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Temperature dependence of the Brillouin spectra in $Sn_2P_2S(Se)_6$ ferroelectric crystals

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A temperature dependence of hypersound velocities at transition from a paraelectric phase to ferroelectric phase in $Sn_2P_2S_6$ crystals was investigated by Brillouin scattering spectroscopy. Based on these data, full set of elastic constants was determined. Similar measurements were also performed for $Sn_2P_2(Se_{0.28}S_{0.72})_6$ mixed crystals in the paraelectric phase near a Lifshitz point. The sound velocity indicatrices' evolution at transition from $Sn_2P_2S_6$ to $Sn_2P_2(Se_{0.28}S_{0.72})_6$ was observed and softening of transverse acoustic phonons in the paraelectric phase near the Lifshitz point was found. An instability of the acoustic phonons is induced by an interaction with a soft optic mode which is the origin of an incommensurate phase appearance in mixed crystals $Sn_2P_2(Se_xS_{1-x})_6$ with $x > x_{\mathrm{LP}} = 0.28$.

Key words: *Brillouin scattering, soft mode, ferroelectrics, Lifshitz point*

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1. Introduction

The compounds $Sn_2P_2S_6$ and $Sn_2P_2Se_6$ are proper uniaxial ferroelectrics with phase transitions (PT) in a region of a crossover from displacive to order/disorder type. A Lifshitz point is observed on a concentration phase diagram of mixed crystals $Sn_2P_2(Se_xS_{1-x})_6$ with coordinates $x_{\mathrm{LP}} \approx 0.28$, $T_{\mathrm{LP}} \approx 286$ K. At this triple point, an incommensurate (IC) phase of the so-called type II appears. Such IC phase is thought to arise from an interaction between a ferroelectric optic soft mode and the acoustic phonons near Brillouin zone center [1–3].

The relationship between the lattice dynamics and the phase transitions has been studied for the $Sn_2P_2S(Se)_6$ crystals by Raman [4,5], Brillouin [6] and neutron scattering [7,8]. In the paraelectric and ferroelectric phases (space groups $P2_1/c$ and Pc, respectively) a clear soft optic mode was observed. Its lineshape indicates the mixed displacive-order/disorder transition. This softening is accompanied with a central component in the Raman and neutron scattering spectra of both $Sn_2P_2S_6$ and $Sn_2P_2Se_6$. This central peak was also observed by Brillouin scattering in $Sn_2P_2S_6$ crystals [6].

An interaction between the soft $TO(X)$ and $TA(u_{xz})$ acoustic modes take place in the ferroelectric phase of $Sn_2P_2S(Se)_6$, as is evident from the dispersion and the phonon lineshapes [7,8]. Consistency between the sound velocities in the ferroelectric phase obtained from ultrasonic measurements [1,9,10] and from the slopes of the acoustic branches in the neutron scattering spectra [7,8] is obtained when piezoelectric corrections are included.

Neutron scattering investigations [7,8] show an important role of the interaction between optic and acoustic phonons in the lattice instability at a non-zero wave vector q_i in $Sn_2P_2Se_6$ crystals. Obviously, this interaction plays the principal role at PT near the Lifshitz point and could be observed in Brillouin scattering spectra when $q_i \to 0$. Investigations of such spectra temperature variations for $Sn_2P_2S_6$ and $Sn_2P_2(Se_{0.28}S_{0.72})_6$ crystals have been carried out in this work.

2. Experimental results

Brillouin scattering spectra stimulated by He-Ne laser irradiation were studied using three pass Fabry-Perot scanned by pressure interferometer with a fineness of 35 and 2.52 cm^{-1} free spectral range. Right angle scattering mode was employed. The crystalline samples were placed in a UTREX cryostat where the temperature was stabilized with an accuracy of 0.25 K. The spectra lines were fitted by Lorentzian.

