Third column electro-optical coefficients of monoclinic Sn$_2$P$_2$S$_6$

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Abstract: All coefficients of the third-column of the unclamped electro-optic tensor of Sn$_2$P$_2$S$_6$ single crystals are determined by direct interferometric techniques. It is found that the largest coefficient $r_{113}^{T}$ for electric field parallel to the $z$-axis is $\approx 67$ pm/V at the wavelength of 633 nm and room temperature.

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1. Introduction

Tin thiohypodiphosphate (Sn$_2$P$_2$S$_6$) is a wide bandgap semiconductor ferroelectric that has received considerable interest in the last few years, specially due to its attractive properties as a fast photorefractive material with optimum response in the near infrared [1–9]. At room temperature Sn$_2$P$_2$S$_6$ belongs to the monoclinic point group $m$. Owing to this low level symmetry and the related large number of independent parameters, several of the characteristic physical, optical and nonlinear optical properties of this material have not been fully determined yet. Concerning optical properties, the refractive indices and their dispersion were characterized in [10] in the range 550-2200 nm, while the second and third order nonlinear optical properties of Sn$_2$P$_2$S$_6$ were discussed in [11]. A direct measure of the values of the coefficients of the first column of the linear electro-optic tensor was performed in [12]. These coefficients correspond to an applied electric field nearly parallel to the material’s spontaneous polarization and are expected to be the largest in Sn$_2$P$_2$S$_6$, the maximum was found for the unclamped coefficient $r_{111}^T$ with a value of 174 pm/V at room temperature and for the wavelength $\lambda = 633$ nm. No direct measurement of the electro-optic coefficients of Sn$_2$P$_2$S$_6$ for field parallel to the crystallo-physical $z$-axis were performed to date. There exist however estimations of the ratios between the coefficients of the third column and those of the first column [13]. The latter are based on the comparison of the diffraction efficiencies of photorefractive gratings in various isotropic and anisotropic diffraction geometries. However, the electro-optic response in photorefractive experiments is also strongly influenced by the fact that the space-charge electric field is periodic [14]. Therefore, the photorefractive electro-optic response is neither fully unclamped nor fully clamped and the degree of clamping depends on the grating orientation and on various additional material parameters involving elasticity, piezoelectricity and elasto-optics [14, 15]. As a consequence, without the knowledge of all the numerous remaining parameters, thorough photorefractive investigations such as in [13] cannot lead alone to the determination of the the unclamped electro-optic coefficients, which require therefore a direct measurement.

In the present work we provide a direct determination of the values for the unclamped electro-optic coefficients of Sn$_2$P$_2$S$_6$ for an applied field parallel to the $z$-axis of the crystal, corresponding to the third column of the electro-optic tensor. The measurements are performed using a Mach-Zehnder type interferometric technique for light propagation along the polar $x$-axis or the $y$-axis of the crystals as well as with the one-beam Senarmont technique. It is confirmed that the third column coefficients are generally smaller than those obtained for field in $x$ direction (first column). Nevertheless, a sizable response is observed also for this field direction, which is nearly perpendicular to the spontaneous polarization. The corresponding largest coefficient
is $r^T_{113} = 67 \pm 7$ pm/V, roughly three times smaller than the overall largest coefficient $r^T_{111}$.

2. Crystal samples and experimental approach

Being Sn$_2$P$_2$S$_6$ of monoclinic symmetry, care must be payed to the coordinate system $xyz$ in which the electro-optic and other tensors are defined. In this paper we stick to the choice discussed in detail in [4], which complies with the one in most earlier literature. It has to be noted that the present choice differs from the one in [12] and [10] by the convention for the sign of the piezoelectric coefficient $d_{333}$, which is negative in the present case. The consequence is a different relative orientation of the positive $x$ and $z$-axes, so that the major axis of the oblique optical indicatrix (associated to the largest refractive index $n_{3}$) is in the second and fourth quadrant of the $xz$-plane (see [4]) instead as the first and third quadrants like in Refs. [10, 12]. For field along the $x$ axis the diagonal elements of the electro-optic tensor (of the type $r_{ii}$) are unaffected, while the nondiagonal element $r_{133}$ switches sign between the two choices. On the other hand, for electric field parallel to the $z$-axis the diagonal elements $r_{ii}$ are switching sign upon inversion of the convention for the positive $z$-axis, while the non-diagonal element $r_{333}$ is unaffected. Therefore, for both the first and the third column coefficients, the relative sign between the diagonal and non diagonal elements depends on the choice for the axes convention.

