Quantum paraelectric state and critical behavior in Sn(Pb)$_2$P$_2$S(Se)$_6$ ferroelectrics

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The dipole ordering in Sn(Pb)$_2$P$_2$S(Se)$_6$ materials may be tuned by chemical substitution realizing a ferroelectric quantum phase transition and quantum glassy or relaxor type phenomena on different parts of the phase diagram. The introduction of Ge impurity increases the temperature of the phase transitions and initiates a more pronounced Ising type critical anomaly in Sn$_2$P$_2$S$_6$ crystal, does not shift the coordinate of the Lifshitz point $x_{LF}$ in Sn$_2$P$_2$(Se$_{1-x}$)$_6$ mixed crystals, induces the appearance of a ferroelectric phase transition in quantum paraelectrics Pb$_2$P$_2$S$_6$ and inhomogeneous polar ordering in (Pb$_{1-x}$Sn$_x$)$_2$P$_2$S(Se)$_6$ crystals. For Pb$_2$P$_2$S$_6$ crystal, the real part of the dielectric susceptibility in the quantum critical regime varies as $1/T^2$ instead of the expected $1/T^3$ behavior of quantum paraelectric systems. This can be partially explained by a screening phenomenon in the semiconductor materials of the Sn(Pb)$_2$P$_2$S(Se)$_6$ system, which weakens the long range electric dipole interactions, and also provides, at high temperatures, a critical behavior near the Lifshitz point (studied by thermal diffusivity) similar to the one predicted in the case of systems with short range interactions. At low temperatures, a quantum critical behavior in Pb$_2$P$_2$S$_6$ crystal can be established by the nonlinear coupling between polar and antipolar fluctuations. An increase in thermal conductivity is induced by Ge impurity in Pb$_2$P$_2$S$_6$ crystal, which is explained through the weakening of the acoustic phonons resonance scattering by soft optic phonons because of the appearance of ferroelectric phase polar clusters.

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I. INTRODUCTION

It was earlier found$^1$ that Ge doping shifts the second order phase transition (P2$_1$/c+Pc) in uniaxial ferroelectric Sn$_2$P$_2$S$_6$ crystal toward higher temperatures. The increase of the phase transition temperature under the influence of Ge impurities is also known for Pb$_{1-x}$Ge$_x$Te and Sn$_{1-x}$Ge$_x$Te ferroelectrics,$^2$ what demonstrates the universal property of Ge impurities in tin or lead containing hosts of elevating the ferroelectric phase transition temperature. By means of X-ray photoelectron spectroscopy, together with first-principles calculations of electronic spectra, it was found$^3$ that the germanium impurity in Sn$_2$P$_2$S$_6$ improves the stereoactivity of the cation sublattice. In Sn$_2$P$_2$S$_6$ ferroelectrics the Sn$^{2+}$ cations stereoactivity and the $P^{4+} + P^{4+} \rightarrow P^{3+} + P^{5+}$ charge disproportionation is related to the nature of the second order phase transition with mixed displacive-order/disorder character.$^{4,5}$

While germanium can only be introduced up to a certain quantity,$^1$ lead can completely substitute tin in (Pb$_y$Sn$_{1-y}$)$_2$P$_2$S$_6$ and (Pb$_y$Sn$_{1-y}$)$_2$P$_2$S$_6$ continuous solid solutions.$^6$ The replacement of tin by lead in the cationic sublattice induces the lowering of the phase transition temperature (see Fig. 1), changing its character to a discontinuous transition across the tricritical point (TCP), and stabilizing the paraelectric phase in the ground state (at $T = 0$ K) for $y > 0.61.$$^7$ The addition of Pb has the effect of diluting the stereoactivity as it weakens the bonding hybridization responsible for ferroelectricity. Formally, the introduction of lead atoms creates a chemical pressure with similar effects to the mechanical pressure.$^5$ The properties of the (Pb$_y$Sn$_{1-y}$)$_2$P$_2$S$_6$ mixed crystals have been described$^7$ within the framework of Blume-Emery-Griffith (BEG) model$^{8,9}$ taking into account the presence of random fields created when substituting tin by lead.

The substitution of S by Se in the anionic sublattice provokes the appearance of an incommensurate (IC) phase at the Lifshitz point (LP) for $x > x_{LF} \approx 0.28$ in Sn$_2$P$_2$(Se$_{1-x}$)$_6$ solid solutions.$^{10}$ The line of tricritical points meet with the line of Lifshitz points at the tricritical Lifshitz point on the $T - x - y$ phase diagram with an interesting topology.$^{11}$

