

# Chemical Bonding and Polarons in $\text{Sn}_2\text{P}_2\text{S}(\text{Se})_6$ Ferroelectrics

YU. VYSOCHANSKII,<sup>1</sup> M. MEDULYCH,<sup>1</sup> A. MOLNAR,<sup>1</sup>  
K. GLUKHOV,<sup>1</sup> A. DZIAUGYS,<sup>2,\*</sup> J. BANYS,<sup>2</sup> R. YEYCH,<sup>1</sup>  
AND M. MAIOR<sup>1</sup>

<sup>1</sup>Uzhgorod University, Uzhgorod, Ukraine

<sup>2</sup>Vilnius University, Vilnius, Lithuania

*For ferroelectric-semiconductor  $\text{Sn}_2\text{P}_2\text{Se}_6$  the low temperature dielectric relaxation was found to be similar to that observed in  $\text{Sn}_2\text{P}_2\text{S}_6$  analog. This relaxation behavior was explained as an evidence of small polaron dynamics in the lattices with different covalence of bonds between atoms at presence of tin and sulfur (selenium) vacancies. The calculations in LDA approach of the electron band structure and the energy levels of intrinsic defects together with analysis of the Raman spectra and photoluminescence temperature behavior give evidences of polaron dynamics joining with donor-acceptor compensation processes.*

**Keywords**  $\text{Sn}_2\text{P}_2\text{S}_6$ ;  $\text{Sn}_2\text{P}_2\text{Se}_6$ ; ferroelectrics; semiconductors; dielectric relaxation; polarons; intrinsic defects

## Introduction

$\text{Sn}_2\text{P}_2\text{S}_6$  (SPS) crystals are ferroelectrics-semiconductors and their properties are related to nonlinear interaction between phonon and electron excitations. The ferroelectric ground state is determined by three-well local potential that is induced by  $\text{Sn}^{2+}$  cation stereoactivity at involving of nonlinear coupling of fully symmetric  $A_g$  and polar soft optical  $B_u$  lattice vibrations [1, 2]. Their optical and semiconductive properties were related to the intrinsic lattice defects like sulfur and tin vacancies [3, 4], and to small electron and hole polarons that could be free or bounded by defects [5].

At substitution of sulfur by selenium, in  $\text{Sn}_2\text{P}_2\text{Se}_6$  (SPSe) compound, the ionicity of the chemical bond obviously becomes smaller than that in the sulfur analog. This important factor decreases the electron-phonon interaction and could effectively change semiconductive and ferroelectric properties. Recently it has been found that lowering of LO-TO splitting of the polar soft optical mode improves the linear interaction between the soft optical and acoustic branches and induces the incommensurate phase on the replacement of S by Se [6]. It is interesting to understand better the relation of the chemical bonding variation with the properties of SPS(Se) crystals. For this aim the dielectric permittivity at low temperatures in the ferroelectric phase at different frequencies has been measured. The obtained dielectric results together with the Raman scattering and photoluminescence

---

Received September 2, 2013; in final form December 9, 2013.

\*Corresponding author. E-mail: andrius.dziaugys@ff.vu.lt

data were analyzed on the background of the first-principles calculation of electron band structure of SPSe crystals with tin and selenium vacancies. Appearance of polaronic effects in SPS and SPSe crystals is compared.

## Dielectric Permittivity Investigations

The dielectric properties have been investigated using the HP4284A capacitance bridge [7] in the frequency range  $10^2$ – $10^6$  Hz and in the temperature interval 30–400 K. The SPS and SPSe crystals were grown by vapor transport (VT) and by Bridgeman (Br) methods [8]. The stoichiometric content of high purity elementary tin, phosphorous, sulfur or selenium was used in the growing processes. The silver paste was used for electrodes at polar cuts of plate shape samples with typical dimensions near  $1 \times 5 \times 5$  mm<sup>3</sup>.

The temperature dependences of dielectric permittivity show clear anomalies at the second order phase transition (PT) near  $T_0 = 337$  K for SPS crystal and at the second order ( $T_i = 220$  K) and the first order ( $T_C = 193$  K) transitions from the paraelectric phase into an incommensurate phase and further to the ferroelectric phase [8]. The values of the Curie-Weiss constant are equal to  $\sim 10^5$  K, similarly to that reported for the paraelectric phases of these crystals in previous investigations [8]. But now we pay attention for relaxation peculiarities at low temperatures in the ferroelectric phase of SPS and SPSe crystals.

For VT grown SPS crystals three anomalies are also observed near 50 K, 170 K and 250 K at the lowest frequency near  $10^3$  Hz (Figure 1). Similar anomalies have been observed in  $\epsilon'(T)$  and  $\epsilon''(T)$  dependences for Bridgeman method grown SPS samples. For SPSe crystal two dielectric anomalies are apparent near 35 K and 90 K at  $10^3$  Hz (Figure 2). All anomalies shift to higher temperatures with increasing frequency which points to their relaxation nature.

