Doctoral Thesis

Photorefractive and nonlinear optical properties of $\text{Sn}_2\text{P}_2\text{S}_6$

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Photorefractive and nonlinear optical properties of Sn$_2$P$_2$S$_6$

A dissertation submitted to the Swiss Federal Institute of Technology Zürich for the degree of Doctor of Natural Sciences presented by Daniel Haertle Dipl. Phys. ETH born on the 9th October 1974 citizen of St. Gallenkappel (SG)

accepted on recommendation of Prof. Dr. P. Günter, examiner Prof. Dr. M. Sigrist, co-examiner Prof. Dr. G. Montemezzani, co-examiner

Zürich 2005
Dedicated to my mother *Sylvia*, for her love and lifelong support in all spheres of life.
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Abstract

Sn₂P₂S₆ is a very interesting material for photorefractive, electro-optical and nonlinear optical applications, and this thesis is devoted to study this crystal in these three fields. The advantage of Sn₂P₂S₆ for these applications are the large transparency range, high nonlinearity, faster response and a narrower bandgap compared to alternatives. Since the interest for this material arose only recently, many linear and nonlinear optical properties were unknown at the beginning of this thesis. We have precisely determined most of them and demonstrated their importance in several promising application schemes, like phase-matched optical parametric generation up to 8 µm, dynamic holography in the interband regime in the visible, and photorefractive beam amplification for diode laser beam cleanup in the infrared.

For nonlinear optical applications phase-matching and therefore precise knowledge on the linear optical properties is essential, so this thesis begins with measurement of optical properties like the position of the indicatrix and its rotation with the wavelength of the light. For the first time it was important in which direction the positive z-axis is defined. A simple method was found to tell the direction of the positive z-axis by using the fact that the indicatrix is rotated in the Cartesian coordinate system. The refractive indices were measured precisely in the wavelength range 550−2300 nm. With interband photorefractive measurements it was shown, that the extrapolation of the refractive indices holds also in the absorption region at least down to 488 nm.

In nonlinear optical applications the generation of a new wavelength has to be phase matched. The refractive index data was used to calculate the phase-matching conditions for second harmonic generation and optical parametric oscillation. Since no program was available for calculating these in crystals with rotated indicatrix, a phase matching program was ameliorated to cope with crystals of such low symmetry. Phase matching was found for second harmonic generation for all wavelengths from 1680 nm up to the end of the transparency range at 8 µm. It was observed experimentally at λ = 1907 nm at the calculated location. With optical parametric oscillation it is possible to create all wavelengths between 1500 and 8 µm by pumping with a Nd:Yag laser at 1064 nm, type I phase matched and with an effective nonlinear optical coefficient $d_{\text{eff}}$ of about 4 pm/V. This is important since the best standard materials for generating infrared wavelengths give access only to wavelengths up to 5 µm, with similar efficiency. To calculate $d_{\text{eff}}$ all 10 nonlinear optical coefficients were measured at $\lambda = 1542$ nm and 1907 nm. Third harmonic generation in Sn₂P₂S₆ was also demonstrated for the first time and two coefficients of the $\chi^{(3)}$ tensor determined.

Both conventional and interband photorefraction were studied in Sn₂P₂S₆. The high gain of this material in conventional photorefraction in the near infrared, allowed to demonstrate phase conjugation at wavelengths up to 980 nm. Two-wave mixing
was studied at several wavelengths up to 1064 nm, which permitted to determine several material constants needed in photorefractive. $\text{Sn}_2\text{P}_2\text{S}_6$ is unique among the good photorefractive materials to allow interband photorefractive experiments at visible light (in the blue and green spectral region). With the two main argon wavelengths both two-wave mixing experiments and diffraction experiments with a non-absorbed beam were performed. Photoconductivity experiments permitted to find a method to calculate the absorption in the interband spectral region, by measuring the photocurrent. This allows to circumvent many hassles in the measurement of the absorption when the light penetrate only a few microns in the material.

From photorefractive measurements it was presumed that $\text{Sn}_2\text{P}_2\text{S}_6$ has large electro-optical coefficients. The relevant ones were measured by a direct method, and resulted even larger than expected. Both the clamped and the unclamped coefficients were measured. The dispersion of the unclamped coefficients was measured and found to be very low. All this grants good possibilities for applications, especially if combined with the equally good nonlinear optical properties.

In a work not related with $\text{Sn}_2\text{P}_2\text{S}_6$ or nonlinear optics, an all-optical device finding differences between two images (optical subtraction) was planned and prototyped. Such a device can match the speed of electronic processing, due to the parallel processing of whole images, and would be particularly useful if all other data processing in the setup is made in the optical domain.
Zusammenfassung


Sowohl der klassische photorefraktive Effekt als auch der sogenannte interband-photorefraktive Effekt wurden in Sn$_2$P$_2$S$_6$ untersucht. Der hohe Gewinnfaktor dieses Materials beim Zwei-Wellen-Mischen im nahen Infraroten erlaubte die Erzeugung von
Zusammenfassung


Grosses photorefraktive Effekte erhält man vor allem in Materialien mit großen elektro-optischen Koeffizienten und guter Photoleitung. Deshalb wurden die relevanten elektro-optischen Koeffizienten durch direkte Messung bestimmt. Sowohl die geklemmten als auch die freien Koeffizienten wurden gemessen, und sie zeigen sehr grosse Werte, z. B. \( r_{111}^T = 174 \pm 10 \, \text{pm/V} \) bei 633 nm, was fünfmal grösser ist als in LiNbO₃. Die Wellenlängenabhängigkeit der freien Koeffizienten wurde im Wellenlängenbereich 600...1300 nm gemessen und ist sehr klein. Dies sind gute Eigenschaften für Anwendungen, besonders wenn man sie mit den ebenso guten nichtlinear-optischen Eigenschaften kombiniert.

In einem weiterem Teil der Dissertation (Anhang B) wird eine voll-optische Anordnung vorgeschlagen, die Unterschiede zwischen zweiern Bildern findet (optische Subtraktion), und ein Prototyp wurde gebaut. Solch eine optische Methode kann die Geschwindigkeit elektronischer Verarbeitung erreichen oder überbieten, weil ein ganzes Bild pro Takt verarbeitet werden kann. Speziell nützlich ist diese Vorrichtung in vollkommen optischen Datenverarbeitungssystemen.
Chapter 1

Introduction

Photonics is a key driving technology of the 21st century [1] and the basis of the present-day internet and long distance communications. Photonics is the science of the harnessing of light, and encompasses its generation, its detection, and manipulation, as for example the management of light through guidance. Many research fields are contributing to photonics, such as quantum electronics, quantum optics, nonlinear optics, electro-optics, integrated-optics, fiber-optics, optical storage, etc.

This thesis studies Sn$_2$P$_2$S$_6$ as an interesting material for photonics. It is shown that tin hypothiodiphosphate (Sn$_2$P$_2$S$_6$) is a very promising material for photorefractive, electro-optical (chapter 3), nonlinear optical (chapter 4) and photorefractive applications (chapters 5 and 6). These studies are accompanied by a thorough study of the linear optical properties of this monoclinic crystal (chapter 2) necessary for the prediction of nonlinear optical interactions. The material contained in chapters 2–6 has been published or is in the course of publication in refereed international journals. The publications reproduced on electro-optics and nonlinear optics reproduced in chapters 3 and 4 were the first to reveal the potentialities of SPS in those fields.

Since this thesis is constructed around 5 journal manuscripts which allow only a limited possibility for a general introduction, we present in the present chapter a short overview of the basics underlying photorefractive, electro-optic and nonlinear optical effects as well as a general description of Sn$_2$P$_2$S$_6$. This introductory chapter is followed by the study of the linear optical properties of Sn$_2$P$_2$S$_6$ in chapter 2. As mentioned above, electro-optical and nonlinear optical properties of Sn$_2$P$_2$S$_6$ are presented in chapters 3 and 4 respectively. In chapter 5 photorefractive measurements are presented, and more specifically two wave mixing and phase conjugation at near infrared wavelengths. The last article, chapter 6, presents interband photorefractive studies in Sn$_2$P$_2$S$_6$, including two wave mixing and interband diffraction experiments at 488 and 514 nm. The appendices contain additional work performed during this thesis. Appendix A reports an easy method for determining the approximate position of the indicatrix in crystal with low symmetry. It is used in chapter 2 for determining the main axes of the indicatrix of Sn$_2$P$_2$S$_6$, but is not specific to this crystal. It was published together with the work of chapter 2. Appendix B reports unpublished work on optical subtraction, i.e. comparison of optical data (such as images) in an all-optical process. Appendix C explains a new method for calculating the absorption in the interband regime, by measuring the photocurrent. This method was found to be valid for all photoconductive materials in which the quadratic carrier recombination
regime can be identified. The latter is characterized by a photocarrier density increasing with the square root of light intensity as a result of interband recombination processes. This appendix is also being submitted for publication.

In the following section, basic concepts and models of nonlinear optics which are important for this work, are introduced. Some of these topics are well introduced and explained in the respective chapters, e.g. electro-optics on page 31 and wavelength conversion in nonlinear optics on page 47. For these topics very little will be written here and we refer to those locations.

1.1 Nonlinear optics

Linear and nonlinear optical effects

Linear and nonlinear optical effects can be described in terms of the linear polarization \( P^L \) and the nonlinear polarizations \( P^{NL} \) of the macroscopic material polarization \( P \) induced in a nonlinear medium by an external electric field \( E \)

\[
P_i = P_i^0 + P_i^L + P_i^{NL}
\]

\[
P_i^0 + \varepsilon_0 \chi^{(1)}_{ij} E_j + \varepsilon_0 \chi^{(2)}_{ijk} E_j E_k + \varepsilon_0 \chi^{(3)}_{ijkl} E_j E_k E_l + \ldots
\]

(1.1)

using the Einstein convention for summation over common indices (with \( i, j, k, l = 1, 2, 3 \)) and with \( P^0 \) the spontaneous polarization, \( \varepsilon_0 \) the vacuum permittivity, \( \chi^{(1)} \) the linear or first-order, \( \chi^{(2)} \) the second-order, and \( \chi^{(3)} \) the third-order susceptibility. For symmetry reasons, the odd-order susceptibilities are present in any material, whereas the even-order ones only occur in noncentrosymmetric materials (in the dipole approximation). The susceptibility tensors \( \chi^{(n)} \) contain all the information about the macroscopic optical properties of the respective material.

If the electrical field \( E \) is that of an electromagnetic wave with frequency \( \omega \), the first two terms of \( P_i^{NL} \) indicated in (1.1) can oscillate with frequencies \( 2\omega \) and \( 3\omega \) respectively, giving rise to new electromagnetic waves with those frequencies. This is the concept of second and third harmonic generation. Since the electric field of the generated upper harmonic wave is proportional to the second and, respectively, third power of the field \( E \) of the fundamental wave, \( E \) and thus the intensity of the wave have to be large for a significant effect.

Electro-optical effect

If the electric field \( E \) is composed by the field \( E^\omega \) of an optical wave plus a static electric field \( E^0 \), the nonlinear polarization \( P_i^{NL} \) in (1.1) will have terms of the same frequency as \( E^\omega \), the first such terms being

\[
P_i^{NL} = 2\varepsilon_0 \chi^{(2)}_{ijk} E_j E_k^0 + 3\varepsilon_0 \chi^{(3)}_{ijkl} E_j E_k^0 E_l^0 + \ldots
\]

(1.2)

This polarization gives a change of the refractive index, which is best written as the change of the tensor \( \varepsilon^{-1} = n^{-2} \) in the form

\[
\Delta \left( \frac{1}{n^2} \right)_{ij} = r_{ijk} E_k^0 + R_{ijkl} E_k^0 E_l^0 + \ldots
\]

(1.3)
where \( r_{ijk} \) is the linear electro-optical tensor, related to \( \chi^{(2)}_{ijk} \), and \( R_{ijkl} \) is the quadratic electro-optical tensor, which is related to \( \chi^{(3)}_{ijkl} \). Contrarily to the nonlinear optical effect, the electro-optical effect does not depend on the intensity of the optical wave \( E^0 \), but only on the static field \( E^0 \). Note that due to dispersion, the linear and nonlinear optical susceptibilities depend on the frequency of the fields inducing the polarization in the material.

### 1.2 Photorefraction

In photorefractive materials the refractive index can be modified by illumination with light. The photorefractive effect can show very high light sensitivity in appropriate material thus permitting the observation of such effects at very low light power (< µW). There are many different effects which can lead to photorefraction as for example photochemical effects, photoinduced reorientation of molecules, Kerr effect at high intensity, or photoinduced thermal effects. In this chapter we will restrict the definition of the photorefractive effect to the light induced refractive index change due to charge transport in electro-optic materials. This definition has become common in literature. Photorefraction gives rise to many interesting effects as for example light induced wave-guiding [2], phase conjugation [3, 4], beam amplification [5], and four wave mixing [6].

In this section the basic theory of photorefraction, starting from the band-transport model will be presented. The special case of direct band-to-band photo-excitation will be considered in section 1.3.

**Physical Processes Involved in the Photorefractive Effect**

The photorefractive effect can be described by the following four processes:

- **Generation of charge carriers through photo-excitation by an inhomogeneous illumination.** The charge carriers can be electrons or holes.

- **Transport of the excited, mobile charges from the illuminated into dark zones due to diffusion or to electric forces (drift).** Additionally, the bulk photovoltaic effect may contribute to the charge displacement.

- **In the dark areas, recombination of the mobile charge carriers into trapped states, e.g. defects, impurities, and self trapping.**

- **Due to this charge redistribution, a space charge electric field is generated which leads to a change of the refractive index via the electro-optic effect, described shortly in section 1.1.**

Figure 1.1 illustrates the involved processes and steps for the special case of hole diffusion. In Fig. 1.2 a simplified band-scheme and the most important processes for photo-excitation, displacement, recombination, and trapping of charge carriers are depicted.

In the following, we introduce the most important mathematical models used to describe the above mentioned physical processes.
Chapter 1. Introduction

I
ne
a.
Light intensity
x
Esc
b.
Charge carrier
density
x
c.
Space charge
field
x
d.
Refractive
index change
x

Generation of mobile charge carriers through photo-excitation.

Charge transport (diffusion, drift and photogalvanic effect).

Trapping of the charge carriers and generation of phase-shifted space-charge field.

Refractive index modulation via electro-optic effect.

Figure 1.1: Mechanisms involved in photorefraction, here illustrated for the case of hole transport. \( \Lambda \) is the grating constant and \( \Phi \) is the phase shift between light intensity and refractive index modulation. For charge transport dominated by diffusion one gets \( \Phi = \Lambda/4 \).

Conventional Model

The so-called conventional model was elaborated by Kukhtarev et al. [7,8,9] considering only photo-excitation and recombination of one species of charge carriers between a single donor level and the corresponding conduction band. This single-level band scheme, along with the involved physical mechanisms, is depicted in Fig. 1.3. Note that while this simplified model describes satisfactorily the processes in a large number of materials showing the photorefractive effect, there exist several crystals where details of the charge transport mechanism are better described by considering additional defect levels [10,11]. Another important limitation is that the photon energies of the light illumination must be smaller than the band-gap energy.

The involved processes can be described by the following set of equations

\[
\frac{\partial N^+_D}{\partial t} = (s_e I + \beta_e)(N_D - N^+_D) - \gamma_e n N^+_D
\]

\[
\frac{\partial n}{\partial t} = \frac{\partial N^+_D}{\partial t} + \frac{1}{e} \nabla J_e
\]

\[
J_e = e n \mu_e \mathbf{E} + k_B T \mu_e \nabla n + e s_e I (N_D - N^+_D) \mathbf{L}_{ph}
\]

\[
\nabla E_{sc} = \frac{e}{\varepsilon_0 \varepsilon_{eff}} (N^+_D - n - N_A)
\]

where the photoexcited charges are assumed to be electrons. The symbols in the above equations are:
1.2. Photorefraction

Figure 1.2: Simplified bandscheme of possible charge transitions in a photorefractive material with the concentration of ionized donors $N_D^+ - N_D^-$ and traps $N_D^+$. Excitation of charge carriers may occur via band-to-band (with a generation rate $s_{dir}I$), trap-to-band ($s_eI$), and band-to-trap transitions ($s_hI$). Excited charges are displaced by diffusion and drift. They can recombine through band-to-band electron-hole recombination (with a recombination rate $\gamma_{dir}$), or be trapped in mid-bandgap levels ($\gamma_e$ and $\gamma_h$). The arrows show the movements of the electrons and thermal excitation is not depicted.

Figure 1.3: Single level band scheme in the conventional model at low intensities. An electron is photoexcited to the conduction band from a mid band-gap level. Diffusion or drift result in a displacement of the electron. Near a trapcenter, the electron can be retrapped.
Chapter 1. Introduction

- $n$ the free electron concentration in the conduction band;
- $N_D$ the donor concentration;
- $N_D^+$ the concentration of ionized donors;
- $N_A$ the concentration of ionized donors (acceptors) in the dark;
- $J_e$ the electron current density;
- $E$ the total electric field;
- $E_{sc}$ the space charge field;
- $I$ the light intensity;
- $L_{ph}$ the photogalvanic transport length vector;
- $s_e$ the photoionization constant for electrons;
- $\beta_e$ the thermal (dark) generation rate for electrons;
- $\gamma_e$ the recombination constant for electrons;
- $\mu_e$ the electrons mobility;
- $\varepsilon_0$ the vacuum dielectric permittivity;
- $\varepsilon_{eff}$ the dielectric permittivity of the material in the direction of $E_{sc}$;
- $e$ the absolute value of the elementary charge;
- $k_B$ the Boltzmann constant;
- $T$ the absolute temperature.

Equation (1.4) is the rate equation for the concentration of the ionized donors. The first term describes the photoionization process ($s_e I$) and the thermal excitation of electrons from the donor level. The second term takes into account the recombination of the electrons ($\gamma_e$) into traps, in our case ionized donors. The second equation (1.5) is the continuity equation for the electron density. The additional term with respect to Eq. (1.4) describes the divergence of the electron current density. Eq. (1.6) describes the different contributions to the electron current density. The first term gives the drift current in the total electric field $E = E_{sc} + E_0$, where $E_0$ is the applied field. The second term describes the diffusion process of the electrons generated by the electron concentration gradient. Thus, this term only gives a contribution for inhomogenous illumination. The last term gives the photogalvanic current, if present. In Sn$_2$P$_2$S$_6$ it is negligible, therefore we do not consider it in the following. The last equation (1.7) is the Poisson equation for the electric field. It describes the spatially modulated part of the electric field generated by the nonuniform distribution of the charge carriers in the crystal. These four equations are valid in this form only for isotropic photoexcitation, i.e., if $s_e$ is independent on the light polarization and intensity, or if the intensity and polarization of the exciting light wave is invariant, i.e., constant, with respect to its propagation direction, like in the case of a plane wave.
1.2. Photorefraction

1.2.1 Photorefractive index gratings

Irradiating a photorefractive material homogeneously, will not generate a space charge field or refractive index grating, but only change some of the bulk material properties like the conductivity or the absorption. In contrast, for an inhomogeneous illumination the charges are locally redistributed and will result in a space charge field. An effective way to produce an intensity pattern is given by the interference of two plane waves. Considering two plane waves with wavevectors $k_1$ and $k_2$ and electric field amplitudes $A_1$ and $A_2$ respectively we obtain a sinusoidal intensity pattern of the form

$$I(x) = I_0(1 + m \cos K \cdot x)$$

where $K = k_1 - k_2$ is the grating vector, $x$ is the position vector, $m = 2 |A_1||A_2|/(|A_1|^2 + |A_2|^2)$ is the modulation depth, and $I_0 = \frac{1}{2} \sqrt{\epsilon_0/\mu_0(|A_1|^2 + |A_2|^2)}$ the mean intensity. For small modulation $m$, such an intensity distribution will build-up a spatial periodic space charge field $E_{sc}$ with the same period. The direction of $E_{sc}$ is oriented parallel to the grating vector $K$ and we will denote in the following the amplitude of the first spatial Fourier component of the space charge field with $E_{sc}$. In order to include in $E_{sc}$ also the phase of the $E_{sc}$ grating with respect to the illumination grating (1.8), we allow complex values of $E_{sc}$ by defining $E_{sc} = \text{Re}(E_{sc} \exp i K \cdot x) K/|K|$. In this way a purely imaginary value of $E_{sc}$ would mean that the space charge grating is shifted by $\pi/2$ with respect to the illumination grating. The exact amplitude of $E_{sc}$ for the conventional model will be given later in this section and for interband photorefraction in the next section.

In an electro-optic material the presence of a periodic space charge field $E_{sc}$ generates a refractive index grating which can be investigated by diffraction experiments of a third plane wave, eventually at a different wavelength. For non centrosymmetric materials which exhibits the linear electro-optic effect (Pockels effect) the change of the dielectric permittivity tensor is defined as

$$\Delta \epsilon^{-1} = r_{eff}(K)E_{sc}.$$ 

(1.9)

where $\epsilon$ is the dielectric permittivity tensor in the material at light wavelength and $r_{eff}(K)$ is a $3 \times 3$ matrix describing the electro-optic effect which considers the un-clamped electro-optic tensor and the additional contributions from the piezo-electric effect [12]. Since in (1.9), and alike in the following formula for $\Delta n$, the oscillating spatial term is not included, the left-hand side of these equations are the complex first spatial Fourier components.

For a certain geometry and light polarization, the amplitude of the spatially periodic refractive index change $\Delta n$ can be expressed as

$$\Delta n \approx -\frac{1}{2} n^3 r_{eff} E_{sc}$$

(1.10)

where $n$ is the refractive index seen by the beam, and $r_{eff}$ is the effective electro-optical coefficient relevant for this geometry. In the following section the magnitude of the space charge field is considered in detail.
Space charge field for sinusoidal illumination

A solution of Eqs. (1.4)–(1.7) can be found in the case where the material is illuminated with an intensity distribution as described by Eq. (1.8).

The space charge field is parallel to the grating vector and its amplitude is $|E_{\text{sc}}|$. Without any external electric field applied to the crystal, the complex amplitude of the space charge field $E_{\text{sc}}$ in case of small modulation depth $m$ is given by

$$E_{\text{sc}} = i m \frac{E_q E_D}{E_q + E_D}$$  \hspace{1cm} (1.11)

where $i$ is the imaginary unit and indicates that the space-charge field grating is shifted by $\pi/2$ compared to the illumination grating. For a better physical interpretation of $E_{\text{sc}}$ we have introduced the diffusion field $E_D$ and the trap limited field $E_q$. The first is defined as

$$E_D = \frac{k_B T}{e} K,$$  \hspace{1cm} (1.12)

and corresponds to the field amplitude of a sinusoidal electric field that exactly counteracts the effect of the charge diffusion process. The trap limited field is

$$E_q = \frac{e}{\epsilon_{\text{eff}} \epsilon_0 K} N_{\text{eff}}$$  \hspace{1cm} (1.13)

and gives a limit for the maximum $E_{\text{sc}}$ that can be generated with the available traps. In Eq. (1.13) $\epsilon_{\text{eff}}$ is the effective dielectric constant for the chosen configuration, and $N_{\text{eff}}$ is the effective trap density defined as

$$N_{\text{eff}} = \frac{N_{D0}^+ (N_D - N_{D0}^+)}{N_D}$$  \hspace{1cm} (1.14)

where $N_{D0}^+ = n_0 + N_A$ is the spatial average of ionized donors with illumination switched on. Although $n_0$, the spatial average of electrons in the conduction band when the light is on, is dependent on the intensity $I_0$ of the light, $n_0$ is in most cases much smaller than $N_A$, so that $N_{D0}^+$, $N_{\text{eff}}$, and $E_q$ are independent on the light intensity in the conventional model.

An important conclusion can be deduced from Eq. (1.11) which shows that if one of the two fields $E_q$ or $E_D$ is much smaller than the other, the total space-charge field is limited by this field. These limiting cases can be observed experimentally by varying the grating constant $K$.

Beam diffraction at an holographic grating

Diffraction gratings are one of the most powerful elements in modern optics. For a diffraction grating two regimes (Bragg and Raman-Nath) can be distinguished. We will focus on Bragg diffraction that is typical for thick (volume) holographic gratings, as mostly the case in photorefractive experiments.

The diffraction efficiency of a grating is defined as $\eta = I_{\text{dif}} / I_{\text{in}}$, where $I_{\text{dif}}$ and $I_{\text{in}}$ are the intensities of the diffracted beam and input beam respectively. For a Bragg grating, $\eta$ was first calculated by Kogelnik using the theory of coupled waves and recently expanded to the case of anisotropic materials by Montemagno and
1.2. Photorefraction

Figure 1.4: Schematic representation of light diffraction at an unslanted holographic grating with grating period $\Lambda$. On the right-hand side the wave-vector momentum conservation for the incident and diffracted beam is depicted. to fulfill the Bragg condition, the difference between the wave-vectors must correspond to the grating vector $K = 2\pi/\Lambda$.

Zgonik [16]. If we have the same absorption $\alpha$ for the incoming and the diffracted wave and a grating of thickness $d$ with refractive index modulation only, one obtains the following equation:

$$\eta = \frac{\sin^2 \sqrt{\nu^2 + \xi^2}}{1 + \xi^2/\nu^2} e^{-\alpha d}$$  \hspace{1cm} (1.15)

with

$$\xi^2 = \frac{\Delta k^2}{4} d^2$$  \hspace{1cm} (1.16)

$$\nu^2 = \frac{k_0^2 A_r^2}{16 n_i n_{dif} g_{in} g_{dif} \cos \vartheta_{in} \cos \vartheta_{dif}} d^2$$  \hspace{1cm} (1.17)

where $\Delta k$ represents the wave-vector mismatch from the Bragg condition projected normal to the sample surface, $g_{in,dif}$ are the projection cosines between electric ($\hat{e}_{in,dif}$) and dielectric displacement ($\hat{d}_{in,dif}$) unit vectors of the incident and diffracted beam respectively, and $\vartheta_{in,dif}$ are the angles inside the material between the Poynting vectors of the incident and the diffracted wave and the normal of the entrance surface (see Fig. 1.4, where $g_{in} = g_{dif} = 1$ was assumed). The coupling constant $A_r$ can be expressed in case of refractive index modulation caused by the electro-optical effect and a space-charge field $E_{sc}$ as

$$A_r = -n_{in}^2 n_{dif}^2 g_{in} g_{dif} \tau_{eff} E_{sc}.$$  \hspace{1cm} (1.18)

Neglecting the anisotropy of the crystal and using (1.10) leads to the approximation

$$\nu^2 = \frac{k_0^2 (\Delta n d)^2}{4 \cos \vartheta_{in} \cos \vartheta_{dif}}$$  \hspace{1cm} (1.19)

often used to determine $\Delta n$ from diffraction experiments.

The dependence of the diffraction efficiency on the beam incidence angle in the air $\vartheta_{in}'$ is shown for a 1 cm thick Sn$_2$P$_2$S$_6$ crystal in Fig. 1.5. The diffraction efficiency

\*The relation between the angle inside the material and in the air is given by Snell’s law
Chapter 1. Introduction

Figure 1.5: Diffraction efficiency $\eta$ as function of the external angle $\vartheta'_\text{in}$ for a 1 cm thick Sn$_2$P$_2$S$_6$ crystal. The other parameters are the grating spacing $\Lambda = 1 \mu$m, $\lambda = 633 \text{ nm}$, $\Delta n = 5 \cdot 10^{-5}$, and the absorption $\alpha = 0.5 \text{ cm}^{-1}$.

presents a strong central peak. On the top of the peak, at Bragg matching ($\Delta k = \xi = 0$), Eq. (1.15) for the diffraction efficiency reduces to $\eta = e^{-\alpha d} \sin^2 \nu$. On the other side, for weak gratings ($\nu^2 \ll 1$) and negligible absorption the curve of Fig. 1.5 is proportional to $\nu^2 (\sin \xi / \xi)^2$. In this case $\eta$ results simply proportional to $\nu^2$ and therefore proportional to the square of the spatial field modulation, $|E_{\text{sc}}|^2$. The position of the side minima and the zero crossing is determined by $\xi$, i.e. by wave-vector mismatch $\Delta k$ and the thickness of the crystal. Another important property of Eq. (1.15) is that for a large value of $\nu \approx 1$ diffraction efficiency as high as 100% can be expected if the absorption is negligible. This allows a very effective way to deviate light beams.

Two wave mixing

Two wave mixing (TWM) is a simple experimental technique, to evaluate the photorefractive properties of a material. The experiment allows to probe the magnitude and the build-up time of the space charge field $E_{\text{sc}}$. From the TWM measurement, the effective trap density $N_{\text{eff}}$ (see Eq. (1.14)), which is mainly responsible for grating spacing dependence of the space charge field, can be determined.

In two wave mixing experiments, two coherent light beams, the signal beam with the intensity $I_S$ and the pump beam with intensity $I_P$, interact in the photorefractive medium. The nonlinear interaction between the two waves may result in energy or phase transfer between the beams.

