The Dielectric and Dilatometric Single Crystal Studies of Phase Transitions in a New Member of Family of Halogenoantimonates(III) \([\text{C(NH}_2\text{)}_3\text{]}_2\text{SbCl}_5 \cdot [\text{C(NH}_2\text{)}_3\text{]}\text{Cl}\)

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The results of dielectric, dilatometric and DSC studies on a new member of the family of alkylammonium halogenoantimonates (\([\text{C(NH}_2\text{)}_3\text{]}_2\text{SbCl}_5 \cdot [\text{C(NH}_2\text{)}_3\text{]}\text{Cl}\)) are presented. This compound undergoes three phase transitions at 146 K, 162 K, and 366 K. The two low temperature transitions are suggested to be of the displacive type and the high temperature one of the order-disorder type. The character of temperature changes of the electric permittivity at the lowest temperature transition suggest a polar phase below the transition temperature.

Key words: Phase transitions; Dielectric; Dilatometric; Halogenoantimonate; Guanidinium.

1. Introduction

Guanidinium \([\text{C(NH}_2\text{)}_3\text{]}^+\) is a relative small and chemically simple cation. Its \(\text{C}\text{–N}_3\) skeleton is planar with \(D_{3h}\) symmetry because of some degree of \(\pi\) overlap of the \(p_z\) orbitals of nitrogen atoms and vacant \(p_z\) orbitals of the carbon. The three \(\text{N}\text{–C}\) bonds have a partial double bond character, which is reflected in their short inter nuclear distances (1.30 Å).

The molecular dynamics of guanidinium salts has been studied by IR [1–4], NMR [5–10] and NQR [5] spectroscopy, and the structure of many simple guanidinium salts is known, e.g. [11–13]. In many guanidinium salts a number of solid-solid phase transitions [6, 8, 14, 15] was found. The correlations between cationic and anionic motions at the phase transitions were studied [8, 9]. The guanidinium cations are characterized by the possibility of \(C_3\) type reorientations in the solid state even at room temperature. In \(\text{GuHClO}_4\) a diffuse phase above 450 K was found, where in addition to molecular reorientations diffusive motions of cations take place [6, 16]. The guanidinium salts are thus interesting from the molecular point of view.

We decided to extend our studies of phase transitions of a number of simple alkylammonium halogenoantimonates(III) and bismuthates(III) to derivatives in which alkylammonium cations were substituted by guanidinium ones.

The halogenoantimonates crystallise in number of different stoichiometries, of which the most popular are \(\text{RMX}_n\), \(\text{R}_2\text{MX}_3\), \(\text{R}_3\text{MX}_6\) and \(\text{R}_3\text{M}_2\text{X}_9\) (\(\text{R} = \text{alkylammonium cation}, \text{M} = \text{antimony}, \text{X} = \text{chlorine, bromine or iodine}\)). They are ionic-molecular salts. Their anionic sublattices are composed of deformed octahedra \(\text{MX}_3^+\) connected with each other by edges, corners or faces forming isolated or polymeric structures. The organic cations are located between the anions, connected to them by hydrogen bonds.

Most attention was devoted to the \(\text{R}_3\text{M}_2\text{X}_9\) subfamily. For \(\text{R} = \text{methyl, dimethyl, trimethyl or tetramethyl cation, interesting materials were obtained. Most of the members of this subfamily exhibited sequences of phase transitions, many of them to ferroelectric and pyroelectric phases. The phase transitions were accompanied by a change of the dynamics of the cationic sublattice. On decreasing the temperature, the reorientations of the cations were consecutively frozen at the phase transitions. Most of the observed transitions were of the order-disorder type.}

Recently, by varying the ratio of \(\text{SbCl}_3\) to guanidinium chloride during the synthesis, two new anti-
mony salts were obtained, namely \[\text{[C(NH}_2\text{)_3]}_3\text{Sb}_2\text{Cl}_9\] and \[\text{[C(NH}_2\text{)_3]}_2\text{SbCl}_5\cdot\text{C(NH}_2\text{)_3]}\text{Cl}\].

Results of dielectric, dilatometric and IR studies on \[\text{[C(NH}_2\text{)_3]}_3\text{Sb}_2\text{Cl}_9\] crystal, show that it undergoes a phase transition at \(T_{cl} = 105\) K. Dielectric dispersion is present above \(T_{cl}\), which may be described by a dielectric relaxator with Arrhenius type of activation. The mechanism of this transition is probably connected with a freezing of \(C_3\) reorientations of guanidinium cations [18].

