FERROELECTRIC PHASE TRANSITIONS IN $Pb_{2x}Sn_{2(1-x)}P_2Se_6$ SYSTEM[*]

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Abstract

Heat capacities of the $Pb_{2x}Sn_{2(1-x)}P_2Se_6$ crystals (x=0, 0.098, 0.251, 0.402 and 1.0) were measured using an adiabatic calorimeter at temperatures between 10 and 350 K. In the crystal of x=0, two heat capacity anomalies corresponding to the ferroelectric commensurate – intermediate incommensurate(C–IC) phase transition temperature T_i, and the incommensurate – paraelectric (IC–N) phase transition temperature T_c, were observed at 193.24±0.10 and 220.07±0.15 K, respectively. The phase transition temperatures decreased with an increase in Pb^{2+} concentration. The anomaly at T_i disappeared at x=0.251 in the mixed systems of the $Pb_{2x}Sn_{2(1-x)}P_2Se_6$. In the crystal of $Pb_2P_2Se_6$ (x=1.0), no phase transition was observed. The normal heat capacities for the mixed crystals were determined by least squares fitting of the Debye and Einstein functions to the experimental data. The anomalous heat capacities gave the phase transition entropies of 8.5 and 1.5 J mol^{-1} K^{-1} for x=0. The large transition entropies are consistent with an order-disorder mechanism in the ferroelectric–paraelectric phase transitions in x=0.

Keywords: binary system, ferroelectrics, heat capacity, phase transition

Introduction

Stannous selenohypodiphosphate, $Sn_2P_2Se_6$, and plumbous selenohypodiphosphate $Pb_2P_2Se_6$ form an alternating lattice consisting of Sn^{2+} or Pb^{2+} and dumbbell shaped $P_2Se_6^{4-}$ ions. The structure of $Sn_2P_2Se_6$ at ambient temperature is reported to be monoclinic with the space group $P2_1/c$ with two formula units per unit cell (z=2) [1–3] . With decreasing temperature, the phase transforms at 220 K to an intermediate incommensurate phase [4] and then transforms to a commensurate ferroelectric phase of the space

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group of Pc with $z=2$ at 196 K [3, 5]. Soft modes have also been reported for $Sn_2P_2Se_6$ using Raman [6], infrared [7] and inelastic neutron scattering [8] experiments. The room temperature phase of $Pb_2P_2Se_6$ is isomorphous with that of $Sn_2P_2Se_6$ and forms solid solution with $Sn_2P_2Se_6$ in the all concentration region [1]. In this study, we describe the effect of the Pb^{2+} ion on the phase transitions in $Pb_{2x}Sn_{2(1-x)}P_2Se_6$ system(x=0, 0.098, 0.251, 0.402 and 1.0) based on the thermodynamic standpoint by the use of the heat capacities measurements.

Experimental

The $Pb_{2x}Sn_{2(1-x)}P_2Se_6$ crystals were prepared in an evacuated quartz tube by the chemical transportation [9] of P, S, and Pb, and/or Sn with a small amount of carrier gas of I_2 in a furnace, equipped with two separate temperature controls. The $Pb_2P_2Se_6$ and $Pb_{1.424}Sn_{0.596}P_2Se_6$ crystals were obtained from melts using a Bridgeman method. The constituents of the samples were determined using inductively coupled plazma-atomic emission spectroscopy (ICP-AES) for Sn and P, and using atomic absorption spectroscopy (AAS) for Pb after the samples were dissolved in HCl/H_2O_2 solution. The ICP-AES and AAS were measured with Perkin Elmer ICP 5500 and Nippon Jarrell Ash A 825 spectrometers. The compositions obtained for Pb, Sn and P, and the best-fit mole fraction, x, in the $Pb_{2x}Sn_{2(1-x)}P_2Se_6$ single crystals are shown in Table 1.