By fitting of the frequency-temperature evolution of obtained dielectric data by Arrhenius relation:

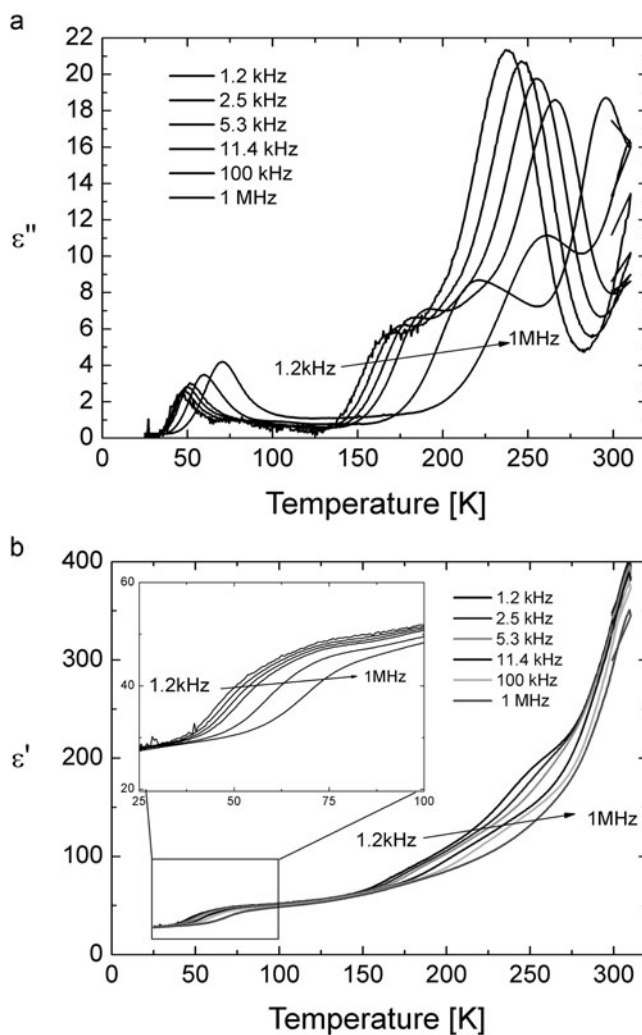
$$v = v_0 \exp(E_A/kT) \quad (1)$$

where  $E_A$  is the activation energy, the following activation energies were found for the sulfur compound 0.08 eV (50 K), 0.27 eV (170 K) and 0.49 eV (250K) for sulfur compound (Figure 3); and 0.06 eV (35 K) and 0.18 eV (90 K) for the selenium compound (Figure 4). For all relaxations the smearing parameter was found to amount to  $\alpha \approx 0.5$ . This parameter comes out of the empirical Cole-Cole formula:

$$\epsilon^* = \epsilon_\infty + \frac{\Delta\epsilon}{1 + (i\omega\tau)^{1-\alpha}} \quad (2)$$

where  $\Delta\epsilon$  represents dielectric strength of the relaxation,  $\tau$  is the mean and most probable Cole-Cole relaxation time,  $\epsilon_\infty$  represents the contribution of all polar phonons and electronic polarization to the dielectric permittivity, and  $0 \leq \alpha \leq 1$  is the parameter of width of Cole-Cole distributions functions; when  $\alpha = 0$  Eq. (2) reduces to the Debye formula. The dielectric dispersion regions in SPS and SPSe crystals where fitted using above mention formula by choosing parameters, which best fit to describe the  $\epsilon^*(\omega)$  dependences.

In previous investigations of SPS crystals the dielectric relaxations at low temperatures were related to a residual disordering in the lattice [9]. Recently they were related to small polaron dynamics at the lowest temperatures and to their dynamics with donor-acceptor compensation processes at elevated temperatures [5]. For the SPSe crystals similar interpretation of low temperature dielectric relaxations could be obviously appropriate

