
On the (P, T, x) -phase diagram of $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$ solid solutions: comparison of temperature dependences of the acoustic wave velocities in $\text{Sn}_2\text{P}_2\text{S}_6$ and $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ crystals under high hydrostatic pressures

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Abstract. We have studied temperature dependences of the longitudinal ultrasonic wave velocity v_{55} for $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ crystals at different hydrostatic pressures. It has been shown that the temperature and pressure behaviours of v_{55} for $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ essentially differ from those found for the pure $\text{Sn}_2\text{P}_2\text{S}_6$ crystals. A partial (P, T, x) -phase diagram for the solid solutions $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$ is constructed and discussed.

Keywords: $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$, ferroelectric phase transition, tricritical point; acoustic wave velocity, hydrostatic pressure

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$\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ crystals belong to the family of solid solutions with a general formula $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$. They undergo a proper paraelectric-to-ferroelectric phase transition at $T_C = 283$ K, with a schematic change $2/m F m$ of their point symmetry [1, 2]. It has been assumed for a long time that the $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ crystals are unique among ferroelectrics in that they correspond to thermodynamic conditions of the Lifshitz point [1–6]. Just at this point of the (x, T) -phase diagram, a second-order paraelectric-to-ferroelectric phase transition, which takes place at $x < 0.28$, should split into two transitions: a second-order paraelectric-to-incommensurate one and an incommensurate-to-ferroelectric transition which is of the first order.

As a matter of fact, the Lifshitz point is one of very special points predicted by the Landau mean-field theory and so it occurs quite rarely. The existence of the Lifshitz point has earlier been unambiguously proved in experiments only for the ferromagnetic crystal MnP [7, 8]. As shown in our recent works, the phase transition in $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ crystals is of the second order [9] though, at atmospheric pressure, it closely corresponds to the conditions of the tricritical point rather than the Lifshitz point [10]. In such a case splitting of the first-order paraelectric-to-ferroelectric phase transition should appear at some higher concentrations of selenium, e.g. at an ordinary triple point at $x \approx 0.4$ [10]. Moreover, the appearance of the tricritical point at $P_{TC} = 4335.7$ bar and $T_{TC} = 259$ K has been revealed [11] on the pressure–temperature (P, T) -phase diagram of the pure $\text{Sn}_2\text{P}_2\text{S}_6$ crystals, rather than the Lifshitz point as assumed in the works [12–14]. Notice that, according to [12–14], the Lifshitz point on the (P, T) -phase diagram of $\text{Sn}_2\text{P}_2\text{S}_6$ appears at the coordinates $(P, T) = (1.9$ kbar, 295 K). All these facts imply that the (P, T, x) -phase diagram of the $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$ crystals should be thoroughly reinvestigated.

In this brief communication we report and discuss a partial (P, T, x) -phase diagram for the $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$ solid solutions obtained on the basis of standard acoustic studies. We also analyse

differences in the temperature and pressure behaviours of the acoustic wave velocities found for $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$ crystals and the pure $\text{Sn}_2\text{P}_2\text{S}_6$ crystals.

The acoustic measurements were performed using a plate of single $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ crystal, with the thickness of $d = 4.97$ mm, perpendicular to the bisector between the crystallographic axes a and c . Hydrostatic pressures were created inside a special chamber, using a pumping station UNGR-20000 and an oil as a pressure transmitter. The sample was cooled by a nitrogen gas flow. The velocity of the longitudinal ultrasonic wave v_{55} was measured with a standard pulse-echo overlap method [15]. The acoustic wave in the sample was excited with LiNbO_3 transducers (the resonance frequency $f = 10$ MHz, the bandwidth $\Delta f = 0.1$ MHz, and the acoustic power $P_a = 1\text{--}2$ W). The measurements of the acoustic wave velocity were performed at constant hydrostatic pressures in a cooling run, with the temperature change rate of about 0.2 K/min.

Fig. 1 shows the experimental results for the temperature dependences of the longitudinal ultrasonic wave v_{55} for $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ under different hydrostatic pressures. The values of the hydrostatic pressure correspond to the phase transition temperatures T_C . For the sake of comparison, the corresponding temperature dependences of the velocity v_{55} for the $\text{Sn}_2\text{P}_2\text{S}_6$ crystals derived at different hydrostatic pressures in the work [11] are also presented in Fig. 1.

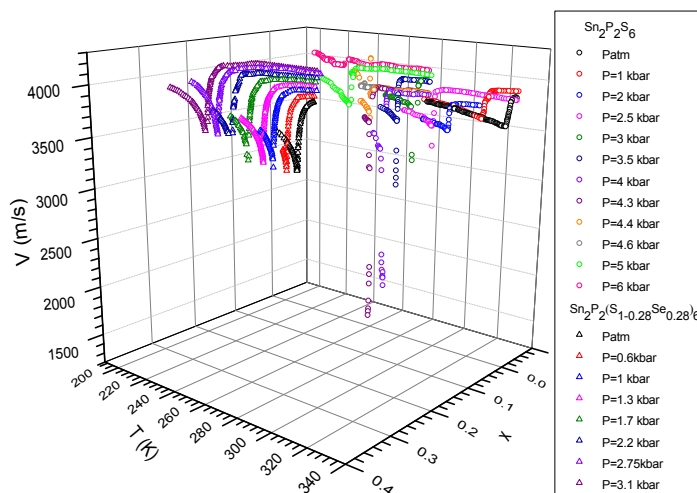


Fig. 1. Temperature dependences of longitudinal acoustic wave velocity v_{55} at different hydrostatic pressures obtained for $\text{Sn}_2\text{P}_2\text{S}_6$ (circles) [11] and $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ crystals (triangles).