The interference between the signal and pump beams produces an intensity pattern in the crystal, and a space charge field described by Eq. (1.11) builds up. If diffusion is the dominant charge transport mechanism for the photoexcited charge carriers, a refractive index grating is built up, which is exactly $\pi/2$ out of phase with respect to the intensity grating. The pump beam is diffracted off the grating and the

\[ n_{\text{in}} \sin \vartheta'_{\text{in}} = \sin \vartheta'_\text{in} \]
diffracted wave is either exactly in phase with the signal or out of phase. Therefore, the signal is either amplified or depleted. For \( I_P \gg I_S \) (undepleted pump approximation) the measured energy transfer can be characterized by the exponential gain \( \Gamma \) which is defined as

\[
\Gamma = \frac{1}{d} \ln \frac{I_{S}^{on}}{I_{S}^{off}},
\]

where \( I_{S}^{off} \) and \( I_{S}^{on} \) are the intensities of the transmitted signal beam before and after turning on the pump beam and \( d \) is the length of the path of the signal beam in the crystal along its energy propagation direction [16]. In chapter 5, TWM is used to determine the material properties \( r_{eff} \) and \( N_{eff} \) of \( \text{Sn}_2\text{P}_2\text{S}_6 \), and more explicit expressions for \( \Gamma \) are given in Sec. 5.3 on page 63. Two wave mixing is also the basic process underlying self-pumped phase conjugation in photorefractive media, which will be treated in detail in that chapter.

### 1.3 The interband photorefractive effect

The conventional model only considers photo-excitation of charges from one midgap impurity level to one of the conduction bands. Accordingly, the absorption constant is small and the excitation process rather slow (milliseconds to seconds). As shown in Fig. 1.2, other transitions are possible as well. Under light illumination with photon energies larger than the band gap, band-to-band transitions occur and dominate over impurity-to-band transitions. Because of a much higher absorption constant in this regime, many more free charge carriers are produced, thus leading to a much faster excitation process. This effect is known as the “interband photorefractive effect”.

#### Basic equations

The most common set of equations describing the charge dynamics is given in [17], and includes one trap level in addition to direct band-to-band excitation. No thermal excitations and no photogalvanic current are considered. The following equations describe the processes illustrated in Fig. 1.2:

\[
\frac{\partial N_D^+}{\partial t} = s_e I(N_D - N_D^+) + \gamma_h p(N_D - N_D^+) - \gamma_e n N_D^+ 
\]

\[
\frac{\partial n}{\partial t} = s_{dir} I(N_V - p) + s_e I(N_D - N_D^+) - \gamma_e n N_D^+ - \gamma_{dir} np + \frac{1}{e} \nabla J_e 
\]

\[
\frac{\partial p}{\partial t} = s_{dir} I(N_V - p) + s_h I(N_V - p) N_D^+ - \gamma_h p(N_D - N_D^+) - \gamma_{dir} np - \frac{1}{e} \nabla J_h 
\]

\[
J_e = e n \mu_e E_{sc} + k_B T \mu_e \nabla n 
\]

\[
J_h = e p \mu_h E_{sc} - k_B T \mu_h \nabla p 
\]

\[
\nabla E_{sc} = \frac{e}{\varepsilon_0 \varepsilon_{eff}} (N_D^+ + p - n - N_A) 
\]
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The symbols have the same meaning as in Eqs. (1.4–1.7) whereas the newly added ones are defined as follows: \( p \) is the free hole concentration in the valence band, \( N_V \) is the density of electrons close enough to the top of the valence band to be photoexcited, \( J_h \) the hole current density, \( s_{\text{dir}} \) the photoexcitation constant for direct band-to-band phototransitions, \( \gamma_h \) the recombination constant for the hole-donor interaction, and \( \mu_h \) the hole mobility. The mathematical complexity of this set of equations is already for one impurity level so high that no closed solution has yet been found. Analytic solutions for \( E_{\text{sc}} \) were found by applying some simplifications [17,18]. Here we present only the solution for pure interband regime, i.e. without considering any trap level \((N_D = N_D^+ = N_A = 0)\), and without an external field. This limit well describes the effect for high light intensities, where the contribution from trap levels becomes negligible.

The resulting amplitude of the space charge field \( E_{\text{sc}} \) for a continuous sinusoidal illumination with a small light intensity modulation \( m \) is given by

\[
E_{\text{sc}} = -i m \frac{E_{\text{qf}} (E_{\text{Rh}} - E_{\text{Re}})}{(E_D + E_{\text{Re}} + E_{\text{Rh}})(E_D + E_{\text{qf}})}
\]  

(1.27)

where \( E_D = K k_B T / e \) represents the diffusion field, \( E_{\text{qf}} \) the free carrier-limited field

\[
E_{\text{qf}} = \frac{e}{\epsilon_{\text{eff}} \epsilon_0 K} \sqrt{\frac{g I_0}{\gamma_{\text{dir}}}},
\]  

(1.28)

and \( E_{\text{Re,Rh}} \) the electron (hole) recombination fields

\[
E_{\text{Re,Rh}} = \frac{1}{K \mu_{e,h}} \sqrt{g I_0 \gamma_{\text{dir}}}.
\]  

(1.29)

The recombination fields can be interpreted as the average electric field needed to drift one electron or hole by a distance \( K^{-1} = \Lambda / 2 \pi \) before a direct band-to-band recombination takes place.

Eq. (1.27) is a little bit more complex than Eq. (1.11), valid for the conventional single level model. Different regimes dominated by one of the fields \( E_{\text{qf}}, E_D, E_{\text{Rh}}, \) and \( E_{\text{Re}} \) are possible. In interband photorefraction the steady state of the space charge field depends not only on the grating spacing \( \Lambda \) but also on the light intensity \( I_0 \). For high intensities \((E_{\text{qf}} \gg E_D)\) and small grating spacings \( \Lambda \) the \( E_{\text{sc}} \) will grow proportional to \( \sqrt{I_0} \).

The dynamics of the build-up is given by a double exponential function [18], and the build-up time constants are proportional to

\[
\tau_{ib} \propto \frac{1}{\sqrt{I_0}}
\]  

(1.30)

in the pure interband regime. The diffraction efficiency of interband gratings is given by (1.15), but with the interband space charge field (1.27) inserted in (1.18). This results, for small efficiencies, in

\[
\eta \propto (\Delta n \tilde{d})^2 \propto \left[ \Delta n \ln \left( \frac{I_0}{I_{\text{ref}}} \right) \right]^2
\]  

(1.31)
where $\tilde{d}$ is the thickness of the grating and $I_{\text{ref}}$ is a reference intensity needed for normalisation. In (1.31) the grating is assumed constant until a certain thickness $\tilde{d}$, which is dependent on the illumination intensity, and then vanishing. This approximation has been shown to yield equal or better results than a model with an exponentially decreasing grating [17].

Usually interband photorefractive experiments are performed with ultraviolet light, since the bandgap of most photorefractive materials lies in that energy range. $\text{Sn}_2\text{P}_2\text{S}_6$ has a smaller bandgap of 2.3 eV and thus visible laser lines, such as of an Argon laser, can be used. More characteristic properties of this material are given in the following section.

1.4 $\text{Sn}_2\text{P}_2\text{S}_6$

1.4.1 Introduction

Tin hypotiodiphosphate ($\text{Sn}_2\text{P}_2\text{S}_6$) is a very interesting material for photorefractive, electro-optical and nonlinear optical applications. In the photorefractive field $\text{Sn}_2\text{P}_2\text{S}_6$ is characterized by a large beam coupling gain in the wavelength range 0.5...1.1 $\mu$m and a relatively fast response, two orders of magnitude faster than $\text{BaTiO}_3$ doped with rhodium, which is the usual photorefractive material in the near infrared. In electro-optics $\text{Sn}_2\text{P}_2\text{S}_6$ is useful because of its large electro-optical coefficients and their nearly absent dispersion in the near infrared. For example the diagonal electro-optical coefficient $r_{111} = 166 \pm 8$ pm/V at $\lambda = 1313$ nm, which leads to a half-wave voltage 15-20 times smaller than in the standard material LiNbO$_3$. And for nonlinear optics $\text{Sn}_2\text{P}_2\text{S}_6$ has large effective nonlinear optical coefficients with phase-matching in a transparency region ranging from 0.53 to 8 $\mu$m.

A good and long introduction to $\text{Sn}_2\text{P}_2\text{S}_6$ is given in the chapter on this material in Ref. [19]. We are mainly interested in the photorefractive properties of $\text{Sn}_2\text{P}_2\text{S}_6$ so we will describe these here first, and then pass on to the crystal’s growth, structure and other properties in the next sections.

1.4.2 Photorefractive properties

Photorefraction with $\text{Sn}_2\text{P}_2\text{S}_6$ started in 1991, when Grabar et al. first observed this effect in $\text{Sn}_2\text{P}_2\text{S}_6$ [20]. A few years later Odoulov et al. remarked that the photorefractive gain at 1.06 $\mu$m can be enhanced considerably by pre-illuminating the crystal with white light [21,22]. A new step forward was made in 2001 when a new ”brown” modification was obtained [23] and in 2003 with tellurium doped crystals, which both outperform normal ”yellow” crystals in photorefractive gain and speed. The main photorefractive parameters of these three types of $\text{Sn}_2\text{P}_2\text{S}_6$ crystals are shown in Table 1.1 in comparison to some standard materials.

1.4.3 Growth of $\text{Sn}_2\text{P}_2\text{S}_6$

The growth of the $\text{Sn}_2\text{P}_2\text{S}_6$ crystal was first described in 1970 by Nitsche et al. [24]. They reported the possibility that single crystals of many metal-phosphorous-sulfur
Table 1.1: Typical photorefractive parameters of various Sn$_2$P$_2$S$_6$ crystals at two light wavelengths $\lambda$: $\alpha_x$, absorption coefficient for $x$-polarized light; $\Gamma_{\text{max}}$, maximal two-wave mixing gain; $\tau$, faster response time at a grating spacing of 1 $\mu$m and scaled to a light intensity of 1 W/cm$^2$; $N_{\text{eff}}$, effective trap density [19].

<table>
<thead>
<tr>
<th>Sn$_2$P$_2$S$_6$ sample</th>
<th>$\lambda$ [nm]</th>
<th>$\alpha_x$ [cm$^{-1}$]</th>
<th>$\Gamma_{\text{max}}$ [cm$^{-1}$]</th>
<th>$\tau$ [ms]</th>
<th>$N_{\text{eff}}$ [10$^{16}$ cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow</td>
<td>633</td>
<td>0.5</td>
<td>4–7</td>
<td>10–50</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>780</td>
<td>0.2</td>
<td>2–5</td>
<td>100</td>
<td>0.2</td>
</tr>
<tr>
<td>Brown</td>
<td>633</td>
<td>5.7</td>
<td>38</td>
<td>4</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>780</td>
<td>1.0</td>
<td>18</td>
<td>10</td>
<td>0.7</td>
</tr>
<tr>
<td>Te-doped (1%)</td>
<td>633</td>
<td>1.0</td>
<td>10</td>
<td>2.5</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>780</td>
<td>0.4</td>
<td>6</td>
<td>7</td>
<td>1</td>
</tr>
<tr>
<td>LiNbO$_3$ (SLN)</td>
<td>633</td>
<td>0.2</td>
<td>20</td>
<td>(5–50)$\cdot10^4$</td>
<td></td>
</tr>
<tr>
<td>KNbO$_3$</td>
<td>633</td>
<td>0.2</td>
<td>2–5</td>
<td>1–2</td>
<td></td>
</tr>
</tbody>
</table>

Compounds Me$_2$P$_2$S$_6$ (Me = Sn, Fe, Cd) can be grown by a vapor transport technique employing pure iodine. Stoichiometric amounts of the constituting elements and the transporter gas were sealed into quartz ampoules and brought to reaction at 650–700$^\circ$C. The ampoule was placed in the hot spot of a horizontal temperature gradient, while the crystal grows in the cold end (ca 20$^\circ$C colder) by chemical transport. A possible reaction equilibrium for this transport is:

\[2(SnI_2)_{\text{gas}} + 0.5(P_4)_{\text{gas}} + 3(S_2)_{\text{gas}} \rightleftharpoons (Sn_2P_2S_6)_{\text{solid}} + 2(I_2)_{\text{gas}}\]

but other reactions, involving volatile phosphorous sulfides and/or phosphorus halides cannot be excluded [25]. Average growth times were of the order of 100 hours. Nowadays there are three different transporter agents used [23]: pure iodine I$_2$, SnI$_2$ and SnI$_4$. With either SnI$_4$ or iodine transporter yellow-colored crystals are obtained, recently a light-brown colored Sn$_2$P$_2$S$_6$ sample was grown using SnI$_2$ as transporter (with enhanced photorefractive parameters) [23].

1.4.4 The crystal structure

The structure at room temperature was investigated in Ref. [26] and at 110$^\circ$ in Ref. [27]. At room temperature the crystal has a ferroelectric [28] monoclinic structure with point group $m$ [26], above the second order phase transition at $T_C = 66 \pm 2^\circ$C [29] the crystal is paraelectric and belongs to the monoclinic point group 2/$m$.

The primitive cell is shown in Fig. 1.6 and is set according to the standard convention [30] that $b$ is perpendicular to the mirror plane, and $c < a$, $\beta > 90^\circ$, $\alpha = \gamma = 90^\circ$. Then the translation vectors are $a = 9.375$ Å, $b = 7.488$ Å and $c = 6.513$ Å, and the angle $\beta$ between $a$ and $c$ is $\beta = 91.15^\circ$ [26]. Note that the crystal axis $b$ is perpendicular to the plane of Fig. 1.6. The elementary cell has two P$_2$S$_6$ units. The whole structure shows a pseudosymmetry through a pseudo twist axis in direction [010]. The P$_2$S$_6$ unit is settled by two distorted trigonal PS$_3$ prisms which are related together through a P-P bond. The bases are rotated so that the whole symmetry is 3$m$. The two Sn$^{2+}$ cations are connected to the (P$_2$S$_6$)$^{4-}$ complex by ionic bonds.
1.4. \( \text{Sn}_2P_2S_6 \)

Figure 1.6: Schematic structure of \( \text{Sn}_2P_2S_6 \). The symmetry plane is parallel to the plane of the figure. The unit cell in the Dittmar notation is indicated by the dashed lines.

The atoms of the unit cell have a space group \( Pn \)\(^{[27]} \) at room temperature, since the atoms get onto each other by a translation by \( \left( \frac{1}{2}, 0, \frac{1}{2} \right) \) and successively a mirror operation about the \( y \)-plane. But note that all the macroscopic physical properties follow the point group symmetry, which is equal to the space group if one ignores the translations (which have no effect macroscopically).

The coordinate system chosen to describe the physical tensor symmetry is a right handed Cartesian \( x, y, z \) system. According to the standard of piezoelectric materials \(^{[30]} \), the \( y \)-axis is perpendicular to the symmetry plane \( (y \parallel b) \), the \( z \)-axis is chosen parallel to the crystal \( c \)-axis and the \( x \)-axis perpendicular to \( y \) and \( z \). The versus of the \( +x \)-axis and the \( +z \)-axis is set so that the piezoelectric constants \( d_{11} \) and \( d_{33} \) are positive. A positive value of \( d_{11} \) means that tension (= release of compression) parallel to the \( x \)-axis will cause a potential difference to be generated with its positive terminal on the \( +x \) face, that is, the face toward which \( +x \) points from inside the crystal. \( +y \) is set in such a way that the system is right handed. Crystals are normally cut along \( xyz \).

1.4.5 Spontaneous polarisation and other physical properties

Existence of ferroelectricity in \( \text{Sn}_2P_2S_6 \) was first reported in Refs. \(^{[28]} \) and \(^{[31]} \). It is given by movement of Sn atoms in a rigid \( P_2S_6 \) framework \(^{[27]} \). In crystals of class \( m \) the direction of the spontaneous polarisation \( P_S \) is not predictable, it must just lie in the \( (010) \) plane. \( P_S \) happens to lie between \( +x \) and \( -z \) \(^{[32]} \), \((14 \pm 2)°\) from \( +x \) \(^{[33]} \).
The value for $P_S$ was found to be 14 $\mu$C/cm$^2$ at 20$^\circ$C and the coercitive field is 750 V/cm \[31\].

As-grown Sn$_2$P$_2$S$_6$ crystals are usually poly-domain. For electro-optical, photorefractive, nonlinear optical or piezoelectric applications crystals need to be poled. This is done by heating the sample well over the phase transition temperature $T_C = 66 \pm 2^\circ$C and slowly cooling it down to room temperature under an applied electric field larger than the coercive field.

During heating of a poled sample, $P_S$ decreases up to the critical temperature, where it goes to zero following the square root dependence typical for second order phase transitions \[28\].

We conclude this introduction to Sn$_2$P$_2$S$_6$ with an overview of its physical properties in Table 1.2.

Table 1.2: Basic physical properties of Sn$_2$P$_2$S$_6$ at room temperature. The tensor elements are in the coordinates defined in chapter 2.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spontaneous polarization $P_s$</td>
<td>15 $\mu$C/cm$^2$</td>
<td>[31,34,35]</td>
</tr>
<tr>
<td>Transparency range</td>
<td>530 nm – 8000 nm</td>
<td>[36, Ch. 4]</td>
</tr>
<tr>
<td>Main refractive indices$^a$</td>
<td></td>
<td>Ch. 2</td>
</tr>
<tr>
<td>$n_1 = 3.0256$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n_2 = 2.9309$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n_3 = 3.0982$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dielectric constant $\varepsilon_{11}$</td>
<td>230 – 300</td>
<td>[37]</td>
</tr>
<tr>
<td>Electro-optic coefficient $r_{111}^T$$^a$</td>
<td>174 pm/V</td>
<td>Ch. 3</td>
</tr>
<tr>
<td>Piezoelectric coefficient $d_{111}$</td>
<td>244 pC/N</td>
<td>[38]</td>
</tr>
<tr>
<td>Density $\rho$</td>
<td>3.54·10$^3$ kg/m$^3$</td>
<td>[26]</td>
</tr>
<tr>
<td>Elastic constant $C_{1111}$</td>
<td>4.2 · 10$^{10}$ N/m$^2$</td>
<td>[39]</td>
</tr>
<tr>
<td>Pyroelectric coefficient $p_1$</td>
<td>7 · 10$^{-4}$ C/(m$^2$ K)</td>
<td>[40]</td>
</tr>
<tr>
<td>Coercive field $E_c$</td>
<td>7.5 · 10$^4$ V/m</td>
<td>[31]</td>
</tr>
<tr>
<td>Heat capacity $C_p$</td>
<td>240 J/(mol K)</td>
<td>[41]</td>
</tr>
<tr>
<td>Thermal conductivity $\lambda_1$</td>
<td>0.5 J/(s m K)</td>
<td>[42]</td>
</tr>
<tr>
<td>Nonlinear optical susceptibility$^b$</td>
<td>$\chi_{111}^{(2)} = 24$ pm/V</td>
<td>Ch. 4</td>
</tr>
<tr>
<td></td>
<td>$\chi_{111}^{(3)} = 17$ · 10$^{-20}$ m$^2$/V$^2$</td>
<td>Ch. 4</td>
</tr>
</tbody>
</table>

$^a$at 632.8 nm
$^b$at 1907 nm
Chapter 2

Refractive indices of Sn$_2$P$_2$S$_6$ at visible and infrared wavelengths

We report on the refractive indices of Sn$_2$P$_2$S$_6$ crystals in the wavelength range 550 – 2300 nm. The measurements are performed at room temperature using the minimum deviation method. The dispersion is described by a two oscillator model yielding the oscillator energies and strengths (Sellmeier parameters) for all polarization directions. The rotation of the indicatrix in the mirror plane and the direction of the optical axes have also been determined in the wavelength range $\lambda = 550 – 2200$ nm.

2.1 Introduction

Tin thiolypodiphosphate (Sn$_2$P$_2$S$_6$) is a wide bandgap semiconductor ferroelectric with interesting nonlinear optical properties [43] and large electro-optical coefficients [44]. In addition it is also a very attractive photorefractive material showing fast photorefractive grating recording times and large refractive index change in the red and near infrared spectral region [21,23]. These properties make Sn$_2$P$_2$S$_6$ an interesting material for several applications where laser diodes are employed (laser stabilization [45], beam cleanup, optical phase conjugation [46]). The wide optical transparency range extending from $\lambda = 0.53$ $\mu$m to $\lambda = 8$ $\mu$m [36] also allows optical parametric generation of infrared wavelengths not accessible with standard nonlinear optical crystals.

For the prediction of the phase-matching conditions, the principal refractive indices and the orientation of the indicatrix in the $xz$-plane have to be known with a reasonable accuracy. Complete and sufficiently accurate data for Sn$_2$P$_2$S$_6$ are not available in the literature. Preliminary refractive indices at room temperature for the visible and near-IR spectral range are given in [47], but no data for some spectral regions (e. g. from 650 to 1300 nm) is given. In addition the accuracy of these data is two orders of magnitude lower than the results reported here. Ref. [48] gives the temperature dependence of the refractive indices at $\lambda = 633$ nm and the relative rotation of the indicatrix between $\lambda = 510 – 810$ nm. The absolute position of the indicatrix has been reported in [44].

†This chapter, together with Appendix A, has been published in Optics Express, 13, p. 2047-2057 (2005) [32].
In this paper measurements of the refractive indices at 295 K in the wavelength range 550 – 2300 nm are presented. The absolute accuracy of the measurements is better than $2 \cdot 10^{-4}$. The dispersion of the data is analyzed and described with a two-oscillator Sellmeier model.

In Sn$_2$P$_2$S$_6$ the indicatrix has a rotational degree of freedom in the mirror plane of the crystal ($xz$-plane). Its angle to the $x$-axis is measured for the wavelength range $\lambda = 550 – 2200$ nm with an accuracy of $0.4^\circ$. Phase-matching conditions can be accurately predicted.

2.2 Crystallographic properties

Sn$_2$P$_2$S$_6$ is a proper ferroelectric with monoclinic point group symmetry $m$ at room temperature. The crystal undergoes a second-order phase transition to the centrosymmetric paraelectric phase (point group $2/m$) at the temperature $T_C = 338$ K [25].

Optical quality Sn$_2$P$_2$S$_6$ single crystals were produced by the conventional vapor-transport technique [25][24] using iodine as a transporter. We used nominally pure samples exhibiting low photorefractive effects.

![Figure 2.1: Position of the indicatrix and spontaneous polarization $P_S$ in the $xz$-plane at room temperature. This is the mirror plane, perpendicular to $b$ and $y$. ($a, b, c$) is the crystallographic system (non-orthogonal for monocline crystals), ($x, y, z$) is the Cartesian coordinate system, and ($x_1, x_2, x_3$) is the dielectric coordinate system.](image)

In this work we refer to the unit cell chosen by Dittmar and Schäfer [26] and the Cartesian coordinate system according to the IEEE standard on piezoelectricity [30], with $y \parallel b$ perpendicular to the mirror plane, $z \parallel c$, the positive direction of the $x$-axis and the $z$-axis so that the piezoelectric coefficients $d_{xxx}$ and $d_{zzz}$ are positive and $+y$ is chosen so that $xyz$ is a right-handed system. In this system $P_S \cdot \hat{x} > 0$ and $P_S \cdot \hat{z} < 0$, with $\hat{x}$ and $\hat{z}$ the unit vectors in $x$ and $z$-direction, as we determined by measuring the pyroelectric current.
2.3 Rotation of the indicatrix

In both the paraelectric and ferroelectric phases the indicatrix of Sn$_2$P$_2$S$_6$ lies in the mirror plane $xz$ and is rotated by an angle $\alpha$ from the $x$-axis to its major axis (see Fig. 2.1).

This rotation angle was measured by determining the rotation angle of the crystal for perfect extinction between crossed polarizers. The crystal was rotated about the $y$-axis, which coincided with the beam direction.

For $\lambda = 632.8$ nm and 295 K one gets an angle of either $\alpha = 43.3 \pm 0.4^\circ$ or $\alpha = -46.7 \pm 0.4^\circ$. This is because the measurement cannot distinguish between the major or the minor dielectric axis. We established that the angle between the major dielectric axis and the $x$-axis is $\alpha = 43.3 \pm 0.4^\circ$ by exploiting the fact that the reflection angle at an internal reflection depends on the rotation of the indicatrix. This to our best knowledge new method is described in Appendix A and can be used for an easy determination of the $+z$-axis.

![Figure 2.2: Measured rotation angle $\alpha$ of the major axis of the indicatrix to the $x$-axis ($T = 300$ K) Error: $\pm 0.4^\circ$. In the inset a comparison is shown with the less precise data calculated from the refractive indices (grey circles).](image)

For the measurement of the indicatrix rotation we used two rectangular samples with dimensions $5.21 \times 7.58 \times 5.83$ mm$^3$ and $5.07 \times 5.38 \times 4.85$ mm$^3$ along $x$, $y$ and $z$ axes respectively and polished faces perpendicular to the $y$-axis. The orientation of the crystallographic axes of these samples was $\pm 6'$ as determined by Laue scattering.

The measurements of $\alpha$ were performed using a Perkins Elmer $\lambda$9 spectrometer as light source and detector. This permitted to automatically scan over the wavelength range of $550 \ldots 2200$ nm for various rotations $\alpha_C$ of the crystal between the two crossed polarizers. We received the complete transmission map as a function of the wavelength $\lambda$ and the angle $\alpha_C$, where the minimum represents the index ellipsoid orientation to be determined. For each wavelength the bottom dozen of points was used to fit a parabola and find the minimum. The results from one sample are displayed in
Fig. 2.2. The error of ±0.4° comes mainly from the uncertainty of the absolute calibration value for \(\alpha\) measured at 632.8 nm. The relative error is much smaller (approximately 0.05°).

No model is known to explain the rotation of the indicatrix in low symmetry crystals. However the data in Fig. 2.2 can be well fitted by the empirical formula (mean absolute deviation = 1/40°)

\[
\alpha(\lambda) = \alpha_\infty + \frac{\alpha_1}{\lambda^2} + \frac{\alpha_2}{\lambda^4}
\]

with \(\alpha_\infty = 53.54°\) being the rotation for infinitely long wavelength, \(\alpha_1 = -5.523°\mu m^2\) and \(\alpha_2 = 0.4510°\mu m^4\) (at \(T = 300\) K).

The temperature dependence of \(\alpha\) is given in Ref. 48 and at \(T = 295\) K and \(\lambda = 633\) nm \(\frac{d\alpha}{dT} = -0.16\) K\(^{-1}\).

One can also calculate the dispersion \(\alpha(\lambda)\) from refractive index measurements of \(n_1\), \(n_3\) and \(n_2\), although this calculation is much less precise than the direct measurement. From our data presented later in this article we get a good agreement with Fig. 2.2 which is shown in the inset of that figure.

![Figure 2.3: Angle 2V between the optical axes, calculated from the refractive indices given by eq. (2.6) and the parameters in Table 2.3](image)

From the principal refractive indices one can also calculate the orientation of the two optical axes of Sn\(_2\)P\(_2\)S\(_6\), i.e. the beam directions, where all polarizations see the same refractive index. In biaxial crystals these beam orientations have to be perpendicular to the middle principal refractive index, \(n_{\text{mid}} = n_1\) for Sn\(_2\)P\(_2\)S\(_6\). Both optical axes are off the same angle \(V\) from the axis corresponding to the minimum refractive index \(n_{\text{min}}(= n_2\) for Sn\(_2\)P\(_2\)S\(_6\)), namely

\[
\tan^2 V = \frac{1}{n_{\text{max}}^2} - \frac{1}{n_{\text{mid}}^2} - \frac{1}{n_{\text{min}}^2}.
\]

The angle 2V between the two optical axes is shown in Fig. 2.3.
2.4 Refractive index measurement

Samples

For the measurement of the three principal refractive indices of Sn$_2$P$_2$S$_6$ by the minimum deviation method [49] two prisms with different crystallographic orientations are necessary. The orientations must be chosen such that the prism-bisecting plane contains at least one principal axis of the index ellipsoid. We cut two such prisms out of a single crystal and a third prism was cut out of another Sn$_2$P$_2$S$_6$ crystal to determine the variations of refractive index between different crystals. The sizes and orientations are given in Table 2.1. The apex angles $\varphi$ are approximately 29° and were chosen to be as large as possible (since the error terms $\frac{\partial n}{\partial \varphi}$ and $\frac{\partial n}{\partial \delta}$ diminish with larger apex angles) with the restriction not to let the incidence angle exceed 55°.

Table 2.1: Size and orientation of the prism samples. Sample 1 and 2 are cut from the same crystal. Both samples 1 and 3 permit to measure $n_1$ and $n_3$, while sample 2 permits to measure $n_2$ and $n_z$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Length [mm]</th>
<th>Orientation</th>
<th>Length [mm]</th>
<th>Orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.0</td>
<td>$z$</td>
<td>7.5</td>
<td>$x$</td>
</tr>
<tr>
<td>2</td>
<td>6.0</td>
<td>$z$</td>
<td>4.3</td>
<td>$y$</td>
</tr>
<tr>
<td>3</td>
<td>5.1</td>
<td>$z$</td>
<td>5.7</td>
<td>$x$</td>
</tr>
</tbody>
</table>

The non-parallel surfaces are polished to a flatness of $\lambda/4$ of a He-Ne wavelength over the central region of the surfaces. This region has a diameter ranging from 65% to 90% of the crystals edge and is larger than the diameter of the beams used in the experiment. The resulting error in the apex angle due to imperfect centering of the beam on the crystal is approximately 0.001°.