In mixed crystals (Pb$_y$Sn$_{1-y}$)$_2$P$_2$S$_6$ and (Pb$_y$Sn$_{1-y}$)$_2$P$_2$S$_6$ at $y > 0.61$ and $y > 0.65$, respectively, the paraelectric phase is stable in the ground state.$^{6,12}$ and pure compounds Pb$_2$P$_2$S$_6$ and Pb$_2$P$_2$Se$_6$ are quantum paraelectrics. The quantum paraelectric state is manifested in the Pb$_2$P$_2$S$_6$ crystal by the growth of the dielectric susceptibility while cooling down to 0 K.$^5$ A similar state also appears in the Sn$_2$P$_2$S$_6$ crystal at hydrostatic pressure $p > 1.5$ GPa.$^{13,14}$

The Pb$^{2+}$ cations have a smaller stereoactivity compared with Sn$^{2+}$ and this determines the suppression of ferroelectricity while substituting tin by lead.$^{5,15}$ In the case of Ge$^{2+}$ cations, the stereoactivity is bigger, which provokes a temperature rise in the ferroelectric phase transition in Sn$_2$P$_2$S$_6$ crystals with germanium impurity.$^1,16$ For Sn$_2$P$_2$(Se$_{1-x}$)$_6$ solutions, both S by
Se and Sn by Ge replacements increase the crystal lattice covalence, and the critical anomaly near the LP becomes sharper.\textsuperscript{17}

In the case of the binary compounds GeS, SnS, PbS or GeS, GeSe, GeTe, it was demonstrated that it is mostly the energy difference between $s$ orbitals of metal atoms and $p$ orbital of chalcogen atoms which determines the stereoelectricity of the cations and the crystal lattice covalency.\textsuperscript{18} For ternary compounds, for example BiNiO$_3$, it was demonstrated\textsuperscript{19} that the energy positions of the valence orbitals of the two cations Bi$^{3+}$ and Ni$^{2+}$ are also important. Therefore, for compounds of the Sn(Pb)$_2$P$_2$S$_6$(Se)$_6$ system with two types of cations (tin or lead metals and phosphorous), a more complex role of the electron valence orbitals hybridization can also be important.\textsuperscript{5,15,20} It was found\textsuperscript{5} that Sn by Pb substitution changes the local potential for spontaneous polarization fluctuation at almost constant intercell interactions. On S by Se substitution, on the contrary, the intersite interaction is changed.

In previous investigations,\textsuperscript{5,6,12} the influence of Sn→Pb and S→Se substitutions on the phase transition from the paraelectric phase into the ferroelectric one has been analyzed. Here we will pay attention to understanding the germanium impurity influence on the phase transitions and the quantum paraelectric state in different segments of the Sn(Pb)$_2$P$_2$S$_6$(Se)$_6$ ferroelectrics phase diagram. The temperature dependence of dielectric susceptibility and thermal diffusivity are analyzed with the use of the quantum anharmonic oscillators (QAO) model\textsuperscript{5,21} for the calculation of the spontaneous polarization fluctuations spectra in the local three-well potential. The appearance of the quantum critical behavior in Pb$_2$P$_2$S$_6$ and (Pb$_{0.98}$Ge$_{0.02}$)$_2$P$_2$S$_6$ crystals, in mixed (Pb$_y$Sn$_{1-y}$)$_2$P$_2$S$_6$ and (Pb$_y$Sn$_{1-y}$)$_2$P$_2$Se$_6$ crystals with 5% of Ge impurity is investigated, together with the appearance of polar ordering at low temperatures induced by germanium.

\section{Experimental data}

We have investigated the temperature dependence of the dielectric susceptibility with a HP4284 precision LCR meter at temperatures from 300 to 20 K during the cooling cycle at a rate of about 1 K/min, and at frequencies ranging from 20 to 1 MHz.\textsuperscript{22,23} The thermal diffusivity $D$ measurements have been performed by a high resolution $ac$ photopyroelectric calorimetry technique in the standard back detection configuration. A closed cycle He cryocryostat operated in cooling and heating modes has been used.\textsuperscript{16} Ge-doped single crystals were obtained by vapor-transport method in a quartz tube using SnI$_2$ as a transport agent. The synthesis of the starting material in the polycrystalline form was carried out using high-purity (99.999\%) elements.\textsuperscript{16,24} The samples were characterized and oriented by X-ray diffraction technique. For complex dielectric susceptibility measurements, the monocristalline plates with the thickness of about 2 mm and plane parallel faces around 15 mm$^2$ with silver paste electrodes on (100) faces were prepared. For thermal diffusivity measurements all samples have been prepared in the form of thin plane-parallel slabs with thicknesses in a range of 0.500-0.550 mm and whose faces were cut in the monoclinic symmetry plane.