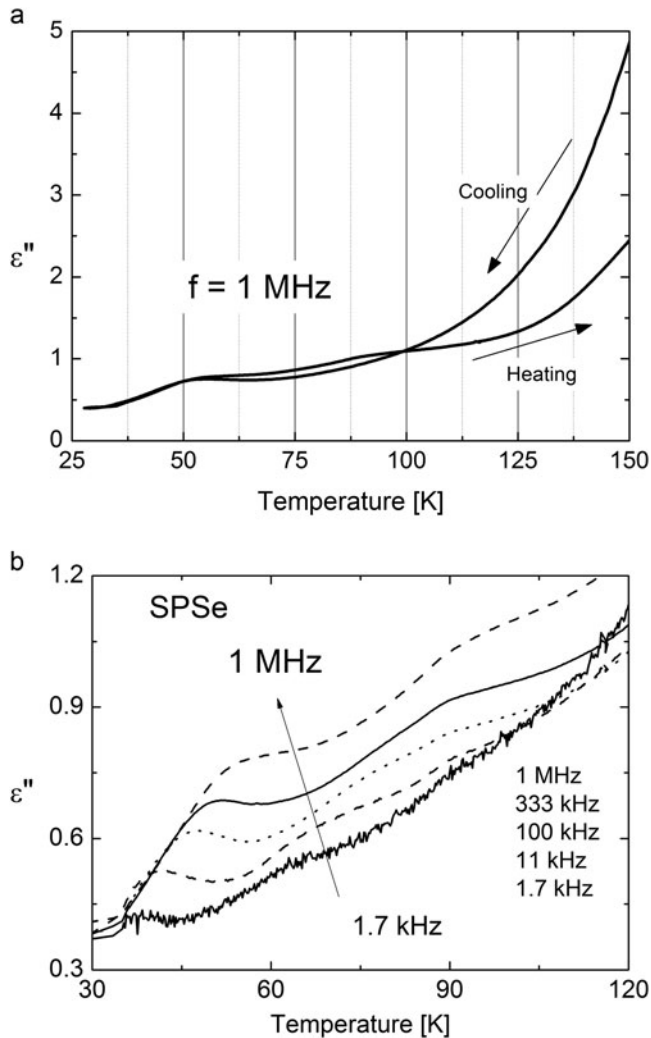


**Figure 1.** Real and imaginary parts of low-temperature dielectric permittivity for SPS crystal at different frequencies.

and the experimental data point to a decrease in the activation energies for the selenide compound.

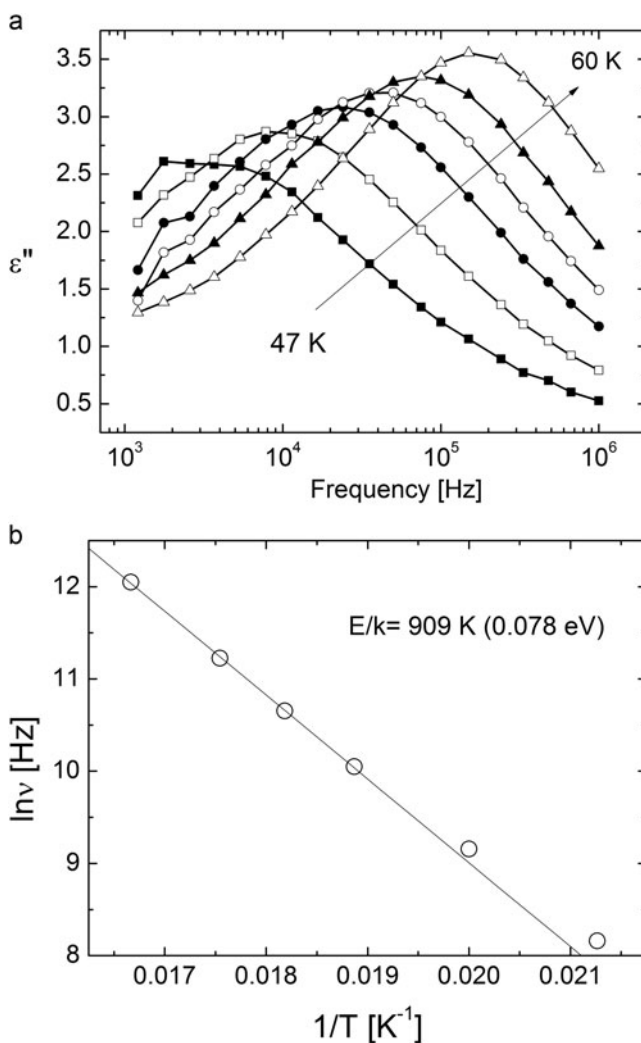
### Discussion of Results

Polaron formation and dynamics are related to peculiarities of chemical bonding and intrinsic defects in the crystal lattice. For SPS crystals the ionic-covalent bonding and the leading role of tin cation stereoactivity in ferroelectricity were established by LDA calculations of the electron band structure for an ideal lattice and for the cases of the sulfur and tin vacancies [2, 3]. Tin vacancy acceptor states ( $E_a \approx 0.1$  eV) and sulfur vacancy donor states ( $E_d \approx 0.5$  eV), placed near the top of the valence band, were found in the energy gap [3, 4].



