Doctoral Thesis

Investigation of epitaxial ferroelectric K$_{1-y}$ Nay Ta$_{1-x}$ Nb$_x$ O$_3$ on Ba doped KTaO$_3$ substrates

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Publication Date:
1999

Permanent Link:
https://doi.org/10.3929/ethz-a-003886442

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Investigation of epitaxial ferroelectric $K_{1-y}Na_yTa_{1-x}Nb_xO_3$ on Ba doped KTaO$_3$ substrates

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY
ZURICH

for the degree of
Doctor of Natural Sciences

presented by

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December 17, 1999
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Abstract

The solid solution system $K_{1-x}Na_xTa_{1-x}Nb_xO_3$ (KNTN) is a very promising material for pyroelectric, nonlinear optical and electro-optical applications. With liquid phase epitaxy thin KNTN films of good quality are grown on $KTaO_3$ substrates which can be used as pyroelectric sensors or optical waveguides. In order to have the possibility of poling the KNTN films or measuring electrical fields in direction perpendicular to the substrate/film interface the substrate must be conducting. In this thesis therefore we doped $KTaO_3$ with barium (Ba). Ba doped $KTaO_3$ crystals of good quality were grown and characterized by optical and electrical measurements, and by ultraviolet photoelectron spectroscopy. Together with ab initio calculations of the electronic ground state the measured results can give a detailed picture of the origin of charge conduction in this material.

The ratio of K/Na atoms in the KNTN films allows the adjustment of the lattice constant and thus the lattice fitting with the substrate within 0.03% (when the film is in the cubic phase). In this work we demonstrated the possibility of poling the film either in-plane or perpendicular to the film/substrate surface, depending on the amount of incorporated Na. Only over small areas of $10 \mu m \times 10 \mu m$ it is possible to pole the film along any crystallographic axis without destroying the film.

Dielectric measurements on KNTN c-films (polar axis of the film perpendicular to the film/substrate interface) showed a very pronounced relaxor behavior even at frequencies around 20 Hz. Two relaxor processes can be distinguished and attributed to the tantalum (Ta) / niobium (Nb) mixing (ferroelectric properties) and the K/Na mixing (polar glass properties).

To explore the physical properties of the KNTN films different types of pyroelectric detector arrangements were built and investigated. The pyroelectric current as well as the voltage
response were measured. The influence of the substrate (on the heat flow in the pyroelectric detector) is discussed and the pyroelectric coefficient was determined. The two independent nonlinear optical susceptibility coefficients $d_{31}$ and $d_{33}$ were measured by Maker-fringe technique.
Zusammenfassung


Durch Ändern des Verhältnisses der K und Na Atome kann die Gitterkonstante im KNTN Film an diejenige im Substrat mit einer Genauigkeit von 0.03 % angepasst werden. In dieser Arbeit wurde gezeigt, dass Filme gewachsen werden können, die entweder entlang der Oberfläche oder senkrecht dazu gepoole werden können. Flächen von bis zu $10 \mu m \times 10 \mu m$ wurden entlang einer beliebigen kristallographischen Achse zerstörungsfrei gepolt.

Messungen der komplexen Dielektrizitätskonstanten zeigten ein ausgeprägtes Relaxor-Verhalten, da schon für Frequenzen von ungefähr 20 Hz eine Abhängigkeit der Dielektrizitätskonstanten von der Frequenz gemessen werden konnte. Über den Frequenzbereich von 20 Hz bis 100 kHz können zwei Relaxor-Prozesse unterschieden werden, die je dem Gemisch von Ta
Zusammenfassung

und Nb Atomen (verantwortlich für die ferroelektrischen Eigenschaften) und demjenigen von K und Na Atomen (das zu polarem Glass führt) zugeschrieben werden können.


Zusätzlich zu den experimentellen Arbeiten wurden Berechnungen der Valenzelektronenverteilung im Grundzustand von KTaO$_3$ und KNbO$_3$ durchgeführt und miteinander verglichen.
Chapter 1

Introduction

Potassium tantalate niobate (KTa$_{1-x}$Nb$_x$O$_3$ or KTN) is a solid solution system which possesses very high quadratic (Kerr) and linear (Pockels) electro-optic effects, which led to considerable interest in this material during the last 35 years [1–5]. Since its constituent crystal potassium tantalate (KTaO$_3$ or KT) and potassium niobate (KNbO$_3$ or KN) have almost identical cubic unit-cell sizes but very different phase transition temperatures from the ferro- to the paraelectric phase (approximately 0 and 708 K, respectively), the phase transition temperature of the solid solution and thus its properties at a given temperature can be controlled by adjusting the tantalum to niobium ratio of the respective crystal [6]. The reason for the solid solution behaviour of these $ABO_3$ compounds with perovskite structure is the isomorphy of both end members and the chemical similarity of the $B$ ions with almost identical ionic radii $r_B = 0.68$ Å for Ta$^{5+}$ and $r_B = 0.69$ Å for Nb$^{5+}$.

There have been numerous attempts to grow large optical-quality KTN crystals, but because of the concentration changes during growth, the crystal always exhibited dark and bright regions parallel to the growth interface (so-called striations) which prevented the wide-spread use of KTN in optical devices [7,8]. KTN crystals without these striations demand a highly temperature stabilized growth equipment with a long term temperature fluctuation $\Delta T < 0.02$ °C at a growth temperature $T > 1000$ °C. A $\Delta T$ of 0.02 °C leads to a variation of the Nb concentration of $\delta x \approx 3 \cdot 10^{-5}$ and a refractive index modulation of $\Delta n \approx 10^{-6}$ [9–11].
Gutmann [12] successfully grew KTN crystalline thin films of constant composition on KTaO₃ substrates. The selection of liquid phase epitaxy (LPE) as the growth method for µm thick films allowed the choice of a dilute system (KF/KTN solution with about 7 mol% KTN), and thus a large variation of the growth rate and reduced sensitivity for small temperature fluctuations. Even though the lattice constant in the cubic phase of KTaO₃ and KTN are quite similar (3.988 Å for KT and 3.994 Å for KTN(x = 0.37), both at 300 K), relaxation defects due to lattice misfit are still observed. A successful method for the reduction of the lattice misfit and the avoidance of lattice misfit induced defects was the partial replacement of K by Na in the KTN lattice. The exchange of A ions in the ABO₃ lattice can be performed to a certain limit of ≈ 20 mol% without degradation of most of the physical properties, which depend mainly on the B-O interaction in the BO₆-octahedra. In practice, the Na incorporation was accomplished by a replacement of part of theKF by NaF in the [(KF)₁₋ₓ(NaF)ₓ] – KTN(x) solution resulting in a film composition of K₁₋ₓNaₓTa₁₋ₓNb₂O₃ (KNTN). The smaller ionic radius of Na⁺ compared to that of K⁺ reduces the lattice constant of the KNTN film and thus a matching with that of KT is possible.

Before the beginning of this thesis the following problems and questions were still unsolved:

- The high electrical resistivity of pure KTaO₃ substrates (ρ ≈ 10¹¹ Ωm) prevents generally any electrical treatment (e.g. the poling of ferroelectric films) or dielectric and electro-optical measurements on the epitaxial film via the substrate.

- Lattice matching of KNTN films on KTaO₃ substrates has mainly be investigated for the cubic (paraelectric) phase. For the tetragonal (ferroelectric) phase, only the influence of Na to the number of induced misfit defects and some in-plane (parallel to the substrate/film interface) poling experiments have been carried out. What remained was the description and optimization of the amount of domains with polarization perpendicular to the substrate/film interface.

During the work of this thesis the following was achieved:

- Barium was established as a new dopant for KTaO₃ (chapter 4). Ba:KTaO₃ substrates have a resistivity as low as 2 · 10² Ωm compared to 10¹¹ Ωm for pure KTaO₃. Optical and
electrical measurements were carried out. The dopant-induced optical absorption shows an $E^{-3}$ dependency (where $E$ is the energy of the photon) which is attributed to free-carrier absorption due to ionized-donor scattering. 0.004 at% Ba is sufficient to lower the specific resistivity of the substrate to 200 $\Omega \cdot \text{m}$ with an acceptable absorption constant $\alpha < 2 \text{ cm}^{-1}$ in the wavelength range from 400 nm to 1 $\mu$m. Ultraviolet photoelectron spectroscopy measurements were used to investigate the shift of the Fermi level by doping and confirmed the picture of ionized donors (Ba) impurities. Theoretical calculations of the electronic ground state of Ba-doped KTaO$_3$ gave the same result.

- Poling of KNTN films perpendicular to the substrate/film interface was demonstrated and the best K/Na concentration was examined (chapter 5.1).

- Dielectric measurements showed a frequency-dependent broad phase transition of KNTN. This relaxor behaviour could be explained by two mechanism connected to the Ta/Nb and K/Na mixings (chapter 5.2).

- Pyroelectric detectors based on KNTN films were built and investigated. The influence of the thermal contact of the film on the pyroelectric response was clearly shown (chapter 5.3).

- In addition to the main themes above, a new method for measuring the ferroelectric hysteresis was developed (appendix 1) and some calculations on the electronic ground-state and band-structure of the materials were carried out (chapter 6 and appendix 2).
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Chapter 2

Fundamentals

2.1 Ferroelectric crystals

Crystals exhibiting a spontaneous polarization \( P_s \), which can be reoriented by an external electric field, are called ferroelectric. Whether ferroelectricity can occur in a crystal depends on its point group. The dipole moment of a crystal is defined as

\[ \mu = \iiint \rho(r) \, r \, dV, \]  

(2.1)

where \( \rho(r) \) is the charge density at point \( r \) and \( dV \) an infinitesimal volume element. With \( \mu^* \) being the dipole moment per unit volume, the spontaneous polarization can be expressed as

\[ P_s = \frac{\iiint \mu^* \, dv}{\text{volume}}. \]  

(2.2)

The measurement of \( P_s \) as a function of the applied electric field gives a hysteresis which looks similar to the form obtained for the magnetization as a function of the applied magnetic field in ferromagnetics. This similarity in the phenomenological description gave ferroelectricity its name.

In general, uniform alignment of electric dipoles only occurs in certain regions of a crystal, while in other regions of the crystal spontaneous polarization may be in another direction. Such
regions of uniform polarization are called ferroelectric domains. These domains are separated by domain walls. The two most common explanations why domains build up in a crystal are

- the domains are caused by electrostatic forces which build up at the crystal’s faces due to the change in spontaneous polarization, especially when cooling down from the paraelectric to the ferroelectric phase (where $dP_z/dT$ is large), and
- the existence of defects and internal stresses, which are present in grown crystals and require domains to minimize the free energy.

2.2 Perovskite structure

The perovskites are an extremely important class of materials which may undergo a series of ferroelectric transitions with decreasing temperature. The name perovskite was given to the natural mineral CaTiO$_3$ by the German chemist and mineralogist Gustav Rose (1798-1873), who named it after the Russian general and mineralogist Lev Alexeievitch Perovsky (1792-1856) in the 1830’s [13]. This name now is applied to a wide range of ABX$_3$ materials with structures similar to that shown in Fig. 2.1. We will restrict ourselves to the group of perovskite
oxides of the chemical form ABO$_3$, where O is an oxygen, A represents a cation with a larger radius and B is a cation with a smaller radius. Perovskites not only are of interest because of their ferroelectric properties. Geophysicists expect the lower mantle of the earth (from the 670 km seismic discontinuity down to the mantle-core boundary) to consist mainly (50 % - 90 %) of a MgSiO$_3$-rich perovskite phase. It seems that the major upper mantle mineral phases, olivine ((Mg, Fe)$_2$SiO$_4$), pyroxene ((Mg, Fe)SiO$_3$) and garnet ((Mg,Fe,Ca)$_3$Al$_2$Si$_3$O$_{12}$), all transform to assemblages dominated by perovskite-structured silicates ((Mg,Ca,Si)(Si,Al,Fe)O$_3$) at the conditions on the Earth’s lower mantle (20 – 30 GPa) [14].

The cubic perovskite structure shown in Fig. 2.1 can be understood as a cubic close-packed arrangement of A and O ions with B ions filling the octahedra interstitial positions. While the A ions give (almost) all their valence electrons to the oxygen, a small part of the B-ion valence electrons are also used for covalent bonding, as can be seen in the calculated valence electron distribution shown in Fig. 2.2. Nevertheless, it serves as quite a good approximation to look at the crystal as purely ionic. Then the packing of the structure can be described by a tolerance factor $t$, which is defined by

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)} \left( \frac{\text{diagonal length}}{\sqrt{2} \cdot \text{side length}} \right)$$

where $R_A$, $R_B$ and $R_O$ are the ionic radii of the A, B and O ions, respectively. For $t = 1.0$ the packing is said to be ideal. A Perovskite structure is obtained for values $0.80 < t < 1.14$, but even for those values the structure may differ from a pure cubic perovskite form. It may be a distorted small-cell perovskite in which ferroelectricity can appear (KNbO$_3$, BaTiO$_3$, ...). Another possibility are the distorted multiple-cell perovskites, where the true unit cell is made up of multiple cubic-perovskite-like but distorted sub-cells, e.g. the oxygen octahedra may be tilted by different angles. Materials with distorted perovskite structure may have different phases and mostly obtain the cubic perovskite structure at high temperatures. They exhibit a variety of electronic and magnetic properties such as ferroelectricity, antiferroelectricity, ferromagnetism, antiferromagnetism, and can be isolators, semiconductors, metals or even superconductors.

### 2.2.1 KTaO$_3$

At zero stress KTaO$_3$ (KT) preserves its cubic perovskite structure at all temperatures from its melting point at 1360 °C to 0 K and therefore is paraelectric throughout this temperature
range. However, it is slightly unstable against a condensation of the ferroelectric mode at low temperature. At higher temperatures (30-300 K) the susceptibility can be fitted to a Curie-Weiss law with a Curie-Weiss temperature $T_0 \approx 13$ K. For temperatures lower than 30 K this Curie-Weiss law does not apply, but $\epsilon(T)$ can be described by another form derived by Barrett [15]. His theory is the quantum-mechanical description of the theory of Slater, who proposed to explain the dielectric behavior of BaTiO$_3$ at least above its Curie temperature [16] by a model.
in which the crystal is treated as if the Ba and O ions were fixed in position and as if each Ti ion acted like an independent harmonic oscillator with small additional anharmonic terms. The only interaction of the Ti atoms is through the electric field. This picture of course can also be applied to KTaO$_3$, where the movement of the Ta atoms is described by independent harmonic oscillators in a matrix of fixed K and O atoms. Barrett wrote the potential energy for the Ta ion in an electric field as

$$
\phi = a (x^2 + y^2 + z^2) + b_1 (x^4 + y^4 + z^4) + 2b_2 (x^2 y^2 + x^2 z^2 + y^2 z^2) - q (x E_x + y E_y + z E_z),
$$

(2.4)

where $x$, $y$ and $z$ are the components of the position vector of the Ta ion measured from its symmetric high-temperature position. $\phi_2$ is treated as perturbation of the potential energy of a simple harmonic oscillator in an electric field, of which the unperturbed energy levels are given by

$$
E_{lmm}^0 = \left(l + \frac{3}{2}\right) \hbar \nu - \frac{q^2 E_x^2}{4a^4},
$$

(2.5)

where $l, m, n \in \mathbb{N}$. The diagonal matrix elements $\langle lmn|\phi_2|lmm\rangle$ in the case of small energy perturbation with respect to $kT$ are found to be

$$
\langle lmn|\phi_2|lmm\rangle = b_1 \left[ \frac{3}{4\beta^2} (2l^2 + 2l + 1) + (2m^2 + 2m + 1) + (2n^2 + 2n + 1) \right]
$$

$$
+ \frac{3q^2}{4a^2\beta} (2l + 1) (E_x^2 + E_y^2 + E_z^2) + (2m + 1) (E_x^2 + E_y^2 + E_z^2) + \frac{q^4}{16a^4} (E_x^4 + E_y^4 + E_z^4)
$$

$$
+ 2b_2 \left[ \frac{1}{4\beta^2} ((2l + 1)(2m + 1) + (2l + 1)(2n + 1) + (2m + 1)(2n + 1)) \right]
$$

$$
+ \frac{q^2}{8a^2\beta} (2l + 1) (E_x^2 + E_y^2) + (2m + 1) (E_x^2 + E_z^2) + (2n + 1) (E_y^2 + E_z^2)
$$

$$
+ \frac{q^4}{16a^4} (E_x^4 E_y^2 + E_y^2 E_z^2 + E_z^2 E_x^2),
$$

(2.6)

where $\beta = 2a/h\nu$. The ionic polarizability resulting from the Ta ion is

$$
\alpha_{Ta}' = \frac{q^2}{2a} \left(1 - \frac{(3b_1 + 2b_2)h\nu}{2a^2} \right) \coth \left( \frac{h\nu}{2kT} \right).
$$

(2.7)
For the dielectric constant it follows that

\[ \varepsilon = \frac{M}{\frac{1}{2} \coth \left( \frac{T}{2T_i} \right) - T_0} \]  \hspace{1cm} (2.8)

with

\[ T_i = \frac{\hbar v}{k} \]
\[ M = \frac{2a^3 \varepsilon_0 v B}{q^2 (3b_1 + 2b_2) kD} \]
\[ T_0 = \frac{2a^3 \varepsilon_0 v}{q^2 (3b_1 + 2b_2) kD} \left( \frac{Dq^2}{2a\varepsilon_0 v} - 1 \right) \]  \hspace{1cm} (2.9)

where \( B \) and \( D \) depend on the values of the electronic polarizabilities of the \( K \) and \( O \) atoms and on the geometry of the lattice. For \( T \gg T_1, \frac{1}{2} \coth(T_1/2T) \) asymptotically approaches \( T \) and in that limit (2.8) follows the Curie-Weiss law. Well under \( T_i \) the dielectric constant \( \varepsilon \) flattens and approaches \( M/(\frac{1}{2} T_i - T_0) \) for \( T \rightarrow 0 \) K. In Barretts theory, the deviation from the Curie-Weiss law results from the quantized nature of the ionic motion of the Ta ion, which has an energy of the lowest quantum level of \( kT_1 \) with \( T_1 \approx 55 \) K [17]. Thus it is the quantized nature of the soft mode, which prevents a phase transition to a ferroelectric state at normal pressure. Materials with such a behavior are called \textit{quantum paraelectrics}. It has been reported, however, that such a quantum paraelectric becomes ferroelectric when it is mixed with ferroelectrics or even other quantum-paraelectrics, or sufficiently strong uniaxial stress is applied [18, 19].

For optical applications it is worth noting that the fundamental bandgap at room temperature is 3.5 eV (3.8 eV at 0 K), and hence pure KT crystals are colorless and transparent in the visible. The refractive index \( n \) at room temperature is 2.223 at a wavelength of \( \lambda = 633 \) nm.

2.2.2 \textbf{KNbO}_3

\textbf{KNBO}_3 (KN) has a melting point of 1050 °C. Despite the very similar chemistry of Nb and Ta, \textbf{KNBO}_3 does not remain in the cubic phase down to lowest temperatures but undergoes a sequence of phase transitions when cooling down. The cubic (\textit{m3m}, paraelectric) to tetragonal (\textit{4mm}, ferroelectric) transition takes place at 435 °C, the tetragonal-orthorhombic (\textit{mm2})
at 225 °C, and the orthorhombic-rhombohedral (3m) at −33 °C. All these transitions are of first order and thus show a thermal hysteresis. If for all the structures a pseudo-cubic unit cell is used, which is very close to the truly cubic unit-cell at high temperatures, then the displacements of the ions, and thus the direction of spontaneous polarization, is parallel to [001] in the tetragonal, [011] in the orthorhombic, and [111] in the rhombohedral phase.

The spontaneous polarization in KNbO₃ is 41 ± 2 μC/cm² at room temperature [20]. KNbO₃ crystals have large nonlinear optical coefficients \(d_{ijk}(2\omega): |d_{31}| = 11.3\) pm/V, \(|d_{32}| = 12.8\) pm/V, \(|d_{33}| = 19.5\) pm/V, (for \(\lambda = 1064\) nm) [21]. In addition, the crystal is very suitable for sum-frequency and second harmonic generation of short wavelength radiations under non-critical phase-matching conditions [22,23] and planar optical waveguides have been produced in KNbO₃ [24,25].

2.2.3 KTa₁₋ₓNbₓO₃ and K₁₋ₓNaₓTa₁₋ₓNbₓO₃

KTA₁₋ₓNbₓO₃ (KTN) is a completely miscible solid solution of KTaO₃ and KNbO₃. The temperature of the phase transition from para- to ferroelectric state can be varied freely by the relative Nb concentration \(x\) between 0 K for \(x = 0\) to 708 K for \(x = 1\) (Fig. 2.3). The reason for the solid solution behavior of the KTaO₃-KNbO₃ system lies in the isomorphy of the Ta and Nb atoms. Their ionic radii are very similar \((r_{Ta} = 0.68\) Å and \(r_{Nb} = 0.69\) Å).