For Pb$_2$P$_2$S$_6$ crystal the $\varepsilon'(T)$ dependence shows monotonic rise at cooling till 20 K (see Fig. 2) with some flattening below 50 K. At lead by germanium substitution (about 2\%), a clear maximum of $\varepsilon''(T)$ near 35 K (at 100 kHz frequency) is observed (see Fig. 3) and below this temperature $\varepsilon'(T)$ displays frequency dependency in the range between 1 kHz and 1 MHz. In the case of (Pb$_{0.98}$Sn$_{0.02}$)$_2$P$_2$S$_6$ and (Pb$_{y}$Sn$_{1-y}$)$_2$P$_2$Se$_6$ mixed crystals, $\varepsilon'(T)$ and $\varepsilon''(T)$ anomalies also appear in the temperature region of 20–50 K (see Fig. 4, 5). These anomalies are induced by germanium impurity.

By the previous dielectric investigations\textsuperscript{15} it was shown that for (Pb$_y$Sn$_{1-y}$)$_2$P$_2$S$_6$ mixed crystals with $y = 0.61$ and $y = 0.66$ in the paraelectric phase $\varepsilon'(T) \sim (T - T_C)^{-2}$. Such dependence was attributed to glassy-like dielectric susceptibility behavior in (Pb$_y$Sn$_{1-y}$)$_2$P$_2$S$_6$ mixed crystals with coexisting paraelectric and ferroelectric states. We have shown that such temperature dependence of the dielectric susceptibility can be attributed to the appearance of the spontaneous polarization quantum fluctuations at low temperatures in the crystals of the investigated system.

For Pb$_2$P$_2$S$_6$ crystal the real part of the dielectric susceptibility increases monotonously with decreasing temperature and in the measured temperature range the saturation behavior is not observed [see Fig. 2(a)]. In the
That is the most prominent criterion of the dielectric susceptibility of quantum paraelectrics, \( \varepsilon \). Accord-

parts of dielectric susceptibility at different frequencies.(FIG. 4. Temperature dependence of the real and imaginary parts of dielectric susceptibility real \( \varepsilon' \) (blue squares) and imaginary \( \varepsilon'' \) (red circles) parts at 100 kHz for \((\text{Pb}_{0.98}\text{Ge}_{0.02})_2\text{P}_2\text{S}_6\) crystal.)

FIG. 5. Temperature dependence of dielectric susceptibility real part of (a) \((\text{Pb}_{0.7}\text{Sn}_{0.25}\text{Ge}_{0.05})_2\text{P}_2\text{S}_6\) and (b) \((\text{Pb}_{0.5}\text{Sn}_{0.25}\text{Ge}_{0.05})_2\text{P}_2\text{S}_6\) at 10 kHz; orange solid line is the fitting according to the Barret's equation (1). The inset shows the reciprocal dielectric susceptibility as a function of the squared temperature (blue lines).

Barrets equation can be used:

\[
\varepsilon(T) = \frac{C}{\left(\frac{T}{T_C}\right) \coth\left(\frac{T}{T_C}\right) - T_C} + \varepsilon_0, \tag{1}
\]

where \( C \) is the Curie-Weiss constant, \( T_C \) is the classical paraelectric Curie temperature, \( \varepsilon_0 \) is a temperature independent constant and \( T_1 \) is the dividing point between the low temperatures where quantum effects are important so \( \varepsilon(T) \) deviates from Curie-Weiss law, and the high temperature region where a classical approximation and Curie-Weiss law are valid. 25, 27

In many cases, \( T_C \leq 0 \) K, and the material does not undergo a ferroelectric phase transition at any finite temperature. When \( T_C \) is finite and \( T_C < T_1 \), the quantum fluctuations break the long range ferroelectric order and stabilize the quantum paraelectric state in the sample. Probable ferroelectric transition occurs at \( T_C \). 26 According to dielectric data of \( \text{Pb}_2\text{P}_2\text{S}_6 \) [see Fig. 2(a)] deviation from Barrett’s equation starts around 75 K. The obtained parameter values \( (T_1 \approx 190 \) K and \( T_C \approx -370 \) K) for \( \text{Pb}_2\text{P}_2\text{S}_6 \) crystal demonstrate that the material does not undergo a ferroelectric phase transition at any finite temperature.

As was mentioned above, when Pb substitutes Sn in Sn\(_2\)P\(_2\)S\(_6\) type crystals, the hybridization of anion and cation orbitals becomes weaker, reducing the phase transition temperature. On the other hand, Ge dopant plays an opposite role; it enhances the total stereoactivity of the cation sublattice in the crystal. Small amount of impurities in quantum paraelectrics could induce ferroelectricity. 29, 30 So, it is possible that germanium impurities can affect quantum paraelectric state of \( \text{Pb}_2\text{P}_2\text{S}_6 \). Figure 2(b) shows the temperature dependence of the real part of dielectric susceptibility for \((\text{Pb}_{0.98}\text{Ge}_{0.02})_2\text{P}_2\text{S}_6\) crystal and confirms a non-classical \( T^2 \) behavior of the inverse dielectric susceptibility. For this, the temperature dependence of the real part of dielectric susceptibility for crystal doped by germanium is fitted by the Barretts equation (1) giving temperatures \( T_1 \approx 200 \) K and \( T_C \approx 40 \) K. Since \( T_C < T_1 \) for \((\text{Pb}_{0.98}\text{Ge}_{0.02})_2\text{P}_2\text{S}_6\), it could be concluded that the quantum critical regime the usual Curie-Weiss law of the inverse dielectric susceptibility \( 1/\varepsilon(T) \sim T \) changes into \( 1/\varepsilon(T) \sim T^2 \). 25, 26 That is the most prominent criterion for quantum critical behavior. For \( \text{Pb}_2\text{P}_2\text{S}_6 \) the inverse dielectric susceptibility \( 1/\varepsilon(T) \) exhibits the expected non-classical \( T^2 \) temperature dependence over the temperature range 50 K–250 K.

