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Dielectric Properties of the $(CH_3NH_3)_5Bi_{2(1-x)}Sb_{2x}Cl_{11}$ Mixed Crystals

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The $(CH_3NH_3)_5Bi_{2(1-x)}Sb_{2x}Cl_{11}$ crystals were examined from the point of view of their applicability in pyroelectric detectors. It was shown that they can be useful so far as the construction of infrared detectors is concerned due to high values of both their pyroelectric coefficient and figure of merit $p/\sqrt{\varepsilon}$ which are both comparable with those of triglycine sulphate crystals.

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1. Introduction

Alkylammonium halogenobismuthate(III) $(CH_3NH_3)_5Bi_2Cl_{11}$ crystallizes at room temperature in the orthorhombic system, space group $Pca2_1$. At increasing temperature the crystal undergoes a transition from the ferroelectric to paraelectric phase with a symmetry $Pcab$ at temperature $T_c = 308$ K. The dielectric, pyroelectric [1], and dilatometric studies indicate a continuous character of the phase transition. Due to the high value of the pyroelectric coefficient, p, the crystals should be taken into account as a material for infrared pyroelectric detector. One of the measures of figure of merit of the detector is a magnitude of $p/\sqrt{\varepsilon}$, where ε is the dielectric permittivity of the crystal. This parameter for $(CH_3NH_3)_5Bi_2Cl_{11}$ at temperatures 300–307 K is even better than that for the triglycine sulphate (TGS) crystals. For the $(CH_3NH_3)_5Bi_{2(1-x)}Sb_{2x}Cl_{11}$ mixed crystals with a small Sb admixture [2] the shift of the maximum value of ε towards higher temperatures has been observed. This is the reason why the studies on pyroelectric and dielectric properties have been undertaken in order to determine their properties and usefulness for construction of the pyroelectric detectors.

2. Experimental part

The $(CH_3NH_3)_5Bi_{2(1-x)}Sb_{2x}Cl_{11}$ crystals were grown up from the aqueous solution with the corresponding molar concentration $x = 0, 0.05, 0.07, 0.13, 0.25$ at

constant temperature 300 K. The measurements of the dielectric permittivity were carried out at a frequency of 1 kHz using the ultra-precision capacitance bridge Andeen-Hagerling 2500 A in a field of 100 V/m along the ferroelectric c-axis. The measurements of the pyroelectric coefficient were performed using the short current method during heating at constant rates 1.14×10^{-2} K/s and 2.27×10^{-2} K/s, respectively. Before the measurements the crystals were polarized by a dc field of 200 kV/m during cooling and then short-circuited for 0.5 h.

3. Results

Figure 1 shows the temperature dependence of the pyroelectric coefficient and the dielectric permittivity for the alkylammonium chlorobismutate crystals. The maximum value of both the pyroelectric coefficient and the dielectric permittivity reveals at the same temperature. This means that the internal field in the crystal equals to zero. The internal bias field is evident as a shift of dielectric hysteresis loop from the center in the E-axis.

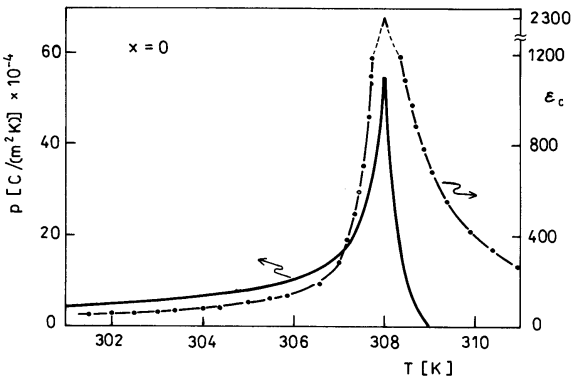

Fig. 1. Temperature dependence of the pyroelectric coefficient and dielectric permittivity, in the alkylammonium halogenobismuthate(III) without admixture ($x = 0$).

Figure 2 presents the temperature dependence of the pyroelectric coefficient and of the dielectric permittivity for the crystal with a 5% molar contents of antimony, Sb ($x = 0.05$). When we compare Fig. 1 and Fig. 2, we can see that the introduction of antimony to the crystal causes a significant reduction of the pyroelectric coefficient value, some diffusion of p at maximum and its shift toward higher temperature. The maximum value of the electric permittivity appears at higher temperatures than that for the maximum value of the pyroelectric coefficient.

The temperature dependence of the pyroelectric coefficient and electric permittivity for crystals containing 7% and 13% of antimony is presented in Figs. 3 and 4, respectively.

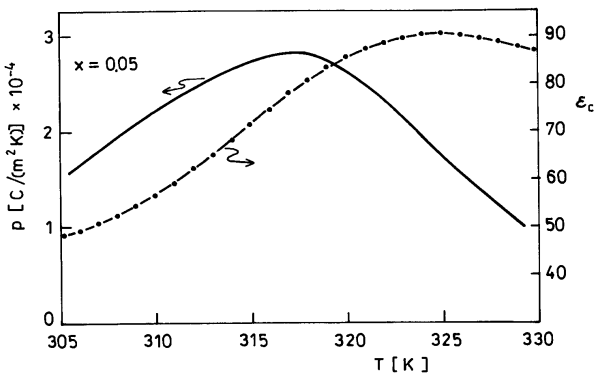

Fig. 2. As in Fig. 1, but for crystals with the 0.05 antimony content.

