

SPECIFIC HEAT OF $(\text{NH}_2(\text{CH}_3)_2)_3\text{Bi}_2\text{I}_9$ T. PLACKOWSKI, D. WŁOSEWICZ, P.E. TOMASZEWSKI, J. BARAN
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The specific heat of title compound was measured by adiabatic calorimeter in the temperature range 80–315 K. The phase transitions at about 304, 285 and 235 K were confirmed. A new structural phase transition at about 125 K was observed as well as new anomaly on differential scanning calorimetry (DSC) curve at about 318 K. The peculiar multiple character of C_p anomalies may be explained in terms of phase transitions or intermediate phases induced by impurities. The specific heat data are in agreement with the independent DSC measurements and with preliminary X-ray studies.

PACS numbers: 64.70.Kb, 65.40.-f

1. Introduction

Since 1985 the numerous structural phase transitions have been discovered and studied in nanohalogeno-metallates with the general composition $\text{A}_3\text{B}_2\text{X}_9$ with organic groups as A cations ($\text{B} = \text{Sb}$ or Bi ; $\text{X} = \text{Cl}$, Br or I). Six types of structure are known for such stoichiometry [1]. Our compound, $(\text{NH}_2(\text{CH}_3)_2)_3\text{Bi}_2\text{I}_9$, crystallizes in type B formed by two layers of isolated bioctahedral B_2X_9 groups. Thus, its properties can be compared with other iodine derivatives only (which have the same structural motive; chlorine and bromine derivatives have the A-type structure with BX_6 structural unit): $(\text{NH}_3\text{CH}_3)_3\text{B}_2\text{I}_9$, $(\text{NH}_2(\text{CH}_3)_2)_3\text{B}_2\text{I}_9$, where $\text{B} = \text{Sb}$ or Bi . Changes of degree of freedom (by freezing of orientational motion with lowering temperature) of alkylammonium cations induce the phase transitions of order-disorder type.

Up till now, there have been no specific heat studies performed for crystals of this novel family of polar crystals.

$(\text{NH}_2(\text{CH}_3)_2)_3\text{Bi}_2\text{I}_9$ belongs at room temperature (phase II) to the orthorhombic system with the space group $Cmc2_1$ with the lattice parameters $a = 0.9011$, $b = 1.558$, $c = 2.252$ nm [2]. The dielectric permittivity, NMR, DSC and optical experiments revealed that this crystal undergoes successive phase transitions at 235, 285 and 304 K (on heating); the existence of phase transition at about 195 K was recently questioned [3, 4]. Above the phase transition at about 304 K the crystal becomes hexagonal (phase I) with the lattice parameters $a = 0.9009$ and $c = 2.251$ nm [2].

2. Experimental

Single crystals of $(\text{NH}_2(\text{CH}_3)_2)_3\text{Bi}_2\text{I}_9$ were grown from concentrated hydroiodic acid by slow evaporation at room temperature. The crystals have the form of pseudohexagonal plates of deep red colour.

The specific heat measurements were performed in the automated adiabatic calorimeter as described in [5]. The sample was located on a flat holder of the heat capacity equivalent to ≈ 200 mg Cu at the room temperature and glued by a weighted amount of Apiezon T grease and aluminium powder mixture. Two independent adiabatic screens were used to minimize energy exchange with the surrounding. The calorimeter operation alternatively combines two different modes: a heat pulse method with better absolute accuracy and a faster continuous method with better resolution. The heating rate for both methods is 10 mK/s. The mass of sample was about 130 mg. Due to small dimensions of the as-grown crystals, the sample consisted of 10 single crystals. At least three continuous runs were done through each of the transitions.

The DSC measurements were made on Perkin-Elmer DSC 7 using single crystal sample of mass of about 10 mg. The scanning rate was 20 K/min.

3. Results and discussion

The temperature dependence of specific heat of $(\text{NH}_2(\text{CH}_3)_2)_3\text{Bi}_2\text{I}_9$ in the range from 110 K to 315 K is presented in Fig. 1. At least five groups of anomalies are clearly visible on the smooth curve of background corresponding to the lattice contribution to the specific heat. The entropy and enthalpy changes, ΔS and ΔH respectively, associated with each phase transition were calculated with the aid of a hypothetical base line. The relative errors of ΔS and ΔH due to uncertainty in base line estimation are of the order of 10%. The numerical data and the nomenclature used by us are presented in Fig. 2 and Table. Because of rather good correspondence between our groups of peaks on $C_p(T)$ and single phase transitions known from literature, we decided to maintain the phase nomenclature hitherto existing and to deal with each group of anomalies as with one transition. The similar effects were observed for several other crystals (e.g. PbZrO_3 , NaNbO_3 , LaBGeO_5) with the explanation by the existence of impurity-induced intermediate phases as one of the possibilities [6, 7].