**Figure 2.** Imaginary part of dielectric permittivity at low temperature for SPSe crystal at different frequencies.

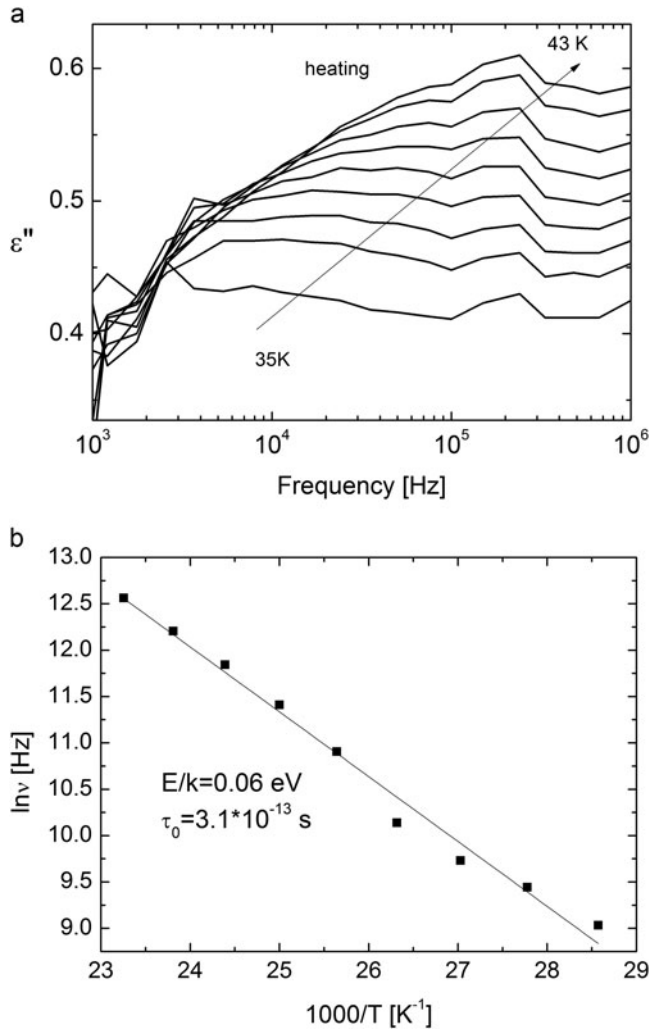
We have calculated in LDA approach of DFT (as it was described earlier [2, 3]) the electron energy spectra and partial densities of states for both paraelectric and ferroelectric phases of SPSe crystal. The stereoactivity of tin cations is still apparent (similar to the SPS crystal case) as high Sn5s orbitals contribution at the top of valence band (Figure 5). Such hybridization could be presented as  $sp^2$  mixing of tin 5s orbitals with selenium 4p orbitals and with further mixing of their resulting antibonding part with tin 5p orbitals. Of course, for highly coordinated positions of tin atoms inside the selenium octahedrons the higher order hybridization like  $sp^2d^3$  more adequately reflects the mixing of valence orbitals for the metal atoms and ligands. The 5s orbitals of tin ions, that are placed mostly in the energy range between 6 and 8 eV (Figure 5), also could be traced across all valence band, even at their bottom – near 15 eV the tin 5s orbitals mixing with phosphorous 3s and sulfur 3s orbitals is observed. This mixing reflects rather strong covalence of bonding in the SPSe



**Figure 3.** Frequency dependence of imaginary part of dielectric permittivity for SPS at low temperatures and the Arrhenius plot of the characteristic frequency  $\nu$  determined from the maximum value of frequency dependence of imaginary part of dielectric permittivity. The solid line represents the best fit by Arrhenius relation.

crystal. The rise of covalence in SPSe crystal is reflected in its basic properties [8] (Table 1): the temperature of crystal melting  $T_m$  and the Debye temperature  $T_D$  are shifted towards lower temperatures when the energy gap decreases.

It is apparent, that the stereoactivity of tin cations in selenide lattice is similar to that found for the SPS crystal. So, for SPSe crystal a similar three-well local potential [1] for the order parameter (spontaneous polarization) fluctuations is presented. It is confirmed by similar values of the soft optical mode frequency in the ferroelectric phase at low temperatures (Table 1). But for SPSe, as result of smaller ionicity, the intercell interaction is weakened and the transition temperature from the paraelectric phase into the polar ferroelectric one lowers. Indeed, by LDA calculations it was determined that for SPSe crystal the Mulliken



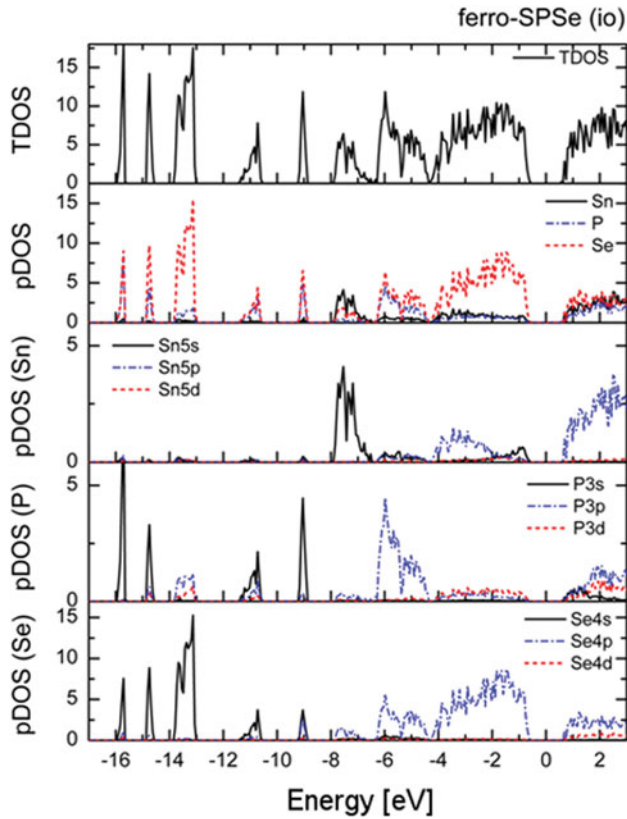
**Figure 4.** Frequency dependence of imaginary part of dielectric permittivity for SPSe at low temperatures and the Arrhenius plot of the characteristic frequency  $\nu$  determined from the maximum value of frequency dependence of imaginary part of dielectric permittivity. The solid line represents the best fit by Arrhenius relation.

