Specific heat anomaly in ferroelectric: Bis(imidazolium) pentachloroantimonate(III) $(C_3 N_2 H_5)_2[SbCl_5]$

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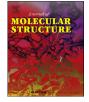
A B S T R A C T

Single crystals of ferroelectric bis(imidazolium) pentachloroantimonate(III) $(C_3N_2H_5)_2[SbCl_5]$ have been grown and the heat capacity was measured by the use of AC calorimetric method. The temperature dependence of excess heat capacity and excess entropy in the ferroelectric phase can be described in the frame of the classical Landau-Devonshire theory of phase transitions. The results of experimental studies were analyzed and the α, γ and δ values of the Landau potential coefficients were calculated. The temperature dependence of the order parameter was also evaluated from the heat capacity data.

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1. Introduction

The materials characterized by a ferroelectric properties have found broad applications in advanced laser technology, mechanical energy transfer and optoelectronics as a nonvolatile ferroelectric memories and piezoelectric actuators [1–4]. Particularly, haloantimonates(III) and halobismuthates(III) based on various aliphatic and heteroaromatic amines evoke much interest because many of these compounds exhibited ferroelectricity, quite often in the room temperature phases. These molecular-ionic compounds, described by the general formula $R_aM_bX_{3b+a}$ (where R-amine, $M = Sb$ and Bi and $X = Cl$, Br, I) are characterized by a rich diversity of the anionic networks. From among of numerous subgroups of this family only several like: RMX_4 [5], $R_3M_2X_9$ [6], $R_5M_2X_{11}$ [7] and R_2MX_5 [8,9] were found to exhibit ferroelectric properties. The paraelectric–ferroelectric phase transitions (PTs) of an 'order-disorder' type of haloantimonates(III) and halobismuthates(III) crystals are usually driven by a change in the reorientational motion of the organic moieties.

The R_2MX_5-subgroup is characterized by several types of the anionic networks (e.g. isolated bioctahedral $[M_2X_{10}]^{4-}$ or polymeric $[MX_5]_\infty^{2-}$ moieties). Two examples of ferroelectrics crystallizing with R_2MX_5 chemical stoichiometry characterized so far, were found to adopt the polymeric anionic network. The first, $(1,1'$-dimethyl-4,4'-bipyridinium)$BiBr_5$, possesses the trans–connected anionic octahedra [8]. The ferroelectric transition ($T_c = 243$ K) is due to a significant distortion of regular trans–connected octahedra of polymeric structure leading to strong acentric polyanionic network, thus the molecular mechanism of the PT seems to be of a 'displacive' type. The second, imidazolium analog, $(C_3N_2H_5)_2[SbCl_5]$ (abbreviated as **ICA**) is characterized by a chain of cis–connected octahedra [9]. Its molecular mechanism of ferroelectric PT is complex because both the 'order-disorder' and 'displacive' contributions are postulated.

Studies of **ICA** single crystals revealed sequence of two PTs at temperatures about 342 K and 180 K [9]. The second order PT at 180 K from phase that we can number II to phase III is paraelectric–ferroelectric one whereas the PT at 342 K from phase I to II is of the first order. The large transition entropy ($\Delta S_{tr} = 12.4$ J K^{-1} mol^{-1}) already estimated for the higher temperature, first order PT (at 342 K) with a DSC method indicates the 'order–disorder' mechanism of this transition [9]. On the other hand the ferroelectric heat anomaly at lower temperature (180 K) was characteristic of a second order PT thus we could not precisely estimate its entropy transition magnitude from DSC studies.

The main goal of our paper is to obtain new experimental data and present more detailed characteristics of the specific heat and entropy anomaly in **ICA** at the continuous

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paraelectric–ferroelectric PT region. The AC calorimetry method gives a possibility to obtain the well-defined temperature dependence of heat capacity close to the ferroelectric (II→ III) PT temperature and precisely analyze critical phenomena [10,11]. Moreover, we shall prove compatibility of the obtained results with the description of ferroelectric PT.

2. Experimental

All materials used in this work were of reagent grade purity and were used as commercially obtained: imidazole (>99% Sigma–Aldrich), Sb_2O_3 (Sigma–Aldrich 99.999%) and HCl (Sigma–Aldrich 48%).

The powder of $(C_3N_2H_5)_2[SbCl_5]$ (**ICA**) was prepared by reaction of imidazole and Sb_2O_3 in a concentrated hydrochloric acid. The salts obtained were twice recrystallized and characterized by an elemental analysis (commercial CHNS vario EL III Elementar apparatus on C, H and N) C: 16.27% (theor. 16.22%), H: 2.52% (theor. 2.55%), N: 12.60% (theor. 12.58%).

