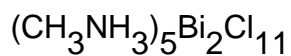


Dielectric dispersions in pentakis methyl ammonium bismuthate single crystals. II.



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Dielectric dispersions in pentakis methyl ammonium bismuthate single crystals: II. $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Cl}_{11}$

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Abstract. The dielectric dispersion of the permittivity ϵ'' in $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Cl}_{11}$ single crystals has been studied in the frequency range from 1 MHz to 20 GHz in the temperature range 150–400 K and from 18 to 40 GHz in the temperature range 300–360 K. Near the high-temperature ferroelectric phase transition (308 K) the dielectric behaviour is determined by the properties of two relaxators: a low-frequency relaxator in the megahertz region showing a critical slowing down and a high-frequency relaxator in the gigahertz region which is thermally activated. The contribution of the high-frequency relaxator vanishes near the temperature of the second phase transition at about 170 K where another contribution of a third relaxator with an extremely small strength appears. The origin of the observed dielectric contributions with respect to the molecular motion of the CH_3NH_3^+ cations is discussed.

1. Introduction

A pentakis(methylammonium)undecachlorodibismuthate $((\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Cl}_{11})$ (MAPCB) single crystal is structurally isomorphic to the bromine analogue $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Br}_{11}$ (MAPBB) and shows a similar sequence of phase transitions. At 308 K it undergoes a paraelectric-to-ferroelectric transition from space group $Pcab$ to $Pca2_1$ accompanied by a large dielectric anomaly along the polar c axis [1–4]. At 170 K a transition between two ferroelectric phases takes place where a parabolic increase in the spontaneous polarization along the c axis is observed [2]. Near the transition a stepwise change in the static permittivity was found [1], which differentiates this crystal from MAPBB in that it exhibits a maximum of the permittivity there [5, 6].

Structural investigations [4] on both the ferroelectric (294 K) and the paraelectric (349 K) phase indicate the important role of the ordering of the methylammonium cations at the phase transition $T_{c1} = 308$ K. In the high-temperature phase, two CH_3NH_3^+ cations of the MAPCB molecule are ordered (formed by $C(i1)\text{--}N(i1)$, $i = 1, 2$, following the notation in [4]) and three others are disordered (formed by $C(i2)\text{--}N(i2)$ and $C(3)\text{--}N(3)$). In the ferroelectric phase, $C(3)\text{--}N(3)$ cations become ordered and the ordering–disordering process of these cations is suggested to be the origin of the phase transition at T_{c1} . The two $C(i2)\text{--}N(i2)$ cations are still disordered at 294 K.

In MAPCB, one may expect interesting dynamic dielectric properties similar to those found in the case of MAPBB [6, 8]. Recently a Debye-type dispersion and a critical slowing

down at T_{c1} were reported in both crystals [7]. However, the other dispersions that we observed in MAPBB [6] are not mentioned there.

2. Experimental details

The MAPCB compound was obtained from the reaction of $(\text{BiO})_2\text{ClO}_3$ and $\text{CH}_3\text{NH}_3\text{Cl}$ in a solution of HCl. It was purified by repeated crystallization. The single crystals were grown from a dilute solution by slow evaporation at 293 K.

The preparation of the samples as well as the methods of the dielectric dispersion measurements were the same as in the case of MAPBB described in [8].

All measurements described in this work were done for the crystallographic c axis of the MAPCB single crystal.

3. Results

Similarly to the case of MAPBB [6, 8] the dynamic dielectric behaviour of MAPCB near T_{c1} can be described as a sum of the dielectric responses from two independent relaxators:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \Delta\varepsilon_1^*(\omega) + \Delta\varepsilon_2^*(\omega) \quad (1)$$

where

$$\Delta\varepsilon_1^*(\omega) = A \Delta\varepsilon / [1 + (i\omega\tau_{\varepsilon_1})^{1-h_1}] \quad (2)$$

$$\Delta\varepsilon_2^*(\omega) = (1 - A) \Delta\varepsilon / [1 + (i\omega\tau_{\varepsilon_2})^{1-h_2}]. \quad (3)$$

τ_{ε_1} and τ_{ε_2} denote the relaxation times, h_1 and h_2 are the parameters characterizing the distribution of relaxation times, and $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ is the total relaxation strength of both relaxators. The parameter A determines the part of the total dispersion strength $\Delta\varepsilon$ due to relaxator 1. This is illustrated in figures 1–3, where Cole–Cole diagrams for both phases as well as the frequency dependence of the imaginary part of the permittivity in the ferroelectric phase are shown. The full curves in these plots were obtained by fitting the experimental data using equations (1)–(3). The contributions of the two relaxators are better separated in frequency as in the case of MAPBB [8] and, in the figures, one can recognize the different temperature dependences of relaxators 1 and 2. While contribution 1 with the relaxation frequency $f_{\varepsilon_1} = 1/2\pi\tau_{\varepsilon_1}$ shows a critical slowing down, the characteristic frequency $f_{\varepsilon_2} = 1/2\pi\tau_{\varepsilon_2}$ of contribution 2 changes within the small temperature range shown in figure 4 nearly linearly with temperature. The critical slowing down, found here for f_{ε_1} , agrees with the results for MAPCB very recently published in [7].