charges of tin atoms are smaller when compare with those of SPS, also the full electronic charge of tin cations rises when sulfur is substituted by selenium. This is reflected by calculated electronic configurations of tin atoms in the case of SPSe ( $\text{Sn} - 5s^{1.858}p^{1.291}d^{0.228}$  in the paraelectric phase;  $\text{Sn}_1 - 5s^{1.870}p^{1.296}d^{0.226}$  and  $\text{Sn}_2 - 5s^{1.869}p^{1.313}d^{0.225}$  in the ferroelectric phase). For SPS crystals the calculations yield ( $\text{Sn} - 5s^{1.866}p^{1.153}d^{0.222}$  in the paraelectric phase;  $\text{Sn}_1 - 5s^{1.851}p^{1.164}d^{0.224}$  and  $\text{Sn}_2 - 5s^{1.850}p^{1.175}d^{0.226}$  in the ferroelectric phase [2]). It is important to mention, that in selenium containing crystal the charge nonequivalence for  $\text{Sn}_1$  and  $\text{Sn}_2$  cations becomes smaller comparatively with such difference in the SPS crystal. The differences of ionic orbitals charge populations together with the difference of atomic coordinates in the elementary cell of the crystal lattice are

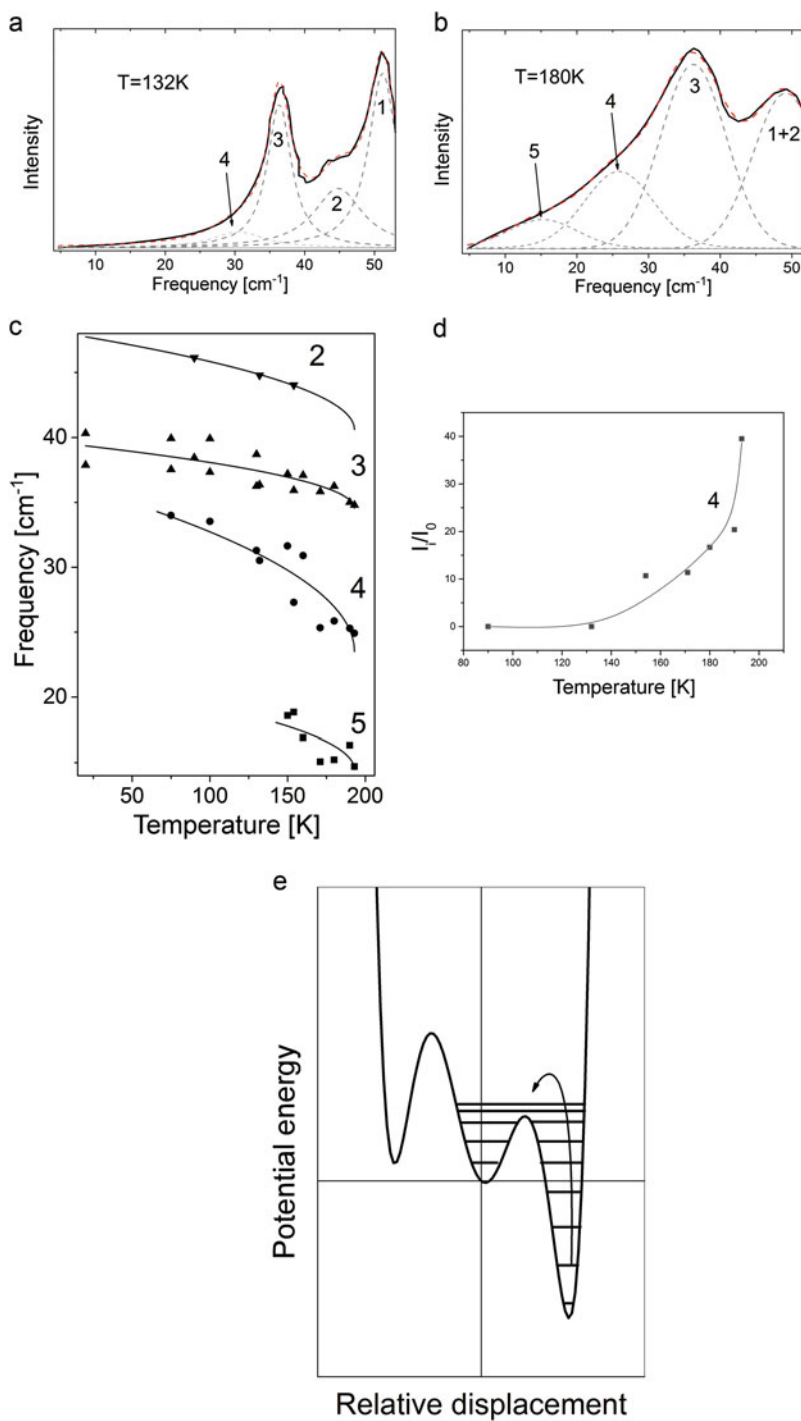
**Table 1**  
Main characteristics of SPS and SPSe crystals