Our experiments were performed using three nominally undoped Sn$_2$P$_2$S$_6$ samples grown at the University of Uzhgorod. Their dimensions are $5.7 \times 4.5 \times 5.0$ mm$^3$ (SPS1), $7.8 \times 10.5 \times 6.0$ mm$^3$ (SPS2) and $3.8 \times 4.6 \times 4.2$ mm$^3$ (SPS3) along $x$, $y$ and $z$ axes, respectively. They were electrically poled by heating above the phase transition temperature $T_C$ at 338 K and slowly cooling them down to room temperature under an electric field of about 1 kV/cm applied along the $x$-axis, which is near to the spontaneous polarization direction. Sample SPS1 was polished on the $x$-surfaces to permit light propagation along the polar $x$-axis, sample SPS2 was polished on the surfaces perpendicular to the monoclinic $y$-axis, which is perpendicular to the crystallographic mirror plane. Sample SPS3 was polished on both $x$ and $y$ surfaces. In all our electro-optic measurements the electric field was applied along the $z$-axis through graphite electrodes on the $z$ surfaces. As discussed below, the above sample combination allowed to perform each type of electro-optic measurements independently on two different samples.

The set-up used to determine the various electro-optic tensor elements is depicted schematically on Fig. 1. For the interferometric measurement of the electro-optic coefficients a beam-splitter devides the beam from a He-Ne laser ($\lambda = 633$ nm) into two arms. The beam in the lower signal arm goes through the Sn$_2$P$_2$S$_6$ crystal which is subjected to an ac-voltage of up to 10 V amplitude and frequency of few kHz. The applied voltage has no bias. By choosing the polarization of the signal beam parallel to an eigenpolarization of the crystal, the applied voltage induces a pure phase modulation on the signal beam through the electro-optic effect. The polarization of the beam in the reference arm is put parallel to the one of the signal wave by means of the upper polarizer, while its absolute phase can be set by moving the piezo-mirror, which permits so to adjust the working point for the measurement. Signal and reference wave recombine at the second beam-splitter and go through an analyzer which is put parallel to both polarizers. A small section of the resulting interference fringe is then detected by the silicon photodetector and analyzed by means of an oscilloscope and/or a lock-in analyzer.

In the interferometric set-up the detected intensity is $I(\Delta \phi) = I_1 + I_2 + 2\sqrt{I_1 I_2} \cos \Delta \phi$, where $\Delta \phi = \Delta \phi_0 + \Delta \phi_\ell$ and $I_1$ and $I_2$ are the intensities coming from each of the two arms. Here $\Delta \phi_0$ is the average phase shift between the waves in the two arms of the Mach-Zehnder interferometer and is adjusted by means of the piezo-mirror, while $\Delta \phi_\ell$ is the electrically induced phase shift. The latter is given by

$$\Delta \phi_\ell = \frac{2\pi}{\lambda} L \Delta n + \frac{2\pi}{\lambda} (n-1) \Delta L = \frac{2\pi L}{\lambda} \left[ -\frac{n^3}{2} r_{eff} + (n-1) d_{eff} \right] E$$

