

Effect of Hydrostatic Pressure on the Phase Transitions in Ferroelectric $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_3\text{COO})_6$ and $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_3\text{COO})_6$

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Effects of hydrostatic pressure on the phase transitions in ferroelectric $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_3\text{COO})_6$ and $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_3\text{COO})_6$ were studied by dielectric loss measurements in a temperature range of -100 to 100°C . The II transition temperature of $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_3\text{COO})_6$ at 1 atm increases with increasing pressure. The III transition temperature of $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_3\text{COO})_6$ increases with increasing pressure, but the shift and 33-degree shift of the transition temperature are -17°C and 33°C , respectively, at 10 kbar. The transition temperature of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_3\text{COO})_6$ increases with increasing pressure, but the shift and 33-degree shift of the transition temperature are -17°C and 33°C , respectively, at 10 kbar. The transition temperature of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_3\text{COO})_6$ increases with increasing pressure, but the shift and 33-degree shift of the transition temperature are -17°C and 33°C , respectively, at 10 kbar. The transition temperature of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_3\text{COO})_6$ increases with increasing pressure, but the shift and 33-degree shift of the transition temperature are -17°C and 33°C , respectively, at 10 kbar.

Phase I and II should be D_2 and C_2 , respectively. Taking into account the results of optical dielectric loss measurements together with the pyroelectric results.

Changes in the dielectric properties of the ferroelectric materials with the hydrostatic pressure have been reported by several authors.¹⁻⁴ It seems that the hydrostatic pressure has an effect on the II-III transition temperature of ferroelectric materials. The results of present effects would provide a piece of information about the transition mechanism. A part of the present study was preliminarily reported elsewhere.⁵

1. Experimental

Single crystals of $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_3\text{COO})_6$ and $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_3\text{COO})_6$ were grown by means of slow evaporation of aqueous solutions around 100°C . The starting materials were lead acetate, calcium propionate, and propionic acid for $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_3\text{COO})_6$ and strontium hydroxide, calcium propionate, and propionic acid for $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_3\text{COO})_6$. Several plates were cut out of the crystals. After attached with silver paste electrodes, the specimen was set in a quartz bomb which had seven electrical feed-throughs. As grown crystals were used in the whole measurements in the present work. Two types of high pressure bomb were used: one was an optical furnace type for measurements above room temperature, another was a Cu-Bomb for low

2. Introduction

At atmospheric pressure, two transitions were observed both in $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_3\text{COO})_6$ and $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_3\text{COO})_6$. In $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_3\text{COO})_6$, the room temperature phase (Phase II) transforms to Phase III at about 9°C , then Phase II transforms to Phase I at about -169°C . The space groups of Phase I and II are determined to be D_2 and C_2 , respectively. Ferroelectricity is observed in Phase II.⁶ A sharp change in spontaneous polarization was reported at the transition temperature.⁷ The order of the second order, while the II-III transition is of the first order, in $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_3\text{COO})_6$ is similar to those in $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_3\text{COO})_6$. It has been observed that the highest temperature phase transition to Phase II at 100°C in $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_3\text{COO})_6$ transforms to Phase II at about 82°C . The dielectric loss of the grown crystals of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_3\text{COO})_6$ shows the antiferroelectric rather broad transition at the II-III transition temperature. The discontinuous change at the II-III transition is "ferroelectric". Earlier structure analysis⁸ showed that the space group of Phase I (D_2) is non-polar D_2 - 6_2 . However, one of the present authors (K.O.) recently revealed that Phase II and III of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_3\text{COO})_6$ are pyroelectric. Recently, Takahagi et al.⁹ found ferroelectric activity of Phase II of well annealed crystal of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_3\text{COO})_6$. Then, the point groups of