Table 1 The elemental analysis and Pb^{2+} ion mole fraction, x, in $Pb_{2x}Sn_{2(1-x)})P_2Se_6$ crystals

x	Pb		Sn		P	
	calcd.	obsd.	calcd.	obsd.	calcd.	obsd.
0.098	5.14	5.26	27.09	27.71	7.84	7.86
0.251	12.62	12.27	21.78	21.38	7.58	7.29
0.402	19.70	19.73	16.82	16.81	7.16	7.34

The heat capacities of $Pb_{2x}Sn_{2(1-x)}P_2Se_6$ were measured using an adiabatic low-temperature calorimeter between 10 and 350 K. The calorimeter consists of the sample cell (~4 cm^3) and double adiabatic jackets surrounding it. They are suspended in the vacuum chamber. The temperature of the cell was measured with a rhodium-iron resistance thermometer calibrated in ITS-90. Details of the calorimetric apparatus were previously described [10]. The normal heat capacities were determined by non-linear optimization of the harmonic heat capacity functions with an originally developed program for numerical analysis of the heat capacity.

Results and discussion

The molar heat capacities of $Sn_2P_2Se_6$(x=0) are shown in Fig. 1. Heat capacity anomalies occurred at 193.24±0.10 and 220.27±0.15 K [11]. The first is the ferroelectric
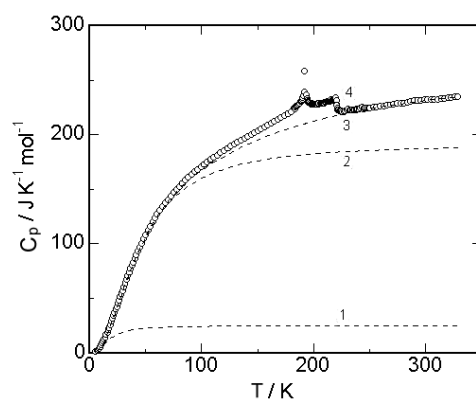
Fig. 1 Molar heat capacities of Sn$_2$P$_2$Se$_6$ (x=0). 1 – Debye term, optimized, 2 – Debye
and Einstein terms, optimized, 3 – calculated normal heat capacities at constant
pressure, 4 – experimental molar heat capacities, open circles

commensurate – intermediate incommensurate (C–IC) (lock-in) phase transition tem-
perature T_c, and the second the incommensurate – paraelectric (IC–N) phase transi-
tion temperature T_i, respectively. The phase transition at 193.24 K has a latent heat
and thus is a first order transition, while that at 220.27 K is second order characterized
by the absence of a latent heat. The normal heat capacity was calculated as follows:
3D (73.9 K), 6E (84.8 K), 6E (207.1 K) and 8E (160.8 K) and internal vibrational
contributions of 6E (662 K) and 1E (312 K) and a C_p–C_v correction, AC_p^2T, in which
A is 1.4442·10^{-7} J mol^{-1}. Here D and E represent Debye and Einstein heat capacity
functions and the number in front of D and E are the number of degree of freedom i.e.,
the masses assigned to the heat capacity function. Numbers in the parentheses are the
characteristic temperature of the harmonic heat capacity function. The best-fit values
of the characteristic temperatures and the coefficient A were determined by the least
squares fitting against the experimental data for T =11–111 K and 348–355 K. The
masses were chosen so as to give the smallest residue for the optimized characteristic
temperatures. The transition enthalpy and entropy were divided at 204.3 K into

Table 2 Phase transition enthalpy and entropy of Pb$_{2x}$Sn$_{2(1-x)}$P$_2$Se$_6$

	Phase transition	T / K	ΔH/J mol^{-1}	ΔS/J K^{-1} mol^{-1}
x=0	C–IC	193.24±0.10	1400±80	8.5±0.4
	IC–N	220.07±0.10	330±20	1.5±0.1
x=0.098	C–IC	164.54±0.10	720±30	5.5±0.3
	IC–N	192.96±0.10	200±10	1.1±0.1
x=0.251	IC–N	142.33±0.10	290±10	2.2±0.1
x=0.402	IC–N	96.08±0.10	170±10	2.1±0.1
x=1	–	–	–	–