In the present paper we report dielectric dilatometric and DSC studies of phase transitions in \[\text{[C(NH}_2\text{)_3]}_2\text{SbCl}_5\cdot\text{[C(NH}_2\text{)_3]}\text{Cl}\] (guanidinium hexachloroantimonate) = GHCA crystals.

2. Experimental

The GHCA crystals were obtained by the reaction of stoichiometric amounts of \(\text{Sb}_2\text{O}_3\) and guanidinium hydrochloride in hot concentrated hydrochloric acid. They were recrystallized from hydrochloric acid at ambient room temperature. Their stoichiometry was confirmed by elemental analysis. The melting point is 155°C. The complex electric permittivity was measured along the three principal crystal directions by an HP4284A precision LCR meter between 1 kHz and 1 MHz in the temperature range from 300 K to 80 K with a cooling rate of 0.2 K/min in the region of phase transitions and about 0.5 K/min elsewhere.

Linear thermal expansions were measured by a thermomechanical analyzer Perkin Elmer TMS-2. The accuracy of thermal expansion determination was about 2%. The results were obtained for dynamical temperature changes of about 0.5 K/min.

The DSC studies were performed on a Perkin-Elmer DSC 7 calorimeter with a heating/cooling rate of 10 K/min.

3. Results

3.1 Dilatometric Results

Figure 1 shows the temperature dependencies of the thermal expansion coefficients \((\Delta l/l)\) measured along the \(a\), \(b\), and \(c\) axes. There are two structural phase transitions; at 146 K discontinuous and at 162 K continuous. The transition near 146 K is accompanied by a distinct spontaneous change in lengths \((\Delta L/L)\) of about \(-1.6 \cdot 10^{-4}\), \(+1.1 \cdot 10^{-4}\) and \(+2.4 \cdot 10^{-4}\) along the \(a\)-, \(b\)-, and \(c\)-axes, respectively.

The volume change \((\Delta V/V)\) at this transition, \(+1.9 \cdot 10^{-4}\), suggests a positive pressure coefficient \((dT_c/dp = \Delta V/\Delta S)\). Except for the phase transitions region, GHCA reveals only a minor difference in the thermal expansions for the three crystallographic axes. Along the \(a\)-axis, dilatation is dominant, the mean value of the linear thermal expansion \(\tilde{\alpha}\) is defined as \((\Delta l_1 - \Delta l_2)/L_0(T_1 - T_2)\), where \(L_0\) is the length of the sample at room temperature) in the studied temperature range being \(5.4 \cdot 10^{-5}\) K\(^{-1}\).
3.2 DSC Studies

The DSC experiment did not reveal any heat anomalies below room temperature. In Fig. 2 a DSC curve is presented. Above room temperature there is one distinct anomaly of the heat flow at $T_{c3} = 366$ K. This anomaly was observed only during the first run on the virgin sample. The enthalpy and entropy of the transition are $\Delta H = 15$ kJ/mole and $\Delta S = 41$ J/K · mole, respectively. As yet it is difficult to say whether this transition is irreversible in nature.

3.3 Dielectric Results

Figures 3 a, b, and c show the temperature dependence of the electric permittivity of GHCA, measured along the $a$, $b$, and $c$ axes on heating. The temperature dependence of $\varepsilon'_a$ is anomalous at 146 K, and that of $\varepsilon'_c$ shows a subtle anomaly at 162 K and a second one similar in shape to that of $\varepsilon'_a(T)$ at 146 K.

The temperature dependence of $\varepsilon'_a$ is different from those observed along the $a$ and $c$ directions. Nevertheless there are also two distinct anomalies at 146 K and 162 K.

The anomalies at $T_{e1} = 146$ K and $T_{e2} = 162$ K correspond to the temperatures of the phase transitions. It should be noted that GHCA shows pronounced anisotropy in dielectric permittivity especially along the $c$-direction.