The large single crystals were grown by a slow evaporation of an aqueous solution. The plates of the approximate thickness 0.3–0.4 mm and the maximum area 12 mm^2 were cut and prepared. In the experiment, we used AC calorimetric specific heat measuring system Sinku–Riko, the model ACC-1M/L, whose regulation accuracy of a heat bath temperature was 0.01 K. The front face of the sample was blackened for better absorption of the heat pulse. It should be taken into account that absolute values of the specific heat could be determined only in a relative way, by comparison with the ac temperature response of the model sapphire sample. The specific heat measurements were performed at a chopping frequency of 1 Hz while cooling and heating with a constant temperature rate of 0.1 K/min. The ac temperature amplitude at frequency of 1 Hz was measured using chromelconstantan thermocouple wires of 25 μm with resolution of 0.0025 K. The pure helium pressure amounts $2.5 \cdot 10^4$ Pa (with the maximum error $0.5 \cdot 10^4$ Pa). The typical magnitude of the temperature oscillation is of about 0.0235 K. The source of heat capacity values for reference sapphire used for the measurements determining Specific Heat Capacity by Differential Scanning Calorimetry was presented in Ref. [12] and is under the jurisdiction of ASTM Committee E37 on Thermal Measurement and is the direct responsibility of Subcommittee E37.01 on Test Methods and Recommended Practices. Current edition approved March 1, 2005. Published April 2005. It should be added that the different value of T_c for the II → III PT reported in Ref. [9] and in present paper result from different techniques, the rate of the temperature changing, the mass of the sample (gradients of the temperature) and the quality of the sample. The complex electric permittivity was measured between 100 and 370 K by an Agilent E4980A Precision LCR Meter in the frequency range between 135 Hz and 2 MHz. The dimensions of the sample were approximately $2 \times 3 \times 1$ mm^3. The plates were silver painted. The overall error in estimation of the real and imaginary parts of the complex electric permittivity was about 5%.

3. Results and discussion

Fig. 1 (a) and (b) present the temperature dependence of the specific heat Cp and the specific heat increment ΔCp, respectively measured during cooling cycle. As the measured molar heat capacity contains two contributions of the excess heat capacity due to ferroelectric PT and the lattice heat capacity they have to be separated. In order to achieve the baseline a polynomial has been fitted to the obtained data including also relatively wide range of ferroelectric phase data. This procedure of settling on made the

parameters of a third order baseline polynomial depended on the limits of a temperature region taken into account. The lower and upper limits of the temperature range were fixed at the ends of experimental dependence of the molar heat capacity presented in Fig. 1(a). The excess of molar heat capacity ΔCp separated from the lattice contribution to the molar specific heat is shown in Fig. 1(b).

The Landau-Devonshire potential function was used to characterized the thermodynamic properties [13]:

$$G = G_0 + \frac{1}{2}\alpha P^2 + \frac{1}{4}\gamma P^4 + \frac{1}{6}\delta P^6 \tag{1}$$

where P stands the order parameter and α coefficient which changes with temperature $\alpha = \alpha_0(T - T_c)$. The estimation of the α, γ and δ coefficients allows us to confirm the order of the phase transition and proximity to the tricritical point. From the Eq. (1) and definition of entropy as $S = -\partial G/\partial T$ it results that:

$$\Delta S = -\frac{1}{2}\alpha_0 P^2 \tag{2}$$

The excess specific heat which can be defined as $\Delta C_p = T\frac{\partial \Delta S}{\partial T}$ follows the equation:

$$\left(\frac{T}{\Delta C_p}\right)^2 = \frac{4\gamma^2}{\alpha_0^4} + \frac{16\delta}{\alpha_0^3}(T_c - T) \tag{3}$$

The Eq. (3) allows to estimate coefficients γ and δ if the coefficient α_0 is known. It can be deduced from the slope of $1/\varepsilon$ vs. T dependence (see Fig. 4 of Ref. [9]). In a range up to 8 K above $T_{(\varepsilon max)}$, the α_0 coefficient is about $5.732 \cdot 10^7$ VmC^{-1} K^{-1}.

Since $(T/\Delta C_p)^2$, (Fig. 2) appeared to be linear in the temperature range $0.1 \le (T_c - T) \le 11$, thus the coefficients δ and γ were estimated from the linear regression: $(T/\Delta C_p)^2 = 5.25187 \cdot 10^{-7} + 6.01563 \cdot 10^{-8} \cdot (T_c - T)$. Taking into consideration value of molar volume Vm = 4270.45 mol/m^3 the calculated coefficients are given in Table 1.

The parameters defined as V = $\gamma(\alpha 0\delta)-1/2$ or more universal dimensionless: K $= \frac{\gamma^2}{4\alpha_0\delta T_c}$ can be used for the estimation of the proximity to the tricritical point. The value of the V-parameter for the second order transitions is positive, but it is negative for the first order transitions. In our case, V = 5.9 clearly shows that the transition is rather far from being the tricritical one. The K-parameter gives 0.049, two orders of magnitude greater value than that obtained for TGSe, which is often regarded as a model crystal exhibiting the tricritical behaviour [17]. Estimated coefficients indicate two possible mechanisms of transitions for the analyzed group of crystals. The data obtained for $[NH_2(CH_3)_2]_3Sb_2Cl_9$ and **ICA** crystals are quite close and suggest similar ways of ordering at ferroelectric transition.

The dipole–dipole interactions of the ferroelectric type in these compounds are intensified by the presence of the polymeric structure of anionic substructure (one- or two-dimensional). It is well known that the crystals with the polymeric anionic structure (1D or 2D) are characterized by an enhanced polarizability which, in the case of the ionic crystals, has a direct connection with the polar properties of the ferroelectric phase [8,14–16]. In the case of the imidazolium analogs (see Table 1, compounds (1), (2) and (3)) some of the coefficients are comparable with each other, however, they are significantly different from those for (4) and (5) (**ICA**). In the imidazolium analogs ((1), (2), (3)) the anionic networks are characterized by the bioctahedral $[M_2X_{11}]^{5-}$ units (0D arrangement) thus the coupling between the cationic and anionic sublattices seems to be weaker.