

## Pressure-Temperature Phase Diagram of $\text{Ca}_2\text{Ba}(\text{C}_2\text{H}_5\text{COO})_6$

Kazuo GESI and Kunio OZAWA

Physics Division, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-11

(Received August 13, 1974)

The pressure-temperature phase diagram of  $\text{Ca}_2\text{Ba}(\text{C}_2\text{H}_5\text{COO})_6$  was drawn in a pressure range of  $p \leq 7$  kbar and a temperature range of  $-100^\circ\text{C} \leq T \leq +200^\circ\text{C}$  from dielectric constant measurements. Four pressure-induced phases IV, V, VI, VII were detected besides atmospheric pressure phases of I, II, III. The phase boundaries and the order of transitions between them were determined. At the transition from the high pressure IV phase to V phase, a pronounced dielectric constant peak was observed. The height of the peak decreases with increasing pressure. Ferroelectric hysteresis loops were not observed around the temperature at the peak of dielectric constant.

### § 1. Introduction

Dicalcium barium propionate  $\text{Ca}_2\text{Ba}(\text{C}_2\text{H}_5\text{COO})_6$  undergoes two polymorphic transitions at 1 atm; the room temperature phase (denoted as phase I) transforms to phase II at about  $-6^\circ\text{C}$ , then phase II transforms to phase III at about  $-70^\circ\text{C}$ .<sup>1-3)</sup> The transition from phase I to phase II is of the first order, while the II-III transition is of the second order.<sup>1-3)</sup> The crystal structure of phase I belongs to the cubic system, and the space group is  $O_h^7\text{-Fd}am^{42)}$  or  $O^4\text{-F}4_13$ ,<sup>5)</sup> but so far detailed structure analysis of phases II and III has not been reported. Unlike to dicalcium strontium and lead propionates, the barium salt does not show any marked dielectric anomalies at the transition temperatures. Nor ferroelectric activity at 1 atm has been found for  $\text{Ca}_2\text{Ba}(\text{C}_2\text{H}_5\text{COO})_6$ .<sup>6)</sup>

We have studied the effect of hydrostatic pressure on the phase transitions of  $\text{Ca}_2\text{Ba}(\text{C}_2\text{H}_5\text{COO})_6$  from dielectric constant measurements. The present work aims to draw the pressure-temperature phase diagram of this substance, and also to check a possibility of ferroelectric activity in pressure-induced phases.

### § 2. Experimental

Single crystals of dicalcium barium propionate were grown by slow evaporation of an aqueous solution containing proper amounts of barium hydroxide, calcium propionate, and propionic acid. A (100) plate attached with silver-paste electrodes was set in a pressure bomb which had seven electrical terminal plugs. Two types of pressure bombs were used; one is an internal furnace type for the

measurements above room temperature, and the other is a Cu-Be bomb for low temperature measurements. The pressure transmitting fluids used were silicon oil (at and above room temperature), and 50-50 mixture of *iso*- and *n*-pentane. Detailed descriptions of the high pressure system were published elsewhere.<sup>7,8)</sup> The phase transitions at high pressures were detected by anomalies in dielectric constant measured with an LCR-meter or a three terminal capacitance bridge.

### § 3. Results

Figure 1 shows the change in capacity of a (100) plate with hydrostatic pressure at different temperatures above room temperature. The room temperature phase (phase I) transforms to a high pressure phase which is denoted as phase IV in this paper. The I-IV transition is clearly of the first order, since it is accompanied with a discontinuity in dielectric constant and with marked thermal (or pressure) hysteresis. The I-IV transition temperature increases with increasing pressure with a rate of  $125 \pm 3$  deg kbar.<sup>-1</sup> In phase IV, the dielectric constant increases with decreasing temperature and reaches a peak as shown in Fig. 2. The peak value of the dielectric constant decreases as pressure increases, when the peak is blurred accordingly. In addition, there is a marked thermal hysteresis between heating and cooling processes at a constant pressure as shown in Fig. 2. We attribute the dielectric constant peak to a phase transition, and denote the lower temperature phase as phase V. Although any discontinuous changes in dielectric constant at the IV-V transition were

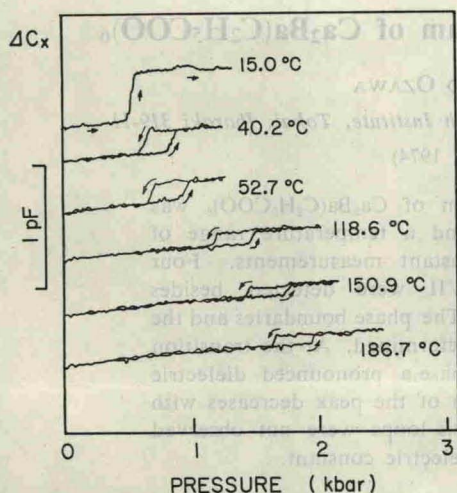


Fig. 1. Relative capacitance change  $\Delta C_x$  of a (100) plate of  $\text{Ca}_2\text{Ba}(\text{C}_2\text{H}_5\text{COO})_6$  with hydrostatic pressure at various temperatures. Measured with an LCR-meter and recorded on an x-y recorder. Area and thickness of the specimen were  $0.14 \text{ cm}^2$  and  $0.39 \text{ mm}$ , respectively. Frequency:  $100 \text{ kHz}$ .

