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A Piecha, G Bator and R Jakubas

Faculty of Chemistry, University of Wrocław, 50-383 Wrocław, Joliot Curie 14, Poland

Abstract
Dielectric dispersion studies in the frequency range between 220 Hz and 1 MHz have been performed on pentakis(imidazolium) undecachlorodibismuthate(III), $(C_3N_2H_5)_5Bi_2Cl_{11}$, single crystals. The measurements have been made over the temperature range between 300 and 140 K. It is found that the dielectric dispersion, observed along the b-axis of the monoclinic symmetry ($P2_1/c$), is monodispersive between 166.5 and 168 K, and polydispersive in the close vicinity of $T_c = 166$ K, for $T < T_c + 0.2$ K. The observed dielectric dispersion is analysed using a single relaxation mode of the Debye type. Over the paraelectric phase the process of the dielectric critical slowing down is observed. This is characteristic of the order–disorder ferroelectric phase transition.

1. Introduction

The phase transitions in $R_aM_bX_{(3b+a)}$ compounds, where R denotes organic cations, M denotes Sb and Bi atoms and X is Cl, Br and I, have been extensively studied. A number of these salts have been shown to exhibit ferroelectric behaviour. The main interest has been focused on the mechanism of the ferroelectric–paraelectric transition [1–4]. It has turned out that the stoichiometry of the anionic moieties plays a crucial role in the generation of polar properties in this class of compound. It is shown that ferroelectricity appears mainly in the compounds characterized by two-dimensional anionic layers, $(M_2X_9^{3-})_\infty$, (five salts) [5–8]. Four ferroelectric salts are found to crystallize in the $R_5M_2X_{11}$ composition, for which anionic moieties constitute discrete bioctahedral units, $Bi_2X_{11}^{5-}$. This type of the anionic form is unique and all salts with this composition, reported to date, appear to be ferroelectric [9–13]. Recently, we have synthesized an incommensurate modulated ferroelectric, $RSbCl_4$ (where R stands 4-aminopyridinium), which is characterized by the one-dimensional anionic form, $(SbCl_4^-)_\infty$ [14].

The $R_5M_2X_{11}$ salts attract much interest because the dielectric characteristics of the methylammonium analogues are comparable to that found in the well-known TGS family of crystals.

Very recently we reported on new ferroelectric compound with the $R_5M_2X_{11}$ composition comprising in the structure the imidazolium cation [13]. Pentakis(imidazolium) undecachlorodibismuthate(III), $(C_3N_2H_5)_5Bi_2Cl_{11}$, has been studied by means of x-ray, differential scanning calorimetry (DSC) and dielectric methods. The room-temperature crystal structure has been determined as monoclinic, space group $P2_1/n$ with $a = 13.616$ Å, $b = 14.684$ Å and $c = 9.045$ Å and $\beta = 96.85°$. Two solid–solid phase transitions, $P\bar{4}n2 \xrightarrow{\text{360 K}} P2_1/n$ (I → II), and $P2_1/n \xrightarrow{\text{166 K}} P2_1$ (II → III), discontinuous and continuous in nature, respectively, have been revealed. The lowest-temperature phase (III) reveals ferroelectric properties with saturated spontaneous polarization of the order of 6×10^{-3} C m^{-2} along the *b*-axis. The ferroelectric phase transition mechanism is governed by the dynamics of the imidazolium cations. It is interesting that both the paraelectric and ferroelectric phases, II and III, demonstrate additionally ferroelastic properties.

In this paper, we report the dynamical dielectric characteristic of $(C_3N_2H_5)_5Bi_2Cl_{11}$ single crystals in the vicinity of the ferroelectric phase transition temperature ($T_c = 166$ K).

