Piezooptic Coefficients and Acoustic Wave Velocities in $Sn_2P_2S_6$ Crystals

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Abstract

Piezooptic coefficients of $Sn_2P_2S_6$ crystals are experimentally determined for λ=623.8 nm and T= 293 K with the aid of interferometric technique. The components of the elastic stiffness tensor for these crystals are calculated on the basis of studies for the acoustic wave velocities. It is shown that acoustooptic figure of merit can achieve extremely high values for $Sn_2P_2S_6$ crystals ($M_2 - 2\times10^{-12}s^3/kg^2$).

Key words: $Sn_2P_2S_6$ crystals, piezooptic coefficients, ultrasonic velocities, semiconductors, ferroelectrics

Introduction

$Sn_2P_2S_6$ crystals belong to semiconductor-ferroelectric materials with nontrivial properties that make them attractive for various practical applications, particularly in optoelectronics. Though electro-, piezo- and magnetooptic coefficients represent the most important parameters of any material, which are crucial in considering the very possibility of its utilization in devices for controlling optical radiation, those coefficients are still not completely studied for $Sn_2P_2S_6$ crystals. Moreover, the above compound represents a wide family of semiconductors $Sn_{2y}Pb_{2(1-y)}P_2S_{6x}Se_{6(1-x)}$ (see, e.g., [1]), whose parameters may be efficiently governed when substituting relevant chemical components. Specifically, such basic properties as the refractive indices and the bandgap energy have proven to be sensitive to this substitution. This could make the mentioned crystal family the most attractive materials for the integrated optics, especially if one takes the expected possibility for growing epitaxial layers into consideration.

$Sn_2P_2S_6$ crystals manifest a proper second-order paraelectric-to-ferroelectric phase transition at 337 K with the change of point symmetry group $2/mFm$, while $Sn_2P_2Se_6$ is characterized with the phase transition into a proper ferroelectric phase with the symmetry m (T_c=193 K). These crystals are semiconductors, with the bandgap energy E_g=1.7 eV at T=293 K [2].

The relevant studies of optical effects in $Sn_2P_2S_6$ crystals induced by different external fields have been originated from the estimations of electrooptic (EO) coefficients on the basis of temperature variations of optical refraction caused by spontaneous electric polarization [3]. Later on, temperature dependence of the effective EO coefficient has been studied in the work [4], where high enough EO figure of merit of these crystals has been detected for the first time. Finally, a detailed study of EO effect in $Sn_2P_2S_6$ crystals has been performed in [5]. It

has been shown that the EO coefficient achieves extremely high values: $r_{11}=1.74\times10^{-10}$ *m/V* at the room temperature and $\lambda=632.8$ *nm*, while at the phase transition temperature it becomes still larger (4.5×10^{-9} *m/V*). One can expect that such the high values of EO coefficients in $Sn_2P_2S_6$ crystals could be caused by a secondary piezo-optic (PO) effect due to piezoelectric effect. Nevertheless, as far as we know, the EO data for $Sn_2P_2S_6$ [3–5] are almost the only available in the literature for $Sn_{2y}Pb_{2(1-y)}P_2S_{6x}Se_{6(1-x)}$ family, in what the effects of optical birefringence induced by external fields are concerned. At least we can only remind the results for the effective PO coefficient of $Sn_2P_2S_6$ crystals presented in the study [6], which has confirmed that the coefficient is indeed high. The PO coefficient reported in [1] is also high ($\pi_{66}=5\times10^{-11}$ *m²/N*) and the same is also true of the corresponding acoustooptic (AO) figure of merit estimated in this work ($M_2=540\times10^{-15}$ *s³/kg*). It is worthwhile that the PO (or elastooptic) coefficients and the ultrasonic wave velocities represent the data necessary for predicting practical applicability of material in acoustooptics.

Following from the mentioned above, we have undertaken detailed studies for the PO, elastooptic, acoustic and AO effects in the crystals of $Sn_{2y}Pb_{2(1-y)}P_2S_{6x}Se_{6(1-x)}$ family. We begin from the PO coefficients and the ultrasonic velocities for $Sn_2P_2S_6$ crystals, which are presented in this work.

