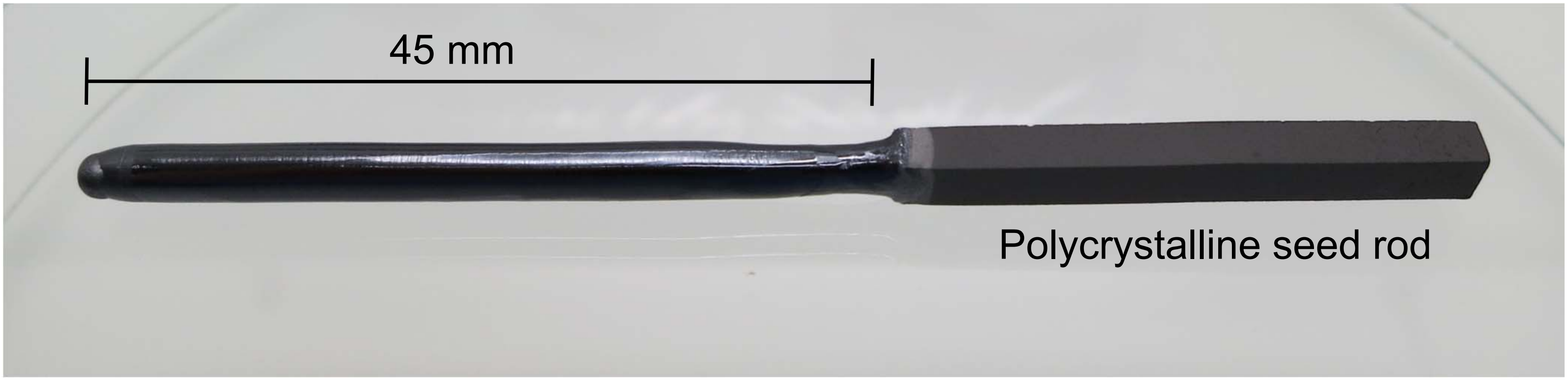




Sketch of the temperature profile T(z) along the z - direction

Example of a melt-grown oxide prepared by the Cyberstar mirror furnace

Hexagonal layered $DyMnO_{3-\delta}$ ($\delta \approx 0.05$) grown with 8 mm / h under argon with a flow rate of 24 liter / h and a lamp power of 2×280 W

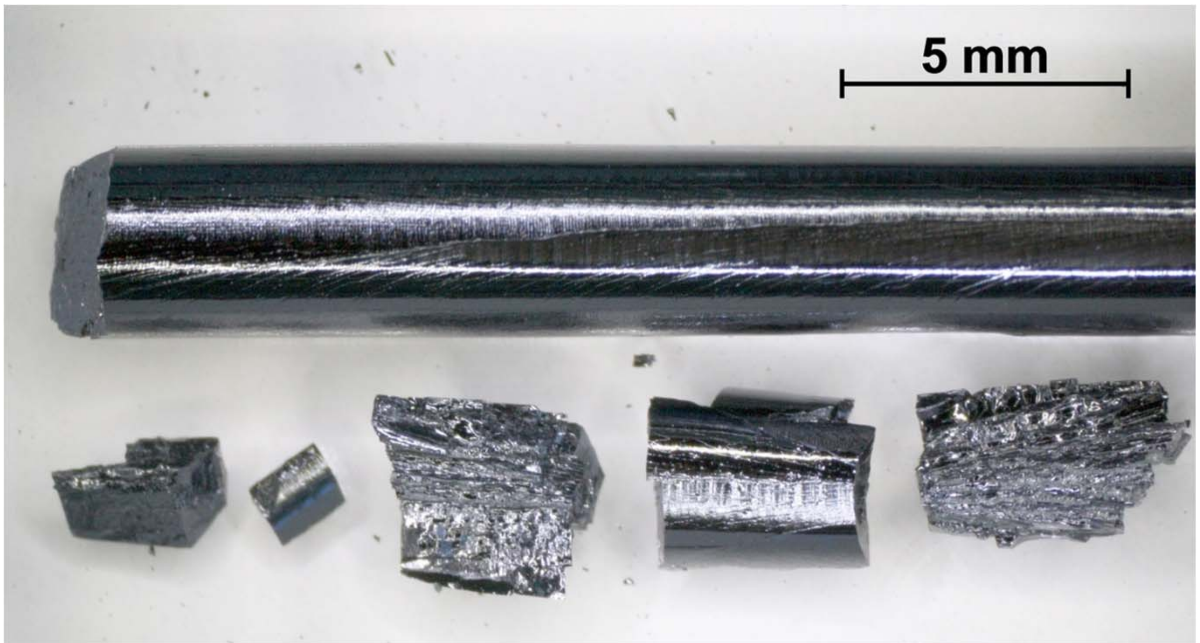


As-grown crystalline $DyMnO_{3-\delta}$ ($\delta \approx 0.05$) with a length of 45 mm and polycrystalline seed rod. Run / Sample number 761

The nominal composition of the seed rod and feed rod was $DyMnO_3$, i.e. the material released somewhat oxygen during the run. That was experimentally verified by an oxygen analyzer ZIROX SGM7 which was used to measure the oxygen content of argon at the gas outlet of the mirror furnace (see part 3). During the pre-initial phase, where the lamps were still off, an oxygen content of 3 ppm was detected. This is a typical value for argon with a specified purity of 99.999 %. During the creation of the molten zone an oxygen content of about 400 ppm was observed for a short time. After starting the floating zone melting process with a zone speed of 8 mm / h the oxygen content did decrease steadily. After one hour and during the subsequent 4 hours the detected oxygen content was always in a range of about 50 – 40 ppm. The presence of a significantly enhanced oxygen content of the argon at the gas outlet of the Cyberstar mirror furnace indicates that the original chemical composition $DyMnO_3$ did release oxygen resulting in a melt-grown sample with composition $DyMnO_{3-\delta}$ with $\delta > 0$. The synthesis of the melt-grown sample went off without any noticeable evaporation. Hexagonal $DyMnO_{3-\delta}$ is ferroelectric and displays magnetic ordering at low temperatures. The preparation of $DyMnO_{3-\delta}$ ($\delta = 0$ and $\delta > 0$) by floating zone melting is reported in some papers, see e.g. S. Harikrishnan et al. , Journal of Physics: Condensed Matter 21 (2009) 096002 and V. Yu. Ivanov et al. , Physics of the Solid State 48 (2006) 1726 - 1729

Example of a melt-grown oxide prepared by the Cyberstar mirror furnace

Hexagonal layered $DyMnO_{3-\delta}$ ($\delta \approx 0.05$) grown with 8 mm / h under argon with a flow rate of 24 liter / h and a lamp power of 2×280 W

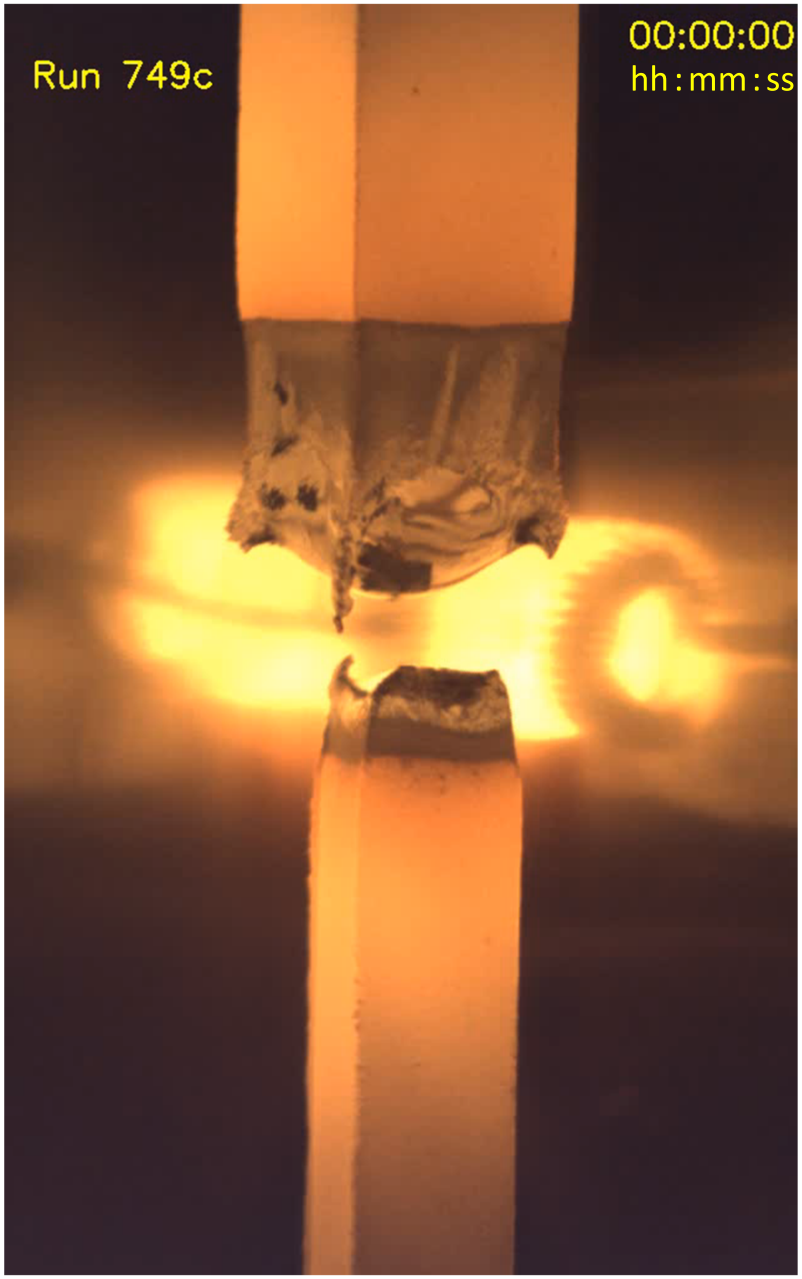


Run / Sample No. 761C

Pieces of the as-grown crystalline sample

The preparation of $DyMnO_{3-\delta}$ ($\delta = 0$ and $\delta > 0$) by floating zone melting is reported in some papers, see e.g. S. Harikrishnan et al. , Journal of Physics: Condensed Matter 21 (2009) 096002 and V. Yu. Ivanov et al. , Physics of the Solid State 48 (2006) 1726 - 1729

Example of a melt-grown oxide prepared by the Cyberstar mirror furnace



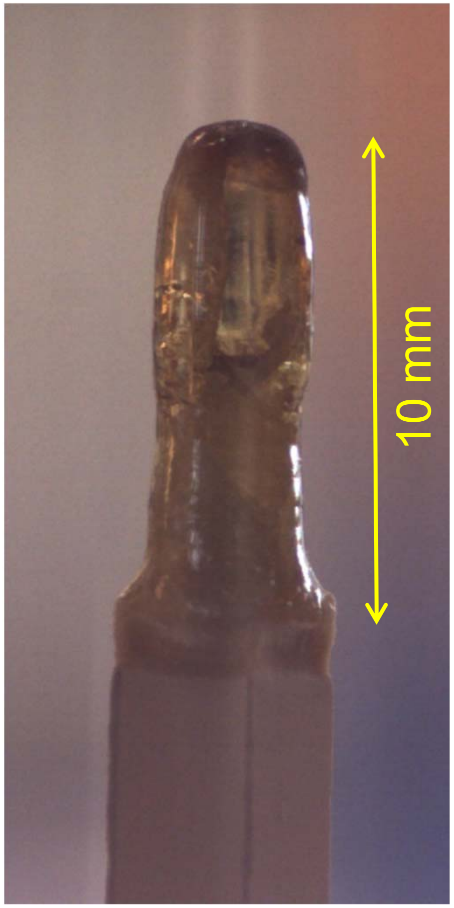
Nb_2O_5 grown with 14 mm / h under synthetic air with a flow rate of 18 liter / h and a lamp power of about 2 × 280 W

On the left: Fast mode video of the floating zone melting process

The video is running only in the ppsx version of this presentation, see page 2

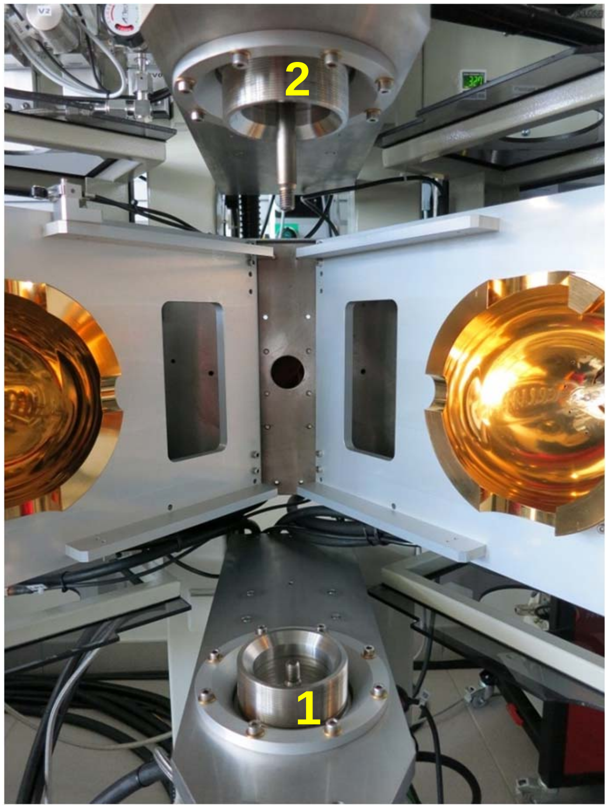
On the right: As-grown crystalline sample after the run in the mirror furnace

Nb_2O_5 is a transparent insulator with a melting point of about 1510 °C

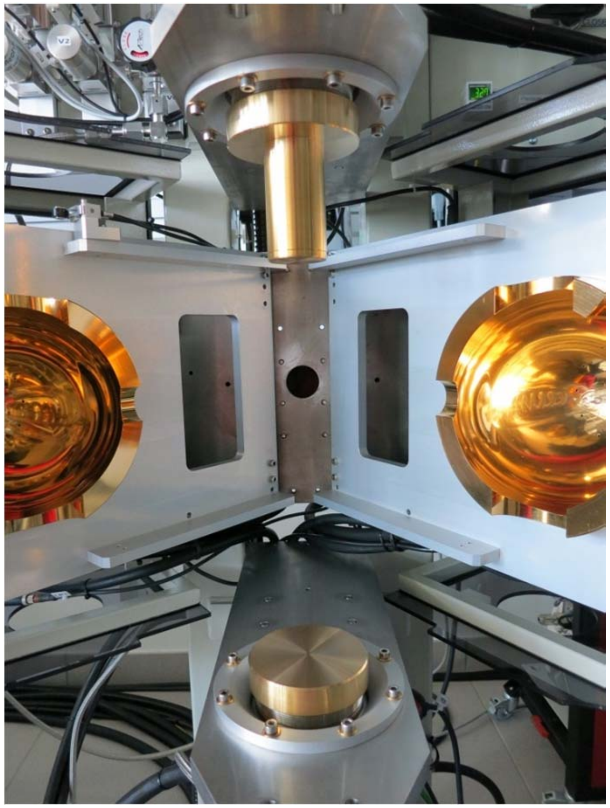


Cyberstar mirror furnace – Protective lids

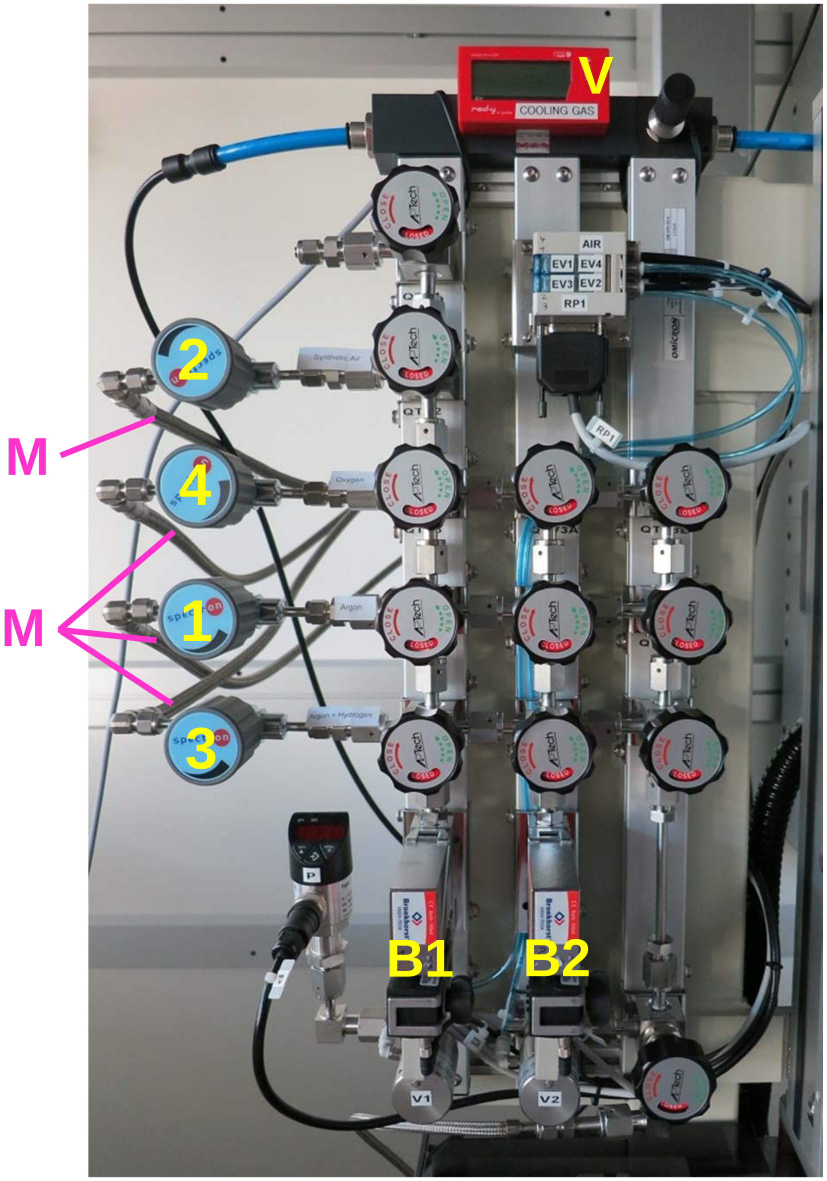
Two lids with an internal thread. Made of brass in the metal workshop of the Department of Materials of the ETH Zurich by C. Roth and M. Elsener



The lids can be screwed on the lower external thread (1) and the upper external thread (2) at the lower and upper space of the mirror furnace. They protect the lower and upper shaft and space when the mirror furnace is not in use



Cyberstar mirror furnace – Gas inlet and gas flow control system



1 – 4 Gas inlet of the mirror furnace: Spectron diaphragm valves DVM-8-OD-6 (rotary dosing valves)

- 4 Oxygen (O_2) or gas mixture Ar + O_2
- 3 Gas mixture 97,2 % Ar + 2,8 % H_2
- 2 Synthetic air or oxygen
- 1 Argon (Ar)

M Flexible metal tubes (Swagelok 6 mm) which connect the gas inlet of the mirror furnace with the gas lines 1 – 4 of the gas supply cabinet which is presented in part 3

B1 B2 Bronkhorst mass flow controller from the “EL-FLOW“ series. Maximum gas flow rate 2000 sccm for B1 and 20 sccm for B2

V Flow meter and regulator from the “red-y compact“ series of Vögtlin Instruments for the cooling gas (compressed air) which cools the lamps. Maximum gas flow rate 300 ln / min

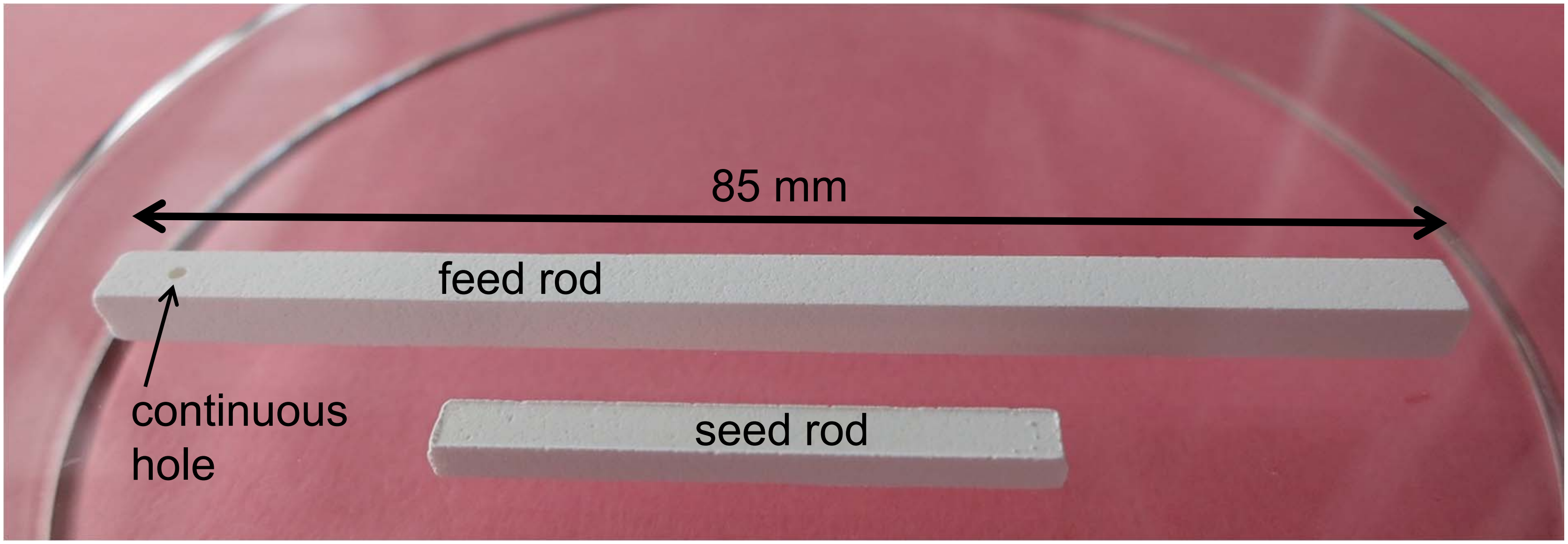
Cyberstar mirror furnace – Special features

- Translational and rotational movement of the lower and upper shaft by electric direct drives without any gears and clutches
- Large range of the translational speed:
  0,01 – 100 mm / h (continuously variable)
  0 – 100 mm / min (continuously variable)
- Large range of the rotational speed:
  0,1 – 99,9 rpm (continuously variable)
- Highly efficient mirror and lamp system, i.e. the molten state can be reached with relatively little power
- Experiments can be performed under various atmospheres / gas types / pressure ranges:
  - high pressure up to 10 bar
  - normal pressure
  - vacuum down to about 0,05 mbar

Part 2 - 2

The design of the
feed rods and seed rods
and desirable properties
of sample holders
for the rods

The design of the feed and seed rods

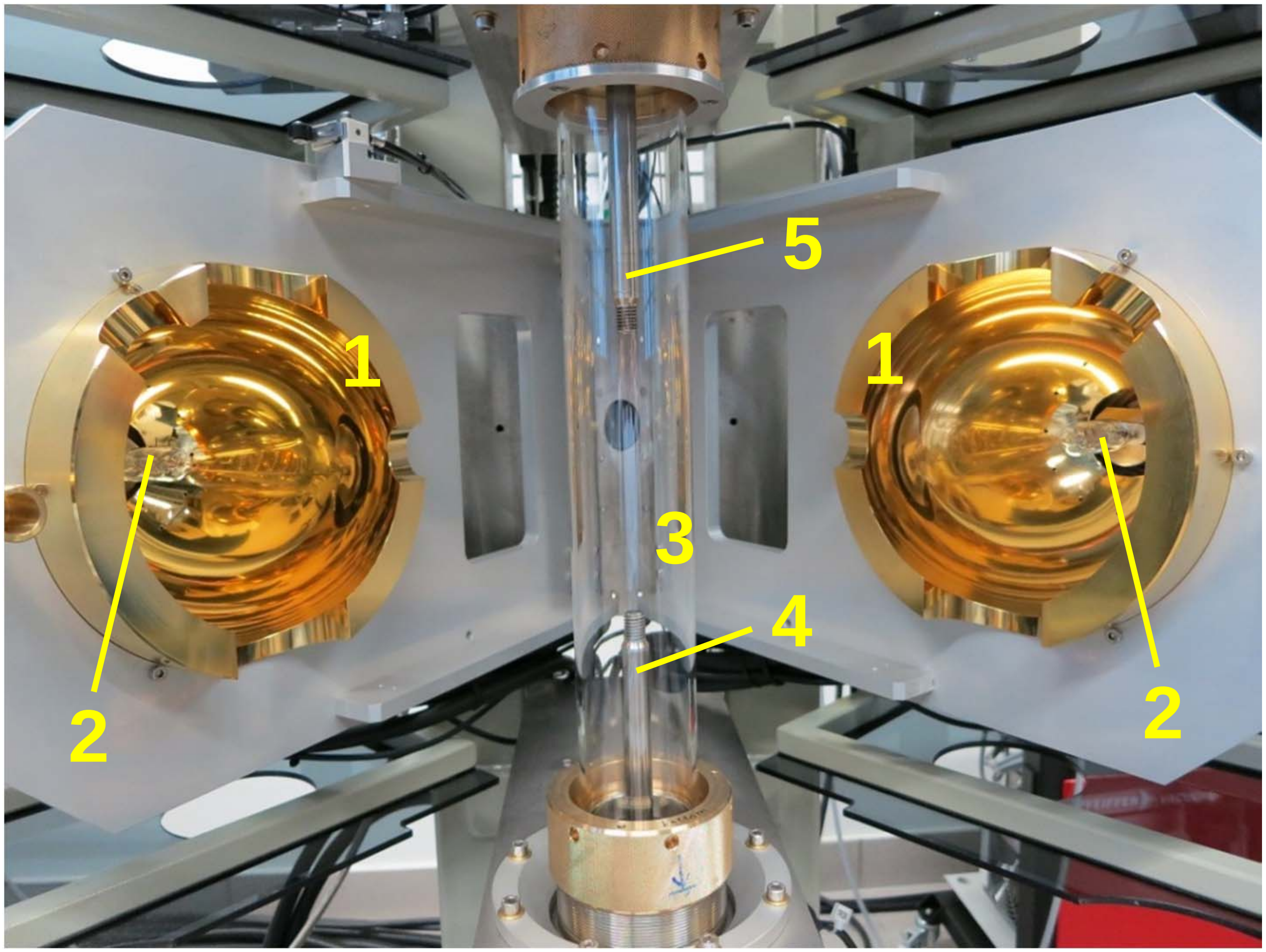


Example of polycrystalline sintered rods with same chemical composition such as $La_2Ti_2O_7$ for floating zone melting in the mirror furnace

- Rectangular rods with such a design can be prepared relatively easily by means of special pressing dies
- The preparation of such rods is described in part 5

By means of special sample holders, which are presented in the following parts, it is relatively easy to fix and center such rods at the lower and upper shaft of the Cyberstar mirror furnace ...

Cyberstar mirror furnace - Mirrors unlocked - Not loaded with rods



1 Elliptical and gold-coated mirror

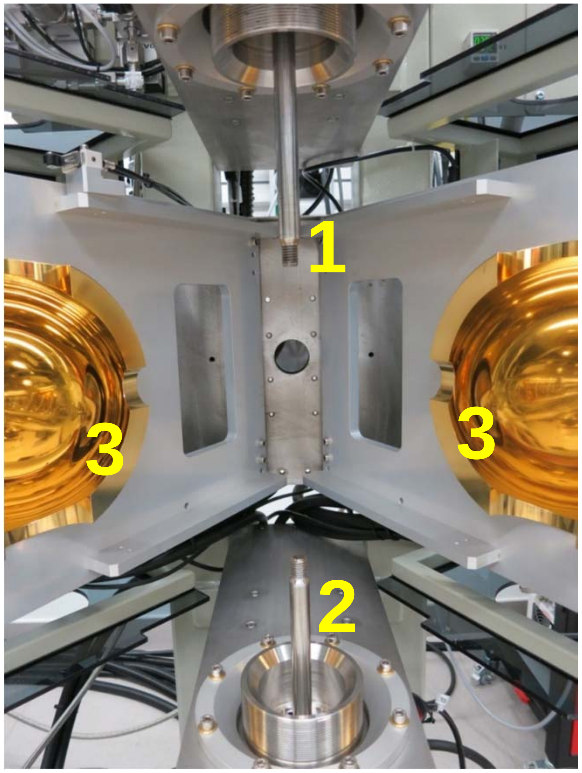
2 Halogen lamp

3 Quartz glass tube

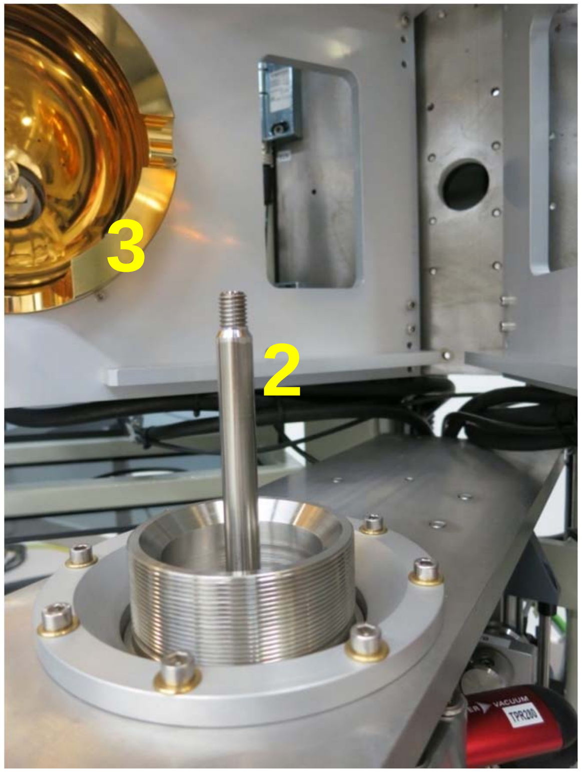
4 Lower shaft

5 Upper shaft

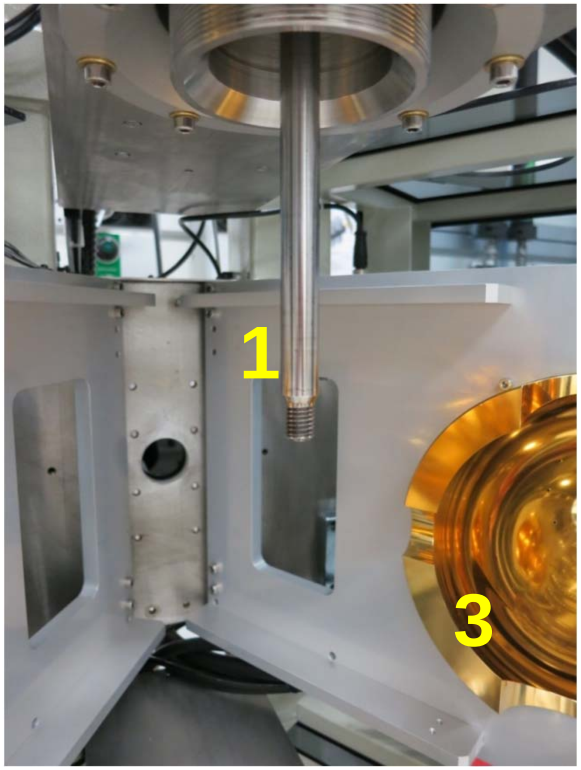
Cyberstar mirror furnace - Mirrors unlocked & Quartz glass tube removed



Lower and upper shaft
and mirrors



Lower shaft



Upper shaft

1 Upper shaft with M10 thread • 2 Lower shaft with M10 thread • 3 Mirror

Lower and upper shaft can be rotated and vertically moved by electric direct drives

Sample holders are needed to fix the seed (feed) rod on the lower (upper) shaft ...

Desirable properties of the sample holders for the seed and feed rod

- Mechanically and chemically stable at elevated temperatures under oxidizing (oxygen or air), inert (argon), or reducing (argon + hydrogen) atmospheres

- No metal-metal connections

  When two screwed metal parts become hot they often form a strong linkage which cannot easily be loosened after cooling down. That can be prevented by means of lubricants but the use of lubricants is not wanted

- Clean and dry design, i.e. no use of lubricants or glue

  In some cases, such as the growth of so-called reduced oxides under argon, the evaporation of lubricants may lead to an unwanted oxidation of the sample

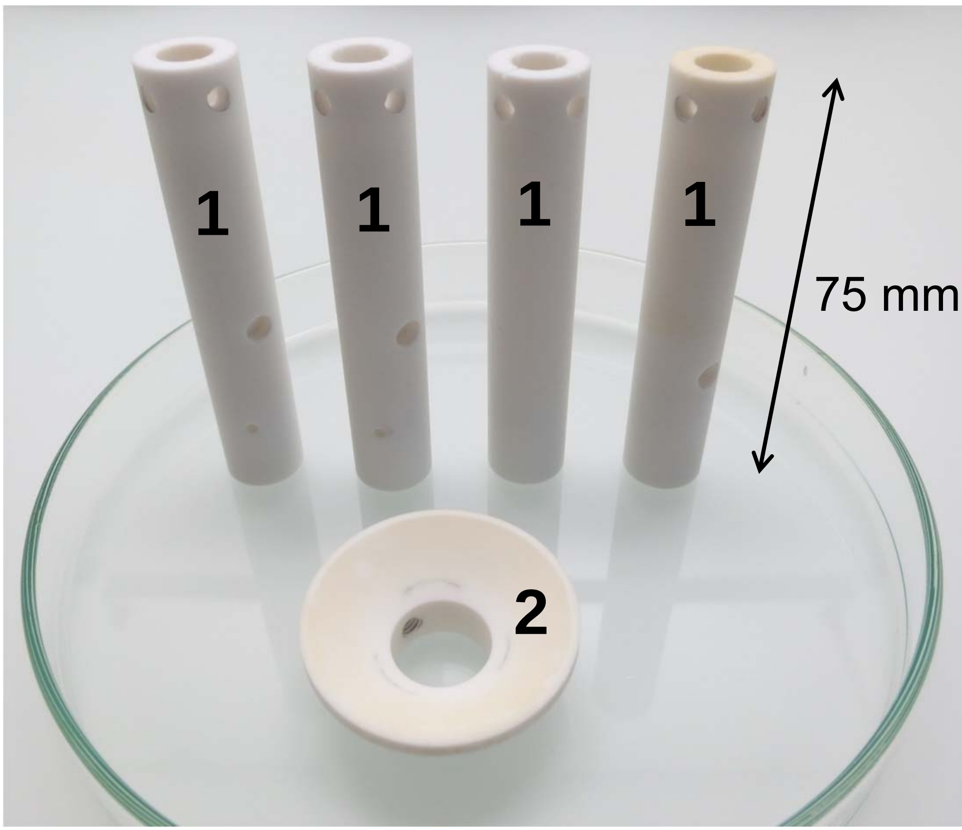
- Easy fixation and centering of the rods

Part 2 - 3

Sample holders
made of Macor
for the feed rod
and seed rod

Sample holders made of Macor for the seed rod and feed rod

Macor is a machinable glass-ceramic composite material which is mechanically and chemically stable up to 800 °C (temporary up to 1000 °C) under various atmospheres. It can be machined in the metal workshop like metals or alloys !

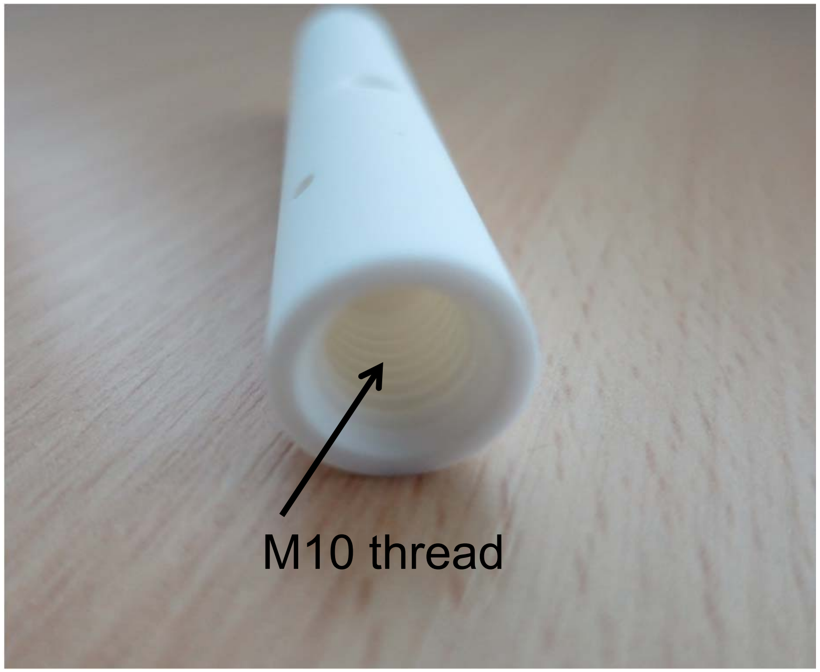


1 Sample holders for the seed rod and feed rod with similar design

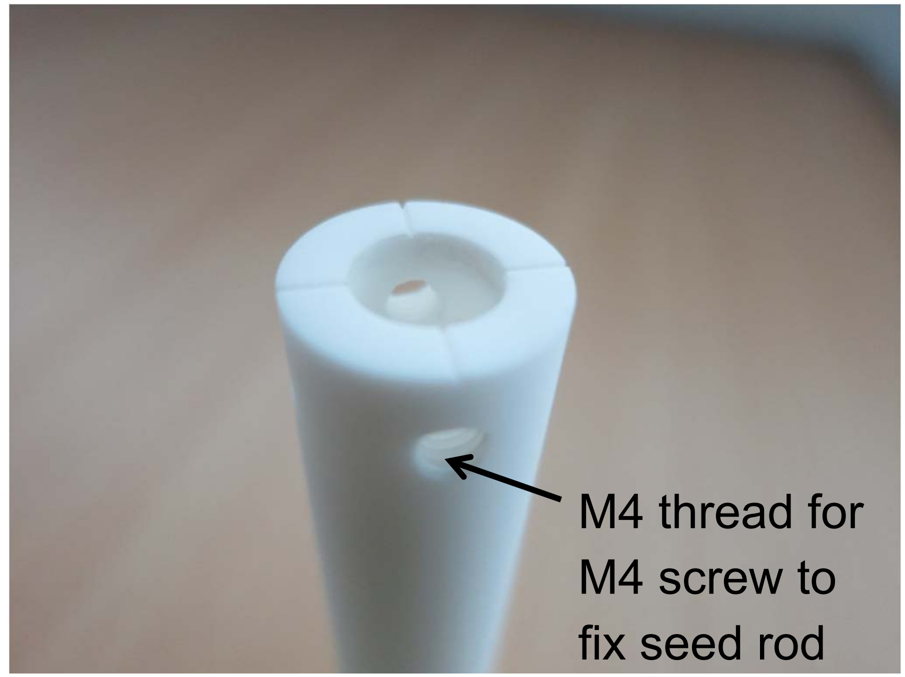
2 Funnel-like component

Made in the metal workshop of the Department of Materials of the ETH Zurich by C. Roth and M. Elsener

Upper and lower end of a Macor sample holder for the seed rod

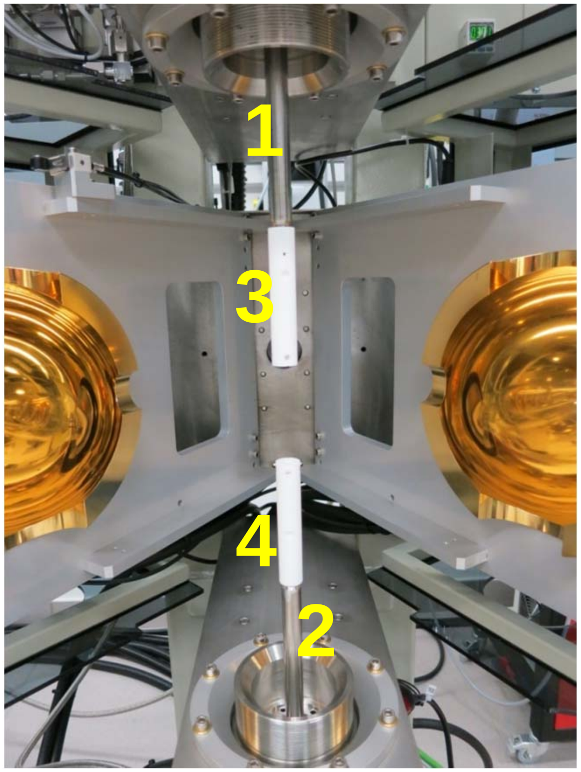


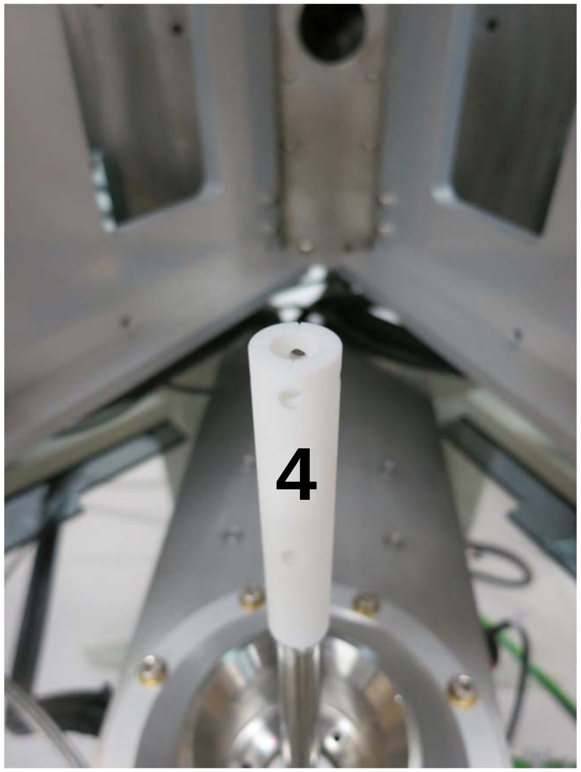
Lower end – can be screwed on the M10 thread of the lower shaft of the mirror furnace



Upper end – seed rod can be inserted from above

Macor sample holders screwed on the upper and lower shaft





1 Upper shaft

2 Lower shaft

3 Sample holder for the feed rod screwed on the upper shaft

4 Sample holder for the seed rod screwed on the lower shaft

Platinum-Rhodium screws

Custom-made M4 type screws for the fixation of the seed and feed rod, purchased and delivered from stone-ware gmbh (Switzerland)

Made of Pt-Rh 90-10 (90 % Pt + 10 % Rh) by Ögussa (Austria)

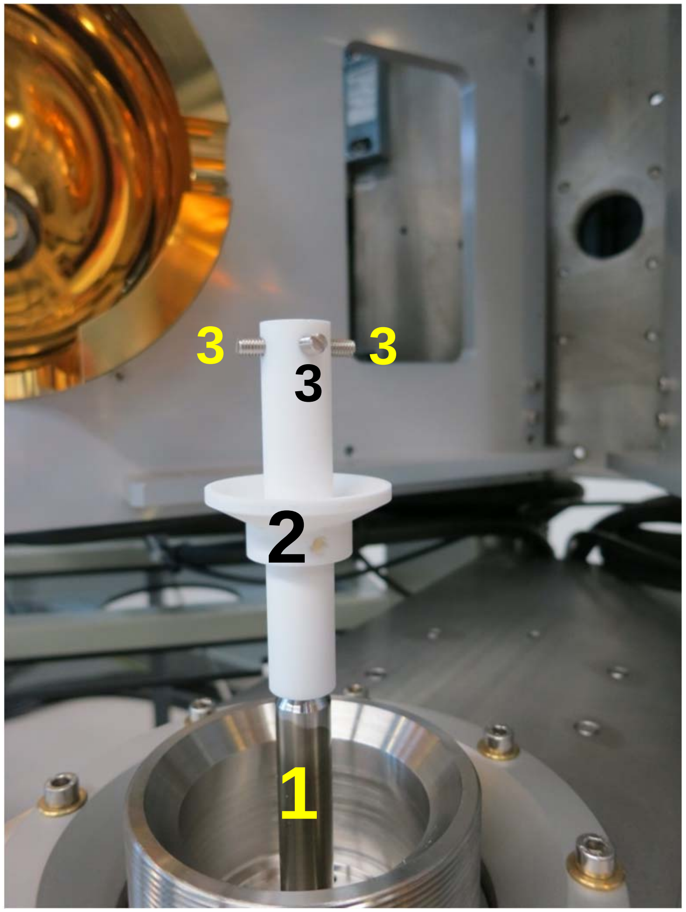
Length 10 mm

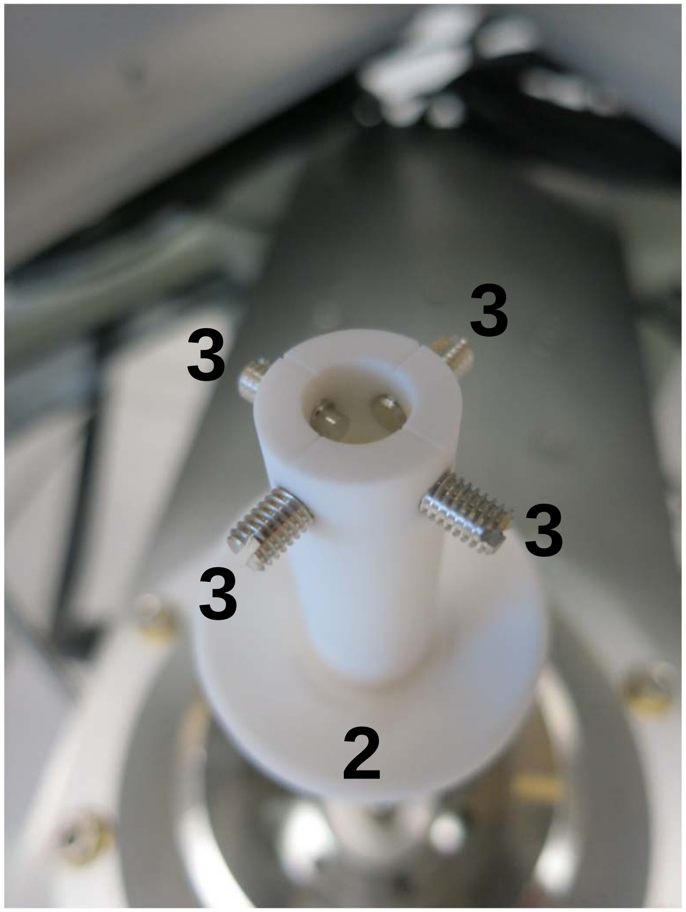
Some screws have a continuous axial hole

Pt-Rh 90-10 is mechanically and chemically stable up to 1450 °C under various atmospheres

The melting point of Pt-Rh 90-10 is about 1850 °C

Sample holder on lower shaft with 4 platinum-rhodium screws



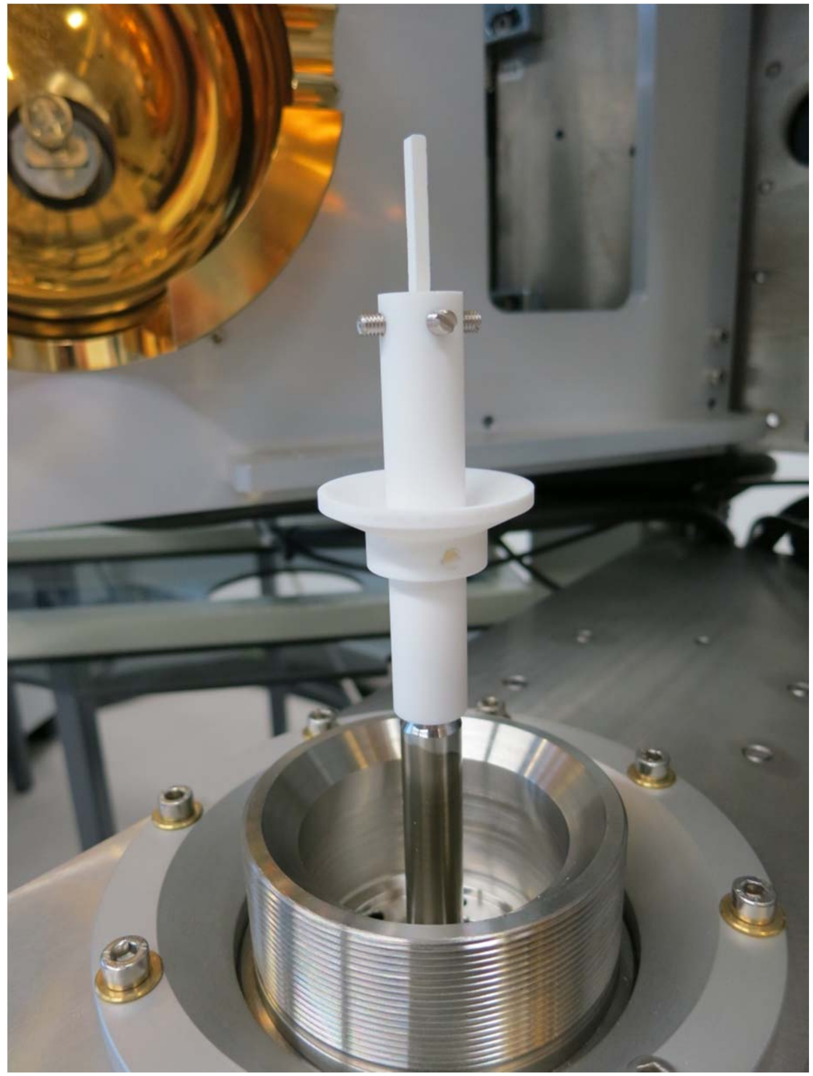


1 Lower shaft

2 Funnel-like part (if there are falling pieces from the feed rod or melt above, then most of them will be collected here)

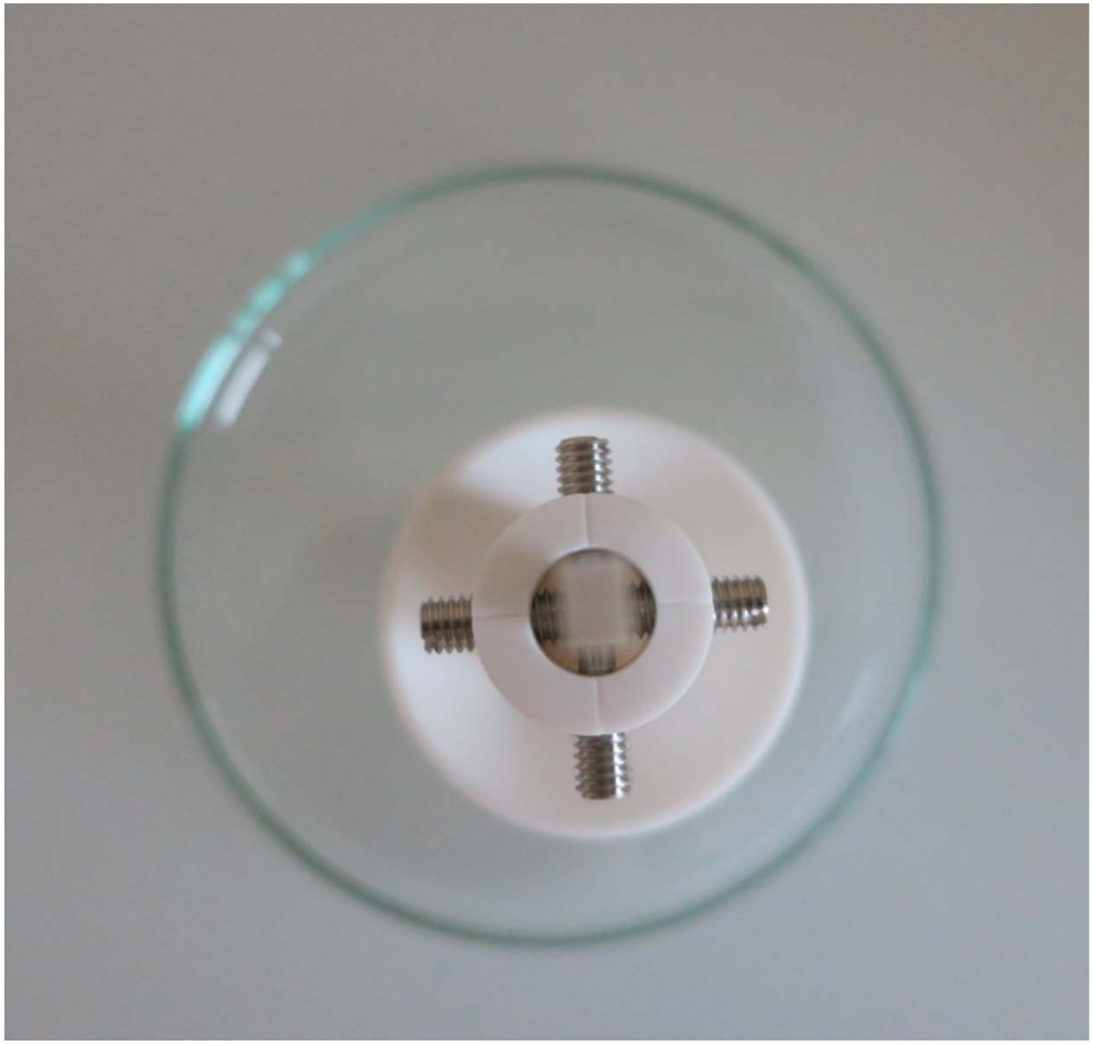
3 M4 platinum-rhodium screw for the fixation of the feed rod

Seed rod inserted, centered and fixed in sample holder at lower shaft



Top view of seed rod inserted, centered and fixed in sample holder

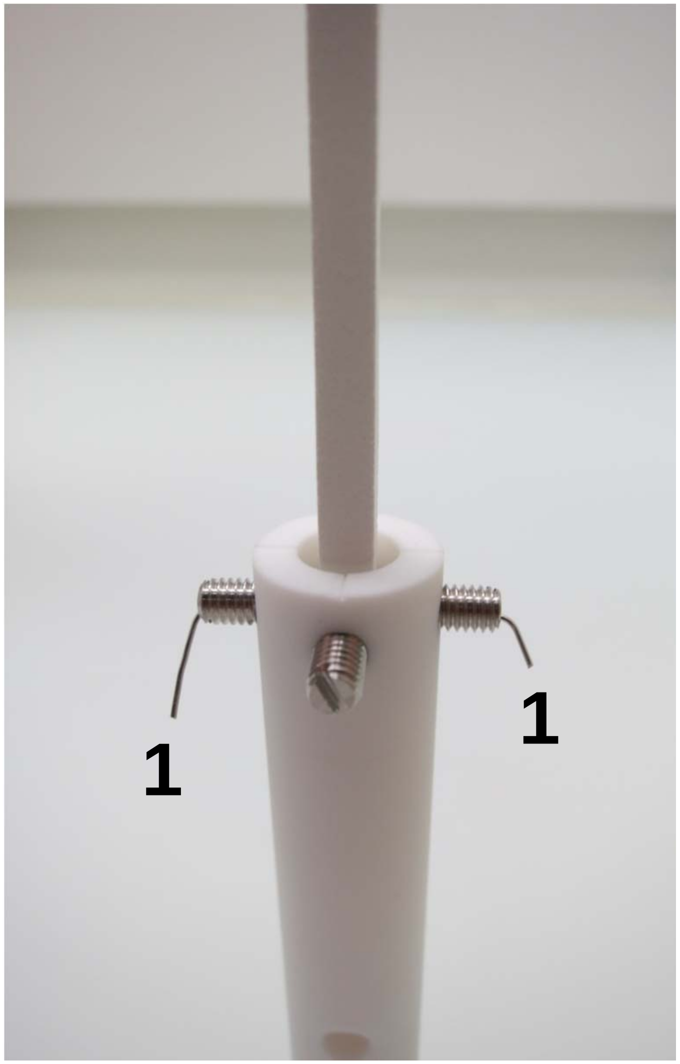
Seed rod and sample holder outside of the mirror furnace



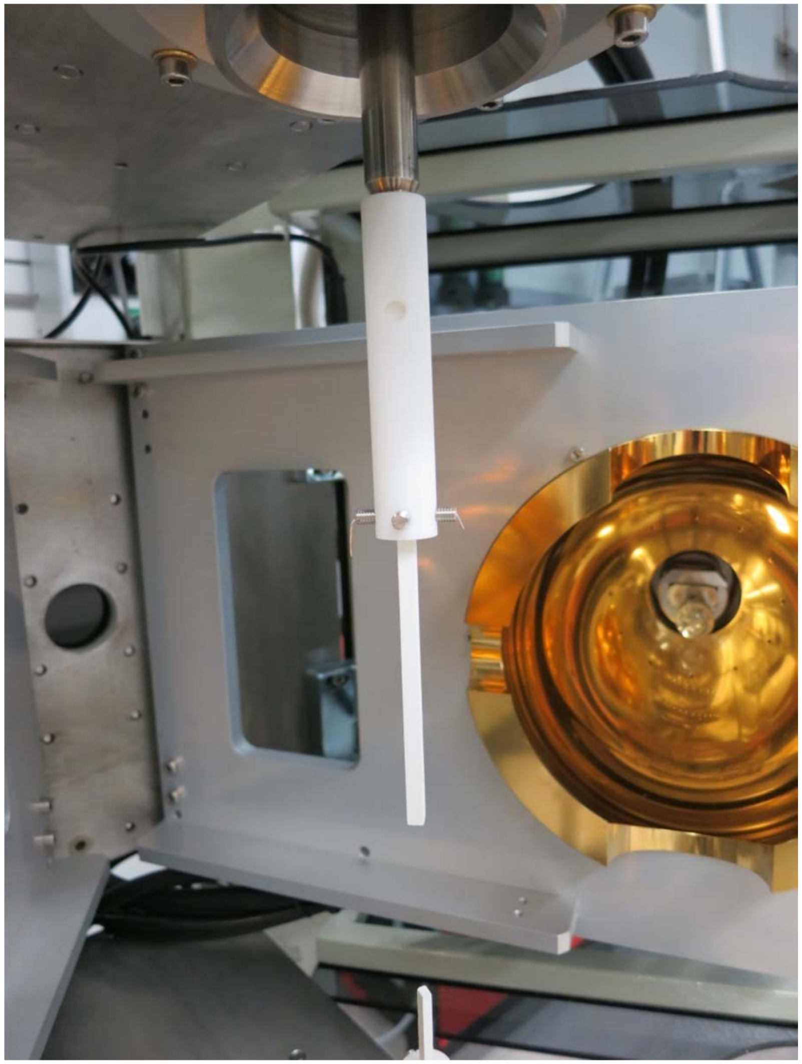
Feed rod inserted, centered and fixed in sample holder

Feed rod and sample holder outside of the mirror furnace

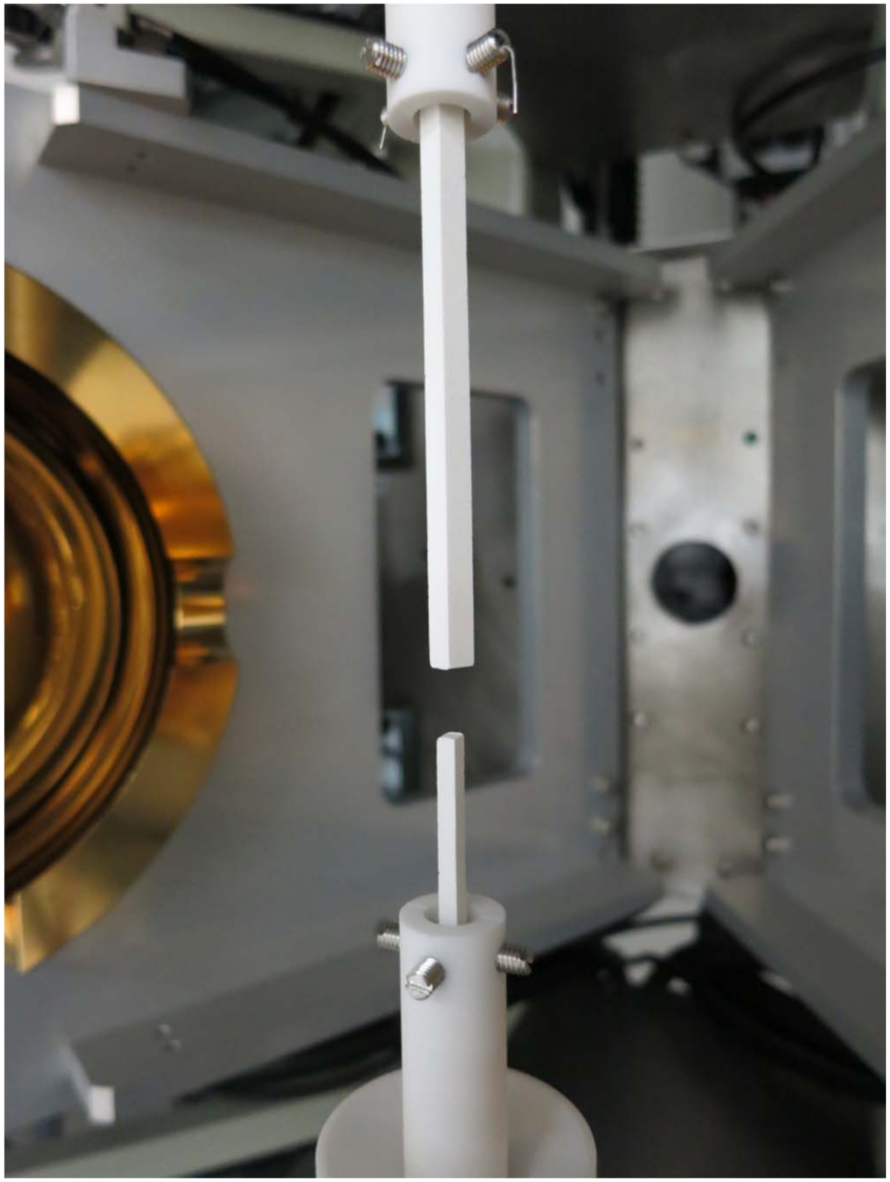
When screwed on the upper shaft in an upside down orientation, then the platinum wire (1) ensures that the feed rod cannot come off. The platinum wire extends continuously through both platinum-rhodium screws and the feed rod. This is possible because the feed rod has a hole and both screws have an axial hole.



Feed rod inserted, centered and fixed in sample holder at upper shaft

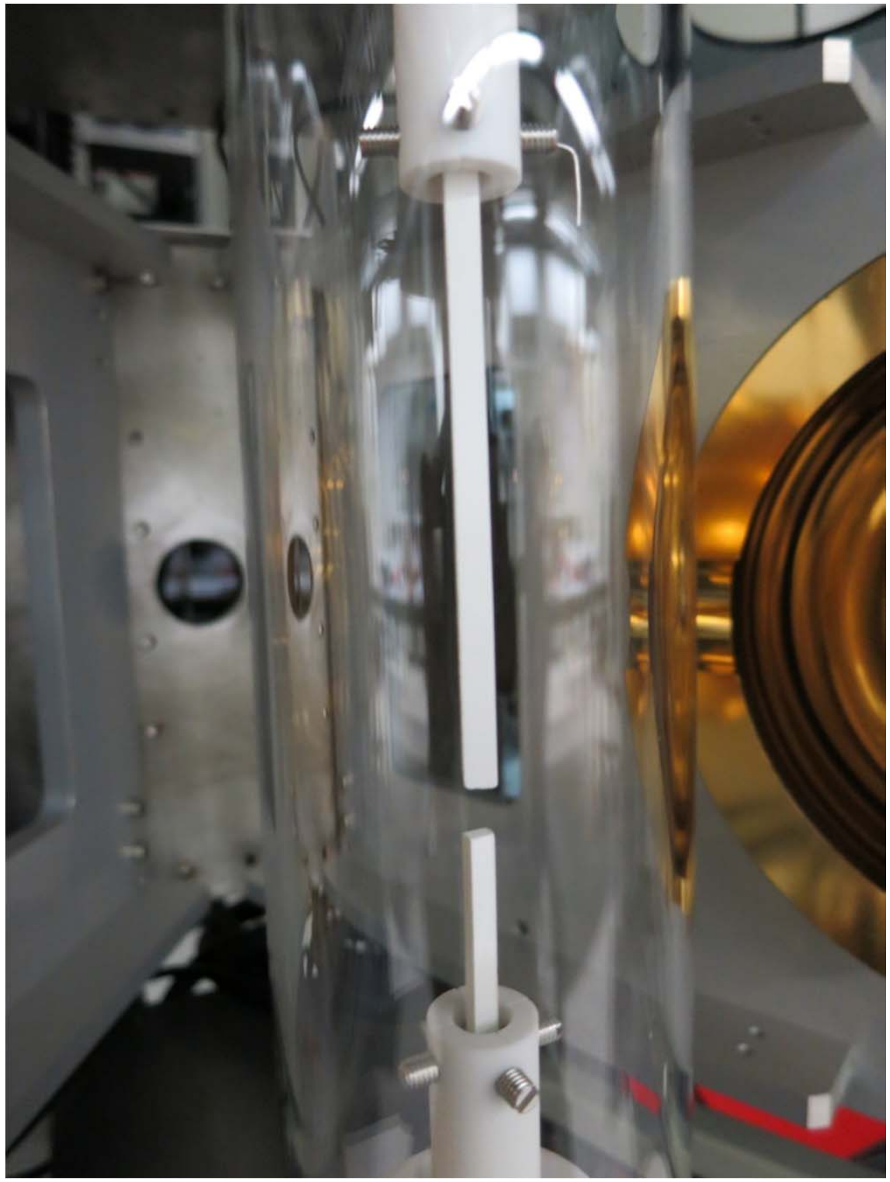


Seed and feed rod fixed by sample holders on lower and upper shaft



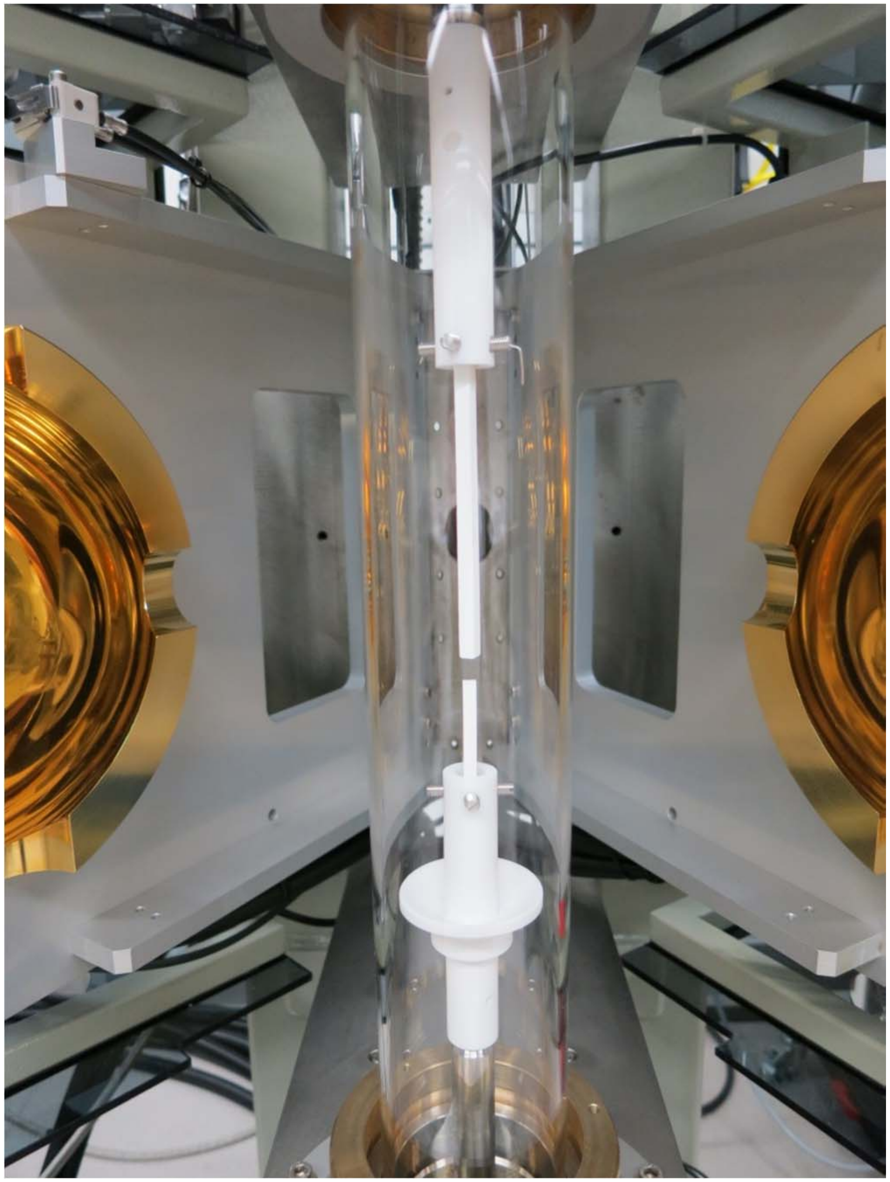
Lower and upper shaft, and thus the seed and feed rod, can be rotated and vertically moved by electric direct drives

Seed and feed rod inside quartz glass tube



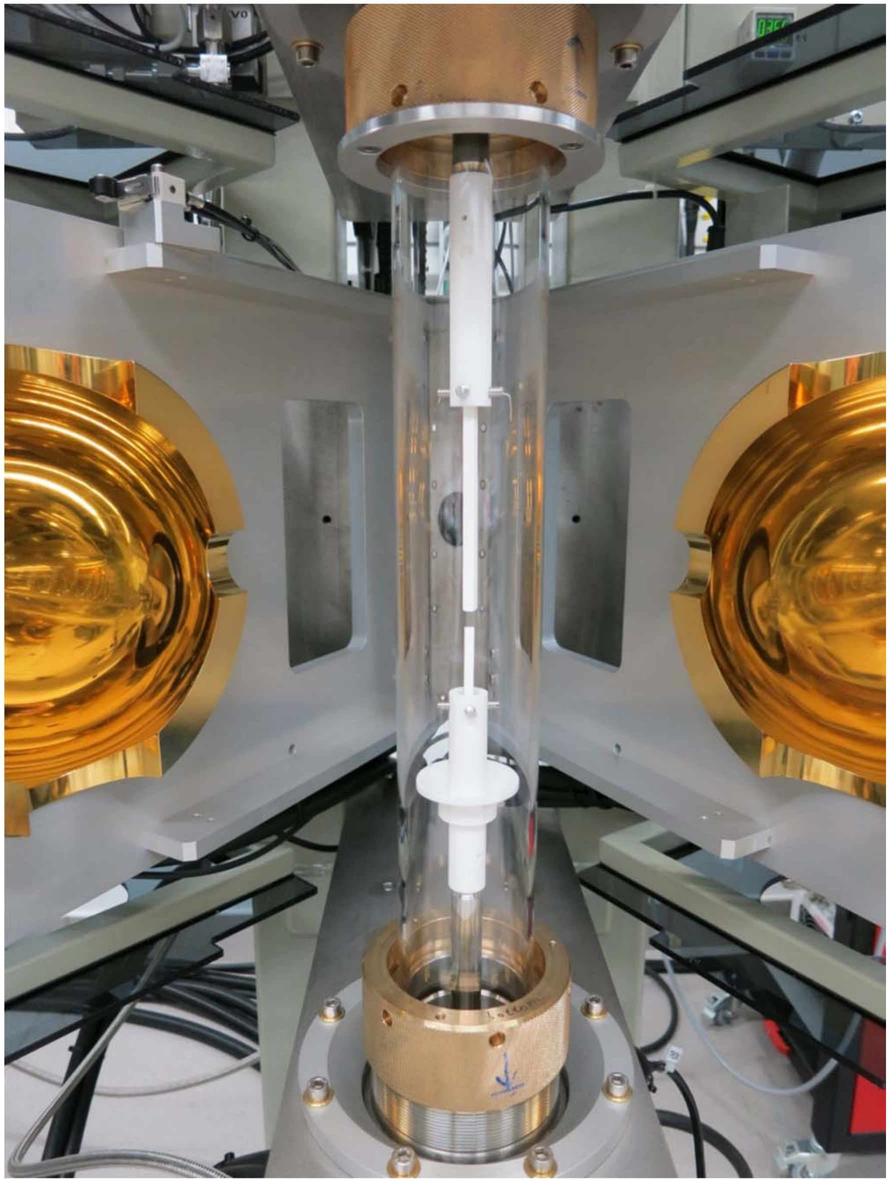
Lower and upper shaft, and thus the seed and feed rod, can be rotated and vertically moved by electric direct drives

Seed and feed rod inside quartz glass tube



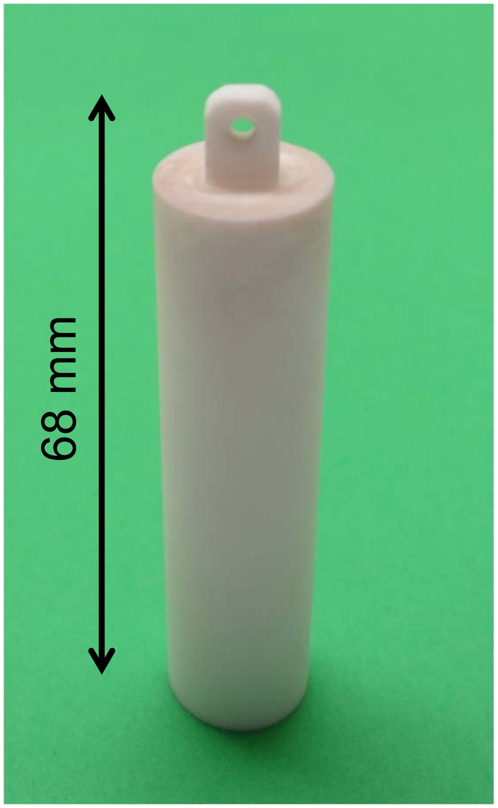
Lower and upper shaft, and thus the seed and feed rod, can be rotated and vertically moved by electric direct drives

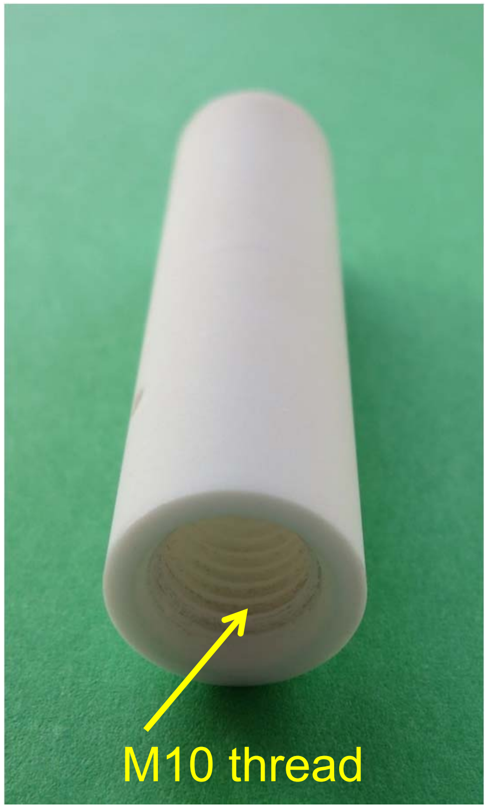
Seed and feed rod inside quartz glass tube

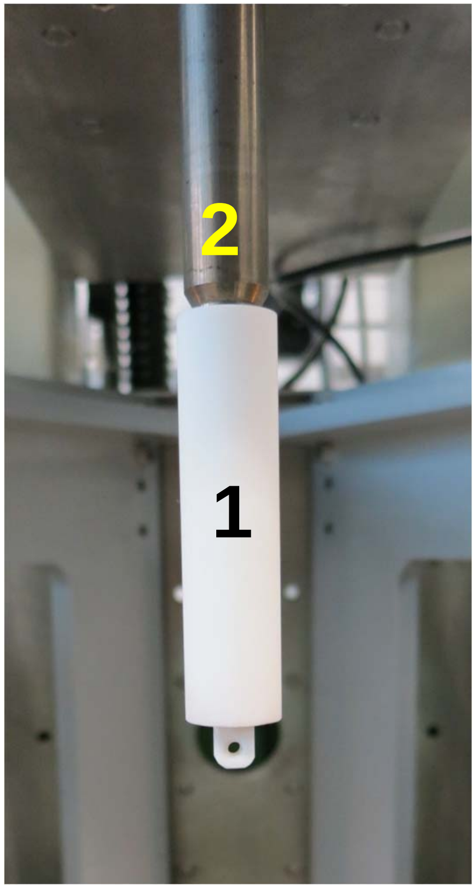


Lower and upper shaft, and thus the seed and feed rod, can be rotated and vertically moved by electric direct drives

Another sample holder construction for the feed rod







Made of Macor in the metal workshop of the Department of Materials of the ETH Zurich by C. Roth and M. Elsener

Sample holder (1) screwed on the upper shaft (2)

A feed rod can be fixed by means of the hole and a (platinum) wire

Part 2 - 4

Sample holders made of yttria stabilized zirconia for the feed rod and seed rod

Sample holders made of yttria stabilized zirconia

Motivation: The sample holders made of Macor, which are presented in the previous part, can be used up to 800 °C and temporary up to 1000 °C. However, if the melt-grown sample has a relatively high melting point, then these maximum operating temperatures are probably not sufficient. Therefore it is desirable to have sample holders which can withstand higher temperatures.

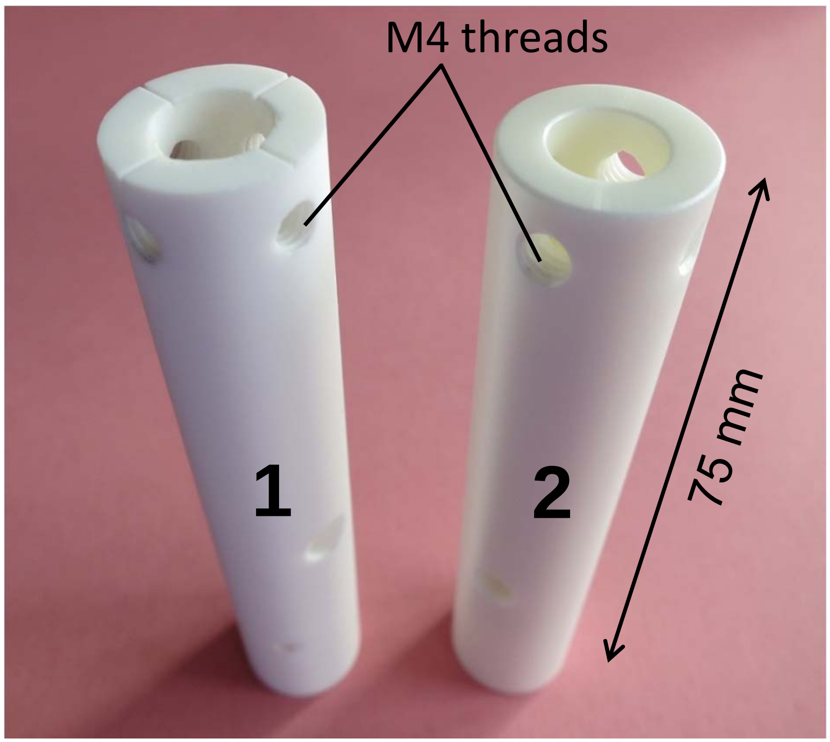
It was considered to produce sample holders made of technical ceramics like

- alumina, i.e. Al_2O_3
- yttria stabilized zirconia, i.e. $(ZrO_2)_{1-y}(\frac{1}{2}Y_2O_3)_y = Zr_{1-y}Y_yO_{2-0.5y}$

These materials can be used up to 1700 °C or 1500 °C. It was decided to use yttria stabilized zirconia because its thermal shock resistance is higher than that of alumina.

Sample holders made of yttria stabilized zirconia

Sample holders for the seed rod and feed rod were made of yttria stabilized zirconia. They are mechanically and chemically stable up to 1500 °C under various atmospheres.



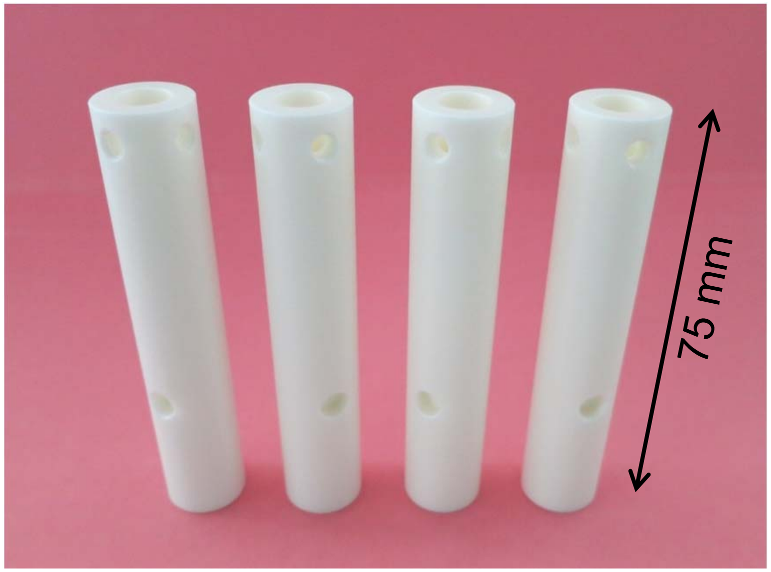
Two sample holders with nearly equal design and dimensions

1 Sample holder made of Macor (see also previous pages). Weight 31 g. Made in the metal workshop of the Department of Materials of the ETH Zurich

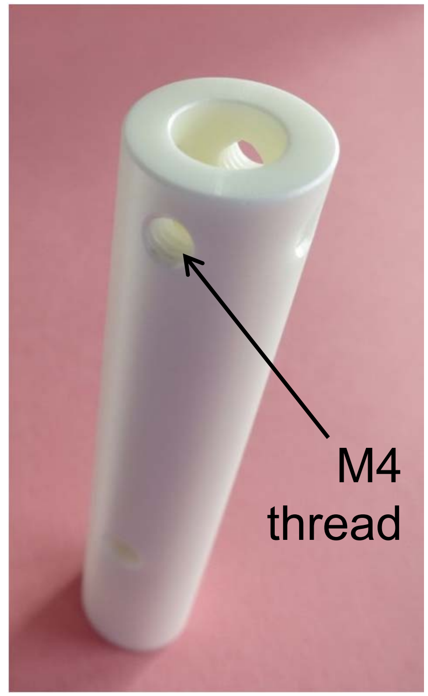
2 Sample holder made of yttria stabilized zirconia (FRIATEC DEGUSSIT FZY). Weight 68 g. Made by FRIATEC AG (Germany). Purchased and delivered from stone-ware gmbh (Switzerland)

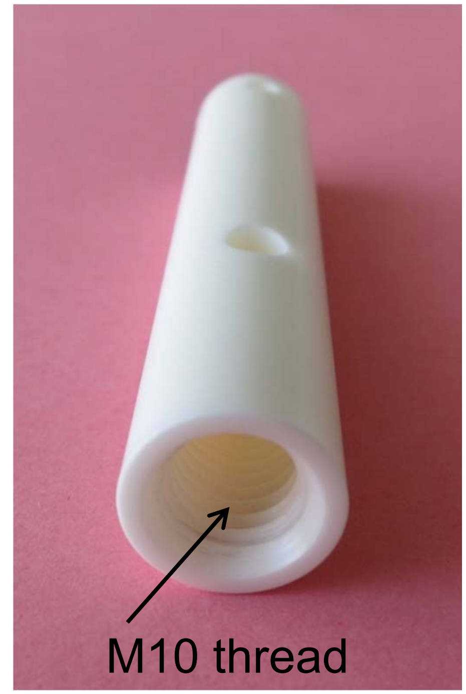
Sample holders made of yttria stabilized zirconia

Made of yttria stabilized zirconia (FRIATEC DEGUSSIT FZY) by FRIATEC AG (Germany) - purchased and delivered from stone-ware gmbh (Switzerland)



Four sample holders with nearly equal design and dimensions were produced, two for the seed rod and two for the feed rod

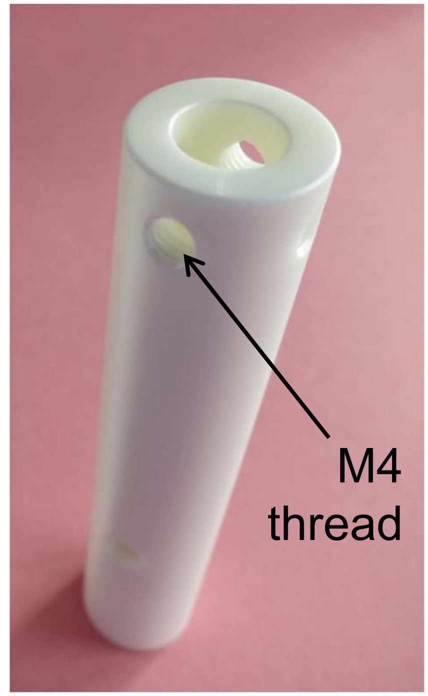




Before using or testing these sample holders it was necessary to solve an issue concerning the threads ...

Sample holders made of yttria stabilized zirconia – The M4 threads

Examples of custom-made M4 platinum-rhodium screws made of Pt-Rh 90-10 by Ögussa (Austria), purchased and delivered from stone-ware gmbh (Switzerland)

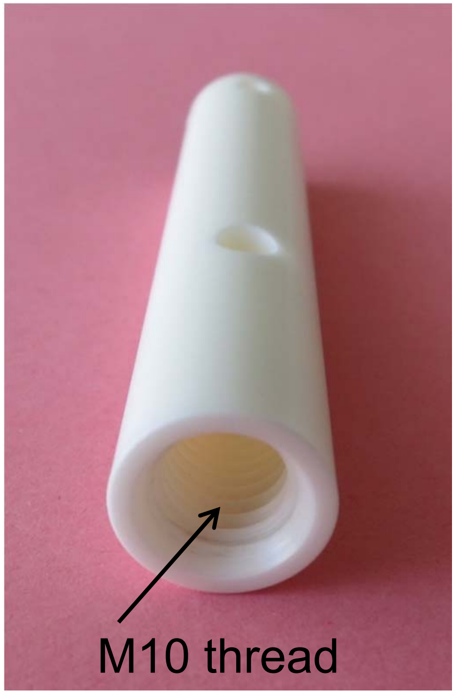


Sample holder made of yttria stabilized zirconia

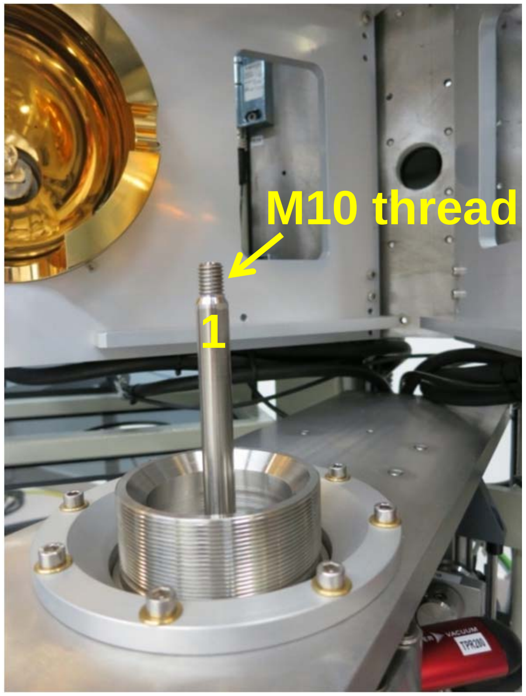
Sample holder with reworked M4 Pt-Rh screws

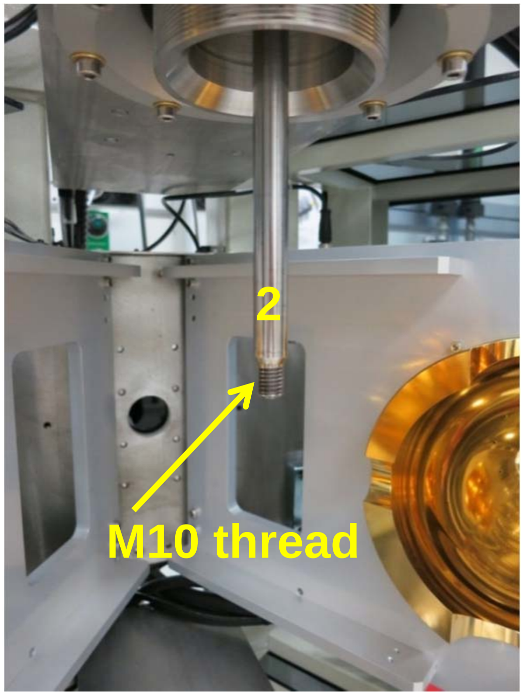
It was realized that the as-delivered M4 Pt-Rh screws did not fit into all M4 threads of the sample holders - just because a small deviation from the ideal thread or screw geometry may lead to a misfit. This issue was solved by M. Elsener from the metal workshop of the Department of Materials of the ETH Zurich by reworking the M4 platinum-rhodium screws with a tap an die.

Sample holders made of yttria stabilized zirconia – The M10 threads



Sample holder made of yttria stabilized zirconia

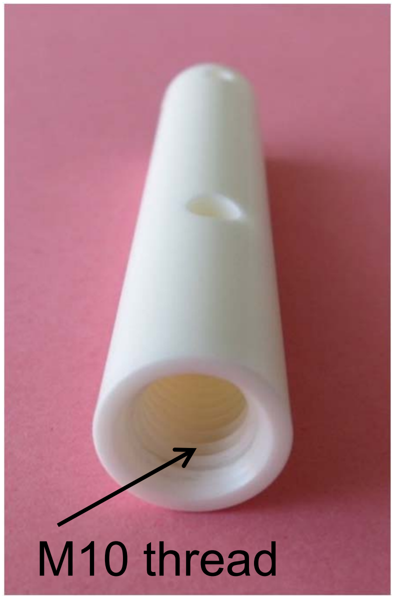




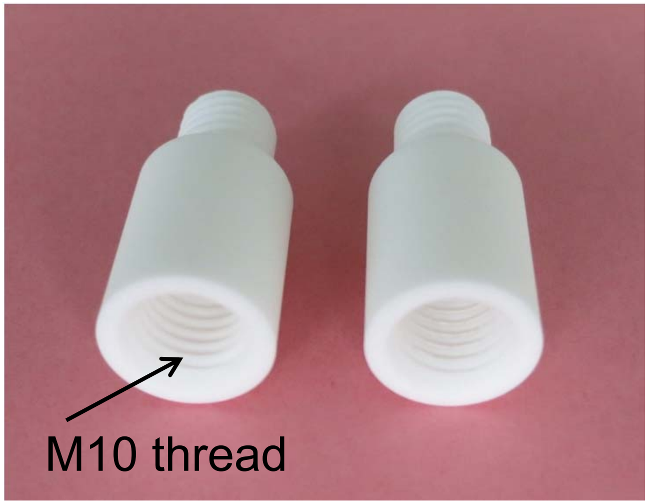
Lower shaft (1) and upper shaft (2) of the mirror furnace

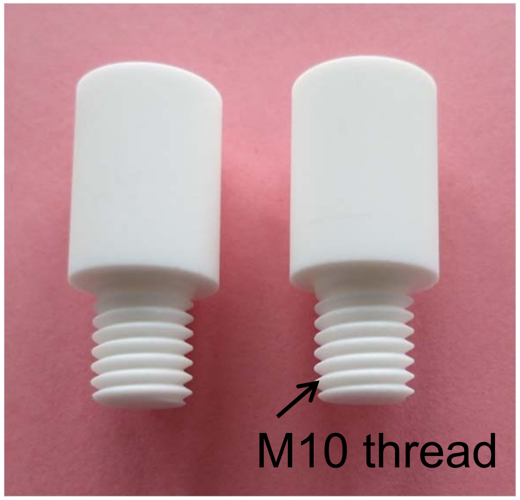
It was realized that not all sample holders can be screwed on the lower or upper shaft of the mirror furnace - just because a small deviation from the ideal thread geometry may lead to a misfit. This issue was solved in the following way ...

Sample holders made of yttria stabilized zirconia – The M10 threads



Sample holder made of yttria stabilized zirconia

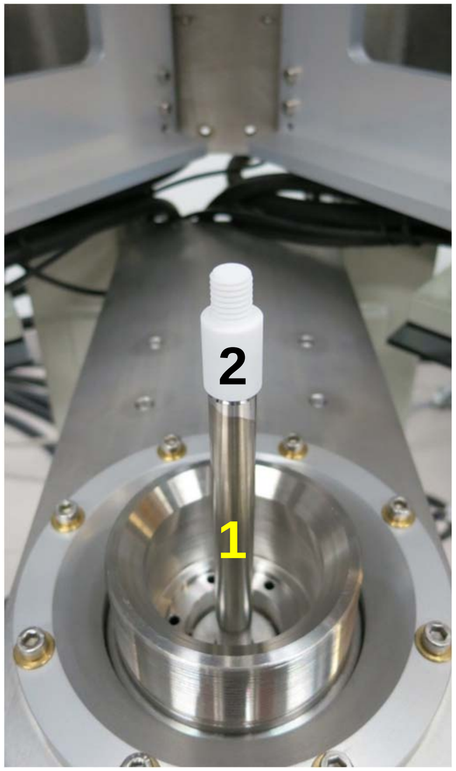




Two Interfaces made of Macor with an external and internal M10 thread

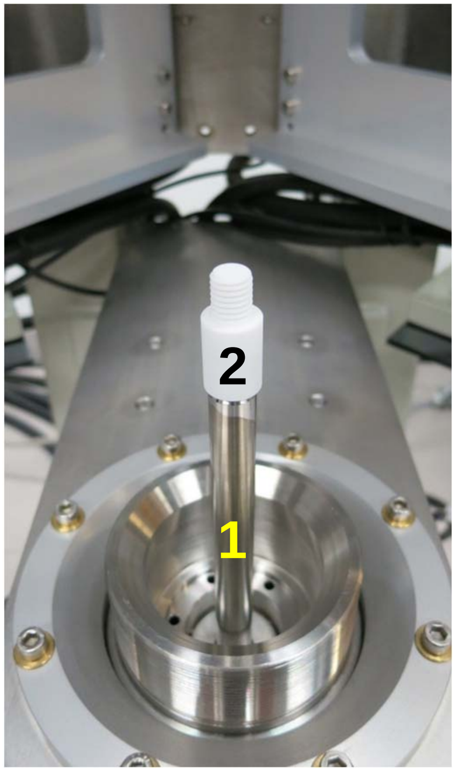
Two M10 interfaces made of Macor were produced by C. Roth and M. Elsener from the metal workshop of the Department of Materials of the ETH Zurich. The external M10 threads of the two Macor interfaces were prepared in such a way that they fit to the internal M10 threads of all sample holders made of yttria stabilized zirconia. Now the sample holders can be used in the following way ...

Sample holder made of yttria stabilized zirconia for the seed rod – 1 / 5

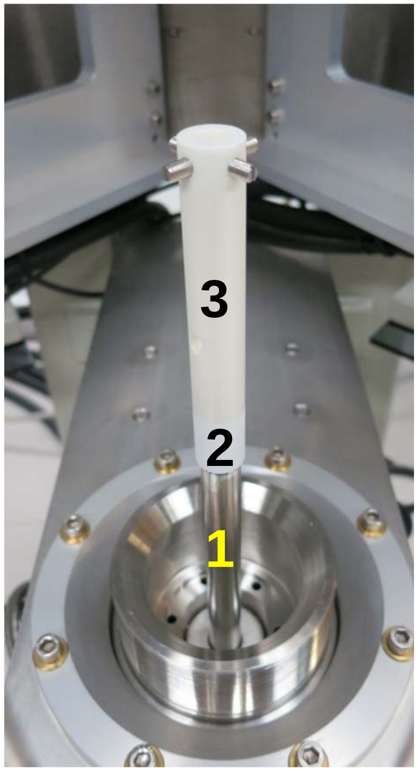


Interface made of Macor (2) screwed on the lower shaft (1)

Sample holder made of yttria stabilized zirconia for the seed rod – 2 / 5

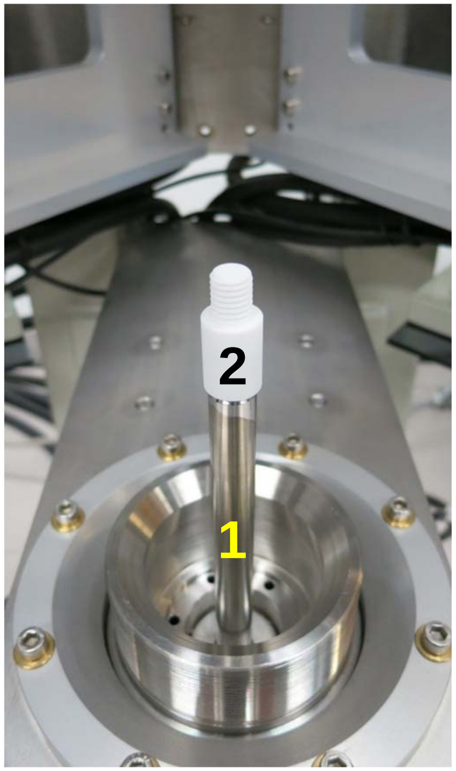


Interface made of Macor (2) screwed on the lower shaft (1)

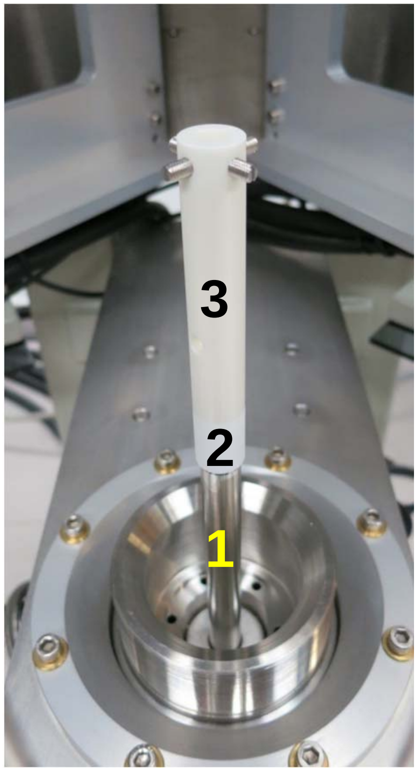


Sample holder made of yttria stabilized zirconia (3) screwed on the interface made of Macor (2)

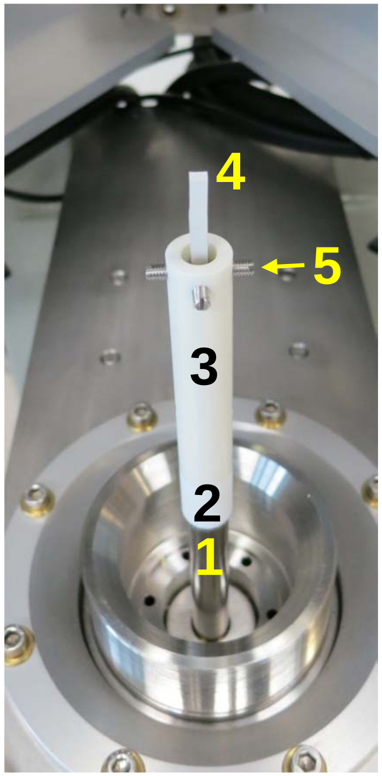
Sample holder made of yttria stabilized zirconia for the seed rod – 3 / 5



Interface made of Macor (2) screwed on the lower shaft (1)

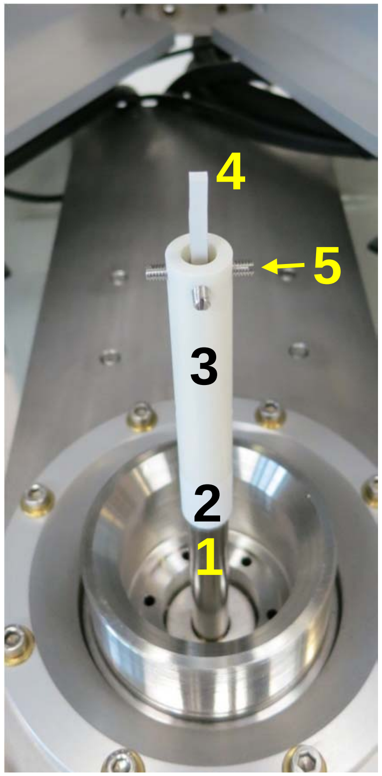


Sample holder made of yttria stabilized zirconia (3) screwed on the interface made of Macor (2)



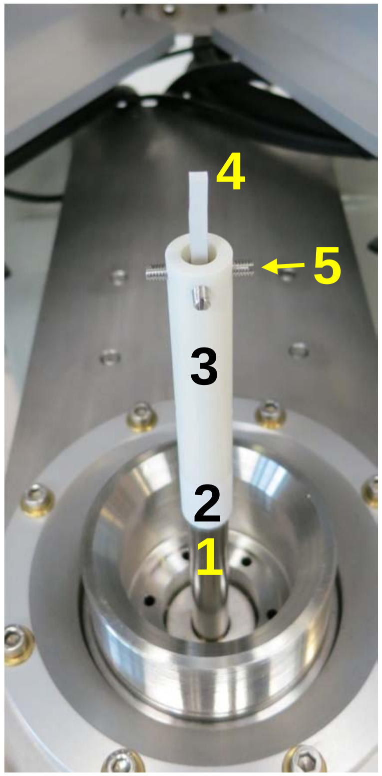
Seed rod (4) inserted and fixed and centered by platinum-rhodium screws (5)

Sample holder made of yttria stabilized zirconia for the seed rod – 4 / 5

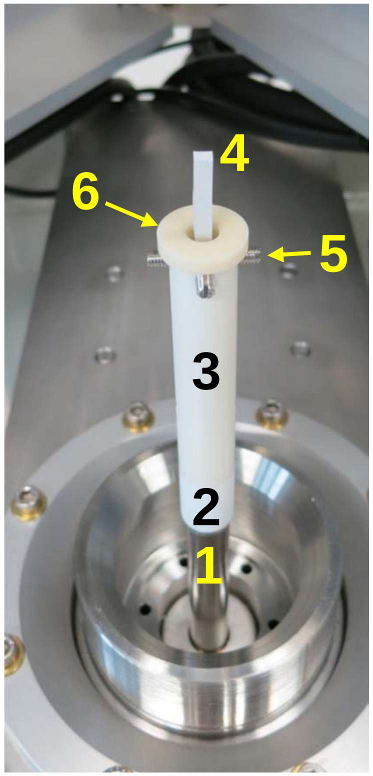


Seed rod (4) inserted and fixed and centered by platinum-rhodium screws (5)

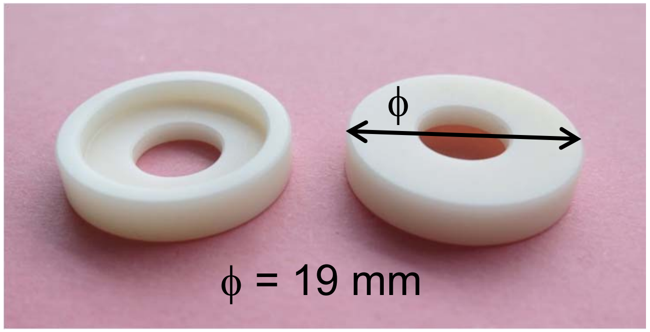
Sample holder made of yttria stabilized zirconia for the seed rod – 5 / 5



Seed rod (4) inserted and fixed and centered by platinum-rhodium screws (5)

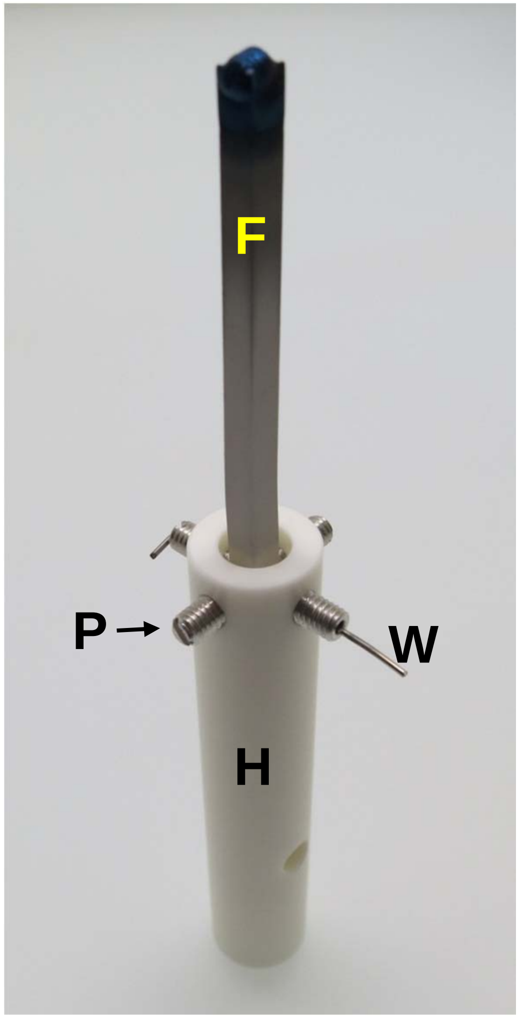


Lid made of alumina (6) put on the top of the sample holder. If molten material drops from above, then the lid may protect parts of the sample holder and the platinum-rhodium screws



Example of a custom-made lid made of alumina (FRIATEC DEGUSSIT AL23) by FRIATEC AG (Germany), purchased and delivered from stone-ware gmbh (Switzerland)

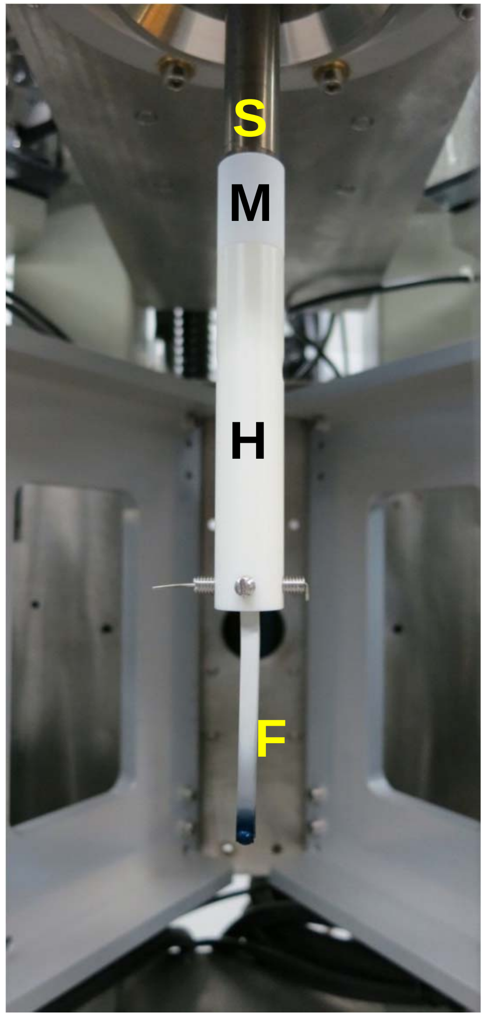
Sample holder made of yttria stabilized zirconia for the feed rod – 1 / 2



Sample holder (H) with inserted feed rod (F) which is fixed and centered by platinum-rhodium screws (P). When screwed on the upper shaft in an upside down orientation, then the platinum wire (W) ensures that the feed rod cannot come off. The platinum wire extends continuously through both platinum-rhodium screws and the feed rod. This is possible because the feed rod has a hole and both screws have an axial hole.

The feed rod in this example appears in black-blue and white color. It is the remaining part of a run where a white strontium niobium oxide (Nb^{5+}) was reduced under argon plus hydrogen which results in a black-blue material where the average Nb valence is smaller than 5+

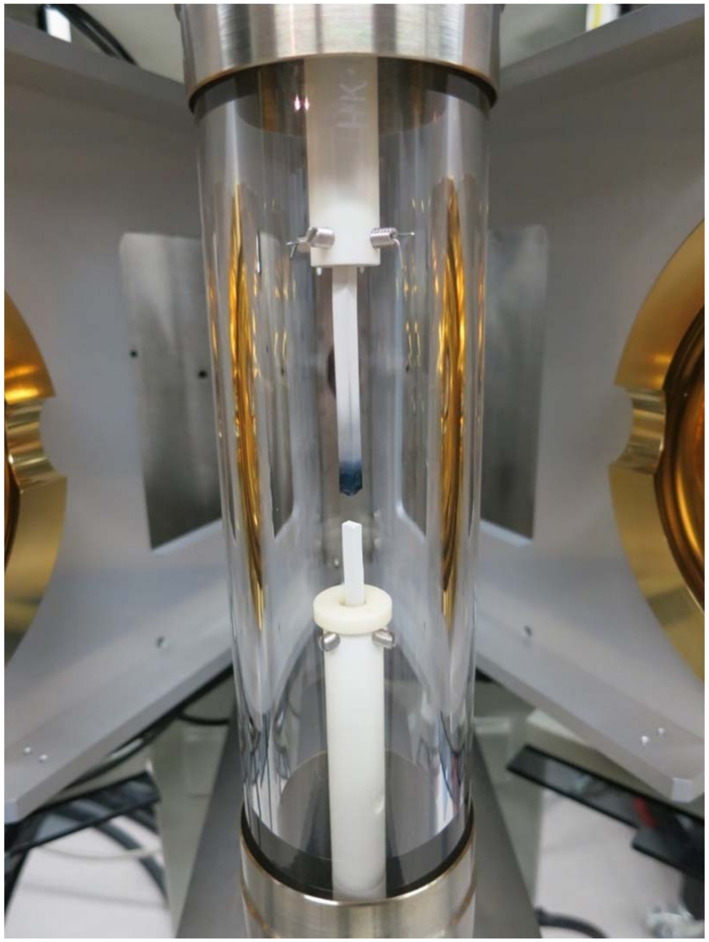
Sample holder made of yttria stabilized zirconia for the feed rod – 2 / 2

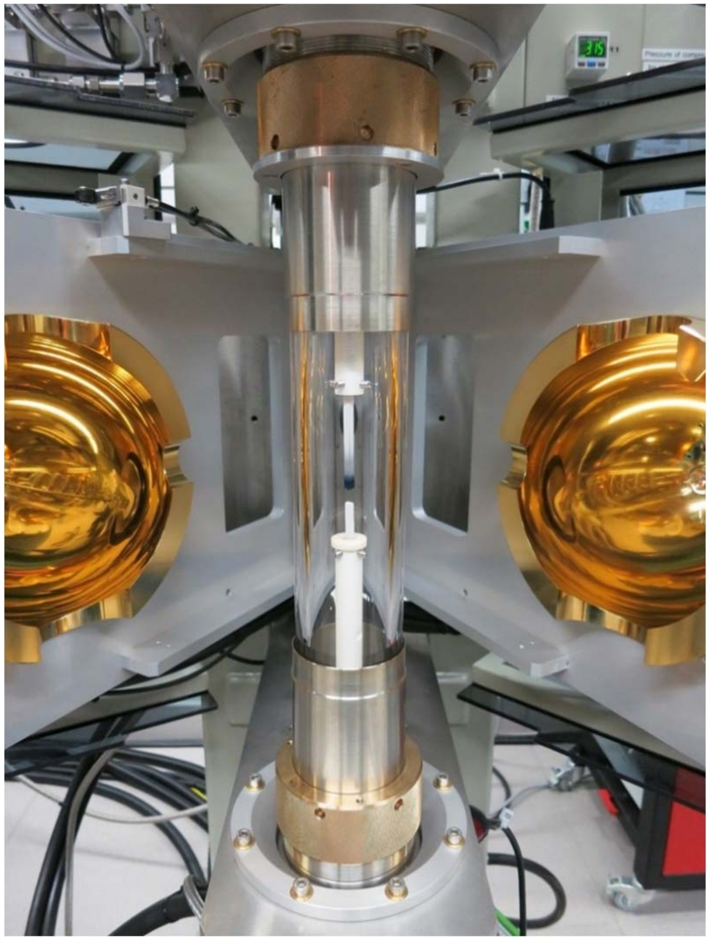


Sample holder (H) with feed rod (F) fixed at the upper shaft (S). The sample holder (H) is screwed on an interface made of Macor (M) which is screwed on the upper shaft (S)

The feed rod in this example appears in black-blue and white color. It is the remaining part of a run where a white strontium niobium oxide (Nb^{5+}) was reduced under argon plus hydrogen which results in a black-blue material where the average Nb valence is smaller than 5+

Sample holders made of yttria stabilized zirconia inside quartz glass tube





Sample holders with fixed and centered seed rod and feed rod inside a quartz glass tube which is appropriate for high gas pressures up to 10 bar

Part 2 - 5

Zirconia-related oxides as technical ceramics: Overview and examples

Zirconia-related oxides as technical ceramics

Yttria stabilized zirconia

$(ZrO_2)_{1-y}(\frac{1}{2}Y_2O_3)_y$
$= Zr_{1-y}Y_yO_{2-0.5y}$

$y \approx 16$ mole percent yttria
$\frac{1}{2}Y_2O_3$ stabilizes cubic phase. No high temperature phase transition

Oxygen ion conductor at elevated temperatures

FRIATEC DEGUSSIT FZY (zirconia partially stabilized with yttria): Usable up to 1500 °C. Bending strength σ_m (DIN EN 843-1) ≈ 400 MPa. High temperature and corrosion resistance

Zirconia ZrO_2

monoclinic
⇳ ≈ 1150 °C
tetragonal
⇳ ≈ 2350 °C
cubic (fluorite type)

Not suitable for high temperature applications because of phase transition(s) at elevated temperatures

Magnesia stabilized zirconia

$(ZrO_2)_{1-y}(MgO)_y$
$= Zr_{1-y}Mg_yO_{2-y}$

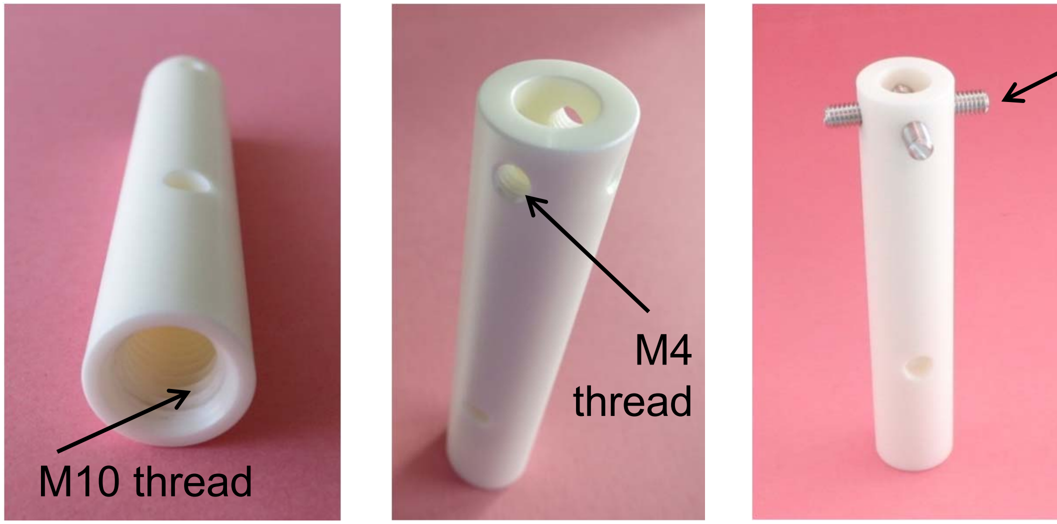
$y \approx 16$ mole percent magnesia
MgO stabilizes cubic phase

FRIATEC FRIALIT FZM (zirconia partially stabilized with magnesia): Usable up to 900 °C. Bending strength σ_m (DIN EN 843-1) ≈ 500 MPa

Valences: Mg^{2+} Y^{3+} Zr^{4+}

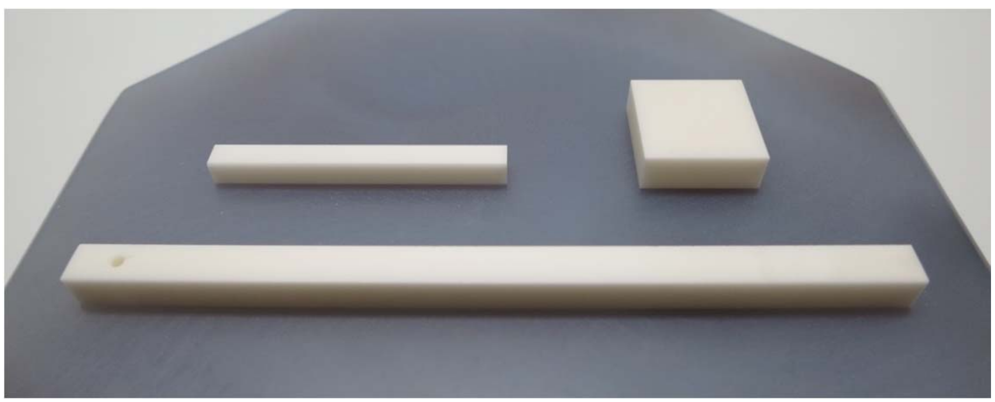
Partially stabilized zirconia contains smaller amounts of additions and consists of two or three of the phases cubic, tetragonal, and monoclinic

Components made of yttria stabilized zirconia



Custom-made sample holder for the mirror furnace (see part 2 - 4). Made of FRIATEC DEGUSSIT FZY

Mortar and pestle (see part 9)



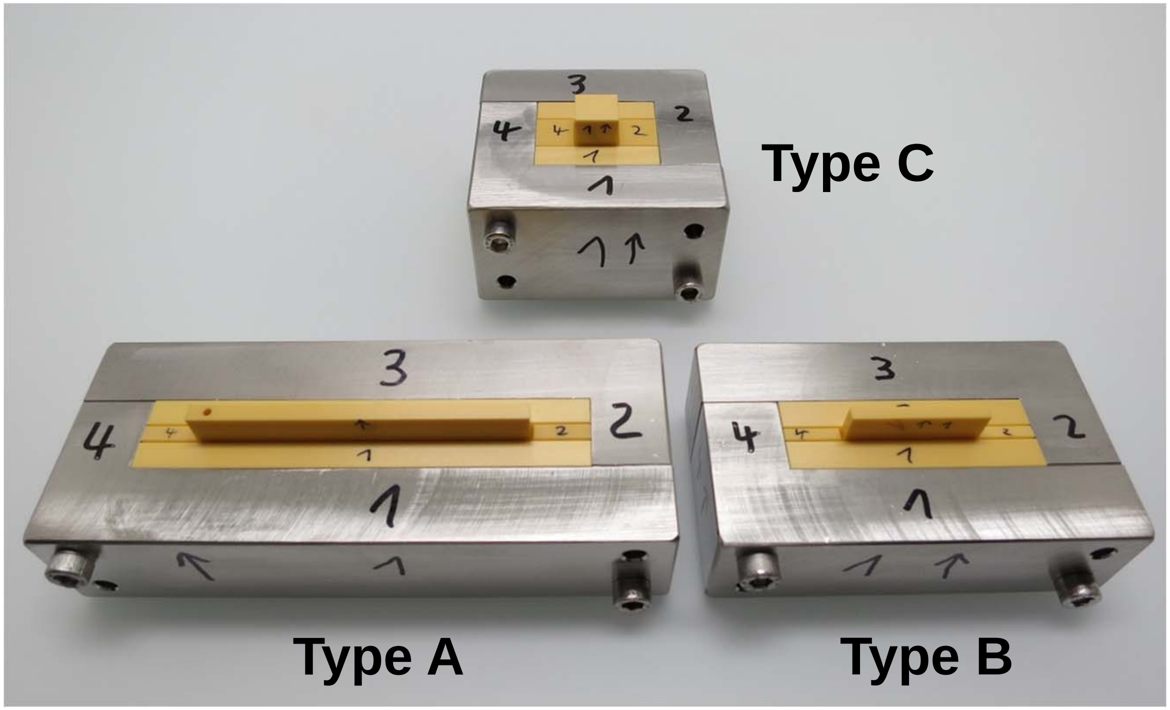
Custom-made lower punches for pressing dies and sintering of pressed powder (see part 5). Made of FRIATEC DEGUSSIT FZY

Yttria stabilized zirconia – Further examples

Oxygen analyzer ZIROX SGM7 which uses a solid electrolyte cell made of yttria stabilized zirconia (operating temperature 750 °C). It is used to measure the oxygen content of argon at the mirror and tube furnace (see part 2 - 1, 3, and 8)

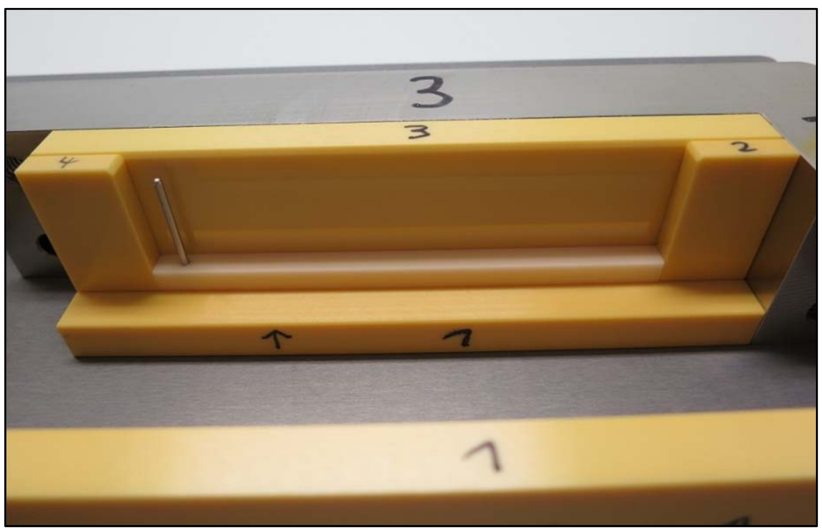
Crystalline yttria stabilized zirconia (cubic) with 20 weight-percent yttria. Grown in USA by a solidification from the melt by the so-called skull melting technique. A gift from L. J. Gauckler in 2011

Components made of magnesia stabilized zirconia



Custom-made pressing dies (see part 5). Yellow parts made of magnesia stabilized zirconia FRIATEC FRIALIT FZM

Type A with rectangular punch for rods with length 85 mm and width 4,5 mm. Type B with rectangular punch for rods with length 35 mm and width 3,5 mm. Type C with square punch for samples with length 14 mm and width 14 mm



Pressing die type A partly disassembled (see part 5). Yellow parts made of magnesia stabilized zirconia FRIATEC FRIALIT FZM

Part 2 - 6

An improved suspension and centering for the feed rod

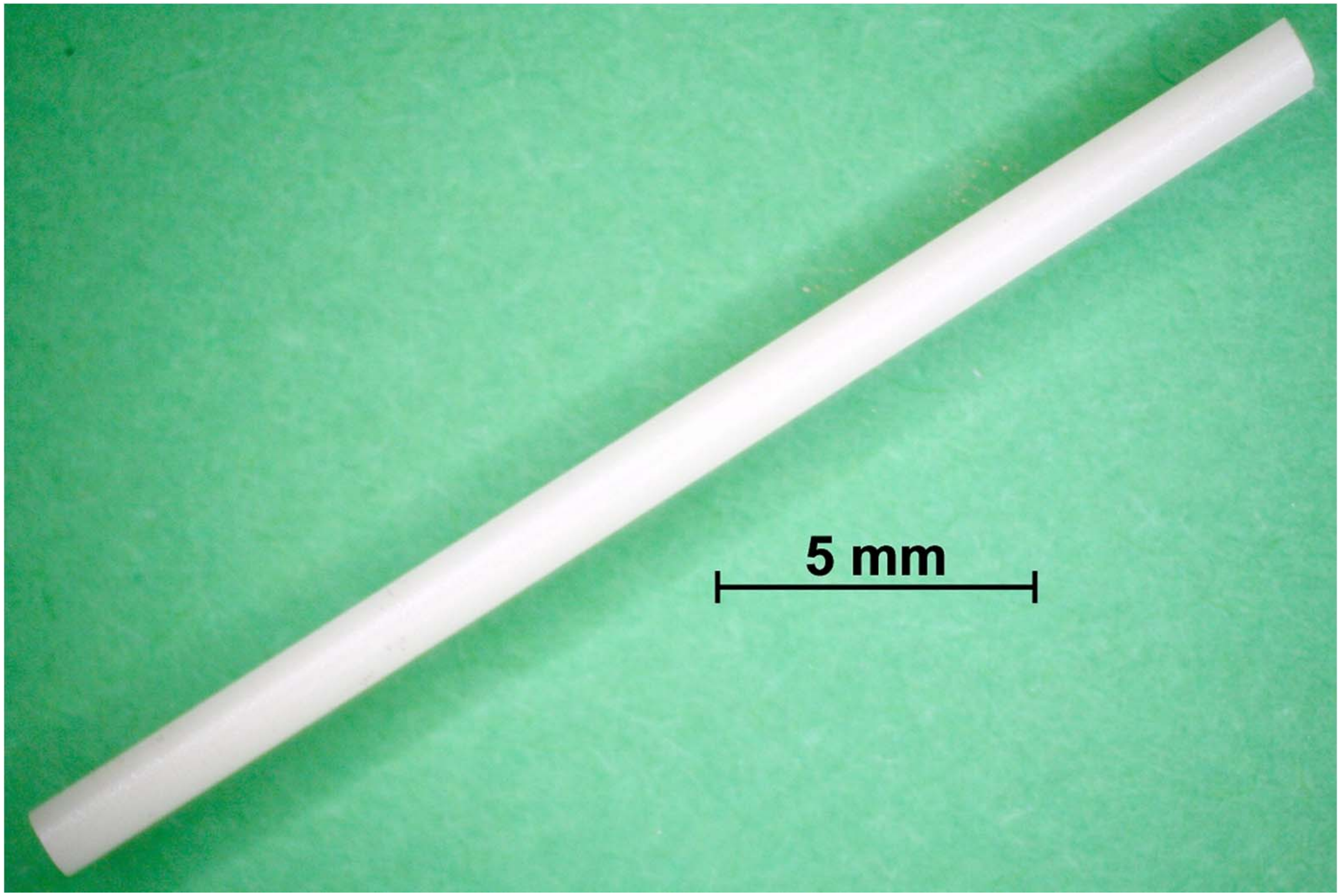
An improved suspension and centering for the feed rod – 1 / 6

As the feed rod was fixed and centered in the sample holder and then screwed on the upper shaft, then it was often observed that the feed rod was tilted with respect to the upper shaft. This tilting was caused by irregularities of the platinum wire that extends continuously through the feed rod and the platinum-rhodium screws.