At low Nb concentrations the cubic structure does not become instable even at lowest temperatures. According to Höchli [27], the critical concentration of Nb ions in a KT crystal to get a ferroelectric state is \(x_c = 0.008\). Unlike the cases of Na and Li dopants in a KTaO₃ crystal, there seems to be no polar glass state for any concentration in the KTN solid solution system. It is important to note however, that a KTN "crystal" is not determined just by indicating the relative concentration \(x\) of the Nb ions. It is not clear how the Ta and Nb ions are distributed on a microscopic level. This distribution depends probably greatly on the way the crystals were grown.

KTN was for a first time produced and investigated by Triebwasser [6]. Theoretical and experimental results of the investigation of linear and quadratic electro-optical effect for ferro- and paraelectrical KTN at room temperature, respectively, were reported by different authors [2–4,28,29]. In the paper of Ingold and Günter [28] a theoretical half-wave voltage
Figure 2.3: Phase diagram of $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ established by Rytz ([26] and references therein). Up to $x \approx 0.01$ no ferroelectric phase at normal pressure can be seen. For $0.01 < x < 0.05$ only a transition from cubic to rhombohedral structure is present, whereas for $x > 0.05$ the crystal undergoes all three phase transition as in the case of $\text{KNbO}_3$ ($x = 1.0$). For $x > 0.3$ the phase transition from para- to ferroelectric state is of first order; for $x < 0.3$ it is of second order.

$V_{\text{min}} = 8.9$ V was postulated for a KTN($x = 0.43$) at $\lambda = 633$ nm. Also the optical properties of pure, Fe and Ti-doped KTN crystals were examined [30,31].

From $\text{KNbO}_3$, KTN inherits all the outstanding pyroelectric, linear and nonlinear electro-optical effects. The mixing with KT introduces a free parameter, $0 \leq x \leq 1$, which in turn can be used to adjust the Curie temperature in the whole range between 708 K (for pure KN) to 0 K (for pure KT). With this, it is possible to tailor the composition of KTN and KNTN in order to get maximal effects at the working temperature; i.e. for pyroelectric applications the Curie temperature should be slightly above the working temperature to maximize the pyroelectric effect.
The solid-liquid phase diagram of KTN imposes a fundamental growth problem encountered for all solid solution systems. The fact that the composition between the melt and the growing crystal is not identical and the growth temperature (see Fig. 2.4) has to be lowered during the growth implies that the growing crystal experience a continuous change of composition. The melt and the crystal composition are both shifted to the lower melting component, here KN. This problem can be avoided by growing thin films of KTN and KNTN, where only a small part of the melt is incorporated in a crystalline layer on a suitable substrate. Because of the very close lattice constant of any KTN with KT, the latter is a perfect choice for the use as substrate, especially because it is not ferroelectric and thus does not contribute in any measurement of ferroelectric-related properties on the film/substrate system.

The addition of Na to KTN, which gives K_{1-y}Na_yTa_{1-x}Nb_xO_3 (KNTN), finally allows the lattice matching of KNTN films on KT substrates, because the smaller Na⁺ ions, which replace the K⁺ ion, decrease the lattice constant of the KNTN film. With this, it can be seen that KNTN films on KT substrates is a very promising candidate for pyroelectric, electro-optical and nonlinear-optical applications.
2.3 Phase transitions in KNbO₃ and KTa₁₋ₓNbₓO₃

Crystals in the cubic perovskite structure are paraelectric because symmetry prohibits a polar axis. If temperature is lowered many of the perovskites undergo transitions to phases with lower symmetry. KNbO₃ as an example changes from cubic to tetragonal, then to orthorhombic and at last to rhombohedral symmetry when cooling down. In general, the temperature $T_C$, which separates the paraelectric from the ferroelectric phase is called the *Curie point or phase transition temperature*. The phase transition from ferroelectric to paraelectric state is called *second-order phase transition* if the spontaneous polarization $P_s$ is a continuous function of temperature $T$; if $P_s(T)$ exhibits a discontinuity at $T_c$, then we have a *first-order phase transition*. In most ferroelectrics, the temperature dependence of the real part $\varepsilon'$ of the dielectric constant $\varepsilon = \varepsilon' + i\varepsilon''$ above the Curie point can be described fairly accurately by the *Curie-Weiss law*

$$\varepsilon'(T) = \varepsilon_0 + \frac{C}{T - T_0} \approx \frac{C}{T - T_c} \quad (\text{for } T > T_c), \quad (2.10)$$

where $C$ is the *Curie constant* and $T_0$ is the *Curie temperature* which equals the Curie point $T_C$ only in the case of a second-order phase transition. For first-order transitions upon cooling the crystal it is $T_0 < T_C$. In relaxor materials the temperature dependence of the dielectric constant displays a broadened peak [32]. When the temperature is higher than $T_m$ (the temperature at which the dielectric constant has its maximum value $\varepsilon_m$), $\varepsilon'(T)$ changes with $T$ according to

$$\frac{1}{\varepsilon'} - \frac{1}{\varepsilon_m} = C'(T - T_m)^\eta, \quad (2.11)$$

where $1 < \eta < 2$ and $C'$ is a constant.

2.3.1 Phenomenological theory

Phenomenological theories of ferroelectricity go back to Müller [33,34], Ginzburg [35,36], and Devonshire [37–39]. The starting point is the Gibbs free energy density $G$ of a piezoelectric crystal without magnetic effects, given by

$$G = U - TS - \sum_i X_i x_i - \sum_i E_i D_i, \quad (i = 1 \ldots 6, \, i = 1 \ldots 3) \quad (2.12)$$
1.3 Phase transitions in KNbO₃ and KTa₀₋ₓNbₓO₃

where the variables are defined in Table 2.1.

<table>
<thead>
<tr>
<th>variable</th>
<th>meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>stress (tensor)</td>
</tr>
<tr>
<td>x</td>
<td>strain (tensor)</td>
</tr>
<tr>
<td>E</td>
<td>electric field (vector)</td>
</tr>
<tr>
<td>D</td>
<td>electric displacement (vector)</td>
</tr>
<tr>
<td>Pₛ</td>
<td>spontaneous polarization (vector)</td>
</tr>
<tr>
<td>S</td>
<td>entropy (scalar)</td>
</tr>
<tr>
<td>T</td>
<td>temperature (scalar)</td>
</tr>
<tr>
<td>U</td>
<td>internal energy (scalar)</td>
</tr>
<tr>
<td>G</td>
<td>Gibbs free energy (scalar)</td>
</tr>
</tbody>
</table>

Table 2.1: Used variables and their meaning. In the text, the following substitutions are made for tensor indices: (11)→ 1, (22)→ 2, (33)→ 3, (23),(32)→ 4, (13),(31)→ 5, and (12),(21)→ 6.

In general, the material response to an applied electric field \( E \) is (phenomenologically) described by

\[
D = \varepsilon_0 E + P = \varepsilon_0 (1 + \chi) E, \tag{2.13}
\]

where \( D \) is the electric displacement, \( \varepsilon \) the permittivity constant, \( P \) the electric polarization, and \( \chi \) the dielectric susceptibility. In ferroelectrics, \( D \) can be approximated by \( P \) because \( \chi \gg 1 \).

Because of the cubic symmetry of KNbO₃ and KTaO₃ at high temperatures the free energy density can be expanded in a Taylor series of the form ([40] and references therein):

\[
G = G_0 + \alpha \left( P^2_x + P^2_y + P^2_z \right) + B_1 \left( P^4_x + P^4_y + P^4_z \right) + B_2 \left( P^2_x P^2_y + P^2_x P^2_z + P^2_y P^2_z \right) + C_1 \left( P^6_x + P^6_y + P^6_z \right) + C_2 \left[ P^4_x (P^2_y + P^2_z) + P^4_y (P^2_x + P^2_z) + P^4_z (P^2_x + P^2_y) \right] + C_3 P^2_x P^2_y P^2_z, \tag{2.14}
\]

where \( G_0 \) is the free energy in the paraelectric phase. Because the system cannot be stable for \( P \to \infty \), it is obvious that \( C_i > 0 \) (\( i = 1, 2, 3 \)). The equilibrium value of the spontaneous
polarization \( \mathbf{P} \) can be obtained by minimizing the free energy Eq. (2.14). Both the condition of extremum

\[
\left( \frac{\partial G}{\partial P_i} \right)_{\mathbf{P}} = 0
\]  

(2.15)

and of minimum need to be satisfied. The latter condition means that where Eq. (2.15) holds the second differential of free energy must be a positively defined quadratic form

\[
d^2G = \sum_{i,k=x,y,z} \frac{\partial^2 G}{\partial P_i \partial P_k} dP_i dP_k > 0. 
\]  

(2.16)

Extremum condition Eq. (2.15) gives the following system of equations for \( \mathbf{P} \):

\[
\begin{align*}
\alpha P_x + 2B_1 P^3_x + B_2 P_x (P^2_x + P^2_z) + 3C_1 P^5_x + 2C_2 P^3_x (P^2_y + P^2_z) + C_3 P^2_x P^2_y P^2_z &= 0, \\
\alpha P_y + 2B_1 P^3_y + B_2 P_y (P^2_x + P^2_z) + 3C_1 P^5_y + 2C_2 P^3_y (P^2_x + P^2_z) + C_3 P^2_x P^2_y P^2_z &= 0, \\
\alpha P_z + 2B_1 P^3_z + B_2 P_z (P^2_x + P^2_y) + 3C_1 P^5_z + 2C_2 P^3_z (P^2_x + P^2_y) + C_3 P^2_x P^2_y P^2_z &= 0. 
\end{align*}
\]  

(2.17)

There is a temperature \( T_0 \), where \( G(T_0, \mathbf{P} = 0) \) is not a local minimum anymore, and spontaneous polarization builds up. Above this temperature, \( \alpha \) in Eq. (2.18) must be positive, and become negative below \( T_0 \) in order to give a negative contribution to free energy for some definite polarization. The simplest form to achieve this requirements is to choose

\[
\alpha = A (T - T_0) \quad \text{with} \quad A > 0. 
\]  

(2.18)

Eqs. (2.17) with (2.18) have four families of solutions, corresponding to zero polarization (cubic symmetry); polarization directed along the fourth order axis (tetragonal symmetry); along the second order axis (orthorhombic symmetry) and along the third order axis (rhombohedral symmetry) (see Fig. 2.5). For the aforementioned symmetries the polarizations and the
2.3 Phase transitions in KNbO$_3$ and KTa$_{1-x}$Nb$_x$O$_3$

The polarization components $P_i$, ($i = t, o, rh$) have the form:

$$P_i^2 = -\frac{B_i}{2C_i} \left( 1 + \sqrt{1 - \frac{4\alpha C_i}{B_i^2}} \right). \quad (2.20)$$

where

Figure 2.5: Schematic plot of the direction vector of spontaneous polarization in the tetragonal (4mm), orthorhombic (mm2) and rhombohedral (3m) phase.
\[
B_t = 2B_1, \quad C_t = 3C_4,
\]
\[
B_0 = 2B_1 + B_2, \quad C_0 = 3(C_1 + C_2),
\]
\[
B_{rh} = B_1 + B_2, \quad C_{rh} = 3C_1 + 6C_2 + C_3.
\]

Let us now discuss the transition from the cubic paraelectric to the tetragonal ferroelectric phase. The spontaneous polarization will occur along the fourfold axis, and we can describe the phase transition using the free energy expansion Eq. (2.14) in only one dimension (say along the z-axis):

\[
G = G_0 + \sum_{\alpha} A(T - T_0) \frac{B_0}{2} P^2 + \frac{C_t}{2} P^4 + \frac{C_t}{3} P^6.
\]

The condition for a minimum, corresponding to Eq. (2.16) becomes

\[
\left( \frac{\partial^2 G}{\partial P^2} \right)_{P_t} > 0,
\]

which using Eqs. (2.12) and (2.13) is equivalent to

\[
\left( \frac{\partial E}{\partial P} \right)_{P_t} = \epsilon_0^{-1} \chi^{-1} > 0.
\]

**Paraelectric phase**

In the paraelectric phase we have \( P_t = 0 \) and consequently

\[
\epsilon_0^{-1} \chi^{-1} = \alpha(T) = A(T - T_0) > 0.
\]

Combining Eqs. (2.24) and (2.25) gives

\[
\chi = \frac{C}{T - T_0} \quad \text{with} \quad C \equiv \frac{1}{\epsilon_0 A},
\]

which is the Curie-Weiss law (hence \( T_0 \) is the Curie-Weiss temperature).
2.3 Phase transitions in KNbO$_3$ and KTa$_{1-x}$Nb$_x$O$_3$

Para- to ferroelectric phase transition

![Diagram of Gibbs energy as a function of the spontaneous polarization $P_s$.](image)

Figure 2.6: Gibbs energy as a function of the spontaneous polarization $P_s$. (a) For a first-order phase transition ($B_t < 0$), (b) for a second-order transition, $B_t > 0$. Left graph (a): (1), (2): $T > T_C$; (3): $T = T_C$; (4): $T_C > T > T_0$; (5), (6): $T < T_0$. Right graph (b): (1): $T > T_C$; (2): $T = T_C$; (3), (4), (5): $T < T_C$.

Let us assume that $B_t$ and $C_t$ vary only slightly in the vicinity of the phase transition temperature and therefore can be approximated by a constant value. It has already been shown that $C_t > 0$ and $\alpha = A(T - T_0)$, $A > 0$. If we examine Eq. (2.20) for $T > T_0$, we see that $\alpha > 0$, and hence a positive solution for $P_t^2$ exists only if $B_t < 0$. In that case we can have not only a local minimum at $P_t = 0$, but also for some finite value $P_t = P_1$. As long as the local minimum at $P_t = 0$ is the global one, the crystal is in the paraelectric state (Fig. 2.6(a), curves (1) and (2)). At the phase transition temperature $T_C > T_0$ (3), all three local minima have the same value and the spontaneous polarization changes discontinuously from zero to a finite value. For $T_C > T > T_0$ (4) there is still a local minimum at $P_t = 0$, which corresponds to a metastable paraelectric state. The ground state is already ferroelectric, but to reach this ground state a potential wall must be overcome. In this temperature region a hysteresis is often observed when measuring the dielectric constant $\epsilon(T)$. When cooling down from the paraelectric high-temperature phase the crystal can still be in the metastable paraelectric phase, while it is for sure in the ferroelectric state when heating the crystal up. The discontinuous change in spontaneous polarization and the observed hysteresis in $\epsilon(T)$ are typical for a such a first-order phase transition.
For $B_\tau > 0$ the Curie-Weiss temperature $T_0$ and the Curie point $T_C$ are equal, and the spontaneous polarization builds up continuously at the phase transition from para- to ferroelectric state. In Fig. 2.6(b) curve (1) corresponds to $T > T_c$. Phase transition occurs at $T = T_c$ (2) and leads to ferroelectric states for $T < T_c$ (3,4,5).

### 2.3.2 The eight-site model

The eight-site model was introduced by Comes [41] as part of an explanation of ferroelectric phases and phase sequences in BaTiO$_3$. It assumes the presence of a local minimum of the potential energy for the Ti-atom in an off-center position along all eight [111] directions. At high temperatures in the cubic phase the Ti-atoms are distributed equally over all eight sites and no macroscopic polarization is present in the crystal. Towards lower temperatures three subsequent order-disorder phase transitions take place and the number of probable sites for the Ti atoms is reduced from the eight sites in the cubic phase to four in the tetragonal phase (giving a polarization in [100] direction), further to only two in the orthorhombic phase (polarization along [110] direction), and at last to only one of the previously eight possible sites in the rhombohedral phase (with a polarization in [111] direction) (see Fig. 2.7). The remaining problem in this model is the driving force for the symmetry-breaking at the phase transitions.

The eight-site model can be formulated as a limiting case of the continuous-spin model with the general form [42]:

$$\mathcal{H}(\{\xi_i\}) = \sum_i V_0(\{\xi_i\}) + \sum_{i,j,\alpha\beta} J_{ij\alpha\beta} \xi_i^\alpha \xi_j^\beta,$$

where the $\{\xi_i\}$ are the lattice Wannier function coordinates representing the degree of local polar distortion. (The lattice Wannier functions are an orthonormal basis of symmetrized localized atomic displacement patterns). In the extreme case where $V_0$ has very narrow and deep wells in the [111] directions, $\xi$ can take only eight discrete values $\xi_0(s_x, s_y, s_z)$, where $s_\alpha = \pm 1$. Then the local potential term becomes a constant, and the energy differences between different configurations are determined by the intersite interactions. It turns out, however, that nearest neighbor interactions and also further neighbor interactions result in a direct cubic to rhombohedral phase transition [42]. Therefore, additional physics must be included in the model to give the right
2.3 Phase transitions in KNbO₃ and KTa₁₋ₓNbₓO₃

cubic-tetragonal-orthorhombic-rhombohedral phase sequence. A simple way to do so is to include strain coupling. The lowest order strain coupling terms allowed by symmetry are linear in strain and quadratic in \( \xi_i \). The simplest nontrivial coupling is

\[
j_i \sum_{\alpha \beta} \left[ (2e_{xx} - e_{yy} - e_{zz}) \xi_{i\alpha} \xi_{j\beta} + (2e_{yy} - e_{xx} - e_{zz}) \xi_{j\alpha} \xi_{j\beta} + (2e_{zz} - e_{xx} - e_{yy}) \xi_{i\alpha} \xi_{j\beta} \right],
\]

with the six-component homogeneous strain tensor \( e_{\alpha\beta} (\alpha, \beta = x, y, z) \).

A model similar to Eq. (2.27) has been used for the phase transitions in KTa₁₋ₓNbₓO₃. Vugmeister [43] considered the single-ion model of ferroelectricity with the Hamiltonian

\[
\mathcal{H}(\{\xi_i\}) = \sum_i \mathcal{H}_i(\{\xi_i\}) + \sum_{i\not=j} V_{ij} \xi_i \xi_j,
\]

Figure 2.7: The eight-site model for the phase sequence in BaTiO₃-type perovskites. In the cubic phase (m3m) all 8 sites are equally probably occupied by the Ti-atom (Nb or Ta-atom in the case of KNbO₃ or KTaO₃, respectively). In the tetragonal phase (4mm) the upper 4 sites are preferentially occupied; in the orthorhombic phase (mm2) two neighbor ones and in the rhombohedral phase (3m) only one site.
where some Ta atoms in the KTaO$_3$ matrix are substituted by Nb (impurity) atoms, $\xi_i$ is the vector describing the displacement of each ion. The single-particle potential $\mathcal{H}_i$ is adopted in the form

$$\mathcal{H}_i = \frac{\alpha}{2} \sum_{\alpha} \xi_{i\alpha}^2 + \frac{\beta}{4} \sum_{\alpha} \xi_{i\alpha}^4$$

for the host lattice ions, and

$$\mathcal{H}_i = \begin{cases} \frac{\alpha}{2} \sum_{\alpha} \left( |\xi_{i\alpha}| - \frac{x_0}{\sqrt{3}} \right)^2 + \frac{\beta}{4} \sum_{\alpha} \xi_{i\alpha}^4; & |\xi_{i\alpha}| > \frac{x_0}{\sqrt{3}} \\ \frac{U}{x_0^2} \left( |\xi_{i\alpha}| - \frac{x_0}{\sqrt{3}} \right); & |\xi_{i\alpha}| \leq \frac{x_0}{\sqrt{3}} \end{cases}$$

for the off-center Nb (impurity) ions. In the model it is assumed that the ferroactive host lattice ions can be described by a single-well, slightly anharmonic potential, while the impurity ion potential possesses eight off-center minima with a barrier height $U$, $a_d$ is the harmonic constant of the impurity, $x_0$ the off-center displacement of the impurity ion in the [111] direction. Within the mean-field theory and using the expression for the average square displacement of the host lattice ion $\langle x_i^2 \rangle$ in the description of KTaO$_3$ as quantum paraelectric the correct phase transition temperature $T_c(x)$ for high and low concentrations $x$ in KTa$_{1-x}$Nb$_x$O$_3$ could be obtained.

### 2.3.3 The microscopic model of Cochran - Anderson

Cochran and Anderson [44] derived a description of the phase transition under the assumption that in some ferroelectrics, the phase transition should be the result of a lattice instability which is caused by a particular ionic motion of all constituent atoms, i.e. from a vibrational mode. In ionic crystals, the vibrational modes are accompanied by an oscillating polarization which induces a local electric field. This local field interacts with the ions through long range Coulomb forces. If, for a particular mode, the long range forces are of the same magnitude but of opposite sign than the short range ones, the vibrational mode is a so-called soft mode. With decreasing temperature, the frequency of soft modes goes to zero at the Curie temperature $T_0$. As a result the crystal becomes unstable, and its structure changes in order to obtain a stable state again. Ferroelectric transitions can usually be associated with the condensation of a soft mode of lattice motion at the Brillouin zone center.
2.3 Phase transitions in KNbO$_3$ and KTa$_{1-x}$Nb$_x$O$_3$

The microscopic model of Cochran and Anderson is a lattice in one dimension with a basis consisting of a fully polarized cation and an anion with a spherical electronic shell (see Fig. 2.8). Between cation and anion we have a short range force constant $f$, and $k$ is the harmonic core-shell force constant. The relative displacements in the $j$-th cell of the cation, the anion, and the electronic shell are labeled by $u_j^+$, $u_j^-$, and $v_j$, respectively. The cation has a mass $m^+$, ionic charge $Z \cdot e$; that of the anion is $m^-$ and $Z \cdot e$ ($e$ is the electron charge), where the spherical electronic shell has a charge $Y \cdot e$ and the core the charge $X \cdot e$ ($X + Y = Z$).

