INFLUENCE OF DEFECTS ON DIELECTRIC PROPERTIES OF $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{X}_{11}$ ($\text{X} = \text{Cl}, \text{Br}$) CRYSTALS

J. MRÓZ, H. PYKACZ

Institute of Physics, Technical University of Wrocław
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

AND R. JAKUBAS

Institute of Chemistry, University of Wrocław
F. Joliot-Curie 14, 50-383 Wrocław, Poland

(Received January 3, 1995; revised version March 31, 1995)

Influence of defects on ferroelectric properties of the $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{X}_{11}$ ($\text{X} = \text{Cl}, \text{Br}$) crystals in the vicinity of ferro-paraelectric phase transition was investigated. γ -irradiation of both crystals insignificantly shifts T_c towards higher temperature. The substitution of chlorine atoms by iodine ones in the $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Cl}_{11}$ crystal drastically reduces the magnitude of the dielectric permittivity but does not influence on the temperature behaviour of the spontaneous polarization.

PACS numbers: 77.70.+a

1. Introduction

$(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{X}_{11}$ ($\text{X} = \text{Cl}, \text{Br}$) crystals belong to a new family of organic-inorganic crystals of the general formula $\text{R}_x\text{M}_y\text{X}_z$ ($\text{R} =$ alkylammonium cation, $\text{M} = \text{Sb}^{+3}$ or Bi^{+3} , $\text{X} = \text{Cl}, \text{Br}, \text{I}$). Many crystals of this group undergo an interesting sequence of phase transitions of an order-disorder type. Some of these phase transitions lead to polar phases [1-4]. $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Cl}_{11}$ (MAPCB, hereafter) and $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Br}_{11}$ (MAPBB, hereafter) crystallize in orthorhombic system (space group $Pca2_1$). Both crystals are ferroelectric at room temperature [5, 6]. MAPCB transforms to the paraelectric phase at 307 K while MAPBB at 311 K. Both crystals have the same symmetry ($Pcab$) in the paraelectric phase. Three out of total five methylammonium cations present in the lattice get ordered at the ferro-paraelectric phase transition. The spontaneous polarization P_s and the dielectric permittivity are comparable in magnitude to those found in the crystals

of TGS family. Very promising from the application point of view are electrooptic properties of these crystals [7].

MAPCB and MAPBB crystals are very sensitive to the influence of various kind of defects. For example, MAPBB crystals grown from aqueous solution with some excess of HBr have strong internal bias field E_b , which significantly modifies temperature dependence of P_s and $\epsilon(T)$, especially in the vicinity of the phase transition at 77 K [8].

The purpose of this paper is to investigate the role of defects produced by γ -irradiation in MAPCB and MAPBB and the influence of iodine admixture in MAPCB on ferroelectric properties of the crystals.

2. Experimental

MAPCB and MAPBB single crystals were obtained by slow evaporation of aqueous solution containing 5:1 mole fraction of $(\text{CH}_3\text{NH}_3)\text{Cl}$ or $(\text{CH}_3\text{NH}_3)\text{Br}$ and $(\text{BiO})_2\text{CO}_3$ with a small excess of HCl or HBr in the solution. Samples 1 mm thick were cut perpendicularly to the c -axis and electroded with conductive silver paste. The samples were irradiated at the room temperature with Co_{60} γ -ray source at a dose rate of 0.1 Mrad/h.

Crystals doped with iodine were grown by several successive recrystallizations of pure MAPCB with some HI added to the solutions. Crystals with two different concentrations of iodine were obtained. The crystal density was taken as a measure of concentration of iodine in the sample. The pure chlorine crystal has a density of 2.31 g cm^{-3} . An increase in density of $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Cl}_{11(1-x)}\text{I}_{11x}$ mixed crystals, being 2.315 g cm^{-3} (sample 1) and 2.330 g cm^{-3} (sample 2), corresponds to the molar fraction of iodine atoms of about 0.3% and 1% mole, respectively. Pure crystals of MAPCB which are colourless turned yellow after being doped with iodine.