Sound velocities V and attenuation α were calculated using formulas:

$$\Omega_0 = \frac{V}{c}\,\omega_0\sqrt{(n_0 - n_{\mathrm{S}})^2 + 4n_0 n_{\mathrm{S}}\sin^2\frac{\theta}{2}}, \qquad \alpha = \frac{\delta\omega}{2V},$$

where Ω_0 is a half-width of the Brillouin component, ω_0 is frequency of He-Ne-laser, θ is scattering angle, n_0, n_{S} are indices of refraction for stimulated and scattered light. The refractive indices were determined by prism method and were taken: $n_0 = n_{\mathrm{S}} = 3.0$ and 3.25 for pure crystals and solid solutions, respectively. The accuracy was about 3% for sound velocities and about 10% for attenuation.

Elastic modules and velocity indicatrices were calculated on the basis of the experimental hypersound velocities by using the known Kristoffel relation

$$\Big(\sum_{jk} c_{ijkl} n_j n_k - \rho v^2 \delta_{il}\Big) p_l = 0,$$

where c_{ijkl} are the elastic constants, n_i are the unit wave vector components, ρ is the density, v is the velocity and p_i are the unit polarization vector components.

We used a crystallographic setup when a Cartesian axis Y coincides with [010] direction, perpendicular to a symmetry plane (010) of a $2/m$ and m point groups. An axis X was placed along [100] direction, and thus the Z axis deviated for $\simeq 1.15°$ from [001] direction. These axes, X and Z, are closed to the directions of a spontaneous

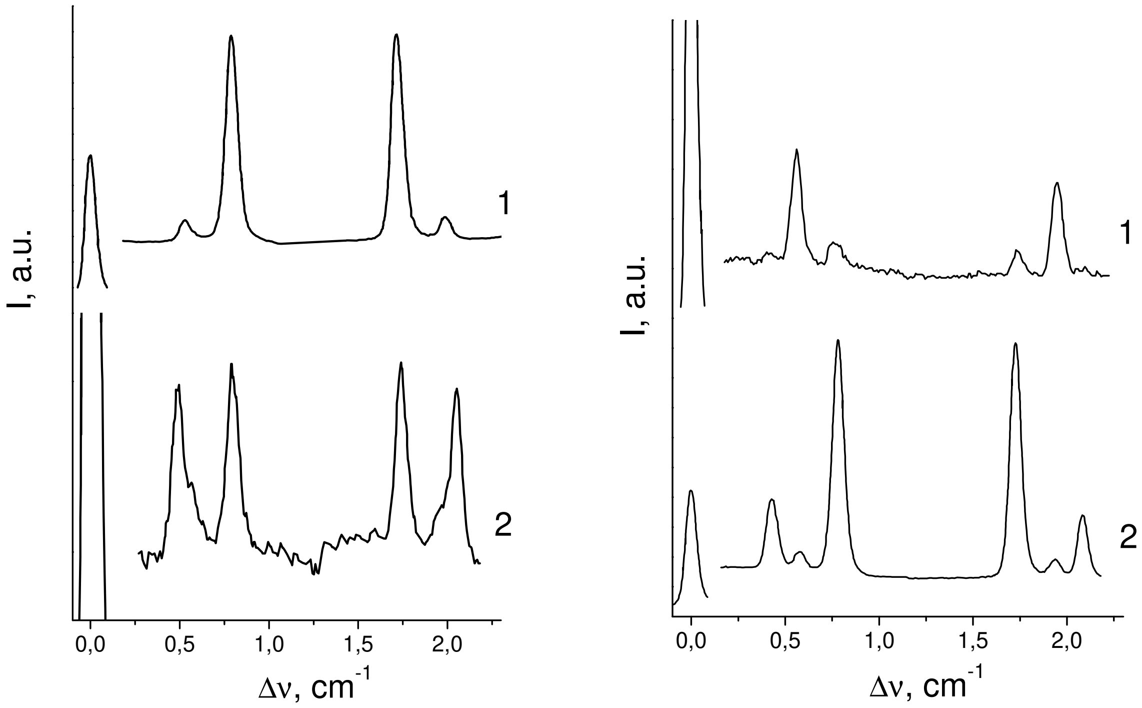

Figure 1. Brillouin spectra of $Sn_2P_2S_6$ crystals for: $\vec{q} \parallel [001]$ – left (1 – $X\overline{Z}(XZ\ X\overline{Z})XZ$, 2 – $X\overline{Z}(Y\ X\overline{Z})XZ$); $\vec{q} \parallel [011]$ – right (1 – $Z(X\ Z)Y$, 2 – $Z(X\ X)Y$) at room temperature.

polarization in the ferroelectric phase and to the directions of a wave vector of modulation in the IC phase, respectively.

