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Phase Transitions in Guanidinium Bromoantimonate(V) $[C(NH_2)_3]SbBr_6$

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$[C(NH_2)_3]SbBr_6$ belongs to a rich family of the molecular-ionic crystals of alkylammonium halogenoantimonates(V). Several members of this family show ferroelasticity. The crystals may be divided into two subgroups: $RSbCl_6$(where R denotes an organic cation, *e.g.* guanidinium, pyrrolidinium, piperidinium) [1–4] and $(R^+)_2$ $(SbCl_6^-)(Cl^-)$ [5,6]. Both types of these crystals consist of isolated $(SbCl_6^-)$ anions and R^+ cations. The salts with more complex composition additionally possess an isolated (Cl^-) anion. Most of these crystals exhibit a complex sequence of phase transitions (PTs). The numerous PTs of the order-disorder type are governed by the dynamics of the cationic and anionic units. In turn, the paraelastic-ferroelastic PTs, usually continuous in nature and strictly connected with deformation of the hydrogen bonds system, appeared to have the displacive mechanism.

In last decade many papers were devoted to studies on solid complexes of $SbCl_6^-$ anions with exotic cations, *e.g.* porphyrin, tris(4-bromophenyl)aminium or thietanium species, [7,8,9]. This is important in biological systems investigations, *e.g.* on photosynthetic reaction or in catalysis.

Very little is yet known about the physical properties of bromoantimonates(V), especially from the point of view of their dynamic properties. To our best knowledge there are only several reports on alkylammonium bromoantimonates(V) [10]. These salts contain, as often as not, in the structure either the Sb(V) or mixed Sb(V) and Sb(III) atoms, *e.g.*, $(C_5H_5NH]_6Sb^{(III)}Sb_3^{(V)}Br_{24}$ [11] or $(C_7H_{13}NH)_4Sb^{(III)}Sb^{(V)}Br_{12}\cdot 2Br_2$ [12]. We should add that bromoantimonates(V), as a rule, are unstable in air. Recently, we were successful in obtaining a new bromoantimonate(V) compound containing guanidinium cation: $[C(NH_2)_3]SbBr_6$.

This communication reports the results of studies on the PTs taking place in a new guanidinium hexabromoantimonate(V), $[C(NH_2)_3]SbBr_6$ (abbreviation – GBA), which were obtained using differential scanning calorimetry (DSC), dilatometry and dielectric method.

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GBA was prepared following a procedure described elsewhere [13]. The single crystals of GBA were grown from an aqueous solution at room temperature during several hours. The chemical formula of the compound was checked by the elemental analysis (found C, 30.95; H, 3.50; N, 14.52%; calc., C, 30.93; H, 3.64; N, 14.44%). The single crystals are of hexagonal-like habit, resembling that of the chloroantimonate(V) analogue – $[C(NH_2)_3]SbCl_6$ (GCA) [2]. The crystals are intensely colored, being deep red (transmitted light from very thin section of the crystal) to black. The GBA crystals are quite unstable in air and after over a dozen hours the black material begins to turn red and after that yellow. This means that crystals have some tendency to decomposition and contain the mixed Sb(III) and Sb(V) states. This process is accompanied by a drastic change in the physical properties of crystals.

Differential scanning calorimetry (DSC) runs were recorded using a Perkin Elmer DSC-7 between 100–400 K. The dilatometric measurements were made with a thermomechanical analyser Perkin Elmer TMA-7 between 100–400 K. The complex electric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ from 300 to 400 K was measured with the HP 4284A Precision LCR Meters in the frequency range between 1 kHz and 1 MHz. The dimensions of the sample were of the order of $3\times3\times1$ mm^3. The overall error was less than 5% and 10% for the real and imaginary part of the complex electric permittivity, respectively. For dielectric and dilatometric measurements we were able to prepare a single crystal sample for only one direction perpendicular to the hexagonal plates (the single crystals as-grown without cutting). Since the morphology of GBA and GCA seems to be identical, this direction was labelled as a c-axis.