In order to describe the temperature dependencies of the dielectric susceptibility of quantum paraelectrics,
long-range ferroelectric order in the sample doped by Ge is broken due to quantum fluctuations below 200 K, and a probable ferroelectric transition occurs in the temperature region between 40 K and 80 K (see Fig. 3). Doping with germanium decreases the real part of susceptibility below 80 K deviating from Barrett’s fit [see Fig. 2(b)].

The peak of the real part of the dielectric susceptibility is broad. Moreover, there are two peaks of the imaginary part of the dielectric susceptibility with a frequency dispersive behavior, and the temperatures of the loss peaks are around 50 K and 100 K at 100 kHz (see Fig. 3). Obviously, this is related to compositional fluctuations in (Pb0.98Ge0.02)2P2S6 crystal. Also, a fast-enough dynamics of local dipoles, and slow dynamics of noninteracting ones, or weakly interacting nanoclusters, can determine the broadness of the phase transition induced by Ge impurity with related frequency–temperature anomalous behavior of dielectric susceptibility that is similar to the one observed in the case of a crossover between dipole glass and ferroelectric relaxor.29,30

As was already mentioned, for (Pb0.9Sn1−y)2P2S6 mixed crystals with compositions y = 0.61 and y = 0.66, which are close to the transition at zero temperature from a polar phase to a paraelectric one, the dielectric susceptibility demonstrates the quantum critical behavior with TC ≈ 35 K and 20 K, respectively.12 We have investigated the influence of Ge dopants on the paraelectric state of Pb2P2S6 type compounds by studying of (Pb0.97Sn0.03Ge0.05)2P2S6 and (Pb0.97Sn0.03Ge0.05)2P2S6 samples. In these crystals the Sn2+ sites of pure Sn2P2S6 were codoped with two different impurities (Pb2+ and Ge2+) which have very different influences on the phase transitions. It is important to realize that Sn substitution has the strongest effect because the ferroelectric phase transition is induced by the stereoactivity of the Sn2+ cation 5s2 electron lone pair.

The temperature dependence of the real part of the dielectric susceptibility for (Pb0.97Sn0.03Ge0.05)2P2S6 and (Pb0.97Sn0.03Ge0.05)2P2S6 crystals is shown in Fig. 4. Susceptibility ε′ increases continuously with decreasing temperature from room temperature till 20 K. The dielectric losses have maximum at low temperature, around 40 K at frequency 1 MHz. The inverse dielectric permittivity 1/ε(T) exhibits the expected non-classical T2 temperature dependence not only in the case of doped (Pb0.98Ge0.02)2P2S6 sample (see Fig. 2), but it is also observed in mixed crystals (Pb0.97Sn0.03Ge0.05)2P2S6 and (Pb0.97Sn0.03Ge0.05)2P2S6 (see Fig. 5). From this follows that the ferroelectric quantum critical behavior is relatively insensitive to quenched disorder in doped samples and mixed crystals.

By fitting the experimental data of Fig. 5(a) to Barrett’s equation (1) it was determined the next parameters: T1 ≈ 70 K, TC ≈ −4 K, and C ≈ 30670 K. The observed temperature behavior of the dielectric susceptibility demonstrates that (Pb0.97Sn0.03Ge0.05)2P2S6 crystal obviously undergoes some inhomogeneous polar ordering at very low temperatures.

Similarly, the temperature dependence of the dielectric susceptibility ε′(T) for the (Pb0.97Sn0.03Ge0.05)2P2S6 crystal is shown in Fig. 5(b). On cooling from 300 till 20 K both ε′ and ε″ increase, their frequency dispersion more clearly appears below 100 K.23 By fitting to the Barrett’s equation (1) [see Fig. 5(b)] it was found that T1 ≈ 55 K, TC ≈ −6 K, and C ≈ 34260 K. It is seen that in the selenide mixed crystal (Pb0.97Sn0.03Ge0.05)2P2S6 the germanium impurity induces inhomogeneous polar ordering at lower temperatures similarly to the case of the sulfide analogue.