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Effects of hydrostatic pressure on the phase transitions in ferroelectric $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{COO})_6$ and $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$ were studied by dielectric constant measurements in a temperature range of $-100\sim+200^\circ\text{C}$ and a pressure range up to about 8.5 kbar. The I-II transition temperatures (8.7°C in the Sr-salt, 60.4°C in the Pb-salt at 1 atm) monotonically increase with increasing pressure with initial slopes of $19.7\text{ deg kbar}^{-1}$ for the Sr-salt and $23.4\text{ deg kbar}^{-1}$ for the Pb-salt, respectively. The II-III transition temperatures (-173°C in the Sr-salt, -88°C in the Pb-salt at 1 atm) increase with increasing pressure, and the first order II-III phase boundaries terminate at critical points of $p_{\text{crit}}=3.35\text{ kbar}$; $T_{\text{crit}}=-35^\circ\text{C}$ in the Sr-salt, and $p_{\text{crit}}=1.73\text{ kbar}$; $T_{\text{crit}}=-41^\circ\text{C}$ in the Pb-salt, respectively. A sharp maximum of low frequency dielectric constant was found at the critical point of the Pb-salt.

§ 1. Introduction

At atmospheric pressure, two transitions were observed both in $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{COO})_6$ and in $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$.¹⁾ In $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{COO})_6$, the room temperature phase (Phase I) transforms to Phase II at about 9°C ,^{1,2)} then, Phase II transforms to Phase III at about -169°C .¹⁾ The space groups of Phase I and II are determined as $D_4^4-P4_12_12$ (or $D_4^8-P4_32_12$)^{3,4)} and $C_4^2-P4_1$ (or $C_4^4-P4_3$)⁵⁾ respectively. Ferroelectric activity has been found in Phase II.²⁾ A slight change in spontaneous polarization was reported at the II-III transition temperature.⁶⁾ The I-II transition is of the second order, while the II-III one is of the first order.¹⁾ In $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$, similar transitions to those in $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{COO})_6$ have been observed; the highest temperature phase (Phase I) transforms to Phase II at about 60°C ,¹⁾ then, Phase II transforms to Phase III at about -82°C .¹⁾ The dielectric constant of as grown crystals of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$ along the tetragonal *c*-axis shows a rather broad maximum at the I-II transition temperature, and shows a discontinuous change at the II-III transition temperature.¹⁾ Earlier structure analysis⁷⁾ reported that the space group of Phase II of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$ is non-polar $D_4^4-P4_12_12$ (or $D_4^8-P4_32_12$). However, one of the present authors (KG) recently revealed that Phase II and III of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$ are pyroelectric.⁸⁾ Very recently Takashige *et al.*⁹⁾ found ferroelectric activity of Phase II of well annealed crystal of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$. Then, the point groups of

Phase I and II should be D_4 and C_4 , respectively, by taking into account the results of optical rotatory power measurements¹⁰⁾ together with the pyroelectric results.

The changes in the physical properties of the two propionates associated with the I-II transitions have been widely studied. On the other hand, it seems that very little has been done as to the II-III transitions. The present study deals with the effect of hydrostatic pressure on the phase transitions in these two ferroelectric propionates. The results of pressure effects would provide a piece of information about the transition mechanism. A part of the present study was preliminarily reported elsewhere.^{11,12)}

§ 2. Experimental

Single crystals of $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{COO})_6$ and $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$ were grown by means of slow evaporation of aqueous solutions around 28°C . The starting materials were lead mono-oxide, calcium propionate, and propionic acid for the Pb-salt, and strontium hydroxide, calcium propionate, and propionic acid for the Sr-salt. Several *c*-plates were cut out of single crystals. After attached with silver-paste electrodes, the specimen was set in a pressure bomb which had seven electrical terminal plugs. As grown crystals were used in the whole measurements in the present work. Two types of high pressure bomb were used; one was an internal furnace type for measurements above room temperature, another was a Cu-Be bomb for low

temperature measurements. Descriptions of the pressure bombs and the pressure system used were published elsewhere.^{13,14)}

The dielectric constant of the specimen was measured with an LCR-meter or a three terminal capacitance bridge as a function of temperature at various pressures up to about 8.5 kbar. Pressure was measured with a manganin gauge, and temperature was measured with an alumel-chromel thermocouple or a copper-constantan thermocouple set closely around the specimen. The transitions at high pressures were detected by anomalies in dielectric constant.