The platinum wire can be replaced by an alumina pin with a diameter of 1 mm (the diameter of the continuous hole in the feed rod is about 1,3 mm). The alumina pin is quite straight and does therefore not lead to a tilting of the feed rod.
The following slides describe this concept ...

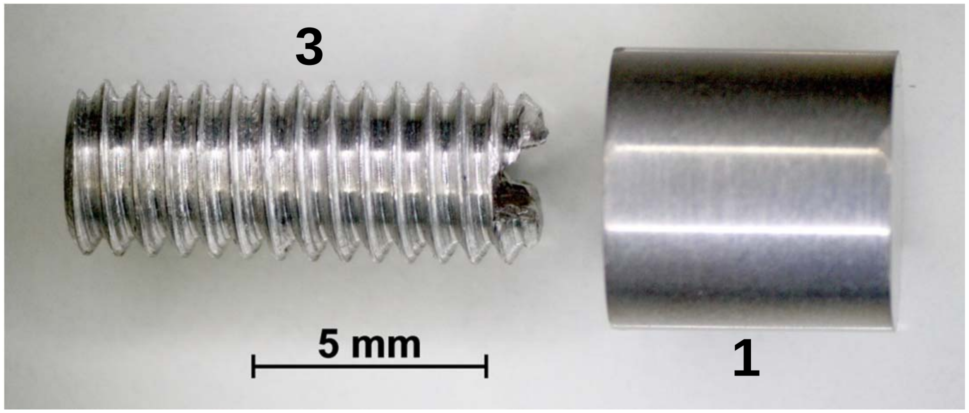
An improved suspension and centering for the feed rod – 2 / 6

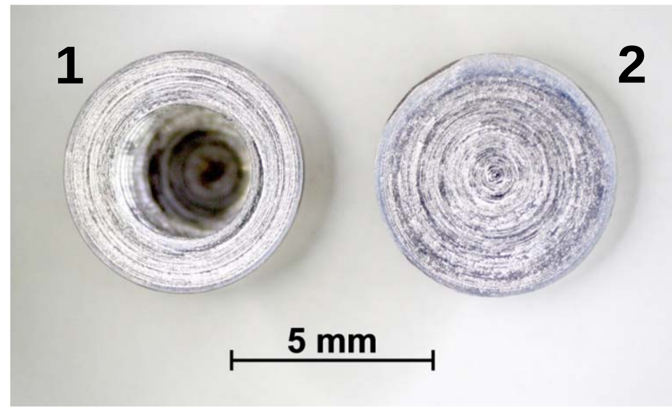
Pin made of alumina (FRIATEC DEGUSSIT AL23) by FRIATEC AG (Germany), purchased and delivered from stone-ware gmbh (Switzerland). The diameter of this alumina pin is 1 mm. It was broken off manually from a longer piece

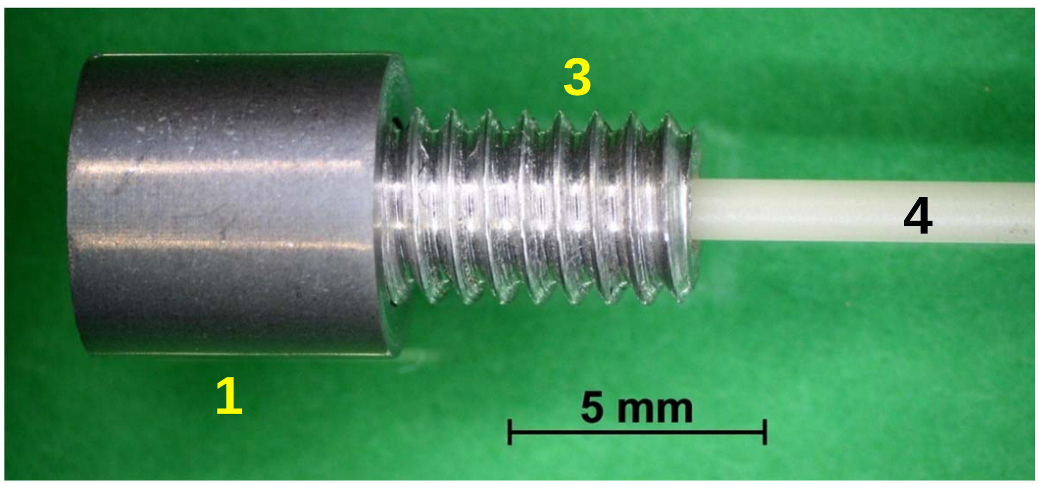


An improved suspension and centering for the feed rod – 3 / 6

Two custom-made Pt-Rh sleeves (1) (2) made of Pt-Rh 90-10 by Ögussa (Austria), purchased and delivered from stone-ware gmbh (Switzerland). The sleeves are 6 mm long and have inside a 5 mm long M4 type thread



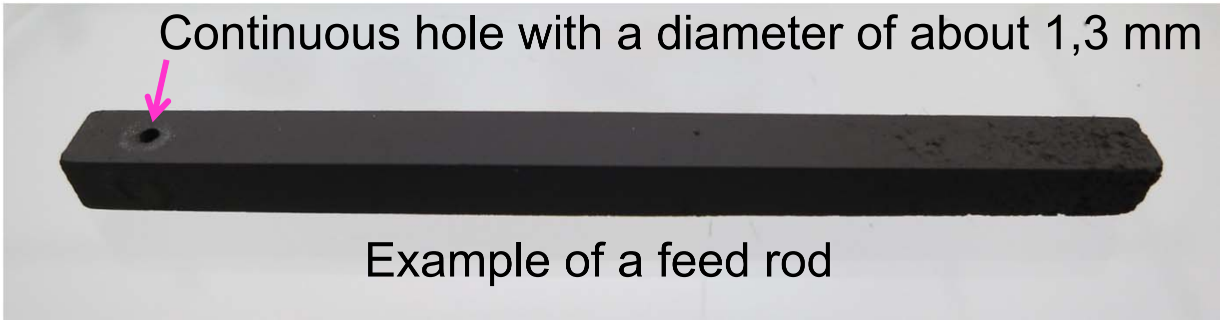


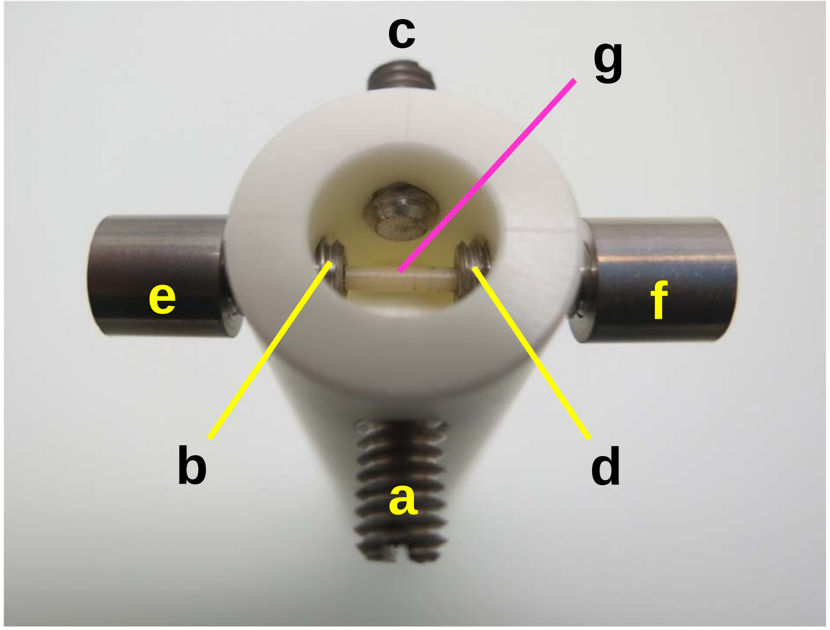


Finger-tight screwed: A Pt-Rh sleeve (1) and a M4 type Pt-Rh screw (3) with a continuous axial hole. An alumina pin (4), see previous page, is inserted into the axial hole of the Pt-Rh screw

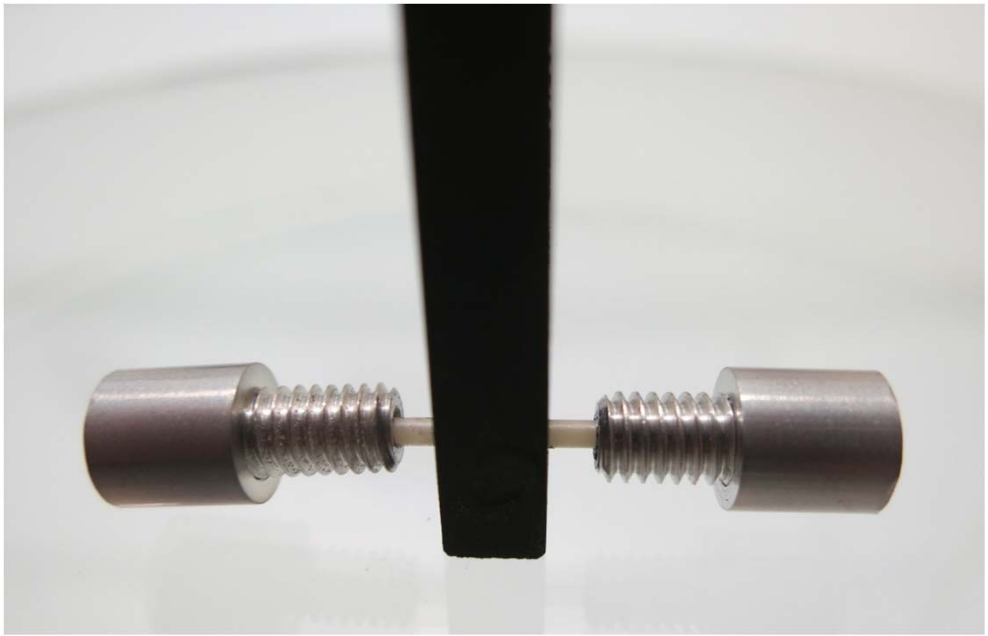
An improved suspension and centering for the feed rod – 4 / 6

These pictures indicate the concept





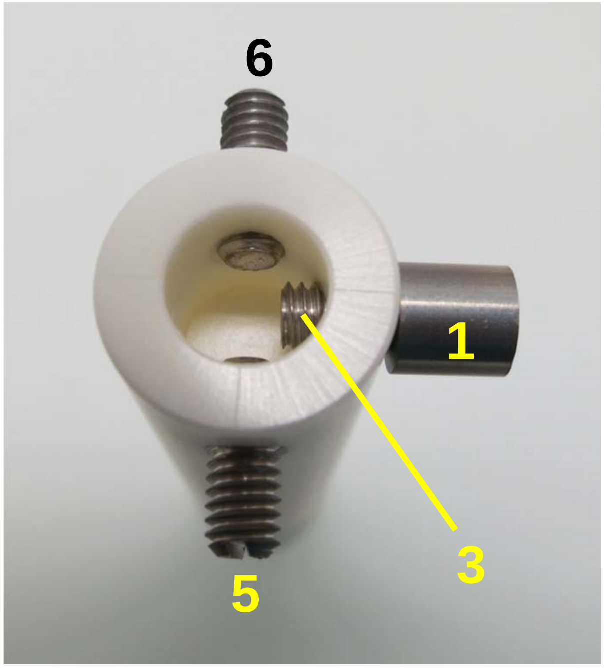
Top view of a sample holder made of yttria stabilized zirconia. Equipped with four Pt-Rh screws (a, b, c, d), two Pt-Rh sleeves (e, f), and an alumina pin (g)

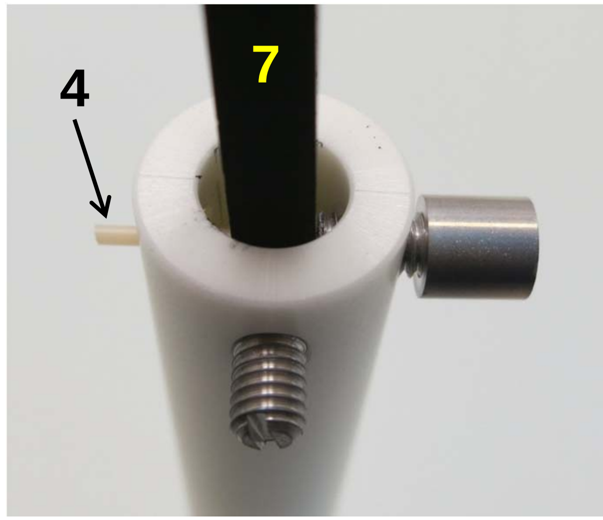


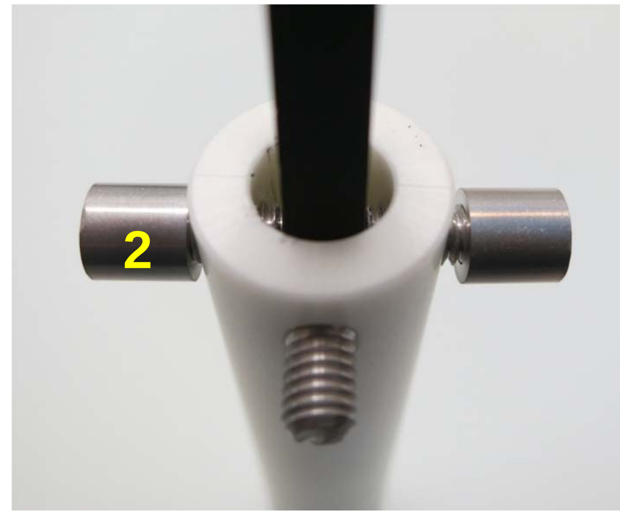
Alumina pin (diameter 1 mm) extends continuously through the feed rod. Both ends of the alumina pin are inserted into the axial hole of the Pt-Rh screws on which the Pt-Rh sleeves are screwed

An improved suspension and centering for the feed rod – 5 / 6

These pictures show the assembling





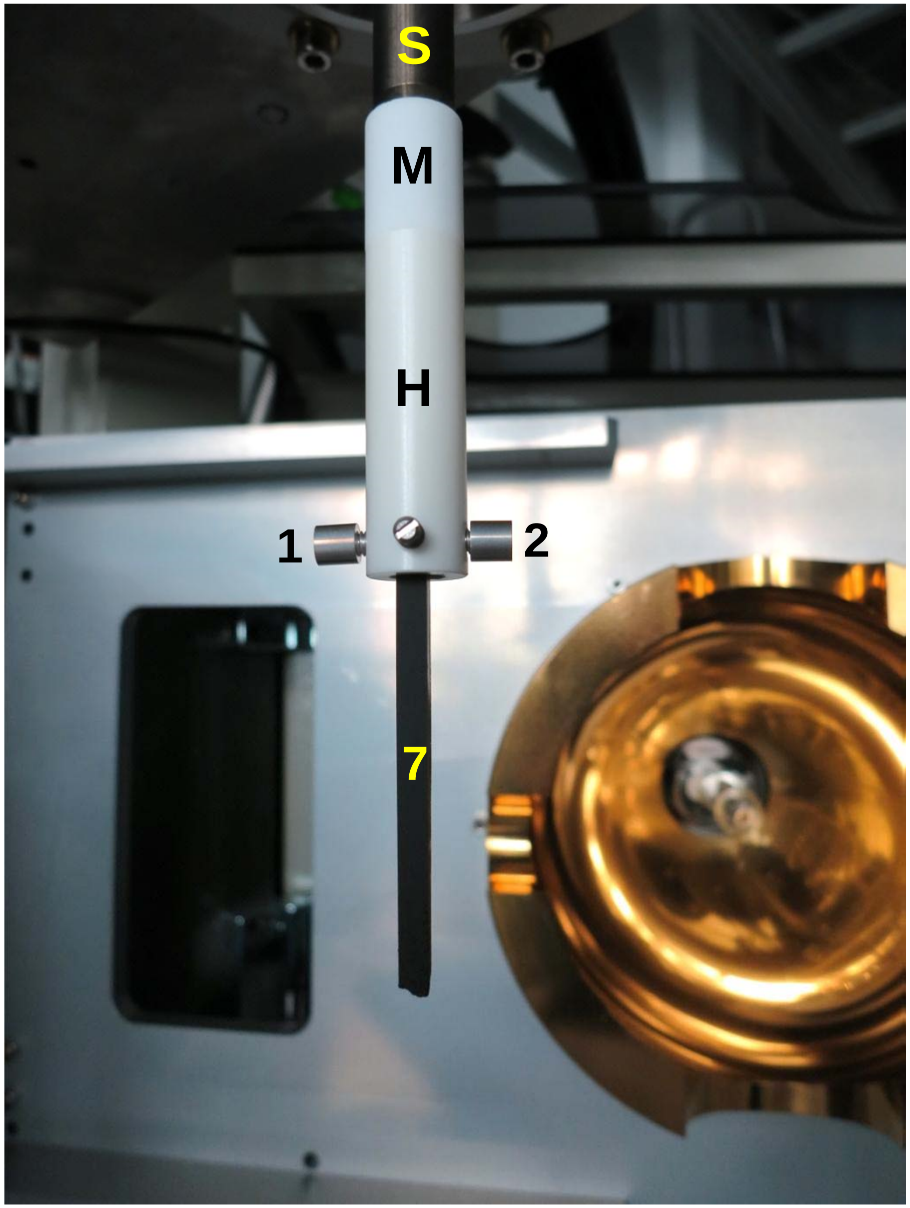


Top view of a sample holder made of yttria stabilized zirconia. Equipped with a Pt-Rh screw (3) on which a Pt-Rh sleeve (1) is screwed, and another Pt-Rh screws (5) (6)

A feed rod (7) is inserted into the sample holder. An alumina pin (4) is inserted through the feed rod and into the axial hole of the Pt-Rh screw (3)

Another Pt-Rh screw with an axial hole, on which another Pt-Rh sleeve (2) is screwed, is screwed into the left M4 type thread of the sample holder. This design prevents a dropping out of the alumina pin

An improved suspension and centering for the feed rod – 6 / 6



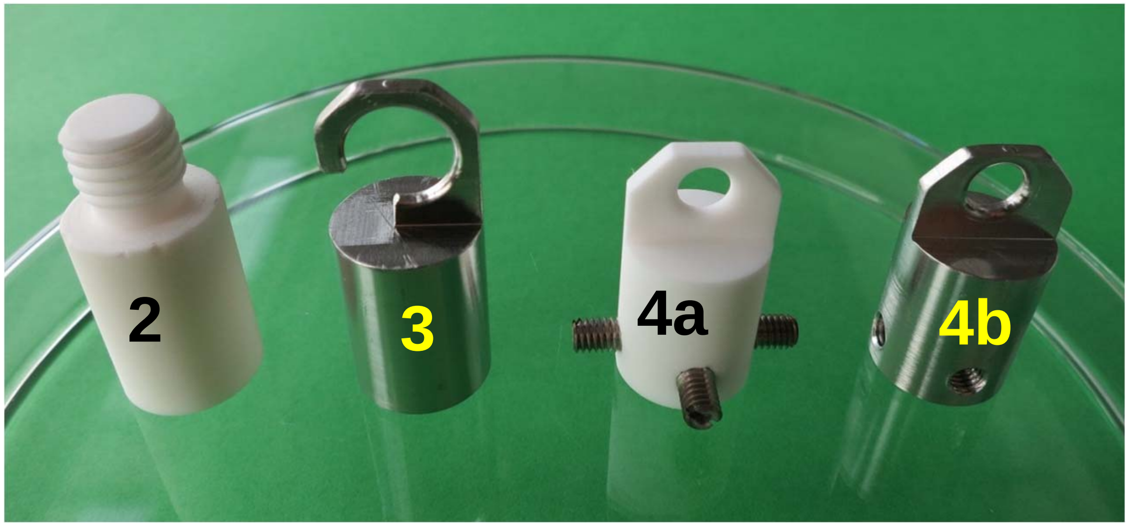
The sample holder (H), made of yttria stabilized zirconia, and the feed rod (7) are fixed and centered at the upper shaft (S). The sample holder (H) is screwed on an interface made of Macor (M) which is screwed on the upper shaft (S). Now the feed rod (7) rests via its continuous hole on the straight alumina pin. That favors a centered, non-tilted alignment of the feed rod (7). The Pt-Rh sleeves (1) (2) prevent a dropping out of the alumina pin.

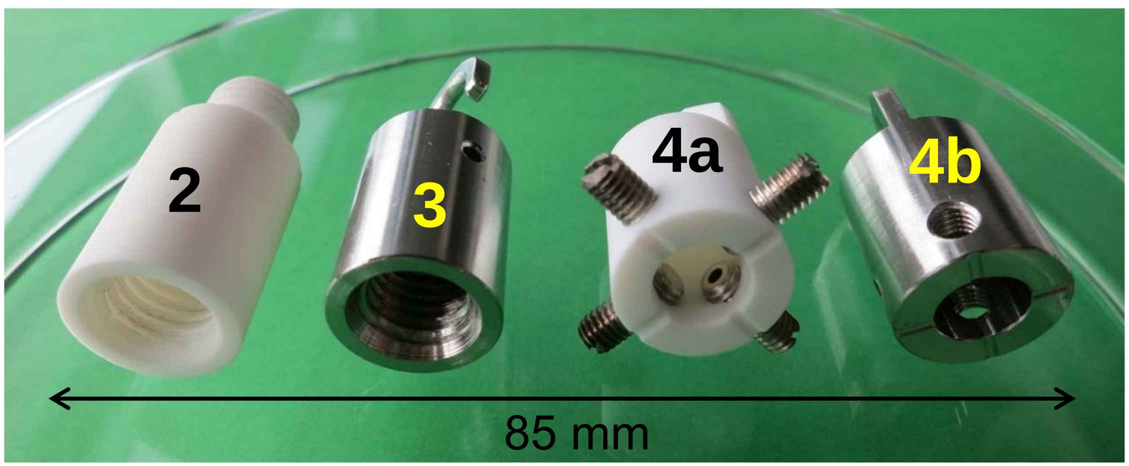
If it is desirable to have a somewhat movable feed rod, then one can tighten the four M4 type Pt-Rh screws not completely so that the feed rod can slightly move and swing

Part 2 - 7

Freely swinging sample holders for the feed rod

Single components for a freely swinging sample holder for the feed rod





2 Interface made of Macor with an external and internal M10 thread

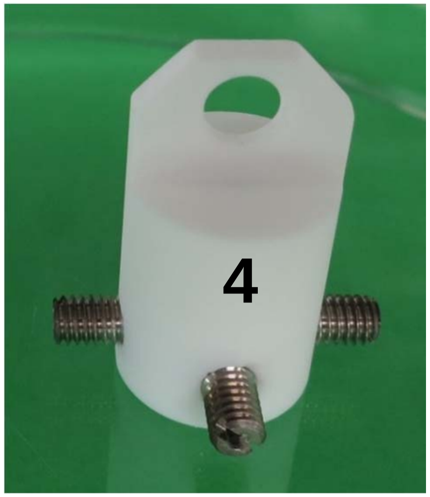
3 Component made of high temperature stainless steel with a hook and an internal M10 thread

4a Sample holder made of Macor for the feed rod, equipped with four M4 type platinum-rhodium screws

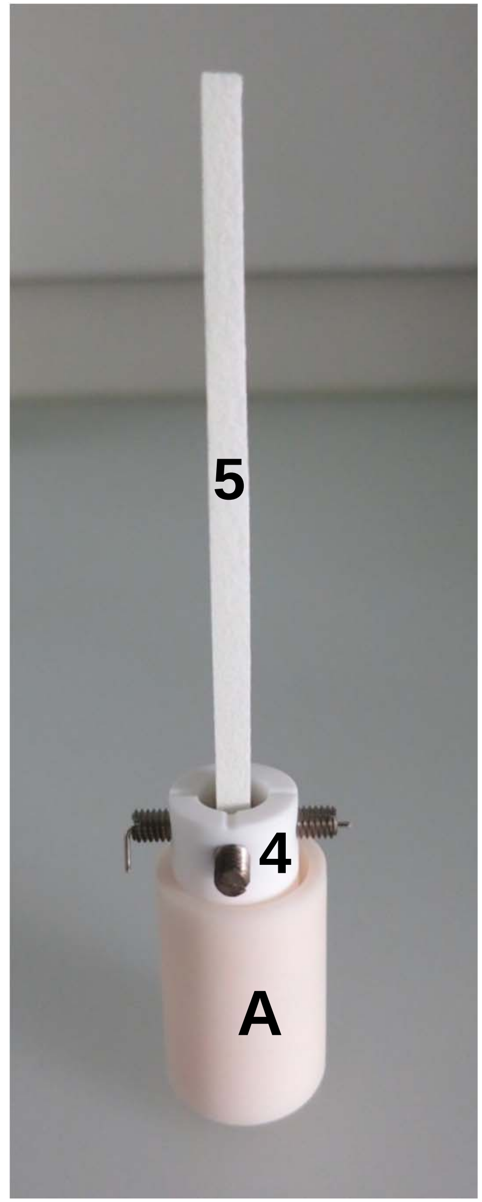
4b Sample holder made of high temperature stainless steel for the feed rod

All parts, except the four platinum-rhodium screws, were made in the metal workshop of the Department of Materials of the ETH Zurich by C. Roth and M. Elsener

A freely swinging sample holder for the feed rod – How it works 1 / 4



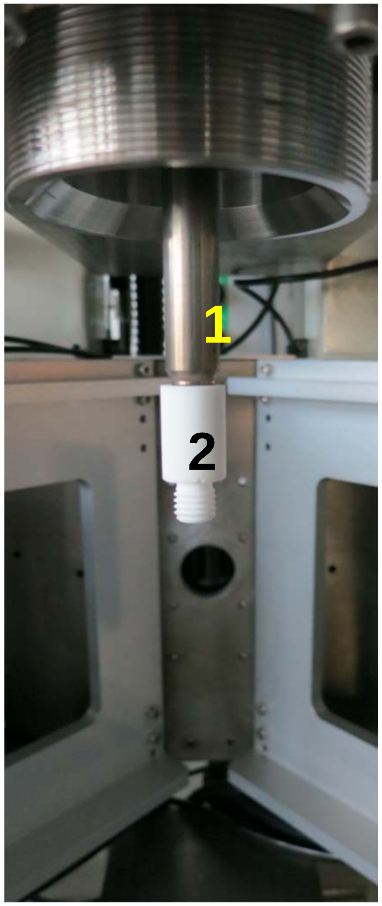
Sample holder made of Macor (4) for the feed rod, equipped with four M4 type platinum-rhodium screws



Feed rod (5) inserted, centered and fixed in the sample holder made of Macor (4)

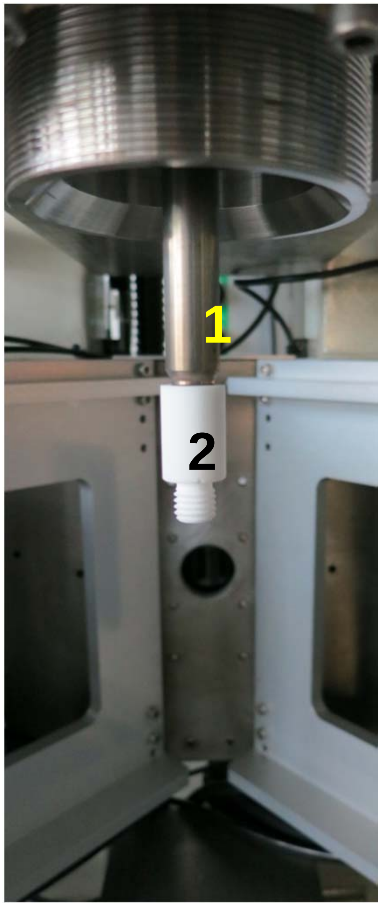
The sample holder (4) stands upside in an alumina crucible (A)

A freely swinging sample holder for the feed rod – How it works 2 / 4

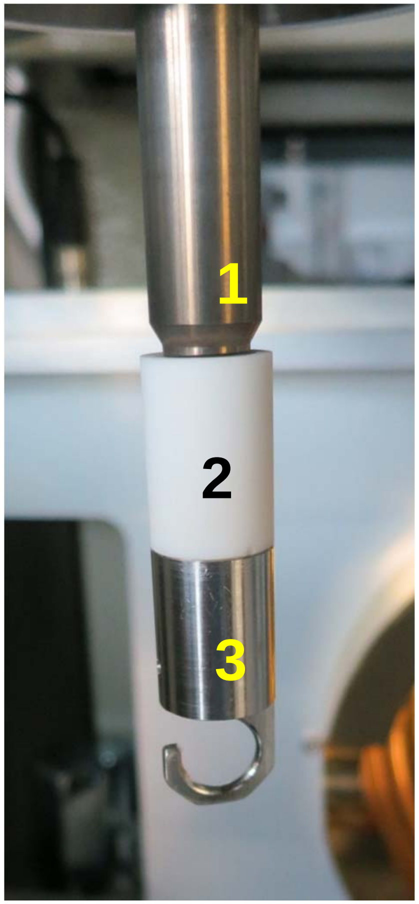


Interface made of
Macor (2) screwed
on the upper shaft (1)

A freely swinging sample holder for the feed rod – How it works 3 / 4

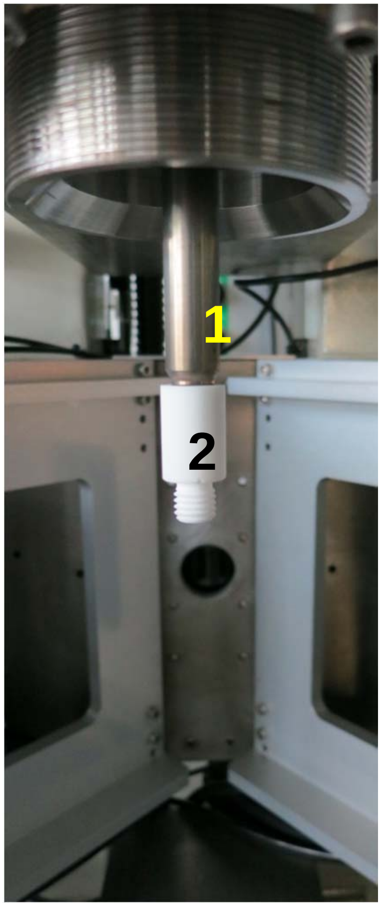


Interface made of Macor (2) screwed on the upper shaft (1)

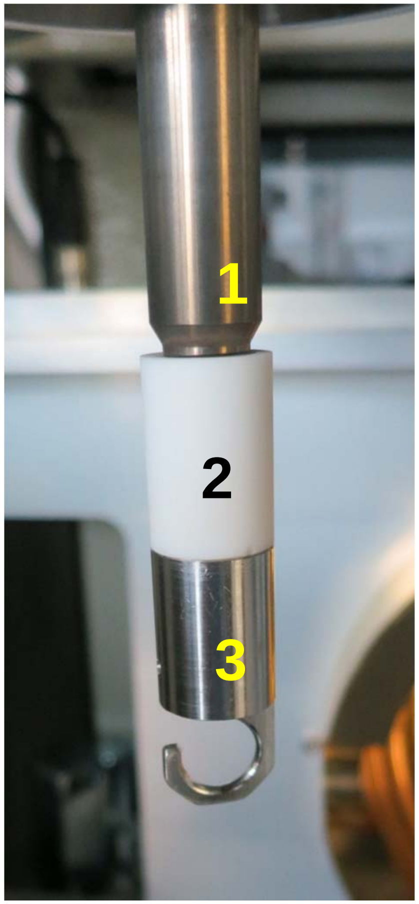


Component with hook (3) screwed on the interface made of Macor (2)

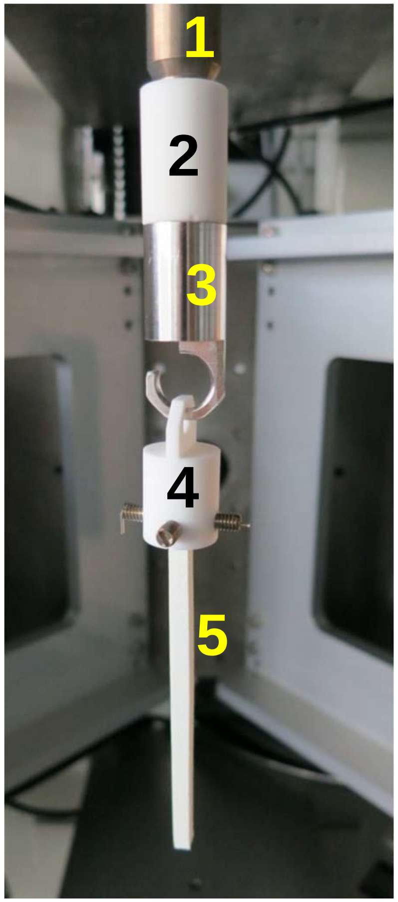
A freely swinging sample holder for the feed rod – How it works 4 / 4



Interface made of Macor (2) screwed on the upper shaft (1)

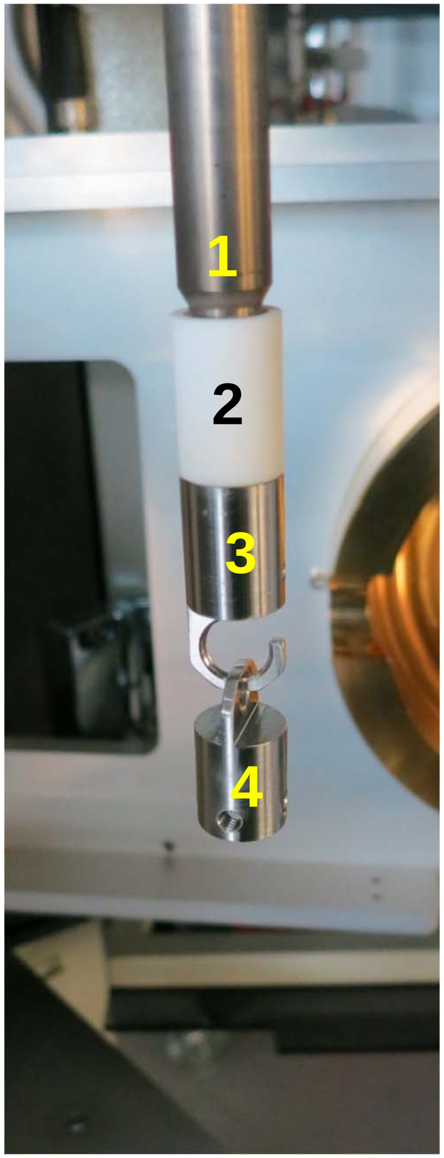


Component with hook (3) screwed on the interface made of Macor (2)



Sample holder made of Macor (4) with fixed feed rod (5) suspended at the component with hook (3)

Another freely swinging sample holder for the feed rod   1 / 2

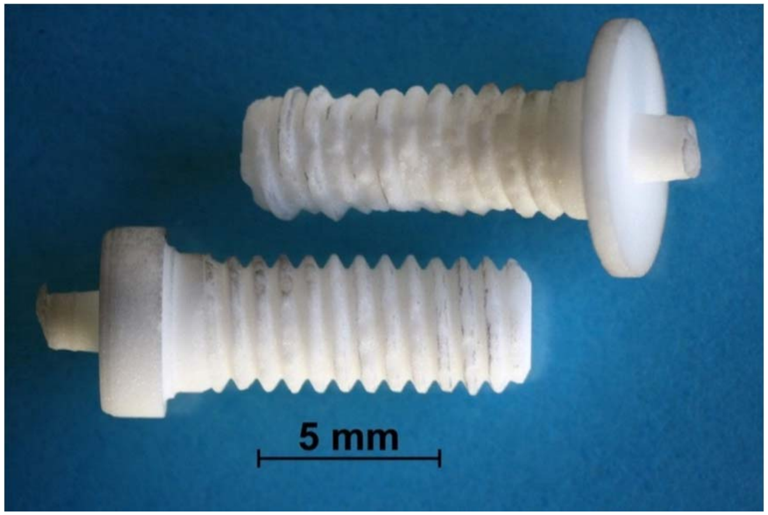


Similar assembly as that which is shown on the previous page but now the sample holder (4) is made of a high temperature stainless steel

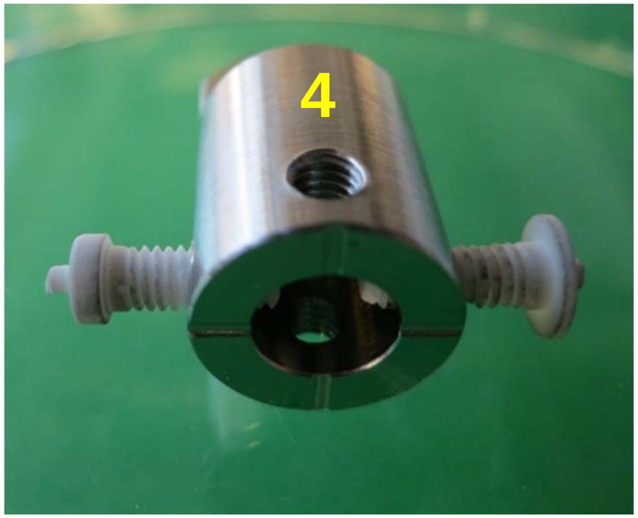
Here the sample holder (4) is shown without feed rod

Another freely swinging sample holder for the feed rod 2 / 2

For the sample holder made of stainless steel it was attempted to produce M4 type screws made of Macor, two with a continuous axial hole and two without an axial hole. It turned out that this is close to the feasibility limit of Macor: The fabrication of M4 type screws with a continuous axial hole was not possible. Thus M4 type screws made of Pt-Rh or stainless steel have to be applied



Two M4 type screws made of Macor. Made in the metal workshop of the Department of Materials of the ETH Zurich by B. Jörg. The threads work well, even if the they do not look perfect !



Sample holder made of stainless steel (4) equipped with two M4 type screws which are shown on the left

Comments to the presented freely swinging sample holders

It was often observed that the feed rod position was off-centered when the presented concept was used. The following reasons seem to be responsible for this unwanted misalignment:

- several adjacent and easily displaceable suspension positions on the hook
- a slightly asymmetric mass distribution of the overall assembly which consists of the sample holder, the M4 type screws, one or two platinum wires, and the feed rod

If it is desirable to have a freely swinging feed rod, then it can be realized also in the following way: For the sample holder concept which is presented in part 2 - 3 , part 2 - 4 and part 2 - 6 one can tighten the four M4 type Pt-Rh screws not completely so that the feed rod can slightly move and swing

Part 2 - 8

Advantages and potential disadvantages of the design of the rods and sample holders

Advantages of the design of the rods and sample holders

- Easy fixation and centering of the seed rod and the feed rod
- Clean and dry handling and installation without any lubricant or glue

Used materials seem to be compatible with each other concerning their linear thermal expansion coefficient α [10^{-6} K^{-1}]:

Macor:	$\alpha \approx 9 - 13$ in the temperature range 20 – 800 °C
Yttria stabilized zirconia: (FRIATEC DEGUSSIT FZY)	$\alpha \approx 11$ in the temperature range 20 – 1000 °C
Pt-Rh 90-10 (M4 screws):	$\alpha \approx 9 - 11$ in the temperature range 20 – 1000 °C
Stainless steel (shaft):	$\alpha \approx 10 - 17$ (depends on composition)
For comparison:	
Alumina (α - Al_2O_3 , corundum):	$\alpha \approx 9$ in the temperature range 20 – 1000 °C
Window glass:	$\alpha \approx 8$
Borosilicate glass:	$\alpha \approx 3$
Quartz glass:	$\alpha \approx 0.5$ in the temperature range 0 – 900 °C

Potential disadvantages of the design of the rods

Density of the rods: The preparation of the rods is described in part 5. The rods are pressed by special pressing dies which are made of magnesia stabilized zirconia or quartz glass. The use of that pressing dies displays several advantages but the allowed pressing force is relatively small. Therefore the density of the as-pressed rods is relatively low. The density of the sintered rods, however, depends on the sintering temperature. Nevertheless, the fabrication of sintered rods with a high density would be facilitated when the density of the as-pressed rods is already relatively high. In general, a high density of the rods is preferred for the floating zone melting process. However, in practice, it was possible to prepare many different crystalline oxide materials by using the as-sintered rods which were not optimized with respect to their density.

Rectangular shape of the rods: Sometimes, depending on the chemical composition of the rods, the feed rod material nearby the molten zone displays a phenomenon which can be called as formation of legs. It means that a part of the feed rod material grows in form of long and thin pieces (legs) away from the rod and molten zone. If this inconvenient phenomenon occurs, then, compared with cylindrical rods, it is more pronounced for rectangular rods. In most cases, however, it is possible to diminish this phenomenon by rotating the feed rod with an appropriate speed of rotation.

Part 3

Presentation of associated devices and technical facilities:

- Turbo pumping station
- Gas supply
- Oxygen analyzer for argon
- Suction for the exhaust gas lines
- Compressed air
- Cooling water unit

Turbo pumping station “HiCube” from Pfeiffer Vacuum

Turbo pumping station with oil-free backing pump. Purchased and delivered from Pfeiffer Vacuum Switzerland.

8 Vacuum line / Flexible metal tube towards tube furnace

7 Angle valve towards tube furnace

6 Vacuum line / Flexible metal tube towards mirror furnace

5 Angle valve towards mirror furnace

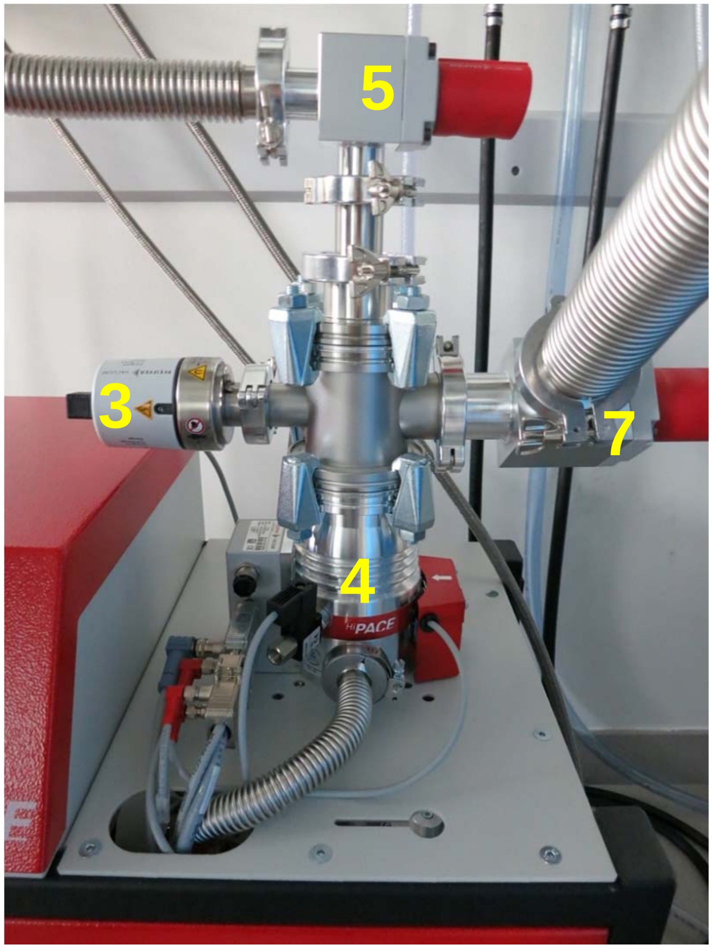
4 Turbo pump “HiPace 80”

3 Pressure gauge PKR 251 for measuring the pressure at the turbo pump

2 Control unit

1 Pressure indicator TPG 261

Turbo pumping station "HiCube" from Pfeiffer Vacuum

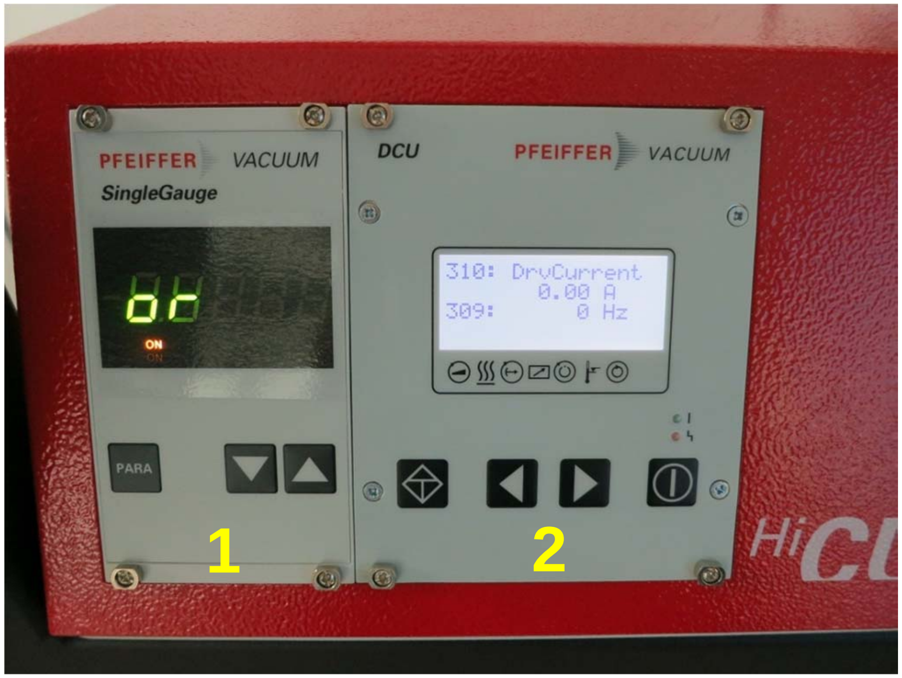


7 Angle valve towards tube furnace

5 Angle valve towards mirror furnace

4 Turbo pump "HiPace 80"

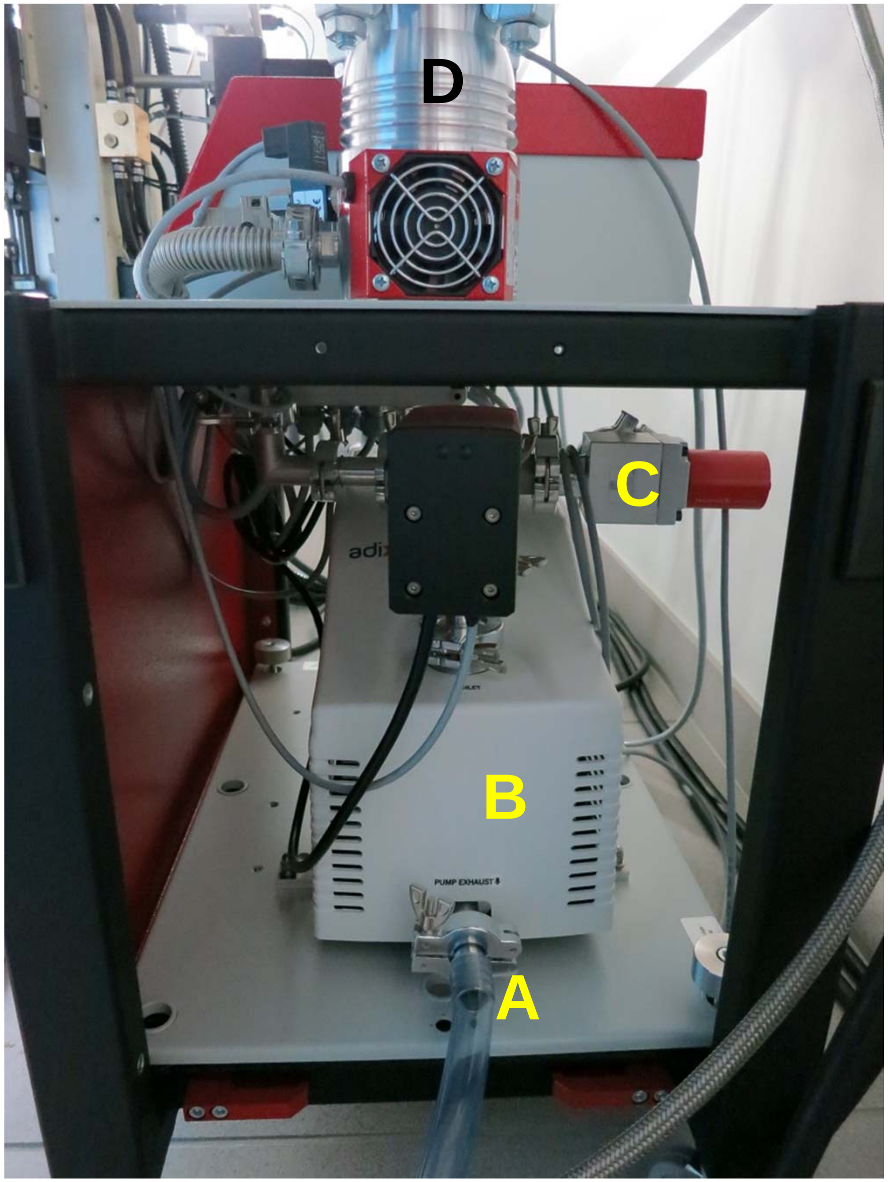
3 Pressure gauge PKR 251 for measuring the pressure nearby the turbo pump



2 Control unit

1 Pressure indicator TPG 261

Turbo pumping station “HiCube” from Pfeiffer Vacuum



Side view

D Turbo pump “HiPace 80”

C Additional angle valve and vacuum port in case of using the backing pump without the turbo pump

B Oil-free backing pump (dry primary pump) ACP 15 from adixen / Alcatel Vacuum Technology

A Gas outlet / Exhaust gas line

Turbo pumping station “HiCube” from Pfeiffer Vacuum

Some technical information

Backing or primary pumps are usually based on aerodynamic principles: Moving parts create in a certain region a compressed gas which results in a pressure difference and pumping effect. The oil-free backing pump ACP 15 from adixen (see previous page) reaches an ultimate pressure of 0,05 mbar.

In turbo pumps the gas atoms or molecules become accelerated to a high speed when they hit a fastly rotating turbine-like part. The rotating part in the turbo pump “HiPace 80” (see previous page) reaches a rotation speed of 90000 rpm. The turbo pump is operated together with a backing or primary pump. Turbo pumps may achieve an ultimate pressure of the order of 10^{-10} mbar. In the quartz glass tube of the Cyberstar mirror furnace (see part 2) and in the alumina tube of the GERO tube furnace (see part 8) the achievable ultimate pressure is of the order of 10^{-2} mbar and 10^{-3} mbar, respectively.

Gas supply for gas-tight devices like the mirror and tube furnace

Highly compressed gas in steel bottles

- Bottle size or volume: 50 Liter
- Gas pressure inside bottle:
  200 bar when completely full
- One bottle contains about 10000 Liter normal pressure gas

1 Argon (Ar) with purity 5.0 = 99,999 %

2 Synthetic air (80 % N_2 + 20 % O_2) or gas mixture Ar + O_2

3 Non-flammable gas mixture 97,2 % Ar + 2,8 % H_2

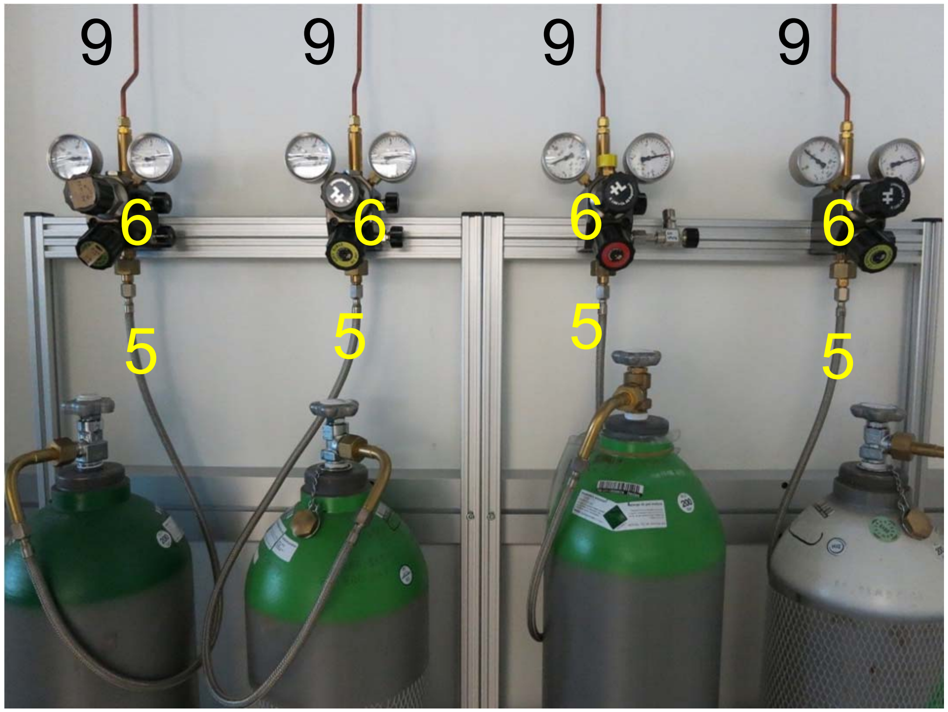
4 Oxygen (O_2) with purity 5.0 = 99,999 %

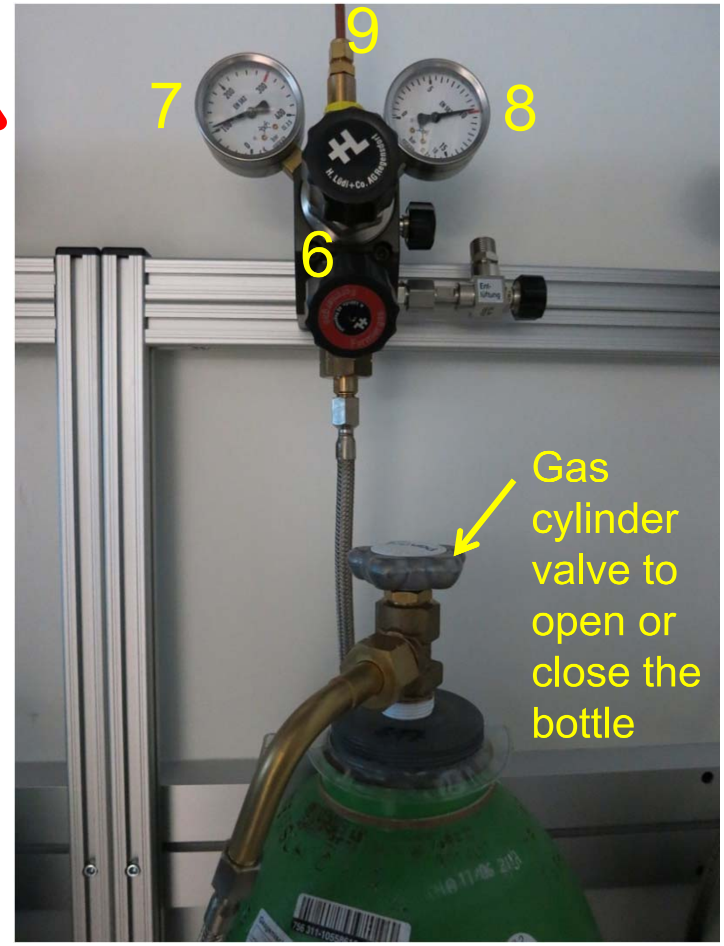
Percentage specifications of purity and composition indicate mole percent

Bottles with a gas pressure up to 200 bar are potentially dangerous and require a proper handling !

Gas supply – A closer view at the gas bottles and line regulators

Up to 200 bar pressure in bottle, flexible metal tube and line regulator ! Proper handling required !





9 Supply line towards gas supply cabinet

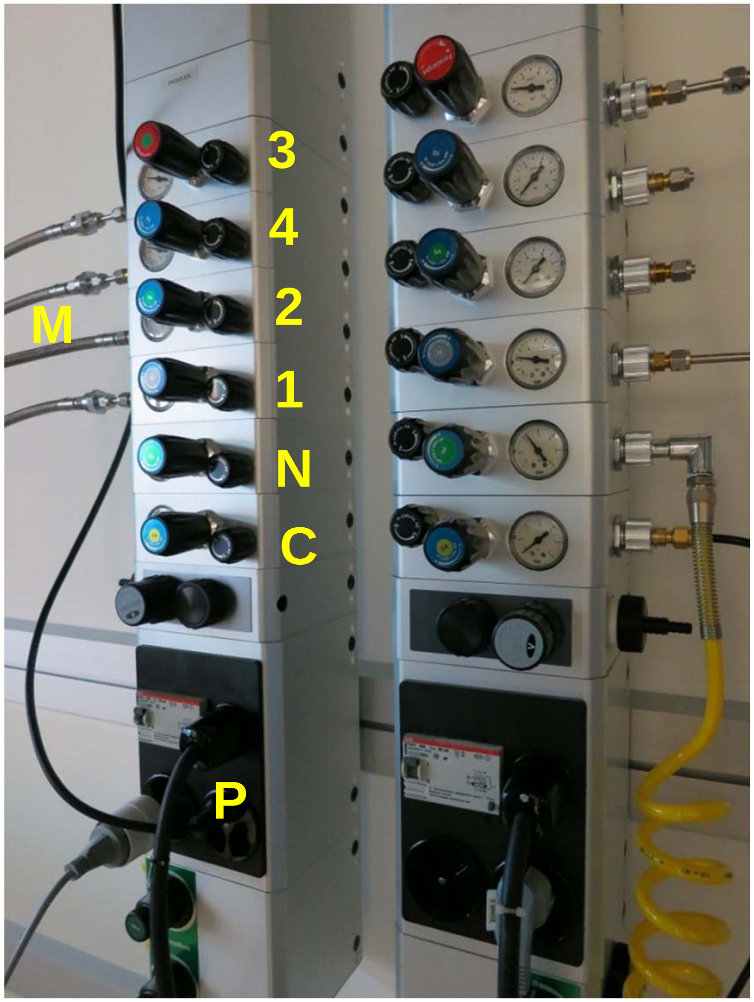
8 Pressure indicator for the adjustable gas pressure inside the supply line (up to 10 bar)

7 Pressure indicator for the gas pressure inside the bottle (up to 200 bar)

6 Line pressure regulator which reduces the high bottle pressure to a low supply line pressure

5 Flexible metal tube which connects the bottle with the line regulator
- gas pressure inside tube up to 200 bar

Gas supply cabinet for the mirror and tube furnace



4 Oxygen (O_2)

3 Gas mixture 97,2 % Ar + 2,8 % H_2 (non-flammable)

2 Synthetic air or gas mixture Ar + O_2

1 Argon (Ar)

M Flexible metal tubes (Swagelok 6 mm) which connect the gas lines 1 – 4 with the gas inlet of the mirror furnace

N Gaseous nitrogen (N_2) from a big liquid nitrogen tank

C Compressed air

P Power supply 230 V single-phase

Two adjacent point-of-use cabinets. The consumption points 1 – 4 are equipped with point-of-use regulators which provide an adjustable downstream pressure in the range 0 – 10 bar (inlet pressure 10 bar). The point-of-use cabinet on the right is used for the gas supply of the tube furnace which is presented in part 8.

A safety note concerning oxygen

When oxygen gas streams with a high speed across grease or oil, then an ignition may happen !

Examples of fatty or oily components:

1) Valves often comprise greased or oiled parts
2) Greased O-rings which are part of a device
3) Oily pumps
4) Short metal tubes (for gas lines) when they were cut and deburred with lubricants

Oxygen gas can reach a high speed by the presence of a large pressure gradient, e.g.

- when evacuating a space which is filled with oxygen
- when flushing an evacuated space with oxygen

Possible solutions when oxygen is used:

1) Use oil- and fat-free valves or valves which contain a special type of grease which is suitable for oxygen
2) If it is necessary to grease some components such as O-rings, then use only a special type of grease which is suitable for oxygen
3) Use oil-free pumps
4) Clean metal tubes

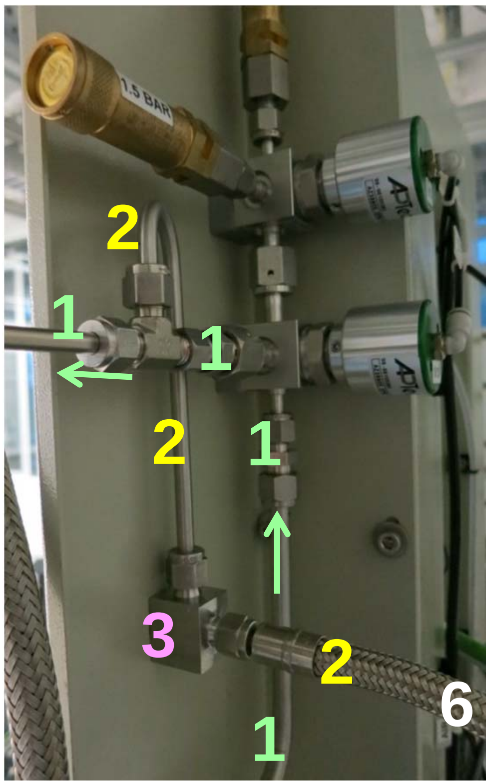
Oxygen analyzer ZIROX SGM7 to measure the oxygen content of argon

- Mirror furnace and tube furnace are at their gas outlet equipped with an oxygen analyzer
- If the process gas is flowing argon, then the oxygen analyzer is used to measure the oxygen content of argon at the gas outlet of the mirror furnace or tube furnace
- Made by German company ZIROX
- Zirconia-based measuring cell which operates at 750 °C
- Requires permanent argon gas flow of about 7 Liter / h which is ensured by an internal pump. Its gas inlet is connected via a flexible metal tube with the gas outlet of the mirror furnace or tube furnace.
- If the mirror furnace or tube furnace is evacuated and subsequently flushed with argon 5.0 (i.e. purity 99,999 %), then an oxygen content of ≤ 2 ppm can be reached

Rear view

Front view

Oxygen analyzer ZIROX SGM7 at the mirror furnace



Gas outlet of the mirror furnace

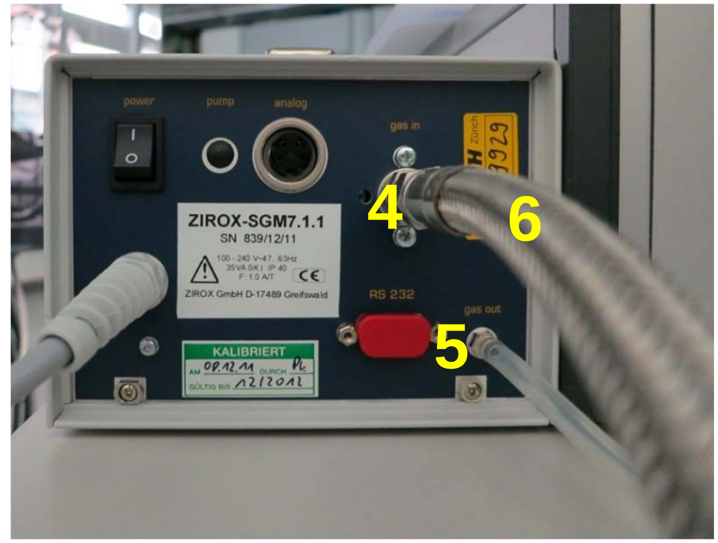
6 Flexible metal tube (Swagelok 6 mm)

4 (5) Gas inlet (outlet) of the oxygen analyzer

3 Ball valve (Swagelok SS-43GS4-A-SC11) to open or close branch line - valve lever on the other side of the panel

2 Branch line towards oxygen analyzer

1 Exhaust gas line of the mirror furnace



Rear view

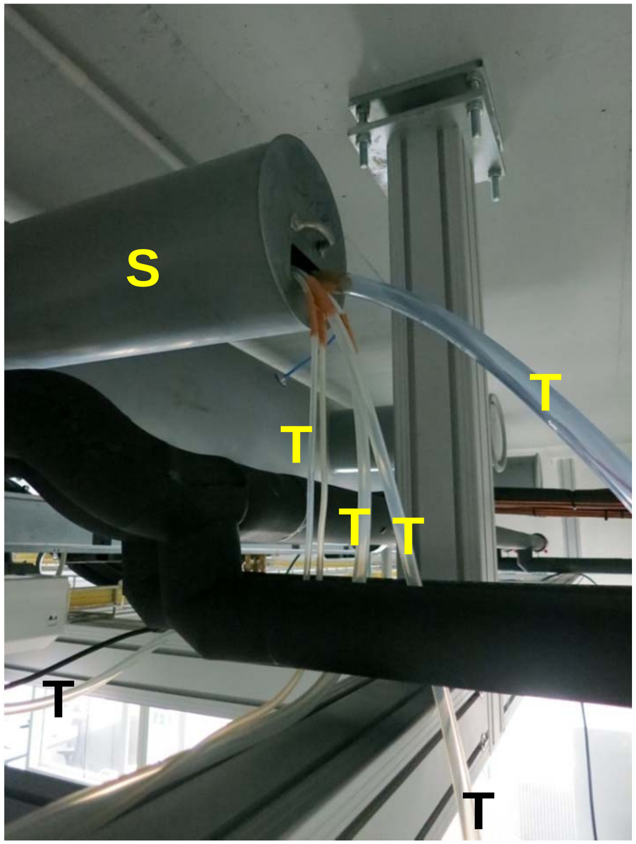
Front view

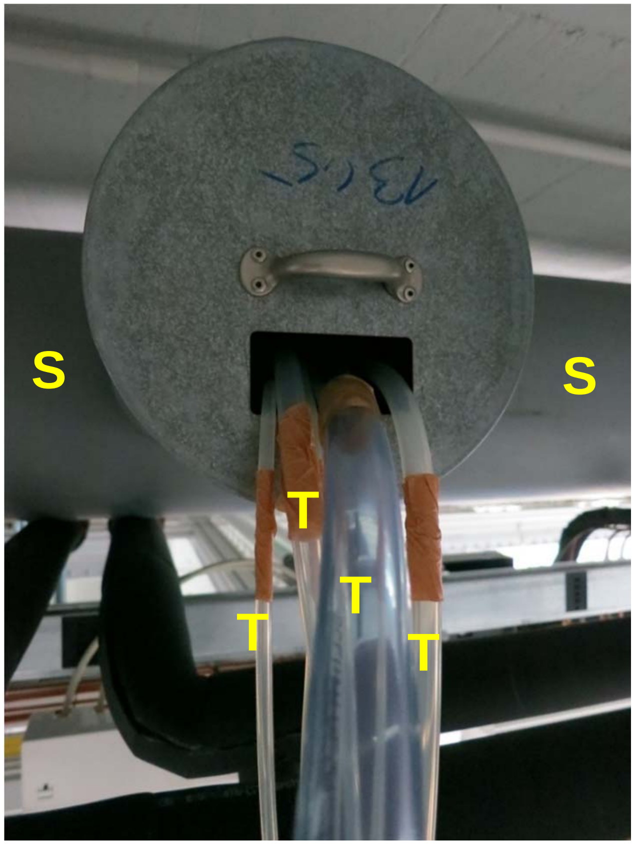
Suction for exhaust gas lines

T = Tube which represents an exhaust gas line that is connected with the gas outlet of a device like

- mirror furnace or tube furnace
- turbo pumping station
- oxygen analyzer ZIROX SGM7

S = Suction line which is located close to the ceiling of the laboratory

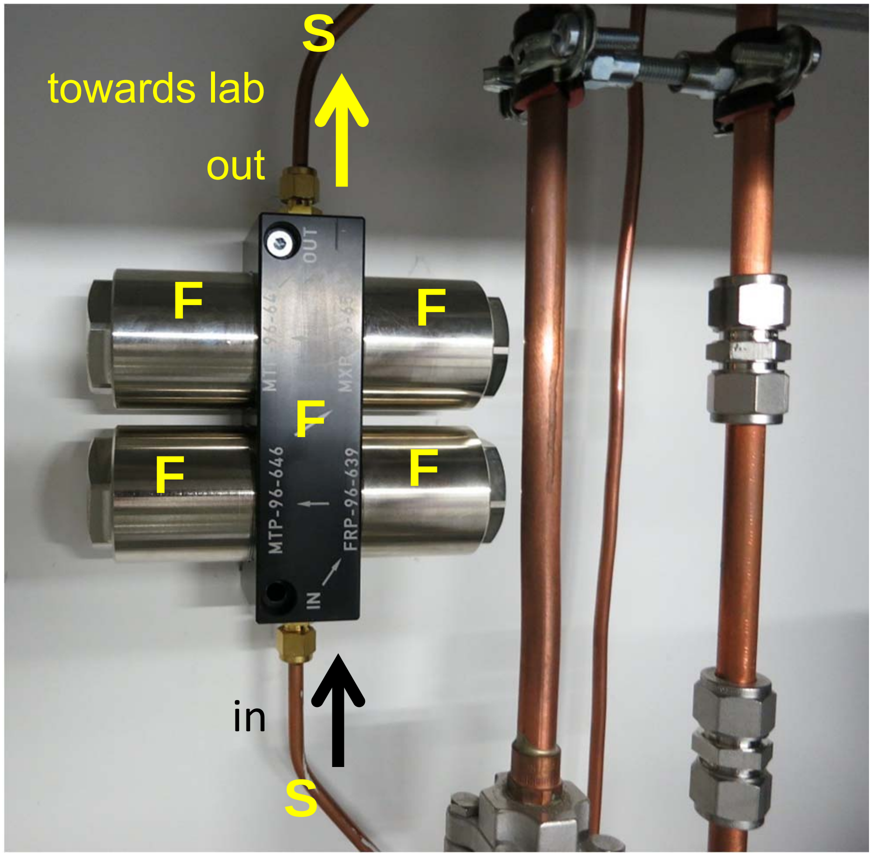




Laboratory is equipped with a permanently running supply air and suction

Compressed air supply

It is used for the electropneumatic valves and cooling of the lamps at the mirror furnace



A short section of the compressed air supply line (S) which is located outside of the laboratory. The supply line is equipped with a filter unit (F) which ensures the provision of clean compressed air at the point-of-use cabinets in the laboratory. The filter unit comprises four different types of filters.

Two adjacent point-of-use cabinets which are located in the laboratory. The consumption point for compressed air (C) is equipped with a point-of-use regulator which provides an adjustable downstream pressure 0 – 6 bar.

Cooling water unit for water-cooled devices like the mirror and tube furnace

- Construction by D. Freund (ETH Zurich) and P. Winkelaar (Winkelaar Rohrleitungstechnik)
- Primary circuit: Technical cooling water with supply temperature 12 °C
- Secondary circuit via water-cooled devices like the mirror furnace and / or tube furnace
- Secondary circuit provides adjustable but constant temperature of supply water and cooling of return flow by a variable themal contact between primary and secondary circuit

Cooling water unit

1 Supply from cooling water unit towards inlet of mirror (m) or tube (t) furnace

2 Return from outlet of mirror (m) or tube (t) furnace towards cooling water unit

Cooling water port

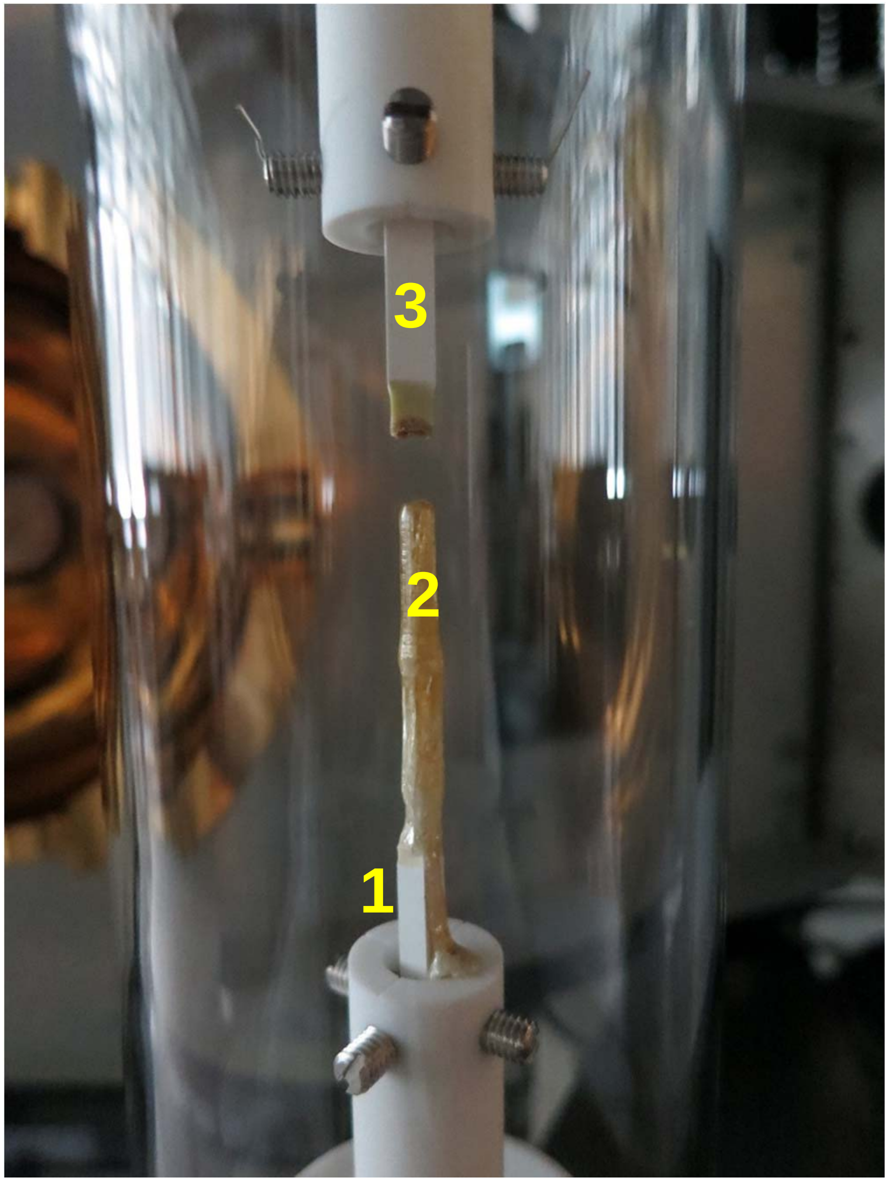
Typical operating parameters:

- inlet temperature at mirror furnace and / or tube furnace 20 °C
- inlet (outlet) pressure at mirror and / or tube furnace 4,5 bar (2 bar) $\rightarrow \Delta p$ = 2,5 bar

Part 4

Examples of melt-grown oxides prepared by the Cyberstar mirror furnace

Examples of melt-grown oxides prepared by the Cyberstar mirror furnace



$Sr_2Nb_2O_7$ 1 / 2

View into the quartz glass tube after the run

3 Remaining part of the feed rod

2 As-grown crystalline sample

1 Seed rod

Experimental details:

Chemical composition of polycrystalline sintered seed rod and feed rod was $Sr_2Nb_2O_7$ which melts at about 1650 °C

Lamp power about 2 × 400 W

Atmosphere: Synthetic air with a flow rate of 24 Liter / h

Feed rod: Translation (rotation) speed 18 mm / h (10 rpm counterclockwise)

Seed rod: Translation (rotation) speed 14 mm / h (10 rpm clockwise)

Examples of melt-grown oxides prepared by the Cyberstar mirror furnace

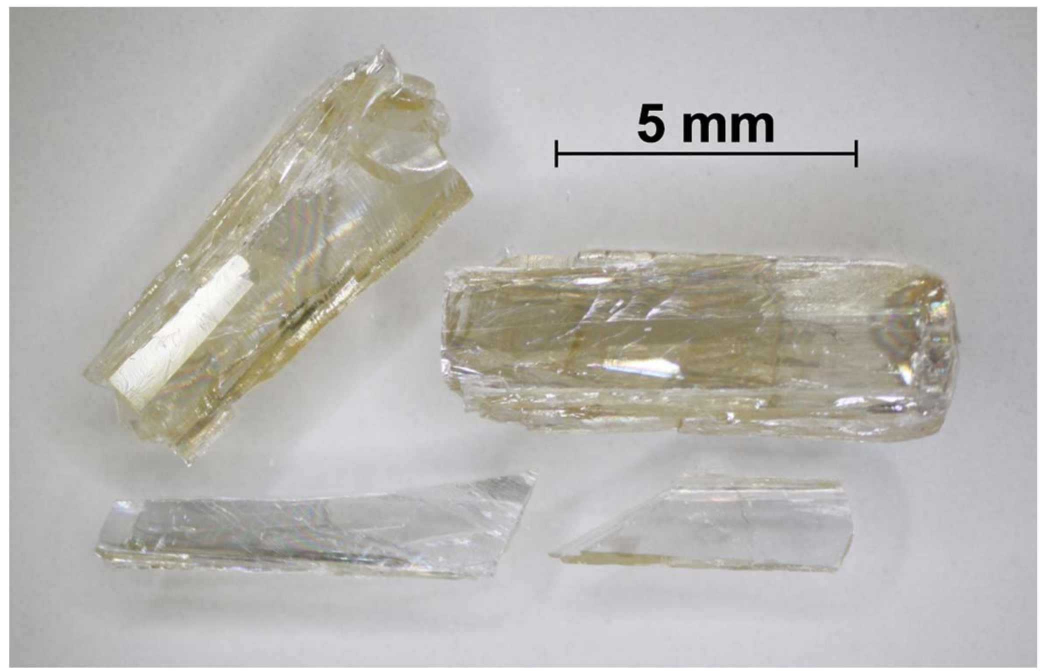
$Sr_2Nb_2O_7$ 2 / 2

$Sr_2Nb_2O_7$ is a transparent and ferroelectric insulator with a high ferroelectric transition temperature (T_c = 1340 °C) and a layered crystal structure

S. Nanamatsu et al , J. Phys. Soc. Jpn. 38 (1975) 817

See also appendix 1 and 5 in this presentation and Progress in Solid State Chemistry 29 (2001) 1 and 36 (2008) 253 and references therein

As-grown crystalline sample



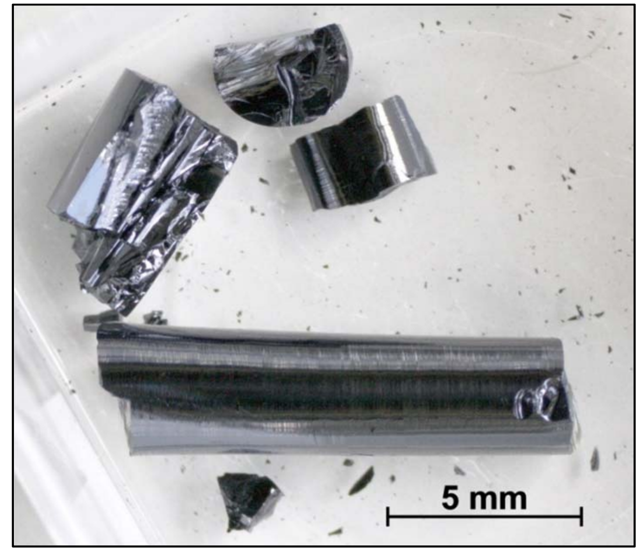
Crystalline pieces obtained by crushing the as-grown sample

Examples of melt-grown oxides prepared by the Cyberstar mirror furnace

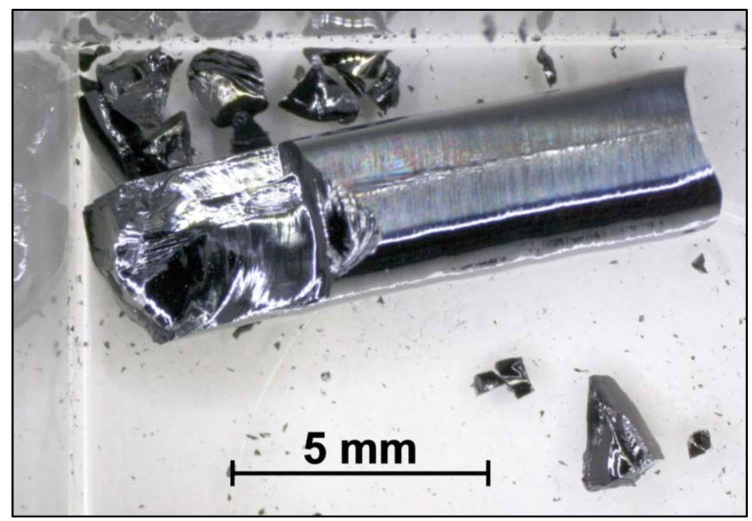
Hexagonal layered $YMnO_3$

Crystalline pieces of as-grown stoichiometric and non-stoichiometric samples

Grown with 8 mm / h under synthetic air with a flow rate of 18 liter / h and a lamp power of about 2 × 355 W or 2 × 400 W



Hexagonal layered $YMnO_3$ is a known multiferroic. It is ferroelectric with $T_c \approx 900$ K and antiferro-magnetic with $T_N \approx 70$ K



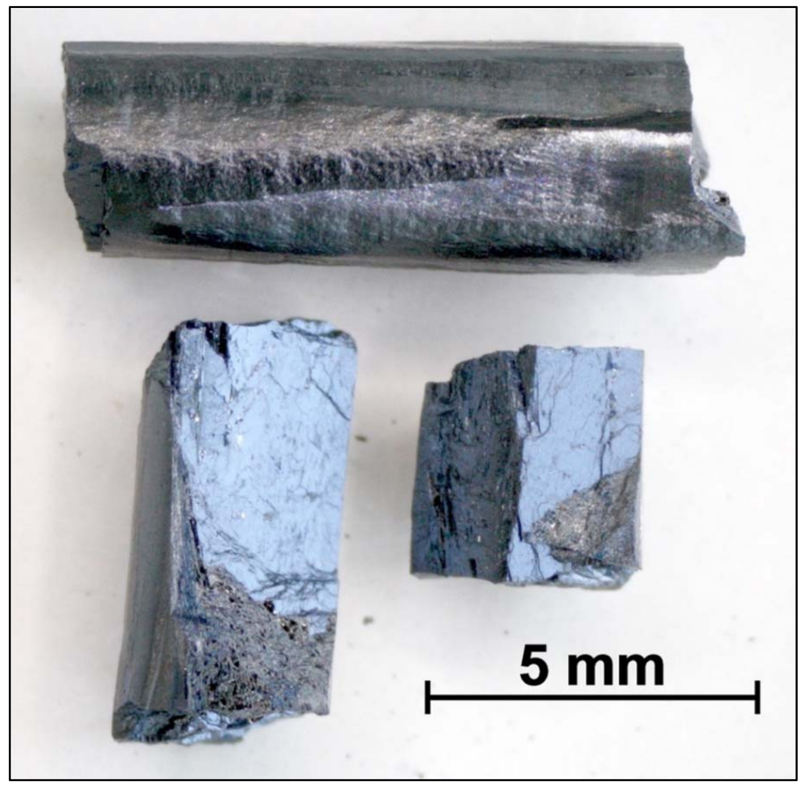
The preparation of hexagonal $YMnO_3$ by a mirror furnace is reported in some papers, see for example C. Fan et al , Journal of Crystal Growth 388 (2014) 54 - 60

Examples of melt-grown oxides prepared by the Cyberstar mirror furnace

A layered oxide of the type $Ca_5Nb_5O_{17}$ grown with 14 mm / h under argon with a flow rate of 24 liter / h and a lamp power of about 2 × 345 W

45 mm long as-grown crystalline sample and polycrystalline seed rod

Crystalline pieces of the as-grown sample



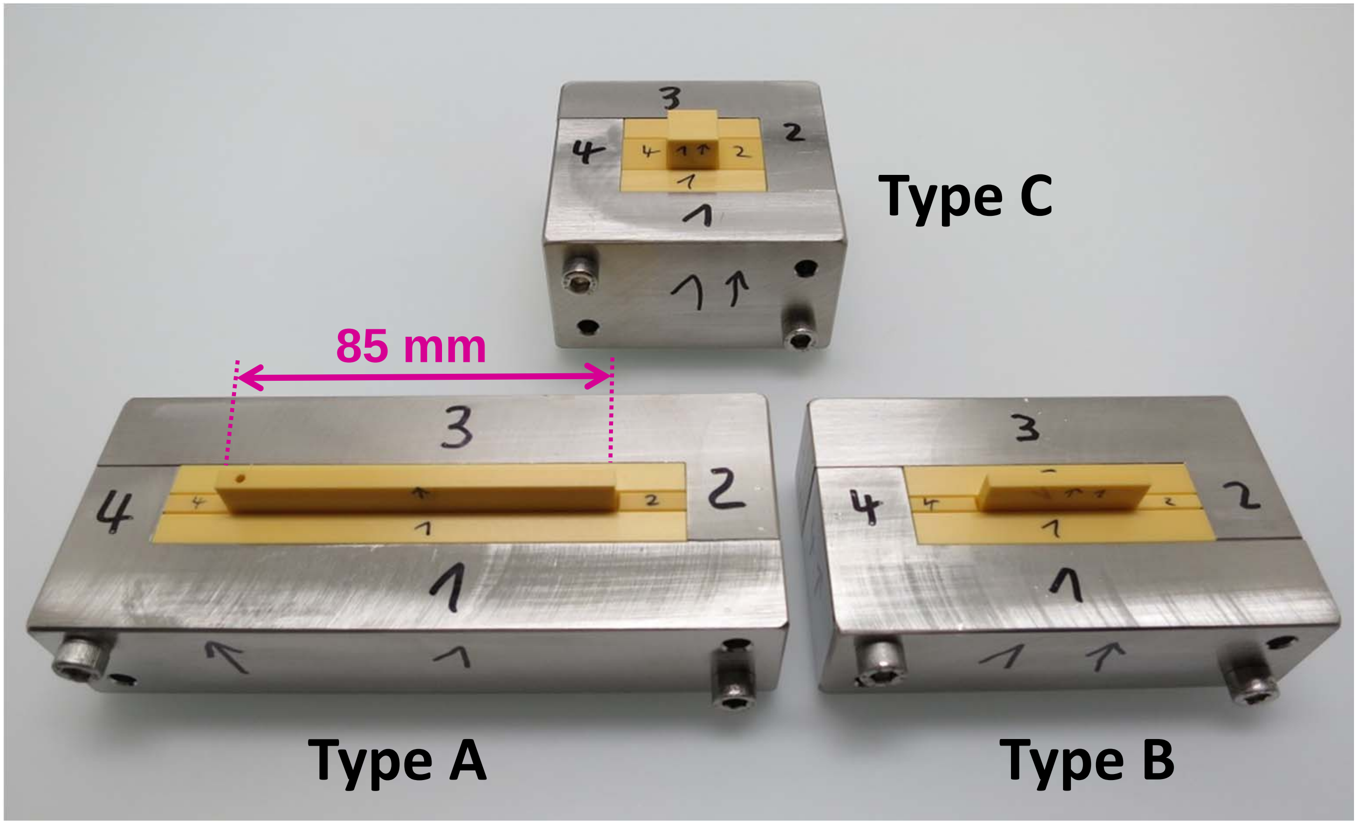
$Ca_5Nb_5O_{17}$ is a quasi-1D metal with a layered crystal structure [1,2]. It is isostructural to $Sr_5Nb_5O_{17}$ [1,3] which is presented in the introduction and in appendix 1 and 5 of this presentation

[1] Progress in Solid State Chemistry 29 (2001) 1
[2] Journal of Solid State Chemistry 178 (2005) 2934
[3] Progress in Solid State Chemistry 36 (2008) 253
and references therein

Part 5

Preparation of rectangular feed and seed rods by special pressing dies made of ceramics or glass, a laboratory press, and sintering

Pressing dies made of technical ceramics



Yellow parts made of magnesia stabilized zirconia (FRIATEC FRIALIT FZM) by FRIATEC AG (Germany), purchased and delivered from stone-ware gmbh (Switzerland)

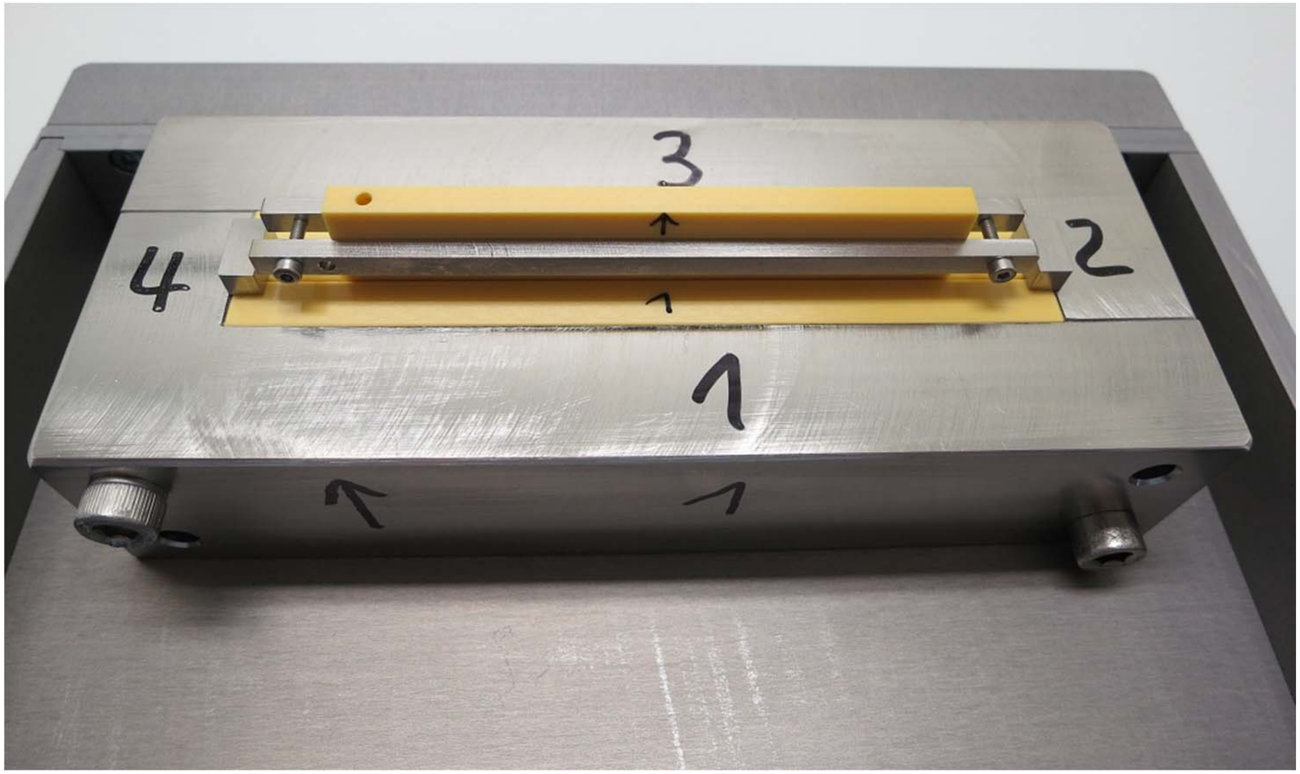
Metal frames made in the metal workshop of the Department of Materials of the ETH Zurich by C. Roth and M. Elsener

Type C with square punch for other samples with length 14 mm and width 14 mm

Type B with rectangular punch for seed rods with length 35 mm and width 3,5 mm

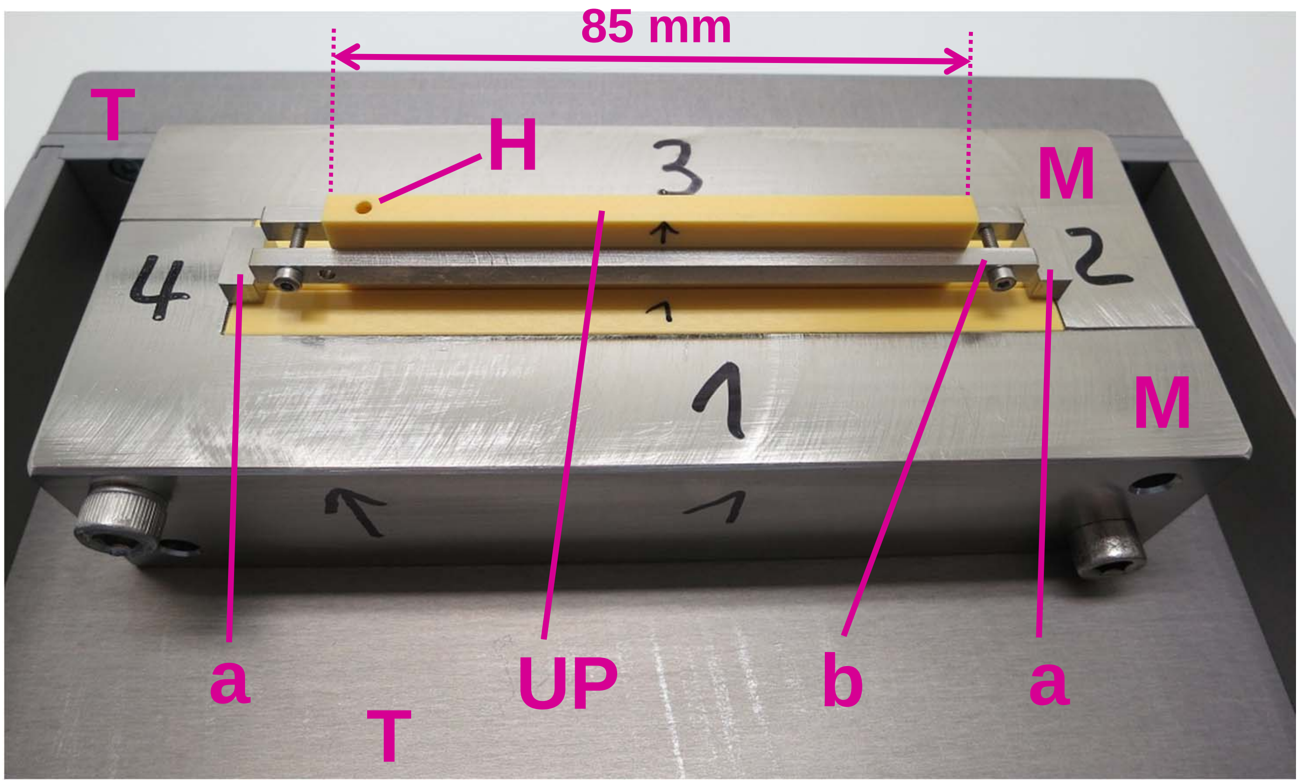
Type A with rectangular punch for feed rods with length 85 mm and width 4,5 mm

Custom-made pressing die for the feed rod



Yellow parts made of magnesia stabilized zirconia (FRIATEC FRIALIT FZM) by FRIATEC AG (Germany), purchased and delivered from stone-ware gmbh (Switzerland)

Custom-made pressing die for the feed rod



Made in the metal workshop of the Department of Materials of the ETH Zurich by C. Roth:

M Two-part frame made of stainless steel

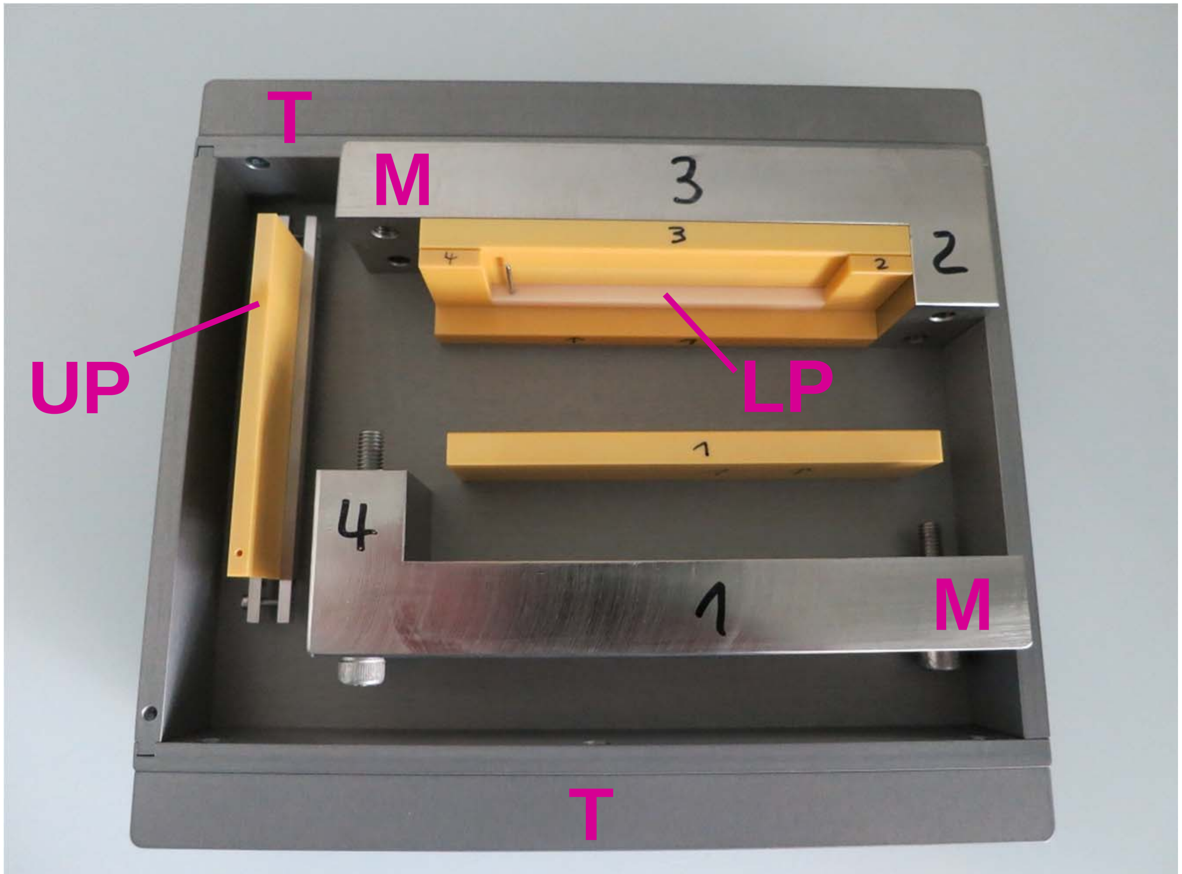
a , b Components made of stainless steel for an estimation of the thickness or height of the pressed powder

T Tray made of eloxed aluminum

Yellow parts made of magnesia stabilized zirconia (FRIATEC FRIALIT FZM) by FRIATEC AG (Germany), purchased and delivered from stone-ware gmbh (Switzerland)

UP Upper punch with length 85 mm and width 4,5 mm and continuous hole H

Pressing die for the feed rod - Top view when partly disassembled



Made in the metal workshop of the Department of Materials of the ETH Zurich by C. Roth:

M Two-part frame made of stainless steel

T Tray made of eloxed aluminum

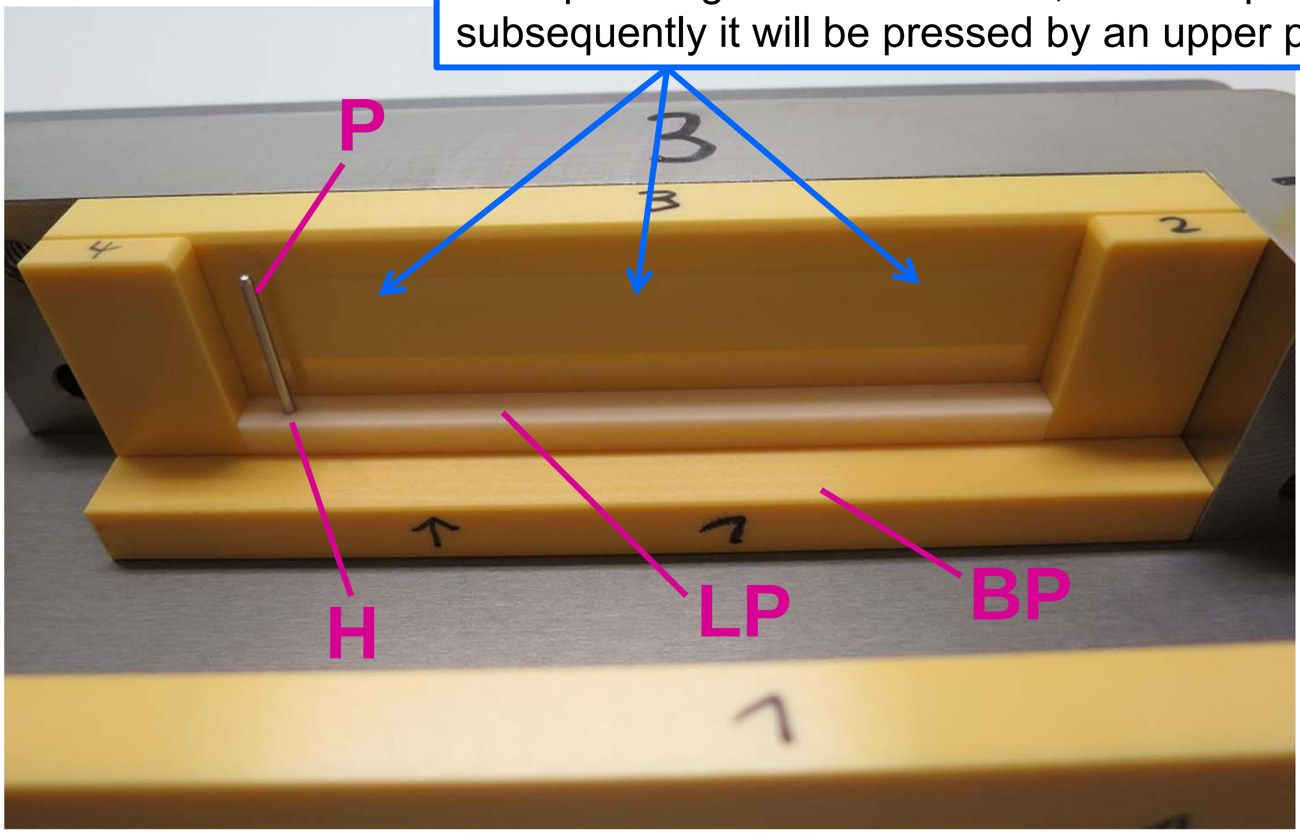
Made by FRIATEC AG (Germany), purchased and delivered from stone-ware gmbh (Switzerland):

- Yellow parts, made of magnesia stabilized zirconia (FRIATEC FRIALIT FZM)
- Lower punch LP, made of alumina (FRIATEC FRIALIT F 99,7)

UP Upper punch LP Lower punch

Pressing die for the feed rod – Partly disassembled

If the pressing die is assembled, then the powder is poured in here and subsequently it will be pressed by an upper punch on the lower punch



P Custom-made pin (diameter 1,3 mm) made of stainless steel, delivered from stone-ware gmbh

LP Lower punch with length 85 mm and width 4,5 mm and continuous hole H

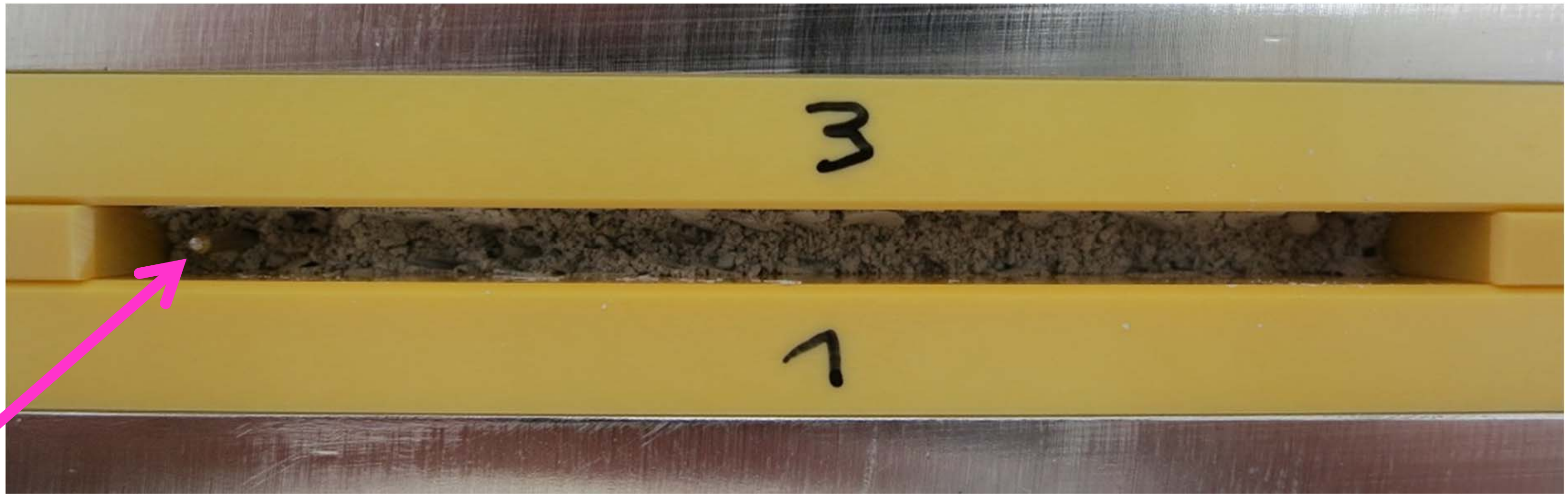
BP Base plate with continuous hole

Pin P runs through lower punch LP and base plate BP

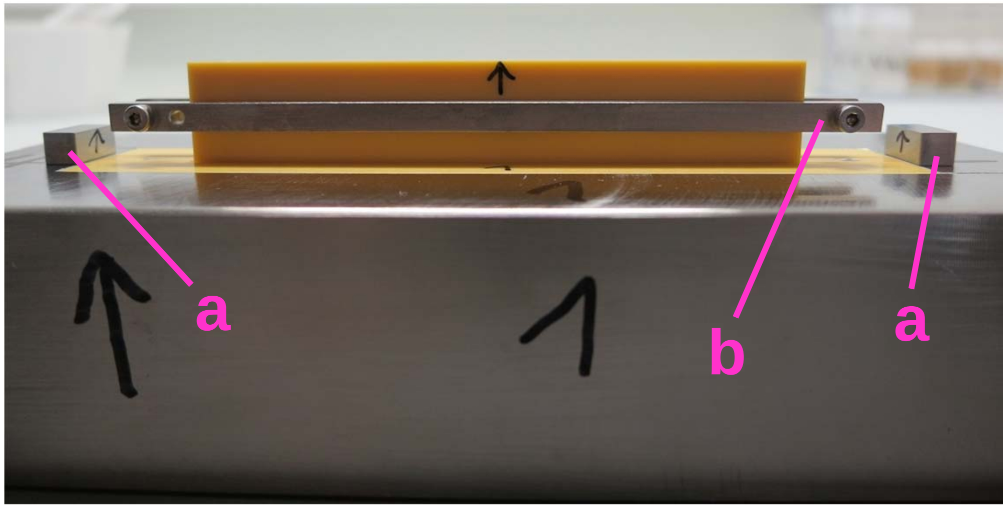
Made by FRIATEC AG (Germany), purchased and delivered from stone-ware gmbh (Switzerland):

- Yellow parts, made of magnesia stabilized zirconia (FRIATEC FRIALIT FZM)
- Lower punch LP with continuous hole H, made of alumina (FRIATEC FRIALIT F 99,7)

Pressing die for the feed rod – Assembled and filled with powder



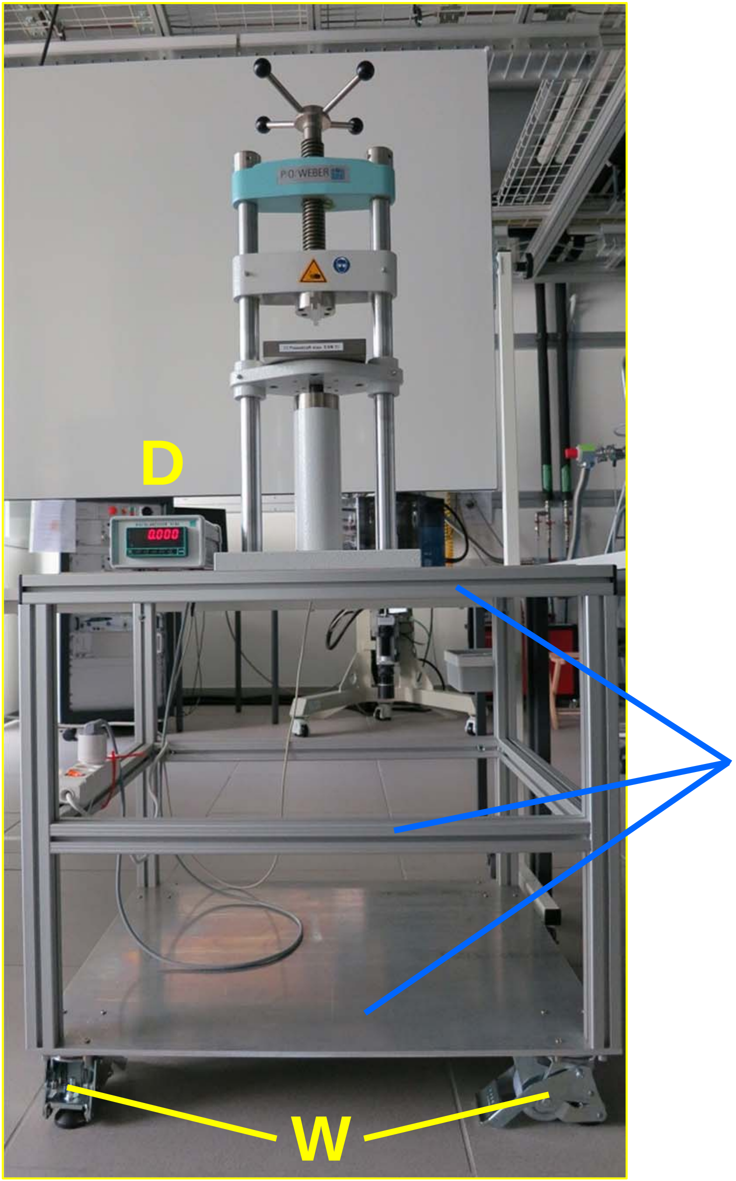
Top view when the lower part of the cavity is filled with powder
Chemical composition of the powder in this example: 0,6 Nb + 0,2 Nb_2O_5



Side view with inserted upper punch

a , b Components for an estimation of the thickness or height of the pressed powder

Press from Paul-Otto Weber GmbH



Non-hydraulic press with force sensor and digital force display (D)

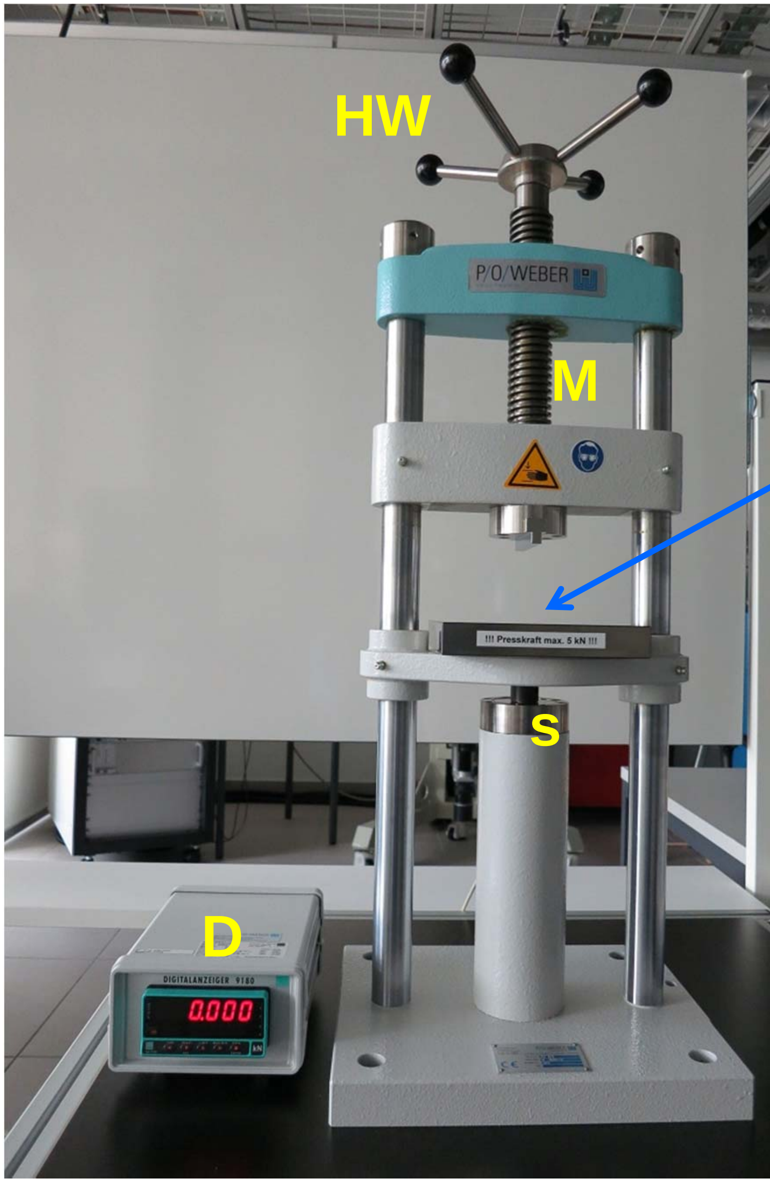
Press made by German company Paul-Otto Weber GmbH

Maximum pressing force 5 kN - The press is designed for relatively small pressing forces because it is used for pressing dies which are made of technical ceramics

Wheeled rack with high-quality lockable wheels (W) which are stable like machine feet

Wheeled rack made in the metal workshop of the Department of Materials of the ETH Zurich by C. Roth and M. Elsener

Press from Paul-Otto Weber GmbH



Non-hydraulic press with force sensor (s) and digital force display (D)

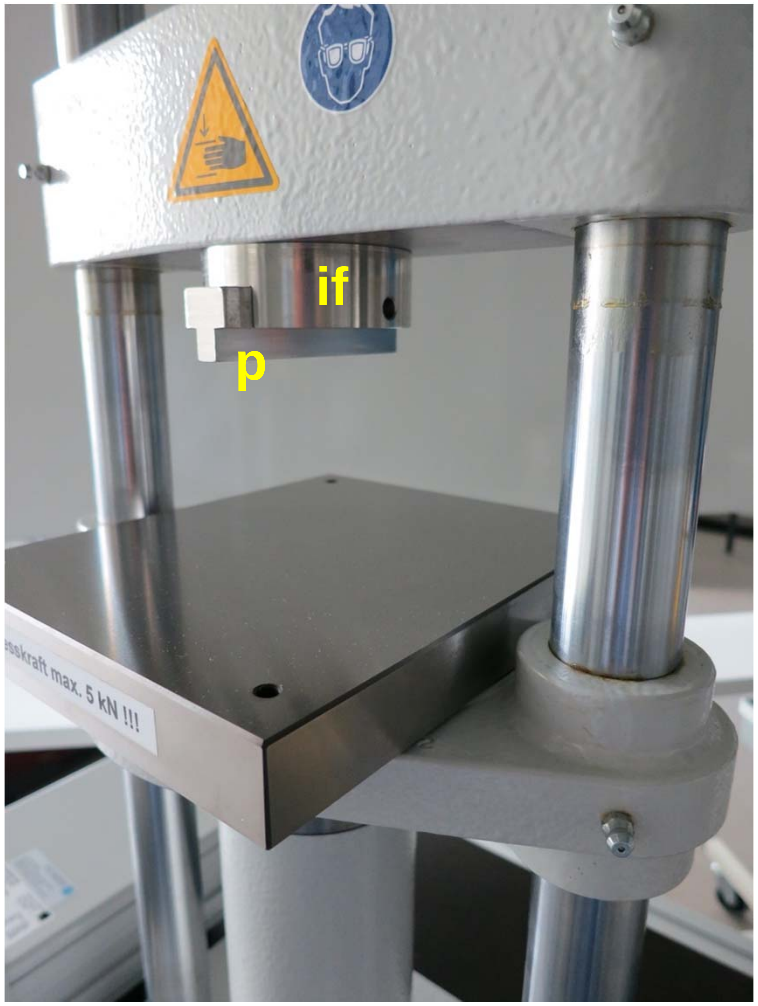
Press made by German company Paul-Otto Weber GmbH

Pressing die will be placed here

Maximum pressing force 5 kN - The press is designed for relatively small pressing forces because it is used for pressing dies which are made of technical ceramics

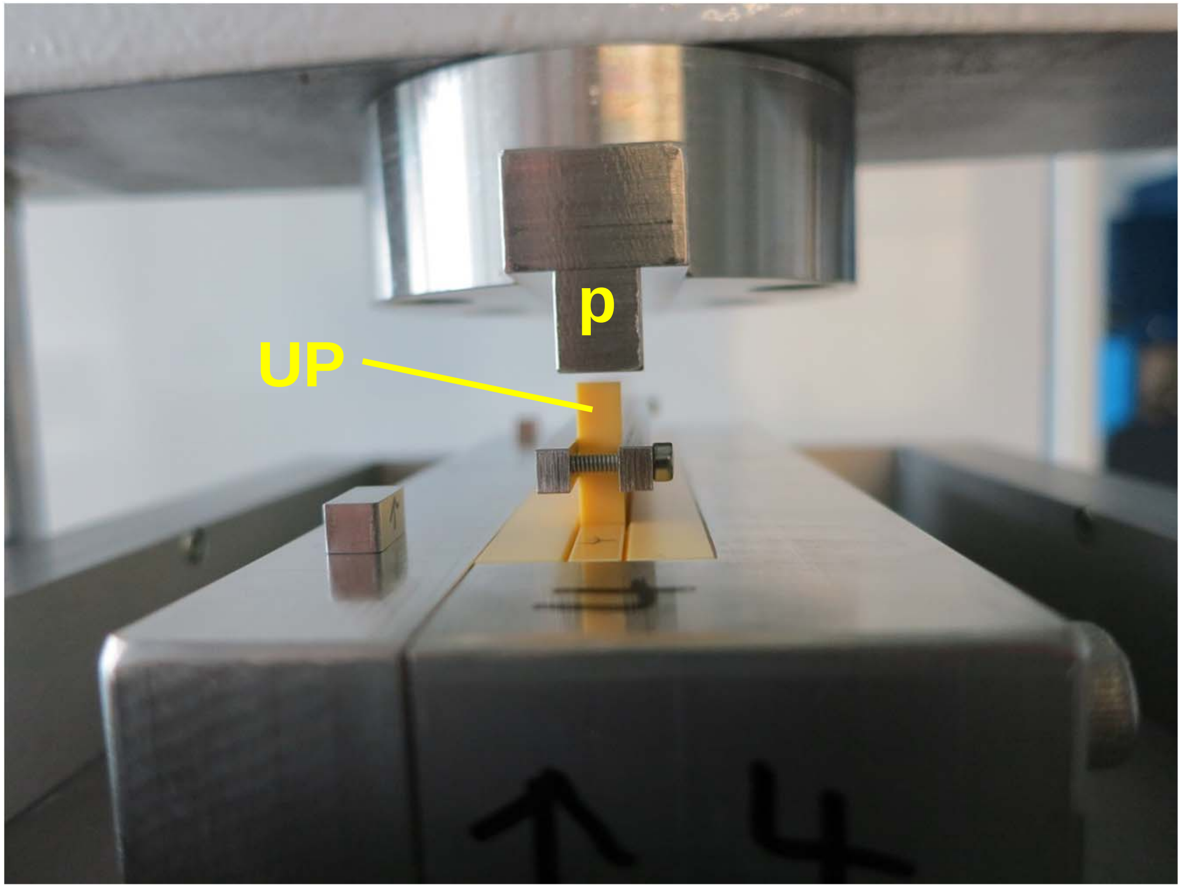
Creation of a pressing force by moving the mandrel (M) via the handwheel (HW) downwards

Press from Paul-Otto Weber GmbH



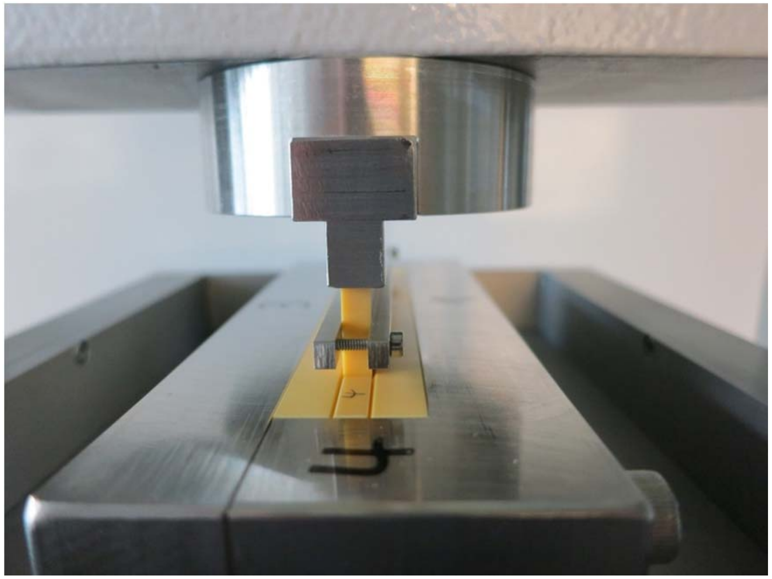
Interface (if) and exchangeable punch (p) made in the metal workshop of the Department of Materials of the ETH Zurich by C. Roth

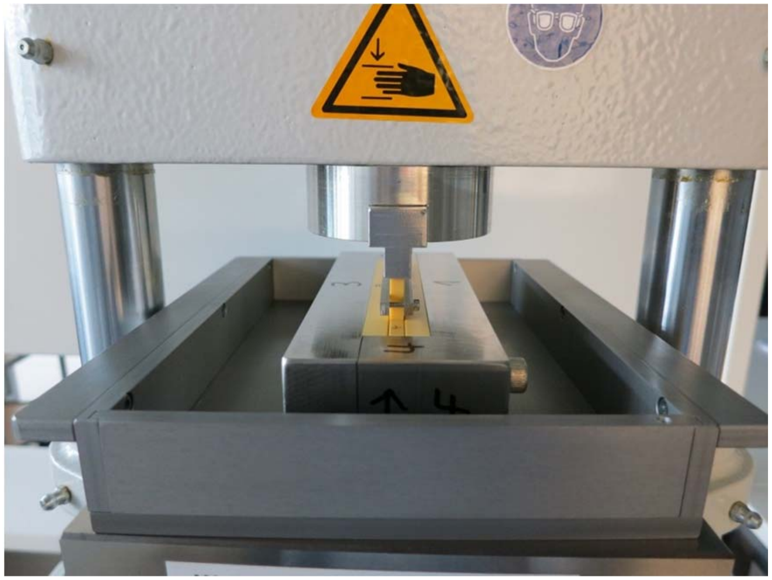
Press with placed pressing die for the feed rod



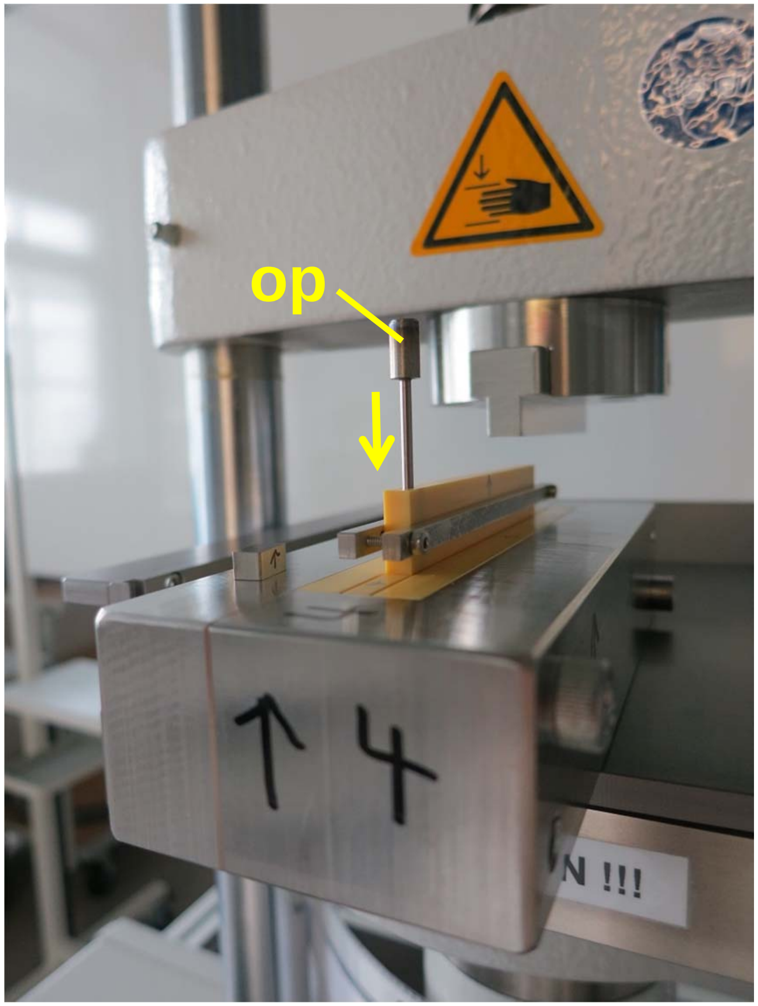
UP Upper punch of the pressing die p Punch of the press

Applying a pressing force of 1 kN on the upper punch of the pressing die





Press with pressing die for the feed rod - Removing the pin after pressing

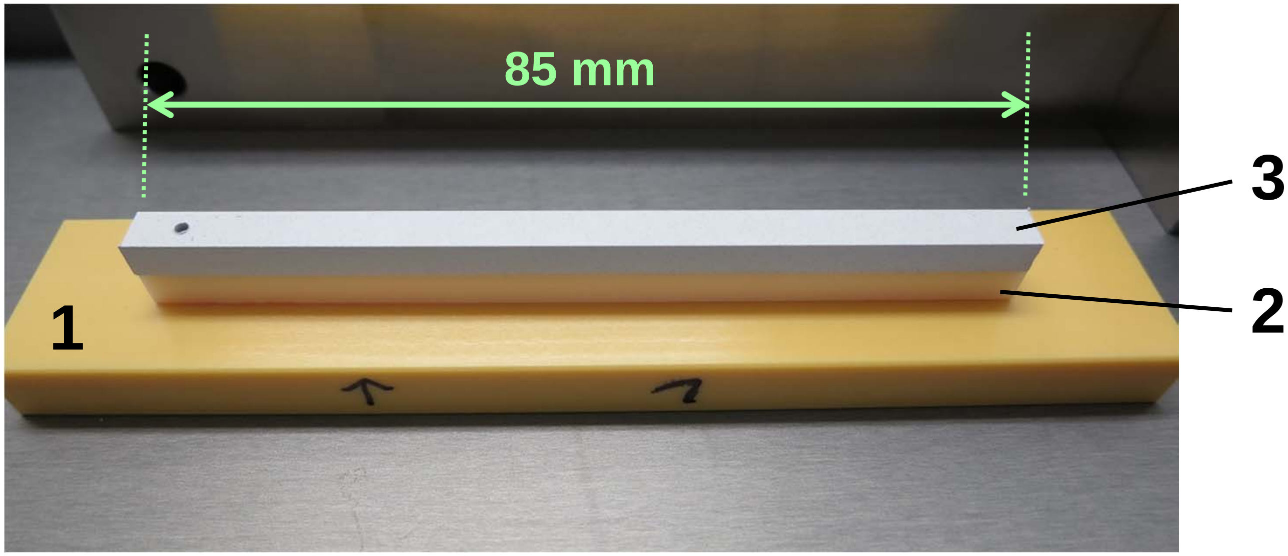


After pressing the pressing die will be moved across the edge so that the pin (p) can come out from below. The pin (p) comes out by pushing with another pin (op) from above.