The specific heat curve shows quite complicated behaviour in the vicinity of phase transitions. As it is shown in Fig. 1, one can notice the multiple-peak anomalies in $C_p(T)$ at different temperatures. All effects, except the transition at about 125 K, are reproducible in the different measurement runs.

The specific heat value at room temperature corresponds well with the value of Dulong-Petit estimation for 26 atoms per formula unit (molecule has 44 atoms with 20 "heavy" atoms).

Now let us describe the consecutive phase transitions or their groups.

— On the DSC curves the small but clearly seen effect was observed at about 318 K indicating on new phase transition I-I' (Fig. 3). It seems that phase I' should have the space group $P6_3/mmc$. Our C_p experiments did not exceed the temperature of 315 K, thus just below the anomaly observed later by DSC.

TABLE

Characteristics of anomalies and thermodynamical data of $(\text{NH}_2(\text{CH}_3)_2)_3\text{Bi}_2\text{I}_9$. The data from DSC are presented in parentheses () and from literature [3, 4] — in square brackets [], the data without brackets are from C_p measurements. The phase transition temperatures were measured as a temperature of anomaly maximum (both for C_p and DSC data). For clarity, each of anomalies group was named by one temperature value corresponding to the main peak or mean value of temperatures. The hysteresis are evaluated from DSC measurements.

| Phase transition(s) | VI-V (≈ 125 K) | V-IV (≈ 215 K) | IV-III (≈ 247 K) | III-II (287 K) | II-I (304 K) | I-I' (≈ 318 K) |
|-----------------------------------|---|----------------------------------|--|--|----------------------------|---|
| Characteristics of anomalies | triple 120.9 123.3 126.8 (127) | cuspid diffused peak (214) | triple: 241 (wide, small) 246.1 (sharp) (244) 250.1 (sharp) | two sharp peaks: 281.6 (small) (283) 286.9 (pronounced) (288) [285] | single, sharp 304 (305) | wide, small (only DSC data) (319) |
| ΔS [J/(mol K)] | 7.1 (0.8) | 0.5 (for peak) (1.4) | 2.4 (1.5) | 5.6 (0.2+5.4) (5.6), [4.3] | 0.9 (0.9), [1.2] | — (0.3) |
| ΔH [kJ/mol] | 0.90 (≈ 0.10) | 0.11 (≈ 0.30) | 0.59 (≈ 0.36) | 1.61 (0.07+1.54) (1.61), [1.2] | 0.27 (0.29), [0.36] | — (≈ 0.08) |
| Hysteresis [K] (from DSC data) | (?) | (≈ 30) | (25) [large] | (6.5 for main peak) [2] | 5 [0.5] | ≈ 10 |

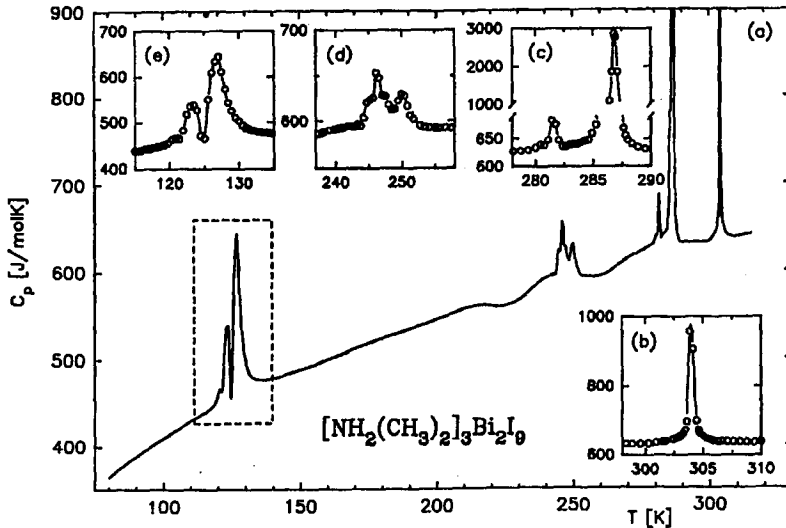


Fig. 1. Specific heat of $(\text{NH}_2(\text{CH}_3)_2)_3\text{Bi}_2\text{I}_9$. The insert pictures show the details of each group of anomalies. The part of main plot surrounded by dashed rectangle and insert (e) present only one example of $C_p(T)$ behaviour in this temperature range; the other possibilities are presented in Fig. 4.