The Brillouin scattering spectra obtained in $Sn_2P_2S_6$ crystals at two different directions are shown in figure 1. Here, the conventional scattering geometry was used when the directions of the input and the scattered light are indicated, and parenthesis contain their polarizations. Spectral lines of longitudinal LA and transverse TA acoustic phonons are clearly seen.

Table 1. Room temperature hypersound velocities of $Sn_2P_2S_6$ crystals along different directions (column 2 – this work, 3 – [9,10], 4 – [7]).

Direction	v_L, v_{T1}, v_{T2}, 10^3 m/c	v_L, v_{T1}, v_{T2}, 10^3 m/c	v_L, v_{T1}, v_{T2}, 10^3 m/c
[100]	3.5, 2.5, 2.2	2.6, 2.4, 2.3	4.1, –, 2.3
[010]	3.0, 2.4, 2.1	3.0, –, 2.0	–
[001]	3.6, 2.4, 2.1	3.8, –, –	3.8, 2.5, –
[110]	4.0, 2.3, 1.5	–	–
[011]	3.5, 2.5, 1.9	–	–
[101]	3.9, 2.4, 1.8	–	–

This way, the hypersound velocities were obtained for six different directions of the phonon propagation in $Sn_2P_2S_6$ (table 1). Based on these data a full set of elastic constants was calculated for room temperature (table 2).

Table 2. Elastic constants of $Sn_2P_2S_6$ crystals at room temperature.

c_{ij}, $\times 10^{10}$ N/m^2						
	4.2	2.0	1.8	0.0	–0.7	0.0
		3.2	1.0	0.0	–0.4	0.0
			4.5	0.0	0.5	0.0
				1.6	0.0	0.1
					2.2	0.0
						2.2

The Brillouin scattering spectra were also investigated at different temperatures in both paraelectric and ferroelectric phases of the $Sn_2P_2S_6$ crystals. It was found that near the second order PT at $T_0 \approx 337$ K the temperature dependencies of longitudinal hypersound velocity and attenuation have strong anomalies along [010] (see for example figure 2) and [011] directions. These anomalies are similar to the ones observed earlier [6] in Brillouin scattering for $Sn_2P_2S_6$ in [010] direction and satisfy the known Landau-Khalatnikov relations [11].

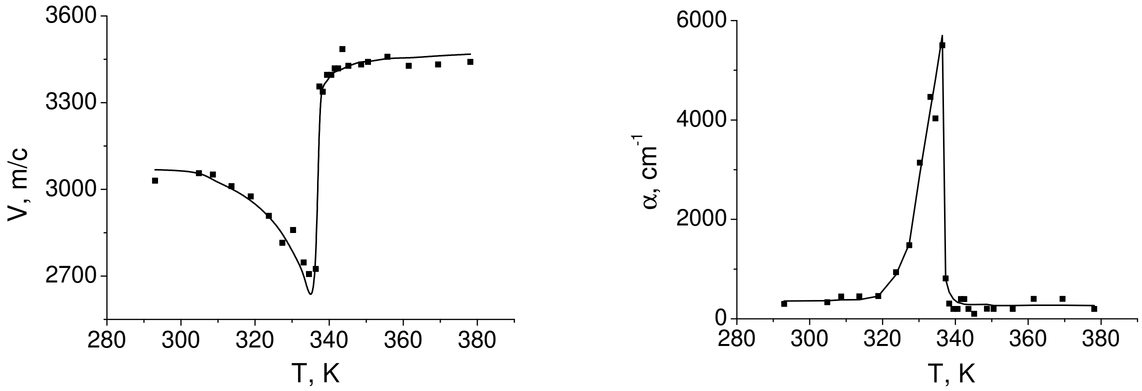

Figure 2. Temperature dependencies of velocity and attenuation of the longitudinal hypersound propagating along [010] direction in $Sn_2P_2S_6$ crystals.