§ 3. Results

(a) $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{COO})_6$

The dielectric constant along the *c*-axis of $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{COO})_6$ shows a λ -type maximum at the I-II transition temperature (the ferroelectric Curie point). The I-II transition temperature shifts towards higher temperatures as pressure

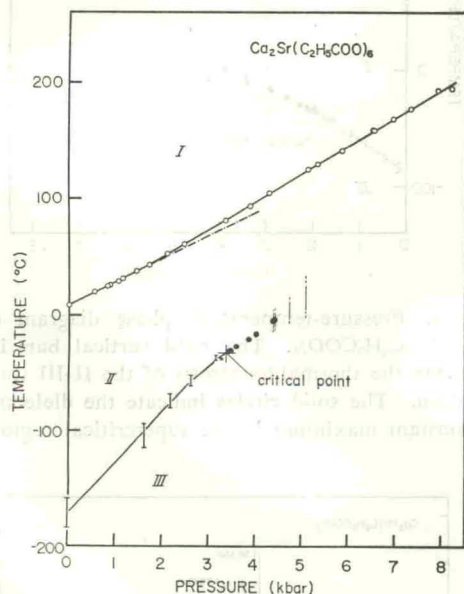


Fig. 1. Pressure-temperature phase diagram of $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{COO})_6$. The bold vertical bars indicate the thermal hysteresis of the II-III transition. The solid circles indicate the maximum of the dielectric constant in the supercritical region. The slash-and-dot line shows the initial slope of the I-II phase boundary.

increases. The maximum value of the dielectric constant gradually decreases with increasing pressure. This is partially due to crashing of the specimen at high pressures.¹¹⁾ The pressure

dependence of the I-II transition temperature is shown in Fig. 1 by open circles. The I-II transition temperature at 1 atm and the initial pressure coefficient $(d\theta_{\text{I-II}}/dp)_{p=0}$ are $8.7 \pm 0.2^\circ\text{C}$ and $19.7 \pm 0.2 \text{ deg kbar}^{-1}$, respectively. The slope of the I-II transition temperature vs pressure curve increases with increasing pressure as seen in Fig. 1; above about 6 kbar, the pressure derivative of the transition temperature is estimated to be 24 deg kbar^{-1} .

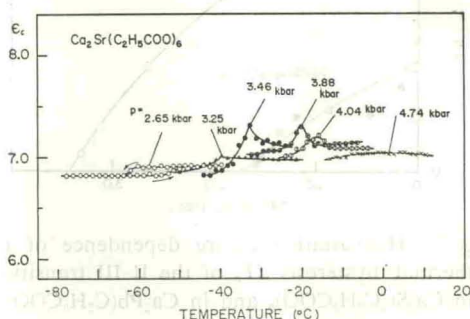


Fig. 2. Temperature dependence of the dielectric constant along the *c*-axis of $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{COO})_6$ at various hydrostatic pressures in the vicinity of the critical point. Frequency: 1 kHz.

At the II-III transition temperature, a discontinuous change in the dielectric constant and a thermal hysteresis of about 25°C was observed at 1 atm; they correspond to the marked first order nature of the transition and usually the crystal was crashed by passing the II-III transition at 1 atm. Figure 2 indicates the temperature dependence of the dielectric constant along the *c*-axis at various pressures. The thermal hysteresis of the II-III transition temperature ΔT_c gradually decreases with increasing pressure, and finally disappears at about 3.35 kbar as shown in Fig. 3. As shown in Fig. 2, the dielectric constant shows a small but distinct λ -type maximum around the critical pressure at which the first order nature of the transition disappears. As pressure increases exceeding the critical pressure the sharpness of the dielectric constant maximum is rounded off, and above about 4.5 kbar the peak of dielectric constant becomes so diffuse that one can hardly recognize the maximum position. The above behavior of the temperature dependence of dielectric constant is reversible unless the crystal is experienced the first order transition below the critical pressure. The pressure dependence of the II-III transition temperature is also shown in Fig. 1.