As a whole, according to the results of the dielectric investigations, it can be concluded that Pb2P2S6 crystals exhibit a quantum paraelectric state. The introduction of small amounts of germanium dopant provokes the appearance of the ferroelectric phase. In mixed crystals a very inhomogeneous polar ordering (like dipole glassy or relaxor state) appears below approximately 100 K.

We can see that the ε′(T) dependence of Eq. (1), considering quantum fluctuations for Pb2P2S6 compound, predicts the value of TC in accordance with T0(y) dependence for (Pb0.9Sn1−y)2P2S6 mixed crystals (see Fig. 1). At this, the value of T1 is strongly suppressed in mixed crystals — from 190 K in Pb2P2S6 and 207 K in the case of (Pb0.98Ge0.02)2P2S6 to T1 ≈ 70 K in the solution with y = 0.7. Such decrease of the crossover temperature T1 from classic to quantum fluctuations behavior can be interpreted as the manifestation of quantum coherence destruction for the electronic component of spontaneous polarization fluctuations, that are determined by phosphorous cations P4+ ↔ P4+ ↔ P3+ ↔ P5+ charge disproportionation. The electronic contribution to spontaneous polarization is connected to the coherent state of polaronic excitons — small hole polarons in SnP2S3 structural groups are coupled with small electronic polarons in nearest SnP2S3 structural groups.5,31 Obviously such polaronic excitons are strongly bounded by defects in mixed crystals what preserves the development of quantum fluctuations when lowering the temperature.

![Temperature dependence of dielectric susceptibility](image)

**Fig. 6.** Temperature dependence of dielectric susceptibility (a) real and (b) imaginary parts for crystals (Pb0.97Sn0.03Ge0.05)2P2S6. Data [12] for (Pb0.91Sn0.09)2P2S6 and (Pb0.96Sn0.04)2P2S6 mixed crystals are also shown for comparison.

In Fig. 6 the temperature dependencies of real and imaginary parts of dielectric susceptibility are compared for (Pb0.97Sn0.03Ge0.05)2P2S6 crystal in comparison with data [12] for (Pb0.96Sn0.04)2P2S6 and
The introduction of the germanium impurity into Sn$_2$P$_2$S$_6$ crystal lattice increases the dip of the thermal diffusivity anomaly near the second order phase transition, which becomes a little broader than in the case of the nominally pure crystal [see Fig. 7(b)] and therefore, it was not possible to perform fittings with great accuracy.\cite{16,33}

For Sn$_2$P$_2$S$_6$ crystal, the germanium dopant shifts the temperature of continuous ferroelectric transition upwards and sharpens the critical anomaly of thermal diffusivity (see Fig. 7).\cite{16} The introduction of germanium impurity into Sn$_2$P$_2$S$_6$ crystal lattice increases the dip of the thermal diffusivity anomaly near the second order phase transition, which becomes a little broader than in the case of the nominally pure crystal [see Fig. 7(b)] and therefore, it was not possible to perform fittings with great accuracy.\cite{16,33}

For the Lifshitz point composition Sn$_2$P$_2$(Se$_0$28S$_0$72)\(_6\) crystal, the critical index $\alpha \approx 0.34$ and the critical amplitudes ratio $A^+/A^- \approx 0.42$ were observed.\cite{34} The introduction of Ge increases the critical temperature from 281.3 K to 284 K [see Fig. 7(c)] but changes neither the character of the transition nor the universality class, as it is uniaxial Lifshitz class with critical exponent $\alpha \approx 0.25$ and $A^+/A^- \approx 0.49$.\cite{32} Such values agree with the theoretical ones estimated for a Lifshitz system without considering strong dipolar interactions. In the case of the Lifshitz point in uniaxial ferroelectrics only small multiplicative corrections to mean field behavior are expected\cite{38} in the critical region. Hence, both the critical exponent and the amplitude ratio values observed for the Sn$_2$P$_2$(Se$_0$28S$_0$72)\(_6\) mixed crystal lead to the conclusion that long-range interactions do not have a strong influence on the critical behavior in this system. This can be related to the partial screening of the dipole-dipole interaction by charge carriers in the Sn$_2$P$_2$(Se$_0$S$_{1-x}$)\(_6\) ferroelectric semiconductors.