Two thermal anomalies were detected between 300–370 K (see Fig. 1a) on the DSC curves. One distinct anomaly observed at 361/356 K, on cooling-heating, corresponds to a first-order PT of an order – disorder type. It is accompanied by a large transition entropy $\Delta S = 12\ J\cdot mol^{-1}\cdot K^{-1}$ (= Rln 4.2). In the low temperature region at about 314 K a small but clearly shaped thermal anomaly is visible due to the continuous PT.

The temperature dependence of the thermal expansion, $\Delta L/L_o$, along the direction perpendicular to the hexagonal-like plate is presented in Fig. 1b. Two anomalies are found during heating and cooling cycles. The anomaly at about 314 K is seen as a change in the slope of the linear part of $\Delta L/L_o(T)$ curve. At higher temperature, close to 361 K, one can observe a drastic, positive thermal expansion of the order of $2\cdot10^{-2}$ (on heating). This anomaly is not perfectly reversible, being of the order of $5\cdot10^{-3}$ during cooling. One can state, however, that the sequence of the PTs revealed by dilatometric technique is in good agreement with that found by DSC.

The real part of the complex electric permittivity, ε'_c, in the vicinity of the high temperature PT (356 K) at the frequency of 1 MHz during cooling is shown in Fig. 1c. This transition is accompanied by a small rapid jump in the ε'_c value by about 1 unit. No relaxation process is found between 1 kHz and 1 MHz. It is interesting that dielectric characteristic of GBA shows a large similarity to that found in its chlorine analogue GCA (see Fig. 7 in [2]). Such dielectric response suggests that dipolar groups, contributing to the electric permittivity value over the high temperature phase I, are

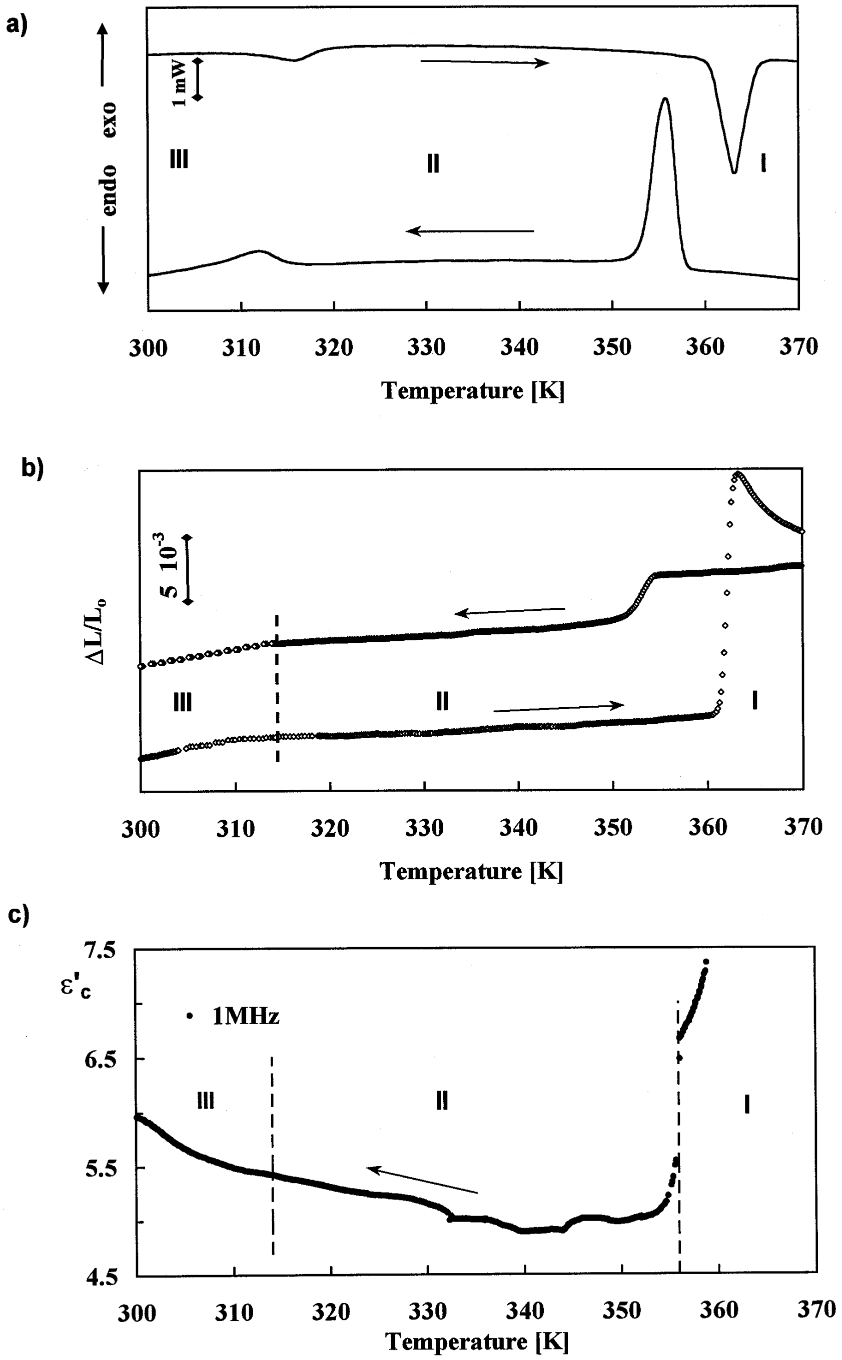
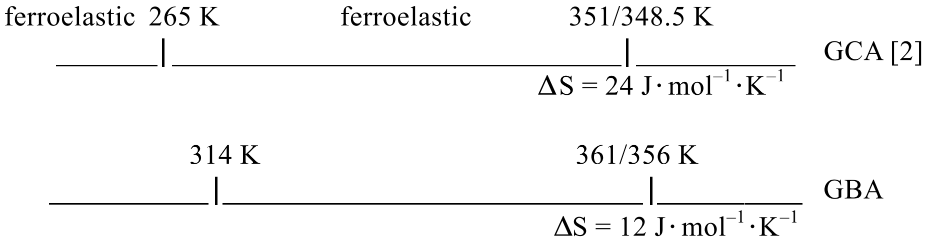