The model system is subjected to long range Coulomb forces (depending on their charges) and the local field $E_{loc}$ is of the form

$$E_{loc}(x) = E_{loc} \mathbf{p} e^{i(kx - \omega t)}, \quad (2.32)$$

where $k$ is the propagating vector, $\mathbf{p}$ the unit polarization vector, $E_{loc}$ the field amplitude and $\omega$ the angular frequency. (We assume a pure transverse uniform field, $\exp(i k x) = 1.$)
The model equations are then given by

\begin{align*}
m^+ \ddot{u}_j^- &= f(v_j + v_{j+1} - 2u_j^+) + ZeE_{loc} \\
m^- \ddot{u}_j^- &= k(v_j - u_j^-) + XeE_{loc} \\
0 &= k(u_j^- - v_j) + f(u_j^- + u_{j-1}^+ - 2v_j) + YeE_{loc},
\end{align*}

(2.33)

where in the last equation the mass of the electronic shell has been taken as zero. Considering only center phonons (q = 0), the displacements now can be substituted by

\begin{align*}
u_j^+ &= U^+ e^{i\omega t} \\
u_j^- &= U^- e^{i\omega t} \\
v_j &= Ve^{i\omega t}.
\end{align*}

(2.34)

With the relative displacements \(U = U^+ - U^-\) and \(W = U^- - V\), together with \(F = 2f\) Eq. (2.33) becomes

\begin{align*}
m^+ \omega^2 U^+ &= F(U + W) - ZeE_{loc} \\
m^- \omega^2 U^- &= kW - XeE_{loc} \\
0 &= kW + F(U + W) + YeE_{loc} \quad \Rightarrow \quad W = \frac{FU + YeE_{loc}}{k + F}
\end{align*}

(2.35)

Inserting the last expression for the relative core-shell displacement \(W\) into the upper two equations in Eq. (2.35) then leads to

\begin{align*}
m^+ \omega^2 U^+ &= \Phi U - \xi eE_{loc} \\
m^- \omega^2 U^- &= -\Phi U + \xi eE_{loc}.
\end{align*}

(2.36)

Here, the effective force constant has been defined as \(\Phi = Fk/(F + k)\) (which takes into account the short-range forces and the intra-ionic forces), and the effective ionic charge is \(\xi = Z + FY/(F + k)\), which includes the Coulomb charge \(Ze\) and the effects of the core-shell deformation. Finally, with the reduced mass \(\mu = (m^+m^-)/(m^+ + m^-)\), we obtain

\(\mu \omega^2 U = (\Phi U - \xi eE_{loc}).\)

(2.37)
This result can now be interpreted: for a softening of a ferroelectric mode \((\omega \rightarrow 0)\) it is necessary to have a balance between short-range forces and long-range Coulomb forces.

Inserting an expression for the local field \(E_{\text{loc}}\) into Eq. (2.37) and using a dielectric constant of the form

\[
\epsilon(\omega) = \epsilon_{\text{lattice}} + \epsilon_{\infty}
\]

\((\epsilon_{\infty} \text{ being the high frequency dielectric constant)}\) one arrives at the famous Lyddane-Sachs-Teller relation

\[
\frac{\epsilon(0)}{\epsilon(\infty)} = \frac{\omega_{LO}^2}{\omega_{TO}^2},
\]

where \(LO\) means a longitudinal optical, and \(TO\) a transversal optical mode. Relation (2.39) implies that the anomaly of the static dielectric constant \((\epsilon(0) \rightarrow \infty)\) is caused by the frequency anomaly of a particular \(TO\) mode \((\omega_{TO} \rightarrow 0)\). This is the soft \(TO\)-mode or ferroelectric mode.

In contrast to the order-disorder transition in the eight-site model the description by soft-modes is a displacive one. While in the displacive scenario it is supposed that the \(Nb\) atoms are oscillating about the central symmetric position in the high-temperature paraelectric phase, in the eight-site model the \(Nb\) atoms are assumed to be statistically distributed over the eight \([111]\)-displaced positions. In \(KNbO_3\) a crossover of both models seems to be the best description ( [45] and references therein). Raman scattering experiments have shown that separate off-center potential minima for \(Nb\) atoms exist, and the hopping between them can be induced by appropriate photon pumping (contradicting a simply displacive description). On the other hand the eight-site picture would imply that a single \(Nb\) impurity in a \(KTaO_3\) crystal had the choice of eight local potential minima around the mass center of the replaced Ta atom. However, in the phase diagram of \(KTa_{1-x}Nb_xO_3\) (Fig. 2.3) up to \(x \approx 0.01\) no ferroelectric phase can be seen. Theoretical calculations of a single \(Nb\)-atom in a supercell configuration did also not show these eight potential minima. Nevertheless, calculations for \(KNbO_3\) in the cubic state give the eight off-center potential minima for a simultaneous \([111]\) displacement of all the \(Nb\) ions (or at least a not-too-small subset thereof). This means that the displacement of the \(Nb\) ions is correlated, and the ferroelectric instability develops as the softening of particular phonon modes. The important difference with the simple displacive model is that the particular vibration pattern may have finite spatial extend, or correlation length, even at very low temperatures.
2.4 Relaxor ferroelectrics

While “normal” ferroelectric material, such as BaTiO₃, KNbO₃, triglycine sulfate (TGS) and many more, show a narrow peak in the real part of permittivity $\varepsilon'(T)$ around the phase transition temperature, there is a group of ferroelectrics, the relaxors, which exhibit a broad and high maximum of $\varepsilon'(T)$. In addition, $\varepsilon'(T)$ has a strong frequency dispersion. While for the real part $\varepsilon'$ of the complex permittivity $\varepsilon = \varepsilon' + i\varepsilon''$ the higher values are obtained at lower measurement frequencies, the maximum of the imaginary part $\varepsilon''(T)$ corresponds to higher measurement frequencies. Relaxor ferroelectrics include many solid solutions and stoichiometric compounds. A huge group of perovskite-based solid solutions are relaxors, i.e. KNb₁₋ₓTaₓO₃ (KTN), (Pb₁₋ₓLaₓ)Zr₁₋ₓTiₓO₃ (PLZT), (Pb₁₋ₓBaₓ)Zr₁₋ₓTiₓO₃ (PBZT) and Pb(Mg₁/₃Nb₂/₃)O₃ (PMN).

For the description of relaxor type ferroelectrics some models are described below (for a more complete overview, see [46]).

2.4.1 Compositional fluctuation model

Already in 1963 Isupov [47] proposed a model which assumes that ferroelectric relaxors consist of discrete microregions which do have different composition. In the case of KTN, this could be an inhomogeneity of the distribution of the B-atoms (Ta and Nb). To each mesoscopic region a separate phase transition temperature can be assigned (depending on the composition), which on the macroscopic scale then gives a diffuse phase transition. Recent studies [48] on the atomic ordering showed that in PMN the ordered regions embedded in a Nb-rich matrix exist also on the nanometer scale. This means that the compositional fluctuations cannot be the only reason in this material.

Another approach is that of Fritzberg [49], who applied the concept of the Känzig region to ferroelectrics. Känzig regions are the smallest regions in which spontaneous polarization appears or disappears because of thermal fluctuations. This could be observed in the temperature region just above the ferroelectric phase transition in BaTiO₃. However, this theory can also not explain why solid solutions should show a broader peak in $\varepsilon'(T)$ at phase transition than the “pure” ferroelectrics of which they consist.
2.4 Relaxor ferroelectrics

2.4.2 Orientational glass

Consider a crystal such as KTaO$_3$, where some K-atoms have been replaced by Li or some Ta by Nb. This replacement can give rise to a dipole moment, if the center of the substitutent is at an off-center position compared to the substituted ion. These dipole moments have an orientational degree of freedom and have been denoted the orientational glass system [27]. The dipoles interact with each other and, below some temperature, freeze in a position without long range order. This behavior is described by the empirical Vogel-Fulcher relationship,

$$\omega_r = \omega_0 \exp \left( -\frac{E_a}{k(T - T_f)} \right),$$

(2.40)

where $\omega_r$ is the relaxation frequency ($\varepsilon''(\omega_r) = \text{max}$), $\omega_0$ is the attempt frequency, $T_f$ the freezing temperature, $k$ the Boltzmann constant, and $E_a$ the activation energy.

2.4.3 Polar glass model

An interpretation of the properties of relaxors has been presented by Viehland [50] in an analogy to magnetic spin-glass systems. He proposed that the cooperative interaction between the dipoles is hindering the individual orientation, and that something like a preferred configuration of orientations within the clusters would represent the precursor to the long-range ferroelectric ordering. A modified Vogel-Fulcher relationship has been used to describe the frequency dependency of dielectric response. This modified relationship is given by:

$$\omega = \omega_0 \exp \left( -\frac{E_a}{k(T_m - T_f)} \right).$$

(2.41)

Here, $T_m$ is the temperature where the dielectric permittivity $\varepsilon'(T)$ has its maximum at frequency $\omega$. $T_f$ can be interpreted as the static freezing temperature for the reorientation of the dipole moments.
2.5 Pyroelectricity

The spontaneous polarization $P_s$ in ferroelectrics is temperature-dependent, and thus charge will build up on the surface of a ferroelectric material when its temperature is changed. The change of spontaneous polarization with temperature, $T$, is called the pyroelectric coefficient $p$: $p = dP_s/dT$. The ancient discovery of pyroelectricity most probably can be attributed to the high electric fields which develop across an insulating pyroelectric material when subjected to a relatively small temperature change. For example, in a crystal such as LiTaO$_3$ with a typical pyroelectric coefficient of $p = 1.9 \cdot 10^{-8}$ C cm$^{-2}$ K$^{-1}$ and a dielectric constant $\varepsilon' = 44$ (around room temperature), a field of 59 kV cm$^{-1}$ (sufficient to break down air) builds up for a temperature change of only 12 °C.

The term *pyroelectricity* is not always used in the same way (for an overview see [51]). Usually only *vectorial* pyroelectricity is encountered, which mathematically is a relation between a scalar (temperature) and a vector (polarization). In practice, the tensorial effect is negligible and will not be considered here. Physically, the vectorial pyroelectricity (the term *vectorial* will be omitted from now on) is the change of positive and negative polarization charges with temperature on certain portions of materials. This phenomenon is the direct pyroelectric effect. The reverse, or *electrocaloric* effect, describes the change in temperature of a pyroelectric material caused by a change in the electric field. Differences in the exact definition of the pyroelectric constant $p$ arise from considering different constrains. The classical approach is that given in [51], which describes a material of infinite dimensions and thus with no boundary effects. In [52], a pyroelectric material with finite dimensions and attached electrodes is considered, which gives expressions which can be used directly in an experimental situation. While in both descriptions the structure is supposed to be unclamped, differences arise from additional forces [52], which act perpendicular to and in the plane of the electrodes. Their origin lies in the electrostatic force due to the electrodes, which also gives an in-plane contribution, because of the finite size of the sample. Here, I will use the classical method for highlighting the fundamental physics behind the pyroelectric effect.

As in the previous section the starting point is Gibbs free energy (2.12). We choose $\mathbf{X}$, $\mathbf{E}$ and $T$ as independent variables. The differential form of (2.12) then is

$$dG = -SdT - \sum_i x_i dX_i - \sum_i D_i dE_i,$$

(2.42)
where \( l \) denotes the tensorial components in reduced form. We may write down elastic, dielectric, and thermal equation of state in the form

\[
x_\ell = - \left( \frac{\partial G}{\partial x_\ell} \right)_{E,T}, \quad D_\ell = - \left( \frac{\partial G}{\partial E_\ell} \right)_{X,T}, \quad S = - \left( \frac{\partial G}{\partial T} \right)_{X,E}.
\]  

(2.43)

The differential forms of these equations of state are:

\[
\begin{align*}
dx_\ell &= \sum_j \left( \frac{\partial x_\ell}{\partial x_j} \right)_{E,T} dX_j + \sum_j \left( \frac{\partial x_\ell}{\partial E_j} \right)_{X,T} dE_j + \left( \frac{\partial x_\ell}{\partial T} \right)_{X,E} dT, \\
\,dD_\ell &= \sum_j \left( \frac{\partial D_\ell}{\partial x_j} \right)_{E,T} dX_j + \sum_j \left( \frac{\partial D_\ell}{\partial E_j} \right)_{X,T} dE_j + \left( \frac{\partial D_\ell}{\partial T} \right)_{X,E} dT, \\
\,dS &= \sum_j \left( \frac{\partial S}{\partial x_j} \right)_{E,T} dX_j + \sum_j \left( \frac{\partial S}{\partial E_j} \right)_{X,T} dE_j + \left( \frac{\partial S}{\partial T} \right)_{X,E} dT.
\end{align*}
\]  

(2.44)

We can now define the coefficients:

- elastic compliance coefficients \( s_{ij} = \frac{\partial x_i}{\partial x_j} \)
- permittivities \( \varepsilon_{ij} = \frac{\partial D_i}{\partial E_j} \)
- piezoelectric constants \( d_{ij} = \frac{\partial D_i}{\partial x_j} \)
- pyroelectric coefficients \( p_i = \frac{\partial D_i}{\partial T} = \frac{\partial S}{\partial E_i} \)
- thermal expansion coefficient \( \alpha_i = \frac{\partial x_i}{\partial T} = \frac{\partial S}{\partial X_i} \)
- specific heat \( c = T \frac{\partial S}{\partial T} / \rho \frac{\partial T}{\partial T} \)

where \( \rho \) is the density.

If, in the variation of the electric displacement \( dD_i \) in (2.44), stress \( X \) and electric field \( E \) are held constant, only the third term on the right-hand side remains and we have

\[
dD_i = \left( \frac{\partial D_i}{\partial T} \right)_{X,E} dT,
\]

(2.45)

where the superscript \( X \) indicates that the crystal sample is under constant stress. Because of \( D = \varepsilon_0 E + P = \varepsilon^{perm} \varepsilon_0 E + P \), and the assumption that the dielectric constant \( \varepsilon^{perm} \) (coming
only from permanent polarization) is temperature-independent, the pyroelectric coefficients can be written as

\[ p_i^X = \left( \partial P_x / \partial T \right)_{X,E}. \]  \hspace{1cm} (2.46)

The pyroelectric effect occurs only in crystals exhibiting spontaneous polarization \( P_s \) or in materials with remanent polarization.

Under the condition of a constant external field \( (dE = 0) \), the equation for the variation of the strain (2.44) is:

\[ dx_i = s_{ij}^{E,T} dX_j + \alpha_i^E dT. \]  \hspace{1cm} (2.47)

and for the electric displacement:

\[ dD_i = d_{ij}^T dX_j + p_i^X dT. \]  \hspace{1cm} (2.48)

Combination (2.47) and (2.48) gives:

\[ dX_j = dx_i / s_{ij}^{E,T} - \alpha_i^E dT / s_{ij}^{E,T} \]
\[ = dD_i / d_{ij}^T - p_i^X dT / d_{ij}^T. \]  \hspace{1cm} (2.49)

Under constant strain \( (dx = 0) \) this gives

\[ p_i^X = \left( \partial D_i / \partial T \right)_X + d_{ij}^T \alpha_i^E / s_{ij}^{E,T}. \]  \hspace{1cm} (2.50)

The term \( \left( \partial D_i / \partial T \right)_X \) is a pyroelectric coefficient at constant strain and is written \( p_i^X \). The total pyroelectric coefficient at constant stress \( X \) is thus given by

\[ p_i^X = p_i^S + d_{ij}^T c_{jk}^{E,T} \alpha_k^E. \]  \hspace{1cm} (2.51)
The first term on the right hand side, which is the pyroelectric coefficient at constant strain, is called the first pyroelectric coefficient or (in older publications) real pyroelectric coefficient. The second term is the second pyroelectric coefficient, which describes the change in polarization, caused by the electric field, which is generated by thermal expansion and piezoelectric effect. The second pyroelectric effect is sometimes called pseudo-pyroelectric effect. Moreover, a third pyroelectric effect may occur in some pyroelectric materials. This effect is caused by a piezoelectric effect induced by a thermal stress, which, in turn, is due to inhomogeneous heating. While the first two effects may have the same order of magnitude, the third effect is always very small.

### 2.6 Nonlinear optic effect

In general the induced polarization $P$ in a medium can be expressed in a Taylor series expansion of the electric field $E$ of the optical wave:

$$P_i = \epsilon_0 \chi^{(1)}_{ij} E_j + \epsilon_0 \chi^{(2)}_{ijkl} E_j E_k + \epsilon_0 \chi^{(3)}_{ijklm} E_j E_k E_l + \ldots,$$  \hspace{1cm} (2.52)

where $P_i$ is the $i$th component of the instantaneous polarization and $E_j$ is the $j$th component of the instantaneous electric field and where summation runs over corresponding indices. $\chi$, $\chi^{(2)}$, $\chi^{(3)}$ are linear, quadratic and cubic optical susceptibility, respectively. The second term in Eq. (2.52) is responsible for the sum- and difference frequency generation (and as a special case also for the second-harmonic generation), and for parametric generation. The third term is responsible for third-harmonic generation and self-focusing.

If we look at two electric fields with frequencies $\omega_1$ and $\omega_2$ interacting in a nonlinear medium, the components of the polarization at the sum frequency $\omega_3 = \omega_1 + \omega_2$ is given by

$$P_{i,3}^{\omega_3}(\mathbf{r}) = \epsilon_0 \left[ \chi_{ijkl}^{(2)}(-\omega_3, \omega_1, \omega_2) E_j^{\omega_1}(\mathbf{r}) E_k^{\omega_2}(\mathbf{r}) + \chi_{ijkl}^{(3)}(-\omega_3, \omega_1, \omega_2) E_j^{\omega_1}(\mathbf{r}) E_k^{\omega_2}(\mathbf{r}) \right],$$  \hspace{1cm} (2.53)

where

$$E_i(\mathbf{r}, t) = \Re \left( E_i^{\omega}(\mathbf{r}) e^{-i\omega t} \right) \quad , \quad P_i(\mathbf{r}, t) = \Re \left( P_i^{\omega}(\mathbf{r}) e^{-i\omega t} \right).$$  \hspace{1cm} (2.54)
In the case of optical frequency doubling this gives

\[ P_i^{2\omega} = \epsilon_0 \frac{1}{2} \chi_{ijk}^{(2)} (-2\omega, \omega, \omega) E_j^{\omega} E_k^{\omega}. \]  

(2.55)

The nonlinear optical coefficients \( d_{ijk} \) are symmetric in \( j \) and \( k \) and thus can be written in a contracted notation with the following mapping of \((i, j)\):

\[
\begin{align*}
(11) & \rightarrow 1 & (22) & \rightarrow 2 & (33) & \rightarrow 3 \\
(23), (32) & \rightarrow 4 & (13), (31) & \rightarrow 5 & (12), (21) & \rightarrow 6.
\end{align*}
\]  

(2.56)

For the point group 4mm the contracted \( d_{ij} \) tensor is

\[
d_{ij}^{\text{4mm}} = \begin{pmatrix}
0 & 0 & 0 & 0 & d_{15} & 0 \\
0 & 0 & 0 & d_{15} & 0 & 0 \\
d_{31} & d_{31} & d_{33} & 0 & 0 & 0
\end{pmatrix}
\]  

(2.57)

in the case of non-absorbing, dispersionless materials the Kleinman relation \([53]\) \( d_{ijk} = d_{ikj} = d_{jki} = d_{kij} \ldots \) indicates \( d_{15} = d_{31} \), and there are only two independent elements left.
Chapter 3

Growth of $K_{1-y}Na_yTa_{1-x}Nb_xO_3$ films on $KTaO_3$ substrates

$K_{1-y}Na_yTa_{1-x}Nb_xO_3$ (KNTN) films with thicknesses of 5 to 40 $\mu$m were grown by liquid phase epitaxy (LPE). The excellent lattice matching of KNTN on pure or Ba-doped $KTaO_3$ (KT) allowed the growth of epitaxial films of high quality. The growth equipment and basics of the growth process will be described in this chapter. In addition, the pulling of pure and doped KT crystals is dealt with. At last the influence of the film composition and the induced lattice mismatch on the formation of domains is examined.