In order to determine the thermal conductivity $k$ of the investigated samples, thermal diffusivity data $D$ have been combined with heat capacity data $c$ using the following equation:

\[ k = cD. \]  

(2)

For (Pb$_{0.98}$Ge$_{0.02}$)$_2$P$_2$S$_6$ crystal the thermal conductivity at low temperatures is bigger than in the case of pure Pb$_2$P$_2$S$_6$ crystal (see Fig. 8). This is related to the induction of polar clusters of the ferroelectric phase when doping with Ge. The dielectric susceptibility of such clusters is smaller than the susceptibility of the paraelectric phase and the frequency of the lowest energy soft polar optic mode near the Brillouin zone (BZ) center is elevated. The growth of the soft optical mode frequency diminishes the probability of the optical phonon resonance scattering by acoustic phonons.\cite{39,40} At low temperatures heat is transferred by acoustic and lowest frequency optical phonons. Acoustic phonons with small wave numbers are involved mostly in normal scattering (N-process) that doesn’t contribute to thermal resistivity. The phonons from the optical branch near the BZ center also participate in Umklapp scattering (U-process) by lattice imperfections, which provide an effective thermal resistivity. So, the hardening of the optical branch lowers the population of the optical phonons and increases the thermal conductivity of (Pb$_{0.98}$Ge$_{0.02}$)$_2$P$_2$S$_6$ crystal at very low temperatures (see Fig. 8).

Such explanation agrees with the comparison of the changes in the temperature dependencies of dielectric susceptibility and thermal conductivity induced by germanium (Fig. 9). On cooling below 100 K, the difference in thermal conductivity between (Pb$_{0.98}$Ge$_{0.02}$)$_2$P$_2$S$_6$ and Pb$_2$P$_2$S$_6$ crystals rapidly rises, and oppositely — dielectric susceptibility of (Pb$_{0.98}$Ge$_{0.02}$)$_2$P$_2$S$_6$ crystal quickly lowers relatively to Pb$_2$P$_2$S$_6$ crystal susceptibility.
Such low temperature evolution of the dielectric susceptibility induced by germanium impurity reflects the hardening (frequency increase) of the lowest polar optic mode near the BZ center.

With the introduction of germanium into the lattice of Pb$_2$P$_2$S$_6$ crystal, the temperature dependence of the thermal conductivity coefficient $k(T)$ in a wide temperature range coincides with Eikens law, i.e. it is proportional to the inverse of temperature (see Fig. 10). Such dependency gives evidence about the dominant role of three-phonon scattering processes in the thermal resistivity. In the case of Sn$_2$P$_2$S$_6$ ferroelectric phase, the introduction of Ge impurity also improves $k \sim T^{-1}$ temperature dependence for the thermal conductivity.

In the case of (Pb$_{0.7}$Sn$_{0.25}$Ge$_{0.05}$)$_2$P$_2$S$_6$ mixed crystals the thermal conductivity temperature behavior (see Fig. 11) is similar to observed in case of glassy materials, what demonstrates an effective phonon scattering in solid solutions with sublattice of mixed tin and lead cations. The addition of germanium impurity induces the dipole glass state, which appeared in the complex dielectric susceptibility frequency dependency below 100 K (see Fig. 4). Only a small contribution to thermal conductivity by germanium addition is observed in the temperature range from 50 K to 120 K. Similar behavior is also observed for (Pb$_{0.7}$Sn$_{0.25}$Ge$_{0.05}$)$_2$P$_2$S$_6$ selenide solid solution.

### III. DISCUSSION OF RESULTS

With the application of the local mode approach to the monoclinic ferroelectrics Sn$_2$P$_2$S$_6$, it was found a three-well potential energy surface. The nonlinear interaction of the vibration modes leads to this complex shape of local potential for spontaneous polarization fluctuations. Such nonlinearity is a result of significant electron-phonon interaction, that can be described as a second order Jahn-Teller effect related to the electron lone pair stereoreactivity of Sn$^{2+}$ cations. The nonlinear lattice dynamics is reflected in the theoretically and experimentally observed complex nature of the soft mode related to continuous phase transition. In the description of the microscopic origin of Sn$_2$P$_2$S$_6$ ferroelectric lattice instability, in addition to the second order Jahn-Teller effect, the $P^{4+} \leftrightarrow P^{4+} \leftrightarrow P^{5+} + P^{5+}$ charge disproportionation was also considered. Such electronic correlations can be described within the presentation of Andersons electron pairs flipping, and thermodynamics of Sn$_2$P$_2$S$_6$ family ferroelectrics can be considered within the framework of BEG model. In this approximation, a change in the local three-well potential by flattening the side wells leads to a decrease of the calculated continuous phase transition temperature and a TCP is reached. Below TCP temperature, the first order ferroelectric phase transition line further drops down to 0 K. In the case of the family of Sn$_2$P$_2$S$_6$ ferroelectric crystals, such an evolution can be induced substituting tin by lead in mixed crystals (Pb$_y$Sn$_{1-y}$)$_2$P$_2$S$_6$ or under hydrostatic compression.

