



Elastic and acousto-optic properties of $\text{Sn}_2\text{P}_2\text{S}_6$ crystals: Effect of ferroelectric phase transition

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ABSTRACT

We report on the studies for temperature dependences of elastic stiffness coefficients in $\text{Sn}_2\text{P}_2\text{S}_6$ crystals. Basing on the construction of acoustic velocity surfaces, we have determined the parameters of the slowest acoustic wave that propagates in $\text{Sn}_2\text{P}_2\text{S}_6$ crystals. The acousto-optic figure of merit for the case of acousto-optic interaction with this wave is estimated as $\sim 0.8 \times 10^{-12} \text{ s}^3/\text{kg}$. We have shown that $\text{Sn}_2\text{P}_2\text{S}_6$ is very close to the conditions of tricritical point on the (x, T) - and (p, T) -phase diagrams of the solid solutions $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$. The critical exponent α of the heat capacity for the $\text{Sn}_2\text{P}_2\text{S}_6$ crystals is equal to 0.42 ± 0.03 .

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1. Introduction

Tin thiohypodiphosphate crystals $\text{Sn}_2\text{P}_2\text{S}_6$ are wide-gap semiconductors that manifest a proper, second-order paraelectric-to-ferroelectric phase transition, with the change $2m \leftrightarrow m$ of their point symmetry at $T_c = 337 \text{ K}$ [1]. These crystals are transparent in a wide spectral range (from $\lambda = 0.53 \mu\text{m}$ to $\lambda = 8.0 \mu\text{m}$ [1], have high enough electrooptic coefficients $r_{11} = 1.74 \times 10^{-10} \text{ m/V}$ at the room temperature and the light wavelength of $\lambda = 633 \text{ nm}$ [2,3], and manifest conspicuous photorefractive properties [4,5]. Moreover, the tin thiohypodiphosphate represents a promising magneto-optic material (the corresponding Verdet constant amounts to $115 \text{ rad/T} \times m$ [6]). In our recent works [7–10] we have experimentally studied and analyzed acoustic properties of $\text{Sn}_2\text{P}_2\text{S}_6$ at the room temperature and demonstrated that the material has great potentials for acousto-optic (AO) applications. The AO figure of merit (AOFM) of $\text{Sn}_2\text{P}_2\text{S}_6$ calculated on the basis of our experimental AO data reaches very high values $M_2 = (1.7 \pm 0.4) \times 10^{-12} \text{ s}^3/\text{kg}$ [9]. In other words, the crystals of $\text{Sn}_2\text{P}_2\text{S}_6$ reveal one of the highest AOFMs known for the AO materials operating in the visible spectral range (see, e.g., the study of AOFM for Hg_2Br_2 crystals [11]). This is why $\text{Sn}_2\text{P}_2\text{S}_6$ can be widely used in optoelectronics, in particular in devices for AO operation of optical radiation.

It is necessary to note that the AOFM value mentioned above has been obtained for the conditions of AO interaction with the

acoustic wave which still is not the slowest one. Being more precise, we have dealt with the waves having the velocities $v_{21} = 2100 \text{ m/s}$ and $v_{23} = 2610 \text{ m/s}$ (here the first and the second indices denote the directions of the wave vector \mathbf{q} and the polarization vector \mathbf{e} of the acoustic wave, respectively) [9]. The AOFM is inversely proportional to the cube of the acoustic wave velocity and so becomes extremely high with lowering velocity ($M_2 = n^6 p_{ef}^2 / \rho v^3$, with n being the refractive index, p_{ef} the effective elasto-optic coefficient, and ρ the crystal density). We have shown in our recent work [10] that the slowest wave in the $\text{Sn}_2\text{P}_2\text{S}_6$ crystals is the transverse wave with the velocity $1550 \pm 120 \text{ m/s}$ at the room temperature. It has also been found that the propagation direction of this wave coincides with neither of the principal crystallographic directions and, moreover, it does not belong to the principal crystallographic planes. One can easily calculate that, for the case of AO interaction with the latter wave, the AOFM can increase by several times, when compared with the value obtained in the work [9], if only the effective elasto-optic coefficient remained approximately the same.