The strength $A \Delta\varepsilon$ of relaxator 1 decreases rapidly when the temperature is lowered in the ferroelectric phase and there is a possibility of studying the properties of relaxator 2 separately at lower temperatures, when the contribution $\Delta\varepsilon_1^*$ may be neglected. Figure 5 shows Cole–Cole diagrams for several temperatures $T < T_{c1}$. The obtained results can be fitted with the Cole–Cole formula (3) for the contribution $\Delta\varepsilon_2^*$ with parameters τ_{ε_2} and h_2 (see full curves in figure 5). The relaxation time τ_{ε_2} obeys the Arrhenius law as shown in figure 6, and the activation energy calculated from the plot for temperatures $T < T_{c1}$ is 0.19 eV. Near and above T_{c1} the Arrhenius plot (inset in figure 6) yields an activation energy of 0.11 eV. The strength of relaxator 2 decreases monotonically with decreasing temperature. Near the temperature of the second phase transition at

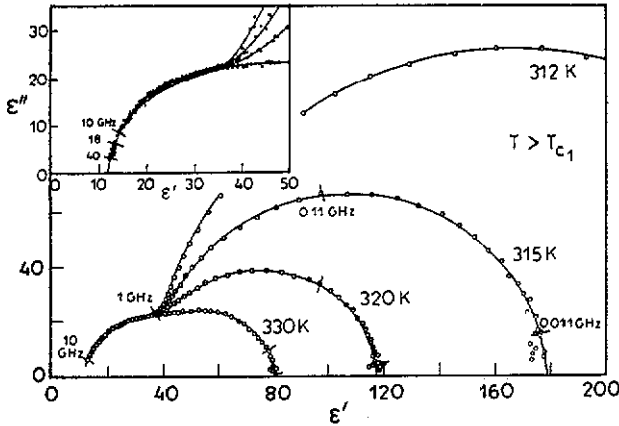


Figure 1. Dielectric dispersion of ϵ_c^* measured in the paraelectric phase. The full curves were obtained by fitting with equations (1)–(3); the fitting parameters, e.g. for $T = 315$ K, were $\tau_{\epsilon_1} = 1.74 \times 10^{-9}$ s, $\tau_{\epsilon_2} = 7.20 \times 10^{-11}$ s, $h_1 = 0.009$, $h_2 = 0.052$, $A = 0.81$ and $\Delta\epsilon = 165$.

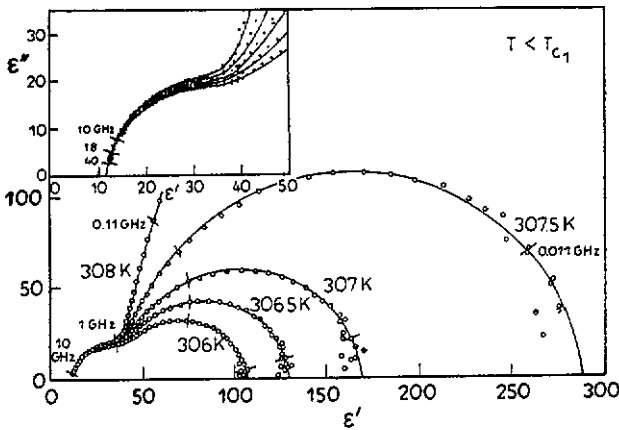


Figure 2. Dielectric dispersion of ϵ_c^* measured in the ferroelectric phase near T_{c1} . The full curves were obtained by fitting with equations (1)–(3); the fitting parameters, e.g. for $T = 307.5$ K, were $\tau_{\epsilon_1} = 4.82 \times 10^{-9}$ s, $\tau_{\epsilon_2} = 8.01 \times 10^{-11}$ s, $h_1 = 0.06$, $h_2 = 0.06$, $A = 0.90$ and $\Delta\epsilon = 278$.