(1)
where $E$ is the applied electric field to the measuring crystal, $L$ is the length of the crystal, $\lambda$ is the vacuum wavelength and $n$ is the refractive index seen by the eigenwave propagating in the crystal. $r_{\text{eff}}$ is the effective electro-optical coefficient active in the particular measuring geometry and is either equal to one of the coefficients of the electro-optic tensor or to a linear combination of them. Finally, $d_{\text{eff}}$ is the effective piezoelectric coefficient causing a crystal length variation in the given measuring geometry. The second term on the right-hand-side of Eq. (1) gives the contribution of the piezoelectric length variation to the phase shift. This contribution is rather small, for equal values of $r_{\text{eff}}$ and $d_{\text{eff}}$ the electro-optic contribution to the phase shift is by a factor $n^3/[2(n-1)]$ larger than the piezoelectric one, this factor equals about 14 in our case. Therefore, by considering the known absolute value of the piezoelectric constants of the crystal [16], it is found that the corrections due to the second term in Eq. (1) are small and fall well within the experimental error given below for the coefficients $r_{223}$, $r_{333}$, $r_{\text{fast}}$ and $r_{\text{slow}}$, which are calculated using the electro-optic phase shift alone. By putting the average phase shift $\Delta \phi_0 = \pi/2$ (linear detection working point) the absolute value of the effective electro-optic coefficient $r_{\text{eff}}$ in Eq. (1) can then be determined as

$$r_{\text{eff}} = \frac{2\lambda d}{\pi Ln^3} \frac{\Delta I_E}{\Delta I_{\text{max}} \Delta V},$$

where $d$ is the inter-electrode distance, $\Delta I_E$ is the peak-to-peak amplitude of the modulated detected signal, $\Delta V$ is the corresponding amplitude of the modulated voltage applied to the crystal, and $\Delta I_{\text{max}} = 4\sqrt{I_1 I_2}$ is the peak-to-peak contrast of the intensity of the interference fringes.

Some measurements were performed also by removing the upper reference arm and using the lower arm in a Senarmont-type configuration which measures the birefringence induced by the applied electric field [17, 18]. In this case both beam splitters are removed and a quarter-wave plate placed between the crystal and the analyzer allows to determine the induced birefrin-
gence (resulting from a combination of electro-optic tensor elements) by means of an intensity measurement after the analyzer. The input polarization to the measuring crystal is at 45 degrees to the two oblique main axes of the indicatrix. If the quarter-wave plate has its axis parallel to the input polarization to the electro-optic crystal, the light leaving the quarter-wave plate is linearly polarized but with its polarization rotated by half the retardation phase angle $\Delta \Phi$ between the two perpendicular eigenwaves in the crystal. For an analyzer oriented at an angle $\beta$ to the input polarization the transfer function of such a set-up is therefore of the kind $T = \cos^2(\beta - \Delta \Phi/2)$ and the effective electro-optic coefficient is determined by an expression of the kind of Eq. (2) by placing the analyzer at the half transmission point.

3. Electro-optic effect and experiments

In our coordinate system $(x,y,z) = (1,2,3)$ the third-rank electro-optic tensor of Sn$_2$P$_2$S$_6$ 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)

with the inherent symmetry ($r_{ijk} = r_{jik}$). We are interested in the coefficients of the third column in the above tensor. After applying an electric field $E = (0,0,E)$ along the $z$-direction the inverse dielectric tensor at optical frequencies, $(1/n^2)_{ij} \equiv (1/e)_{ij}$, is modified as

$$ \left(\frac{1}{n^2}\right)_{ij}(E) = \begin{pmatrix} (1/n^2)_{11} & 0 & (1/n^2)_{13} \\ 0 & (1/n^2)_{22} & 0 \\ (1/n^2)_{13} & 0 & (1/n^2)_{33} \end{pmatrix} + \begin{pmatrix} r_{113}E & 0 & r_{133}E \\ 0 & r_{223}E & 0 \\ r_{133}E & 0 & r_{333}E \end{pmatrix}. $$

(4)

the outer-diagonal elements $(1/n^2)_{13}$ in the unperturbed tensor on the right-hand side account for the fact that the main axes of the index ellipsoid (optical indicatrix) are rotated (in the $xz$-plane) with respect to the crystallographic axes.

