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High Temperature Magnetic and Thermal Properties of $(Pb_ySn_{1-y})_2P_2S_6$ Chalcogenides

S. Il'kovič[a], M. Reiffers[a,*], V. Šebeň[a], K. Šterbáková[a], V. Burger[a], L. Parma[a], O. Čobal'[b], I. Rizak[c] and V. Rizak[b]

[a]Faculty of Sciences, University of Prešov, 17. novembra 1, SK 080 78 Prešov, Slovakia

[b]Uzhgorod National University, Uzhgorod, Ukraine

[c]National Aerocosmic University — KHAI, Kharkiv, Ukraine

The results of study of Pb influence on high temperature magnetic and thermal properties of the chalcogenides $(Pb_ySn_{1-y})_2P_2S_6$ are presented. The increasing Pb content shifts phase transition to the ferroelectric state at about 337 K towards lower temperatures while magnetic field till 3 T has no influence on this transition. The measured susceptibility and magnetisation data are discussed.

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1. Introduction

In $Sn_2P_2S_6$ compound tin atoms are formally in the divalent state Sn^{2+}. Due to electronic configuration, structure formation has big probability of the spd^2-hybridization and the presence of four coplanar bounds and therefore crystal structure of the $Sn_2P_2S_6$ is three-dimensional. In the case of the oxidation state Sn^{4+} there will occur the sp^3d^1-hybridization and the presence of six bounds, which obviously causes the existence of layered compound $Sn_2P_2S_6$ [1, 2].

$Sn_2P_2S_6$ is a ferroelectric semiconductor, where at room pressure the transition from paraelectric into ferroelectric state occurs at $T_0 = 337$ K.

The study of the isomorphous substitution of the sulphur for the selenium in $Sn_2P_2S_6$ revealed that the phase transition shifted to lower temperatures. In $Sn_2P_2Se_6$ there was observed the diffraction evidence of the incommensurate phase with anomalous behaviour of physical properties above T_0 [3, 4].

There are two main reasons of the interest to study this crystal within the $(Pb_ySn_{1-y})_2P_2(Se_xS_{1-x})_6$ system. First is the vicinity of the Lifshitz point on $T-X$ diagram in substitution of sulphur for the selenium, when the phase diagram splits into two lines (first and second order of phase transition, which limits incommensurate phase). The second point of interest is that on $P-T$ diagram the transition temperature decreases with concentration of lead up to 0 K and reaches value $y = 0.61$ for sulphur series and value $y = 0.4$ and $y = 0.64$ for selenium series, respectively [5–7]. The temperature was determined from dielectric constant measurements.

Our main aim was the study the influence of Pb on the ferroelectric phase transition of $(Pb_ySn_{1-y})_2P_2S_6$ samples, where Pb content varies from 0 till 0.8, using the measurements of the temperature dependence of heat capacity, susceptibility and magnetisation in the temperature range 50–400 K and in the applied magnetic up to 3 T.

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 of the relaxation method. Magnetisation and susceptibility was measured by vibrating sample magnetometer (VSM).

Polycrystalline samples of $(Pb_ySn_{1-y})_2P_2S_6$ and single crystalline $Sn_2P_2S_6$ 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 Fig. 1 the temperature dependence of heat capacity $C(T)$ of $(Pb_ySn_{1-y})_2P_2S_6$ samples is shown in the temperature range 50–350 K. The main observation is that concentration of the lead has influence on the temperature dependence of the heat capacity. The maximum at $T_0 = 337$ K for $y = 0$ is connected with the transition from paraelectric to ferroelectric state. This temperature T_0 is decreasing with increasing concentration of Pb in polycrystalline samples of $(Pb_ySn_{1-y})_2P_2S_6$. Moreover, the intensity of this maximum is decreasing and more

* corresponding author; e-mail: reiffers@saske.sk

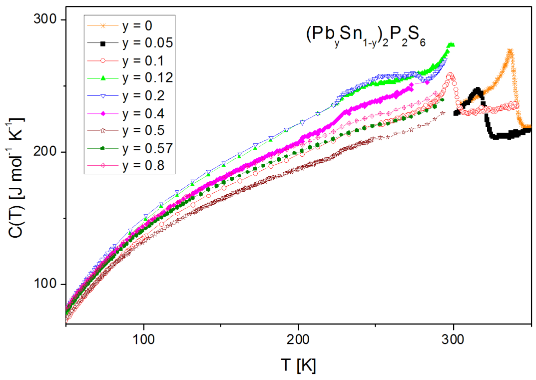

Fig. 1. Temperature dependence of the heat capacity $C(T)$ of $(Pb_ySn_{1-y})_2P_2S_6$.

smearing with increasing Pb-concentration. This is due to an increase of structure imperfectness.

We have determined the phase transition temperatures from ferroelectric to incommensurate paraelectric phase depending up to lead concentration. We have used temperature characteristics of the heat capacity for the all measured samples in the temperature region from 200 K to 350 K as one could see in detail in Fig. 2. The reason why some measurements have been done only below or above 300 K is due to the experimental method (different type of the Appiezon grease, producing good thermal contact with calorimeter for measurements of heat capacity below and above room temperature). Our results are summarized in Table. We should mention that small shoulder in the vicinity of 230 K (sometimes presented for Pb concentration above 0.4) is due to the Appiezon grease.