The II-III transition temperature at 1 atm and the initial pressure coefficient are estimated as $-173 \pm 2^\circ\text{C}$ and $43.5 \pm 0.5 \text{ deg kbar}^{-1}$, respectively. Here we assumed that the equilibrium transition temperature is at the middle point

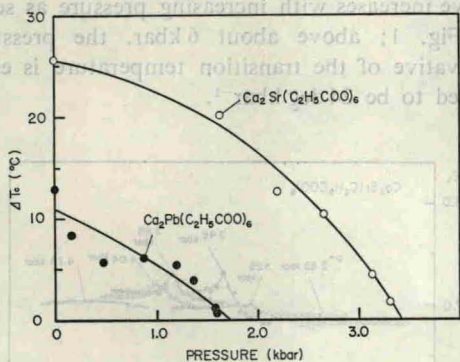


Fig. 3. Hydrostatic-pressure dependence of the thermal hysteresis ΔT_0 of the II-III transitions in $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_3\text{COO})_6$ and in $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_3\text{COO})_6$.

of the thermal hysteresis observed. The observed II-III transition temperature at 1 atm is comparable to -169°C reported by Nakamura *et al.*¹¹ As seen in Fig. 1, the II-III phase boundary gradually deviates from the linear relation, and the pressure coefficient becomes smaller as pressure approaches to the critical pressure. The critical point exists at $p_{\text{crit}} = 3.35 \pm 0.05 \text{ kbar}$ and $T_{\text{crit}} = -35.0 \pm 0.5^\circ\text{C}$. Above the critical pressure, the temperature at which the dielectric constant shows the maximum increases with increasing pressure with a rate of $28.5 \pm 0.2 \text{ deg kbar}^{-1}$ as shown by closed circles in Fig. 1.

(b) $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_3\text{COO})_6$
The pressure dependence of the I-II transition of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_3\text{COO})_6$ is shown in Fig. 4. The relation between the transition temperature and pressure can be expressed by a linear function over the pressure range studied. The observed I-II transition temperature at 1 atm and the pressure coefficient are $60.4 \pm 0.3^\circ\text{C}$ and $23.4 \pm 0.2 \text{ deg kbar}^{-1}$, respectively. The former value is in good agreement with 59.8°C obtained by Nakamura *et al.*¹¹ for as grown crystal.

At the II-III transition temperature, the dielectric constant along the *c*-axis shows a discontinuous change and thermal hysteresis of about 13°C at 1 atm. As pressure increases the thermal hysteresis ΔT_0 decreases, and completely vanishes at a critical pressure of 1.73 kbar as shown in Fig. 3. Figure 5 indicates the tem-

perature dependence of the dielectric constant along the *c*-axis at various pressures. At around the critical pressure a sharp λ -type maximum of the dielectric constant is seen. Above the critical pressure, the sharpness of the peak decreases with increasing pressure, and above about 4 kbar the maximum becomes very obscure. The pressure dependence of the II-III transition temperature is shown in Fig. 4 by bold vertical bars. The II-III transition temperature at 1 atm and the initial pressure coefficient are estimated as $-88.3 \pm 0.5^\circ\text{C}$ and $28.4 \pm$

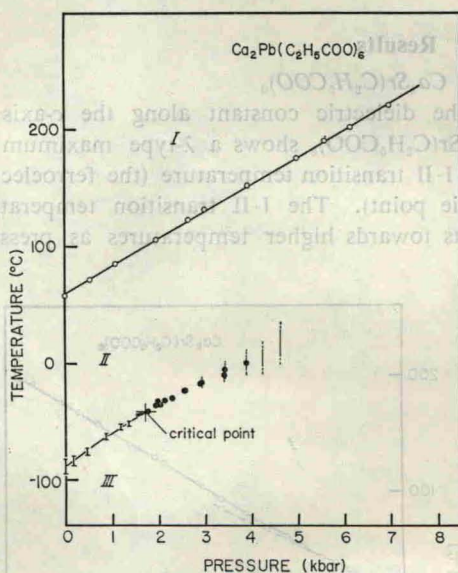


Fig. 4. Pressure-temperature phase diagram of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_3\text{COO})_6$. The bold vertical bars indicate the thermal hysteresis of the II-III transition. The solid circles indicate the dielectric constant maximum in the supercritical region.