Experimental procedure and results

Synthesis of $Sn_2P_2S_6$ compounds and the growth of single crystals have been performed on the basis of chemical vapour transport reactions [7]. In order to implement PO experiments, after X-ray orientation procedure we have prepared a sample with the shape of parallelepiped ($5.43\times5.08\times4.13$ *mm³*) and the faces perpendicular to principal crystallographic directions for the light propagation and the application of compressive mechanical stresses. All the

experimental measurements have been performed on single-domain samples. It is necessary to remind that $Sn_2P_2S_6$ crystals belong to low-symmetry monoclinic point group. Thus, the orientation of optical indicatrix (OI) depends on the wavelength, temperature, etc. Y axis of the crystallographic coordinate system coincides with the corresponding axis of the OI, while X and Z axes of the latter are rotated by $\simeq45°$ in XZ plane with respect to crystallographic directions (at the room temperature and the wavelength of radiation 632.8 *nm*). The form of the PO tensor for the point symmetry group *m* is as follows:

	σ_1	σ_2	σ_3	σ_4	σ_5	σ_6
ΔB_1	π_{11}	π_{12}	π_{13}	0	π_{15}	0
ΔB_2	π_{21}	π_{22}	π_{23}	0	π_{25}	0
ΔB_3	π_{31}	π_{32}	π_{33}	0	π_{35}	0
ΔB_4	0	0	0	π_{44}	0	π_{46}
ΔB_5	π_{51}	π_{52}	π_{53}	0	π_{55}	0
ΔB_6	0	0	0	π_{54}	0	π_{66}

$$(1)$$

It does not depend on the orientation of OI with respect to the axes of crystallographic system, unlike the magnitude of PO coefficients. Thus, for avoiding ambiguity in the determination of PO coefficients we have used the crystallographic coordinate system, with a possibility of further recalculation of the coefficient to the principal coordinate system (i.e., the system of the OI) after all the coefficients in Eq. (1) are determined.

It is seen that the matrix (1) is rather complicated and includes twenty independent coefficients. In the present paper we represent the results for the nine of them: π_{11}, π_{12}, π_{13}, π_{21}, π_{22}, π_{23}, π_{31}, π_{32}, and π_{33}. Let us consider equation for the OI perturbed by the mechanical stress σ_2 and written in the crystallographic system:

$$(B_1 + \pi_{12}\sigma_2)X^2 + (B_2 + \pi_{22}\sigma_2)Y^2 + \\ +(B_3 + \pi_{32}\sigma_2)Z^2 + 2\pi_{52}\sigma_2 ZX = 1 \quad (2)$$

One can find that the mechanical stress leads to a small rotation of OI around the Y axis:

$$\tan 2\xi_Y = \frac{\pi_{52}\sigma_2}{B_1 - B_3 + (\pi_{12} - \pi_{32})\sigma_2}, \qquad (3)$$

which is of the order of $10^{-3} - 10^{-4}\,rad$. This small OI rotation cannot essentially affect the accuracy of determination of π_{12}, π_{22} and π_{32}, when the incident light is polarized parallel to X, Y and Z axis, respectively. The same is true for the other components of compressive stresses. Thus, one can neglect the influence of the components π_{51}, π_{52} and π_{53}. However, it is necessary to remember that the mechanical stress components σ_1 and σ_3 in the crystallographic system correspond to the components σ_5 and $-\sigma_5$ in the coordinate system of OI.

We studied the PO effect with interferometric technique based on employing Mach-Zehnder interferometer (see Fig. 1) and determining optical retardation that corresponds to a half-wave mechanical stress $^{\lambda/2}\sigma_m$.

The PO coefficients were calculated with the formula (see, e.g., [8])

$$\pi_{im} = \frac{2\delta\Delta_k}{^{\lambda/2}\sigma_m n_i^3 d_k}, \qquad (4)$$

where $\delta\Delta_k$ is the optical retardation change, n_i the refractive index for $i-th$ polarization of the incident light and d_k the sample thickness along the direction of light propagation.