Both the velocity of the slowest wave mentioned above and its propagation direction have been derived in the study [10] using the following procedure: the elastic stiffness tensor has been rewritten in a so-called acoustic eigen coordinate system rotated around b axis by the angle $\theta = [\arctan(2C_{46}/(C_{66} - C_{44}))]/2 = -(16 \pm 5)^\circ$ with respect to the initial coordinate system, in order to meet the conditions $C'_{46} = C'_{15} = C'_{25} = C'_{35} \approx 0$ for the elastic stiffness tensor components written in this new system. In fact, such an 'eigen acoustic coordinate system' does not exist at all. Really, only the tensor component $C'_{46} \equiv 0$ in this system, while

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the other coefficients C'_{15} , C'_{25} and C'_{35} remain nonzero, though being small enough. Since the parameters of the slowest wave (the directions of its propagation and polarization) for $\text{Sn}_2\text{P}_2\text{S}_6$ have been obtained in the work [10] with assuming of exact equality to zero of the coefficients C'_{15} , C'_{25} and C'_{35} , these parameters could serve as a rough approximation only.

On the other hand, a decrease in the acoustic wave velocities occurring with approaching the phase transition temperature T_C , as revealed for some of the longitudinal waves propagating in $\text{Sn}_2\text{P}_2\text{S}_6$ [12], can in principle lead to further increase in the AOFM. However, in our recent work [13] reporting the temperature dependences of both the longitudinal and transverse acoustic wave velocities in the $\text{Sn}_2\text{P}_2\text{S}_6$ crystals, we have shown that the above temperature dependences should impose no notable variation of the AOFM, though the relevant results are also approximated.

For determining the propagation direction of the slowest acoustic wave and possible variations of its parameters with temperature, the acoustic velocity surfaces are to be constructed for different temperatures. In order to find the minimal velocity, it would be necessary to cut these surfaces by a plane that rotates, e.g., around the b axis and then determine the minimal velocities within all of these planes. Prior to this, the temperature dependences of all the elastic stiffness coefficients for $\text{Sn}_2\text{P}_2\text{S}_6$ crystals are needed. On the other hand, efficient applications of these crystals should be based on high enough stiffness coefficients in a wide temperature range, including the point $T_C = 337$ K which is close to the room temperature. In connection with this, it is worthwhile to notice that some of the stiffness coefficients for the $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ crystals tend almost to zero near the phase transition temperature [14], thus making the crystals inconvenient for practical applications.

Following from the above considerations, the aim of the present work is to study the temperature behavior of all the stiffness coefficients in the $\text{Sn}_2\text{P}_2\text{S}_6$ crystals in the vicinity of the Curie temperature. Besides, we will also touch the problem of critical exponents for the $\text{Sn}_2\text{P}_2\text{S}_6$ crystals, which are close to a so-called tricritical point both on 'selenium concentration–temperature' (x, T) [14] and 'hydrostatic pressure–temperature' (p, T) [15,16] phase diagrams peculiar for the solid solutions of $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$. Issuing from the temperature dependences of the elastic stiffness coefficients, we will determine the critical exponent α describing temperature dependence of the heat capacity $C_p \sim (T_C - T)^{-\alpha}$. It is important that the latter index is close to 0.5 for the case of $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ crystals, which corresponds to thermodynamic system in the vicinity of its tricritical point [14].

2. Data processing

The lattice parameters of $\text{Sn}_2\text{P}_2\text{S}_6$ are equal to $a = 0.9378$ nm, $b = 0.7448$ nm, $c = 0.6513$ nm, and $\beta = 91.15^\circ$ (at the room temperature and the atmospheric pressure), where the crystallographic axis b is perpendicular to the symmetry mirror plane [17], while the spontaneous polarization vector is almost parallel to the a axis. The elastic stiffness coefficients have been determined with respect to the crystallographic axes $a = 1$, $b = 2$, and $c = 3$. Here we report on complete determination of the elastic matrix $C_{klmn} = C_{ij}$ (with $i, j = 1-6$; $1 = 11$, $2 = 22$, $3 = 33$, $4 = 23$, $5 = 13$ and $6 = 12$), via measurements of the phase ultrasonic velocities along different crystallographic directions. The temperature dependences of the velocities of longitudinal and transverse ultrasonic waves have earlier been obtained with a standard pulse–echo overlap method and presented in our recent work [13].¹ Since $\text{Sn}_2\text{P}_2\text{S}_6$ belongs to the

monoclinic point symmetry group m at the room temperature, there are 13 independent nonzero elastic coefficients (C_{11} , C_{22} , C_{33} , C_{44} , C_{55} , C_{66} , C_{12} , C_{13} , C_{23} , C_{15} , C_{25} , C_{35} , and C_{46}), and the same holds true of the point group $2/m$ describing the paraelectric phase.