Figure 1. **a)** DSC curve of the $[C(NH_2)_3]SbBr_6$ between 300 and 370 K recorded on heating and cooling, scanning rate 10 K· min^{-1}; **b)** temperature dependence of the linear thermal expansion, $\Delta L/L_o$, measured along the *c*-axis on cooling and heating at a rate of 2 K·min^{-1}; **c)** temperature dependence of the real part of the complex electric permittivity measured along the *c*-axis on cooling.

performing a quite fast reorientation. The expected macroscopic relaxation time should be shorter than $1 \cdot 10^{-8}$ s.

It seems interesting to compare the phase transition sequence disclosed in these two closely related compounds GBA and GCA:



The important conclusion resulting from the above diagram is that GCA and GBA show a large similarity in their dynamic properties. The corresponding PTs occur in a comparable temperature region. The high temperature PTs are characterized by relatively large transition entropies, ΔS, and identical dielectric response, which suggests an obvious affinity of this PT mechanism. The high temperature PTs for both compounds are classified as an order – disorder type. The ^{1}H NMR studies on GCA showed [14] that the reorientation of $[C(NH_2)_3^+]$ cations (the C_3-type) contributed mainly to the PT mechanism at 351 K. On the other hand, the increment of the electric permittivity, accompanying the PT at 348.5 K in GCA and at 356 K in GBA cannot be the result of the motion of organic cations. It is obvious that the motion of flat guanidinium cation, being of high symmetry (C_3), does not lead to a change in the resultant dipole moment of the unit cell. The preliminary X-ray temperature dependent studies on GCA admit the $SbCl_6$ octahedra tilting in the vicinity of the 351 K PT. Thus, the freezing of this motion may be the reason for the appearance of the dielectric increment around the high temperature PT of both guanidinium compounds.

Taking into account the PT diagrams of GCA and GBA and large similarities of the physical properties studied, one can suggest that GBA is a potential ferroic (ferroelastic) crystal below 361 K.

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