$T_{c2} = 170$ K and at frequencies higher than 1 GHz a new contribution to the permittivity becomes visible. In figure 7, Cole–Cole plots are displayed for an MAPCB sample with a diameter of 2 mm and a thickness of 1 mm at temperatures near T_{c2} . For this sample the obtained permittivity values are at the limit of accuracy of the measurement method used and larger samples would be necessary for a quantitative evaluation. Therefore, the conclusions from figure 7 can be qualitative only. Nevertheless the vanishing of the contribution from relaxator 2 below 200 K and the simultaneous appearance of a new contribution from relaxator 3 are clearly seen in figure 7. The strength of this contribution does not exceed 2 units and also vanishes below T_{c2} (figure 7(b)).

The above description of the dynamic dielectric behaviour of MAPCB near T_{c2} is qualitatively similar to that observed in MAPBB near $T_{c2} = 77$ K [8]. The difference

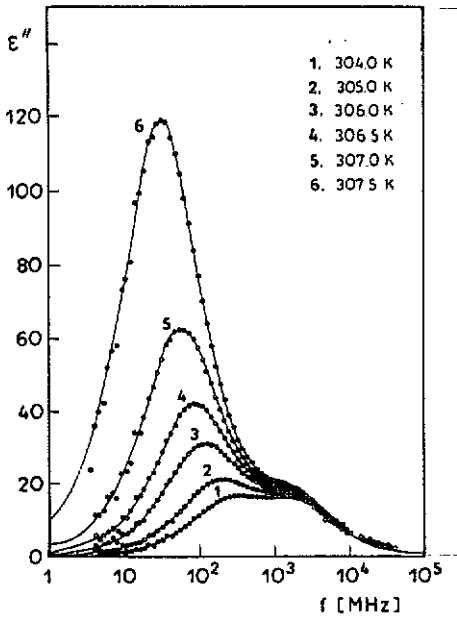


Figure 3. Frequency dependence of the imaginary part of the complex permittivity ϵ'' : ferroelectric phase.

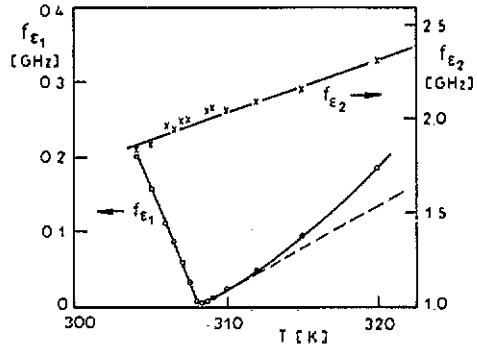


Figure 4. Temperature dependence of the relaxation frequency f_{ϵ_1} (relaxator 1) and f_{ϵ_2} (relaxator 2).

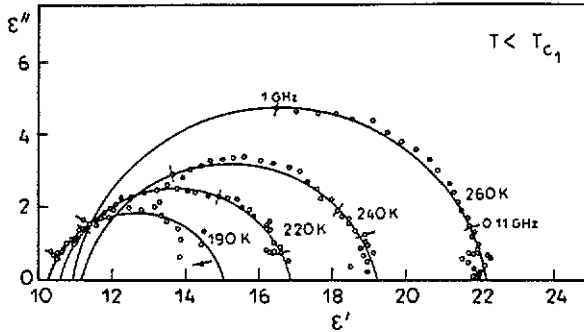


Figure 5. Dielectric dispersion of ϵ'' far below T_{c1} in the frequency range 1 MHz-1 GHz.

seems to be quantitative only; in MAPCB the strength of relaxator 3 is much smaller. Unfortunately, because of insufficient accuracy of the measurement, an estimation of the temperature dependence of the characteristic frequency of this contribution was not possible.

A summary of the temperature dependence of all observed dielectric contributions is displayed in figure 8. Near the ferroelectric phase transition at $T_{c1} = 308$ K there are two contributions to the permittivity of MAPCB apart from ϵ_{∞} : one from relaxator 1 whose strength is $\Delta\epsilon_1 = A \Delta\epsilon$ and the other from relaxator 2 whose strength is $\Delta\epsilon_2 = (1 - A) \Delta\epsilon$. The contribution $\Delta\epsilon_1^*$ which has a critical temperature dependence decreases rapidly on reducing the temperature below T_{c1} and for $T < 300$ K it is small compared with $\Delta\epsilon_2^*$. The thermally activated contribution $\Delta\epsilon_2^*$ decreases monotonically and vanishes near the temperature T_{c2} of the second phase transition. Simultaneously with

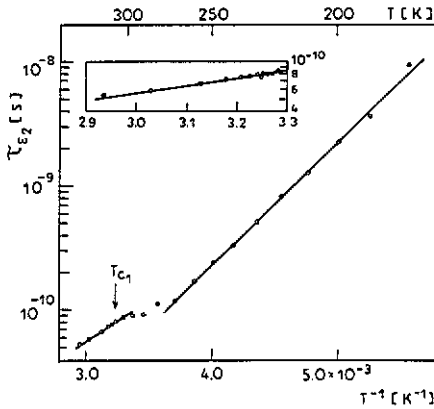


Figure 6. Arrhenius plot of the relaxation time τ_{ϵ_2} .