Experiment

Refractive index measurements were performed at 295 K using the minimum-deviation method. The samples were mounted under a cover and thermally stabilized by a Peltier element to better than ±0.03 K. The refractive indices were measured at 43 different wavelengths between 550 and 2300 nm. In the visible and near IR region (up to 1181 nm) a xenon spectral lamp was used together with a monochromator. The wavelength passband of this assembly was 1 nm. The absolute setting of the wavelength was checked with laser lines at 632.8 nm and 1313.4 nm. It was found to be better than $\Delta \lambda = 0.5$ nm. The wavelengths above 820 nm corresponded to spectral lines of the xenon lamp. Above 1181 nm an optical parametric amplifier (TOPAS, Light Conversion Ltd) pumped by a 150 fs Ti:Sapphire laser (Clark-MXR) was employed. The wavelength bandpass of this system was several tens of nm, but due to lower dispersion and the geometry of the set-up, measurements with good precision were nevertheless possible. Additional measurements were performed at 632.8 nm.
Chapter 2. Refractive indices of Sn$_2$P$_2$S$_6$

with a He-Ne laser, as well as at 1313.4 using a diode pumped YLF laser (ADLAS model DPY 203C, $\Delta \lambda = 0.5$ nm) and at 1565 and 1605 nm with a stabilized diode laser (Santec TSL-220, $\Delta \lambda = 0.005$ nm).

The deflected light was focused on a camera mounted on a rotatable arm controlled by a stepping motor. The rotation stage had a resolution of 0.005 degrees and a positional accuracy of 0.01 degrees. For wavelengths below 950 nm a silicon CCD camera has been used, beyond it a Vidicon camera (Micronviewer 7290A-06E). The cameras were attached to a laser beam analyzer for a precise determination of the position of the peak (more precise than the rotational accuracy). This allowed also the measurement at the central wavelength of the fs-pulse and the accuracy was not limited by its large bandwidth.

The refractive index can be determined by measuring the angle of minimum deviation $\delta$ and the apex angle $\varphi$ of the prism, and using:

$$n = \frac{\sin[(\delta + \varphi)/2]}{\sin(\varphi/2)} \quad (2.3)$$

The accuracy of the refractive index measurements depends on the accuracy of the angular measurements, temperature, wavelength, and of the orientation of the prism-bisecting plane with respect to the crystallographic axes and is given by:

$$\Delta n = \Delta n_{\text{sys}} + \Delta n_{\text{stat}} = \frac{\partial n}{\partial \varphi} \Delta \varphi + \frac{\partial n}{\partial \varphi} \Delta \varphi_z + \sqrt{\left(\frac{\partial n}{\partial \delta} \Delta \delta\right)^2 + \left(\frac{\partial n}{\partial T} \Delta T\right)^2 + \left(\frac{\partial n}{\partial \varphi_{\text{Fl}}} \Delta \varphi_{\text{Fl}}\right)^2} \quad (2.4)$$

The apex angle leads to a systematic error $\Delta n_{\text{sys}}$ of the refractive index. We determined the apex angle using a using a Michelson interferometer in which one mirror was substituted by the prism. The statistical accuracy of the apex measurement was 0.001°, giving a contribution of $\frac{\partial n}{\partial \varphi} \Delta \varphi = 7 \cdot 10^{-5}$ to $\Delta n$. Another systematic error is introduced by the orientational inaccuracy $\phi_z$ of the principal refractive index axes with respect to the prism-bisecting plane. The orientation of the crystal is controlled by x-ray scattering to 3 arcmin, and the process of fabricating the prisms introduces an error of less than 45 arcmin. For the main refractive indices this gives an error $\frac{\partial n}{\partial \phi_z} \Delta \phi_z < 2 \cdot 10^{-5}$. But this error would grow by two orders of magnitude and dominate all others when measuring $n_z$, since $n_z$ is not extremal in this deviation.

To the systematic error the measurement of the angle of minimum deviation adds a statistical error ($\Delta n_{\text{stat}}$) with terms given by the inaccuracy of $\delta$, temperature $T$ and flatness of the surfaces of the prisms expressed by an angle $\varphi_{\text{Fl}}$. The dominant term is due to $\Delta \delta$. Measuring the double minimum deviation angle, $\Delta \delta$ becomes 0.005 degrees and $\frac{\partial n}{\partial \delta} \Delta \delta \approx 1.2 \cdot 10^{-4}$. The error caused by the inaccuracy of the temperature depends on the wavelength and polarization. Values of the temperature dispersion are available only at a few wavelengths in the visible [48] and there $\frac{\partial n}{\partial T} \Delta T$ is between $1.7 \cdot 10^{-5}$ (for $n_2$) and $3.6 \cdot 10^{-5}$ (for $n_1$). The last contribution for the
2.5. Results

The principal refractive indices of Sn\textsubscript{2}P\textsubscript{2}S\textsubscript{6} at 295 K are shown in Fig. 2.4. The largest refractive index \( n_3 \) reaches 3.3 at \( \lambda = 550 \text{ nm} \) close to the absorption edge at 530 nm, while the smallest refractive index \( n_2 \) goes down to 2.69 in the infrared.

The measurements give us the lengths \( n_1, n_2 \) and \( n_3 \) of the principal axes of the indicatrix. As can be seen in Fig. 2.1, the indicatrix is rotated by the angle \( \alpha \) around the \( b \)-axis with respect to the crystallographic axes. Therefore the refractive indices for light polarization along the Cartesian axes \( x, y \) and \( z \) are

\[
\begin{align*}
n_x &= \left( \frac{\sin^2 \alpha}{n_1^2} + \frac{\cos^2 \alpha}{n_3^2} \right)^{-\frac{1}{2}} \\
n_y &= n_2 \\
n_z &= \left( \frac{\cos^2 \alpha}{n_1^2} + \frac{\sin^2 \alpha}{n_3^2} \right)^{-\frac{1}{2}}
\end{align*}
\]  

(2.5)

where \( \alpha \) is the angle between the axis \( x \) and axis 3 (largest refractive index). Table 2.2 displays the refractive indices at room temperature for some selected wavelengths.

The error due to \( \Delta \varphi \) grows with larger refractive index, while the one due to \( \Delta \delta \) diminishes approximately by the same amount, leading to a total error \( \Delta n \) which is approximately constant over the whole wavelength range.

The inaccuracy \( \Delta n_{\text{stat}} \) comes from the imperfect flatness of the prism’s surfaces, so that the apex angle changes if the beam comes away from the centric position. In our experiment \( \frac{dn}{\partial \varphi_{\text{fr}}^{\text{f}}} \Delta \varphi_{\text{fr}} \) ranged from \((1 \ldots 7) \cdot 10^{-5}\) depending on the prism used.

\[\Delta n \approx 2 \cdot 10^{-4}\]

Figure 2.4: Principal refractive indices of Sn\textsubscript{2}P\textsubscript{2}S\textsubscript{6} at \( T = 295 \text{ K} \) in the wavelength range 550…2300 nm. The point signs do not correspond to the error bars \((\Delta n \approx 2 \cdot 10^{-4})\) and for \( n_1 \) and \( n_3 \) (\( \lambda < 1650 \text{ nm} \)) data points from two crystals are displayed. The continuous lines correspond to a two-oscillators Sellmeier model with the parameters given in Table 2.3.
Table 2.2: Refractive indices of Sn$_2$P$_2$S$_6$ at selected wavelengths ($T = 295$ K). The values of $n_x$ and $n_z$ are calculated using eq. (2.5) and the measured values of $n_1$, $n_3$ and $\alpha$.

<table>
<thead>
<tr>
<th>$\lambda$ [$\mu$m]</th>
<th>$n_1$</th>
<th>$n_2$</th>
<th>$n_3$</th>
<th>$n_x$</th>
<th>$n_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5500</td>
<td>3.1682</td>
<td>3.0529</td>
<td>3.2887</td>
<td>3.2341</td>
<td>3.2173</td>
</tr>
<tr>
<td>0.6328</td>
<td>3.0256</td>
<td>2.9309</td>
<td>3.0982</td>
<td>3.0629</td>
<td>3.0588</td>
</tr>
<tr>
<td>0.8080</td>
<td>2.8980</td>
<td>2.8162</td>
<td>2.9438</td>
<td>2.9184</td>
<td>2.9215</td>
</tr>
<tr>
<td>0.8600</td>
<td>2.8774</td>
<td>2.7974</td>
<td>2.9199</td>
<td>2.8957</td>
<td>2.8997</td>
</tr>
<tr>
<td>1.0640</td>
<td>2.8270</td>
<td>2.7511</td>
<td>2.8623</td>
<td>2.8410</td>
<td>2.8469</td>
</tr>
<tr>
<td>1.3134</td>
<td>2.7966</td>
<td>2.7231</td>
<td>2.8282</td>
<td>2.8085</td>
<td>2.8154</td>
</tr>
<tr>
<td>1.5500</td>
<td>2.7808</td>
<td>2.7085</td>
<td>2.8107</td>
<td>2.7918</td>
<td>2.7991</td>
</tr>
<tr>
<td>2.0000</td>
<td>2.7653</td>
<td>2.6941</td>
<td>2.7935</td>
<td>2.7753</td>
<td>2.7831</td>
</tr>
<tr>
<td>2.3000</td>
<td>2.7597</td>
<td>2.6889</td>
<td>2.7873</td>
<td>2.7694</td>
<td>2.7773</td>
</tr>
</tbody>
</table>

The curves of Fig. 2.4 were obtained by using a two-term Sellmeier oscillator model:

$$n^2(\lambda) - 1 = \frac{S_1 \lambda^2}{1 - (\lambda_1/\lambda)^2} + \frac{S_2 \lambda^2}{1 - (\lambda_2/\lambda)^2},$$  \hspace{1cm} (2.6)

$S_1$ and $S_2$ are the Sellmeier oscillator strengths, $\lambda_1$ and $\lambda_2$ represent the oscillator wavelengths, and $E_i = \frac{hc}{\lambda_i}$ are its energies. This model, with four adjustable parameters, represents the experimental data of each crystal to within $2 \cdot 10^{-4}$. Sellmeier expressions with only one oscillator term could not describe the measurements accurately enough. This can be seen graphically in Fig. 2.5 where we plot $n^2(\lambda) - 1$ versus $\lambda^{-2}$ for the same data as in Fig. 2.4. A one-oscillator would show a straight line in this figure. The Sellmeier coefficients for the data in Fig. 2.4 and 2.5 as well as for calculated values of $n_x$ and $n_z$ are given in Table 2.3. The main oscillator has an energy $E_1$ varying between 5.04 and 5.12 eV (242 – 246 nm) depending on the polarization and is 15 – 22 times stronger than the weaker oscillator positioned in the violet region (406 – 431 nm). The oscillator energies observed are in accordance with the band structure of Sn$_2$P$_2$S$_6$ [50, 51]. Note that Sn$_2$P$_2$S$_6$, as most inorganic crystals, obeys to the empirical law of Wemple and DiDomenico [52, 53] that the ratio $E_0/S_0 = (6 \pm 0.5) \cdot 10^{-14}$ eVm$^2$, where $E_0$ and $S_0$ are the oscillator energy and strength in a one-oscillator Sellmeier model.

The optical properties of Sn$_2$P$_2$S$_6$, and to an even greater extent the nonlinear optical properties, depend on the growth conditions and may vary from crystal to crystal. To test the reproducibility of the refractive indices we measured $n_1$ and $n_3$ in two Sn$_2$P$_2$S$_6$ crystals from different bowls (samples nr. 1 and nr. 3). For each crystal and both polarizations the data points lie within a standard deviation $\sigma_{\text{exp}} = 3 \cdot 10^{-4}$ from the corresponding fit. This indicates a good reproducibility even upon a change in polarization. However the refractive indices of sample nr. 3 are approximately $1 \cdot 10^{-3}$ lower than in sample nr. 1, which is more than the error of the measurement. In order to assess the crystal quality, we performed rocking curve [54] measurements on the two crystals. For sample nr. 1 we measured a FWHM of 36 arcsec for the (400) peak and 16 arcsec for the (600) one. Sample nr. 3 had FWHMs of 80 and 90 arcsec,
respectively. This indicates that both samples have a good crystallographic ordering, but crystal nr. 1 is nearer to the perfect crystalline structure. Since the goal is to measure the refractive indices for the perfect Sn$_2$P$_2$S$_6$ structure, and more defects are likely to reduce the refractive indices, we used only the data from sample nr. 1 in this paper. Sample nr. 2, which was used for measuring $n_2$, was cut from the same bowl as sample nr. 1.

2.6 Conclusions

Refractive indices, indicatrix rotation and direction of the optical axes of Sn$_2$P$_2$S$_6$ have been determined at room temperature. It has been shown that the refractive indices

![Figure 2.5: Principal refractive indices of Sn$_2$P$_2$S$_6$ at $T = 295$ K in the wavelength range 550...2300 nm. The coordinate axes are chosen so that a one-oscillator Sellmeier model would appear as a straight line. The continuous lines are from eq. (2.6) using the parameters shown in Table 2.3.](image)

Table 2.3: Sellmeier coefficients for dispersion of the refractive index of Sn$_2$P$_2$S$_6$ at $T = 295$ K. The given values are the fit parameters for calculating the refractive indices with (2.6), while the error is the one of the physical properties.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$S_1$ [$\mu$m$^{-2}$]</th>
<th>$\lambda_1$ [nm]</th>
<th>$E_1$ [eV]</th>
<th>$S_2$ [$\mu$m$^{-2}$]</th>
<th>$\lambda_2$ [nm]</th>
<th>$E_2$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_1$</td>
<td>93.15 ± 1</td>
<td>251.6 ± 4</td>
<td>4.93 ± 0.08</td>
<td>3.41 ± 1</td>
<td>427.7 ± 7</td>
<td>2.90 ± 0.05</td>
</tr>
<tr>
<td>$n_2$</td>
<td>90.52 ± 1</td>
<td>245.9 ± 6</td>
<td>5.04 ± 0.12</td>
<td>4.06 ± 1</td>
<td>406.5 ± 10</td>
<td>3.05 ± 0.07</td>
</tr>
<tr>
<td>$n_3$</td>
<td>91.51 ± 1</td>
<td>250.4 ± 4</td>
<td>4.95 ± 0.08</td>
<td>4.77 ± 1</td>
<td>440.2 ± 7</td>
<td>2.82 ± 0.05</td>
</tr>
<tr>
<td>$n_x$</td>
<td>94.12 ± 2</td>
<td>242.6 ± 7</td>
<td>5.11 ± 0.14</td>
<td>5.68 ± 1</td>
<td>426.2 ± 9</td>
<td>2.91 ± 0.06</td>
</tr>
<tr>
<td>$n_z$</td>
<td>96.53 ± 2</td>
<td>241.9 ± 7</td>
<td>5.13 ± 0.14</td>
<td>5.45 ± 1</td>
<td>421.6 ± 9</td>
<td>2.94 ± 0.06</td>
</tr>
</tbody>
</table>
can be well described by a two oscillator Sellmeier equation with a strong UV oscillator 
($\lambda_1 = 242 - 252$ nm) and a weaker oscillator in the violet ($\lambda_2 = 406 - 440$ nm). 
At 300 K and $\lambda = 550$ nm the major axis of the indicatrix is oriented at an angle 
$\alpha = 40.2 \pm 0.4^\circ$ off the $x$-axis towards the $z$-axis. This deviation increases with 
longer wavelengths, reaching an extrapolated angle of $53.5^\circ$ at infinite wavelength.
Chapter 3

Electro-optical properties of Sn$_2$P$_2$S$_6$

The electro-optical properties of monoclinic Sn$_2$P$_2$S$_6$ single crystals are measured by direct interferometric technique for electric fields applied parallel to the crystallographic x-axis that lies near the spontaneous polarization vector. The room temperature free electro-optical coefficient $r_{111}^T$ reaches $174 \pm 10$ pm/V at $\lambda = 633$ nm and shows only weak dispersion in the wavelength range between $\lambda \approx 0.6 \ldots 1.3$ $\mu$m. Corresponding values of $r_{221}^T$ and $r_{331}^T$ at $\lambda = 633$ nm are $92 \pm 8$ pm/V and $140 \pm 18$ pm/V, respectively. The temperature dependence of the electro-optical coefficients near the structural phase transition at $T_C = 65^\circ$C is well described by a Curie-Weiss law with a peak value $r_{111}^T \approx 4500$ pm/V. The ratio between the free and clamped electro-optical coefficients is determined at the wavelength $\lambda = 633$ nm by applying a fast pulsed electric field instead of an AC field and measuring the temporal evolution of the electrically induced refractive index change. The values are $r_{111}^S/r_{111}^T = 0.30 \pm 0.02$, $r_{221}^S/r_{221}^T = 0.12 \pm 0.02$ and $r_{331}^S/r_{331}^T = 0.30 \pm 0.09$.

3.1 Introduction

Tin thiohypodiphosphate (Sn$_2$P$_2$S$_6$) is a wide bandgap semiconductor ferroelectric with interesting nonlinear optical properties [43] and wide optical transparency range extending from $\lambda = 0.53$ $\mu$m to $\lambda = 8$ $\mu$m [36]. In addition it is also photorefractive with fast photorefractive grating recording times and large refractive index change in the red and near infrared spectral region [21][23], opening interesting possibilities for applications in connection with laser diode sources.

For electro-optics or photorefractive applications the knowledge of the electro-optical properties is of fundamental importance. Unfortunately, to date individual components of the electro-optical (EO) tensor of Sn$_2$P$_2$S$_6$ are still unknown. Presently available data on electro-optical properties are restricted to estimations based on the spontaneous electro-optical effect induced by the spontaneous polarization [48], to measurements of the field-induced birefringence giving values for some mixed coefficients [55] and to effective values indirectly estimated from photorefractive beam-

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1This chapter has been published in Optics Communications 215(4-6), 333-43 (2003) [44], with some minor changes that are described in footnotes in this chapter.
coupling experiments \cite{21,23,56,57,58}.

In the present work we report on the direct determination of the most important electro-optical tensor components of Sn$_2$P$_2$S$_6$, i.e. those for applied electric fields oriented parallel to the crystallographic $x$-axis, that is nearly parallel to the spontaneous polarization. A standard interferometric set-up with AC applied fields was used \cite{59,60,61}. Measurements are performed in the wavelength range between 594 and 1313 nm at room temperature as well as in the temperature range between room temperature and the phase transition for $\lambda = 633$ nm. Finally, the ratios of clamped to free electro-optical coefficients were determined by applying fast rising electric pulses to the crystal using the method described earlier in Ref. \cite{62}. The large values of the electro-optical coefficients determined here (up to 174 pm/V at room temperature and 4510 pm/V near the phase transition temperature of 65°C for $\lambda = 633$ nm) and its weak dispersion towards the infrared confirm that this material seems attractive for electro-optical or photorefractive applications at red and infrared wavelengths.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{structure.png}
\caption{Structure of Sn$_2$P$_2$S$_6$. The symmetry plane is parallel to the plane of the figure. The unit cell is indicated by the dashed lines.}
\end{figure}

### 3.2 Crystallographic and optical properties

Sn$_2$P$_2$S$_6$ is a proper ferroelectric with monoclinic point group symmetry $m$ at room temperature. The crystal undergoes a second-order phase transition to the centrosymmetric paraelectric phase (point group $2/m$) at the temperature $T_C = 338$ K \cite{25}. For the unit cell chosen by Dittmar and Schäfer \cite{26} which we refer to in this work, the lattice parameters are $a = 0.9378$ nm, $b = 0.7448$ nm, $c = 0.6513$ nm, and $\beta = 91.15^\circ$. We choose the right-handed coordinate system which is shown in Fig. 3.1 together with the crystallographic axes. In accordance to the IEEE standard on piezoelectric materials \cite{30}, the $z$-axis is defined parallel to the [001] crystallographic direction.
3.2. Crystallographic and optical properties

(c-axis), while the y-axis is normal to the symmetry plane and corresponds to the crystallographic b-axis. Finally, the x-axis is chosen perpendicular to y and z and deviates by 1.15° from the [100] direction and by approximately 13 degrees from the spontaneous polarization vector $P_S$ [38,63]. Also according to the IEEE standard [30], the positive direction of the x-axis and the z-axis is set so that the piezoelectric constants $d_{111}$ and $d_{333}$ are positive and $+y$ is chosen so that $xyz$ is a right-handed system. In this system $P_S \cdot \hat{x} > 0$ and $P_S \cdot \hat{z} < 0$, where $\hat{x}$ and $\hat{z}$ are the unit vectors in x and z-direction. Note that the coordinate system used here corresponds up to a rotation of 1.15° about y to the coordinate system used in most of the previous investigations of electro-optical, nonlinear optical and photorefractive properties. Alternative choices for the coordinate system may be related to the main axes of the low-frequency dielectric tensor or of the optical indicatrix, the latter choice was used for instance in Ref. [48]. We prefer the use of the coordinate system described above because the crystallographic axes do not suffer from the variations in the orientation of the dielectric tensor and of the optical indicatrix observed by varying temperature, frequency of the electric field, or light wavelength [48].

The linear optical properties of SPS were first reported in Ref. [48] where on the basis of the available data on the temperature variations of the refractive indices, dielectric constant and spontaneous polarization $P_S$, the "spontaneous" linear EO coefficients in the ferroelectric phase as well as the quadratic (Kerr) polarization-optical constants in the paraelectric phase have been evaluated. Precise refractive index data is reported in chapter 2 of this thesis (page 28) and in the corresponding article [32].

\[ \text{\footnotesize The paper publishing the content of this chapter has been written before the detailed analysis of refractive indices and orientation of the axes described in chapter 2. Therefore in that paper [44] the historical coordinate system is used, with } a \parallel x \text{ instead of } c \parallel z, \text{ thus being rotated by } 1.15° \text{ about } y \text{ towards the IEEE standard system used here.} \]

\[ \text{\footnotesize In paper [44] there is a section analysing the refractive index data from Ref. [47] using a single} \]

---

Figure 3.2: Position of spontaneous polarization and indicatrix in the xz-plane at room temperature.
3.3 Electro-optical effect

The third-rank electro-optical tensor for materials of monoclinic point group $m$ contains 10 independent components. In our coordinate system $(x, y, z) = (1,2,3)$ it has the form

$$r_{ijk} = \begin{pmatrix}
    r_{111} & 0 & r_{113} \\
    r_{221} & 0 & r_{223} \\
    r_{331} & 0 & r_{333} \\
    0 & r_{322} & 0 \\
    r_{131} & 0 & r_{133} \\
    0 & r_{122} & 0
\end{pmatrix}$$

(3.1)

with the inherent symmetry ($r_{ijk} = r_{jik}$). The inverse dielectric tensor at optical frequency is

$$\left(\frac{1}{n^2}\right)_{ij} = \begin{pmatrix}
    \frac{1}{n_{11}^2} & \frac{1}{n_{13}^2} \\
    \frac{1}{n_{13}^2} & \frac{1}{n_{33}^2}
\end{pmatrix}$$

(3.2)

with the outer-diagonal terms $\frac{1}{n_{13}^2}$ being responsible for the rotation of the main axes of the indicatrix with respect to the crystallographic axes. After applying an electric field $E = (E, 0, 0)$ along the $x$-axis the change of this tensor is expressed as

$$\Delta \left(\frac{1}{n^2}\right)_{ij} = r_{ijk}E_k = \begin{pmatrix}
    r_{111}E & 0 & r_{131}E \\
    0 & r_{221}E & 0 \\
    r_{131}E & 0 & r_{331}E
\end{pmatrix},$$

(3.3)

where Einstein’s summation convention over equal indices is used. In the measurements described below we have used only input light polarizations that correspond to an eigen-polarization in the sample, leading only to a phase modulation of the signal beam. The corresponding change of the main axes of the indicatrix is then $\Delta \left(\frac{1}{n^2}\right) = \Delta \left(\frac{1}{n_{ij}^2}\right) d_i d_j$. Here $\mathbf{d}$ is the unit vector along the polarization direction. By choosing appropriate geometries individual elements or linear combinations of the four independent electro-optical coefficients $r_{111}, r_{221}, r_{331}, r_{131}$ can be determined.

3.4 Samples

Optical quality $\text{Sn}_2\text{P}_2\text{S}_6$ single crystals were produced by the conventional vapor-transport technique using iodine as a transporter. We used nominally pure samples exhibiting low photorefractive effects. Samples with dimensions $5.21 \times 7.58 \times 5.83$ mm$^3$, $5.44 \times 5.72 \times 2.79$ mm$^3$ and $5.07 \times 5.38 \times 4.85$ mm$^3$ along $x$, $y$ and $z$ axes respectively were polished, and electrically poled by heating above $T_C$ and slowly cooling them down to room temperature under an electric field of about $1$ kV/cm applied along the $x$-direction. Gold evaporated electrodes were used for poling and oscillator Sellmeier model. This section has been taken out since more precise refractive index data is available in chapter 2. The results presented in this chapter are calculated with the old refractive indices, but the change when using the new ones is negligible.

$^\dagger$Note that here refractive index $n$ is in the Cartesian system corresponding to the crystallographic axes. Therefore $n_{11}$ is $n_x$ and not to be confused with the principal refractive index $n_1$. 
3.5 Experiments

for inducing the refractive index changes by the electric field. The single domain state was controlled using light scattering by domain walls in Sn$_2$P$_2$S$_6$ described in [64]. This method permits an easy visualization of polydomain areas within the sample.

3.5 Experiments

Unclamped electro-optical coefficients

In our study the linear EO coefficients were measured using a standard Michelson interferometer [59,60,61]. This method allows the determination of the individual components of the EO tensor including their sign. The experimental set-up was similar to the one used in [59,60] and is shown in Fig. 3.3. The typical value for the applied electric field amplitude was $E \cong 3 \text{ V/cm}$. For the investigation of the wavelength dependence of the tensor components $r_{111}$ and $r_{221}$ the measurements were carried out at six different light wavelengths: 594 and 633 nm (He-Ne laser), 817 and 877 nm (Ti:Sapphire laser), 1064 nm (Nd:YAG laser) and 1313 nm (Nd:YLF laser). The studied Sn$_2$P$_2$S$_6$ samples were mounted free in one arm of the interferometer, and the light intensity in the output interference picture was measured by a photodetector. When an electric field $E = (E, 0, 0)$ is applied to the sample the induced phase shift between the interfering beams is

$$
\Delta \phi = \frac{2\pi}{\lambda} L \Delta n + \frac{2\pi}{\lambda} (n - 1) \Delta L
$$

(3.4)

$$
= -\frac{\pi}{\lambda} L n^3 r_{\text{eff}} E + \frac{2\pi}{\lambda} L (n - 1) d_{\text{eff}} E
$$

(3.5)

where $L$ is the length of the path in the crystal (twice the length of the crystal), $n$ is the refractive index seen by the eigenwave, $r_{\text{eff}}$ is the effective electro-optical coefficient, which is either equal to one of the coefficients appearing in (3.3) or to a linear combination of them and $d_{\text{eff}}$ is the effective piezoelectric coefficient. The second term on the right-hand-side of (3.5) is due to the piezoelectric length change of the crystal and was evaluated using the known piezoelectric constants of the crystal [38]. This piezoelectric effect represents a relatively small correction to the electro-optical coefficients measured (about 3% for $r_{111}$, 8% for $r_{221}$ and 10% for $r_{331}$).

If the applied field is a weak modulated sine-wave signal with frequency $\Omega$ ($V = E \cdot d \ll V_\pi$ where $V_\pi = \frac{\lambda}{L n^3 r_{\text{eff}}}$), the measured intensity at the interferometer output is of the form

$$
I = I_1 + I_2 - 2\sqrt{I_1 I_2} \frac{2\pi}{\lambda} L \left(n^3 r_{\text{eff}} - 2(n - 1)d_{\text{eff}}\right) E \sin(2\pi \Omega t).
$$

(3.6)

where $I_1$ and $I_2$ are the intensities of the beams in the two arms of the interferometer. In our measurements the working point was adjusted by means of the external piezoelectrically movable mirror in Fig. 3.3 and the amplitude of the modulated signal in (3.6) was determined using a lock-in amplifier. Finally the value of the effective electro-optical coefficients $r_{\text{eff}}$ were determined by using (3.5) and (3.6). Note that for the measurements of the temperature dependence the set-up in Fig. 3.3 was slightly modified by placing the Sn$_2$P$_2$S$_6$ crystal inside an oven allowing to change the sample temperature above the phase transition at 65 °C.
At low frequencies of the applied field ($\Omega < 500$ Hz) we found that significant photoconductive screening of the applied field occurs already for intensities of the optical beam in the order of $100 \mu$W/cm$^2$ ($\lambda = 633$ nm). This would lead to reduced values of the measured electro-optical coefficient. This effect disappears if the electric field frequency is increased to $\Omega \approx 1$ kHz. Therefore all the measurements were performed at the low intensity described above and at $\Omega \approx 1$ kHz. For the measurements of the electro-optical coefficients $r_{ij}$ the electric field has to be applied parallel to the $x$-axis, which is close to the spontaneous polarization. Since the dielectric constant is maximal parallel to the spontaneous polarization, we expect the largest EO tensor elements in this configuration.