As seen from Fig. 1, the phase transition from the paraelectric to ferroelectric phase in the both crystals is clearly revealed as anomalous changes in the velocity v_{55} occurring in the vicinity of T_C . Since the reflected signal practically disappears at the hydrostatic pressures higher than 3.1 kbar, the studies of the acoustic wave velocity for $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ under those conditions have become impossible. Such behaviour can probably be caused by a notable obliquity of the acoustic energy flow or appearance of a well-defined phase boundary that leads to scattering of the acoustic wave. It is worth noticing that further decrease in the hydrostatic pressure down to 3.1 kbar yields in restoring of the reflected signal.

The overall temperature-pressure behaviours of the v_{55} velocity differ essentially for the both crystals. The ‘depth’ of the velocity minimum observed at T_C for the pure $\text{Sn}_2\text{P}_2\text{S}_6$ crystals increases with increasing hydrostatic pressure and acquires its highest value at $P_{TC} \approx 4.3$ kbar and $T_{TC} = 259$ K (see Fig. 2). As shown in our recent work [11], this behaviour of the v_{55} parameter observed for the above crystals is caused by existence of the tricritical point on the (P, T) -phase diagram and the corresponding change in the order of phase transition from second to the first one

at $P \approx 4.3$ kbar. On the other hand, the difference of the so-called ‘background’ velocity in the paraelectric phase and the minimal velocity at T_C ($v_{55}^{pp} - v_{55}^{T_C}$) for the $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ crystals increases quite weakly with increasing pressure (see Fig. 2). Moreover, this velocity difference depends almost linearly on the pressure for the case of $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$.

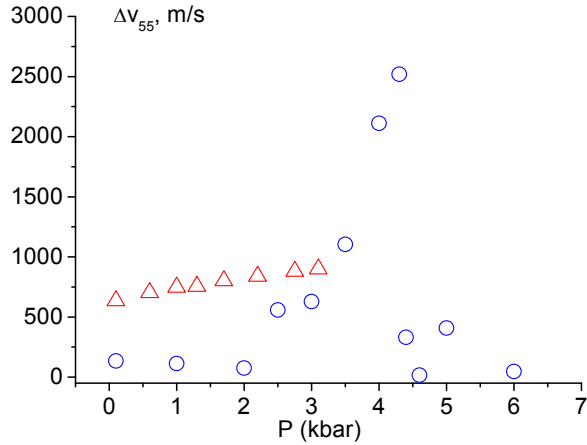


Fig. 2. Pressure dependence of difference of the velocity v_{55} in the paraelectric phase and the minimal velocity at T_C : circles correspond to $\text{Sn}_2\text{P}_2\text{S}_6$ and triangles to $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ crystals.

Since the $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ crystals stay in the conditions of the tricritical point already at the atmospheric pressure, so different temperature and pressure behaviours of the same sound velocity in the both crystals suggest that, contrary to the pure $\text{S}_2\text{P}_2\text{S}_6$ compound, the $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ solid solutions should ‘move away’ from the tricritical point with increasing hydrostatic pressure.

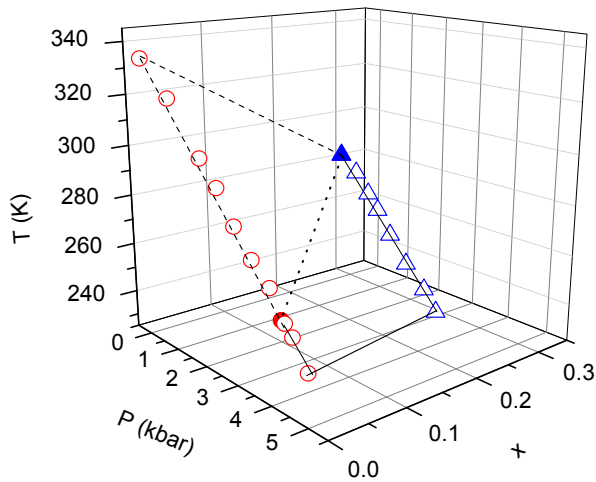


Fig. 3. (P, T, x) -phase diagrams for $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$ solid solutions: open circles correspond to $\text{Sn}_2\text{P}_2\text{S}_6$ and open triangles to $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ crystals; a full circle and a full triangle correspond to the tricritical points; solid and dashed lines are lines of the first-order and second-order phase transitions, respectively; dotted line represents schematically a line of tricritical points.

Using our experimental data concerned with the baric shifts of the Curie temperature for the both crystals, one can construct a partial (P, T, x) -phase diagram for the $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$ solid solutions given by Fig. 3. It is readily seen from Fig. 3 that the Curie temperature decreases linearly with increasing pressure in the both cases. In fact, the lines of the phase transition for the both crystals are parallel. The latter fact suggests that this part of the (P, T, x) -phase diagram represents a plane. Hence, the tricritical points in the both crystals should be connected by some straight line or a curve in the (P, T, x) -space, which is schematically represented by a dotted line in Fig. 3. Let us finally notice that no phase transition splitting is observed on the phase diagram of $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ for the pressures as high as 3.1 kbar.

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Анотація. В роботі досліджено температурні залежності швидкості поздовжньої ультразвукової хвилі v_{55} у кристалах $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ при різних гідростатичних тисках. Показано, що температурна і тискова залежності швидкості v_{55} в кристалах $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ суттєво відрізняються від відповідних залежностей в кристалах $\text{Sn}_2\text{P}_2\text{S}_6$. Отримана і проаналізована частина (P, T, x) -фазової діаграми для твердих розчинів $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$.