Pressing die for the feed rod – View after pressing the powder

Pin and upper punch are removed - Top view into the cavity on the pressed powder

View of the pressed rectangular feed rod when the laterals are removed



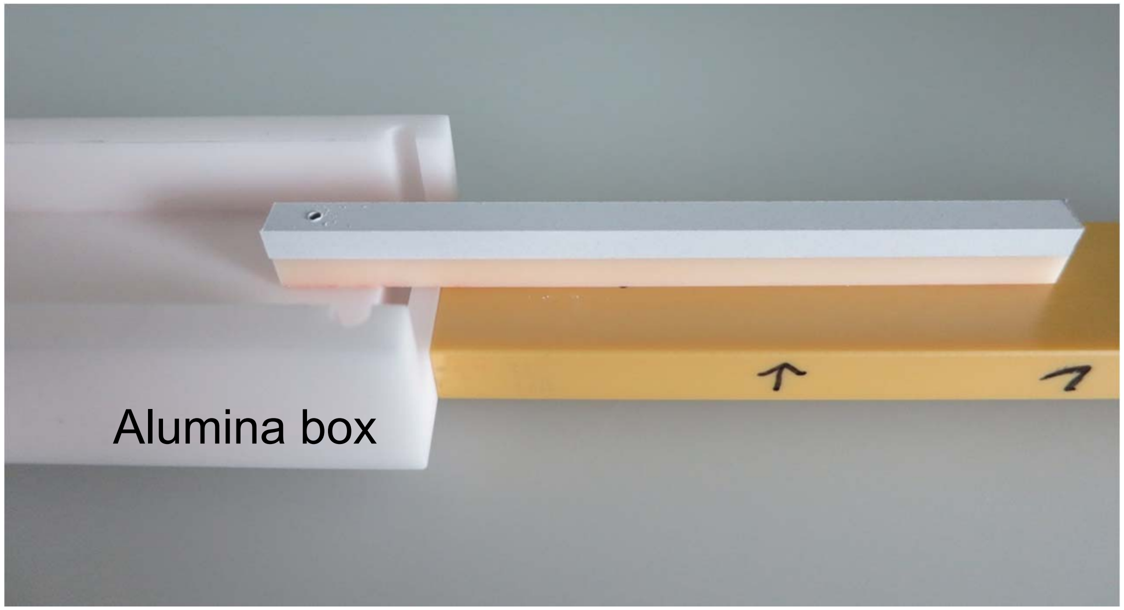
3 Rectangular rod with a continuous hole - made of pressed powder
Chemical composition of the pressed powder in this example: 0,6 Nb + 0,2 Nb_2O_5

2 Lower punch - made of alumina (FRIATEC FRIALIT F 99,7)

1 Base plate - made of magnesia stabilized zirconia (FRIATEC FRIALIT FZM)

The pressed rod is mechanically not stable. If it is touched in a not very careful way, then it becomes damaged or destroyed. However, the rod is needed in a mechanically stable form. Therefore the lower punch and the pressed rod will be placed into an alumina box and heated to an appropriate high temperature under a suitable atmosphere which results in sintering and chemical solid state reactions.

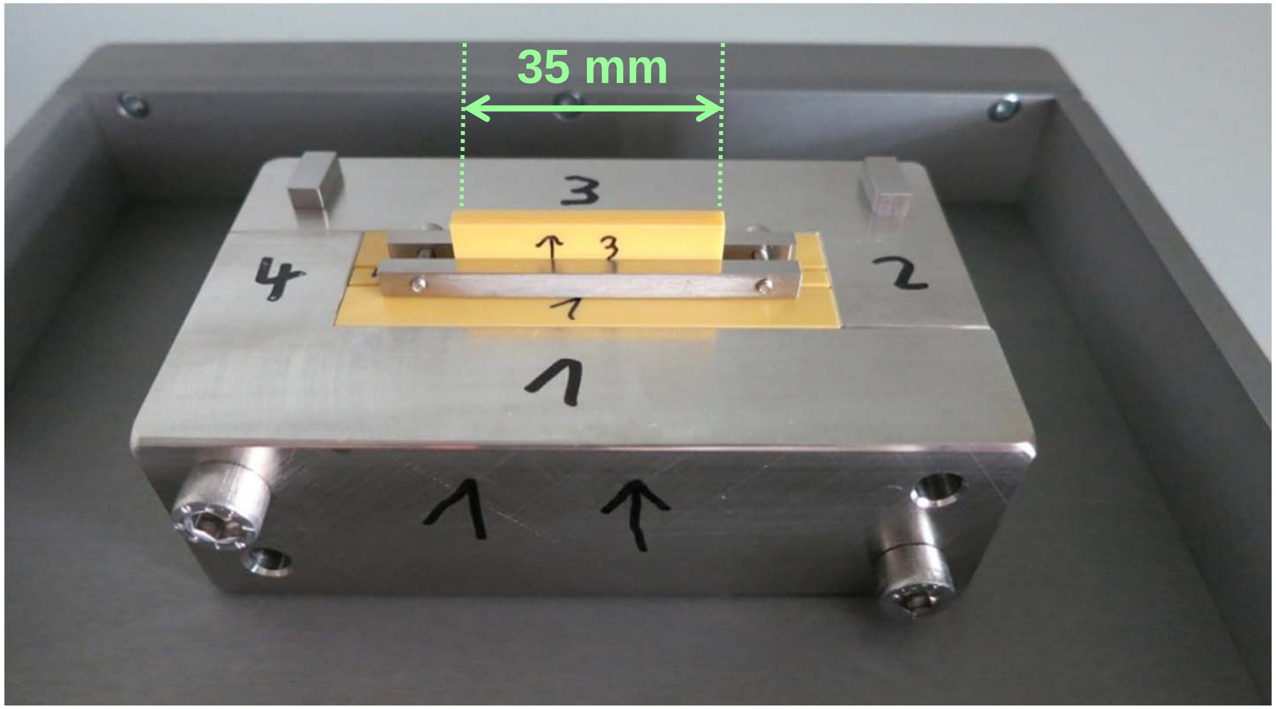
Moving the lower punch and pressed feed rod into an alumina box



Box and lower punch made of alumina (FRIATEC FRIALIT F 99,7) by FRIATEC AG (Germany), purchased and delivered from stone-ware gmbh (Switzerland)

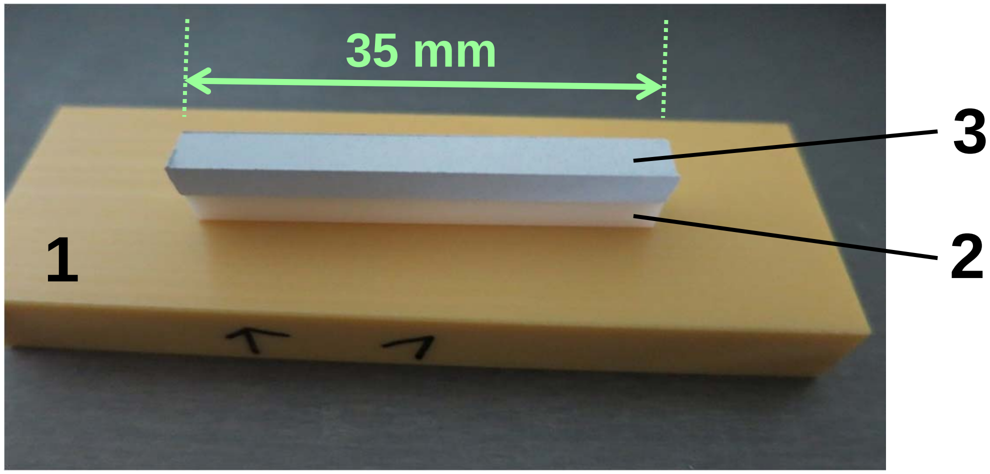
This alumina box is especially suitable for the tube furnace

Custom-made pressing die for the seed rod



The preparation of the seed rod is similar to that of the feed rood. It is somewhat easier because the feed rod is smaller and does not involve a hole.

Example of a pressed rectangular seed rod



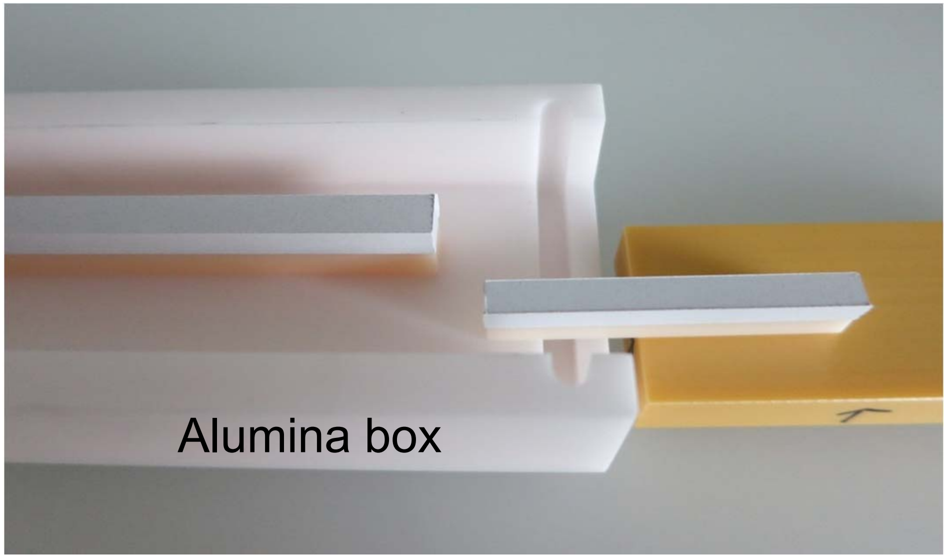
3 Rectangular rod with a continuous hole - made of pressed powder
Chemical composition of the pressed powder in this example: 0,6 Nb + 0,2 Nb_2O_5

2 Lower punch - made of alumina (FRIATEC FRIALIT F 99,7)

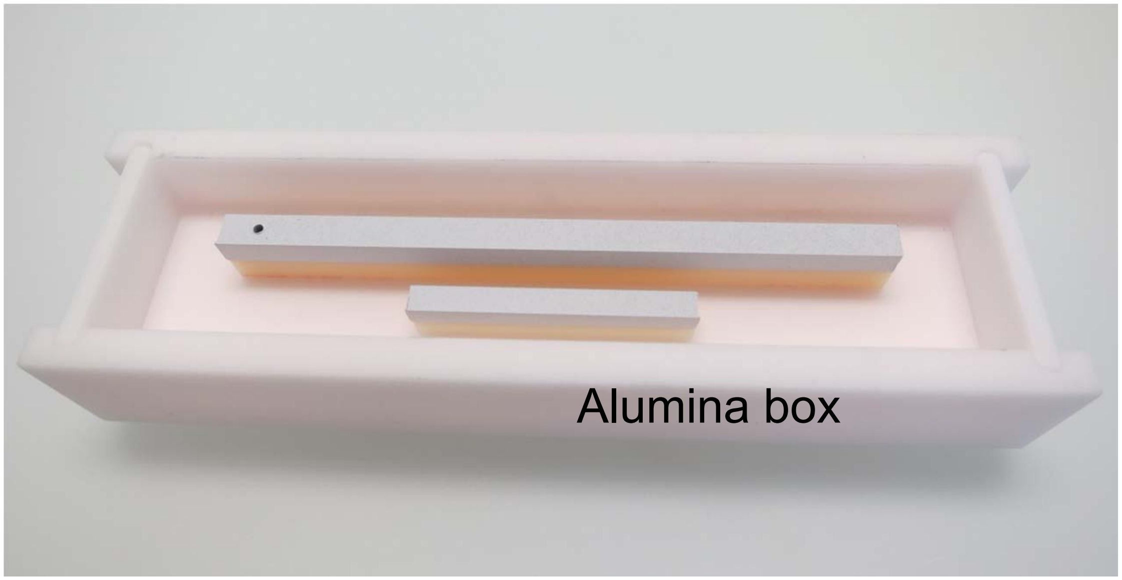
1 Base plate - made of magnesia stabilized zirconia (FRIATEC FRIALIT FZM)

The pressed rod is mechanically not stable. If it is touched in a not very careful way, then it becomes damaged or destroyed. However, the rod is needed in a mechanically stable form. Therefore the lower punch and the pressed rod will be placed into an alumina box and heated to an appropriate high temperature under a suitable atmosphere which results in sintering and chemical solid state reactions.

Moving the lower punch and pressed feed rod into an alumina box



Box and lower punch made of alumina (FRIATEC FRIALIT F 99,7) by FRIATEC AG (Germany), purchased and delivered from stone-ware gmbh (Switzerland)

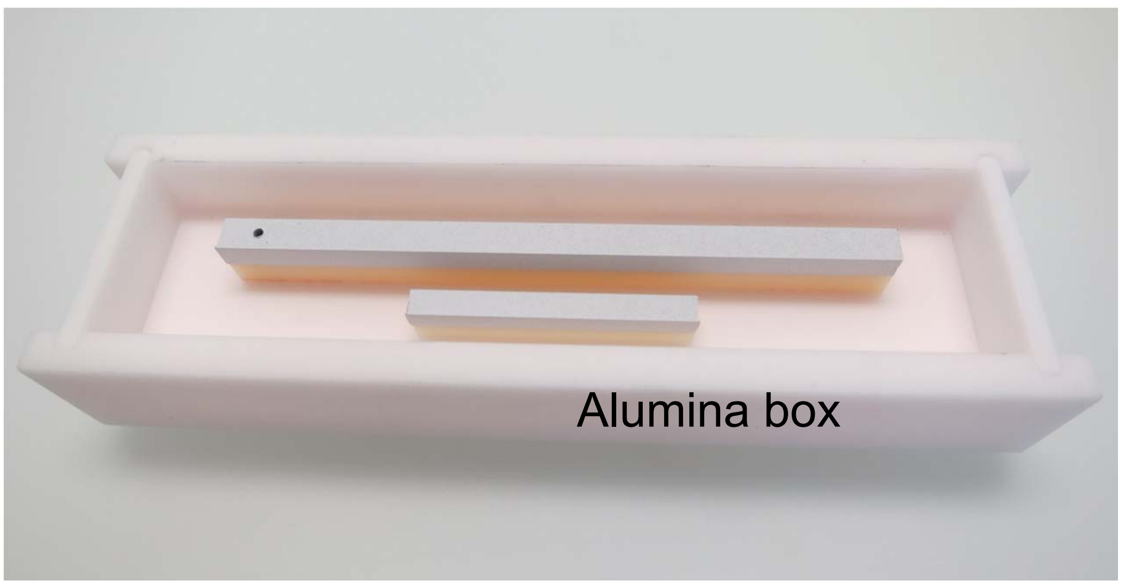


Pressed feed and seed rod on their lower alumina punch in the alumina box

This alumina box is especially suitable for the tube furnace

Pressed rods ready for sintering

The pressed rods are mechanically not stable. If they are touched in a not very careful way, then they become damaged or destroyed. However, the rods are needed in a mechanically stable form. Therefore the pressed rods, their lower alumina punch and the alumina box will be placed in a furnace and heated to an appropriate high temperature under a suitable atmosphere which results in sintering and chemical solid state reactions.

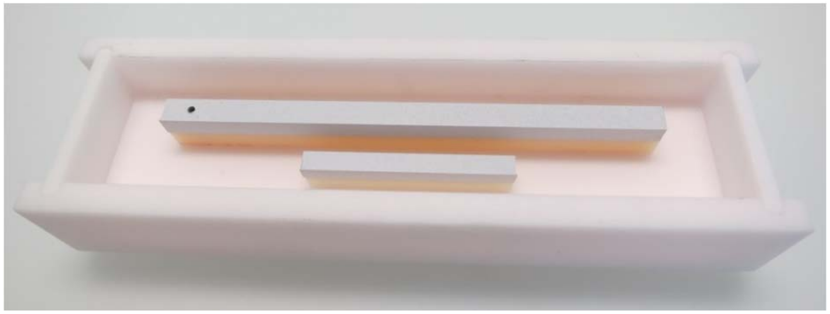


Pressed feed and seed rod on their lower alumina punch in the alumina box

Chemical composition of the pressed rods in this example: 0,6 Nb + 0,2 Nb_2O_5

This alumina box is especially suitable for the tube furnace

Rods before and after sintering

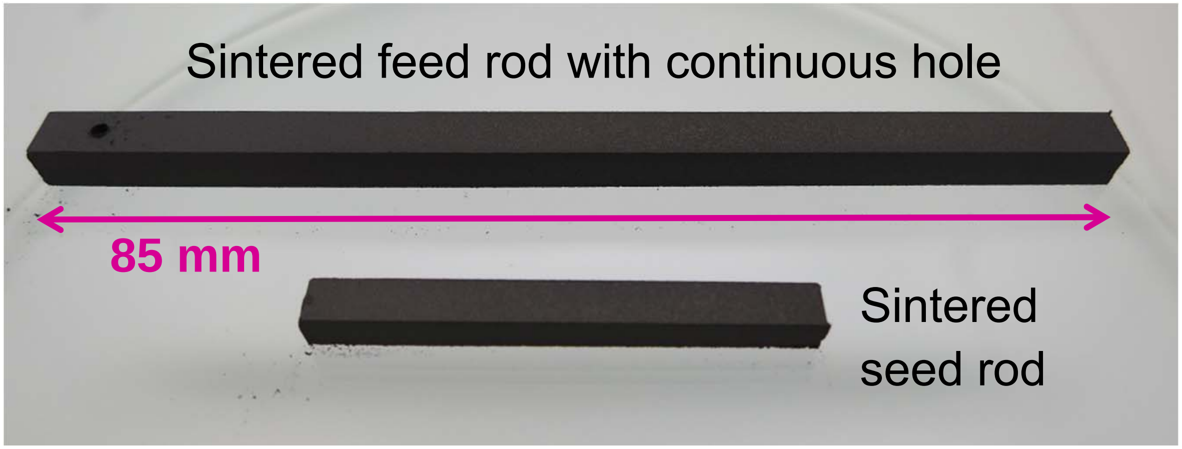


Pressed rods on their lower alumina punch in an alumina box before sintering

Chemical composition of the powder in this example: 0,6 Nb + 0,2 Nb_2O_5

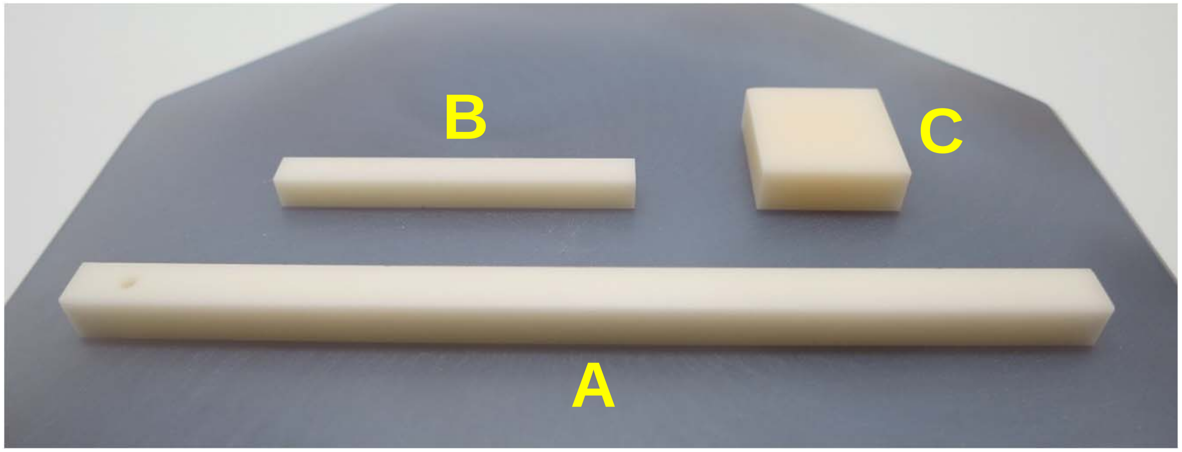
Pressed rods on their lower alumina punch in an alumina box after sintering them for 1 h at 1150 °C under argon

The color change of the rods from white-grey to black is due to chemical solid state reactions like 0,6 Nb + 0,2 $Nb_2O_5 \rightarrow NbO$

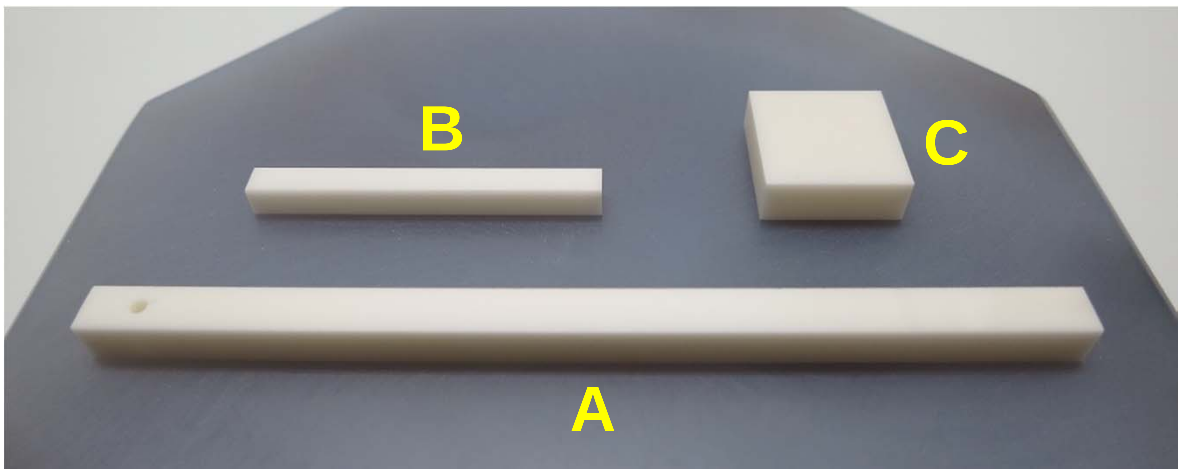


Several types of lower punches on which the powder is pressed

Lower punches for the pressing die type A (feed rod), type B (seed rod) and type C



Lower punches made of alumina (FRIATEC FRIALIT F 99,7)
- usable up to 1950 °C

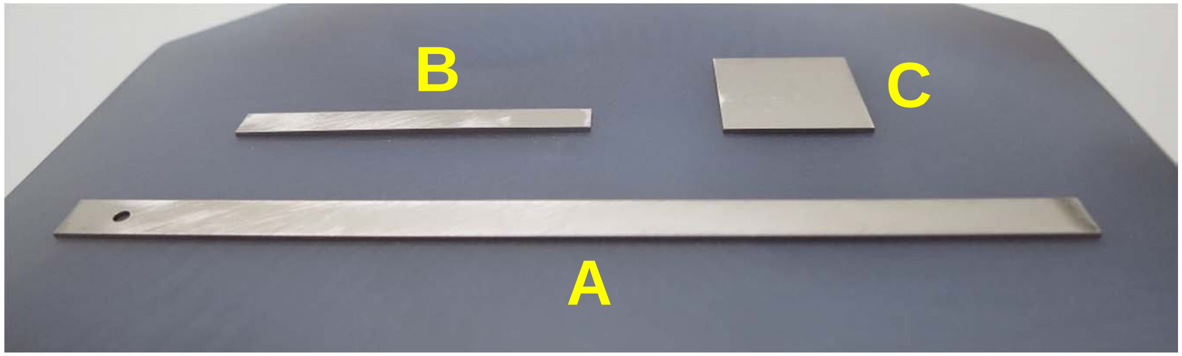


Lower punches made of yttria stabilized zirconia (FRIATEC DEGUSSIT FZY)
- usable up to 1500 °C

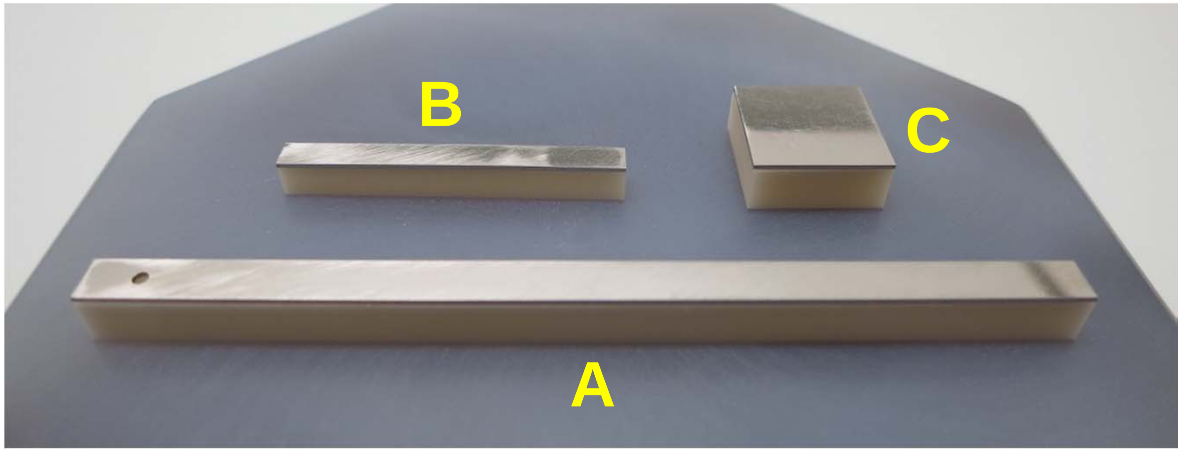
Made by FRIATEC AG (Germany), purchased and delivered from stone-ware gmbh (Switzerland)

Another option for the lower punch on which the powder is pressed

0,5 mm thick plates made of FKS-Platinum for the lower punches of the pressing die type A (feed rod), type B (seed rod) and type C – Made by Ögussa (Austria), purchased and delivered from stone-ware gmbh (Switzerland)



FKS-Platinum is a dispersion hardened platinum which contains 0,16 % zirconia
- usable up to 1400 °C



Lower punches made of alumina (see previous page) covered with FKS-Platinum plates. If this arrangement is used in the pressing dies, then the powder is pressed directly on the FKS-Platinum plates.

Advantages of the design of the pressing dies and rods

- Pressing powder into rectangular shapes without abrasion of metallic or magnetic components on the surface of the pressed powder

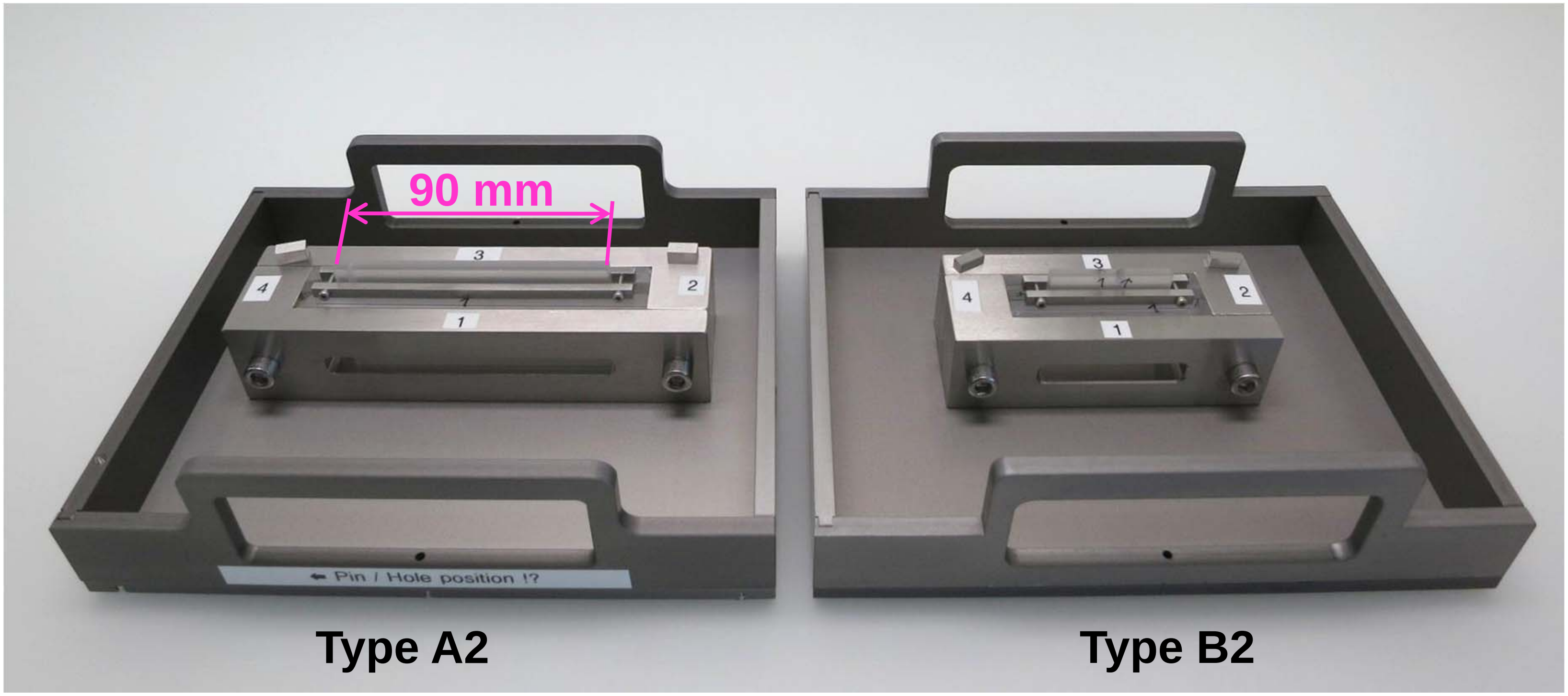
- Pressing dies are stainless, carefree, and can be easily cleaned

- Feed rod with continuous hole allows an easy, clean and safe fixation in the mirror furnace

Potential disadvantages are described in part 2 - 6

Another pressing dies made of quartz glass ...

Pressing dies made of quartz glass



Type A2 with rectangular punch for feed rods with length 90 mm and width 5 mm

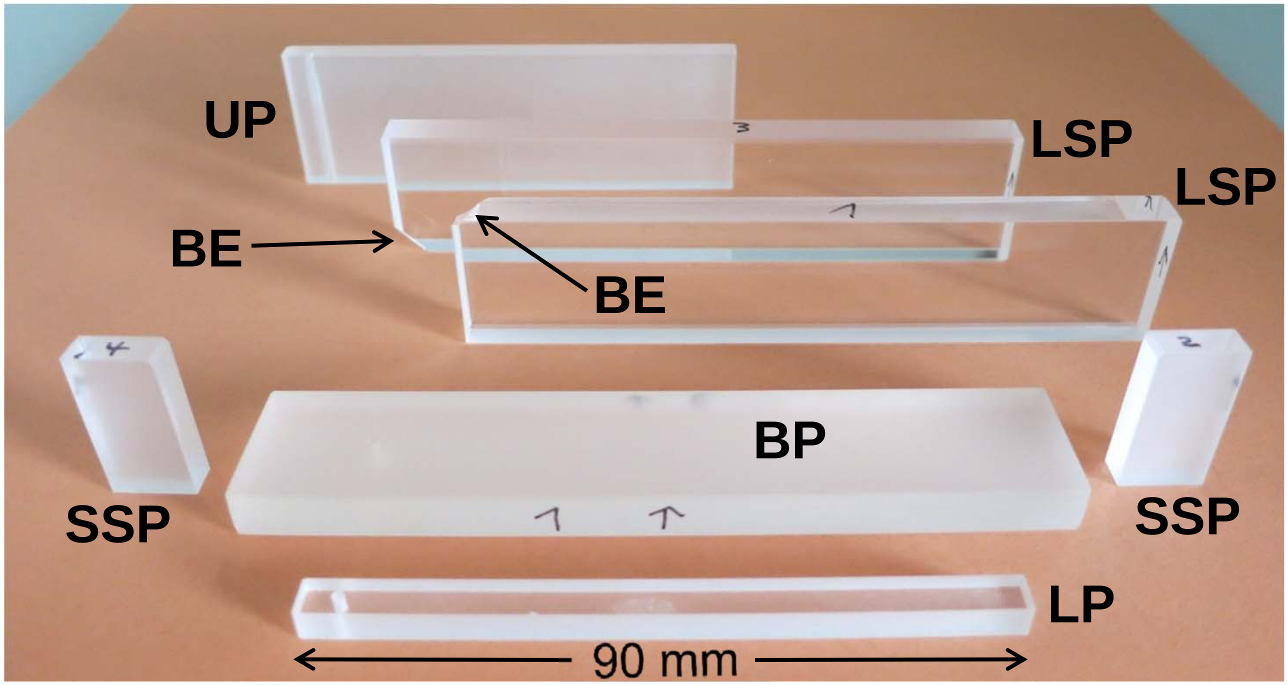
Type B2 with rectangular punch for seed rods with length 40 mm and width 4 mm

Glass parts purchased and delivered from EMATAG AG (Switzerland)

Metal frames, trays and other metal parts made in the metal workshop of the Department of Materials of the ETH Zurich by C. Roth and M. Elsener

Pressing die type A2 – Single glass components

Single components purchased and delivered from EMATAG AG (Switzerland)



Polished surfaces are transparent

Smoothed surfaces are non-transparent

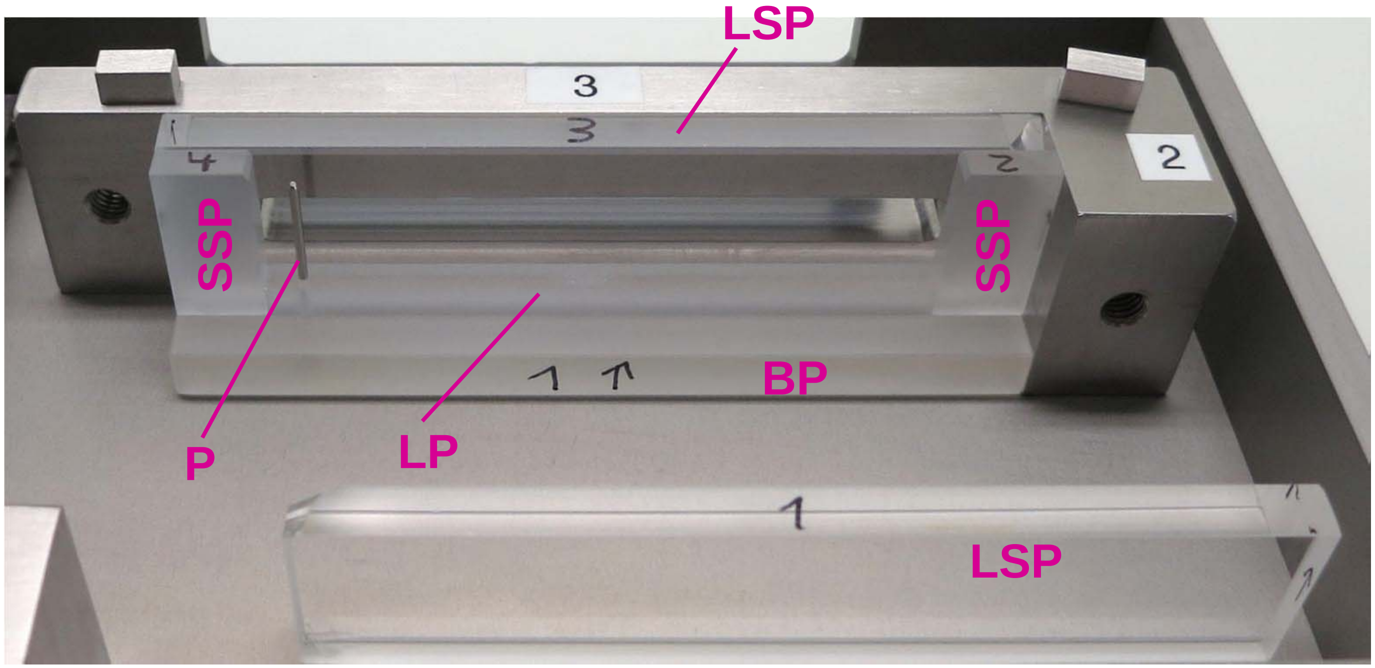
SSP Short side panel
LSP Long side panel
UP Upper punch with continuous hole
BP Base plate with continuous hole

made of quartz glass (type GE124) [SSP, LSP, UP, BP]

LP Lower punch with continuous hole - made of sapphire
BE Broken edge - the damage at these locations does not affect the overall usability of this pressing die

The production of such glass components is nearby the feasibility limit because the required precision $\geq |\pm 0{,}01|$ mm for the dimensions is quite demanding

Pressing die type A2 – Partly assembled



Glassy parts and lower punch purchased and delivered from EMATAG AG (Switzerland)

Metal parts made in the metal workshop of the Department of Materials of the ETH Zurich by C. Roth

P Custom-made pin (diameter 1,3 mm) made of stainless steel, purchased and delivered from stone-ware gmbh (Switzerland). The pin extends through the lower punch LP and the base plate BP

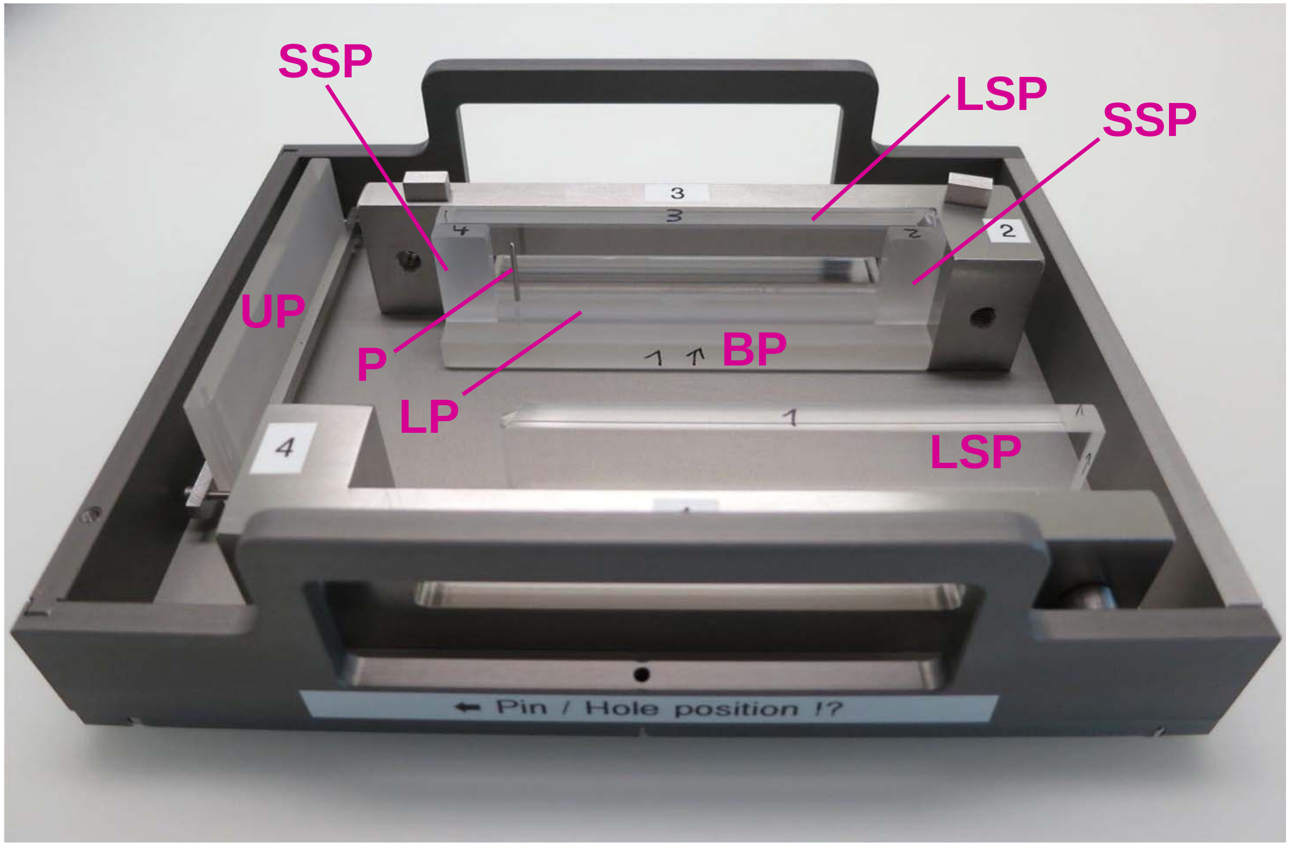
LP Lower punch made of sapphire

BP Base plate made of quartz glass

LSP Long side panel made of quartz glass

SSP Short side panel made of quartz glass

Pressing die type A2 – Partly assembled



Glassy parts and lower punch purchased and delivered from EMATAG AG (Switzerland)

Metal parts made in the metal workshop of the Department of Materials of the ETH Zurich by C. Roth

P Custom-made pin (diameter 1,3 mm) made of stainless steel, purchased and delivered from stone-ware gmbh (Switzerland). The pin extends through the lower punch LP and the base plate BP

LP Lower punch made of sapphire

BP Base plate made of quartz glass

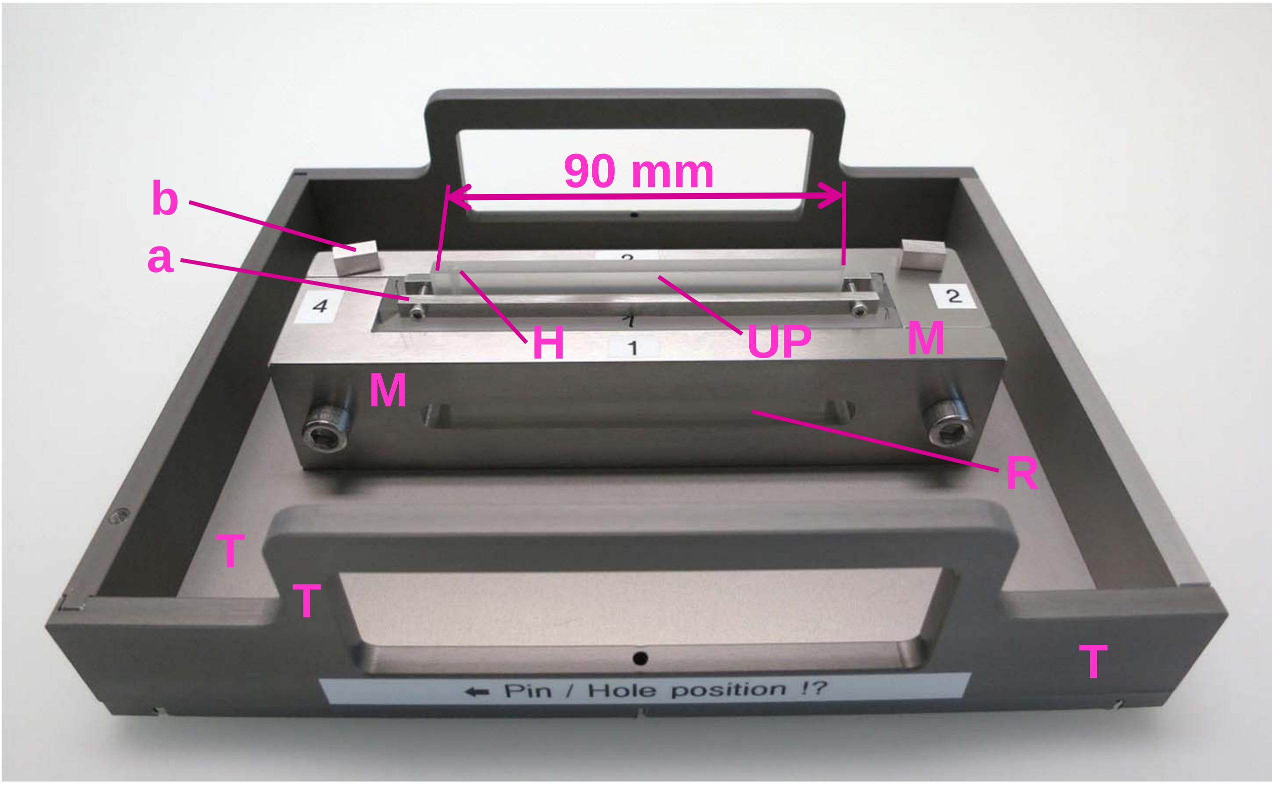
UP Upper punch made of quartz glass

LSP Long side panel made of quartz glass

SSP Short side panel made of quartz glass

Pressing die type A2 – Completely assembled

Pressing die type A2 – Completely assembled



Glassy parts made of quartz glass and sapphire - purchased and delivered from EMATAG AG (Switzerland)

UP Upper punch with length 90 mm and width 5 mm and continuous hole H

R Recess in the metal frame with height 8 mm and length 90 mm - it makes it possible to view into the interior of the pressing die

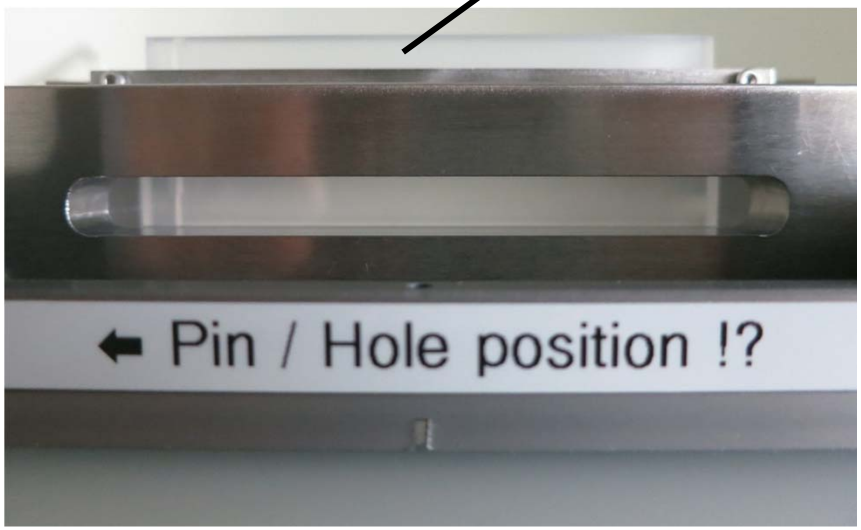
Metal parts made in the metal workshop of the Department of Materials of the ETH Zurich by C. Roth:

M Two-part frame made of stainless steel

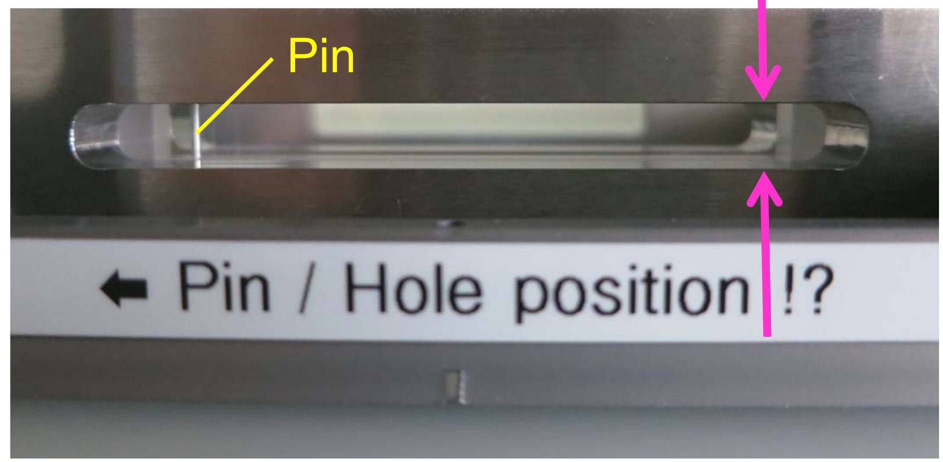
a , b Components made of stainless steel for an estimation of the thickness or height of the pressed powder

T Tray made of eloxed aluminum

Pressing die type A2 – Side views through a glassy side panel



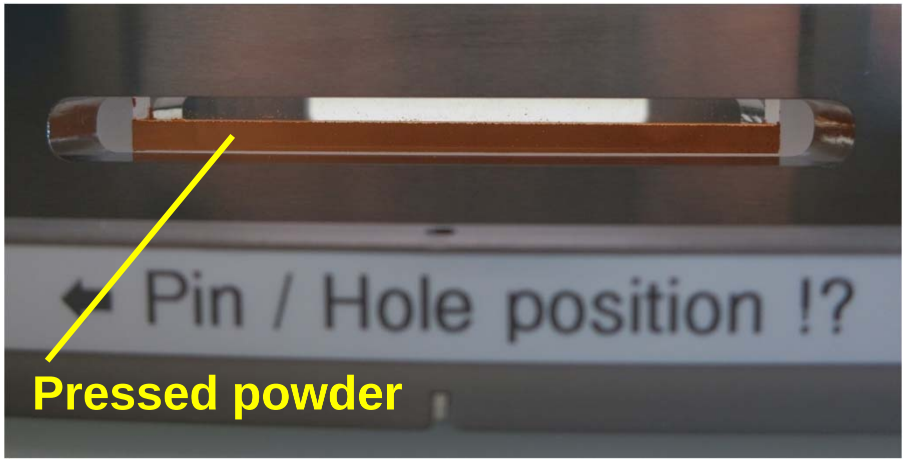
Side view when the upper punch is inserted



Side view when the upper punch is removed

Pressing die type A2 – Side views through a glassy side panel

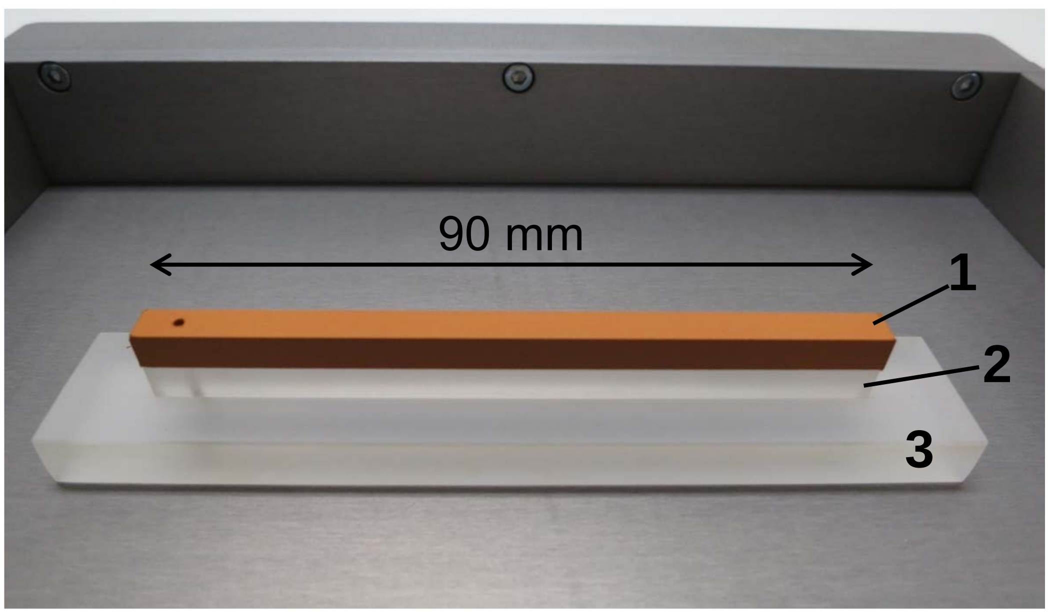
Side view when powder is filled into the pressing die



Side view after pressing with a force of 1 kN and when the upper punch is removed. The height of the pressed powder is about 4 mm

Pressing die type A2 – Example of an as-pressed rod

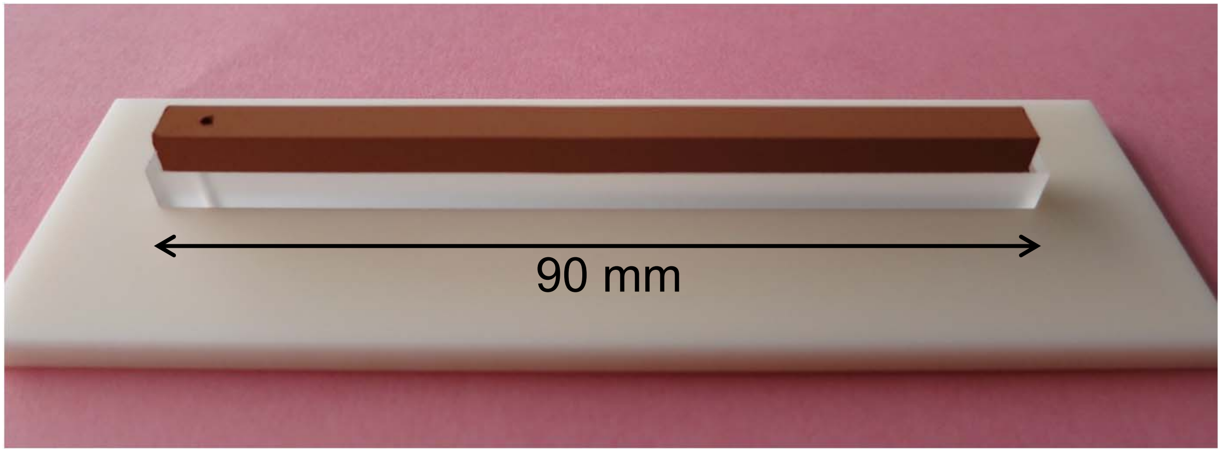
An as-pressed rod inside the pressing die when the metal frame is removed. The applied pressing force was 1 kN



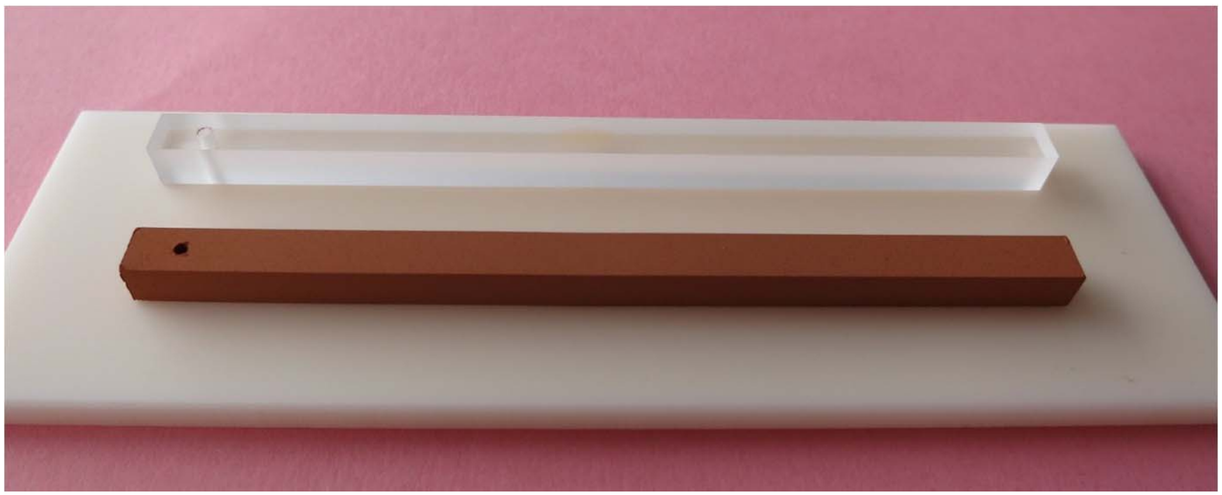
View when the side panels are removed:

As-pressed rod (1) on a lower punch (2) which is made of sapphire. The lower punch (2) is located on the base plate (3) which is made of quartz glass

Pressing die type A2 – Example of a sintered rod



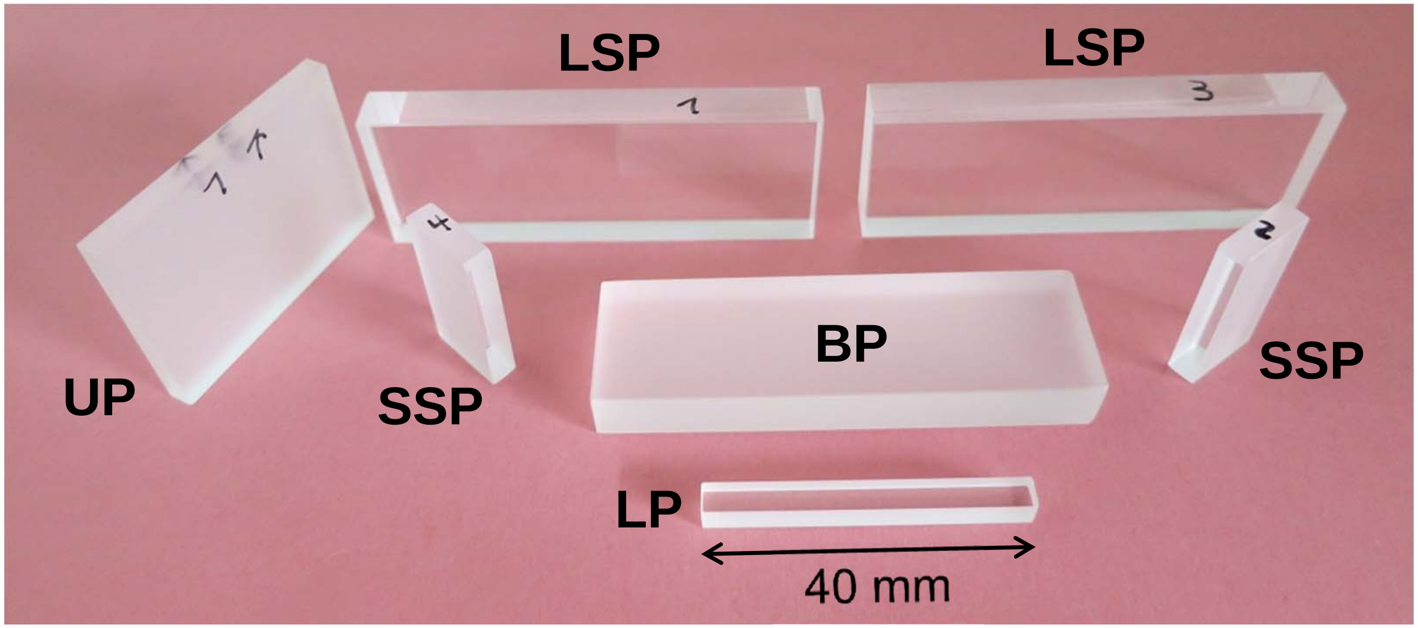
Sintered feed rod on the lower punch made of sapphire. The rod was sintered on the lower punch for 4 h at 1290 °C in air. Compared with the as-pressed rod (see previous page) the sintered rod is somewhat shorter, i.e. a shrinkage took place



View when the sintered rod is taken away from the lower punch

Pressing die type B2 – Single glass components

Single components purchased and delivered from EMATAG AG (Switzerland)



Polished surfaces are transparent

Smoothed surfaces are non-transparent

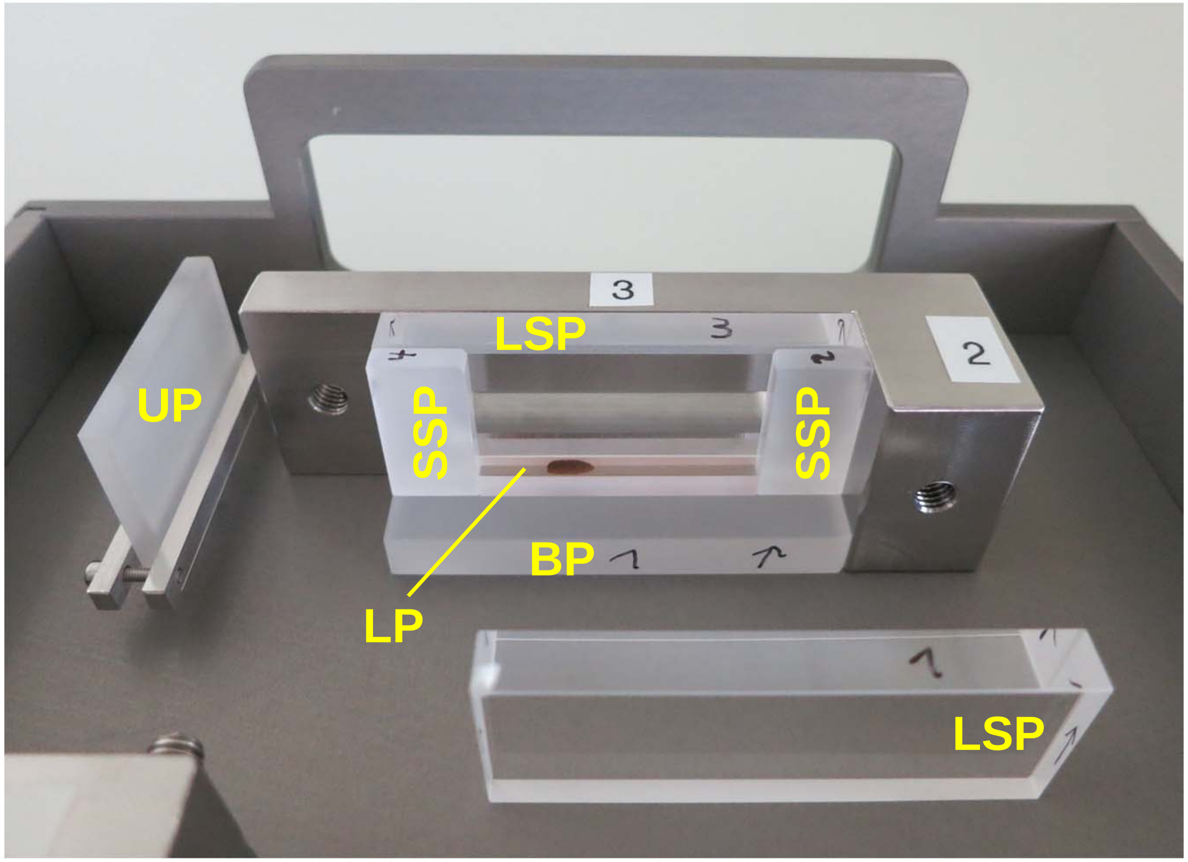
SSP Short side panel
LSP Long side panel
UP Upper punch
BP Base plate

(SSP, LSP, UP, BP: made of quartz glass (type GE124))

LP Lower punch made of sapphire

The production of such glass components is nearby the feasibility limit because the required precision $\geq |\pm 0{,}01|$ mm for the dimensions is quite demanding

Pressing die type B2 – Partly assembled



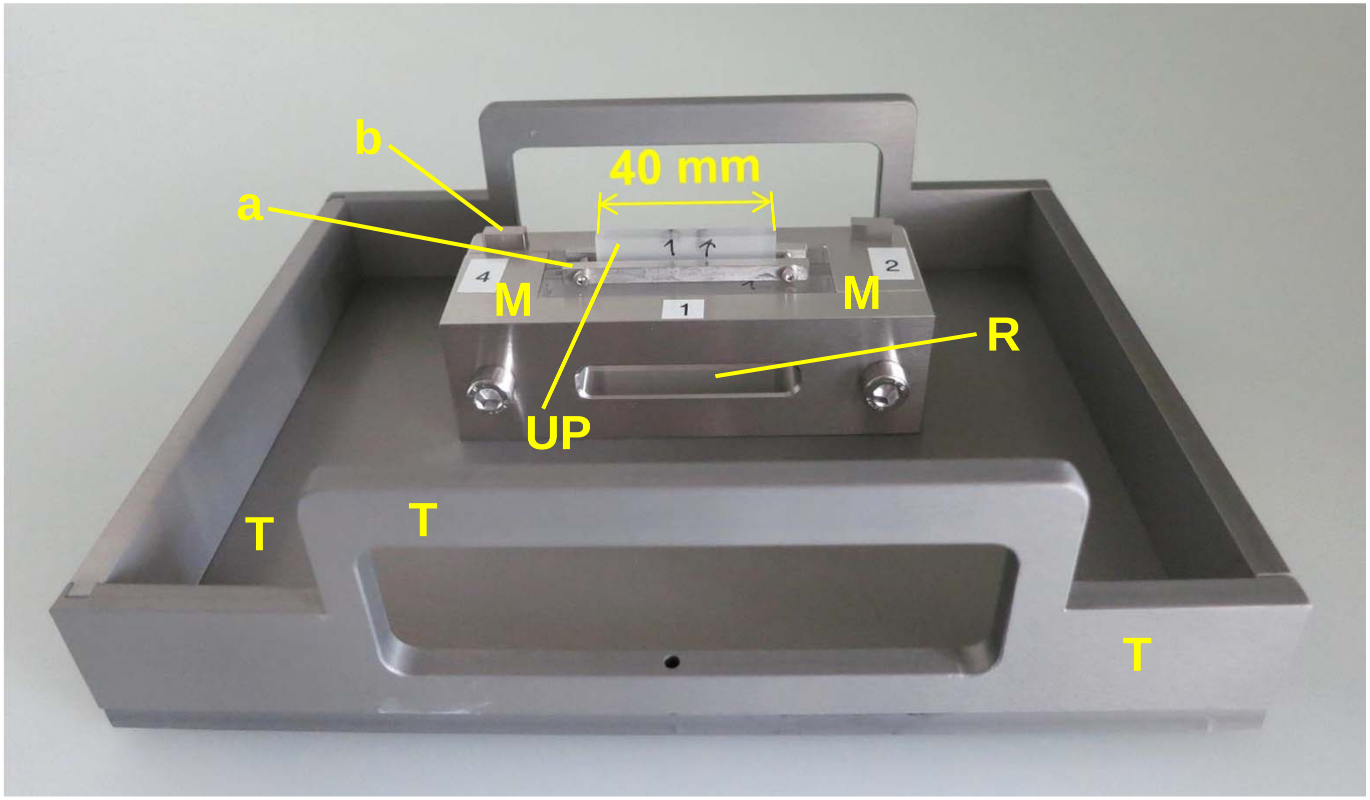
Glassy parts and lower punch purchased and delivered from EMATAG AG (Switzerland)

Metal parts made in the metal workshop of the Department of Materials of the ETH Zurich by C. Roth

UP Upper punch made of quartz glass
LP Lower punch made of sapphire - the reason for the brown color on the surface is explained later
BP Base plate made of quartz glass glass
LSP Long side panel made of quartz glass
SSP Short side panel made of quartz glass

Pressing die type B2 – Completely assembled

Pressing die type B2 – Completely assembled



Metal parts made in the metal workshop of the Department of Materials of the ETH Zurich by C. Roth:

M Two-part frame made of stainless steel

a , b Components made of stainless steel for an estimation of the thickness or height of the pressed powder

T Tray made of eloxed aluminum

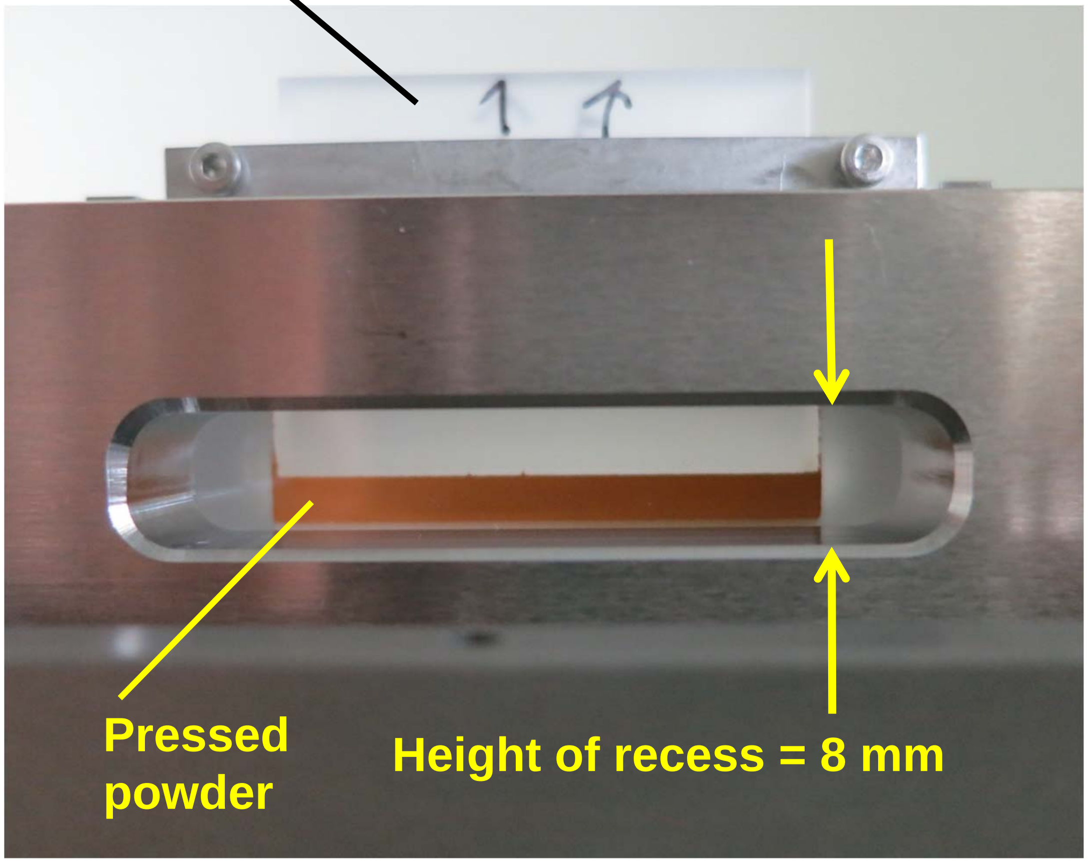
Glassy parts made of quartz glass and sapphire - purchased and delivered from EMATAG AG (Switzerland)

UP Upper punch with length 40 mm and width 4 mm

R Recess in the metal frame with height 8 mm and length 40 mm - it makes it possible to view into the interior of the pressing die

Pressing die type B2 – A side view through a glassy side panel

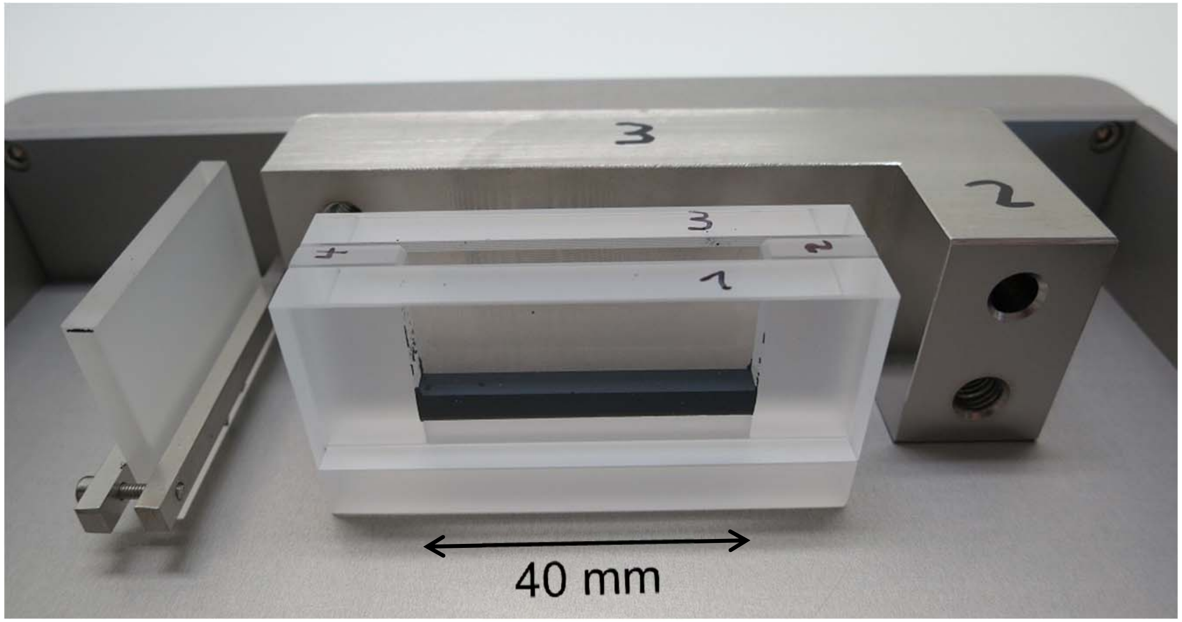
Upper punch



Side view with inserted upper punch after pressing powder with a force of 0,8 kN

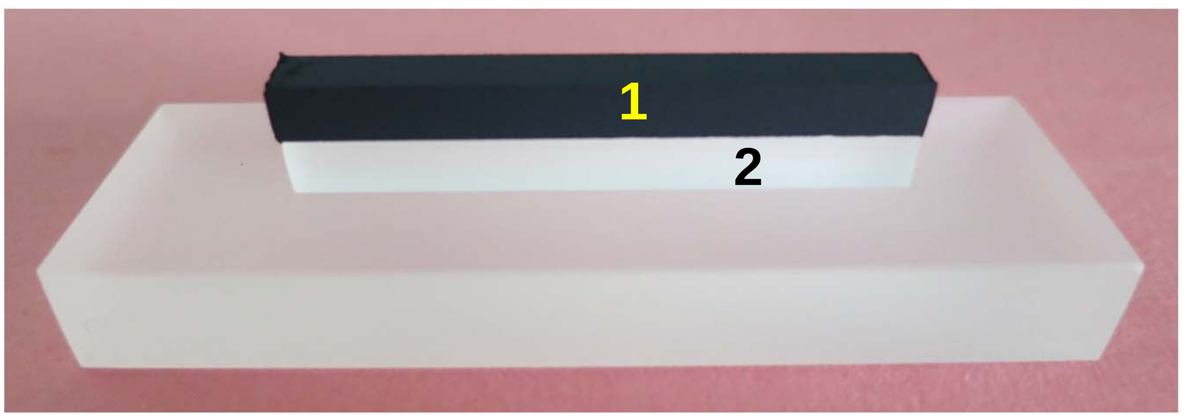
The height of the pressed powder is about 3 mm

Pressing die type B2 – Example of an as-pressed rod



An as-pressed rod inside the glass components. The applied pressing force was 0,5 kN. The chemical composition of the pressed powder in this example is

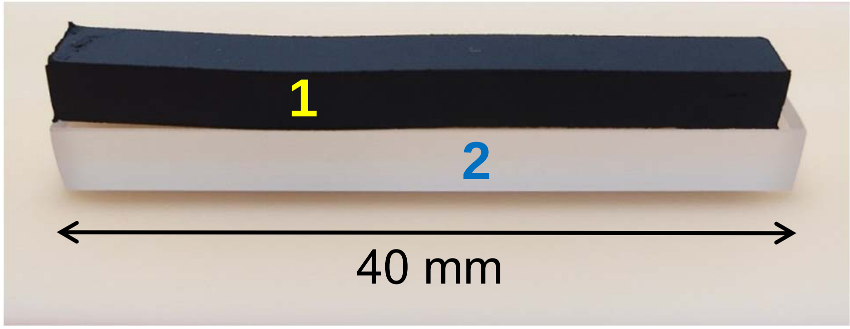
$Y_2O_3 + Mn_2O_3 = 2\ YMnO_3$



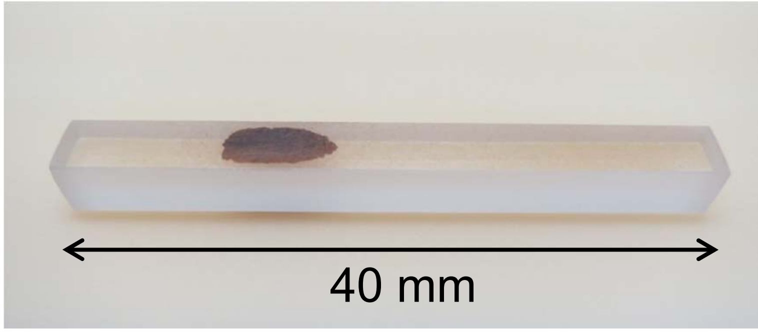
View when all side panels are removed: As-pressed rod (1) on the lower punch (2) which is made of sapphire

Note: These pictures were taken at a date when the metal frame with recess was not yet available. Therefore in this example the pressing die was assembled with the metal frame type B

Pressing die type B2 – Example of a sintered rod

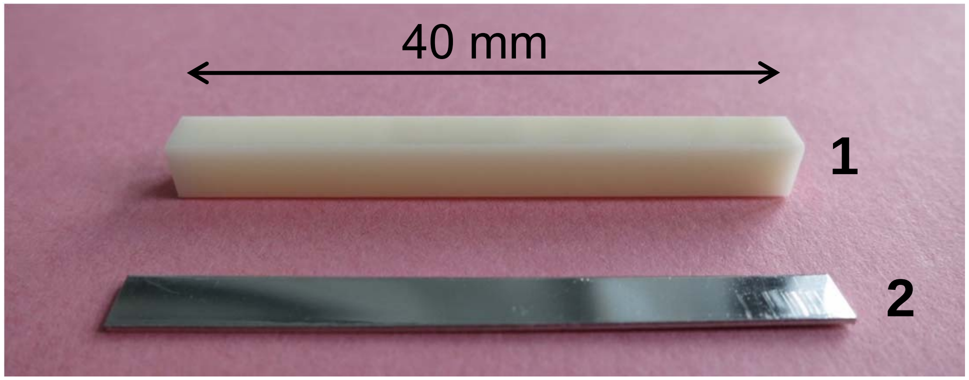


Sintered rod (1) on a lower punch made of sapphire (2). In this example the chemical composition of the rod is $Y_2O_3 + Mn_2O_3 = 2\ YMnO_3$ and it was sintered for 4 h at 1410 °C in air. The rod is somewhat bent but still usable as seed rod for floating zone melting



Appearance of the lower punch made of sapphire when the sintered rod is taken away. The sintering did lead to a brown spot. It indicates that a chemical solid state reaction between $Y_2O_3 + Mn_2O_3 = 2\ YMnO_3$ and sapphire took place at a specific location. Nevertheless, this lower punch can be used for the preparation of another seed rods because its surface is still fine

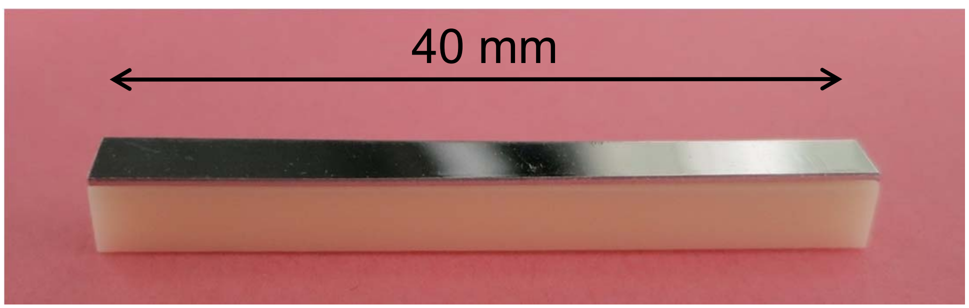
Pressing die type B2 – Another options for the lower punch



Lower punch (1) made of alumina (FRIATEC FRIALIT F 99,7) by FRIATEC AG (Germany)

Sheet (2) with thickness 0,5 mm made of FKS-Platinum by Ögussa (Austria)

Purchased and delivered from stone-ware gmbh (Switzerland)



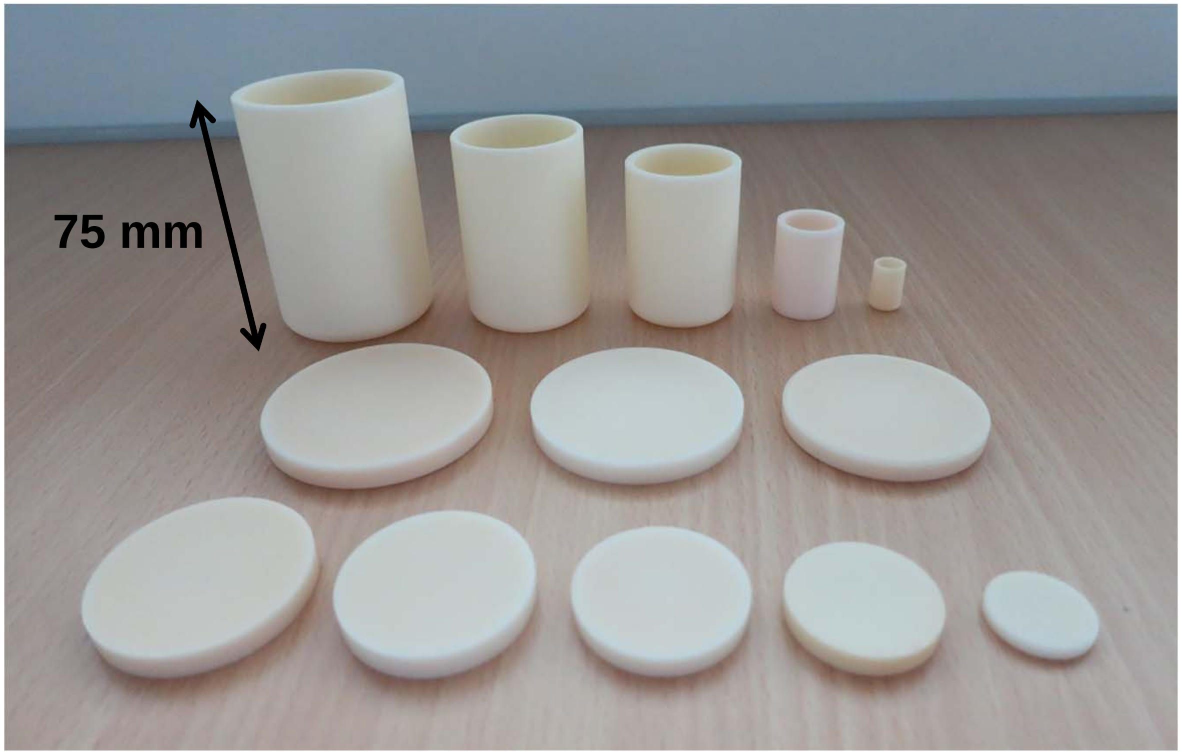
Lower punch made of alumina covered with the sheet made of FKS-Platinum. If this arrangement is used within the pressing die, then the powder is pressed directly on the FKS-Platinum sheet

FKS-Platinum is a dispersion hardened platinum which contains 0,16 % zirconia

Part 6

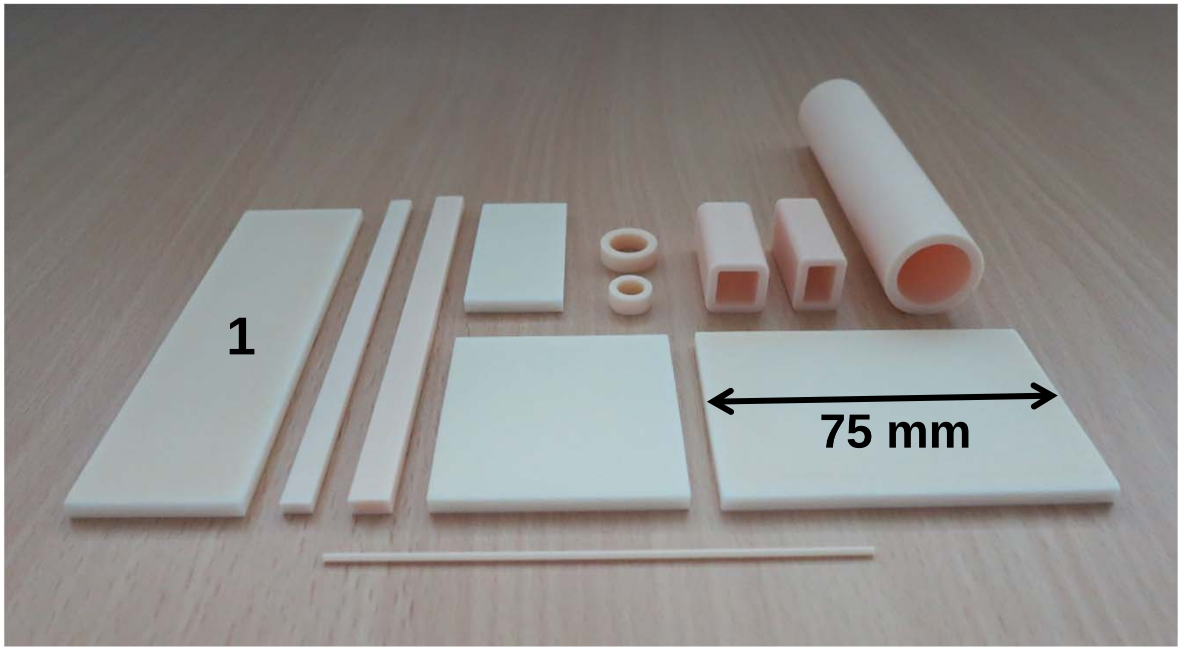
Presentation of various
FRIATEC components
made of
high temperature ceramics

Examples of FRIATEC components made of high temperature ceramics



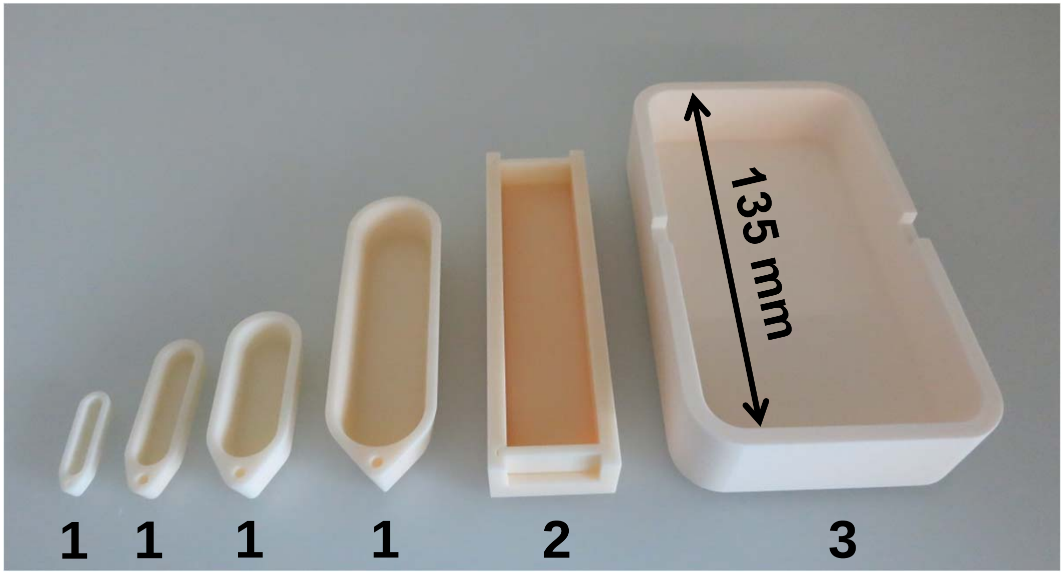
Crucibles and discs / lids made of alumina by FRIATEC AG (Germany), purchased and delivered from stone-ware gmbh (Switzerland).
These are FRIATEC standard products made of the alumina type FRIATEC DEGUSSIT AL 23 which can be used up to 1950 °C.

Examples of FRIATEC components made of high temperature ceramics



Plates, rods, and tubes made of alumina (FRIATEC DEGUSSIT AL 23) by FRIATEC AG (Germany), purchased and delivered from stone-ware gmbh (Switzerland). These are mainly standard products. Plate 1 represents a custom-made design. The length of the rods and tubes is choosen by the customer.

Examples of FRIATEC components made of high temperature ceramics



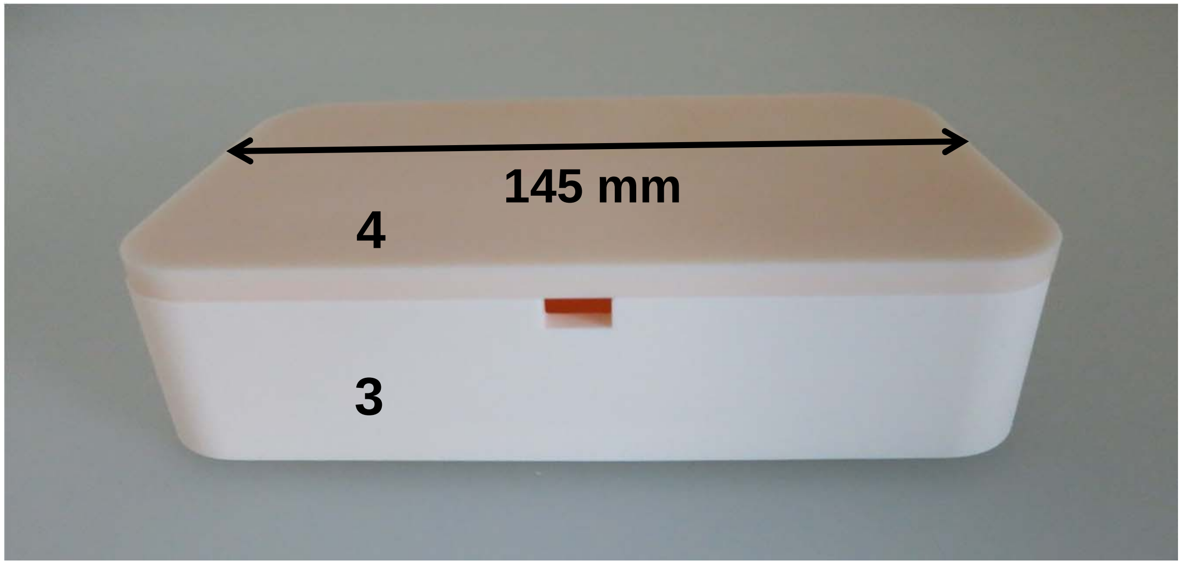
Boats (1) and boxes (2, 3) made of alumina by FRIATEC AG (Germany), purchased and delivered from stone-ware gmbh (Switzerland)

3 Standard product with customized modifications. Made of the alumina type FRIATEC DEGUSSIT AL 24. This box is especially suitable for the chamber furnace, see part 7.

2 Custom-made design made of the alumina type FIRIATEC FRIALIT F 99,7. This box is especially suitable for the tube furnace, see part 5 and 8.

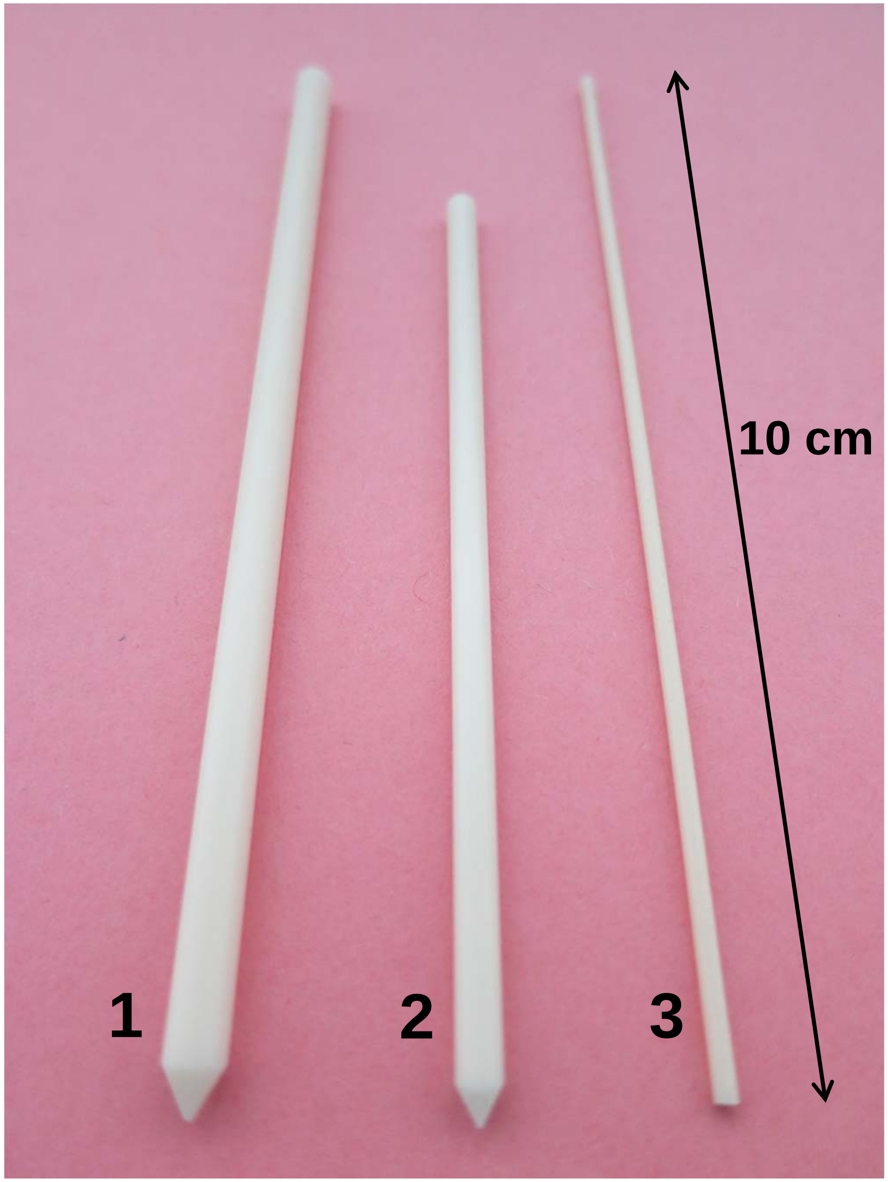
1 Standard products made of the alumina type FRIATEC DEGUSSIT AL 23

Examples of FRIATEC components made of high temperature ceramics



Box (3) with lid (4) made of alumina by FRIATEC AG (Germany), purchased and delivered from stone-ware gmbh (Switzerland). This box is shown without lid on the previous page and is made of the alumina type FRIATEC DEGUSSIT AL 24. The custom-made lid is made of the alumina type FRIATEC DEGUSSIT AL 23. This box is especially suitable for the chamber furnace, see part 7.

Examples of FRIATEC components made of high temperature ceramics



Rods made of alumina (FRIATEC DEGUSSIT AL 23) by FRIATEC AG (Germany), purchased and delivered from stone-ware gmbh (Switzerland)

3 Standard product with diameter 1,5 mm

2 Custom-made design with diameter 3 mm and sharp tail. It can be used as scratch pen to clean parts such as alumina crucibles.

1 Custom-made design with diameter 4 mm and sharp tail. It can be used as scratch pen to clean parts such as the lower alumina punch of the pressing dies.

Part 7

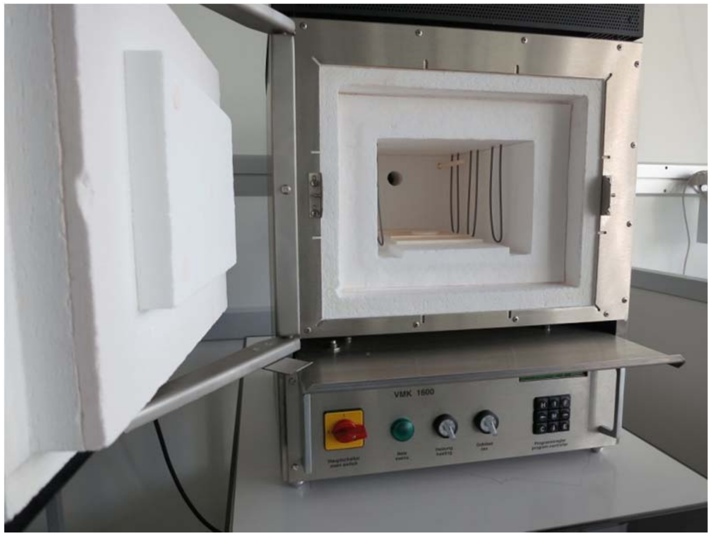
Presentation of the Linn High Therm chamber furnace

Laboratory chamber furnace from Linn High Therm

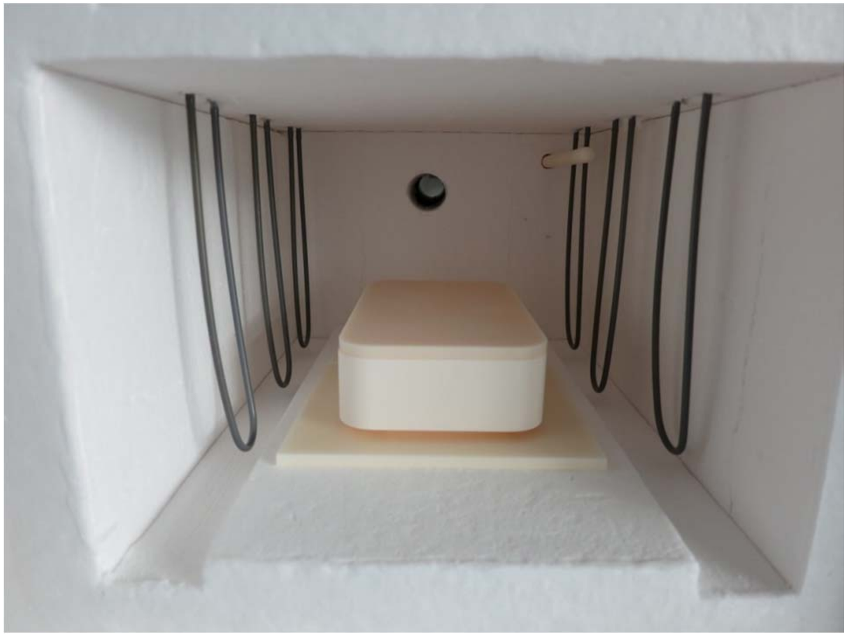
Non-gas-tight laboratory chamber furnace VMK 1600 from German company Linn High Therm

For removing moisture of starting materials, pre-reactions, calcination, sintering or synthesis of polycrystalline materials in air

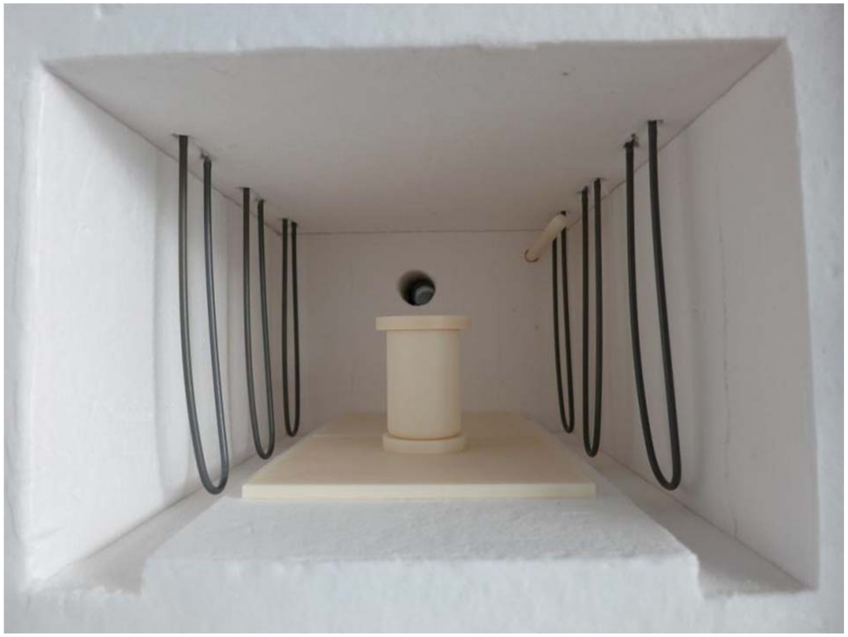
Maximum permanent operating temperature 1550 °C



Laboratory chamber furnace from Linn High Therm



Heating chamber loaded with a box and lid made of alumina. Pressed seed and feed rods can be sintered in this alumina box.



Heating chamber loaded with a crucible and lid made of alumina. The crucible is filled with powder, e.g. for removing moisture of starting materials, pre-reactions, calcination, or synthesis of polycrystalline materials.