	$\text{Sn}_2\text{P}_2\text{S}_6$	$\text{Sn}_2\text{P}_2\text{Se}_6$
$T_{\text{melt}}$ [K]	1051	947
$T_{\text{D}}$ [K]	100	80
$E_{\text{g}}$ [eV] at 77 K	2.5	2.0
$T_0$ [K]	337	
$T_{\text{i}}, T_{\text{C}}$ [K]		220, 193
$P_{\text{s}}$ [ $\mu\text{C cm}^{-2}$ ]	16	10
$\Delta U_{\text{loc}}$ [eV]	$\approx 0.01$	$\approx 0.01$
$\omega_{\text{soft mode}}$ [ $\text{cm}^{-1}$ ] at 77 K	41	39

proportional to the spontaneous polarization  $P_{\text{s}}$  that appears in the ferroelectric phase. Indeed, the  $P_{\text{s}}$  value of the SPSe crystal is smaller than that of the in SPS (Table 1). From this follows that in SPSe crystal the local three-well potential is less deformed by internal electric mean field of the spontaneous polarization in comparison with that of the SPS crystals.

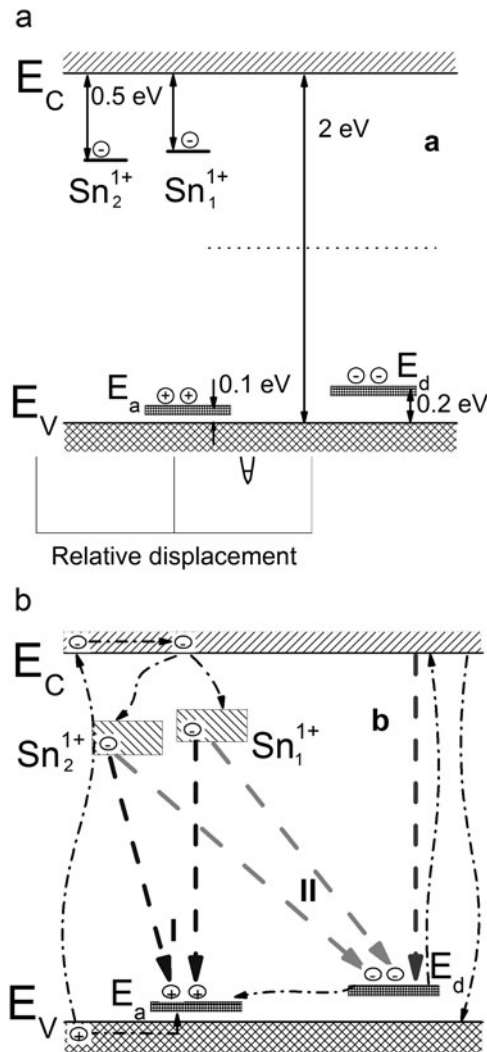


**Figure 5.** Total and partial electron densities of states for SPSe crystal in the ferroelectric phase.



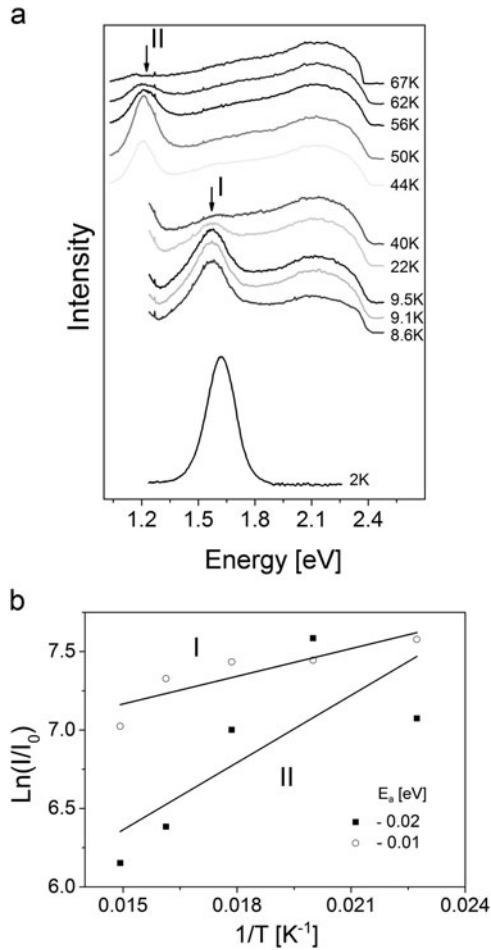
**Figure 6.** The low frequency Raman spectra for SPSe crystals in the ferroelectric phase at 132 K and 180 K (a, b). The spectra are fitted by Gaussian contours with numbers 1, 2, 3, 4 and 5, the addition spectral lines (numbers 4 and 5) are shown by arrows. The temperature dependencies of the Raman lines frequencies (c) and relative intensity for the addition line with number 4 (d). The local three-well anharmonic potential with illustration of nonequidistant phonon energy levels (e).





