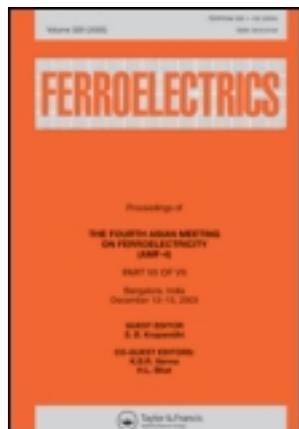


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GROWTH AND DIELECTRIC PROPERTIES OF FERROELECTRIC PROPIONATES†

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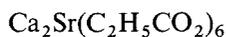
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Large single crystals of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{CO}_2)_6$ and $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{CO}_2)_6$ have been grown by the solution-growth technique. Dielectric and pyroelectric properties of these salts have been measured for as-grown and annealed samples. The results are analyzed in light of a free energy model appropriate to a second-order pseudo-proper ferroelectric.

INTRODUCTION

Dicalcium strontium propionate,



(abbreviated DSP), has two phase transition points near -169°C and 8.5°C . Two phase transitions were also found for dicalcium lead propionate, $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{CO}_2)_6$, (DLP), near -82°C and 58°C .¹ Both compounds have been found to be ferroelectric between the high and low phase transition points.^{2,3} The crystal symmetries of these compounds in the ferroelectric phase and above the upper transition point are C_4 and D_4 , respectively.^{2,3,4}

In this paper we report on the growth of single crystals of DLP and DSP from solution and measurements of their dielectric and pyroelectric properties. The results of these measurements are analyzed in light of a Landau-type free energy expansion for a second-order pseudo-proper ferroelectric.^{5,6}

EXPERIMENTAL TECHNIQUE

Growth

Large single crystals of DSP and DLP were grown using the solution crystal growth technique (Figure 1). Growth took place in a modified Holden-type crystallizer, which had a temperature stability of $\pm 0.005^\circ\text{C}$.

Crystals of DSP and DLP were grown from saturated solutions by slow heating from 40°C to 45°C instead of isothermal evaporation. The raw material used for growth of DSP and DLP was obtained by mixing aqueous solutions of calcium propionate and lead (or strontium) propionate in stoichiometric amounts. A water: propionic acid solvent system was employed using a volume ratio of 95:5. Seeds of the materials to be grown were glued to Lexan seed holders at a radial distance of 4 cm. Each seed was $\sim 5 \times 5 \times 5$ mm in size and they were oriented along the [001] axis whenever possible. The flow velocity of solution across the seeds was calculated to be ~ 20 cm/sec. Typically, the growth runs lasted from 40-60 days. During this period the average heating and growth rates were $0.1^\circ\text{C}/\text{day}$ and 0.1 mm/day, respectively. After an initial capping period, the crystals grew clear to

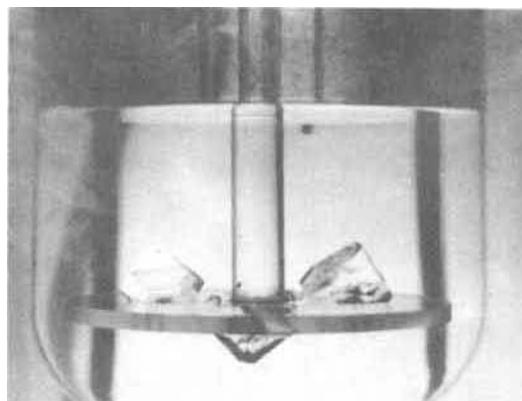


FIGURE 1 Crystals of DLP during growth. Each crystal is ~ 20 mm in height.

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heights ranging from 10 to 20 mm each. All runs contained varying amounts of spurious nucleation which formed on the walls of the glass container and the seed holder.