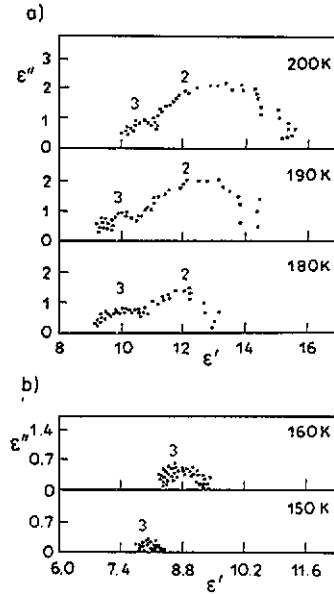


Figure 7. Cole-Cole plots of ϵ'' for several temperatures (a) above and (b) below T_{c2} .

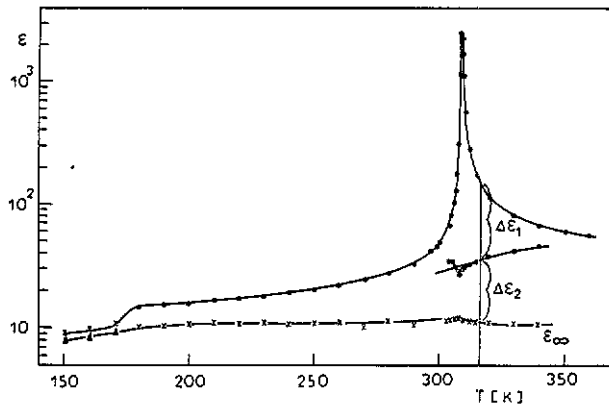


Figure 8. Temperature dependence of the permittivity ϵ_c of MAPCB. The full points are obtained as the static permittivity $\epsilon_s = \Delta\epsilon - \epsilon_\infty$ (equations (1)–(3)); $\Delta\epsilon_1$ and $\Delta\epsilon_2$ denote the strengths of relaxators 1 and 2, respectively.

this vanishing the contribution from relaxator 3 of extremely small strength appears, with some analogy to MAPBB [8].

4. Discussion

Discussing the origin of the dielectric contributions found in MAPCB we make use of the results of the structural investigations published in [4]. According to this work the phase transition at $T_{c1} = 308$ K takes place owing to the ordering–disordering process of non-paired C(3)–N(3) cations, located in the middle of each edge of the orthorhombic unit

cell. We suggest that the cooperative motion of these cations is the origin of the observed critical contribution $\Delta\epsilon_1^*$.

A very important role in the dynamic dielectric behaviour of MAPCB is played, in our opinion, by the dynamics of the cation pair C(*i*2)–N(*i*2), *i* = 1, 2, which is disordered above and below T_{c1} . This disorder is due to two physically different equilibrium positions for each C(*i*2)–N(*i*2) cation which can jump from one position to the other. The jump consists of a rotation of the C–N bond and a translation of the centre of the C–N bond [4]. This thermally activated reorientational motion of the dipolar C(*i*2)–N(*i*2) molecules is most probably the origin of the observed thermally activated contribution $\Delta\epsilon_2^*$. The difference between the activation energies above ($\Delta U = 0.11$ eV) and below ($\Delta U = 0.19$ eV) T_{c1} may be explained by the structural changes at the transition.

The contribution $\Delta\epsilon_2^*$ vanishes at a temperature of about 170 K. As no indication exists that the dynamics of the C(*i*2)–N(*i*2) cations are changing at T_{c2} , one may assume that these cations attain a high degree of order due to the energy splitting of the equilibrium positions. Simultaneously the dispersion of relaxator 3 is observed with an extremely small strength $\Delta\epsilon_3$, which also vanishes a few kelvins below T_{c2} . This contribution, in analogy to a similar one observed for MAPBB, indicates that a further cooperative ordering interaction may exist in this crystal, too. As a result the parabolic increase in the spontaneous polarization below T_{c2} may occur as observed in [2].

For confirmation of this concept and for a more quantitative picture, further measurements in other crystallographic directions are necessary. One may expect that in the *a* and *b* directions, when the critical dielectric contribution is absent, the properties of the thermally activated contribution may be better evaluated and a quantitative connection with the structural characteristics may be established.

Acknowledgment

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