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Electrical properties of imperfect TGFB

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Abstract : Studies of ferroelectric hysteresis loop and electrical conductivity of imperfect (X-ray irradiated- and *L*-alanine admixtured) TGFB crystals in the temperature range (from 325 up to 350 K) are performed. Peculiar changes of the spontaneous polarization P_s during irradiation are observed. It exhibits no change at the early stage of irradiation (below the threshold dose $D_0 = 9.10^3$ rad), hereafter, it begins to decay in a fairly rapid manner and the ferroelectric hysteresis loop is deteriorated and smeared out. The bias filed E_b as well as the coercive field E_c build up steadily during irradiation. Unusual effect of the field and heat treatment on the loop pattern in the region of low dose irradiation was obtained. In this region, the loop develops split pattern, due to irradiation, changed by the field to single loop pattern and *vice-versa* in the absence of the field. This process could be maintained, provided that the field is not removed for a longer time, where the split loop pattern becomes permanent, such case could be returned to more unstable (metastable) state by gentle heat treatment, and again, the field successes to operate this cycle. Effect of *L*-alanine admixture on the ferroelectric hysteresis loop are measured and interpreted. Electrical conductivity (σ) exhibits anomaly at T_c. Increase and decrease of σ around D_0 due to increase of ionization radiation as well as gradual decrease of σ due to increase of *L*-alanine concentration are observed and discussed.

Keywords : Electrical properties, phase transition, imperfect triglycine fluoroberyllate.

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1. Introduction

Triglycine fluoroberyllate (hereafter TGFB) is one of a triglycine family with very similar structure and ferroelectric properties [1–3]. The unit cell parameters are almost identical with those of this family, but the unit cell volume is slightly smaller for TGFB, which suggests strong dipol-dipole interaction in this material. It undergoes a phase transition of second order at the Curie temperature $T_c = 346$ K, along its polar axis [2]. The structure has monoclinic symmetry with space group $P2_1$ in the ferroelectric phase below T_c, changed to space group $P2_1/m$, but without change of monoclinic symmetry, in the paraelectric phase above T_c [1]. The use of ferroelectrics as detectors and memories has created a need of studing the effect of imperfection on the physical properties of these materials, which have been analysed repeatedly [4,5].

Imperfections generate bias field, suppression of domain wall's motion and shifting of T_c [6,7]. The work is devoted to show the effect of imperfections (X-ray irradiation, *L*-alanine admixture) on the ferroelectric hysteresis and electrical conductivity of TGFB at different temperatures near T_c.

2. Experimental

Triglycine fluoroberyllate TGFB $[(NH_2CH_2COOH)_3H_2BeF_4]$ crystals were grown in its ferroelectric phase from the aqueous solution by slow evaporation [8]. The crystals were cleaved into thin slices of thickness = 2 mm, normal to ferroelectric *b* axis. Crystals of this thickness produce a few percent attenuation of X-ray irradiation. Preparation of X-ray irradiated —, *L*-alamine admixtured crystals were described in the previous work [9]. Ferroelectric hysteresis loops were obtained using the modified Sawyer-Tower circuit at a frequency of 50 Hz [10]. In some cases, the reversion of nucleation may occur before that of the applied field, due to the presence of internal (or external) stress or if the free charges below the crystal surfaces cannot reach their new equilibrium distribution during each half-cycle of the loop. This phenomenon could be minimized by cycling the loop at very low frequency. The electrical conductivity σ was measured using the method mentioned in the previous work [11].

3. Results and discussion

Temperature dependence of P_s which is equal to the saturation value of the electric displacement extrapolated to zero field in the hysteresis loop of non- and X-ray irradiated

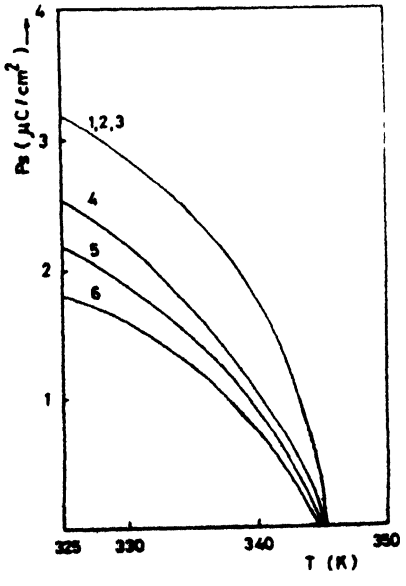

Figure 1. P_s-temperature dependence of non- (curve 1), and irradiated samples (curves 2, 3) for $D < D_0$ and (curves 4–6) for $D > D_0$.