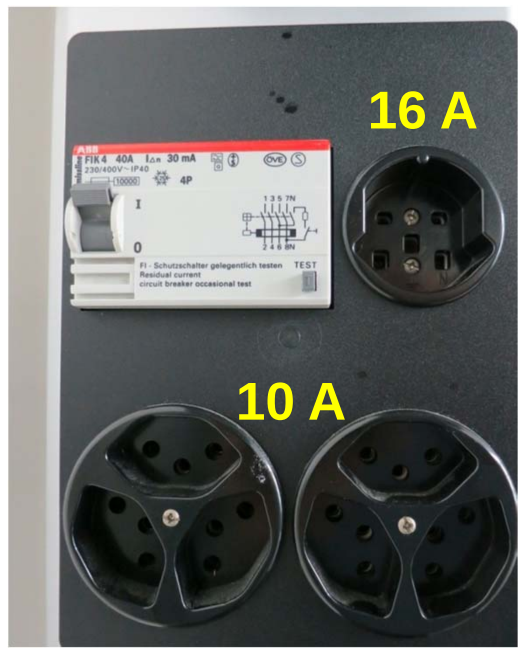
Box, crucible, and lids made of alumina by FRIATEC AG (Germany), purchased and delivered from stone-ware gmbh (Switzerland)

Laboratory chamber furnace from Linn High Therm

Power supply

- 230 V single phase
- Maximum current consumption 11,3 A during heating
  - measured by a clamp meter

Swiss plug for 230 V / 16 A single phase



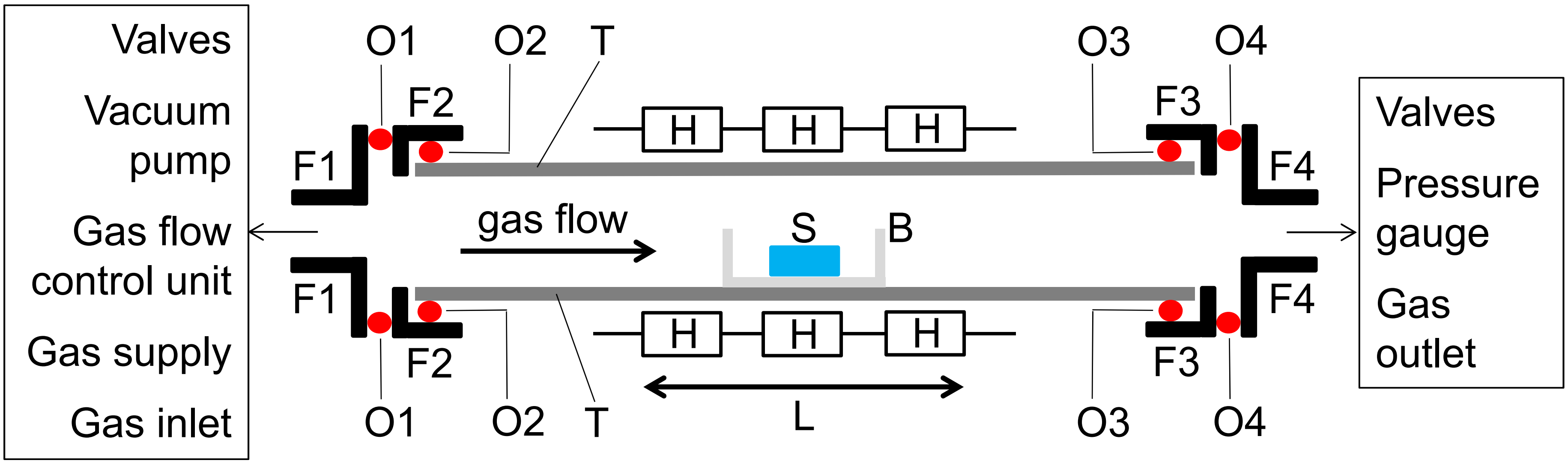
Swiss sockets 230 V single phase

Part 8

Presentation of the GERO tube furnace

Sketch of the construction of a gas-tight tube furnace

Aim: Gas-tight chamber in which samples can be heated under a non-air atmosphere such as oxygen, argon, argon plus hydrogen, or vacuum



F1 , F2 , F3 , F4 = Water-cooled flanges

O1 , O2 , O3 , O4 = O-rings

T = tube, e.g. made of alumina (Al_2O_3)

B = Sample box, e.g. made of alumina

S = Sample

H = Heating elements

L = Length of heated tube segment, e.g. 60 cm at the tube furnace which is shown on the next page

GERO tube furnace

Alumina tube inside (not visible)   Gas outlet (not visible from this view)

Gas-tight tube furnace HTRH 100-600 / 16 from German company GERO

For the synthesis or sintering of polycrystalline materials under a non-air atmosphere such as argon

Maximum operating temperature 1600 °C, 1450 °C under vacuum

Tolerable heating and cooling rate ≤ 300 °C / h because of ceramic alumina tube

1 Turbo pumping station “HiCube” from Pfeiffer Vacuum with oil-free backing pump

2 Supply of gases like Ar and the non-flammable gas mixture 97.2 % Ar + 2.8 % H_2

3 Gas flow control system   4 Gas inlet at the tube   5 Control unit

6 Oxygen analyzer ZIROX SGM7 to measure the O_2 content of Ar at the gas outlet

7 Cooling water port for the water-cooled flanges

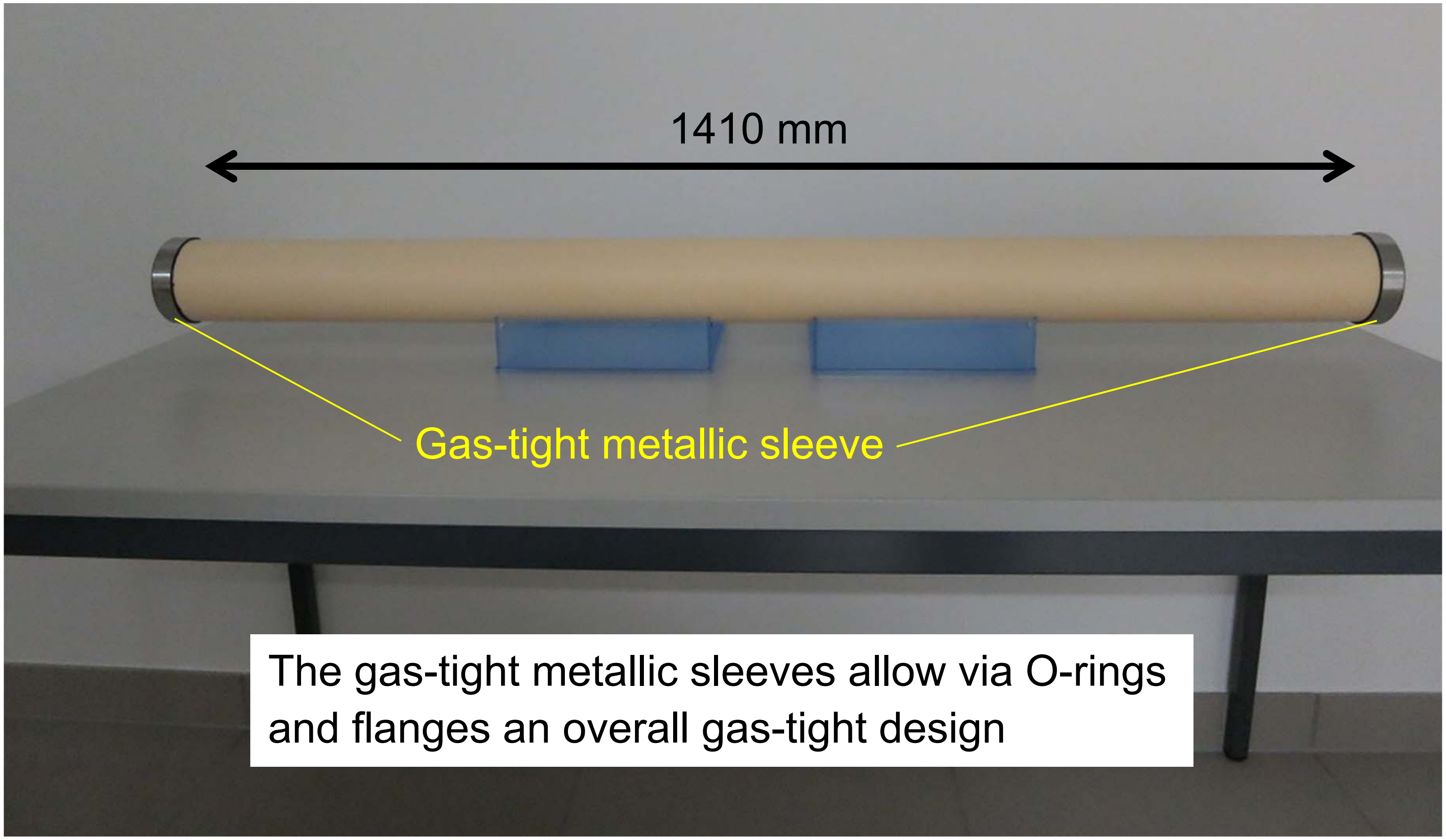
Type of alumina tube which is used in the tube furnace

Length 1410 mm • Inner diameter 85 mm • Outer diameter 100 mm

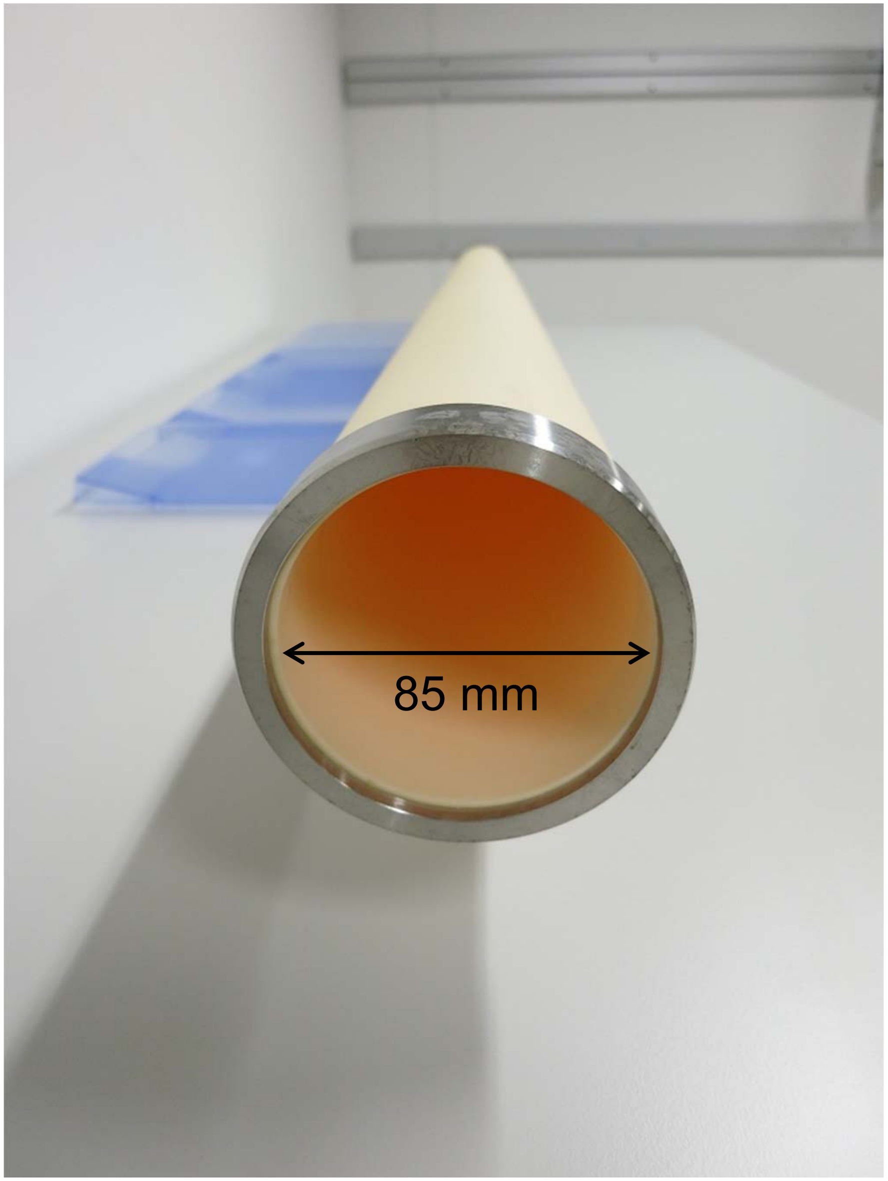
Mass 10,5 kg • Alumina (Al_2O_3) type: FRIATEC DEGUSSIT AL 23

Alumina tube made by FRIATEC AG (Germany)

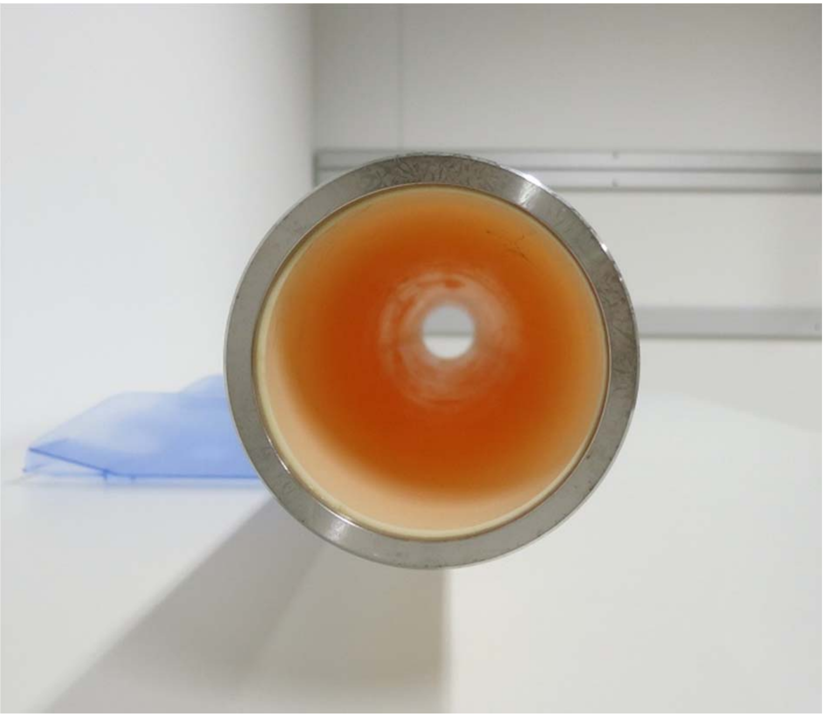
Metallic sleeves attached by GERO



Type of alumina tube which is used in the tube furnace

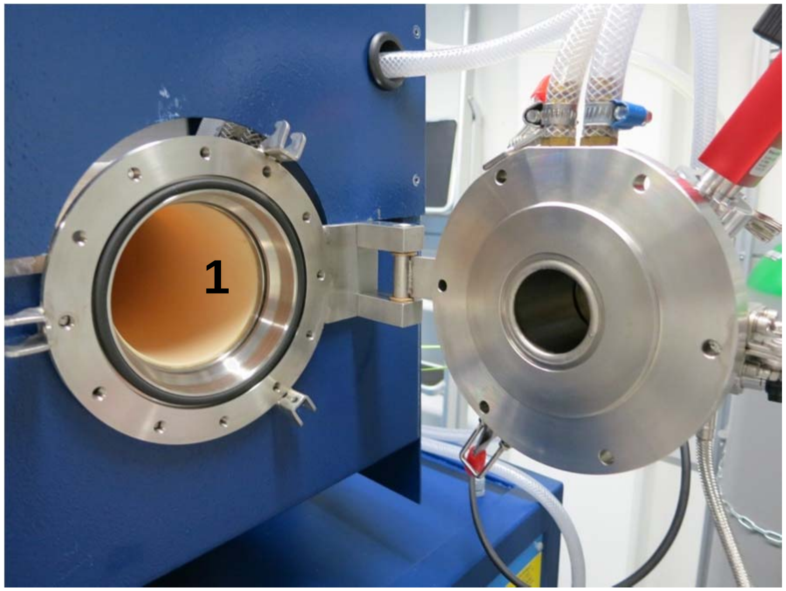


Another views of the alumina tube



Tube furnace – Gas outlet side - Alumina tube - Insertion of samples

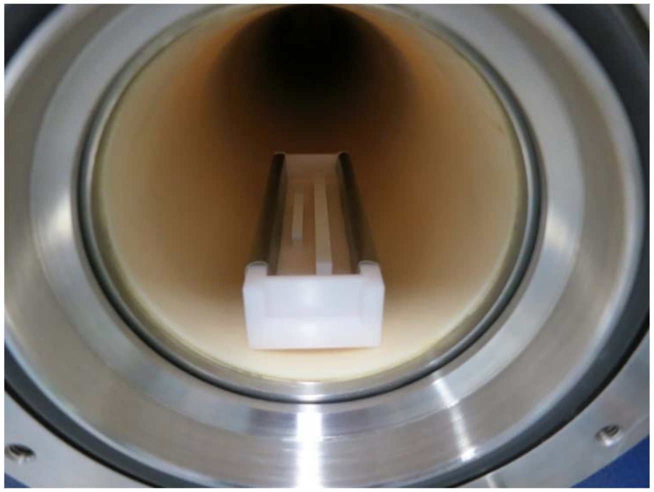
Flange / Door closed



Flange / Door open - Alumina tube (1) is visible

Alumina tube and alumina box made by FRIATEC AG

Alumina box with samples - pressed powder in form of two rods - and two Nb foils which act as oxygen getter



Box with samples in the tube at its end position

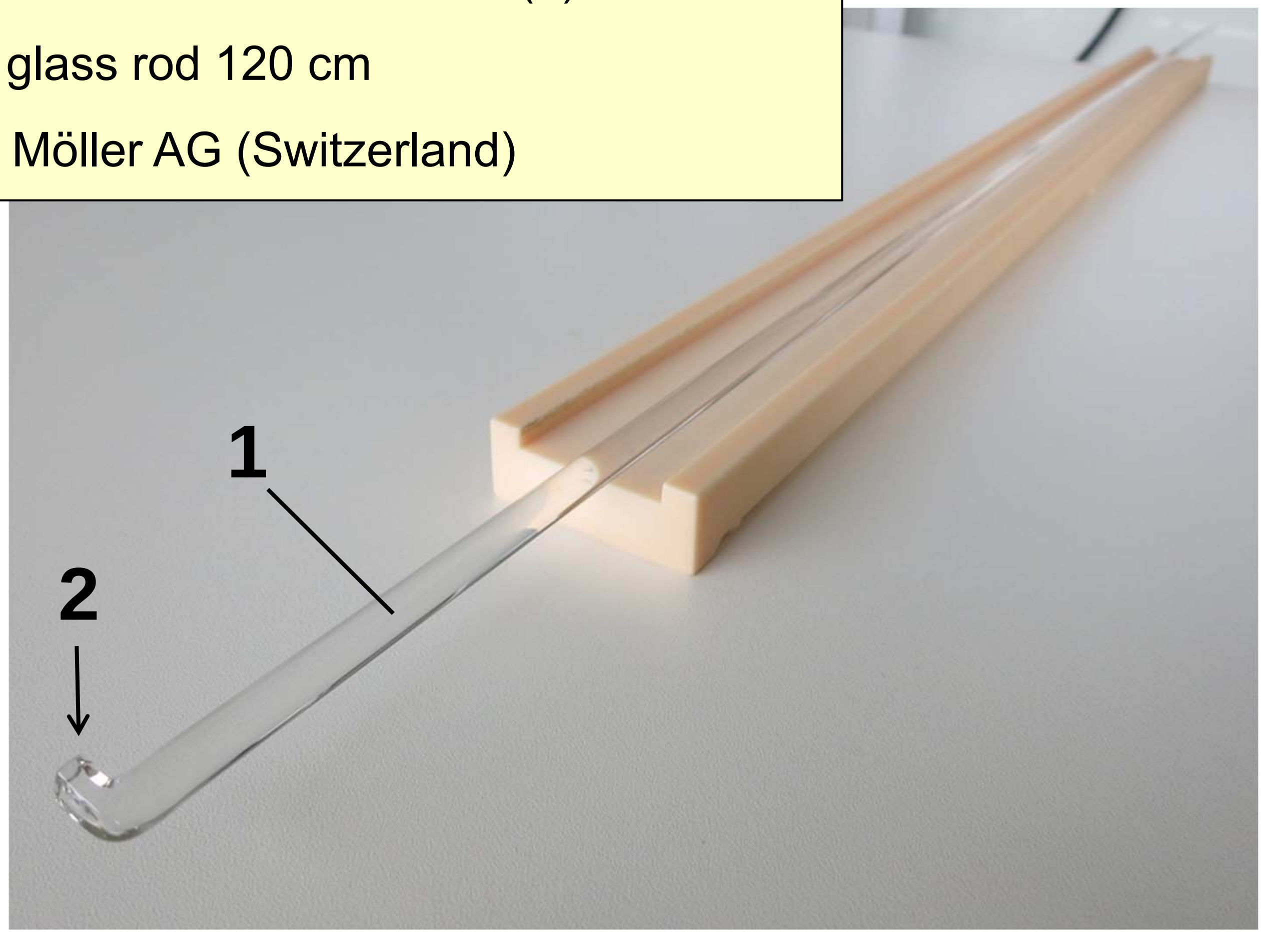
Must be moved about 65 cm halfway down by means of a long glass rod

Glass rod to move the alumina box into or out of the alumina tube

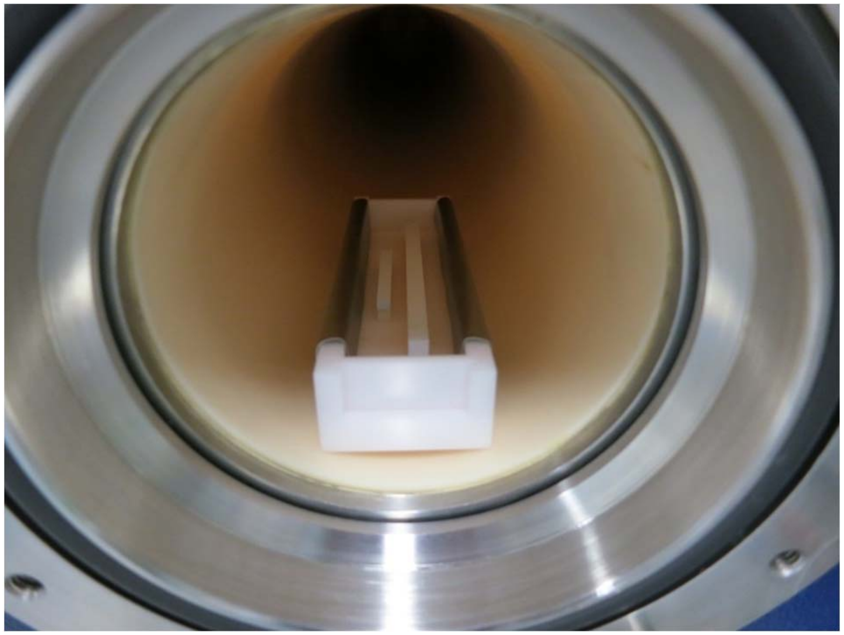
Glass rod (1) with a hook-like bracket (2) at one end

Length of the glass rod 120 cm

Made by Willi Möller AG (Switzerland)



Tube furnace – Alumina box and samples in the alumina tube

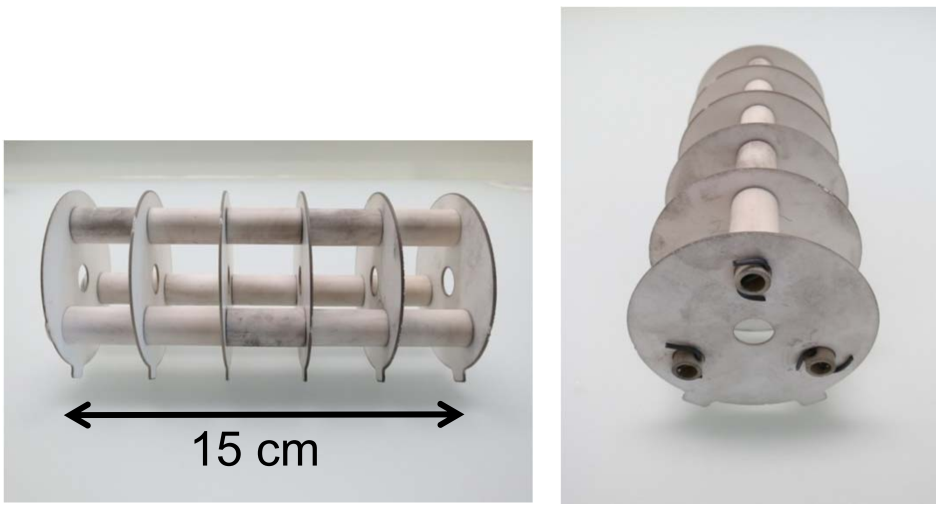


Alumina box placed in the alumina tube at its end position. The alumina box is loaded with samples. In this example the specimen are pressed powder in form of two rods.

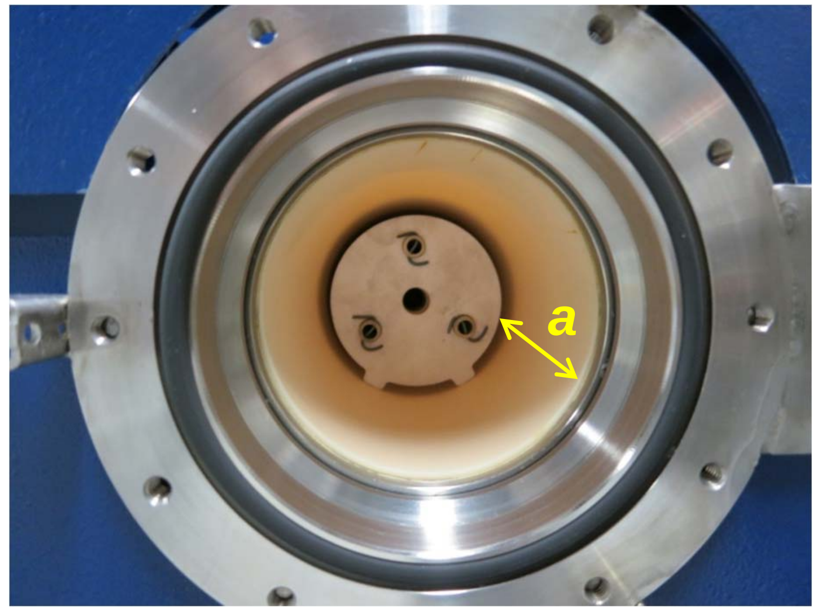
Alumina box and samples placed in the middle of the alumina tube. The glass rod shown on the previous page was used to move the alumina box into this position. The distance from the end to the middle of the alumina tube is about 70 cm.

Tube furnace – Radiation shields

After placing the alumina box and samples in the middle of the alumina tube, a radiation shield is inserted into the tube nearby its end. A second radiation shield is located at the gas inlet side of the tube. The radiation shields are made of alumina and they reduce the temperature of outer components nearby the flanges. Assuming, for example, the middle range of the alumina tube is heated to 1250 °C. Then some components nearby the flanges reach a temperature of about 30 °C (65 °C) when (no) radiation shields are used.



Two views of a radiation shield

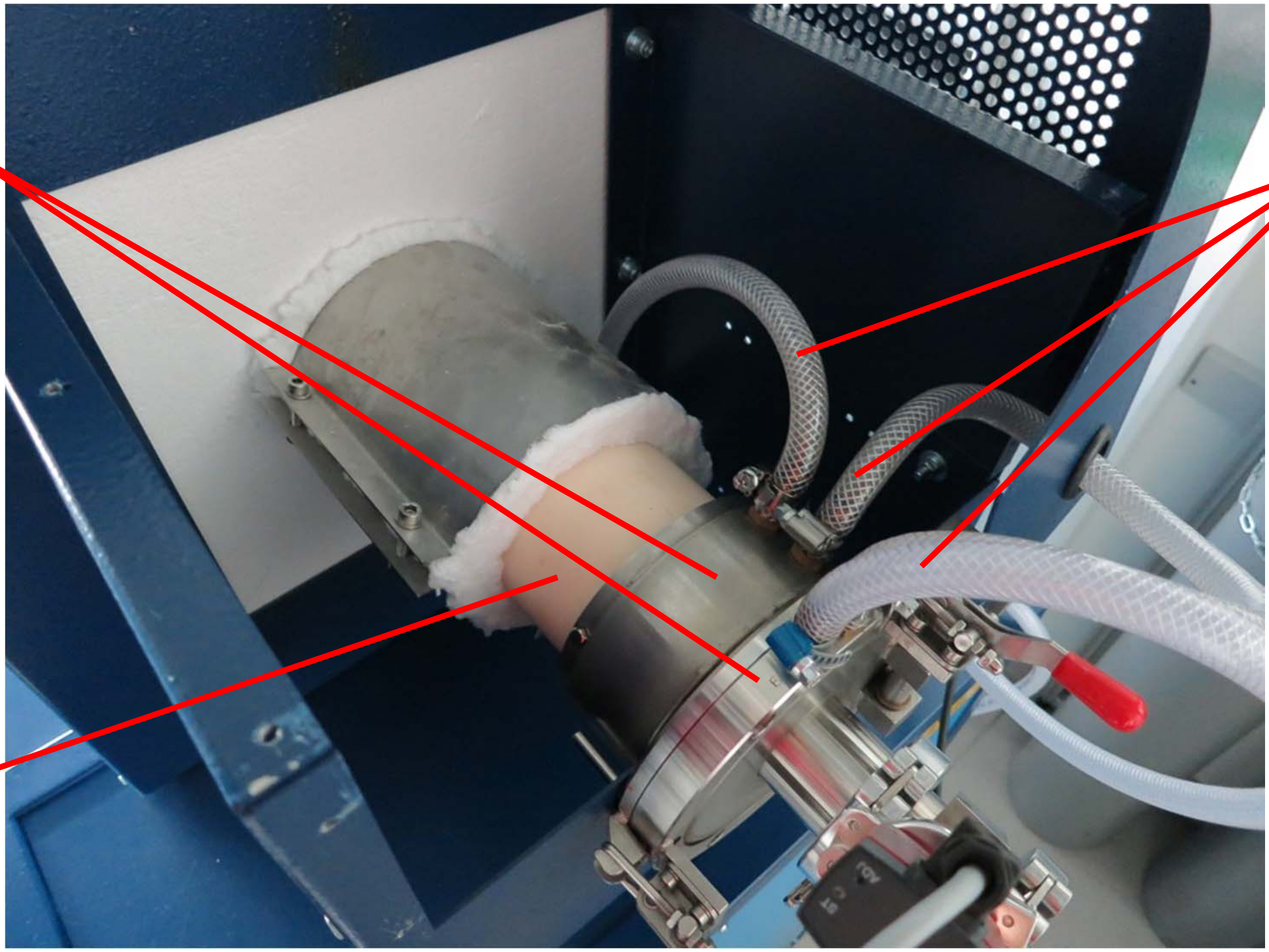


Radiation shield in the alumina tube at its gas outlet side. The distance *a* is about 10 cm.

Tube furnace – Alumina tube and flange at the gas outlet

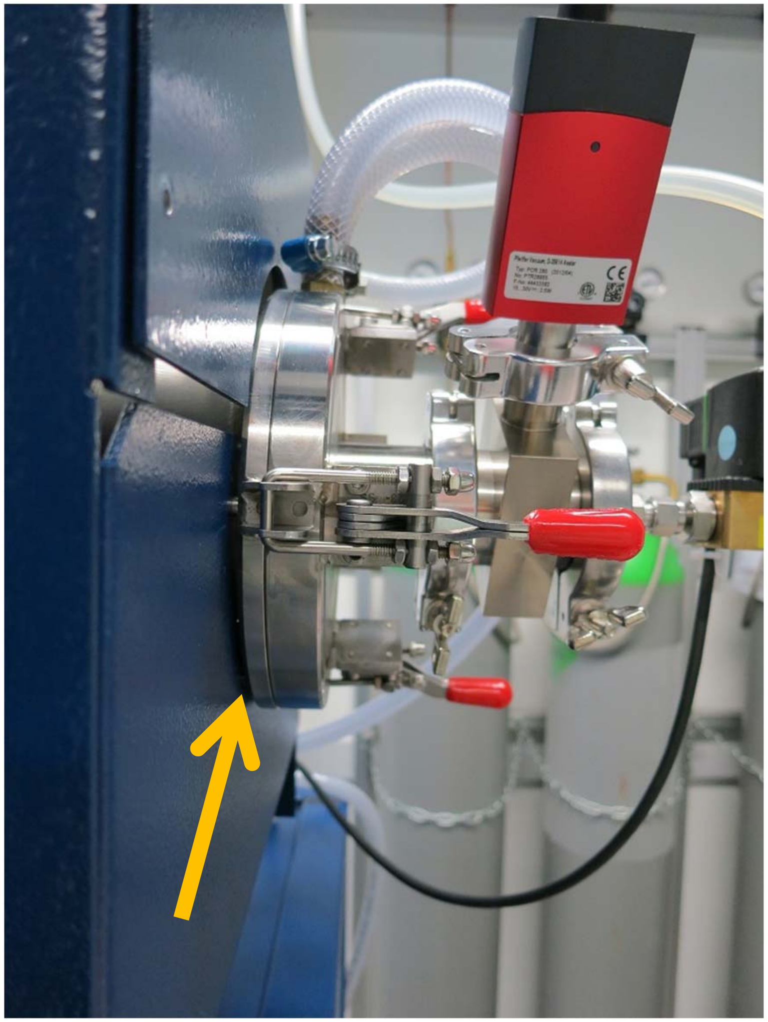
View when the upper protective plate is hinged aside

- Flange is water-cooled
- Only a small part of the alumina tube is visible
- Construction at the gas inlet is similar

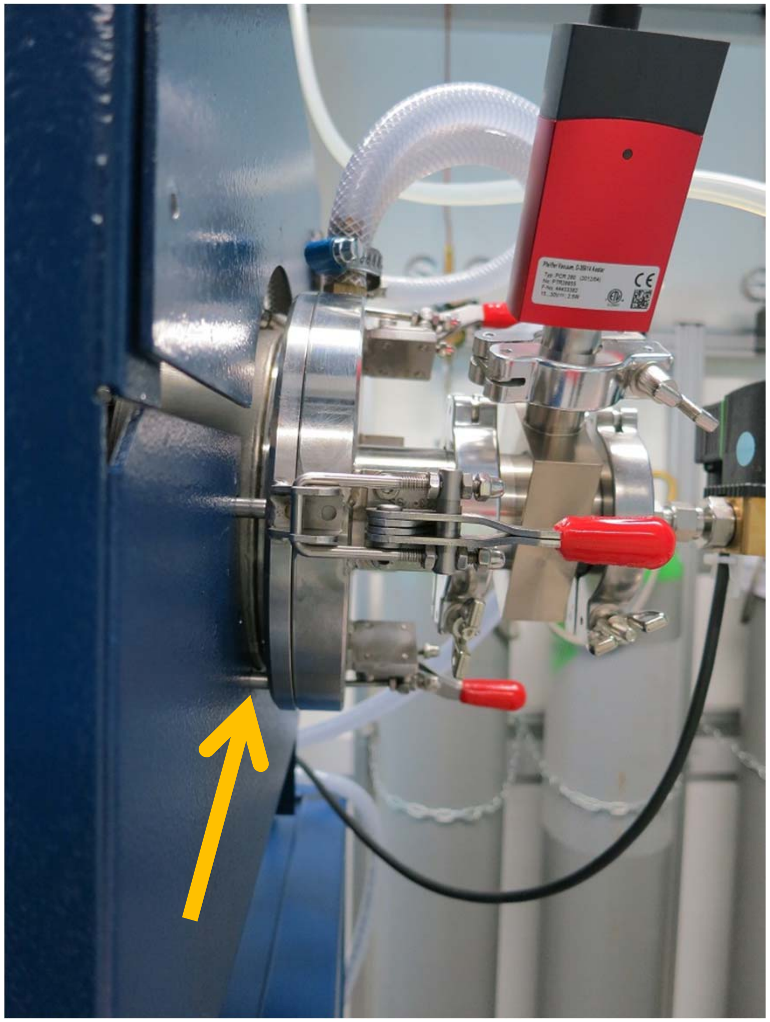


Tube furnace – Movable flange at the gas outlet

Flange is movable because of the thermal expansion of the alumina tube upon heating

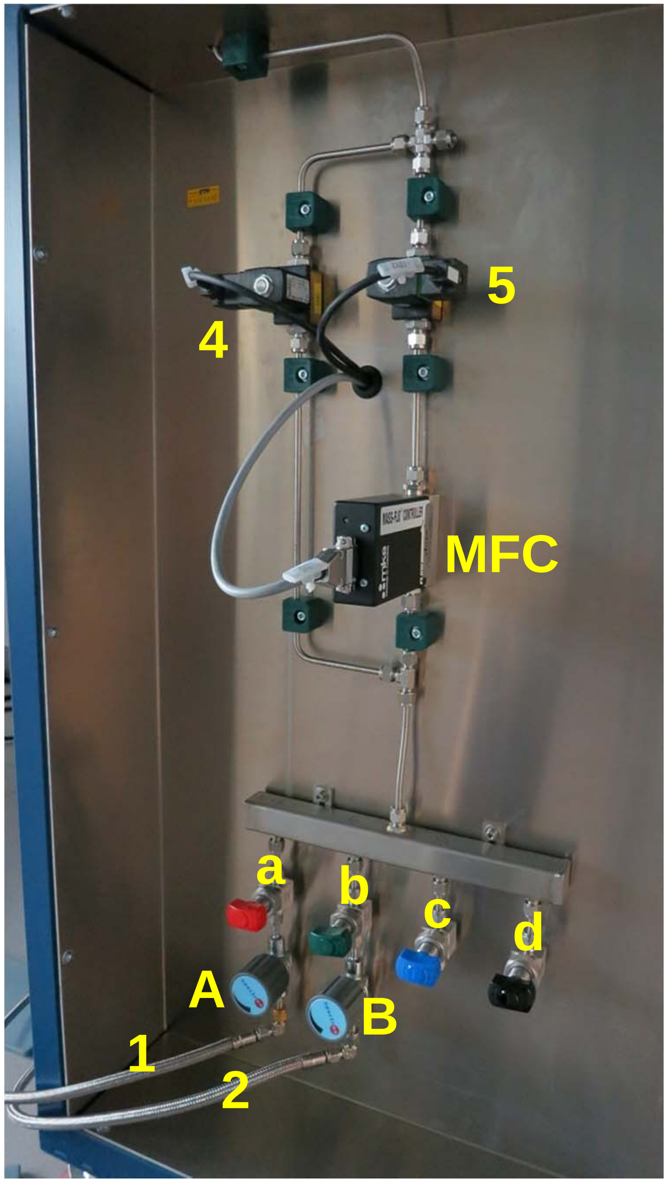


Flange position when temperature of the whole alumina tube is about 20 °C



Flange position when temperature of the middle part of the alumina tube is 1250 °C. Tube and flange are moved about 1 cm to the right

Tube furnace – Gas inlet and gas flow control



4 , 5 Electromagnetic valves

MFC Mass flow controller 1179 B from MKS Instruments, maximum gas flow rate 2000 sccm = 120 Liter / h

a - d Swagelok diaphragm valves 6LVV-DPS6M

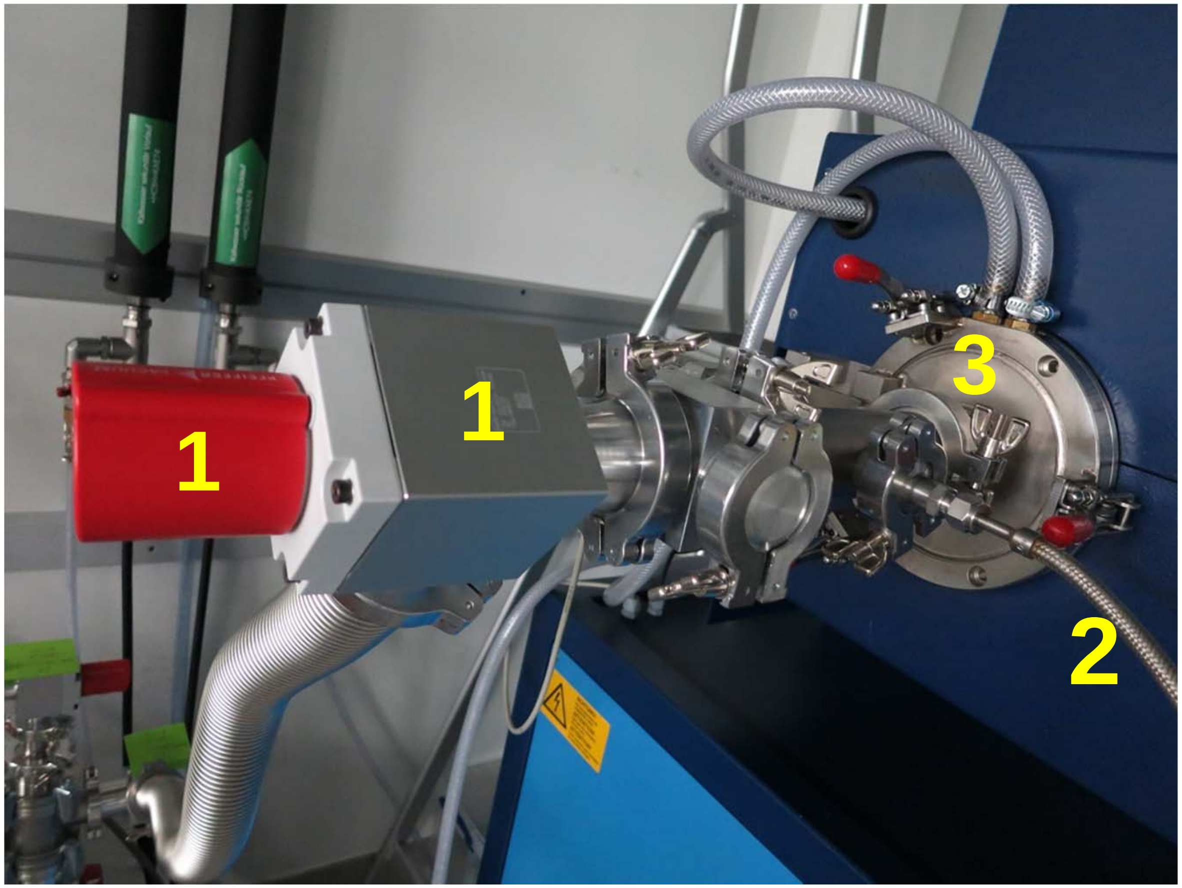
A , B Spectron diaphragm valves DVM-8-OD-6 (rotary dosing valves)

1 , 2 Gas supply via flexible metal tubes (Swagelok 6 mm). They are connected to a gas supply cabinet which is presented in part 3. Gas types:

2 Argon (Ar)

1 97,2 % Ar + 2,8 % H_2

Tube furnace – Gas inlet at the tube and valve towards pump

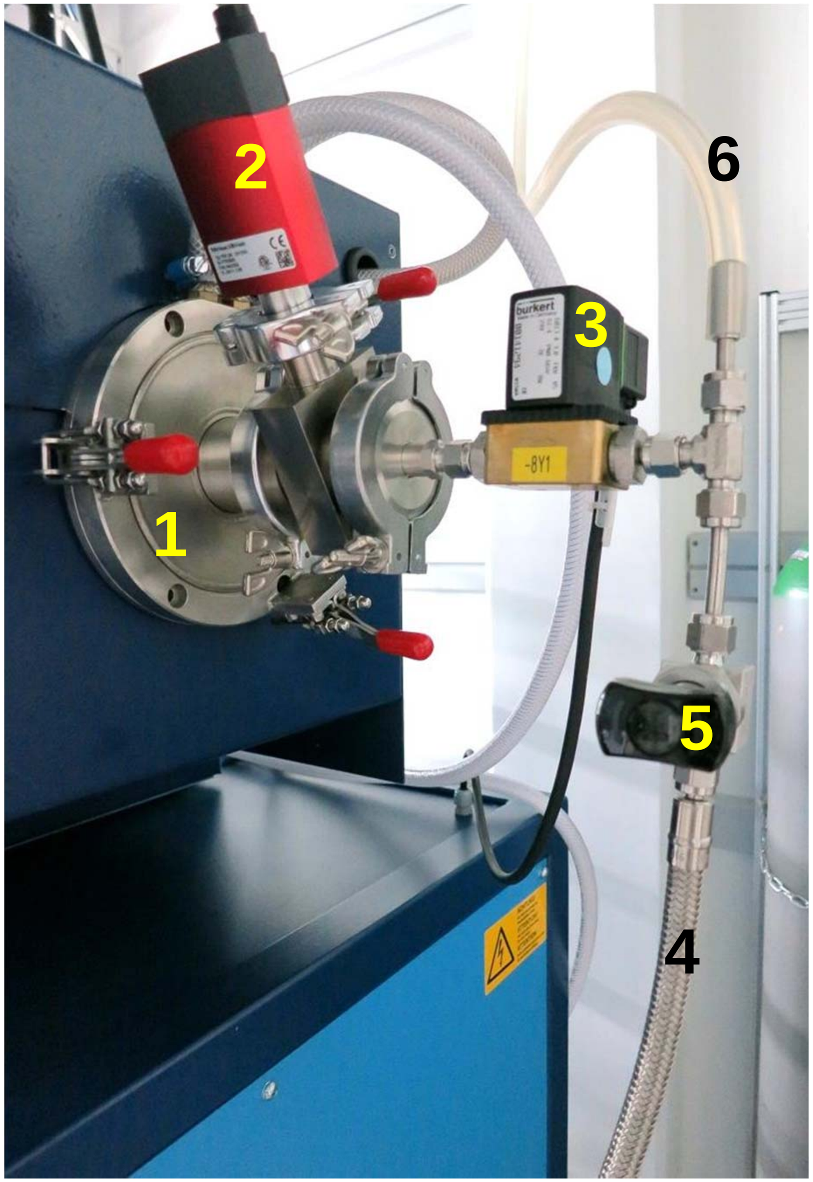


3 Flange / Door at the gas inlet side of the tube

2 Gas supply at the gas inlet side of the tube

1 KF 40 type angle valve from Pfeiffer Vacuum towards turbo pumping station

Tube furnace – Gas outlet



6 Exhaust gas line

5 Swagelok diaphragm valve 6LVV-DPS6M
towards oxygen analyzer ZIROX SGM7

4 Flexible metal tube (Swagelok 6 mm)
towards gas inlet of the oxygen analyzer
ZIROX SGM7

3 Electromagnetic valve

2 Pressure gauge PCR 280
from Pfeiffer Vacuum

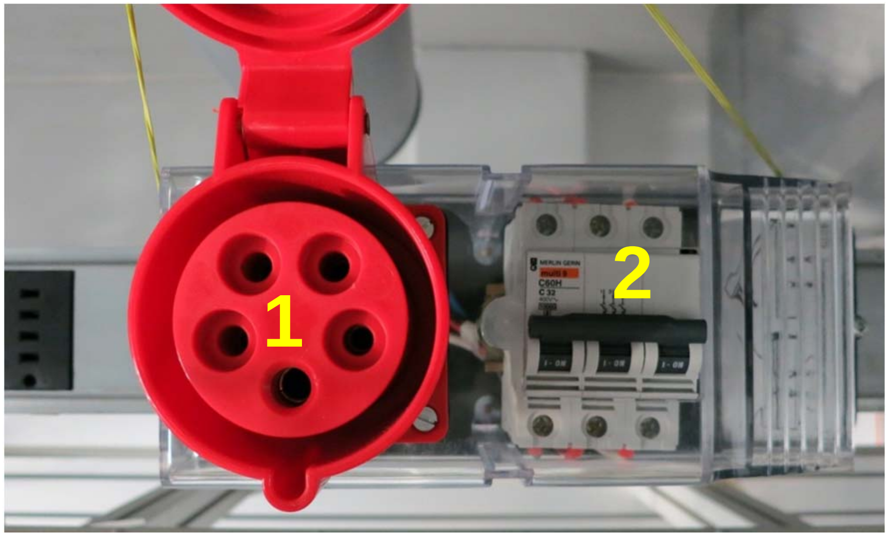
1 Flange / Door which is used to insert or
remove an alumina box which contains
the sample

Tube furnace – Power supply by 400 V / 32 A triphase

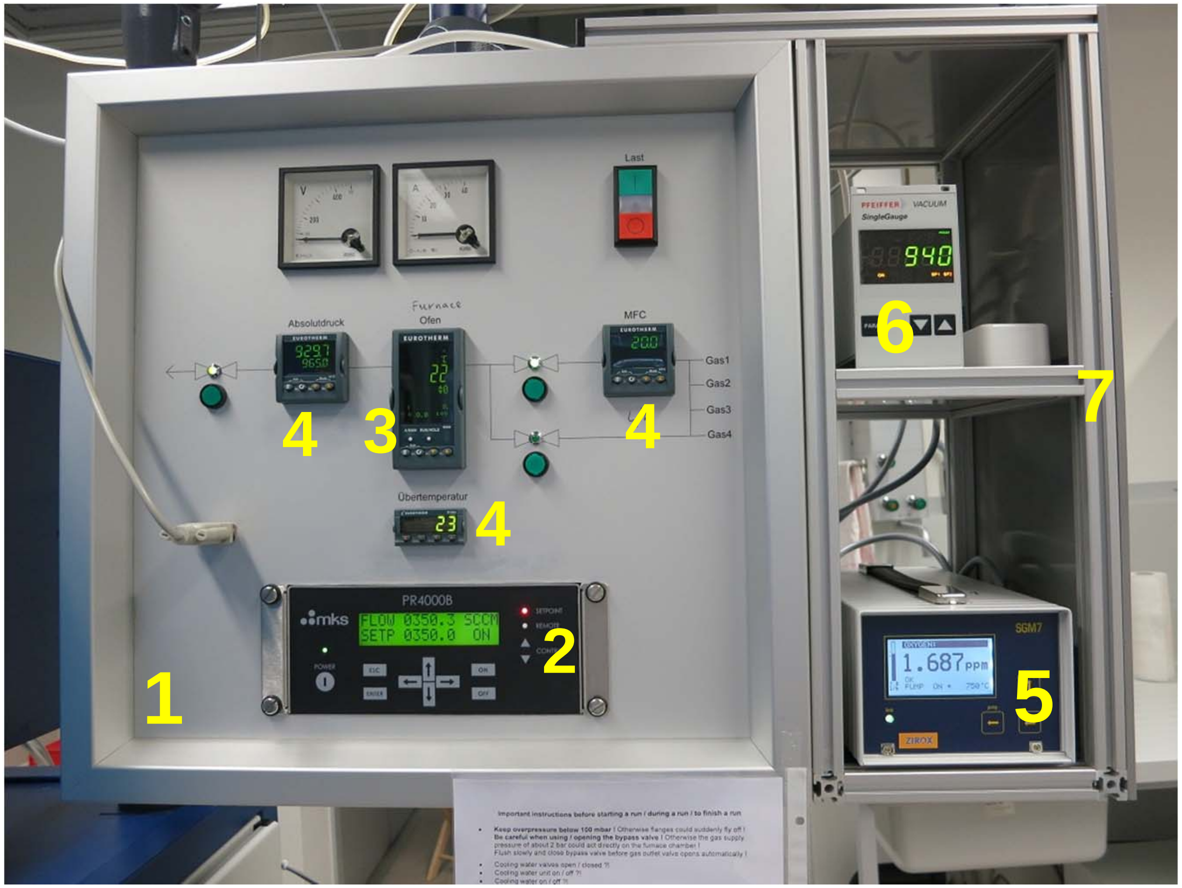
Maximum power consumption
of the tube furnace 11,5 kVA

CEE type plug for 400 V / 32 A triphase (3)

Located close to the ceiling of the laboratory:
CEE type socket for 400 V / 32 A triphase (1)
and automatic fuse (2)



Tube furnace – Control unit



7 Metal shelf - made in the metal workshop of the Department of Materials of the ETH Zurich by M. Elsener

6 Pressure indicator TPG 261 from Pfeiffer Vacuum for the pressure at the gas outlet

5 Oxygen analyzer ZIROX SGM7 to measure the oxygen content of argon at the gas outlet

4 Eurotherm devices which display the pressure at the gas inlet (1000 – 1 mbar), the temperature of a second thermocouple, and the gas flow rate

3 Eurotherm control unit for the temperature run

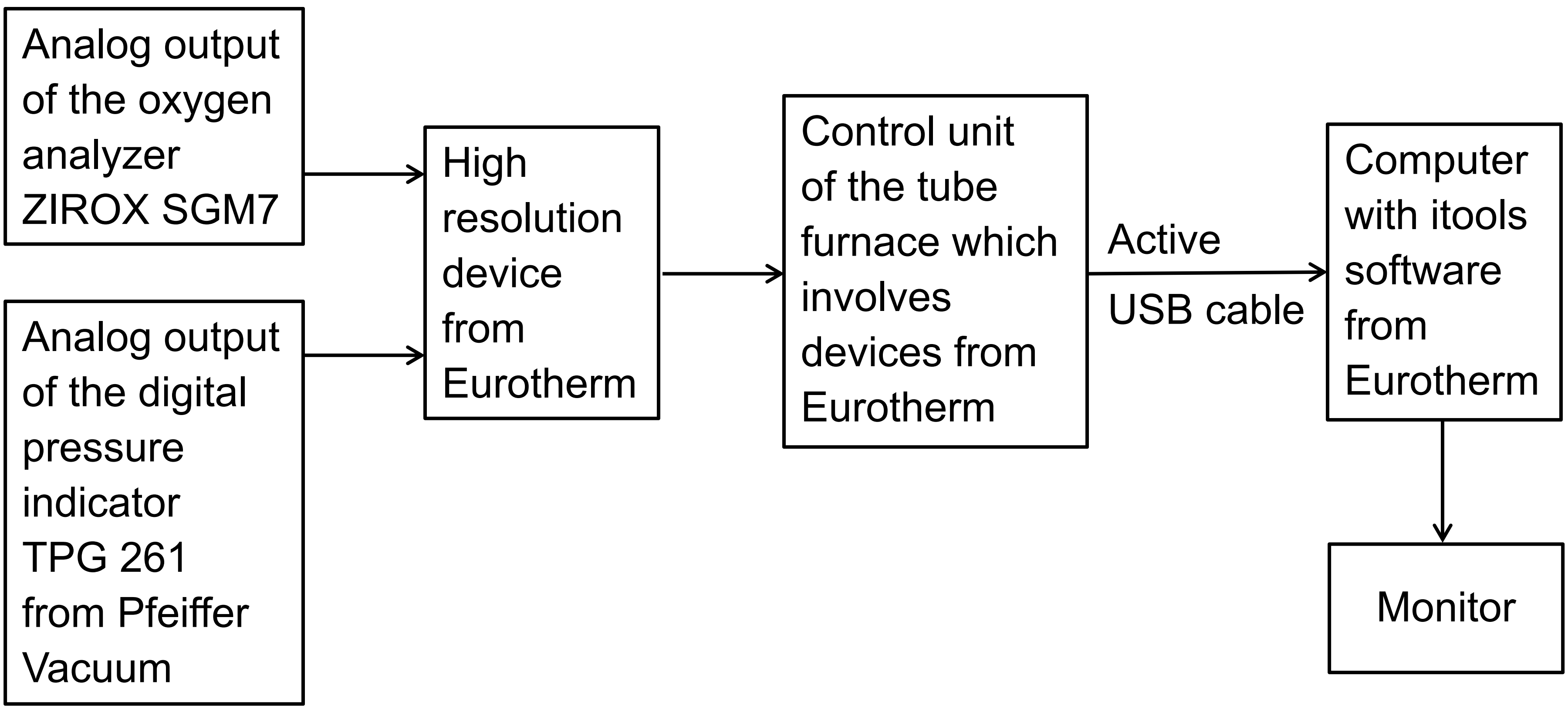
2 Gas flow control unit PR 4000 B from MKS Instruments

1 Control unit of the tube furnace

Tube furnace – Data recording

The tube furnace is equipped with a data logger and the following quantities can be recorded as function of time:

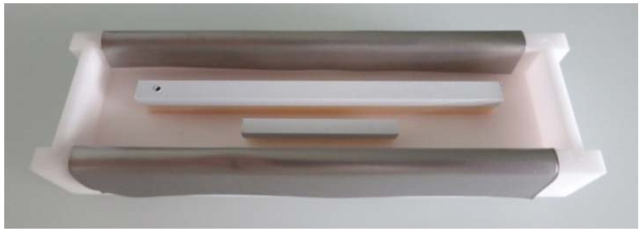
- Set and actual value of temperature • Gas flow rate • Pressure
- Oxygen content of argon at the gas outlet if argon is used as process gas



The following pages shows the time-dependent course of some quantities from three different experiments

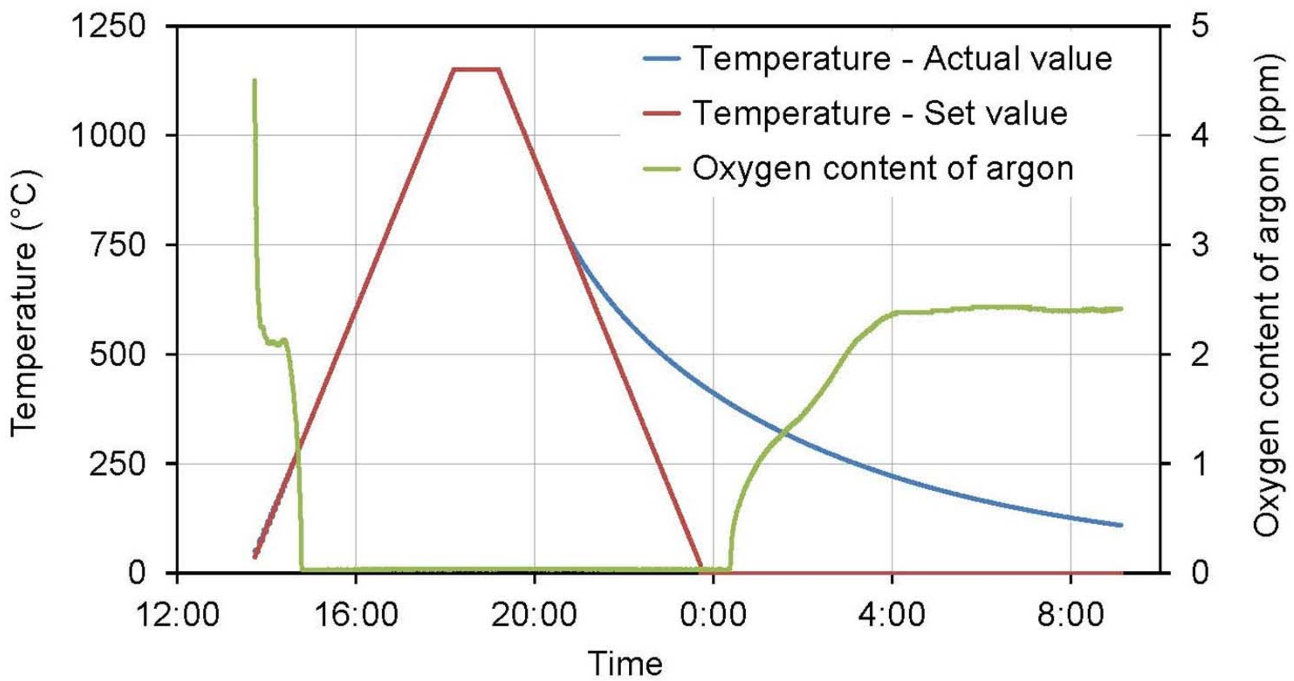
Tube furnace – Example 1 of a temperature run

Purpose of this run: Sintering of pressed rods at 1150°C under argon



Sample inside alumina tube: Pressed powder in form of two rods (seed and feed rod for the mirror furnace) and two niobium foils in an alumina box. Chemical composition of the pressed powder in this example: 0,6 Nb + 0,2 Nb_2O_5

Before starting the run the alumina tube was evacuated by a turbo pumping station and subsequently flushed with argon • Argon gas flow rate 300 sccm = 18 Liter / h • Oxygen content of argon measured at the gas outlet by the oxygen analyzer ZIROX SGM7 • Oxygen content drops at elevated temperatures to zero because the niobium foils act as oxygen getter



Set value of heating and cooling rate 250 °C / h

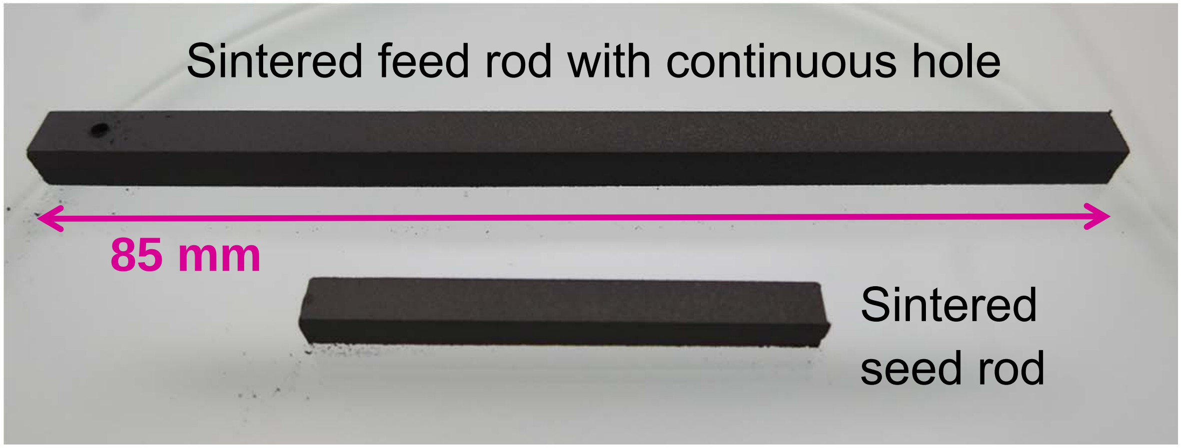
Below 750 °C the actual cooling rate becomes much smaller than its set value

Tube furnace – Example 1 of a temperature run

Rods after sintering at 1150°C under argon

The color change of the rods from white-grey (see previous page) to black is due to chemical solid state reactions like

$0{,}6\ Nb + 0{,}2\ Nb_2O_5 \rightarrow NbO$



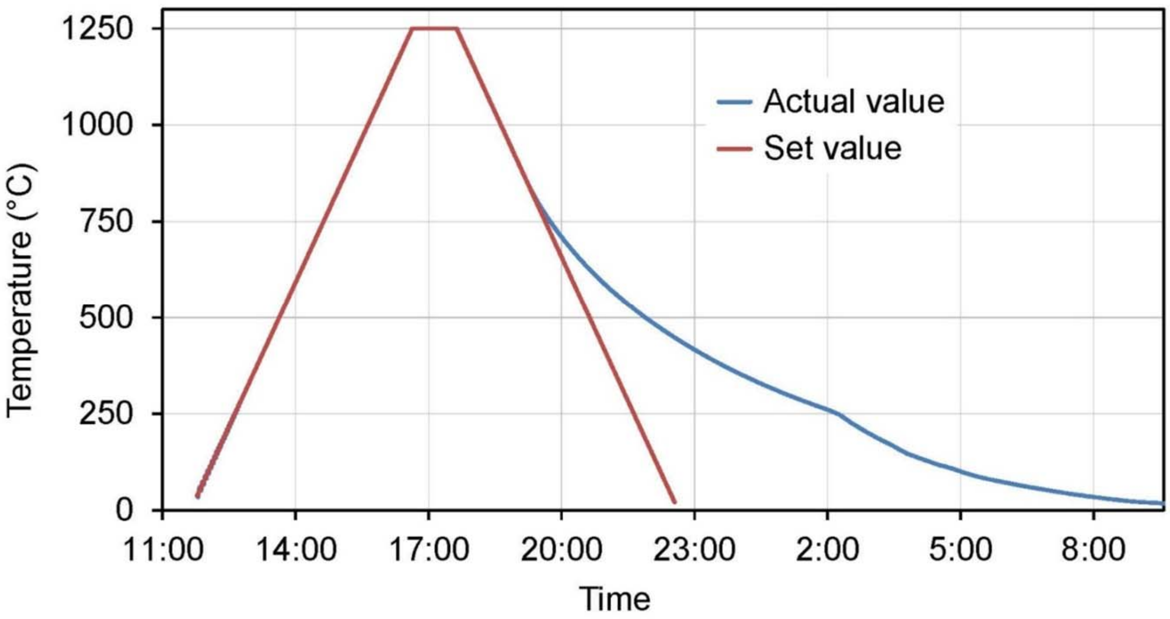
The sintered rods are mechanically stable and can be processed in the mirror furnace

Tube furnace – Example 2 of a temperature run

Purpose of this run: Try to determine the actual oxygen content of Fe_2O_3 powder by reducing it to Fe metal at 1250 °C under 97.2 % Ar + 2.8 % H_2

Sample inside alumina tube: Fe_2O_3 powder in an alumina boat and alumina box

Gas type 97.2 % Ar + 2.8 % H_2 • Before starting the run the alumina tube was evacuated by a turbo pumping station and subsequently flushed with 97.2 % Ar + 2.8 % H_2 • Gas flow rate 450 sccm = 27 Liter / h

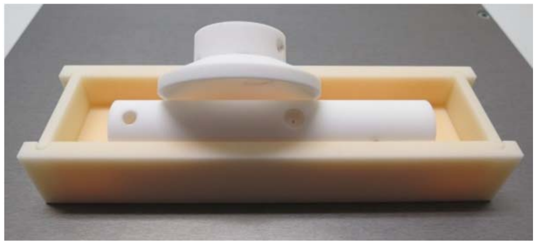


Set value of heating and cooling rate 250 °C / h

Below 750 °C the actual cooling rate becomes much smaller than its set value

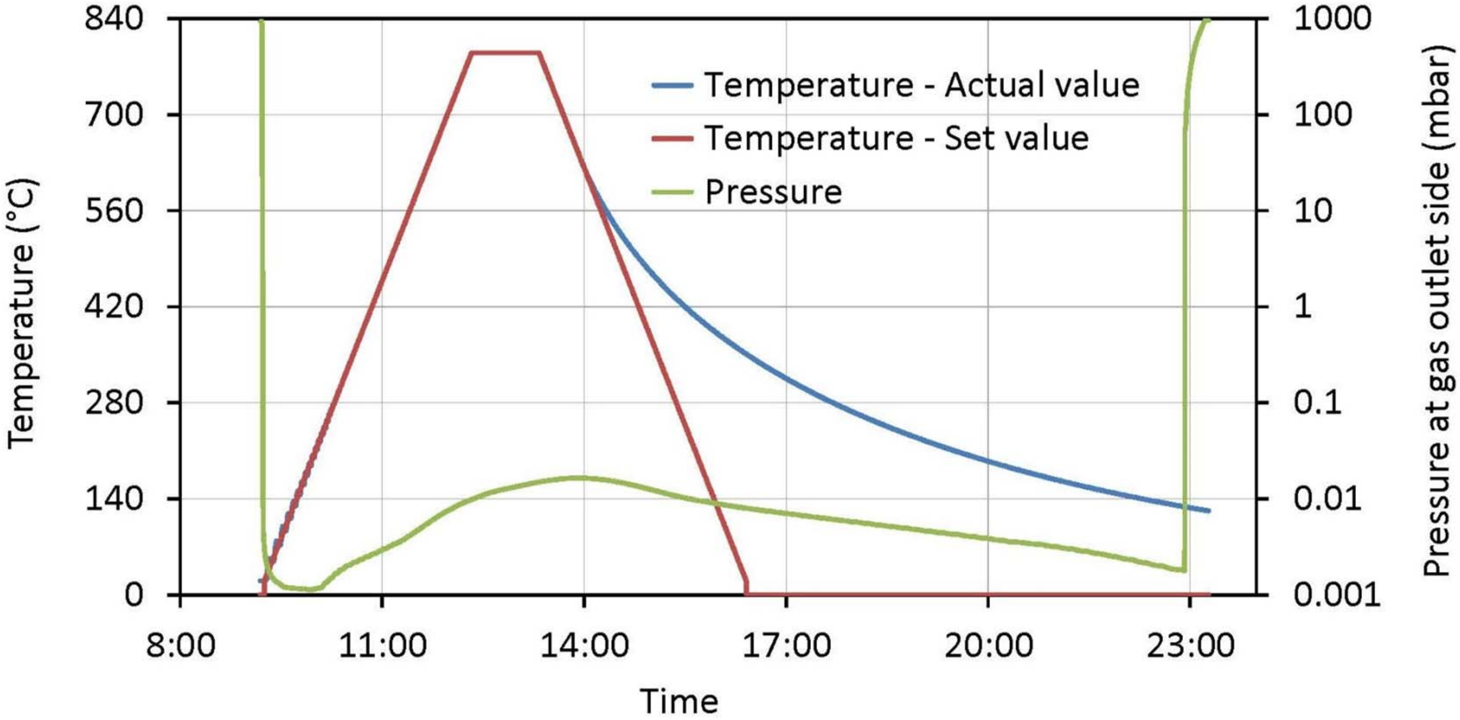
Tube furnace – Example 3 of a temperature run

Purpose of this run: Bake-out of parts made of Macor at 790 °C under vacuum



Sample inside alumina tube: Two components made of Macor for the mirror furnace in an alumina box

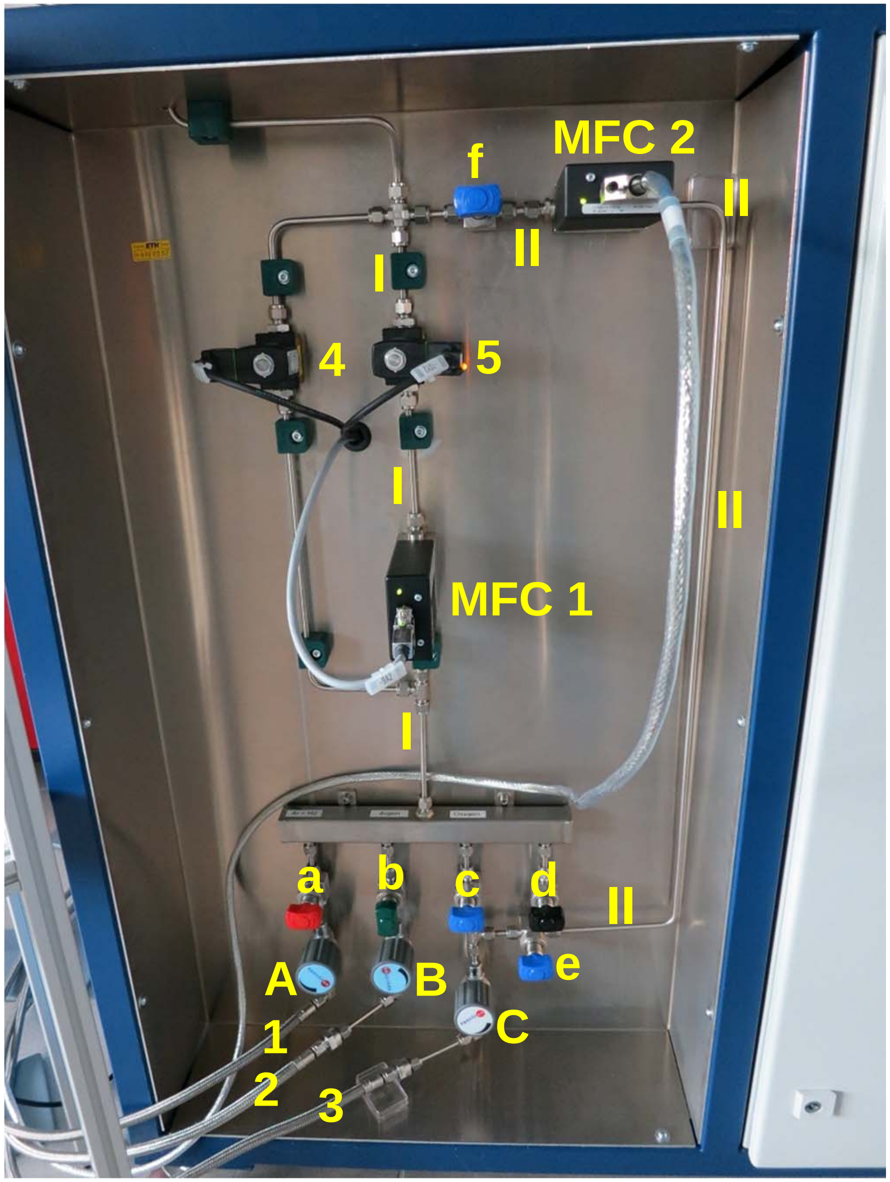
- The alumina tube was permanently pumped out by a turbo pumping station
- Termination of the run at about 130 °C by flushing the alumina tube with argon



Set value of heating and cooling rate 250 °C / h

Below 550 °C the actual cooling rate becomes much smaller than its set value

Tube furnace – Modified gas inlet and gas flow control 1 / 2



Modification in May 2014 by adding an additional gas line (II) and mass flow controller (MFC 2). That allows the mixture of two gases via gas line I and II and MFC 1 and MFC 2

4 , 5 Electromagnetic valves

MFC 1 (2) Mass flow controller 1179 B from MKS Instruments with maximum gas flow rate 2000 (10) sccm

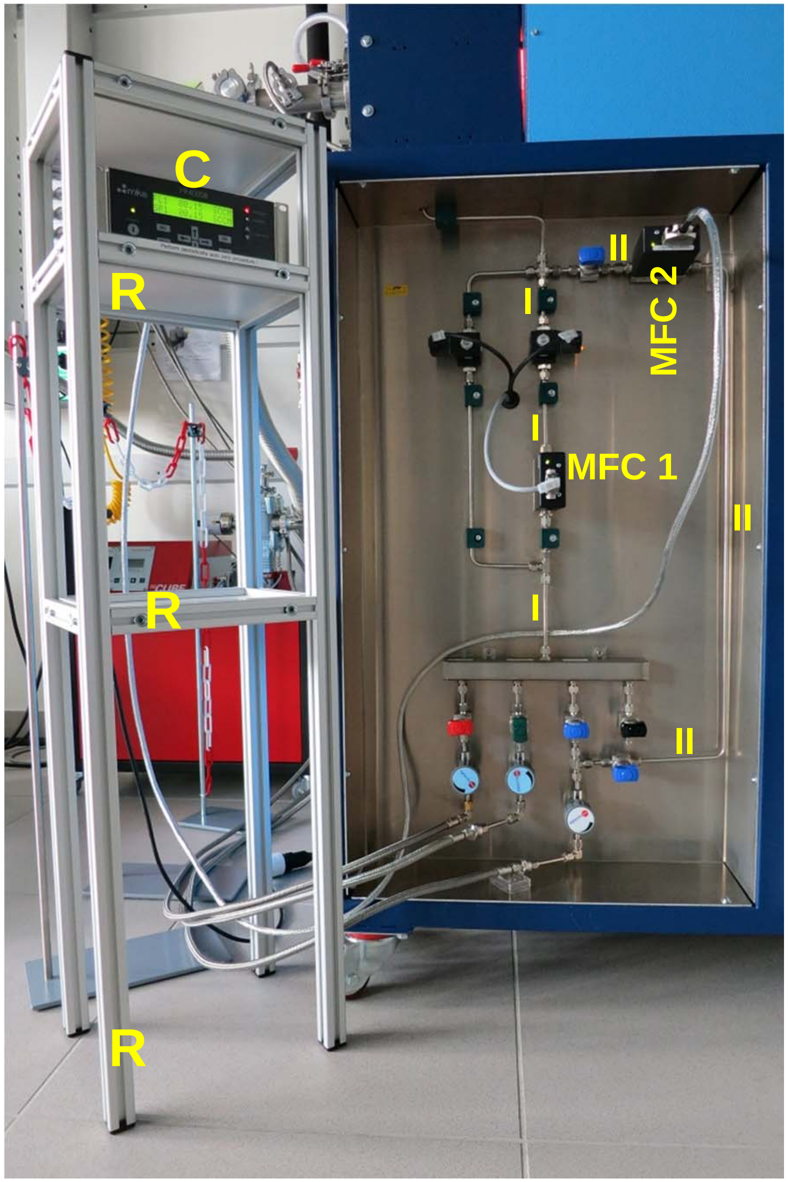
a , b , c , d , e , f Swagelok diaphragm valves 6LVV-DPS6M

A , B , C Spectron diaphragm valves DVM-8-OD-6 (rotary dosing valves)

1 , 2 , 3 Gas supply via flexible metal tubes (Swagelok 6 mm). They are connected to a gas supply cabinet which is presented in part 3. Gas types: (1) 97,2 % Ar + 2,8 % H_2 , (2) Ar , (3) oxygen or synthetic air or mixture Ar + O_2

Metal tubes (Swagelok 6 mm) such as gas line II prepared by M. Elsener from the metal workshop of the Department of Materials of the ETH Zurich

Tube furnace – Modified gas inlet and gas flow control 2 / 2



Modification in May 2014 by adding an additional gas line (II) and mass flow controller (MFC 2). That allows the mixture of two gases via gas line I and II and MFC 1 and MFC 2

C Gas flow control unit PR 4000 B from MKS Instruments for MFC 2

R Rack for gas flow control unit (C). Prepared by M. Elsener from the metal workshop of the Department of Materials of the ETH Zurich

Part 9

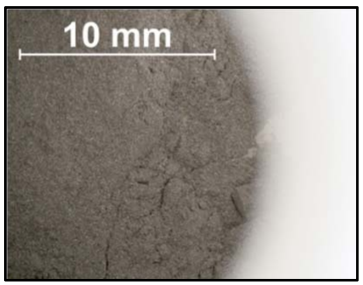
Preparation of oxide powder mixtures: Starting materials, analytical balance, and special mortars and pestles

Examples of commercially available starting materials

Fe_2O_3 powder

WO_3 powder

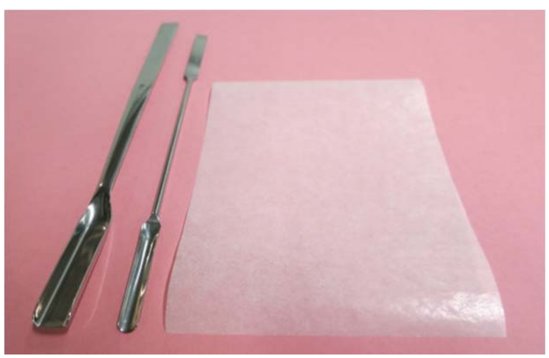
$SrCO_3$ powder



Nb powder

Nd_2O_3 powder

Storage of starting materials in an alumina crucible in a desiccator
- Mn_2O_3 powder in this example

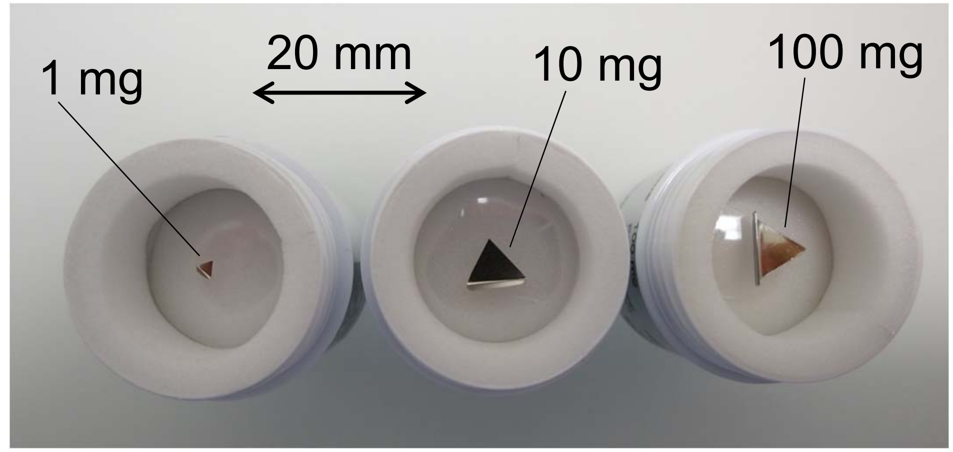


Spatula and weighing paper

Analytical balance MS 204 from Mettler Toledo

Analytical balance MS 204 from
Mettler Toledo (Switzerland)

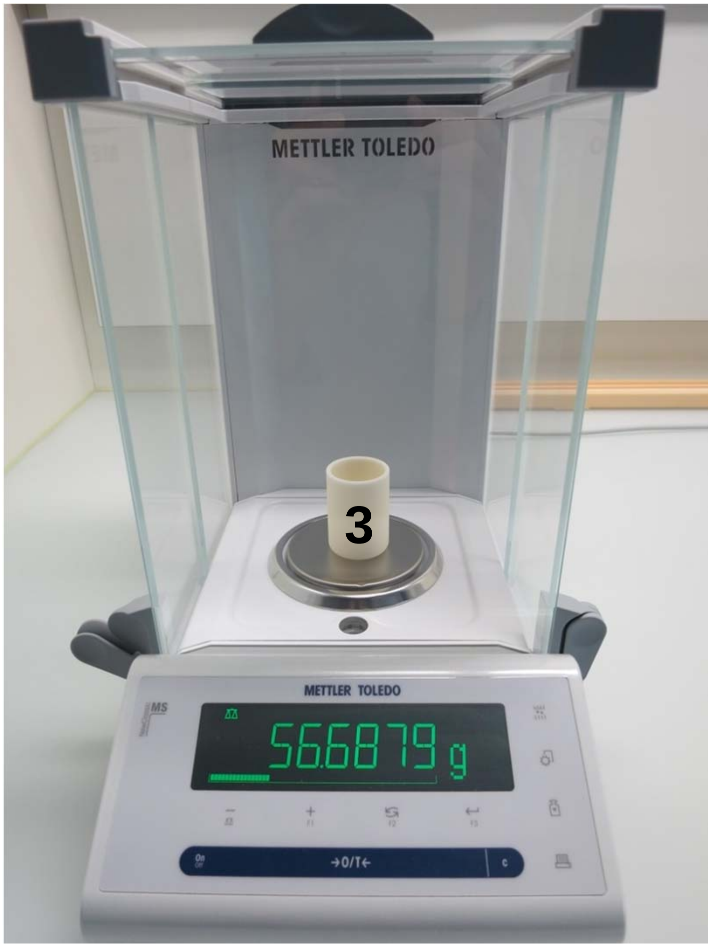
- Readability 0,1 mg
- Typical standard deviation of repeatability with respect to a load of 20 g: 0,05 mg
- Maximum capacity 220 g



Calibration weights from Mettler Toledo (Switzerland) made of special stainless steel

Analytical balance MS 204 from Mettler Toledo

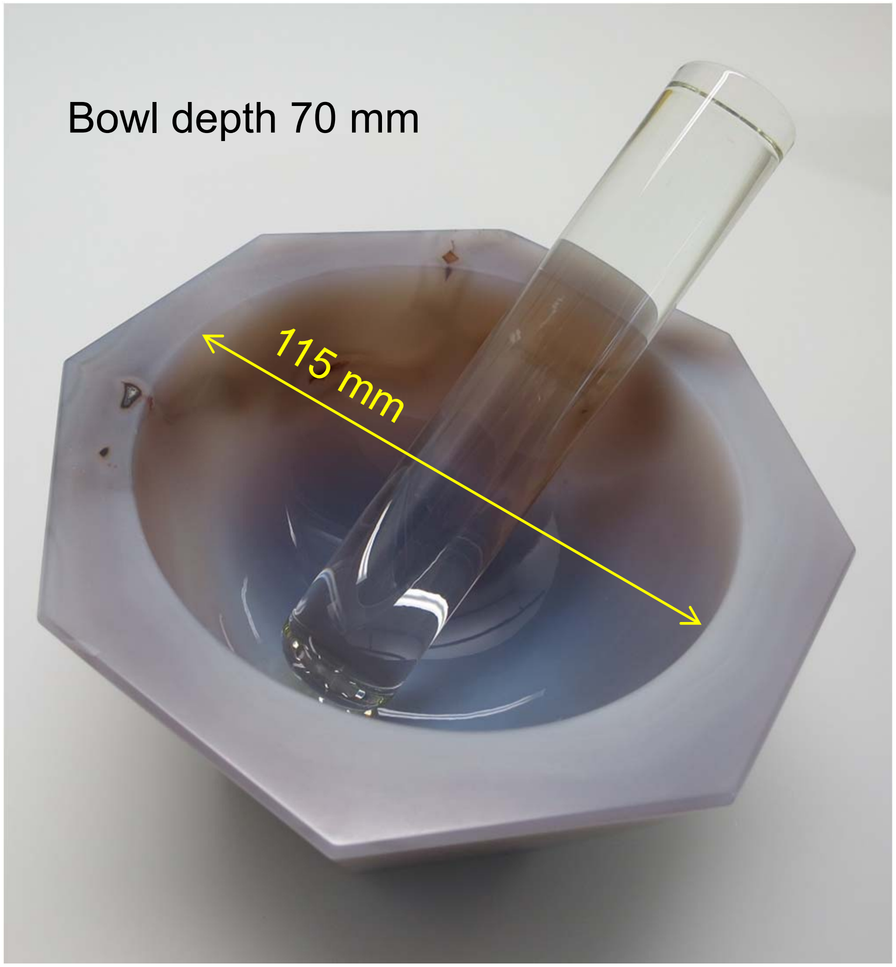
Weighing powder (1) on weighing paper (2). In this example the chemical composition of the powder is Nd_2O_3



Weighing an alumina crucible (3). The crucible can be empty or filled with as-grinded, pre-reacted or sintered powder.

Agate mortar and a pestle made of glass

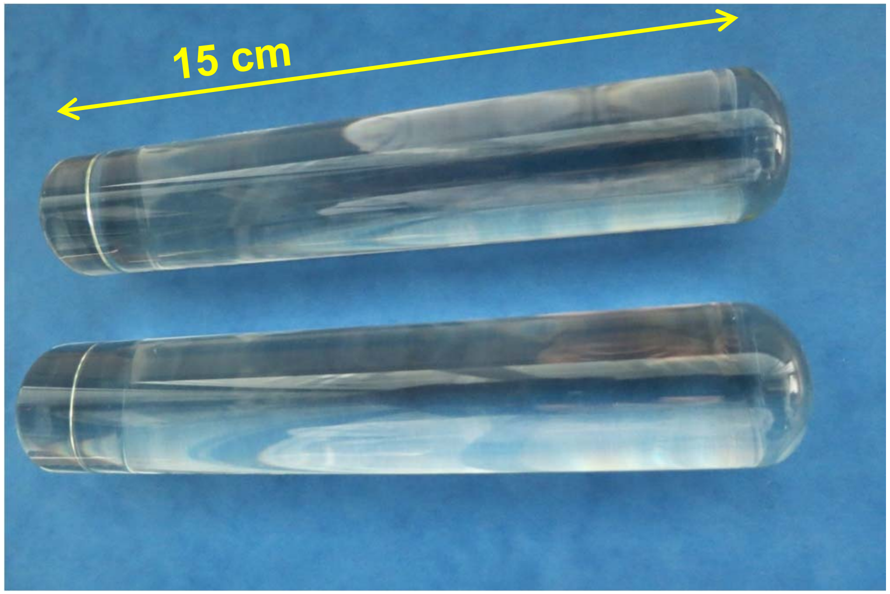
- Mortar made of agate, custom-made design from
  Lemke GmbH / Technical Stones - Laboratory Agate Goods (Germany)
- Pestle made of glass, custom-made design from Willi Möller AG (Switzerland)

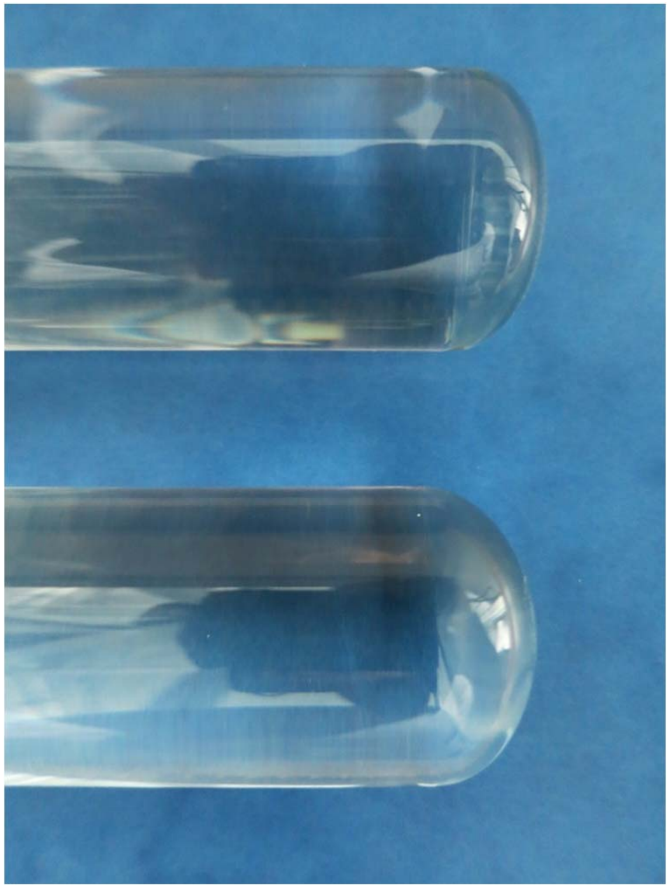


The use of an agate mortar and a pestle made of glass works surprisingly well !

Pestles made of glass

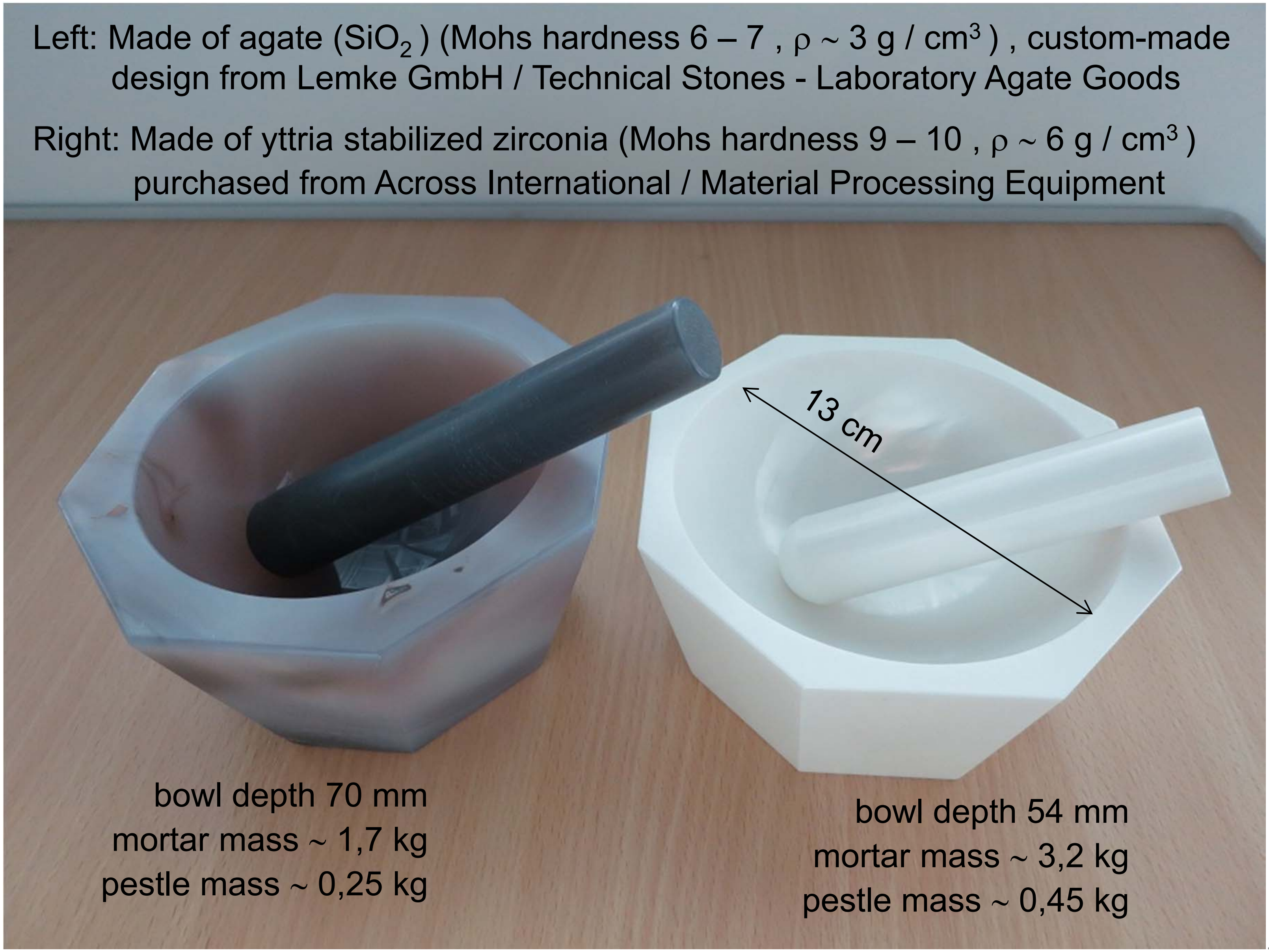
Custom-made design from Willi Möller AG (Switzerland)





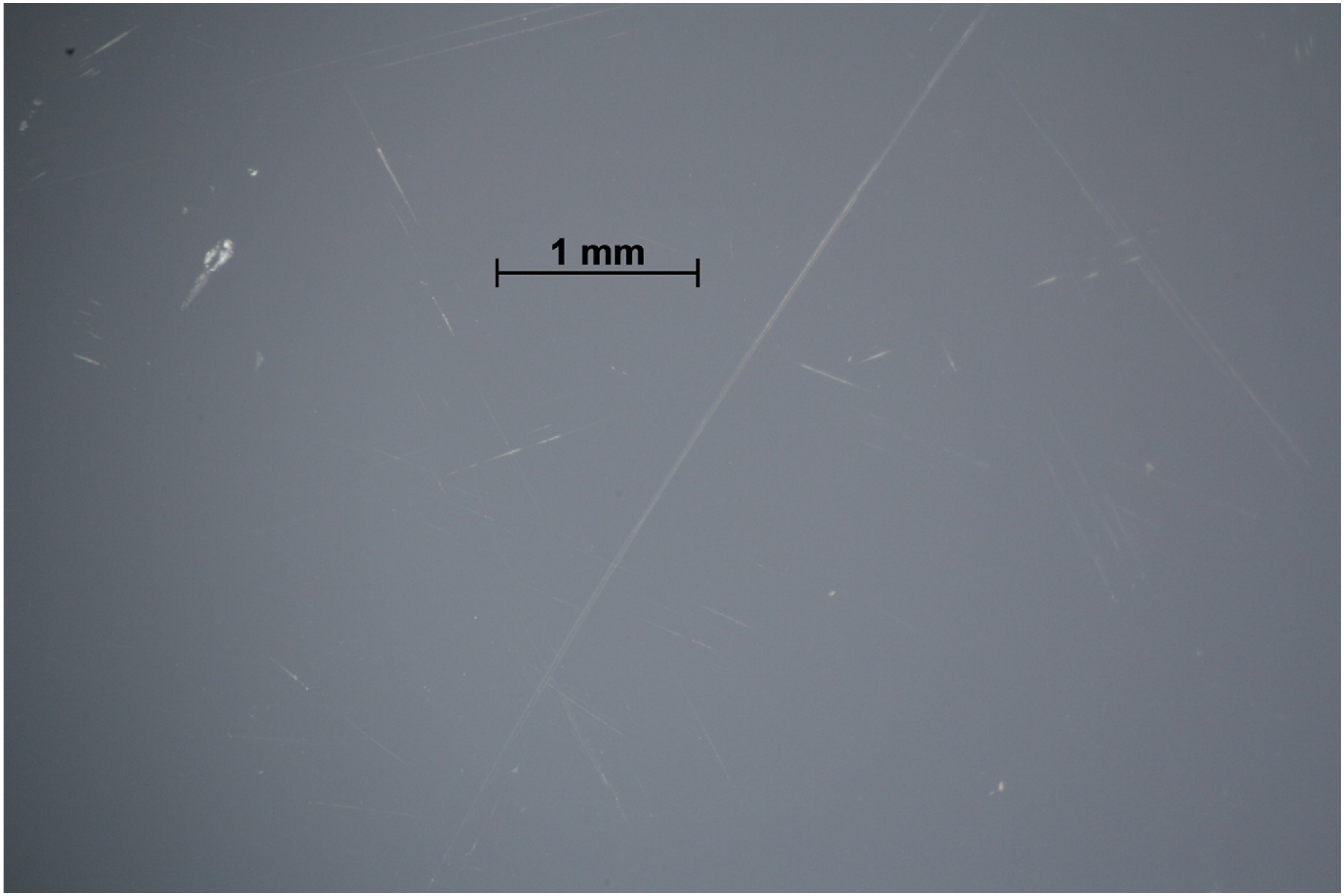
Two slightly different designs of the striking surface

Mortars with pestle of similar size and design (as-delivered condition)



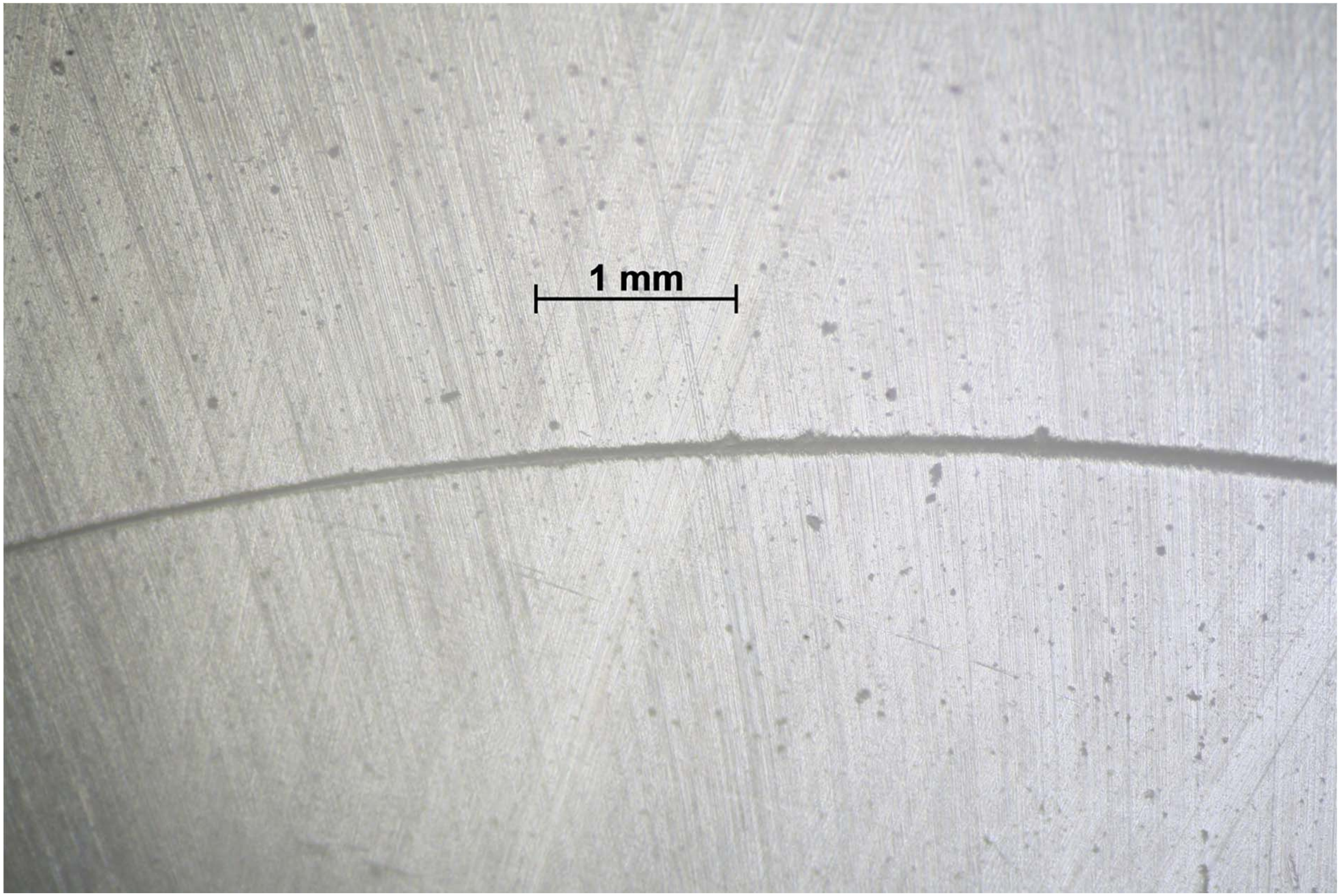
Inner surface / Striking surface of the agate mortar

As-delivered condition and same scale as on next page

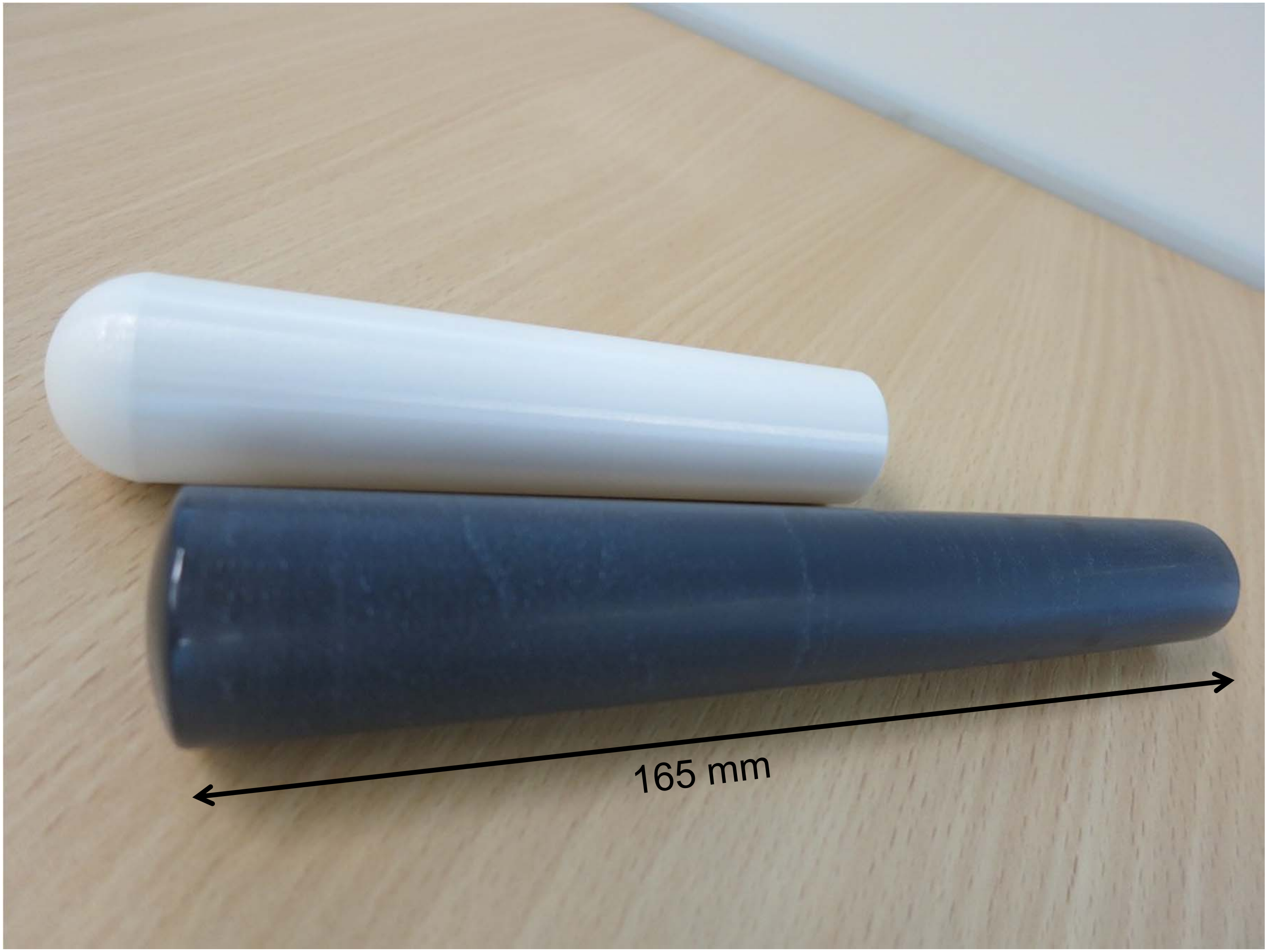


Inner surface / Striking surface of the yttria stabilized zirconia mortar

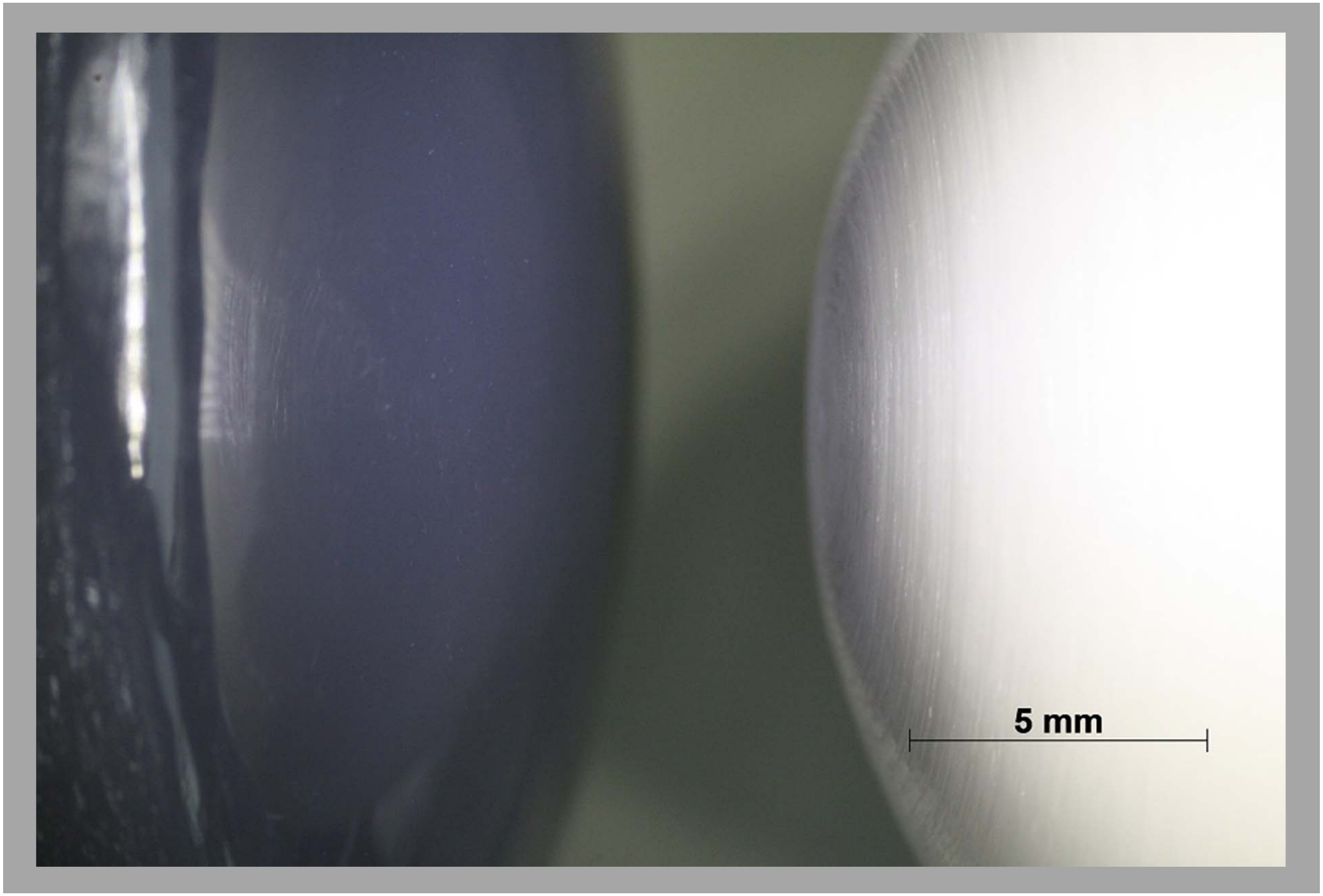
As-delivered condition and same scale as on previous page



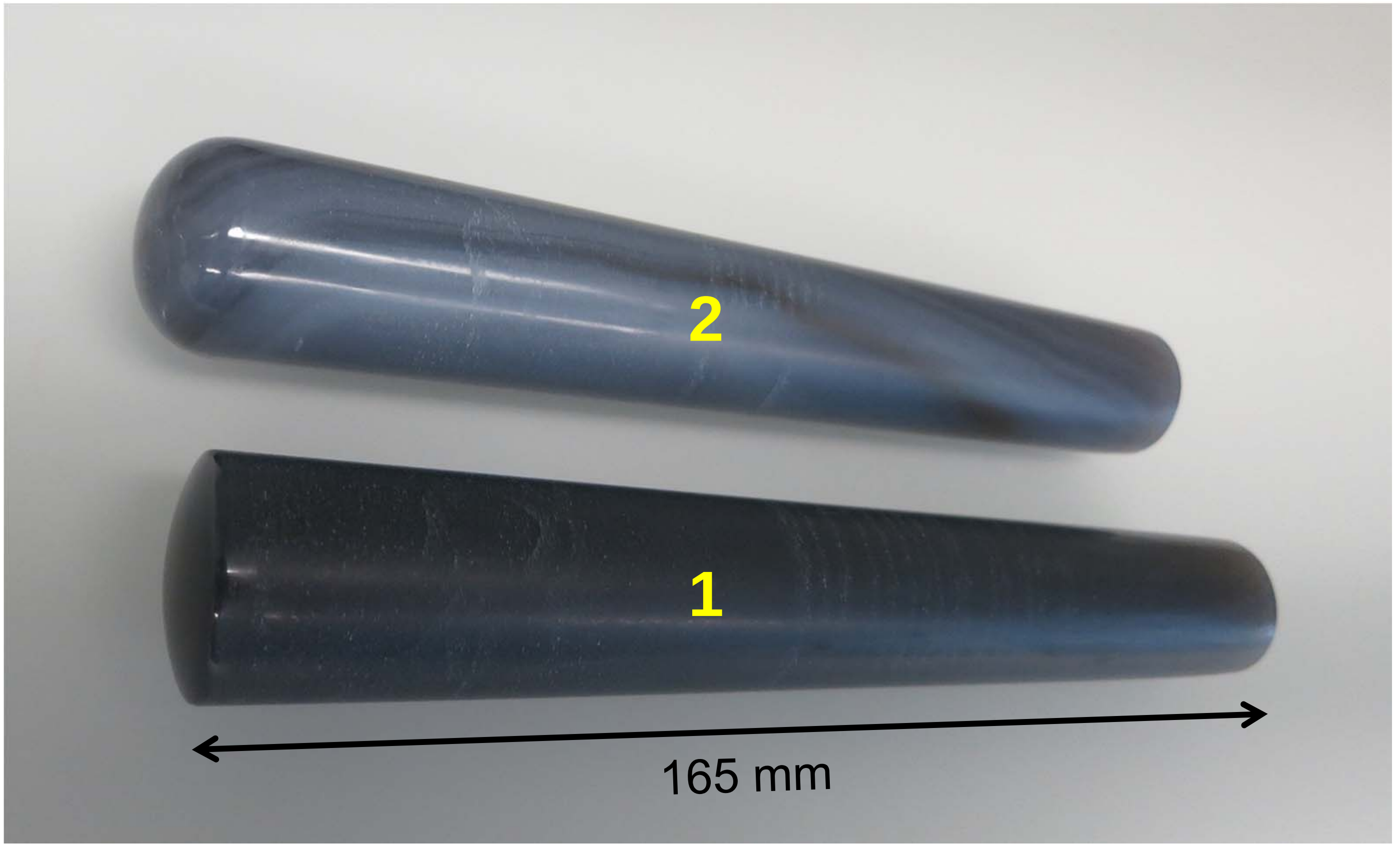
Another view of the pestles (as-delivered condition)



Striking surface of the pestles (as-delivered condition)



Two pestles made of agate



2 Pestle with a more rounded striking surface

1 Pestle with a relatively flat striking surface. This pestle is also shown on the two previous pages

Custom-made design from Lemke GmbH / Technical Stones – Laboratory Agate Goods

It was observed that the use of design 1 did lead relatively fast to grooves at the striking surface of the pestle and mortar. This unwanted effect is significantly diminished when design 2 is used. This phenomenon is possibly related to the relatively large slope of the mortar`s striking surface which results from its relatively large bowl depth.

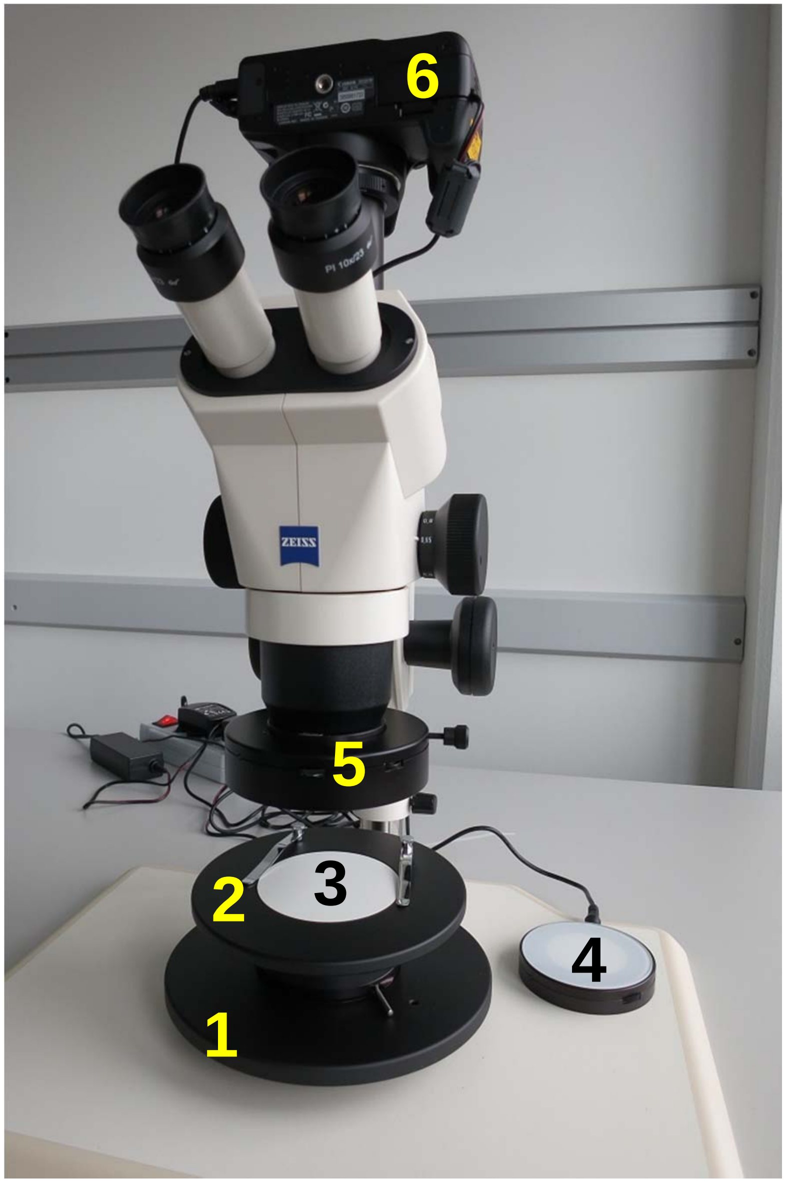
Part 10

Presentation of a
Zeiss optical microscope
and examples of pictures

Optical microscope Stemi 2000-C from Zeiss

The digital camera is connected with a computer on which the Zeiss software AxioVision is installed. That enables taking photos and image processing.