Dielectric measurements were performed at the frequency 1 kHz using an automatic capacitance bridge (type E315A) at a constant cooling/heating rate of 0.1 K/min.

The spontaneous polarization was measured by a charge integration technique using an electrometer (Unitra 219).

The internal bias field was measured as a shift of the ferroelectric hysteresis loop using a Sawyer-Tower circuit in a few seconds without compensation.

A pyroelectric coefficient was measured by the short-circuit current method.

3. Results

Figure 1a shows the temperature dependence of the dielectric permittivity for the MAPCB crystal along the c -axis for the four various doses of γ -irradiation, in the range 1–13.4 Mrad. The higher dose, the smaller peak value of ϵ at the phase transition temperature T_c . Similar changes were observed for the MAPBB crystal (Fig. 1b). The T_c temperature is slightly higher in γ -irradiated samples than in virgin ones. A similar effect was obtained, for example, in PbTiO_3 crystal [9, 10]. Usually, in γ -irradiated ferroelectrics the T_c temperature is lower than in virgin crystals which was explained by reduction of ferroelectrically active dipole moments in γ -irradiated samples [11].

Fig. 1. Dielectric permittivity vs. temperature for MAPCB (a) and MAPBB (b) irradiated by various doses.

Fig. 2

Fig. 3

Fig. 2. Temperature dependence of the internal bias of MAPCB and MAPBB irradiated with a dose of 5.5 Mrad and 13.4 Mrad, respectively.

Fig. 3. Internal bias vs. dose of γ -irradiation in MAPCB.

Figure 2 shows the temperature dependence of the internal bias E_b for MAPCB and MAPBB crystals irradiated with 5.5 Mrad and 13.4 Mrad, respectively. The temperature dependence of E_b is non-linear. The E_b field disappears in the paraelectric phase. The magnitude of the E_b field is a linear function of the dose of γ -irradiation for both crystals in the studied range up to 13.4 Mrad at room temperature. As an example, the results for MAPCB crystals are shown in Fig. 3. Very similar characteristic of internal bias vs. γ -dosage was reported in TGS and Rochelle salts [12].

Figure 4 shows the temperature dependence of dielectric permittivity ϵ for

Fig. 4. Dielectric permittivity vs. temperature in $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Cl}_{11(1-x)}\text{I}_{11x}$ mixed crystals with $x = 0.3\%$ mole and $x = 1\%$ mole.

mixed crystals $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Cl}_{11(1-x)}\text{I}_{11x}$ along the ferroelectric c -axis for the two samples with $x = 0.3\%$ mole and $x = 1\%$ mole. The magnitude of the dielectric constant is reduced for mixed crystal and its anomaly at T_c gets much broader. The T_c temperature is increased by 1.5 K for 0.3% mole of I as compared with $T_c = 307$ K in pure MAPCB crystal. Mixed crystal $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Cl}_{11(1-x)}\text{I}_{11x}$ containing of 1% mole I drastically changes its properties. ϵ_{max} decreases by about two orders of magnitude as compared with pure chlorine crystal and is shifted towards higher temperature by 9 K. The mixed crystals containing iodine atoms are characterized by the high internal bias field. The E_b field strength was so high that it was impossible to observe ferroelectric hysteresis loop by means of Sawyer-Tower circuit. The high E_b field is responsible for reduction and shift of the peak value of dielectric permittivity.

Dielectric permittivity presented in Fig. 4 (and also in Figs. 1a and b) was measured in conditions when E_b field was not compensated by an external electric field.

The replacement of Cl by Br atoms in pure analog, MAPCB, causes a positive shift of the transition temperature. The observed shift of the transition towards higher temperature after the replacement of Cl with I atoms is in agreement with what was expected.