Simple expressions linking the velocities and the elastic coefficients are available only for the four of the elastic stiffness matrix components ($C_{22} = \rho v_{22}^2$, $C_{44} = \rho v_{32}^2$, $C_{66} = \rho v_{12}^2$, and $C_{46} = 0.5 \sqrt{(\rho v_{21}^2 - \rho v_{23}^2)^2 - (C_{44} - C_{66})^2}$). All the other coefficients are linked by more complicated relations or by complex systems of equations. Then cumbersome, both in experimental and computational aspects, procedures for deriving the remaining nine elastic coefficients are required for the monoclinic system [18,19]. To determine those coefficients, one should measure the velocities of quasi-longitudinal (QL) and quasi-transverse (QT) ultrasonic waves for at least six different directions ($[100]$, $[010]$, $[001]$, $[110]$, $[101]$, and $[011]$). As a result, the errors for the elastic stiffness coefficients would be high enough ($\sim 15\%$).

The acoustic velocity surfaces have been constructed using the well known Christoffel equation, the software packages 'Origin 7.0', 'Mathcad' and 'Maple 13', and the experimental data for the elastic stiffness coefficients. The exact propagation direction and the velocity of the slowest wave have been determined after rotating the elastic stiffness tensor around the crystallographic axis b (the step of 10°) and constructing cross sections of the acoustic velocity surfaces for each rotation angle.

3. Results and discussion

3.1. Temperature dependences of elastic stiffness coefficients

Under normal conditions, the elastic stiffness coefficients obtained in the present work for $\text{Sn}_2\text{P}_2\text{S}_6$ agree well with the data obtained in our recent work [10]. The temperature dependences of the elastic stiffness coefficients are presented in Fig. 1. As seen from Fig. 1, only some of the coefficients reveal notable temperature dependence in the vicinity of T_C , namely C_{11} , C_{22} , C_{23} , C_{12} , and C_{13} . The other coefficients (C_{33} , C_{15} , C_{25} , C_{35} , and C_{66}) have a step-like anomaly at the phase transition temperature, while the coefficients C_{44} , C_{55} , and C_{46} are almost temperature-independent.

3.2. Acoustic wave velocity surfaces

The cross sections of the acoustic velocity surfaces calculated for different temperatures are presented in Fig. 2. The velocity of the slowest wave QT_2 (with the wave vector belonging to the crystallographic coordinate plane ac) is equal to 1407 m/s. The wave vector of this wave is rotated by 55° with respect to the a axis, while the polarization vector belongs to the ac plane (see Fig. 2a). As follows from the cross sections of the acoustic wave velocity surfaces by the plane $a'b$ (where the angle between the a and a' axes is equal to 55° – see Fig. 3), this wave is found to be the slowest acoustic wave for the $\text{Sn}_2\text{P}_2\text{S}_6$ crystals. There are four different propagation directions of the slowest wave in $\text{Sn}_2\text{P}_2\text{S}_6$ (see Fig. 2).

Inside the temperature range of the ferroelectric phase, the direction of propagation of this wave remains almost the same (see Fig. 2a–c), while in the paraelectric phase the \mathbf{q} vector is rotated by 39° with respect to the a axis (see Fig. 2d and e). This fact is caused by a jump-like rotation of the surface for the QT_2 wave around the b axis occurring at the phase transition.

It is seen from Fig. 4 that the velocity of the slowest wave manifests very weak temperature dependence in the both phases. The slowest transverse wave propagates along the direction rotated by 55° with respect to the a axis in the ac plane and has its polarization lying in the same plane. It should excite the

¹ The $\text{Sn}_2\text{P}_2\text{S}_6$ crystals studied by us have been grown with a vapor-transport technique at the Uzhgorod National University (Ukraine).

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