The QAO model with the description of electronic recharging and lattice instability as pseudospin fluctuations in an anharmonic potential of three-well shape was proposed for a description of the temperature-pressure diagram of Sn$_2$P$_2$S$_6$ and of the temperature-composition diagram of (Pb$_y$Sn$_{1-y}$)$_2$P$_2$S$_6$ ferroelectric mixed crystals. In the QAO model, the real crystal lattice is represented as a system of one-dimensional interacting quantum anharmonic oscillators. A shape of the phase diagram calculated for the BEG model [see Fig. 12(a)] correlates with the experimental observations. Here the on-site energy $\Delta$ changes with the variation of crystals chemical composition at almost constant intersite interaction $J$. The dimensionless parameter $\delta = \Delta/J$ was estimated by using the following characteristics of the (Pb$_y$Sn$_{1-y}$)$_2$P$_2$S$_6$ mixed crystals $T - \delta$ phase dia-
The shape of the local potential was determined with shown points for the Pb\textsubscript{2}P\textsubscript{2}S\textsubscript{6} crystal where 0.1\(T_x \approx 7\) K.

We present the measured dielectric susceptibility \(1/\varepsilon'(T)\) over the range 27–80 K for Pb\textsubscript{2}P\textsubscript{2}S\textsubscript{6} crystal in different temperature scales (see Fig. 13). From the comparison of Fig. 13(a) and Fig. 13(b), it is seen that \(1/\varepsilon'\) varies as \(T^2\) in the region 27–80 K and does not satisfy the \(T^3\) quantum critical behavior. Above 80 K this crystal exhibits classical Curie-Weiss behavior [see Fig. 13(c, d)]. We emphasize that for Pb\textsubscript{2}P\textsubscript{2}S\textsubscript{6} crystal the critical exponent is close to \(\gamma = 2.0\), that is calculated and observed for multiaxial quantum critical systems like SrTiO\textsubscript{3},\textsuperscript{27,44} and does not follow the theoretically predicted for uniaxial ferroelectrics value \(\gamma = 3.0\),\textsuperscript{45,46} which have been experimentally found in the case of BaFe\textsubscript{12}O\textsubscript{19} and SrFe\textsubscript{12}O\textsubscript{19} crystals.\textsuperscript{45}

The \(1/T^2\) low temperature variation found for the dielectric susceptibility of Pb\textsubscript{2}P\textsubscript{2}S\textsubscript{6} close to the quantum critical point instead of the expected uniaxial behavior of \(1/T^3\) can be explained at first glance by a screening phenomenon in semiconductor materials of the Sn(Pb)\textsubscript{2}P\textsubscript{2}S(Se)\textsubscript{6} system which weakens the electric dipole interaction. Such explanation is seen as appropriate for the above discussed critical behavior near the Lifshitz point in Sn\textsubscript{2}P\textsubscript{2}(Se\textsubscript{0.25}S\textsubscript{0.75})\textsubscript{6} mixed crystal, which agrees with the theoretically predicted for systems with short-range interactions.\textsuperscript{17,34} But, for Pb\textsubscript{2}P\textsubscript{2}S\textsubscript{6} crystals at low temperatures, the electric conductivity is very small (below 10–14 Ohm\textsuperscript{−1} cm\textsuperscript{−1}),\textsuperscript{47} and screening effects cant be effective with a low concentration of the free charge carriers.

Figure 14 demonstrates, that for both Sn\textsubscript{2}P\textsubscript{2}S\textsubscript{6} and Pb\textsubscript{2}P\textsubscript{2}S\textsubscript{6} crystals the soft optic branch in the paraelectric phase is flat: soft phonons frequency slightly changes with the increase of wave number and moves from the
BZ center to the edge, where the crossing with acoustic phonon branches occurs. On cooling to the continuous phase transition temperature $T_0 \approx 337$ K for Sn$_2$P$_2$S$_6$ crystal, in addition to the development of polar fluctuations near the BZ center, the antipolar fluctuations also strongly develop in the paraelectric phase. Here, critical behavior can be described as a crossover between Ising and XY universality classes, what is expected near critical points with coupled polar and antipolar order parameters and competing instabilities in the reciprocal wave vectors space. A similar situation obviously exists in the quantum paraelectric phase of Pb$_2$P$_2$S$_6$ crystal, where on cooling down to 0 K the flat optic phonon branch softens across wide reciprocal space in BZ. Besides, the long wavelength polar fluctuations grow together with a development of short wavelength antipolar fluctuations and, therefore, their nonlinear coupling can modify the quantum critical behavior.

### IV. CONCLUSIONS

The dipole ordering temperature of Sn(Pb)$_2$P$_2$S(Se)$_6$ materials may be tuned by chemical substitution realizing a ferroelectric quantum phase transition and quantum glassy or relaxor type phenomena in different parts of the phase diagram. The introduction of Ge impurity initiates several important phenomena: it increases the temperature of the phase transitions and improves the spontaneous polarization in the crystal; it doesn’t shift the coordinate of the Lifshitz point $x_{LP}$ in Sn$_2$P$_2$(Se$_x$S$_{1-x}$)$_6$ mixed crystals; it initiates a more pronounced critical anomaly in Sn$_2$P$_2$S$_6$ crystals; it induces the appearance of a phase transition in the quantum paraelectric Pb$_2$P$_2$S$_6$ and inhomogeneous polar ordering in (Pb$_{0.7}$Sn$_{0.3}$)$_2$P$_2$(Se)$_6$ crystals. The quantum fluctuations are destroyed in the mixed crystals, what follows from the comparison of the low temperature behavior of the thermal diffusivity and the complex dielectric susceptibility at different frequencies.