2. Experimental details

Single crystals of $(C_3N_2H_5)_5Bi_2Cl_{11}$ were grown by a slow evaporation method at constant room temperature (25 °C) from an aqueous solution of a stoichiometric mixture of imidazolium chloride and bismuth(III) chloride with a large excess of HCl acid. The material was twice re-crystallized. The complex dielectric constant, $\varepsilon^* = \varepsilon' - i\varepsilon''$, was measured with an HP 4284A Precision LCR Meter in the frequency range between 100 Hz and 1 MHz. The ac measuring voltage was 1 V. The samples for dielectric measurements were prepared by cutting the crystal perpendicularly to the *b*-axis of the monoclinic symmetry. The specimen with graphite electrodes had dimensions of $5 \times 5 \times 1$ mm^3. The overall error was less than 5% for the real and imaginary part of the complex dielectric constant.

3. Results and discussion

The frequency and temperature dependence of the real part of ε^* along the *b*-axis determined in a cooling run is shown in figure 1. The temperature of the sample was varied continuously at a rate of 0.2 K min^{-1}. Dielectric dispersion becomes remarkable in the frequency range between 220 Hz and 100 kHz. Figure 2 shows the frequency dependence of ε''_b at various temperatures over the paraelectric phase (II). The data in figures 1 and 2 were subsequently re-plotted as ε''_b versus ε'_b (Cole–Cole plots) as shown in figure 3.

The experimental values of the complex dielectric constant $\varepsilon^*(\omega)$ were fitted with the Cole–Cole formula:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega\tau)^{(1-\alpha)}}, \tag{1}$$

where ε_0 and ε_∞ are the low and high frequency limits of the dielectric constant, respectively, ω is angular frequency, τ is the characteristic relaxation time and α is a parameter which represents a measure of distribution of the relaxation times. All parameters (ε_0, ε_∞, τ and α) at selected temperatures were estimated by using the results of $\varepsilon^*(\omega)$ at several frequencies between 220 Hz and 1 MHz. The fit parameters of the low frequency relaxation process are listed in table 1.

It is clearly seen from figure 3 that the Cole–Cole plots deviate only slightly from semi-circles at temperatures $T - T_c > 0.2$ K (α ranges between 0.04 and 0.08 approaching T_c).
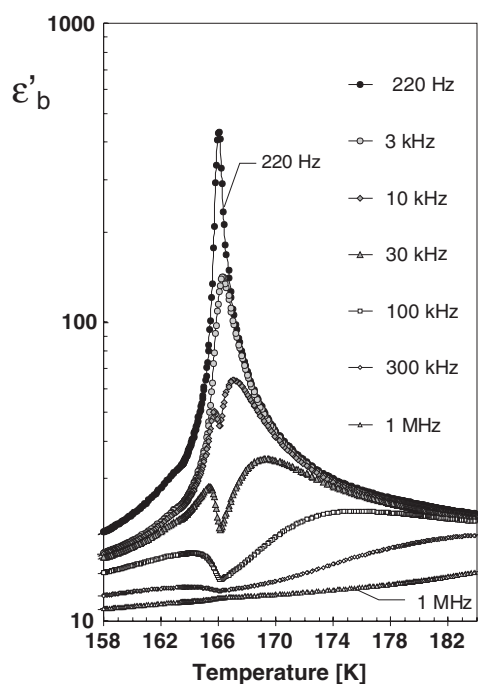
Figure 1. Temperature dependence of the real part (ε') of the dielectric constant at various frequencies along the *b*-axis in the close vicinity of $T_c = 166$ K for decreasing temperature.
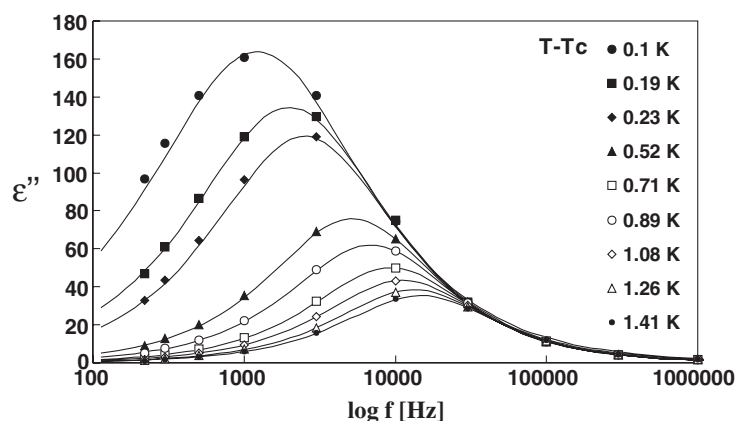

Figure 2. Frequency dependences of ε_b'' at various temperatures over the paraelectric phase (II).