two-phase transitions. The phase transition enthalpies and entropies based on above the normal heat capacities are 1400±80 J mol^{-1} and 8.5±0.4 J mol^{-1} K^{-1} for the lower ferroelectric – incommensurate (lock–in) phase transition (C–IC) and 330±30 J mol^{-1} and 1.5±0.1 J mol^{-1} K^{-1} for the upper incommensurate – paraelectric (IC–N) phase transition, respectively. A previous heat capacity data of Maior [12] gave that the entropies of C–IC and IC–N phase transitions are 1.7 and 4.4 J mol^{-1} K^{-1}, respectively for Sn$_2$P$_2$Se$_6$. These are much smaller than the present values and probably reflects the difference in the base line. The entropy of the lock–in (C–IC) transition of K$_2$SeO$_4$ [13], which belongs to displacive type ferroelectrics [14, 15], is 0.012 J mol^{-1} K^{-1}. This entropy is much smaller than that in Sn$_2$P$_2$Se$_6$. These large entropy values of Sn$_2$P$_2$Se$_6$ (x=0) suggest that the incommensurate structure is compatible with the order – disorder mechanism. The sum of transition entropies of the lower (lock–in) and upper (IC–N) transitions is equal to 10.0 J mol^{-1} K^{-1}, which is significantly larger than R ln2=5.76 J mol^{-1} K^{-1}, and it is a clear evidence for an order – disorder mechanism. As to the microscopic mechanism of the disorder, two possibilities are considered. One is an orientational disorder of P$_2$Se$_6^{4-}$ ions with the two equivalent orientations satisfying the site symmetry of the space group of the crystal in the high-temperature paraelectric phase. The transition entropy of this model amounts to Rln2= 5.76 J mol^{-1} K^{-1} and this value is smaller than the experimental value. The second possibility is the positional disorder of the Sn^{2+} ions. If there are two energetically equivalent positions for an Sn^{2+} ion, the entropy becomes 2R ln2=11.5 J mol^{-1} K^{-1}. The experimental value is slightly smaller than this value and the latter model is consistent with the experimental value. Recent X-ray measurements for Sn$_2$P$_2$Se$_6$ single crystals suggest the existence of two sites for an Sn^{2+} ions, supporting the cationic disorder model [3]. Until now, the phase transition at 220 K has been considered to be a displacive type because of the existence of the soft mode. However, the large entropy values favor an order – disorder mechanism. Therefore, Sn$_2$P$_2$Se$_6$ belongs to the same group of compounds as Sn$_2$P$_2$S$_6$, in which the ferroelectric – paraelectric transition is controlled by both the order – disorder and displacive mechanisms [11].
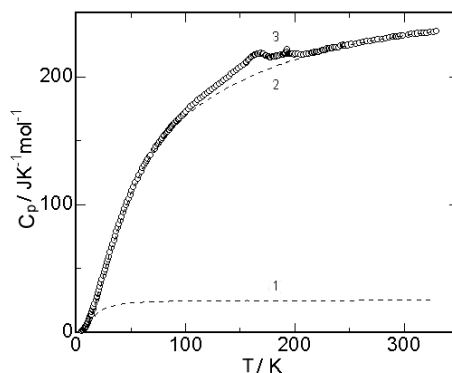

Fig. 2 Molar heat capacities of Pb$_{0.196}$Sn$_{1.804}$P$_2$Se$_6$ (x=0.098), 1 – Debye term, optimized, 2 – calculated normal heat capacities at constant pressure, 3 – experimental molar heat capacities, open circles

