Principal components of piezo-optic tensor for Pb$_3$Ge$_3$O$_{11}$ crystals

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Abstract. Using an interferometric technique and a half-wave stress method, we determine experimentally the principal components $\pi_{11}$, $\pi_{12}$, $\pi_{13}$, $\pi_{33}$ and $\pi_{33}$ of the piezo-optic tensor $\pi_{ij}$ for lead germanate crystals. Following from the above data, elasto-optic coefficients $p_{i\alpha}$ are calculated. The coefficient of acousto-optic (AO) figure of merit $M_2$ is estimated for the case of AO interactions with longitudinal acoustic waves. It is shown that, issuing from its maximal $M_2$ parameter ($M_2 = 24.3 \times 10^{-15}$ s/kg), Pb$_3$Ge$_3$O$_{11}$ can be compared to beta-barium borate or lead molybdate crystals. Moreover, this parameter exceeds essentially the values known for such notorious AO materials as, e.g., lithium niobate, crystalline quartz and fused silica.

Keywords: piezo-optic effect, interferometric methods, Pb$_3$Ge$_3$O$_{11}$ crystals.

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1. Introduction

Lead germanate Pb$_3$Ge$_3$O$_{11}$ belongs to the point group of symmetry 3 under normal conditions [1]. This trigonal-pyramidal group is characterized by a very complicated form of its piezo-optic tensor that contains 30 nonzero components, 12 of which are independent (11 invariant) [2]. In what the number of nonzero and/or independent piezo-optic components is concerned, the point symmetry group 3 is similar to the monoclinic groups, for which the piezo-optic tensor contains 20 nonzero components and 19 invariant ones. One can state that, from the viewpoint of piezo-optic effect, the point group 3 is indeed close to the low-symmetry groups, despite the fact that the crystals belonging to the group 3 are optically uniaxial. Similar situation is also peculiar for the rhombohedral symmetry group $\overline{3}$. This concerns all the other properties of the groups 3 and $\overline{3}$ described by the tensors of ranks higher than two.

As a consequence, experimental determination of all components of the piezo-optic tensor for the crystals belonging to the groups 3 and $\overline{3}$ is not a simple problem. In the present work, we begin to solve this problem for the first time. The main challenge here concerns determination of so-called non-principal and non-diagonal components of the piezo-optic matrix. We remind that the principal components are given by $\pi_{ij}$ with $i, j = 1, 2, 3$ and the diagonal ones, $\pi_{ii}$, are characterized by $i = j = 1, \ldots, 6$. The main difficulties that appear when determining the non-principal and non-diagonal components of the piezo-optic tensor have earlier been thoroughly formulated and experimentally solved on the example of monoclinic triglycine sulfate ($\text{NH}_2\text{CH}_2\text{COOH}_2 \times \text{H}_2\text{SO}_4$) [3] and tetragonal-dipyramidal calcium tungstate (CaWO$_4$) [4].

In the present work we start our studies of the piezo-optic coefficients (POCs) for the Pb$_3$Ge$_3$O$_{11}$ crystals from experimental determination of their principal POCs, i.e. the matrix
components \( \pi_{11}, \pi_{12}, \pi_{13}, \pi_{31} \) and \( \pi_{33} \). Moreover, below we calculate the appropriate elasto-optic coefficients and estimate acousto-optic (AO) figure of merit that corresponds to the largest elasto-optic coefficients for lead germanate.

2. Experimental methods

PbGeO\(_3\) crystals have been grown at the Oles Honchar Dnipro National University (Ukraine), using a known Czochralski method. Our crystals have the shape of a hexagonal prism, with the height \( \sim 3.5 \) cm and the cross section \( \sim 2 \times 1 \) cm\(^2\).

To study the principal POCs, we have prepared samples of so-called direct cuts. These have two faces perpendicular to crystallographic axes \( c \) and \( a \) and one face parallel to \( ac \) plane. The samples have a cubic shape, with the sizes \( \sim 6 \times 6 \times 6 \) mm\(^3\). The Cartesian crystal-physical coordinate system \( XYZ \) has been chosen according to the rules \( Z \parallel c, \ X \parallel a \) and \( Y \perp ac \). The principal POCs \( \pi_{im} \) (with the indices \( i \) and \( m \) corresponding respectively to the light polarization direction and the mechanical stress component \( \sigma_m \)) have been measured using a Mach–Zehnder interferometer. A sample under uniaxial mechanical stress was inserted into one of its arms, a so-called sample arm.