The coefficients $r_{111}$ and $r_{221}$ were measured with a beam propagation vector along $z$-axis and polarization along the $x$-axis and the $y$-axis, respectively. The other two coefficients $r_{331}$ and $r_{131}$ were calculated from two measurements with beam propagation along the $y$-axis and polarizations $\alpha$ and $\alpha + \frac{\pi}{2}$ off the $x$-axis, the two eigenpolarizations in this geometry. From the measurement of $r_\alpha$, $r_\alpha + \frac{\pi}{2}$ we obtain

$$r_{331} = r_\alpha + r_\alpha + \frac{\pi}{2} - r_{111}$$
$$r_{131} = \frac{r_\alpha \cos^2 \alpha - r_\alpha + \frac{\pi}{2} \sin^2 \alpha - r_{111} \cos 2\alpha}{\sin 2\alpha}$$

by rotating the coordinate system by an angle $\alpha$ about the $y$-axis, where $r_\alpha$ and $r_\alpha + \frac{\pi}{2}$ are the measured effective coefficients. Since $r_{331}$ and $r_{131}$ are obtained by summing and subtracting the results of different measurements, the relative errors of their values are larger than those of $r_{111}$ and $r_{221}$.

The values of the measured electro-optical coefficients at $\lambda = 633$ nm and room temperature are given in Table 3.1. The values are the average of measurements on two crystals (three crystals for $r_{111}$ and $r_{221}$) and three different positions per crystal. The dispersion of the values from different positions and crystals is generally within the experimental error given in Table 3.1. This table shows that Sn$_2$P$_2$S$_6$ possesses
3.5. Experiments

Table 3.1: Electro-optical coefficients of Sn$_2$P$_2$S$_6$ at $\lambda = 633$ nm and room temperature.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>unclamped EO coefficients [pm/V]</td>
<td></td>
</tr>
<tr>
<td>$r_{111}^T$</td>
<td>$+174 \pm 10$</td>
</tr>
<tr>
<td>$r_{221}^T$</td>
<td>$+92 \pm 8$</td>
</tr>
<tr>
<td>$r_{331}^T$</td>
<td>$+140 \pm 18$</td>
</tr>
<tr>
<td>$r_{131}^T$</td>
<td>$-25 \pm 15$</td>
</tr>
<tr>
<td>clamped EO coefficients [pm/V]</td>
<td></td>
</tr>
<tr>
<td>$r_{111}^S$</td>
<td>$+50 \pm 5$</td>
</tr>
<tr>
<td>$r_{221}^S$</td>
<td>$+11 \pm 3$</td>
</tr>
<tr>
<td>$r_{331}^S$</td>
<td>$+42 \pm 10$</td>
</tr>
<tr>
<td>$r_{131}^S$</td>
<td>$-11 \pm 8$</td>
</tr>
<tr>
<td>ratio $r^S/r^T$</td>
<td></td>
</tr>
<tr>
<td>$r_{111}^S/r_{111}^T$</td>
<td>$0.30 \pm 0.02$</td>
</tr>
<tr>
<td>$r_{221}^S/r_{221}^T$</td>
<td>$0.12 \pm 0.02$</td>
</tr>
<tr>
<td>$r_{331}^S/r_{331}^T$</td>
<td>$0.30 \pm 0.09$</td>
</tr>
</tbody>
</table>

very large electro-optical coefficients $r_{111}$ and $r_{331}$, confirming the suitability of this crystal for electro-optical and photorefractive applications. The reduced half-wave voltage $V_{\pi} = \frac{\lambda}{n^2 r}$ of Sn$_2$P$_2$S$_6$ is very low compared to other materials, since both $n$ and $r$ are large. For $\lambda = 633$ nm and $r_{111}^T$ the reduced half-wave voltage is $V_{\pi} = 124$ V. As a comparison, for the standard material LiNbO$_3$ is $V_{\pi} = \frac{\lambda}{n^2 r_{333}} = 1885$ V.

The wavelength dependence of $r_{111}$ and $r_{221}$ at room temperature is shown in Fig. 3.4 and 3.5. The experimental values are compared with the results of a one oscillator model which uses polarization potentials $\frac{dE_0}{dP}$ (change of the oscillator energy $E_0 = \frac{hc}{\lambda_0}$ with crystal polarization) and dispersion constants

$$K = -\frac{\partial (S_0 \lambda_0)}{S_0 \partial \lambda}$$

as parameters $^5$, $^6$.

$$r = \epsilon_0 (\epsilon - 1)(1 - \frac{1}{n^2})^2 \frac{dE_0}{dP} \frac{1}{S_0 hc \lambda_0} \left( (1 - K) + (1 + K) \frac{\lambda_0^2}{\lambda^2} \right). \quad (3.9)$$

In (3.9) $\epsilon_0$ is the dielectric permittivity of vacuum, $S_0$ and $\lambda_0$ are the oscillator strength and wavelength of a single-oscillator Sellmeier model and $K$ describes the change of the interband oscillator strength induced by polarization changes. Eq. (3.9) is derived from the so called polarization potential model, which assumes a “sensible” parametrization of the linear susceptibility followed by differentiation with respect to the applied crystal polarization.

In paper $^4$ the values of the one-oscillator Sellmeier coeff-

<table>
<thead>
<tr>
<th>$n_i$</th>
<th>$S_0 / \mu m^{-2}$</th>
<th>$\lambda_0$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_1$</td>
<td>$76 \pm 4$</td>
<td>$292 \pm 7$</td>
</tr>
<tr>
<td>$n_2$</td>
<td>$75 \pm 5$</td>
<td>$284 \pm 5$</td>
</tr>
<tr>
<td>$n_3$</td>
<td>$68 \pm 3$</td>
<td>$313 \pm 6$</td>
</tr>
</tbody>
</table>

§ In paper $^4$ the values of the one-oscillator Sellmeier coef-

§ coficients were given in a table in section 3.2. The values for the three principal refractive indices reported there are:
Chapter 3. Electro-optical properties of Sn$_2$P$_2$S$_6$

Figure 3.4: Dispersion of $r_{111}^T$ at room temperature. The theoretical curve is given by Eq. (3.9) and the parameters reported in the text.

Figure 3.5: Dispersion of $r_{221}^T$ at room temperature. The theoretical curve is given by Eq. (3.9) and the parameters reported in the text.
3.5. Experiments

As can be seen in Fig. 3.4 and 3.5 the dispersion of $r_{111}$ and $r_{221}$ is small, with electro-optical coefficients at $\lambda = 1313 \text{ nm}$ nearly as large as in the red. Note however, that the absorption is smaller in the infrared region, which would benefit electro-optical devices operating at these wavelengths. With $\epsilon_{11} = 230$ we can determine $\frac{dE_0}{dP} = (1.6 \pm 0.4) \times 10^{-19} \text{ Vm}^2$ and $K = -0.4 \pm 0.4$. For $r_{111}$, while for $r_{221}$ they are $\frac{dE_0}{dP} = (1.6 \pm 0.4) \times 10^{-19} \text{ Vm}^2$ and $K = -0.4 \pm 0.4$.

![Figure 3.6: Temperature dependence of $r_{111}^T$ ($T < T_C$) and $R_{1111}^T$ ($T > T_C$, grey region) at $\lambda = 633 \text{ nm}$. The theoretical line is according to (3.10) and (3.13) with the parameters $T_C = 64.4 \degree\text{ C}$ and $AC\epsilon_0 g = 1863 \sqrt{\degree\text{ C pm/V}}$ for the ferroelectric phase, and $T_C = 64.4 \degree\text{ C}$ and $\epsilon_0 D^2 g = 57.2 \times 10^{-15} \text{ C}^2\text{m}^2/\text{V}^2$ for the paraelectric phase. The inset shows the same data near the phase transition temperature, in the same y-scale.](image)

The temperature dependence of $r_{111}$ and $r_{221}$ for $T < T_C$ is shown in Fig. 3.6 and 3.8. As expected, the electro-optical coefficients grow according to mean field theory of second order phase transitions with a Curie-Weiss law $\epsilon = \frac{C}{2(T_C - T)}$ and $P_S = A(T_C - T)^{\frac{1}{2}}$. Therefore the electro-optical coefficients are

$$r \approx 2\epsilon_0(\epsilon - 1)gP_S$$

$$\approx AC\epsilon_0 g(T_C - T)^{-\frac{1}{2}}$$

(3.10)

where $C$ is the Curie constant, $A$ is a material constant that can be fitted from the temperature dependence of $P_S$ and $g$ is a suitable quadratic polarization-optic coefficient. The full line in Fig. 3.6 and 3.8 is according to (3.10). In Fig. 3.7 and 3.9 $r_{111}^{-2}$ and $r_{221}^{-2}$ are shown as a function of temperature. In proximity of $T_C$ ($T_C - T \ll 10 \degree\text{ C}$), $r^{-2}$ depends linearly on $T_C - T$.

Above $T_C$ the crystal is in the paraelectric phase and the linear EO tensor $r$ vanishes due to the centrosymmetric structure. The quadratic EO tensor $R$ is then the lowest order electro-optical tensor. Superposing a DC electric field $E_{dc} = (E_{dc}, 0, 0)$
Figure 3.7: Same curve as in Fig. 3.6 but in inverse square scale for $r_{111}$ below $T_C$ and inverse square root scale for $R_{1111}$ above $T_C$.

Figure 3.8: Temperature dependence of $r_{221}^T$ ($T < T_C$) and $R_{2211}^T$ ($T > T_C$, grey region) at $\lambda = 633$ nm. The line is a fit according to (3.10) and (3.13) with the fitted parameters $T_C = 64.8^\circ C$ and $AC\epsilon_0g = 808.5 \, \sqrt{\circ C} \, \text{pm/V}$ for the ferroelectric phase, and $T_C = 64.3^\circ C$ and $\epsilon_0D^2g = 28.8 \cdot 10^{-15} \, \circ C^2 \, \text{m}^2/\text{V}^2$ for the paraelectric phase. The inset shows the same data near the phase transition temperature, in the same $y$-scale.
3.5. Experiments

The sinusoidal signal field allows to measure a first order effect of $R$:

$$\Delta \left( \frac{1}{n^2} \right)_{ij} = R_{ijkl} E_k E_l$$

$$= R_{ij11} (E_{dc} + E_0 \sin(\Omega t))^2$$

$$= (R_{ij11} E_{dc}) E_{dc} + 2(R_{ij11} E_{dc}) E_0 \sin(\Omega t) +$$

$$+ (R_{ij11} E_0) E_0 \sin^2(\Omega t) + \cdots$$

(3.11)

The first term in (3.11) does not depend on the modulation field so that it generates only a static deformation of the indicatrix. The second term describes a change in the indicatrix linear to the applied signal field so that this term is detected in the lock-in at the frequency $\Omega$ as an equivalent linear EO tensor

$$r_{ij}^\Omega = 2R_{ij11} E_{dc}.$$ 

(3.12)

The third term describes the pure quadratic electro-optical effect. In our measurements at temperatures above $T_C$ the applied bias field was $E_{dc} = 20 \text{ V/cm}$.

Above the critical point $T_C$ the temperature dependence of the quadratic EO coefficient can be approximately described by the function

$$R \simeq \epsilon_0^2 (\epsilon - 1)^2 g$$

$$\simeq \epsilon_0^2 \frac{D^2}{(T - T_C)^2} g.$$ 

(3.13)

$D$ is a modified Curie constant and $g$ is a suitable quadratic polarization-optic coefficient. The constants $\epsilon_0^2 D^2 g$ for $R_{1111}$ and $R_{2211}$ are given in Fig. 3.6 and 3.8 respectively. Fig. 3.7 shows $R_{1111}$ in inverse square root scale showing the linear relationship of $R^{-1/2}$ versus $(T - T_C)$. The similar curve for $R_{2211}$ is shown in Fig. 3.9.
Clamped electro-optical coefficients

Recently we have introduced a new method for determining the ratio $r^S/r^T$ between the clamped and unclamped (free) electro-optical coefficients. This method is based on applying a fast electric field pulse to the crystal instead of an AC field and considering the time dependence of the field-induced refractive index change. This allows to separate the fast (clamped) part $r^S$ of the electro-optical tensor from the slower contribution due to acoustic phonons. The instantaneous intensity change upon applying the voltage pulse (step in Fig. 3.10) is proportional to $r^S$, while the stationary value is proportional to $r^T$. With the acoustic contribution to $r^T$ also a mechanical ringing of the crystal appears, induced by the piezoelectric effect.

![Graph](image.png)

Figure 3.10: Measurement of ratio $r^S/r^T$: a sharp square electric field pulse starts at $t = 0$ s and lasts 10 ms. $r^S/r^T$ is given by the ratio of the height of the step at $t = 0$ s ($\sim r^S$, inset) and the extrapolated signal at $t = 0$ s ($\sim r^T$), which is scaled to unity in this figure. The oscillations are due to resonant mechanical oscillations with frequencies $\nu_1 = 255 \text{ kHz}$ and $\nu_2 = 382 \text{ kHz}$ and the exponential decay of the signal is due to screening of the electric field in the illuminated region.

The same interferometric set-up as above was used (Fig. 3.3), but the sine wave generator was replaced by a pulse generator (Tabor 8201) to create square pulses with rise time shorter than 12 ns. The typical pulse voltage amplitude for an approximately cubic crystal of side length $\approx 0.5$ cm was 1 V. The output signal of the interferometer was detected by a fast photodiode attached directly to an oscilloscope and averaged over 140 pulses. For these measurements a larger light intensity of the order of 100 mW/cm$^2$ had to be used. Even though nominally pure crystals were used, the large photoconductivity of Sn$_2$P$_2$S$_6$ crystals at $\lambda = 633$ nm leads to a strong screening of the applied field already before the end of the pulse. Therefore, the unclamped contribution to the signal has to be found by extrapolating the signal curve to the beginning of the pulse. This can be done because the build-up time of the screening
is much longer than the response time of the acoustic electro-optical contribution.

The oscillations in Fig. 3.10 are given by resonant mechanical modes of the crystal and are fitted with $\nu_1 = 255$ kHz and $\nu_2 = 382$ kHz. The same crystal was analyzed using an impedance spectrometer, which permits to roughly calculate its dielectric function through its capacitance. Among the many resonances of $\epsilon_{11}(\omega)$, resonances at $\nu_1$ and $\nu_2$ were clearly visible.

The measured ratios $r^S/r^T$ and the clamped electro-optical coefficients $r^S$ are shown in Table 3.1. The dominant part of $r^T$ is given by the contribution from acoustic phonons, a combination of the piezoelectric and the elasto-optic effect, and the anisotropy in the $y$-direction is more pronounced for the electro-optical coefficient $r^S$ than for the acoustic contribution to $r$.

3.6 Discussion

Direct measurement of the electro-optical effect was reported earlier by Kroupa et al. in [55] by measuring the birefringence for the longitudinal geometry, where both the light beam propagation and the applied electric field are directed along the $x$-direction. Only an effective value of the electro-optical coefficient of the type $r_a = r_{331} - \left(\frac{n_z}{n_x}\right)^3 r_{221}$ can be obtained in this geometry, with $n_z$ being the refractive index for light polarization parallel to the $z$-axis. We obtain the value $r_a = 62 \pm 20$ pm/V based on Table 3.1. This is slightly higher than the approximated value of 51 pm/V that can be extrapolated to room temperature from the data in [55].

In order to get an additional confirmation for our data, we also performed experiments using the same type of setup as in [55], but with the light propagating along the $z$-direction and field along the $x$-direction. The effective coefficient in this configuration is $r_c = r_{111} - \left(\frac{n_z}{n_x}\right)^3 r_{221} = 100 \pm 5$ pm/V. This agrees well with the value $r_c = 96 \pm 13$ pm/V calculated from the electro-optical coefficients $r_{111}$ and $r_{221}$ measured interferometrically (Table 3.1).

The electro-optical coefficients measured in this work are also higher than the ones estimated by using light diffraction from photorefractive gratings, $r^\text{PR}_{111} \approx 130$ pm/V at $\lambda = 900$ nm [57] and $r^\text{PR}_{111} \approx 37 - 53$ pm/V at $\lambda = 1064$ nm [21]. This is expected due to the partial clamping of the piezo-elasto-optical contributions to the electro-optical effect that occur with a spatially modulated field [12] and possible electron-hole competition [65,66] or other effects reducing the apparent electro-optical coefficient in photorefractive measurements [67].

Note also, that the ratio $r^T_{221}/r^T_{111} = 0.54 \pm 0.04$ pm/V at $\lambda = 1064$ nm is higher than $r^\text{PR}_{221}/r^\text{PR}_{111} = 0.38 \pm 0.02$ measured by Hellwig et al. at the same wavelength, while $r^\text{PR}_{221}/r^\text{PR}_{331} = 0.66 \pm 0.10$ pm/V at $\lambda = 633$ nm compares well to $r^\text{PR}_{221}/r^\text{PR}_{331} = 0.59$ at $\lambda = 1064$ nm [58]. Also here the discrepancy between our ratios and those obtained by photorefractive investigations might be attributed to the same reasons.

The polarization-optic coefficients $f_{ijm}$ that relate the change of the optical indicatrix with the crystal polarization $P$ as $\Delta (1/n^2)_{ij} = f_{ijm}P_m$ are often regarded as more fundamental constants since they show much smaller variations from material to material than the electro-optical coefficients. The electro-optical coefficients $r_{ijk}$ are related to $f_{ijm}$ by the expression $r_{ijk} = \epsilon_0 f_{ijm} (\epsilon_{mk} - \delta_{mk})$, where $\delta_{mk}$ is the
Kronecker’s delta. For the elements $r_{ij}$ in point group $m$ this expression reduces to

$$r_{ij} = \epsilon_0 f_{ij} (\epsilon_{11} - 1) + \epsilon_0 f_{ij3} \epsilon_{13},$$

(3.14)

for $ij = 11, 22, 33$ and $13=31$. The dielectric tensor in Sn$_2$P$_2$S$_6$ is rotated by only about 13 degrees with respect to the crystallographic $x$-axis and the ratio between $\epsilon_{11}$, which is the largest element of the dielectric tensor, and the outer diagonal element $\epsilon_{13}$ is $\epsilon_{11}/\epsilon_{13} \approx 6$. It is therefore reasonable to assume that the main contribution to the elements $r_{ij}$ in Eq. (3.14) comes from the first term on the right-hand side. By neglecting the second term one obtains a rough estimation for the polarization-optic coefficients of the form $f_{ij} \approx r_{ij}/(\epsilon_0 \epsilon_{11})$. Using $\epsilon_{11} \approx 230$ and the values shown in Table 3.1 one obtains $f_{111} \approx 0.089$ m$^2$/C, $f_{221} \approx 0.046$ m$^2$/C, $f_{331} \approx 0.072$ m$^2$/C and $f_{131} = f_{311} \approx 0.012$ m$^2$/C. These values are of the same order of magnitude as the polarization-optic coefficients observed in several inorganic oxide crystals such as KNbO$_3$ or BaTiO$_3$ [68]. This indicates that the main reason for the observed high electro-optical coefficients of Sn$_2$P$_2$S$_6$ is the large dielectric constant.

It is possible to estimate the quadratic polarization-optic coefficients $g_{ijkl}$ of the upper paraelectric phase from the electro-optical coefficients $r_{ijk}$. From crystal optic measurements Grabar et al. [48] determined four elements of the quadratic polarization-optic tensor in the coordinate system corresponding to the main axes of the indicatrix. By transforming their values to the coordinate system used in this work one obtains:

- $g_{1111} \approx 0.256$ m$^4$/C$^2$
- $g_{2211} \approx 0.13$ m$^4$/C$^2$
- $g_{3311} \approx 0.154$ m$^4$/C$^2$
- $g_{1311} \approx -0.035$ m$^4$/C$^2$.

(3.15)

It has been generally assumed [52, 53] that the quadratic polarization-optic coefficients $g_{ijkl}$ do not depend on temperature (at least not in first approximation). Therefore in ferroelectric materials the linear electro-optical effect is regarded as the same quadratic effect of the centrosymmetric high temperature phase biased by the spontaneous polarization $P_S$. That is

$$\Delta \left( \frac{1}{n^2} \right)_{ij} = g_{ijkl} P_k P_l$$

(3.16)

with polarization $\mathbf{P} = P_S + \mathbf{P}_{\text{nd}}$ and $\mathbf{P}_{\text{nd}} = \epsilon_0 (\epsilon - \delta) \mathbf{E}$. In Sn$_2$P$_2$S$_6$ one has $P_S = (P_S \cos \gamma, 0, P_S \sin \gamma)$ with $P_S \approx 14$ µC/cm$^2$ and $\gamma \approx 13^\circ$ at room temperature. Combining (3.3) with (3.16) one gets

$$r_{ijk} = 2\epsilon_0 (\epsilon_{mk} - \delta_{mk}) g_{ijkl} P_{S1}.$$

(3.17)

It follows that

$$r_{ij1} = 2\epsilon_0 (\epsilon_{11} - 1) g_{ij11} P_S \cos \gamma + 2\epsilon_0 \epsilon_{31} g_{ij13} P_S \cos \gamma + 2\epsilon_0 (\epsilon_{11} - 1) g_{j133} P_S \sin \gamma + 2\epsilon_0 \epsilon_{31} g_{j133} P_S \sin \gamma$$

(3.18)

---

Note that the left-hand scale of Fig. 2 in Ref. [48] has to be reduced by a factor 10, consequently the last equation of page 2088 in [48] should read $(M_{S1} + M_{S3} + M_{S5})/2 = 5.01 \cdot 10^{-2}$ m$^4$/C$^2$ in that reference.
3.7. Conclusions

with \( ij = 11, 22, 33 \) and \( 13 = 31 \).

In order to estimate the polarization-optic coefficients \( g_{ij11} \) given in (3.15) from the measured coefficients \( r_{ij1} \) we make some simplifying assumptions. We consider the spontaneous polarization to be directed exactly along the \( x \)-direction \( (\gamma = 0) \) and we assume that the polarization induced by the applied electric field \( P_{\text{ind}} \) also has only an \( x \)-component, that is we neglect the influence of the component \( \epsilon_{31} \) of the dielectric tensor. Eqs. (3.18) then reduces to

\[
 r_{ij1} = 2\epsilon_0(\epsilon_{11} - 1)g_{ij11}P_S
\]

(3.19)

From (3.19) with \( P_S \approx 14 \mu \text{C/cm}^2 \) and \( \epsilon_{11} \approx 230 \) one can estimate the quadratic polarization-optic coefficients

\[
\begin{align*}
g_{1111} &\approx 0.31 \text{ m}^4/\text{C}^2 \\
g_{3311} &\approx 0.25 \text{ m}^4/\text{C}^2 \\
g_{1311} &\approx -0.044 \text{ m}^4/\text{C}^2.
\end{align*}
\]

(3.20)

These values agree relatively well with the results of crystal-optic measurements of Ref. [48] shown in (3.15). The values are higher than the ones from Ref. [48] indicating that the contribution of the second to fourth term in (3.18) has the same sign as those appearing in (3.20). As a consequence the coefficients \( g_{ii13} \) are suggested to be positive because \( \epsilon_{31} \) is positive.

3.7 Conclusions

Free and clamped electro-optical coefficients of \( \text{Sn}_2\text{P}_2\text{S}_6 \) for an electric field parallel to the crystallographic \( x \)-axis were determined with a direct interferometric technique for various wavelengths and temperatures. Both low-frequency electro-optical measurements in a stress-free sample and measurements in the inertia-clamped samples using a step-like electric field were performed. The room temperature free electro-optical coefficient \( r_{111}^T \) reaches \( 174 \pm 10 \text{ pm/V} \) at \( \lambda = 633 \text{ nm} \) and shows only weak dispersion in the near infrared. It increases with temperature up to the ferroelectric to paraelectric phase transition at 65 °C, where a peak value of \( r_{111}^T \approx 4500 \pm 110 \text{ pm/V} \) has been measured. The large values of \( r_{111}^T \) and \( r_{331}^T \) make of \( \text{Sn}_2\text{P}_2\text{S}_6 \) a very promising material for electro-optical and photorefractive applications.
Chapter 3. Electro-optical properties of $Sn_2P_2S_6$
Chapter 4

Nonlinear optical coefficients and phase-matching conditions in Sn$_2$P$_2$S$_6$

Phase-matching conditions and second and third order nonlinear optical coefficients of Sn$_2$P$_2$S$_6$ crystals are reported. The coefficients for second harmonic generation (SHG) are given at $\lambda = 1542$ nm and 1907 nm at room temperature. The largest coefficients at these wavelengths are $d_{111} = 17 \pm 1.5$ pm/V and $d_{111} = 12 \pm 1.5$ pm/V, respectively. The third-order susceptibilities $\chi^{(3)}_{1111} = (17 \pm 6) \cdot 10^{-20}$ m$^2$/V$^2$ and $\chi^{(3)}_{2222} = (9 \pm 3) \cdot 10^{-20}$ m$^2$/V$^2$ were determined at $\lambda = 1907$ nm. All measurements were performed by the Maker-Fringe technique. Based on the recently determined refractive indices, we analyze the phase-matching conditions for second harmonic generation, sum- and difference-frequency generation and parametric oscillation at room temperature. Phase-matching curves as a function of wavelength and propagation direction are given. Experimental phase-matched type I SHG at 1907 nm has been demonstrated. The results agree very well with the calculations. It is shown that phase-matched optical parametrical oscillation is possible in the whole transparency range up to 8 $\mu$m with an effective nonlinear coefficient $d_{\text{eff}} \approx 4$ pm/V.

4.1 Introduction

Tin thiohypodiposphate (Sn$_2$P$_2$S$_6$) is a wide bandgap semiconductor ferroelectric with very attractive photorefractive properties and large electro-optical coefficients [21,46]. In addition, the wide optical transparency range extending from $\lambda = 0.53$ $\mu$m to $\lambda = 8$ $\mu$m [36] holds promise for optical parametric generation up to infrared wavelengths not accessible with standard nonlinear optical crystals. This requires the knowledge of the nonlinear optical coefficients and phase matching conditions. Up to now no coefficient had been determined; the only publication on nonlinear optics in Sn$_2$P$_2$S$_6$ reports a value for $d_{211}$ [43], but unfortunately without specifying the coordinate system being used (in Sn$_2$P$_2$S$_6$ $d_{211}$ is zero due to symmetry in the standard coordinate system). In this work we determine or estimate

\[\text{This chapter has been published slightly abbreviated in Optics Express 13(10), 3765–76 (2005) 69.}\]
all 10 second-order nonlinear coefficients, as well as the third-order nonlinear optical susceptibilities \( \chi^{(3)}_{1111} \) and \( \chi^{(3)}_{2222} \) using the Maker-Fringe technique.

In Ref. [32], the refractive indices and the indicatrix rotation of Sn\(_2\)P\(_2\)S\(_6\) are given for the wavelength range 550 – 2300 nm at room temperature. The Sellmeier coefficients determined there allow to describe the refractive indices with an accuracy of \( 2 \cdot 10^{-4} \) in the wavelength interval indicated. These data allow us to calculate phase-matching conditions for second harmonic generation (SHG), sum- and difference-frequency generation (SFG and DFG) and optical parametric oscillation (OPO). Calculated phase-matching conditions are compared with experimental data at \( \lambda = 1907 \) nm. A configuration for optical parametric oscillators pumped with the fundamental wavelength of a Nd:YAG laser, capable of producing radiation from 1 to 8 \( \mu \)m in the infrared, is described.

### 4.2 Optical frequency conversion in Sn\(_2\)P\(_2\)S\(_6\)

For phase-matched parametric interactions among three waves at the frequencies \( \omega_1 \), \( \omega_2 \), and \( \omega_3 \), where \( \omega_3 = \omega_1 + \omega_2 \), the wave vectors \( k_i \) of the interacting waves must satisfy

\[
k_3 = k_1 + k_2.
\]

That is, if all the \( k_i \) are parallel to one another, then

\[
\frac{n_3}{\lambda_3} = \frac{n_1}{\lambda_1} + \frac{n_2}{\lambda_2}
\]

where the \( n_i \) are the refractive indices for the waves at frequencies \( \omega_i \) and the \( \lambda_i \) are the corresponding vacuum wavelengths. We use the Cartesian coordinate system as defined in Ref. [32], unit cell of Dittmar and Schäfer [26], \( y \parallel b \) is perpendicular to the mirror plane of the crystal, \( z \parallel c \), the positive direction of the \( x \)-axis and the \( z \)-axis so that the piezoelectric coefficients \( d_{xxx} \) and \( d_{zzz} \) are positive and \( +y \) so that \( xyz \) is a right-handed system. The spherical coordinates are defined in Fig. 4.1.