3.1 Liquid phase epitaxy of $K_{1-y}Na_yTa_{1-x}Nb_xO_3$

3.1.1 Basics of the epitaxial growth process

The overgrowth of single crystalline material on a crystalline substrate is called epitaxy. Whereas in homoepitaxial growth experiments substrate and film are of the same materials and of the same structure, the hetero-epitaxial growth describes the development of a crystalline film on a crystal with another chemical composition. In the following description, only heteroepitaxy will be considered.
Chapter 3. Growth of KTN films on KT substrates

The growth of two dimensional layers starts with the heterogeneous nucleation by the building of an adsorption layer, the coalescence and the orientation of the individual adsorbed atoms or molecules to a lattice arrangement and the filling in of the incomplete layers. After the nucleation the growth of thin films continues, under ideal conditions, in a layer by layer growth perpendicular to the substrate/layer interface, similar to the bulk crystal growth from solution. Any disturbance, e.g. a sudden variation of the supersaturation or the composition, can change this two dimensional growth mode called Frank-van der Merwe mode [12]. This growth mode can also be influenced by the lattice constant difference, the lattice misfit, and the difference between substrate/layer and layer/layer interaction. If the lattice misfit exceeds a certain limit the two dimensional Frank-van der Merwe growth mode will be replaced by the three dimensional Volmer-Weber mode, where inside the adsorption layer only three dimensional crystals can be formed. A further growth mode, the Stranski-Krastanov mode, can be observed when the atom-atom interaction between the substrate and the layer is different from the interaction between the atoms in the layer. In this case, the formation of the first two dimensional monolayer(s) shields the substrate/layer interaction, and enables a three dimensional growth of these first monolayers.

Liquid phase epitaxy (LPE), which means the growth of epitaxial films from solutions, complicates this process, because the transport of the layer forming atoms, the interaction at the layer boundary and the growth occur in a dispersive solution. Because of the temperature sensitivity of this process, any variation of the growth temperature will influence these interactions, changing the growth rates and the composition for solid solution system compounds like KTN and KNTN. To ensure a high crystal quality of the epitaxial layers the growth using LPE techniques should be performed in a highly temperature stabilized furnace at a low supersaturation or near the thermodynamical equilibrium. To ensure a homogeneous film thickness and composition the solution should be stirred by crucible or substrate rotation.

### 3.1.2 Growth of K\(_{1-y}\)Na\(_y\)Ta\(_{1-x}\)Nb\(_x\)O\(_3\) thin films

In this thesis K\(_{1-y}\)Na\(_y\)Ta\(_{1-x}\)Nb\(_x\)O\(_3\) (KTN) films with phase transition temperatures between 25 °C and 65 °C were grown. Compositions in the solution and those in the film are given in Table 3.1. Depending on the growth temperature the growth rate varies from 0.1 µm/min to 5 µm/min. Even larger growth rates result in the preferred nucleation on defects including
spiral growth mode leading to macroscopic spirals or growth hillocks. Generally, high growth rates reduce the crystal quality and demand a plane polishing of the epitaxial film surfaces.

The use of KF as solvent for KTN reduces the necessary growth temperature to about 920 °C and prevents K-deficiency in the film. A temperature stability of \( \Delta T < 0.1 \) °C during the dipping time is of prime importance, because even small fluctuations create chemical inhomogeneities (variation of the Nb/Ta ratio) during the growth. This requirement was fulfilled by using a 3-zone furnace, with a large crucible embedded in a high thermal mass (Fig. 3.1). For a detailed description of the LPE apparatus see [12]. To protect the ceramic parts of the furnace from gaseous KF an Argon atmosphere was used. The KTaO\(_3\) substrates were provided with a small furrow at the edges, mounted with a Pt-wire on the substrate holder and cleaned successively in acetone, H\(_2\)O, HF, H\(_2\)O and acetone. After this treatment the substrate was inserted into
Table 3.1: Growth data for tetragonal $K_{1-y}Na_yTa_{1-x}Nb_xO_3$ films obtained from $(KF)_{1-z}$ $(NaF)_z$-KTN(xs) solution. $x_f$ and $y_f$ are the composition in the film and $T_c$ the measured phase transition temperature.

<table>
<thead>
<tr>
<th></th>
<th>$x$ (melt)</th>
<th>$x_s$</th>
<th>$c_{KTN}$ [mol%]</th>
<th>$z_{NaF}$</th>
<th>$T_{gr}$ [$^\circ$C]</th>
<th>$x$ (film)</th>
<th>$y$ (film)</th>
<th>$T_C$ [(^\circ)C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>KTN contentration</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaF concentration</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>growth temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x_f$</td>
<td>$0.04\ldots0.11$</td>
<td>$0.39$</td>
<td>$0.78$</td>
<td>$0.05\ldots0.12$</td>
<td>$0.45$</td>
<td>$0.82$</td>
<td>$0.05\ldots0.12$</td>
<td>$0.03\ldots0.10$</td>
</tr>
</tbody>
</table>

the hot furnace with a speed of $\approx 1$ cm/min to a level of 1 cm above the solution. After a temperature equilibration time of 10 min it was dipped into the solution. The dwell time between reaching the growth temperature and the dipping process was at least 30 min. This time was necessary for the reduction of the temperature fluctuations induced by the control process of the temperature program. The epitaxial growth was always performed in the center of the solution. After the expired growth time the substrate with the epitaxial layers were rapidly ($\approx 1$ cm/sec) pulled out of the solution and slowly ($\approx 0.5$ cm/min) out of the furnace. As-grown films had a bluish tint, which arose due to a slight oxygen deficiency. After annealing at 950 $^\circ$C for 20 h in an oxygen atmosphere, they became transparent and insulating with a specific resistivity of around 1M$\Omega$ cm.

3.2 Production of a suitable substrate

3.2.1 The ideal substrate

A good substrate for LPE of KNTN thin films for optical waveguiding must fulfill several conditions. It should

- have a lattice constant very close to that of the film, to minimize strain and misfit dislocations in the film,
3.2 Production of a suitable substrate

- have a refractive index which is smaller than that of the film, to offer the possibility of optical waveguiding in the film, and

- be (semi-) conducting to allow poling of the film perpendicular to the substrate/film interface, electrical measurements (e.g. dielectric constant, pyroelectricity), and electro-optical applications.

As already pointed out by Gutmann [54], KT is a good candidate as it satisfies the first two of the three requirements listed above. The only drawback is that KT is an insulator. Therefore, a voltage applied to the substrate/film system would result in a much higher electric field in the substrate than in the film. One possible way of overcoming this problem, while still having the excellent lattice matching between the KNTN film and the KT substrate, is the doping of KT with an heterovalent ion.

In the literature quite a large number of publications can be found on K⁺ or Ta⁵⁺-ion doping in KT (see Table 3.2). Their findings are not consistent at all and it seems that one dopant can incorporate at different sites and may or may not generate an oxygen vacancy to bind the additional conduction electron of the dopant. KT seems to have an outstanding tolerance for misfits in ionic size and charge, as stated in [55].

Because of the similar ionic radius of Ba²⁺ \( (r_{\text{Ba}^{2+}} = 1.61 \text{ Å}) \) and K⁺ \( (r_{\text{K}^{+}} = 1.64 \text{ Å}) \) and because the second valence electron of Ba is not needed for ionic bonding with the O₃⁻-octahedra, we substituted some of the K⁺-ions in KT by Ba²⁺-ions to increase electrical conductivity. As already mentioned, it is important to check if Ba really incorporates at the K-site and if no oxygen vacancy is created, which would reduce electron conductivity. The corresponding measurements will be presented in Sec. 4.3.

3.2.2 Growth of the crystals

The growth of Ba:KTaO₃ crystals was performed in two steps. First, K₂CO₃ and Ta₂O₅ were calcinated at \( \approx 820 \text{ °C} \), giving a KTaO₃ powder and CO₂:

\[
\text{K}_2\text{CO}_3 + \text{Ta}_2\text{O}_5 \rightarrow 2\text{KTaO}_3 + \text{CO}_2^2. \tag{3.1}
\]
Table 3.2: Some publications on doping KT

<table>
<thead>
<tr>
<th>dopant</th>
<th>substitutes</th>
<th>investigation</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn⁴⁺</td>
<td>Ta⁵⁺</td>
<td>resistivity of doped and undoped KT</td>
<td>[56]</td>
</tr>
<tr>
<td>Gd³⁺, Eu²⁺</td>
<td>K⁺</td>
<td>electron spin resonance</td>
<td>[57]</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>K⁺</td>
<td>semiconductivity, Ca concentration 4.3·10¹⁸ to 1.3·10¹⁹</td>
<td>[58]</td>
</tr>
<tr>
<td>Fe³⁺, Ni³⁺</td>
<td>Ta⁵⁺, K⁺</td>
<td>electron paramagnetic resonance</td>
<td>[59]</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>Ta⁵⁺</td>
<td>electron spin resonance</td>
<td>[60]</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>Ta⁵⁺+V₀</td>
<td>electron paramagnetic resonance; Co²⁺ does not build in very good</td>
<td>[61]</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>-</td>
<td>electron spin resonance</td>
<td>[62]</td>
</tr>
<tr>
<td>Ti³⁺</td>
<td>Ta⁵⁺+V₀</td>
<td>electron paramagnetic resonance</td>
<td>[63]</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>Ta⁵⁺</td>
<td>temperature dependence of the cubic crystalline splitting parameter</td>
<td>[64]</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>unclear</td>
<td>correlation of hydrogen diffusion with relative concentration of Fe³⁺ sites</td>
<td>[65]</td>
</tr>
<tr>
<td>Yb³⁺; U⁵⁺; Cu²⁺; Co²⁺; Mn²⁺; Fe³⁺; Ni³⁺</td>
<td>K⁺; Ta⁵⁺; unclear; Ta⁵⁺; Ta⁵⁺; Ta⁵⁺+V₀; (K⁺, Ta⁵⁺)</td>
<td>when doped with impurities, KT appears to have a tolerance misfit in ionic size and charge not normally found in other crystals</td>
<td>[55]</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>(Ta⁵⁺, K⁺)</td>
<td>electric-field effect in electron paramagnetic resonance</td>
<td>[66]</td>
</tr>
</tbody>
</table>

In the second step, K₂CO₃ was added to the KTaO₃ powder to get a K-rich solution when heated to ≈ 1400 °C. Doping was achieved by adding a small amount of BaCO₃ to the solution:

\[
\text{KTaO}_3 + \text{K}_2\text{CO}_3 + \text{BaCO}_3 \rightarrow \text{Ba:KTaO}_3 + \text{K}_2\text{O} + \text{CO}_2^2. \quad (3.2)
\]

Due to the similar ionic radii of Ba²⁺ and K⁺, it is very probable that Ba incorporates at K sites. That is why the amount of dopants in the melt will be given in atomic ppm (at ppm), where the
3.2 Production of a suitable substrate

The smooth change of doping concentration (in macroscopic dimensions), as seen in Fig. 3.2, is in contrast to the one reported for Ca in [68], where three subsequently pulled Ca doped crystals from the same melt showed all the same abrupt color change from dark blue in the first half to colorless in the second half. Nevertheless such an abrupt change could also be

number of Ba atoms is compared to the number of K atoms in the precalcinated KTaO₃ ceramic. (The K atoms of the KO₂ additive will not be taken into account, because the excess of K in the melt is only needed to give stoichiometric composition in the crystal).

Out of this solution, Ba-doped KT crystals were grown by the Czochralsky method. Table 3.3 resumes the used growth parameters. First trials with only 10 at ppm Ba gave almost clear samples, with only a pale blue part just below the seed. Crystals, for which 250 at ppm were added to the melt, showed a larger dark blue region in the first-grown part. Towards the end, the crystal became paler, and finally no Ba was left in the melt and thus undoped clear KT was grown. Fig 3.2 shows an as-grown Ba doped KT crystal. The samples showed light blue/white striations perpendicular to the pulling direction, induced by concentration inhomogeneities parallel to the growth interface [67].

Figure 3.2: Upper crystal: as-grown Ba:KTaO₃. (from left to right:) Ba incorporates very well, resulting in a Ba-rich dark blue region just below the seed, then no more Ba is contained in the melt and the crystal’s color changes over pale blue to totally clear (pure KTaO₃). Lower Crystal: pure KTaO₃ for comparison.
Table 3.3: Parameters used for the Czochralski growth of Ba:KT crystals.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>melt composition</td>
<td>Ba:KT (10 - 250 ppm Ba) with 5 mol% K₂O</td>
</tr>
<tr>
<td>superheating</td>
<td>1400 °C for 8 h</td>
</tr>
<tr>
<td>growth temperature</td>
<td>1320 °C</td>
</tr>
<tr>
<td>crucible</td>
<td>Pt, volume V = 63 cm³</td>
</tr>
<tr>
<td>atmosphere</td>
<td>air flow, 300 cm³/min</td>
</tr>
<tr>
<td>seed</td>
<td>KT (100)</td>
</tr>
<tr>
<td>seed rotation</td>
<td>15 rpm</td>
</tr>
<tr>
<td>crucible rotation</td>
<td>25 rpm, accelerated crucible rotation (ACRT)</td>
</tr>
<tr>
<td>pulling rate</td>
<td>0.25 mm/h</td>
</tr>
<tr>
<td>pulling time</td>
<td>≈ 5 d</td>
</tr>
<tr>
<td>cooling rate</td>
<td>50 °C/h</td>
</tr>
</tbody>
</table>

seen in a crystallized sample after heating the melt to ≈ 1400°C, and subsequently cooling it slowly down to room temperature (Fig. 3.3). It seems that it is energetically favorable for the Ba²⁺-ions to incorporate close to another. If there is enough time for diffusion, the dopant ions will move together. However, during Czochralski growth the crystallized part has a low enough temperature not to allow Ba²⁺-ion movement on a macroscopic scale. It is well possible that the observed striations are the result of such ionic movement on a microscopic scale.

### 3.3 Lattice matching

One of the mayor problems in the heteroepitaxial growth of μm thick films is the misfit between epitaxial film and substrate. The misfit \( f \) describes the lattice constant difference for the inter-growth plane relative to the lattice constant of the substrate.

\[
f = \frac{a_f - a_s}{a_s},
\]

(3.3)

where \( a_f \) and \( a_s \) are the lattice constants of the film and the substrate, respectively. If \( f \) exceeds a critical value which depends on the thickness of the film, relaxation defects will occur, which reduce the energy stored in the lattice strain of the epitaxial film.
The influence of the lattice misfit and the film thickness on the formation of lattice misfit defects is theoretically treated in [69-72]. If one monolayer of a material is grown, which has chemically similar atoms as the substrate, a critical misfit \( f_c \approx 0.09 \) is allowed without misfit dislocations. Strain releasing defects will be formed at \( f = 0.14 \). For increasing film thickness, however, the critical misfit decreases to \( f_c = 0.04 \) for 5 monolayers (e.g. Ge on Si) and \( f_c \leq 10^{-3} \) to \( 10^{-5} \) for \( \mu \text{m} \) thick films.

Lattice constants of KTN\((x = 0.37, \text{no Na})\) film [73] and KT substrate [74] are shown in Fig. 3.4. The equilibrium volume fraction \( \phi_c \) of \( c \)-domains in a film can be calculated by the theory of [75] and [76]. For tetragonal epitaxial ferroelectric films (with lattice constants \( a \) and \( c \)) on a cubic substrate (with lattice constant \( b \)), the strain in \( a \)- and \( c \)-domains is given by

\[
\sigma_a = \frac{b - a}{a} \quad \text{and} \quad \sigma_c = \frac{b - c}{c},
\]  

(3.4)
Figure 3.4: Lattice constants of the KTaO₃ substrate and the KTₐ₋ₓNbₓO₃ film (x = 0.37, y = 0.0) as a function of temperature for a wider (a) and smaller (b) temperature range. To get c-oriented films, the lattice constant of the substrate must be close to or smaller than that of the film in a-direction. Addition of Na reduces the lattice constant of the film and it can, at growth temperature, be matched to that one of KT. The drawback is that, at low temperatures, this gives a mixture of a- and c-domains. The regions of $a_1/a_2/a_1$ (a-domains parallel to both in-plane axes), $a/c/a$ (preferentially in-plane domains), $c/a/c$ (preferentially out-of-plane domains) and c-domain pattern is shown.
3.3 Lattice matching

respectively. \( E \) being Young’s modulus and \( v \) Poisson’s ratio, the strain energy per unit volume can readily be expressed by

\[
\eta_a = \frac{E}{2(1-v^2)} \left( \sigma_a^2 + \sigma_c^2 + 2v \sigma_a \sigma_c \right) \quad \text{for } a\text{-domains}
\]

\[
\eta_c = \frac{E}{1-v} \sigma_a^2 \quad \text{for } c\text{-domains.} \tag{3.5}
\]

Both energy densities are equivalent if:

\[
\frac{\sigma_a}{\sigma_a - \sigma_c} = \frac{1}{2(1+v)}. \tag{3.6}
\]

The relative coherency \( e_r \) can be defined as the ratio of one misfit strain \( \sigma_a \) to the tetragonal strain \( \sigma_T = (c-a)/a \):

\[
e_r = \frac{\sigma_a}{\sigma_T} = \frac{b-a}{c-a}. \tag{3.7}
\]

In the case of both domains having the same strain energy densities, the threshold coherency strain will be:

\[
e_r^* = \frac{b_{c/a} - a}{c - a} = \frac{\sigma_a}{\sigma_a - \sigma_c} \approx \frac{\sigma_a}{\sigma_a - \sigma_c} = \frac{1}{2(1+v)}. \tag{3.8}
\]

which defines the lattice constants of the substrate, \( b_{c/a} \) in the case of same probability for \( a \)- and \( c \)-domains:

\[
b_{c/a}(T) = e_c (c(T) - a(T)) + a(T). \tag{3.9}
\]

For \( b > b_{c/a} \), \( a \)-domains are favored, whereas in the opposite case more \( c \)-domains appear. Furthermore the boundaries between monovariant and polyvariant domain patterns can be considered. The transition from \( c \)-monovariant to \( c/a_1/c \)-domains takes place for \( e_r = e_c - \Delta E \); that from \( a \)-monovariant to \( a_1/c/a_1 \) domain pattern at \( e_r = e_c + \Delta E \). For sufficiently thick films and a Poisson ratio of \( v = 0.3 \) one gets \( \Delta E = 0.2219 \) [77]. This theory applied to the case of K(N)TN-films gives the boundaries for the different domain pattern as shown in Fig. 3.4.
For a given substrate/film system, in general, the lattice matching condition at growth temperature (to minimize the misfit dislocations), and that at room temperature (to get $c$-films, where the polarization is perpendicular to the substrate/film interface), cannot be fulfilled at the same time. However, in the case of KTN, the addition of Na into the solid solution for the growth of $K_{1-x}Na_xTa_{1-x}Nb_xO_3$ (KNTN) films allows an additional parameter in the lattice fitting. Because of the smaller ionic radius of $Na^+$ (which replaces $K^+$) the lattice constant of the KNTN film can be scaled down. In Fig. 3.4, this corresponds to shifting downwards the curves corresponding to the lattice constant of KTN. Perfect lattice matching at growth temperature would yield a $c/a/c$-domain pattern at room temperature. But already with a small misfit in the high temperature region is it possible to get $c$-films at room temperature.
Chapter 4

Conducting Ba-doped KTaO$_3$ crystals

4.1 Optical measurements

For the investigation of the optical absorption constant from the UV to the IR-range, an UV / VIS / NIR Perkin Elmer Lambda 9 spectrometer for wavelengths between $\lambda = 0.3 \mu$m and 2.5 $\mu$m (4.1 and 0.5 eV), and a Fourier transformed infrared (FT-IR) spectrometer (Perkin Elmer Paragon 1000PC) for the range of $\lambda = 1.3$ to 10 $\mu$m (0.96 to 0.13 eV) has been used. A crystal like that shown in Fig 3.2 has been cut into thin slices of $\approx 1$ mm, perpendicular to the growth direction, which gave pieces of approximately constant doping concentration [78]. Fig 4.1 shows the transmission of some of the slices. It can be seen that the blue colour arises from a strong absorption towards the red and infrared wavelengths. The absorption coefficient $\alpha$ has been calculated from the transmission data (a constant Fresnel reflection coefficient $R = 0.14$ has been assumed) and is displayed in Fig. 4.2. No precaution has been taken to eliminate the influence of the surrounding atmosphere and the effect of multiple reflections, which causes additional absorption, especially in the IR range. To get the doping-induced absorption, the difference in the absorption of the Ba-doped and the pure crystal was taken, which also eliminates any additional background absorption due to the environment. This difference $\Delta \alpha$ is shown on the right-hand-side of the graph. The induced absorption $\Delta \alpha$ can accurately be fitted by the sum of an $E^{-3}$ dependency ($E$ being the energy of the photon):

$$\Delta \alpha = A_1 E^{-3}. \quad (4.1)$$
Chapter 4. Conducting Ba-doped KTaO₃ crystals

Figure 4.1: Transmission of slices of Ba-doped (b-e) and pure KTaO₃ (a). Thickness is around 1 mm.

The power law of the absorption coefficient with energy can be attributed to the absorption due to free electrons. Classically this gives an $E^{-n}$-dependency with $n = 2$. In addition to the classical value, other powers $n$ can be found in the literature:

- for scattering caused by acoustic phonons, $n = 1.5$ [79], [80].
- for optic polar modes of vibration of the lattice, $n = 2.5$ [81]
- for free carrier absorption due to ionized-donor scattering, $n = 3$ [82], [80], and $n = 3.5$ [79].