The change \( \delta \Delta_k \) in the optical path between the sample and reference arms is described by the following relation (see, e.g., Ref. [5]):

\[
\delta \Delta_k = -\frac{1}{2} \pi_{im} \sigma_m d_k n_i^3 + S_{im} \sigma_m d_k (n_i - 1).
\] (1)

Here \( n_i \) denotes the refractive index of the material, \( d_k \) the sample thickness along the light propagation direction \( k \), and \( S_{im} \) the elastic compliance coefficients that define Poisson strains along the direction \( k \).

The \( \delta \Delta_k \) value can be determined issuing from a well-known method of half-wave stresses [6]. According to this method, we measure the parameter \( \delta \Delta_k = \lambda/2 \) (with \( \lambda = 632.8 \) nm being the light wavelength) which is achieved under the operative stress \( \sigma_m = \sigma_m d_k \). Taking the above definitions into account, one can rewrite Eq. (1) as

\[
\pi_{im} = -\frac{\lambda}{2\sigma_m n_i^3} + \frac{2S_{im}}{n_i^2} (n_i - 1).
\] (2)

Thus, the POCs \( \pi_{im} \) can be determined from the experimental data \( \sigma_m \). As an example, one can use the following experimental conditions to determine \( \pi_{33} \): (i) \( k = 1, i = 3, m = 3 \) or (ii) \( k = 2, i = 3, m = 3 \). According to the conditions (i) and (ii), we rewrite Eq. (2) as

\[
\pi_{33} = -\frac{\lambda}{\sigma_{33} n_3^3} + \frac{2S_{33}}{n_3^2} (n_3 - 1)
\] (3)

and

\[
\pi_{33} = -\frac{\lambda}{\sigma_{33} n_3^3} + \frac{2S_{33}}{n_3^2} (n_3 - 1).
\] (4)

Eqs. (3) and (4) differ only by the elastic compliance components. In principle, the equality \( S_{33} = S_{23} \) is valid for the isotropic materials, the crystals of cubic system and the optically uniaxial crystals. Nonetheless, these two relations for \( \pi_{33} \) are important since they facilitate measuring the POC \( \pi_{33} \) in two different experimental geometries. This is convenient for checking the data obtained experimentally. The alternative relations for the other principal POCs can be formulated in a similar manner. Finally, it is easy to prove that the relationships like Eqs. (3) and (4) are not the same for the \( \pi_{11} \) and \( \pi_{22} \) coefficients, since they contain unequal elastic compliances \( S_{11} \) and \( S_{12} \).
3. Results and discussion

Table 1 displays the operative stresses $\sigma_1^o$ obtained experimentally and the principal POCs calculated on their basis for the Pb$_3$Ge$_3$O$_{11}$ crystals. The refractive indices $n_o = n_1 = n_2 = 2.116$ and $n_e = n_3 = 2.515$ ($\lambda = 632.8$ nm) [7] have been used for calculating $\pi_{im}$, together with the elastic compliances $S_{12} = -6.4$ and $S_{13} = -2.2$ (in the units $10^{-12}$ m$^2$/N = 1 B) [8]. Unfortunately, we cannot calculate exactly the errors for the POC, since the errors for the elastic stiffness coefficients have not been indicated in Ref. [8]. Following from our recent studies, we present in Table 1 only the error values estimated in the present work.

Table 1. Results of our interferometric experiments performed for the Pb$_3$Ge$_3$O$_{11}$ crystals.

| Experiment # | Experimental conditions | $\sigma_{im}^o$, kgf/cm | $\pi_{im}$, B * |
|--------------|-------------------------|-------------------------|----------------|
| 1            | 1 2                     | $\sigma_{11}^o = 19$   | $\pi_{11} = 2.08\pm0.39$ |
| 2            | 3                      | $\sigma_{31}^o = 29$   | $\pi_{31} = 0.76\pm0.27$ |
| 3            | 1 1                     | $\sigma_{11}^o = 24$   | $\pi_{11} = 2.32\pm0.29$ |
| 4            | 2                      | $\sigma_{21}^o = 29$   | $\pi_{21} = 1.83\pm0.24$ |
| 5            | 2 2                     | $\sigma_{22}^o = 19.5$ | $\pi_{22} = 1.99\pm0.38$ |
| 6            | 3                      | $\sigma_{32}^o = 29$   | $\pi_{32} = 0.76\pm0.27$ |
| 7            | 2 3                     | $\sigma_{22}^o = 25$   | $\pi_{22} = 2.21\pm0.28$ |
| 8            | 1                      | $\sigma_{12}^o = 33$   | $\pi_{12} = 1.55\pm0.21$ |
| 9            | 3 1                     | $\sigma_{33}^o = 21.5$ | $\pi_{33} = 2.51\pm0.31$ |
| 10           | 2                      | $\sigma_{23}^o = 48$   | $\pi_{23} = 0.90\pm0.15$ |
| 11           | 3 2                     | $\sigma_{33}^o = 20$   | $\pi_{33} = 2.73\pm0.33$ |
| 12           | 1                      | $\sigma_{13}^o = 46$   | $\pi_{13} = 0.96\pm0.16$ |