Phase-matching conditions may be satisfied in materials with sufficient birefringence either by rotating the direction of the laser beams with respect to the main axes of the optical indicatrix (angle tuning), by adjusting the wavelengths of the interacting beams (wavelength tuning), or by temperature tuning of the birefringence of the crystal.

The advantage of wavelength and temperature tuning is that the interacting beams can travel collinearly with one of the main axes of the optical indicatrix. In this case, termed noncritical phase matching, the Poynting vectors of all the interacting beams (wavelength tuning), or by temperature tuning of the birefringence of the crystal.

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For angle tuning, there is critical phase matching: The Poynting vectors are in general not parallel to the wave vectors, and the interacting beams walk off from one another. A discussion of the walk-off angles for biaxial crystals was made in Ref. [70]. The efficiency of the frequency conversion depends on the interaction length of the waves in the crystal, which in turn depends on the diameter of the beams and on the walk-off angle. Angle tuning is advantageous if the interaction length is of the order
4.2. Optical frequency conversion in Sn$_2$P$_2$S$_6$

![Figure 4.1: Coordinate system of Sn$_2$P$_2$S$_6$ and polar angles defining the direction of the wave vector $\mathbf{k}$.](image)

of the crystal length; the method can find application for powerful pulsed lasers when the beams do not need to be tightly focused or a long crystal length is not required.

The induced nonlinear-optical polarization $\mathbf{P}(\omega_3)$ as a function of the electric fields $\mathbf{E}(\omega_{1,2})$ of the fundamental waves is described by

$$P_i^{(\omega_3)} = \epsilon_0 \sum_{jk} d_{ijk}^{(\omega_3,\omega_1,\omega_2)} E_j^{(\omega_1)} E_k^{(\omega_2)},$$

(4.3)

where $\epsilon_0$ is electric constant and $d_{ijk}$ are the nonlinear-optical coefficients. For second harmonic generation ($\omega_1 = \omega_2$), $d_{ijk}$ is symmetric in the last two indices, and the contracted notation can be used.

For general directions of the wave vectors and polarizations in the crystal the projection of the induced polarization at frequency $\omega_3$ along the direction of polarization of the emitted wave with frequency $\omega_3$ can be written as

$$|\mathbf{P}(\omega_3)| = 2\epsilon_0 d_{\text{eff}} |\mathbf{E}(\omega_1)| |\mathbf{E}(\omega_2)|$$

(4.4)

with

$$d_{\text{eff}} = \sum_{ijk} d_{ijk}^{(\omega_3,\omega_1,\omega_2)} \cos(\beta_i^{(\omega_3)}) \cos(\beta_j^{(\omega_1)}) \cos(\beta_k^{(\omega_2)}),$$

(4.5)

where $\beta_i^{(\omega)}$ is the angle between the electric-field vector of the wave at frequency $\omega$ and the axis $i$ of the Cartesian coordinate system. In a birefringent crystal the electric field direction in general is not perpendicular to the wave vector. The walk-off angle has to be taken into account in order to calculate the angles $\beta_i$. A discussion of phase matching in biaxial crystals, including analytical expressions for the walk-off angles and $d_{\text{eff}}$ for different geometries, can be found in Refs. 70, 71, 72.

For type I SHG the induced nonlinear polarization is given by:

$$|\mathbf{P}(2\omega)| = \epsilon_0 d_{\text{eff}} |\mathbf{E}(\omega)|^2,$$

(4.6)

where $d_{\text{eff}}$ can again be derived from Eq. (4.5). The difference between Eqs. (4.6) and (4.4) is consistent with a continuous transition to the degenerate case, described by (4.6), from the sum-frequency case, described by (4.4), with two distinguishable fundamental fields.
Chapter 4. Nonlinear optical properties of Sn$_2$P$_2$S$_6$

The frequency dependence of the nonlinear-optical coefficients can be approximately described with Miller’s rule [73]:

$$d_{ijk}^{(\omega_3,\omega_1,\omega_2)} = \epsilon_0 \chi_{ii}^{(\omega_3)} \chi_{jj}^{(\omega_1)} \chi_{kk}^{(\omega_2)} \delta_{ijk},$$

(4.7)

where $\delta_{ijk}$, the Miller indices, are almost independent of the frequency [74] and $\chi_{ii} = n_i^2 - 1$ are the diagonal elements of the linear susceptibility. Therefore, to estimate the wavelength dependence of the nonlinear-optical coefficients $d_{ijk}$, one can assume the Miller indices to be constant and use the approximate dispersion formula (4.7) with the wavelength dependence of the refractive indices determined in [32].

4.3 Second harmonic generation

In SHG the frequencies of the incoming beams are equal ($\omega_1 = \omega_2$) and the $d$ tensor becomes symmetric in its last two indices. This allows to write it in its reduced form [75], which for the symmetry group $m$ of Sn$_2$P$_2$S$_6$ is

$$\begin{pmatrix}
  d_{11} & d_{12} & d_{13} & 0 & d_{15} & 0 \\
  0 & 0 & 0 & d_{24} & 0 & d_{26} \\
  d_{31} & d_{32} & d_{33} & 0 & d_{35} & 0
\end{pmatrix}.$$

If one neglects absorption and the dispersion of the $d$ coefficients (Kleinman symmetry), the number of independent coefficients drops from 10 to 6, being $d_{15} = d_{31}$, $d_{32} = d_{24}$, $d_{26} = d_{12}$, and $d_{35} = d_{13}$.

The nonlinear optical susceptibilities $d_{ip}$ were determined by a standard Maker-Fringe technique [76,77] with added suppression of laser beam intensity fluctuations. The fundamental wavelengths were $\lambda = 1542$ nm (first Stokes-line generated in a high pressure Raman cell filled with methane and pumped by a Surelite Nd:YAG laser at $\lambda = 1064$ nm, 7 ns, Q-switched at 2 Hz) and 1907 nm (same laser with the Raman cell filled with high pressure H$_2$ and Q-switched at 10 Hz). The samples used were an $x$-plate and a $z$-plate, from crystals grown at Uzhgorod University (Ukraine), oriented by Laue diffraction (precision $\pm 6^\circ$), polished to optical quality and poled by heating above $T_C = 66^\circ C$ and slowly cooling in an applied electric field of 1 kV/cm.

The $d$ coefficients were found by fitting the Maker-Fringe curves and comparing them to the ones of a reference crystal of $\alpha$-quartz. Fig. 4.2 shows an example of a Maker-Fringe measurement of Sn$_2$P$_2$S$_6$ with the corresponding fitted curve. The curve is not symmetrical with respect to the angle $\zeta = 0^\circ$, corresponding to beams perpendicular to the crystal, since the indicatrix is not perpendicular to the Cartesian axes, and therefore the coherence length is minimal at an angle $\zeta \neq 0^\circ$. Nevertheless the theoretical curve describes the experiments nicely. The modified Kleinman symmetries $\delta_{15} = \delta_{31}$ and $\delta_{35} = \delta_{13}$ where used during fitting, while the other Kleinman symmetries where not used, since enough Maker-Fringe curves were available for those coefficients.

The resulting coefficients $d_{ip}$ of Sn$_2$P$_2$S$_6$ are shown in Table 4.1. Note that due to the contribution of several tensor elements in the Maker-Fringe experiments, some of their values could be determined only with a relatively low accuracy. The largest value is the diagonal coefficient $d_{111} = 17 \pm 1.5$ pm/V at $\lambda = 1542$ nm and $d_{111} =$
4.3. Second harmonic generation

Figure 4.2: Maker-Fringe measurement in Sn$_2$P$_2$S$_6$ at $\lambda = 1907$ nm and fitted theoretical curve. The sample was a $z$-plate, which was rotated around its $y$-axis. The abscissa is the external angle between the fundamental beam ($p$-polarized) and the $z$-axis of the crystal. Detected was the $p$-polarized part of the second harmonic signal, yielding a measurement of $d_{11}$ at the angle $\zeta = 0^\circ$ and a combination of $d_{11}, d_{13}, d_{15}, d_{31}, d_{33}$ and $d_{35}$ for other rotation angles.

Figure 4.3: Temperature dependence of $d_{111}$ at $\lambda = 1907$ nm measured during heating until over the phase transition (a). The solid curve is according to $d_{111} = A(T_C - T)^{1/2}$ with $A = 4.2 \text{K}^{-1/2} \text{pm/V}$ and $T_C = 65.7 \degree \text{C}$. In b) the coordinates are chosen so that the dependence of Fig. a) is linear in the temperature range just below the phase transition.
Chapter 4. Nonlinear optical properties of Sn$_2$P$_2$S$_6$

Table 4.1: All second order nonlinear optical tensor elements $d_{ip}$ of Sn$_2$P$_2$S$_6$ at two wavelengths of the fundamental beam. The coefficients are given according to the standard conventions [75] (e. g. $d_{15} = d_{113} = d_{131}$) and a $\alpha$-quartz reference value of $d^2_{111} = 0.286\ \text{pm/V}$ at $\lambda = 1542\ \text{nm}$ and $d^2_{111} = 0.277\ \text{pm/V}$ at $\lambda = 1907\ \text{nm}$ [75].

<table>
<thead>
<tr>
<th>$d_{ip}$ at 1542 nm [pm/V]</th>
<th>$d_{ip}$ at 1907 nm [pm/V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{11}$</td>
<td>17 ± 1.5</td>
</tr>
<tr>
<td>$d_{12}$</td>
<td>5.2 ± 0.6</td>
</tr>
<tr>
<td>$d_{13}$, $d_{35}$</td>
<td>8 ± 7</td>
</tr>
<tr>
<td>$d_{15}$, $d_{31}$</td>
<td>8 ± 10</td>
</tr>
<tr>
<td>$d_{24}$</td>
<td>1.3 ± 0.3</td>
</tr>
<tr>
<td>$d_{26}$</td>
<td>2.9 ± 0.3</td>
</tr>
<tr>
<td>$d_{32}$</td>
<td>6 ± 3</td>
</tr>
<tr>
<td>$d_{33}$</td>
<td>4 ± 2</td>
</tr>
</tbody>
</table>

12 ± 1.5 pm/V at 1907 nm, which is higher than most of the largest coefficients of standard materials for nonlinear optics. Of special interest is also that Sn$_2$P$_2$S$_6$ has very large electro-optical coefficients ($r^2_{111} = 161 ± 8\ \text{pm/V}$ at $\lambda = 1064\ \text{nm}$ [44]), allowing to combine electro-optical with nonlinear-optical effects.

Fig. 4.3 shows the temperature dependence of the largest $d$ coefficient at $\lambda = 1907\ \text{nm}$. At this wavelength the influence of temperature on the optical properties is negligible with respect to the change in nonlinear optical properties of second order. The $d$ coefficient is proportional to the electrical polarization [78], which below $T_C$ is given mainly by the acentricity parameter, i.e. the spontaneous polarization $P_S$. Therefore Fig. 4.3 represents the temperature dependence of the spontaneous polarization $P_S$. Close to the phase transition ($T_C - T < 7°\ \text{C}$) we see the decrease proportional to the square root of $T_C - T$ (Fig. 4.3b). The fact that $d_{111}$ does not vanish completely above $T_C$ is explained by thermal fluctuations in the critical region just above the second-order phase transition, induced by residual defects [78].

4.4 Third harmonic generation

The same laser source as in the case of SHG at $\lambda = 1907\ \text{nm}$ was used for the THG measurements, which were performed using the Maker-Fringe technique in an evacuated chamber (10$^{-2}$ bar). As reference we used an $\alpha$-quartz crystal and the value $\chi^{(3)}_{1111} = 1.99 \cdot 10^{-20}\ \text{m}^2/\text{V}^2$ [77].

The measurements showed that Sn$_2$P$_2$S$_6$ has very large $\chi^{(3)}$ coefficients:

$$\chi^{(3)}_{1111} = (17 ± 6) \cdot 10^{-20}\ \text{m}^2/\text{V}^2$$
$$\chi^{(3)}_{2222} = (9 ± 3) \cdot 10^{-20}\ \text{m}^2/\text{V}^2$$

corresponding to 850 and 470 times $\chi^{(3)}_{1111}$ of $\alpha$-quartz and 16 and 8.5 times $\chi^{(3)}_{2222}$ of KNbO$_3$ [77].
4.5 Phase matching

4.5.1 Second harmonic generation

In Sn$_2$P$_2$S$_6$ phase-matched SHG is possible for a fundamental wavelength in the range between 1680 nm and 8 $\mu$m. The whole range is achievable by type I phase matching (incident photons have the same polarisation), while type II phase matching (incident photons are of orthogonal polarisation) is possible for $\lambda > 2324$ nm. The upper boundary of 8 $\mu$m is given only by the end of the transparency range (see Fig. 4.4), which is due to phonon-phonon interactions [36].

![Figure 4.4](image_url)

Figure 4.4: Absorption constant of Sn$_2$P$_2$S$_6$ at room temperature for non-polarized light propagating along the z-axis. It shows the large transparency range extending from $\lambda = 0.53$ $\mu$m to $\lambda = 8$ $\mu$m. This curve is calculated from measured transmission (by a PE $\lambda 9$ spectrometer for $\lambda < 1.6$ $\mu$m and a PE Paragon FT-IR spectrometer above that wavelength) and taking into account multiple Fresnel reflections.

The refractive indices used for calculating the phase-matching conditions are based on experimental data in the range of 550 – 2300 nm [32]. This data is precise ($\Delta n = 2 \cdot 10^{-4}$) and fits very well to a two-oscillator Sellmeier model, which was used to extrapolate the refractive indices at longer wavelengths. Nevertheless the precision at larger wavelengths cannot be predicted and could decrease rapidly. For the calculation of $d_{\text{eff}}$, we numerically evaluated (4.5), taking into account the dispersion of the $d_{ijk}$, given by Eq. (4.7). Some analytical expressions for $d_{\text{eff}}$ for a biaxial crystal can be found in Refs. 71 and 72.

Fig. 4.5 shows the phase-matching wavelengths versus the beam direction for type I and type II SHG. The phase-matching loci at the available laser line of $\lambda = 1907$ nm are drawn by the white dashed line. Some experimental points measured at this wavelength are also plotted, demonstrating the accuracy of the calculated phase-matching curve.

In Fig. 4.6 the regions of internal directions not accessible in crystals cut along the Cartesian $x, y, z$-axes are indicated by the grey area. For those directions oblique cuts are necessary in order to access the wished internal direction from air. In the
Figure 4.5: Directions of phase matching in Sn$_2$P$_2$S$_6$ for frequency doubling at room temperature; a) Type I, b) Type II. φ and θ are the spherical coordinates of the k vector in the crystal (see Fig. 1.1). Some contour curves are labeled with their corresponding fundamental wavelength in nanometers. The dashed white line corresponds to the predicted phase-matching for the laser line at 1907 nm and the white circles are experimental points.

Figure 4.6: The grey region indicates the directions that are not accessible from air in crystals cut along the Cartesian x, y, z-axes. This figure was calculated for the wavelengths in Fig. 4.5a, but since the dependence on the angles φ and θ is much larger than that on the wavelength, it can be assumed valid for every configuration shown in this paper.
4.5. Phase matching

Figure 4.7: Effective coefficients $d_{\text{eff}}$ for phase-matched SHG directions and corresponding wavelengths as in Fig. 4.5. a) Type I, b) Type II.

Figure 4.8: Internal walk-off angle for type I phase-matched SHG directions and corresponding wavelengths as in Fig. 4.5a.
Chapter 4. Nonlinear optical properties of Sn$_2$P$_2$S$_6$

following figures this region is either exactly equal or only slightly different than in Fig. 4.6. All contour plots display the data for the beam directions $k$ with polar coordinates in the range $\phi \in [0^\circ, 180^\circ]$ and $\theta \in [0^\circ, 90^\circ]$ inside the crystal. In order to get the whole definition range $\phi \in [0^\circ, 360^\circ]$ and $\theta \in [0^\circ, 180^\circ]$ of the spherical coordinates, the following symmetries should be applied

$$
\begin{align*}
\phi &\rightarrow 180^\circ - \phi & \text{for } \theta \in [90^\circ, 180^\circ] \\
\theta &\rightarrow 180^\circ - \theta \\
\phi &\rightarrow 360^\circ - \phi & \text{for } \phi \in [180^\circ, 360^\circ].
\end{align*}
$$

The effective nonlinear optical coefficient is shown in Fig. 4.7 for phase matching of type I and II. It ranges between 0 and 5 pm/V, with high values of $d_{\text{eff}} > 3$ pm/V for all fundamental wavelengths $\lambda > 1980$ nm. Compared to other materials, $d_{\text{eff}}$ of Sn$_2$P$_2$S$_6$ is similar to the ones of LiNbO$_3$ and KTP, and larger than in most other standard materials.

Fig. 4.8 shows the walk-off angle inside the crystal for type I phase matching (PM). For the largest part of directions it lies between 1° and 2°. The corresponding data for type II PM is similar. A special point is given where the walk-off angle is zero, which corresponds to non-critical phase matching. In Sn$_2$P$_2$S$_6$ this can occur only for a beam direction parallel to the fixed main axis of the indicatrix, i.e. $k \parallel y$, corresponding to $(\phi, \theta) = (90^\circ, 90^\circ)$ in the figures. The fundamental wavelength for non-critical PM is $\lambda = 3212.5$ nm for type I and $4536.5$ nm for type II. Again, compared to other standard nonlinear optical materials, the walk-off angles are similar to the ones of LiNbO$_3$, and larger than in KTP, but smaller than in BBO.

The figures in this section already give an indication of the possibilities for SFG, since the curves describing phase-matched SFG or OPO collapse in one point with $\lambda_1 = \lambda_2$ for the directions for phase-matched SHG with fundamental wavelength $\lambda_1$. The positions of these points were given by the curves in Fig. 4.5.

### 4.5.2 Sum-frequency generation and optical parametric oscillation

In this section we discuss the phase-matching possibilities for SFG or parametric oscillation. The phase-matching condition is given by Eq. (4.2). In the case of SFG two optical waves at frequencies $\omega_1$ and $\omega_2$ interact to produce a wave at the sum frequency $\omega_3 = \omega_1 + \omega_2$. For parametric oscillation inside a resonant cavity a strong pump wave at frequency $\omega_3$ can produce an idler wave at frequency $\omega_2$ and, through difference frequency generation, a signal wave at frequency $\omega_1 = \omega_3 - \omega_2$. We consider here only configurations in which all wave vectors are collinear. There are two different possibilities for achieving phase matching: (I) The two waves with wavelengths $\lambda_1$ and $\lambda_2$ share the same polarization, and the sum frequency wave $\lambda_3$ is polarized orthogonal to $\lambda_1$ and $\lambda_2$ or (II) the two waves at the wavelengths $\lambda_1$ and $\lambda_2$ are polarized orthogonal to each other. In analogy to SHG we call these two cases type I and type II SFG.

In OPO for each beam direction a continuous range of pumping wavelengths can be phase-matched. The phase-matched wavelengths for some propagation directions
4.5. Phase matching

Figure 4.9: Angle-tuning for phase-matched sum-frequency generation or optical parametric oscillation. (a) Type I, (b) Type II. Beam propagation is in the $xy$-plane ($\theta = 90^\circ$). $\lambda_3$ is the wavelength of the pumping beam, while $\lambda_1$ and $\lambda_2$ are the wavelengths of the signal and the idler. The bold lines correspond to non-critical phase matching.

in the $xy$-plane are given in Fig. 4.9. With type I PM (left) the curves for $\lambda_1$ and $\lambda_2$ join smoothly at the wavelength which produces phase-matched second-harmonic radiation. For type II SFG (right) the phase-matching lines intersect where phase-matched SHG is possible. In Fig. 4.9 the non-critical PM condition ($\mathbf{k} \parallel y$) is shown by a thick line: here with wavelength tuning of $\lambda_3 \in [1000, 1606]$ nm it is possible to get all the wavelengths between 1150 and 8000 nm.

The same result can be achieved by angle-tuning with a fixed pumping wavelength: this can be seen by staying on a vertical line in Fig. 4.9 and choosing the corresponding value of $\phi$ for the desired wavelengths $\lambda_1$ or $\lambda_2$. For the Nd:YAG laser wavelength $\lambda_3 = 1064$ nm this can be also seen in Fig. 4.10a, looking at the bottom horizontal line, where $\theta = 90^\circ$. At this wavelength $\lambda_{1,2} \in [1238, 7572]$ nm can be obtained using PM of type I. For the same configuration at the laser diode wavelength of $\lambda_3 = 808$ nm, $\lambda_1 > 2747$ nm can be accessed (Fig. 4.10b). Type II PM is also possible, with operating wavelengths similar to type I PM (see Fig. 4.9b). Generally one can access by type II PM the same signal and idler wavelengths as with type I, but the required tuning range of $\lambda_3$ is larger and the conversion efficiency lower.

For the efficiency of these frequency conversions refer to Fig. 4.11, where $d_{\text{eff}}$ and the walk-off angle are displayed for $\mathbf{k}$ in the $xy$-plane ($\theta = 90^\circ$). These two parameters depend very little on the interacting wavelengths, and $d_{\text{eff}} > 3$ pm/V for type I PM in the range $\phi = 30^\circ \ldots 150^\circ$, while for type II $d_{\text{eff}}$ is around 2 pm/V in the whole range of $\phi$. The largest contributions to $d_{\text{eff}}$ around the non-critical PM direction ($\theta = \phi = 90^\circ$) are given by $d_{111}$ and $d_{133}$, with these two contributions having the same sign for type I and different one for type II PM. With $\phi$ moving away from $90^\circ$, the term with $d_{133}$ becomes dominant for type I, while for type II many terms roughly balance each other. The efficiency for general beam directions is shown in Fig. 4.12 for $\lambda_3 = 808$ nm. It is highest for $\theta$ near $90^\circ$, and remains large as long as the internal angle between $\mathbf{k}$ and the $xy$-plane does not exceed $20 - 30^\circ$. The same figure at $\lambda_3 = 1064$ nm is very similar. By pumping at that wavelength, with a crystal cut perpendicularly to ($\theta = 90^\circ, \phi = 45^\circ$), one can for example access all wavelengths...
Figure 4.10: Phase-matched SFG or OPO of type I for $\lambda_3 = 1064 \text{ nm}$ (a) and $\lambda_3 = 808 \text{ nm}$ (b). The contour lines have constant signal wavelength $\lambda_1$ and $\lambda_2$, where $\frac{1}{\lambda_1} + \frac{1}{\lambda_2} = \frac{1}{\lambda_3}$. The contour line labels are $\lambda_1$ in micrometers. In the outer white region at $\lambda_3 = 1064 \text{ nm}$ no type I PM is possible. In the inner white region one of the phase-matched wavelengths diverges.

Figure 4.11: Effective nonlinear optical coefficient (continuous line) and walk-off angle (dashed line) for phase-matched SFG or OPO with beam propagating in the $xy$-plane ($\theta = 90^\circ$). The dependence of $d_{\text{eff}}$ and the walk-off angle on the wavelengths of the interacting beams is weak. The data above is calculated for $\lambda_1 = 2400 \text{ nm}$.
4.6 Conclusions

The nonlinear optical coefficients of ferroelectric Sn$_2$P$_2$S$_6$ were measured for $\lambda = 1542$ nm and 1907 nm at room temperature. The largest coefficients at these wavelengths are $d_{111} = 17 \pm 1.5$ pm/V and $d_{111} = 12 \pm 1.5$ pm/V, respectively. Third order susceptibilities $\chi^{(3)}_{1111} = (17 \pm 6) \cdot 10^{-20}$ m$^2$/V$^2$ and $\chi^{(3)}_{2222} = (9 \pm 3) \cdot 10^{-20}$ m$^2$/V$^2$ were measured at $\lambda = 1907$ nm. The temperature dependence of $d_{111}$ confirmed the temperature dependence of the spontaneous polarization within a temperature range of about 7°C below the Curie temperature $T_C \approx 66^\circ$C.

Based on the new refractive-index data for Sn$_2$P$_2$S$_6$, we have analyzed various nonlinear optical second-order interactions. Phase-matching configurations for various wavelengths and beam propagation directions have been studied. The principal polarization directions, walk-off angles, acceptance angles, and effective nonlinear-optical coefficients have been calculated numerically for arbitrary beam propagation directions in this biaxial crystal. Phase matching has been found to be possible in a large variety of configurations.

The advantages of this crystal are its large transparency range extending from 0.53 to 8 µm, the possibility for phase matching in the whole transparent range, the good nonlinear efficiency $d_{\text{eff}} \approx 4$ pm/V at phase matching, the very large electro-optical coefficients and the absence of hygroscopicity. The walk-off angle ranges between 0 and 2°, similarly to LiNbO$_3$ but larger than in KTP. Damage threshold studies will be required to fully assess the potentiality of this crystal for high-power near infrared frequency conversion.
Chapter 5

Sn$_2$P$_2$S$_6$ crystals for fast near infrared photorefraction and phase conjugation

The photorefractive properties of Sn$_2$P$_2$S$_6$ crystals in the wavelength range from 633 nm to 1064 nm are investigated. Conventional "yellow" and modified "brown" crystals with a variation of non-stoichiometric defects are examined. Brown crystals respond much faster and exhibit substantially higher photorefractive gain than yellow crystals, up to 18 cm$^{-1}$ at 780 nm and 8.5 cm$^{-1}$ at 1064 nm. Ring-cavity self-pumped phase conjugation is demonstrated using both types of crystals. The phase-conjugate response of brown Sn$_2$P$_2$S$_6$ is two orders of magnitude faster than in yellow Sn$_2$P$_2$S$_6$ or Rh doped BaTiO$_3$, with a grating recording time below 50 ms for 30 mW power at 860 nm. Various thresholding effects are analyzed in order to determine the optimal wavelength range for the two types of crystals. We find an optimum in the range 650–950 nm for yellow and in the range 850–1100 nm for brown Sn$_2$P$_2$S$_6$.

5.1 Introduction

Photorefractive materials have been studied intensively in the last few decades due to their utilization in a variety of applications [82, 83, 84]. Recently it has been of considerable interest to improve their response in the near infrared wavelength range of widely available laser diodes. Unfortunately the conventional photorefractive materials tend to be less sensitive in the near infrared and only a few materials have been shown to exhibit substantial photorefractive response. Semiconductor photorefractive crystals are relatively fast but have small nonlinearity and require high external electric fields. Among conventional photorefractive materials, reduced Rh doped KNbO$_3$ [85] and Rh doped BaTiO$_3$ [86] have been shown to exhibit relatively large nonlinearity, but rather slow response. Especially Rh:BaTiO$_3$ has been optimized intensively in the last years by many groups to obtain photorefractive gain values of as large as $\Gamma = 23$ cm$^{-1}$ at light wavelength $\lambda = 1.06 \mu$m with a response time of 75 seconds with a light power of 20 W/cm$^2$ (Ref. [87,88]). Self-pumped phase conjugation

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$^\dagger$This chapter has been accepted for publication in JOSA B (2005) [81].
in near infrared is commonly obtained using Rh:BaTiO$_3$, but the response time is still in the order of 10 s at $\lambda = 1.06$ $\mu$m and 5 W/cm$^2$ (Ref. 89).

Here we consider another near-IR sensitive material, tin hypothiodiphosphate (Sn$_2$P$_2$S$_6$). In contrast to most conventional ferroelectrics which are insulators, Sn$_2$P$_2$S$_6$ has a smaller band gap of 2.3 eV at room temperature which results in pronounced semiconductor features. Photorefractive response of Sn$_2$P$_2$S$_6$ is much faster than that of Rh:BaTiO$_3$ or Rh:KNbO$_3$, also without applying external fields. At $\lambda = 633$ nm and 1 W/cm$^2$ with conventional yellow Sn$_2$P$_2$S$_6$ the response time is of the order of 10 ms (Ref. 90). The measured gain coefficients were up to 7.5 cm$^{-1}$ at $\lambda = 633$ nm and up to 6 cm$^{-1}$ at $\lambda = 1.06$ $\mu$m, the latter obtained by using a focused laser beam with intensity of about 50 W/cm$^2$ and pre-illumination [22,21]. With external electric field a gain factor of more than 15 cm$^{-1}$ was achieved at $\lambda = 0.9$ $\mu$m (Ref. 57). A strong electron-hole competition has been observed in yellow Sn$_2$P$_2$S$_6$, which leads to transient behavior and decreases the gain in the steady state [21].