The transverse hypersound velocities propagated in the symmetry plane (010) of $Sn_2P_2S_6$ crystals, especially in the [001] direction, do not have a pronounced anomaly at PT from the paraelectric phase to the ferroelectric one (figure 3).

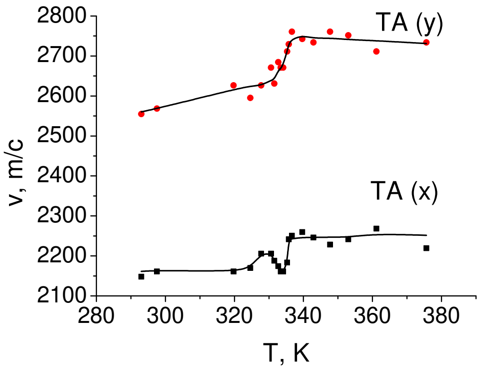

Figure 3. Temperature dependence of transverse acoustic phonon velocities propagating along [001] direction in $Sn_2P_2S_6$ crystals.

The Brillouin scattering spectra for $Sn_2P_2(Se_{0.28}S_{0.72})_6$ crystals at room temperature are shown in figure 4. The polarization of scattered light was not analyzed due to a weak intensity of Brillouin components. As the Lifshitz point in $Sn_2P_2(Se_{0.28}S_{0.72})_6$ occurs at the