In pure Pb$_2$P$_2$Se$_6$ (x=1.0) no phase transition was observed in the heat capacity measurements between 10 and 330 K although its crystal structure is isomorphous with that of Sn$_2$P$_2$Se$_6$ (x=0). The heat capacities of x=0.098 in the Pb$_{2x}$Sn$_{2(1-x)}$P$_2$Se$_6$ system are shown in Fig. 2, in which an estimated base line using a similar method to Sn$_2$P$_2$Se$_6$ is shown in the figure. The heat capacity anomalies were found at 164.54±0.10 and 192.96±0.10 K, which probably correspond to C–IC and IC–N phase transitions, respectively. These values are lower than that in pure Sn$_2$P$_2$Se$_6$. This shows that the introduction of Pb^{2+} ion into Sn$_2$P$_2$Se$_6$ induces the lowering of the phase transition temperatures. This phase transition temperature lowering due to Pb^{2+} ion introduction in the mixed crystal, was also observed in Pb$_{2x}$Sn$_{2(1-x)}$P$_2$S$_6$ system [16]. In the Sn$_2$P$_2$S$_6$, a similar ferroelectric – paraelectric phase transition was observed (ΔS=8.6 J mol^{-1} K^{-1}) although there is no incommensurate phase [11]. The interesting point is that in the phase transitions for x=0.098, the upper transition has a characteristic of first-order and lower one of second-order, although the upper IC–N transition is second-order and lower C–IC phase transition first-order for x=0. There is a possibility that the pure Sn$_2$P$_2$Se$_6$ crystals are mixed in the crystals of x=0.098 because the first-order C–IC transition in x=0 is very close to the first-order transition in x=0.098. We should remeasure the heat capacity of x=0.098 after annealing at temperatures above melting point. The normal heat capacity was calculated in the similar way as with Sn$_2$P$_2$Se$_6$: 3D (66.5 K), 7E (89.4 K), 7E (159.3 K), 7E (219.5 K) and 6E (656.3 K) and a C_p–C_v correction, AC_p^2T, in which A is 1.942·10^{-7} J mol^{-1}. The phase transition enthalpies and entropies based on above the normal heat capacities are 720±30 J mol^{-1} and 5.5±0.3 J mol^{-1} K^{-1} for the lower ferroelectric – incommensurate (lock-in) phase transition, and 200±10 J mol^{-1} and 1.1±0.1 J mol^{-1} K^{-1} for the upper incommensurate – paraelectric (IC–N) phase transition, respectively. The sum of two phase transitions is 6.6 J mol^{-1} K^{-1}. The reduced phase transition entropy of the mixed crystal for one mole of Sn$_2$P$_2$Se$_6$ is 7.3 J mol^{-1} K^{-1} because no phase transition was observed in the Pb$_2$P$_2$Se$_6$ (x=1.0). For the mixed crystal of x=0.251 in the Pb$_{2x}$Sn$_{2(1-x)}$P$_2$Se$_6$ system, only one heat capacity anomaly was observed at 142.33±0.10 K. The phase transition temperature more decreased than that of the crystals of x=0.098. The
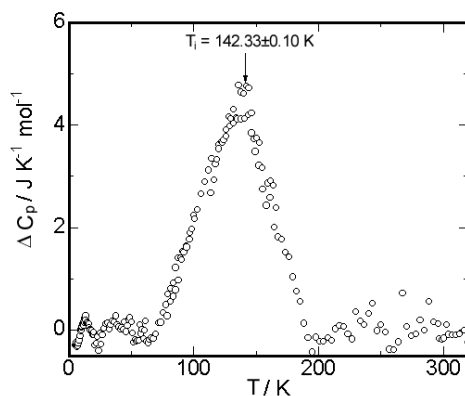

Fig. 3 The excess heat capacities of Pb$_{0.502}$Sn$_{1.498}$P$_2$Se$_6$ (x=0.251) as a function of temperature

normal heat capacity for x=0.251 was calculated in the same way as with x=0.098: $3D$ (61.25 K), $7E$ (86.02 K), $7E$ (158.1 K), $7E$ (217.9 K) and $6E$ (660.0 K) and a C_p–C_v correction, AC_p^2T, in which A is 1.640·10^{-7} J mol^{-1}. The excess heat capacities above normal heat capacities for x=0.251 are shown in Fig. 3. The phase transition enthalpy and entropy based on above the normal heat capacities are 290±10 J mol^{-1} and 2.2±0.1 J mol^{-1} K^{-1}. The reduced phase transition entropy of the mixed crystals for one mole of Sn$_2$P$_2$Se$_6$ is 2.9 J mol^{-1} K^{-1}. The value of phase transition entropy in the x=0.251 is much lower than that of x=0 and 0.08. This shows that the lower first-order lock-in C–IC phase transition is probably almost frozen-in. The compound of x=0.402 in the only one phase transition was observed at 96.08±0.10 K. The normal heat capacity was calculated in the same way as with x=0.098 and 0.251: $3D$ (55.65 K), $7E$ (87.83 K), $7E$ (148.1 K), $7E$ (236.8 K) and $6E$ (640.8 K) and a $C_p - C_v$ correction, AC_p^2T, in which A is 1.499·10^{-7} J mol^{-1}. The excess heat capacities above normal heat capacities for x=0.402 are shown in Fig. 4. The phase transition enthalpy and entropy based on above the normal heat capacities are 170±10 J mol^{-1} and 2.1±0.1 J mol^{-1} K^{-1}. The reduced phase transition entropy in the mixed crystal for one mole of Sn$_2$P$_2$Se$_6$ is 3.5 J mol^{-1} K^{-1}. The value of phase transition entropy in the x=0.402 is much lower than that of x=0 and 0.08 and close to that of 0.251. This also shows that the lower first-order transition is probably also frozen-in.
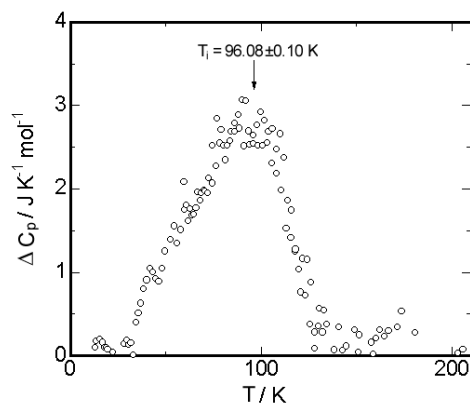