Sample Preparation

The dielectric and pyroelectric measurements were done on samples cut perpendicular to the tetragonal C axis and polished to a thickness of 50–110 μm . Samples of DSP and DLP were annealed in evacuated quartz ampoules. DLP was annealed at 270°C for 21.5 hours and DSP at 340°C for 64 hours.^{7,8} Electrodes were formed on both faces with evaporated antimony.

Dielectric constant measurements were performed in a field of 8–10 V/cm at 8 kHz. The pyroelectric coefficient was measured using the dc technique of Byer and Roundy and the ac technique of Chynoweth.

RESULTS AND DISCUSSION

Dicalcium Lead Propionate

Results of dielectric measurements on as-grown and annealed DLP are shown in Figure 2. These results are similar to those reported by Takashige, *et al.*⁷ In the as-grown sample, the dielectric constant, ϵ , increases from a value of 4.3 at 25°C to a value of 8.2 at about 56°C. A higher peak value of ϵ and a shift to the low temperature side are seen for the annealed sample. The difference in the dielectric behavior of as-grown and annealed

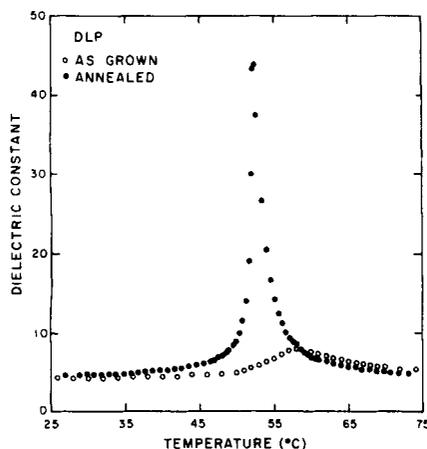


FIGURE 2 Dielectric constant vs. T for as-grown and annealed DLP.

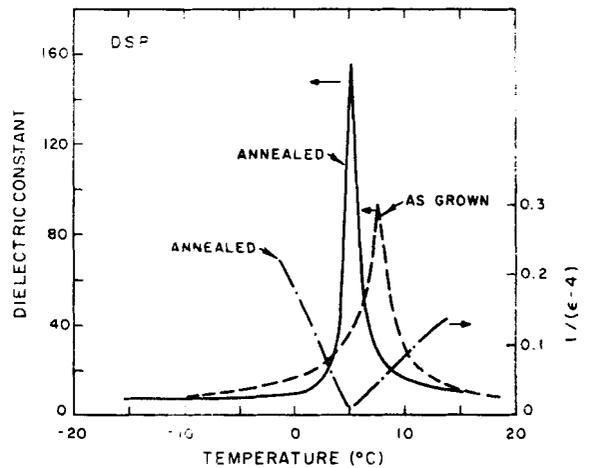


FIGURE 3 a) Dielectric constant vs. T for as-grown (dashed line) and annealed (solid line) DSP, b) Curie-Weiss plot (dash-dot line) for annealed DSP.

DLP can be ascribed to the large internal bias field normally present in as-grown DLP.⁷

The influence of the internal bias field is also manifested by the absence of any anomaly in the temperature dependence of the pyroelectric coefficient. In unannealed samples, the pyroelectric coefficient, p , rises from a value of 1.2 nC/cm² K at 30°C to a peak value of 7.0 nC/cm² K at 55°C and decays slowly thereafter.

Dicalcium Strontium Propionate

Results of dielectric constant measurements on DSP are shown in Figure 3. Similar to DLP, the annealing of DSP causes a rise in the peak value of ϵ and a shift towards lower temperature. Figure 3 also shows a Curie-Weiss plot for the annealed sample close to the transition temperature. The Curie constants above and below the transition temperature are 62 K and 28 K, respectively. These values are consistent with the data in the literature.^{8,9,10}

Comparing the dielectric behavior of DLP and DSP, it can be seen that, unlike DLP, as-grown DSP does not exhibit large internal bias fields. In as-grown DLP, the internal bias field of the order of 10 kV/cm.⁷ The internal bias in as-grown DSP was estimated from hysteresis loops to be less than 0.5 kV/cm. This small bias field cannot totally account for the differences in the behavior of ϵ for annealed and as-grown DSP. For example, as the transition point is approached, the dielectric constant of annealed DSP rises more steeply in the