Pure chlorine and mixed chlorine-iodine crystals show a quite similar temperature dependence of the spontaneous polarization P_s , especially in the vicinity of $T_c = 307$ K, with only slight reduction of the magnitude of P_s (Fig. 5). An internal electric field due to polar iodine admixture stabilizes the spontaneous polarization in a similar way as an external electric field does. Analogous effects were observed in other ferroelectrics, for example, doped $\text{Li}_2\text{Ge}_7\text{O}_{15}$ [13, 14].

The result of measurements of the pyroelectric coefficient for 1% mole iodine concentration in MAPCB crystal is shown in Fig. 6. The pyroelectric measurements revealed that the change of the temperature dependence of P_s in MAPCB containing I atoms with respect to the pure analog may be due to the appearance

Fig. 5. Spontaneous polarizations vs. temperature for $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Cl}_{11(1-x)}\text{I}_{11x}$ crystals (1 — $x = 0.3\%$ mole, 2 — $x = 1\%$ mole).

Fig. 6. Temperature dependence of the pyroelectric coefficient in the vicinity of the phase transition for $x = 1\%$ mole iodine containing crystal.

of the high internal bias. The samples appeared to be also in a single domain state, because the observed spontaneous polarization in mixed crystals is comparable to that found in MAPCB. The above-mentioned features are beneficial for technical application.

4. Conclusions

1. γ -irradiation of MAPCB and MAPBB crystals insignificantly shifts T_c towards higher temperature. This is quite unique for ferroelectric crystals for which T_c usually gets lower.
2. An internal bias E_b that appears due to γ -irradiation depends linearly on the dose of γ -irradiation.
3. Substitution of iodine for chlorine in MAPCB crystal significantly increases the T_c temperature, reduces the magnitude of the dielectric permittivity but does not change the character of the temperature dependence of the spontaneous polarization.
4. The grown crystal with high iodine admixture (here 1% mole) is in a single domain state with the high internal bias field.

References

- [1] R. Jakubas, *Solid State Commun.* **60**, 389 (1986).
- [2] R. Jakubas, L. Sobczyk, J. Matuszewski, *Ferroelectrics* **74**, 339 (1987).
- [3] R. Jakubas, L. Sobczyk, *Phase Transit.* **20**, 163 (1990).
- [4] H. Ishihara, K. Watanabe, A. Iwata, K. Yamada, Y. Kinoshita, T. Okuda, V.G. Krishnan, S. Dou, A. Weiss, *Z. Naturforsch. A* **47**, 65 (1992).
- [5] R. Jakubas, *Solid State Commun.* **69**, 267 (1989).
- [6] R. Jakubas, L. Sobczyk, J. Lefebvre, *Ferroelectrics* **100**, 143 (1989).
- [7] A. Miniewicz, R. Jakubas, *J. Mol. Electron.* **7**, 55 (1991).
- [8] H. Pykacz, J. Mróz, R. Jakubas, *Acta Phys. Pol. A* **84**, 105 (1993).
- [9] S.P. Soloviev, I.I. Kuzmin, V.V. Zakurkin, *Ferroelectrics* **1**, 19 (1970).
- [10] B. Hilczer, in: *Proc. IV Intern. Summer School on Defects, Zakopane 1973*, Eds. T. Igielski, M. Jastrzębska, Z. Damm, PWN Warszawa 1974, p. 157.
- [11] J.A. Gonzalo, J.R. Lopez-Alonzo, *J. Phys. Chem. Solids* **25**, 303 (1964).
- [12] K. Okada, J.A. Gonzalo, J.M. Rivera, *J. Phys. Chem. Solids* **28**, 689 (1967).
- [13] M.D. Volnyanskii, A.Yu. Kudzin, I.I. Makarenko, *Fiz. Tverd. Tela* **29**, 3471 (1987) [*Sov. Phys. Solid State* **29**, 1991 (1987)].
- [14] M.D. Volnyanskii, A.Yu. Kudzin, T.V. Shvets, *Fiz. Tverd. Tela* **33**, 2228 (1991) [*Sov. Phys. Solid State* **33**, 1257 (1991)].