PROC. JSSF-2, KYOTO, 1980
J. PHYS. SOC. JPN. 49 (1980) SUPPL. B, pp. 21–23.

Effect of Heat-treatment on Ferroelectric Hysteresis Loop of $Ca_2Sr(C_2H_5COO)_6$

Jun HATANO, Takeyo TSUKAMOTO and Hideo FUTAMA

Department of Applied Physics, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo, 162

Annealing effects on characteristic parameters of domain dynamics of dicalcium strontium propionate are examined by ferroelectric hysteresis measurement. The annealing brings about the remarkable increase of the coercive field which is accompanied by the lowering of the transition temperature. By an analysis on the basis of the simple model of two-dimensional domain growth, it is concluded that the increase of coercive field is attributed to that of activation field of sideways wall-motion.

§1. Introduction

Domain structure of dicalcium strontium propionate, $Ca_2Sr(C_2H_5COO)_6$ (abbreviated as DSP), was studied by Someya and Kobayashi[1] by means of an electron-mirror microscope technique and, recently, by Hosokawa *et al.*[2] with direct optical method. Both of them reported island domains: specklike islands by the former and pseudo-octagonal islands by the latter. Mochizuki and Futama[3] made an attempt to reveal the domains using a powder-pattern technique. It was suggested that the obtained patterns reflect the internal strain introduced during crystal growth.

As-grown crystals of DSP, usually contain internal bias field. An annealing at about 300°C eliminates the internal bias field and lowers the transition temperature by a few degrees.[3,4] In annealed crystals, no domains can be observed.[3] In the present study, the effect of the heat-treatment on characteristic parameters of domain dynamics are examined by ferroelectric hysteresis loop measurements.

§2. Experiments

Shapes of ferroelectric *D-E* hysteresis loop generally depend not only on temperature but also on impressing rate of field at which the hysteresis loop is traced, $S(=\mathrm{d}E/\mathrm{d}t)$. An ordinary Sawyer-Tower bridge with a triangular wave generator of wide range of S was used as the loop tracer. The advantage of triangular wave instead of sinusoidal one is that the magnitude of S is constant during a trace of the hysteresis loop.

The strength of the internal bias field in DSP varies with the location of electrode attached on the specimen.[3] Gold was evaporated on a small area so selected as not to spread over two or more regions which have different biases; on the area, uniform deposition of powder was observed. The annealing was made in a vacuum ampoule. In Fig. 1, powder patterns, both for as-grown and for annealed crystals, are delineated by a modified powderpattern technique.[5]

The temperature dependence of coercive field E_c, measured under constant S is shown in Fig. 2. The E_c values are remarkably raised with the annealing which is accompanied by the lowering of the transition temperature T_c. In Fig. 3, the S dependence of E_c measured under constant temperature difference $\Delta T(=T_c-T)$, is shown in log-log scale. The E_c values gradually increase with S.

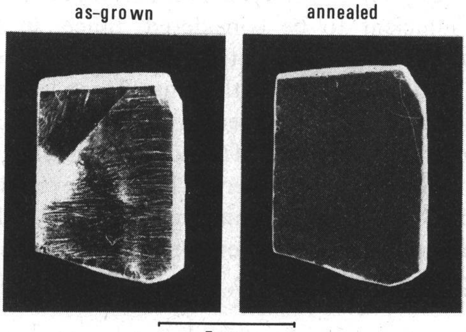

Fig. 1. Powder patterns on *c*-plates of DSP at − 30°C, of as-grown crystal (left), of annealed (320°C, 50 hours and 330°C, 70 hours) crystal (right).

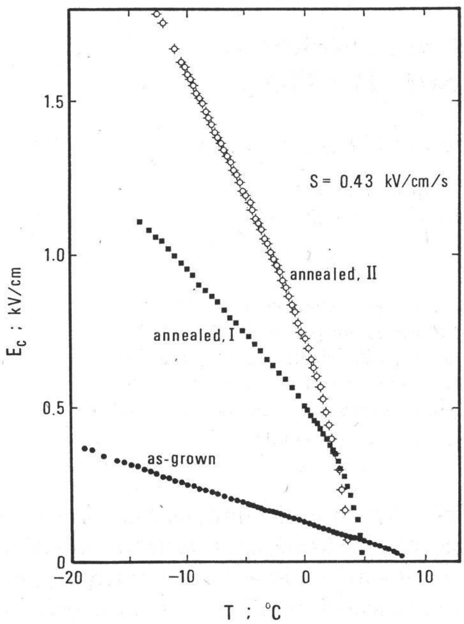

Fig. 2. Temperature dependence of the coercive field measured under the condition, $S = 0.43$ kV/cm/s, for the crystal: as-grown, annealed (I) [320°C, 50 hours] and annealed (II) [320°C, 50 hours and 330°C, 70 hours].