TGFB crystals, are shown in Figure 1. P_s decreases with increasing temperatures and disappears at T_c (Figure 1, curve 1). It is found that P_s of non-irradiated TGFB is slightly

higher than that of triglycine sulphate (TGS) [12,13] which suggests stronger interaction among the dipoles in TGFB and consequently indicates that the unit cell volume is slightly smaller than that in TGS [1]. Effect of irradiation leads to shift the curie temperature T_c to lower temperatures and shows no noticeable change in P_s, in the limit of experimental errors, till the critical value of irradiation ($D_0 = 9 \times 10^3$ rad), Figure 1 (curves 2,3), hereafter it decays rapidly rather than gradually, Figure 1 (curves 4–6). The shape of the hysteresis loop remains unchanged as P_s is constant, but as it decays, the quality of the loop deteriorates and smeared out. Little information on the ferroelectric mechanism in TGFB leads to the discussion of P_s-behaviour as a function of irradiation in terms of a phenomenological model [14,15] based on a potential energy diagram, (Figure 2).

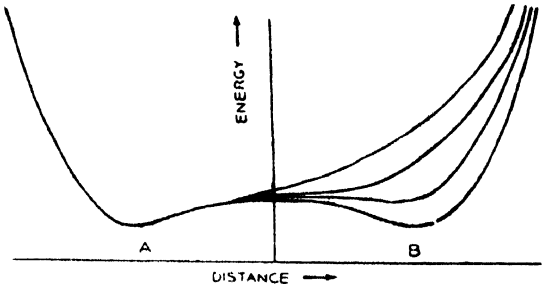

Figure 2. Diagram of the double-minimum potential energy curve.

The ion responsible for the ferroelectric mechanism has either of the two potential minima A or B, in the undamaged state. The effect of the irradiation is supposed to modify one side of the energy diagram with respect to the other and in particular, the minimum A, in which the ion resides, is relatively unaffected by the irradiation. If during the irradiation, the minimum B is steadily raised relative to that at A and the horizontal distance between the two minima is maintaining constant, one can account for the initial constancy of P_s. If the minimum B is gradually obliterated, the crystal will become polar and non-ferroelectric, as confirmed by the persistense of the pyroelectric effect after the hysteresis loop has been considerably deteriorated [16,17]. It is not intended that this is the true explanation for the effect, but merely to show that it is possible to arrive at such model which accounts for it.

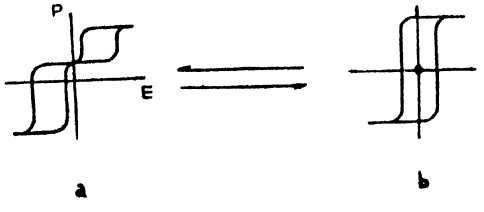

Figure 3. Changes of ferroelectric hysteresis loop due to : (a) irradiation effect, (b) field effect.

Figure 3 shows schematically, the behaviour of a hysteresis pattern with small doses of irradiation ($<D_0$). The irradiated crystals show a split-loop pattern, (Figure 3(a)), but when the field is applied immediately after irradiation and maintained for one minute, the two parts of the loop slide towards each other along the field axis and eventually merge to

form a normal hysteresis loop (Figure 3(b)), though with slightly greater coercive field than the initial one. If the field is then removed for about a minute the split-loop is again obtained. Alternatively, if the field is maintained throughout the irradiation, there is no splitting observable at the end of irradiation. But again, briefly removing the field, the crystal adopt a split-loop pattern which anneals back to a single loop as the field is again maintained. The process of relaxing to a split-loop pattern with the field off and its subsequent annealing with the field on could be repeated continuously provided that the field was not removed for too long a period, say ≥ half an hour. If the field was removed for longer time, the split-loop pattern becomes permanent. It the crystal was heated to about (~100°C) for a minute and then cooled rapidly to room temperature, it returned to its previous unstable state where the loop pattern could be cycled by the field between the split- and single-loop patterns. It was also found that dc-fields annealed out the split-loop pattern in a way similar to that of the ac-field. The above remarks could be applied, in particular, to crystals that had been damaged only slightly, that is by an amount less than that required to make P_s decreases. This means that, the whole crystal reflects a relatively minor amount of local damaging, and the hysteresis loop retains its entity throughout the initial stages of irradiation. Increase of damaging, which contains several cells, tends to destroy the dipole coupling across these damaged portions and hence reduces P_s at $D > D_0$. Such explanation could possibly fit the variation of P_s *versus* irradiation, but it would not account for the biasing effect. On the other hand, irradiation damage effects might be ascribed to a migration of the imperfections produced by irradiation into the domain walls [18]. Imperfections segregating in this way could serve to trap the domain wall. Such a mechanism appears attractive in that, one could readily account for the memory effects.