By means of dielectric measurements it was shown that for Pb$_2$P$_2$S$_6$ crystal the real part of the dielectric susceptibility increases monotonously with decreasing temperature in the range from 300 K till 20 K. It was found that in the quantum critical regime the usual Curie-Weiss law of the inverse of dielectric susceptibility $1/\varepsilon'(T) \sim T$ changes into $1/\varepsilon'(T) \sim T^2$, which is the prominent criterion for quantum critical behavior. The nature of long-range dipole interactions in uniaxial materials predicts a dielectric susceptibility varying as $1/T^2$ close to the quantum critical point. But we found that the dielectric susceptibility varies as $1/T^2$ as expected and observed in better known multi-axial systems. This result can be partially explained by a screening phenomenon in semiconductor materials of the Sn(Pb)$_2$P$_2$S(Se)$_6$ system which is effective at relatively high temperatures and weakens the electric dipole interactions. But due to the free charge carriers low concentration at low temperatures, evidently the nonlinear coupling between polar and antipolar fluctuation is surely related to the modification of the observed quantum critical behavior in Pb$_2$P$_2$S$_6$ crystal.

The temperature dependence of the dielectric susceptibility has been analyzed in terms of the Barrett model that also demonstrates the presence of a quantum paraelectric state in Pb$_2$P$_2$S$_6$ type crystals. Small amounts of germanium impurity in (Pb$_{0.98}$Ge$_{0.02}$)$_2$P$_2$S$_6$ crystal induce the appearance of the ferroelectric phase, what is manifested in the decrease of the real part of the dielectric susceptibility below 75 K, deviating from the Barrett’s fit, and the appearance of a broad peak around 40 K. The observed behavior of the dielectric susceptibility temperature dependence demonstrates that (Pb$_{0.7}$Sn$_{0.3}$)$_2$P$_2$S$_6$ + 5% Ge crystal doesn’t undergo a ferroelectric phase transition with polar ordering at macroscopic scale at any finite temperature, implying that a relaxor or dipole glass state appears below 50 K. The temperature dependence of the dielectric susceptibility at different frequencies for (Pb$_{0.7}$Sn$_{0.3}$)$_2$P$_2$S$_6$ + 5% Ge sample is similar to the observed one for the sulfide mixed crystal. The thermal properties of Pb$_2$P$_2$S$_6$, (Pb$_{0.98}$Ge$_{0.02}$)$_2$P$_2$S$_6$, (Pb$_{0.7}$Sn$_{0.25}$Ge$_{0.05}$)$_2$P$_2$S$_6$ and (Pb$_{0.7}$Sn$_{0.25}$Ge$_{0.05}$)$_2$P$_2$S$_6$ single crystals have been studied, as it was earlier performed for Sn$_2$P$_2$S$_6$ crystal doped by germanium, where Ge impurity sharpens the Ising type critical anomaly at the continuous ferroelectric transition. It was found that for (Pb$_{0.98}$Ge$_{0.02}$)$_2$P$_2$S$_6$ crystal the thermal conductivity at low temperature (near 50 K) is bigger than in the case of pure Pb$_2$P$_2$S$_6$ crystal. This is obviously related to the Ge induction of polar clusters of the ferroelectric phase. The dielectric susceptibility of such clusters is smaller than the susceptibility of the paraelectric phase and the frequency of the lowest energy soft optical mode near the BZ center is obviously elevated. The increase in the soft optical mode frequency diminishes the probability of acoustic phonons resonance scattering by optic phonons. At low temperatures, heat is transferred by the acoustic and the lowest frequency optical phonons. Acoustic phonons with the small wave numbers are involved mostly in normal scattering processes that don’t contribute to the thermal resistivity. The phonons from the optical branch near the BZ center also participate in Umklapp scattering by lattice imperfections which
provides an effective thermal resistivity. Thus, the hardening of the optical branch lowers the population of the optical phonons and increases the thermal conductivity of (Pb0.08Ge0.02)2P2S6 crystal. In the case of (Pb0.75Pb0.25Te0.05)2P2S(Se)6 mixed crystals, the thermal conductivity behaves on cooling, like in glassy materials, which demonstrates an effective phonon scattering in solid solutions with sublattice of mixed tin and lead cations. Here germanium impurity induces the dipole glass state, which is manifested in the complex dielectric susceptibility frequency dependence below 100 K.

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