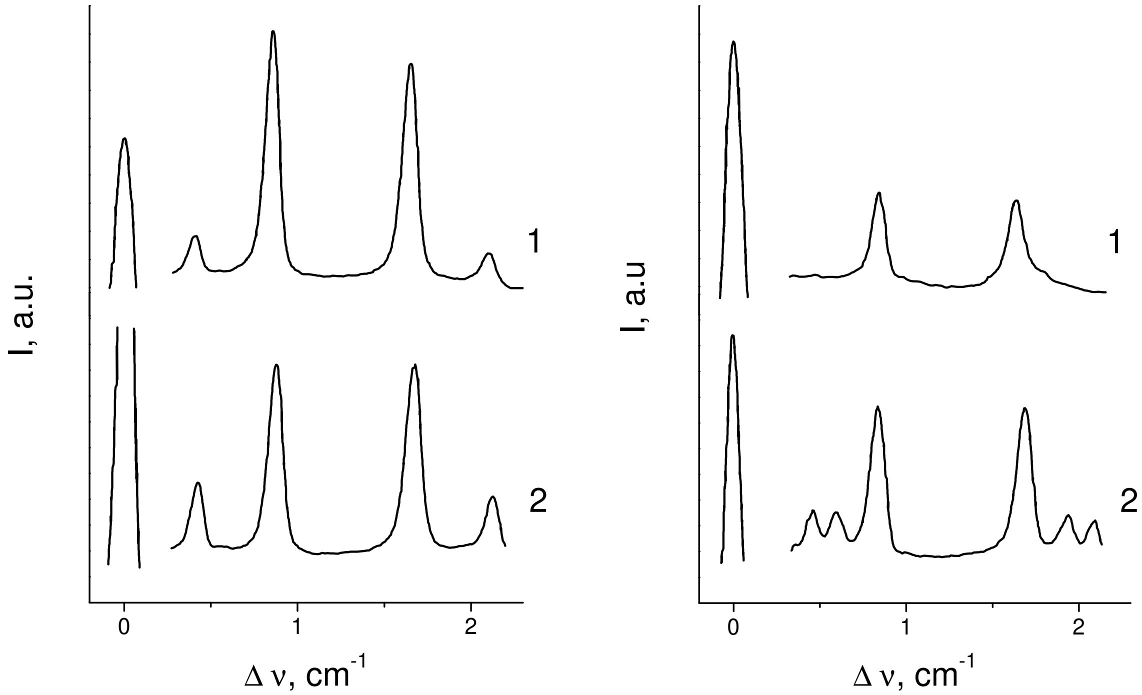

Figure 4. Brillouin spectra of $Sn_2P_2(Se_{0.28}S_{0.72})_6$ crystals for: $\vec{q} \parallel [101]$ – left (1 – $Z(X\ 0)X$, 2 – $X(Z\ 0)X$; $\vec{q} \parallel [011]$ – right (1 – $X(Z\ 0)Y$, 2 – $Z(X\ 0)Y$) at room temperature.

$T_{\mathrm{LP}} \approx 286$ K, the hypersound velocities and elastic constants collected in table 3 and table 4 reflect the elastic anisotropy of the investigated crystals in the paraelectric phase at approximately $T_{\mathrm{LP}} + 8$ K.

The bulk compressibility calculated from the above data for the $Sn_2P_2S_6$ and $Sn_2P_2(Se_{0.28}S_{0.72})_6$ crystals at room temperature is equal approximately to $4.2 \cdot 10^{-11}$ m^2/N for both compounds.

Table 3. Room temperature hypersound velocities of $Sn_2P_2(Se_{0.28}S_{0.72})_6$ crystals along different wavevector directions.

Direction	v_L, v_{T1}, v_{T2}, 10^3 m/c this work	v_L, v_{T1}, v_{T2}, 10^3 m/c [10]
[010]	–	3.0, –, –
[001]	3.7, 2.2, 1.6	–
[110]	3.6, 2.3, 1.6	–
[011]	3.4, 2.4, 1.8	–
[101]	3.6, –, 1.7	–
$[10\bar{1}]$	3.5, –, 1.7	–
[111]	3.5, 2.4, 1.7	–
$[11\bar{1}]$	3.5, 2.3, 1.9	–

The examples of velocity indicatrices for the paraelectric and the ferroelectric phases of the $Sn_2P_2S_6$ crystals and for the paraelectric phase of the $Sn_2P_2(Se_{0.28}S_{0.72})_6$ crystals are shown in figure 5. We can see a transformation of the orientation dependence of sound velocities in the paraelectric phase near T_0 or T_{LP} at transition from $Sn_2P_2S_6$ to $Sn_2P_2(Se_{0.28}S_{0.72})_6$. Herein, a softening of the quasi-transverse acoustic phonons, that are polarized and propagated in (010) plane and related to the u_{xz} elastic deformation, was found in the paraelectric phase near the Lifshitz point.

Table 4. Elastic constants of $Sn_2P_2(Se_{0.28}S_{0.72})_6$ crystals at room temperature.

c_{ij}, $\times 10^{10}$ N/m^2						
	5.3	0.6	2.0	0.0	1.3	0.0
		4.4	1.0	0.0	0.0	0.0
			5.2	0.0	–1.2	0.0
				1.8	0.0	0.3
					1.3	0.0
						2.1