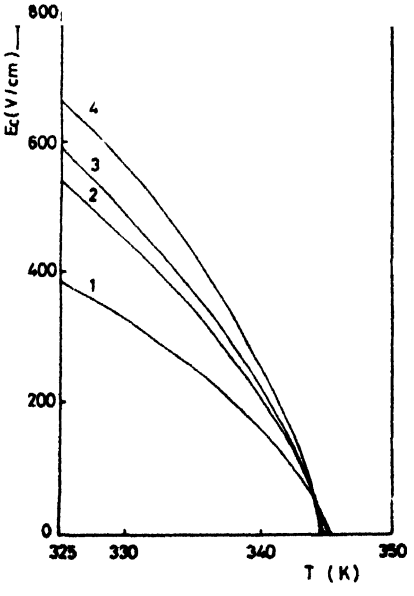

Figure 4(a). E_c-temperature dependence of non- (curve 1) and irradiated samples (curves 2–4).

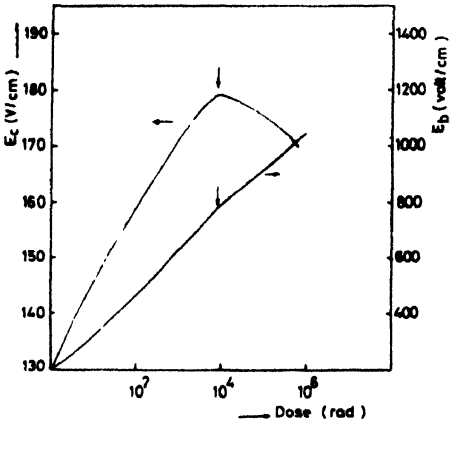

Figure 4(b). Variations of E_c and E_b with irradiation (at 300 K).

Figure 4(a), shows the temperature dependence of the coercive field E_c for non-irradiated (curve 1) and irradiated samples (curves 2–4). E_c is defined as half the width of the hysteresis loop whatever, the value of the bias field. It decreases with increasing temperature and disappears at T_c. Steady increase of E_c (Figure 4(a), curves 2–4) and shifting of T_c toward lower temperatures due to irradiation, were observed. Figure 4(b) exhibits isothermal (at 300 K) E_c-irradiation dependence. At first, E_c increases steadily *versus* the irradiation to a maximum value, at which P_s starts to decrease, after that it goes into a steady decline. Figure 4(b) shows also the isothermal (at 300 K) variation of the bias field E_b (obtained from the hystersis loop) as a function of irradiation, which has pronounced effect along the ferroelectric *b* axis.

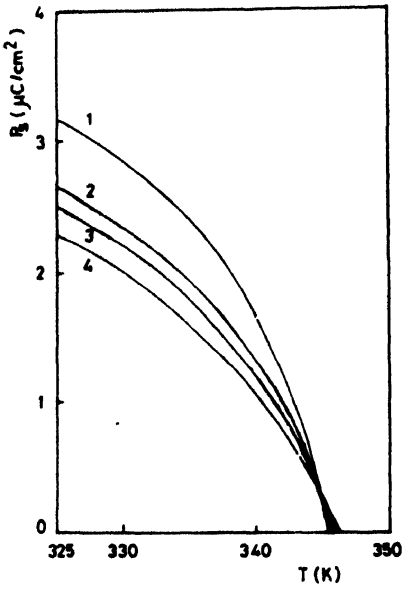

Figure 5. P_s-temperature dependence of pure sample (curve 1) and various *L*-alanine admixtured samples (curves 2–4).

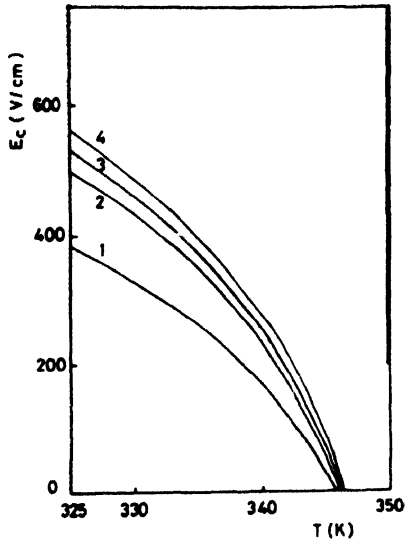

Figure 6. E_c-temperature dependence of pure sample (curve 1) and various *L*-alanine admixtured samples (curves 2–4).