This means that over this temperature region we deal with a nearly monodispersive relaxation process. On the other hand, in the close vicinity of T_c the α parameter increases up to 0.2.

It is well known from literature that most ferroelectrics exhibit monodispersive properties, even in the close vicinity of T_c [15]. In our case the distribution of relaxation times may be explained in two possible ways: (i) the presence of three dielectric relaxators (three kinds of dynamically disordered dipolar imidazolium cations), (ii) the temperature gradient on the sample. The imidazolium relaxators are not well frequency separated and they simultaneously
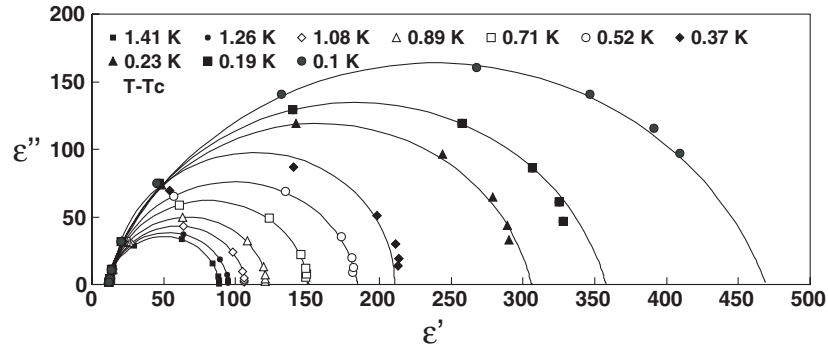
Figure 3. Cole–Cole plots of ε_b'' versus ε_b' at several temperatures over the paraelectric phase (II) showing the relaxation nature of the dielectric dispersion. The dashed lines indicate constant frequency loci.

Table 1. Fit parameters of the relaxation process in $(C_3N_2H_5)_5Bi_2Cl_{11}$.

T (K)	ϵ_0	ϵ_∞	α	τ (10^5 s)
167.41	88.62	12.17	0.05	1.1
167.26	95.00	12.00	0.05	1.2
167.22	98.55	12.16	0.05	1.3
167.08	106.98	12.22	0.06	1.4
167.00	111.14	12.13	0.06	1.5
166.89	121.75	12.09	0.06	1.7
166.74	142.27	12.01	0.07	2.1
166.71	150.93	12.00	0.07	2.3
166.56	177.75	11.92	0.08	2.8
166.52	185.00	11.89	0.08	3.1
166.22	306.02	10.68	0.13	6.3
166.19	357.93	9.93	0.16	8.0
166.11	469.32	8.42	0.21	12.9

contribute to the dielectric constant. The distribution is usually better observed approaching the T_c temperature. In some ferroelectrics, however, the appearance of the distribution of relaxation times may be due to the temperature fluctuation in the sample. For example, Yoshimitsu *et al* [16] revealed the relationship between the experimental value α and the width of temperature fluctuation. In our opinion in $(C_3N_2H_5)_5Bi_2Cl_{11}$ either the temperature gradient or the presence of the non-equivalent relaxators are equally probable.