* Brewster is defined as 1 B = $10^{-12}$ m$^2$/N

Taking the equality $\pi_{11} = \pi_{22}$ into account, one can see that the POC $\pi_{11}$ has been determined basing on the measurements in four different geometries (see lines 1, 3, 5 and 7 in Table 1). Notice also that the errors in the lines 3 and 7 are much smaller than those appearing in the lines 1 and 5. Then the final $\pi_{11}$ error has been calculated from the results presented in the lines 3 and 7. The other POCs have been determined from the measurements in two different geometries, since we have $\pi_{12} = \pi_{21}$, $\pi_{13} = \pi_{31}$ and $\pi_{32}$. Finally, the resultant POCs are presented in terms of their mean arithmetic values and mean arithmetic errors (see Table 2).

By their magnitude, the largest POCs ($\pi_{11}, \pi_{12}$ and $\pi_{13}$) for lead germanate are comparable with the POCs of such known piezo-optic crystals as GaP (of which maximal POC is equal to 1.44 B [5]), CaWO$_4$ (1.86 B [4]), LiNbO$_3$ (2.06 B [9]), SiO$_2$ (3.11 B [10]) and $\beta$-BaB$_2$O$_4$ (3.7 B [11]).
Table 2. Principal POCs and elasto-optic coefficients found for the lead germanate crystals.

| POCs, B | $\pi_{11}$ | $\pi_{12}$ | $\pi_{31}$ | $\pi_{13}$ |
|---------|------------|------------|------------|------------|
| Present work | 2.27±0.28 | 1.69±0.23 | 0.93±0.16 | 0.76±0.27 | 2.62±0.32 |
| $p_{11}$ | $p_{12}$ | $p_{31}$ | $p_{33}$ |
| Present work | 0.217±0.026 | 0.193±0.022 | 0.159±0.019 | 0.116±0.022 | 0.274±0.040 |
| Ref. [13] | 0.223 | 0.213 | 0.129 | 0.194 | 0.202 |

The elasto-optic coefficients have been calculated, using a well-known tensor formula $p_{ij} = \pi_{ik}C_{km}$ with $C_{mn}$ being the elastic module tensor. For the point group of symmetry 3 we have

$$p_{11} = \pi_{11}C_{11} + \pi_{12}C_{12} + \pi_{13}C_{13} + \pi_{14}C_{14} + \pi_{15}C_{15},$$

$$p_{12} = \pi_{12}C_{12} + \pi_{13}C_{13} + \pi_{14}C_{14} - \pi_{15}C_{15},$$

$$p_{31} = \pi_{31}(C_{11} + C_{12}) + \pi_{33}C_{13},$$

$$p_{33} = 2\pi_{33}C_{13} + \pi_{33}C_{33}. $$

The elastic modules have been taken from Ref. [8]: $C_{11} = 6.84$, $C_{12} = 2.68$, $C_{13} = 1.79$, $C_{33} = 9.43$, $C_{14} = 0.0$, $C_{15} = -0.12$ (all in the units of $10^{10}$ N/m$^2$). The POCs $\pi_{14}$ and $\pi_{15}$ needed for the calculations have been determined in the work [12]: $\pi_{14} = -(0.35±0.09)$ B and $\pi_{15} \leq 0.09$ B. Since these coefficients are rather small and the same holds true for the elastic modules $C_{14}$ and $C_{15}$, one can neglect the fourth and fifth terms in the first and second lines of Eqs. (5). The elasto-optic coefficients calculated in this manner are presented in Table 2.

It is seen from Table 2 that the elasto-optic coefficients determined by us agree well with those measured in Ref. [14] using an AO-based Dixon–Cohen method. The only exceptions are the elasto-optic coefficients $p_{31}$ and $p_{33}$, especially the largest $p_{33}$ coefficient.

Now let us consider an isotropic AO Bragg diffraction inside the principal crystal-physical planes, under the conditions that quasi-longitudinal acoustic waves (AWs) interact with optical waves and the AWs propagate close to the principal coordinate axes. A schematic view of the appropriate wave-vector diagrams is given in Fig. 1. Note that a purely longitudinal AW propagates along the principal axis $Z$. The quasi-longitudinal AW propagating along the $Y$ axis also becomes purely longitudinal since $C_{14}$ is equal to zero [8]. Finally, a quasi-longitudinal AW propagating along the $X$ axis is nearly longitudinal, with the angle of non-orthogonality of its polarization not exceeding $\sim 1.5$ deg. Hence, in our further analysis one can neglect the non-orthogonality of the longitudinal AWs that propagate along the principal directions.