The accuracy for determination of the PO coefficients directly obtained from the experiment was equal to 15%. The measurements were performed under constant field conditions for the case of He-Ne laser (the wavelength of radiation $632.8nm$) and the temperature $T = 393K$. The experimental geometry and the values of PO coefficients are presented in Table 1.

The measurements of the velocity of longitudinal and transverse ultrasonic waves were performed on single crystals by the pulse-echo overlap method. The accuracy of the velocity measurements was about 0.5%. However the total error for the absolute value of acoustic wave velocities was higher and depended also on the misalignment of sample orientation. The acoustic waves in samples were excited, using $LiNbO_3$ transducers (the resonance frequency f=10 MHz, the bandwidth
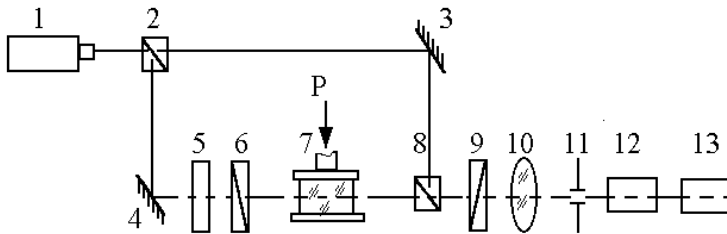

Fig. 1. Experimental setup for PO measurements: 1 – He-Ne laser, 2, 8 – semi-reflecting mirror cubes, 3, 4 – mirrors, 5 – $\lambda/4$ plate, 6, 9 – polarizers, 7 – setup for application of mechanical stresses, 10 – objective lens, 11 – diaphragm, 12 – photodetector, 13 – multimeter.

Table 1. Experimental geometry and PO coefficients of $Sn_2P_2S_6$ crystals.

Light wave vector direction	Polarization of incident light, mechanical stress component	Module of PO coefficient, pm^2/N
X	Z, σ_2	$\pi_{32} = 9.94$
X	Y, σ_2	$\pi_{22} = 8.48$
Z	X, σ_2	$\pi_{12} = 4.63$
X	Y, σ_1	$\pi_{21} = 8.8$
Y	Z, σ_1	$\pi_{31} = 13.7$
Y	X, σ_1	$\pi_{11} = 15.6$
X	Z, σ_3	$\pi_{33} = 2.61$
Y	X, σ_3	$\pi_{13} = 2.2$
X	Y, σ_3	$\pi_{23} = 1.49$

Δf=0.1 MHz and the acoustic power P_a=1–2 W). Notice that the acoustic velocities and the elastic modules are presented below for the crystallographic system but not the principal coordinate system of the elastic modules.

Some of the ultrasonic waves velocities for Sn₂P₂S₆ crystals and all the components of elastic stiffness tensor have previously been determined with different methods, including the pulse echo overlap method, Brillouin scattering spectroscopy and the neutron scattering [1,9–13]. Large dispersion of these data is probably caused by the use of samples grown with different techniques and a low accuracy of sample orientation. The accuracy of these measurements is not satisfactory for AO applications of the mentioned crystals. Our results for the ultrasonic wave velocities are presented in Table 2. These data agree more or less with the results published previously. It is necessary to note that, since the sign of the coordinate system is not determined in the present measurements, the wave velocities for the acoustic waves, whose polarization or propagation directions are not parallel to the principal crystallographic axes, are determined with the accuracy up to the sign of coordinate system. We have also observed the dependence of acoustic velocities on pre-illuminating conditions. The results presented below are obtained for the non-illuminated samples.

Table 2. Ultrasonic wave velocities for Sn₂P₂S₆ crystals at $T = 293K$.