§3. Calculations

Calculations of E_c as a function of S were made on the basis of a simple two-dimensional model of domain growth.[6, 7] In the model, the nucleus densities of domain are proposed to depend linearly on the applied field, $[n(E) = n_0 + kE]$, and so-called exponential law of sideways velocity of domain wall, $[v(E) = v_\infty \exp(-\delta/E)]$, is assumed, where v_∞ and δ are an extrapolated velocity and an activation field, respectively. So far as the completely saturated hysteresis loop is concerned, only a first quarter of one cycle of the triangular wave is sufficient to be considered. Since, in this period of the field, the time dependent field can be written as $E=St$, the time dependent nucleus-density is represented as $n(t)=n_0+kSt$. For brevity, any kind of relaxation of nucleation for field is neglected here. The total (extended) area $A_{ex}(t)$ of the domains per unit area of electrodes regardless of overlapping is obtained by superposition principle,

$$A_{ex}(t)=n_0 a(t)+kS\int_0^{t_c} a(t-u)\,\mathrm{d}u, \qquad (1)$$

where $a(t)$ is the area of a growing domain. The coalescence of the domains is taken into consideration by the Avrami theorem;[8] then, the time dependent polarization $P(t)$ is represented as a function of $A_{ex}(t)$. The coercive field under consideration is given by $E_c = St_c$, where t_c is a solution of $P(t_c)=0$. The final equation to be solved for cylindrical domains is

$$N\left[\int_0^{t_c} \exp\left(-\frac{\delta}{Sx}\right)dx\right]^2 + KS\int_0^{t_c}\left[\int_0^{u} \exp\left(-\frac{\delta}{Sx}\right)dx\right]^2 du = \frac{\ln 2}{\pi}, \qquad (2)$$

where $N=n_0 v_\infty^2$ and $K=kv_\infty^2$. This equation was numerically solved by an iteration method. The results are given by solid curves in Fig. 3, where the parameters δ, N and K are determined by the best fitting to the experimental results. As a consequence, the increases in δ and N, and the decrease in K occur with the annealing. As the increasing N (i.e. n_0 or v_∞) should make E_c decrease, and change in K are not so effective for E_c value in the present S region, it is concluded that the rise in E_c of DSP with the annealing are attributed mainly to the increase of δ values.

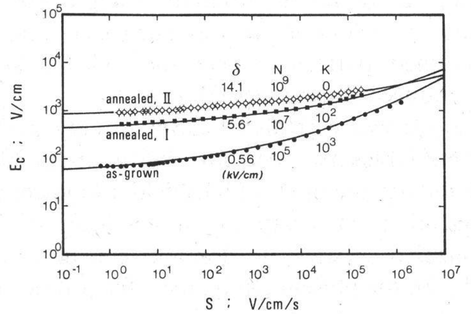

Fig. 3. The S dependence of E_c measured under the condition $T_c - T = 11°$. Solid curves are calculated for the values of δ, N and K which are shown in the figure.

§4. Discussion

The shapes of observed and calculated hysteresis loops are shown in Fig. 4, in which the internal bias field of the as-grown crystal is eliminated by an external *d.c.* field. The agreement between the observed and the calculated results is very well for the annealed crystals. In the as-grown crystal, however, so-called backswitching phenomenon is observed. It can be considered that a part of the domain walls are pinned by some crystal defects. In the early

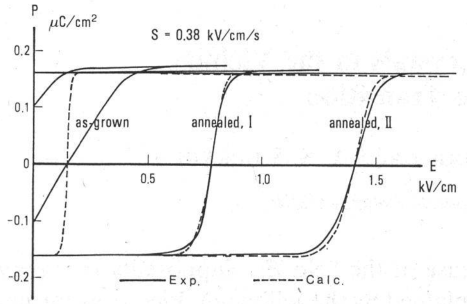

Fig. 4. Observed and calculated hysteresis loops at $S=0.38$ kV/cm/s. Solid curves are experimental results observed at $T_c - T = 11$. Dotted curves are theoretical results calculated for the same values of δ, N and K as shown in Fig. 3.

stage of annealing, these pinning centers disappear and, at the same time, the internal bias field is diminished. For an origin of the internal bias field, a different kind of defects should be considered, which cause irreversible dipoles of same sense throughout the volume. These two kinds of defects are easily diminished or homogenized in the early stage of the annealing. In the advanced stage, however, the E_c values keep rising and the transition temperature continues to lower even after the above two kinds of defects have disappeared. This fact implies that another kind of defect, such as small change in chemical composition or deviation from stoichiometry, is created homogeneously. Since they necessarily affect on the nature of interaction between dipoles, they are possible origins of the advanced annealing effects.

References

1) T. Someya and J. Kobayashi: Phys. Status Solidi a **4** (1971) K161.
2) T. Hosokawa, J. Kobayashi and Y. Uesu: Appl. Phys. Lett. **36** (1980) 907.
3) J. Mochizuki and H. Futama: J. Phys. Soc. Jpn. **23** (1967) 127.
4) K. Deguchi and E. Nakamura: J. Phys. Soc. Jpn. **40** (1976) 478.
5) J. Hatano, F. Suda and H. Futama: Jpn. J. Appl. Phys. **12** (1973) 1644.
6) J. Janta: *Proc. Int. Meeting Ferroelectricity, Kyoto, 1969*, J. Phys. Soc. Jpn. **28** (1970) Suppl. p. 340.
7) J. Hatano: J. Phys. Soc. Jpn. **45** (1978) 1291.
8) E. Fatuzzo: Phys. Rev. **137** (1962) 1999.