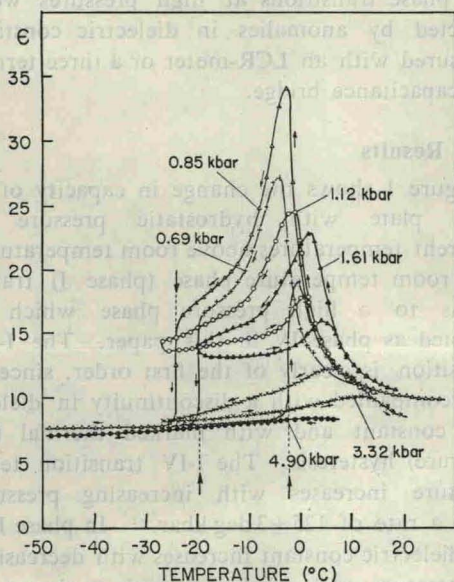


Fig. 2. Temperature dependence of the dielectric constant of (100) plates of  $\text{Ca}_2\text{Ba}(\text{C}_2\text{H}_5\text{COO})_6$  at various pressures. The peak and thermal hysteresis at the IV-V transition are shown. The discontinuous change in dielectric constant at the II-V transition is shown by vertical arrows. Frequency:  $1 \text{ kHz}$ .

not observed, the IV-V transition is probably of the first order. Structural inhomogeneity which is brought about by passing the first

order I-IV boundary would round off discontinuous changes in the dielectric constant. The marked thermal hysteresis in phase V would be due to a long time constant for getting to the equilibrium state in phase V. Figure 3 shows changes in the dielectric constant at the II-V (or III-V) transition. The II-V and III-V transitions are also of the first order, and the transition pressure increases with decreasing temperature. The estimated slope of the II-V (or III-V) phase boundary is  $-(71 \pm 2) \text{ deg kbar}^{-1}$ . The II-IV-V triple point is found at  $T = -(5 \pm 2)^\circ\text{C}$ ,  $p = 0.55 \pm 0.05 \text{ kbar}$ .

The dielectric anomalies at the I-II transition at high pressures are shown in Fig. 4 (a). The

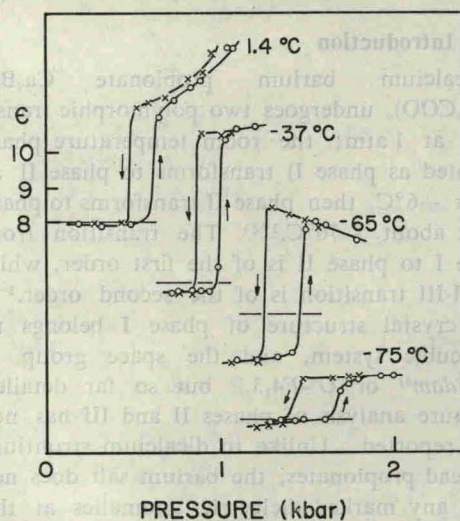


Fig. 3. Dielectric constant anomalies of (100) plates at the II-V and III-V transitions of  $\text{Ca}_2\text{Ba}(\text{C}_2\text{H}_5\text{COO})_6$ . The thin horizontal line on each curve shows the level of  $\epsilon = 8.0$ . Frequency:  $1 \text{ kHz}$ .

I-II transition temperature rises with increasing pressure with a slope of  $34 \pm 2 \text{ deg kbar}^{-1}$ , then, the I-II phase boundary terminates at the I-II-IV triple point at  $T = 9 \pm 1^\circ\text{C}$ ,  $p = 0.42 \pm 0.05 \text{ kbar}$ . Figure 4(b) measured at  $0.55 \text{ kbar}$  shows a dielectric constant anomaly which we have assigned to the II-III transition. The assignment, however, is not very conclusive, since the anomaly at the II-III transition is slight even at  $1 \text{ atm}$ .

Above about  $2 \text{ kbar}$ , other dielectric anomalies are seen at low temperatures as shown in Fig. 4(c). The anomalies would correspond to a phase transition from phase V to a new high pressure phase, which is denoted as phase VI. The dielectric anomaly suggests that the V-VI