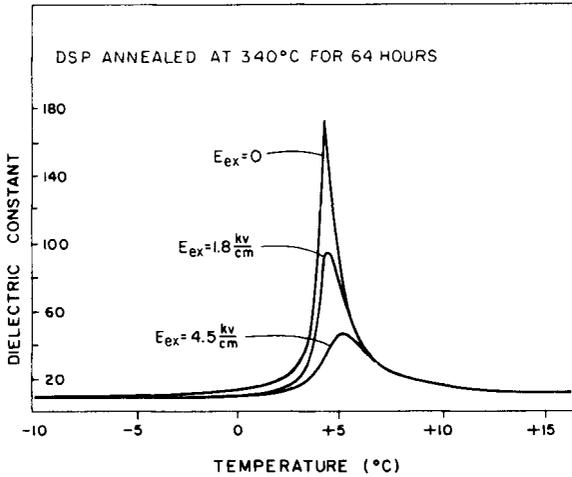


FIGURE 4 Dielectric constant vs. T under varying external bias fields for annealed DSP.

ferroelectric phase than in the paraelectric phase, as expected. However, the opposite is found in the as-grown samples. Annealed DSP under external bias fields does not exhibit this anomalous behavior. This can be seen in Figure 4. As the applied field increases, the peak of ϵ broadens and shifts to the higher temperature side. These results agree with the theoretical prediction for field dependence of ϵ in second-order pseudo-proper ferroelectrics.¹¹

The temperature dependence of the spontaneous polarization, P_s , was measured in annealed DSP using the charge integration technique (Figure 5). The P_s values obtained are consistent

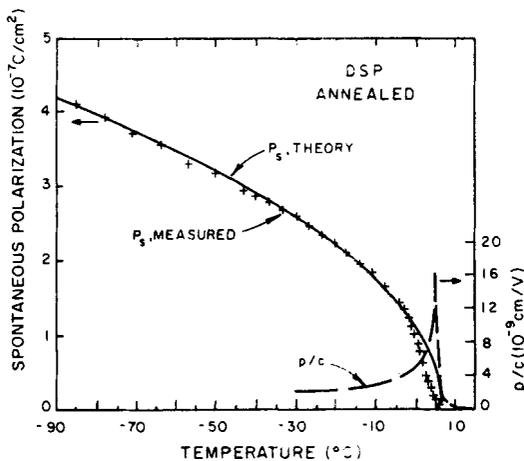


FIGURE 5(a) Spontaneous polarization vs. T (solid line = theoretical curve, crosses = measured points) for annealed DSP, b) p/c vs. T for annealed DSP.

with the data of Matthias *et al.*² however, they are lower than those reported by Takashige *et al.*⁷ The curve through the experimental points was obtained by a linear least square fitting of the equation: $P_s = K (T_0 - T)^{1/2}$, to the data up to 0°C. For K and T_0 we found the values of $K = 4.26 \times 10^{-8} C/cm^2 K^{1/2}$ and $T_0 = 6.86^\circ C$. The deviation of the experimental points from the theoretical curve in the close vicinity of T_c is in accordance with the observation of Deguchi *et al.*⁹

Figure 5 also shows the temperature dependence of the ratio p/c (c = heat capacity) measured on an annealed sample of DSP by the dynamic technique. A small external field of 0.35 kV/cm was used to keep the sample from depoling near the transition temperature. The p/c scale was calibrated at $-30^\circ C$ by taking the values of $p = 3.5 \times 10^{-9} C/cm^2 K$ from charge integration measurements, and $c = 1.65 J/cm^3 K$ from the literature.¹

Further investigation of the dielectric properties of DLP and DSP is needed to quantitatively discuss differences in their behavior.

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