In crystals with pronounced electron-hole competition, which we call Type I yellow Sn$_2$P$_2$S$_6$ crystals, the photorefractive gain is also very sensitive to pre-illumination, and the exponential gain coefficient can increase by a factor of 2–3 after pre-exposure with white light [21]. The competition of two out-of-phase gratings in Type I yellow Sn$_2$P$_2$S$_6$ crystals with different decay times results in splitting of the spectrum of the steady-state gain factor [92]. This leads to a specific dynamics of the self-pumped phase conjugation in a ring cavity with a high index-contrast amplitude [91]. Different response characteristics were obtained in the so-called Type II yellow Sn$_2$P$_2$S$_6$ crystals [93]. For these crystals no transient gain and pre-illumination influence were detected. Recently, a brown modification of Sn$_2$P$_2$S$_6$ was obtained with improved gain of up to $\Gamma = 38$ cm$^{-1}$ at $\lambda = 633$ nm and even faster response [23,46]. Brown Sn$_2$P$_2$S$_6$ crystals are also not sensitive to pre-illumination with white light and do not show a pronounced electron-hole competition. Self-pumped phase conjugation was demonstrated in brown Sn$_2$P$_2$S$_6$ at $\lambda = 780$ nm with a very fast response which is below 50 ms at 1 W/cm$^2$ (Ref. 46).

In this paper we report on the wavelength dependence of photorefractive properties and self-pumped phase conjugation in both yellow Type II and brown Sn$_2$P$_2$S$_6$ towards longer wavelengths up to $\lambda = 1.06$ $\mu$m. We discuss the optimization of the phase-conjugate performance at different wavelengths considering absorption, photorefractive gain, intensity, dark conductivity, and the transmission of a phase-conjugation cavity. Thresholding behavior of the phase-conjugate reflectivity in Sn$_2$P$_2$S$_6$ is analyzed regarding ring-cavity losses, light intensity, and photorefractive coupling strength.

### 5.2 Crystal properties

Sn$_2$P$_2$S$_6$ crystals used in our measurements were grown by the chemical vapor-transport reaction technique [25]. Several transport agents can be selected to grow Sn$_2$P$_2$S$_6$ by this technique: I$_2$, SnI$_2$, or SnI$_4$. The choice of the transport gas affect the growth speed and the stoichiometry level of the grown crystals. Conventional yellow crystals that we used in our experiments were grown employing SnI$_4$ as a transport gas. Modified brown crystals, presumably of a lower stoichiometry level [23], were grown
5.3. Two-wave mixing

All photorefractive experiments were performed at room temperature. The measurements were carried out at different wavelengths: \( \lambda = 633 \text{ nm} \) (He-Ne laser, maximal cw power \( P_{\text{max}} = 5 \text{ mW} \)), 780 nm (external cavity diode laser, \( P_{\text{max}} = 300 \text{ mW} \), Rainbow Photonics AG, Zurich), 860 nm (Ti:Sapphire laser, \( P_{\text{max}} = 200 \text{ mW} \)), 980 nm
(laser diode, \( P_{\text{max}} = 100 \text{ mW}, \text{SLI} \)), 1064 nm (Nd:YAG laser, \( P_{\text{max}} = 200 \text{ mW} \)). In order to avoid that reflections and phase-conjugate feedback are affecting laser oscillation, a Faraday isolator was inserted in front of all the lasers used.

For the measurements of the two-beam coupling gain the usual experimental setup was used with the crystal \( x \)-axis oriented in the incidence plane \( xz \) and perpendicular to the bisector of the two incident beams. Both waves were extraordinary polarized in the plane of incidence. The intensity ratio of the pump wave to the weak signal wave was at all the wavelengths high enough to neglect the pump wave depletion. The yellow and brown \( \text{Sn}_2\text{P}_2\text{S}_6 \) crystals used for this measurement were respectively \( z = 5.7 \text{ mm} \) and \( z = 2.4 \text{ mm} \) thick.

Figure 5.2 shows the measured dependence of the two-wave mixing gain \( \Gamma \) on the grating spacing \( \Lambda = \lambda/2 \sin \theta \), where \( 2\theta \) is the external angle between the intersecting beams. Measurements at light wavelengths \( \lambda = 780 \text{ nm} \) and 1064 nm are shown. Large values of the two-wave mixing gain coefficients are observed in the brown crystal, with a maximum of \( \Gamma = 18 \text{ cm}^{-1} \) at 780 nm and \( \Gamma = 8.5 \text{ cm}^{-1} \) at 1064 nm. The corresponding response time \( \tau_{\text{twm}} \) for an intensity of 0.2 W/cm\(^2\) at 780 nm is approximately 15 ms, and 0.26 s at 1064 nm and 3.6 W/cm\(^2\). In the yellow sample the measured gain coefficients are much lower (see Fig. 5.2), with a maximum of about 2.5 cm\(^{-1}\) at 780 nm with the response time of approximately 0.2 s for an intensity of 0.2 W/cm\(^2\). In both yellow and brown \( \text{Sn}_2\text{P}_2\text{S}_6 \) the response becomes faster at larger grating spacings. For the diffusion case and assuming an isotropic photoexcitation cross-section one gets for the stationary two-wave mixing exponential gain coefficient within the weak probe beam approximation \[7,16\]

\[
\Gamma = \frac{2\pi}{\lambda} n_S n_P^2 \cos \beta_P \frac{\hat{e}_S \cdot \hat{e}_P}{\cos \theta_S} r_{\text{eff}} \text{Im}(E_{\text{sc}}),
\]

\(5.1\)

where \( n_S \) and \( n_P \) are the refractive indices seen by the signal and the pump beam, \( \beta_P \) the angle between the pump beam Poynting vector and the wave vector, \( \theta_S \) the angle between the Poynting vector of the signal beam and the sample normal, \( \hat{e}_S \) and \( \hat{e}_P \) the electric field unit vectors of the interacting beams, and \( r_{\text{eff}} \) the effective
5.4. Ring-cavity self-pumped phase conjugation

The imaginary part of the steady-state space charge electric field in the case of diffusion dominated charge transport is given by

$$\text{Im}(E_{sc}) = \frac{E_D E_q}{E_D + E_q},$$  \hspace{1cm} (5.2)

where $E_D = (k_B T/e)(2\pi/\Lambda)$ is the diffusion electric field and

$$E_q = (e/\epsilon_0\epsilon_{\text{eff}})(\Lambda/2\pi)N_{\text{eff}}$$  \hspace{1cm} (5.3)

the trap-limiting field. Here $k_B$ is the Boltzmann constant, $T$ the absolute temperature, $e$ the unit charge, $\epsilon_0$ the electric constant, $\epsilon_{\text{eff}}$ the effective dielectric constant, and $N_{\text{eff}}$ the effective concentration of traps. For our geometry we assume $\cos \beta_p \simeq 1$ and $\hat{e}_S \cdot \hat{e}_P \simeq \cos 2\theta_S$. For the effective dielectric constant we take $\epsilon_{\text{eff}} \approx 300$ for brown samples and $\epsilon_{\text{eff}} \approx 230$ for yellow samples [23]. The refractive indices can be calculated using the Sellmeier model with the parameters given in Ref. 47 and taking into account the indicatrix rotation, that gives for our geometry approximately $n_S = n_P \approx 2.93$ at 780 nm and 2.84 at 1064 nm. The solid curves in Fig. 5.2 present the theoretical approximations according to Eq. (5.1). From the model parameters we can estimate the effective electro-optic coefficient $r_{\text{eff}}$ and the effective concentration of traps $N_{\text{eff}}$. The obtained parameters are listed in Table 5.1. Due to a larger effective concentration of traps the optimal coupling in brown Sn$_2$P$_2$S$_6$ is observed at smaller grating spacings than in yellow Sn$_2$P$_2$S$_6$. A lower gain obtained in yellow samples is mainly due to hole-electron compensation effects, which are not significant in brown samples [23]. The higher value obtained in brown Sn$_2$P$_2$S$_6$ is a result of a larger effective electro-optic coefficient. Even though in general the effective electro-optic coefficient is not expected to correspond to one of the elements of the unclamped electro-optic tensor [12], we have a surprisingly good correspondence with the directly measured electro-optic coefficient $r_{111}^{T} = (168 \pm 13) \text{ pm/V}$ at $\lambda = 780$ nm (Ref. 44). A slight decrease of $r_{\text{eff}}$ with $\lambda$ is also in agreement with the results of the direct measurements [44]. The decrease of the effective concentration of traps $N_{\text{eff}}$ with $\lambda$ confirms that more than one band-gap level is involved in photorefraction of Sn$_2$P$_2$S$_6$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda$ [nm]</th>
<th>$r_{\text{eff}}$ [pm/V]</th>
<th>$N_{\text{eff}} [10^{16} \text{ cm}^{-3}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>yellow</td>
<td>780</td>
<td>41 ± 2</td>
<td>0.14 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>1064</td>
<td>38 ± 5</td>
<td>0.044 ± 0.009</td>
</tr>
<tr>
<td>brown</td>
<td>780</td>
<td>178 ± 9</td>
<td>0.67 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>1064</td>
<td>161 ± 7</td>
<td>0.43 ± 0.04</td>
</tr>
</tbody>
</table>

5.4 Ring-cavity self-pumped phase conjugation

The experimental setup for the ring-cavity self-pumped phase conjugation is depicted in Fig. 5.3. The light beams were polarized in the plane of the ring-cavity loop and
Figure 5.3: Experimental set-up for the ring-cavity self-pumped phase conjugation with Sn$_2$P$_2$S$_6$. Without the external loop the input beam 3 was fanned towards the +x direction. All beams are polarized in the plane of the loop. The transmission grating is written by the beam 3 with its self-diffracted beam 4 and by the beams 1 and 2 counter propagating in the loop.

almost parallel to the x-axis in the crystal to use the largest electro-optic coefficient $r_{111}$. The external angle $2\theta$ was adjusted at each laser wavelength approximately to the angle corresponding to the maximum measured two-wave mixing gain $\Gamma$ (Fig. 5.2). The crystals were rotated by $\beta \approx 45^\circ - 50^\circ$ with respect to the incident beam for reducing the Fresnel losses. In these experiments a yellow crystal with dimensions $x \times y \times z = 8.05 \times 8.91 \times 9.72$ mm$^3$ and a brown crystal with $x \times y \times z = 4.40 \times 5.68 \times 2.42$ mm$^3$ were used. We have coated the crystals with approximately 100 nm thick Al$_2$O$_3$ layer to reduce the reflection losses by about 50% at normal incidence in a wide wavelength range (800–1100 nm). The ring-cavity length was about 40–45 cm and one of the mirrors in the cavity was vibrating to ensure that the input beam 3 and the feedback beam 1 are not coherent. In this case the reflection gratings created by pairs of beams (1,3), (2,4), (1,4), and (2,3) cannot be formed in the crystal. The generated phase conjugated signal is then a result of the coupling via the transmission grating formed by the incident beam 3 and its self-diffracted beam 4 as well by their feedback beams 1 and 2. The intensity of the phase-conjugated wave 2 is measured by a photodiode placed after a beam splitter. The phase-conjugate reflectivity $R$ is defined as the ratio between the measured intensity of the phase-conjugated wave 2 and the input wave 3.

Figure 5.4 shows the time evolution of the phase-conjugate reflectivity $R$ after turning on the input beam 3. In the beginning the phase-conjugated signal emerges from the noise gratings of the scattered input beam. After the external loop is restored, the desired transmission grating dominates and the phase-conjugated signal increases sharply and finally it saturates at its maximum value. We define the reflectivity rise time as the time in which the reflectivity rises from 10% to 90% of its saturation value.

5.4.1 Theoretical background

The measured data for the saturated reflectivity were compared to a plane-wave solution of the coupled equations for the case of large coupling (depleted-pump) assuming negligible absorption [94]. The boundary conditions for our ring-cavity self-pumped
5.4. Ring-cavity self-pumped phase conjugation

![Graphs showing phase-conjugate reflectivity R over time for different Sn\textsubscript{2}P\textsubscript{2}S\textsubscript{6} samples](image)

Figure 5.4: Time evolution of the phase-conjugate reflectivity \( R \) after turning on the input beam 3 using (a) brown Sn\textsubscript{2}P\textsubscript{2}S\textsubscript{6} of 2.4 mm thickness and (b) yellow Sn\textsubscript{2}P\textsubscript{2}S\textsubscript{6} of 9.7 mm thickness. The input beam is at \( \lambda = 860 \text{ nm} \) and has a diameter of 1.2 mm and powers of 30 mW (a) and 90 mW (b).

phase conjugator are \( A_1(0) = t_0 A_3(0), A_2(0) = t_0 A_4(0) \), and \( A_4(L) = 0 \), where \( A_i(z) \) is the electric field amplitude of the \( i \)-th wave at the position \( z \) along the propagation, where the position \( z = 0 \) is at the crystal boundary on the side of the ring cavity and \( z = L \) at the input beam boundary. The parameter \( t_0 \) accounts for the changes of the beam amplitudes and phases after being reflected by both mirrors in the cavity and being transmitted through the sample surface at \( z = 0 \). The total light intensity is equal to \( I_0 = |A_1|^2 + |A_2|^2 + |A_3|^2 + |A_4|^2 \) and is independent of \( z \) if the absorption is neglected. The four coupled-wave equations can be integrated to obtain the solution in the form \[94\]

\[
|t_0|^2 \frac{\tanh \kappa L}{s + \sigma \tanh \kappa L} = \frac{s - I_0 \tanh \kappa L}{(sI_0 - s^2) \tanh \kappa L + (I_0 - \sigma)s},
\]

where

\[
\sigma = I_0 \frac{|t_0|^2 - 1}{|t_0|^2 + 1},
\]

\[
s = \sqrt{\sigma^2 + (I_0 - \sigma)^2 |\rho|^2},
\]

\[
\kappa = \frac{s \Gamma^*}{4I_0}
\]

and \( |\rho|^2 \) is the phase-conjugate reflectivity defined as

\[
|\rho|^2 = \left| \frac{A_2(L)}{A_3(L)} \right|^2.
\]

By inserting Eqs. (5.5)-(5.7) into (5.4) one obtains the transcendental equation for the reflectivity \( |\rho|^2 \), which depends on the coupling constant \( \Gamma L \) and \( |t_0|^2 = T_0 \) that we refer to as the loop transmission. The measured reflectivity is equal to \( R = |\rho|^2 |t_L|^4 \) where \( t_L \) accounts for the changes of amplitudes and phases of interacting beams after being transmitted through the sample surface at \( z = L \).
In the case when absorption is not negligible, the optical energy is not conserved in the crystal and the coupled-wave equation cannot be integrated analytically. Numerical calculations [95], however, have shown that the absorption can be considered together with the other cavity losses, if the ratio between the linear absorption and the gain \( \alpha/\Gamma \) is less than about 0.1, which is mostly fulfilled in our experimental situations (see Table 5.2).

### 5.4.2 Loop transmission dependence

Besides the two-beam coupling mechanism and the initial spatial distribution of the incident light, the ring-cavity losses are of crucial importance for the self-pumped phase conjugation. To study the characteristics of the ring-cavity scheme, the cavity transmission was decreased additionally by adding neutral density (ND) filters into the ring as shown in Fig. 5.3. The results of the dependence of the saturated reflectivity \( R \) on the loop transmission \( T \) are shown in Fig. 5.5 for yellow and brown Sn\(_2\)P\(_2\)S\(_6\) samples at various wavelengths. By decreasing the transmission of the loop the maximum reflectivity decreases until the threshold is reached. Comparing measured reflectivities to theoretical given by Eq. (5.4) two crystal parameters can be determined [46]: \( \Gamma_L \), the coupling strength, and \( T_0 \), the loop transmission without the ND filter. Theoretical curves in Fig. 5.5 result in gain values \( \Gamma \) and loop transmissions \( T_0 \) as given in Table 5.2. Higher loop transmission \( T_0 \) (and consequently higher phase-conjugate reflectivity) in the yellow sample is a result of lower absorption losses in this crystal. The rise time was not much affected by small additional losses, but increased considerably when approaching the transmission threshold [46].

The obtained gain values \( \Gamma \) (Table 5.2) can be compared to the values measured by the two-wave mixing (Fig. 5.2). In the yellow sample of 0.97 cm thickness the

![Figure 5.5: Measured saturated phase-conjugate reflectivity \( R \) as a function of loop transmission \( T \) using (a) brown Sn\(_2\)P\(_2\)S\(_6\) of 2.4 mm thickness and (b) yellow Sn\(_2\)P\(_2\)S\(_6\) of 9.7 mm thickness. The solid curves are calculated from Eq. (5.4) with parameters listed in Table 5.2 where also the input beam intensities \( I_0 \) for this experiment are given.](image)
5.4. Ring-cavity self-pumped phase conjugation

Table 5.2: Characteristic parameters of phase conjugation in Sn$_2$P$_2$S$_6$ crystals of thickness $L$ that correspond to the experimental results at different wavelengths $\lambda$ with maximum input intensities $I_0$. $R_0$ is the measured saturated reflectivity and $\tau_0$ is the phase conjugation rise time. The photorefractive gain $\Gamma$ and the maximal loop transmission $T_0$ are the model parameters of Eq. (5.4) obtained from measurements as a function of loop transmission. The effective background intensity $I_\beta$ is a model parameter of the dependence of reflectivity on intensity. The relative errors of the parameters $I_0$, $R_0$, $\tau_0$, $\Gamma$, and $T_0$ are in the range of 10-20%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda$ [nm]</th>
<th>$\alpha_x$ [$\text{cm}^{-1}$]</th>
<th>$I_0$ [W/cm$^2$]</th>
<th>$R_0$ [%]</th>
<th>$\tau_0$ [s]</th>
<th>$\Gamma$ [cm$^{-1}$]</th>
<th>$T_0$ [%]</th>
<th>$I_\beta$ [W/cm$^2$]</th>
</tr>
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<tbody>
<tr>
<td>brown</td>
<td>633</td>
<td>5.65</td>
<td>0.27</td>
<td>1.8</td>
<td>0.077</td>
<td>36</td>
<td>2.5</td>
<td>0.01 ± 0.005</td>
</tr>
<tr>
<td></td>
<td>(L = 2.42 mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>780</td>
<td>0.88</td>
<td>4.0</td>
<td>35</td>
<td>0.011</td>
<td>20</td>
<td>45</td>
<td>0.1 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>860</td>
<td>0.33</td>
<td>2.5</td>
<td>48</td>
<td>0.045</td>
<td>18</td>
<td>62</td>
<td>0.2 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>980</td>
<td>0.14</td>
<td>5.2</td>
<td>35</td>
<td>0.42</td>
<td>14</td>
<td>62</td>
<td>0.3 ± 0.1</td>
</tr>
<tr>
<td>yellow</td>
<td>633</td>
<td>0.49</td>
<td>0.27</td>
<td>23</td>
<td>1.6</td>
<td>6.8</td>
<td>28</td>
<td>0.04 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>(L = 9.72 mm)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>780</td>
<td>0.21</td>
<td>4.0</td>
<td>55</td>
<td>2.4</td>
<td>5.6</td>
<td>62</td>
<td>0.45 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>860</td>
<td>0.16</td>
<td>8.0</td>
<td>60</td>
<td>9.3</td>
<td>4.0</td>
<td>82</td>
<td>1.1 ± 0.3</td>
</tr>
</tbody>
</table>

obtained values from the phase conjugation are about twice as high as in the yellow sample of 0.57 cm used in the two-wave mixing experiment. The theory we are using is derived for the plane wave approximation and convenient for thin photorefractive crystals without considerable distortion of the beam because of the photorefractive fanning. A slight variation in the properties of the two yellow Type II samples used in the experiments is also possible. The obtained values from the two different experiments for the brown sample of 0.24 cm thickness are on the other hand in a very good agreement.

5.4.3 Intensity dependence

Phase conjugation performance is affected also by the input beam intensity. The response rate increased linearly with intensity in the measured intensity regime as expected for the two-beam coupling time constant [46]. The results of the dependence of the saturated phase-conjugate reflectivity on the input intensity are shown in Fig. 5.6. The reflectivity increases for lower intensities above some threshold intensity and then it saturates at the maximum value limited by the ring-cavity characteristics. This kind of intensity thresholding was explained with the excitation of carriers due to the thermal effects and by background uniform illumination competing with the spontaneous build-up of the grating. To model the intensity dependence we can take into account the background uniform illumination $I_\beta$ in the coupled-wave equations, which changes the parameter $\kappa$ defined in (5.7) to

$$\kappa = \frac{s\Gamma^*}{4(I_0 + I_\beta)}, \quad (5.9)$$

The solid lines shown in Fig. 5.6 represent the intensity dependences of the reflectivity with the previously obtained parameters $\Gamma L$ and $T_0$ and the effective background illuminations parameters $I_\beta$ as listed in Table 5.2. Since the saturation of the reflectivity...
is already well reached at the input intensities used for the loop transmission dependence measurements, the curves in Fig. 5.5 do not change considerably by taking into account $I_\beta$. The smaller $I_\beta$ in the brown sample can be explained by an increased photoconductivity in brown Sn$_2$P$_2$S$_6$ compared to conventional yellow Sn$_2$P$_2$S$_6$.

### 5.4.4 Dependence of the phase conjugation response on the grating coupling strength

Figure 5.7 shows the measured gain $\Gamma$ in brown and yellow Sn$_2$P$_2$S$_6$ versus the light wavelength $\lambda$, as obtained from the phase conjugation experiments (see Table 5.2) and at $\lambda = 1064$ nm from the two wave mixing experiments. The dashed lines correspond to the theoretical coupling strength threshold for the ring-cavity self-pumped phase conjugation $\Gamma L = 2$ (Ref. 94) for the brown sample with $L = 2.4$ mm and the yellow sample with $L = 9.7$ mm. For example, at $\lambda = 1064$ nm the gain is at the threshold for the phase-conjugate wave generation in the brown sample, therefore one needs a thicker sample to observe the phase conjugation above this wavelength.

Although the gain is much higher and the phase-conjugate response is much faster in brown Sn$_2$P$_2$S$_6$ than in yellow Sn$_2$P$_2$S$_6$, the saturated reflectivity was lower in brown Sn$_2$P$_2$S$_6$ (see Fig. 5.4 or Table 5.2). This was attributed to a lower loop transmission as a consequence of a higher absorption in brown Sn$_2$P$_2$S$_6$. Therefore phase-conjugate reflectivities can be higher at longer light wavelengths $\lambda$ provided that the performance is not yet limited by the coupling strength that decreases with $\lambda$. To check whether the reflectivities in the Sn$_2$P$_2$S$_6$ samples are also limited by the coupling strength, theoretical dependences of the reflectivity as functions of the coupling strength were plotted in Fig. 5.8 considering the corresponding loop transmission parameters. Above the coupling-strength threshold the reflectivity increases with $\Gamma L$ until it saturates at a value equal to the transmission of the loop reduced by the reflection losses at the input crystal surface. For the experimental points in
5.4. Ring-cavity self-pumped phase conjugation

Figure 5.7: Photorefractive gain $\Gamma$ as a function of the light wavelength $\lambda$ in a) brown Sn$_2$P$_2$S$_6$ and b) yellow Sn$_2$P$_2$S$_6$. The dashed lines correspond to the coupling strength threshold $\Gamma L = 2$ for the brown sample with $L = 2.4$ mm and the yellow sample with $L = 9.7$ mm. The dotted lines present approximations of the dependences $\Gamma(\lambda)$ used to estimate the theoretical limits of the phase-conjugate reflectivities.

Fig. 5.8 that already reach the saturation, the reflectivity is limited by the loop-cavity transmission and not by the coupling strength. One can conclude that the grating strength started to be a limiting factor for the investigated yellow sample at 860 nm, and for the brown sample at 980 nm. At all other measured wavelengths the reflectivity is limited only by the loop-cavity transmission.

Figure 5.8: Theoretical dependences of saturated reflectivity $R$ on the coupling strength for loop transmissions $T_0$ obtained at different wavelengths (Table 5.2): 633 nm (dash-dotted line), 780 nm (dotted line), 860 nm (solid line), 980 nm (dashed line). Experimental points for a) brown Sn$_2$P$_2$S$_6$ and b) yellow Sn$_2$P$_2$S$_6$ are also included. Note that since the losses at the mirrors inside the cavity were higher at 980 nm but the absorption losses were lower at 980 nm, the curves for brown Sn$_2$P$_2$S$_6$ at 980 nm and 860 nm almost coincide.

5.4.5 Optimization of the phase-conjugation performance

From the examples of the loop transmission and the coupling strength threshold shown above, one can conclude that there exists an optimal crystal thickness for
Chapter 5. Photorefraction and phase conjugation with Sn\textsubscript{2}P\textsubscript{2}S\textsubscript{6}

the ring-cavity self-pumped phase conjugation at each wavelength. If the reflectivity is limited by the coupling strength, using a thicker crystal could result in a better performance. If it is limited by the cavity transmission, it could be advantageous to use a thinner crystal. Figure 5.9 shows the calculated phase-conjugate reflectivities as functions of the crystal length considering the parameters listed in Table 5.2. At each wavelength there is a maximum in the phase-conjugate reflectivity that corresponds to the optimal crystal length. The dotted vertical lines correspond to the brown and yellow crystals investigated. One can conclude that both are of the optimal thickness for wavelengths of about 860 nm. For shorter wavelengths it will be advantageous to use thinner crystals, for longer wavelengths thicker ones. Selecting a crystal according to the maximum reflectivity presented in Fig. 5.9 will assure the lowest possible absorption losses without starting to limit the reflectivity due to the coupling strength. Such a crystal can be then antireflection coated for a selected wavelength minimizing the reflection losses at the crystal surface.

Figure 5.9: Theoretical dependences of saturated reflectivity \( R \) on the crystal length for loop transmissions \( T_0 \), photorefractive gains \( \Gamma \) and absorption constants \( \alpha \) obtained at different wavelengths (Table 5.2): 633 nm (dash-dotted line), 780 nm (dotted line), 860 nm (solid line), 980 nm (dashed line). Experimental points for a) brown Sn\textsubscript{2}P\textsubscript{2}S\textsubscript{6} and b) yellow Sn\textsubscript{2}P\textsubscript{2}S\textsubscript{6} are also included with the dotted vertical lines corresponding to the investigated crystal thicknesses.

Figure 5.10: Optimized phase-conjugate reflectivity \( R \) (left scale) as a function of the light wavelength \( \lambda \) for a) brown Sn\textsubscript{2}P\textsubscript{2}S\textsubscript{6} and b) yellow Sn\textsubscript{2}P\textsubscript{2}S\textsubscript{6} crystal of the optimal thickness \( L \) (right hand scale).
5.5. Conclusions

Considering the above optimization procedure we have calculated the optimal reflectivities as functions of the wavelength for yellow and brown Sn$_2$P$_2$S$_6$. For this purpose we have approximated the dependences $\Gamma(\lambda)$ presented in Fig. 5.7 with linear functions. Such linear dependences have no physical meaning, we only use them as first approximations for our calculation. We assume further only absorption losses, therefore the loop transmission parameter is $T_0 = \exp(-2\alpha L)$, where the absorption constant values $\alpha$ are plotted in Fig. 5.1. At each light wavelength $\lambda$ we can then calculate the dependence of the saturated reflectivity $R$ as a function of the crystal thickness $L$, similar as in Fig. 5.9. Figure 5.10 shows the dependence of the reflectivity maximum and the crystal length at the maximum as a function of $\lambda$. In optimized crystals, reflectivities up to about 90 percent are possible using brown Sn$_2$P$_2$S$_6$ and up to about 65 percent using yellow Sn$_2$P$_2$S$_6$. The optimal wavelength range for using brown Sn$_2$P$_2$S$_6$ is 850–1100 nm with crystals 0.25 to 0.7 cm thick. The optimal wavelength range for using yellow Sn$_2$P$_2$S$_6$ is 650 to 950 nm with crystals 0.6 to 1.7 cm thick.

5.5 Conclusions

Photorefractive properties and self-pumped phase conjugation in yellow and brown Sn$_2$P$_2$S$_6$ crystals were studied in the near infrared wavelength range. Compared to the most popular photorefractive material for the near-infrared applications, Rh doped BaTiO$_3$, Sn$_2$P$_2$S$_6$ crystals are especially advantageous because of the dynamic response, which is typically two orders of magnitude faster. The photorefractive gain in the near-infrared, 18 cm$^{-1}$ at 780 nm and 8.5 cm$^{-1}$ at 1064 nm, is high enough to allow many potential applications. We are especially interested in applying phase conjugation in the near infrared. Thresholding behavior regarding the ring-cavity transmission, light intensity, and photorefractive coupling strength for the ring-cavity self-pumped phase conjugation was investigated in detail. The presented analysis allows us to optimize the phase-conjugation performance. The optimal wavelength range for using yellow Sn$_2$P$_2$S$_6$ is 650–950 nm and for using brown Sn$_2$P$_2$S$_6$ 850–1100 nm with optimal phase-conjugate reflectivities of up to 90%. Besides optimizing the available yellow and brown Sn$_2$P$_2$S$_6$ crystals of different stoichiometry level we are also looking for new crystal modifications with dopants to further improve the photorefractive performance of Sn$_2$P$_2$S$_6$. 
Chapter 5. Photorefraction and phase conjugation with $\text{Sn}_2\text{P}_2\text{S}_6$
Chapter 6

Interband holography at visible wavelengths in Sn$_2$P$_2$S$_6^†$

We present fast-response, continuous-wave holographic investigations using Sn$_2$P$_2$S$_6$ crystals and interband illumination at 514 nm and 488 nm. We demonstrate two-wave mixing and Bragg diffraction at 514 nm with grating response times of around 100 microseconds at a moderate light intensity of 0.6 W/cm$^2$, two orders of magnitude faster than measured for conventional photorefractive effects. In two-wave mixing holes are the main charge carriers, and a large gain of up to 52±8 cm$^{-1}$ was measured.