**Figure 7.** Energy diagram (a) for acceptor ( $E_a$ ), donor ( $E_d$ ) and small electronic polarons ( $\text{Sn}_1^{1+}$ ,  $\text{Sn}_2^{1+}$ ) energy levels in SPSe crystals with vacancies of tin and selenium. In (b) the electron excitation and recombination processes are shown. The arrows with numbers I and II show the recombination processes related to similar number spectral bands of photoluminescence (Figure 8). The vertical red arrow denotes the recombination process from conduction band onto free donors.

The side well of the local potential for SPS crystal was calculated to be of  $\Delta U \approx 0.01$  eV [1]. For ferroelectric ground state the local potential is determined by internal field of the spontaneous polarization, and the energy barrier between deepness side well and central well could be estimated in range of 0.02 – 0.03 eV. In such a case for SPSe crystal this barrier could be smaller and probably is ranged within 0.01 – 0.02 eV interval. These estimations could be appropriate for explanation of lowering of the paraelectric phase stability border from  $T_0 = 337$  K in SPS to  $T_i = 220$  K in SPSe, and also, for a rise of the lattice anharmonicity, as shown by clear growth of the Debye-Waller parameter [8], and by broadening and asymmetry of Raman spectral lines on heating above 200 K in SPS crystal and above 100 K in the case of SPSe crystal [5, 10].



**Figure 8.** Photoluminescence for SPSe crystals at different temperatures [11, 12] and temperature dependence of the intensity for the spectral lines with numbers I and II determined by fitting with Gaussian contours.

Low energy Raman scattering in the ferroelectric phase of SPSe crystals was interpreted earlier as results of optical mode softening and mixing with some continuum of excitations [10]. Now we suppose that the observed growth of the low frequency tail of soft optical mode (Figure 6) originates from the addition spectral lines that are related to the not equidistant phonon energy levels in strongly anharmonic local potential (Figure 6c).

The analysis of thermodynamic characteristics and electron band structure of sulfide and selenide compounds and also investigations of intrinsic lattice defects show that such as most probable vacancies of tin ( $V_{Sn}$ ) and sulfur ( $V_S$ ) or selenium ( $V_{Se}$ ) are desirable. Our LDA calculations yielded the activation energies  $E_a \approx 0.1$  eV for  $V_{Sn}$  acceptors and  $E_d \approx 0.1 - 0.3$  eV for  $V_{Se}$  donors. This is comparable with early obtained values  $E_a \approx 0.1$  eV and  $E_d \approx 0.4 - 0.5$  eV for similar vacancies in the SPS lattice [3, 4]. One can suppose that due to smaller ionicity the electron-phonon interaction in SPSe crystals are weaker than that in SPS crystals. Basing on this the gap energy levels could be proposed for SPSe (Figure 7), similarly to early [5] taken scheme for SPS crystal. For SPSe the energy levels for small

electron polarons localized at  $\text{Sn}_1^+$  and  $\text{Sn}_2^+$  cations are located by  $\approx 0.5$  eV below the bottom of the conduction band. Also, possibly the energy difference between the levels is smaller in selenium crystal because of weaker nonequivalence of tin cations in comparison with the situation in SPS crystal.

With proposed energetic scheme the temperature evolution of photoluminescence in SPSe (Figure 8) could be explained. The spectral band I near 1.6 eV could be devoted to radiative recombination of electron polarons with small hole polarons that are related to  $\text{Se}^-$  ions. We suppose that the energy level of light induced hole polarons (localized at  $\text{Se}^-$  ions) is placed at 0.1 eV above of the valence band top, similarly to the energy level of acceptor centers at  $\text{Se}^-$  ions localized near tin vacancies. The band II near 1.2 eV is obviously related to recombination of electron polarons with free (ionized) donor centers at selenium vacancies. Wide photoluminescence spectral line in the region 1.9–2 eV obviously appears in result of recombination from conduction band onto free donors, what is shown by vertical red arrow in Figure 7b. At such interpretation, heating induces temperature suppression of the band I with activation energy near 0.01 eV that follows from relaxations across energy barrier in the three-well local potential (Figure 6e) [1, 2]. Higher activation energy (near 0.02 eV) for the band II could be related to the donor-acceptor compensation that support hopping of the bonded small hole polarons in SPSe crystal lattice, similarly to earlier described processes [5].

Generally speaking, the appearance of relaxation processes in dielectric permittivity and data on the lattice anharmonicity obtained from Raman spectroscopy studies, together with photoluminescence information about in gap centers temperature repopulation in lattices with tin and sulfur or selenium vacancies confirm formation of small radius hole and electron polarons and their relaxation dynamics difference in SPS and SPSe crystals.