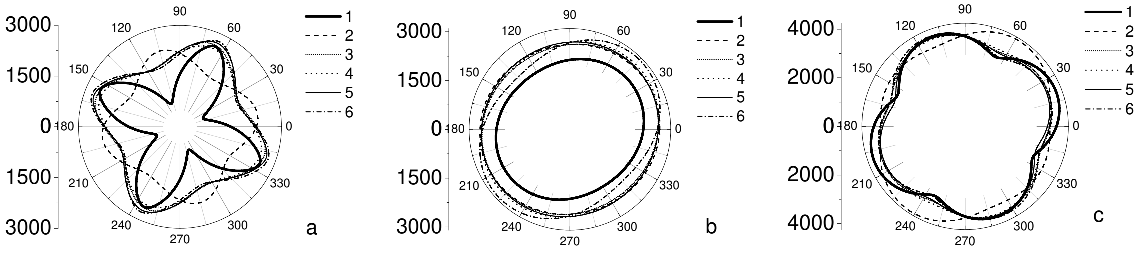

Figure 5. Velocity indicatrices of acoustic phonons propagated in the symmetry plane (010) in the paraelectric phase of $Sn_2P_2(Se_{0.28}S_{0.72})_6$ crystals at room temperature (1), and for $Sn_2P_2S_6$ crystals in the ferroelectric phase (2 – 337 K) and in the paraelectric phase (3 – 338.5, 4 – 340, 5 – 351, 6 – 372 K); (a) – transverse phonons polarized in the symmetry plane (010), (b) – transverse phonons polarized in the [010] direction, (c) – longitudinal phonons polarized in the symmetry plane (010).

3. Discussion

The results of Brillouin scattering investigations for $Sn_2P_2Se_6$ crystals are generalized based on the transverse acoustic phonon instability found in the paraelectric phase near the Lifshitz point. Let us consider the origin of this instability for proper ferroelectrics $Sn_2P_2(Se_xS_{1-x})_6$.

The interaction of the order parameter fluctuation with elastic degrees of freedom plays an essential role in the mechanism of the PT to the IC phase in proper ferroelectrics. A shift of the rigidity dispersion minimum of the order parameter η from the Brillouin zone center results in the rise of the coupling of a soft optical phonon with the acoustic ones. In the case of $Sn_2P_2S_6$-like crystals along q_y, the linear interaction between the soft TO mode and the transverse acoustic TA mode polarized along the X axis is involved. This interaction is proportional to the wave vector modulus, and both modes attain the similar B symmetry at $q_y \neq 0$. Moving away from the Brillouin zone center along q_z, the soft TO mode and mixed quasi-longitudinal and quasi-transverse acoustic vibrations polarized in the XZ plane attain the same A' symmetry which permits a linear interaction. These situations are characterized by the occurrence of $(\partial\eta/\partial Y) \cdot u_{xy}$-like or $(\partial\eta/\partial Z) \cdot u_{xz}$-like gradient invariants. Thus, critical wave vector of the IC phase and its temperature range, which are defined by a form of generalized rigidity dispersion, depend considerably on the elastic modules. If dispersion surface of the soft optical mode is close to isotropic one, the direction characterized by the smallest velocity of a transverse elastic wave is most favorable for modulation wave production.

Note that in $Sn_2P_2S_6$-like crystals along q_y, the TO mode interacts linearly only with the lower TA branch, whereas the interaction with LA branch occurs along q_z too, and this branch may serve as a mediator which gains the linear coupling between the soft TO and TA phonons. Moreover, due to a full-symmetric character of u_{xz} shift, the $\eta^2 u_{xz}$ invariant is available. A term $\eta^2 u_{xy}$ is forbidden by symmetry, and thus, for transverse acoustic phonons, propagating along Z axis, non-linear interaction with the order parameter fluctuations is allowed in the lowest order (for longitudinal phonons this holds true for $\eta^2 u_{ii}$). Due to the increase of the fluctuations on the approach to the PT from the paraelectric phase, this circumstance promotes the reduction of the velocity of TA phonons with q_z. Fluctuational variation of the velocity of TA phonons with q_y must be much smaller since only biquadratic non-linear coupling of $\eta^2 u_{xy}^2$ is allowed. These facts agree qualitatively with softening of quasitransverse acoustic phonons that are polarized in (010) plane and propagate near the direction of the modulation wave vector in the IC phase of $Sn_2P_2(Se_xS_{1-x})_6$ crystals (figure 5).