The AO figure of merit for lead germanate (see Table 3) has been calculated using a standard relation $M_{z} = n^{6}p_{eff}^{2}/\rho v^{3}$, where $p_{eff}$ implies the effective elasto-optic coefficient, $\rho = 7330$ kg/m$^3$ [8] the crystal density and $v$ the velocity of the longitudinal AW. The latter has been taken from Ref. [14].

The highest AO figure of merit, $24.3\times10^{-15}$ s$^3$/kg, can be reached at the type I of AO interactions with the longitudinal AW propagating along the Z axis. Almost the same AO figure of merit, $21.2\times10^{-15}$ s$^3$/kg, is achieved for the interaction geometries given by Eqs. (3), (5) and (7). Note that, according to the maximal AO figure of merit, Pb$_3$Ge$_2$O$_{11}$ is comparable with $\beta$-barium borate [12] and lead molybdate crystals [14]. Moreover, the maximal figure of merit for the lead germanate crystals exceeds essentially the appropriate values for such known AO materials as, e.g., lithium niobate [15, 16], crystalline quartz and fused silica [15]. Nonetheless, the longitudinal AWs propagating along the principal crystal-physical axes manifest usually large enough
attenuations in the high-frequency range [14]. Then it would be necessary to decrease the operative acoustic frequency down to MHz range, if one needs to use the AO parameters of lead germanate mentioned above. On the other hand, one can consider the AO interactions in the other geometries, as well as the interactions with the other AWs. In the latter case, all of the elasto-optic tensor components need to be determined. These points will be a subject of our forthcoming works.

Fig. 1. Schematic wave-vector diagrams for XZ (a) and XY (b) planes: $k_{aw}$ is the acoustic wave vector, while $k_i$ and $k_d$ are the wave vectors of the incident and diffracted optical waves, respectively. Double-sided arrows and crossed circles indicate polarizations of the optical waves.

| Type of isotropic interaction | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|------------------------------|---|---|---|---|---|---|---|---|
| AW velocity, m/s             | 3470 | 3470 | 3010 | 3010 | 3010 | 3010 | 3010 | 3010 |
| Refractive index              | $n_e$ | $n_o$ | $n_e \approx n_o$ | $n_e$ | $n_o$ | $n_e$ | $n_o$ | $n_e$ |
| $p_{eff}$                     | $p_{33}$ | $p_{13}$ | $p_{11}$ | $p_{12}$ | $p_{11}$ | $p_{31}$ | $p_{11}$ | $p_{31}$ |
| AO figure of merit, $10^{-15}$ s$^3$/kg | 24.3 | 7.4 | 21.2 | 16.8 | 21.2 | 7.1 | 21.2 | 7.1 |
4. Conclusions
In the present work we have determined experimentally the principal POCs for the lead germanate crystals. On the basis of those results, the elasto-optic coefficients have been calculated and the AO figure of merit of Pb$_3$Ge$_2$O$_{11}$ has been estimated for the case of AO interactions with the longitudinal AWs propagating close to the principal crystal-physical directions. It has been found that the highest AO figure of merit, 24.3×10$^{-15}$ s$^2$/kg, is reached at the AO interaction with the longitudinal AW propagating along the Z axis. Almost the same AO figures of merit are peculiar for a number of different interaction geometries. As a result, the AO parameters of the Pb$_3$Ge$_2$O$_{11}$ crystals are comparable with the characteristics of many known AO materials. However, due to high attenuation typical in the GHz frequency range for the longitudinal AWs propagating along the principal crystal-physical axes, lead germanate must be used in some other geometries of AO interactions (e.g., the interactions with shear AWs) or in the lower-frequency range.

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Анотація. З використанням інтерферометричної методики і методу пів-хвильових напружень в роботі визначені головні компоненти п’єзооптичного тензора $\pi_{im}$ ($\pi_{11}$, $\pi_{12}$, $\pi_{13}$, $\pi_{31}$, $\pi_{33}$) кристалів германату свинцю. На основі експериментально отриманих п’єзооптичних коефіцієнтів розраховані відповідні коефіцієнти пружно-оптичного тензора $p_{in}$, а також оцінено значення коефіцієнтів акусто-оптичної якості. Виявлено, що максимальне значення $M_2=24.3 \times 10^{-15} \text{с}^3/\text{кг}$ для кристалів Pb₅Ge₃O₁₁ є співмірним з відповідними коефіцієнтами кристалів $\beta$-борату барію і молібдату свинцю. Крім того, це значення для германату свинцю значно перевищує відповідні коефіцієнти для таких відомих акустооптичних матеріалів, як ніобат літію і кристалічний та плавлений кварц.