Figure 2 shows the crystal configurations for the measurement of the electro-optic coefficients $r_{223}$, $r_{333}$, $r_{fast}$ and $r_{slow}$, for which the propagating wave is an eigenwave of the crystal. As will be discussed in more detail later, $r_{fast}$ is associated to the fast eigenwave for light propagation in $y$ direction, while $r_{slow}$ is associated to the corresponding slow eigenwave. Each configuration was tested in two different crystal samples. Sample SPS3 was used in all configurations, while sample SPS1 was used for the configurations of Fig. 2(A) and Fig. 2(B) only, and sample SPS2 was used for the configurations of Fig. 2(C) and Fig. 2(D) only.

Since the measurement give direct information only on the sign of the product $rE_3$, it is important to know the correct positive orientation of the axes $x$, $y$ and $z$ in order to assign the sign to the electro-optic coefficients. A combination of different techniques was used for this purpose. First, the positive direction of the $y$ axis can be determined by observing the rotation direction of the optical indicatrix upon increasing temperature, which is counterclockwise around the positive $y$ axis [19]. Second, in the samples showing sufficient photorefractive effect the positive direction of the $x$-axis can be determined by observing the main direction of beam fanning for a $p$-polarized wave propagating along the $z$ direction. Finally, the orientation of the two oblique main axes of the indicatrix (fast axis corresponding to the refractive index $n_1$ and slow axis corresponding to $n_3$) can be determined by observing the non specular angle of reflection on the $z$ crystal surface of a $p$-polarized wave propagating in the $xz$-plane of the crystal. This method is described in the appendix of [10]. A combination of the above techniques prior
to the electro-optic measurements allowed to determine the crystal axes orientations depicted on Fig. 2.

Fig. 2. Crystal configurations for the interferometric measurement of the third-column electro-optic coefficients of \( \text{Sn}_2\text{P}_2\text{S}_6 \). A) Measurement of \( r_{223} \); B) \( r_{333} \); C) \( r_{\text{slow}} \); D) \( r_{\text{fast}} \). The thick double arrow give the polarization direction of the corresponding eigenwave. For \( \text{Sn}_2\text{P}_2\text{S}_6 \) the angle \( \alpha \) in C) and D) is \( \alpha \approx 43.3 \) deg for \( \lambda = 633 \) nm and room temperature. The positive direction of the applied electric field \( E_3 \) is always towards the bottom (+\( \hat{z} \)).

The electrically induced change of the scalar inverse refractive index squared for the eigenwaves of the configurations of Fig. 2 is obtained as

\[
\Delta \left( \frac{1}{n^2} \right) = \Delta \left( \frac{1}{n^2} \right)_{ij} \hat{d}_i \hat{d}_j. \tag{5}
\]

Here \( \hat{d} \) is the unit vector along the polarization direction of the eigenwave and \( \Delta (1/n^2)_{ij} \) is the second term on the right-hand side of Eq. (4). The Einstein summation rule over equal indices is used in the above tensor contraction. With \( \Delta n = -n^4 \Delta (1/n^2)/2 \) the above expression gives immediately the refractive index change \( \Delta n \) in Eq. (1). The configurations of Fig. 2(A) and Fig. 2(B) deliver then directly the electro-optic coefficients \( r_{223} \) and \( r_{333} \), respectively. For the configuration of Fig. 2(C) the measured effective electro-optic coefficient according to Eq. (2) corresponds to the slow eigenwave (refractive index \( n_3 \)) and is found with \( \hat{d} = (-\cos \alpha, 0, \sin \alpha) \) in Eq. (5). This delivers

\[
r_{\text{slow}} = r_{113} \cos^2 \alpha + r_{333} \sin^2 \alpha - 2r_{133} \sin \alpha \cos \alpha \approx \frac{1}{2} (r_{113} + r_{333}) - r_{133}, \tag{6}
\]
where the last approximated expression on the right-hand side is obtained by substituting the polarization angle $\alpha = 43.3 \pm 0.4 \ \text{deg}$ [10] by the value of 45 deg. Similarly, the effective electro-optic coefficient measured for the fast eigenwave is

$$
\Delta n \equiv -\frac{n_3}{2} r_c E_3 = - \left( \frac{n_3}{2} r_{\text{fast}} - \frac{n_3}{2} r_{\text{slow}} \right) E_3,
$$