6.1 Introduction

Tin hypothiodiphosphate (Sn$_2$P$_2$S$_6$) is a ferroelectric crystal with large electro-optical coefficients, $r_{111}^T = 174$ pm/V at room temperature and $\lambda = 633$ nm [44]. Its band-gap of 2.3 eV is smaller than in oxyde ferroelectrics, and permits interband photorefraction at visible wavelengths in the blue-green. In the conventional photorefractive regime, in the red and near infrared region, Sn$_2$P$_2$S$_6$ shows relatively fast photorefractive grating recording times and large refractive index changes [21,22,23,96,57,46,90]. In addition Sn$_2$P$_2$S$_6$ is transparent over a large wavelength range 0.53 – 8 µm.

There are several advantages of the interband photorefractive effect compared to the conventional photorefractive effect. One is the faster response or that the grating is very robust to illumination with sub band-gab photons. Additionally the crystal doesn’t have to be doped. The interband photorefractive effect is very interesting for applications where fast switching or large processing speed is required. It has already been implemented to demonstrate incoherent-to-coherent light converters [97], optical joint Fourier-transform correlators [98], fast dynamical light-induced waveguides [2] and tunable optical filters for wavelength division multiplexing [99].

The possibility for fast hologram recording via interband photorefraction in the visible was demonstrated in our preliminary experiments [100]. In the pulsed regime, effects ascribed to the interband photorefractive effect were already used to demonstrate optical correlation at high repetition frame rates using the wavelength 532 nm [98]. Interband photorefraction has been studied previously in KNbO$_3$ [17] and LiTaO$_3$ [101].

$^†$The content of this chapter is going to be published in a paper by R. Mosimann as first author.
where UV light has to be used. Visible light compared to UV light offers several advantages in terms of availability of laser sources, standard optical devices, easier detection etc.

In this paper we present our results on the recording of interband photorefractive gratings in Sn$_2$P$_2$S$_6$ at green ($\lambda = 514$ nm) and blue ($\lambda = 488$ nm) wavelengths using continuous-wave illumination. The intensity dependence of the diffraction efficiency of a Bragg grating is measured and the strong influence of the rotation of the optical indicatrix with the wavelength on the Bragg angle is investigated. We use the absorption measured with a new method described in Appendix [102], which permits to use photoconductivity measurements instead of absorption measurements where the absorption is too large for direct determination. We further present two-wave mixing experiments at $\lambda = 514$ nm which show very high gain coefficients of up to 52 cm$^{-1}$.

6.2 Experimental

6.2.1 Sample preparation

Sn$_2$P$_2$S$_6$ single crystals were produced by the conventional vapor-transport technique [25, 24] using iodine as a transporter. At room temperature Sn$_2$P$_2$S$_6$ has a ferroelectric monoclinic structure with point group $m$. In this work we use the standard coordinate system with the z-axis parallel to the crystallographic c-axis, $y \parallel b$ normal to the mirror plane, and $x$ normal to $y$ and $z$. The indicatrix is rotated in the $xz$-plane, and its rotation angle $\alpha_{\text{ind}}$ is defined as the angle between the $x$ axis and the major principal axis of the indicatrix. This angle is wavelength and temperature dependent [32,48]. The poling was performed by heating the crystal above the second order phase transition at $T_C = 338 \pm 2$ K and slowly cooling it down to room temperature with an electric field of about 1 kV/cm applied along the $x$-direction. We used a bulk crystal and a thin $z$-plate. The dimensions of the thick Sn$_2$P$_2$S$_6$ crystal were $5.07 \times 5.38 \times 4.85$ mm$^3$ along the $x$, $y$ and $z$ axes. The thin plate had dimensions $7.3 \times 8.3 \times 0.045$ mm$^3$ and was attached to a substrate of quartz with a thickness of 3 mm. The single domain state was verified using the method described in Ref. [64].

6.2.2 Bragg diffraction and two-wave mixing

Photorefractive Bragg diffraction was performed in a nondegenerate four-wave mixing configuration in the longitudinal geometry as illustrated in Fig. 6.1. In this geometry all three beams enter the crystal through the same surface. The depth of the grating is of the order of $2/\alpha = 4 - 200 \mu\text{m}$ for absorptions $\alpha$ between $\lambda = 488$ and 514 nm (see App. C) [102], and therefore the interaction length for the readout beam is quite short. The read out beam was $p$-polarised in all the measurements, while the writing beams were either $p$-- or $s$-polarised. The diffracted probe beam (HeNe laser) had a wavelength of $\lambda = 633$ nm and thus a photon energy of $h\nu = 2.0$ eV, which is

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*The factor of 2 in this estimation of the grating thickness comes from the fact that in the interband regime relevant in our case the grating strength $\Delta n(z) \sim \sqrt{I(z)}$, where $I(z) = I_0 \exp(-\alpha z)$ is the total light intensity. Ref. [17] reports grating thicknesses much larger than $2/\alpha$ in KNbO$_3$, but in the measurements in Sn$_2$P$_2$S$_6$ presented here the estimation is quite good according to the results of the Bragg diffraction.*
6.3. Results and discussion

6.3.1 Bragg diffraction

Determination of the Bragg angle

The external Bragg angle \( \theta_{B,r} \) of the reading beam is commonly calculated by

\[
\sin \theta_{B,r} = \frac{\lambda_r}{\lambda_w} \sin \theta_{B,w},
\]

if the writing beams are incident symmetrically to the sample, and \( \theta_{B,w} \) is the external incidence angle of the writing beam, \( \lambda_r \) the read-out beam wavelength and \( \lambda_w \) the writing beam wavelength. In \( \text{Sn}_2\text{P}_2\text{S}_6 \) this equality in general doesn’t hold because the indicatrix is rotated in the \( xz \)-plane and therefore no main axes are perpendicular to

Figure 6.1: Experimental setup and crystal orientation for longitudinal Bragg diffraction measurements. The grating is written by two recording beams at 514 nm or 488 nm incident symmetrically with respect to the sample surface. The read-out beam at 633 nm is here on the left side of the writing beam, later we refer to this configuration as "read-out from the left side". "Read-out from the right side" means that the read out beam is on the right side of the right writing beam, according to the crystal orientation indicated on the scheme.

smaller than the band-gap energy in \( \text{Sn}_2\text{P}_2\text{S}_6 \) (2.3 eV). Therefore it is expected not to influence the interband grating. An acousto-optical modulator with a rise time of less than 0.5 \( \mu \)s was used to turn the recording beam on and off. After the crystal the diffracted beam power was measured with a photodiode.

For the two-wave mixing experiment we used the same setup as the Bragg diffraction experiment without the read-out beam and introduced a filter (1%) to weaken one of the writing beams. The weak beam is called the signal beam, the strong one the pump beam. The bulk crystal was exchanged with a thin \( \text{Sn}_2\text{P}_2\text{S}_6 \) plate of 45 \( \mu \)m thickness glued on a quartz substrate. After the sample we focused the beam on the photodiode, for collecting all the light passing through the absorbing thin plate.

6.3 Results and discussion
the crystal surface. Additionally this rotation changes with the wavelength ($\alpha_{\text{ind}}^{514\text{nm}} = 39.9^\circ$, $\alpha_{\text{ind}}^{633\text{nm}} = 43.3^\circ$) [32]. We choose $p$-polarised read-out beams, since the effective electro-optical coefficient is then near to $r_{111}^T$, which is the largest coefficient in this material [44]. This implies, however, that the rotation of the indicatrix has to be taken into account in every measurement, as explained in the following.

Let us first consider the case where also the two writing beams are polarised in the plane of the incidence. In this case the two writing beams have different refractive indices in the crystal. Because of this the grating fringes are not perpendicular to the surface of the crystal. This shifts the Bragg angle, and the direction of this shift is determined by the direction of the optical indicatrix with respect to the direction of the incident beams.

In the second case the writing beams are $s$-polarised. In this case both writing beams have the same refractive index and the grating is perpendicular to the surface. However, there will be still a shift of the Bragg angle with respect to (6.1), due to the $p$-polarised read-out beam, for which the refractive index will be different if coming from the left or from the right side of the writing beams.

![Figure 6.2: Diffraction efficiency $\eta$ as a function of the read-out angle and the phase-mismatch $\Delta k$. The left figure was read out from the left side of the writing beam, the right one from the right side (see Fig. 6.1). All the beams, the writing and the read out beams, were $p$-polarised. The measured diffraction efficiency has been approximated with the theoretical dependence obtained for phase-only transmission gratings [15]:

$$\eta = \frac{\sin^2 \sqrt{\nu^2 + \xi^2}}{(1 + \xi^2/\nu^2)} e^{-\alpha d},$$

(6.2)
with

\[ \xi^2 = \frac{\Delta k_r^2}{4} d^2, \]  

(6.3)

and

\[ \nu^2 = \left( \frac{\pi \Delta n \tilde{d}}{\lambda \sqrt{\cos(\theta_s) \cos(\theta_p)}} \right)^2, \]

(6.4)

where \( d \) is the thickness of the crystal, \( \tilde{d} \) the thickness of the grating, \( \theta_s \) the internal angle of the signal wave, \( \theta_p \) the internal angle of the pump wave, \( \Delta k_r \) the phase mismatch and \( \Delta n \) the effective refractive index change. This measurement has also been performed for \( s \)-polarised writing beams at \( \lambda = 514 \text{ nm} \) and \( \lambda = 488 \text{ nm} \). In Table 6.1 the values for the external Bragg angles calculated from the known refractive indices \(^{32}\) and the measured values are shown. The calculation of the Bragg angle is very sensitive to the values of the refractive indices, which were extrapolated from Sellmeier parameters obtained from data (\( \lambda = 550 - 2300 \text{ nm} \)) outside the absorption regime. Still the calculated and the measured angles match very well. This indicates also that the refractive indices can be extrapolated very accurately with a Sellmeier formula \(^{32}\) to lower wavelengths until at least 488 nm. The error for the refractive indices used to calculate the bragg angles is 0.01, resulting from the error in the determination of the bragg angle of 0.4°.

While the direction of the \(+x\)-axis can be easily determined by the direction of the polar axis, the direction of the \(+z\)-axis is more difficult to determine \(^{32}\). The direction of the shift of the Bragg angle from (6.1) can be used to determine the direction of the \(+z\)-axis with respect to the entrance surface. The resulting \(+z\)-axis is shown in Fig. 6.3 and corresponds to the direction presented in \(^{32}\).

![Figure 6.3: The orientation of the indicatrix, \(x\)- and \(z\)-axis as determined from the Bragg diffraction measurements. The \(z\)-axis is pointing into the crystal. \(k_{1,\text{air}}\) and \(k_{2,\text{air}}\) are the incident writing wave vectors, \(k_1\) and \(k_2\) the Wave vectors in the crystal, \(K\) the grating vector and \(\alpha_{\text{ind}}\) the rotation of the indicatrix.](image-url)
Table 6.1: Measured external Bragg angles compared to the Bragg angles calculated with taking into account the rotation of the indicatrix and without rotation (Eq. 6.1).

<table>
<thead>
<tr>
<th>$\lambda$ [nm]</th>
<th>Writing pol.</th>
<th>$\Theta_B$ $^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>calc. with (6.1)</td>
<td>calculated</td>
</tr>
<tr>
<td>514 (left side)</td>
<td>$p$</td>
<td>19.6</td>
</tr>
<tr>
<td>514 (right side)</td>
<td>$p$</td>
<td>-19.6</td>
</tr>
<tr>
<td>514</td>
<td>$s$</td>
<td>19.6</td>
</tr>
<tr>
<td>488</td>
<td>$s$</td>
<td>20.8</td>
</tr>
</tbody>
</table>

Intensity dependence

The photoconductivity measurements in our sample show that purely interband regime is reached for intensities above 1 mW/cm$^2$ at 488 nm and 10 mW/cm$^2$ at 514 nm. Therefore we are in the purely interband regime for all measurements in this paper, without considering a considerable contribution of the trap grating, that might be formed deeper inside the crystal, as observed previously in KNbO$_3$ [17] and LiTaO$_3$ [101].

The dependence of the Bragg diffraction efficiency on the intensity of the writing beam was studied with both $p$- and $s$-polarised writing beams and at the wavelengths of 488 nm and 514 nm. The intensity of the writing beams was changed with a filter in front of the crystal and the intensity of the read-out beam was $I_{\text{HeNe}} = 130$ mW/cm$^2$.

The diffraction efficiency is defined as the ratio between the diffracted and the incident light intensities. Fig. 6.4 shows the square root of the diffraction efficiency as a function of the intensity at 488 nm for the $s$-polarisation. This relation can be approximated by [17]

$$\sqrt{\eta} \propto \frac{\Delta n}{\alpha} \ln \left( \frac{I_0}{I_{\text{ref}}} \right),$$  \hspace{1cm} (6.5)

where $\Delta n$ is the average amplitude of the refractive index change, $\alpha$ is the absorption constant at the wavelength of the writing beams, $I_0$ is the total incident writing intensity, and $I_{\text{ref}}$ is a reference intensity needed for normalisation. This behaviour is expected if we assume that increasing the writing intensity increases the effective thickness of the grating and that the depth dependence of the grating is a step function. This depth dependence was shown to describe the experimental results in KNbO$_3$ better than an exponential decrease [17]. The straight line in Fig. 6.4 is a good indicator that we are in the interband regime. Additionally, note that we can observe only one regime and not two different ones as in LiTaO$_3$ [101].

Dynamics of the grating build up

The dynamics of the diffraction efficiency cannot be explained with a simple model, because the intensity of the writing beam is exponentially decreasing with the depth inside the crystal. For the build up of the holographic grating this means that the
6.3. Results and discussion

Figure 6.4: Dependence of the square root of the diffraction efficiency on the writing light intensity at 488 nm. The line represents the best fit according to relation (6.5). The writing beams are $s$-polarised, the read out beam $p$-polarised. Grating spacing $\Lambda = 0.9 \, \mu m$.

Figure 6.5: The build-up of the grating for 514 nm and all beams $p$-polarized for two different writing intensities. The two time components are found to be $\tau_1 = 75 \, \mu s$ and $\tau_2 = 140 \, \mu s$ for the higher intensity and $\tau_1 = 85 \, \mu s$ and $\tau_2 = 230 \, \mu s$ for the lower intensity.
build up time, the amplitude and the phase of the grating will depend on the depth. The diffracted beam at the back side of the crystal is formed by the coherent sum of all the amplitudes of the diffracted light at different depths. The build-up was modeled with a semi-heuristic double exponential function of the form

$$\eta = \left[ \sqrt{\eta_1 (1 - \exp(-t/\tau_1))} + \sqrt{\eta_2 (1 - \exp(-t/\tau_2))} \right]^2.$$  \hspace{1cm} (6.6)

This yields a fast ($\tau_1$) and a slow time constant ($\tau_2$). For 650 mW/cm$^2$ writing beam intensity, 130 mW/cm$^2$ read-out beam intensity, a grating spacing of $\Lambda = 1.0 \mu$m and both the read-out and the writing beams $p$-polarised, $\tau_1$ was about 75 $\mu$s and $\tau_2$ 140 $\mu$s. For 449 mW/cm$^2$ writing beam intensity $\tau_1$ was 85 $\mu$s and $\tau_2$ 230 $\mu$s, which is as expected slower then for the higher writing beam intensity.

This is very fast compared to the build-up time measured in brown Sn$_2$P$_2$S$_6$ at $\lambda = 780$ nm for 1 W/cm$^2$, which is $\tau = 50$ ms [46]. It is also more then 2 orders of magnitude faster then in LiTaO$_3$ at about the same writing intensity [101] and almost as fast as in KNbO$_3$, where build up times of about 10 $\mu$s were shown in transversal geometry at 1 W/cm$^2$ and with an external applied field as an enhancement [103].

### 6.3.2 Two-wave mixing in a thin plate

Two-wave mixing experiments were performed in a 45 $\mu$m thick Sn$_2$P$_2$S$_6$ plate, with $p$-polarised light of wavelength $\lambda = 514$ nm and an intensity of $I_0 = 650$ mW/cm$^2$. In the Bragg diffraction experiments described in section 6.3.1 we measured a grating thickness of $\tilde{d} = 32 \mu$m for a similar writing intensity. For the calculation of the two wave mixing gain we assume a constant grating of that thickness and no gain thereafter. This is justified by the fact that deeper in the crystal the grating cannot be formed while the light intensity becomes smaller than the dark intensity. The gain coefficient can be expressed as

$$\Gamma = \frac{1}{\tilde{d}} \ln \frac{I_{w/pump}}{I_{w/o\,pump}}$$  \hspace{1cm} (6.7)

and

$$\Gamma = \frac{4\pi}{\lambda \cos \theta_s} \Delta n,$$  \hspace{1cm} (6.8)

where $I_{w/pump}$ and $I_{w/o\,pump}$ are the signal beam intensities with and without the pump beam turned on, $\Delta n$ is the effective refractive index change and $\theta_s$ the internal incidence angle of the signal wave.

The result of $\Gamma = 52 \pm 8$ cm$^{-1}$ shows a very high gain and the corresponding refractive index contrast $\Delta n = (2.1 \pm 0.5) \cdot 10^{-4}$ corresponds well to the value of $\Delta n$ calculated from Bragg diffraction in section 6.3.1.

To check if the amplification of the signal we measured really comes from energy transfer from the pump wave to the signal wave and not some other effect, we rotated the plate by 180° around $y$, so that spontaneous polarisation is inverted, and we measured a weakening of the signal beam, as expected for photorefractive two-wave mixing. With this experiment we can also identify the main charge carriers at the measured interband wavelengths. If the signal beam gets amplified with the spontaneous polarisation pointing in direction of the amplified beam, the main charge
carriers are holes, since the corresponding electro-optic coefficient is positive [44]. This is the situation that occurs in Sn$_2$P$_2$S$_6$, so the main charge carrier is the same as has been identified for conventional photorefraction [44, 46]. In the case of the interband photorefraction this implies that $\mu_h > \mu_e$, where $\mu_h$ is the mobility of the holes and $\mu_e$ the mobility of the electrons [17,104].

6.4 Conclusions

We have investigated interband photorefractive effects in Sn$_2$P$_2$S$_6$ at the visible wavelengths of $\lambda = 488$ nm and $\lambda = 514$ nm. We measured the Bragg angle for the reading beam at 633 nm in longitudinal geometry for different writing beam wavelengths and polarisations. We observed a considerable shift of the Bragg angle, which was shown to be an effect of the rotation of the indicatrix with respect to the sample surface and with the wavelength. An average refractive index change of $\Delta n = (1.9 \pm 0.3) \cdot 10^{-4}$ at 514 nm was calculated out of the angle dependence of the diffraction efficiency. The temporal response of the interband effect was investigated and the build-up time constants were found to be of the order of 100 $\mu$s at a writing beam intensity of 600 mW/cm$^2$ and therefore more than two orders of magnitude faster than for the conventional photorefractive effect at 633 nm.

With a thin plate of Sn$_2$P$_2$S$_6$ we demonstrated two-wave mixing effects at a wavelength of 514 nm with a very high gain coefficient of $\Gamma = 52 \pm 8$ cm$^{-1}$ for $p$-polarised light. Because of the energy transfer in the direction of the spontaneous polarisation, we concluded that the main charge carriers at 514 nm are holes, and therefore $\mu_h > \mu_e$. We calculated the average refractive index change $\Delta n = (2.1 \pm 0.5) \cdot 10^{-4}$ at 514 nm, which corresponds remarkably well with the number calculated from Bragg diffraction.
Chapter 7

Conclusions and future prospects

7.1 Conclusions

This thesis has presented a detailed study of Sn$_2$P$_2$S$_6$ crystals in terms of its optical, electro-optical, nonlinear optical and photorefractive properties. It was shown that Sn$_2$P$_2$S$_6$ is a very interesting material with a great potential for applications in these fields.

In the first part of the thesis linear optical properties of Sn$_2$P$_2$S$_6$ are reported, which were useful for the subsequent photorefractive and nonlinear optical experiments. The Cartesian axes were defined unambiguously with respect to the crystallographic axes. The rotation of the indicatrix in the mirror plan and the three main refractive indices were precisely determined in the wavelength range 550–2300 nm. With a new technique based on the study of the diffraction angles at a photorefractive grating under interband illumination it was shown, that the extrapolations of the refractive indices and of the rotation of the indicatrix hold also in the absorption region at least down to 488 nm.

The refractive index data was used to calculate the phase-matching conditions for second harmonic generation and optical parametric oscillation. Applications in nonlinear optics use only phase-matched geometries. Phase matching for second harmonic generation was found to be possible for all wavelengths from 1680 nm up to the end of the transparency range at 8 µm. It was observed experimentally at $\lambda = 1907$ nm at the calculated location. With optical parametric oscillation it is possible to create all wavelengths between 1500 and 8 µm by pumping with a Nd:Yag laser at 1064 nm, type I phase matched and with an effective nonlinear optical coefficient $d_{\text{eff}} \approx 4 \text{ pm/V}$. The best standard materials for generating infrared wavelengths arrive only up to 5 µm, with similar efficiency. To calculate $d_{\text{eff}}$ all 10 nonlinear optical coefficients were measured at $\lambda = 1542$ nm and 1907 nm. Third harmonic generation in Sn$_2$P$_2$S$_6$ was demonstrated and two coefficients of $\chi^{(3)}$ determined. To calculate the phase-matching conditions a software program was ameliorated to cope with crystals of monoclinic symmetry.

Both conventional and interband photorefraction were studied in Sn$_2$P$_2$S$_6$. The high gain of this material in conventional photorefraction in the near infrared, allowed to demonstrate phase conjugation at wavelengths up to 980 nm. Two-wave mixing was studied at several wavelengths up to 1064 nm, which permitted to determine several material constants needed in photorefraction. Sn$_2$P$_2$S$_6$ is unique among the good
photorefractive materials to allow interband photorefractive experiments at visible light (in the blue and green spectral region). With the two main argon wavelengths both two-wave mixing experiments and diffraction experiments with a non-absorbed beam were performed. Photoconductivity experiments permitted to find a novel method to calculate the absorption in the interband spectral region, by measuring the photocurrent. This allows to circumvent many hassles in the measurement of the absorption when the light penetrate only a few microns in the material.

From photorefractive measurements it was presumed that Sn$_2$P$_2$S$_6$ has large electro-optical coefficients. The relevant ones were measured by a direct method, and resulted even larger than expected. Both the clamped and the unclamped coefficients were measured. The dispersion of the unclamped coefficients was measured and found to be very low. Also the temperature dependences of the linear and the quadratic electro-optical coefficients were investigated, and a good following of the Curie-Weiss law was recognized at the phase transition, with a peak electro-optical coefficient $r_{111}^T \approx 4500 \pm 110$ pm/V.

The large diagonal electro-optical coefficients grant good possibilities for applications, especially if combined with the equally good nonlinear optical properties. For example infrared wavelengths up to 8 $\mu$m can potentially be generated in an optical parametric oscillator, while changing or stabilizing the generated frequency by an electric field instead of rotating or heating the crystal. Another application we consider possible (see next section for a detailed explanation), is a holographic element based on the photorefractive properties of Sn$_2$P$_2$S$_6$, which cleans up laser diode beams. May the results of this work lead one step closer towards these goals!

### 7.2 Future Prospects

In this section, open questions are addressed and future experiments, that continue the research of this work, will be proposed.

**Nonlinear optical laser beam cleanup**

The aim is to obtain good quality (nearly diffraction limited and narrow bandwidth), high-power beams out of high-power semiconductor diode laser arrays. There are two main approaches to reach this: one involving an external seeder laser, and one involving a self-organized frequency selective phase conjugate external cavity. A simplified schematics showing the first approach is given in Fig. 7.1. An available narrowbandwith external cavity laser is used to seed the emission of the high-power laser diode array and force it to oscillate at the same frequency. One uses a double phase conjugate mirror between the seeder and the laser array in order to insure that the seeding light is effectively injected in each emitter portion. The spectrally cleaned laser radiation obtained in such a way will be submitted to laser beam cleanup (spatial profile) by two-wave mixing.

The above mentioned second approach involves a phase conjugate external cavity. A self-pumped phase conjugate mirror will form the end of this cavity, which should contain also a frequency selective element (grating or Fabry-Perot) in order to limit the emission bandwidth. The necessary nonlinear optical elements could be based on
Figure 7.1: Schematics of seeded configuration with double phase conjugate mirror for improving the coherence and brightness of high-power laser diode arrays.

Sn$_2$P$_2$S$_6$ or rhodium doped KNbO$_3$.

Light induced waveguides and switches

Figure 7.2: Possible schematic setup for the realization of a $m \times n$ optical interconnect. $m$ input fibers may be arbitrarily connected to $n$ output fibers via light induced channel waveguides.

Experiments are now underway in our group to dynamically induce waveguides in Sn$_2$P$_2$S$_6$, similarly as have been obtained in K NbO$_3$.

The long term aim is to realize a $m \times n$ optical interconnector, schematically drawn in Fig. 7.2. An array of $m$ optical fibers is connected to a planar waveguide electro-optic crystal. By imaging a reconfigurable waveguide structure (defined, e.g., by a spatial light modulator) onto the crystal surface, arbitrary connections to an
output array of $n$ optical fibers may be induced. Thus, any of the $m$ input fibers can be connected to any of the $n$ output fibers.

Besides $\text{Sn}_2\text{P}_2\text{S}_6$, other materials are of interest. $\text{KNbO}_3$ has already been used to make dynamically induced waveguides \cite{105} with UV light and $\text{LiTaO}_3$ may be used to create fast responding gratings in the deep UV. The advantage of $\text{Sn}_2\text{P}_2\text{S}_6$ is its relatively fast response and a narrower bandgap, which makes possible to use visible light instead of UV light.

To realize reconfigurable optical interconnects using light induced waveguides, one important next step is to confine the guided light in two dimensions instead of only one dimension. The possibilities to realize two-dimensional confinement are described in the next three sections.

**Thin plate**

The use of crystals that are only a few $\mu$m thick, thus defining a waveguiding layer by itself. One way to obtain such thin crystals is by polishing bulk samples. However, for the required thicknesses this method is very difficult to realize. A better alternative would be the epitaxial growth of thin crystal films on a suitable substrate with a lower refractive index than the one of the grown film. An example for such light induced waveguides in a thin crystal film is given in Fig. 7.3. Here, a fixed waveguide array is induced by imaging a waveguide pattern onto the crystal surface. Using proper masks, which may be fixed or reconfigurable, any desired waveguide pattern may be induced.

![Waveguide array with discrete waveguides in a thin crystal film created by top surface illumination and the interband photorefractive effect. Not shown are an externally electric field and the probe beam propagating parallel to the plane of incidence.](image)

**Ion implantation**

Also ion implantation may be used to create a waveguiding layer, as has been demonstrated, for instance, for $\text{KNbO}_3$ \cite{106,107}. Recently, in our laboratory, waveguiding layers were fabricated by ion implantation also in $\text{Sn}_2\text{P}_2\text{S}_6$. The lateral confinement is achieved by irradiation of a single crystal with low-dose MeV $\text{He}^+$ ions. This leads to
7.2. Future Prospects

the formation of a partially amorphorized layer of decreased refractive index buried a
few microns below the surface defining a barrier waveguide. Such a refractive index
profile is shown for illustration in Fig. 7.4. By using such a barrier waveguide in

combination with light induced waveguides, it should be possible to create a channel
waveguide, i.e., confined in two dimensions. However, the ion irradiation also leads
to a higher conductivity in the amorphorized layer. This complicates the impression
of a voltage over the crystal as shortages might arise easier. Special geometries, with
multiple barrier layers, that are only defined partially and do not cover the entire
crystal might solve this problem.

Light induced 3D confinement

Figure 7.4: Schematic refractive index profile (in percentage index change with
respect to the bulk index) of a implanted barrier waveguide as a function of depth.

![Graph showing refractive index profile](image)

Figure 7.5: Schematic setup for obtaining three-dimensional addressing and steer-
ing of light induced waveguides. Not shown are an externally applied electric field
and imaging optics for the controlling light.

![Diagram showing light induced 3D confinement](image)
A third approach to achieve two dimensional confinement and three-dimensional dynamic beam steering is depicted in Fig. 7.5. Here, a proper external illumination from two sides of the crystal is used in combination with an externally applied electric field in order to induce a channel with increased refractive index in the bulk of the crystal. Since the waveguides would be created in the bulk of the crystalline sample, in order to avoid an excessive absorption of the controlling light, the conventional photorefractive effect instead of the interband photorefractive effect has to be chosen. This, however, at the cost of a somewhat slower response. The channel waveguide is defined by the overlapping volume of the two perpendicular illumination layers inside the crystal. Steering of the wave guided in such a channel is possible if the external illumination is changed dynamically, for instance by using two electrically addressed spatial light modulators.
Appendix A

Method for determining the major axis of the indicatrix

We explain here in detail a novel method for determining if the major axis of the indicatrix of Sn\textsubscript{2}P\textsubscript{2}S\textsubscript{6} is rotated by $\alpha = 43.3^\circ$ or $\alpha = -46.7^\circ$ from the $x$-axis, and how it can be used to determine the $+z$ direction.