Complete system purchased and delivered from Carl Zeiss AG (Switzerland)



6 Digital camera Canon EOS 1000 D

5 LED light source for an illumination of the sample from above

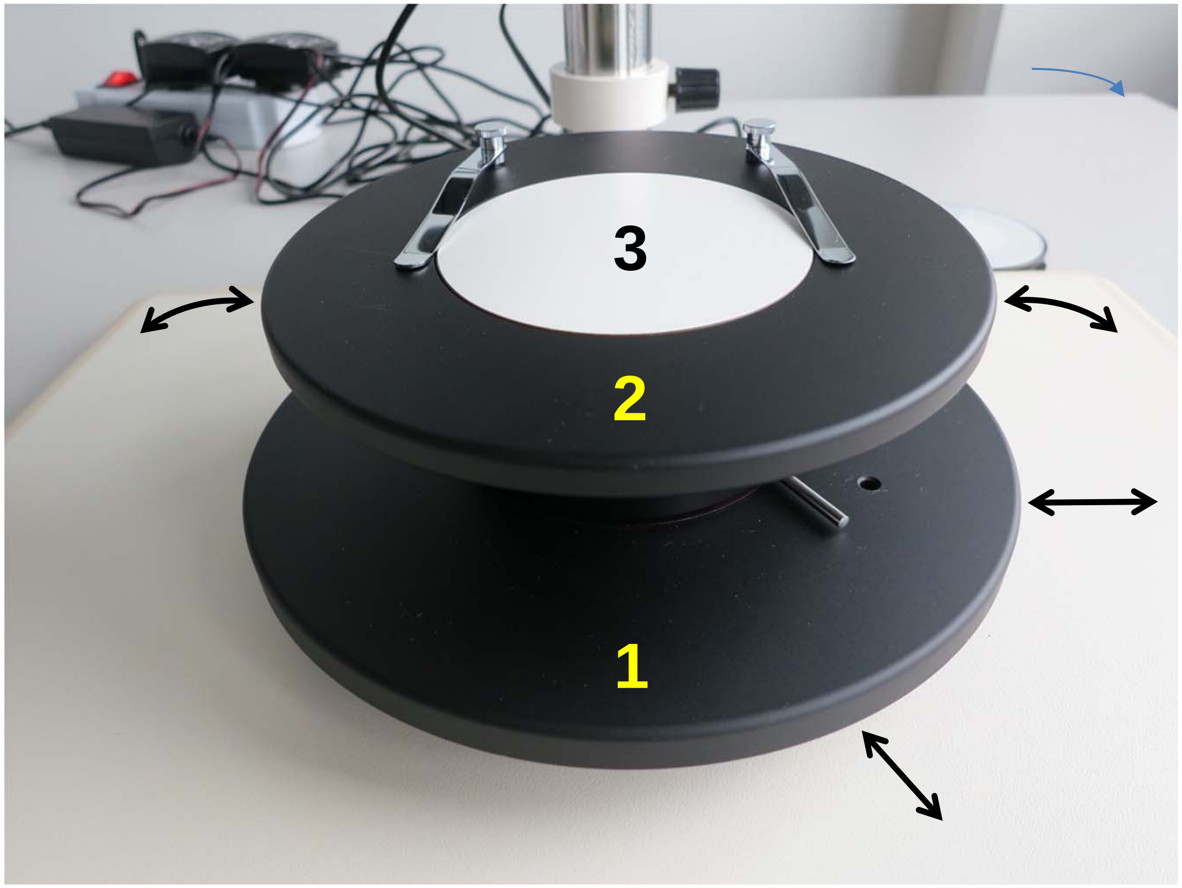
4 LED light source for an illumination of the sample from below – Can be inserted at position 3

3 Sample will be placed here

2 Upper part of the stage, tiltable in any direction out of the x-y plane

1 Lower part of the stage, movable in any direction within the x-y plane

Optical microscope Stemi 2000-C from Zeiss



Adjustable microscope stage

3 Sample will be placed here

2 Upper part of the stage, tiltable in any direction out of the x-y plane

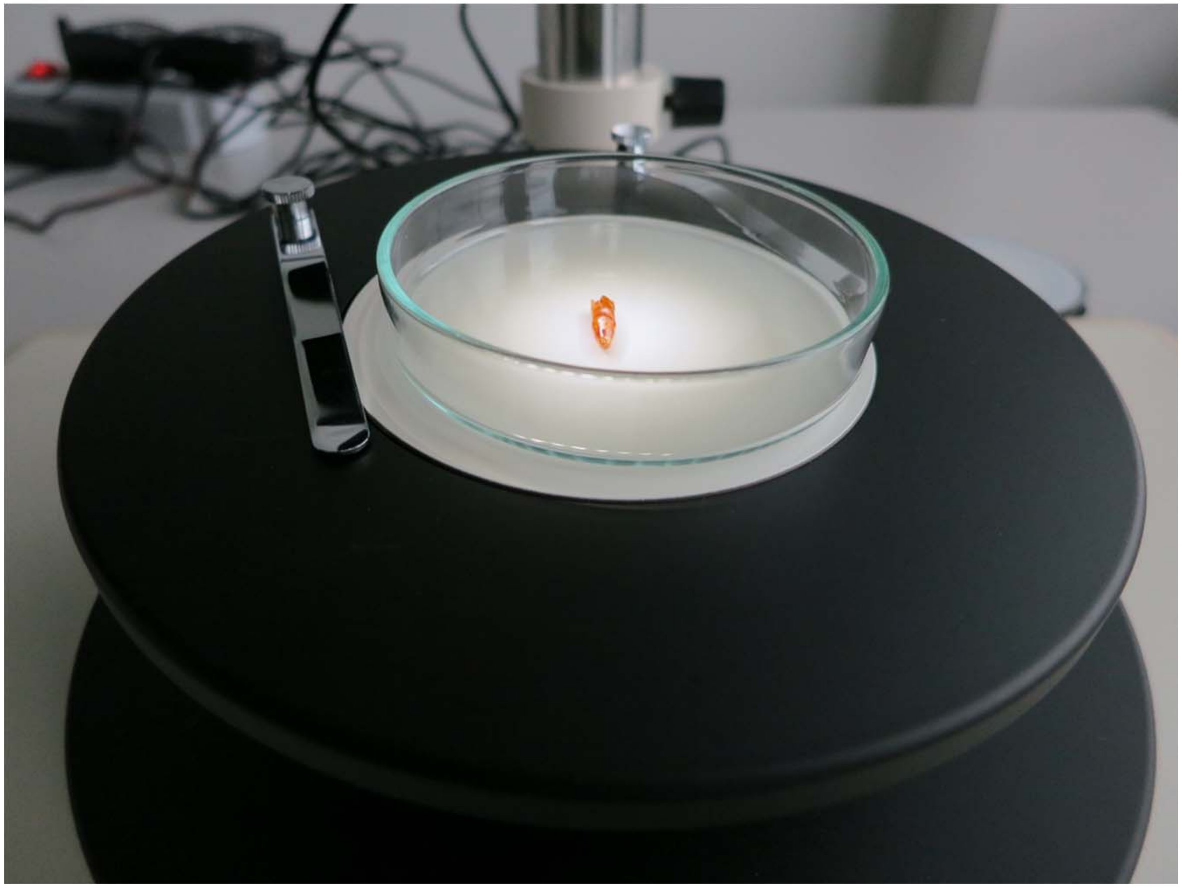
1 Lower part of the stage, movable in any direction within the x-y plane

Optical microscope Stemi 2000-C from Zeiss

LED light source for an illumination of the sample from above

The illumination of the sample can be varied by an adjustable brightness and by switching on / off selected sections of the circular LED arrangement

Optical microscope Stemi 2000-C from Zeiss

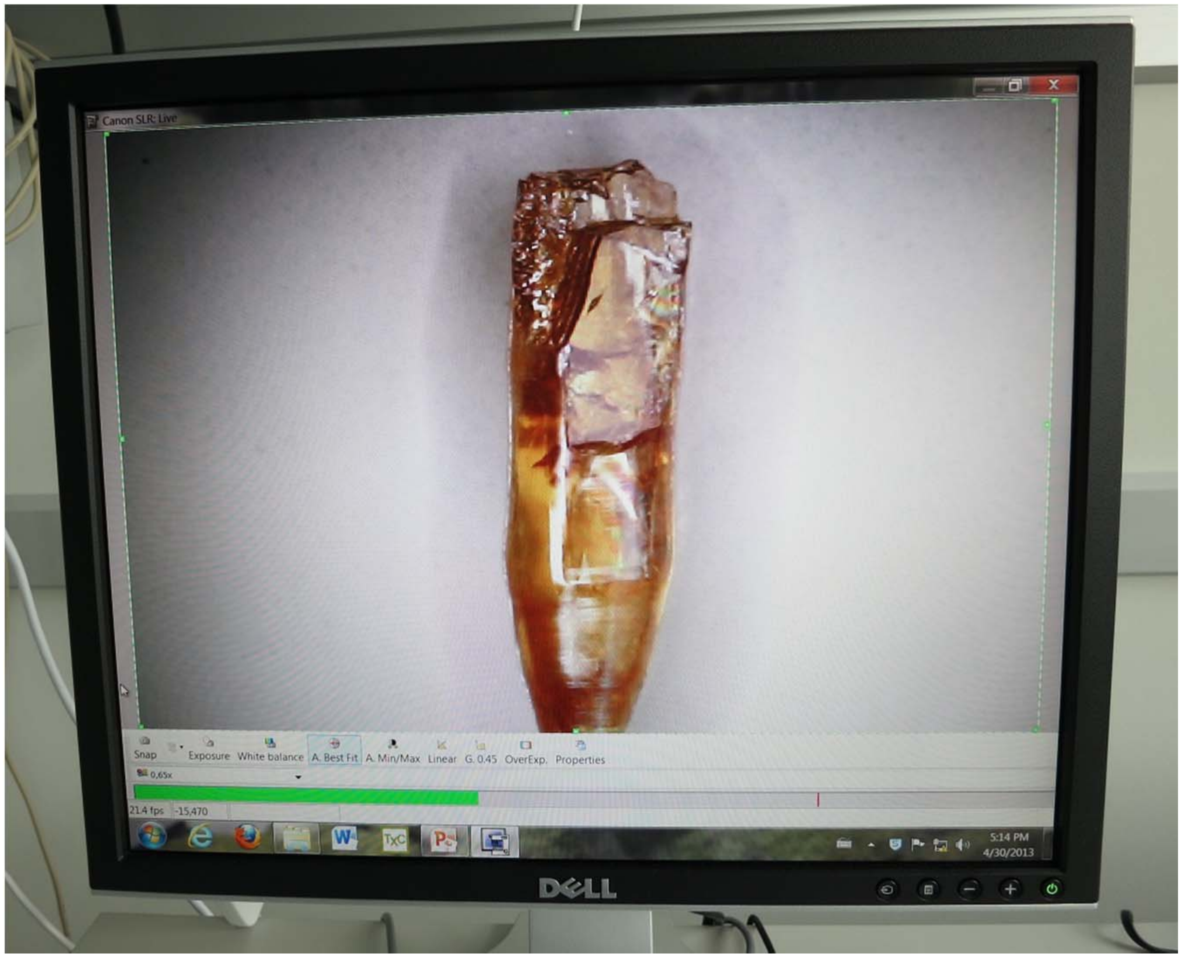


Melt-grown crystalline sample in a glass bowl on the stage

Chemical composition of this sample $La_{1.6}Sm_2Eu_{0.4}Ti_4O_{14}$

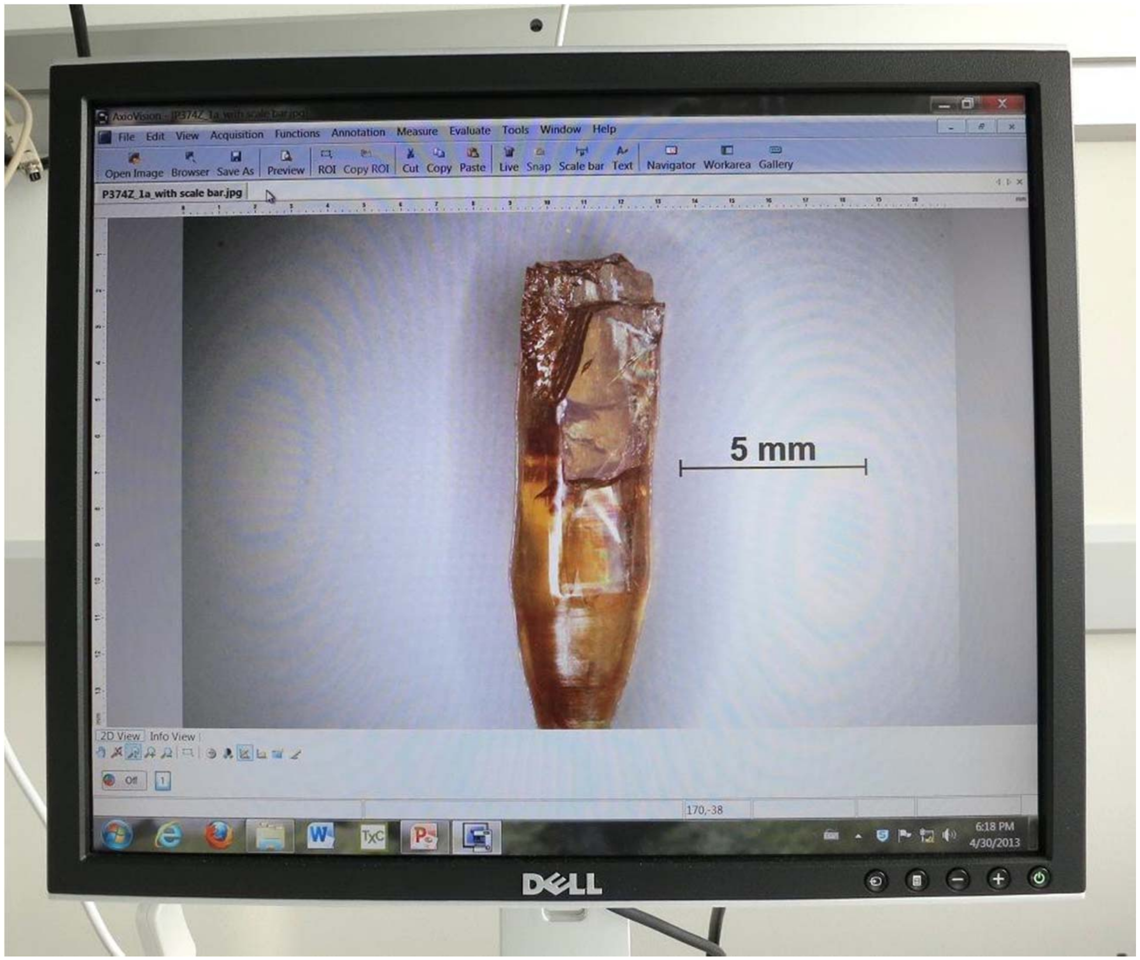
Sample prepared at the University of Augsburg • Progress in Solid State Chemistry 36 (2008) 253

Optical microscope Stemi 2000-C from Zeiss



How it appears on the monitor: Live image of the sample shown on the previous page

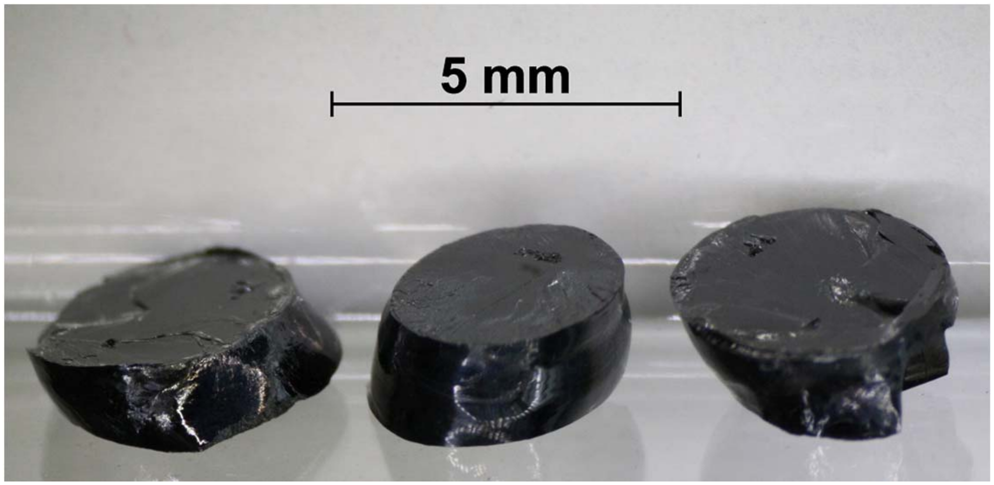
Optical microscope Stemi 2000-C from Zeiss



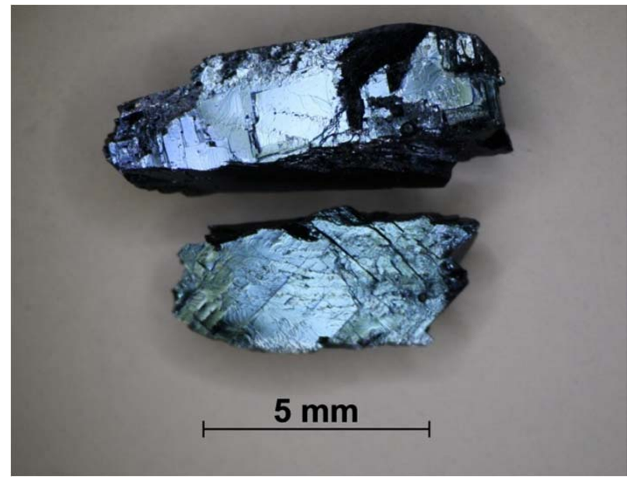
After taking the picture of the sample shown on the previous page: Image with inserted scale bar

Optical microscope Stemi 2000-C from Zeiss

Examples of pictures of melt-grown crystalline samples
which were taken by the Zeiss microscope



$Sr_{4.6}La_{0.4}Nb_4O_{15.06}$



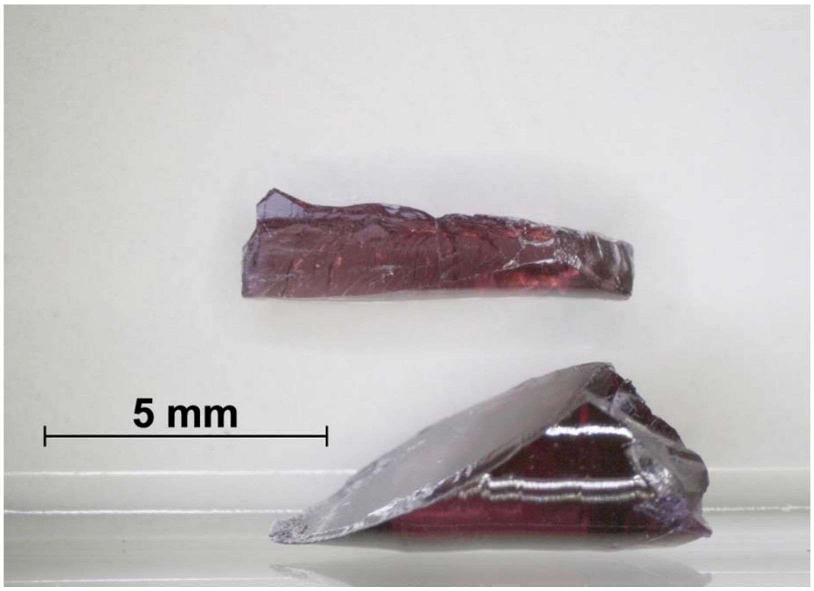
$BaCa_2Nb_3O_{10.07}$

Progress in Solid State Chemistry 36 (2008) 253

Samples prepared at the University of Augsburg - Photos taken at the ETH Zurich

Optical microscope Stemi 2000-C from Zeiss

Examples of pictures of melt-grown crystalline samples which were taken by the Zeiss microscope



$Nd_4Ti_4O_{14}$

$Pr_5Ti_4AlO_{17}$

Progress in Solid State Chemistry 36 (2008) 253

Samples prepared at the University of Augsburg - Photos taken at the ETH Zurich

Optical microscope Stemi 2000-C from Zeiss

Examples of pictures of melt-grown crystalline samples which were taken by the Zeiss microscope

$La_5Ti_4FeO_{17}$

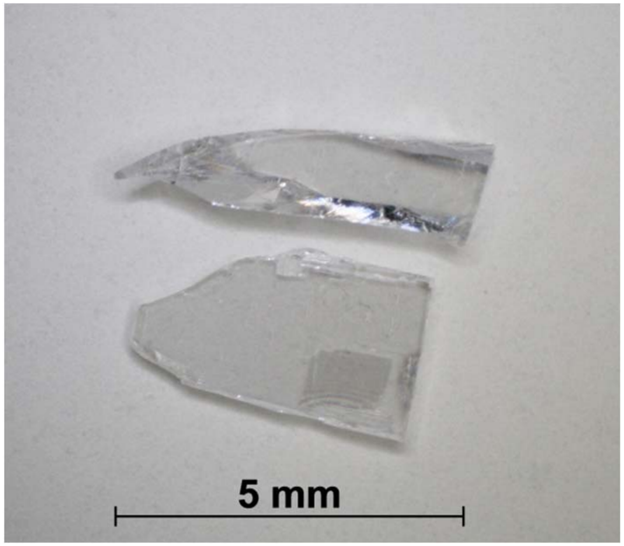
$La_6Ti_4Fe_2O_{20}$

Progress in Solid State Chemistry 36 (2008) 253

Samples prepared at the University of Augsburg - Photos taken at the ETH Zurich

Optical microscope Stemi 2000-C from Zeiss

Examples of pictures of melt-grown crystalline samples which were taken by the Zeiss microscope



$Sr_4Nb_4O_{14}$

Samples prepared at the University of Augsburg

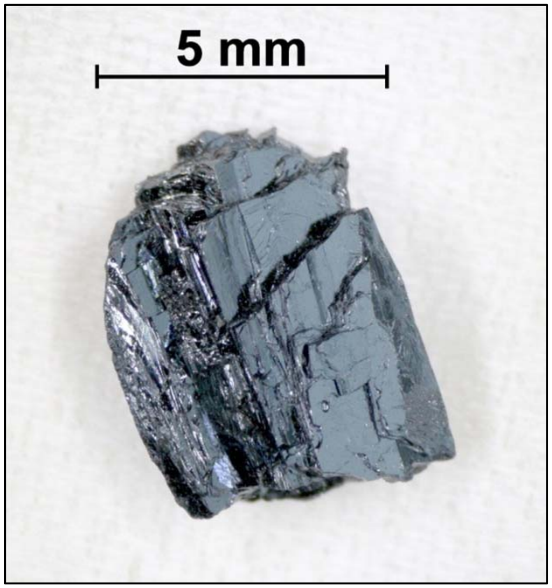
Progress in Solid State Chemistry 36 (2008) 253

Samples prepared at the ETH Zurich

Photos taken at the ETH Zurich

Optical microscope Stemi 2000-C from Zeiss

Examples of pictures of melt-grown crystalline samples which were taken by the Zeiss microscope



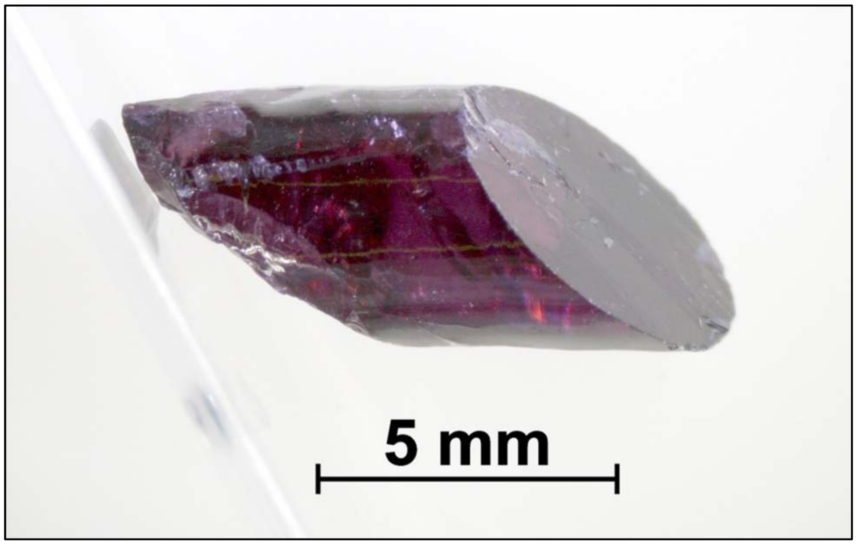
$Sr_{3.2}La_{0.8}Nb_4O_{14}$

Progress in Solid State Chemistry 29 (2001) 1 and 36 (2008) 253

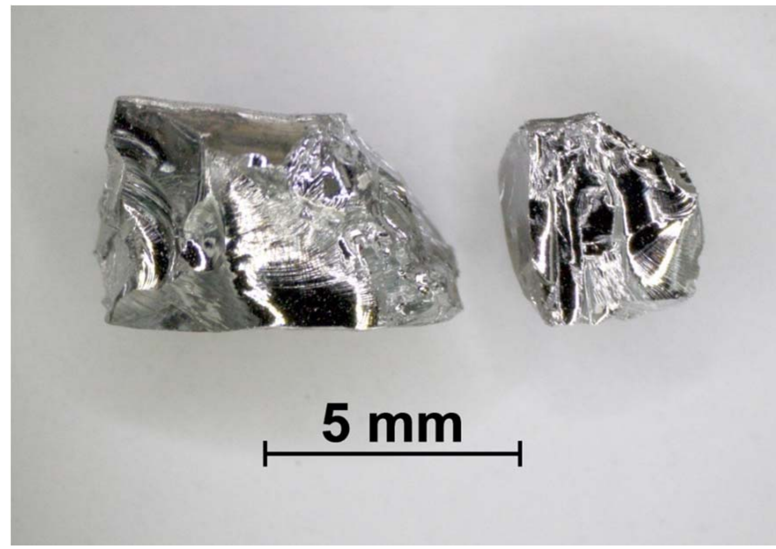
Samples prepared at the University of Augsburg - Photos taken at the ETH Zurich

Optical microscope Stemi 2000-C from Zeiss

Examples of pictures of melt-grown crystalline samples which were taken by the Zeiss microscope



$Nd_4Ti_4O_{14}$



$TiO_{0.27}$

Samples prepared at the IBM Zurich Research Laboratory - Photos taken at the ETH Zurich

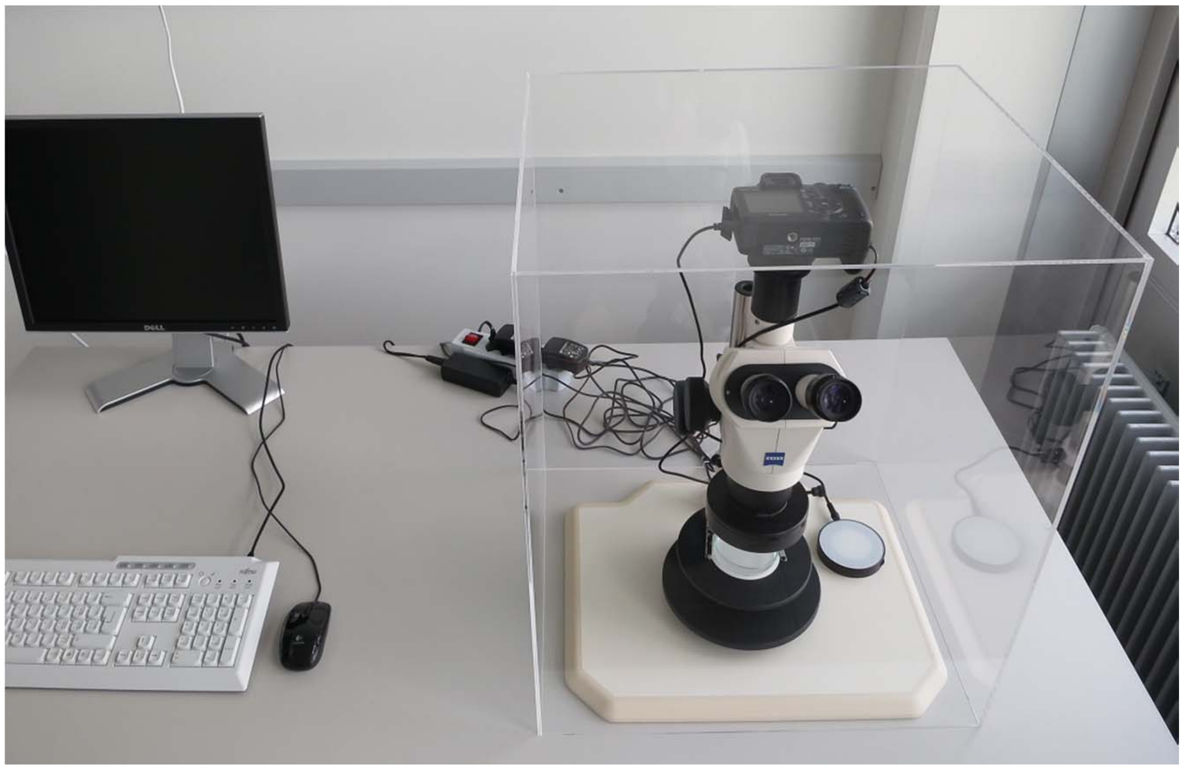
Optical microscope Stemi 2000-C from Zeiss

Examples of pictures of platinum-rhodium screws (see part 2) which were taken by the Zeiss microscope

Platinum-Rhodium screws (custom-made design) purchased and delivered from stone-ware gmbh (Switzerland) and made by Ögussa (Austria) - Photos taken at the ETH Zurich

Optical microscope Stemi 2000-C from Zeiss

Monitor and keyboard of the associated computer & Microscope
under a transparent protective box made of acrylic glass



Acrylic glass box (custom-made design)
made by Semadeni AG / Switzerland

Part 11

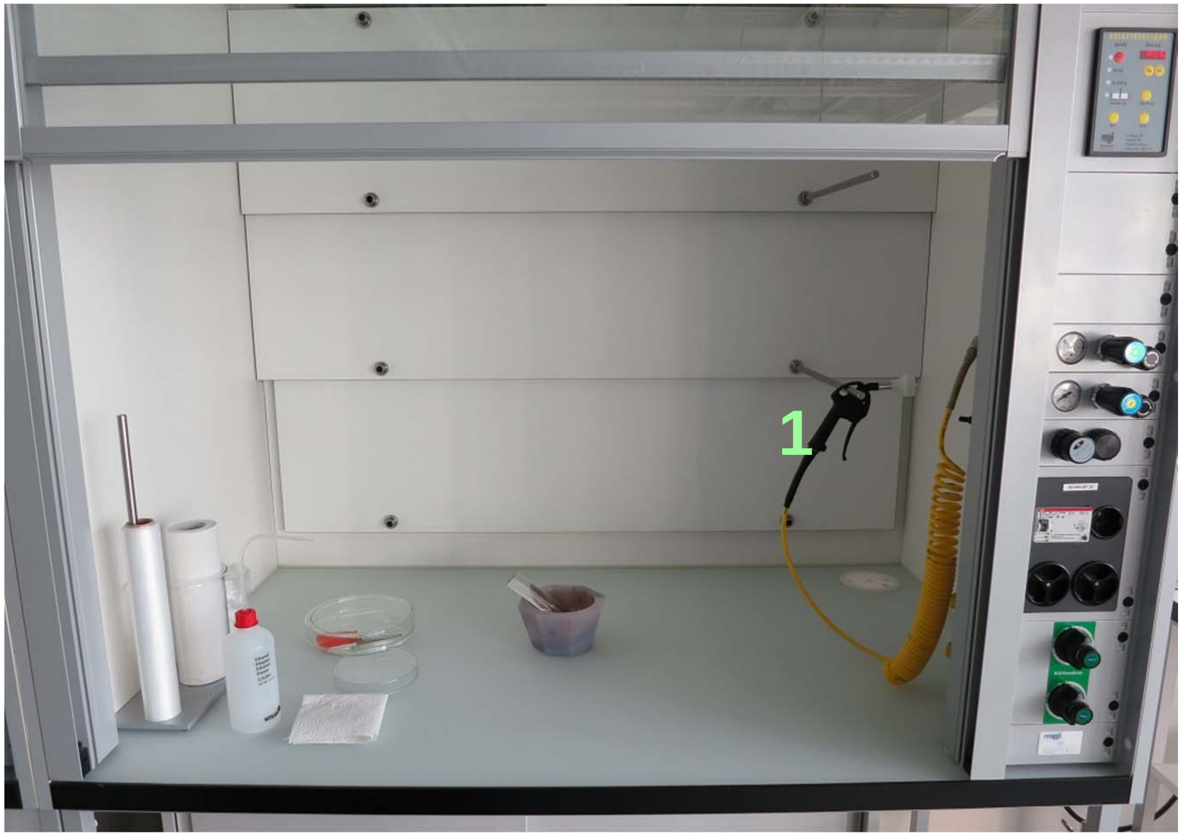
Presentation of miscellaneous equipment

Laboratory hood

The hood allows a safe working with chemicals and powder such as grinding or mixing by a mortar and pestle or the preparation of seed and feed rods

Adjusted suction capacity 200 m^3 / h

Laboratory hood



The hood allows a safe working with chemicals and powder such as grinding or mixing by a mortar and pestle or the preparation of seed and feed rods

Adjusted suction capacity 200 m^3 / h

The gas filter gun (1) is used for cleaning and is presented on the following page

Gas filter gun for cleaning

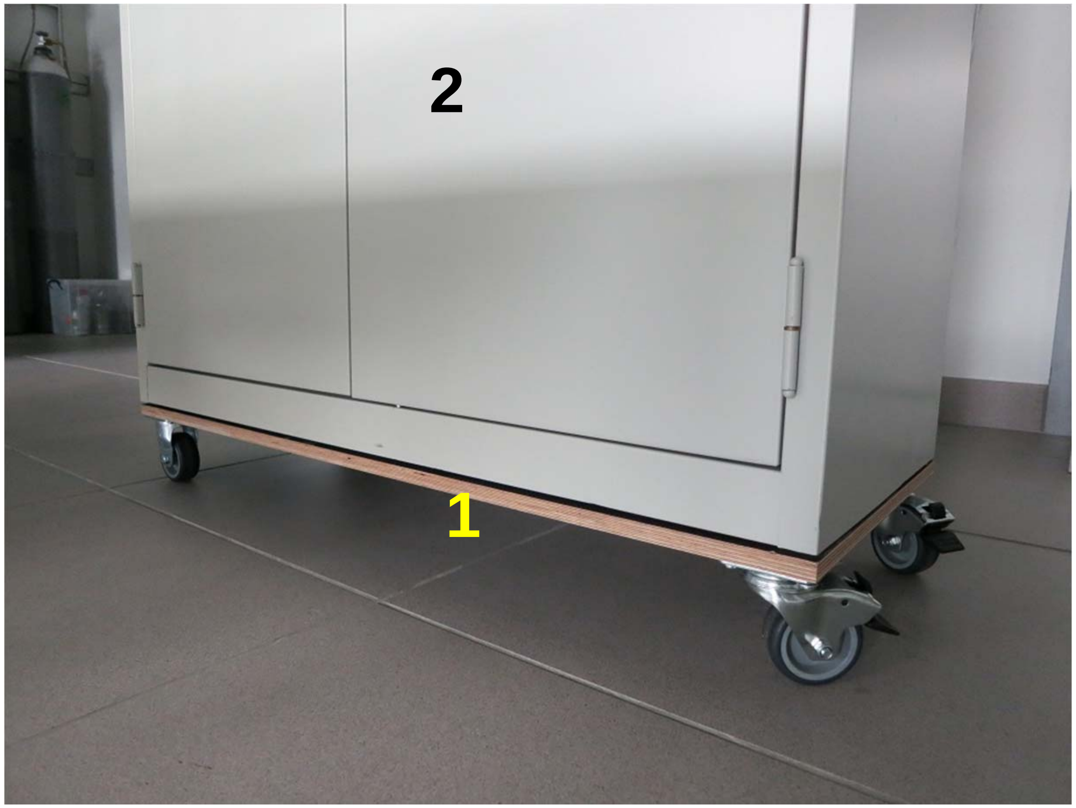
Gas filter gun GF-30A from SKAN AG (Switzerland)

It enables the generation of a directed and particle-free stream of gas such as air

It comprises a PTFE membrane filter (2) with a pore size of 0,45 μm

For cleaning of various components such as parts of pressing dies, crucibles, mortars, and pestles

Wheeled stages for metal cabinets



2 Metal cabinet

1 Example of a wheeled stage

The wheeled stages were made in the metal workshop of the Department of Materials of the ETH Zurich by M. Elsener, C. Roth and B. Jörg

Part 12 – Thermogravimetry

12 - 1 What is thermogravimetry and sketch of its technical implementation

12 - 2 Presentation of the NETZSCH thermogravimetric analyzer

12 - 3 Examples of thermogravimetric measurements and results

Part 12 - 1

What is thermogravimetry and sketch of its technical implementation

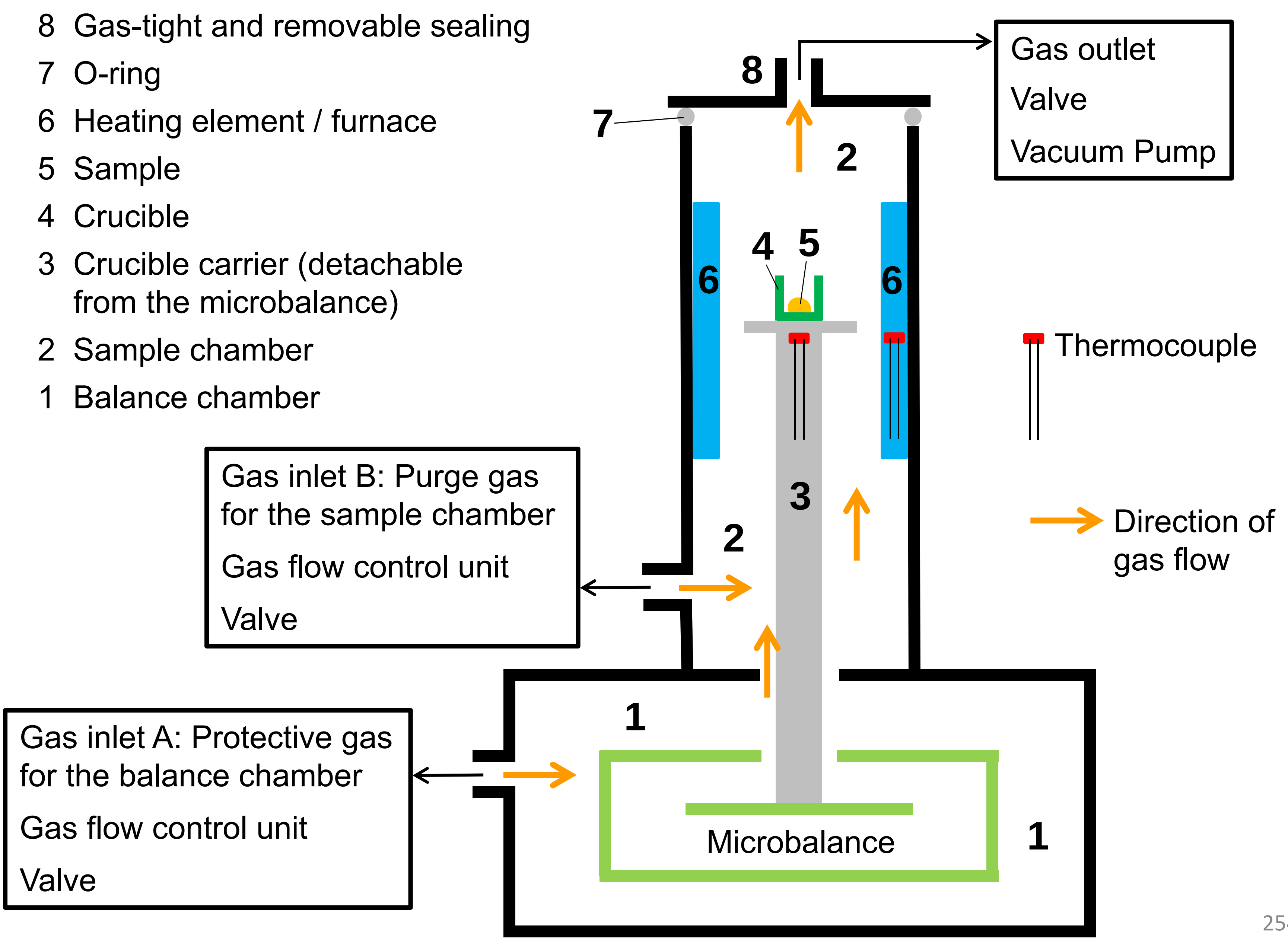
What is thermogravimetry ?

Thermogravimetry means the measurement of the weight or mass of a material or sample as a function of temperature under a specific atmosphere. A thermogravimetric analysis may reveal some materials properties such as

- release of oxygen (reduction), moisture, or CO_2 - at which temperature it begins, at which temperature it is finished, how much
- uptake of oxygen (oxidation) - at which temperature it begins, at which temperature it is finished, how much
- oxygen content and chemical composition
- exothermic or endothermic phase changes if the thermogravimetric analyzer and the data evaluation provides a so-called calculated DTA signal
- components of released gases if the thermogravimetric analyzer is equipped with a mass spectrometer

The thermogravimetry is technically implemented by a combination of a microbalance and a small furnace. The principle of a thermogravimetric analyzer is sketched on the following page …

Thermogravimetric Analyzer – Sketch of principle

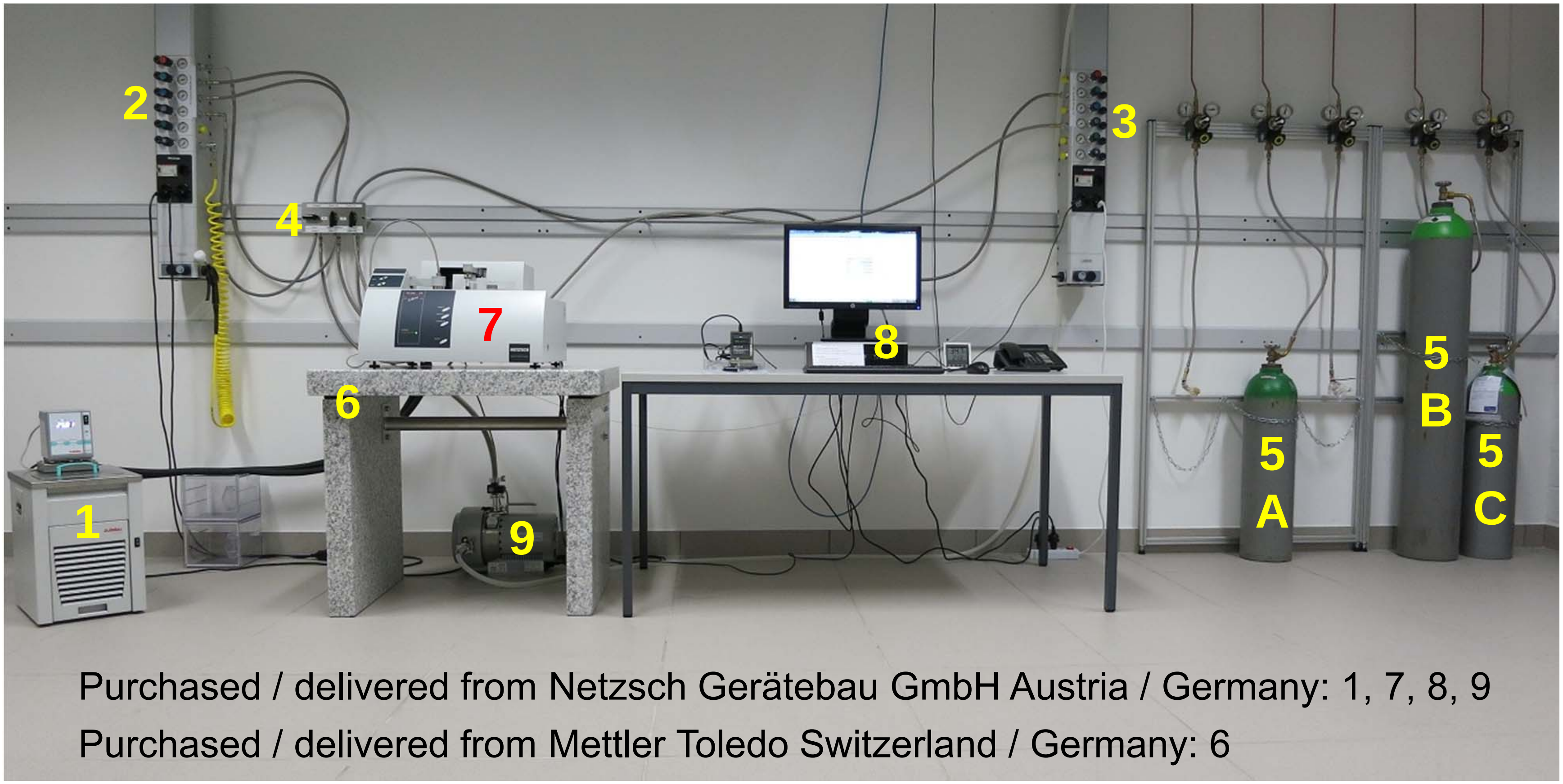


Part 12 - 2

Presentation of the NETZSCH thermogravimetric analyzer

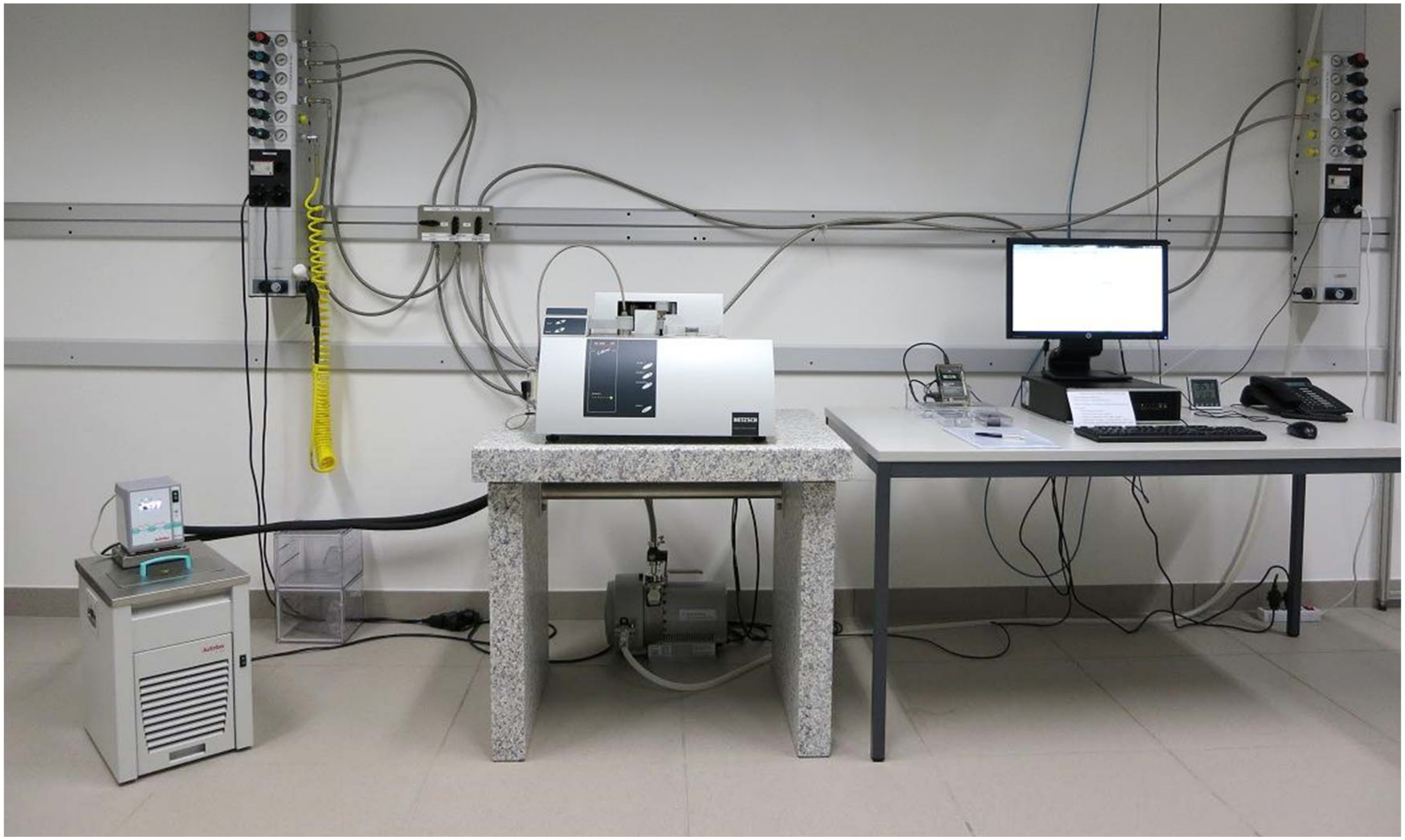
Thermogravimetric analyzer NETZSCH TG 209 F1 Libra – Overall system

Thermogravimetric analyzer NETZSCH TG 209 F1 Libra – Overall system



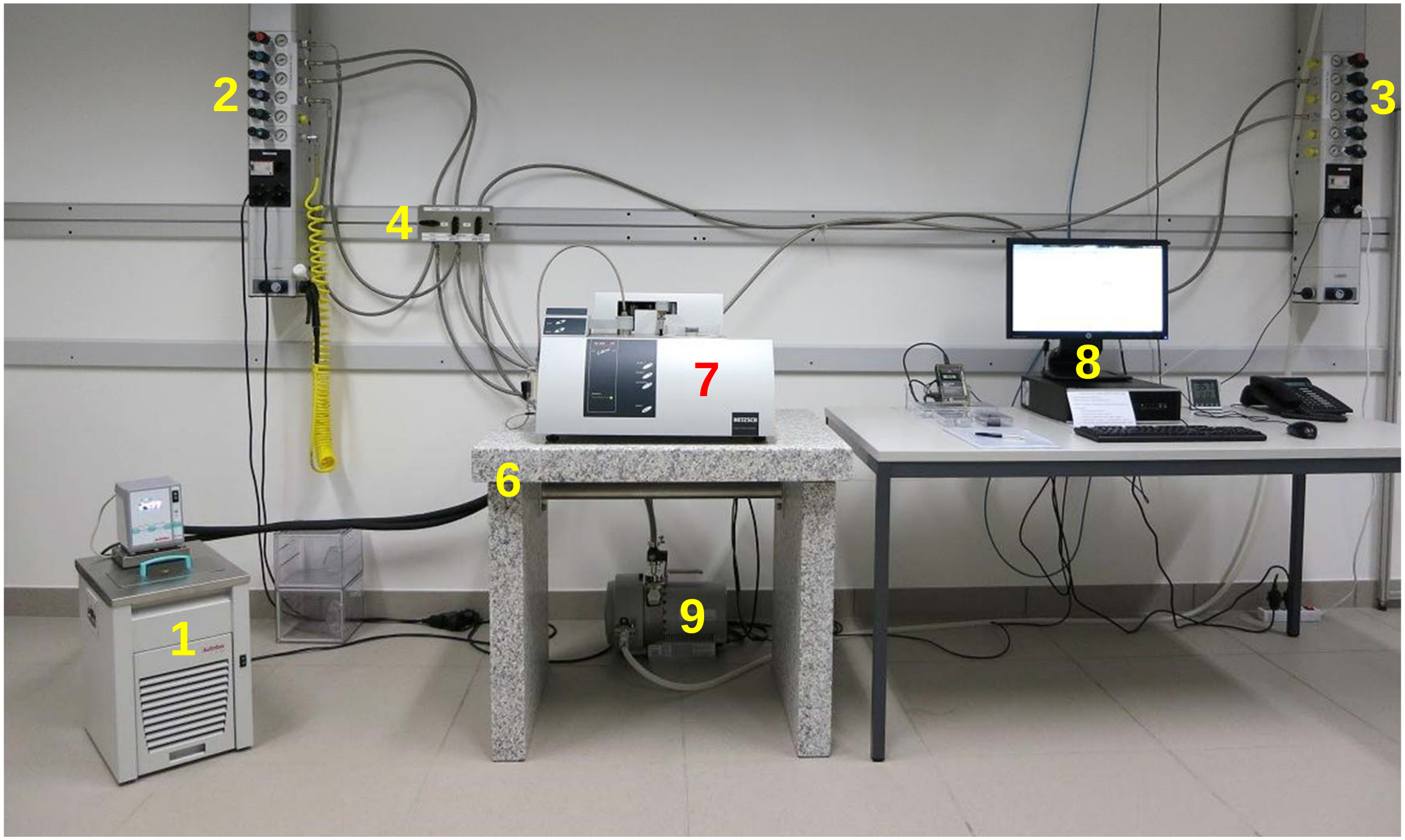
1 Refrigerated and heated water circulator for temperature stabilization of the microbalance
2 Gas supply cabinet for the purge gas for the sample chamber (synthetic air, Ar or Ar + H_2)
3 Gas supply cabinet for the protective gas for the balance chamber (synthetic air or Ar)
4 Switching valves for the protective gas and purge gas
5 Gas supply / gas bottles: Ar (A) • Synthetic air (B) • 97,2 % Ar + 2,8 % H_2 (C)
6 Balance table made of granite 7 Thermogravimetric analyzer 8 Computer and monitor
9 Oil-free scroll vacuum pump for evacuating the balance chamber and sample chamber

Thermogravimetric analyzer NETZSCH TG 209 F1 Libra – Overall system



Closer view of overall system without gas bottles

Thermogravimetric analyzer NETZSCH TG 209 F1 Libra – Overall system



Closer view of overall system without gas bottles

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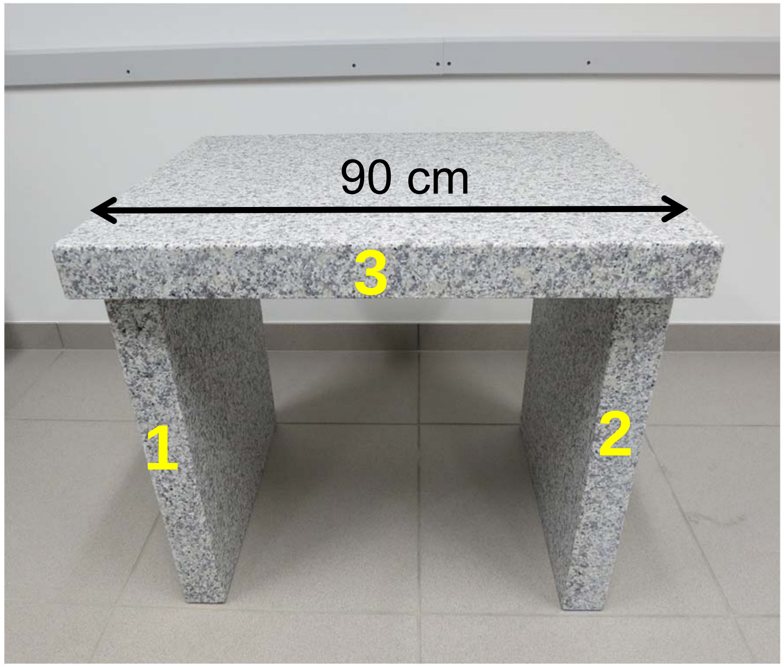
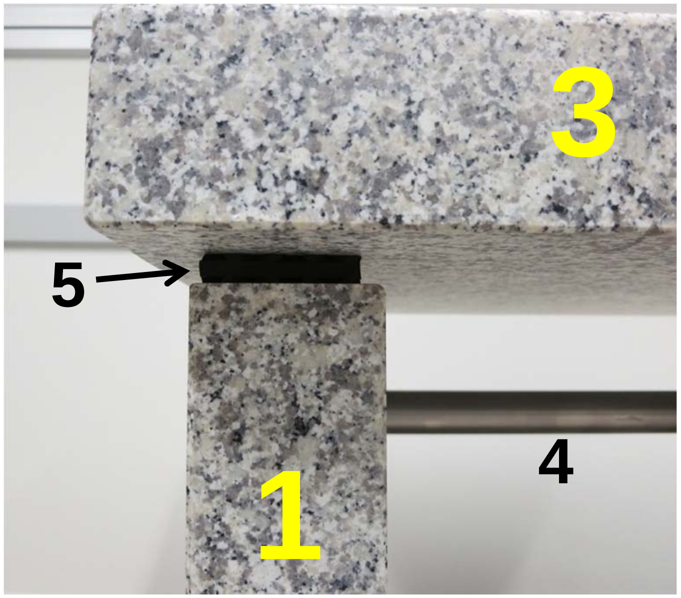
Balance table for the thermogravimetric analyzer





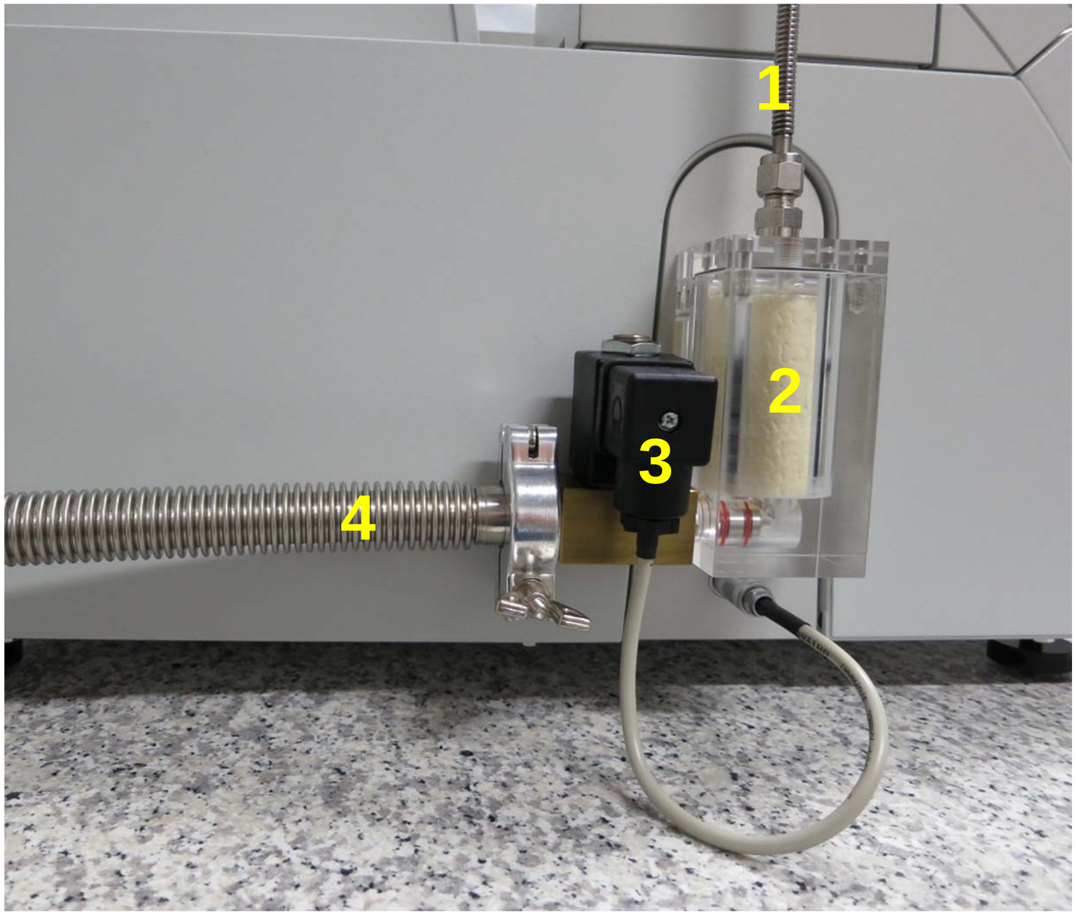
The balance table consists of three very heavy granite slabs (1, 2, 3) , a crossbar (4) , and four rubber feet on which the upper granite slab (3) rests. One of the four rubber feet is shown in the right picture (5). The rubber feet ensure a vibration-damped bearing of the upper granite slab (3).

Purchased / delivered from Mettler Toledo Switzerland / Germany. Delivery and assembling by H. - A. Pförtner and I. Rinke from the company Pförtner Kleintransporte.

Thermogravimetric analyzer (TGA) NETZSCH TG 209 F1 Libra

1 Gas outlet (flexible metal tube)
2 Motor-driven and gas-tight sealing of the sample chamber
3 Robot for the transport of a crucible from the crucible platform into the sample chamber and vice versa
4 Crucible platform

TGA NETZSCH TG 209 F1 Libra – Left-hand side



1 Gas outlet (flexible metal tube)

2 Gas filter

3 Electromagnetic valve

4 Flexible metal tube towards vacuum pump

TGA NETZSCH TG 209 F1 Libra – Rear side

1 Gas inlet 1 for the purge gas for the sample chamber

2 Gas inlet 2 for the purge gas for the sample chamber

3 Gas inlet for the protective gas for the balance chamber

4 Gas outlet. Connected is a thin and long teflon tube (5) which minimizes the effect of external pressure fluctuations

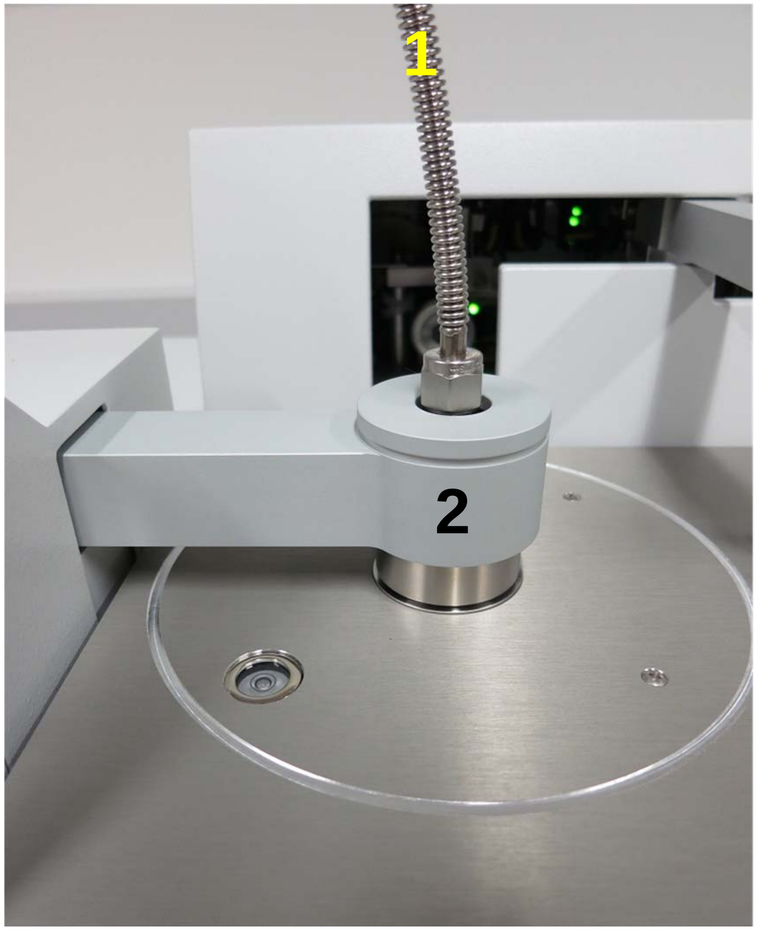
6 / 7 Water inlet / outlet for the temperature stabilization of the microbalance

TGA NETZSCH TG 209 F1 Libra – Some technical features

- Temperature range 20 – 1100 °C
- Heating and cooling rates 0.001 – 200 °C / min
- Microbalance resolution 0.1 µg
- Microbalance range 0 – 2000 mg
- Microbalance with integrated calibration weight and computer-controlled calibration procedure
- Integrated and computer-controlled gas flow system with 3 gas lines and 3 mass flow controllers
- Allowed protective gas types or atmospheres for the balance chamber: Air, nitrogen, inert gas such as argon, or vacuum
- Vacuum-tight design (down to 0.01 mbar)
- Easy change of the gas type by computer-controlled evacuation and filling of the balance chamber and sample chamber
- Calculated DTA signal (c-DTA)

TGA NETZSCH TG 209 F1 Libra – Sample chamber 1 / 2

1 Gas outlet (flexible metal tube)
2 Motor-driven and gas-tight sealing of the sample chamber
3 Sample chamber

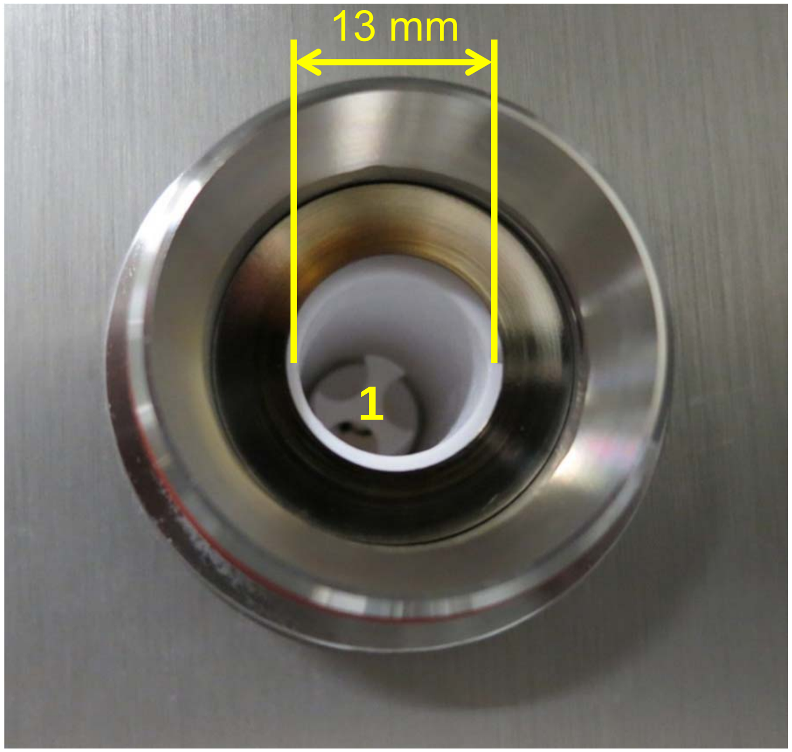


Sample chamber closed

Sample chamber (3) open

TGA NETZSCH TG 209 F1 Libra – Sample chamber 2 / 2

Top view of the open sample chamber

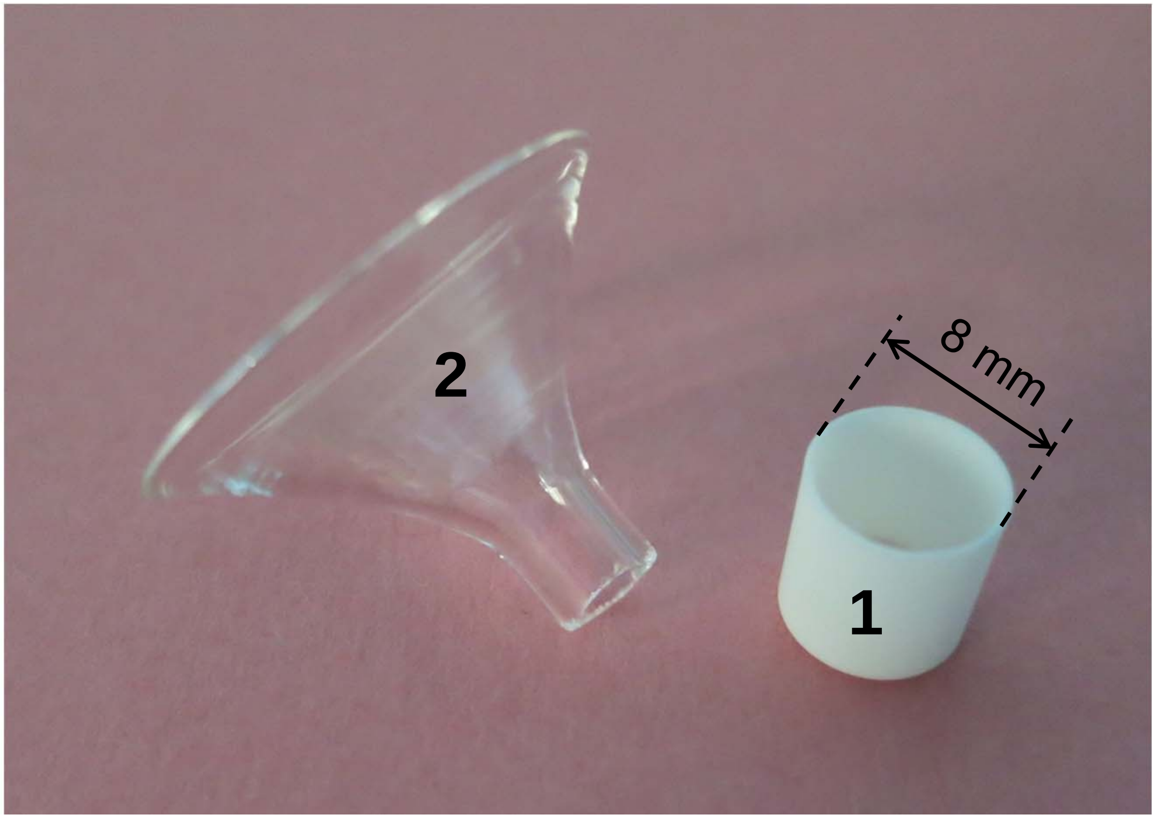


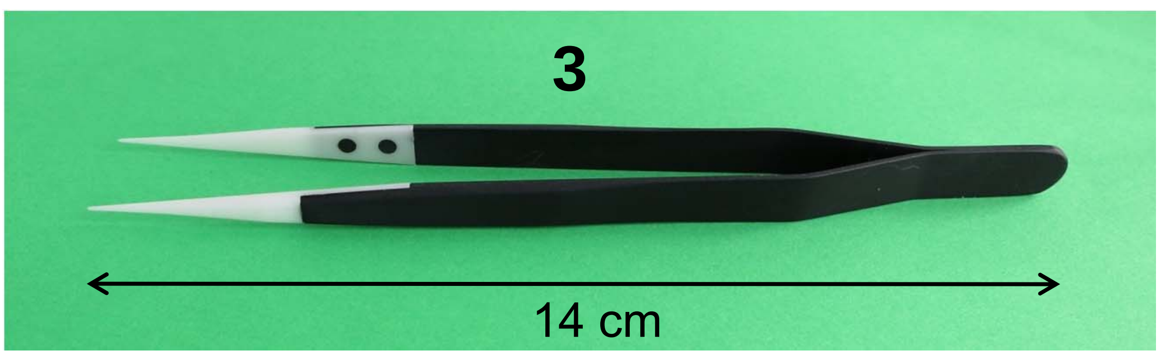
Motor-driven crucible carrier (1) down

Motor-driven crucible carrier (1) up

In this position it can be loaded with a crucible

TGA NETZSCH TG 209 F1 Libra – Example of a suitable crucible





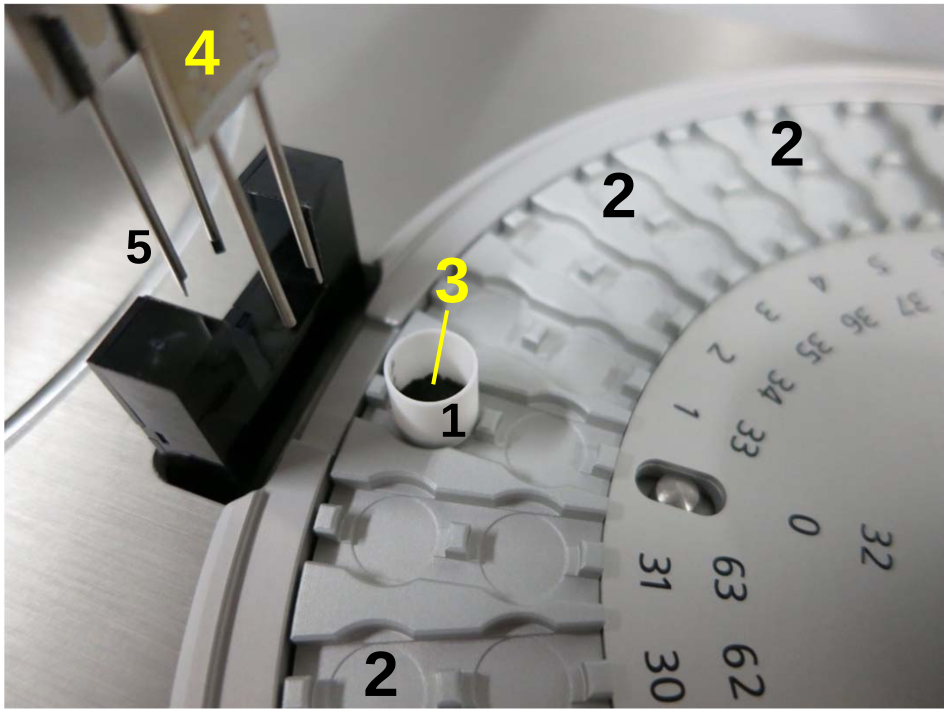
1 Crucible made of alumina with diameter 8 mm, height 8 mm, and mass 320 mg. Purchased / delivered from Netzsch Gerätebau GmbH Austria / Germany

2 Small custom-made glass funnel from Willi Möller AG (Switzerland). It can be inserted into the alumina crucible and makes its filling with powder relatively easy

3 Ceramic tweezer for gripping the crucible. The tips (white) are made of ceramics and the legs (black) are made of an aluminum alloy. Purchased and delivered from Plano GmbH (Germany)

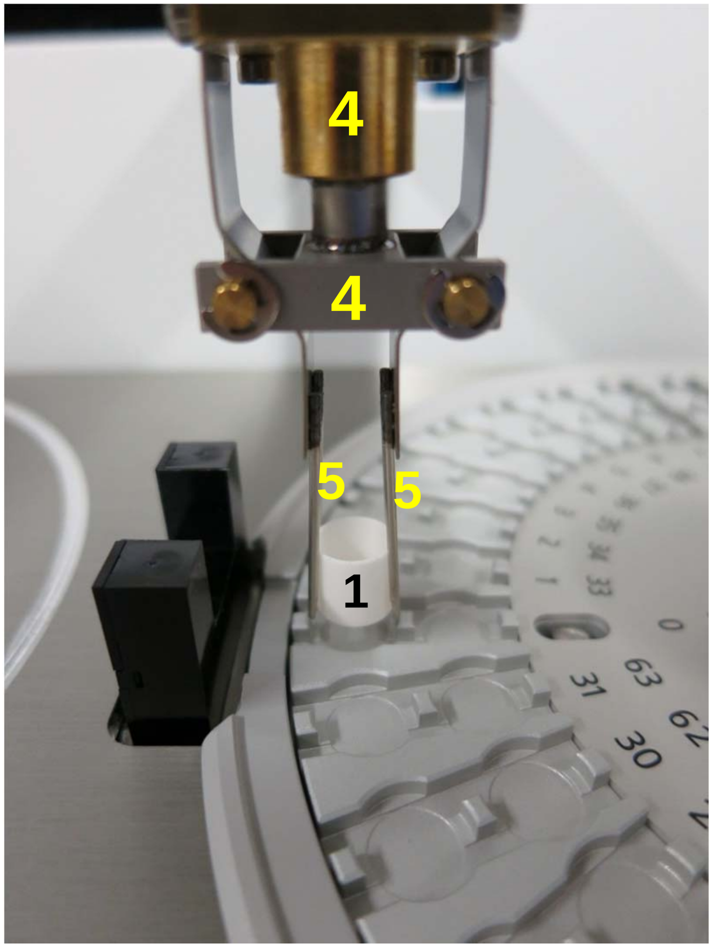
TGA NETZSCH TG 209 F1 Libra – Loading procedure 1 / 4

5 Gripper arm of the robot (overall there are four gripper arms)



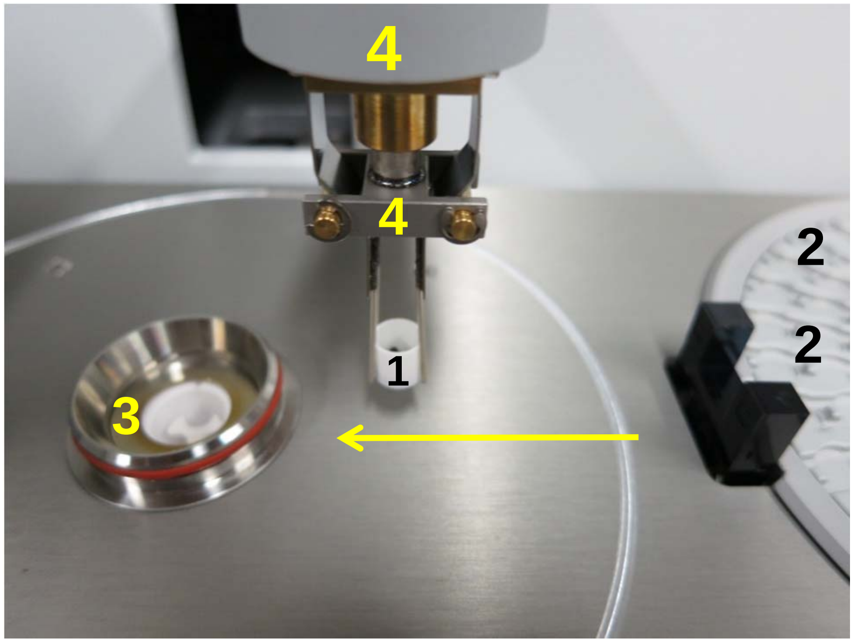
A crucible (1) on the crucible platform (2). The crucible (1) is filled with a sample (black powder) (3) and was manually placed onto the crucible platform (2)

→



The robot (4) has gripped and lifted the crucible (1)

TGA NETZSCH TG 209 F1 Libra – Loading procedure 2 / 4



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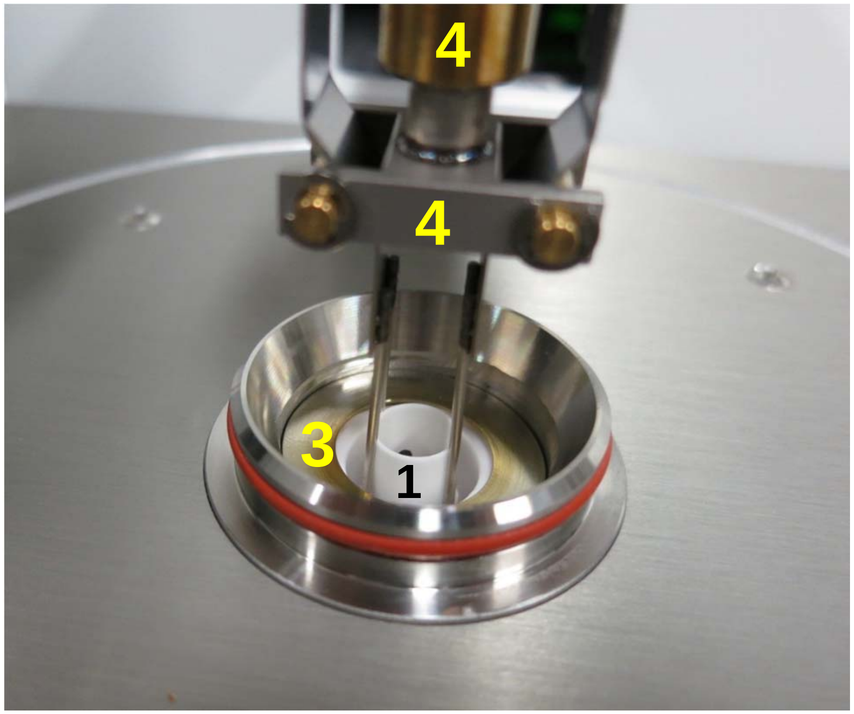


The robot (4) transports the gripped and lifted crucible (1) from the crucible platform (2) towards the open sample chamber (3)

The robot (4) places the crucible (1) onto the crucible carrier within the sample chamber (3)

TGA NETZSCH TG 209 F1 Libra – Loading procedure 3 / 4

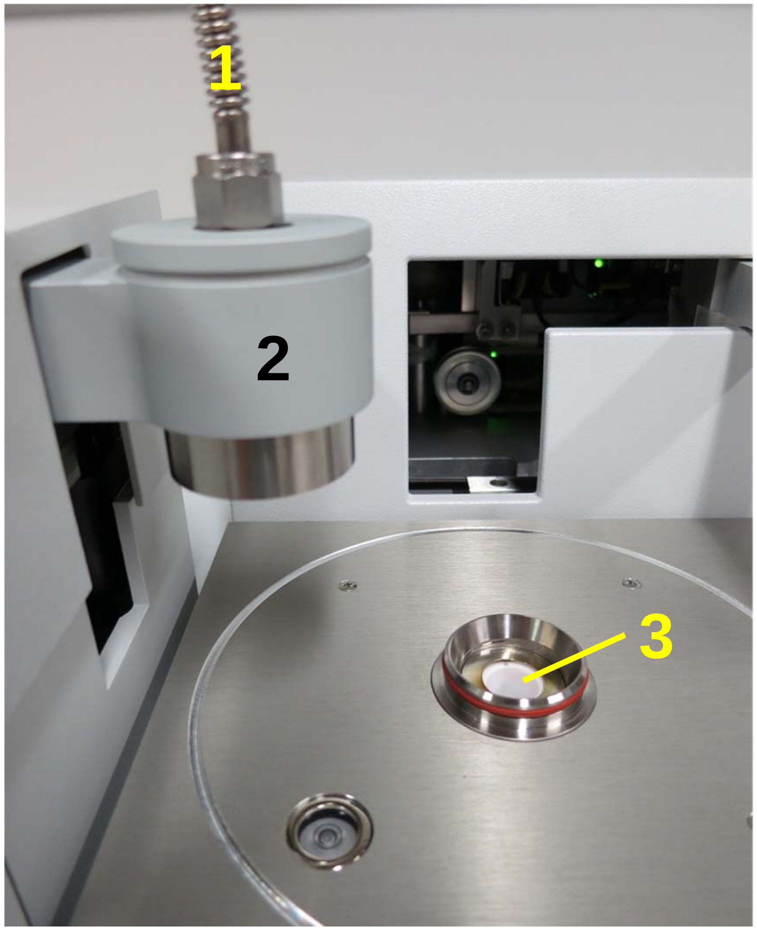
Crucible (1) on the crucible carrier in its lifted position within the sample chamber (2). The crucible (1) contains a sample (black powder) (3) and was placed onto the crucible carrier by the robot

→

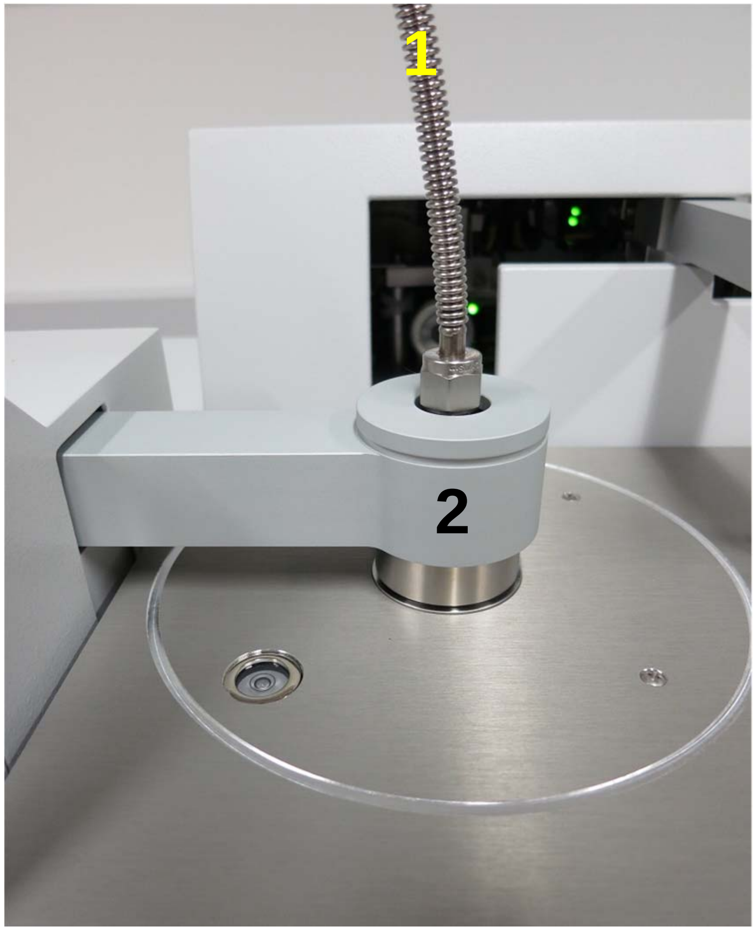
Crucible (1) on the crucible carrier in its bottom position within the sample chamber (2). The crucible (1) contains a sample (black powder) (3)

TGA NETZSCH TG 209 F1 Libra – Loading procedure 4 / 4

1 Gas outlet (flexible metal tube)
2 Motor-driven and gas-tight sealing of the sample chamber
3 Sample chamber



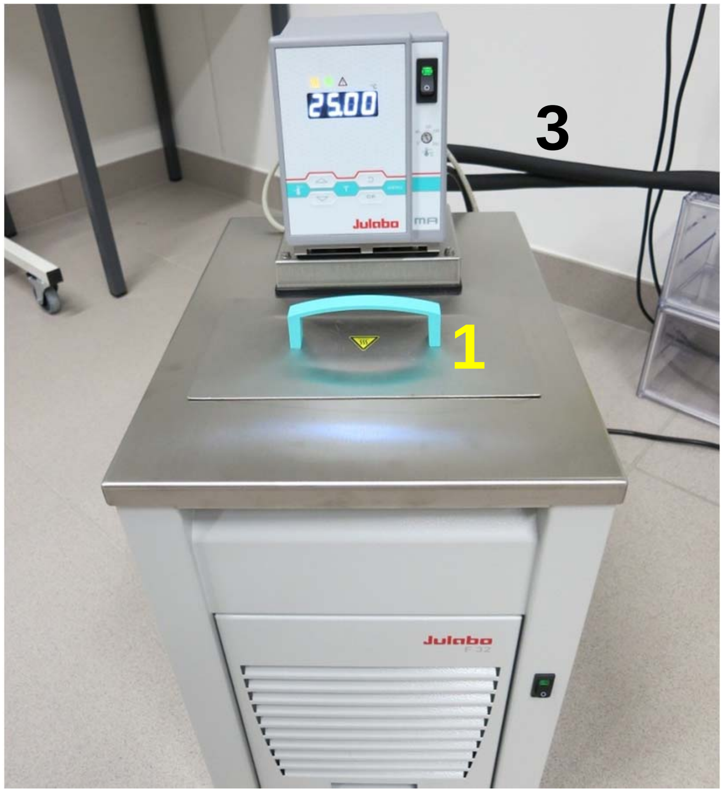
Sample chamber (3) open



Sample chamber closed

TGA NETZSCH TG 209 F1 Libra – Water circulator for the microbalance

Refrigerated and heated water circulator Julabo F32
for the temperature stabilization of the microbalance



1 Lid of the water bath

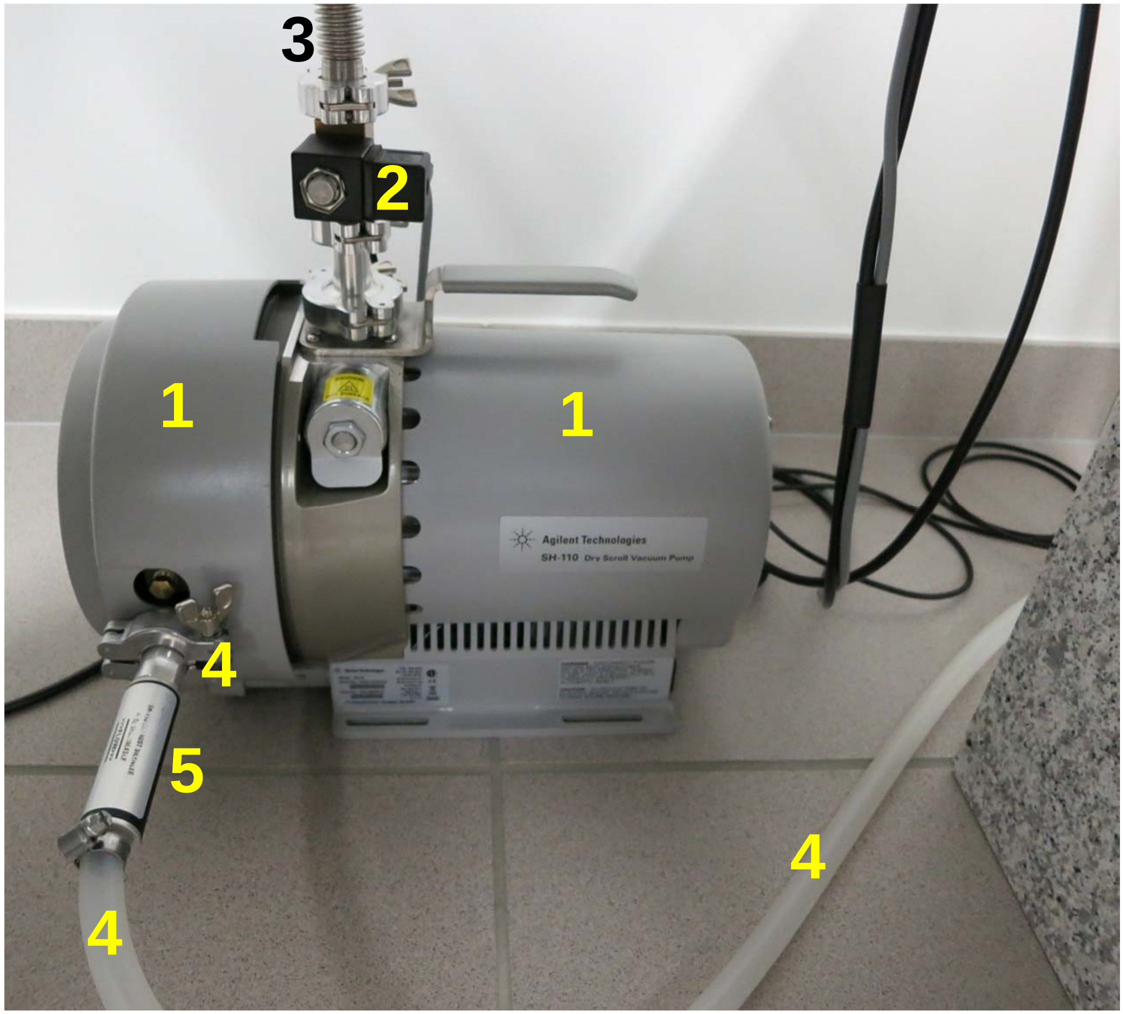
2 Water bath

3 Tubes towards water inlet and water oulet of the thermo-gravimetric analyzer

Lid (1) is removed and
water bath (2) is visible

TGA NETZSCH TG 209 F1 Libra – Oil-free vacuum pump

Vacuum pump for the evacuation of the balance chamber and sample chamber of the thermogravimetric analyzer. The vacuum pump is part of the computer-controlled evacuation and gas flow system



1 Oil-free / dry scroll vacuum pump from Agilent Technologies, type SH-110

2 Electromagnetic valve

3 Flexible metal tube towards thermo-gravimetric analyzer

4 Gas outlet / Exhaust gas line

5 Silencer

TGA NETZSCH TG 209 F1 Libra – Gas supply 1 / 5

Up to 200 bar pressure in bottle, flexible metal tube and line regulator ! Proper handling required !

Gas bottles and line regulators

8 Supply line towards gas supply cabinet

7 Pressure indicators for the gas pressure inside the bottle (up to 200 bar) and inside the supply line (up to 10 bar)

6 Line pressure regulator which reduces the high bottle pressure to a low supply line pressure

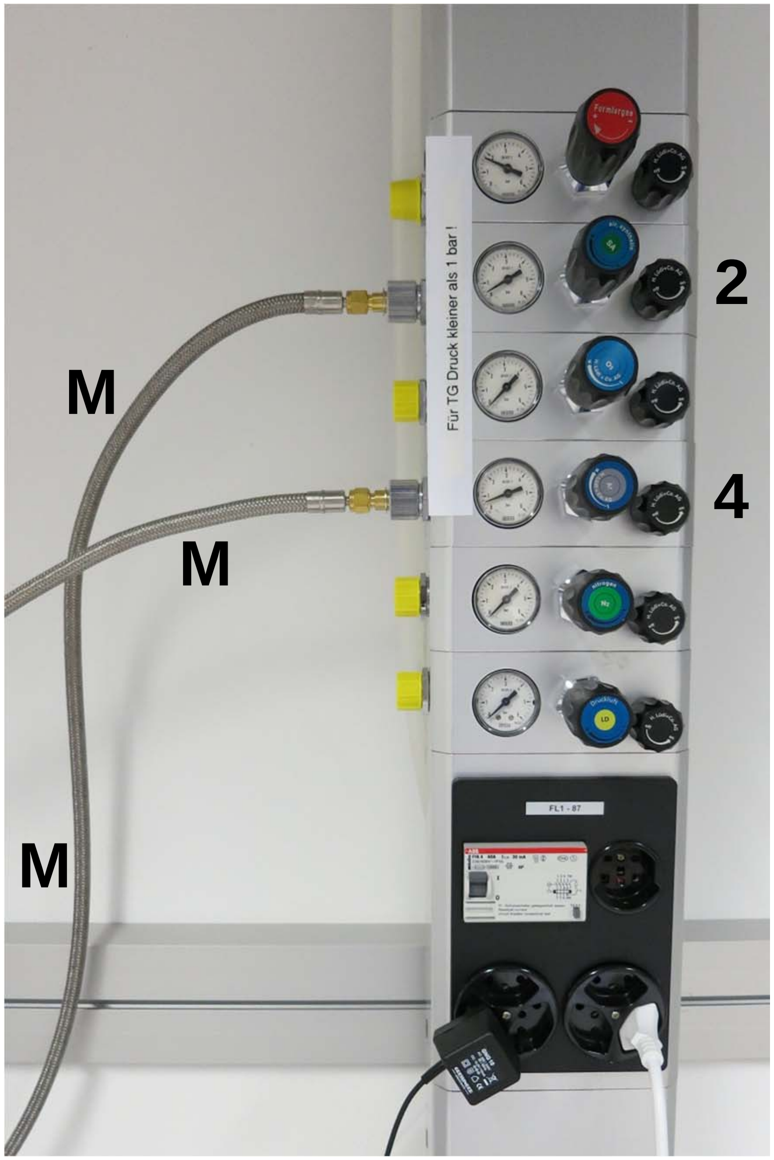
5 Flexible metal tube which connects the bottle with the line regulator

4 Ar

2 Synthetic Air (20 % O_2 + 80 % N_2)

1 97,2 % Ar + 2,8 % H_2 (non-flammable)

TGA NETZSCH TG 209 F1 Libra – Gas supply 2 / 5



Gas supply cabinet which is used for the protective gas for the balance chamber

2 Synthetic air

4 Argon

M Flexible metal tube (Swagelok 6 mm) towards switching valve

Gas supply cabinet which is used for the purge gas for the sample chamber

1 Argon + Hydrogen

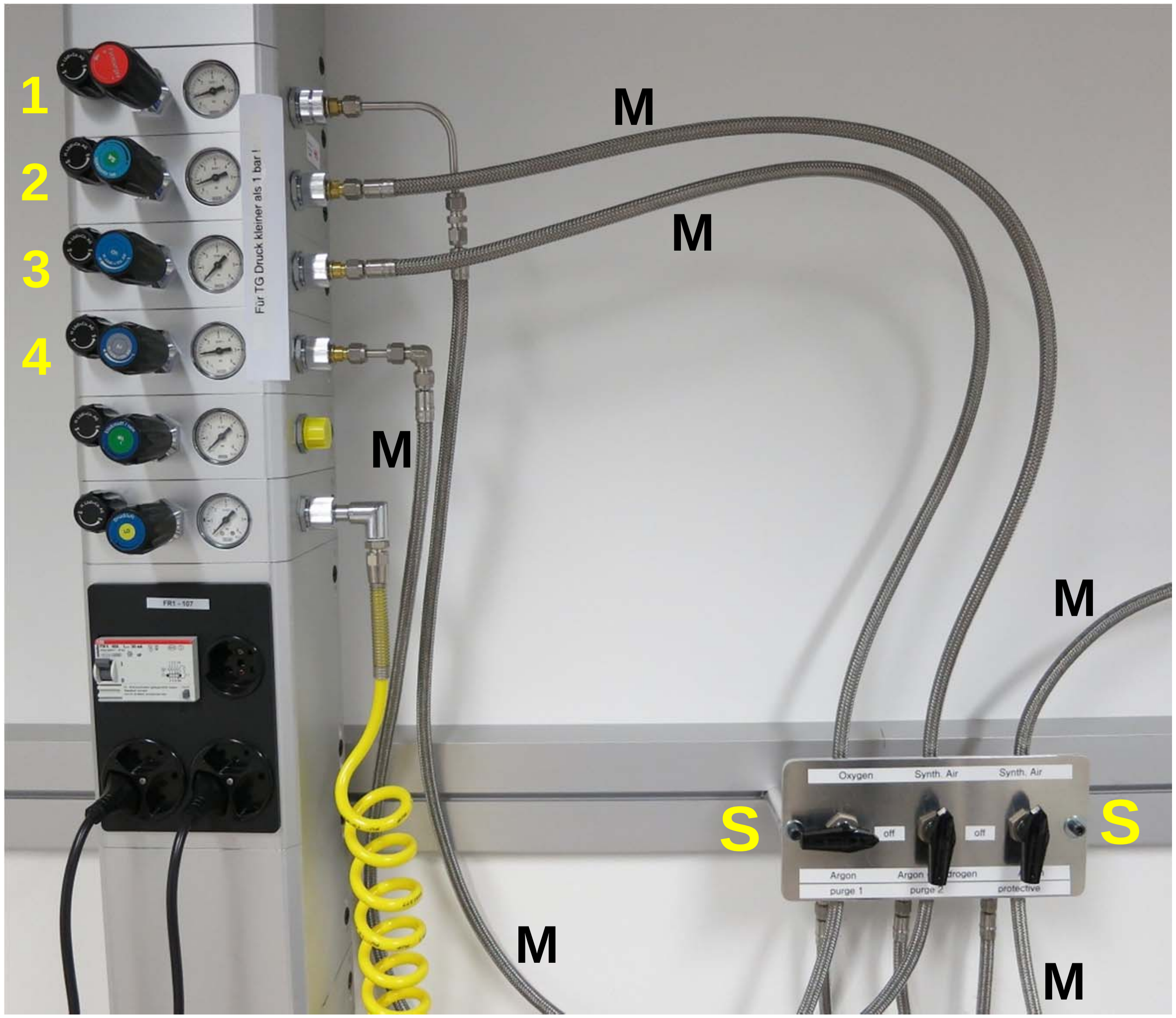
2 Synthetic air

3 Oxygen

4 Argon

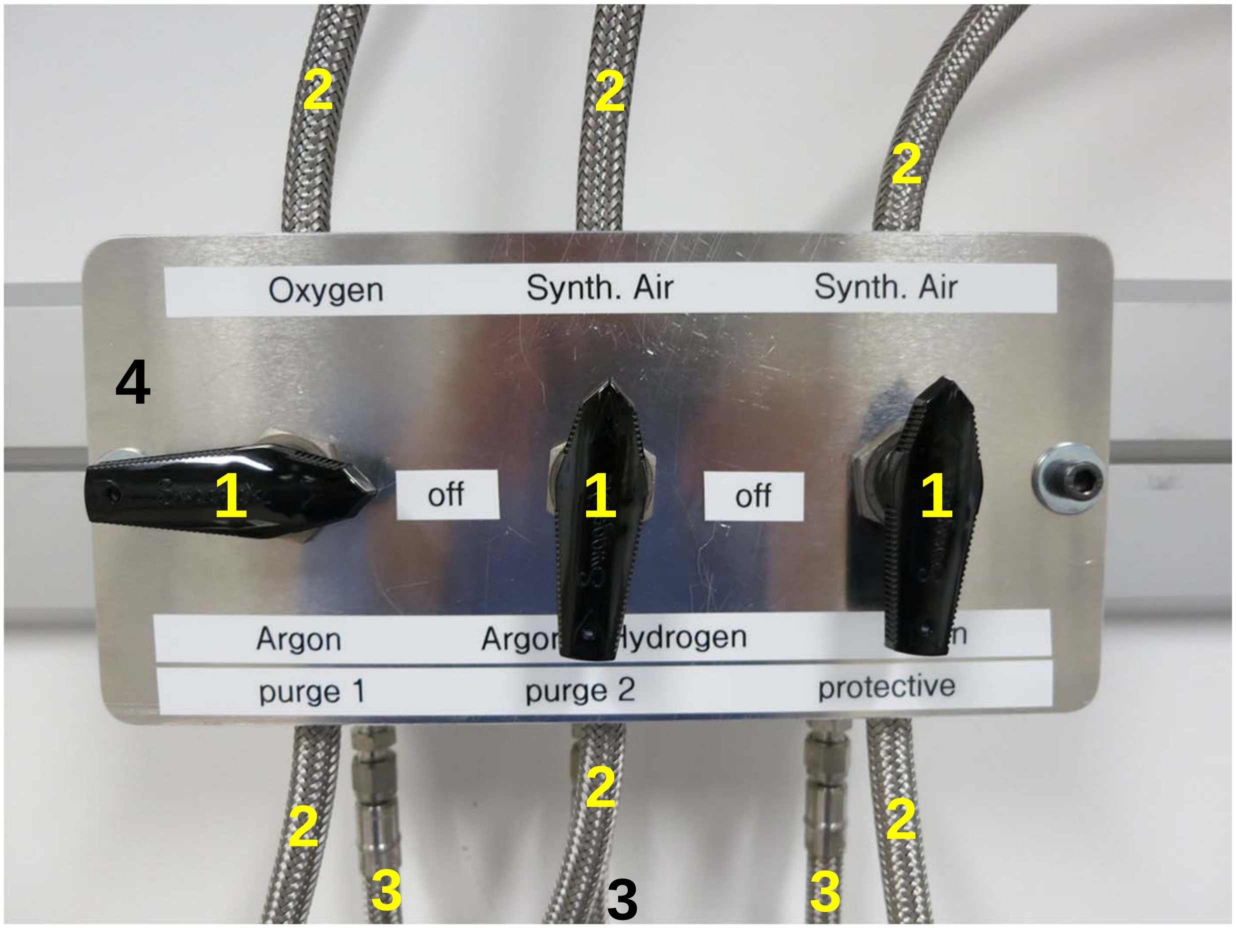
M Flexible metal tube (Swagelok 6 mm) towards switching valves

S Switching valves



TGA NETZSCH TG 209 F1 Libra – Gas supply 4 / 5

Gas switching valves for the protective gas for the balance chamber (synthetic air or argon) and the purge gas for the sample chamber (oxygen, synthetic air, argon, or argon + hydrogen)



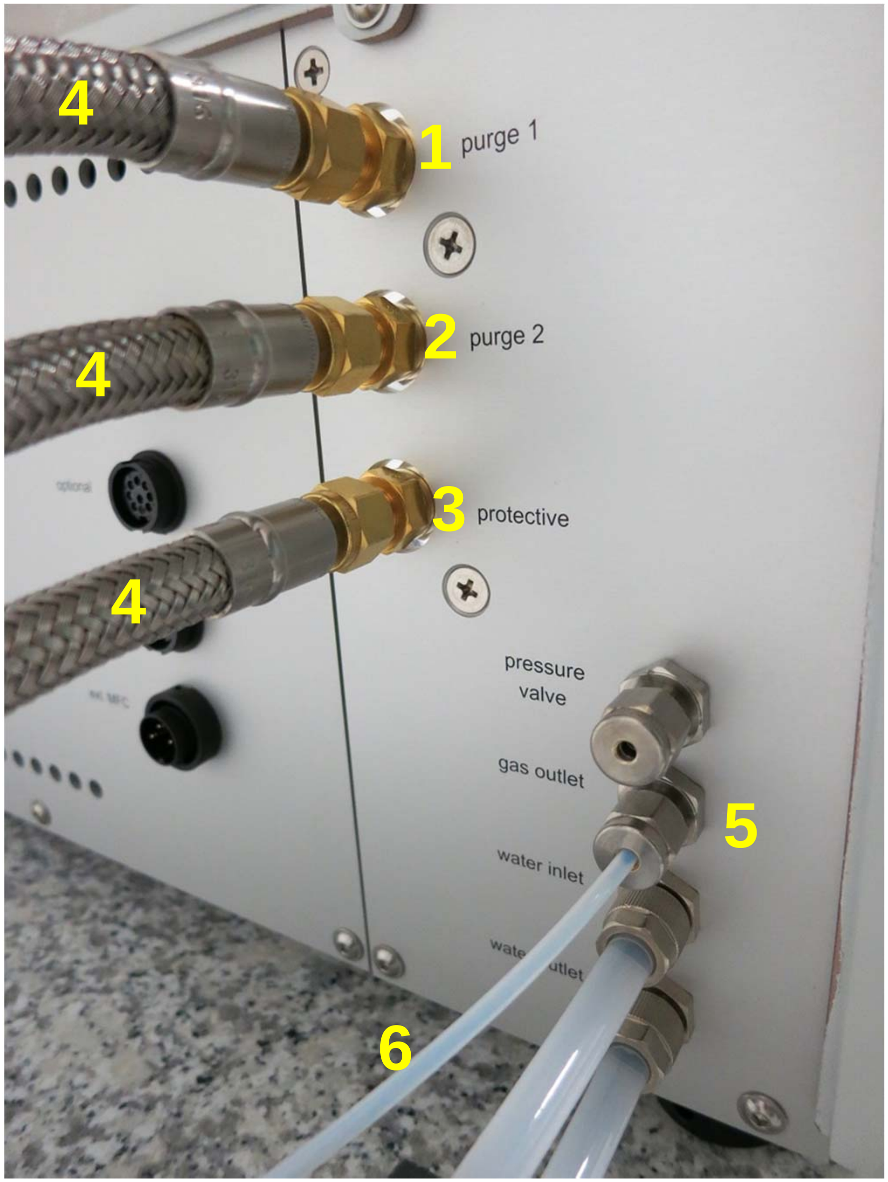
1 Swagelok lubricant-free 3-way ball valve SS-43GXS6MM-1466 with 6 mm fittings

2 Flexible metal tube (Swagelok 6 mm) from gas supply cabinet to switching valve

3 Flexible metal tube (Swagelok 6 mm) from switching valve to thermogravimetric analyzer

Metal plate (4) and mounting parts made by C. Roth and M. Elsener from the metal workshop of the Department of Materials of the ETH Zurich

TGA NETZSCH TG 209 F1 Libra – Gas supply 5 / 5



Rear side of the thermogravimetric analyzer

1 Gas inlet 1 for the purge gas for the sample chamber

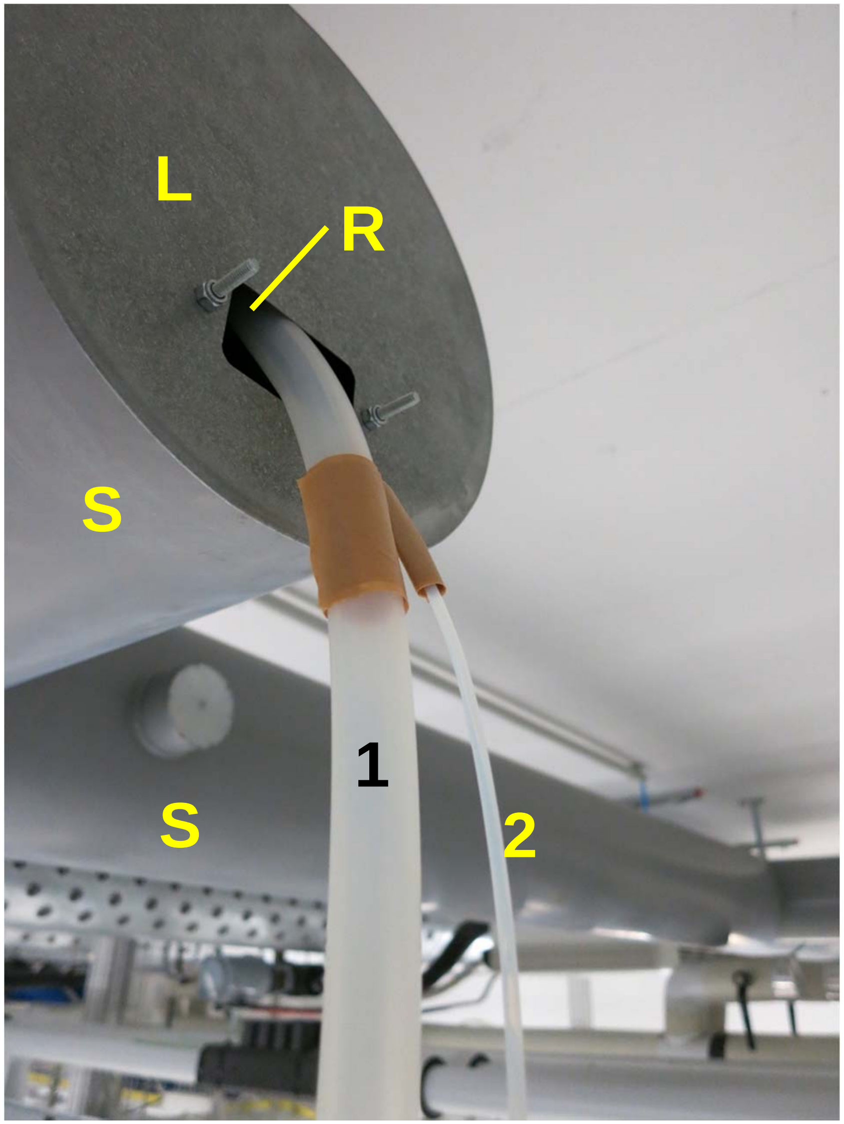
2 Gas inlet 2 for the purge gas for the sample chamber

3 Gas inlet for the protective gas for the balance chamber

4 Flexible metal tube (Swagelok 6 mm) towards switching valves which are shown on the previous slide

5 Gas outlet. Connected is a thin and long teflon tube (6) which minimizes the effect of external pressure fluctuations

TGA NETZSCH TG 209 F1 Libra – Suction for exhaust gas lines



S Suction line which is located close to the ceiling of the laboratory

L Lid of the suction line

R Recess in the lid. Manufactured by M. Elsener from the metal workshop of the Department of Materials of the ETH Zurich

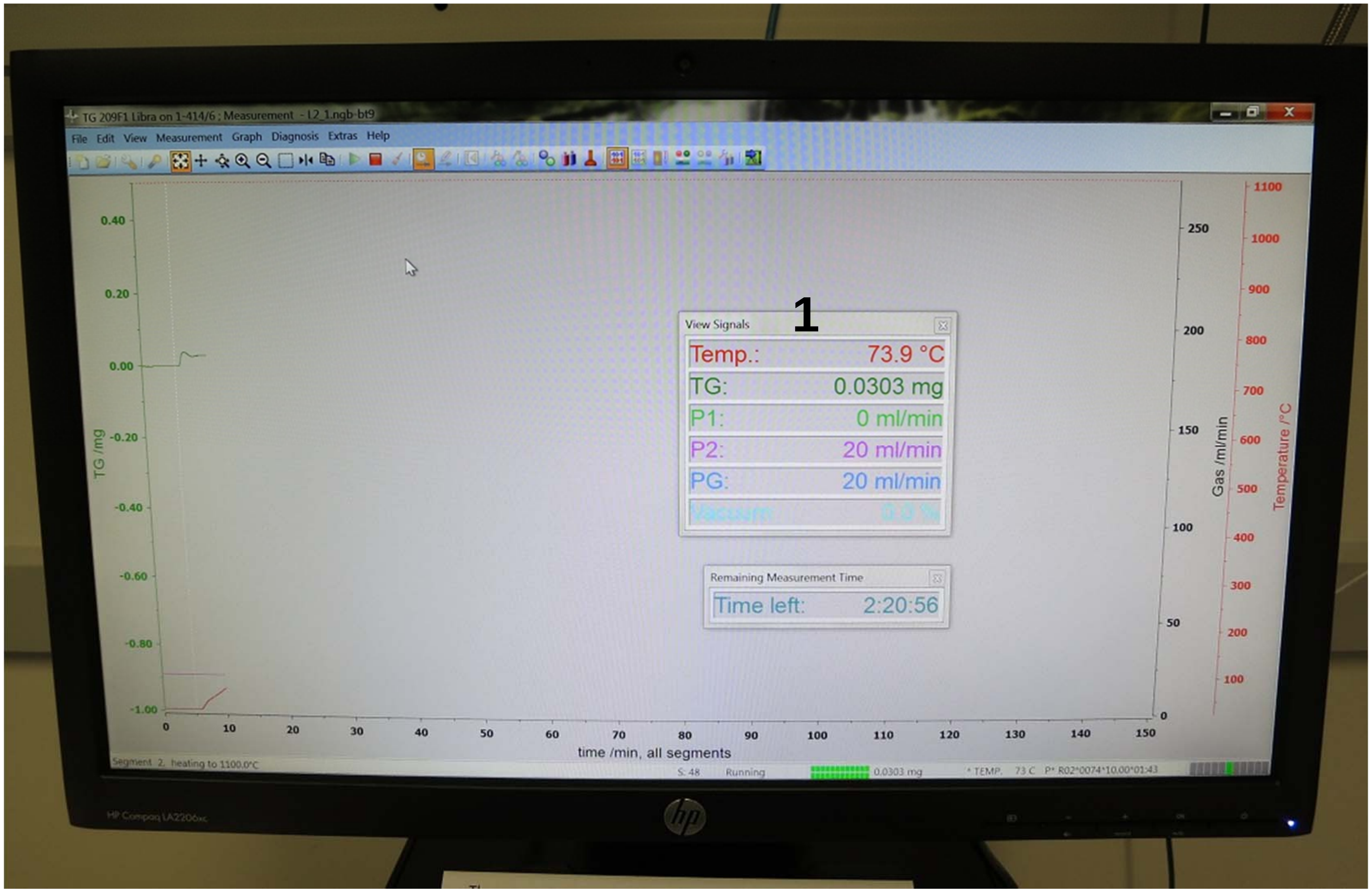
1 Tube which is connected with the gas outlet of the vacuum pump

2 Thin and long teflon tube which is connected with the gas outlet of the thermogravimetric analyzer. It minimizes the effect of external pressure fluctuations

Laboratory is equipped with a permanently running supply air and suction

TGA NETZSCH TG 209 F1 Libra – A snapshot from the monitor

A screenshot from a running thermogravimetric measurement



The display box (1) shows the current numerical values of some relevant quantities like the temperature of the crucible and sample, the TG value, i.e. the mass or weight in mg (after taring), and the gas flow rate of the purge gas and protective gas

Part 12 - 3

Examples of thermogravimetric measurements and results

The baseline or buoyancy correction 1 / 5

On the crucible and the crucible carrier acts a buoyancy force which depends on the

- design of the crucible and crucible carrier (shape, dimensions, material, density, mass)
- gas type and gas flow rate
- temperature program T(t)

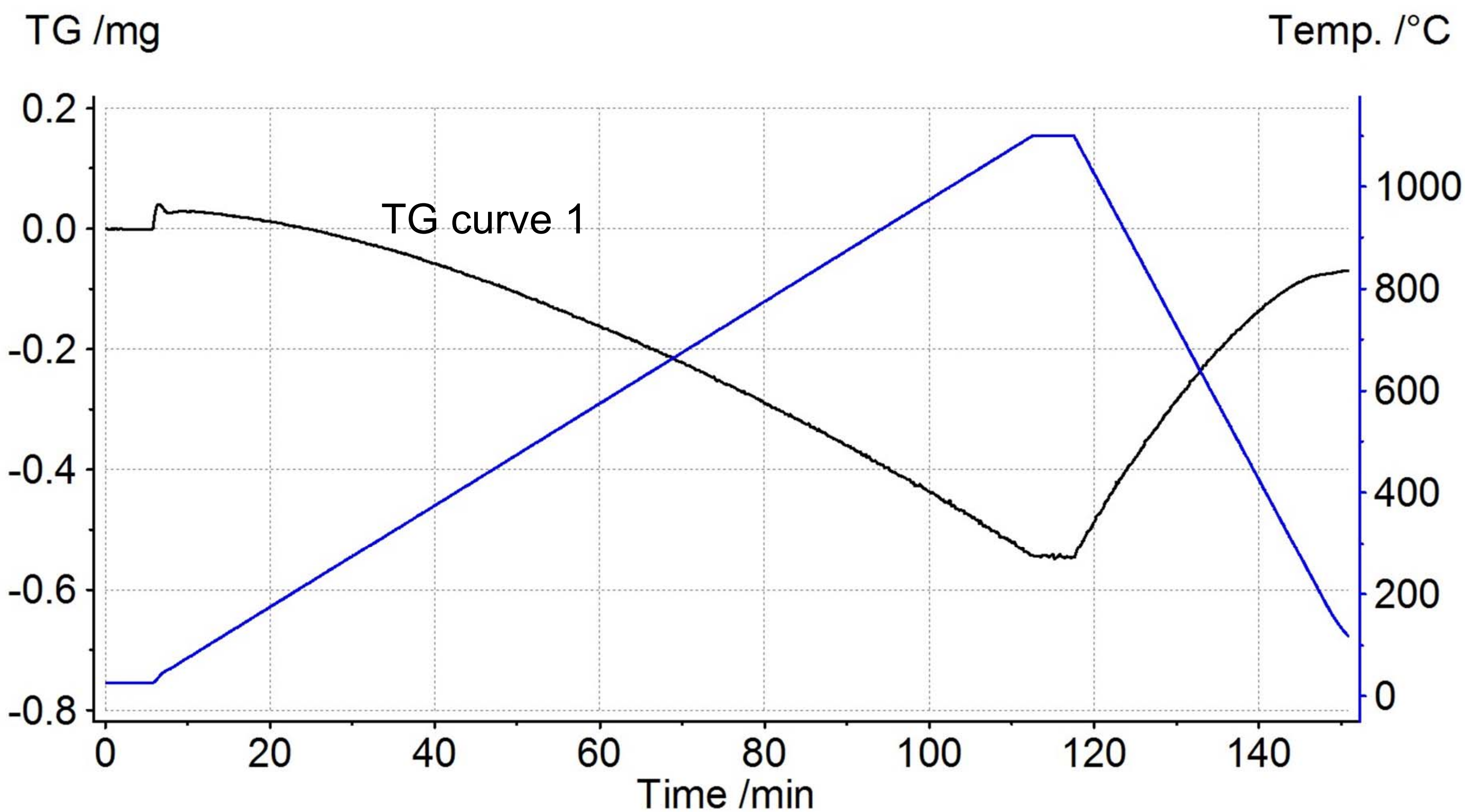
The buoyancy force acts onto the microbalance and is observable in terms of a corresponding weight or mass. That has to be taken into account when a crucible plus sample is measured. Therefore for a specific gas type, gas flow rate, temperature program T(t), and crucible type a measurement with the empty crucible will be performed. The resulting weight or mass versus T(t) curve represents the corresponding buoyancy curve or baseline. The buoyancy or empty crucible curve will be subtracted from the corresponding crucible plus sample curve.