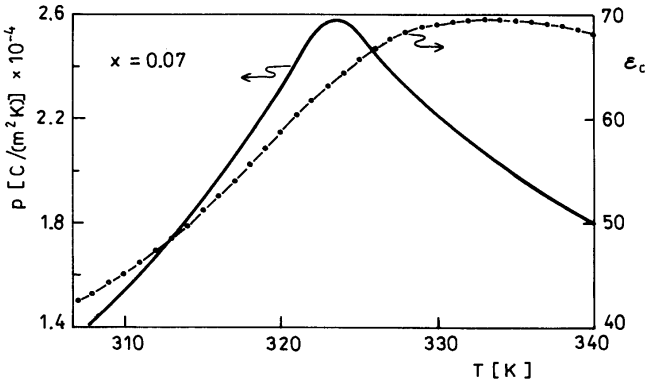

Fig. 3. As in Fig. 1, but for crystals containing 0.07 mole of antimony.

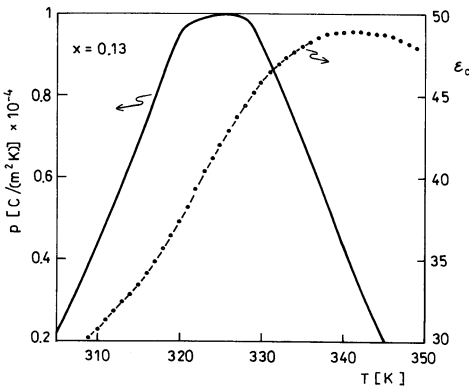

Fig. 4. As in Fig. 1, but for crystals containing 0.13 mole of antimony.

The character of the plots is similar to those in Fig. 2. On increasing antimony content the maximum value of the pyroelectric coefficient decreases while

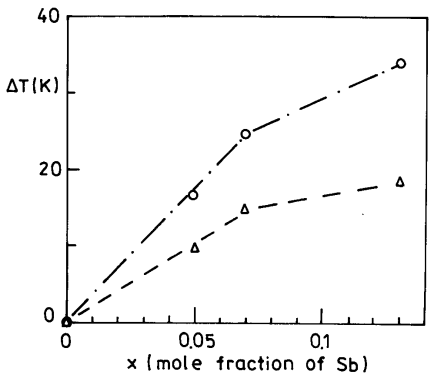

Fig. 5. The shift of the maximum value of the pyroelectric coefficient (Δ) and of the dielectric permittivity (○) on the temperature scale versus molar content of antimony in the crystal.

its diffusion as well as the shift in temperature scale rises. For crystals with 25% molar content of Sb the large diffusion of the maximum values of both pyroelectric coefficient and dielectric permittivity occurs. The results are not shown in figures. Figure 5 shows the temperature shift corresponding to the maximum value of the pyroelectric coefficient and dielectric permittivity *versus* the molar content of antimony in the crystal, x. The determination of the molar content of Sb is burdened by an error of 3%.

4. Discussion

The result of the antimony introduction to the crystal is an appearance of polarization at higher temperature as well as an emergence of a strong internal bias field in the crystal.

The effect of internal bias field on pyroelectric and dielectric properties of ferroelectric crystals with phase transition of the second order type in the light of the thermodynamic theory is presented in papers [3–5]. It is known that the internal bias field, E_{b}, influences the peak value of the pyroelectric coefficient and it does not influence its temperature position. The presence of E_{b} affects also the magnitude of permittivity, ε, and shifts the temperature of $\varepsilon_{\max}$. The evidence for it is both the diffusion of the maximum of the pyroelectric coefficient and the shift of $\varepsilon_{\max}$ on temperature scale. A magnitude $T(\varepsilon_{\max}) - T(p_{\max})$ is a measure of the internal bias field E_{b}, where $E_{\mathrm{b}} \sim \Delta T^{3/2}$. For the application as the pyroelectric detectors the ratio $p/\sqrt{\varepsilon}$ is important. For crystals at $x = 0$, $T = 305$ K it is very large and equals to 8×10^{-5} C/(m^2 K). The unfavorable feature of the detectors with $x = 0$ is a narrow working temperature range and a change of sensitivity with temperature. In crystals ($x = 0.05$, $T = 315$ K) and ($x = 0.07$, $T = 320$ K) the figure of merit is equal to 3.3×10^{-5} C/(m^2 K) and 3.0×10^{-5} C/(m^2 K), respectively. The promising feature of the crystals with the antimony content is a

remarkably wider working temperature range as well as the polarity of the crystal. The figure of merit of these crystals is comparable with that of the TGS crystals.

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