(10)

where $r_c$ is the effective electro-optic coefficient determined in this configuration and $\hat{n}$ is an arbitrary value for the reference refractive index that can be established freely among one of the known refractive indices of the sample. If we choose $\hat{n} = n_z$ (see [10]) the expression for $r_c$ becomes

$$
r_c = r_{113} \frac{n_1^2 \sin^2 \alpha - n_3^2 \cos^2 \alpha}{n_z^2} + r_{333} \frac{n_1^2 \cos^2 \alpha - n_3^2 \sin^2 \alpha}{n_z^2} + r_{133} \frac{n_1^3 + n_3^3}{n_z^3} \sin 2\alpha.
$$

(11)

Even though this expression appears complicated, it can be strongly simplified if one considers that $n_1 \approx n_3 \approx n_z$ and one takes $\alpha = 45 \ \text{deg}$. In this case one gets $r_c \approx 2 r_{133}$, therefore the effective coefficient $r_c$ is expected to be roughly twice the non diagonal electro-optic coefficient $r_{133}$.

We present now the results obtained for the values of the different elements of third column of the unclamped electro-optic tensor. Our experiments have shown that all the directly measured coefficients $r_{223}$, $r_{333}$, $r_{\text{fast}}$ and $r_{\text{slow}}$ have the same sign and are positive. The corresponding values for the wavelength of 633 nm are given in Table 1 together with measured value for the effective coefficient $r_c$ defined in Eqs. (10) and (11). The value $r_c$ (meas.) results from the measurement in the Senarmont configuration while $r_c$ (calc.) is calculated from the measured $r_{\text{fast}}$ and $r_{\text{slow}}$ using Eq. (10) or Eq. (11) with $\alpha = 43.3 \ \text{deg}$. The two approaches are found to give a good agreement. The values of $r_{113}$ and $r_{133}$ in Table 1 are calculated with Eqs. (8) and (9) from the experimental data for $r_{\text{fast}}$, $r_{\text{slow}}$ and $r_{333}$. Note that the scattering of the measured data among our investigated samples and measuring positions lies within the given experimental error.

For comparison Table 1 contains also the unclamped electro-optic coefficients for electric field in $x$-direction from [12]. Note that the coefficient $r_{131}$ is reported in Table 1 with the opposite sign with respect to [12]. This is a consequence of the different convention for the positive orientation of the crystallographic axes taken in this work with respect to [12], as discussed in Section 2 and in [4].
Table 1. Unclamped Electro-Optical Coefficients of Sn$_2$P$_2$S$_6$ at $\lambda = 633$ nm

| Coefficient | Value [pm/V] | Reference |
|-------------|--------------|-----------|
| $r_{223}$   | +21.7 ± 3.8  | This work |
| $r_{333}$   | +24.7 ± 3.7  | This work |
| $r_{fast}$  | +58.9 ± 5.1  | This work |
| $r_{slow}$  | +32.6 ± 2.3  | This work |
| $r_c$ (meas.) | +26.5 ± 1.5 | This work |
| $r_{113}$   | -67 ± 7      | This work |
| $r_{133}$   | +14.4 ± 3.0  | This work |
| $r_c$ (calc.) | +23.1 ± 5.6 | This work |
| $r_{111}$   | +174 ± 10    | [12]      |
| $r_{221}$   | +92 ± 8      | [12]      |
| $r_{331}$   | +140 ± 18    | [12]      |
| $r_{131}$   | +25 ± 15     | [12]      |