4. Discussion

GHCA crystallizes in monoclinic P2$_1$/c space group with $a = 9.732$, $b = 21.875$, $c = 8.554$ Å, and $\beta = 91.55^\circ$. The anionic sublattice of this crystal is composed of polymeric chains (Sb$_2$Cl$_5^-$)$_n$ which extend along the $c$ direction and isolated chlorine ions Cl$^-$ located between the chains. The chains are composed of distorted SbCl$_6^{5-}$ octahedra connected with each other by corners in such a way that four chlorine atoms of the co-ordination sphere of the antimony...
atom are terminal and two are bridging. In the channels formed by the anionic chains, between the separate chlorine ions the guanidinium cations are located, connected to the chlorine atoms by hydrogen bonds.

From the stoichiometric point of view, \([\text{C(NH}_2\text{)}_3\text{]}_2\text{SbCl}_5 \cdot [\text{C(NH}_2\text{)}_3\text{]}\text{Cl}\) is equal to \([\text{C(NH}_2\text{)}_3\text{]}_2\text{SbCl}_6\). We use, however, the above notation to stress its molecular structure, since \(R_2MX_6\) compounds should have anionic sublattice built of isolated \(MX_6^{2-}\) units, whereas the \(R_2MX_5\) crystals are characterized by the presence of \((MX_5^2)\)\(_n\) polyanionic chains.

The structure of this crystal has been solved and will be published elsewhere \([19]\).

The most intensively studied phase transformations of alkylammonium halogenoantimonates were devoted to the \(R_3MX_9\) subfamily. The mechanisms of these solid-solid phase transitions were proved to be connected with the dynamics of the cationic sublattice. The majority of the studied transitions was of the order-disorder type. The cations show large reorientations in the high temperature phase. On decreasing the temperature, these reorientations are consecutively frozen.

Our DSC studies on GHCA in the low temperature region did not reveal any heat anomalies. This suggests that the transitions at \(T_{c1}\) and \(T_{c2}\) are of the displacive type, contrary to order-disorder mechanisms of transitions most characteristic to other members of alkylammonium family.

This may be explained by the presence of many hydrogen bonds between the nitrogen atoms of the cations and chlorine atoms of the anions. Since in GHCA we have 3 nitrogen atoms per one cation in comparison to 1 in alkylammonium compounds, the probability of fixing of the guanidinium cations in the crystal lattice at room temperature is larger. As a result, the order disorder transition connected with the reorientations of cations may be expected at higher temperatures. The high temperature transition at \(T_{c3}\), which is accompanied by large changes in enthalpy and entropy, is most probably connected with a breaking of the hydrogen bonds. Since it is not clear whether it is irreversible, we must leave its interpretation till the results of further studies will be available.

The observed dielectric response of GHCA crystals near the transition temperature region at \(T_{c1}\), i.e. a distinct anisotropy of \(\varepsilon'\) favouring the \(c\) axis and a drastic drop of the \(\varepsilon'_c(T)\) curve close to \(T_{c1}\) indicates the presence of dipole units in the crystalline lattice.

The absence of dielectric dispersion up to 1 MHz suggests only that the rate of reorientations of dipoles may be expected in the microwave region or at higher frequencies.

The largest permittivity (50) is observed along the \(c\) direction above \(T_{c1}\) and coincides with the direction of the polyanionic chains.

In our case the dipoles can be represented as arising from the co-ordinated displacements of the isolated \(\text{Cl}^-\) ions relative to the guanidinium cations. The resulting high values of the electric permittivity may be due to collective shifts of such ions from their equilibrium positions.

The much smaller values of the permittivity along the \(a\) and \(b\) directions may be explained by the screening effect of the polyanionic chains (lack of interactions between the cations present in neighbouring holes).

5. Conclusions

1. The temperature dependence of the thermal expansion coefficients (\(\Delta l/l\)) shows two anomalies below room temperature at \(T_{c1} = 146\ \text{K}\) and \(T_{c2} = 162\ \text{K}\), suggesting the presence of two phase transitions.
2. The temperature dependence of the electric permittivity confirms the presence of two transitions at these temperatures.
3. The DSC studies did not show any anomalies below room temperature. Above room temperature one distinct anomaly of heat flow was observed at \(T_{c3} = 366\ \text{K}\).
4. The mechanism of two low temperature transitions is most probably of the displacive type, whereas the transition at \(T_{c3}\) is of the order-disorder type.
5. The shape of the temperature dependence of the electric permittivity along the \(c\) direction at \(T_{c1}\) suggests a polar order below \(T_{c1}\).
6. The elevated value of the electric permittivity along the \(c\) direction may be explained by the presence of collective interactions between the isolated chlorine atoms and the guanidinium cations.

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