V_{ij}	Direction of wave propagation	Wave displacement vector direction	Velocity, m/s
V_{11}	[100]	[100]	3580 ± 40
V_{22}	[010]	[010]	2870 ± 40
V_{33}	[001]	[001]	3600 ± 20
V_{23}	[010]	[001]	2610 ± 40
V_{21}	[010]	[100]	2100 ± 20
V_{32}	[001]	[010]	2500 ± 50
V_{31}	[001]	[100]	2880 ± 60
V_{12}	[100]	[010]	2220 ± 50
V_{13}	[100]	[001]	2470 ± 25
V_{55}	[101]	[101]	3890 ± 20
$V_{\overline{55}}$	$[\overline{1}0\overline{1}]$	$[\overline{1}0\overline{1}]$	3870 ± 20
$V_{5\overline{5}}$	[101]	$[\overline{1}0\overline{1}]$	2260 ± 20
V_{52}	[101]	[010]	2200 ± 20
$V_{\overline{5}5}$	$[\overline{1}0\overline{1}]$	[101]	2460 ± 25
$V_{\overline{5}2}$	$[\overline{1}0\overline{1}]$	[010]	1740 ± 20
V_{44}	[011]	[011]	3150 ± 30
$V_{4\overline{4}}$	[011]	$[0\overline{1}\overline{1}]$	2580 ± 30
V_{41}	[011]	[100]	1890 ± 20
V_{66}	[110]	[110]	4060 ± 40
$V_{\overline{66}}$	$[\overline{1}\overline{1}0]$	$[\overline{1}\overline{1}0]$	3910 ± 40
$V_{6\overline{6}}$	[110]	$[\overline{1}\overline{1}0]$	2290 ± 20
$V_{\overline{6}6}$	$[\overline{1}\overline{1}0]$	[110]	2270 ± 20
V_{63}	[110]	[001]	1560 ± 20
$V_{\overline{6}3}$	$[\overline{1}\overline{1}0]$	[001]	1560 ± 20

On the basis of Christoffel equation we have calculated some components of the elastic stiffness tensor: $C_{11}=4.5\times10^{10}$ N/m^2, $C_{22}=2.9\times10^{10}$ N/m^2, $C_{33}=4.5\times10^{10}$ N/m^2, $C_{12}\approx4.4\times10^{10}$ N/m^2 (with using of V_{66} at calculation), $C_{13}\approx0.8\times10^{10}$ N/m^2 (with using of V_{55} and $V_{5\bar{5}}$ at calculation), $C_{23}\approx1.1\times10^{10}$ N/m^2 (with using of V_{41} at calculation) $C_{44}=2.2\times10^{10}$ N/m^2, $C_{55}=2.2\times10^{10}$ N/m^2, $C_{66}=1.8\times10^{10}$ N/m^2, $C_{46}=0.4\times10^{10}$ N/m^2, $C_{35}=0.5\times10^{10}$ N/m^2, $C_{15}=0.2\times10^{10}$ N/m^2.

Conclusions

The results presented in this paper give rise to extensive investigations of piezo-, elasto- and AO properties of $Sn_{2y}Pb_{2(1-y)}P_2S_{6x}Se_{6(1-x)}$ crystals. The results obtained by us show that the velocities of the chosen acoustic waves in $Sn_2P_2S_6$ crystals are quite low. This fact, together with the large PO coefficients (some of them are of the order of 10 pm^2/N) and large refractive indices, enables one to predict extremely high AO figures of merit for the above crystals. For example, if we estimate the M_2 value on the basis of the lowest acoustic wave velocity $V=1560$ m/s and the other averaged data ($n\approx3.0$, $\pi\approx7$ pm^2/N, $C\approx2.8\times10^{10}$ N/m^2 and $p\approx0.2$), we get $M_2 - 2\times10^{-12}s^3/kg^2$. This is at least more than two times larger than the corresponding value for the best AO material, TeO_2 crystals. However, determination of complete matrices of the PO and elastooptic coefficients, as well as the elastic stiffness coefficients and elastic compliances, would be necessary for precise enough evaluation of the AO figure of merit and optimization of AO interaction geometry. The appropriate results will be a subject of our forthcoming papers.

Acknowledgement

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