Quite similar results for the free-carrier absorption in KTaO₃ have been reported in [56], but for oxygen-deficient crystals. For the least oxygen-deficient sample, Wemple gets an absorption coefficient $\alpha \propto E^{-2.7\pm0.1}$, which he attributes to polar-mode-scattering free-carrier absorption, for which a theoretical $E^{-2.5}$-dependency is predicted. For the more heavily doped samples (in the sense of doping with oxygen vacancies), Wemple also obtains a $E^{-3}$-dependency of the absorption constant. Looking at the left graph in Fig. 4.2, a direct fit of curve (b) would also
4.1 Optical measurements

Figure 4.2: Absorption constant $\alpha$ (left) and induced change $\Delta \alpha$ (right) for doped ((b)-(e)) and undoped (a) KTaO$_3$. 
yield an exponent $n \approx 2.7$. It is only in the difference $\Delta \alpha = \alpha_{\text{doped}} - \alpha_{\text{undoped}}$, where the same $E^{-3}$-dependency is also valid for the lightly doped samples (right graph in Fig. 4.2). This means that for lightly doped samples the induced absorption coefficient $\Delta \alpha$ must be examined because there is a small contribution of the host lattice (corresponding to the undoped crystal), which counteracts the $E^{-3}$-dependency of the absorption constant.

In contrast to [56], no shift of the band-edge as a function of the doping concentration could be observed (see Fig. 4.3). The band-edge data for the most heavily doped and the undoped KTaO$_3$-crystal correspond within 0.005 eV to $E = 3.6$ eV (Wemple reported a shift of 0.025 eV).

### 4.2 Electrical conductivity measurements

For the electrical measurements, 100 Å Ta/1000 Å Au were evaporated on both sides of KT samples. Current-voltage measurements showed excellent ohmic behavior in the range from 0.01 V to 1.0 V. Investigations of electrical conductivity carried out at 10 Hz, using a low
4.2 Electrical conductivity measurements

Figure 4.4: A) resistivity $\rho$ vs inverse temperature for Ba:KT with different doping concentrations (labels of curves correspond to Fig. 4.2). B) conductivity - temperature product $\sigma T$ vs inverse temperature.

frequency impedance analyzer HP4192A, gave the same values for the conductivity as DC experiments. Because of the higher sensitivity, the temperature dependence of the conductivity was determined using the low frequency impedance analyzer. Fig. 4.4 shows the resistivity, $\rho$, and conductivity-temperature product, $\sigma \cdot T$, in the temperature range from 300 K to 16 K. For all samples, the low-temperature conductivity can be described by
with an activation energy of $E_0 \approx 0.5$ meV and $k$ being the Boltzmann constant. While the low-temperature value of the conductivity is directly related to the doping concentration and the free carrier absorption, the high temperature ($T > 100$ K) value seems to contain also other conductivity mechanisms.

It can be seen that, at room temperature or above, the resistivity of a Ba:KT substrate is $\rho < 300 \ \Omega m$ and thus sufficiently small compared to that of a KNTN film ($\rho \approx 10^6 \ \Omega m$). Even for a $10 \ \mu m$ thick KNTN on a $3 \ mm$ thick Ba:KT substrate, only $1\%$ of an applied voltage over both, film and substrate, would be dissipated in the substrate. Also at low temperatures a Ba-doped KT shows a high enough conductivity for most applications. Let us look shortly at the needed conductivity for a KNTN ($10 \ \mu m$)/Ba:KT (1 mm) structure. We require that at least $99\%$ of an applied voltage over the structure is present in the KNTN film. This means, that the resistance in the Ba:KT substrate is at most $1\%$ of the resistance in the KNTN film. The latter has a resistivity of $10^7 \Omega m$ and thus the resistivity of the Ba:KT substrate (which is 100 times thicker) must be less than $10^3 \ \Omega m$. Fig. 4.4 shows that this requirement is fulfilled already with the quite low doping concentration of $0.004 \ at\%$ Ba. Looking at Fig. 4.2 it can be seen that for such doping concentration the absorption constant $\alpha$ in the wavelength range from $0.4 \ \mu m$ to $1.0 \ \mu m$ is at most $3 \ cm^{-1}$. Because of this quite low absorption constant, Ba doped KT crystals are very useful as conductive substrate in optical waveguides.

### 4.3 Ultraviolet photoelectron spectroscopy measurements

With the help of photoelectron spectroscopy (PES) it is possible to investigate electronic properties of materials. For this a probe is exposed to light with sufficient high energy to hit out some electrons of the probe. From their kinetic energy the binding energy can be calculated.

Roughly three types of EPS which differ in the photon energy are generally used. For photon energies up to $100 \ eV$ one speaks of ultraviolet photoelectron spectroscopy (UPS). In the range from $100 \ eV$ to $1000 \ eV$ the term soft X-ray photoelectron spectroscopy (SXPS) is used, whereas methods with even higher energies ($> 1000 \ eV$) are referred to as X-ray photoelectron
4.3 Ultraviolet photoelectron spectroscopy measurements

spectroscopy (XPS). For investigations of the band structure of weakly-bound electronic states UPS is the method of choice.

Even though photoemission is an unitary quantum mechanical effect one can describe it by three independent steps [83]:

- an incident photon excites a bound electron.
- the excited electron moves to the surface experiencing only inelastic collisions
– and leaves the probe to the vacuum.

To leave the surface of the probe, the excited electrons must possess sufficient kinetic energy to overcome the crystal potential $\Phi - E_0$, where $\Phi$ is the work function and $E_0$ the surface potential. In addition to conservation of energy also conservation of momentum must be fulfilled. Let us suppose that the probe has cubic symmetry (as it will be the case for KT). If only the electrons are detected which move perpendicular to the crystals main surface and thus parallel to a unit cell vector, then the following equations must hold:

\[
\begin{align*}
E_{\text{kin}} &= E_{\text{phot}} - (\Phi + E_0) - E_b \\
E_{\text{kin}} &= \frac{\hbar^2 k^2}{2m} \\
k &= k_{\text{Bloch}},
\end{align*}
\]

where $E_{\text{phot}} = h\nu$ is the photon energy, $E_b$ the binding energy of the electron and $k_{\text{Bloch}}$ the corresponding Bloch-vector which must lie on the $\Gamma - X$-line in the first Brillouin zone. This situation is shown in Fig. 4.5. A graphical solution for finding the possible electronic states which can be seen by UPS in the situation described above is to plot the kinetic energy reduced to the first Brillouin zone into the band structure plot, where zero kinetic energy corresponds to $E_\text{Fermi} + E_0 - E_{\text{phot}}$. Adding $\Phi - E_0$ to the energy of the cross points of the kinetic energy curve with the band structure then gives the observed peaks in the UPS measurement.

For the investigation of pure and Ba doped KT the He I$\alpha$ and He II$\alpha$ lines (21.218 eV and 40.814 eV, respectively) were used. While the He I$\alpha$ line has a stronger intensity and thus gives a better signal/noise ratio, the He II$\alpha$ line allows the determination of lower-lying bands because of its higher energy. In the measurements with the He II$\alpha$ line also the He I$\alpha$ line is present, which means that the structures seen with the He II$\alpha$ line appear again shifted by $40.814 \text{ eV} - 21.218 \text{ eV} = 19.596 \text{ eV}$ towards lower energies. The structure in the He II$\alpha$ line begins at energies lower than $-4 \text{ eV}$; this means that they are only reliable down to $-4 \text{ eV} - 19.6 \text{ eV} = -24 \text{ eV}$.

The probe was a slice of a Ba:KT crystal as that shown in Fig. 3.2, which was cut along the growth direction. Like this, one part was Ba doped while the other was undoped. This allowed the detection of the UPS signal for Ba doped and pure KT with the same conditions. The signal of both He lines is shown in Fig. 4.6. UPS measurements on metals gave the position of the
Figure 4.6: UPS signal from a pure (B) and a Ba-doped KT (C). Both, He I $\alpha$ and He II $\alpha$ line measurements are shown. The smaller graph (A) above the UPS signals shows the calculated band structure along $k \in (\Gamma, X)$. The doping results in a shift of the Fermi energy by $\approx 0.5$ eV towards the conduction band electrons.
Fermi level. In Fig. 4.6, the energy was chosen such that the Fermi level corresponds to 0 eV. The K 3p core state allows a precise determination of the shift of the Fermi level, because it is almost constant for all different Bloch vectors. With this, the UPS measurements show that the Fermi energy for Ba doped samples shifts by \( \approx 0.5 \) eV towards the conduction band. As in Fig. 4.6 the Fermi level is held constant at 0 eV, this corresponds to shifting downwards the energy of the valence band and the core electrons. The finding, that the Fermi level shifts towards the conduction band, can only be explained by electron conduction. Hole conduction would result in a lowering of the Fermi level. Electron conduction, in turn, is explicable only by K\(^{+}\)-site doping - the partial replacement of Ta\(^{5+}\)-ions by Ba\(^{2+}\) ions would give hole conduction. Also the case of Ba\(^{2+}\)-ions at K\(^{+}\)-sites with additional oxygen vacancies (V\(_{O}\)) (one vacancy V\(_{O}\) for two replaced K\(^{+}\)-ions) can be excluded, because such a situation would not alter the Fermi energy that much.

### 4.4 Conclusion

With the help of UPS measurements a shift of the Fermi level towards the conduction band of \( \approx 0.5 \) eV was measured. Conductivity measurements gave good electrical conductivity values, and because of the upwards-shift of the Fermi level a n-type conductivity can be concluded. This means, that Ba replaces the K\(^{+}\)-ions, and that the second valence electron of the Ba-atom creates a state very close to the conduction band. This is also in agreement with the measured dependency of the doping-induced optical absorption coefficient with photon energy, \( \Delta \alpha(E) \), because the \( E^{-3} \)-dependency is expected in the case of ionized donor scattering.

Ba-doped KT thus is a very suitable substrate for the epitaxial growth of KTN-films, as it still has the excellent lattice matching properties of pure KT, and, in addition, is conductive. The resistivity of the Ba:KT substrate can be tailored during its growth by the amount of BaCO\(_{3}\) which is added to the melt.
Chapter 5

Electrical, dielectric and pyroelectric properties of $K_{1-y}Na_yTa_{1-x}Nb_xO_3$ films

5.1 Poling experiments

5.1.1 Poling of KNTN films which are lattice matched to the substrate at growth temperature

I already mentioned that exact lattice fitting is only possible for a small temperature range. To test the possibility of poling a lattice matched (at growth temperature) KNTN film ($x = 0.45$, $y = 0.12$; $T_c = 55^\circ C$), two semi-transparent, thin Au-electrodes were evaporated on the film and on the reverse side of the Ba:KT substrate. The as-grown, annealed film is shown in Fig. 5.1 a). Many in-plane domains can be seen, whose boundaries lie at 45° to the film main axes. The film was partially poled by heating it to 80 °C above $T_c$, and slowly cooling it down to room temperature, while applying voltage pulses with a frequency of 2 Hz perpendicular to the film surface. Electrical fields of less than 16 kV cm$^{-1}$ did not alter the domain structure considerably. After a poling procedure with an electric field of 16 kV cm$^{-1}$, the film partially cracked in the direction of the crystallographic axes (Fig. 5.1 b). These cracks lower the energy contained in the strain of the induced out-of-plane-domains. Where two orthogonal cracks meet a dark area is visibly apparent, which therefore corresponds to domains with their polar axis perpendicular to the substrate/film interface. If the film can only relax in one dimension (along
Figure 5.1: Domains in a KNTN (x = 0.45, y = 0.12) film, as seen under crossed polarizers in an optical microscope. (a) as grown (after annealing), the arrows in the lower right corner show the crystallographic axis of substrate and film, (b) after heating above $T_c$ and cooling down to room temperature, with a poling field of 16 kV cm$^{-1}$, (c) as in (b) but with a poling field of 29 kV cm$^{-1}$ (same scale as in (a)). Poling is accompanied by cracks along the film crystallographic axes. Poling perpendicular to the film (dark regions) is possible at the cross-points of cracks - there the film is free to expand in the plane. (The same scale has been used in all pictures.)

the crack lines but more than $\approx 10 \mu$m away from a point with an orthogonal crack line), bright areas corresponding to the two possible in-plane domains are observed. Even higher electric fields cause even more cracks, as can be seen in Fig. 5.1 c), which shows the film after applying a poling field of 29 kV cm$^{-1}$. The critical length over which strain is gathered, without letting the film crack or forming domains with the polar axis in other directions, is around 10 to 15 $\mu$m.
5.1 Poling experiments

Figure 5.2: Experimental set-up for atomic force microscope measurements: an a.c. voltage is applied between the conduction tip and the counter electrode. The resulting polarization dependent oscillations of the cantilever are sensed by laser deflection and measured by two lock-in amplifiers [84].

To conclude it is not possible to grow KNTN films on KT substrates which are lattice matched at growth temperature and can be poled in a- or in c-direction. For most applications, however, c-domains (with a polarization perpendicular to the film / substrate interface) are preferred. Such films can be obtained by adding about 75% of the Na which would be needed to grow (at grow temperature) perfectly lattice matched films (see Fig. 3.4). Films of this composition still are of good crystalline quality and can be poled by periodically applying an electric field while cooling from the cubic to the tetragonal phase. Under an optical microscope no domains at all can be seen in this films. Only such films were used in the following measurements.

5.1.2 Polarization experiments with the atomic force microscope

Scanning force microscopy with voltage modulation technique provides a powerful tool for studying domains in micro- and submicrometer scale. In this mode of operation, an AC voltage which is applied between the conducting tip and the bottom electrode of the sample, creates
an additional force resulting in vibrations of the cantilever. In addition to topographic surface features both, amplitude and phase of the induced vibration are monitored and allow the imaging of the in-plane and out-of-plane polarization in the sample. Fig. 5.2 is a schematic of the experimental set-up.

First, a scan was done with a DC electric field applied between tip and bottom electrode of the sample, which should pole the film. After about 1/3 of the area had been scanned, the polarization of the electric field was switched, and almost at the end of the scan it was reverted again. Then, the whole area was scanned again, this time without any poling DC field. The out-of-plane polarization of this scan is shown on the left-hand-side of Fig. 5.3. The topographic scan did not show the three bands observed in the polarization scan, which proves that really the polarization is observed. Then, the tip was programmed to draw a cross with the two upper and the two lower edge points connected, again with a DC electrical field applied. In a second scan of the same area, the written domains appeared as bright lines, again proving the possibility of
5.2 Dielectric measurements

5.2.1 Measurement and interpretation

The dielectric permittivity $\varepsilon$ has been measured as a function of temperature and frequency. For this, a KNTN sample ($T_C = 60 ^\circ$C, out-of-plane poled), grown on Ba:KT substrate, was placed in an oven with a high thermal mass and then slowly heated up to 120 $^\circ$C. The frequency dependence of $\varepsilon$ was then repeatedly measured at 50 frequencies from 12 Hz to 100 kHz, while slowly cooling down at a rate of 3 $^\circ$C per hour. The real part of the dielectric permittivity, $\varepsilon'$, shows a frequency-dependence which is typical of relaxor ferroelectrics [85]. Nevertheless, there are three special features. Firstly, a very high peak dielectric constant of $\approx 1.4 \cdot 10^4$ can
be observed. Secondly, \( \varepsilon' \) depends on the frequency even for such low values as from 20 to 200 Hz, as can be seen in Fig. 5.4. To see the third feature, the dielectric permittivity \( \varepsilon' \) has been plotted for a range of frequencies of \( 550 \text{ Hz} \leq f \leq 91 \text{ kHz} \) on a logarithmic scale (Fig. 5.6). In the Cole-Cole plot (Fig. 5.5) the imaginary part \( \varepsilon''(f) \) of dielectric constant is shown as

![Figure 5.4: Frequency dispersion of dielectric permittivity \( \varepsilon' \) (left axis) and its inverse (right axis) at frequencies between 20 Hz and 200 Hz. The underlying grey lines show that for 20 Hz the slopes of the inverse dielectric constant above the transition temperature and that below the transition temperature have a ratio 2:1. At higher frequencies, however, this ratio gets smaller. The frequency-dependent Curie constant varies from \( 1.9 \cdot 10^5 \text{ K} \) for 20.7 Hz to \( 1.5 \cdot 10^5 \text{ K} \) for 185 Hz.](image)

function of its real part \( \varepsilon'(f) \) for \( 50 \text{ Hz} < f < 100 \text{ kHz} \) at different temperatures. The points just below the real axis indicate the center of a fitted circle. Above phase transition temperature the frequency dispersion of the complex dielectric constant \( \varepsilon \) can be summarized by
5.2 Dielectric measurements

Figure 5.5: Cole-Cole plot of the complex dielectric constant. Curves are labelled by their temperature in °Celsius. The points just below the real axis show the center of the fitted circle at the indicated temperatures in °Celsius.

\[
\frac{\epsilon(T, \omega)}{\epsilon(T, 0)} - \frac{\epsilon(T, \infty)}{\epsilon(T, 0)} = \frac{1}{1 + (i\omega \tau(T))^{\beta(T)}}
\]

(5.1)

in which the parameter \( \beta \) indicates the degree of distribution of the relaxation time [86]. In Fig. 5.5 the line connecting the center of the circle to the point \( \epsilon_\infty \) makes an angle \( \alpha \) with the real axis, which is connected to the \( \beta \) by \( \beta = 1 - 2\alpha/\pi \). All dipoles have the same relaxation time \( \tau \) if \( \beta = 1 \) (\( \alpha = 0 \)). Then the center of the arc lies on the real axis. As \( \beta \) decreases, the distribution of \( \tau \) increases. In Fig. 5.5 \( \beta = 0.87 \) for temperatures between 120 °C to 65 °C, indicating quite a narrow distribution of relaxation times above the phase transition temperature. Below
Figure 5.6: Logarithmic plot of $\varepsilon'(T)$ for frequencies $550 \, \text{Hz} \leq f \leq 91 \, \text{kHz}$. Two peaks, (a) and (b), can be distinguished. Peak (a) is dominant at higher frequencies, $f > 25 \, \text{kHz}$; peak (b) is the major one at lower frequencies.
the phase transition temperature, however, the interaction of the dipoles increases and with that
the width of the relaxation time distribution, giving for temperatures below 55 °C a β of 0.76.

In a normal relaxor ferroelectric one would expect the maximum of $\varepsilon'(T)$ to shift towards
higher temperatures when moving to higher frequencies [85]. This is also what can be seen for
frequencies up to 30 kHz (peak (b) in Fig. 5.6). The interesting fact is that, for even higher
frequencies, this maximum vanishes and a second one can be seen close to the ferroelectric
phase transition temperature (peak (a)), around $T_c = 60$ °C. Presumably, this second maximum
could also be seen at lower frequencies if it was not hidden by the stronger second peak.

To understand the two peaks in $\varepsilon'$, let us shortly examine the composition of KNTN. The
end compositions of $K_{1-x}Na_xTa_{1-x}Nb_xO_3$ are the ferroelectric (at room temperature) $KNbO_3$
(KN) (for $x = 1, y = 0$) and the incipient ferroelectric $KTaO_3$ (KT) (for $x = 0, y = 0$). Mixing
these two compounds gives the solid solution, $KTa_{1-x}Nb_xO_3$ (KTN). Another way to look at
KTN is as Nb-doped KT. This gives a perovskite-like structure with mixed B-site ions, and
the random substitution locally leads to regions which are richer in the Nb concentration than
others. This is the basic approach of the compositional fluctuation model outlined in sec. 2.4.2.
When comparing $\varepsilon'(f, T)$ obtained for KNTN films with that of measurements of other relax¬
orls with B-site ion-mixing, we find that the Ta-Nb mixing in KNTN gives the diffuse phase
transition - peak (a), seen in the high-frequency measurements of $\varepsilon'$ (Fig. 5.6). Such a B-site
ion-mixing does not result in the extreme low-frequency dependency of $\varepsilon'$.

In addition to the B-site mixing, there is also an A-site mixing in KNTN, where $K^+$-ions
are partially replaced by $Na^+$-ions. Contrary to the case of $Nb^{5+}$ and $Ta^{5+}$, where both ions
have almost identical radii, the $Na^+$ ion is smaller than that of the substituted $K^+$. When we
define the ionic misfit as

$$m_i = \frac{r_i - r_h}{r_h},$$ (5.2)

where $r_i$ and $r_h$ are the dopant and host ionic radii respectively, the numerical values are [87]:

<table>
<thead>
<tr>
<th>dopant</th>
<th>site</th>
<th>ionic misfit $m_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>Ta</td>
<td>-0.04</td>
</tr>
<tr>
<td>Na</td>
<td>K</td>
<td>-0.3</td>
</tr>
</tbody>
</table>
Therefore, the Na-ions can be shifted out of the equilibrium position of the corresponding K-ions. This induces an additional dipole moment and leads to a polar glass-like behavior.