Let us analyze the beam propagation given in Fig. A.1 — where a beam enters a crystal, makes an internal reflection and subsequently exits — for the case that the indicatrix does not lie perpendicular to its surfaces, as happens in monoclinic crystals, or even in uniaxial ones if they are cut obliquely to the optical axis.

\[ \begin{align*}
\theta_{in} & \quad \theta_{in} \\
\theta_{out} & \quad \theta_{out} \\
k & \quad k_f
\end{align*} \]

Figure A.1: Schematic of an internal reflection for $p$-polarized light. The outgoing angle $\theta_{out}$ is not equal to $\theta_{in}$ if the indicatrix is rotated in the $xz$-plane. The energy propagation (Poynting) vector is not parallel to the wave vector $k$ in the crystal, but follows it proximately in the case of this figure. In part b) the normal index surface (see text) is drawn. As in Fig. 2.1, $\alpha$ is the rotation angle of the major axis of the indicatrix from the $+x$-axis, and therefore the rotation angle of the major axis of the normal index surface from the $+z$-axis.

For a polarization that sees the rotation of the indicatrix, i.e. that is in the plane of the rotation, the angle $\theta_{out}$ under which the beam leaves the crystal (exit angle), is different from the incidence angle $\theta_{in}$. The difference $\theta_{out} - \theta_{in}$ in Sn\textsubscript{2}P\textsubscript{2}S\textsubscript{6} is approximately $10^\circ$ for the orientation given in Fig. A.1 and changes sign if the crystal is rotated by $180^\circ$ around $x$ or $z$.

For understanding why the angle $\theta_{out}$ is not equal to $\theta_{in}$, we assume that the indicatrix is rotated in the $xz$-plane, the crystal is cut along the Cartesian axes, and both the beam propagation and beam polarization are in the $xz$-plane (see Fig. A.1).
Appendix A. Determination of major dielectric axis

We can then describe the indicatrix by an ellipse rotated by an angle $\alpha$ as defined in Fig. 2.1. In the $D$-space of the light polarization, the distance between the origin and each point of the indicatrix ellipse corresponds to the refractive index for that polarization direction. In the $k$-space, which is orthogonal to the $D$-space, the indicatrix rotated by 90° (which is called normal index surface [108]) is therefore the refractive index for a given $k$ direction.

For a given wavelength, energy conservation forces all the possible wave vectors $k$ to lie on this normal index surface. At the internal reflection the boundary conditions (translation symmetry in $x$ direction) imply that

$$k_i \cdot x = k_r \cdot x$$

so that $k_r$ is given by the intersection of the normal index surface with a vertical line in Fig. A.1b. One sees that the reflection angle $\theta_r$ (between the internal reflected wave vector $k_r$ and the normal to the crystal surface) is not equal to the internal incidence angle $\theta_i$, if the normal index surface (and thus the indicatrix) does not lie perpendicular to the surface.

$\theta_{out}$ is larger than $\theta_{in}$ if the major axis of the normal index surface is in the II,IV quadrants, so the one of the indicatrix in the I,III quadrants and 0° < $\alpha$ < 90°. For 90° < $\alpha$ < 180°, $\theta_{out}$ is diminished, and for certain small incidence angles ($\theta_{in}$ < 8° and $k_{in,x}$ < 0 for Sn$_2$P$_2$S$_6$) $\theta_{out}$ even becomes negative, i.e. $k_{out}$ points up in Fig. A.1.

![Figure A.2: Calculation of the variation $\theta_{out} - \theta_{in}$ versus the rotation of the indicatrix in the $xz$-plane for Sn$_2$P$_2$S$_6$ (Fig. A.1).](image)

Fig. A.2 displays $\theta_{out} - \theta_{in}$ versus the rotation angle of the indicatrix for different incidence angles $\theta_{in}$. The change in $\theta_{out}$ is maximal at $\alpha = \pm 45°$, while for the indicatrix parallel to the crystal surfaces ($\alpha = 0°$, 90°, 180°) there is no change. The dependence on $\theta_{in}$ is not as strong as on $\alpha$ and does not change the sign of $\theta_{out} - \theta_{in}$. For typical main refractive indices $n_1$ and $n_3$, the maximum value of $\theta_{out} - \theta_{in}$ is nearly constant for $\theta_{in}$ < 20° and increases for larger $\theta_{in}$ due to the sine function in the Snell’s law.

In this article we used the effect described here to determine that the major axis of the indicatrix lies in the I,III quadrants of the coordinate system determined by measuring the sign of the piezoelectric coefficients.
We also established that the spontaneous polarization $P_S$ points in the direction of $+x$. It is now possible to use the internal reflection method to find the $+z$ direction and $P_S$ for $+x$, which is much easier than the other methods, such as Laue diffraction, the measurement of the sign of the piezoelectric coefficients, the dispersion of the indicatrix rotation $\alpha$, or, for crystals where $\alpha$ is not near $m \cdot 45^\circ \ (m \in \mathbb{Z})$, just a precise measurement of $\alpha$. 
Appendix A. Determination of major dielectric axis
Appendix B

Interferometric error detection

In this appendix I report the work done on detecting differences between images in an all-optical way. I found a new method for achieving this goal without a nonlinear optical element, and implemented a working prototype. However, the flatness requirements for one critical component of the setup are stricter than commercially available, so only approximately half of the available image could be compared. For this reason and the fact that electronic computation also solves this task efficiently, we decided to stop this project. I will nevertheless describe here in detail the work performed.

The aim of this project was to compare images in an optical way, rather than through electronics. This has the advantage, that whole images ($\approx 10^6$ bits) can be processed in one step, rather than the bitwise processing of an electronic computer. Here it has to be noted, that also computer can be parallel to a certain degree. At this time 32-bit and 64-bit processors are common. This means that in one cycle simple operations like binary addition or XOR are performed for 32 or 64 bits simultaneously. In addition computers with more than one processor are available. For desktop computers one processor is still the most common, for servers 1 – 4 and for high end computers 16 to hundreds. In addition massively parallel computers can be built, or even custom electronic hardware that performs only a limited number of operations, but this in an extremely parallel way and extremely fast.

An additional advantage of optical data processing is that there are certain operations which can be added at no cost. For example, a Fourier transform can be performed by a single lens, and without requiring additional clock cycles. In electronic computers the fastest algorithms for Fourier transformation (FFT) requires a number of clock cycles in the order of $N \log N$, where $N$ is the number of pixels in the picture.

Optical processing is also particularly useful and fast, if the signal (the picture, in our case) is already in an optical form. In that case we don’t need to convert the signal to the electronic form and back, rendering unnecessary the use of spatial light modulators (SLM, converts an electronic image to an optical one) and CCD cameras, these two being the slowest components in most optical processing setups.

The amount of data processed per unit time is equal to the amount of data processed in one step times the repetition rate. For electronic computers this repetition rate is the clock rate (in the order of 1 GHz), while for an optical setup it is the repetition rate of the slowest component. In my setup we generate light pulses by a
laser, codify a page of data (for example an image) on the beams by two spatial light modulators, and detect the processed page by a CCD camera. Good repetition rates for a pulsed laser are in the order of $10^5$ Hz, for a SLM $10^4 - 10^5$ Hz and for a CCD camera $10^4 - 10^5$ Hz. Using holographic memories instead of the SLM image rates of $10^4 - 10^5$ Hz were demonstrated [98, 109]. If we take a repetition rate of $10^4$ Hz and 10^6 bits per page our optical system has a throughput of $10^{10}$ bit/s, which is in the same order of magnitude than a 64-bit 1 GHz processor.

Optical error detection consists in highlighting the areas where two pictures are different. Normally it is done so that there is no light in the output where the images are equal. Since the fastest SLMs are binary, which means its pixels are either on or off (1 or 0), the optical error detection corresponds to optical subtraction which in turn is the optical equivalent of the binary XOR operation. A XOR $B$ is true if either $A$ or $B$ is true, but not both. In other words it is true if $A$ and $B$ are different.

Figure B.1: Schematic description of the working principle of the setup. See text for a detailed explanation. Components: PBS: polarizing beam splitter, SLM: spatial light modulator, $\lambda/2$: retardation plate, POL: polarizer, M: mirror.

How the optical setup works is explained on the basis of Fig. B.1. Linearly polarized light (45$^\circ$ to the horizontal) is incident on the beamsplitter from the bottom of the picture. The long thin arrow indicates the propagation vector and the thick arrow in the unit circle the polarization of the beam. When there are two polarization arrows, then the grey one indicates the polarization for the "on" state of an SLM pixel (value 1) while the black one is for the "off" state (value 0). At the exit of the interferometer, on the right of the beam splitter, the light coming from the two arms adds coherently. The polarization of the beams modulated by the two SLMs are indicated on the right side of the beam splitter. The SLMs generate phase modulated light, SLM1 horizontally polarized and SLM2 vertically polarized. The resulting polarization for the four possible states of SLM1 and SLM2 is given in the column SLM1+2. A polarizer at $-45^\circ$ is passed through by the polarization corresponding
to the true values of SLM1 XOR SLM2, and this light is detected by a CCD camera. For the false values of XOR no light passes through the polarizer.

The description above skipped the part explaining how phase-modulated light of a desired polarization is produced by an SLM and a beam splitter. The polarizing beam splitter splits the incoming beam into its horizontal polarization (which is transmitted) and its vertical polarization (reflected to the left). The transmitted beam is reflected by a mirror, which does not affect the polarization, and passes a $\lambda/2$ plate with the optical axis at $+45^\circ$. The polarization is reflected at the optical axis of the wave plate, becoming vertical. Both SLMs thus receive vertically polarized incident light and are operated in phase modulation mode. Each pixel of the SLMs is a mirror and a $\lambda/2$ plate with a variable optical axis, which can be set to either $-22.5^\circ$ from the vertical ("off" state) or $+22.5^\circ$ from the vertical ("on" state). The polarization of the light reflected by the SLMs thus varies from pixel to pixel, and is $\pm45^\circ$ from the vertical, depending on the state of the pixel. From the SLM1 the horizontally polarized part is passing through the polarizing beam splitter. The light reflected by SLM2 first passes through the fixed $\lambda/2$ plate and then the vertically polarized part is reflected to the right by the beam splitter.

A lens or a camera objective images the two SLMs on the CCD. In order that both images are at focus, the two arms of the interferometer must have the same length ($\pm0.1\text{ mm}$). A magnifying camera objective was used in our setup, because of its better quality than a single lens and the possibility to match pixels from the SLMs to pixels of the CCD by choosing the right magnification. Since the SLM is square only a CCD with the same square aspect ratio can be pixel matched with the SLMs in both directions. We used ferroelectric SLMs (model SLM-256-A from Displaytech), which can operate at a speed of 1200 images/s and have a resolution of $256\times256$ pixels. As light source we used a He-Ne laser ($\lambda = 632.8\text{ nm}$).

![Figure B.2: Setup in true scale. The components forming the two arms of the interferometer are mounted very solidly on a 12 mm thick anticorodal plate.](image)

$^1$The modulator can work at 200 images/s, but the liquid crystal requires to be operated with the image and the reverse image exposed for the same length of time.
Appendix B. Interferometric error detection

The stability of the two arms of the interferometer is critical: When a phase shift $\Delta \phi = 0$ between the wavefronts of the two interfering images gives us the XOR of the two images, a phase shift $\Delta \phi = \lambda$ results in a NOT XOR and $\Delta \phi = \lambda/2$ in a uniform grey image. The maximal acceptable phase shift is $\Delta \phi \approx \lambda/5$, which implies a stability and flatness of the reflecting SLMs of $\lambda/10$. It also means that one has to control the position of one SLM up to $\lambda/10$ in the direction of the beam. In our setup this was achieved by a piezoelectric translator under SLM1. The stability for translations in the other two directions is less critical. Here we just have to insure that the pixels of the two SLMs overlap well in the image in the CCD. The pixels of our SLMs are squares with a side length of 18 $\mu$m, so two manual microtranslators (resolution $\approx 1 \mu$m) under SLM1 were used for displacements transversal to the beam. In order to get the correct interference on the whole image, the SLMs have to be parallel up to $\lambda/10$ over the the SLM size of 4 mm. Therefore the orientation has to be adjusted with a precision of 10-20 $\mu$rad about the two directions perpendicular to the beam. For the rotation about the beam direction an accuracy of 500 $\mu$rad is needed to match the pixels. In our setup we used an extremely precise 3-D rotator to align SLM2. The length of the interferometer arms was kept as short as possible (65 mm, see Fig. B.2), in order to enhance the stability and minimize the diffraction losses due to the aperture of the beam splitter, which was ca. 20 mm.

![Figure B.3: XOR of two pictures. Top row: theoretical result. Bottom: experimental result, as detected by the CCD camera, without any image processing.](image)

The result of the optical XOR of two pictures is displayed in Fig. B.3, below the electronically calculated, perfect XOR. One sees that the setup performs the XOR operation in a large part of the image, but as already stated at the beginning of this appendix, it is not able to deliver XOR on the complete image. This is due a loss of coherence of the interfering pictures, because of non-flat SLMs. At a distance of approximately half the diagonal of the image the contrast drops to zero ($\Delta \phi = \lambda/2$),
which means, that assuming one SLM is completely flat, the other has a flatness of around $\lambda/4$. I tried to correct the curvature of the SLM in two ways: Applying pressure at selected spots behind the SLM, and heating the central region of the SLM by illuminating it with an additional He-Ne laser. Both ways showed no effect.
Appendix B. Interferometric error detection
Appendix C

Absorption constant determination through photocurrent measurements in the interband regime

We present a new method to determine the absorption constant of crystals by measuring the photocurrent in the typical interband region (10$^{-1}$ to 10$^{3}$ cm$^{-1}$) using bulk samples. Despite not requiring the use of specially prepared thin plates or samples with sharp edges, the technique presented here reaches a good degree of precision. The validity of the method is verified in Sn$_2$P$_2$S$_6$ and near stoichiometric LiTaO$_3$ by comparing it to existing and newly measured absorption data with existing techniques. New more precise absorption data for Sn$_2$P$_2$S$_6$ in the wavelength range 488 . . . 514 nm is presented.

C.1 Introduction

Many photonics and technical devices ranging from lasers, light emitting diodes, photodetectors, electro-absorption modulators [110], to solar cells involve transitions of charges between bands, which is connected to a high light absorption. Other example of applications where light is being strongly absorbed are those related to interband dynamic holography, to which we are specially interested. Incoherent-to-coherent optical converters [97], light-induced waveguides [2], high-frame-rate joint fourier-transform correlators [98] and dynamically reconfigurable wavelength filters have been demonstrated recently based on this process [99]. The knowledge of the absorption constant is a crucial factor for these applications.

The most common technique for measuring absorption constants in the order of 10 $- 10^3$ cm$^{-1}$ involves a direct measurement of the sample transmission. This method is quite precise but requires a thin plate of a few µm thickness. If the light at the wavelength at which one wants to determine the absorption constant induces a secondary physical effect (such as a light-induced absorption at another wavelength or the formation of a holographic phase grating) it is possible to determine

$^1$The content of this chapter is going to be published in a paper by R. Mosimann as first author.
the absorption constant by a scanning method [17,111,101]. This method can be valid provided that the strength of the secondary physical effect is a monotonic function of light intensity. It can reach a precision of about 25% but very sharp edges of the crystal are needed, since the measurement involves probing light traveling only a few micrometers below the crystal surface. If the secondary effect is light-induced absorption one may refer to this technique as the induced absorption method. The absorption can also be extracted from pyroelectric measurements [112]. This method, however, needs in general a very precise electrometer, requires the prior knowledge of several material constants and is very sensitive to external influences. A different approach for measuring the absorption constant is to measure the reflectivity. It is possible either to measure the wavelength dependence at normal incidence and then evaluate the absorption with the Kramers-Kronig relations or to measure its angle dependence at a certain wavelength and evaluate with the Fresnel formulas [113,114]. Both of these methods are only well suited for very high absorption constants in the order of $10^4 - 10^5 \text{cm}^{-1}$.

The most precise way to determine the absorption constant is with a direct transmission measurement. Since the necessary thin plate is difficult to produce, using one of the mentioned methods is often much easier to apply. Here we present a new method to determine the absorption constant beyond the absorption edge by measuring the photocurrent. Compared to the other methods it does not require any special crystal preparation or the knowledge of other material constants, such as refractive indices, which are mostly not known in the absorbing regime.

In this paper we first present in section 2 a theoretical introduction to the method. In a second part we report the measurements of the photocurrent for Sn$_2$P$_2$S$_6$ at a wavelength of $\lambda = 514 \text{nm}$ and $\lambda = 488 \text{nm}$ and compare this data to a direct transmission measurement with a thin plate of 45 $\mu\text{m}$ thickness. The photocurrent was also measured for near-stoichiometric LiTaO$_3$ for $\lambda = 257 \text{nm}$ and compared to existing absorption data.

C.2 Theoretical explanation

We consider a photoconducting dielectric crystal illuminated by light of photon energy larger than the band gap. We are interested in the dependence of the electric current, generated by an applied electric field $E$, on the absorption constant if a sample is fully illuminated on one surface. Fig. C.1 shows the orientation of the crystal we consider. The light is incident on the $z$ surface and the field is applied parallel the $x$-axis of the crystal.

According to the theoretical analysis of the charge transport induced by interband illumination in photoconductive crystals [17] we can basically distinguish two different regimes. For low light intensities and considering only one impurity levels inside the band gap of the material, carriers recombine predominantly into the impurity level and the photoconductivity is directly proportional to the light intensity, similarly as for conventional off-resonant charge excitation [115]. For high light intensities the interband regime becomes dominant as also experimentally confirmed in KNbO$_3$ [17] and LiTaO$_3$ [101]. In this regime the free-hole concentration $p_0$ and the free-electron concentration $n_0$ are proportional to the square root of the light intensity $I_0$ as in
C.2. Theoretical explanation

Figure C.1: Orientation of the crystal axes. The $E$-field is applied in the $x$ direction and light of interband frequency illuminates the $z$-surface.

the limit of very high intensity $n_0 \cong p_0 \cong \sqrt{gI_0/\gamma_{dir}}$ [17], where $\gamma_{dir}$ is the band-to-band recombination rate, $g$ the photoexcitation constant, defined as $g = \alpha/h\nu$, where $h$ is the Planck constant, $\nu$ the frequency and $\alpha$ the absorption constant. The photoconductivity $\sigma$ is then

$$\sigma = e(p_0\mu_h + n_0\mu_e) \propto e(\mu_h + \mu_e) \sqrt{\frac{\alpha I_0}{\nu}} \propto \sqrt{\frac{\alpha}{\nu}} e^{-\frac{\alpha}{2}}, \quad (C.1)$$

where we assumed an exponential decrease of intensity in the beam propagation direction $z$, and where $e$ is the electron charge, $\mu_e$ the mobility of the electrons and $\mu_h$ the mobility of the holes. The integrated electric current measured by an amperemeter in series with the crystal can now be calculated as:

$$I_{el} = \int_0^E j_e(z) b \, dz = const \, E \sqrt{\frac{\alpha}{\nu}} b \int_0^E e^{-\frac{\alpha z}{2}} \, dz, \quad (C.2)$$

where $b$ is the length of the crystal in the $y$ direction, $j_e(z) = \sigma E$ is the depth-dependent electric current density for a field applied in the $x$ direction and $const$ is a proportionality factor including intrinsic material constants. By solving the last integral we get

$$I_{el} \propto \frac{1}{\sqrt{\alpha \nu}}, \quad (C.3)$$

which shows that the integrated current is inversely proportional to the absorption constant $\alpha$. This relationship is valid provided that the wavelength and intensity are such that the interband processes dominate, so that the photoconductivity increases according to the square root of intensity. If this is the case equation (C.3) can be used to determine the absorption constant by a comparative process provided that a lower absorption value (at another wavelength or for a different polarization) has been determined directly by another conventional method. The basic principle is shown in the example of Fig. [C.2] where we have assumed that the absorption for $y$-polarization is smaller than the one for $x$-polarization. As mentioned above one value of $\alpha$ (the one for which $\alpha$ is smallest, point A) still needs to be measured
directly. This wavelength is typically chosen close to the transparency range, where the absorption can be determined by standard methods with a high precision. Then the photocurrent, normalized to the same intensity \( I_{el} \propto \sqrt{I_0} \), for both wavelengths \( \lambda_1 \) and \( \lambda_2 \) and both polarizations is measured. By using the following relationships

\[
\frac{\sqrt{\alpha_{y-pol,\lambda_1} \sqrt{\nu_1}}}{\sqrt{\alpha_{x-pol,\lambda_1} \sqrt{\nu_1}}} = \frac{I_{el,x-pol,\lambda_1}}{I_{el,y-pol,\lambda_1}},
\]

\[
\frac{\sqrt{\alpha_{y-pol,\lambda_1} \sqrt{\nu_1}}}{\sqrt{\alpha_{x-pol,\lambda_2} \sqrt{\nu_2}}} = \frac{I_{el,x-pol,\lambda_2}}{I_{el,y-pol,\lambda_1}},
\]

\[
\frac{\sqrt{\alpha_{y-pol,\lambda_1} \sqrt{\nu_1}}}{\sqrt{\alpha_{y-pol,\lambda_2} \sqrt{\nu_2}}} = \frac{I_{el,y-pol,\lambda_2}}{I_{el,y-pol,\lambda_1}},
\]

one can determine the absorption for the points B–D, which are not accessible by direct transmission measurements. Note that the factor \( \sqrt{\nu_1} / \sqrt{\nu_2} \) in \( \text{(C.5)} \) and \( \text{(C.6)} \) takes into account that the same intensity \( I_0 \) does not contain the same number of photons at different wavelengths.

Figure C.2: A schematic absorption spectra showing the principle of our method. For point A the absorption is lower and can be determined for example by direct transmission measurements. By using equations \( \text{(C.4)} \)–\( \text{(C.6)} \) one can calculate the absorption for the points B–D if the photocurrent is measured at the corresponding wavelength and polarization.

### C.3 Experimental verification

To verify this method we chose two different materials. As first material we used the narrow-bandgap ferroelectric crystal Sn\(_2\)P\(_2\)S\(_6\), a promising material for fast hologram recording via interband photorefraction in the visible \(^{100}\). In this crystal optical correlation at high repetition rates was demonstrated \(^{98}\) using the wavelength 532 nm. In the interband region the absorption constant has been previously calculated using the Urbach rule \(^{116,117}\).
C.3. Experimental verification

The second material is near-stoichiometric LiTaO$_3$ (SLT), which is attractive for several electro-optical or nonlinear optical applications like nonvolatile holographic data storage [118] or frequency doubling into the UV [119] and is transparent down to $\lambda \approx 280$ nm. In SLT deep UV fast interband photorefraction has recently been demonstrated [101]. The absorption constant in this regime has been measured with the method of the induced absorption [101] and by direct measurements in this sample [120].

C.3.1 Absorption measurement for Sn$_2$P$_2$S$_6$

We first measured the absorption constants in Sn$_2$P$_2$S$_6$ using the direct transmission method. We used a thin plate of Sn$_2$P$_2$S$_6$ with dimensions $7.3 \times 8.3 \times 0.045$ mm$^3$ along the $x$, $y$ and $z$ axes. In this work we use the standard coordinate system with the $z$-axis parallel to the crystallographic $c$-axis, $y \parallel b$ normal to the mirror plane, and $x$ normal to $y$ and $z$. The thin plate was attached to a substrate of quartz with a thickness of 3 mm. The crystal was poled along the $x$-axis. The absorption constant in the interband regime was measured by the direct transmission method at four Ar-ion laser lines. In all the experiments the contribution of the reflections between the substrate and the Sn$_2$P$_2$S$_6$ plate were taken into account as well as multiple Fresnel reflections in the crystal itself. We used the recently published two-oscillator Sellmeier parameters for the refractive indices of Sn$_2$P$_2$S$_6$ [32]. The results are shown in Table C.1. Our results confirm the Urbach calculations in Ref. 116. In the Urbach measurements in Ref. 117 it seems as if the axes were defined differently, because the values would match quite well if the polarizations were exchanged.

<table>
<thead>
<tr>
<th>Wavelength [nm]</th>
<th>Absorption constant $\alpha$ [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x$-pol</td>
</tr>
<tr>
<td>514</td>
<td>490 ± 20</td>
</tr>
<tr>
<td>501</td>
<td>1450 ± 50</td>
</tr>
<tr>
<td>496</td>
<td>1730 ± 65</td>
</tr>
<tr>
<td>488</td>
<td>2600 * ± 800</td>
</tr>
</tbody>
</table>

* obtained from photocurrent measurements

The Sn$_2$P$_2$S$_6$ crystal for the photocurrent measurement had the dimensions $5.07 \times 5.38 \times 4.85$ mm$^3$ along the $x$, $y$ and $z$ axes. It was poled along the $x$-axis and had silver electrodes painted onto the $x$-surfaces. We applied an electric field between 200 and 600 V/cm parallel to the $x$-axis, which is nearly parallel to the spontaneous polarization. The sample was homogeneously illuminated with green ($\lambda = 514$ nm) or blue ($\lambda = 488$ nm) light polarized either parallel to the $x$- or $y$-axis of the crystal. We determined the photocurrent by measuring the voltage drop over a reference resistor of 125 k$\Omega$ put in series with the crystal. A multimeter with a large input impedance (1 G$\Omega$) was used for the measurement.
For increasing light intensity, as we get to the purely inteband regime, we expect the different ratios of $I_{el}$ to approach a constant value corresponding to equations (C.4)–(C.6). Fig. C.3 shows the light intensity dependence of $I_x/I_y$ at a wavelength of 488 nm. After reaching a certain intensity, enough charge carriers remain in the conduction band and the photocurrent follows the expected square root dependence on the intensity. In this regime the ratio reaches a constant value, which can be used to calculate the absorption ratio.

![Graph showing the ratio of the photocurrent of the x-polarization and the y-polarization as a function of the intensity. The wavelength is $\lambda = 488$ nm and the applied field is 600 V/cm. For high intensities a common value is reached.]

The results for $\lambda = 488$ nm and $\lambda = 514$ nm obtained from the photocurrent measurement and the ones from the direct measurement with the thin plate match quite well, as seen in Table C.2.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$\sqrt{\alpha_{x-pol, 514 \text{ nm}}}$</th>
<th>$\sqrt{\alpha_{y-pol, 514 \text{ nm}}}$</th>
<th>$\sqrt{\alpha_{x-pol, 488 \text{ nm}}}$</th>
<th>$\sqrt{\alpha_{y-pol, 488 \text{ nm}}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photocurrent</td>
<td>0.54 ± 0.08</td>
<td>0.22 ± 0.04</td>
<td>0.42 ± 0.09</td>
<td></td>
</tr>
<tr>
<td>Direct measurement</td>
<td>0.47 ± 0.02</td>
<td>0.25 ± 0.01</td>
<td>0.53 ± 0.02</td>
<td></td>
</tr>
</tbody>
</table>

The resulting absorption constants for Sn$_2$P$_2$S$_6$ from the values in Table C.2 are $\alpha_{514 \text{nm}, x-pol} = 380 \pm 120 \text{ cm}^{-1}$ and $\alpha_{488 \text{nm}, y-pol} = 2050 \pm 850 \text{ cm}^{-1}$ with the absorption constant $\alpha_{514 \text{nm}, y-pol}$ as the starting point. These values agree within the experimental error with the directly measured values in Table C.1.

For $\lambda = 488$ nm and the x-polarization the absorption coefficient could not be measured directly anymore since the absorption was too high even for the thin
C.4 Conclusions

With the relatively simple measurement of the photocurrent and known absorption data at the lower edge of the transmission region, the absorption constant can be determined within the interband region with a precision of about 35%, which is better or as good as existing methods other than thin sample light transmission. This method doesn’t need the knowledge of any other material constants. Furthermore the crystal doesn’t need any special preparation, such as a thin plate or polished sharp edges.

For Sn$_2$P$_2$S$_6$ the photocurrent measurements have been compared with data obtained with a direct measurement of the absorption in a very thin plate. These
values match quite well and confirm the reliability of the new technique. Also for near-stoichiometric LiTaO$_3$ the obtained data matches the existing values and shows the advantage compared for instance to the indirect method based on the evaluation of the photo-induced absorption.

In the form presented here, the technique can be used for any photoconductive crystal, which, illuminated by light that induces interband transitions, shows a broad regime in which the photoconductivity depends on the square root of light intensity. However, provided that all the absorbed light gives rise to photoconduction, the same method can be adapted also to materials that do not satisfy fully the above condition. This is the case if the intensity dependence of the photoconductivity exhibits a regime with a characteristic exponent (other than 1/2 or 1) over a sufficiently broad range of light intensities.
Bibliography


List of publications

Articles


Conference proceedings


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