The following example illustrates this procedure …

The baseline or buoyancy correction 2 / 5

- Alumina crucible with diameter 8 mm, height 8mm, mass 320 mg
- Gas flow (20 + 20) ml / min synthetic air
- T(t): 25 - 1100 °C with heating rate 10 °C / min, dwell time 5 min, cooling rate 30 °C / min

Empty crucible / Buoyancy effect of crucible and crucible carrier / Baseline

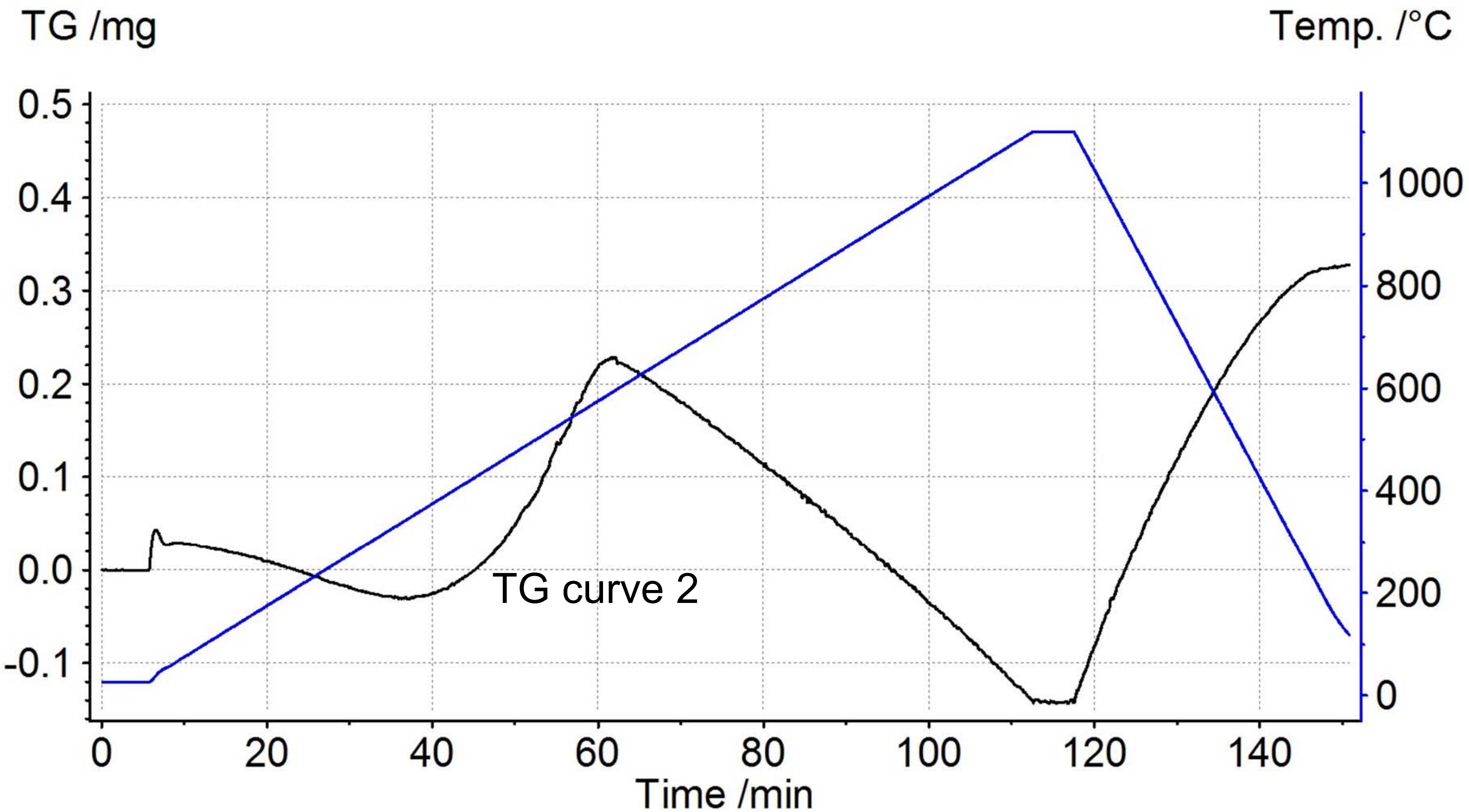


TG = Weight or mass measured by the microbalance (after taring)

The baseline or buoyancy correction 3 / 5

- Alumina crucible with diameter 8 mm, height 8mm, mass 320 mg
- Gas flow (20 + 20) ml / min synthetic air
- T(t): 25 - 1100 °C with heating rate 10 °C / min, dwell time 5 min, cooling rate 30 °C / min

Crucible plus sample (85 mg $Sr_{0.95}NbO_{3.38}$ powder) without buoyancy correction



TG = Weight or mass measured by the microbalance (after taring)

The baseline or buoyancy correction 4 / 5

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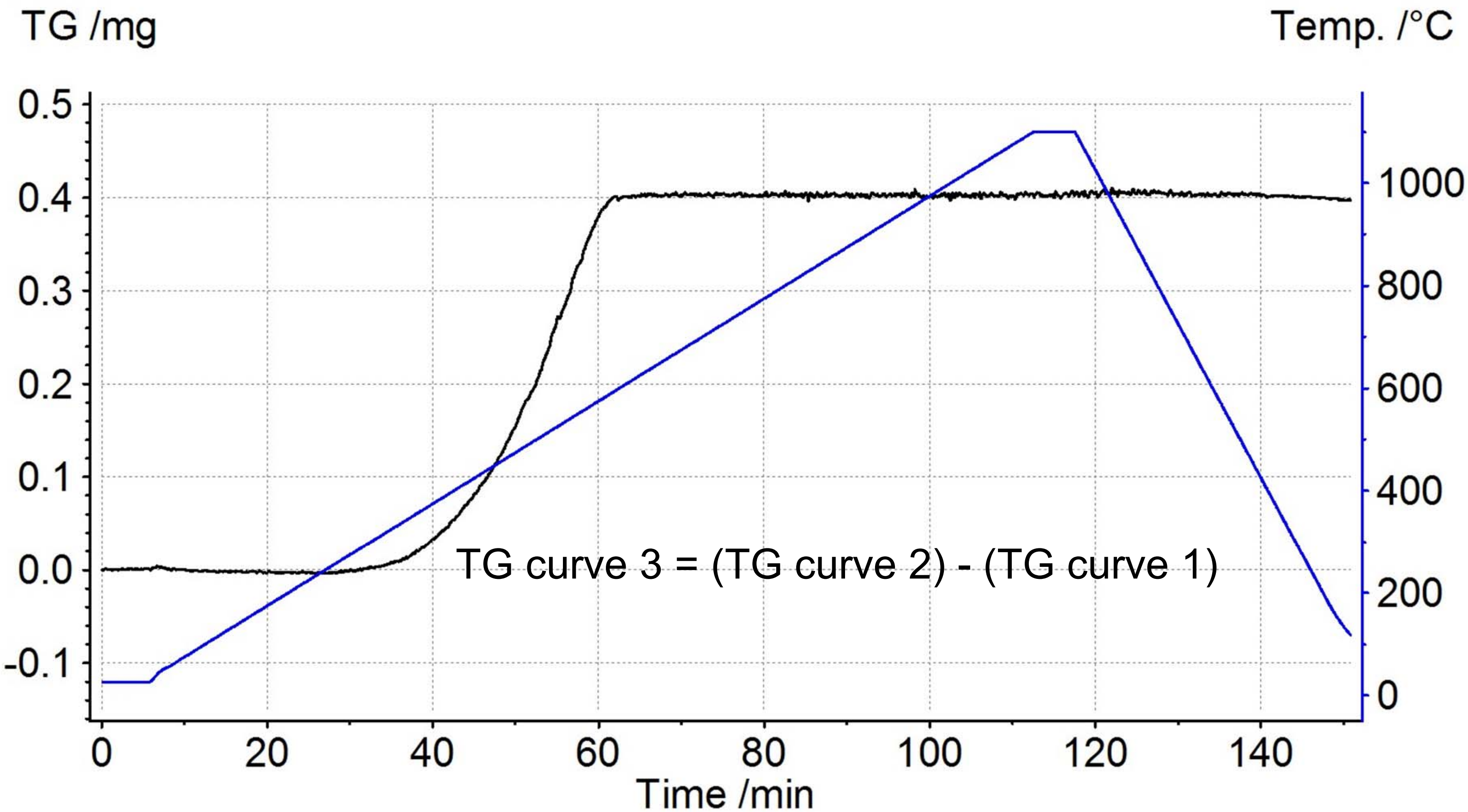


TG = Weight or mass measured by the microbalance (after taring)

The baseline or buoyancy correction 5 / 5

- The TG curves which are shown in the following examples comprise always the buoyancy correction

- The buoyancy effect of the crucible and crucible carrier can be neglected when the sample shows a relatively large weight or mass change

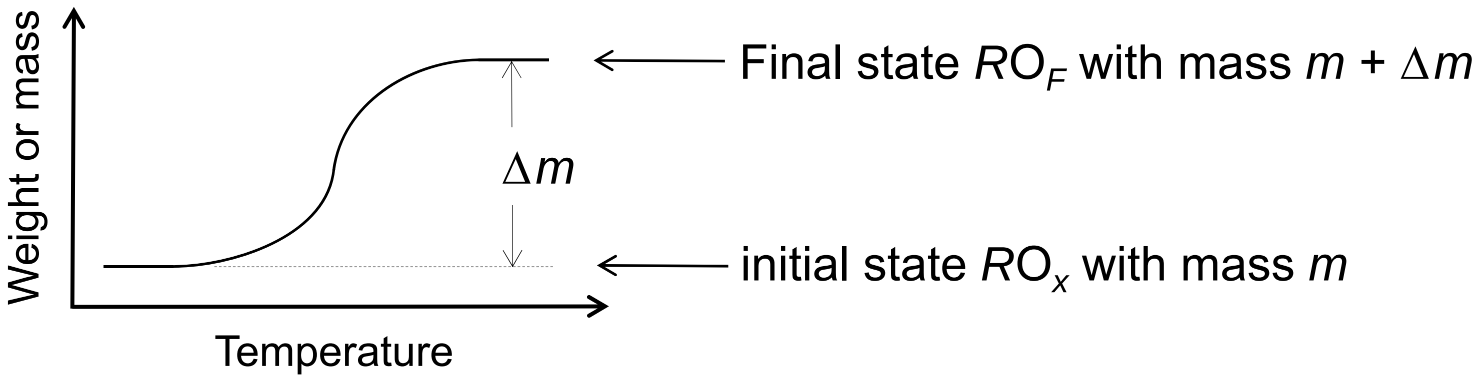
- After a thermogravimetric run it is in the most cases possible to remove the sample from the crucible. Then the crucible can be cleaned. After a bake-out at elevated temperatures the crucible is completely clean and ready for the next run. If the next run is performed under the same conditions, then the same buoyancy correction can be used

Determination of the oxygen content of oxides 1 / 2

The oxygen content x of an oxide RO_x can be determined by thermogravimetric analysis if it can be oxidized or reduced without evaporation to a well-known and well-defined final composition RO_F according to

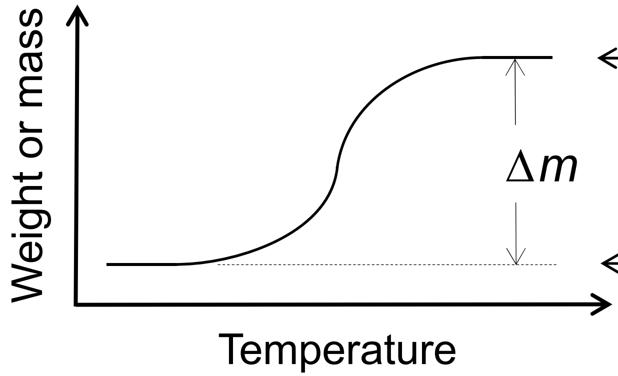
$$RO_x + \frac{1}{2}(F - x)\,O_2 \rightarrow RO_F \qquad \text{Eq. (1)} \qquad F > x \text{ (oxidation) or } F < x \text{ (reduction)}$$

The following figure sketches the case of $F > x$ (oxidation):



For example, so-called reduced titanates and niobates, such as $LaTiO_x$ and $SrNbO_x$ with $x < 3.5$, oxidize at elevated temperatures under an oxidizing atmosphere to a well-defined fully oxidized composition, such as $LaTiO_{3.5}$ and $SrNbO_{3.5}$, where all Ti and Nb ions are in their highest valence state Ti^{4+} and Nb^{5+}, respectively. The oxygen valence is usually O^{2-} and the chemical formulas of oxides correspond to the charge neutrality, i.e. the sum of all positive and negative electrical charges (valences) per formula is zero

Determination of the oxygen content of oxides 2 / 2



From $RO_x + \frac{1}{2}(F - x)\,O_2 \rightarrow RO_F$, the above sketch, and the rule of three it follows

$$\frac{\Delta m}{m + \Delta m} = \frac{(F - x)\,M(O)}{M(RO_F)} \quad \Rightarrow \quad x = F - \frac{\Delta m\, M(RO_F)}{(m + \Delta m)\, M(O)} \qquad \text{Eq. (2)}$$

M(O) = Molar mass of oxygen = 15.999 g / mole

$M(RO_F)$ = Molar mass of RO_F

m = Weight or mass of RO_x

Δm = Mass difference between the initial state RO_x and final state RO_F

After the thermogravimetric measurement of Δm the oxygen content x of RO_x can be calculated by Eq. (2). The following pages present some examples …

Mn_2O_3 1 / 4

Mn_2O_3 powder is commercially available and can be used as starting material for the synthesis of complex oxides such as $YMnO_3$.
It is one of several known manganese oxides like
MnO (Mn^{2+}) , Mn_3O_4 ($Mn^{2.67+}$) , Mn_2O_3 (Mn^{3+}) , and MnO_2 (Mn^{4+})

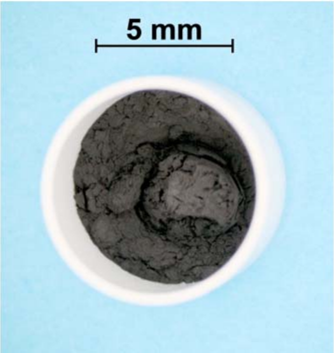
Thermogravimetric analysis can be used to check the chemical composition of Mn_2O_3

It is known that $Mn_2O_3 = MnO_{3/2} = MnO_{1.5}$ converts at elevated temperatures into $Mn_3O_4 = MnO_{4/3} = MnO_{1.33}$ according to

$$MnO_{3/2} \rightarrow MnO_{4/3} + \frac{1}{12} O_2 \uparrow$$

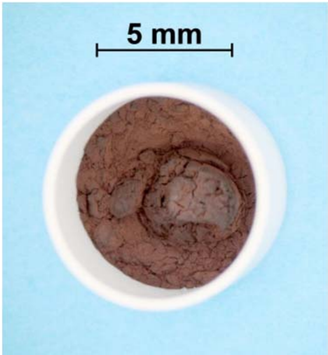
We consider the Mn_2O_3 powder as MnO_x and try to determine its oxygen content x thermogravimetrically in terms of Eqs. (1) and (2) with $F = 4/3$. The following pages shows the results of a thermogravimetric run …

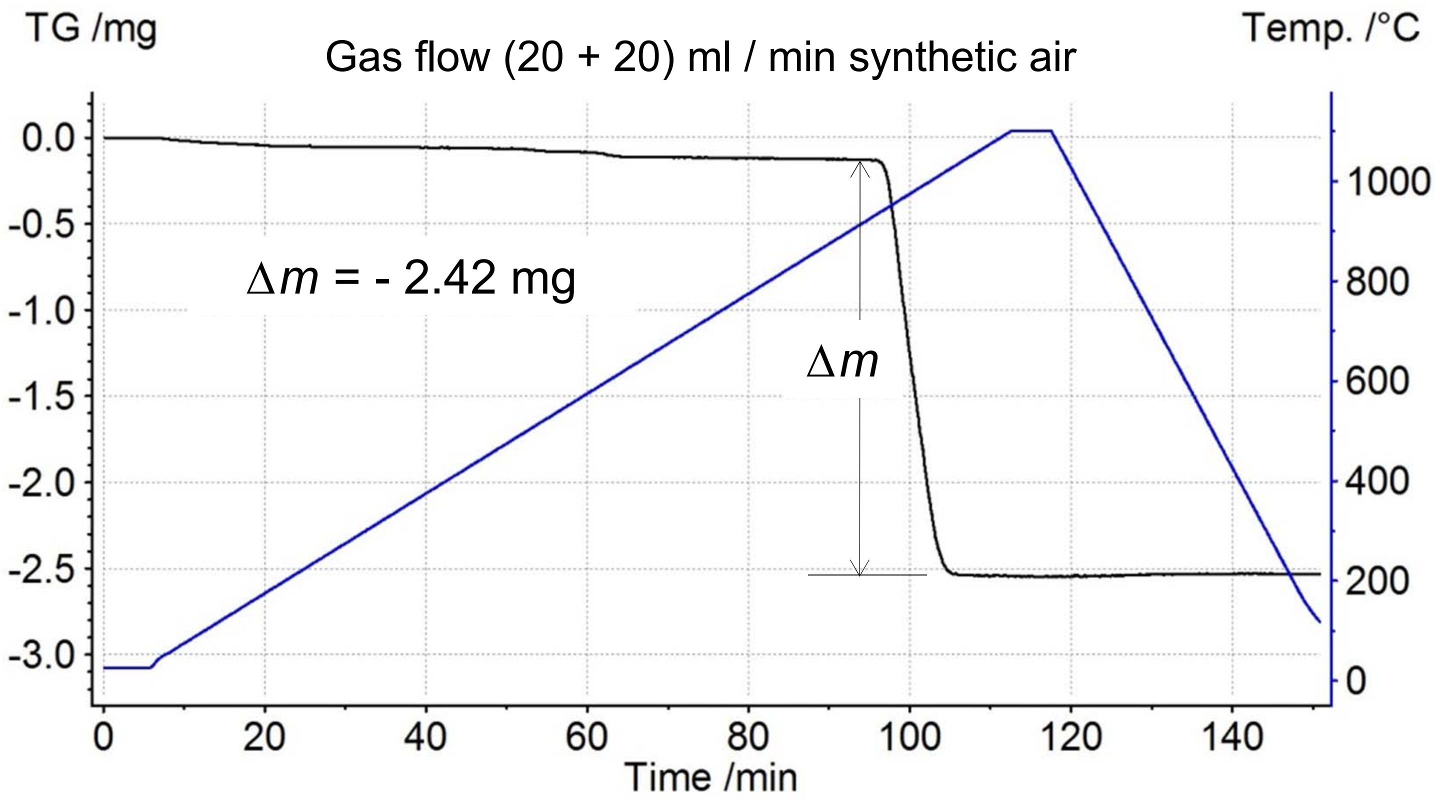
Mn_2O_3 2 / 4



71.30 mg Mn_2O_3 powder from MaTeck (Lot No. 250708) in an alumina crucible before starting the run

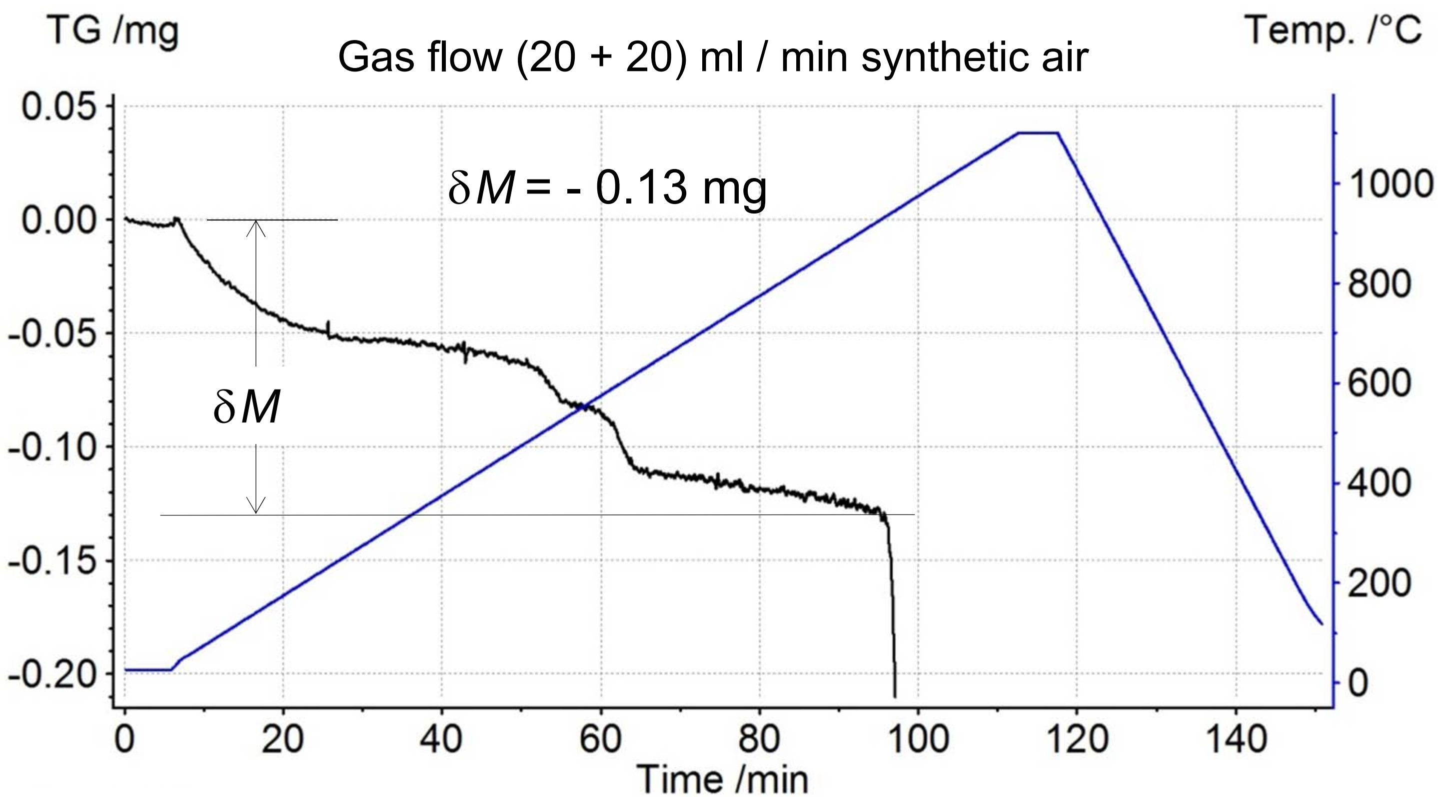
Powder in the crucible after the run. The color is indicative of Mn_3O_4





TG = Weight or mass measured by the microbalance (after taring)

View of the TG curve on an enhanced TG scale



TG = Weight or mass measured by the microbalance (after taring)

We assume that the relatively small weight or mass change δM is due to a release of moisture

Evaluation in terms of Eqs. (1) and (2)

m = (weighed-in quantity of MnO_x powder) – (weight of moisture)
m = (71.30 – 0.13) mg = 71.17 mg

Δm = - 2.42 mg

$F = 4/3$

$M(RO_F) = M(MnO_{4/3})$ = 76.271 g / mole

M(O) = 15.999 g / mole

From Eq. (2) we obtain

x = 1.501 and thus $MnO_x = MnO_{1.50} = Mn_2O_{3.00}$

This indicates that the Mn_2O_3 powder is really Mn_2O_3

Pieces of as-grown crystalline $Sr_{0.95}NbO_x$

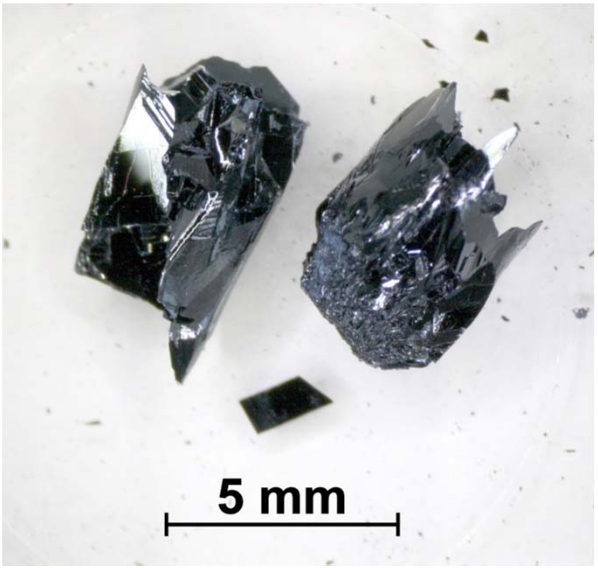
Sample No. 713C

The melt-grown crystalline sample was prepared by the Cyberstar mirror furnace by reducing the fully oxidized composition $Sr_{0.95}NbO_{3.45}$ under 97.2 % Ar plus 2.8 % H_2 . Powder x-ray diffraction indicates a single phase material with a perovskite-related layered structure of the type $n = 5$ of $A_nB_nO_{3n+2} = ABO_x$ (A = Sr and B = Nb). The ideal $n = 5$ type composition is $SrNbO_{3.40}$ and $Sr_{0.95}NbO_x$ represents a non-stoichiometric $n = 5$ type material. For $x = 3.45$ all Nb ions are in their highest valence state 5+ . We want to determine the oxygen content x of $Sr_{0.95}NbO_x$ thermogravimetrically in terms of Eqs. (1) and (2) with $F = 3.45$ …

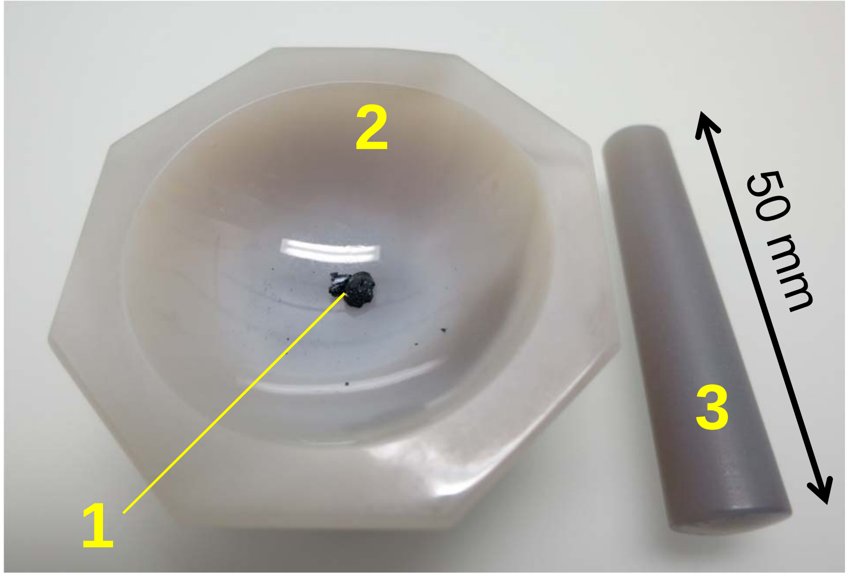
Note: Oxides of the type $A_nB_nO_{3n+2} = ABO_x$ display interesting physical and structural properties. Among them are e.g. quasi-1D metals and the highest-T_c ferroelectrics. Furthermore, they might have a potential to create new superconductors and novel materials which are simultaneously ferroelectric and ferromagnetic. References: www.theory.mat.ethz.ch/lab/presentation2.pdf (11 MB pdf) and Progress in Solid State Chemistry 29 (2001) 1 and 36 (2008) 253

Preparation of powder for the thermogravimetric measurement

It is advisable to grind a part of the as-grown crystalline sample into powder because an increased surface area facilitates the (thermogravimetric) oxidation from $Sr_{0.95}NbO_x$ to $Sr_{0.95}NbO_{3.45}$

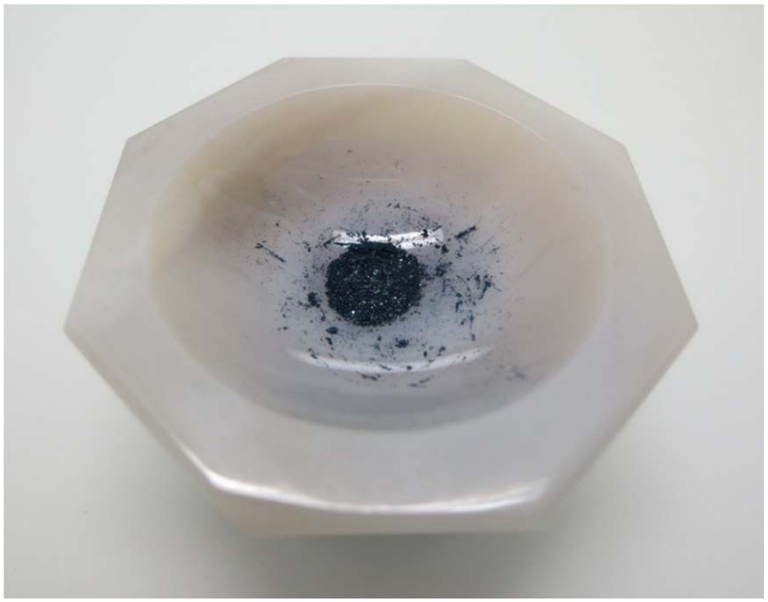


Pieces of as-grown crystalline $Sr_{0.95}NbO_x$. Run / Sample No. 713C



A small crystalline piece (1) with a mass of about 89 mg was removed from the as-grown sample and put into a small agate mortar (2). Also shown is the associated pestle made of agate (3)

Preparation of powder for the thermogravimetric measurement

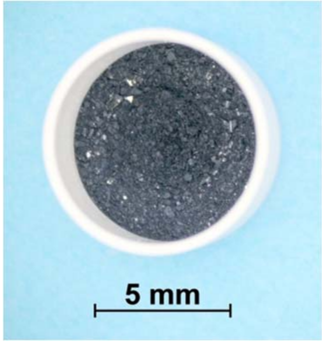


$Sr_{0.95}NbO_x$ powder obtained by grinding the small crystalline piece which is shown on the previous page

Note: During the grinding the mortar was covered by a plastic sheet. The plastic sheet did contain a hole through which the pestle was plugged. In this way the flying away of small parts was diminished

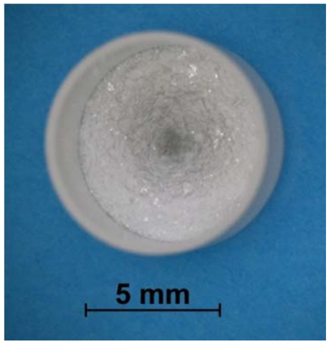
A closer view of the $Sr_{0.95}NbO_x$ powder

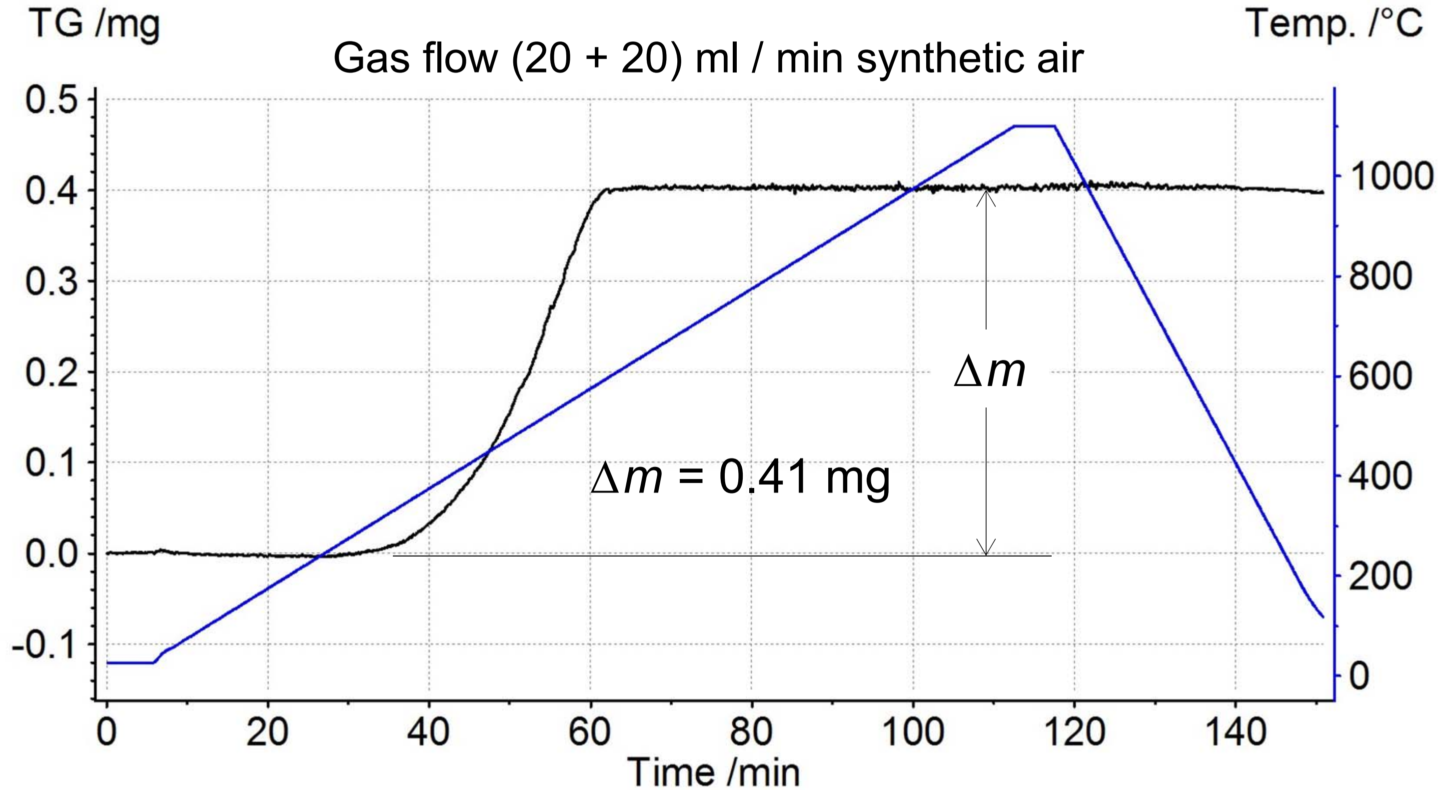
This powder was used for a thermogravimetric run whose results are shown on the next page …



84.84 mg $Sr_{0.95}NbO_x$ powder in an alumina crucible before starting the run

Powder in the crucible after the run. The white color indicates that all Nb ions are in their highest valence state Nb^{5+}





TG = Weight or mass measured by the microbalance (after taring)

Evaluation in terms of Eqs. (1) and (2)

m = weighed-in quantity of $Sr_{0.95}NbO_x$ powder = 84.84 mg

Δm = 0.41 mg

F = 3.45

$M(RO_F) = M(Sr_{0.95}NbO_{3.45})$ = 231.343 g / mole

M(O) = 15.999 g / mole

From Eq. (2) we obtain x = 3.38 and thus the sample composition is $Sr_{0.95}NbO_{3.38}$

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With that we can also calculate the (average) valence v of the Nb ions and the (average) number of 4d electrons per Nb. The (invariable) valence states Sr^{2+} and O^{2-} and the charge neutrality requirement lead to the equation
$0.95 \times (+2) + v + 3.38 \times (-2) = 0$ which results in v = 4.86, i.e.

for $Sr_{0.95}NbO_{3.38}$ the average Nb valence is $Nb^{4.86+}$

We consider the following known valence states / 4d electron configurations of Nb:

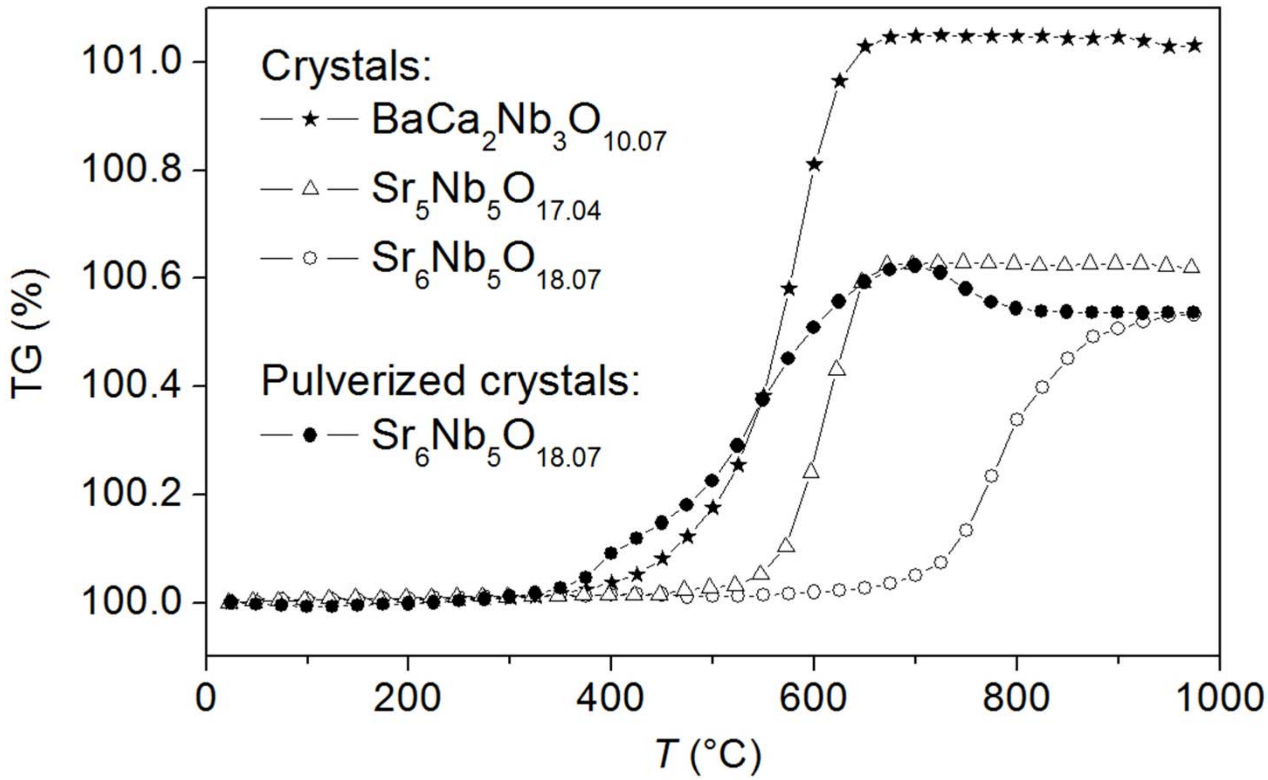
Nb^{5+} / $4d^0$ (fully oxidized state) and Nb^{4+} / $4d^1$ (a so-called reduced state)

From the rule of three we obtain $Nb^{4.86+}$ / $4d^{0.14}$, i.e. for $Sr_{0.95}NbO_{3.38}$
the average number of 4d electrons per Nb is 0.14

Another examples of thermogravimetric oxidation of niobates

TG = Weight or mass measured by the microbalance relative to the weight or mass of the sample at the beginning

Progress in Solid State Chemistry 36 (2008) 253 (Fig. 34)

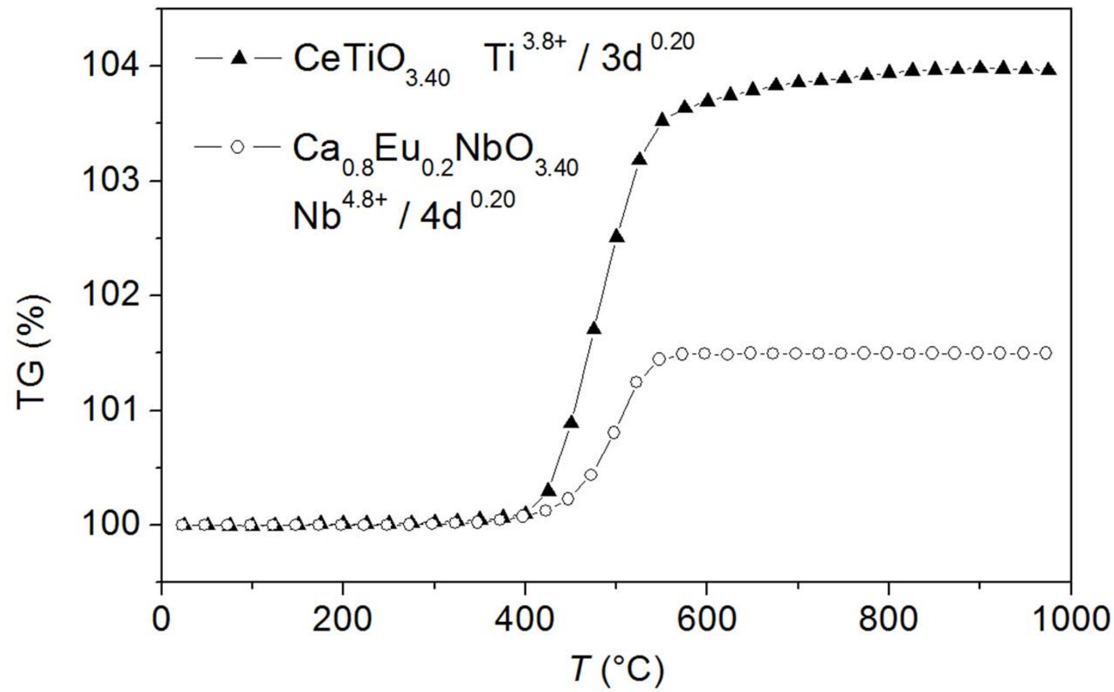


Thermogravimetric behavior of the oxidation of some so-called reduced niobates up to an oxygen content or chemical composition where all Nb ions are in their highest valence state 5+. The melt-grown crystalline samples were prepared and thermogravimetrically investigated at the University of Augsburg (Germany). The specimen were heated in static air from room temperature to 995 °C with a heating rate of 9 or 10 °C / min by a NETZSCH thermogravimetric analyzer TG 209. The specified oxygen content of the three different reduced niobates was determined by their TG curves in the same way as described for $Sr_{0.95}NbO_x$ on the previous pages. Pictures and physical properties of the three different crystalline materials are presented in appendix 1 in this presentation

Another examples of thermogravimetric oxidation of special oxides

TG = Weight or mass measured by the microbalance relative to the weight or mass of the sample at the beginning

Progress in Solid State Chemistry 36 (2008) 253 (Fig. 35)



Thermogravimetric oxidation of two so-called reduced $A_nB_nO_{3n+2}$ = ABO_x compounds of the type n = 5 with Ce^{3+} and Eu^{2+} at the A site, namely $CeTiO_{3.40}$ and $Ca_{0.8}Eu_{0.2}NbO_{3.40}$, respectively. The oxidation implies not only $Ti^{3.8+} \rightarrow Ti^{4+}$ and $Nb^{4.8+} \rightarrow Nb^{5+}$ but also $Ce^{3+} \rightarrow Ce^{4+}$ and $Eu^{2+} \rightarrow Eu^{3+}$, i.e. the fully oxidized composition is $CeTiO_4$ and $Ca_{0.8}Eu_{0.2}NbO_{3.60}$, respectively. The melt-grown crystalline samples were prepared and thermogravimetrically investigated at the University of Augsburg (Germany). The specimen were heated in static air from room temperature to 995 °C with a heating rate of 9 °C / min by a NETZSCH thermogravimetric analyzer TG 209. The specified oxygen content of the two compounds was determined by their TG curves in the same way as described for $Sr_{0.95}NbO_x$ on the previous pages

Pr_6O_{11} powder is commercially available and can be used as starting material for the synthesis of complex oxides such as $Pr_2Ti_2O_7$.
It is one of several known praseodymium oxides like

$Pr_2O_3 = PrO_{1.5}$ (Pr^{3+}) - color **light green** and sensitive to moisture

$Pr_6O_{11} = PrO_{1.83}$ ($Pr^{3.67+}$) - color **dark brown**

PrO_2 (Pr^{4+})

It is known that $Pr_6O_{11} = PrO_{11/6} = PrO_{1.83}$ converts at elevated temperatures into $Pr_2O_3 = PrO_{3/2} = PrO_{1.50}$ according to

$$PrO_{11/6} \rightarrow PrO_{3/2} + \frac{1}{6} O_2 \uparrow \qquad \text{Eq. (3)}$$

The theoretical weight or mass change associated with Eq. (3) can be calculated from Eq. (2) with x = 1.83 and F = 1.50, namely $(\Delta m/m)_{th}$ = - 3.13 %

We consider the Pr_6O_{11} powder as PrO_x and it was tried to determine its oxygen content x thermogravimetrically in terms of Eqs. (1) and (2) with F = 1.5.
The following page shows the results of some thermogravimetric runs …

Pr_6O_{11} 2 / 3

3 separate runs with **dark brown** Pr_6O_{11} powder (Alfa / Lot 61180082) in an alumina crucible

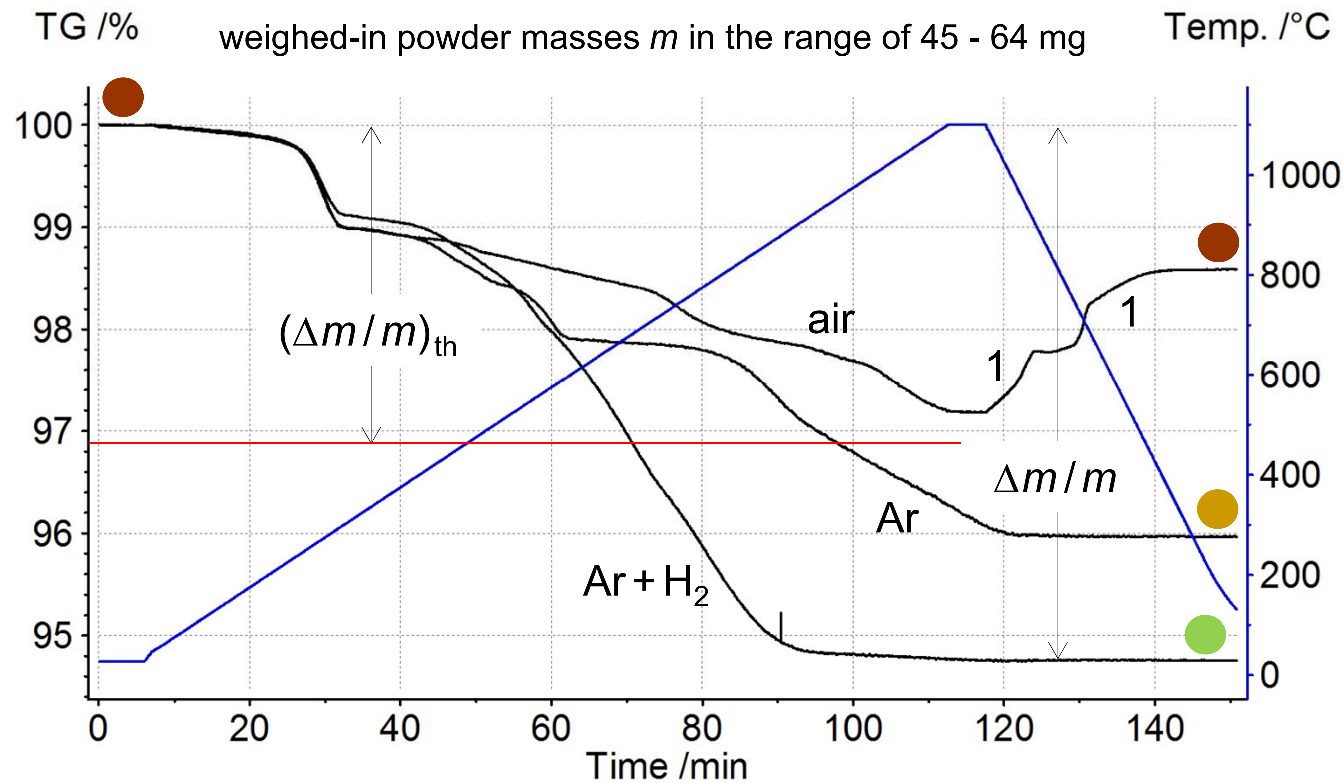
Run "air": Gas flow (20 + 20) ml / min synthetic air - Sample color **dark brown** after the run

Run "Ar": Gas flow (20 + 20) ml / min Ar - Sample color **light brown** after the run

Run "Ar + H_2": Gas flow 20 ml / min Ar + 20 ml / min (97.2 % Ar plus 2.8 % H_2)
Sample color **light green** after the run

TG = Weight or mass measured by the microbalance relative to the weight or mass of the sample at the beginning

1 = Sample takes up oxygen upon cooling



$(\Delta m / m)_{th}$ = - 3.13 % = relative weight or mass change of Pr_6O_{11} = $PrO_{1.83} \rightarrow PrO_{1.50}$

Evaluation and conclusion

The TG curves and the color of the powder after the run reveal that a complete reduction of $Pr_6O_{11} = PrO_{1.83}$ to $Pr_2O_3 = PrO_{1.50}$ was achieved only under $Ar + H_2$ when the highest attainable temperature is 1100 °C:

- Its corresponding relative weight or mass change $\Delta m / m$ = - 5.2 % is significantly larger than the theoretical or calculated value $(\Delta m / m)_{th}$ = - 3.1 % associated with the reduction $Pr_6O_{11} = PrO_{1.83} \rightarrow PrO_{1.50} = Pr_2O_3$
- If we consider the Pr_6O_{11} powder as PrO_x , then we obtain from Eqs. (1) and (2) with m = 63.70 mg , Δm = - 3.34 mg , F = 1.50, $M(RO_F) = M(PrO_{1.50})$ = 164.907 g / mole , and M(O) = 15.999 g / mole an oxygen content x = 2.07. However, this can be considered as wrong because for PrO_x the highest possible oxygen content is x = 2 which is also difficult to achieve

This indicates that the investigated Pr_6O_{11} powder deviates significantly from the composition Pr_6O_{11} . Further analysis techniques such as powder x-ray diffraction and / or a thermogravimetric analyzer equipped with a mass spectrometer are required to clarify its actual composition. Possible components are for example praseodymium oxide PrO_x , moisture, praseodymium hydroxide $Pr_2(OH)_3$ (Pr^{3+}), and praseodymium carbonate hydrate $Pr_2(CO_3)_3 \bullet xH_2O$ (Pr^{3+})

Part 13 – Measuring magnetic properties of samples by a SQUID magnetometer

13 - 1 Sketch of principle

13 - 2 SQUID magnetometer Quantum Design MPMS3 at the Department of Materials of the ETH Zurich

13 - 3 Mounting a sample within a straw

13 - 4 Another SQUID magnetometers

Part 13 – Measuring magnetic properties of samples by a SQUID magnetometer

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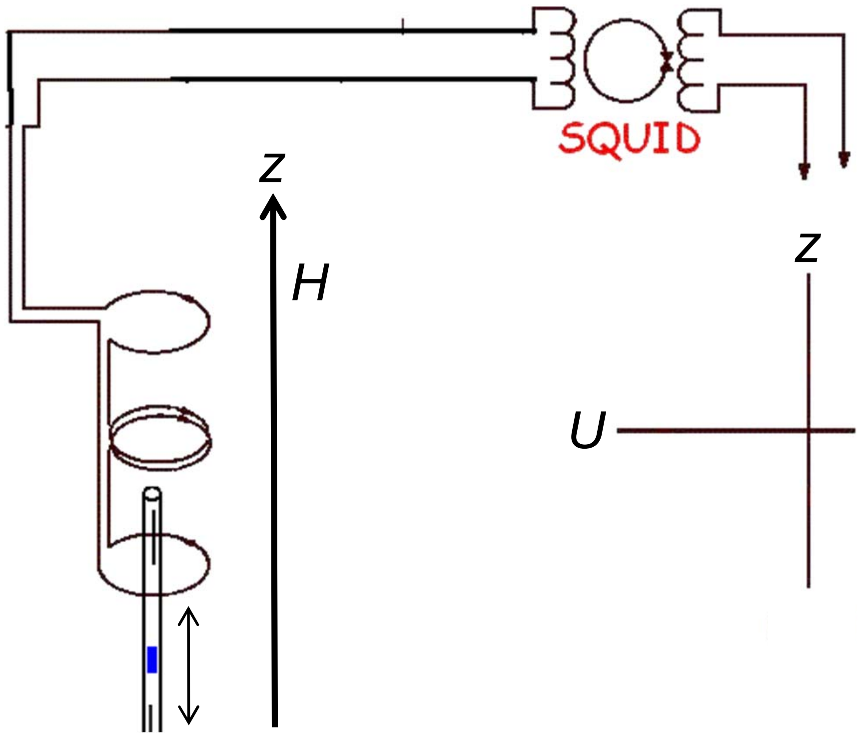
Measuring magnetic properties of a sample by a SQUID magnetometer

SQUID = Superconducting QUantum Interference Device

The magnetic moment *M* of a sample in a magnetic field *H* s measured by moving the sample along the *z*-direction through pick-up coils (gradiometer). From the induced voltage *U*(*z*(*t*)) the magnetic moment *M* of the sample can be determined. Sketch of principle:



Origin of image or animation (the animation runs in the ppsx version of this presentation, see page 2, or in the following link):

http://1.bp.blogspot.com/-PtAkq4t_Acw/Tg-fWC-rMmI/AAAAAAAAAPs/QBYosxxU_S4/s1600/extract_anim2.gif

An external magetic field *H* along the *z*-direction (within the magnetometer) prompts the sample to generate a magnetic moment *M*. The magnetometer measures the magnetic moment *M* of the sample as function of temperature *T* or external magnetic field *H*. The results of such measurements reveal if the sample is paramagnetic, (anti)ferromagnetic, dia-magnetic, or superconducting

Molar magnetic susceptibility χ of a single phase sample with mass *m* and molar mass m_A:

$\chi = M\, m_A / (H\, m)$

Part 13 – Measuring magnetic properties of samples by a SQUID magnetometer

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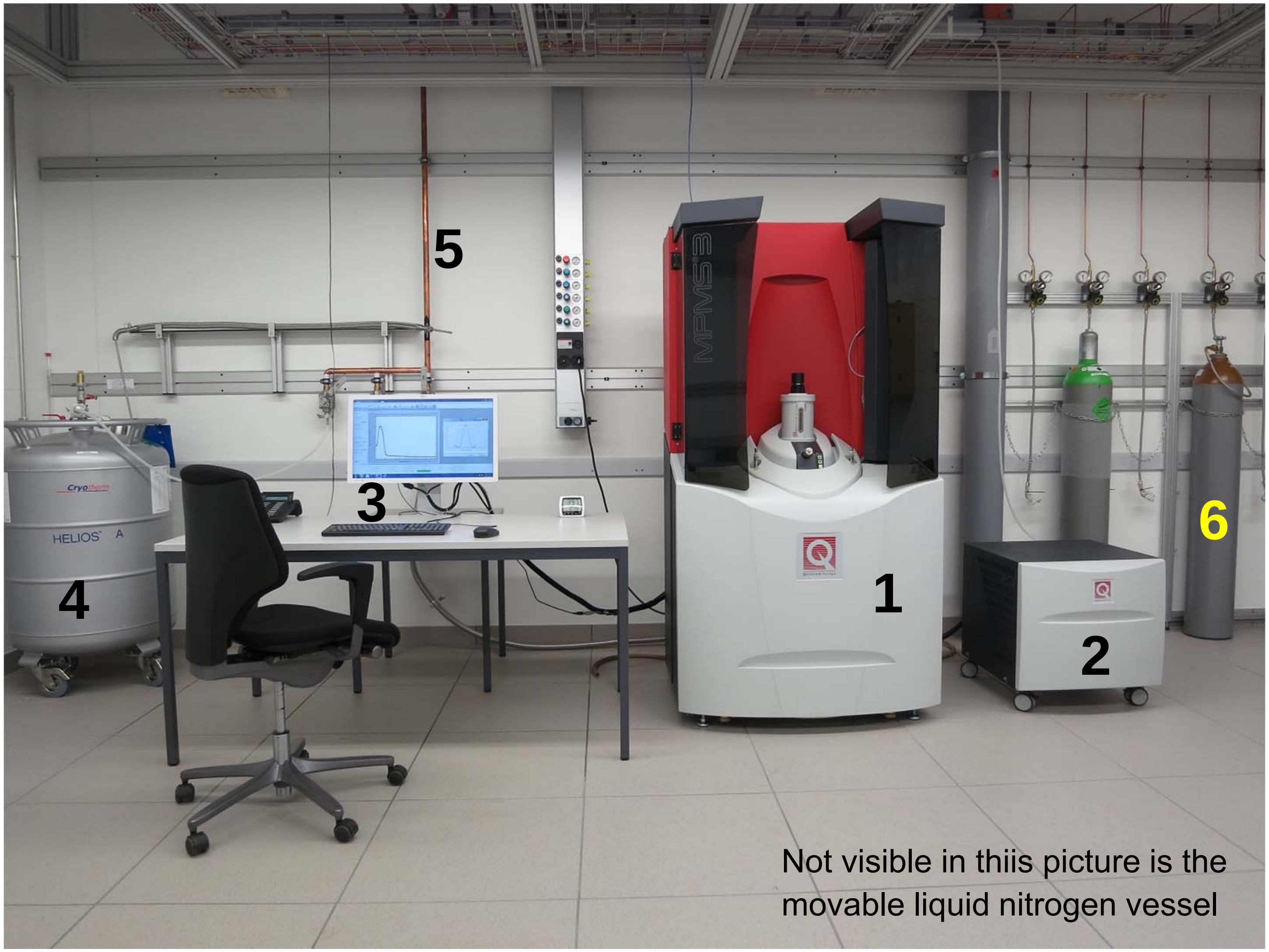
SQUID magnetometer Quantum Design MPMS3 at the ETH Zurich



The MPMS3 is commonly operated by three independent chairs of the Department of Materials of the ETH Zurich

1 SQUID magnetometer MPMS3

2 Associated and continuously running pump for gaseous helium

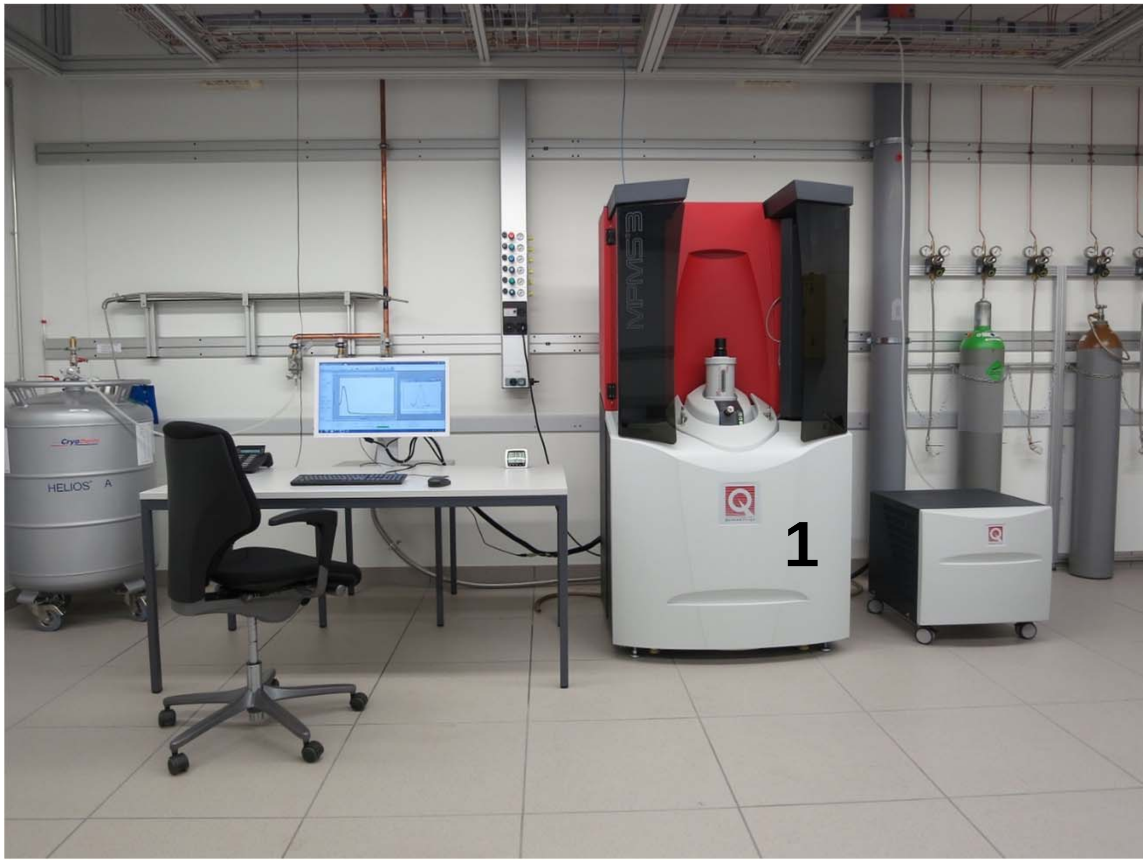
3 Monitor and keyboard of the computer-controlled MPMS3

4 Movable liquid helium vessel. It is used to fill once a week the MPMS3 with liquid helium

5 Recovery line for gaseous helium

6 Helium gas bottle

SQUID magnetometer Quantum Design MPMS3 at the ETH Zurich



The MPMS3 is commonly operated by three independent chairs of the Department of Materials of the ETH Zurich

The SQUID magnetometer MPMS3 (1) comprises among others a dewar which is filled with liquid helium, another dewar which is filled with liquid nitrogen, and a sample chamber. The bottom part of the sample chamber is surrounded by

- a system that stabilizes or changes the temperature in the sample chamber at the location of the sample
- a superconducting magnet that creates a magnetic field *H* at the location of the sample
- superconducting pick-up coils (gradiometer) for the detection of the magnetic moment *M* of the sample
- a coil for the generation of an alternating magnetic field (AC option)

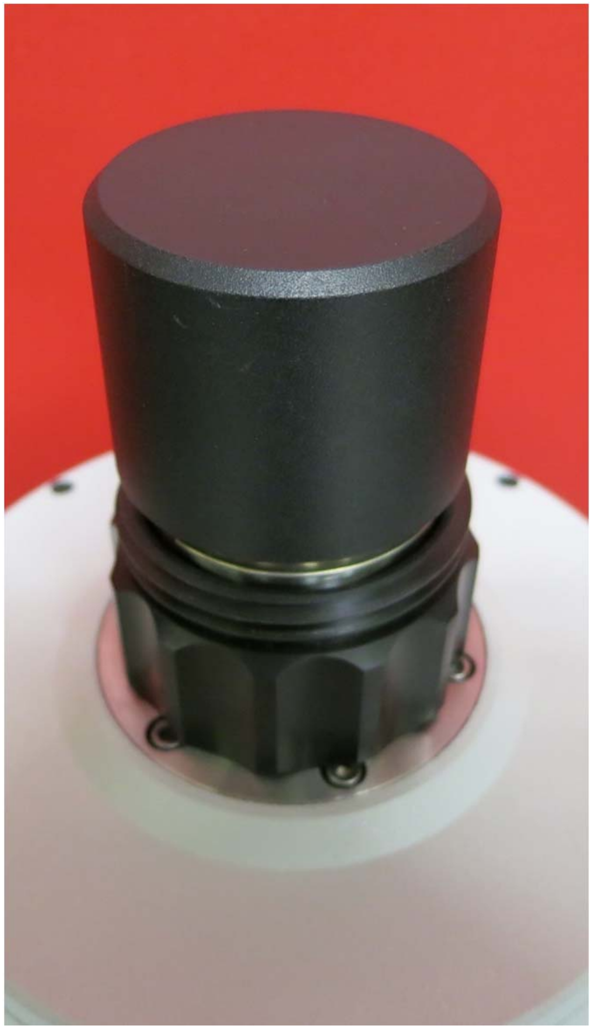
A closer view of the MPMS3

8 Port for filling the MPMS3 with liquid nitrogen

9 Port for filling the MPMS3 with liquid helium

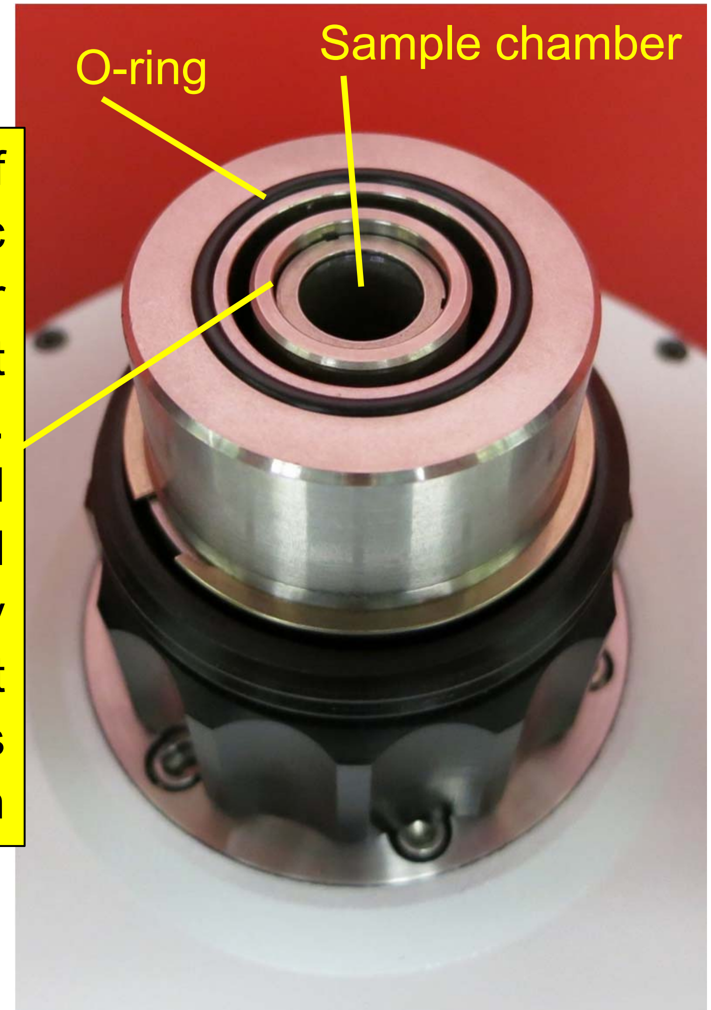
L Lid or sealing of the sample chamber

D Electromagnetic direct drive for the movement of the sample which is fixed on or in a sample holder that is attached at a sample rod



Sample chamber sealed, gas-tight and vacuum-tight

Upper end of electromagnetic direct drive for the movement of the sample. An inserted sample rod will be fixed by permanent magnets at this position



Sample chamber open. Diameter and depth of sample chamber 9 mm and about 1 m, respectively

Some technical features and available options 1 / 2

- Range of measurable magnetic moments *M* from about 10^{-7} emu to 10 emu
- Range of magnetic field *H* from - 70 kOe to + 70 kOe
- Field changing rate from 4 Oe / sec to 700 Oe / sec
- Liquid helium and nitrogen capacity 70 and 60 liter, respectively

Magnetic field units

1 Oe (Oersted) = 1 G (Gauss)

1 T (Tesla) = 10^{4} Oe = 10^{4} G

For comparison: The earth`s magnetic field is about 0.5 G

Some technical features and available options   2 / 2

Temperature range	**Atmosphere in the sample chamber**	**Usable sample holders & Remarks**
Normal mode 2 – 400 K	Gaseous helium with a low pressure in the range of about 2 – 12 Torr	Straw, quartz glass, or brass Fixation of the sample on the quartz glass or brass holder by special glue Straw not suitable for VSM type measurements
Oven option 310 – 1000 K	Vacuum	Special heated sample holder Fixation of the sample by special glue

Measurement mode	**Sample movement through the pick-up coils (gradiometer)**	**Remarks**
DC scan	Linear, e.g. 30 mm (scan length) in 4 sec	
VSM	Oscillation with a frequency of 14 Hz	Higher sensitivity than DC and therefore especially suitable for thin films
AC	Sample does not move continuously but consecutive data acquisition at three different positions within the gradiometer	The sample is excited by an oscillating magnetic field. Frequency 0.1 – 1 kHz Maximum amplitude 10 Oe

Mounting a sample for DC scan measurements 1 / 3

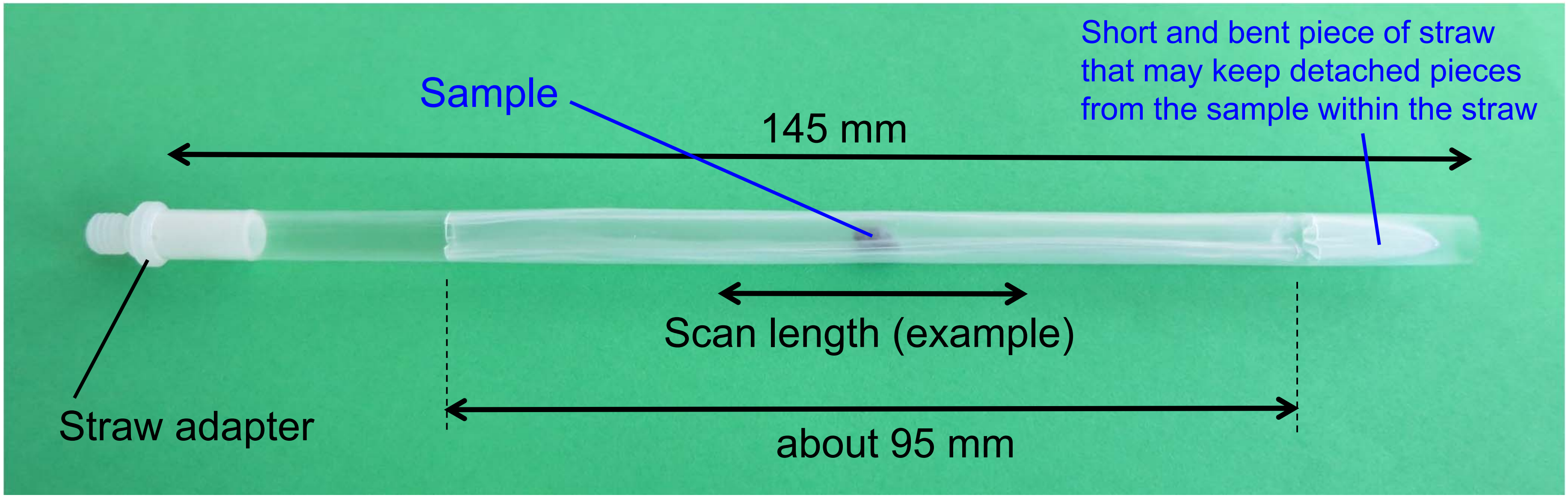
Example: Mechanical fixation of a sample within a straw by pieces of another straw

This tool makes it easy to place the sample at the right position

The 145 mm long straw was cut from a 20 cm long straw. The 95 mm long pieces which are located within the 145 mm long straw were cut from another 20 cm long straw. This arrangement does not produce a significant magnetic moment from the straw material because its mass is (nearly) homogeneously distributed over a length of about 95 mm which is smaller than the scan length during a measurement. The scan length is for example 30 mm. The straw material is suitable for temperatures from 400 K to 2 K but extensive exposure times above 330 K should be avoided. The fixation of a sample within a straw is described in more detail in part 13 - 3

Mounting a sample for DC scan measurements 2 / 3

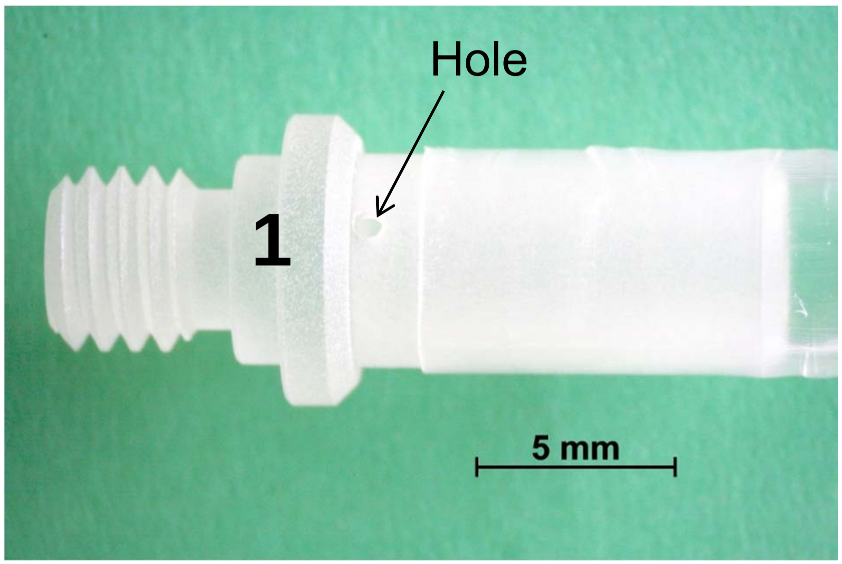
Example: Mechanical fixation of a sample within a straw by pieces of another straw



The 145 mm long straw was cut from a 20 cm long straw. The 95 mm long pieces which are located within the 145 mm long straw were cut from another 20 cm long straw. This arrangement does not produce a significant magnetic moment from the straw material because its mass is (nearly) homogeneously distributed over a length of about 95 mm which is smaller than the scan length during a measurement. The scan length is for example 30 mm. The straw material is suitable for temperatures from 400 K to 2 K but extensive exposure times above 330 K should be avoided. The fixation of a sample within a straw is described in more detail in part 13 - 3

Mounting a sample for DC scan measurements 3 / 3

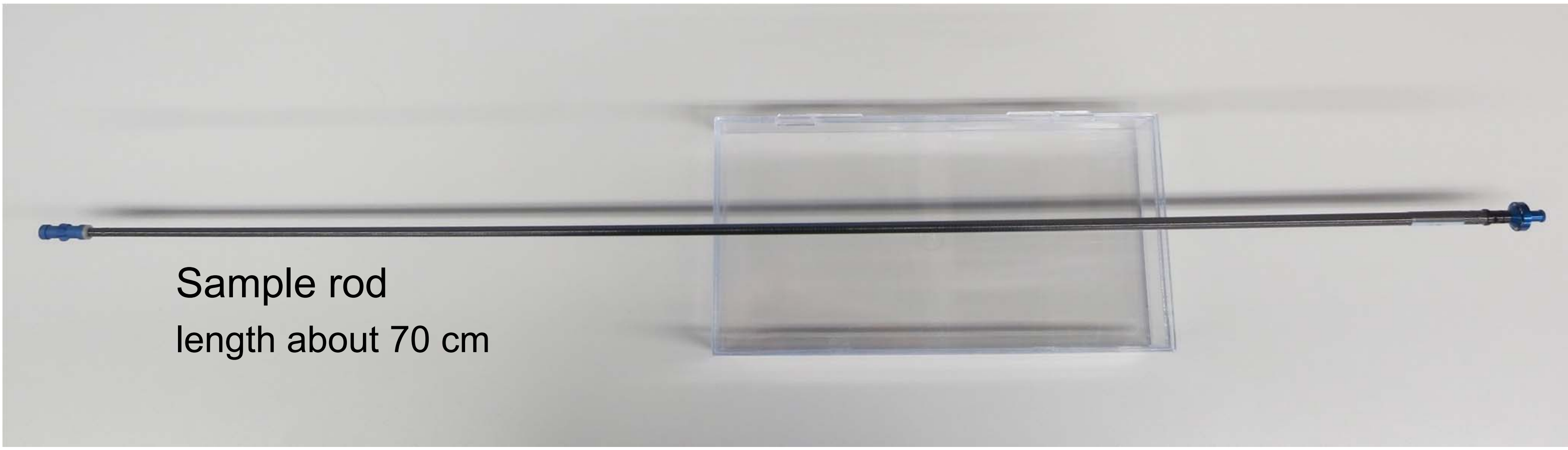
Example: Mechanical fixation of a sample within a straw by pieces of another straw



After inserting the mounted sample into the sample chamber the sample chamber will be several times evacuated and flushed with helium. For several reasons it is important that the inner space of the straw is not completely sealed so that it can be likewise evacuated and flushed with helium. Otherwise, for example, air may remain within the straw which can disturb the measurement of the magnetic moment of the sample below 90 (54) K because oxygen becomes then liquid (solid) and paramagnetic.

An access to the inner space of the straw can be ensured by the hole in the straw adapter (1). Therefore the straw adapter should not be completely pushed into the straw. Furthermore, the short and bent piece of straw (2) usually does not seal the right or bottom end of the straw completely. If the right or bottom end of the straw is completely sealed, e.g. by an appropriate lid, then the hole in the straw adapter (1) can ensure access to the inner space

Sample rod at which the straw or another sample holder will be attached



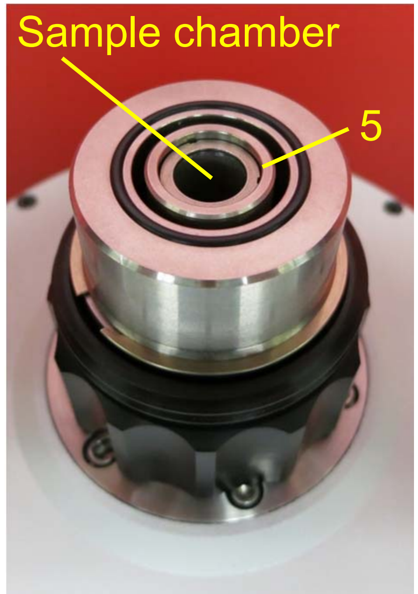
Left or bottom end of the sample rod

Right or upper end of the sample rod

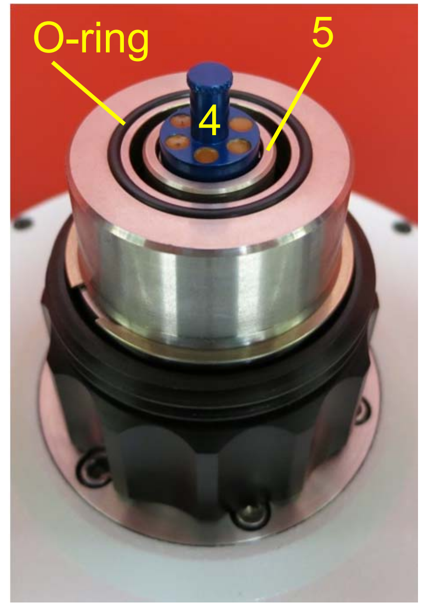
Inserting sample rod and sample into the sample chamber

Straw (1) with sample (2) attached at the sample rod (3)

Length of sample rod plus straw about 85 cm



Sample chamber open. Diameter and depth of sample chamber 9 mm and about 1 m, respectively



Sample rod and sample inserted into the sample chamber. Upper part of the sample rod (4) is fixed by permanent magnets at the upper part of the electro-magnetic direct drive (5)

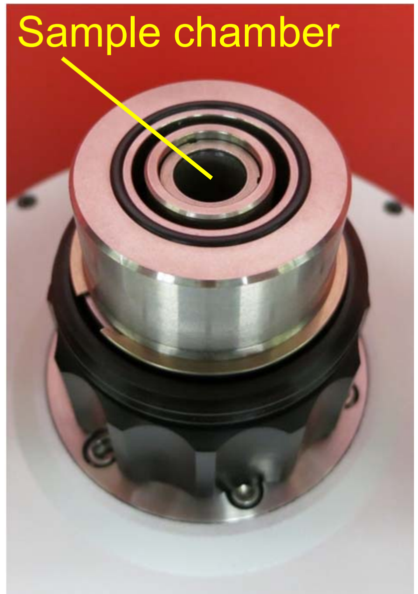
Note

When inserting the sample into the sample chamber the sample crosses a section where there is a magnetic field of 200 Oe. This field is due to the electromagnetic direct drive and cannot be switched off

The sample chamber may be opened only if the temperature in the sample chamber is 300 K and if the sample chamber is flooded with helium

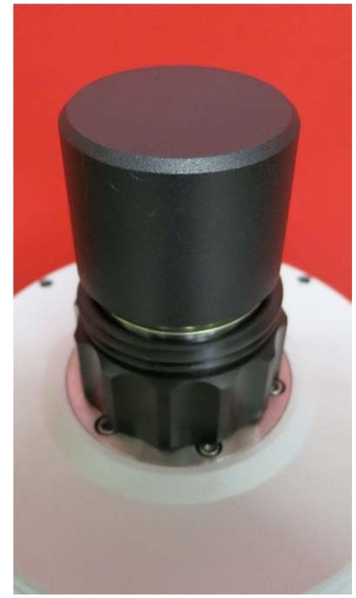
Straw (1) with sample (2) attached at the sample rod (3)

Inserting sample rod and sample into the sample chamber



Sample chamber open

Sample rod and sample inserted into the sample chamber

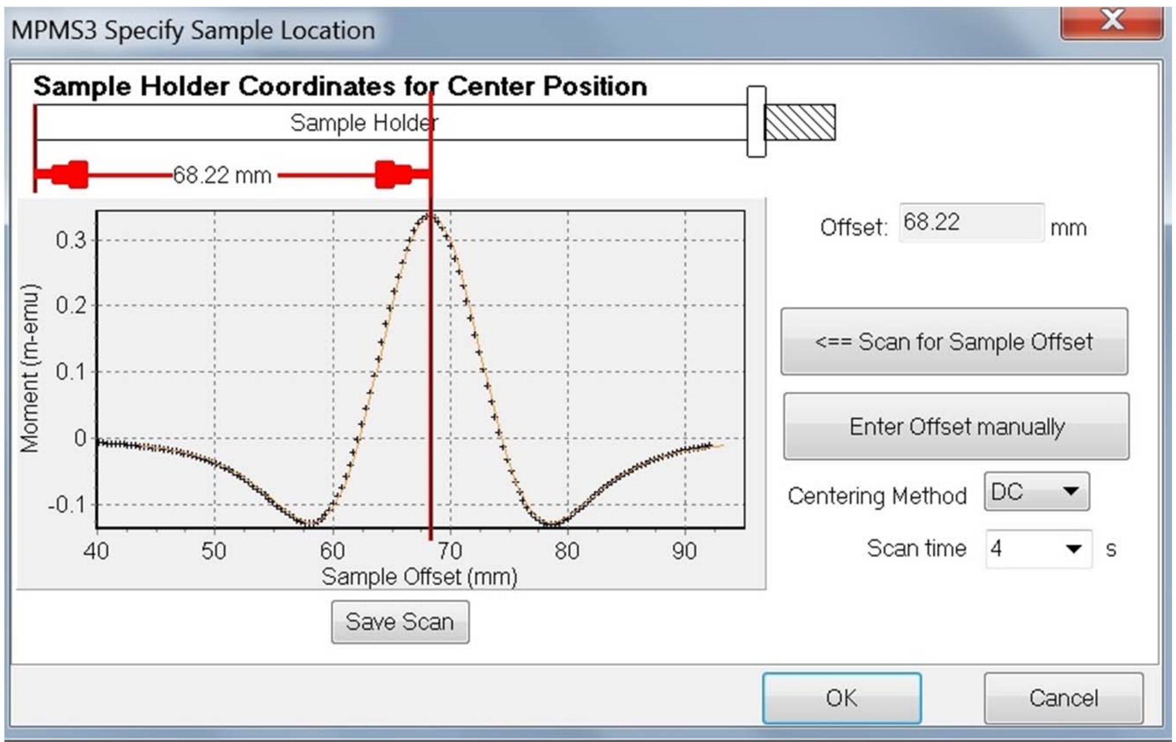


Sample chamber closed

After closing the sample chamber will be several times evacuated and flushed with helium and subsequently sealed. The atmosphere in the sample chamber is usually gaseous helium witt a low pressure of about 2 - 12 Torr

Locating the sample

Before starting a measurement such as *M*(*T*) or *M*(*H*) by DC scans the sample must be located. That can be done by an automatic procedure which is called Scan for Sample Offset. It results in a curve which is called Moment versus Sample Offset from which also the magnetic moment *M* of the sample can be determined. This type of curve is obtained by processing the corresponding voltage versus sample position curve which is sketched in the animation in part 13 - 1



This screen shot from the MPMS3 monitor shows an example of a nice-looking result of a Scan for Sample Offset

m = 72 mg (mass of the sample)

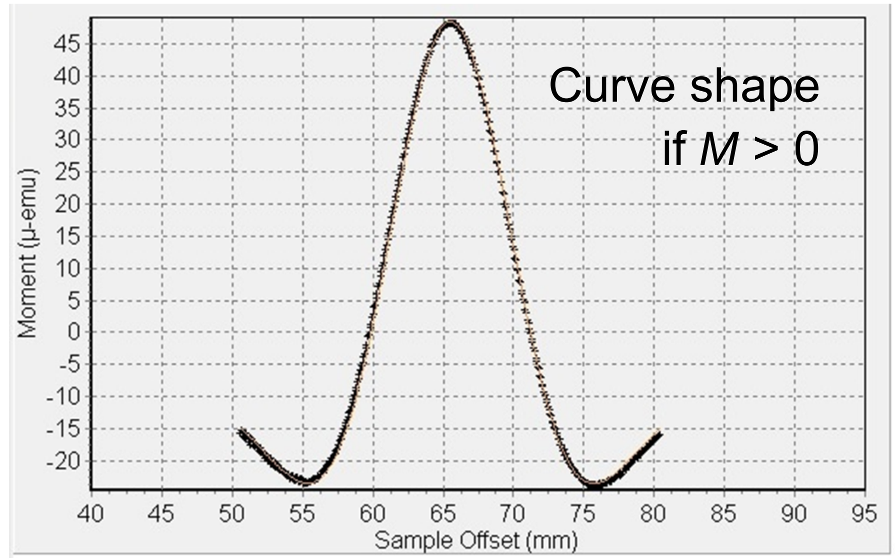
$M = 2.3 \times 10^{-4}$ emu

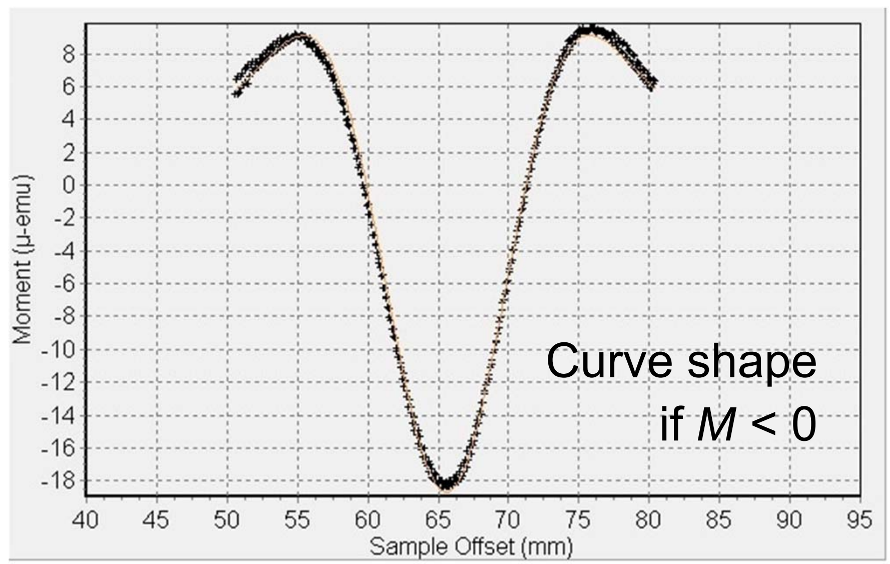
H = 400 Oe

T = 300 K

Measuring the magnetic moment M of a sample in a magnetic field $|H| > 0$ by DC scans: Two examples of processed curves of the voltage vs. sample position

The curves on the right are screen shots from the MPMS3 monitor of two DC scans with a scan length of 30 mm and a scan period of 4 sec. This type of curve is called Moment versus Sample Offset and from it the magnetic moment M of the sample can be calculated. This type of curve is obtained by processing the corresponding voltage versus sample position curve which is sketched in the animation in part 13 - 1

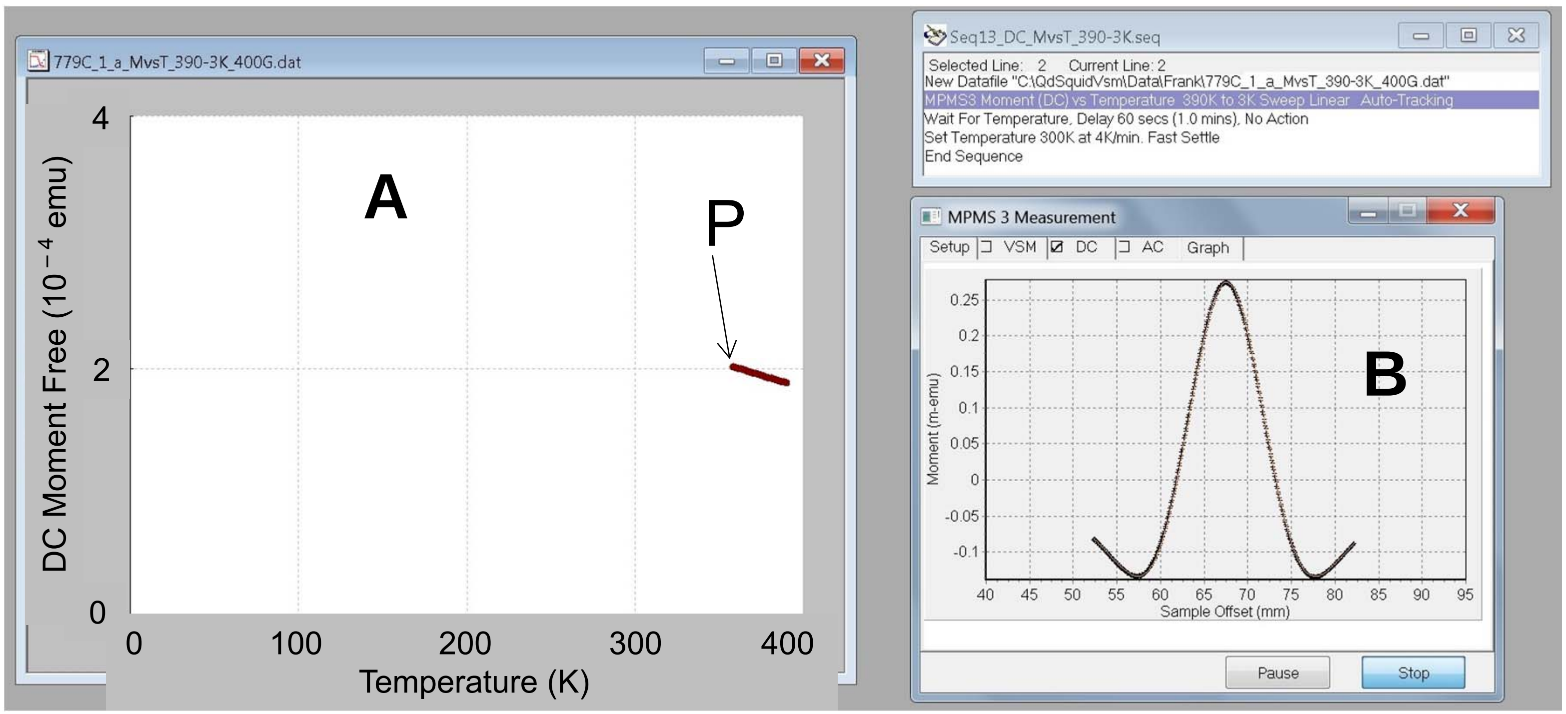




SQUID magnetometer Quantum Design MPMS3 at the ETH Zurich

Example of a screen shot from a running DC measurement

A sample with mass 72 mg is slowly and continuously cooled from 390 K to 3 K with a sweep rate of - 1.3 K. Data acquisition every 1.5 K by one DC scan with 30 mm scan length, 4 sec scan time and automatic tracking of the sample location. Magnetic field *H* = 400 Oe. Before starting the run the sample was located at 300 K, then heated with 7.5 K / min from 300 K to 390 K and once again located at 390 K

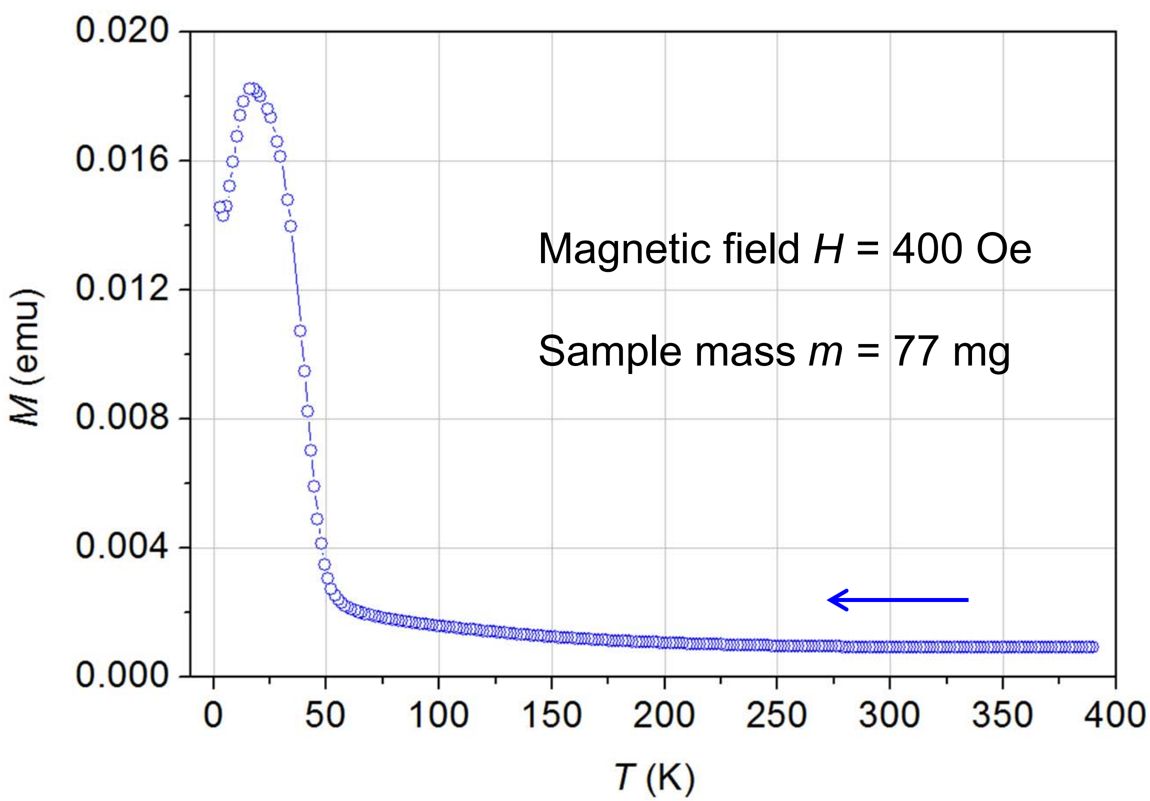


The magnetic moment *M* of the sample, here called DC Moment Free, as function of temperature is displayed in graphics A. Graphics B displays the curve Moment versus Sample Offset (see previous pages) of the DC scan from the most recent data point P

SQUID magnetometer Quantum Design MPMS3 at the ETH Zurich   16 / 51

Example of a result of a DC measurement: Magnetic moment *M* versus *T*

A sample from ongoing research was slowly and continuously cooled from 390 K to 3 K with a sweep rate of - 1.3 K. Data acquisition every 1.5 K by one DC scan with 30 mm scan length, 4 sec scan time and automatic tracking of the sample location. Duration of this run about 5 hours. The obtained *M* (*T*) curve indicates below 50 K the presence of long-range magnetic ordering



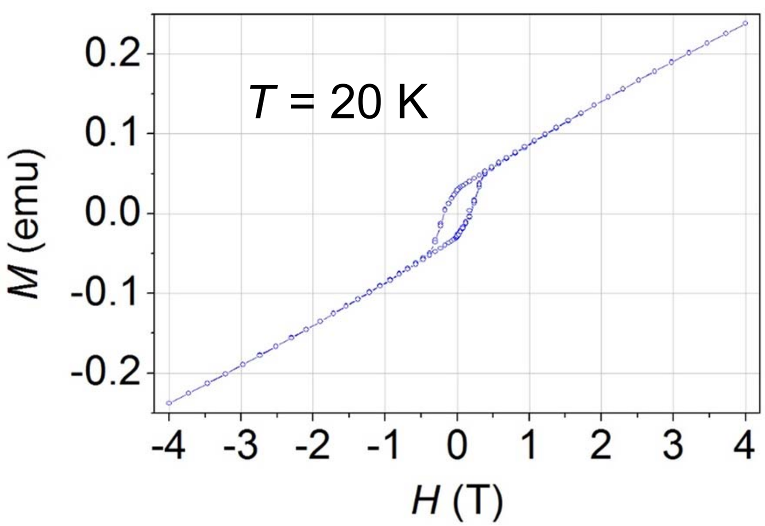
Before starting the run the sample was located at 300 K, then heated with 7.5 K / min from 300 K to 390 K and once again located at 390 K. Duration of this part about 30 minutes

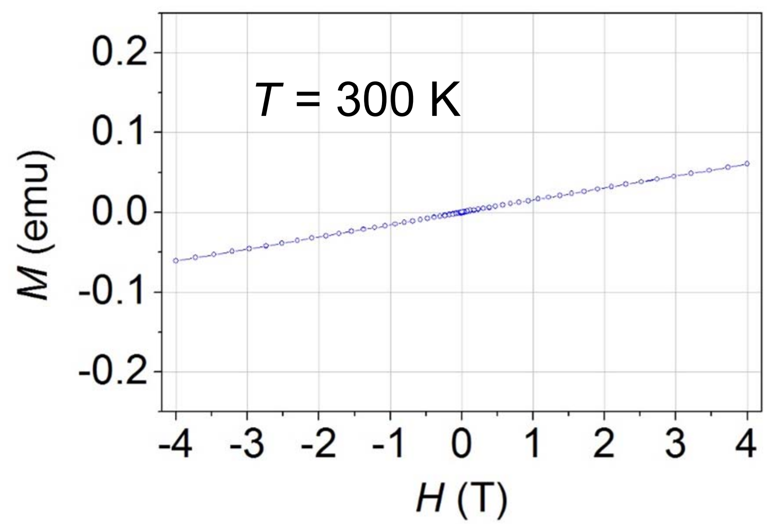
After the run the sample was heated from 3 K to 300 K with a rate of 4 K / min. Duration about 75 minutes. At 300 K the sample can be removed from the sample chamber

SQUID magnetometer Quantum Design MPMS3 at the ETH Zurich

Another example of results of DC measurements: $M(H)$ curves

The magnetic moment M as function of the magnetic field H of a sample from ongoing research was measured at various temperatures such as 300 K and 20 K. The field range and sequence was $0 \rightarrow 4\text{ T} \rightarrow 0 \rightarrow -4\text{ T} \rightarrow 0 \rightarrow 4\text{ T} \rightarrow 0$.
The data acquisition was performed at fields which were specified by a created sequence. The MPMS3 software allows an easy creation of various sequences with diverse linear or non-linear spacings between successive field values.
Data acquisition by two DC scans with 30 mm scan length and 4 sec scan time.
The obtained $M(H)$ curve at 20 K shows a hysteresis which indicates the presence of ferromagnetism. When plotting the obtained $M(H)$ curve at 300 K on the same scale then there is no hysteresis visible





Sample mass m = 127 mg

Residual magnetic fields and measurements at low fields

Even if the magnetic field is set to zero the actual field is not really null. There is always a residual field which is due to the superconducting magnet. The residual field is typically of the order of 1 or 5 Oe. However, if the superconducting magnet was used at high magnetic fields, then the residual field can be even larger such as 30 Oe. If, for example, the set field is 20 Oe and the residual field is - 30 Oe, then the actual field is
20 Oe + (- 30 Oe) = - 10 Oe. This is a significant difference, especially when considering the sign of the field. The residual field can be reduced to a normal value in the following way, preferably before inserting and locating the sample:

Set the field (from zero) to a value above 10000 Oe such as 15000 Oe. Subsequently the field will be set to zero in the so-called oscillating mode (usually the field is changed in the so-called linear mode). Then the field goes several times and with decreasing amplitude through null and changes its sign. This corresponds to a degaussing which reduces the residual field.

Potential incorrect conclusions of results of measurements in low magnetic fields can be avoided by verifying the actual field. It can be determined by a palladium sample or the so-called fluxgate of the ultra-low field option which are presented on the following pages

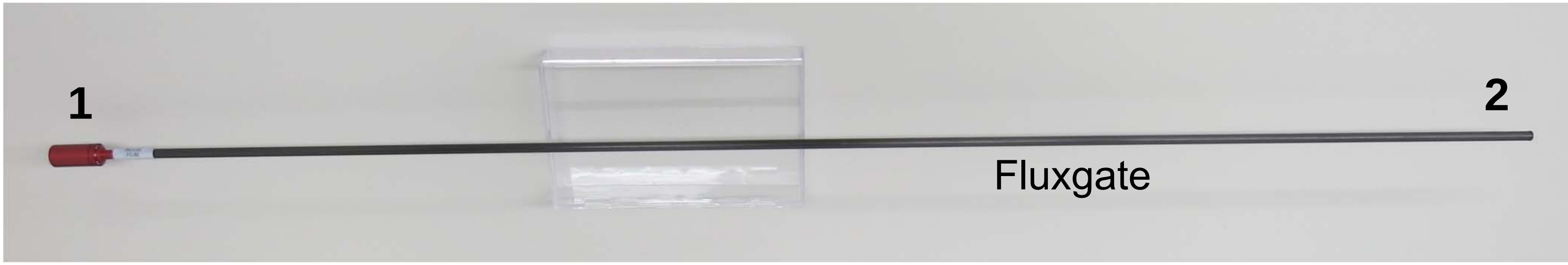
The palladium (Pd) sample

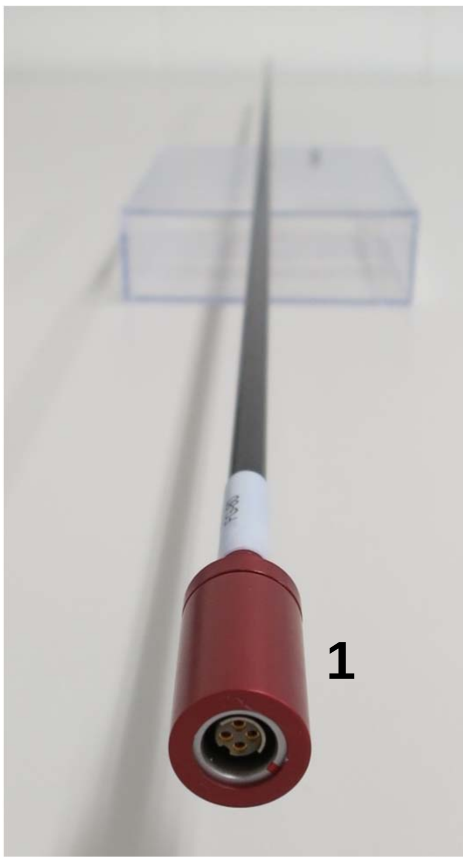
The palladium (Pd) sample can be used for various checks, especially

- for periodic verifications if the measured values of the magnetic moment M are correct
- to determine the sign and magnitude of the actual magnetic field H, particularly when the set field is relatively small such as 25 Oe

The palladium (Pd) sample has a cylindrical shape and its mass is for example m = 263 mg. It is mounted in a quartz glass tube / holder. The quartz glass tube is sealed at its left or upper end (1) and at its right or bottom end (2). Therefore measurements with the palladium (Pd) sample should be performed only at 298 K or 300 K. The adapter at the left or upper end (1) can be screwed into the sample rod. The mass susceptibility of palladium (Pd) at 298 K is well-known, namely $M / (m H) = 5.28 \times 10^{-6}$ emu / (Oe g). It is best verified by measuring M at two different fields H_2 and H_1 such as H_2 = 2 T and H_1 = 1 T and then it can be calculated by $[M(H_2) - M(H_1)] / [m (H_2 - H_1)]$

Measuring low magnetic fields and field profiles by the so-called fluxgate 1 / 3





The so-called fluxgate of the ultra-low field option is a rod (length about 85 cm) that can be inserted into the sample chamber. It allows the measurement of low magnetic fields and field profiles in a field range from - 10 Oe to + 10 Oe. The right or bottom end (2) comprises a sensor for the measurement of low magnetic fields. The left or upper end (1) is equipped with a socket for a special plug and cable.

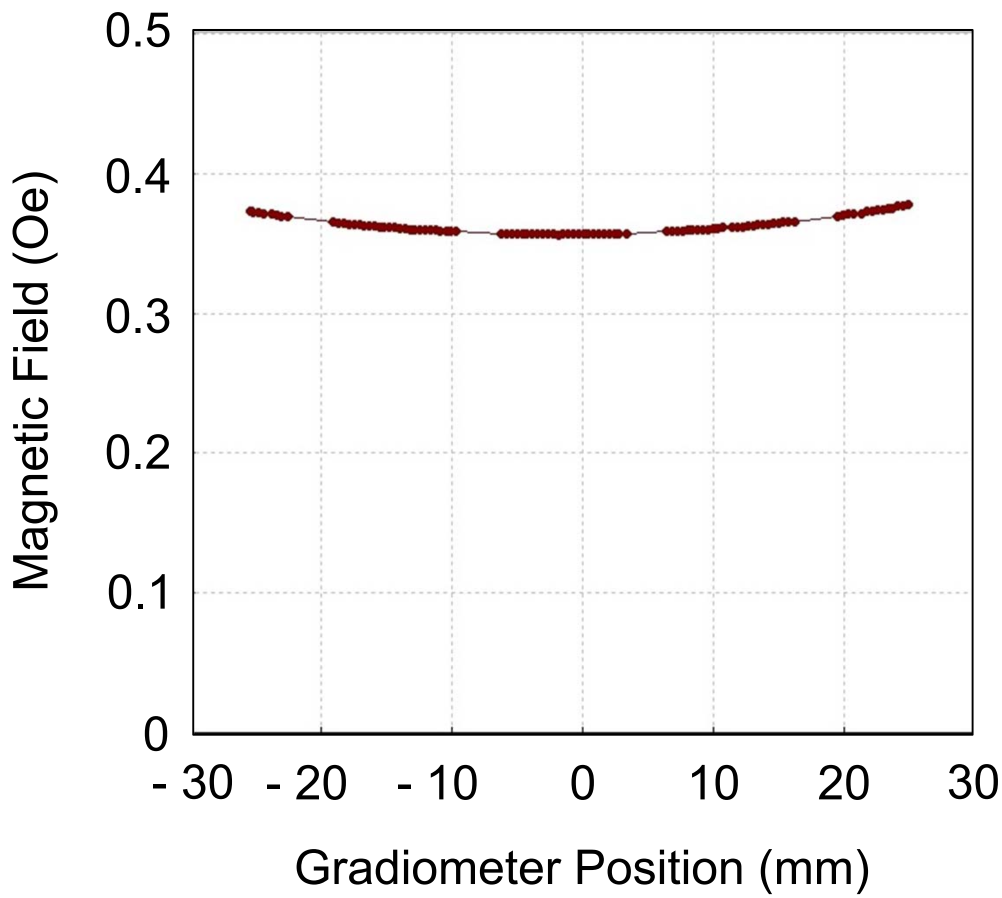
Please note that the fluxgate must not be used in fields whose magnitude is significantly larger than 10 Oe because the sensor could then be damaged

Measuring low magnetic fields and field profiles by the so-called fluxgate 2 / 3

The fluxgate is kept in a magnetically shielded tube which is integrated into the MPMS3 and made of mu-metal

The fluxgate can be inserted into the sample chamber when the temperature of the sample chamber is 300 K and when the sample chamber is flooded with helium

Measuring low magnetic fields and field profiles by the so-called fluxgate 3 / 3



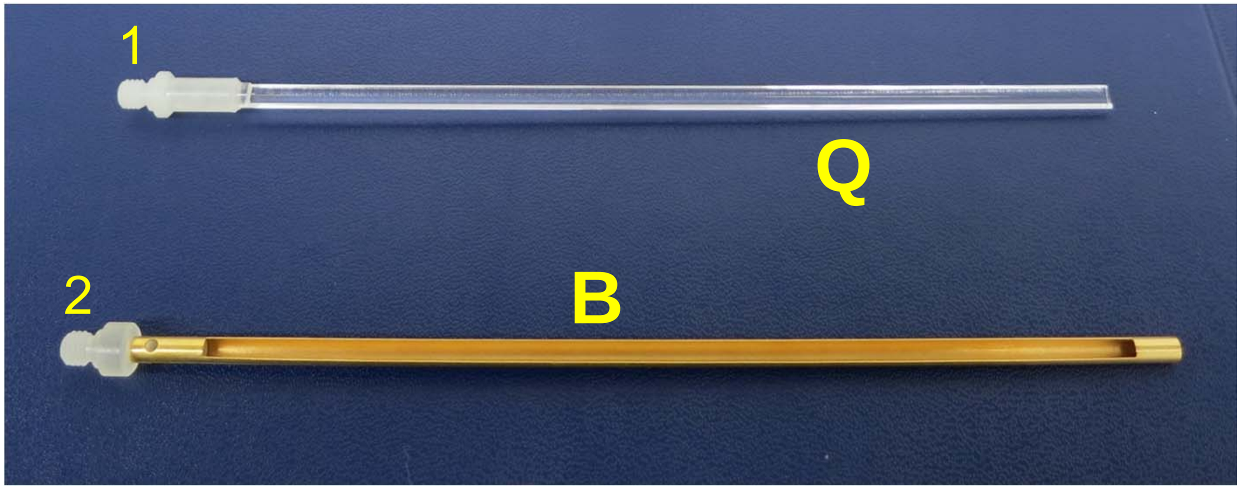
Example of a result of a field profile measurement obtained from the fluxgate and a computer-controlled procedure of the ultra-low field option.
In this example a so-called magnet reset was performed before starting the field profile measurement procedure.
The magnet reset comprises a temporary heating of parts of the superconducting magnet above its superconducting transition temperature and results in a low residual field

In this example the residual field is about 0.4 Oe which is approximately of the same magnitude as the earth`s magnetic field

Another sample holders

On the previous pages an example of sample mounting is presented, namely a sample which is mounted within a straw. Another sample holders are shown below, one is made of quartz glass (Q) and the other one is made of brass (B). Both sample holders do not create a magnetic moment because their mass per length is homogeneous over a long distance. The adapter (1) (2) at the left or upper position can be screwed into the sample rod. The sample can be fixed on or in the sample holder by so-called GE varnish (G). If the sample generates only a small magnetic moment, then it is perhaps necessary to take the magnetic moment of the GE varnish into account. That can be done by measuring $M(T)$ or $M(H)$ of a small amount of the GE varnish without any sample.

After the run the GE varnish and the sample can be removed from the sample holder by ethanol or isopropyl alcohol



The oven option 1 / 2

The oven option allows the measurement of $M(T)$ or $M(H)$ in a temperature range from about 310 K – 1000 K under vacuum. The vacuum in the sample chamber is created by a turbo pump (and a backing pump) which is integrated into the MPMS3.