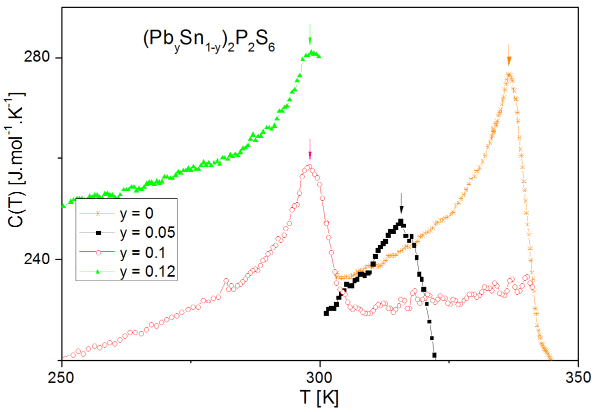

Fig. 2. Shift of the phase transition temperature at the temperature dependence of the heat capacity $C(T)$ of $(Pb_ySn_{1-y})_2P_2S_6$.

We have measured the influence of an applied magnetic field till 3 T. We have observed no influence. From this there yields the confirmation of a fact that Pb substitution does not change the ferrolectricity of

TABLE

Influence of the lead concentration to the phase transition temperatures of $(Pb_ySn_{1-y})_2P_2S_6$ determined from heat capacity measurement.

Concentration of the lead (y) [%]	Phase transition temperature T_0 [K]
0	337
0.05	316
0.1	298
0.12	298
0.2	≈ 250
≥ 0.4	no anomaly

$(Pb_ySn_{1-y})_2P_2S_6$ samples due to the ordering (polarization) of dipoles.

In order to confirm such a conclusion we have measured the temperature dependence of magnetic moment of $(Pb_ySn_{1-y})_2P_2S_6$ samples in the temperature range 50–400 K, which are presented in Fig. 3. The observed dependences show very small or negligible temperature dependence in all temperature range, which is due to the small temperature independent Pauli paramagnetic susceptibility. In Fig. 4 the value of the normalized magnetic moment as function of concentration is shown. One could see that this value is almost independent of Pb--concentration, which again support the observation that character of ferrolectric behaviour remains the same.

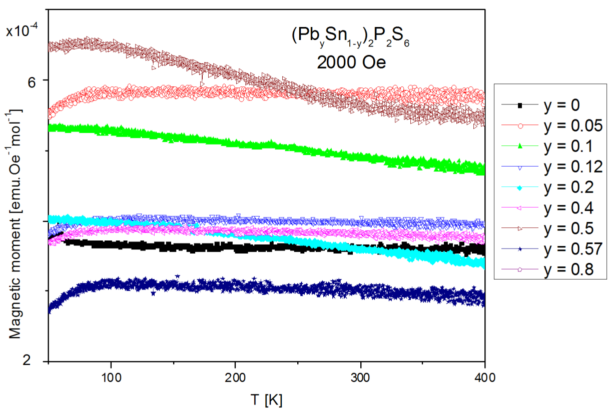

Fig. 3. Temperature dependence of magnetic moment of $(Pb_ySn_{1-y})_2P_2S_6$.

In Fig. 5 the magnetic moment is shown as function of an applied magnetic field up to 3 T at constant temperature. The increasing curves are characteristic for a paramagnetic behaviour with small hysteresis in the vicinity of 0 T. However, for Pb-concentration $y > 0.4$ the dependence come to the saturated value of magnetic moment for the applied magnetic field higher than approximately 0.05 T. For this concentration the transition to ferroelectric state is not present as it follows from our heat capacity measurements and from dielectric measure-

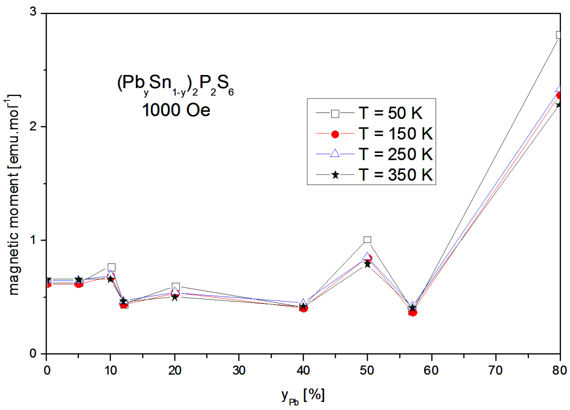

Fig. 4. Value of a normalized magnetic moment of $(Pb_ySn_{1-y})_2P_2S_6$ as function of Pb concentration.

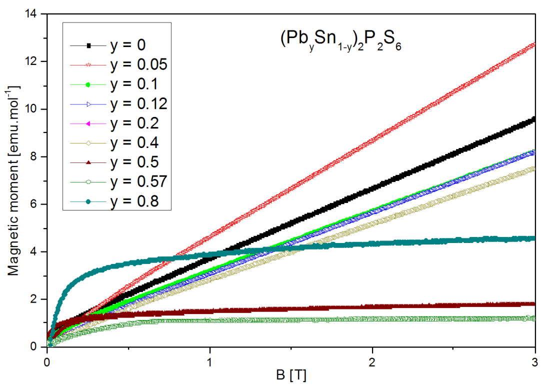

Fig. 5. Magnetisation of $(Pb_ySn_{1-y})_2P_2S_6$ as function of an applied magnetic field at constant temperature.

ments [6]. This is possible sign of increasing contribution from magnetic moment. In order to confirm it further measurements are necessary.

4. Conclusion

In conclusion, we performed the measurements of high temperature (50–400 K) magnetic and thermal properties of the chalcogenides $(Pb_ySn_{1-y})_2P_2S_6$ where Pb content varies from 0 till 0.8 in order to study the Pb influence on the ferroelectric phase transition at about 337 K. We observed the decrease of transition temperature to lower temperatures with increasing Pb content. The application of magnetic field till 3 T has no influence on this transition. The temperature behaviour of susceptibility shows the temperature independent Pauli paramagnetic contribution. The magnetic dependences of magnetisation displayed the saturation of small magnetic moment with increasing magnetic field for $y > 0.4$. In order to exactly explain the observed behaviour, further measurements are necessary.

Acknowledgments

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