The relaxation frequencies \( f_r \) of KNTN obey the Vogel-Fulcher relationship (2.40), as is illustrated in Fig. 5.7, where the frequency of the maximum in \( \varepsilon'' \) is plotted for different temperatures \( T \). Fitting the data gives an activation energy \( E_a = (11 \pm 1) \) meV, freezing temperature \( T_f = (0 \pm 5) \) °C, and attempt frequency \( f_0 = 2.0 \cdot 10^5 \) Hz. The Vogel-Fulcher relationship is observed down to 65 °C.

The temperature \( T_m \) of maximal \( \varepsilon'(f) \) can also be extracted from the measurement, and the modified Vogel-Fulcher relationship (2.41) is applicable as shown in Figs. 5.8 and 5.9. Two
frequency regions with distinct freezing temperature $T_f$ can be observed. While for frequencies $f > 3$ kHz a $T_f = 0$ °C is needed to fit data to the modified Vogel-Fulcher relationship, in the case of $12$ Hz $< f < 1$ kHz a $T_f = 0$ K is obtained (corresponding to a normal Arrhenius relaxation). The activation energies for the higher and lower frequency parts are $T_{a}^h = 13$ meV (in good agreement with that obtained in Fig. 5.7) and $T_{a}^l = 5$ eV, respectively.

It is interesting to note that, in a plot of real part of dielectric permittivity $\epsilon'(f)$ against frequency (Fig. 5.10), the curves corresponding to the ferroelectric phase ($20$ °C $\leq T \leq 50$ °C) show a $f^p$-dependency in the low-frequency-part with a fitted value of $p = -0.11 \pm 0.01$. 

Figure 5.8: Modified Vogel-Fulcher relationship of the frequency $f$ and the temperature $T_m$, where the maximal real part of dielectric permittivity, $\epsilon(f)$, occurs. A freezing temperature of $T_f = (0 \pm 5)$ °C is fitted for frequencies $f > 3$ kHz.
Investigation of dielectric permittivity $\varepsilon(f, T) = \varepsilon'(f, T) + i\varepsilon''(f, T)$ of KNTN films reveals

- high values in $\varepsilon'$ in a broad peak around the phase transition temperature, from para- to ferroelectric phase,

- strong frequency-dependency of $\varepsilon$, also at low frequencies $12 \text{ Hz} < f < 1 \text{ kHz}$,

- two distinct peaks in $\varepsilon'(T)$ for frequencies $f > 10 \text{ kHz}$.

These properties can be explained by the mixing of ions at the B-site (Ta and Nb) and A-site (K and Na) in the perovskite ABO$_3$-structure. While the former is primarily responsible for the
Figure 5.10: (a) Log-lin and (b) log-log plot of $\epsilon(f)$. For frequencies smaller than 1 kHz $\epsilon' \propto f^\nu$ can be observed.
ferroelectric phase transition, the latter introduces a polar glass behavior due to the freedom of the Na⁺-ions to move out of the equilibrium position of the replaced K⁺-ions.

As seen in Fig. 5.4 the Curie-constant of the KNTN-film in the low-frequency limit is $C = 1.9 \cdot 10^5$ K. With this value Eq. (2.26) determines the coefficient $\alpha$ in the expansion of the free energy density (2.17)

$$\alpha = A(T - T_0) = \frac{1}{\epsilon_0 C}(T - T_0) = 5.9 \cdot 10^5 \text{ Jm/C}^2\text{K} \cdot (T - T_0). \quad (5.3)$$

5.3 Pyroelectric measurements

5.3.1 Theory

The simplest and most efficient theory of describing the voltage and current response of a pyroelectric detector in an experimental set-up as shown in Fig. 5.11 is that of Cooper [88]. His model describes a ferroelectric crystal, with two electrodes on opposite faces which is illuminated with a periodical intensity. The electrodes with an area $A$ are separated by the thickness of the crystal, $d$. If one of the electrodes is illuminated by an incident radiation, which will be absorbed, the surface charge $Q = P_s \cdot A$ will change if the spontaneous polarization $P_s$ is temperature-dependent (see Fig. 5.12). This change will cause a pyroelectric current, which can either be measured directly with the aid of an ampere meter (ideally having zero resistance), or as a voltage drop across a large resistance $R_V$. The starting point for the description

---

**Figure 5.11:** Experimental set-up for the measurement of the pyroelectric current and voltage response.
5.3 Pyroelectric measurements

of the heat flow is the one-dimensional heat equation:

\[
C_{th} \frac{d(\Delta T)}{dt} + G_{th} \Delta T = \eta \Delta W, \tag{5.4}
\]

where \( C_{th} \) is the thermal capacitance of the element, \( G_{th} \) the average heat conductance from the detector to the surrounding, and \( \eta \) the effective absorptivity of the radiation-absorbing electrode. If \( \Delta W \) is a periodic function with radian frequency \( \omega \), \( \Delta W = W_0 e^{i\omega t} \), and the temperature change \( \Delta T \) is assumed to show the same periodicity, then (5.4) becomes

\[
\Delta T(i\omega C_{th} + G_{th}) = \eta \Delta W. \tag{5.5}
\]

**Figure 5.12:** One-dimensional model of a pyroelectric detector which is illuminated by a periodic intensity \( \Delta W \).

The change in the spontaneous polarization \( \Delta P_s \) is described by the pyroelectric coefficient \( p \) through

\[
\Delta P_s = p \Delta T \tag{5.6}
\]
and the pyroelectric current \( I = I_0 e^{j\omega t} \) is then

\[
I = \frac{d(A \Delta P_i)}{dt} = \frac{A \rho \eta \frac{d\Delta W}{dt}}{i\omega C_{th} + G_{th}} \tag{5.7}
\]

which gives for the amplitude

\[
I_0 = \frac{A \rho \eta i\omega W_0}{i\omega C_{th} + G_{th}} = \frac{A \rho \eta W_0}{C_{th} - \frac{i\omega C_{th}}{\omega}} \tag{5.8}
\]

(The real part of \( I_0 \) is in-phase with the incident radiation, the imaginary part \( \pi/2 \) out-of-phase.)

This current can either flow through the crystal or through the input resistance in the detecting instrument, \( R_i \). If \( R_i \) is much smaller than the resistance of the crystal, \( R_c \), then Eq. (5.8) can directly be measured through \( R_i \), and the current responsivity \( r_I \), defined by \( r_I \equiv |I|/|\Delta W| \) is given by

\[
r_I = \frac{A \rho \eta}{C_{th} - \frac{i\omega C_{th}}{\omega}} = \frac{A \rho \eta}{\sqrt{C_{th}^2 + G_{th}^2/\omega^2}}. \tag{5.9}
\]

Defining a thermal time constant as

\[
\tau_{th} \equiv \frac{C_{th}}{G_{th}} \tag{5.10}
\]

(5.9) can be expressed as

\[
r_I = \frac{A \rho \eta}{C_{th} \sqrt{1 + (\omega\tau_{th})^{-2}}}. \tag{5.11}
\]

If, instead of a small external resistance \( R_i \), a large one is used, the voltage measured across this external resistance \( R_V \) is the product of the current \( I \) with the total impedance \( Z' \), which gives for the amplitude \( V_0 \) of the measured voltage

\[
V_0 = Z' \cdot I = \left( \frac{1}{R_V} + \frac{1}{R_c} + i\omega C_{el} \right)^{-1} \left( \frac{A \rho \eta W_0}{C_{th} - \frac{i\omega C_{th}}{\omega}} \right). \tag{5.12}
\]
5.3 Pyroelectric measurements

$C_{el}$ means the electrical capacity of the crystal, and $G_{el}$ the total conductance of the two parallel resistances $R_{cr}$ and $R_V$. Again, a time constant can be defined as

$$\tau_{el} = \frac{C_{el}}{G_{el}}, \quad (5.13)$$

which is called the electrical time constant. With this, the voltage responsivity $r_V \equiv |V|/|\Delta W| = |V_0|/|W_0|$ becomes

$$r_V = \frac{A p \eta}{C_{el} C_{th} \omega \sqrt{1 + (\omega \tau_{el})^{-2}} \sqrt{1 + (\omega \tau_{th})^{-2}}}. \quad (5.14)$$

The following three main regions are distinguishable (see Fig. 5.13):

- For frequencies which are considerably smaller than the inverse of both electrical and thermal time constants, the voltage responsivity depends linearly on frequency, $r_V \propto \omega$.

- For frequencies much larger than the inverse of both time constants, the voltage responsivity is proportional to the inverse of the frequency, $r_V \propto \omega^{-1}$.

- In the intermediate region, $\tau_1^{-1} \ll \omega \ll \tau_2^{-1}$, $r_V$ becomes independent of the frequency $\omega$.

5.3.2 KNTN pyroelectric detectors

To study the pyroelectric effect in KNTN and the influence of the substrate, three types of pyroelectric detectors have been built:

- a hybrid pyroelectric detector, with the KNTN film attached to a silicon substrate (which will henceforth be called type 1a),

- a hybrid pyroelectric detector, with a nearly free-standing KNTN film (type 1b), and

- a detector consisting of a KNTN film, grown on Ba doped KT (type 2).
Chapter 5. Properties of KNTN films

In all cases, the upper electrode was a Ta/Au electrode, which absorbed 3% of the incoming light from a laser diode (the rest was reflected). A thin layer of ink increased this value by a factor of 3, which gives \( \eta = 0.09 \) for the effective absorptivity of the electrode.

Hybrid pyroelectric detector (type 1)

For the hybrid pyroelectric detectors, 40 \( \mu \)m KNTN \( (x = 0.39, \ y = 0.11) \) films were grown on a pure KT wafer with a thickness of 1.5 mm [89]. The wafer was then split through the middle using a diamond saw. Both halves were polished on the film side until a smooth surface was obtained. After polishing, the films were prepared with an evaporated 5 nm Ta/100 nm Au contact. Tantalum was found to form a good ohmic contact to KNTN (Fig. 5.14).

In parallel, a silicon wafer was oxidized, and coated on the front face with 5 nm of Ti and 100 nm of Au. This layer was patterned to match the contacts on the KNTN film. Gold was chosen, as it provides excellent wetting contacts for the indium bonding.

Both wafers were bonded in the area of contacts, face to face, with a thin layer of indium (\( \approx 2 \mu \)m), resulting in an intimate contact between the KNTN film and the silicon wafer. In the next step, the KT substrate was mechanically removed by polishing, leaving only about an 12 \( \mu \)m thick KNTN film bonded to the silicon wafer. The top contacts to the KNTN layer, which
again consisted of a Ta/Au layer, and had an area of 1.5 mm², were defined by the photoresist lift-off technique.

Type 1a detectors were completed after this process. To get almost free-standing, thermally isolated structures, a window was opened in the oxide layer, on the back of the Si wafer and aligned with the top contacts. Using the remaining oxide layer as a mask, the Si wafer was anisotropically etched from the reverse side in a KOH solution, until the front etch-stop oxide layer was reached. The whole processing procedure resulted in practically free-standing KNTN
Figure 5.15: Schematic cross section of a hybrid KNTN pyroelectric structure with an attached (left, type 1a) and a free-standing (right, type 1b) detector.

membranes measuring $1.5 \times 1 \text{ mm}^2$. Fig. 5.15 shows a schematic of the fabricated pyroelectric structure.

KNTN film on Ba:KT (type 2)

As a comparison, a KNTN film grown on Ba:KT has also been used as a pyroelectric detector. Clearly, the substrate has strong influence on thermal properties, such as $G_{th}$ and $C_{th}$. Another difference is that poling of the KNTN film is much more complicated when still in contact with the KT substrate (and thus under strain caused by small lattice mismatch) than in the case of a KNTN film which has been attached to the Si wafer. The main advantage of using such a detector of type 2 lies in the simplicity of its fabrication, for which the film only has to be grown, annealed and coated with a Ta/Au electrode on both sides of the film/substrate.
5.3.3 Experimental setup

The pyroelectric effect was measured using the dynamic method [90]. The pyroelectric voltage and current response was detected at different frequencies and temperatures, using the experimental set-up shown schematically in Fig. 5.11. A laser diode, emitting at 670 nm was used to periodically heat the sample. A TTL signal from a lock-in amplifier (SR 830) was used to modulate the laser diode between 0.1 Hz and 10 kHz with a modulation depth of 90 %. Only the first harmonic of the pyroelectric response on the incident rectangular light pulse was measured (at the modulation frequency of the laser diode). As most model calculations of the pyroelectric detectors relate a sinusoidal input to a sinusoidal output signal at the same frequency, having the results in the same form enables an unrestricted application of the derived formulas. However, since the sinusoidal signal at the modulating frequency corresponds only to the first term in a Fourier series, the amplitude of the corresponding sinusoidal incident modulation has to be calculated. The rectangular incident radiation can be written as:

\[ I_{\text{rect}}(\nu, t) = \frac{I_0}{2} + \frac{2I_0}{\pi} \sum_{k=0}^{\infty} \sin((2k+1)2\pi\nu t) \frac{1}{2k + 1}, \quad (5.15) \]

where \( \nu \) is the modulation frequency and \( I_0 \) the amplitude of the rectangular pulse. In order to obtain the amplitude of the incident radiation, which causes a sinusoidal response at the frequency \( \nu \), only the coefficient of the first harmonic element in the series has to be taken into account. The amplitude of the corresponding sinusoidal modulation is then found as \( 2I_0/\pi \).

The laser diode, used for measurements, exhibited a peak power of 1.9 mW, of which 90 % (1.7 mW) were modulated. As such, the amplitude of the corresponding sinusoidal input radiation \( W_0 \), at the same frequency, was 1.1 mW.

The pyroelectric current was measured directly with the lock-in amplifier through a resistance of 1 k\( \Omega \), while the voltage response was obtained over a 10 M\( \Omega \) input resistance. The lock-in amplifier offers the possibility not only to get the absolute value of the responsivities but also the corresponding phase. Re-writing the expression for the amplitude of the pyroelectric current (5.8), in order that in- and out-of-phase parts (real and imaginary parts) can easily be distinguished, gives:

\[ I_0 = \frac{A p \eta W_0}{C_{\text{th}}^2 + (\frac{G_{\text{th}}}{\omega})^2} \cdot \left( C_{\text{th}} + i \frac{G_{\text{th}}}{\omega} \right), \quad (5.16) \]
The thermal time constant (5.10) can most easily be obtained from (5.16), as it is the inverse of the frequency where the out-of-phase value has its maximum. Because of the symmetry of (5.16) only the ratios $p/G_{th}$, $p/C_{th}$ and $\tau_{th} = C_{th}/G_{th}$ can be extracted (if $A$, $\eta$, and $W_0$ are known).
5.3 Pyroelectric measurements

10

^sr

10-

\* (ï&) [V/W]

5(^) IV/W

ah

Figure 5.17: Decay of pyroelectric voltage responsivity with time. First, the larger real part decays with a half life time of 100min; after 2h, the decay of the imaginary part becomes dominant.

5.3.4 Pyroelectric coefficient and pyroelectric figures of merit

Temperature and time-dependency of pyroelectric effect

The measured dependency of dielectric permittivity $\epsilon'$ (measured at 160 Hz), and that of the voltage responsivity $r_v$, is plotted in Fig. 5.16. The film was heated with a ramp of 100 °C/h. While $\epsilon'$ exhibits its maximum at the Curie temperature $T_C = 40$ °C, the maximal pyroelectric responsivity is obtained around 10 °C below $T_C$. This can partly be explained by the fact that, for a fixed frequency, $r_v(T) \propto p(T)/\epsilon(T)$. It is interesting to note that also for temperatures considerably higher than $T_C$, a pyroelectric effect can still be observed. Fig. 5.17 shows the evolution of $r_v$ with time at 80 °C (40 °C above $T_C$). It is notable, that there are still ferroelectric domains at this temperature, which decay quite slowly.
Frequency-dependency of current and voltage responsivity

Hybrid detectors (type 1)  Fig. 5.18 shows the measured in-phase (a), out-of-phase (b) and absolute value (c) of the pyroelectric current in a hybrid detector at 288 K \((T_C = 312 \, \text{K})\). The
5.3 Pyroelectric measurements

The inverse of the radian frequency of the peak position in the imaginary (out-of-phase) part directly gives the thermal time constant $\tau_{th}$. In the case of the thermally isolated structure (type 1b), this gives $\tau_{th,1b} = 1/(2\pi \cdot 65 \text{ Hz}) = 2.5 \text{ ms}$, whereas for the film attached to Si, the time constant is $\tau_{th,1a} = 1/(2\pi \cdot 200 \text{ Hz}) = 0.8 \text{ ms}$. This illustrates that by etching the Si under the KNTN film, the thermal time constant can be extended by more than a factor of 3. The current responsivity for frequencies smaller than 100 Hz is substantially enhanced, whereas for higher frequencies the modulated heat has no time to reach the bottom side of the film, and consequently isolation offers no improvement.

The corresponding voltage responsivity is shown in Fig 5.19. To get the value of the electrical time constant $\tau_{el}$, the ratio of the low-frequency $\omega \ll \tau_{th}$, $\tau_{el}$ values of $r_I$ and $r_V$ gives $G_{el}$, whereas the ratio at frequencies $\omega \gg \tau_{th}$, $\tau_{el}$ gives $\omega C_{el}$. Table 5.1 gives the values for $G_{el}$, $C_{el}$, and $\tau_{el}$ as calculated from the data of Figs. 5.18 and 5.19.

The most direct method of estimating the pyroelectric coefficient $p$ is by looking at the real part or the absolute value of $I_0/(\eta W_0)$ at high frequencies. In that case,
Table 5.1: Measured $G_{el}$ and $C_{el}$ and the calculated electrical time constants $\tau_{el}$ for the investigated hybrid pyroelectric detectors.

<table>
<thead>
<tr>
<th>detector</th>
<th>$G_{el}(10\text{Hz})$ [S]</th>
<th>$C_{el}(1\text{kHZ})$ [F]</th>
<th>$\tau_{el} = C_{el}/G_{el}$ [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>type 1a</td>
<td>$(5.8 \pm 0.3) \cdot 10^{-6}$</td>
<td>$(4.0 \pm 0.2) \cdot 10^{-9}$</td>
<td>$(6.9 \pm 0.7) \cdot 10^{-4}$</td>
</tr>
<tr>
<td>type 1b</td>
<td>$(6.3 \pm 0.4) \cdot 10^{-6}$</td>
<td>$(4.6 \pm 0.2) \cdot 10^{-9}$</td>
<td>$(7.3 \pm 0.8) \cdot 10^{-4}$</td>
</tr>
</tbody>
</table>

where $N_A = 6.02 \cdot 10^{23} \text{mol}^{-1}$ is the Avogadro constant, $V_{\text{unit cell}} = (4.0 \cdot 10^{-10})^3 \text{m}^3$ is the volume of a unit cell, $d = 12 \cdot 10^{-6} \text{m}$ is the thickness of the film, and $c_p = 100 \text{J mol}^{-1} \text{K}^{-1}$ is the specific heat capacity at constant pressure [73]. With these values, the pyroelectric coefficient at a temperature of $24 \text{K}$ under $T_C$ is calculated as

$$p_{24\text{K below } T_C} = (5.2 \pm 0.6) \cdot 10^{-4} \text{C m}^{-2} \text{K}^{-1}. \quad (5.18)$$

The same way as estimating $p_{24\text{K below } T_C}$ (shown just above) the pyroelectric coefficient has been determined in the temperature range from $5^\circ\text{C}$ to $75^\circ\text{C}$. The relative error of the absolute value of $p(T)$ is 15%. Out of the pyroelectric coefficient $p(T)$ the spontaneous polarization $P_s$ can be calculated by

$$P_s(T) = \int_{T_h}^{T} p(T') \, dT', \quad (5.19)$$

where $T_h$ is a temperature well above the phase transition temperature such that $p(T_h) = 0$. The measured pyroelectric coefficient and the calculated spontaneous polarization $P_s$ are shown in Fig. 5.20.

**KNTN on Ba:KT detector (type 2)** In the case of a KNTN film on a conducting Ba:KT substrate, the theoretical description must also include the effect of the substrate (see [91], [92]). Two effects can be observed in Fig. 5.21. First, the exponent of the responsivity at higher frequencies is not $-1$, as it is in the case of the type 1 detectors, but is somewhat smaller, about...
0.67. This can surely be explained by the additional effect of the substrate. While the temperature wave, which originates from the absorbed radiation, penetrates into both film and substrate, only the temperature change in the film gives a pyroelectric effect. But this penetration depth is frequency-dependent; at higher frequencies the penetration depth is smaller, and more of the total temperature change takes place in the film. This effect disturbs the $\omega^{-1}$-dependency caused by the thermal time constant $\tau_{th}$ in the case of no substrate. The second effect is that the thermal
Figure 5.21: Log-log plot of the absolute value of the voltage responsivity $r_V$ of a KNTN film on Ba:KT substrate. At high frequencies a $\omega^{-0.67}$-dependency is observed, due to the frequency-dependence of the penetration depth of the temperature wave.