Figure 4 shows the temperature dependence of the characteristic relaxation time, τ, over the paraelectric phase close to the paraelectric–ferroelectric transition. It should be noticed that the dielectric process in the $(C_3N_2H_5)_5Bi_2Cl_{11}$ crystal is characterized by an apparent critical slowing down in the vicinity of T_c. The relaxation time, τ, fulfils quite well the Curie–Weiss behaviour, $\tau \propto (T-T_c)^{-1}$, as shown in figure 4. Such a behaviour of the macroscopic relaxation time confirms the order–disorder nature of the phase transition in the $(C_3N_2H_5)_5Bi_2Cl_{11}$ crystal. For ferroelectrics with the order–disorder mechanism of the phase transition the dynamics of the dielectric relaxator may be described by the microscopic relaxation time, τ_0, defined according to the formula [17]

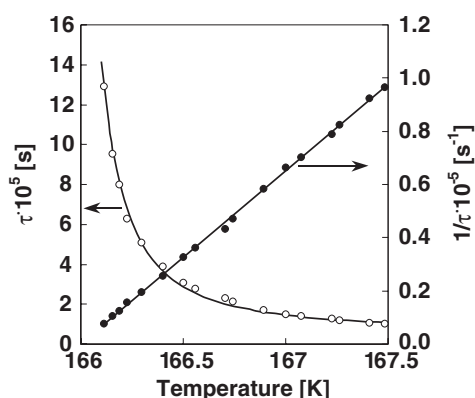$$\tau_0 = \tau \cdot \varepsilon_\infty/(\varepsilon_0 - \varepsilon_\infty). \tag{2}$$

Figure 4. Temperature dependence of τ and τ^{-1} obtained from the Cole–Cole formula.
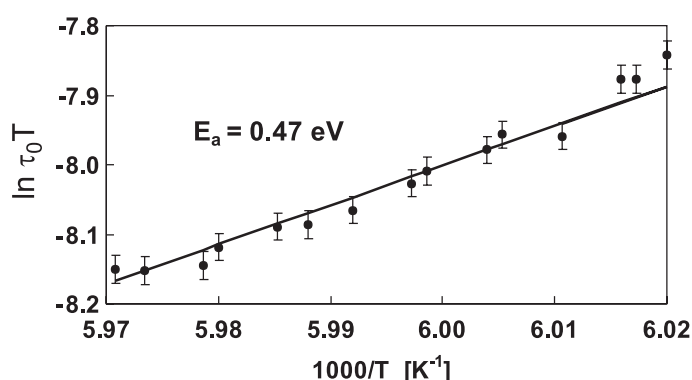

Figure 5. The activation energy obtained by means of the Eyring equation.

Then the activation free energy ΔF^* may be calculated according to the Eyring equation:

$$\tau_0 = (h/kT) \exp(\Delta F^*/kT). \tag{3}$$

It can be seen from figure 5 that the Eyring equation is well obeyed in the case of the $(C_3N_2H_5)_5Bi_2Cl_{11}$ crystal. In the temperature range $T > T_c + 0.2$ K the ΔF^* value equals 0.47 eV, whereas on approaching T_c the activation energy slightly increases. Such a tendency is characteristic of ferroelectric materials. It should be emphasized that the ΔF^* value, being 0.47 eV, is quite large even for relaxation processes encountered in molecular–ionic salts containing organic cations large in size [12, 22]. This large value of the activation energy may be explained by two possible reasons. First, the imidazolium cations, with two heteratoms (nitrogen atoms) in the aromatic ring, form a complex network of hydrogen bondings. Second, the steric hindrance additionally affects the activation energy value.

It is also interesting that the $(C_3N_2H_5)_5Bi_2Cl_{11}$ crystal is characterized by extremely slow dynamics, since the soft mode slows down at T_c up to 1 kHz. Such a situation is encountered quite rarely in order–disorder ferroelectrics. There are known some examples of ferroelectrics characterized by relatively slow dynamics. The molecular ferroelectric, cyclohexane-1,1′-diacetic acid, appeared to have quite similar dielectric response to that of the title crystal [18–20]. However, the strength of relaxator in this molecular ferroelectric is significantly smaller (by one order) in comparison to that found in the $(C_3N_2H_5)_5Bi_2Cl_{11}$

crystal possessing great dipolar units (strongly polarizable aromatic organic cations). For the other ionic ferroelectric, $AgNa(NO_3)_2$, (order–disorder type) the critical dielectric relaxation frequency reaches at T_c the extremely small value of 400 Hz [21]. The motions of the NO_2^- dipoles in $AgNa(NO_3)_2$ are described by a large activation energy of about 0.53 eV, which is comparable to that found in $(C_3N_2H_5)_5Bi_2Cl_{11}$ and assigned to the dynamics of the imidazolium cations. One can conclude that all transitions in ferroelectrics discussed above belong to the interesting class of phase transitions taking place in the extremely slow motion limit.