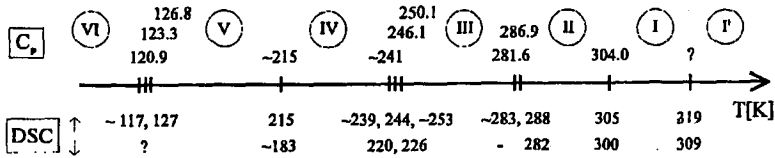


Fig. 2. Phase transitions diagrams of $(\text{NH}_2(\text{CH}_3)_2)_3\text{Bi}_2\text{I}_9$. The upper data are from C_p measurements while the lower ones are from DSC (in this case two sets of data correspond to the heating and cooling processes).

— The phase transition I-II at 304 K is clearly visible as single peak on specific heat (Fig. 1b and Fig. 3). This is a first-order phase transition of paraferroelastic type [3]. The crystal changes its symmetry from hexagonal (phase I with the space group $P6_3mc$) to orthorhombic (phase II with the space group $Cmc2_1$) [2]. NMR data indicate free isotropic cation reorientations in the phase I while in phase II they have slightly lower reorientation frequency [4].

— The greatest anomaly at 286.9 K (high and sharp peak) corresponds to the phase transition I-II and is accompanied by a small peak at 281.6 K (i.e. 5 degrees below) (Fig. 1c). The DSC data confirm the existence of this small anomaly. On cooling (DSC data) the higher peak displaces toward low temperature thus overlapping the smaller anomaly. The transition is of the first-order type in agreement with the literature [3, 4]. Measured value of entropy change satisfies well the relation $\Delta S = 5.6 \approx R \ln 2 = 5.76$ which may indicate that this is an order-disorder

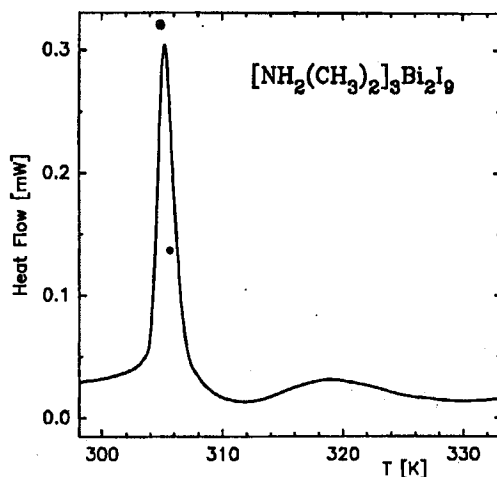


Fig. 3. DSC plot showing the phase transitions I'-I and I-II.

type phase transition, i.e. some two energetically equivalent orientational states existing in the phase II are frozen in phase III due to II-III transition. Because of relatively free rotation of organic cations in both phases known from NMR data [4], the change of configurational entropy should be connected with the inorganic Bi_2I_9 anions sublattice. This seems to be confirmed by preliminary X-ray powder and single crystal determination of the crystal structure at room temperature phase II (the splitting of atoms in the structure) [8].

— The III-IV phase transition anomaly on $C_p(T)$ at about 247 K consists of at least three peaks in the range of ten degrees, one of them is wide (Fig. 1d).

— The more complicated situation exists in the vicinity of IV-V phase transition at about 215 K (Fig. 1a). The character of the observed anomaly seems to be unclear and it may be interpreted in two ways. When we assume that this is a continuous type transition, we could treat this $C_p(T)$ anomaly as a cusp. Hence, using an entropy conserving construction drawn on C_p/T versus T plot, we could resolve a change of specific heat as $\Delta C_p \approx 11 \text{ J}/(\text{mol K})$ and estimate transition temperature as about 219 K. On the contrary, the large temperature hysteresis seen on DSC data may indicate that the III-IV phase transition is of the first-order type and the change of entropy could be very roughly assessed as $\Delta S \approx 0.5 \text{ J}/(\text{mol K})$. However, the DSC curves are difficult to interpret in this case due to small size of the effect.