The time constant of the type 2 detector becomes much larger than in the isolated type 1b detector, 8 ms instead of 0.8 ms. For the detector of type 1b, the heat conductivity was mostly determined by the 2 $\mu$m In-layer, which has, at 288 K, a heat conductivity of 0.83 W cm$^{-1}$ K$^{-1}$. In perovskite crystals it is of the order of 0.01 W cm$^{-1}$ K$^{-1}$. Even though the heat penetrates deeper into the substrate, the heat losses may be smaller because of the lower heat conductivity.

### 5.3.5 Discussion

Three different types of pyroelectric detectors were built on the basis of KNTN films. A high value for the pyroelectric coefficient was found, $p_{23K \text{below } T_C} = (5.2 \pm 0.6) \cdot 10^{-4}$ C m$^{-2}$ K$^{-1}$, and the influence of the substrate/heat sink was investigated. KNTN is not the material of choice for low-cost pyroelectric detectors, because the LPE growth requires quite high temperatures, and because Na is an atom which should not be used in connection with Si-based semiconductors. In Tab. 5.2 the pyroelectric coefficient at room temperature is given for some materials (after [17]). The pyroelectric effect even could be enhanced by a factor of two, if the phase transition temperature would be chosen such that the maximal effect occurs at the
Table 5.2: Pyroelectric effect at room temperature of some materials.

<table>
<thead>
<tr>
<th>material</th>
<th>$p \left[10^{-4} \text{ C m}^{-2} \text{ K}^{-1}\right]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGS</td>
<td>3.0 [93]</td>
</tr>
<tr>
<td>LiTaO$_3$</td>
<td>1.9 [94]</td>
</tr>
<tr>
<td>PLZT (6/80/20)</td>
<td>7.6 [95]</td>
</tr>
<tr>
<td>KNTN (this work)</td>
<td>5.2</td>
</tr>
</tbody>
</table>

working temperature (see Fig. 5.16). The polarization, however, should then be stabilized by an additional electric D.C. field which must be applied permanently, and the crystal would have to be temperature-stabilized. Like this, KNTN is interesting in pyroelectric applications, were high pyroelectric response is needed.

5.4 Nonlinear optical properties

The nonlinear optical coefficients $d_{ij}$ of a K$_{0.90}$Na$_{0.10}$Ta$_{0.69}$Nb$_{0.31}$O$_3$ were measured using the Maker-fringe technique introduced by Maker in 1962 [96]. Using the Maker-fringe technique a plane parallel sample is rotated around an axis perpendicular to the incoming laser beam. Due to the different phase velocities of the fundamental and frequency-doubled beams in the material the intensity of the second-harmonic wave $I^{2\omega}$ generated in the sample shows oscillations. The envelope of such curves is evaluated at zero-degree incidence and compared to the Maker-fringes of a reference crystal (quartz in most cases).

Our experimental set-up is shown in Fig. 5.22. The measurement of the components $d_{ij}$ were performed with a Q-switched Nd:Yag laser, using a wavelength $\lambda^\omega = 1064 \text{ nm}$, a pulse width of $\tau = 25 \text{ ns}$ and a repetition rate of $f = 10 \text{ Hz}$. The frequency doubled power was detected with a photo-multiplier for angles from $-45^\circ$ to $45^\circ$ (0° corresponding to normal incident of the fundamental wave) and processed with a gated integrator. The epitaxial film had a thickness of 25 $\mu$m and was fully out-of-plane oriented (polar axis perpendicular to the surface). The film and the reference were mounted on a goniometer attached to a rotating stage having a resolution of 0.1 °C. The polarizer before the sample was adjusted to let through either s- or p-polarized light, after the sample the analyzer was in p-position. The second
harmonic intensity with a wavelength of $\lambda^{2\omega} = 532$ nm was recorded with an attenuation filter. Fig. 5.23 shows the Maker-fringe curves for the cases of s- and p-polarized incident light. To get absolute values for the nonlinear optical coefficients $d_{31}$ and $d_{33}$ a quartz plate with a thickness of 1.9 mm was used as a reference ($d_{31}^{\text{Quartz}} = 0.4$ pm/V [97]). The fit of the second-harmonic intensity in the $\text{sp}$ configuration (s-polarized incident fundamental beam, p-polarized second-harmonic generated beam) gives a value of $d_{31} = 1.7 \pm 0.2$ pm/V. The $\text{pp}$-configuration allows the determination of the ratio $d_{33}/d_{31}$. This ratio depends critically on the exact values of the refractive indices. It was calculated as $d_{33}/d_{31} = (6 \pm 2)$, giving an absolute value of $d_{33} = 10 \pm 4$ pm/V.

The obtained values compare well with those of Gutmann [12]. Investigating a 13 $\mu$m thick KNTN film he obtained $d_{31} = 0.3 \pm 0.1$ pm/V and $d_{33} = 0.8 \pm 0.2$ pm/V before a poling treatment, and $d_{31} = 1.4 \pm 0.4$ pm/V, $d_{33} = 4.1 \pm 1$ pm/V afterwards. Therefore it can be concluded, that the used film in our experiment was fully out-of-plane oriented and of good quality. Schwyn Thöny [98] measured a value of $d_{33} = 5$ pm/V for KNbO$_3$ films on MgO substrates. Because of the strain due to the lattice misfit those films were tetragonal at room temperature, but of course had a much higher phase transition temperature than in our case. Bearing in mind that the nonlinear optic coefficients get smaller near the phase transition temperature, which is
5.4 Nonlinear optical properties

Figure 5.23: Maker-fringe curves for a K$_{0.90}$Na$_{0.10}$Ta$_{0.69}$Nb$_{0.31}$O$_3$ film with a thickness of 25 μm. The fundamental wavelength was $\lambda_o = 1064$ nm. In the sp configuration (upper graph) the incident light beam was s-polarized; in the pp-configuration it was p-polarized.

about 30 °C for the composition of our used KNTN film, the measured values for $d_{31}$ and $d_{33}$ can be considered quite high.
5.5 Estimation of the linear electro-optic coefficient $r$

With the help of the relative dielectric constant $\varepsilon$ (see Fig. 5.4) and the spontaneous polarization $P_s$ (Fig. 5.20) the linear electro-optic coefficient $r$ can be estimated as it is

$$r = \varepsilon_0 \cdot f \cdot (\varepsilon - 1), \quad (5.20)$$

where $f$ is the polarization-optic coefficient. $f$ is given by

$$f = 2 \cdot g \cdot P_s, \quad (5.21)$$

with the quadratic polarization-optic coefficient $g$ which is to a good approximation independent of temperature and used material, $g \approx 1.8 \text{ m}^4\text{C}^{-2}$. With the measured values (at 20°) of $\varepsilon = 6 \cdot 10^3$ and $P_s = 1.5 \cdot 10^{-2} \text{ C/m}^2$ the electro-optic coefficient $r$ is

$$r \approx \varepsilon_0 \cdot 2 \cdot g \cdot P_s \cdot (\varepsilon - 1) = 300 \text{ pm/V}. \quad (5.22)$$

Because of this high value of the linear electro-optic coefficient $r$ KNTN films are good candidates for electro-optical applications.
Chapter 6

Electronic ground state properties of KTaO$_3$ and KNbO$_3$

In the chemical formula of KTaO$_3$ (KT) and KNbO$_3$ (KN) the only difference lies in the transition metal Ta or Nb ion. Looking at the electronic configuration of those two atoms, the Nb has closed K, L and M shells, 2 electrons in the $N_s$, 6 ion the $N_p$ and 4 in the $N_d$ state. In addition, there is one electron in the $O_s$ state. Ta, on the other hand, has closed K, L, M and N shells; there are 2 electrons in the $O_s$ state, 6 in the $O_p$, 3 in the $O_d$ and 2 in the $P_s$ state.

KN has a series of ferroelectric phase transitions, starting with the cubic to tetragonal transition at 415 °C, followed by a tetragonal to orthorhombic transition and finally settling into a rhombohedral ground state. In contrast, the structure of KT remains cubic perovskite down to 0 K.

It has been proposed ([99] and references therein) that the structural differences may arise from the difference in the $d$ orbitals of Ta and Nb. While the higher $d$ binding energy in Nb favors greater covalency in KN, the smaller $4d$ orbital compared to the $5d$ orbital in Nb leads to higher covalent binding in KT than in KN.

The electronic structures of KT and KN were calculated within the local density approximation (LDA) (see Appendix B). In both cases, a cubic structure was investigated. For KT a lattice constant of 3.98 Å was used; for KN it was set to 4.00 Å. A mesh of $6 \times 6 \times 6$ k-points was used for Brillouin zone integration, and the kinetic cut-off energy was about 100 hartree.
6.1 Electronic density

Figure 6.1: Valence electron density (in e/Å³) in the (001) plane through the center of the niobium or tantalum ion. top: for KNbO₃; middle: for KTaO₃; and bottom: difference of that of KNbO₃ and that of KTaO₃.
The density of the valence electrons in the (001) plane containing four oxygen ions at the sides and one niobium or tantalum ion in the middle is given in Figs. 6.1 and 6.2. Figs. 6.3 and 6.4 show the valence electron density in the (101) plane, which has four potassium ions in the
corner, two oxygen ions in the middle of the two longer sides, and again a niobium or tantalum ion in the middle.

Figure 6.3: Valence electron density (in e/Å³) in the (101) plane through the center of the potassium and the niobium or tantalum ion. top: for KNbO₃; middle: for KTaO₃; and bottom: difference of that of KNbO₃ and that of KTaO₃.
The mostly ionic character of both, KN and KT, can be seen in Figs. 6.1 to 6.4, as most of the valence electron density is distributed in shells around the oxygen ions. While potassium gives away its valence electron, there is a small fraction of the valence electrons of the niobium or tantalum ions, which in the crystal remain close to the parent atom. The density around the niobium or tantalum ion partially has the symmetry of the s-orbital, the other part shows a
Chapter 6. Electronic ground state properties of KTaO$_3$ and KNbO$_3$

d-orbital symmetry with maxima of densities located between the centers of Nb or Ta and the oxygen ions, thus forming a covalent binding. In the difference of the valence electron density of KN and KT (graphs at the bottom in Fig. 6.1 to 6.4) it becomes visible that in KT the electron density between Ta and O is higher than in KN between Nb and O. In KN, on the other hand, the density is higher close to the center of the Nb ion. As the covalent binding between Ta and O is higher in KT than that between Nb and O in KN, it is clear that a ferroelectric phase transition is less likely to occur in KT than in KN, as the cubic structure in the former material is stronger stabilized by this bindings.

6.2 Band structure calculations and comparison with experiments

To understand the influence of the Ba dopant in KT, it is important to know the electronic structure of the pure and the doped material. For this purpose, band structure calculations on pure and Ba doped KT were performed within the density functional theory (DFT) and the local density approximation (LDA). For a description of the code see the appendix.

Until now, band structure calculations have been the domain of high-end computers. Due to the increasing performance of personal computers, it has become possible to undertake LDA calculations on a PC or notebook (under Windows NT).

6.2.1 Calculations for pure KT

Band structure calculations within the local density approximation have been performed on supercomputers by a few authors. Neumann [100] calculated the electronic structure of cubic KNbO$_3$ and KTaO$_3$ using the self-consistent scalar-relativistic linear muffin-tin orbital method and determined ground-state properties such as the lattice constant, bulk modulus and cohesive energy. Ground-state and phonon properties of pure and doped KNbO$_3$ and KTaO$_3$ were investigated by Postnikov [101] using the full-potential linear muffin-tin orbital method (FP-LMTO). The same did Singh [99] using a local orbital extension of the general potential linearized augmented plane waves method (LAPW) and a Brillouin zone sampling of $6 \times 6 \times 6$ $\mathbf{k}$-points. The photoemission spectra from the (100) surface of cubic KTaO$_3$ by excitation with unpolarized Ne
Figure 6.5: Calculated band structure of KTaO$_3$. Zero energy is chosen to be at the calculated Fermi-energy. The straight line at $\approx -14$eV correspond to the K(3p) core electrons which have not been included in the calculation (because of the use of pseudopotentials).
I and He I radiation was calculated by Grass [102] using the self-consistent tight-binding linear muffin-tin orbital method (TB-LMTO) as well as the FP-LMTO. In this work the plane-wave formalism was used together with nonlocal pseudopotential as introduced by Bachelet [103].

Fig. 6.5 shows the band structure of pure KT along the $\Gamma$ (000) - $X$ ($0\frac{1}{2}0$) - $M$ ($\frac{1}{2}\frac{1}{2}0$) - $R$ ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$) - $\Gamma$ - $M$ points (in units of $2\pi/c$, where $c$ is the lattice constant) in the first Brillouin zone (see Fig. 6.6). As the band structure shown in Fig. 6.5 consists only of the valence electrons used in the calculation (18 from the three oxygen, 5 from the tantalum and 1 from the potassium atom), it does not show the additional band of the K(3p) core electrons which have an energy of $\approx -14$ eV (represented by a straight line at that energy in Fig. 6.5). A lattice constant of 3.98 Å has been used for the cubic unit cell. For the integration over the Bloch-vectors a grid of $6 \times 6 \times 6$ k-points was employed which resulted in 10 special k-points in the irreducible part of the Brillouin zone. The number of plane waves for the wavefunctions was 24 in each direction (48 for the density and related variables), which corresponds to a cut-off energy of 2734 eV (100.5 hartree). For the band-structure calculation electronic energies for 30 Bloch-vectors between the high-symmetry points were calculated.

The fundamental band gap is always underestimated in LDA calculations because they are justified for the ground state of a material only. To also arrive at the right energies of the excited
states, quasiparticle band-structure calculations are required, which would involve a far lengthier process. It turned out, however, that even though in LDA calculations the fundamental band gap is underestimated, the relative position of the energies in the conduction band is described quite accurately. Therefore, Fig. 6.5 predicts an indirect band gap from the $R$ to the $\Gamma$ point. This result is also confirmed by two photon absorption measurements [104]. Comparing the obtained band-structure with that of Singh [99] it is interesting to note that around the $M$-point the pure plane wave formalism predicts stronger degenerated states as does the LAPW formalism. This could be due to the fact that a plane waves sampling does not prefer any region in space and consequently does not destroy symmetries.

### 6.2.2 Electronic structure of Ba doped KTaO$_3$

It is much more demanding to perform electronic structure calculations for doped materials, as this requires many more atoms to be considered. To get an idea where the additional valence electron goes to if a K-atom is replaced by a Ba-atom, a supercell consisting of $2 \times 2 \times 2$ unit cells has been employed. From the 8 K-atoms, one was substituted with Ba. This corresponds to a doping concentration of 12.5 %. Actually, such a super-unit cell does not exist as it cannot be expected that the dopants incorporate periodically, and the size of the unit cell changes discontinuously with concentration. Nevertheless, the result of the calculation was that for this model system, the Fermi-energy moves into the lowest lying conduction band, which predicts good electrical conductivity. The other bands remain almost unchanged except that their energy is lowered when measured from the Fermi level.

### 6.2.3 Comparison with the band structure of KNbO$_3$

It is not very surprising that the band structure of KT and KN look quite similar. In both materials we have the same indirect band gap from the $R$-point in the highest-lying valence to the $\Gamma$-point in the lowest lying conduction band. Nevertheless there are differences, particularly for Bloch vectors along $MR$. At the $R$-point, three 3-fold degenerated states (spin-degeneracy is not considered here) are shown for KT in the valence states, whereas in KN the 3-fold degenerated state around $-5$ eV splits up in a 2-fold and a non-degenerated one, which has a higher energy (around $-4.5$ eV).
Figure 6.7: Band structure of KTaO$_3$ (left) and KNbO$_3$ (right) in the cubic perovskite structure. Zero energy was chosen to lie at the top of the valence band.

As it is typical for LDA calculations, the fundamental band gaps are underestimated. But the difference in the band gap energy is 0.5 eV and thus in agreement with the difference in the experimental gaps of 3.8 eV for KT and 3.3 eV for KN. Another interesting thing is that the dispersion of the lowest lying conduction band is much more pronounced in KT than in KN. While it is more than 4 eV in the former material, it is only about 3.5 eV in the latter.

6.3 Origin of ferroelectricity in KNbO$_3$

The energy minima along the [111] direction was calculated for the case of simultaneous shifts of the KNbO$_3$ ions. Fig. 6.8 shows the calculated energy differences if all Nb atoms in a cubic lattice with a lattice constant of 4.00 Å are shifted along the [111] direction. The calculation of such energy differences under small shifts is very sensitive to the k-point sampling and thus
6.3 Origin of ferroelectricity in KNbO$_3$

![Graph showing change in total energy for a simultaneous shift of the Nb ions along the [111] direction.](image)

Figure 6.8: Change in total energy for a simultaneous shift of the Nb ions along the [111] direction

Quite time consuming. If a potential of the form:

$$V(x) = ax^2 + bx^4$$

(6.1)

is assumed, then a fit of the calculated data gives $a = -2.35$ eV/Å$^2$ and $b = 18.63$ eV/Å$^4$. The difference between the energy at the center position ($x = 0$) and the minimal energy at 0.25 Å is therefore

$$\Delta E = \frac{a^2}{4b} = 0.07 \text{ eV}. \quad (6.2)$$

If the barrier height $\Delta E$ is low relatively to $kT_0$ ($k$ being the Boltzmann constant and $T_0$ the phase transition temperature) then a purely displacive transition is to be expected [87]. In the high symmetry phase (at high temperature) the potential seen by the Nb$^{5+}$ ions is almost harmonic. When the temperature falls towards the transition, the anharmonic contribution increases so that the Nb$^5$ ions vibrate in one of the minima. Therefore, the equilibrium position of the Nb$^5$ ions has been displaced from $x = 0$ to $x = x_{\text{min}}$. In the other case of $\Delta E > kT_0$, exclusive order-disorder behavior is to be expected, as in the eight-site model.
KNbO$_3$ has a phase transition temperature of about 700 K, and thus $kT_0 = 0.06$ eV. This is quite exactly the same value as the calculated height of the barrier height of the potential, which is $\Delta E = 0.07$ eV. With this it can be concluded, that neither the purely displacive nor the purely order-disorder transition model can be applied to KNbO$_3$, but it is a mixture of both.
Appendix A

Novel method for measuring the ferroelectric hysteresis by harmonic analysis

A.1 Introduction

Measurement of the ferroelectric hysteresis loop is one of the conventional techniques for investigating ferroelectric materials. Usually, this is done using the Tower-Sawyer circuit [105], which gives good results as long as the material under investigation is highly insulating and has no linear stray capacitance. In most materials and setups this is not the case, and it is necessary to use a more sophisticated circuit to compensate for the losses and linear capacitance of the ferroelectric sample plus crystal holder or substrate. One common method is to use a modified Sawyer-Tower circuit, which involves additional resistors and capacitors [106, 107].

Here, a different measurement and compensation technique is described. Instead of recording the voltage over the reference capacitance in a Sawyer-Tower circuit in the time domain, it is measured in the frequency domain decomposed in the different harmonics. This can easily be done using a lock-in amplifier. Measurement of the first 25 to 30 in- and out-of-phase harmonics provide the necessary information to get the resistance and linear capacitance of the sample, and its ferroelectric hysteresis loop in the time domain by Fourier transformation of the corrected harmonics.
Figure A.1: Slightly modified Sawyer-Tower circuit. The total polarization $P_{tot}$ due to an applied field $E_f$ is given by $\varepsilon_0 \chi_f E_f + P_d$. The resistances $R_f$ and $R_n$ account for possible losses in the ferroelectric and the measuring device (lock-in amplifier), respectively.

A.2 Theory

A.2.1 Fourier coefficients of the hysteresis loop

First we derive an analytical expression of the fourier coefficients of the hysteresis loop $P_d(t)$, where $P_d$ is the polarization in a ferroelectric material due to the switching of dipoles. Fig. A.1 shows a schematic of the slightly modified Sawyer-Tower circuit employed, where the possible loss in the ferroelectric material is modeled by a resistance $R_f$ in parallel with the ferroelectric capacitor $C_f$.

Following the theory given in [108], the electric displacement $\mathbf{D}$ due to an applied electric field $E_f$ in a ferroelectric capacitor with total ferroelectric polarization $P_{tot}$ can be described by

$$D = |\mathbf{D}| = \varepsilon_0 E_f + P_{tot}$$

$$= \varepsilon_0 E_f + \varepsilon_0 \chi_f E_f + P_d$$

$$= \varepsilon_0 \varepsilon_f E_f + P_d,$$

where $\chi_f$ means the electric susceptibility, and $\varepsilon_f = 1 + \chi_f$ is the linear dielectric constant. The direction of $\mathbf{D}$ is perpendicular to the electrodes.
The electric field in the ferroelectric is given by the applied voltage, $V$, and the thickness of the film, $d_f$:

$$E_f = \frac{V}{d_f}. \tag{A.2}$$

Using Maxwell’s first equation

$$\nabla \cdot \mathbf{D} = \rho \tag{A.3}$$

it follows, that

$$\sigma_f = \frac{\epsilon_0 \epsilon_f V}{d_f} + P_d, \tag{A.4}$$

where $\sigma_f$ is the surface charge density on the ferroelectric capacitor.