4. Discussion and conclusions

It is seen in Table 1 that the third-column electro-optic coefficient of Sn$_2$P$_2$S$_6$ have a sizable value, the largest one ($r_{113} \approx 67$ pm/V) correspond to more than twice the electro-optic response of the standard electro-optic material LiNbO$_3$. Nevertheless this maximum value is still about a factor of three smaller than the largest first-column electro-optic coefficient ($r_{111}$), confirming that a field in the x-direction, which is near to the crystal spontaneous polarization, delivers the largest response.

As mentioned in the introduction, estimations for the ratios of electro-optic coefficients were given in [13] on the base of photorefractive anisotropic and isotropic Bragg diffraction investigations in different configurations. Even though the two kinds of measurement are not directly comparable, we list in Table 2 the ratios of coefficients obtained from direct electro-optic measurements and those estimated in [13]. In general these ratios are not expected to be identical in the two cases due to the fact that, as discussed in Section 1, the photorefractive estimation (associated to periodic electric fields) is related to effective coefficients, which can differ significantly from the unclamped coefficients measured here (associated to a homogeneous electric field). Nevertheless Table 2 shows that, with the exception of the ratio $r_{133}/r_{333}$ and in less extent of $r_{223}/r_{221}$, the general trend for the relative magnitude of the tensor elements is maintained in the two cases. These results may suggest that in Sn$_2$P$_2$S$_6$, unlike in BaTiO$_3$ or KNbO$_3$ [20], the influence of the mechanical coupling associated to the periodic field is not such as to revolutionize too strongly the ordering of the electro-optic coefficient magnitude. Note again that in Table 2 we have reversed the signs of the ratios $r_{133}/r_{333}$ and $r_{131}/r_{111}$ with respect to [13]. This is because the convention taken in [13] for the positive direction of the z axis was the same as in [12], but was opposite as the one taken in this work and in [4].

In conclusions, we have determined directly the unclamped electro-optic coefficients of Sn$_2$P$_2$S$_6$ for electric field parallel to the crystallographic z axis, which is nearly perpendicular to the material’s spontaneous polarization. The measurements were performed by means of a Mach-Zehnder interferometer as well as in the one-beam Senarmont type configuration. The largest electro-optic coefficient for field in z- direction is $r_{113} \approx 67$ pm/V. Despite being smaller than all the diagonal coefficients for field in x-direction, this value is more than twice
### Table 2. Ratio of Electro-Optic Coefficients from Direct Electro-Optic Measurements and Estimated from Photorefractive Diffraction Experiments

| Coefficient ratio | Direct electro-optic measurement (This work and [12]) | Photorefractive measurement ([13]) |
|-------------------|-------------------------------------------------------|-----------------------------------|
| $r_{113}/r_{333}$ | 2.7 ± 0.7                                              | 1.7 ± 0.6                         |
| $r_{223}/r_{333}$ | 0.87 ± 0.28                                            | 0.69 ± 0.03                       |
| $r_{133}/r_{333}$ | 0.58 ± 0.20                                            | 1.8 ± 0.4                         |
| $r_{223}/r_{221}$ | 0.24 ± 0.06                                            | 0.14 ± 0.02                       |
| $r_{331}/r_{111}$ | 0.80 ± 0.15                                            | 0.87 ± 0.02                       |
| $r_{221}/r_{111}$ | 0.53 ± 0.08                                            | 0.53 ± 0.02                       |
| $r_{131}/r_{111}$ | 0.14 ± 0.09                                            | 0.12 ± 0.07                       |

as large than to the one of the largest coefficient ($r_{333}$) of the standard electro-optic material LiNbO$_3$. Thus, the present study confirm the interest of Sn$_2$P$_2$S$_6$ for any electro-optic and/or photorefractive configuration in the $xz$-plane of the material.

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