We suppose that this phase transition and the previous one correspond to broad anomaly observed on dielectric permittivity at about 230 K [3] or 220 K [4] and were attributed to second-order [3] or "mixed" transition [4] (perhaps due to small resolution of used methods?). There are no comments in [4] about small anomaly on dielectric permittivity at about 205 K seen in Fig. 5 from [4].

— It is interesting that for second run of DSC the new anomaly appeared at about 172 K. However, the phase transition at about 195 K reported in [3] was

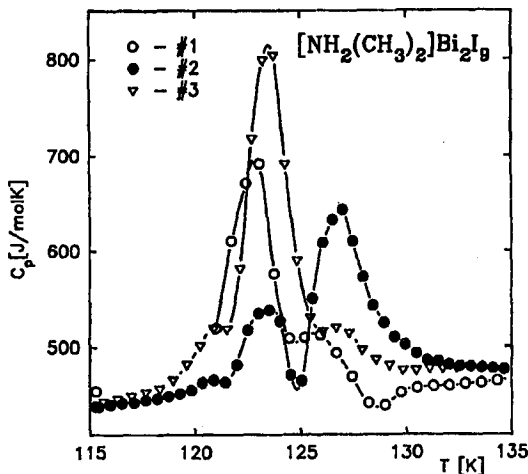


Fig. 4. Different distribution of peak intensities at the phase transitions at about 125 K. The numbers correspond to the consecutive temperature runs.

not observed by other methods. The question about the existence of this phase transition is still open.

— The necessity of the existence of the phase transition V–VI below 140 K can be easily supposed from the published temperature dependence of dielectric permittivity (unfortunately, measurements were done down to 130 K only [3, 4]). Really, at about 125 K such phase transition(s) was observed both in C_p and DSC experiments. The character of triple-peak anomaly changes from one temperature cycle to another (different distribution of well resolved peak intensities), but the positions of each peak remain nearly the same (Fig. 4). It is perhaps without great significance, but the same distribution (curves 1 and 3) was observed when sample was cooled down from room temperature thus without previous heating above the phase transition I–II at 304 K. In the case of curve 2, the cooling was realized step by step from the temperature exceeding 304 K. The entropy change ΔS measured for all peaks together remains nearly constant: 7.8–7.1–8.7 J/(mol K) for three consecutive runs (ΔH are 0.99, 0.92 and 1.12 kJ/mol, respectively).

4. Conclusions

1. The specific heat value at room temperature corresponds well with the value of Dulong–Petit estimation for 26 atoms per formula unit.

2. The smooth shape of background may suggest that during phase transitions the structural changes are only of reconstruction type without significant rebuilding of the structure. It corresponds well with the NMR data suggesting the occurrence of new degrees of freedom during heating in consecutive phase transitions.

3. Except phase transition I–II, we observed a groups of anomalies instead of single phase transition described in literature [3, 4]. In general, the “splitting” of

the $C_p(T)$ peaks could be attributed to several reasons: structural defects and inhomogeneity of the sample (coming from crystal growing process), premonitory phenomena or intermediate phases (e.g. of incommensurate character). However, the existence of impurity-induced intermediate phases were reported for several crystals (e.g. PbZrO_3 , NaNbO_3 , LaBGeO_5) showing the similar behaviour of $C_p(T)$. Thus it could be suggested that pure $(\text{NH}_2(\text{CH}_3)_2)_3\text{Bi}_2\text{I}_9$ might give only single $C_p(T)$ anomalies instead of their groups.

4. For the first time the phase transition at about 125 K was observed (V–VI), as predicted from dielectric permittivity measurements data. Also a new phase transition at about 318 K was revealed by DSC measurements.

5. The first-order II–III phase transition at about 287 K was interpreted as an order–disorder type. The measured change of configurational entropy, $\Delta S = 5.6 \approx R \ln 2$, may suggest a reducing of possible configurations of Bi_2I_9 sublattice by factor of 2.

Further studies, particularly on crystal structure, are desirable for understanding the mechanism of phase transitions in $(\text{NH}_2(\text{CH}_3)_2)_3\text{Bi}_2\text{I}_9$.

The authors express their gratitude to Dr. J. Zaleski (Wrocław, Opole, Poland) for supplying the single crystals of $(\text{NH}_2(\text{CH}_3)_2)_3\text{Bi}_2\text{I}_9$.

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