Figure 5 shows the temperature dependence of P_s for pure (curve 1) and various *L*-alanine admixtured (curves 2–4) samples. Decrease of P_s and changing of T_c to higher temperatures are obtained. It is observed that there is a macroscopic irreversible polarization associated with *L*-alanine admixture which polarizes the host in one sense. This can be understood in terms of the structures of TGFB [1,3], glycine [19] and *L*-alanine [20]. It is known that the three glycine molecules (I, II, III) all participate in the polarization reversal of TGFB, but the main reversible dipole is that associated with glycine I. During polarization reversal, the glycine molecule changes into its mirror image by rotation and may substituted by *L*-alanine of similar structure, so that reversal of this substituted molecule does not take place, by simple rotation [20].

Figure 6 (curve 1) shows that E_c decreases gradually with temperature and disappears at T_c. Increase of E_c (Figure 6, curves 2–4) and shifting of T_c toward higher

temperatures due to increase of *L*-alanine concentration, are also observed. Increase of E_b due to *L*-alanine concentration is also obtained.

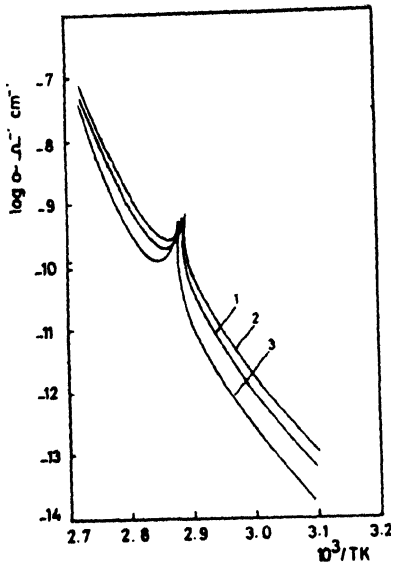

Figure 7. Variation of log σ *versus* $10^3/T$ of non- (curve 1) and irradiated samples (curve 2) for $D < D_0$ and (curve 3) for $D > D_0$.

Figure 7 shows the variation of log σ *vs* $10^3/T$ of non-irradiated (curve 1) and irradiated (curves 2, 3) in the same temperature range. The striking feature of the present result is a gradual transition at T_c, which is typical for the second order transition. The rise in σ at T_c, may attributed to the large scale availability of the protonic carriers released during the rearrangement process of the crystal lattice and/or rotation of sulphate and glycine ions at T_c [21,3]. The plots of non- and irradiated samples have two distinct regions characteristic of ionic crystals [22]. In the lower phase $< T_c$, σ-curves approach slightly, while above T_c the approach is more pronounced and they may tend to merge into a single line. Effect of irradiation on damaging the chemical bonds and creation of some charged carriers with high mobilities leads to increase σ at the first stage $< D_0$ Figure 7 (curve 2), followed by σ-decrease at the second stage $> D_0$ (Figure 7, curve 3), which attributed to the activities of trapping centers (predominent). *L*-Alanine admixtures have the general effect of reducing σ. This reduction is mainly contributed by either vacancies or interstitials trapping.

4. Conclusion

Different changes of ferroelectric hysteresis loop due to X-ray irradiation are observed. P_s shows no change at the first stage ($\leq D_0$), then it begins to decay rapidly and the hysteresis loop is smeared out. At the early stage of irradiation $\leq D_0$ the crystal develops split loop patterns, each subsidiary loop being biased to the same extent but in opposite directions. A split-loop pattern changed into a normal single loop one as a result of

applying external field, but when it is removed, the crystal relaxes back to its split loop form. The irradiated crystal could be cycled by the field between the single and split-loop patterns under certain condition. If the split-loop pattern fails to respond to further field treatment, after removing it for longer time, the sample is subjected to gentle heat treatment to maintain the cycling process between the two forms of the loop patterns. The results are discussed in terms of the conventional double minimum potential energy curve used for describing the ferroelectric mechanisms. E_c and E_b build up steadily during irradiation. P_s of un imperfected TGFB is slightly higher than that of TGS, due to stronger dipoles interactions in the former. Decrease of P_s and increase of E_c and E_b as a function of L-alanine concentration are observed and attributed to domain's clamping and change of internal fields respectively. Measurments of σ show anomaly at T_c. Increase of irradiation, leads to an increase and decrease of σ around D_0 due to release of charged carriers and traping process respectively. Decrease of σ due to increase of L-alanine concentration is due to vacancies and interstitials trapping.

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