The oven option comprises a special sample holder (1) which is made of ceramics. It can be electrically heated by intrinsic filaments. The adapter (2) at the left or upper end can be mechanically and electrically connected with a special sample rod whose upper or right part is shown on the next page. The sample is fixed on the sample holder by a special cement (3) and will be subsequently wrapped by a copper foil (4). After the run the special cement and the sample can be removed from the sample holder by ethanol or isopropyl alcohol

The oven option 2 / 2

Upper part of the special sample rod with electrical cable (1) and plug (2)

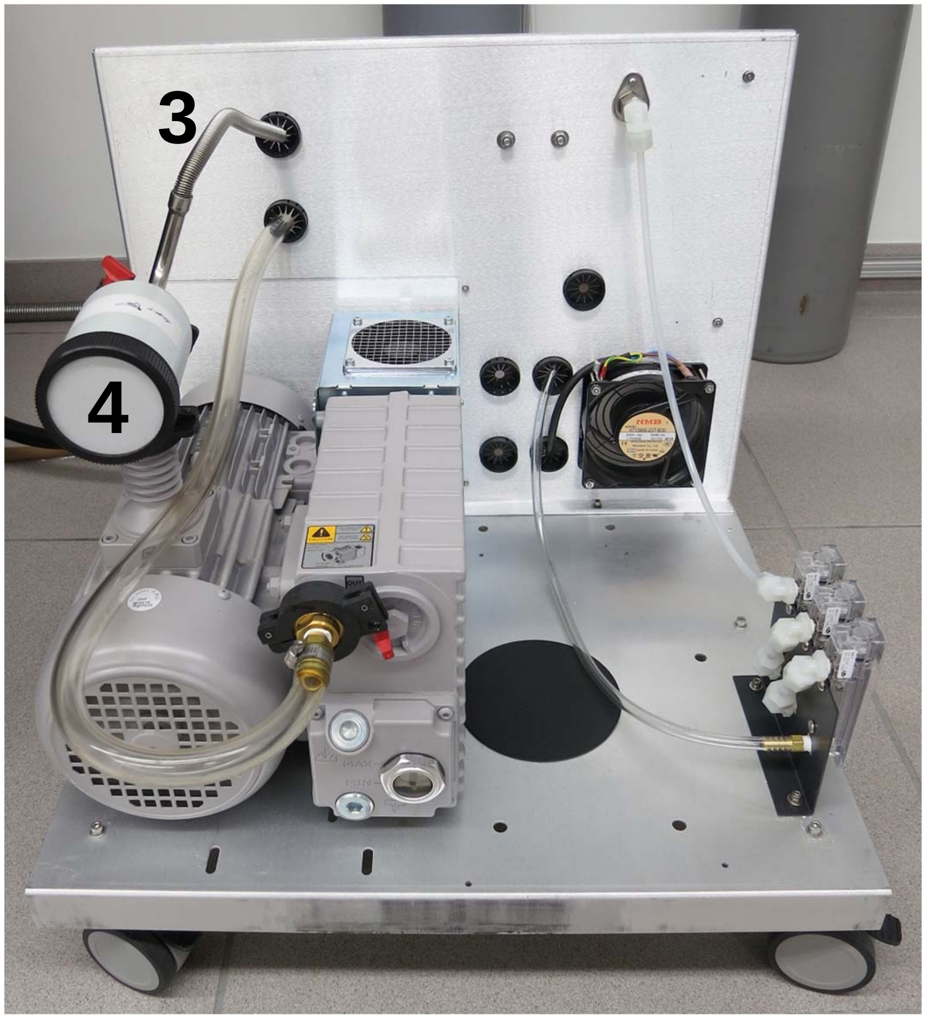
After inserting the sample rod, sample holder and sample into the sample chamber, it will be closed by a special lid (3) which consists of two parts (4) and (5). For comparison the usual lid (6) is also shown here. The special lid (3,4,5) allows a vacuum-tight sealing of the sample chamber and a vacuum-tight feedthrough of the electrical wires. The plug (2) will be plugged in one of the inner sockets (7) and the outer sockets (8) allow an electrical connection with the control unit of the MPMS3

Associated and continuously running pump (Agilent rotary vane pump MS40+) 1 / 4

To the MPMS3 (1) belongs a permanently running pump (2) for gaseous helium.
It is an important part of the temperature control system of the MPMS3.
This pump is also used to evacuate the sample chamber and acts as backing pump for the turbo pump which is running when the oven option is used

Flow meter for the helium gas flow. It is integrated in the pump (2) and located on its right-hand side

Associated and continuously running pump (Agilent rotary vane pump MS40+) 2 / 4

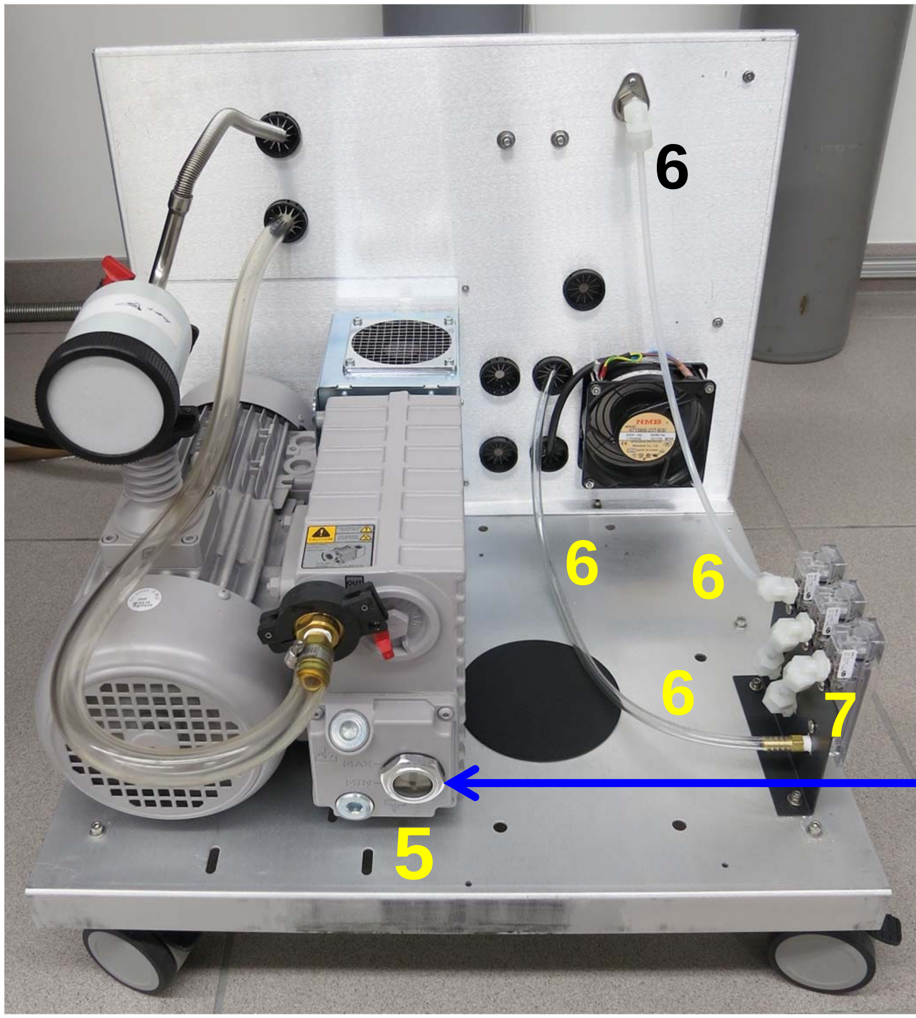


Front view of the pump when the casing is removed

3 Gas inlet line that is connected with the MPMS3. Via this line gaseous helium is pumped from the MPMS3

4 Oil filter in the gas inlet line.
It consists of a container which is filled with small spherical particles which are made of porous alumina that absorbs oil. A periodic inspection is necessary. If the alumina particles appear dark - which indicates the absorption of a large amount of oil - then they have to be replaced

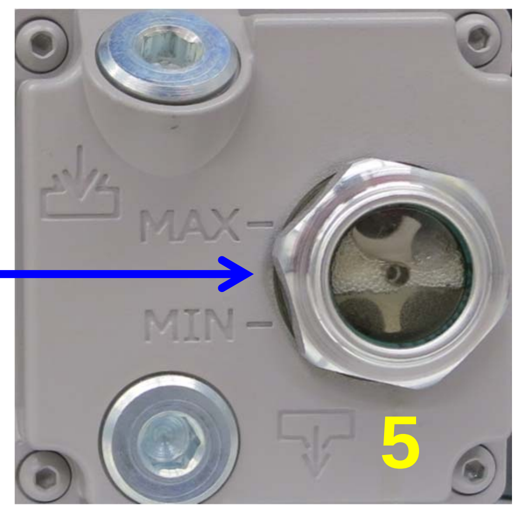
Associated and continuously running pump (Agilent rotary vane pump MS40+) 3 / 4



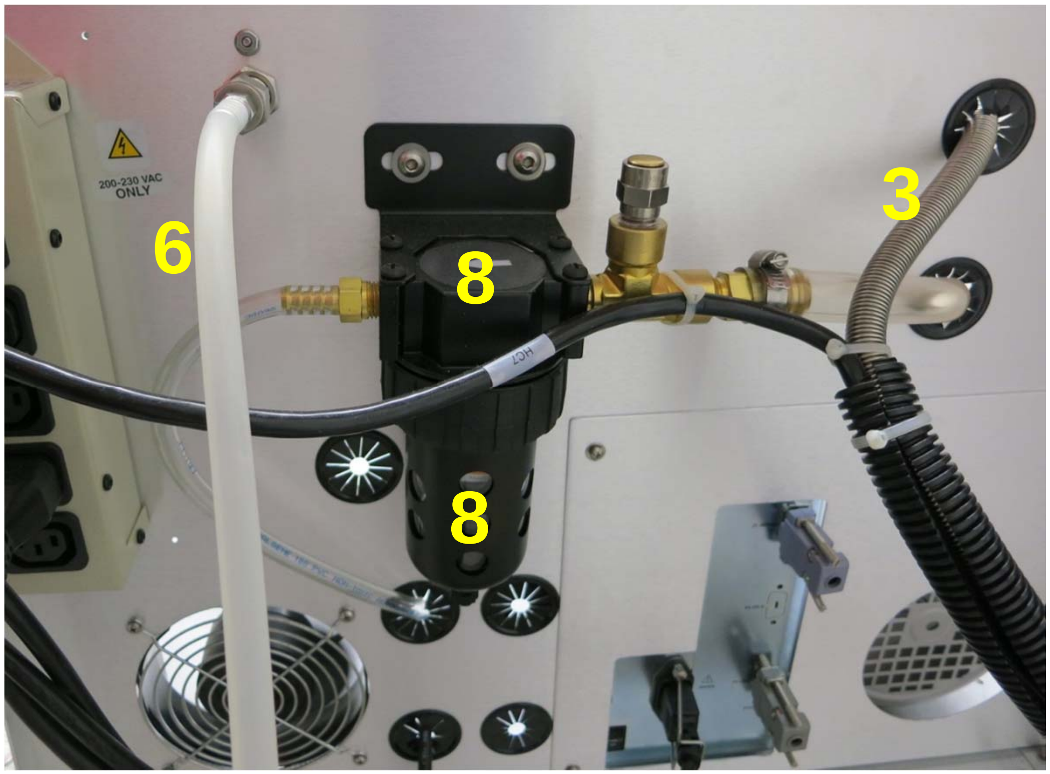
5 Oil level indicator of the pump. The oil level must be periodically inspected. The oil in the pump must be replaced after 8000 operating hours (333 days)

6 Gas outlet line

7 Flow meter for the helium gas flow



Associated and continuously running pump (Agilent rotary vane pump MS40+) 4 / 4



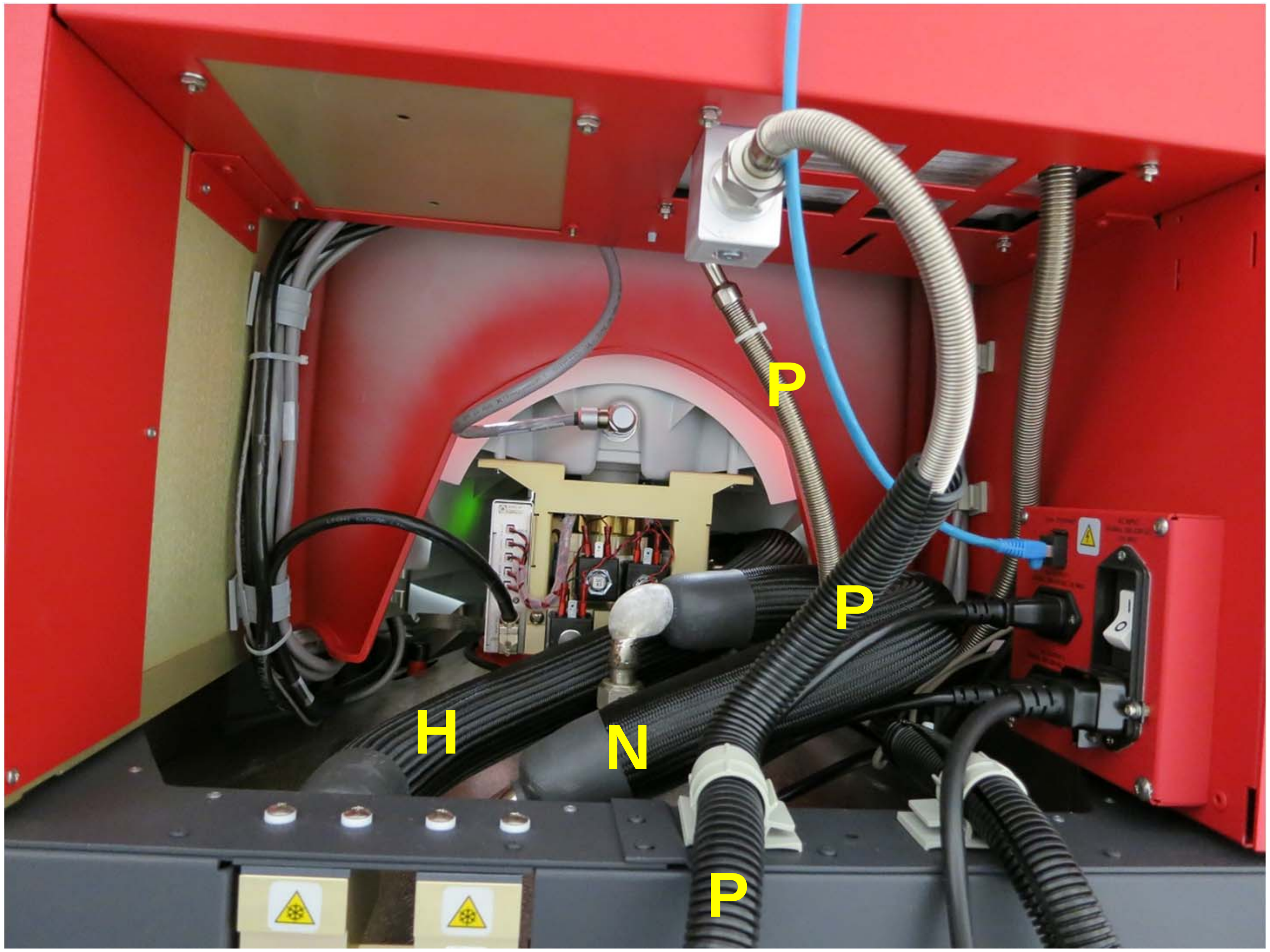
Rear view of the pump

3 Gas inlet line that is connected with the MPMS3. Via this line gaseous helium is pumped from the MPMS3

8 Oil trap in the gas outlet line. It needs a periodic inspection and, if necessary, accumulated oil has to be removed

6 Gas outlet line which is connected with the helium recovery line

Pictures from the rear side of the MPMS3 1 / 3



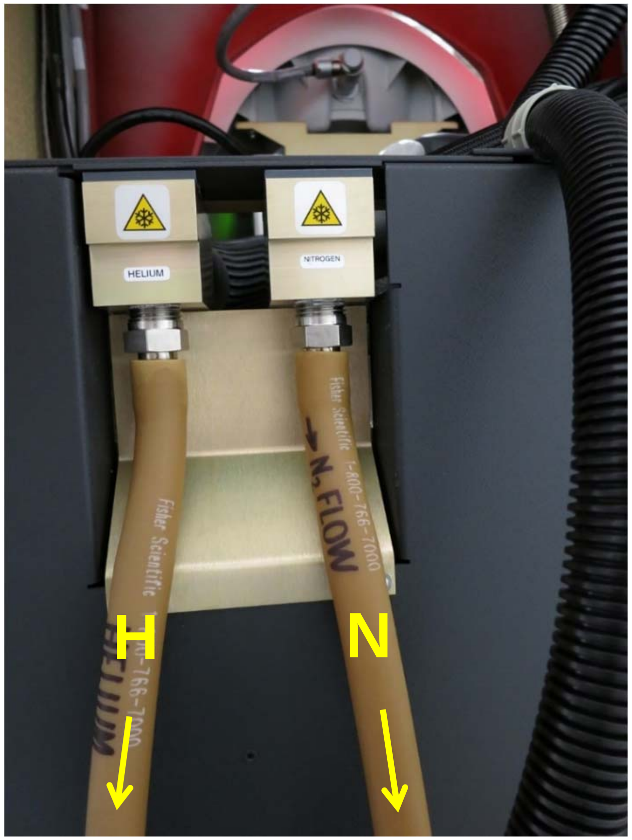
H N

H Gas outlet of the liquid helium dewar. It is connected with the helium recovery line

N Gas outlet of the liquid nitrogen dewar

P This line is connected with the gas inlet (3) of the pump which is shown on the previous page

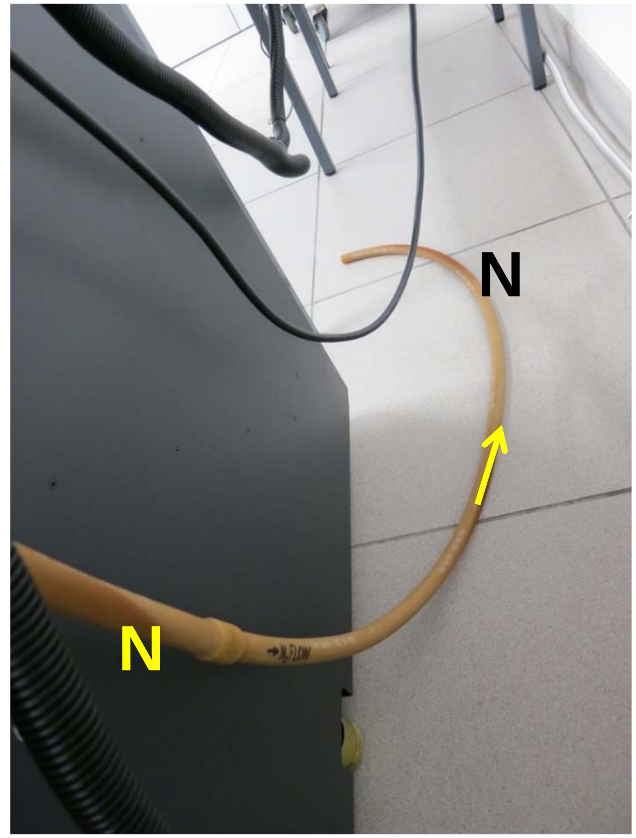
Pictures from the rear side of the MPMS3 2 / 3



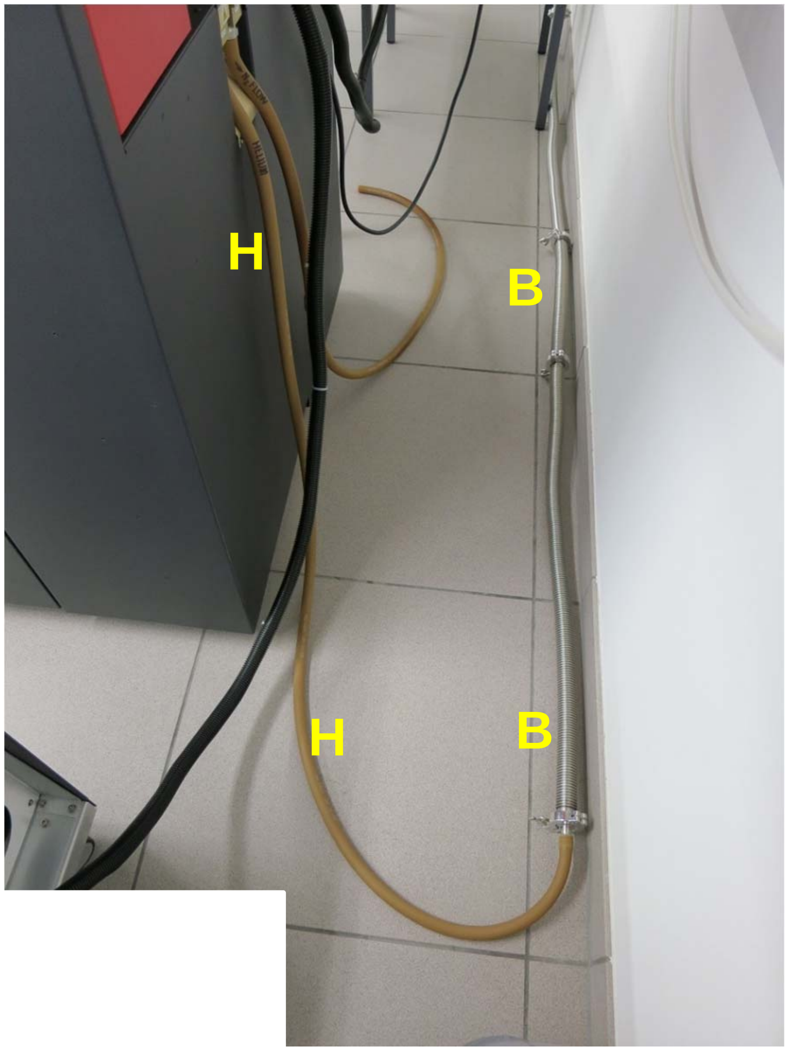
↓ Stream of gaseous helium or nitrogen

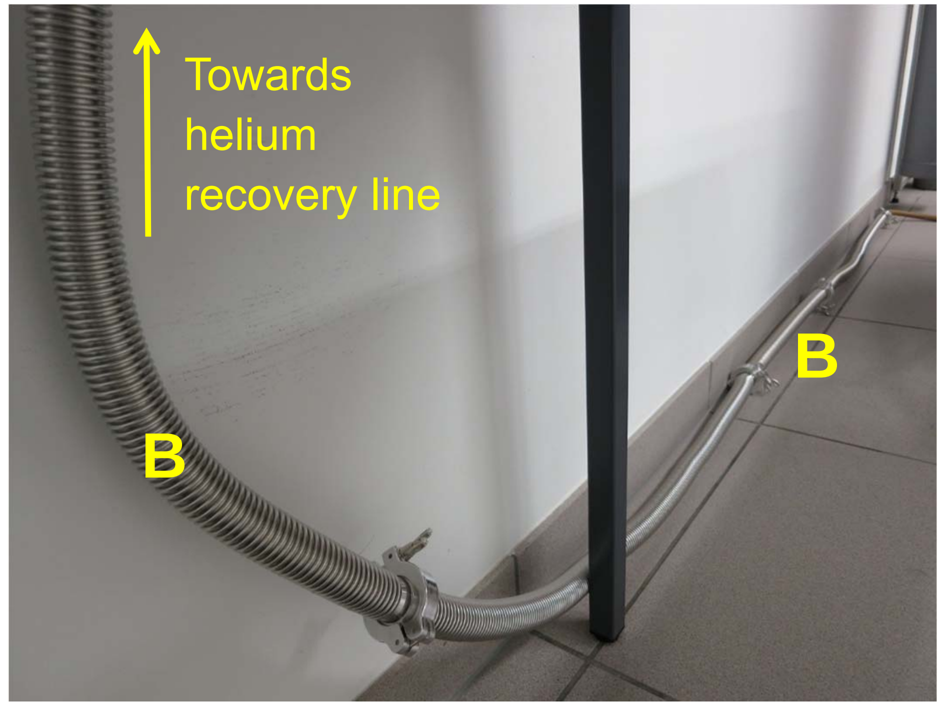
H Gas outlet line of the liquid helium dewar. The gaseous helium which arises permanently at the surface of the liquid helium is piped via this line into the helium recovery line

N Gas outlet line of the liquid nitrogen dewar. The gaseous nitrogen which arises permanently at the surface of the liquid nitrogen is piped via this line into the ambient air



Pictures from the rear side of the MPMS3 3 / 3





The gas outlet line (H) of the liquid helium dewar and the helium recovery line is connected with bellows (B). The bellow line (B) is several meters long. This design prevents a strong icing of large parts of the helium recovery line when the MPMS3 is filled with liquid helium

Movable liquid nitrogen vessel 1 / 3

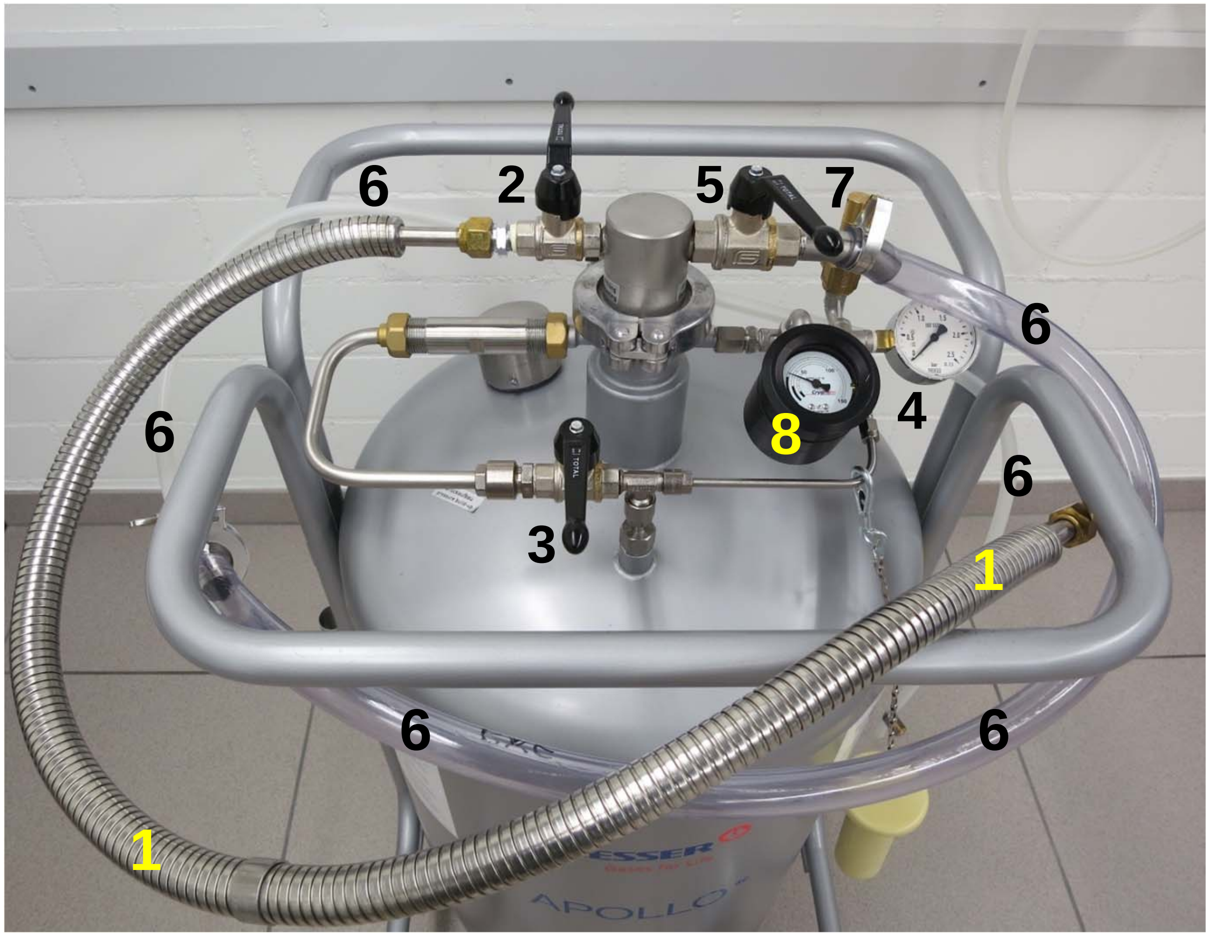
It is used to fill once a week the MPMS3 with liquid nitrogen

- Capacity 100 liter
- Equipped with a fill level display
- Integrated pressurization: It allows the transfer of liquid nitrogen from the vessel into the MPMS3 without any external gas pressure

The movable liquid nitrogen vessel is once a week filled with liquid nitrogen at a liquid nitrogen filling station which is available in the same building where the MPMS3 is located

The capacity of the liquid nitrogen dewar of the MPMS3 is 60 liter. About 35 liters liquid nitrogen are required to backfill the dewar when it is filled once a week

Movable liquid nitrogen vessel 2 / 3



1 Flexible metal tube for the transfer of liquid nitrogen from the vessel into the MPMS3

2 Valve to open / close the transfer line

3 Valve to activate / deactivate the integrated pressurization

4 Display of the pressure of gaseous nitrogen within the vessel

5 Valve to open / close the outlet for gaseous nitrogen. Usually open to prevent the emergence of an over-pressure of gaseous nitrogen

6 Long plastic tube at the outlet for gaseous nitrogen. It prevents the penetration of moisture into the vessel when valve 5 is open

7 Overpressure safety valve. It opens if the pressure of gaseous nitrogen within the vessel is too high

8 Fill level display

SQUID magnetometer Quantum Design MPMS3 at the ETH Zurich   35 / 51

Movable liquid nitrogen vessel   3 / 3

Liquid nitrogen (temperature 77 K) is potentially dangerous for various reasons.
Proper handling required !
Use appropriate safety equipment like cold protection glooves, safety glasses, and a lab coat !

Movable liquid helium vessel 1 / 3

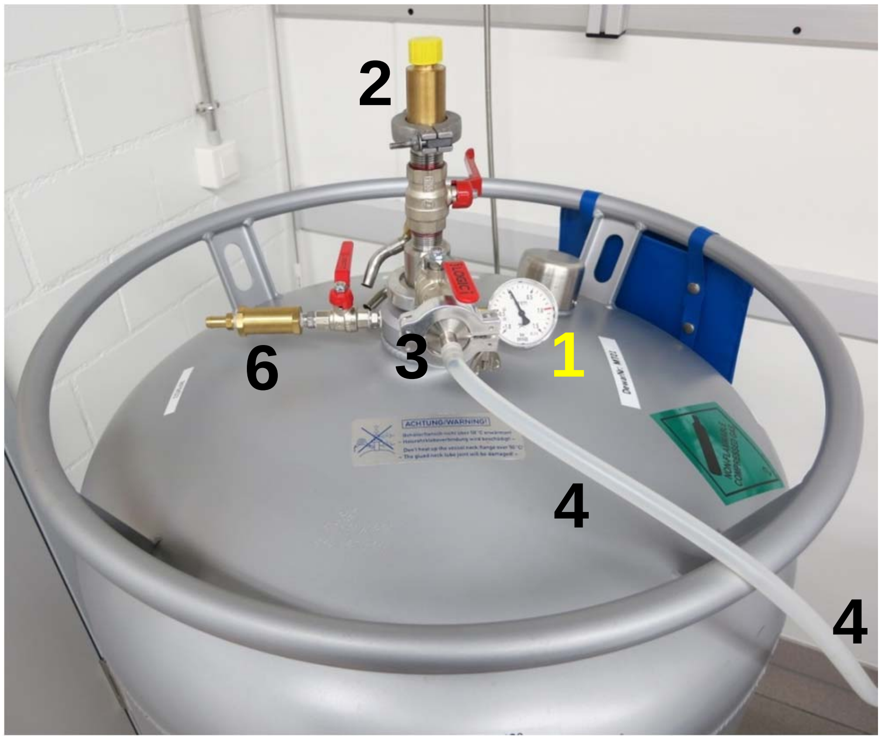
It is used to fill once a week the MPMS3 with liquid helium

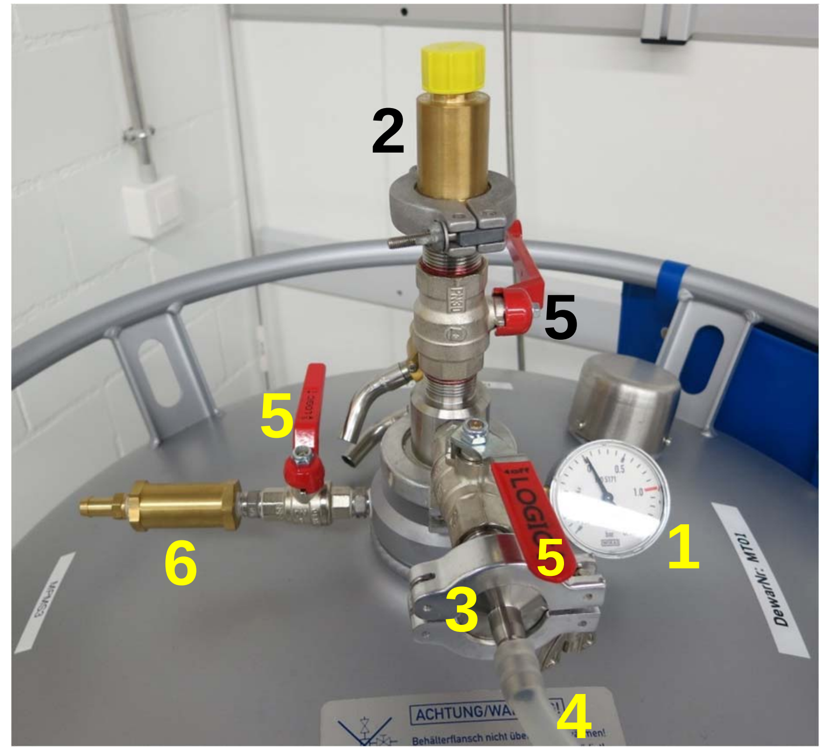
Capacity 100 liter

The movable liquid helium vessel is twice a week filled with liquid helium at the gas liquefaction facility of the ETH Zurich. The vessel is transported by truck from the building where the MPMS3 is located to the gas liquefaction facility and returned likewise by truck

The capacity of the liquid helium dewar of the MPMS3 is 70 liter. About 40 liters liquid helium are required to backfill the dewar when it is filled once a week

Movable liquid helium vessel 2 / 3





1 Manometer which displays the helium gas pressure within the vessel

2 Port for the helium transfer tube which connects the liquid helium vessel with the MPMS3

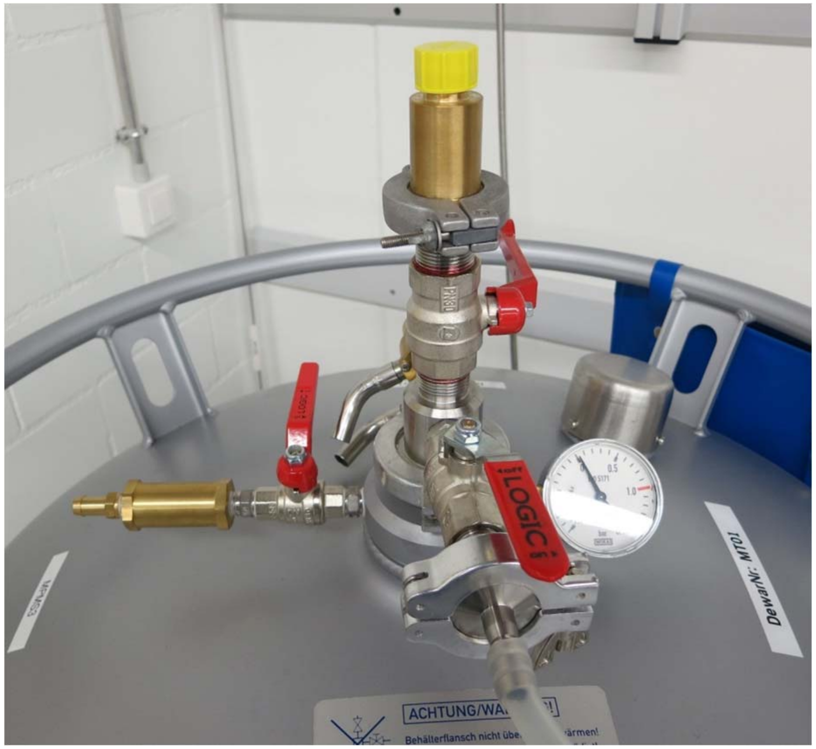
3 Port for the release of gaseous helium which arises permanently at the liquid helium surface. The gaseous helium can be piped into a helium recovery line

4 Hose towards the helium recovery line

5 Manual valve

6 One of several overpressure / safety valves

Movable liquid helium vessel 3 / 3



Liquid helium (temperature 4 K) is potentially dangerous for various reasons.
Proper handling required ! Use appropriate safety equipment like
cold protection glooves, safety glasses, and a lab coat !

Liquid helium transfer tube and recovery line for gaseous helium

1 Transfer tube for liquid helium. This tube connects the movable liquid helium vessel with the MPMS3 liquid helium port when the MPMS3 is filled with liquid helium

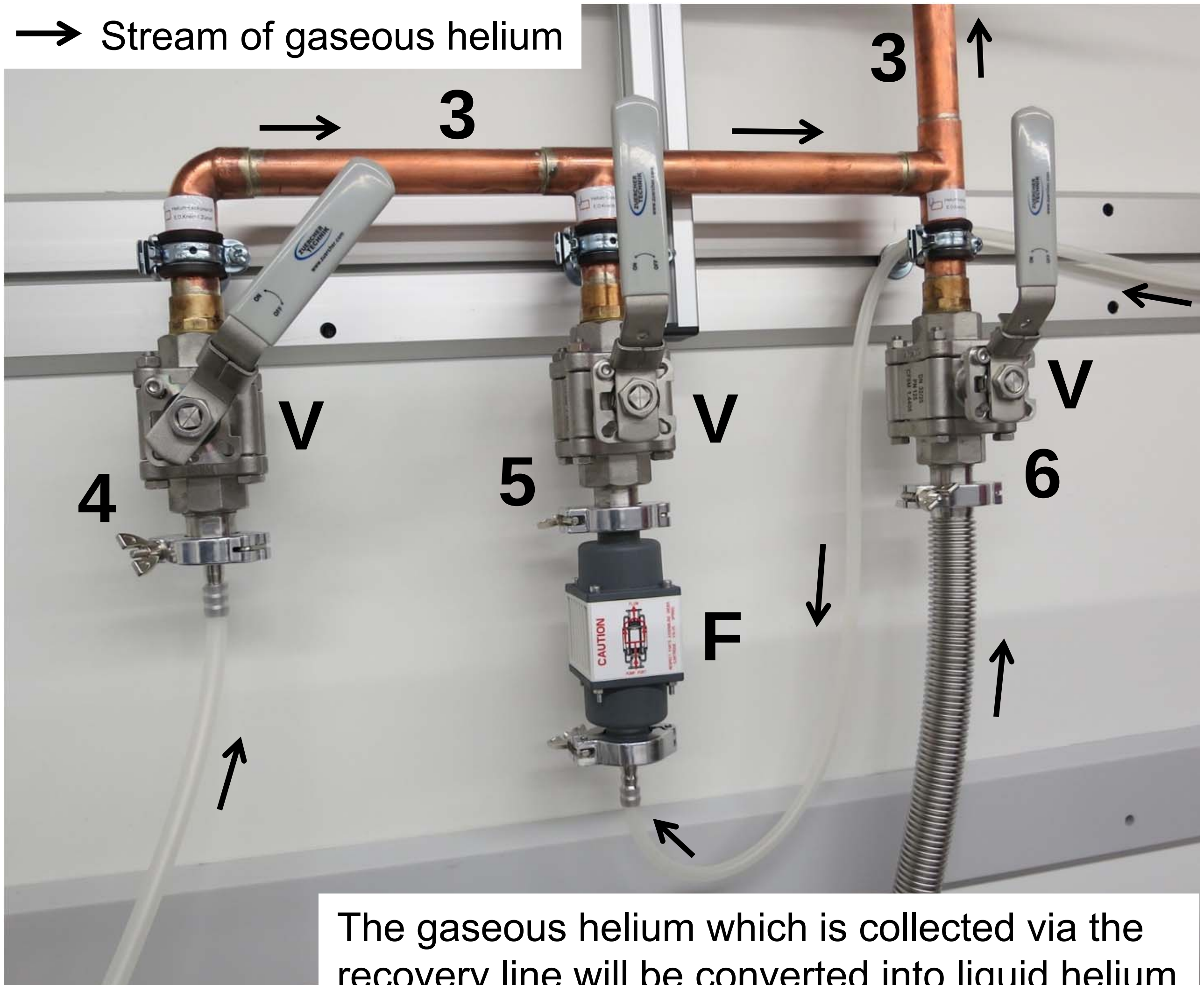
2 Shelf for the liquid helium transfer tube. Made by M. Elsener from the metal workshop of the Dept. of Materials of the ETH Zurich

3 Recovery line for gaseous helium

4
5
6 } Ports at the helium recovery line (3). See next page ...

Ports at the recovery line for gaseous helium

→ Stream of gaseous helium



The gaseous helium which is collected via the recovery line will be converted into liquid helium

3 Recovery line for gaseous helium

4 This port is connected with the movable liquid helium vessel

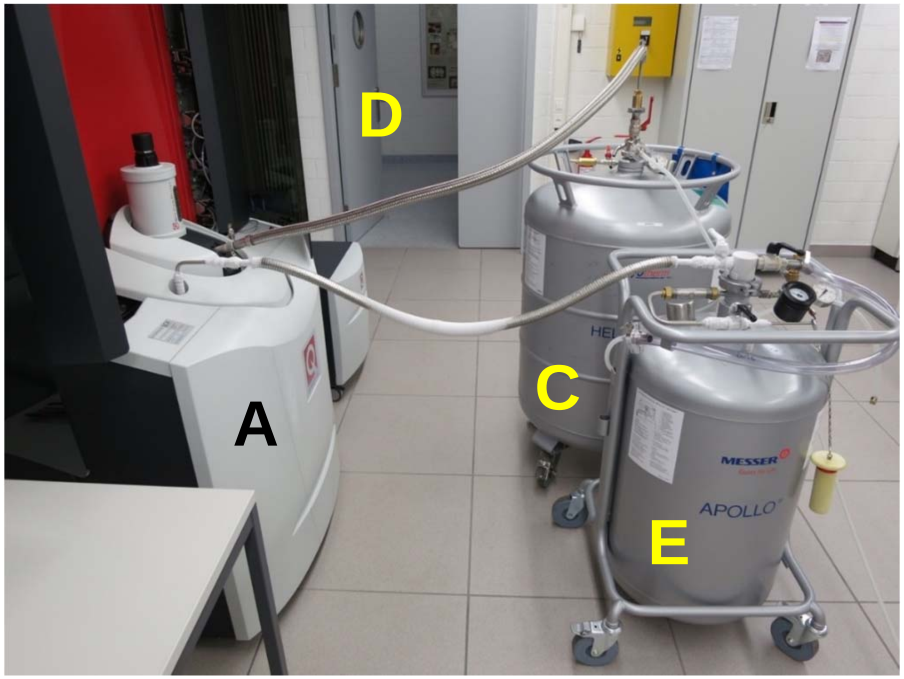
5 This port is connected with the gas outlet of the pump

F Filter unit that ensures an oil-free recovery line. It contains a cartridge which has to be replaced periodically

6 This port is connected with the liquid helium dewar of the MPMS3

V Manual valve to open or close the port

Filling the MPMS3 with liquid nitrogen and liquid helium



A MPMS3

E Movable liquid nitrogen vessel

C Movable liquid helium vessel

The filled MPMS3 can be used for about 12 days before the permanently decreasing liquid helium level reaches a critical value. Our MPMS3 is filled with liquid helium and liquid nitrogen once a week. That makes it easy to implement a simple and periodic filling schedule when three persons fill the MPMS3 alternately and the liquid helium level usually does not reach a critical value.

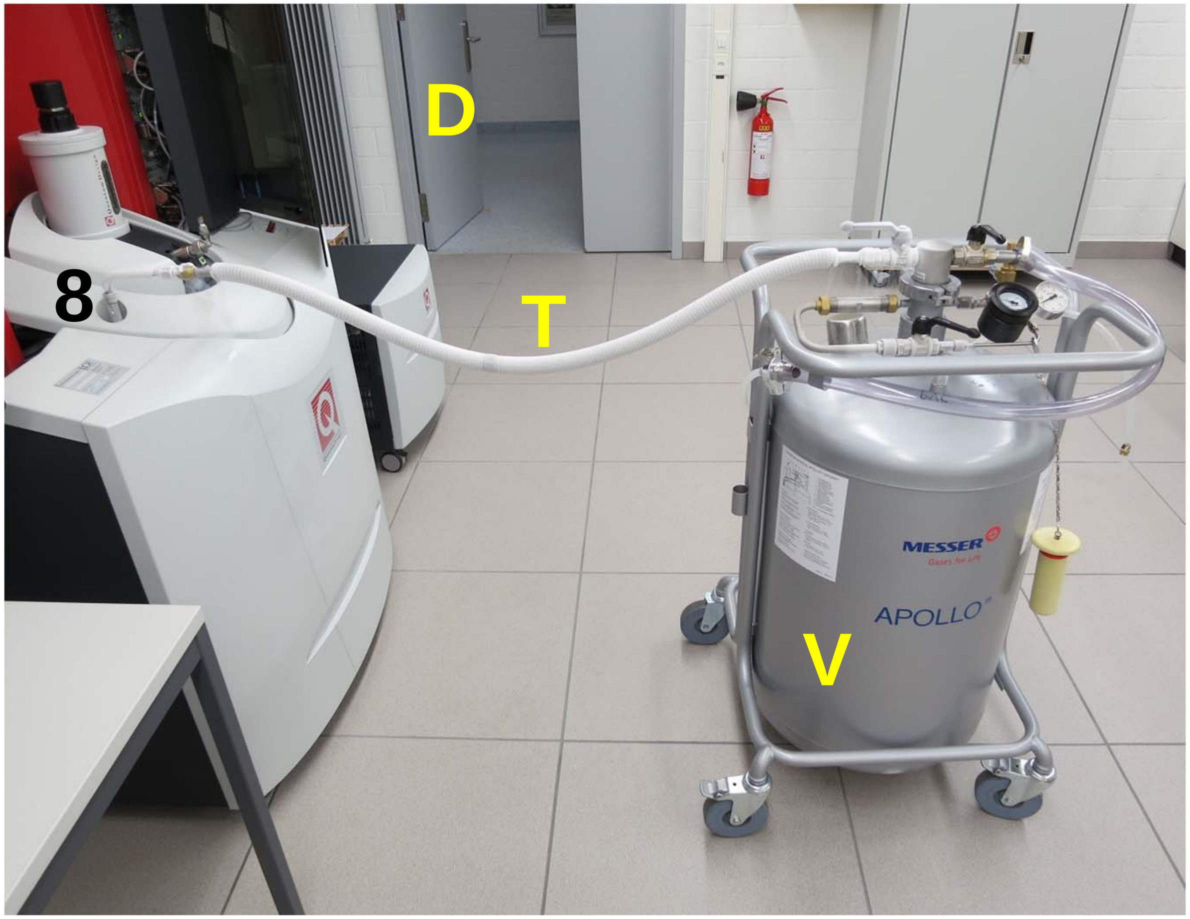
The MPMS3 lab is located in the basement and has no windows. It is equipped with a permanently running supply air and suction, a device to cool the air in the lab, and a monitoring and alarm system for the oxygen content of the air in the lab.

For safety reasons one door (D) of the MPMS3 lab remains open during the filling procedure.

The entire filling procedure takes about 1 hour

Liquid nitrogen (temperature 77 K) and liquid helium (temperature 4 K) are potentially dangerous for various reasons. Proper handling required ! Use appropriate safety equipment like cold protection glooves, safety glasses, and a lab coat !

Pictures from filling the MPMS3 with liquid nitrogen 1 / 2



V Movable liquid nitrogen vessel

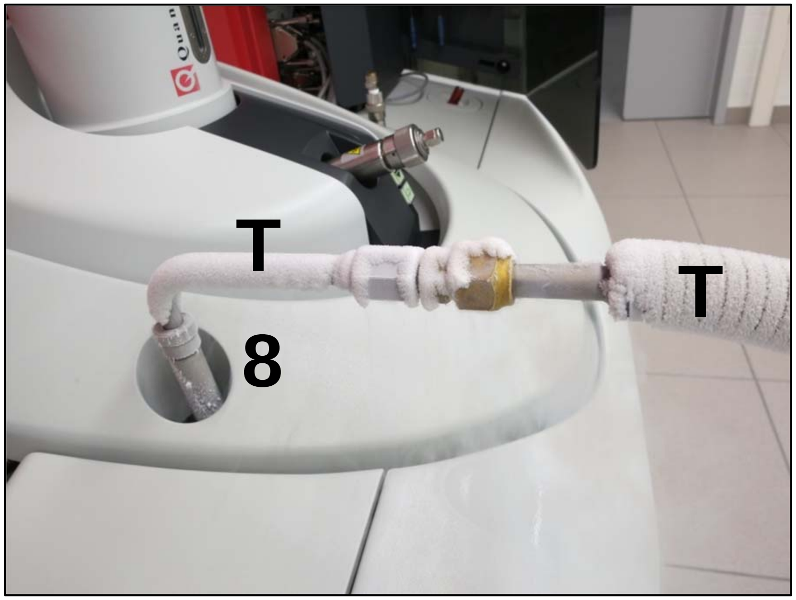
T Liquid nitrogen transfer tube. It is iced because liquid nitrogen is flowing through it

8 Liquid nitrogen port of the MPMS3

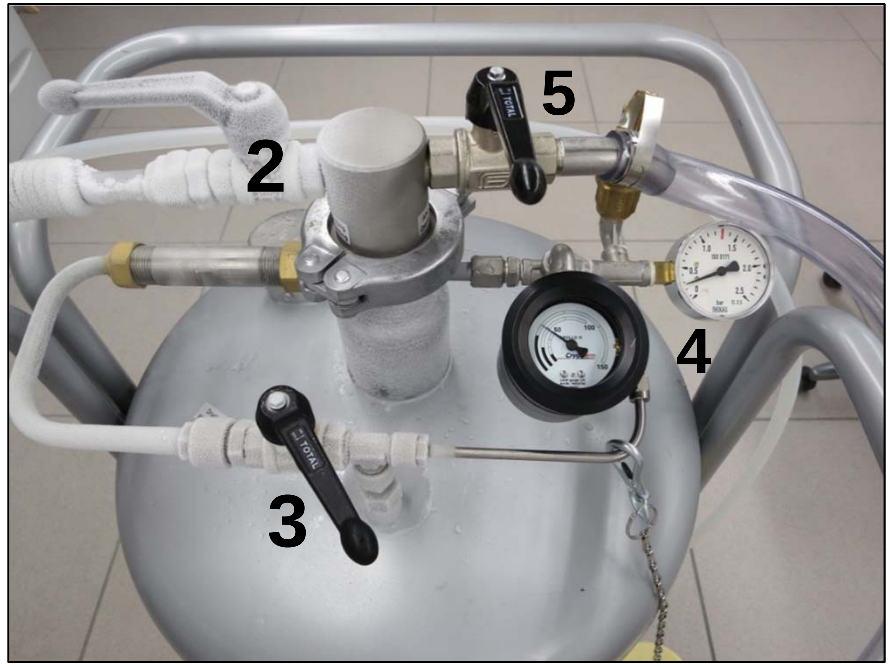
D One of two doors of the MPMS3 lab. For reasons of safety the door remains open during the filling procedure

Liquid nitrogen (temperature 77 K) is potentially dangerous for various reasons.
Proper handling required ! Use appropriate safety equipment like
cold protection glooves, safety glasses, and a lab coat !

Pictures from filling the MPMS3 with liquid nitrogen 2 / 2



The liquid nitrogen port (8) of the MPMS3, the transfer tube (T), and the manual valve (2) are iced because liquid nitrogen is flowing through them



The transfer or flow of liquid nitrogen is enabled by the integrated and activated self-pressurization: The valve (3) of the self-pressurization line is open, the gas outlet valve (5) is closed, and the pressure (4) of gaseous nitrogen within the vessel is about 0,3 bar in this example

⚠ Liquid nitrogen (temperature 77 K) is potentially dangerous for various reasons. Proper handling required ! Use appropriate safety equipment like cold protection glooves, safety glasses, and a lab coat !

Pictures from filling the MPMS3 with liquid helium 1 / 4

C Movable liquid helium vessel
S Liquid helium transfer tube
9 Liquid helium port of the MPMS3

The liquid nitrogen transfer tube (T) of the movable liquid nitrogen vessel (E) is still connected with the liquid nitrogen port (8) of the MPMS3, even if the transfer of liquid nitrogen is already terminated. The tube (T) will be removed from the port (8) at the end of the entire filling procedure. Then the warming up of the tube (T) and the port (8) is so far advanced that they can be disconnected from each other without using a hair dryer or heat gun. Furthermore, after such a relatively long waiting time there is no backflow of liquid nitrogen from the MPMS3 dewar when (T) and (8) are disconnected from each other

Liquid helium (temperature 4 K) and liquid nitrogen (temperature 77 K) are potentially dangerous for various reasons. Proper handling required ! Use appropriate safety equipment like cold protection glooves, safety glasses, and a lab coat !

Pictures from filling the MPMS3 with liquid helium 2 / 4

C Movable liquid helium vessel

S Liquid helium transfer tube

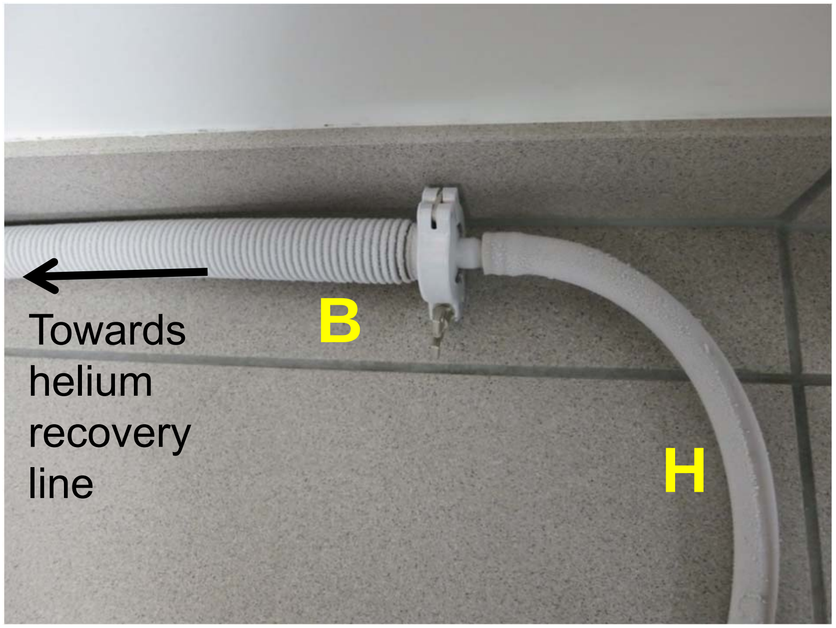
9 Liquid helium port of the MPMS3

For reasons of safety the lab door (D) remains open during the filling procedure

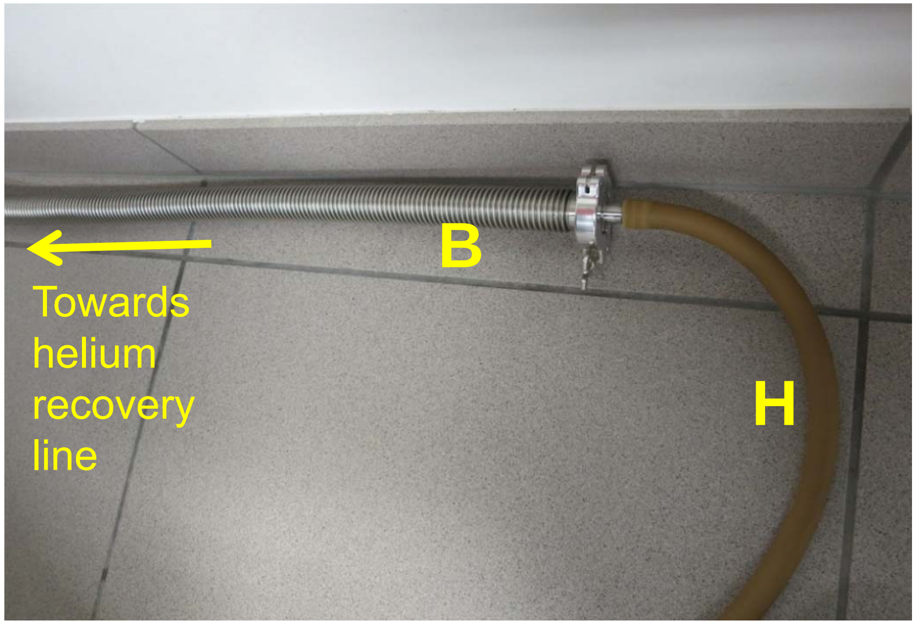
The liquid helium transfer tube (S) does not ice up when liquid helium is flowing through because this transfer tube consists of an inner and an outer tube. The liquid helium is flowing through the inner tube. The outer tube is evacuated and acts as an insulating vacuum that prevents icing

Liquid helium (temperature 4 K) and liquid nitrogen (temperature 77 K) are potentially dangerous for various reasons. Proper handling required ! Use appropriate safety equipment like cold protection glooves, safety glasses, and a lab coat !

Pictures from filling the MPMS3 with liquid helium 3 / 4



The gas outlet line (H and B) of the liquid helium dewar of the MPMS3 and the helium recovery line are partly iced when the MPMS3 is filled with liquid helium, especially at the beginning of the filling where a lot of gaseous and cold helium arises



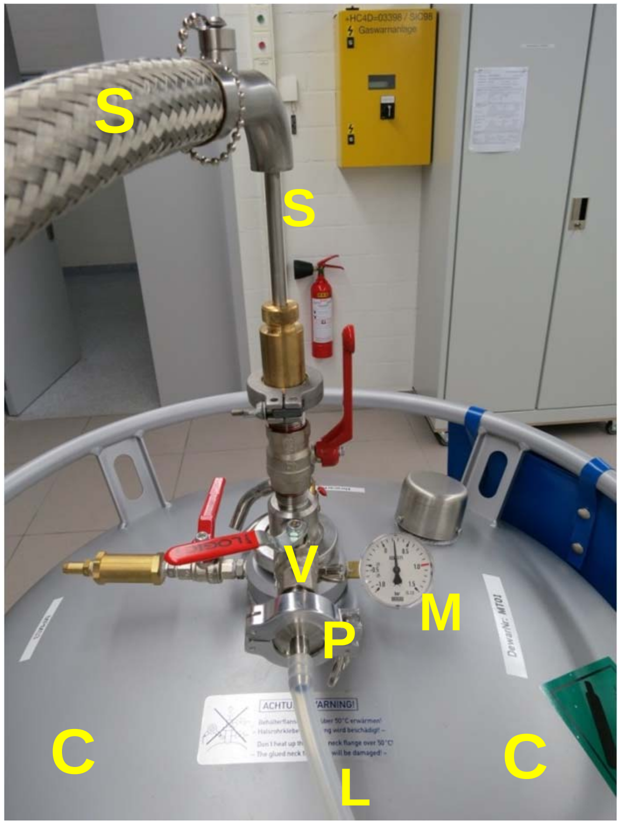
Usual or non-iced appearance of the gas outlet line (H and B) of the liquid helium dewar of the MPMS3

Liquid helium (temperature 4 K) is potentially dangerous for various reasons. Proper handling required ! Use appropriate safety equipment like cold protection glooves, safety glasses, and a lab coat !

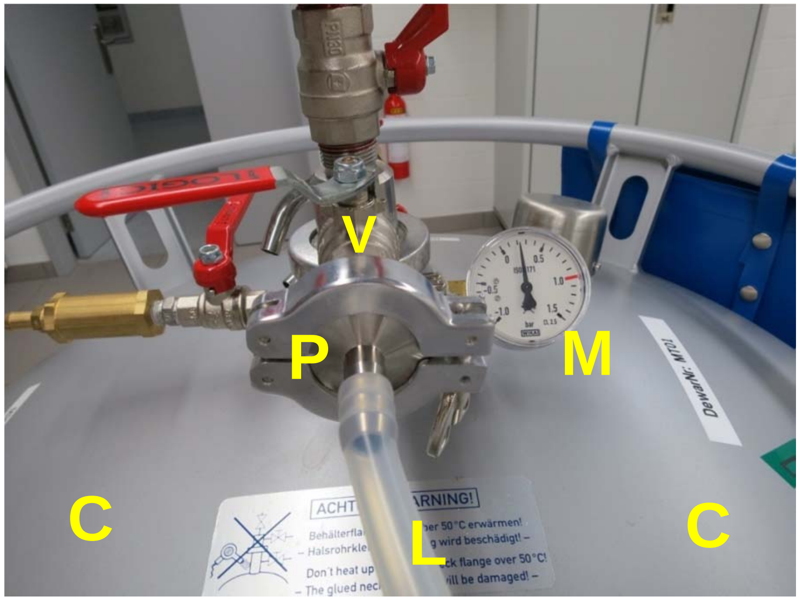
Pictures from filling the MPMS3 with liquid helium 4 / 4

C Movable liquid helium vessel
S Liquid helium transfer tube

P Port which can be used for pressurization
L Tube for pressurization
V Valve to open or close the pressurization line
M Manometer that displays the helium gas pressure



The transfer of liquid helium from the vessel (C) into the MPMS3 is enabled by a pressurization of the vessel (C) via port (P) and tube (L) which is connected with a helium gas supply (see next page). The helium gas pressure is about 200 mbar (M) in this example



Liquid helium (temperature 4 K) is potentially dangerous for various reasons. Proper handling required ! Use appropriate safety equipment like cold protection glooves, safety glasses, and a lab coat !

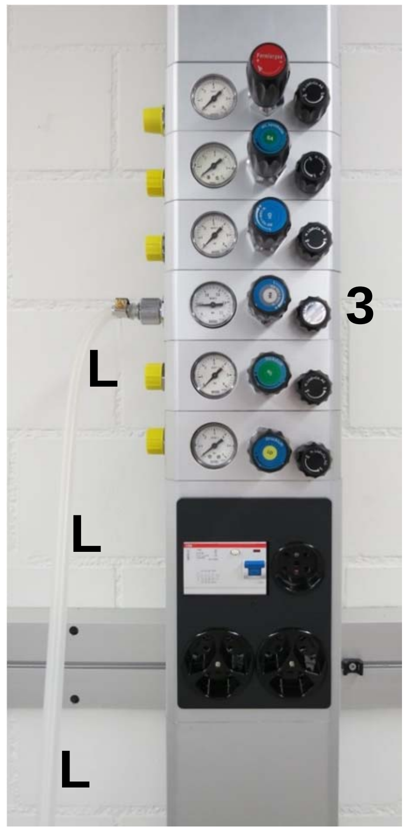
Helium gas supply for the pressurization of the movable liquid helium vessel

The transfer of liquid helium from the movable liquid helium vessel into the MPMS3 requires a pressurization of the movable liquid helium vessel (see previous page)

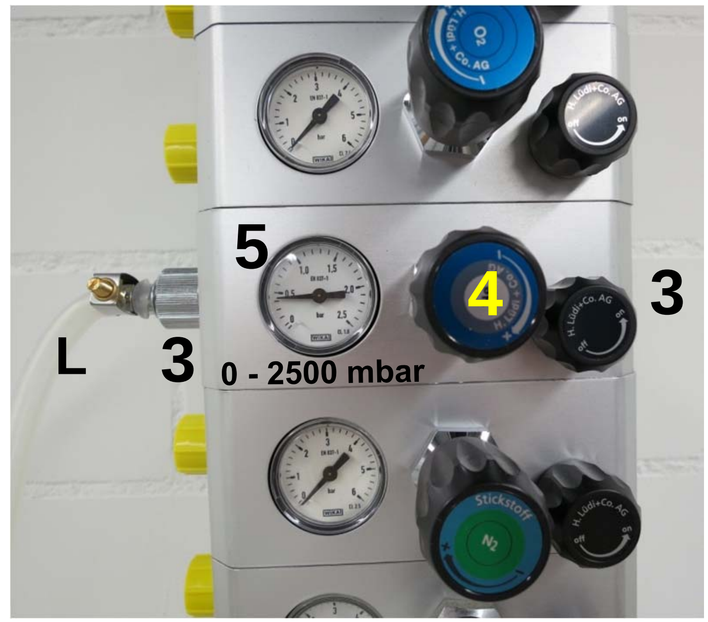
2 Supply line towards gas supply cabinet

Gas bottles with a gas pressure up to 200 bar are potentially dangerous and require a proper handling !

Highly compressed helium gas in a steel bottle (1) of the size 50 liter



More details of the design of a gas supply are presented in part 3 of this presentation



Gas supply cabinet. The consumption point (3) for helium is equipped with a point-of-use pressure regulator (4) and a pressure indication (5). The tube (L) can be connected with the liquid helium vessel (see previous page)

Monitoring the oxygen content of the air in the MPMS3 lab 1 / 2

As already mentioned on some of the previous pages, liquid nitrogen (temperature 77 K) and liquid helium (temperature 4 K) are potentially dangerous for various reasons. If a large amount of liquid nitrogen or liquid helium evaporates suddenly during a special event or accident, then the MPMS3 lab could be flooded with huge amounts of gaseous nitrogen or helium which displace the oxygen in the air of the MPMS3 lab. Therefore the MPMS3 lab is equipped with an oxygen monitoring and alarm system. If the oxygen content in the lab atmosphere decreases below a certain threshold value, then an acoustical alarm (bugle) (1) and optical alarm (flashlight) (2) is triggered. In case of oxygen alarm the lab must be left immediately and it is not allowed to enter the lab

Wall-mounted oxygen sensor in the MPMS3 lab

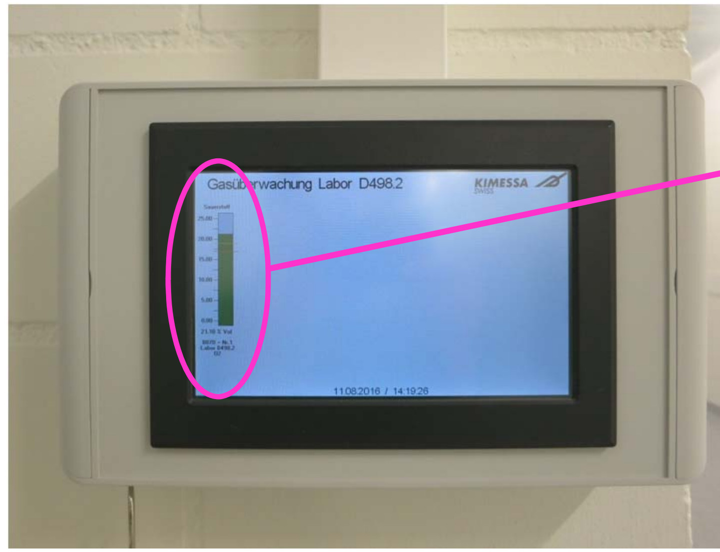
Wall-mounted control cabinet (yellow box) of the oxygen monitoring and alarm system in the MPMS3 lab

Ceiling-mounted bugle (1) and flashlight (2) in the MPMS3 lab

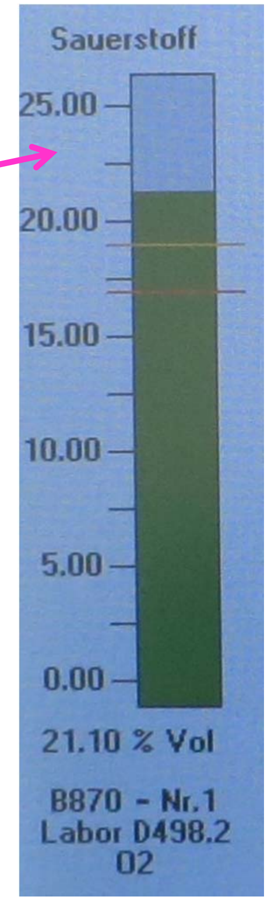
SQUID magnetometer Quantum Design MPMS3 at the ETH Zurich   50 / 51

Monitoring the oxygen content of the air in the MPMS3 lab   2 / 2

Wall-mounted flashlights (3 and 4) outside of the MPMS3 lab nearby its door 1 and door 2



Wall-mounted monitor which displays the oxygen content in the MPMS3 lab. It is located outside of the MPMS3 lab nearby its door 1



☺ Acknowledgement ☺

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Special thanks to

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S. Schaile for the installation of the MPMS3, its putting into operation, and the instruction

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M. Trassin for being part of the team who operates and supervises the MPMS3

Part 13 – Measuring magnetic properties of samples by a SQUID magnetometer

13 - 1 Sketch of principle

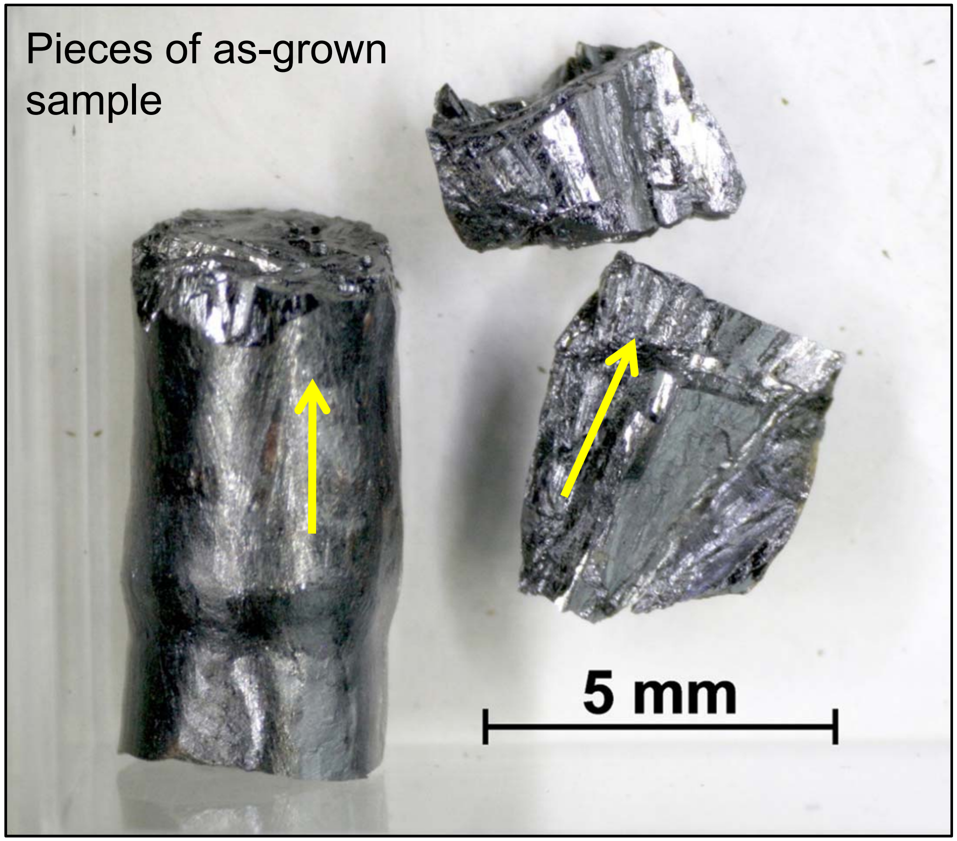
13 - 2 SQUID magnetometer Quantum Design MPMS3 at the Department of Materials of the ETH Zurich

13 - 3 Mounting a sample within a straw

13 - 4 Another SQUID magnetometers

Mounting a sample for magnetic measurements 1 / 7

Example: A melt-grown crystalline oxide material with layered crystal structure



Yellow arrow indicates axial z-direction of the as-grown sample

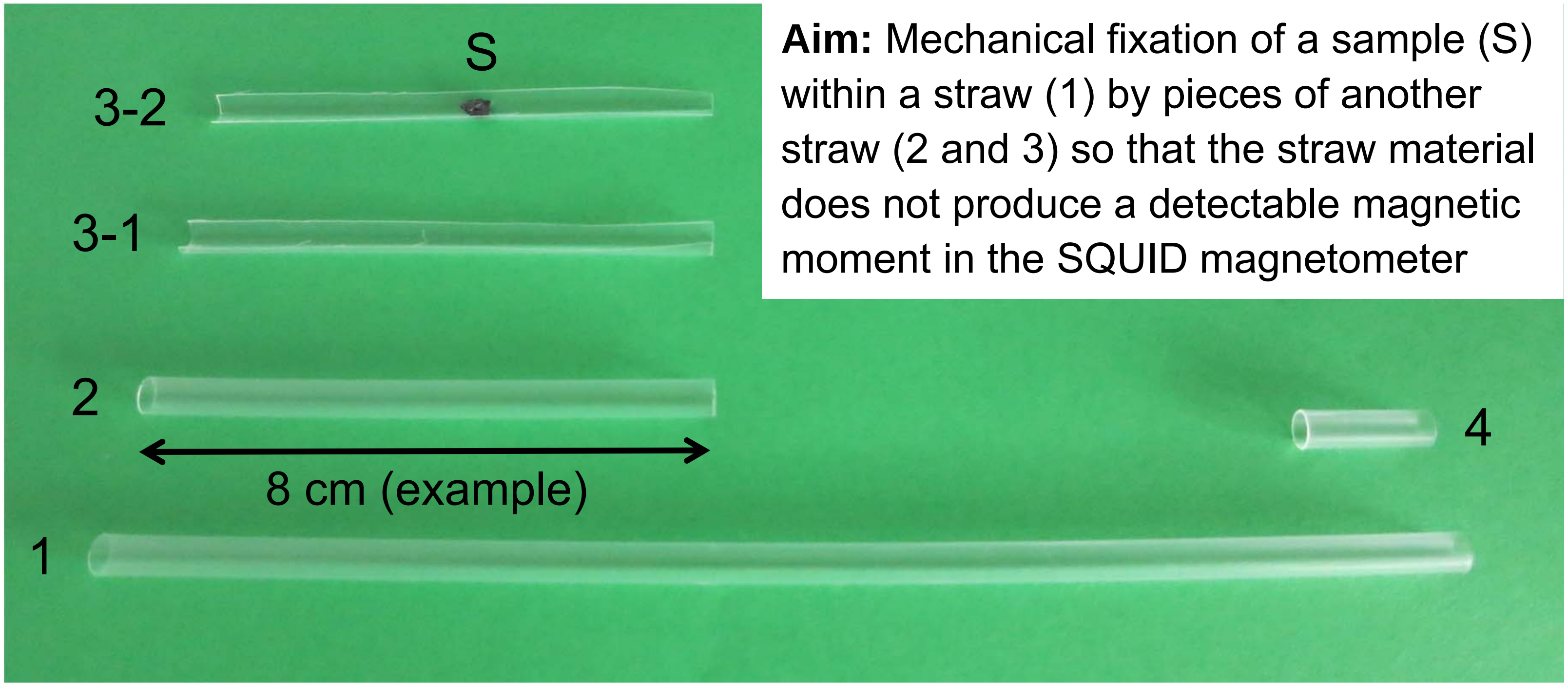
Mounting a sample for magnetic measurements 2 / 7

Example: A melt-grown crystalline oxide material with layered crystal structure

This crystalline piece was prepared from one of the pieces which are shown on the previous page. It mass is 72 mg. It is intended to measure its magnetic properties by a SQUID magnetometer.

The yellow arrow indicates the axial *z* - direction of the as-grown sample (see previous page). The layers are grown parallel to the *z* - direction, i.e. the *c* - axis is oriented perpendicular to the *z* - direction. The magnetic field *H* will be parallel to the *z* - direction, i.e. along the layers. The orientation of the *a* - and *b* - axis is not known

Mounting a sample for magnetic measurements 3 / 7



Aim: Mechanical fixation of a sample (S) within a straw (1) by pieces of another straw (2 and 3) so that the straw material does not produce a detectable magnetic moment in the SQUID magnetometer

An enlarged picture of the sample (S) is shown on the previous page. This type of straw material can be used in a temperature range from 2 K to 400 K but extensive exposure times above 330 K should be avoided

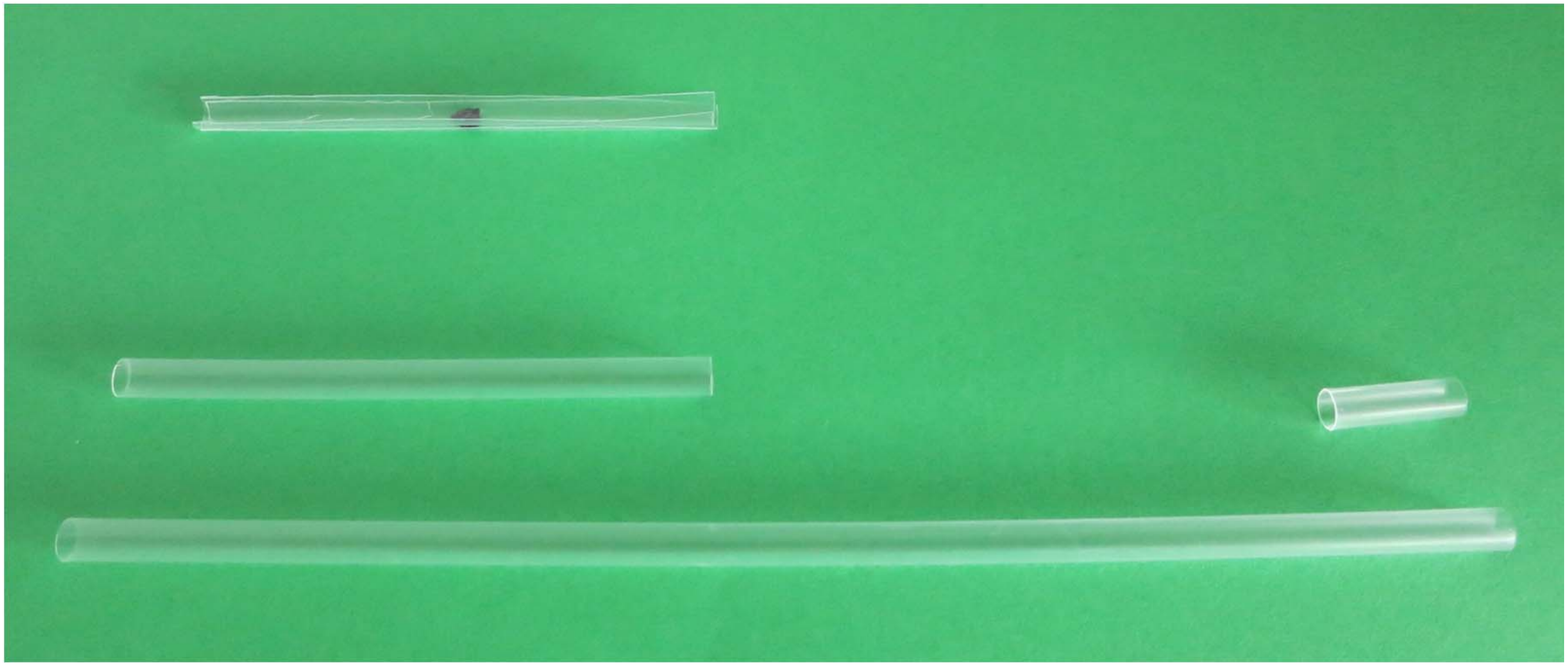
1 A whole straw

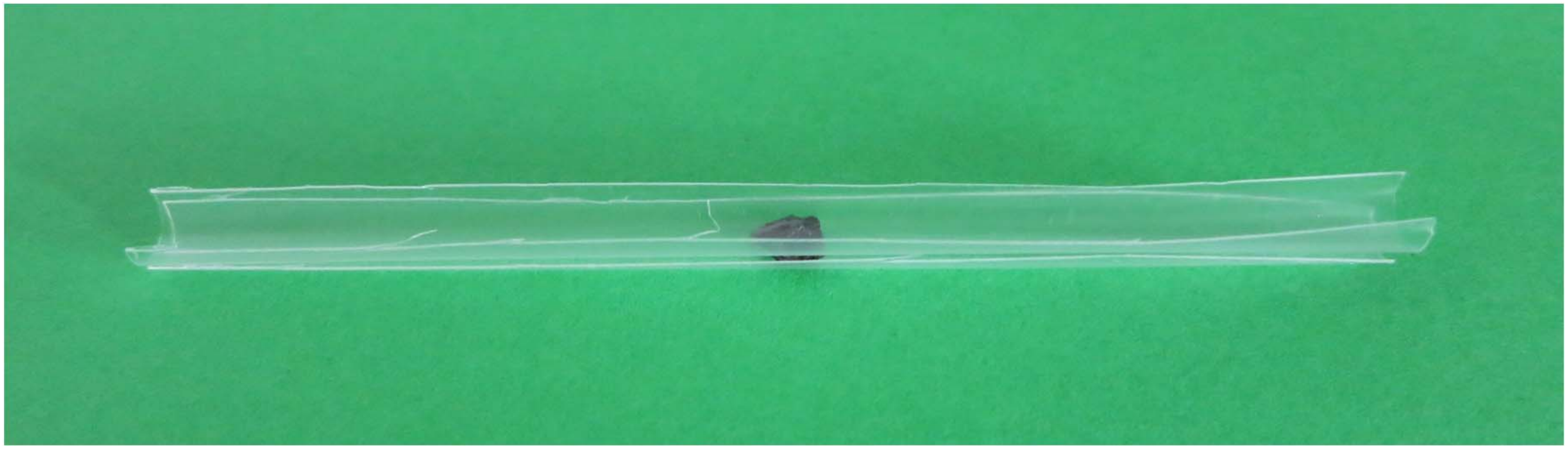
2 A piece of straw cut from a second straw, length for example 8 cm

3 Another 8 cm long piece cut from a second straw. It is cut along its axial direction so that two half pieces (3-1 and 3-2) are obtained

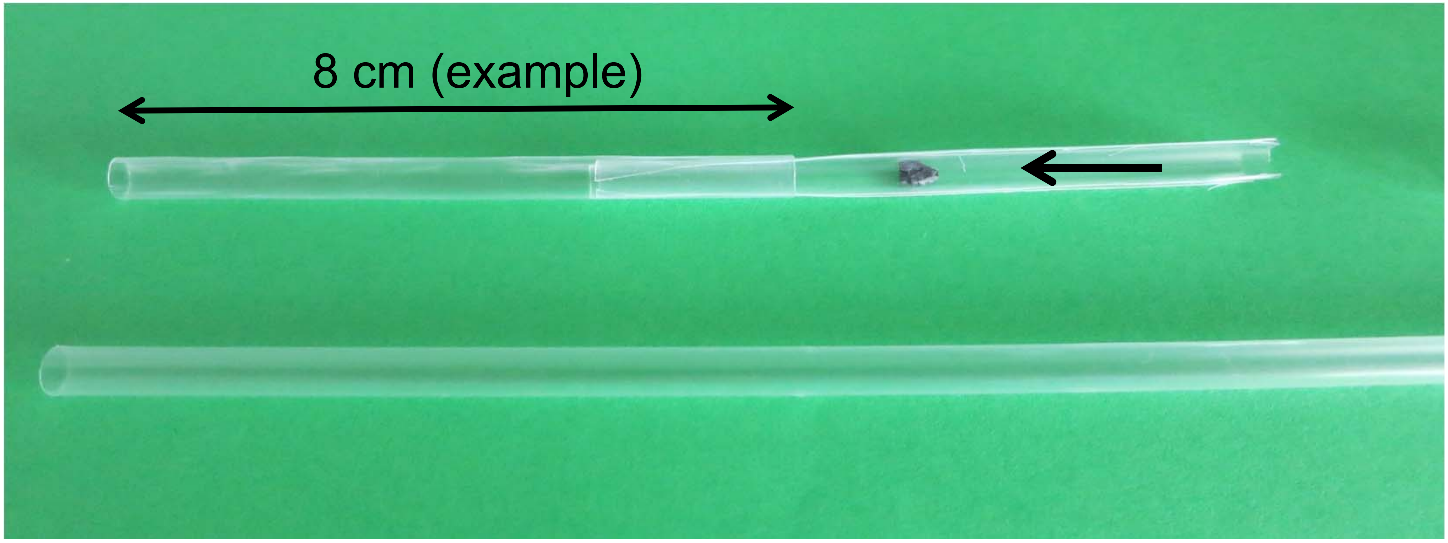
4 A short piece cut from a second straw

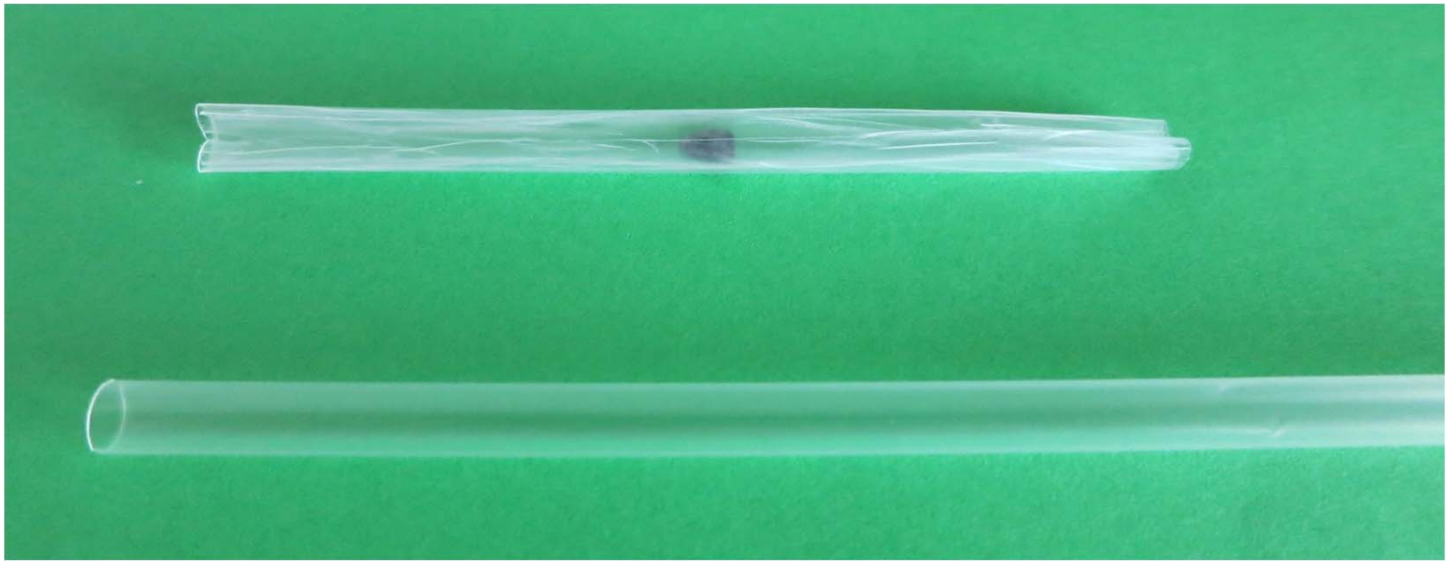
Mounting a sample for magnetic measurements 4 / 7



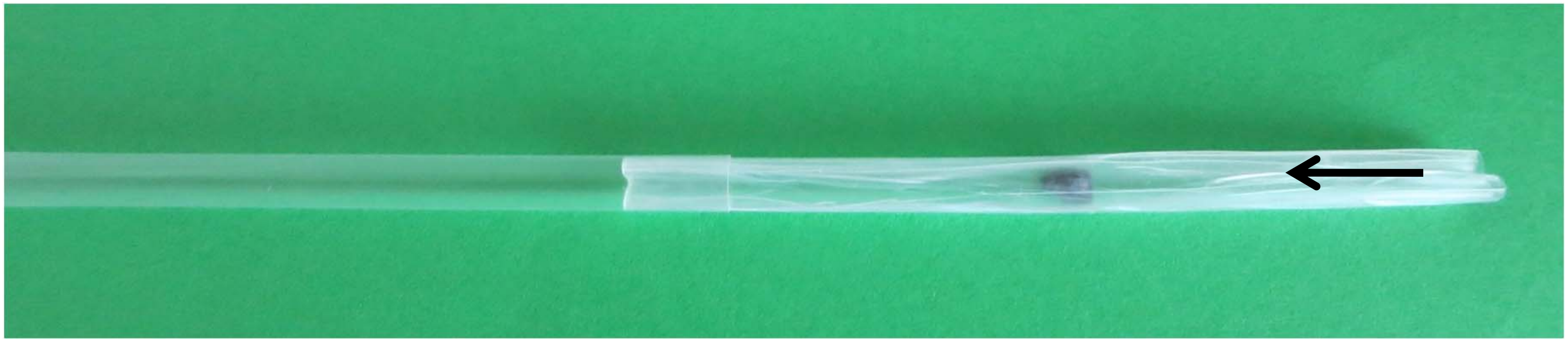


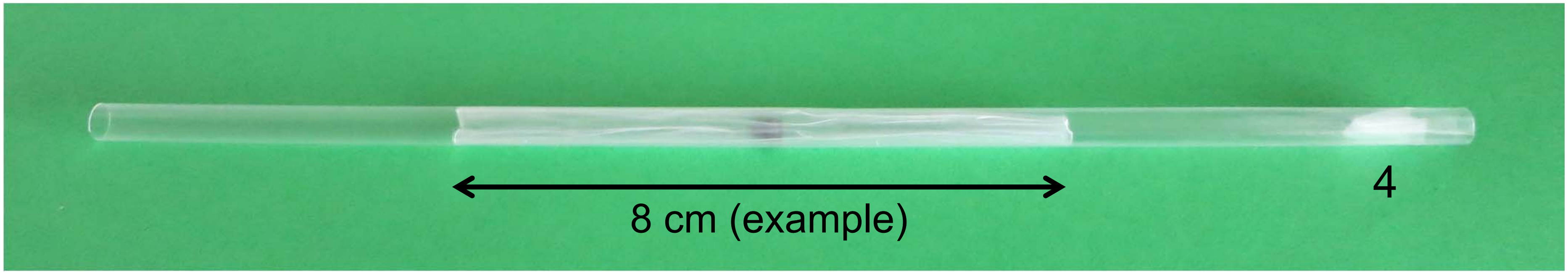
Mounting a sample for magnetic measurements 5 / 7





Mounting a sample for magnetic measurements 6 / 7

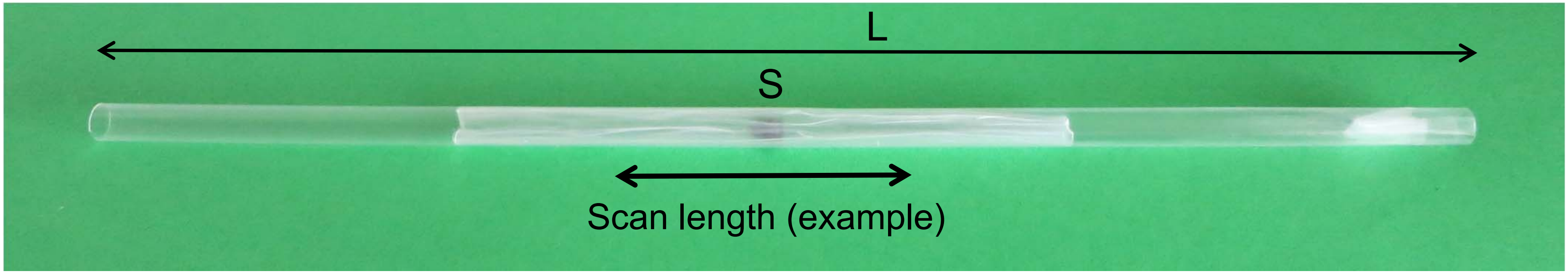




The alumina rod is used to push the 8 cm long part into the whole straw. The short piece (4) was cut from a second straw, bent, and then pushed into the whole straw. It can be used to prevent that something from the sample drops into the bottom of the SQUID magnetometer

Mounting a sample for magnetic measurements 7 / 7

Sample (S) is now ready for a magnetic measurement by a SQUID magnetometer



Advantages of this concept:

- No detectable magnetic moment from the straw material because its mass per length is homogeneously distributed over the scan length
- Clean fixation without any glue

The scan length is for example 4 cm long. Over this length the straw is moved through the pick-up coils (gradiometer) in the SQUID magnetometer.

The appropriate position of the sample (S) and overall length L of the straw depends on the type of the SQUID magnetometer

Part 13 – Measuring magnetic properties of samples by a SQUID magnetometer

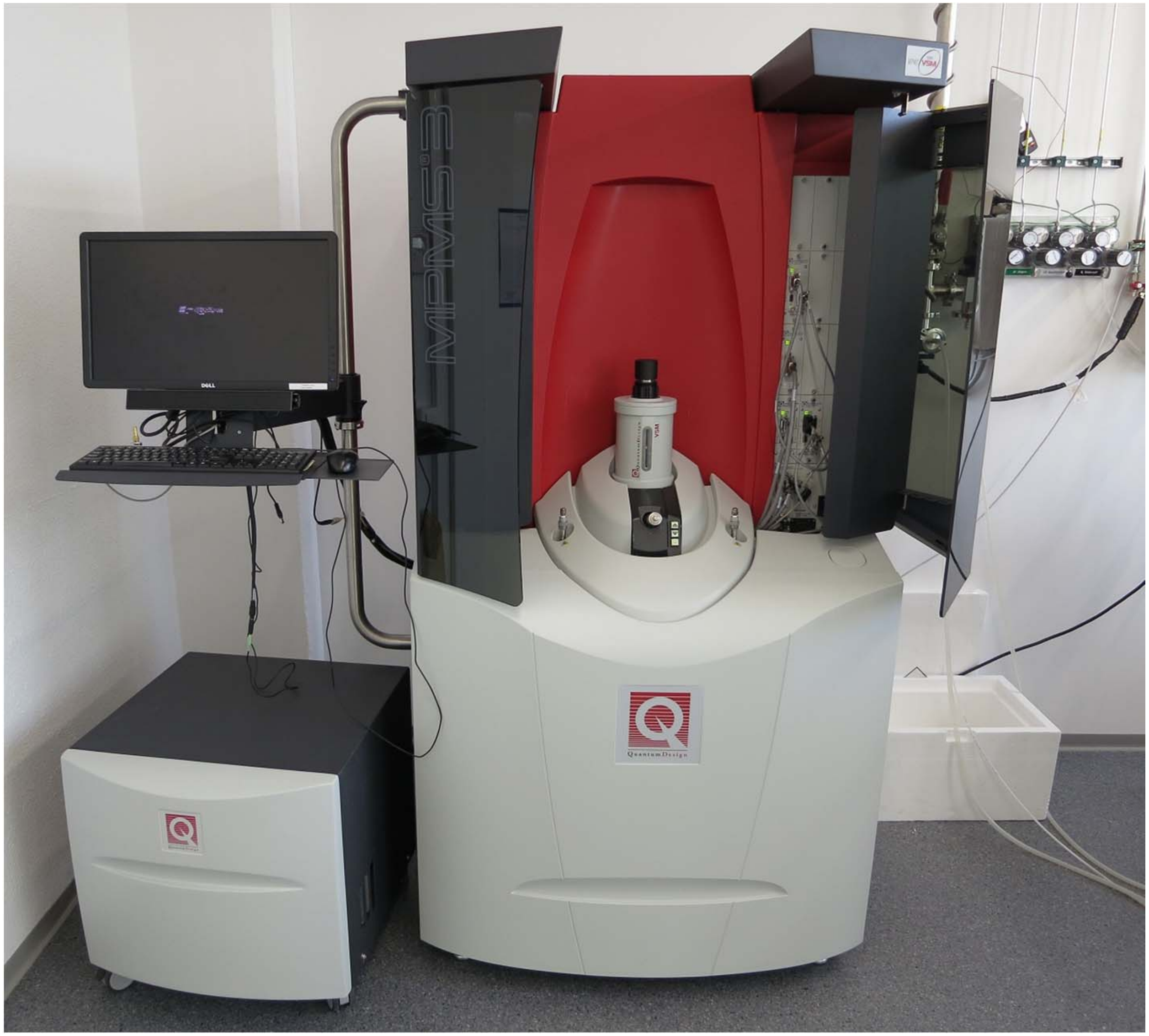
SQUID magnetometer Quantum Design MPMS XL at Paul Scherrer Institute PSI

Acknowledgement

M. Medarde PSI Villigen

M. Morin PSI Villigen

SQUID magnetometer Quantum Design MPMS3 at Paul Scherrer Institute PSI



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Appendix 1

Presentation of the GERO mirror furnace which was used from 1999 – 2007 at the Institute of Physics of the University of Augsburg (Germany) and examples and pictures of melt-grown crystalline oxides

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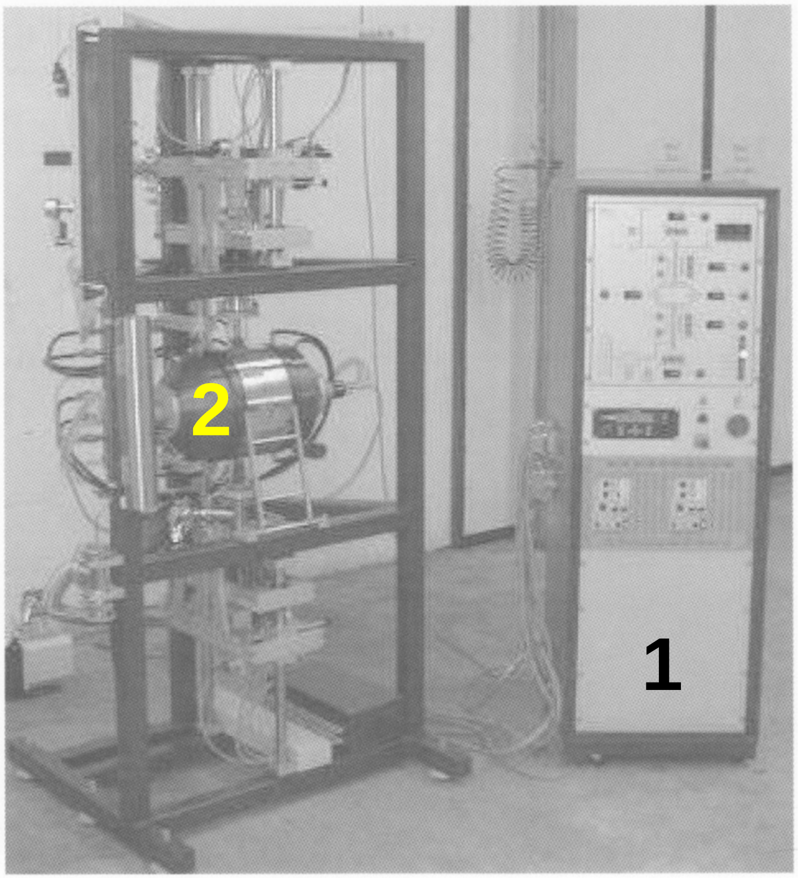
K. Wiedenmann University of Augsburg

and many others from (Carbolite) GERO GmbH and the University of Augsburg !

GERO mirror furnace – General view

Photo from GERO



2 Mirrors in their locked status

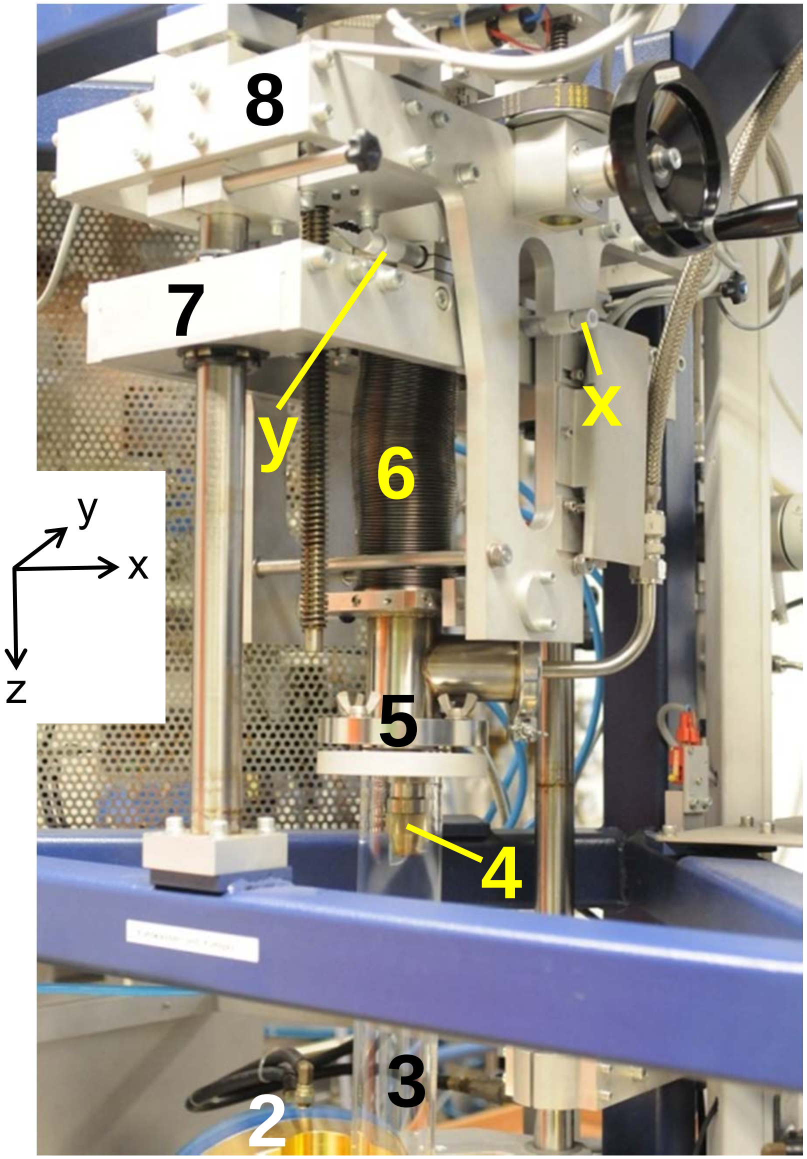
1 Control cabinet

Made by German company GERO in 1998 – Remake of a system which was designed and built at the IBM Zurich Research Laboratory

Special features:

- Direct projection of the image of the molten zone and solid zones by two lenses and two screens, i.e. presence of a front and rear image without using a video camera and monitor
- x-y-position of the feed rod within the quartz glass tube can be adjusted anytime from the outside (see next page), even if the floating zone melting process is running

GERO mirror furnace – A view of the stages above the mirrors



2 Upper part of the left mirror

3 Quartz glass tube

4 Drill chuck within quartz glass tube. The drill chuck (stainless steel and grease-free) is screwed on the upper shaft and is used for the fixation of the feed rod holder.

5 Flange which connects via an O-ring the quartz glass tube with metallic components in a gas-tight manner

6 Metal / Vacuum bellows which is connected with a x-y-positioning stage. The upper shaft is located within the bellows.

x , y Adjusting screws for the x-y-position

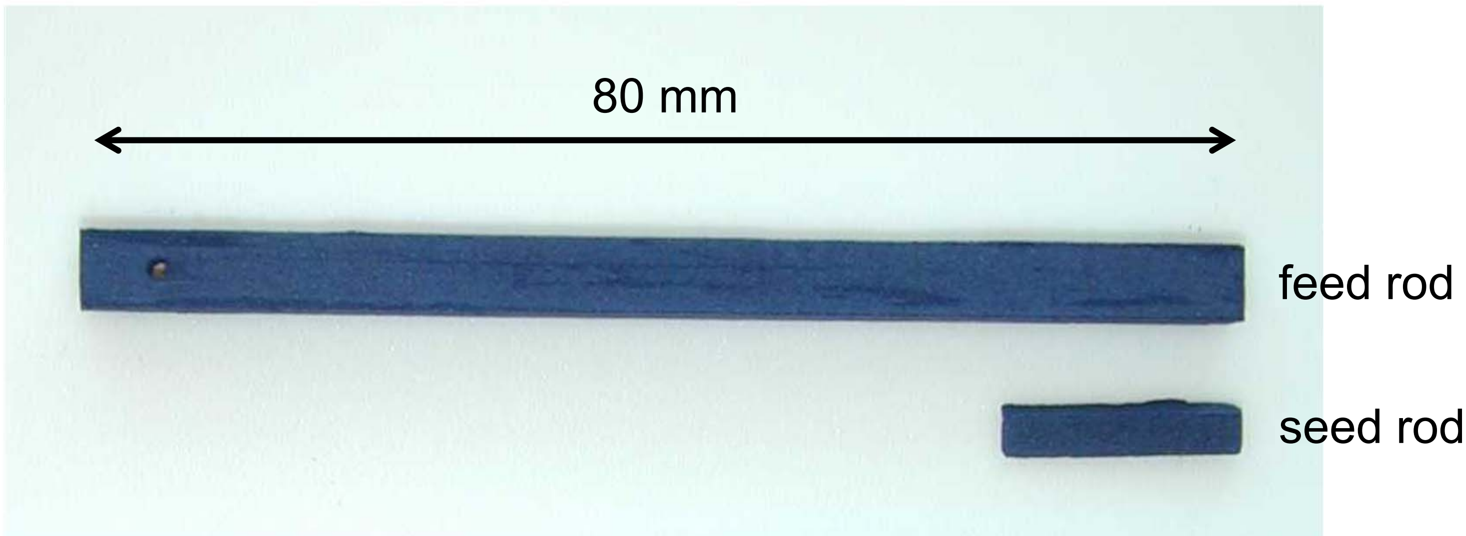
7 , 8 Upper stages

The upper stage (7) comprises a x-y-positioning stage (hardly visible in this picture) which enables from the outside an adjustment of the x-y-position of the upper shaft and feed rod within the quartz glass tube.

Location of furnace: Institute of Physics of the University of Augsburg / Germany • Made by German company GERO in 1998 – Remake of a system which was designed and built at the IBM Zurich Research Laboratory • Photo taken at the University of Augsburg by K. Wiedenmann

Seed and feed rods

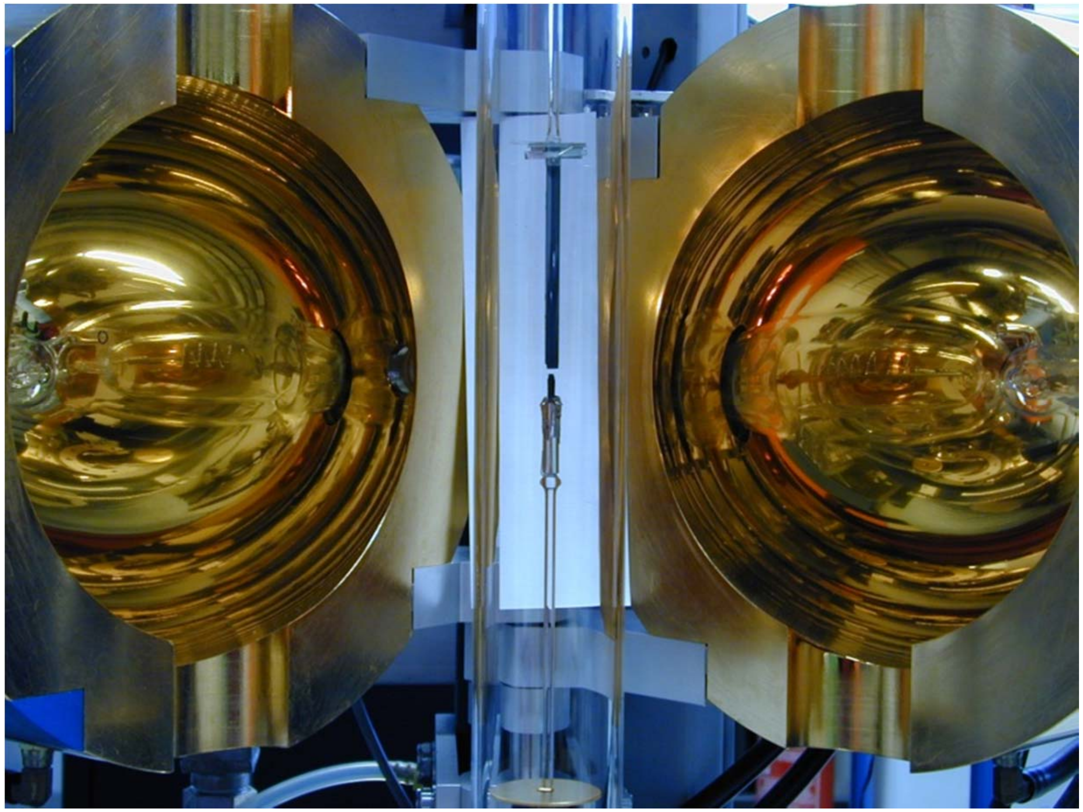
Example of a seed and feed rod which were prepared and used at the Institute of Physics of the University of Augsburg for the GERO mirror furnace



Rectangular sintered polycrystalline rods

Progress in Solid State Chemistry 36 (2008) 253

GERO mirror furnace – A closer view when the mirrors are unlocked



Mirrors unlocked

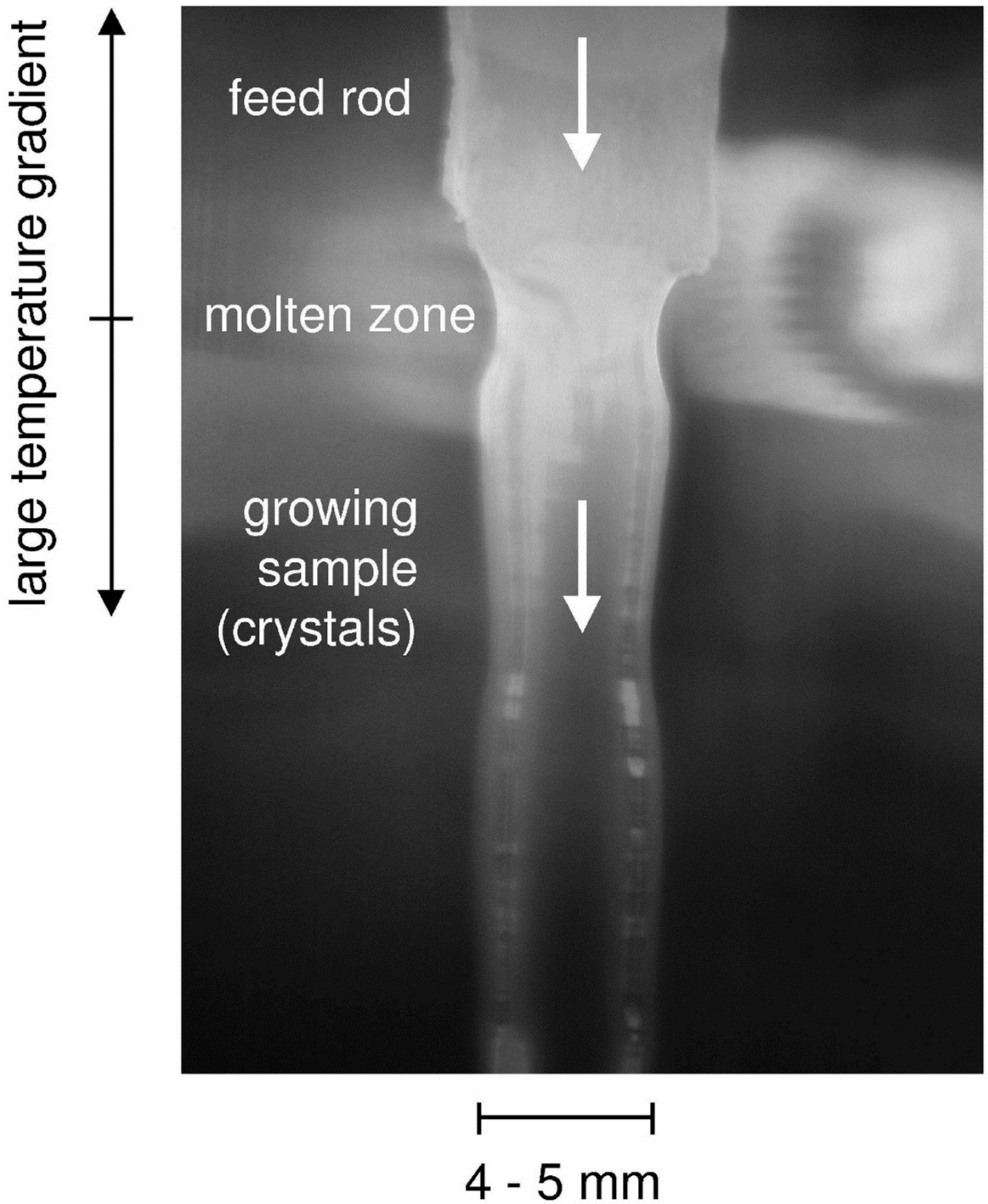
Sample holders and seed and feed rod inside quartz glass tube

Location of furnace: Institute of Physics of the University of Augsburg / Germany

Made by German company GERO in 1998 – Remake of a system which was designed and built at the IBM Zurich Research Laboratory

Photo taken at the University of Augsburg by K. Wiedenmann

GERO mirror furnace – Snap-shot from a floating zone melting process



Single phase crystals can be readily obtained if the solidification is (nearly) congruent, i.e. if the melt and the solidified material have (nearly) the same chemical composition. If this is true depends on the chemical composition and is often not known or predictable, especially for unexplored chemical compositions.

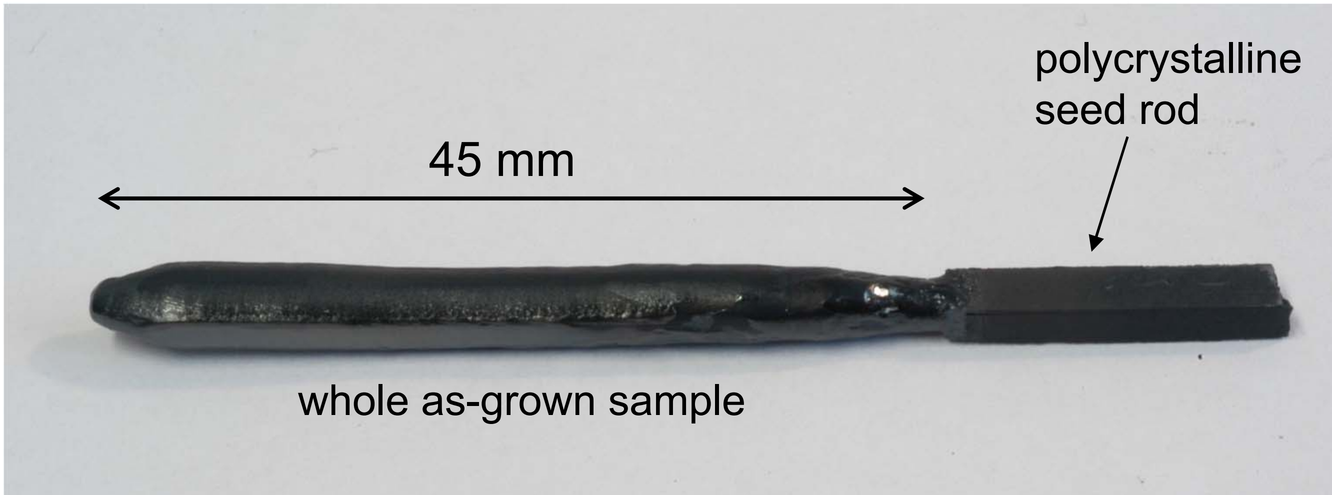
Photo taken at the University of Augsburg by K. Wiedenmann

Examples of melt-grown oxides prepared by the GERO mirror furnace

$Ca_4EuNb_5O_{17}$ – Eu^{2+} / $4f^{7}$ and $Nb^{4.8+}$ / $4d^{0.2}$

grown with 15 mm / h in argon • blue-black electrical conductor

structure type n = 5 of the layered perovskite-related series $A_nB_nO_{3n+2} = ABO_x$



part of the as-grown sample

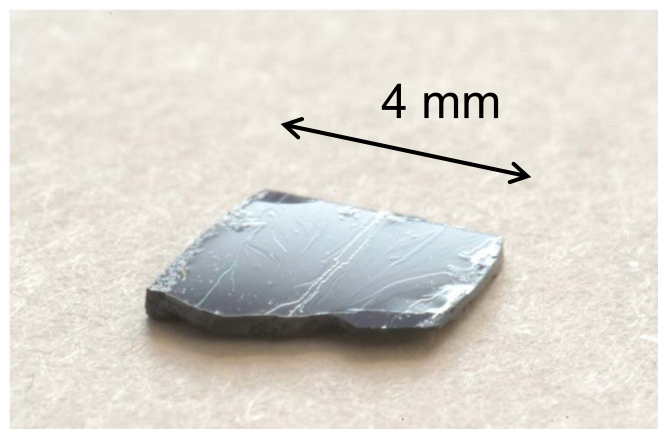
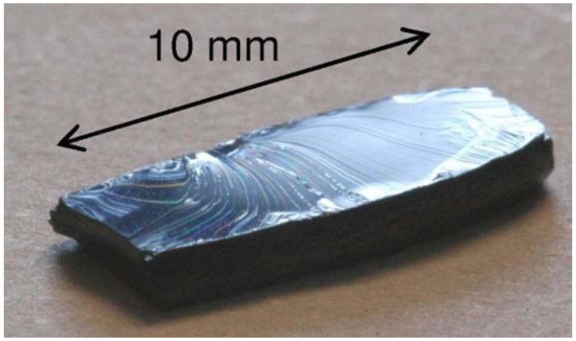


plate-like crystal obtained by crushing / cleaving the as-grown sample

Progress in Solid State Chemistry 36 (2008) 253

Examples of melt-grown oxides prepared by the GERO mirror furnace

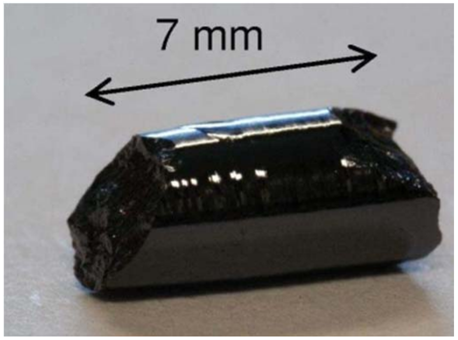
Plate-like crystal and part of as-grown sample of brown-black antiferromagnetic insulators grown with 15 mm / h in air



$LaSrFeO_4$ – Fe^{3+} / $3d^5$

structure type j = 1 of layered perovskite-related $A_{j+1}B_jO_{3j+1}$

Ruddlesden-Popper phase



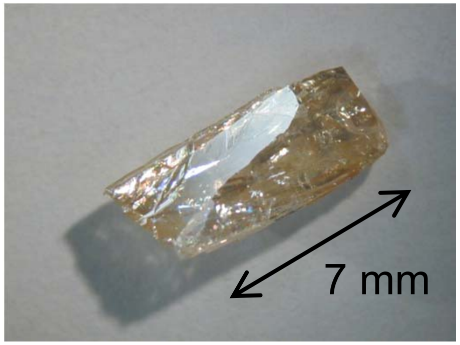
$LaFeO_3$ – Fe^{3+} / $3d^5$

structure type perovskite ABO_3

Progress in Solid State Chemistry 36 (2008) 253

Examples of melt-grown oxides prepared by the GERO mirror furnace

Niobates of the layered hexagonal perovskite-related series $A_mB_{m-1}O_{3m}$



part of as-grown sample

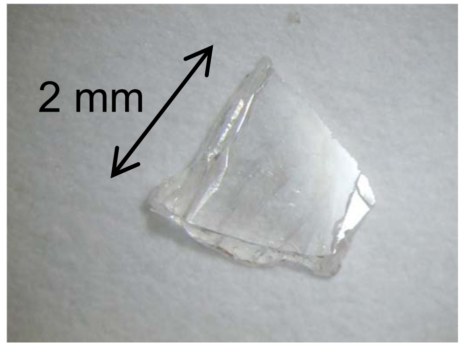


plate-like crystal

$Sr_5Nb_4O_{15}$ – Nb^{5+} / $4d^0$

grown with 15 mm / h in air

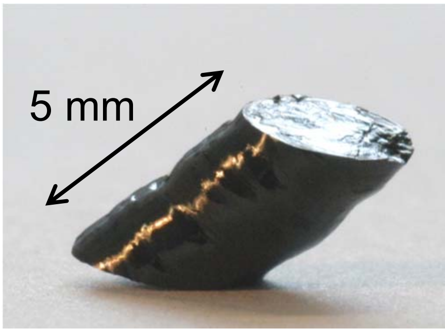
structure type m = 5

yellow transparent insulator

Progress in Solid State Chemistry 36 (2008) 253

Examples of melt-grown oxides prepared by the GERO mirror furnace

Niobates of the layered hexagonal perovskite-related series $A_mB_{m-1}O_{3m}$



part of as-grown sample

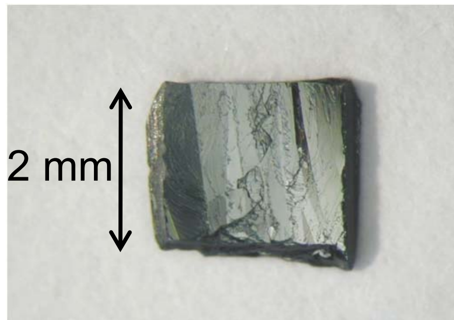


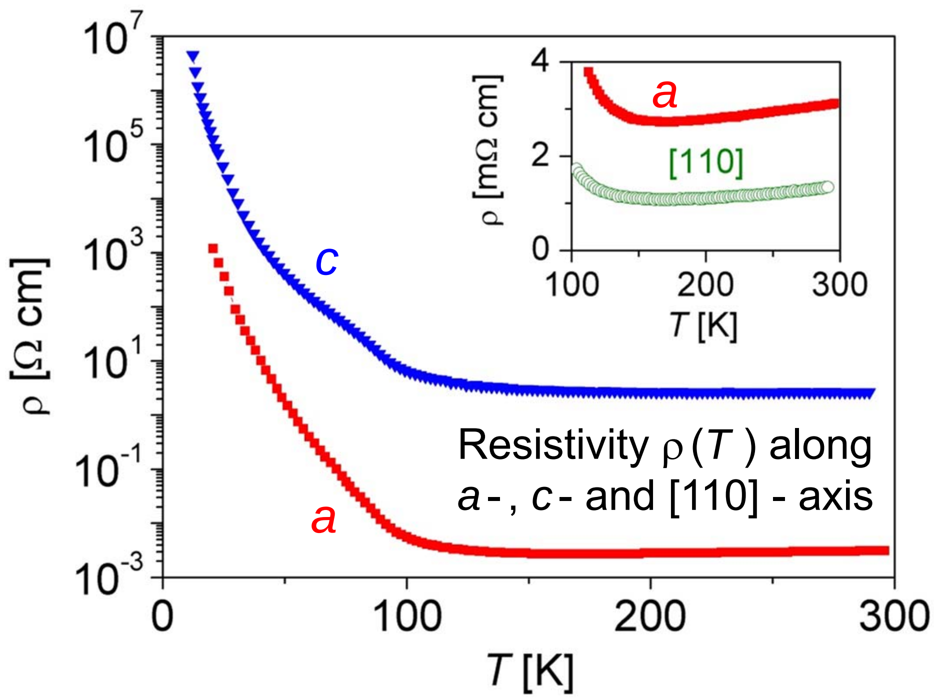
plate-like crystal

$Sr_6Nb_5O_{18.07}$ – $Nb^{4.83+}$ / $4d^{0.17}$

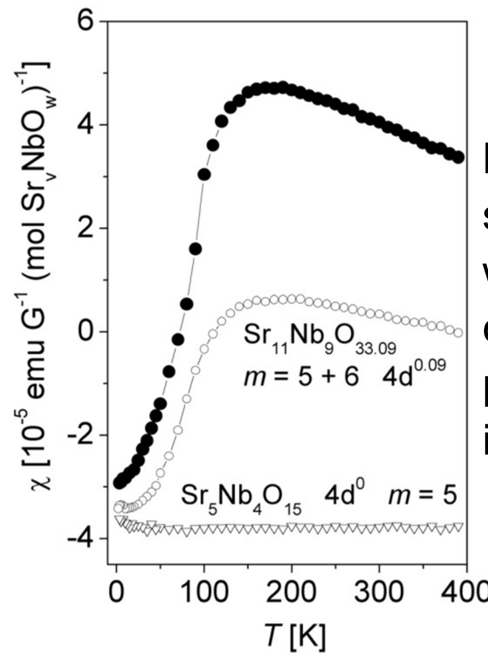
grown with 8 mm / h in argon

structure type m = 6

blue-black quasi-2D metal and temperature-driven metal-to-semiconductor transition at 160 K



Resistivity $\rho(T)$ along a-, c- and [110] - axis

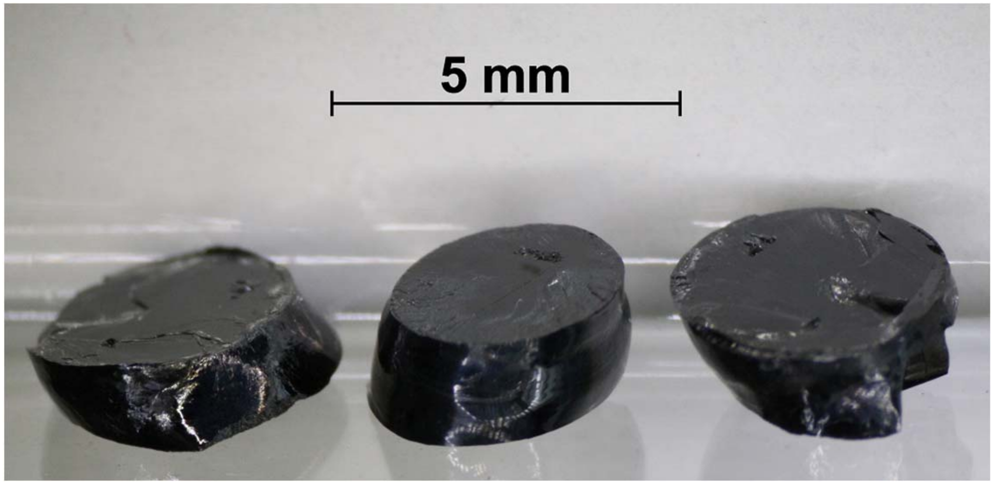


Magnetic susceptibility $\chi(T)$ without Curie contribution from paramagnetic impurities

Progress in Solid State Chemistry 36 (2008) 253

Examples of melt-grown oxides prepared by the GERO mirror furnace

Niobates of the layered hexagonal perovskite-related series $A_mB_{m-1}O_{3m}$



$Sr_{4.6}La_{0.4}Nb_4O_{15.06}$ – $Nb^{4.93+}$ / $4d^{0.07}$

grown with (15 - 6) mm / h by reducing the fully oxidized Nb^{5+} composition $Sr_{4.6}La_{0.4}Nb_4O_{15.20}$ in 98 % Ar + 2 % H_2

structure type m = 5

blue-black electrical conductor

Observation at layered structures: Usually the layers grow parallel or 45 degrees declined to the axial direction of the as-grown sample

Concerning own experiments this material is so far the only example where the layers did grow perpendicular to the axial direction of the as-grown specimen !

Progress in Solid State Chemistry 36 (2008) 253

Samples prepared at the University of Augsburg - Photo taken at the ETH Zurich

Examples of melt-grown oxides prepared by the GERO mirror furnace

Layered perovskite-related Dion-Jacobson phases $A'A_{k-1}B_kO_{3k+1}$ without alkali metals

part of as-grown sample

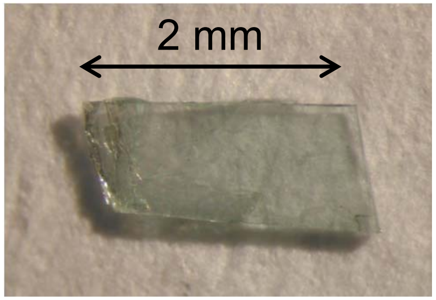


plate-like crystal

$BaLa_2Ti_3O_{10}$ – Ti^{4+} / $3d^0$

grown in air

structure type k = 3

light green transparent insulator

Progress in Solid State Chemistry 36 (2008) 253

Examples of melt-grown oxides prepared by the GERO mirror furnace

Layered perovskite-related Dion-Jacobson phases $A'A_{k-1}B_kO_{3k+1}$ without alkali metals

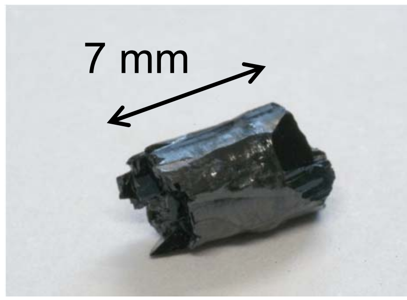
Blue-black anisotropic 3D metals with quasi-2D (layered) crystal structure

$BaCa_{0.6}La_{0.4}Nb_2O_7$

$Nb^{4.8+}$ / $4d^{0.2}$

grown in argon

structure type k = 2



part of as-grown sample

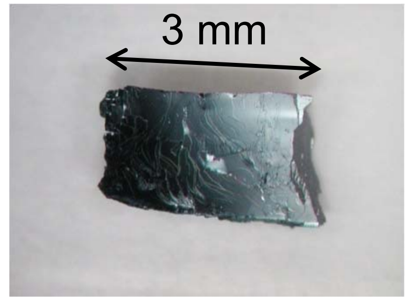
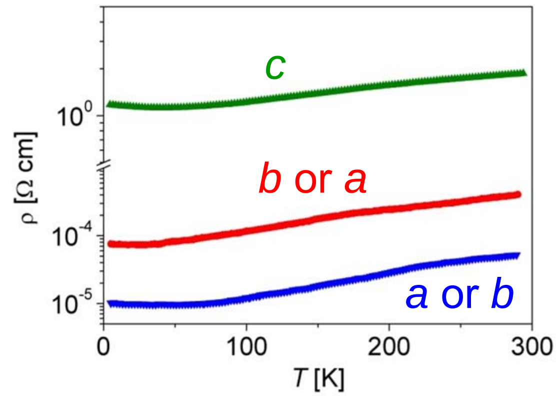


plate-like crystal



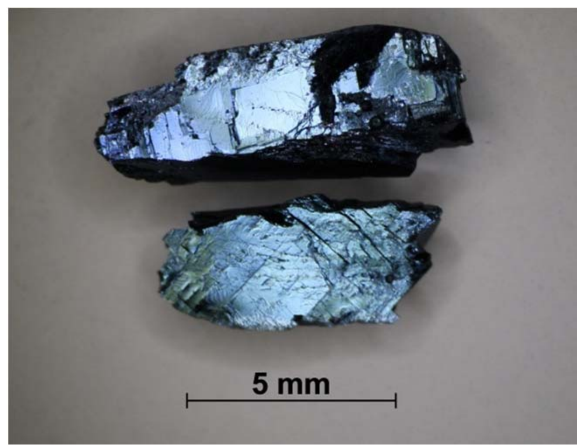
Resistivity ρ(*T*) along *a*- , *b*- and *c*-axis

$BaCa_2Nb_3O_{10.07}$

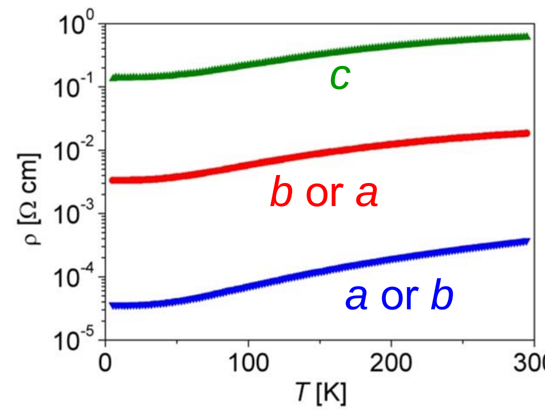
$Nb^{4.71+}$ / $4d^{0.29}$

grown in argon

structure type k = 3



parts of as-grown sample



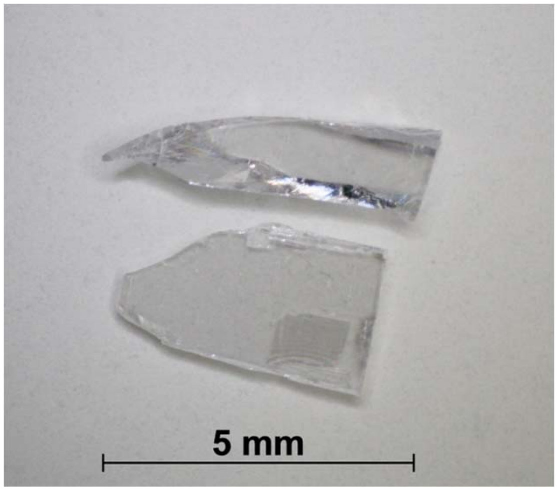
Progress in Solid State Chemistry 36 (2008) 253

Samples prepared at the University of Augsburg - Photo of $BaCa_2Nb_3O_{10.07}$ taken at the ETH Zurich

Examples of melt-grown oxides prepared by the GERO mirror furnace

Layered perovskite-related $A_nB_nO_{3n+2} = ABO_x$

Plate-like crystals / Pieces from as-grown samples



$Sr_4Nb_4O_{14} = SrNbO_{3.50}$

Nb^{5+} / $4d^0$

Grown in air

White transparent
high-T_c ferroelectric insulator
$T_c = 1615$ K

Structure type $n = 4$

$Sr_{3.2}La_{0.8}Nb_4O_{14} = Sr_{0.8}La_{0.2}NbO_{3.50}$

$Nb^{4.8+}$ / $4d^{0.2}$

Grown in argon

Weakly metallic quasi-1D conductor
Optical spectroscopy indicates presence of ferro-electric soft mode → Is this a ferroelectric metal ?

