Heat capacity and electrical resistance of (Pb$_y$Sn$_{1-y}$)$_2$P$_2$S$_6$ chalcogenides

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Abstract. We present the results of study of heat capacity and electrical resistance of the (Pb$_y$Sn$_{1-y}$)$_2$P$_2$S$_6$ chalcogenides where Pb content varies from 0 till 0.8. We have studied the temperature behaviour of heat capacity from the point of Pb influence on change of transition temperature at the temperature region 50 – 400 K. Moreover, we present the results of study of temperature dependence of electrical resistance and influence of an applied magnetic field up to 3 T. The electrical resistance was studied in the temperature range 50 - 400 K due to low temperature semiconducting behaviour. We studied the influence of Pb content on phase transition and relaxation processes.

1. Introduction

The system M$_2$P$_2$S$_6$ (where M = Sn, Pb) crystallizes in monoclinic system with two formula units in a unit cell [1]. This system has a three-dimensional lattice. The presence of (P$_2$S$_6$)$^4$ anions demonstrate covalent bound, and at the other side the bound between Sn(Pb) atoms and sulphur atoms has ionic character [2,3]. In Sn$_2$P$_2$S$_6$ compound is tin atom in divalent state Sn$^{2+}$, which surrounds PS$_3$ pyramids and creates three-dimensional crystal structure. The case of Sn$^{4+}$ state causes the existence of layered compound Sn$_2$P$_2$S$_6$. In the Pb$_2$P$_2$S$_6$ compound f-orbitals participate at the chemical bond formation, and therefore Pb$_2$P$_2$S$_6$ crystals have higher thermal stability [4, 5].

Sn$_2$P$_2$S$_6$ compound is ferroelectric semiconductor with phase transition from paraelectric into ferroelectric phase at the temperature $T_0 = 337$ K. This phase transition temperature is influenced by concentration of the lead atom performing the substitution of the tin atom in the (Pb$_y$Sn$_{1-y}$)$_2$P$_2$X$_6$ (X = S, Se) [6]. The study of this system is interesting from another reason. When the sulphur atom is substituted by selenium one, the curve of the phase transition is splitted at about 20% of the selenium concentration to two curves (second order phase transition from paraelectric to incommensurate phase and first order phase transition from incommensurate to ferroelectric phase). The optical measurements of the light absorption, heat capacity [7] and thermal conductivity [8], spontaneous polarization and permittivity constant in this system and the temperature dependence are in agreement with previous results [9].

Our main aim was to study the influence of Pb substitution on this transition by heat capacity and electrical resistance measurements.
2. Experimental
All measurements were performed by VERSALAB commercial device (Quantum Design) in the temperature range 50 – 400 K and in an applied magnetic field up to 3 T. Heat capacity was measured using the two-tau model by the relaxation method. Electrical resistance was measured by ETO (Electric Transport Module) module.
Polycrystalline samples of (Pb\textsubscript{y}Sn\textsubscript{1-y})\textsubscript{2}P\textsubscript{2}S\textsubscript{6} and single crystalline Sn\textsubscript{2}P\textsubscript{2}S\textsubscript{6} were grown using gas-transport reaction method. We have prepared the samples with concentration of Pb y = 0, 0.05, 0.1, 0.12, 0.2, 0.4, 0.5, 0.57 and 0.8.

3. Results and discussion
In the Fig. 1 is temperature dependence of the heat capacity of (Pb\textsubscript{y}Sn\textsubscript{1-y})\textsubscript{2}P\textsubscript{2}S\textsubscript{6} in the temperature diapason from 50K to 400K. We have also measured the temperature dependence of the electrical conductance (and resistance) shown in the Fig. 2. The mechanism responsible for conductance is intrinsic conductance and conductance caused by pyroeffect. The positions of the peaks, represents phase transition from paraelectric to ferroelectric phase.

![Graph of heat capacity vs. temperature for (Pb\textsubscript{y}Sn\textsubscript{1-y})\textsubscript{2}P\textsubscript{2}S\textsubscript{6}.]

**Figure 1.** Temperature dependence of heat capacity of (Pb\textsubscript{y}Sn\textsubscript{1-y})\textsubscript{2}P\textsubscript{2}S\textsubscript{6}.

We have determined the peaks from heat capacity and the electrical resistance measurements, and they are in a good agreement, as with previous measured data [9, 10, 11]. In the Fig. 3 is phase diagram taken from heat capacity and electrical resistance measurements. The phase transitions at the concentrations y = 0, 0.05, 0.1 are clearly detected, but we can’t determined the phase transitions in other concentrations.
In the coordinate system logarithm of conductance vs. 1000/T has this dependence in paraelectric phase linear character [12]. Our measured results are in the Fig. 4. The conductance shows almost linear behaviour in high temperature regions. On the other hand, the behaviour of logarithm of conductance in ferroelectric has strongly nonlinear character.

From our recent measurements [13] we considered, that magnetic field up to 3 T have no influence to heat capacity of the studied samples, so we expected no influence of magnetic field to electric resistance or conductance. In order to confirm this we measured the electric resistance of prepared samples in zero applied field and magnetic field 3 T (Fig. 5). The experiment yielded to conclusion that the magnetic field has small influence on conductance, especially in paraelectric phase. This difference is connected with pyroelectricity. When the system is heated, or cooled, the polarization of the material changes, which raises the voltage across material [14]. When the temperature stays constant, the pyroelectric voltage gradually disappears due to leakage current.
For this reason we performed the measurement of the relaxation of the electric resistance (Fig. 6). After continuous increasing of the temperature at 12 K/min rate we stopped temperature increasing at 250K and then waited for about 540 s. The resistance slightly rises, what is presented in the insert in Fig. 6. The character of the resistance relaxation is in long scale exponential, what demonstrates the second insert (right). We can see that this effect occurs when the temperature increases. When the temperature decreases, the effect is negligible. Further experiments to clarify this behavior are necessary.

4. Conclusion
We have observed the agreement with temperatures of phase transition from heat capacity and resistance measurements. Heat capacity measurements show no magnetic field influence, but temperature dependence of conductance is slightly different (in zero applied field and in magnetic field 3 T), what is caused by pyroelectricity, what demonstrates relaxation time measurements.

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