Fig. 4 The excess heat capacities of Pb$_{0.804}$Sn$_{1.196}$P$_2$Se$_6$ (x=0.402) as a function of temperature

The phase transition temperatures were plotted in Fig. 5 *vs.* the Pb^{2+} ion mole fractions in the Pb$_{2x}$Sn$_{2(1-x)}$P$_2$Se$_6$ system. The open symbols show our data determined by heat capacity measurements and closed symbols show the data reported by Maior *et al.* using dielectric measurements [17]. The circles and triangles show T_c and T_i, respectively. Both the IC–N and C–IC transition temperatures decrease with an increase in the Pb^{2+} mole fraction. Our data are lower than those of Maior but our data seem to be correct because we determined the mole fraction of the mixed crystals accurately using atomic absorption spectroscopy, however Maior *et al.* did not determine the mole fraction. The phase transition temperatures decreased with an increase
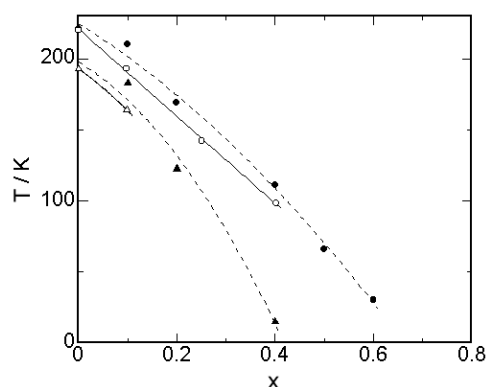
Fig. 5 The phase transition temperature plotted as a function of the Pb^{2+} ion mole fractions in $Pb_{2x}Sn_{2(1-x)}P_2Se_6$. ○, △ – present data, ●, ▲ – [17]

in the Pb^{2+} concentration. The decrease of phase transition temperatures due to an increase in Pb^{2+} mole fraction in the $Pb_{2x}Sn_{2(1-x)}P_2Se_6$ system shows a similar behavior to the system of $Pb_{2x}Sn_{2(1-x)}P_2S_6$ in which only a ferroelectric-paraelectric phase transition was observed [16]. The crystal structure of normal phase in $x=0$ is isomorphous with the room-temperature phase in $x=1.0$. The decrease of the phase transition temperature is interpreted as follows: the ionic radius of the Pb^{2+} ion is larger than that of the Sn^{2+} ion, and so the addition of the Pb^{2+} ions increases the space available for Sn^{2+} ions in the mixed crystals. In the mixed crystals, the motion of the Sn^{2+} ion becomes easier because of the addition of the Pb^{2+} ion, and the phase transition temperature decreases because the Sn^{2+} ion is able to move at a smaller thermal energies.

Conclusions

In the solid solution of $Pb_{2x}Sn_{2(1-x)}P_2Se_6$ system, C–IC and IC–N phase transitions temperatures are lowered with an increase in Pb^{2+} ions and first-order C–IC phase transition might be frozen in around $x=0.241$ with increasing Pb^{2+} ions. This is interpreted as follows. The increase of Pb^{2+} ion increase the space in which the Sn^{2+} ion is movable. However, due to the lowering of phase transition temperature, the phase transitions frozen in successively because the Sn^{2+} ion became unable to move which control the phase transition.

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