The x-ray studies on $(C_3N_2H_5)_5Bi_2Cl_{11}$ show that in the crystal lattice four nonequivalent types of the imidazolium cations exist, which differ by their dynamical ordering and surroundings. Far away from the critical temperature, T_c, they are indistinguishable because all of them are highly disordered. As a result a monodispersive dielectric relaxation is observed in a wide temperature region in the paraelectric phase. Approaching T_c (for $T < T_c + 0.2$ K) the contributions of nonequivalent cations to the complex electric permittivity becomes different, thus the observed polydispersive behaviour of the relaxation process may be explained *inter alia* from this point of view.

Up till now there are known four ferroelectric salts with $R_5Bi_2X_{11}$ (R—organic cations) stoichiometry. Two of them, containing methylammonium cations in the structure, $(CH_3NH_3)_5Bi_2Cl_{11}$ and $(CH_3NH_3)_5Bi_2Br_{11}$, crystallize in the orthorhombic symmetry ($Pca2_1$) in the paraelectric phase. Dielectric relaxation in these analogues was found to appear in the microwave frequency region with the macroscopic relaxation time, τ, close to 1×10^{-9} s and activation energy of about 0.11 eV [23, 24]. The pyridinium, $(C_5H_5NH)_5Bi_2Br_{11}$, and imidazolium, $(C_3N_2H_5)_5Bi_2Cl_{11}$, derivatives, despite their structural similarities with the methylammonium analogues, were found to crystallize in the paraelectric phase in the monoclinic symmetry ($P2_1/n$). Moreover, their dielectric parameters, particularly the values of τ and ΔF^*, differ significantly from those for the methylammonium salts. The dielectric relaxation is shifted towards lower frequencies and in the close vicinity of T_c the relaxation time is equal to $\sim 1 \times 10^{-3}$ s [12] and $\sim 1 \times 10^{-4}$ s (present paper) for pyridinium and imidazolium derivatives, respectively. The activation energy in both cases is quite large, being about 0.3–0.5 eV. The relatively large magnitude of ΔF^* and the long macroscopic relaxation time for salts containing aromatic cations, in comparison to the parameters found for the methylammonium salts, may be explained in terms of the size of the reorienting organic cations. The distinctly larger moment of inertia of the pyridinium and imidazolium cations in comparison to that of the methylammonium ones may be one of the factors justifying the slowing down of the macroscopic relaxation times by nearly 5–6 orders.

It should be noticed that the dielectric dynamical properties of the isomorphous imidazolium and pyridinium salts are different. The relaxation process within the comparable frequency region is extended over the 150 K above $T_c = 118$ K in $(C_5H_5NH)_5Bi_2Br_{11}$, whereas in $(C_3N_2H_5)_5Bi_2Cl_{11}$ it is limited to 2–3 K ($T_c = 166$ K). Additionally, the strength of the dielectric relaxator in the latter compound ($\Delta\varepsilon \approx 480$) is distinctly larger than that in the former salt ($\Delta\varepsilon \approx 200$). The dipole–dipole interactions, leading to the ferroelectric ordering, are stronger in the molecular–ionic systems containing organic cations that are smaller in size ($CH_3NH_3^+ < C_3N_2H_5^+ < C_5H_5NH^+$).

The reported experimental results allow us to conclude that

(1) $(C_3N_2H_5)_5Bi_2Cl_{11}$ revealed an extremely low frequency soft mode above 166 K (~ 1 kHz at T_c); and
(2) the shape of the dielectric response is typical for the clearly second-order phase transition with a fully classical (mean field) dynamics.

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