Differentiating (A.4) one gets

$$\frac{d\sigma_f}{dt} = \frac{dV}{dt} \cdot \frac{\epsilon_0 \epsilon_f}{d_f} + \frac{dP_d}{dt} = \frac{dV}{dt} \cdot \frac{C_f}{A_f} + \frac{dP_d}{dt} \tag{A.5}$$

with $A_f$ being the area of contact on one side and

$$C_f = \frac{\epsilon_0 \epsilon_f A_f}{d_f}. \tag{A.6}$$

Looking at node (a) in Fig. A.1, the following identities must hold:

$$\sigma_n(t) \cdot A_n = C_n \cdot V_{out}(t) \tag{A.7}$$

and

$$-\sigma_f \cdot A_f + \sigma_n \cdot A_n = \int_{t_0} V_{in} - V_{out} \frac{dt}{R_f} - \int_{t_0} V_{out} \frac{dt}{R_n} + Q_0, \tag{A.8}$$
where \(Q_0\) means the total charge before \(t_0\). Taking the derivative of (A.8) with respect to time \(t\), and using (A.7) one gets:

\[
\frac{V_{in} - V_{out}}{R_f} - \frac{V_{out}}{R_n} = - \left( \frac{d(V_{in} - V_{out})}{dt} \frac{C_f}{A_f} + \frac{dP_d}{dt} \right) A_f + C_n \frac{dV_{out}}{dt} \tag{A.9}
\]

which can be written as:

\[
\frac{dP_d}{dt} = -\frac{V_{in}}{A_f R_f} + V_{out} \left( \frac{1}{R_f A_f} + \frac{1}{R_n A_f} \right) - \frac{dV_{in}}{dt} \frac{C_f}{A_f} + \frac{dV_{out}}{dt} \left( \frac{C_n}{A_f} + \frac{C_f}{A_f} \right) \tag{A.10}
\]

In the Sawyer-Tower circuit we applied a voltage \(V_m(t)\) of the form

\[
V_{in}(t) = V_0 \sin(\omega t), \tag{A.11}
\]

where \(v_a = \omega/2\pi\) is the frequency.

Assuming \(V_{out}\) and \(P_d\) to be quasi-periodic functions of time (which means that their Fourier coefficients vary slowly compared to \(2\pi/\omega\)), they can be written as:

\[
P_d(t) = \sum_{k \geq 1} P_{k1} \sin(k\omega t) + P_{k2} \cos(k\omega t) \tag{A.12}
\]

\[
V_{out}(t) = V_0 + \sum_{k \geq 1} V_{k1} \sin(k\omega t) + V_{k2} \cos(k\omega t). \tag{A.13}
\]

Inserting (A.11-A.13) into (A.10) and comparing the Fourier coefficients one gets:

\[
P_{k1} = \frac{1}{A_f} \left[ V_{k1} \left( C_n + C_f \right) - V_0 C_f \delta_{k1} + \frac{V_{k2}}{k\omega} \left( \frac{1}{R_f} + \frac{1}{R_n} \right) \right] \tag{A.14}
\]

\[
P_{k2} = \frac{1}{A_f} \left[ V_{k2} \left( C_n + C_f \right) + \frac{V_0}{\omega R_f} \delta_{k1} - \frac{V_{k1}}{k\omega} \left( \frac{1}{R_f} + \frac{1}{R_n} \right) \right]
\]

\[
V_0 = 0
\]
A.2 Theory

By measuring the first 25 to 30 harmonics, $V_{k_1}$ and $V_{k_2}$, of $V_{\text{out}}$, it is possible to calculate the dielectric polarization $P_d(t)$ and to get the hysteresis loop by drawing it against the applied field

$$E_f = \frac{V_{\text{in}} - V_{\text{out}}}{d_f} = \frac{V_a \sin(\omega t) - \sum_{k \geq 1} V_{k_1} \sin(k\omega t) + V_{k_2} \cos(k\omega t)}{d_f}. \quad (A.16)$$

If $C_n$ is chosen large enough we arrive at $V_{k_1} \ll V_a$ and so $P_d$ can be drawn against

$$E_f \approx \frac{V_a \sin(\omega t)}{d_f}. \quad (A.17)$$

A.2.2 Energy in one loop

To get an expression for the energy used for one hysteresis cycle, the electrical input power into the circuit (and, therefore, the input current $I_{\text{in}}(t)$) is needed. $I_{\text{in}}$ is given by the change of charge on the crystal surface and the current flowing through the resistance $R_f$

$$I_{\text{in}}(t) = \frac{d(\sigma_f(t) A_f)}{dt} + \frac{V_{\text{in}}(t) - V_{\text{out}}(t)}{R_f}$$

$$= C_f \frac{d(V_{\text{in}}(t) - V_{\text{out}}(t))}{dt} + A_f \frac{dP_d(t)}{dt} + \frac{V_{\text{in}}(t) - V_{\text{out}}(t)}{R_f}$$

$$= \frac{V_{\text{out}}(t)}{R_n} + C_n \frac{dV_{\text{out}}(t)}{dt} \quad (A.18)$$

where for the last step, (A.10) has been used.

The electrical energy used during one hysteresis loop is given by

$$E_{el} = \int_{\text{loop}} V_{\text{in}}(t) I_{\text{in}}(t) \, dt$$

$$= \int_{\text{loop}} V_{\text{in}}(t) \left( \frac{V_{\text{out}}(t)}{R_n} + C_n \frac{dV_{\text{out}}(t)}{dt} \right) \, dt. \quad (A.19)$$

with

$$\delta_{k1} = \begin{cases} 1 : & k = 1 \\ 0 : & k > 1 \end{cases} \quad (A.15)$$
By subtracting the energy dissipated in the resistances $R_f$ and $R_n$ from (A.19), one obtains the energy used for one hysteresis loop

$$E_{hyst} = E_{el} - \int_{\text{loop}} \left( \frac{(V_{in}(t) - V_{out}(t))^2}{R_f} + \frac{V_{out}^2(t)}{R_n} \right) dt$$

$$= \int_{\text{loop}} \left( \frac{V_{out}(t)}{R_n} \frac{V_{in}(t) - V_{out}(t)}{R_n} - \frac{(V_{in}(t) - V_{out}(t))^2}{R_f} + C_n \frac{dV_{out}(t)}{dt} \right) dt$$

$$= -V_a V_{12} \pi \omega C_n + V_a \pi \left( V_{11} \left( \frac{1}{R_n} + \frac{1}{R_f} \right) - \frac{V_a - V_{11}}{R_f} \right)$$

$$- \pi \sum_k (V_{k1}^2 + V_{k2}^2) \left( \frac{1}{R_n} + \frac{1}{R_f} \right). \quad (A.20)$$

### A.3 Experiments

#### A.3.1 (Almost) ideal case: TGS

Triglycine sulfate (TGS) can be considered an (almost) ideal ferroelectric because of its high resistivity and its relatively low coercive field. For illustrational purposes, we measured the ferroelectric hysteresis at room temperature with a frequency of 0.09 Hz. This quite low frequency ensures that most of the ferroelectric domains can switch back and forth during one cycle. The drawback is that the magnitude of the induced voltage, over the reference capacity $C_n$, decays over the resistivity of the crystal, $R_f$, and the input resistivity of the lock-in, $R_n$. While the former is quite high in the case of TGS, the influence of the second can readily be seen in Fig. A.2. In this figure, graph (a) shows the hysteresis loop as one gets it in the case of the original, uncompensated Tower-Sawyer circuit. This is equivalent to using $R_f = R_n = \infty$ and $C_f = 0$ in (A.14) (which gives the well-known simple relation $P_d = C_n/A_f \cdot V_{out}$ between the polarization $P_d$ and the measured voltage $V_{out}$). The influence of $R_n$ can easily be shown in the step from graph (a) to (b), where the known value $R_f = 10 \, \text{M} \Omega$ is used in formula (A.14). In order to close the hysteresis loop in the saturation regime at high applied fields, a value of $R_f = 30 \, \text{G} \Omega$ must be used, which then gives the curve in Fig. A.2(c). Finally, the slope in the saturation regime can be counterbalanced by a capacity of the film (coming only from the linear dielectric constant of the ferroelectric material) of $C_f = (0.13 \pm 0.01) \, \text{nF}$.

Because of the strong interaction of KNTN films with the (doped or undoped) KT substrate, no “normal” ferroelectric hysteresis could be measured on these films.
Figure A.2: Hysteresis loop of TGS. (a) directly from measured voltages over reference capacity. (b) corrected for loss in lock-in amplifier. (c) additionally corrected for loss in ferroelectrics. (d) with correction for linear dielectric constant.
Appendix B

Calculations within the local density approximation

Local density approximation (LDA) nowadays is a widely used tool for the computation of ground-state properties of materials. The quantum mechanical description of particles using wavefunctions generally requires the storage of many coefficients when expanding this wavefunction, using a general basis set, and thus demands large computer memories. In addition, the operations on these wavefunctions cost much time and hence computers with a high processing speed are needed. For these reasons the use of LDA has until recently been restricted to supercomputers. Because of the ever-increasing capacity of personal computers (PC), it has also become feasible to perform LDA calculations on PCs. To my knowledge, no LDA based program for PCs was available until now. My program, written to operate on Windows NT 4.0, offers the possibility of ab-initio ground-state calculations of crystals, without the necessity of accessing expensive high-end computers.

B.1 Theory

One of the major problems in quantum mechanical calculations of electron systems is the interaction of the electrons with themselves. Hohenberg and Kohn [109] originated the density-functional theory (DFT), by showing that all aspects of the electronic structure of electrons
in a non-degenerate ground-state, are fully determined by the electron density \( n(r) \). Kohn and Sham [110] then derived a system of self-consistent one-particle equations which together build the ground-state density. These equations are

\[
\left( -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{ion}}(r) + V_H(r) + V_{\text{XC}}(r) \right) \phi_i(r) = \epsilon_i \phi_i(r), \tag{B.1}
\]

where \( \phi_i \) is the electron wave function of the state \( i \). On the left-hand side of (B.1), the first term is the kinetic energy of a non-interacting wavefunction \( \phi_i \), the second is the electrostatic potential of the present ions, the third is the Hartree potential of the electrons, given by

\[
V_H(r) = e^2 \int \frac{n(r')}{|r - r'|} d^3r'. \tag{B.2}
\]

The interaction of the electrons is incorporated into the exchange-correlation potential \( V_{\text{XC}} \), which is generally non-local. Local density approximation (LDA) now assumes that the density does not change too much locally, and hence \( V_{\text{XC}} \) can be approximated by that of a (locally) uniform electron gas. Several parameterizations exist for this uniform gas [110–113], which in practical applications give almost the same results.

For a general periodic system a good choice for the set of basis functions are plane waves. Bloch’s theorem states that electronic wave functions can then be written as

\[
\phi_{i,k} = e^{ikr} f_{i,k}(r), \tag{B.3}
\]

where \( f_{i,k} \) can be expanded in the discrete set of plane waves whose wave vector is a reciprocal basis vector of the crystal,

\[
f_i(r) = \sum_G c_{i,G} e^{G \cdot r}. \tag{B.4}
\]

The Bloch vector \( k \) in (B.3) can be any vector in the first Brillouin zone, and occupied states at any \( k \)-vector will contribute to the electron density. Electronic wavefunction with similar \( k \)-vector will be almost identical, and thus the integral over the first Brillouin zone can be replaced by a sum over discrete \( k \)-points. One possible way of finding discrete Bloch-vectors,
of which the sum will well approximate the integral over the first Brillouin zone, is to take a 3-dimensional mesh in the zone and reduce the points by the symmetry-relations of the crystals. In a cubic crystal, a $6 \times 6 \times 6$-mesh with 216 $k$ points will reduce to 10 special points. The electron density is then approximated by

$$n(r) = \sum_k w_k \sum_G g_G |f_{i,k}|^2,$$

(B.5)

where $w_k$ is the weight of the $k$-point (depending on how many mesh points were mapped onto this special point), and $g_G$ the occupation number of the wavefunction $\phi_{i,k}$. Reciprocal $G$-vectors with high absolute value correspond to high kinetic energy. Because of that, the sum over $G$ can be limited to those vectors for which $|G| < G_{\text{max}}$, where $G_{\text{max}}$ is the cut-off energy.

Finding the self-consistent solution in the LDA calculation requires two iterative loops. The first one is shown in Fig. B.1 and gives the self-consistent solution of the electron density $n(r)$. A second, inner iterative loop is needed to find the lowest eigenstates of the Kohn-Sham equation (B.1). A powerful method for undergoing this task is the preconditioned conjugate-gradients method [114,115].

The straightforward iterative discovery of the self-consistent solution of $n(r)$ must be stabilized and accelerated by a suitable density-mixing method, such as the modified Broyden’s method as proposed by Johnson [116].

**B.2 Computational cost**

Coefficients of the periodic part $f_{i,k}$ of electronic wavefunctions $\phi_{i,k}$ are stored in an array of $N_1 \times N_2 \times N_3 = N$ elements such that all corresponding plane waves up to a certain kinetic cut-off energy $G_{\text{max}}$ are included. As the density is the sum of the absolute squares of the wavefunctions $\phi$, kinetic energies up to $2G_{\text{max}}$ may occur, which demands arrays of $8N$ elements for all densities and potentials. Without use of pseudopotentials, the application of the Hamilton on the wavefunction (B.1) requires an expansion up to $3G_{\text{max}}$ - as only the coefficients up to $G_{\text{max}}$ are needed (for the calculation of the new wavefunction), it is sufficient to calculate $H\phi$ on a grid with kinetic energies up to $2G_{\text{max}}$. With the use of pseudo-potentials this argument does not hold any more, but in the case of smooth pseudo-potentials the errors are very small and can
be neglected. It is even possible to expand densities and potentials only up to $1.5G_{\text{max}}$, which of course induces errors but has the advantage of needing less memory. These induced errors vanish when going to higher cut-off energies $G_{\text{max}}$.

$n(r)$ and $V_{\text{XC}}(n(r))$ are calculated in real $r$ space and need a number of operations which scales as the order of $N$ (shortly written $O(N)$). Coefficients of the wavefunctions are stored in reciprocal $G$ space, and Fast Fourier Transformation (FFT) is used to transform the array from one to the other space, thereby using $O(N \log N)$ operations. Electrostatic potentials are best calculated by Poisson’s equation.
B.2 Computational cost

\[ \nabla^2 E(\mathbf{r}) = -\rho(\mathbf{r}), \]  

(B.6)

where \( \rho(\mathbf{r}) \) is the charge density. Together with the kinetic potential this is preferentially done in \( \mathbf{G} \)-space, where both operators are diagonal and thus need only \( O(N) \) operations. Ion-ion interaction must only be calculated once as long as the ions do not move. Their Coulomb energy can easily be determined using Ewald's method [117].

So far, the FFT is the limiting factor in LDA calculations using plane waves. The disadvantage of plane waves, however, is the huge number of them needed to describe the strongly oscillating core electrons in heavier atoms. However, most physical properties of solids depend much stronger on the valence than on the core electrons. It is possible to incorporate the effect of the core electrons in pseudopotentials, which when applied to the valence electrons give very similar waves outside the core regions while removing the strong oscillations inside the core. The drawback is that no useful pseudopotential exists which operate diagonal on the valence electrons wavefunctions either in \( \mathbf{r} \)- or \( \mathbf{G} \)-space. The most general form of a pseudopotential is

\[ V_{ps} = \sum_{lm} |lm\rangle V_l \langle lm|, \]  

(B.7)

where \( |lm\rangle \) are the spherical harmonics and \( V_l \) is the pseudopotential for angular momentum \( l \). This means that the wavefunction must be decomposed into spherical harmonics. Bachelet et al. parameterized nonlocal pseudopotentials for all atoms from H to Pu [103]. As for all the angular momentum components \( l > 3 \) the pseudopotential \( V_{l=3} \) is used, this pseudopotential can be taken as the local one and only the \( l = 0, 1, 2 \) components of the wavefunction have to be calculated. The applied nonlocal pseudopotentials then are \( V_0(\mathbf{r}) - V_3(\mathbf{r}) \), \( V_1(\mathbf{r}) - V_3(\mathbf{r}) \), and \( V_2(\mathbf{r}) - V_3(\mathbf{r}) \), respectively. Around each atomic position a radial grid is build on which the wavefunctions are decomposed into the spherical harmonics by use of Lebedev's spherical quadrature formula [118]. This part is quite time-consuming and needs roughly about 50% of the computational time. Because the nonlocal parts vanish for sufficient large distances from the atoms (about 3-4 Å), the decomposition does not depend on \( N \) and thus for larger calculations the time spend in this routine gets shorter compared to the time spend in other routines.
B.3 Comparison with commercial available codes

Harris et al [119] compared two commercial available codes (the CASTEP code, distributed by Molecular Simulations, Inc., and the PLANE_WAVE code, distributed by Biosym technologies, Inc.) with a self-developed one. All these codes are based on the plane-wave expansions of the valence electron distribution and the use of LDA.

Their model system consisted of a hydrogen atom in a box with a length of 10 Å. The large cell ensures that the H-atoms are non-interacting. In order to compare the correctness and the convergence of the codes, Harris et al calculated the total energy of the model system for different expansion lengths of the FFT grid. They found that all the codes converge to the same total energy of around 0.4458 hartrees, but at very different convergence rates. The problem of their research is that they did not specify which grid length they meant, i.e., if it is the length of the expansion of the wavefunction or that of the density (or potentials). The energies, which they got for the H-atom, compared to the data I got for the same model system by use of the self-written program (XTALCALC), suggest, that

- the mentioned grid length is that of the densities and potentials, and
- in the PLANE_WAVE code the density is expanded up to $2G_{\text{max}}$, while in the CASTEP code it seems that it is expanded only up to $1.5G_{\text{max}}$.

Fig. B.2 shows the calculated total energy $E$ per hydrogen atom as a function of the length $L$ of the wavefunction - FFT grid (in each dimension). To get the limit of $E$ for very large $L$, $E(L \to \infty)$, the data were fitted by a power-function $f = \text{const} + m \cdot L^{-n}$, with an negative exponent $n$ between 2.4 and 2.5. In the case of the CASTEP and the XTALCALC code this gave a convergence limit of 0.4459 hartree, in the case of the PLANE_WAVE code it was 0.4457 hartree. Within the fitting errors these convergence limits are identical. Fig. B.2 shows that all three programs have about the same convergence rate and the same convergence limit, the first statement in contrast to what has been found in [119], and the second one proofing the correctness of the self-written code.
Figure B.2: Energy per hydrogen atom as a function of the expansion length $L$ of the wave-function - FFT grid in each dimension. Data for the CASTEP and the PLANE_WAVE code are from [119]. The dashed line is a fit of the XTALCALC data with a power function and an exponent of $-2.5$. 
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My thanks are given to all who supported, assisted or simply participated on my work. In particular I would like to express my gratitude to

<table>
<thead>
<tr>
<th>Name</th>
<th>Acknowledgement</th>
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<tbody>
<tr>
<td>Prof. Dr. P. Günter</td>
<td>for giving me the opportunity to work as a Ph. D. student in his Nonlinear Optics Laboratory</td>
</tr>
<tr>
<td>Prof. Dr. M Zgonik</td>
<td>for carefully reading this manuscript</td>
</tr>
<tr>
<td>Dr. Z. Sitar</td>
<td>for many fruitful discussions, their great support and for supervising my thesis as teamleaders</td>
</tr>
<tr>
<td>Dr. Daniel Fluck</td>
<td></td>
</tr>
<tr>
<td>Hermann Wüest</td>
<td>for the growth of the substrate crystals and the discussions at the coffee table</td>
</tr>
<tr>
<td>Jaroslav Hajfier</td>
<td>for polishing the substrates and films</td>
</tr>
<tr>
<td>Dr. Stefan Pfändler,</td>
<td>for many contributions to this work and sharing life as Ph. D. students in the Nonlinear Optics team</td>
</tr>
<tr>
<td>Dr. Thomas König</td>
<td></td>
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<tr>
<td>Dr. F. Gitmans</td>
<td></td>
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<tr>
<td>Dr. Tomas Pliska</td>
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<tr>
<td>Dr. Simon Brülsauer</td>
<td></td>
</tr>
<tr>
<td>Karolina Brüngger</td>
<td></td>
</tr>
<tr>
<td>Michael Kiy</td>
<td>for introducing me to UPS and doing some measurements</td>
</tr>
<tr>
<td>Markus Abplanalp</td>
<td>for sharing his knowledge of AFM and examining some films</td>
</tr>
<tr>
<td>Edwin Hausammann</td>
<td>for his expertise in technical construction</td>
</tr>
<tr>
<td>My parents, Agnes and</td>
<td>for giving me the possibility to study at the ETH</td>
</tr>
<tr>
<td>Eduard Pierhöfer</td>
<td></td>
</tr>
<tr>
<td>My wife Regula Kuratli and</td>
<td>for their understanding and their great support during the time of writing.</td>
</tr>
<tr>
<td>my daughter Livia</td>
<td></td>
</tr>
<tr>
<td>Louise Pierhöfer-Dawson</td>
<td>for reading and correcting the manuscript.</td>
</tr>
</tbody>
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