Earlier, the relationship between the softening observed by neutron scattering optic and acoustic branches and the incommensurate transition for $Sn_2P_2Se_6$ crystal was considered in a simple model for the dispersion curves and interaction strengths, valid in the low q continuum limit [8]. Such a model is suggested by the analysis of the spectra with the assumption of real coupling between optic and acoustic phonons. It was assumed that all of the soft fluctuation behavior is contained in a "bare" temperature dependent optic mode (polarization P_x), which interacts with a temperature independent acoustic mode (strain u_{xz}) via a temperature independent and real interaction strength. In this interaction model, a small change in the material's parameters (an increase of the soft optic mode dispersion and acoustic phonons velocity or a decrease of their interaction parameter) will change the position of the instability from $q_i \neq 0$ to $q_i = 0$ [8]. The sensitivity of the reciprocal-space position of the instability to the material parameters permits to investigate the origin of the Lifshitz point on the temperature - composition phase diagram of $Sn_2P_2(Se_xS_{1-x})_6$ crystals. However, to carry out the quantitative analysis, the investigations of temperature dependence of the mixed soft optic-acoustic phonons spectra near the PT are required.

It is important to notice that the PT from the paraelectric to IC phase in $Sn_2P_2Se_6$ simulated in continuous approximation occurs at too low temperature [8]. This may result from the presence of a central peak, which stabilizes the soft branch above T_i and related to the order/disorder component of the phase transition [3]. Obviously, the mixed optic-acoustic phonons do not completely condense, but only trigger the phase transition. At the same time a mechanism of strong interaction between the soft optic and acoustic branches near the Brillouin zone center in $Sn_2P_2Se_6$ crystals could be related to the disorder of the tin atoms in the paraelectric phase [12]. Taking into account that the condensed mode has got a mixed optic-elastic character and contains both oscillation and relaxation components, further spectroscopic investigations of the complex spectra of polarization dynamics are required. It is also interesting to refine the displacement and disordering components together with polarization and elastic contributions into the modulation wave in the IC phase of $Sn_2P_2(Se_xS_{1-x})_6$ crystals.

4. Conclusions

For $Sn_2P_2S_6$ and $Sn_2P_2(Se_{0.28}S_{0.72})_6$ crystals, the sound velocities were obtained for several propagation directions and a full set of elastic constants for the ferroelectric and the paraelectric phases, respectively, was determined. In the region of the second order ferroelectric phase transition, the strong temperature dependence of sound velocities was observed along [010] and [011] directions, while the weak dependence along [100] direction takes place. Transverse acoustic modes along [001] direction did not show a clear temperature dependence. There was found a transformation of the orientation dependence of sound velocities at transition from pure $Sn_2P_2S_6$ to mixed crystal $Sn_2P_2(Se_{0.28}S_{0.72})_6$. The softening of transverse acoustic phonons propagated and polarized in the (010) symmetry plane was found in paraelectric phase near the Lifshitz point in $Sn_2P_2(Se_{0.28}S_{0.72})_6$ crystal. This instability is related to the origin of the IC phase appearance in the $Sn_2P_2(Se_xS_{1-x})_6$ crystals and obviously determines the peculiarities of the modulation wave.

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Температурна залежність спектрів розсіювання Мандельштама-Бріллюена в сегнетоелектричних кристалах $Sn_2P_2S(Se)_6$

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Методом розсіювання Мандельштама-Бріллюена досліджено температурну залежність швидкостей гіперзвуку при переході з параелектричної у сегнетоелектричну фазу в кристалах $Sn_2P_2S_6$. На основі цих даних визначено повний набір пружних модулів. Такі ж вимірювання проведені для твердого розчину $Sn_2P_2(Se_{0.28}S_{0.72})_6$ у параелектричній фазі біля точки Ліфшиця. Спостерігається еволюція індикатриси швидкостей при переході від $Sn_2P_2S_6$ до $Sn_2P_2(Se_{0.28}S_{0.72})_6$ та зм'якшення поперечного акустичного фонона в параелектричній фазі біля точки Ліфшиця. Нестабільність акустичного фонона спричинена взаємодією з м'якою оптичною модою, що є природою виникнення несумірної фази в твердих розчинах $Sn_2P_2(Se_xS_{1-x})_6$ з $x > x_{\mathrm{LP}} = 0.28$.

Ключові слова: *розсіювання Мандельштама-Бріллюена, м'яка мода, точка Ліфшиця*

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