Structure type $n = 4$

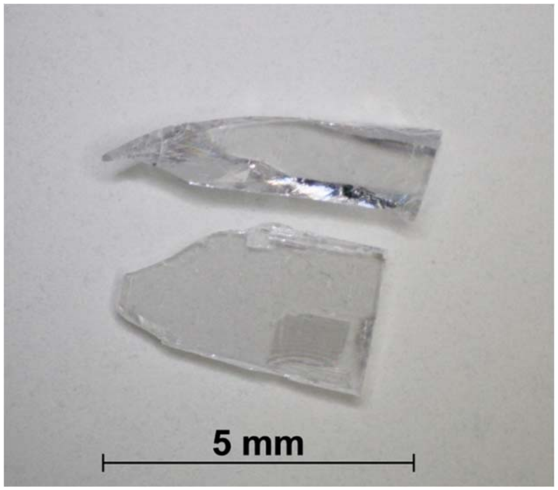
Progress in Solid State Chemistry 29 (2001) 1 and 36 (2008) 253 • Physical Review B 70 (2004) 245123

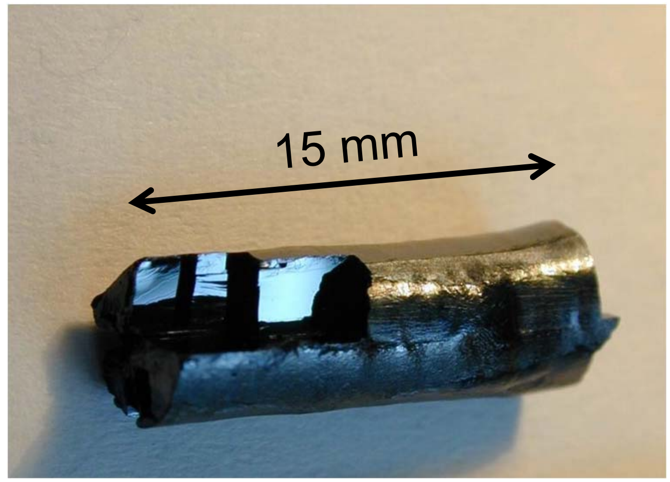
Samples prepared at the University of Augsburg - Photos taken at the ETH Zurich

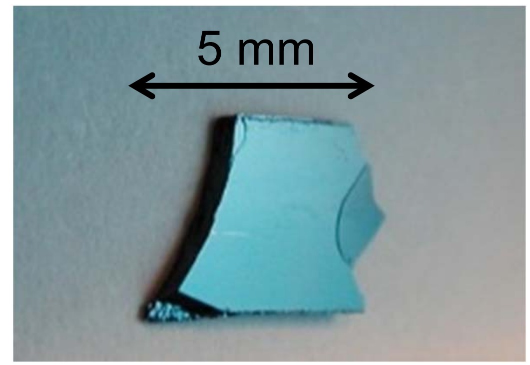
Examples of melt-grown oxides prepared by the GERO mirror furnace

Layered perovskite-related $A_nB_nO_{3n+2} = ABO_x$

Plate-like crystals / Pieces from as-grown samples







$Sr_4Nb_4O_{14} = SrNbO_{3.50}$

Nb^{5+} / $4d^0$

Grown in air

White transparent
high-T_c ferroelectric insulator
T_c = 1615 K

Structure type n = 4

$Sr_5Nb_5O_{17.05} = SrNbO_{3.41}$

$Nb^{4.82+}$ / $4d^{0.18}$

Grown in argon

Blue-black quasi-1D metal
Quasi-1D metals of the type $A_nB_nO_{3n+2} = ABO_x$ might have a potential to create new superconductors

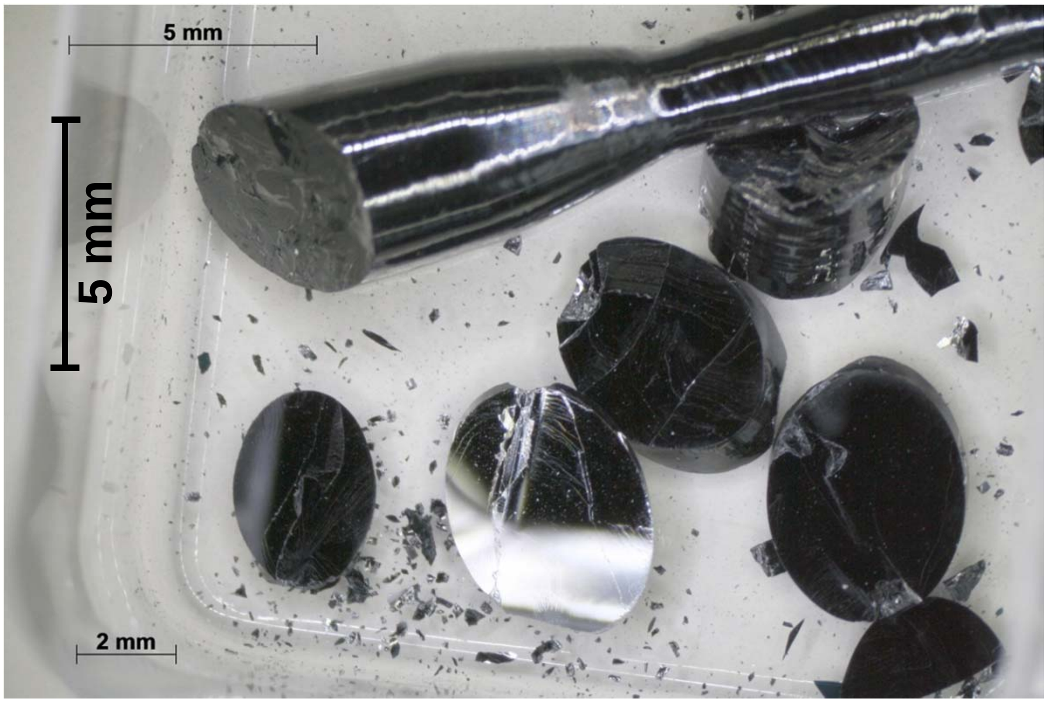
Structure type n = 5

Progress in Solid State Chemistry 29 (2001) 1 and 36 (2008) 253
Physical Review B 70 (2004) 245123 • Physical Review Letters 89 (2002) 236403
Samples prepared at the University of Augsburg - Photo of $Sr_4Nb_4O_{14}$ taken at the ETH Zurich

Examples of melt-grown oxides prepared by the GERO mirror furnace

Layered perovskite-related $A_nB_nO_{3n+2} = ABO_x$

Pieces from as-grown sample



$La_{0.95}TiO_{3.38}$

$Ti^{3.90+}$ / $3d^{0.10}$

Grown in argon

Black electrical conductor (quasi-1D metal ?)

Structure type n = 4.5 (!)

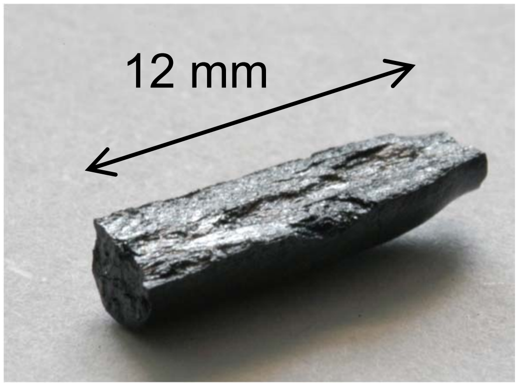
Non-stoichiometric, i.e. significant *A* and O site deficiencies with respect to ideal n = 4.5 type composition $ABO_{3.44}$ or $LaTiO_{3.44}$

Progress in Solid State Chemistry 36 (2008) 253

Sample prepared at the University of Augsburg - Photo taken at the ETH Zurich

Examples of melt-grown oxides prepared by the GERO mirror furnace

$A_nB_nO_{3n+2}$ = ABO_x samples which do not appear in form of large and nice crystals



part of as-grown sample

$La_{0.6}Ca_{0.4}Ti_{0.6}Nb_{0.4}O_{3.40}$ – $d^{0.2}$

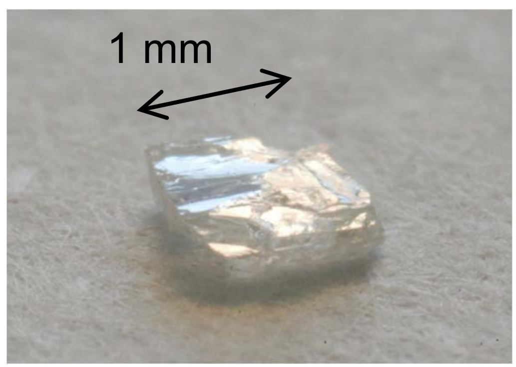
grown by reducing the fully oxidized Ti^{4+} and Nb^{5+} composition $La_{0.6}Ca_{0.4}Ti_{0.6}Nb_{0.4}O_{3.50}$ in 98 % Ar + 2 % H_2

structure type non-stoichiometric / oxygen-deficient n = 4

blue-black electrical conductor

polycrystalline appearance

part of as-grown sample



small piece
obtained by cleaving

$Sr_{0.67}La_{0.33}TaO_{3.67}$ – Ta^{5+} / $5d^{0}$

grown in air

structure type n = 3

light colored transparent insulator

only small and
irregular shaped crystals

Progress in Solid State Chemistry 36 (2008) 253

Examples of melt-grown oxides prepared by the GERO mirror furnace

Layered perovskite-related $A_nB_nO_{3n+2}$ = ABO_x with B = Ti^{4+} / $3d^0$ and Fe^{3+} / $3d^5$

Pieces of as-grown samples which were grown in air with 15 mm / h

$La_5Ti_4FeO_{17}$ (structure type n = 5)

$La_6Ti_4Fe_2O_{20}$ (structure type n = 6)

These brown-black insulators are most probably antiferroelectric (n = 5) or ferroelectric (n = 6) and their magnetic properties are discussed in connection with the search for new materials which are simultaneously ferroelectric and ferromagnetic

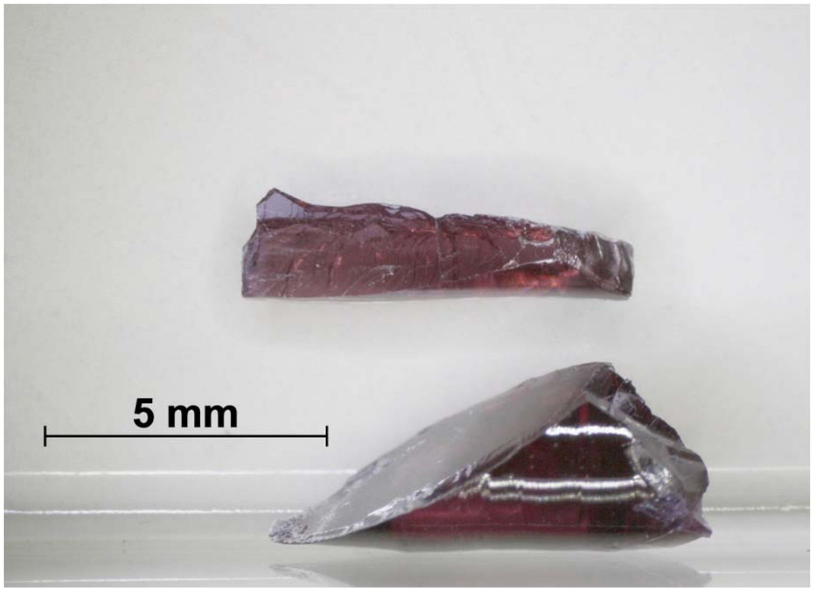
Progress in Solid State Chemistry 36 (2008) 253 • Journal of Physics: Condensed Matter 25 (2013) 076003

Samples prepared at the University of Augsburg - Photos taken at the ETH Zurich

Examples of melt-grown oxides prepared by the GERO mirror furnace

Layered perovskite-related $A_nB_nO_{3n+2}$ = ABO_x type insulators with beautiful colors

Pieces from as-grown samples which were grown with 15 mm / h in air



$Nd_4Ti_4O_{14}$ = $NdTiO_{3.50}$

Nd^{3+} / $4f^3$ and Ti^{4+} / $3d^0$

structure type n = 4

$Pr_5Ti_4AlO_{17}$ = $PrTi_{0.8}Al_{0.2}O_{3.40}$

Pr^{3+} / $4f^2$ and Ti^{4+} / $3d^0$

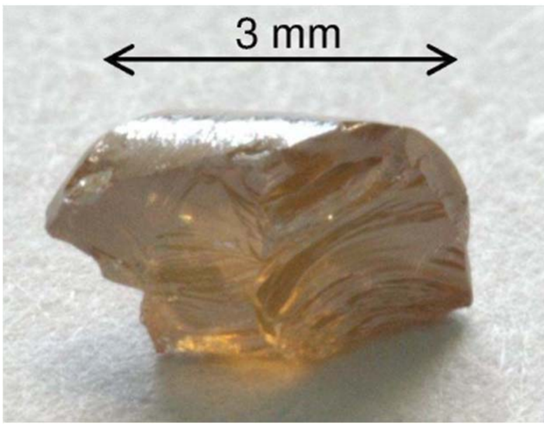
structure type n = 5

Progress in Solid State Chemistry 36 (2008) 253

Samples prepared at the University of Augsburg - Photos taken at the ETH Zurich

Examples of melt-grown oxides prepared by the GERO mirror furnace

Pieces from as-grown samples which are structurally not related to perovskite



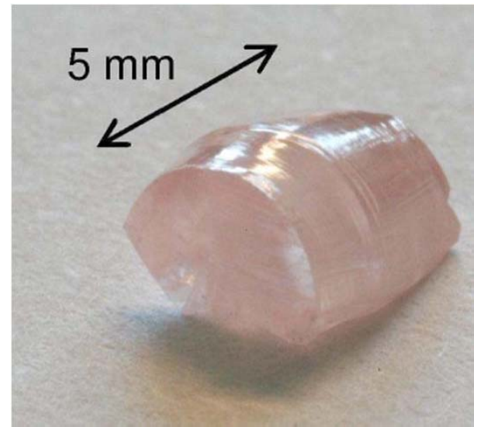
$Sm_2Ti_2O_7 = SmTiO_{3.50}$

Sm^{3+} / $4f^5$ and Ti^{4+} / $3d^0$

grown with 15 mm / h in air

structure type pyrochlore

yellow transparent insulator



$EuNbO_4$

Eu^{3+} / $4f^6$ and Nb^{5+} / $4d^0$

grown with 10 mm / h in air

structure type fergusonite

pink transparent insulator

Progress in Solid State Chemistry 36 (2008) 253

Appendix 2

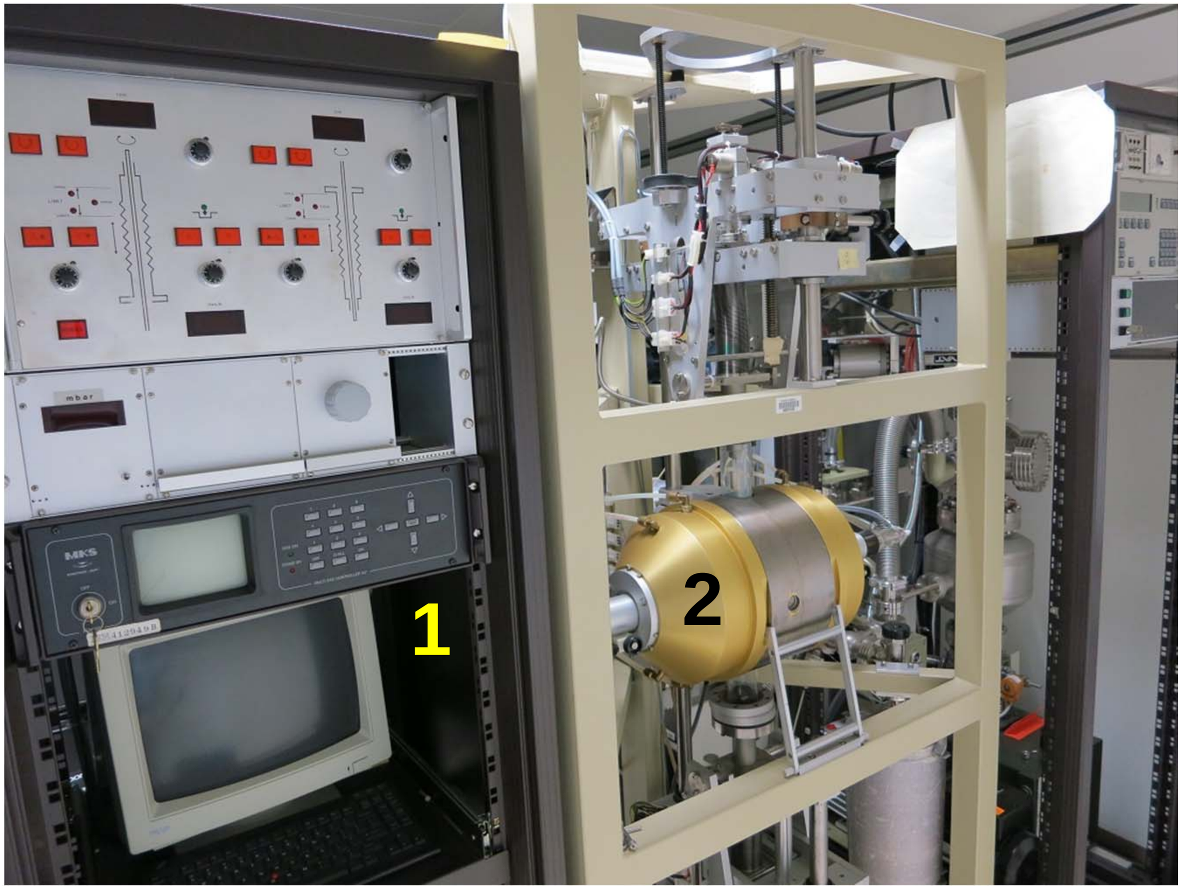
Presentation of the IBM mirror furnace which was used from 1989 – 1992 at the IBM Zurich Research Laboratory (Switzerland) and examples and pictures of melt-grown crystalline oxides

Acknowledgement

J. G. Bednorz IBM Zurich Research Laboratory
D. Widmer IBM Zurich Research Laboratory
and many others from the IBM Zurich Research Laboratory !

A. Reller University of Augsburg (formerly at University of Zurich)
H. Schmalle University of Zurich
F. Waldner University of Zurich
T. Williams Monash University (formerly at University of Zurich)

IBM mirror furnace – General view



Location of furnace:
IBM Zurich Research Laboratory (Switzerland)

Made by IBM and other companies in 1985 and 1986 based on a design by J.G. Bednorz and D. Widmer

Photo taken at the IBM Zurich Research Laboratory in April 2013

2 Mirrors in their locked status

1 Control cabinet

IBM mirror furnace – A closer view when the mirrors are unlocked

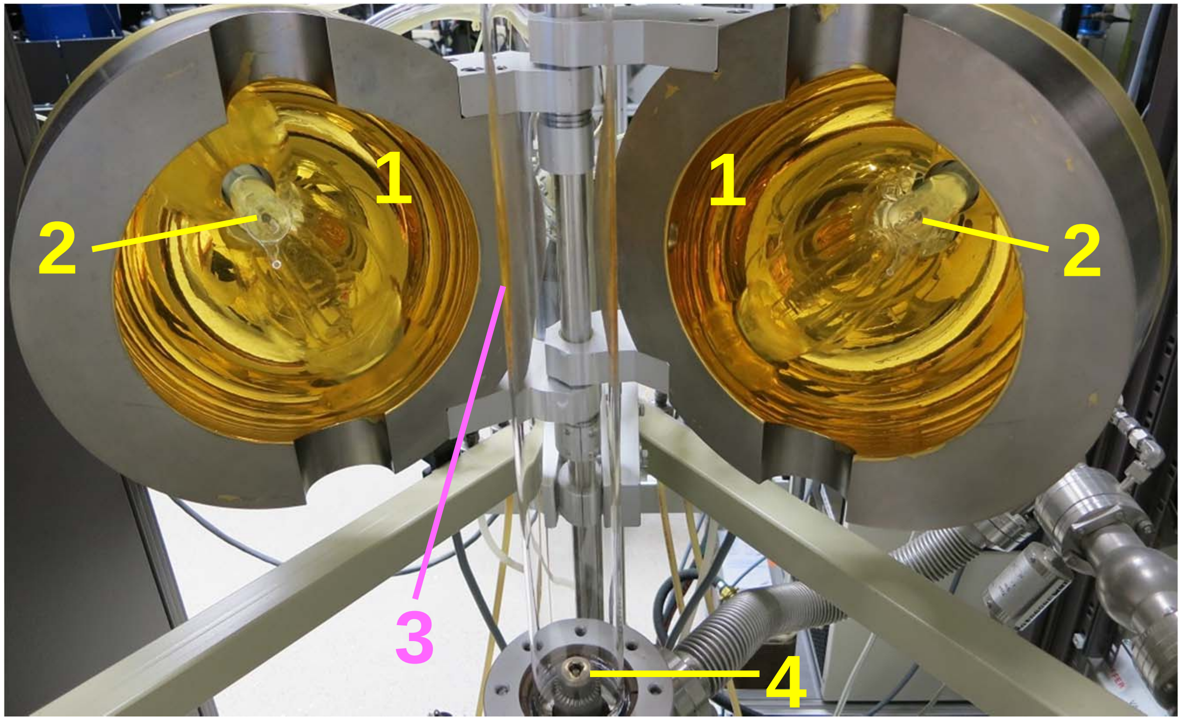


Photo taken at the IBM Zurich Research Laboratory in April 2013

1 Elliptical and gold-coated mirror

2 Halogen lamp, maximum power 1000 W

3 Quartz glass tube

4 Inside quartz glass tube: Drill chuck which is screwed on the lower shaft. The drill chuck is used to clamp the sample holder in which the seed rod is fixed. The same desgin is used at the upper shaft for the feed rod.

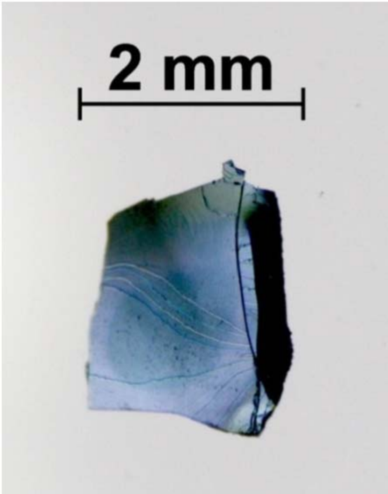
- Mirrors and lamps are cooled by cooling water and a flow of compressed air
- Mirrors are gold-coated because that enhances their infrared reflectivity
- Heating-up and melting of the feed and seed rod material takes mainly place by its infrared absorption

IBM mirror furnace – Special features

- Direct projection of the image of the molten zone and solid zones by two lenses and two screens, i.e. presence of a front and rear image without using a video camera and monitor

- x-y-position of the feed rod within the quartz glass tube can be adjusted anytime from the outside even if the floating zone melting process is running. Some technical details of that construction are shown in appendix 1 which presents the GERO mirror furnace that is based on the IBM design.

Examples of melt-grown oxides prepared by the IBM mirror furnace



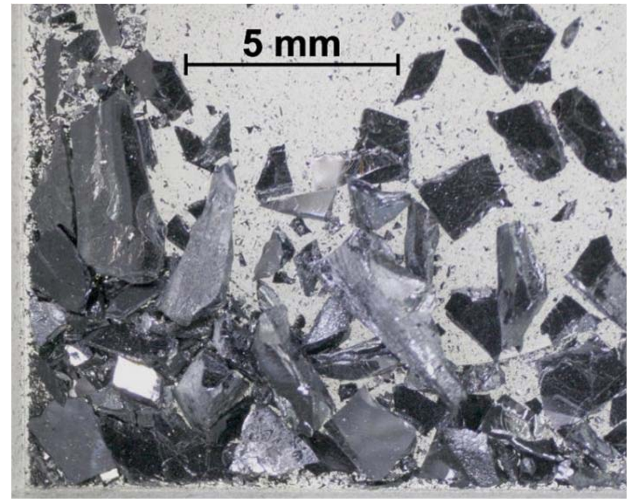
Sr_2RuO_4 – Ru^{4+} / $4d^4$

Structure type $j = 1$
of $A_{j+1}B_jO_{3j+1}$

Grown under air

Samples prepared in 1991 at the IBM Zurich Research Laboratory

Photos taken at ETH Zurich in 2013



Original intention: Try to prepare $j = 2$ type $Sr_3Ru_2O_7$ but melt-grown samples contained always $j = 1$ and not $j = 2$

Sr – Ru – O experiments difficult because of strong evaporation of RuO_x → Nevertheless inside nice crystals

Resistivity measurements 300 K – 4 K on Sr_2RuO_4 crystals revealed metallic behavior along layers

Thin films of the high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$ were deposited on the *ab* - plane of Sr_2RuO_4 crystals
→ In crystalline form Sr_2RuO_4 was the first metallic substrate for the epitaxial growth of high-T_c superconductors

Later Y. Maeno et al. did search for superconductivity in Sr_2RuO_4 below 4 K → Indications for superconductivity below 1 K in polycrystalline samples but zero resistivity was not achieved → Above-mentioned crystals were still available and revealed unambiguous presence of superconductivity with $T_c \sim 1$ K. Despite of its low T_c it gained considerable attention because of its unconventional superconducting properties (spin-triplet pairing)

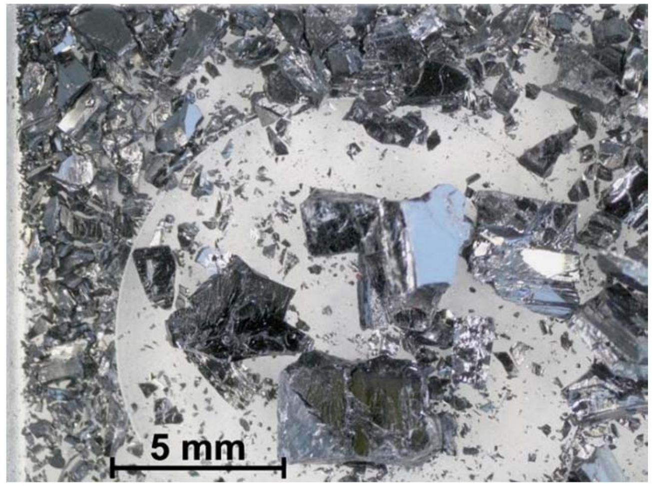
Isostructural to $(La,Ba)_2CuO_4$ which is the parent compound of high-T_c superconductors
in which J. G. Bednorz and K. A. Müller discovered in 1986 superconductivity up to 30 K

Applied Physics Letters 60 (1992) • Nature 372 (1994) 532 • 1138 Physics Today 54 (2001) 42
Progress in Solid State Chemistry 30 (2002) 103 • Reviews of Modern Physics 75 (2003) 657 • Physica C 514 (2015) 339

Examples of melt-grown oxides prepared by the IBM mirror furnace

$La_5Ti_5O_{17}$ – $Ti^{3.8+}$ / $3d^{0.2}$

Grown under argon • Structure type n = 5 of layered perovskite-related $A_nB_nO_{3n+2}$



Examples of crystalline pieces of $La_5Ti_5O_{17}$ which were obtained by crushing the as-grown sample

Samples prepared at the IBM Zurich Research Laboratory

Photos taken at the ETH Zurich

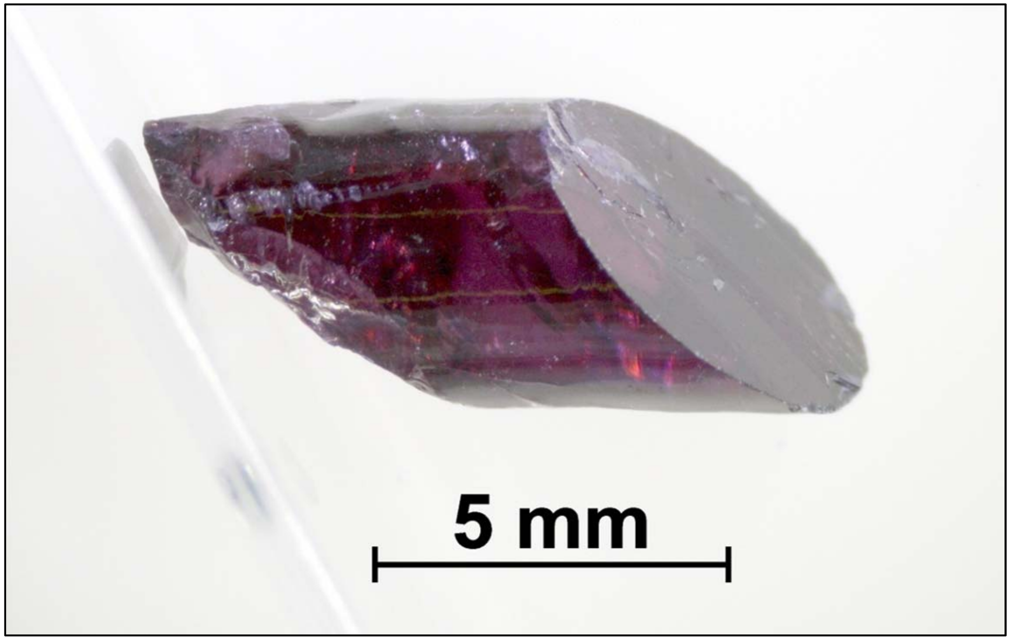
$La_5Ti_5O_{17}$ was prepared at the IBM Zurich Research Laboratory and later also at the University of Augsburg. The crystals did reveal that $La_5Ti_5O_{17}$ is a quasi-1D metal. A recent study indicates within the crystallographic unit cell the presence of metal-insulator-like interfaces which are similar to those which are realized in thin film heterostructures. Electrical conductors of the structure type $A_nB_nO_{3n+2}$ might have a potential to create new superconductors.

Advanced Materials 25 (2013) 218 • Progress in Solid State Chemistry 36 (2008) 253 and 29 (2001) 1
Physical Review B 69 (2004) 224105 • Acta Crystallographica C 59 (2003) i15 • Physical Review B 67 (2003) 035105 and B 74 (2006) 054105 • Journal of Solid State Chemistry 103 (1993) 375 and 93 (1991) 534

Examples of melt-grown oxides prepared by the IBM mirror furnace

$Nd_2Ti_2O_7 = Nd_4Ti_4O_{14}$ – Ti^{4+} / $3d^0$

Grown under air • Structure type n = 4 of layered perovskite-related $A_nB_nO_{3n+2}$



Example of a crystalline piece of $Nd_4Ti_4O_{14}$ which was obtained by crushing the as-grown sample

Sample prepared at the IBM Zurich Research Laboratory

Photo taken at the ETH Zurich

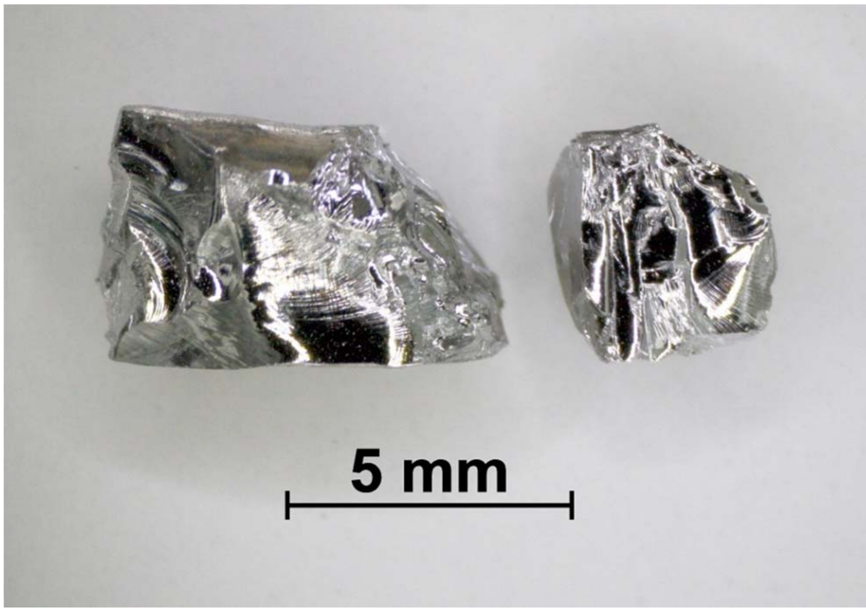
$Nd_2Ti_2O_7 = Nd_4Ti_4O_{14}$ is a violet and transparent high-T_c ferroelectric insulator with T_c > 1770 K

Japanese Journal of Applied Physics 13 (1974) 1473
Progress in Solid State Chemistry 36 (2008) 253

Examples of melt-grown oxides prepared by the IBM mirror furnace

TiO_x with x = 0.27

Grown under argon • Structure type α-Ti or $TiO_{0.33}$ = Ti_3O



Examples of crystalline pieces of $TiO_{0.27}$ which were obtained by crushing the as-grown sample

Samples prepared at the
IBM Zurich Research Laboratory

Photo taken at the ETH Zurich

Oxygen has an unusually large solubility in α-Ti. It ranges from x = 0 to x $\approx$ 0.5. For x $\approx$ 0.33 and x $\approx$ 0.5 there is an ordered phase Ti_3O and Ti_2O, respectively. Ti_3O = $TiO_{0.33}$ melts congruently. The crystalline pieces of $TiO_{0.27}$ have a metal-like or alloy-like appearance and they can be considered as something that is inbetween a metal or alloy and an oxide.

Bulletin of Alloy Phase diagrams 8 (1987) 148

Appendix 3

Another and very special floating zone melting furnaces

High pressure mirror furnace from the company SciDre 1 / 3

The German company Scientific Instruments Dresden GmbH (SciDre) offers a mirror furnace which has several special and extraordinary features such as

- Gas pressure up to 150 (300) bar
- Vacuum down to 10^{-5} mbar
- Temperature up to 3000 °C by a xenon arc lamp with a power shutter in the light beam, step-less adjustable from 0 to 100 %
- Precise motor-driven lamp positioning unit, workable also during a run
- Temperature measurement by a two-color pyrometer with a patented stroboscopic measurement method

Company website: http://scidre.de

A picture of their mirror furnace is shown on the following page …

High pressure mirror furnace from the company SciDre 2 / 3

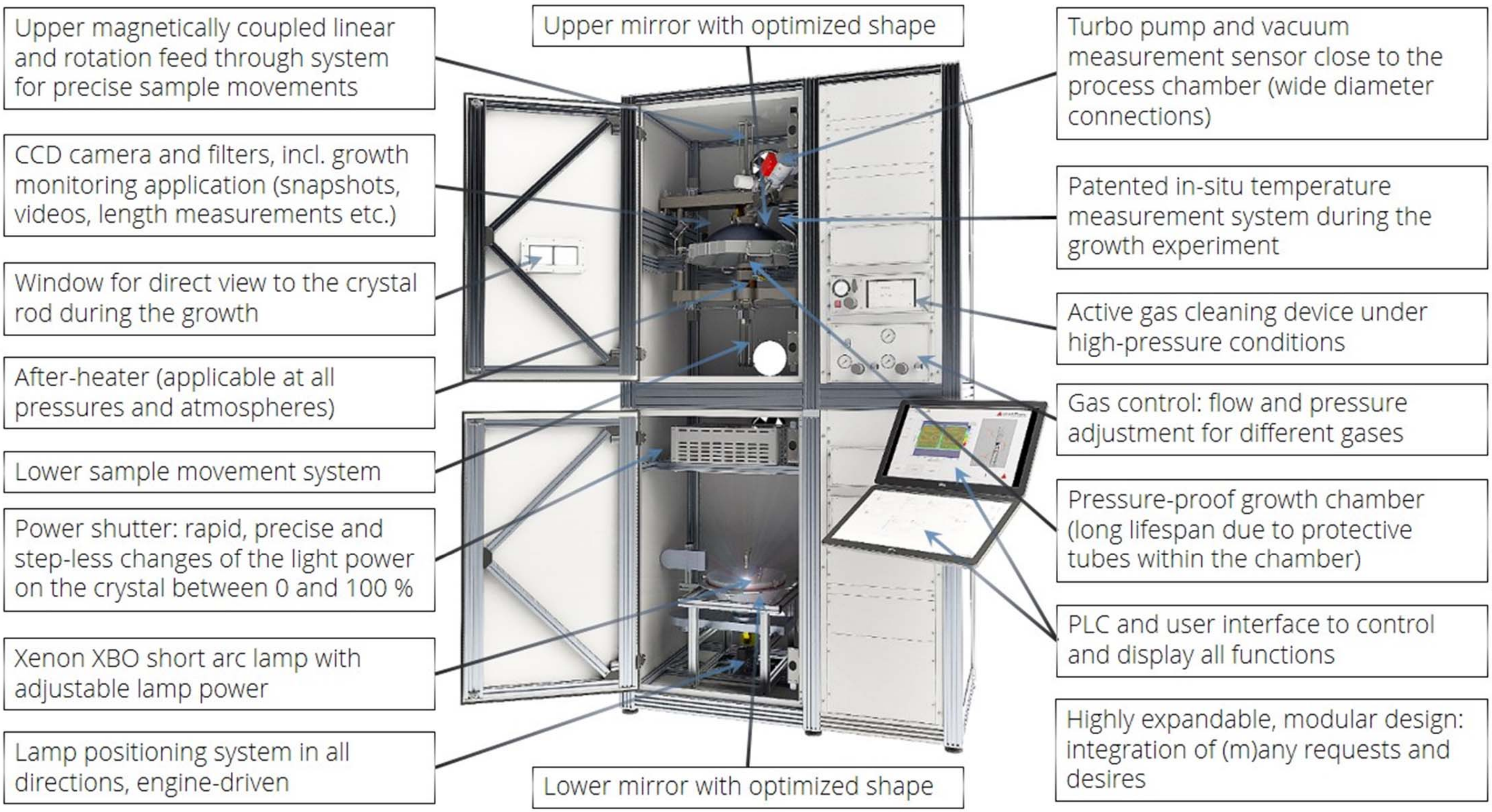


Image source: http://scidre.de or http://scidre.de/index.php?id=12

Acknowledgement

K. Conder PSI Villigen

P. Sass Scientific Instruments Dresden GmbH (SciDre)

S. Wurmehl Leibniz Institute for Solid State and Materials Research Dresden (IFW)

K. Schmiedel Leibniz Institute for Solid State and Materials Research Dresden (IFW)

Laser-heated furnace from the company Crystal Systems Corporation 1 / 2

The Japanese company Crystal Systems Corporation offers a laser-heated floating zone melting furnace. The laser heating achieves along the vertical direction a sharper focusing of the radiation and a stronger temperature gradient than the conventional lamp-based heating in a mirror furnace. This feature is advantageous for the melt-grown synthesis of some materials

Company website: http://www.crystalsys.co.jp/english/index_e.html

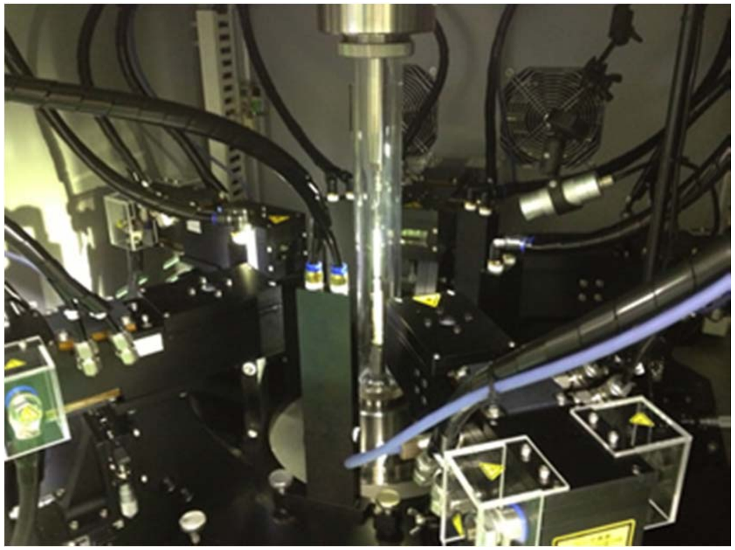


Image source:
http://www.crystalsys.co.jp/english/product04_e.html

Further information:

http://www.crystalsys.co.jp/english/product04_e.html

https://staff.aist.go.jp/t.ito/eng_index.html

The following information were specified on a poster during the poster session of the 2nd Workshop Floating Zone Technique which took place from 4 to 6 April 2016 at the Leibniz Institute for Solid State and Materials Research Dresden (IFW) in Dresden in Germany:

A comparison between two types of floating zone melting systems		
	Laser-heated furnace from Crystal Systems Corporation	Lamp-heated mirror furnace from Quantum Design
Heating by Maximum power	5 laser diodes 5×200 W	2 halogen lamps 2×650 W
Vertical temperature gradient $\Delta T / \Delta z$	> 150 °C / mm	30 °C / mm
Vertical speed range	0.01 – 300 mm / h	0.1 – 14 mm / h

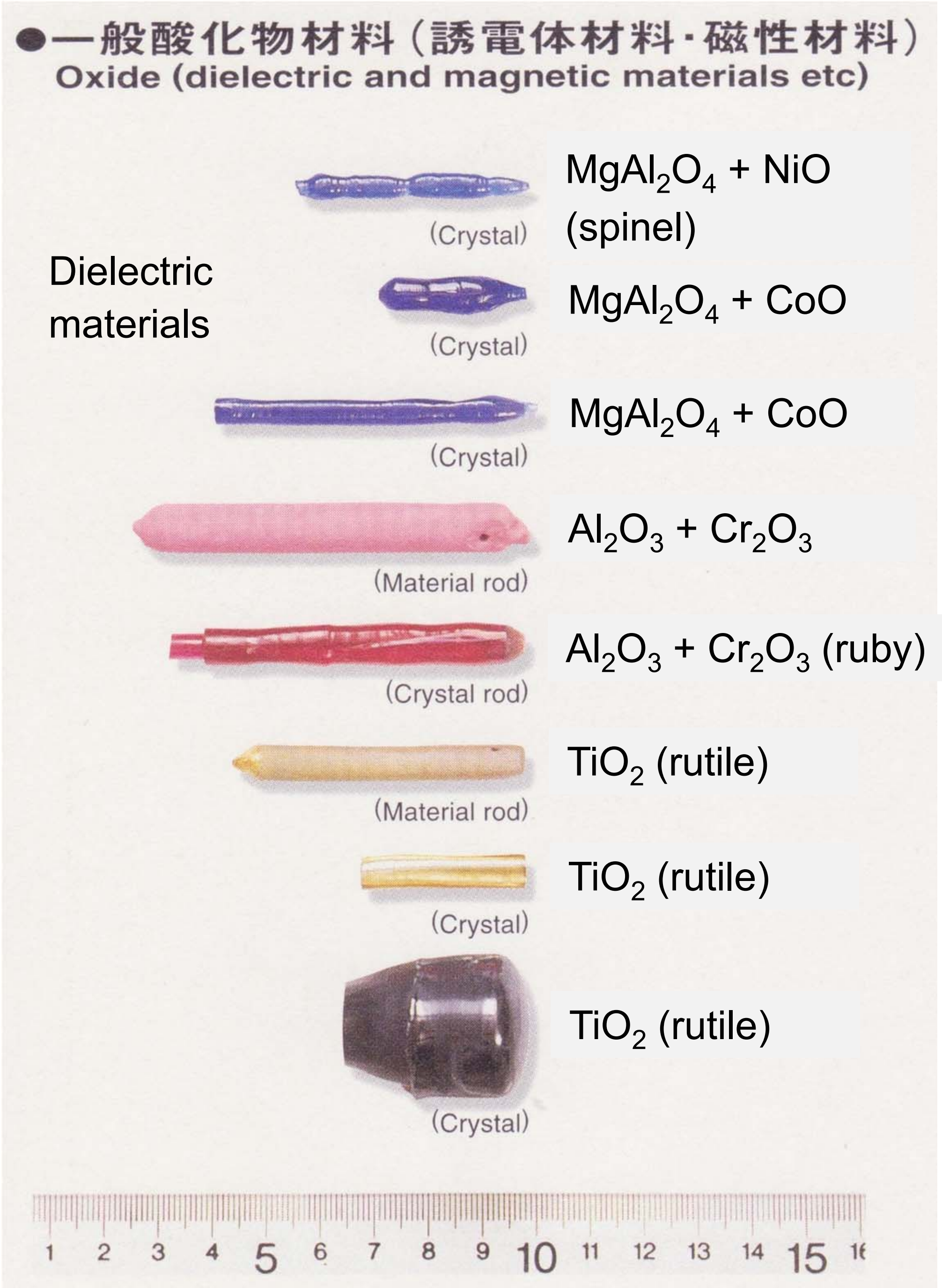
Appendix 4

Pictures of melt-grown crystalline oxides from an IR image furnace (mirror furnace) brochure of the Japanese company NEC Machinery corporation

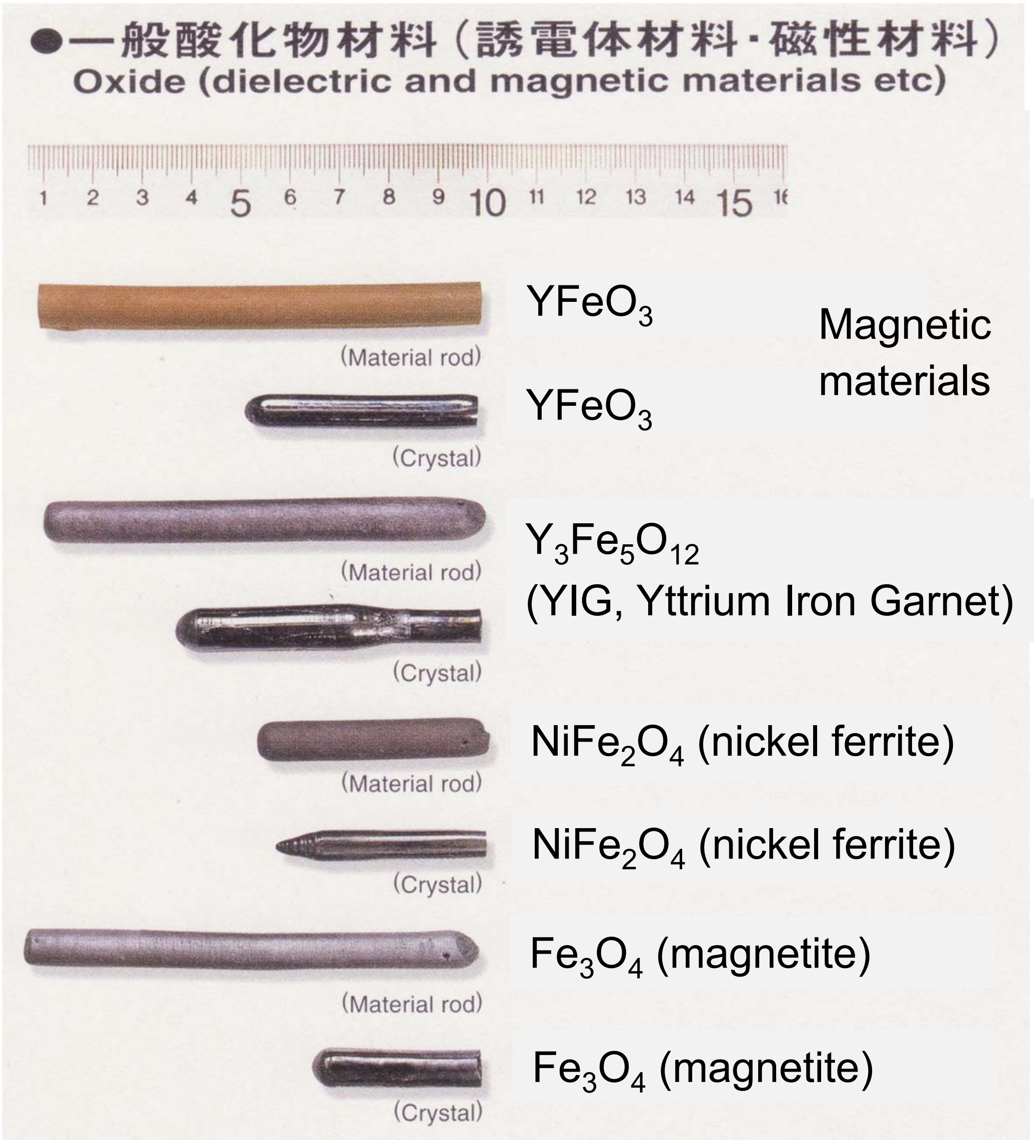
Note: The NEC type mirror furnaces are meanwhile available from the company Canon Machinery Inc. (model names SC1 and SC2): www.canon-machinery.co.jp/english/products/sp-conduct/index.html

The pictures which are presented on the following three pages are from a NEC mirror furnace (IR image furnace) brochure whose cover page is shown on the right

Note: The NEC type mirror furnaces are meanwhile available from the company Canon Machinery Inc. (model names SC1 and SC2): www.canon-machinery.co.jp/english/products/sp-conduct/index.html



Pictures of melt-grown crystalline oxides from a NEC mirror furnace brochure



Pictures of melt-grown crystalline oxides from a NEC mirror furnace brochure

Pictures of melt-grown crystalline oxides from a NEC mirror furnace brochure

Note 1: The Cu-O-based superconductors do not melt congruently. They can be prepared by floating zone melting only if a very small growth speed such as 0.1 mm / h is used, see for example the paper by C. Maljuk and C. T. Lin in Crystals 6 (2016) 62

Sr_2RuO_4	$Nd_{1.85}Ce_{0.15}CuO_4$	$La_{1.9}Sr_{0.1}CuO_4$	$La_{1.93}Sr_{0.07}CuO_4$	$Bi_2Sr_2CaCu_2O_y$
$T_c \approx 1$ K	$T_c \approx 20$ K	$T_c \approx 25$ K	$T_c \approx 15$ K	$T_c \approx 90$ K

Note 2: The superconducting transition temperatures T_c are not specified in the NEC brochure but listed by the author of this presentation. They represent published values which can be found in papers and reports about these materials

Appendix 5

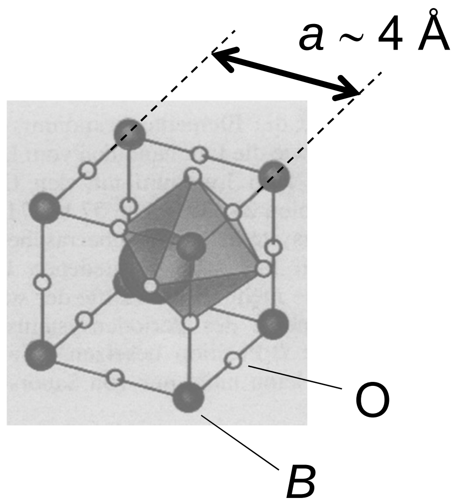
Examples of crystal structures: Layered perovskite-related oxides

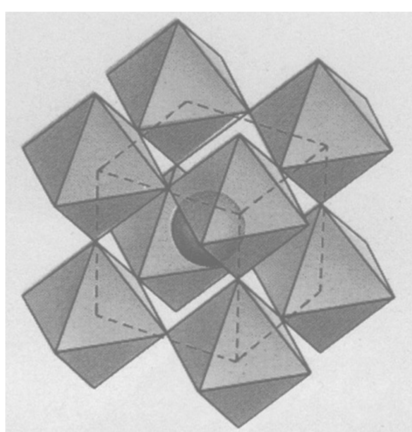
Examples of references

- Links which are presented in the preface of this presentation
- Progress in Solid State Chemistry 36 (2008) 253 , 30 (2002) 103 and 29 (2001) 1
- Journal of Physics: Condensed Matter 25 (2013) 076003

The perovskite structure *ABO*$_3$

a = 3.9 Å for cubic $SrTiO_3$





***ABO*$_3$**

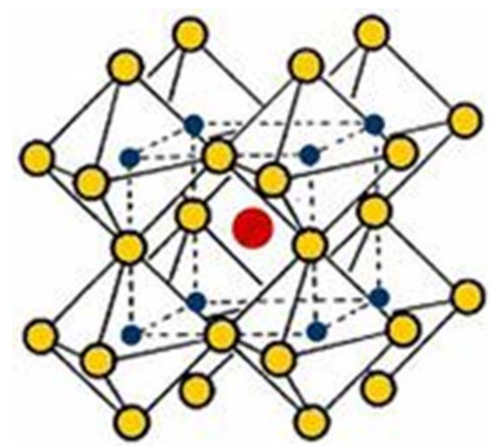
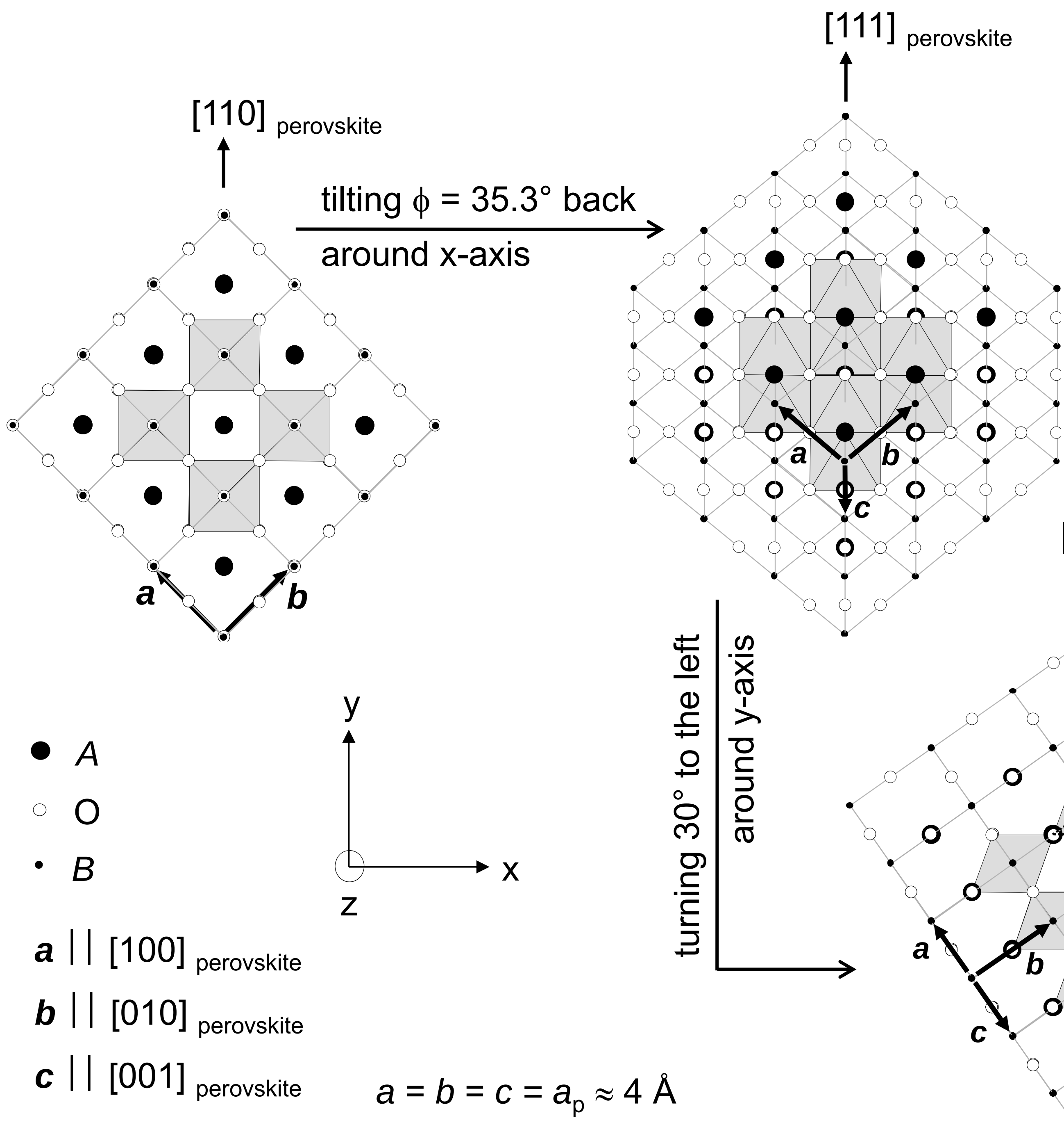
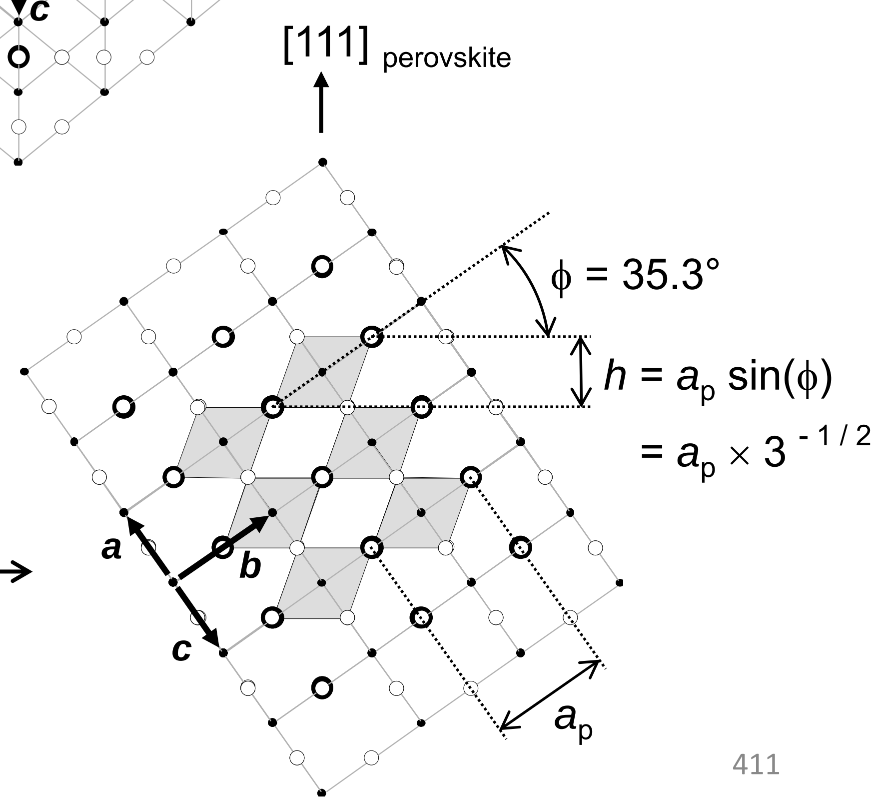


Image:
www.iam.kit.edu/wpt/184.php

Most perovskites *AB*O$_3$ are not cubic because of structural distortions

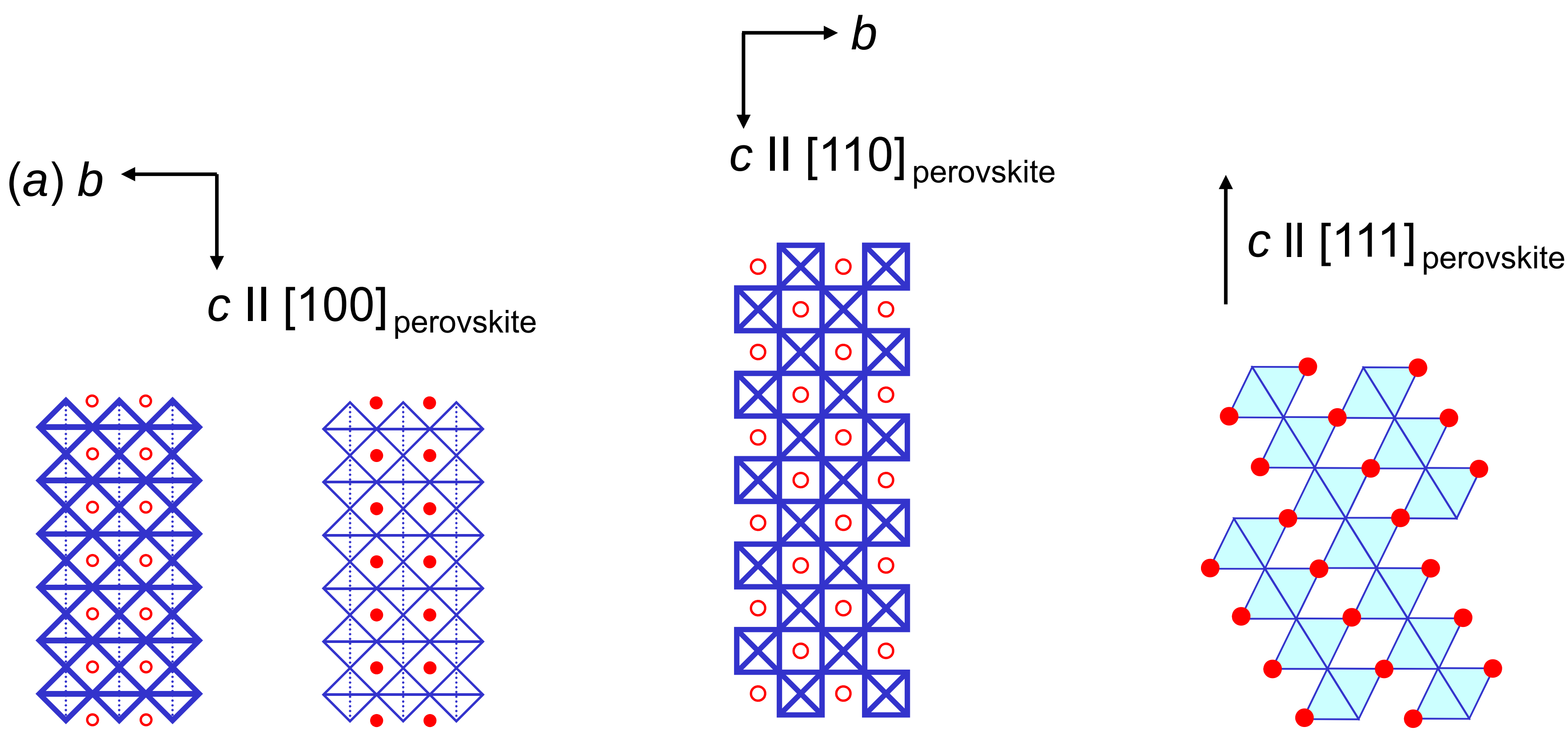
Viewing the 3D perovskite structure ABO_3 from different directions and their 2D projections





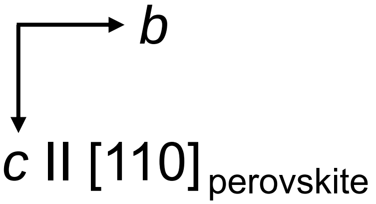
Viewing the perovskite structure ABO_3 from different directions and their 2D projections

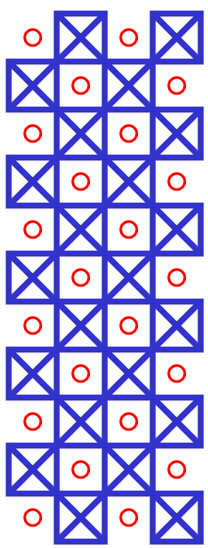

= BO_6 octahedra (O located at corners, B hidden in center)



Creation of perovskite-related layered structures ABO_{3+y} ($A_{1+w}BO_{3+y}$) from ABO_3 by cutting ABO_3 along specific planes and inserting additional O (and A) until all BO_6 octahedra are restored ...

Example of the creation of a perovskite-related layered structure ABO_{3+y} from ABO_3

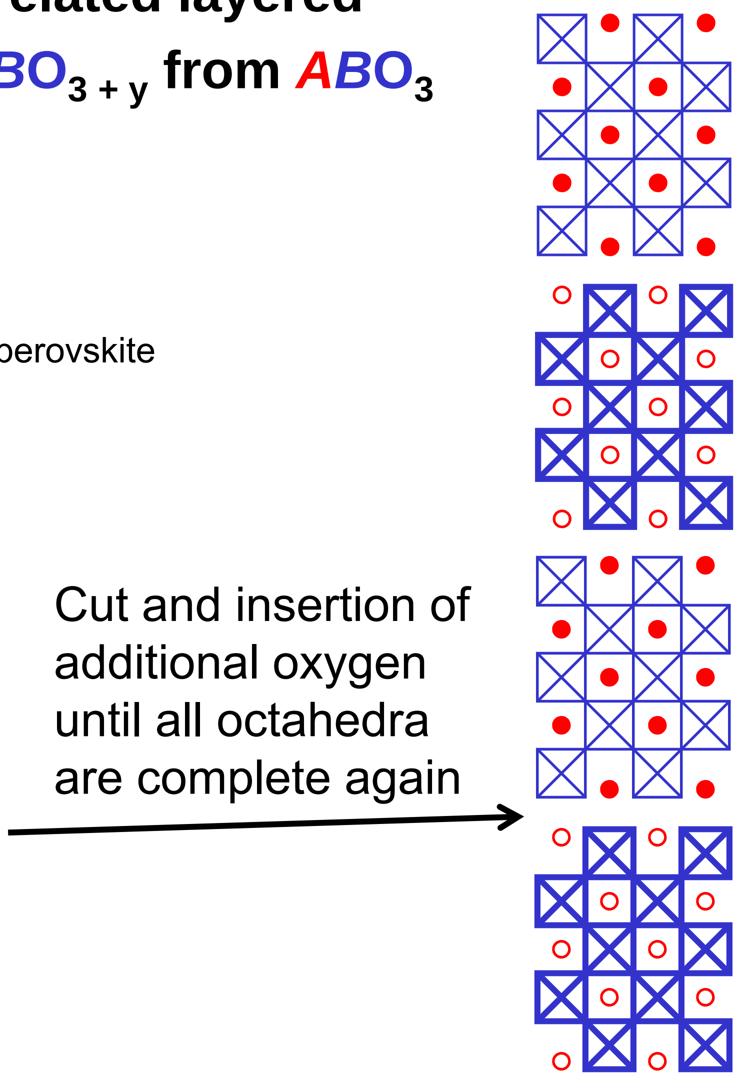




ABO_3 perovskite

$n = \infty$ of $A_nB_nO_{3n+2} = ABO_x$

Cut and insertion of additional oxygen until all octahedra are complete again

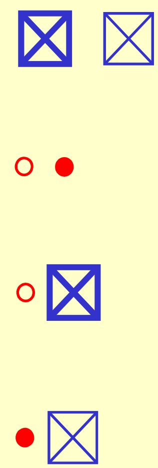


$ABO_{3.40} = A_5B_5O_{17}$

$n = 5$ of $A_nB_nO_{3n+2} = ABO_x$

 = BO_6 octahedra (O located at corners, B hidden in center)

Indications of height differences perpendicular to the drawing plane:



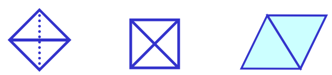
2D sketch of perovskite-related layered oxides of the type

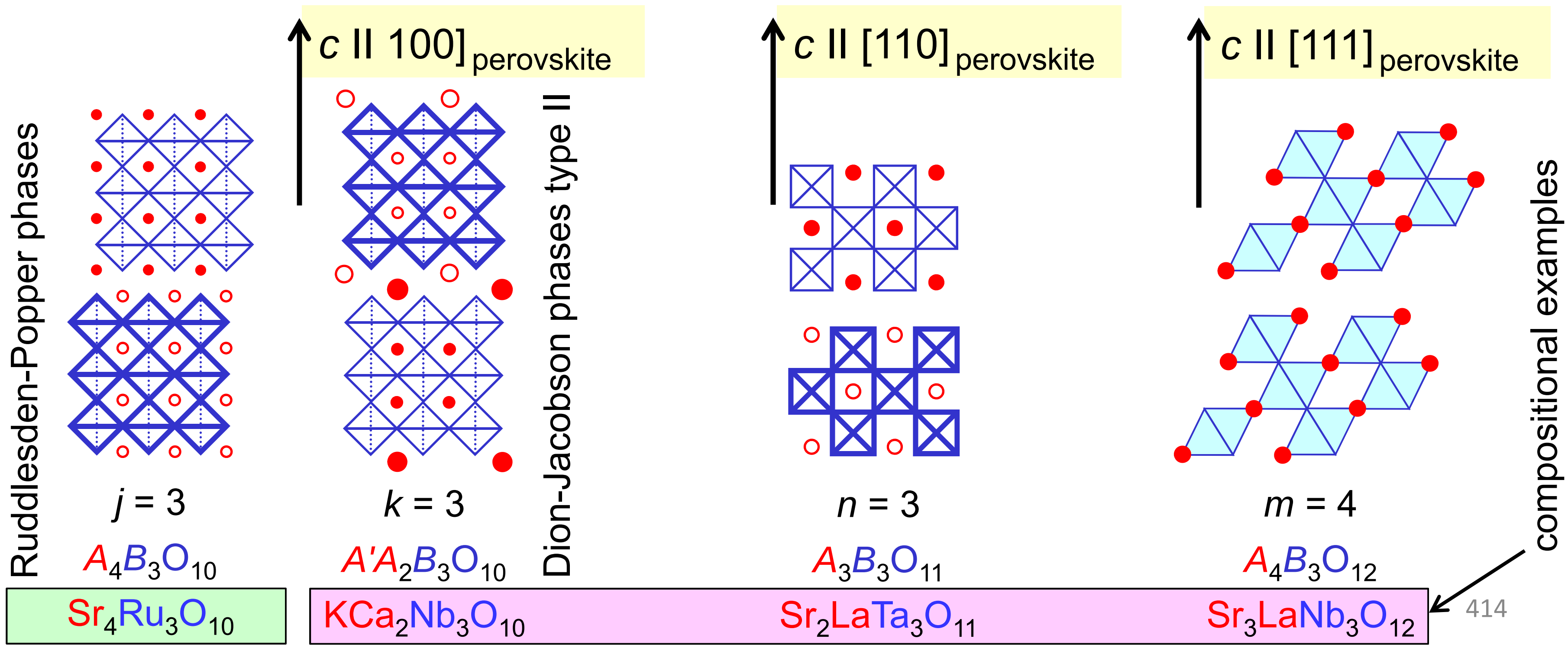
$A_{j+1}B_jO_{3j+1}$, $A'A_{k-1}B_kO_{3k+1}$, $A_nB_nO_{3n+2}$, and hexagonal $A_mB_{m-1}O_{3m}$

B = Al, Ti, V, Cr, Mn, Fe, Cu, Ru ... Comprises *j* = 1 type $(La,Ba)_2CuO_4$ in which J. G. Bednorz and K. A. Müller discovered in 1986 superconductivity up to 30 K

B = Ti, Nb, Ta

- Layers are constituted by corner-shared BO_6 octahedra and extend along *ab*-plane
- Layer thickness along *c*-axis: *j* = *k* = *n* = *m* – 1 BO_6 octahedra
- *j* = *k* = *n* = *m* = ∞ → Perovskite structure ABO_3


= BO_6 octahedra (O located at corners, *B* hidden in center)



2D sketch of the perovskite-related structure of $A_nB_nO_{3n+2}$ = ABO_x

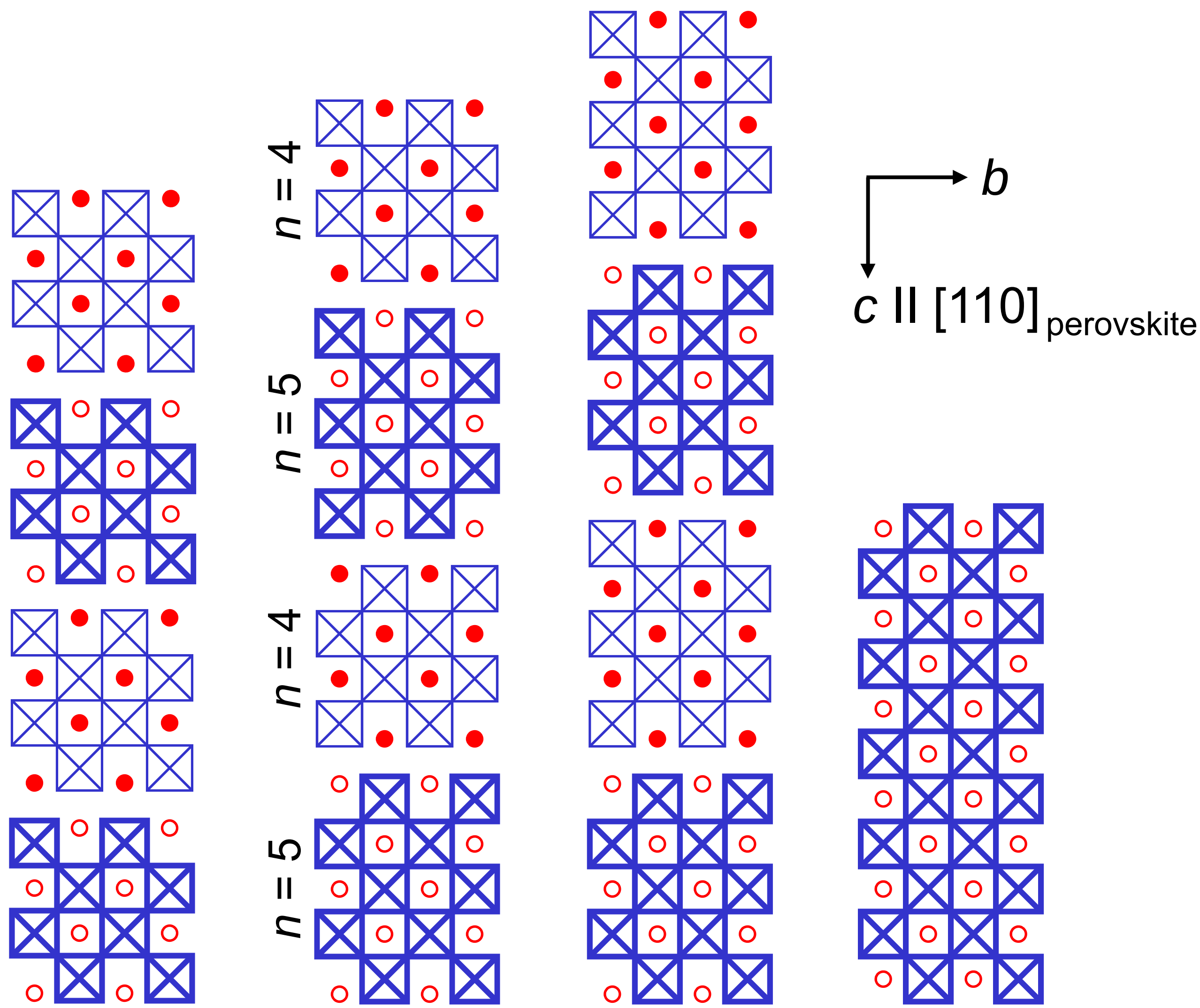
B = Ti, Nb, Ta

☒ = BO_6 octahedra (O located at corners, B hidden in center)

n = layer thickness
= number of BO_6 octahedra along c-axis per layer

Existence of non-integral series members such as n = 4.5

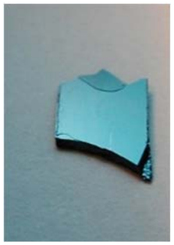
Ordered intergrowth of layers with different thickness



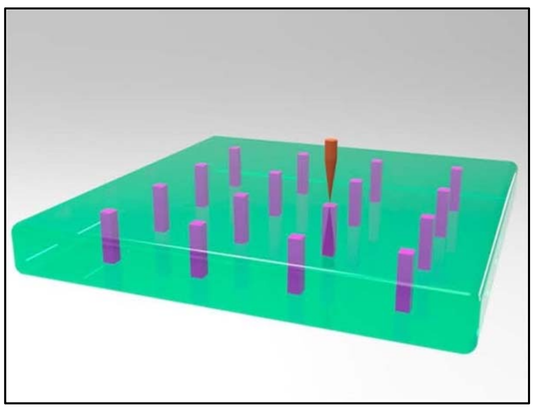
n = 4	n = 4.5	n = 5	$n = \infty$
$ABO_{3.50}$	$ABO_{3.44}$	$ABO_{3.40}$	ABO_3 perovskite

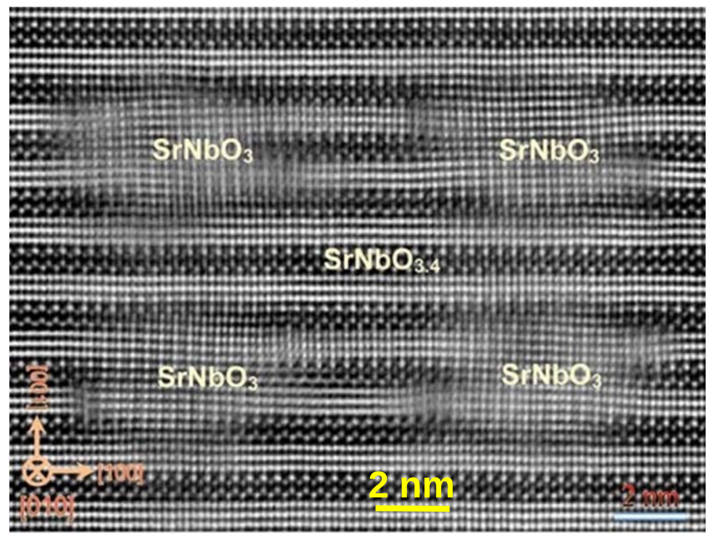
compositional examples →	$SrNbO_{3.50}$	$SrNbO_{3.44}$	$SrNbO_{3.40}$	$SrNbO_3$
physical properties →	ferroelectric	quasi-1D metals		metal

Recently created: $SrNbO_3$ nanopillars ($n = \infty$) in a $SrNbO_{3.4}$ matrix ($n = 5$)



A crystalline piece of melt-grown $n = 5$ type $SrNbO_{3.4}$ - prepared by the IBM mirror furnace - was thinned and locally reduced and transformed to $n = \infty$ type perovskite $SrNbO_3$ by an electron beam in a scanning transmission electron microscope (STEM)



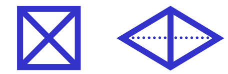


HAADF STEM image of patterned $SrNbO_3$ nanopillars in a $SrNbO_{3.4}$ matrix

If one could find a system in which the matrix is para- or diamagnetic and the transformed phase is ferromagnetic, then such a nanodevice can perhaps be applied as storage media for perpendicular magnetic recording

C. Chen et al , Nano Letters 15 (2015) 6469

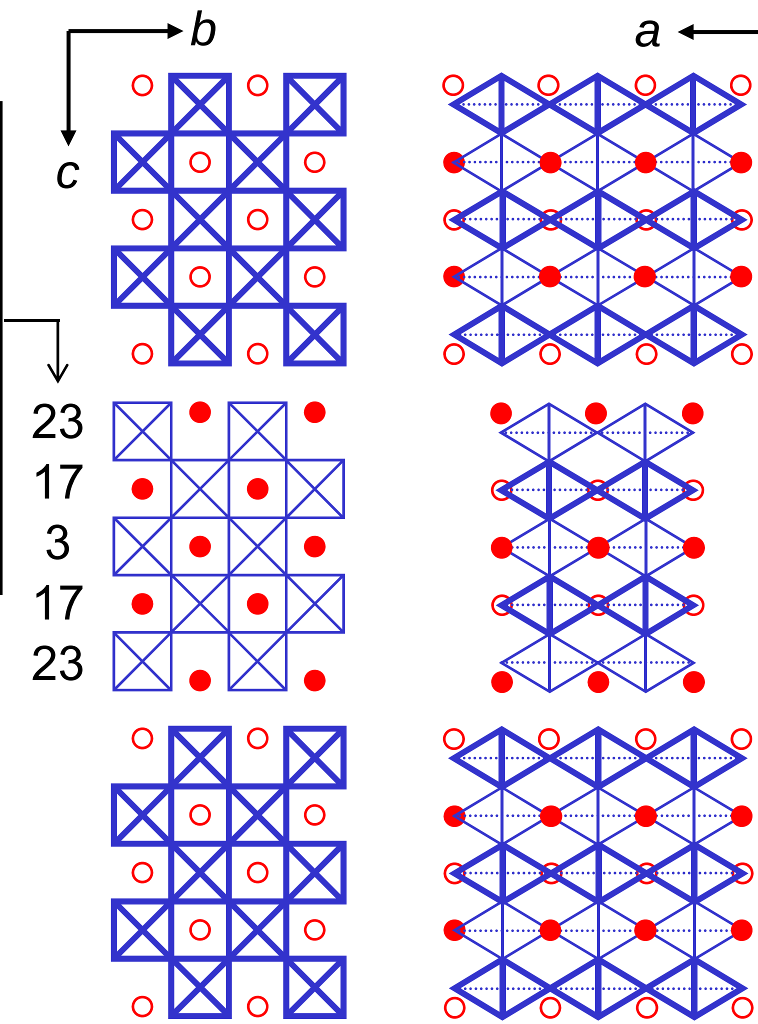
T. Williams et al , Journal of Solid State Chemistry 103 (1993) 375

BO$_6$ octahedra (O located at corners, *B* hidden in center) = 

2D sketch of the pronounced structural anisotropy of $A_nB_nO_{3n+2}$ = ABO_x by using *n* = 5 as example

Distortion of BO_6 octahedra in percent

typical values for *n* = 5



$A_5B_5O_{17}$ = $ABO_{3.40}$

B – O linkage:

- zig-zag along *b*-axis
- chains along *a*-axis
- interruptions along *c*-axis
  ⇨ layered crystal structure

Why are oxides of the type $A_nB_nO_{3n+2}$ = ABO_x interesting ?

- They comprise the highest-T_c ferroelectrics

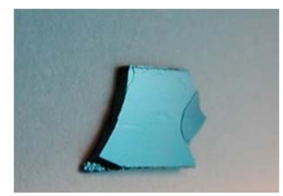
  Example: n = 4 type $La_4Ti_4O_{14}$ = $La_2Ti_2O_7$ = $LaTiO_{3.50}$ with T_c = 1770 K

- They comprise quasi-1D metals where the delocalized electrons are embedded in a ferroelectric-like environment with high dielectric permittivity

  Example: n = 5 type $Sr_5Nb_5O_{17}$ = $SrNbO_{3.40}$

- Many possible chemical compositions including non-stoichiometric compounds

- Many compounds can be synthesized in a single phase and crystalline form via a solidification from the melt by using a mirror furnace

Example: n = 5 type $Sr_5Nb_5O_{17}$

- They might have a potential to create new multiferroics and superconductors

Appendix 6

Some aspects about (raw) materials on earth

Some aspects about (raw) materials on earth

Examples of raw materials: Ores, minerals, fossil oil, natural gas

Mining and refining / processing of ores or minerals yield e.g. metals or oxides in pure form $\rightarrow$ Use or further processing in science, research, technology, industry, and daily life

(Raw) Materials are also related to items / topics / keywords like

- Politics, geopolitics, and political decisions
- Economy, economic interests, vested interests
- Economic dependency
- Environment, ecology, and pollution
- Recycling and disposal
- Wealth, industrial countries
- Poverty, developing countries, inhumane (working) conditions
- Conflicts and wars

The following slides present just a few topics and examples ...

Conflicts around coltan

Coltan stands for columbite-tantalite and is industrially known as tantalite. It is a dull black ore from which the elements niobium (Nb) and tantalum (Ta) are extracted. The niobium-dominant mineral in coltan is columbite $(Fe,Mn)Nb_2O_6$ and the tantalum-dominant mineral is tantalite $(Fe,Mn)Ta_2O_6$

Coltan is used primarily for the production of tantalum capacitors, used in many electronic devices. Many sources mention coltan's importance in the production of mobile phones, but tantalum capacitors are used in almost every kind of electronic device. The anode of tantalum electrolytic capacitors is made of tantalum on which a very thin insulating Ta_2O_5 layer is formed, which acts as the dielectric of the capacitor.

"The central African countries of Democratic Republic of Congo and Rwanda and their neighbours used to be the source of significant tonnages. But civil war, plundering of national parks and exporting of minerals, diamonds and other natural resources to provide funding of militias has caused the Tantalum-Niobium International Study Center to call on its members to take care in obtaining their raw materials from lawful sources. Harm, or the threat of harm, to local people, wildlife or the environment is unacceptable."

A piece of columbite-tantalite

Size 60 x 25 x 21 mm

Text and picture mainly from https://en.wikipedia.org/wiki/Coltan and https://en.wikipedia.org/wiki/Tantalum_capacitor .

Further reference: Documentary film "Blood Coltan" http://topdocumentaryfilms.com/blood-coltan

☺ Thanks to Nicola Spaldin from the ETH Zurich for calling attention to this topic during her speech at the master graduation ceremony in 2012 at the Department of Materials of the ETH Zurich ☺

Unpleasant examples of recycling and disposal of electronic waste

Inhumane conditions (example from Ghana in Africa): Children disassemble und burn electronic waste and seek for valuable materials such as aluminum or copper without any considerations about safety, health, and environment

Image from a German-language report
www.3sat.de/page/?source=/scobel/160141/index.html

Images from a report in the Washington Post from 15 April 2015:
www.washingtonpost.com/news/in-sight/wp/2015/04/15/the-children-who-make-a-living-in-the-toxic-world-of-discarded-electronics

The 15 + 2 = 17 rare earth elements:

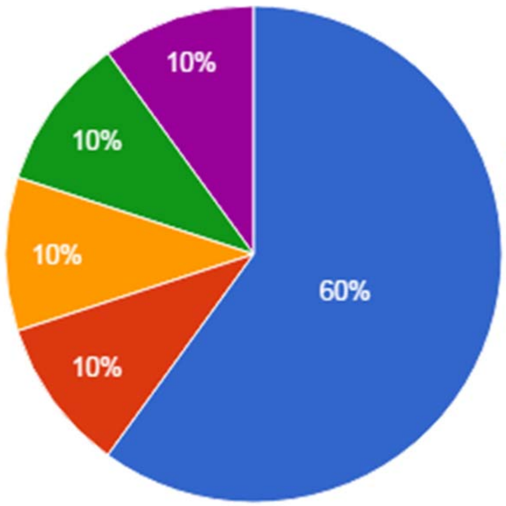
Lanthanides: Lanthanum La (57) – Lutetium Lu (71)
Yttrium Y (39)
Scandium Sc (21)

↑ Atomic number

Image from https://de.wikipedia.org/wiki/Metalle_der_Seltenen_Erden

Rare earth deposits for example in monazite type phosphate minerals $RePO_4$
Re = Rare earth element(s)

The rare earth elements 02 / 10



Other

Glass polishing
by CeO_2 powder

Ceramics / Glass

Metallurgy / Alloys →

Catalysts

Examples: Permanent magnets such as $Nd_2Fe_{14}B$ and $SmCo_5$ and hydrogen storage alloys of the type $LaNi_5$ for rechargeable nickel-metal-hydride batteries

Uses of rare earth elements in the United States during 2013

Many vehicles use rare earth catalysts in their exhaust systems for air pollution control.
A large number of alloys are made more durable by the addition of rare earth metals.
Glass, granite, marble and gemstones are often polished with cerium oxide (CeO_2) powder.
Many motors and generators contain magnets made with rare earth elements. Phosphors used in digital displays, monitors and televisions are created with rare earth oxides.
Most computer, cell phone and electric vehicle batteries are made with rare earth metals

Pie chart and text mainly from http://geology.com/articles/rare-earth-elements

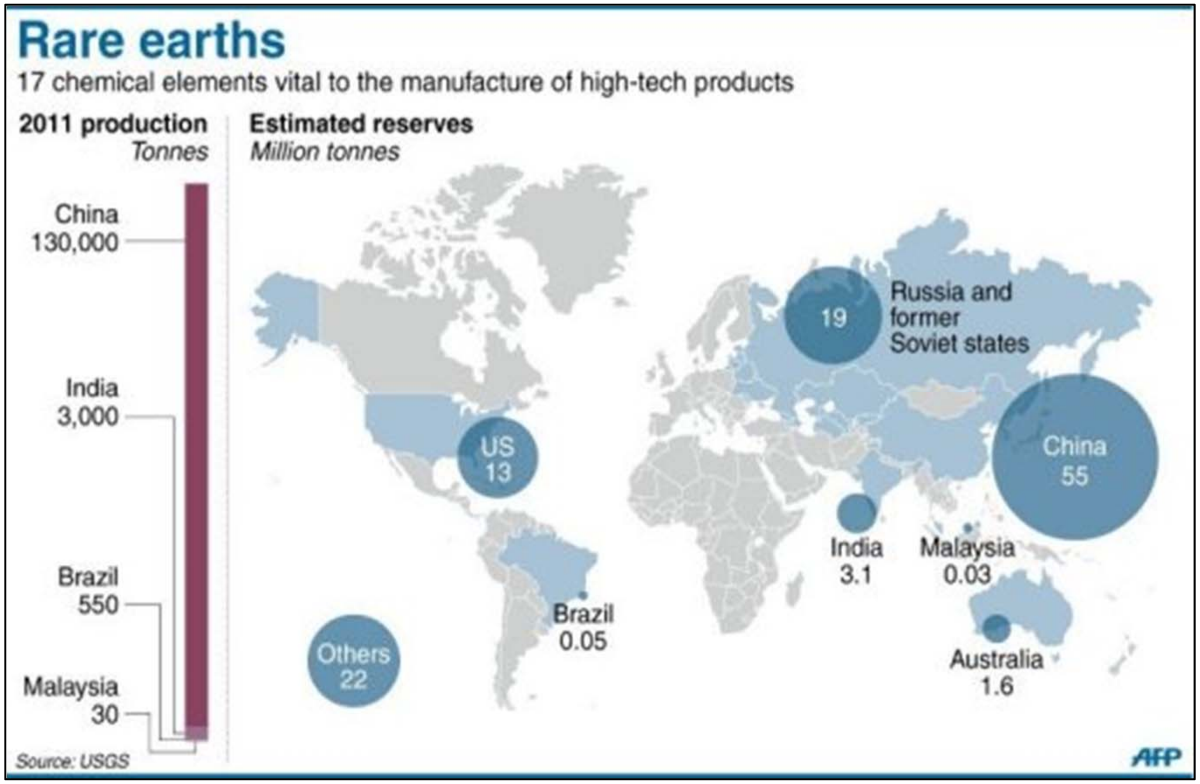
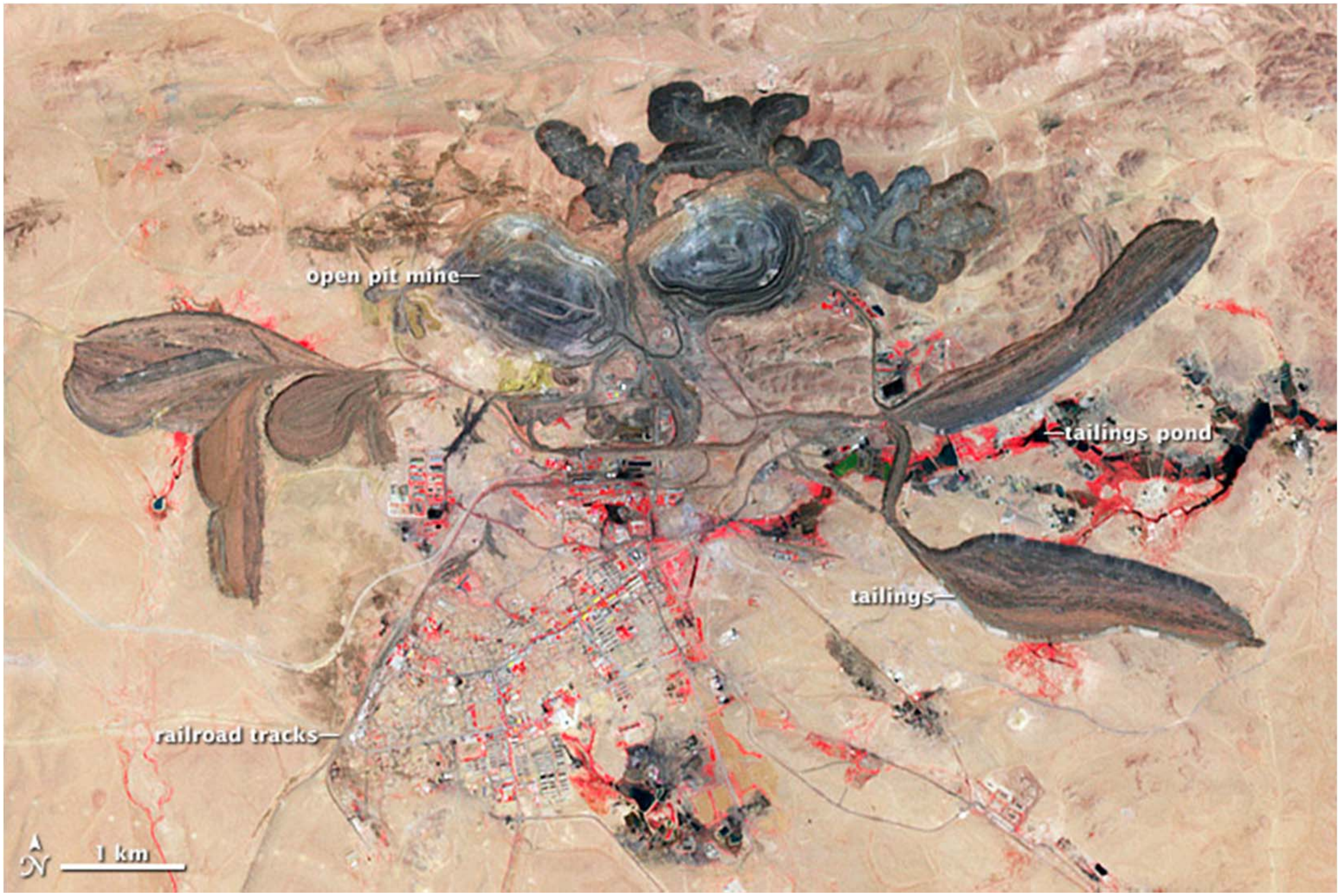


Image: http://phys.org/news/2012-07-china-stockpiling-rare-earths.html

Mining, refining, and recycling of rare earths have serious environmental consequences if not properly managed

See, for example, https://en.wikipedia.org/wiki/Rare_earth_element



Satellite image of the Bayan Obo Mining District in China (2006)

http://earthobservatory.nasa.gov/IOTD/view.php?id=77723&src=eoa-iotd

https://en.wikipedia.org/wiki/Rare_earth_element

The rare earth elements 05 / 10

Former mining of rare earth minerals at the village Ytterby in Sweden

Ytterby quarry

Terbiumvägen (Terbium Road) and Gruvvägen (Mine Road) close to the Ytterby mine

At a quarry and mine near the village, the rare earth mineral yttria (Y_2O_3) was discovered and named after the village. This crude mineral eventually proved to be the source of four new elements that were named after the mineral ore and the village. These elements are yttrium (Y), erbium (Er), terbium (Tb), and ytterbium (Yb) and were first described in 1794, 1842, 1842, and 1878, respectively

Text and pictures from https://en.wikipedia.org/wiki/Ytterby

☺ Thanks to Nicola Spaldin from the ETH Zurich for telling about Ytterby ☺

The rare earth elements 06 / 10

Image from a German-language report www.focus.de/finanzen/news/tid-25584/oel-gas-seltene-erden-deutschland-geht-auf-rohstoffjagd-seltene-erden-aus-sachsen_aid_742295.html

Rare earth deposits also in Saxony in East Germany !

Two German-language reports about that are presented on the two following pages ...

www.faz.net/aktuell/wirtschaft/rohstoffe-seltene-erden-erstmals-in-deutschland-bestaetigt-12046040.html

31. Januar 2013 **Seltene Erden erstmals in Deutschland bestätigt**

Im sächsischen Storkwitz ist das einzige bekannte Vorkommen seltener Erden offiziell bestätigt worden. Es bist bis zu 8 Milliarden Euro wert. Schon ab 2017 könnte das Vorkommen ausgebeutet werden.
In der Nähe von Leipzig ist das erste seltene Erden Vorkommen in Deutschland und Mitteleuropa nun offiziell bestätigt worden. Etwa 20 100 Tonnen der seltenen Rohstoffe schlummern nach Angaben der Seltenerden Storkwitz AG (SES), einer hundertprozentigen Tochter der Deutschen Rohstoff AG, im Boden des sächsischen Dorfes Storkwitz. Das ergab die Untersuchung eines unabhängigen australischen Gutachters.
Hinter seltenen Erden verbergen sich 17 Elemente wie Lanthan, Europium und Yttrium — ohne sie ist nahezu kein modernes Technologieprodukt denkbar. Sie werden wegen ihrer speziellen Eigenschaften etwa in Akkus, Flachbildschirmen oder internetfähigen Handys eingesetzt.
Dazu wurden weitere 4000 Tonnen Niob bestätigt, welches vor allem in der Autoindustrie Verwendung findet. Mit dem grauen Metall kann etwa Stahl veredelt werden, womit wiederum leichtere Autos gebaut werden können — und damit lässt sich am Ende Kraftstoff sparen. Auch als Supraleiter könnte Niob sich einen Namen machen. Fachleute schätzen den Wert der nun bestätigen Funde auf mindestens 2 Milliarden Euro.
Die jetzt bestätigten Funde könnten dabei nur der Anfang sein. Untersucht wurde der Erzkörper nur bis 600 Meter Tiefe — er reicht aber bis mindestens 1200 Meter Tiefe, wie das Gutachten zeigt. Ziel der SES ist es, mindestens 80 000 Tonnen Seltene Erden nachzuweisen. Damit wäre das Vorkommen nach jetzigen Preisen mehr als 8 Milliarden Euro wert.
Eine Förderung ab 2017 ist realistisch
Derzeit läuft eine Wirtschaftlichkeitsprüfung zur Ausbeutung der Lagerstätte, sagte SES-Vorstand Bernhard Giessel dieser Zeitung. „Wir beabsichtigen, so schnell wie möglich an die Börse zu gehen, um Kapital für weitere Bohrungen zu sammeln“, sagte Giessel. Dann könnten schon in diesem Sommer wieder neue Bohrungen stattfinden, um den Erzkörper weiter auszuleuchten. In zwei Jahren könnte dann die Pilotproduktion beginnen, weitere zwei Jahre würde es dauern, die nötige Infrastruktur zu errichten. „Eine Förderung von 2017 an ist aber realistisch“, sagt Giessel optimistisch.
Das Vorkommen ist schon 1973 entdeckt wurden, als das DDR-Unternehmen Wismut nach Uran suchte. Bis 1985 wurde es danach intensiv ausgekundschaftet. Das Vorkommen ist durch den starken Preisanstieg seltener Erden im Jahr 2010 wieder interessant geworden. Heute wird der Markt von China dominiert, das 97 Prozent aller Seltenen Erden fördert — obwohl im Land nur ein Drittel der weltweiten Reserven lagern. Aktuell werden weltweit jährlich etwa 130 000 Tonnen gefördert.
Sachsen ist für Rohstoffunternehmen wegen seiner jahrhundertealten Bergbautradition von besonderem Interesse.
Kaum ein Ort auf der Welt ist bergbautechnisch so gut erforscht wie Sachsen. Dazu gibt es noch viele Fachleute vor Ort, da bis in die neunziger Jahre hinein Bergbau betrieben wurde. Im vogtländischen Gottesberg wird derzeit das größte bekannte unerschlossene Zinn- und Kupfervorkommen der Welt weiter erforscht.

www.freiepresse.de/WIRTSCHAFT/WIRTSCHAFT-REGIONAL/Interesse-an-Seltenen-Erden-in-Nordsachsen-erloschen-artikel9239399.php

4. Juli 2015 **Interesse an Seltenen Erden in Nordsachsen erloschen. Die Erkundungserlaubnis für das größte Vorkommen in Mitteleuropa wurde zurückgegeben. Delitzsch bleibt vorerst auf seinen Bodenschätzen sitzen**

Storkwitz/Freiberg. Der wahrscheinlich größte Schatz Seltener Erden in Mitteleuropa wird vorerst nicht geborgen. Dem 160 Seelen-Dorf Storkwitz bei Delitzsch, unter dessen Getreidefeldern etwa 40.000 Tonnen der mineralischen Metalle liegen, bleibt auf absehbare Zeit ein Bergwerk erspart. Die bereits 2007 an die Deutsche Rohstoff AG erteilte Erkundungslizenz für dieses Gebiet wurde an das Sächsische Oberbergamt in Freiberg zurückgegeben, bestätigte Behördenleiter Bernhard Cramer der "Freien Presse". Das Feld sei damit wieder frei für mögliche andere Investoren.

Dabei hatte die Deutsche Rohstoff AG für die Erkundung eigens eine Tochterfirma, die Seltene Erden Storkwitz (SES) AG gegründet. Die startete 2012 die erste Probebohrung. Ein schräg angesetzter Bohrer holte Kerne bis aus 590 Meter Tiefe zutage. Die Freiberger Firma Uvr-fia, eine ingenieurtechnische Einrichtung für verfahrenstechnische Forschung, sei dann mit Aufbereitungstests beauftragt worden, sagte Jörg Reichert, Vorstand des Unternehmens Ceritech, das im Sommer 2014 die Seltene Erden Storkwitz ablöste. Die entscheidende Frage sei ja, wie sich der ohnehin niedrige Gehalt von 0,4 bis 0,5 Prozent im Erzkörper wirtschaftlich gewinnen ließe, so der promovierte Geologe.

China dominiert den Weltmarkt

Die Versuche hätten gezeigt, dass die Aufbereitung wenig effektiv wäre. Aus diesem Grund habe man sich von dem Projekt verabschiedet - obwohl bereits 2,2 Millionen Euro investiert worden waren.

Die 2012 vorgenommenen Bohrungen hatten die Erkenntnisse bestätigt, die DDR-Geologen zwischen 1971 und 1989 gewonnen hatten. Sie erkundeten damals ein 50 Quadratkilometer großes Gebiet - mit maßgeblicher Beteiligung der Wismut. Im Ergebnis wurden Vorräte von etwa 20.000 Tonnen prognostiziert, weiß Uwe Lehmann, Referatsleiter im sächsischen Landesamt für Umwelt, Landwirtschaft und Geologie. Daraus ableitend seien für einen noch tieferen Bereich weitere Vorräte geschätzt worden. Die Experten gingen von zusammen 40.000 Tonnen Seltene Erden aus.

Für 2013 / 2014 war eine weitere große Probebohrung geplant, die diese Schätzungen präzisieren sollte. Doch da der geplante Börsengang der SES nicht erfolgte, fehlte auch das Geld für das zweite Bohrprogramm. Zudem seien seit 2012 die Weltmarktpreise für Seltene Erden stark gesunken, sagte Vorstand Reichert. China überschwemme und dominiere den Markt, was selbst gestandene Unternehmen in Schwierigkeiten gebracht hat. Im Januar hob China die vor fünf Jahren selbst verhängte Exportquote auf, die vorher den Zufluss von Seltenen Erden auf den Weltmarkt beschränkte. Das dürfte das Aus für den Bergbaukonzern Molycorp gewesen sein, einziger Produzent von Seltenen Erden in den USA und seit fünf Jahren an der Börse. "Er hat gerade Insolvenz angemeldet", beschreibt Reichert die Lage auf dem Weltmarkt. Auch Lynas, ein australisches Bergbauunternehmen für Seltene Erden, die in Malaysia verarbeitet werden, steckt in der Krise. Der Aktienkurs fiel von 2,60 australische Dollar auf 3 Cent, ein Minus von 98,73 Prozent.

Bürger sehen Absage gelassen

Jörg Reichert und die Ceritech haben die Seltenen Erden trotzdem nicht abgeschrieben. "Wir arbeiten an alternativen Projekten", sagte der Leipziger. Dabei gehe es um die Gewinnung Seltener Erden aus mineralischen Halden. Derzeit liefen Versuche mit ersten Proben.

Der Oberbürgermeister der Stadt Delitzsch, zu der Storkwitz gehört, Manfred Wilde, hat entspannt auf die Absage reagiert: "Wir sind nicht enttäuscht, denn die Rohstoffe bleiben uns ja." Die Wirtschaft floriere auch ohne Bergbau: mit BMW, Porsche und dem Flughafen - jeweils nur zehn Fahrtminuten entfernt. "Wir sind auf jeden Fall positiv ins Gespräch gekommen. Und ich bin sicher, wenn die Weltmarktpreise und die Nachfrage steigen, wird man sich an Storkwitz erinnern."

Seltene Erden

Zu den Seltenen Erden gehören 17 metallische Rohstoffe. Der derzeitige weltweite Bedarf beträgt 100.000 bis 120.000 Tonnen pro Jahr. Einige Experten sehen einen rückläufigen Bedarf, weil zum Beispiel der Durchbruch der Elektromobilität bisher ausgeblieben ist. Genau hier würden große Mengen dieser Hightech-Metalle in den Batterien gebraucht. 92 Prozent des Bedarfs wird derzeit von China gedeckt.

Europe's rare earth element resource potential: An overview of REE metallogenic provinces and their geodynamic setting

K. M. Goodenough et al , Ore Geology Reviews 72 (2016) 838 – 856

http://dx.doi.org/10.1016/j.oregeorev.2015.09.019

Abstract
Security of supply of a number of raw materials is of concern for the European Union; foremost among these are the rare earth elements (REE), which are used in a range of modern technologies. A number of research projects, including the EURARE and ASTER projects, have been funded in Europe to investigate various steps along the REE supply chain. This paper addresses the initial part of that supply chain, namely the potential geological resources of the REE in Europe. Although the REE are not currently mined in Europe, potential resources are known to be widespread, and many are being explored. The most important European resources are associated with alkaline igneous rocks and carbonatites, although REE deposits are also known from a range of other settings. Within Europe, a number of REE metallogenetic belts can be identified on the basis of age, tectonic setting, lithological association and known REE enrichments. This paper reviews those metallogenetic belts and sets them in their geodynamic context. The most well-known of the REE belts are of Precambrian to Palaeozoic age and occur in Greenland and the Fennoscandian Shield. Of particular importance for their REE potential are the Gardar Province of SW Greenland, the Svecofennian Belt and subsequent Mesoproterozoic rifts in Sweden, and the carbonatites of the Central Iapetus Magmatic Province. However, several zones with significant potential for REE deposits are also identified in central, southern and eastern Europe, including examples in the Bohemian Massif, the Iberian Massif, and the Carpathians

Rare Earth Elements: Industrial Applications
and Economic Dependency of Europe

G. Charalampideset et al , Procedia Economics and Finance 24 (2015) 126 - 135

doi 10.1016/S2212-5671(15)00630-9

Abstract

Rare Earth Oxides are used in mature markets (such as catalysts, glassmaking and metallurgy), which account for 59% of the total worldwide consumption of rare earth elements, and in newer, high-growth markets (such as battery alloys, ceramics, and permanent magnets), which account for 41% of the total worldwide consumption of rare earth elements. China currently controls completely the mining activity, the enrichment technologies and metallurgy, and end-metal products of rare earths, resulting for both Europe and the U.S.A. in full industrial dependency. Due to high demand and limited availability of rare earth elements (REEs), Europe is unable to meet its industrial needs today for the manufacturing sector. Therefore the EU has included them in the group of 14 critical minerals. The balance of demand and supply in the world market of Rare Earth Metals was always rather unstable. The most significant increase of prices took place during the years 2009-2011, followed by a sudden and substantial fall in prices due mainly to the actual, persistent heavy economic crisis of the industrialized countries. The EU, in order to limit the dependency of REE imports, would have to employ alternative measures to secure REE supply security by adopting an admixture of trade policies, industrial adjustment and innovation and budget allocations in the member states.

Environmentally friendly production of Rhine gold in Germany 1 / 2

Rhine gold granules. Picture from 2013 by Jutta Werling from Aurum Rhenanum

Aurum Rhenanum
www.aurum-rhenanum.com

Modern Rhine gold production

Different scientific surveys have proved that the area on the upper Rhine ranks among the gold-richest regions of Europe. The Rhine gold is located in formerly active river deposits, which now provide gravel and sand.

Many attempts were required to find the optimum process for separating the Rhine gold from the other materials. This separation process is purely mechanical and thus ecologically sound.

200 tons gravel and sand yield on average 1 gram Rhine gold

Environmentally friendly production of Rhine gold in Germany 2 / 2

Rhine gold granules. Picture from 2013 by Jutta Werling from Aurum Rhenanum

Note: Pure gold or Rhine gold is usually not used for jewelry because of its softness

Two rings made of a Rhine gold alloy of the type 750, i.e. they consist of 75 % Rhine gold. The other alloy components are usually silver and / or copper. Diameter about 2 cm. Manufactured in 2013 by goldsmith Karin Demmler in Constance in Germany

☺ Acknowledgement ☺

Karin Demmler www.schmuck-karindemmler.de

Jutta Werling www.aurum-rhenanum.com and www.brazilgems.de

Environmental Science Center at the University of Augsburg

Environmental Science Center, Institute for Materials Resource Management, and Chair of Resource Strategy at the University of Augsburg in Germany

Image from
www.uni-augsburg.de/einrichtungen/innocube

Chair of Resource Strategy:
Prof. Armin Reller and his team

Image from (October 2016)
www.mrm.uni-augsburg.de/en/groups/reller

The research conducted by the Chair of Resource Strategy focuses on the following areas:
• Management of resources with a particular focus on water as well as mineral and metallic resources • Resource flows and production chains • Multidisciplinary research on the environment • Education for sustainable development • Material histories
• Educational models for sustainable development and resource conservation
• Environmental management

Reference: www.mrm.uni-augsburg.de/en/groups/reller/forschung

Appendix 7

The Periodic Table of the Chemical Elements

The Periodic Table of the Chemical Elements

WebElements: the periodic table on the world-wide web

www.webelements.com

Key: element name / atomic number / symbol / atomic weight (mean relative mass)

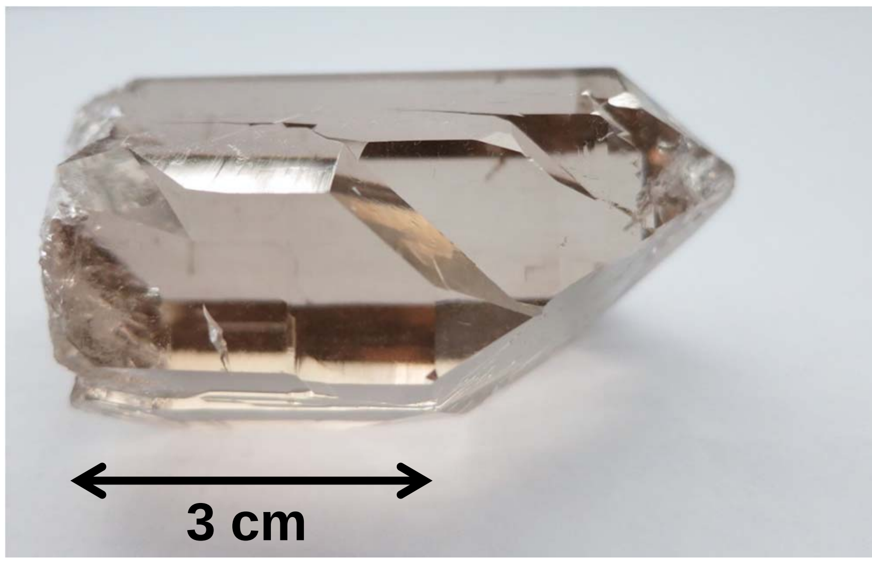
1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
hydrogen 1 **H** 1.0079																		helium 2 **He** 4.0026
lithium 3 **Li** 6.941	beryllium 4 **Be** 9.0122												boron 5 **B** 10.811	carbon 6 **C** 12.011	nitrogen 7 **N** 14.007	oxygen 8 **O** 15.999	fluorine 9 **F** 18.998	neon 10 **Ne** 20.180
sodium 11 **Na** 22.990	magnesium 12 **Mg** 24.305												aluminium 13 **Al** 26.982	silicon 14 **Si** 28.086	phosphorus 15 **P** 30.974	sulfur 16 **S** 32.065	chlorine 17 **Cl** 35.453	argon 18 **Ar** 39.948
potassium 19 **K** 39.098	calcium 20 **Ca** 40.078		scandium 21 **Sc** 44.956	titanium 22 **Ti** 47.867	vanadium 23 **V** 50.942	chromium 24 **Cr** 51.996	manganese 25 **Mn** 54.938	iron 26 **Fe** 55.845	cobalt 27 **Co** 58.933	nickel 28 **Ni** 58.693	copper 29 **Cu** 63.546	zinc 30 **Zn** 65.38	gallium 31 **Ga** 69.723	germanium 32 **Ge** 72.61	arsenic 33 **As** 74.922	selenium 34 **Se** 78.96	bromine 35 **Br** 79.904	krypton 36 **Kr** 83.80
rubidium 37 **Rb** 85.468	strontium 38 **Sr** 87.62		yttrium 39 **Y** 88.906	zirconium 40 **Zr** 91.224	niobium 41 **Nb** 92.906	molybdenum 42 **Mo** 95.96	technetium 43 **Tc** [98]	ruthenium 44 **Ru** 101.07	rhodium 45 **Rh** 102.91	palladium 46 **Pd** 106.42	silver 47 **Ag** 107.87	cadmium 48 **Cd** 112.41	indium 49 **In** 114.82	tin 50 **Sn** 118.71	antimony 51 **Sb** 121.76	tellurium 52 **Te** 127.60	iodine 53 **I** 126.90	xenon 54 **Xe** 131.29
caesium 55 **Cs** 132.91	barium 56 **Ba** 137.33	57-70 *	lutetium 71 **Lu** 174.97	hafnium 72 **Hf** 178.49	tantalum 73 **Ta** 180.95	tungsten 74 **W** 183.84	rhenium 75 **Re** 186.21	osmium 76 **Os** 190.23	iridium 77 **Ir** 192.22	platinum 78 **Pt** 195.08	gold 79 **Au** 196.97	mercury 80 **Hg** 200.59	thallium 81 **Tl** 204.38	lead 82 **Pb** 207.2	bismuth 83 **Bi** 208.98	polonium 84 **Po** [209]	astatine 85 **At** [210]	radon 86 **Rn** [222]
francium 87 **Fr** [223]	radium 88 **Ra** [226]	89-102 **	lawrencium 103 **Lr** [262]	rutherfordium 104 **Rf** [267]	dubnium 105 **Db** [268]	seaborgium 106 **Sg** [271]	bohrium 107 **Bh** [272]	hassium 108 **Hs** [270]	meitnerium 109 **Mt** [276]	darmstadtium 110 **Ds** [281]	roentgenium 111 **Rg** [280]	ununbium 112 **Uub** [285]	ununtrium 113 **Uut** [284]	ununquadium 114 **Uuq** [289]	ununpentium 115 **Uup** [288]	ununhexium 116 **Uuh** [293]	ununseptium 117 **Uus** —	ununoctium 118 **Uuo** [294]

*lanthanoids	lanthanum 57 **La** 138.91	cerium 58 **Ce** 140.12	praseodymium 59 **Pr** 140.91	neodymium 60 **Nd** 144.24	promethium 61 **Pm** [145]	samarium 62 **Sm** 150.36	europium 63 **Eu** 151.96	gadolinium 64 **Gd** 157.25	terbium 65 **Tb** 158.93	dysprosium 66 **Dy** 162.50	holmium 67 **Ho** 164.93	erbium 68 **Er** 167.26	thulium 69 **Tm** 168.93	ytterbium 70 **Yb** 173.06
**actinoids	actinium 89 **Ac** [227]	thorium 90 **Th** 232.04	protactinium 91 **Pa** 231.04	uranium 92 **U** 238.03	neptunium 93 **Np** [237]	plutonium 94 **Pu** [244]	americium 95 **Am** [243]	curium 96 **Cm** [247]	berkelium 97 **Bk** [247]	californium 98 **Cf** [251]	einsteinium 99 **Es** [252]	fermium 100 **Fm** [257]	mendelevium 101 **Md** [258]	nobelium 102 **No** [259]

Symbols and names: the symbols and names of the elements, and their spellings are those recommended by the International Union of Pure and Applied Chemistry (IUPAC - http://www.iupac.org/). Names have yet to be proposed for the most recently discovered elements beyond 112 and so those used here are IUPAC's temporary systematic names. In the USA and some other countries, the spellings **aluminum** and **cesium** are normal while in the UK and elsewhere the common spelling is **sulphur**.
Group labels: the numeric system (1–18) used here is the current IUPAC convention.
Atomic weights (mean relative masses): Apart from the heaviest elements, these are the IUPAC 2007 values and given to 5 significant figures. Elements for which the atomic weight is given within square brackets have no stable nuclides and are represented by the element's longest lived isotope reported at the time of writing.

Image as well as more detailed information: www.webelements.com

Thank you for your attention



Crystal grown by nature

Mountain crystal / smoky quartz from Switzerland