## Conclusions

Low temperature dielectric permittivity relaxation anomalies in the ferroelectric phase of SPS and SPSe crystals have been observed and explained as appearance of small polaron dynamics. Lowering of the chemical bonds ionicity decreases electron-phonon interaction for selenide compound that appears as shift of the dielectric relaxation processes from 50 K in SPS to 35 K in SPSe. Basing on electron band structure calculations the stereoactivity of tin cations in selenide crystal was found to be similar to that in sulfide compound, but smaller ionicity of the former determines smaller temperature range of the ferroelectric phase. Also, the anharmonicity of SPSe lattice starts to growth on heating at lower temperature (near 100 K, instead near 200 K as for the SPS case) that is clearly observed in the Raman spectral lines width and asymmetry temperature dependence. By first-principles calculations the in-gap energy level positions for tin and sulfur (selenium) vacancies have been found and the photoluminescence spectra were explained as radiative recombination of electron polarons at  $\text{Sn}^+$  cations with hole polarons at  $\text{S}^-$  or  $\text{Se}^-$  anions with participation of the acceptor-donor compensation in elevated temperature range. The photoluminescence temperature suppression correlates with Raman data on the lattices anharmonicity and with the dielectric relaxation data.

## Funding

We wish to acknowledge the support of the Research Council of Lithuania funding this work according to the project “Postdoctoral Fellowship Implementation in Lithuania”.

## References

1. K. Rushchanskii, Yu. Vysochanskii, and D. Strauch, Ferroelectricity, nonlinear dynamics and relaxation effects in monoclinic  $\text{Sn}_2\text{P}_2\text{S}_6$ . *Phys Rev Letters*. **99**, 207601-1–4.(2007).
2. K. Glukhov, K. Fedyo, and Yu. Vysochanskii, Electronic structure and phase transition in ferroelectric  $\text{Sn}_2\text{P}_2\text{S}_6$  crystal. *Int J Mol Sci*. **13**, 14356–4384.(2012).
3. Yu. Vysochanskii, K. Glukhov, K. Fedyo, and R. Yevych, Charge transfer and anharmonicity in  $\text{Sn}_2\text{P}_2\text{S}_6$  ferroelectrics. *Ferroelectrics*. **414**, 30–40.(2011).
4. Yu. Vysochanskii, K. Glukhov, M. Maior, K. Fedyo, A. Kohutych, V. Betsa, I. Prits, and M. Gurzan, Ferroelectric and semiconducting properties of  $\text{Sn}_2\text{P}_2\text{S}_6$  crystals with intrinsic vacancies. *Ferroelectrics*. **418**, 124–133.(2011).
5. Yu. Vysochanskii, A. Molnar, R. Yevych, K. Glukhov, and M. Medulych, Ferroelectricity and polarons in  $\text{Sn}_2\text{P}_2\text{S}_6$  crystals. *Ferroelectrics*. **440**, 31–41.(2012).
6. R. M. Yevych, Yu. M. Vysochanskii, M. M. Khoma, and S. I. Perechinskii, Lattice instability at phase transitions near the Lifshitz point in proper monoclinic ferroelectrics. *J Phys: Condens Matter*. **18**, 4047–4064.(2006).
7. J. Macutkevic, P. Kuzhir, A. Paddubskaya, S. Maksimenko, J. Banys, A. Celzard, V. Fierro, S. Bistarelli, A. Cataldo, F. Micciulla, and S. Bellucci, Electrical transport in carbon black-epoxy resin composites at different temperatures. *J Appl Phys*. **114**, 033707-1–8.(2013).
8. Yu. M. Vysochanskii, T. Janssen, R. Currat, R. Folk, J. Banys, J. Grigas, and V. Samulionis, *Phase Transitions in Ferroelectric Phosphorous Chalkogenide Crystals*, Vilnius: Vilnius University Publishing House, 2006.
9. M. Iwata, A. Miyashita, Y. Ishibashi, K. Moriya, and S. Yano, Low temperature dielectric dispersion in  $\text{Sn}_2\text{P}_2\text{S}_6$ . *J Phys Soc Jpn*. **67**, 499–501.(1998).
10. P. H. M. van Loosdrecht, M. M. Maior, S. B. Molnar, Yu. M. Vysochanskii, P. J. M. van Bentum, and H. van Kempen, Raman study of the ferroelectric semiconductor  $\text{Sn}_2\text{P}_2\text{Se}_6$ . *Phys Rev B*. **48**, 6014–6018.(1993).
11. B. Padlyak, R. Vlokh, O. Grabar, Yu. Vysochanskii, I. Dmitruk, W. Ryba-Romanowski, and R. Lisiecki, Luminescence properties of  $\text{Sn}_2\text{P}_2\text{Se}_6$  crystals. *Opt Mater*. **31**, 1831–1834.(2009).
12. R. Vlokh, O. Grabar, Yu. Vysochanskii, and I. Dmitruk, Luminescence and reflection spectra of  $\text{Sn}_2\text{P}_2\text{Se}_6$  semiconductors-ferroelectrics at low temperatures. *Ukr J Phys Opt*. **7**, 24–26.(2006).