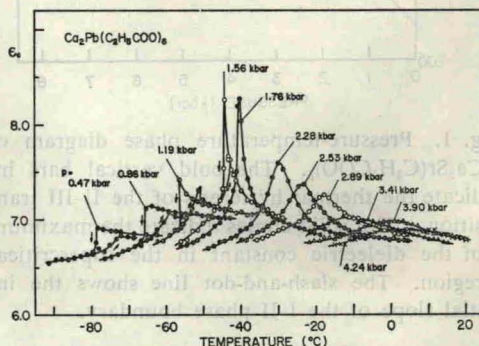


Fig. 5. Temperature dependence of the dielectric constant along the *c*-axis of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_3\text{COO})_6$ at various hydrostatic pressures in the vicinity of the critical point. Frequency: 1 kHz.

0.5 deg kbar⁻¹, respectively. The pressure coefficient of the II-III transition temperature gradually decreases as pressure approaches the critical pressure. The critical point at which the first order II-III phase line terminates exists at $p_{\text{crit}} = 1.78 \pm 0.05$ kbar and $T_{\text{crit}} = -40.5 \pm 0.5^\circ\text{C}$. Above the critical pressure the temperature at which the dielectric constant shows the maximum increases with increasing pressure with a rate of 18.1 ± 0.5 deg kbar⁻¹. The behavior is shown in Fig. 4 by closed circles.

§ 4. Discussion and Conclusion

The pressure-temperature phase diagrams of $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{COO})_6$ and $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$ shown in Figs. 1 and 4 quite resemble each other. The fact suggests that the phase transition mechanisms of the two salts are close to each other. This is the reason why we intended to reexamine the polarity in Phase II of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$.⁹⁾ The discovery of the ferroelectric activity in Phase II of the Pb-salt⁹⁾ and the results of the optical rotatory power¹⁰⁾ also supported the above expectation.

Recently, Kobayashi *et al.*¹⁵⁾ interpreted the ferroelectric transition in $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{COO})_6$ in terms of improper ferroelectricity. A simple phenomenological treatment of improper ferroelectrics¹⁶⁾ shows that the pressure coefficient of an improper ferroelectric Curie temperature is expressed as

$$dT_c/dp = -CQ_h/(2\pi), \quad (1)$$

where C is the Curie constant, and $Q_h = 2Q_{13} + Q_{33}$ is the volume electrostrictive coefficient which is defined as $Q_h = \Delta v_s/P_s^2$, where Δv_s and P_s are respectively the spontaneous change in volume and the spontaneous polarization. Kobayashi *et al.*¹⁵⁾ showed that the ratio $\Delta v_s/P_s^2$ in Phase II of $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{COO})_6$ is considered to be a constant only in a limited temperature region below the Curie temperature. At -13°C , where the proportionality between Δv_s and P_s^2 is held, the spontaneous strains along the a - and the c -axis are estimated to be $(x_1)_s = 0.16 \times 10^{-3}$ and $(x_3)_s = -1.0 \times 10^{-3}$, respectively.¹⁵⁾ At the same temperature, the spontaneous polarization is $0.32 \mu\text{C cm}^{-2}$.¹⁵⁾ Then, one gets the volume electrostrictive coefficient as $Q_h = \{2(x_1)_s + (x_3)_s\}/P_s^2 = -7.8 \times 10^{-10}$ cgs esu. The value is almost 10^2 as large as that observed for proper ferroelectrics such as triglycine sulfate. The above value of Q_h together with the Curie constant $C = 156 \text{ K}^{17)}$ yields $dT_c/dp = 20$ deg kbar⁻¹.

The estimation is in very good agreement with the observed value of 19.7 deg kbar⁻¹. On the other hand, the electrostrictive coefficients Q_{13}^d which are deduced from the piezoelectric coefficients d_{31} and the dielectric susceptibility along the c -axis χ_{33} by the relation $Q_{13}^d = d_{31}/(2\chi_{33}P_s)$ show strong temperature dependence especially in the vicinity of the Curie temperature.^{18,25)} The anomalous behavior of Q_{13}^d can be interpreted by assuming the material being improper ferroelectric.^{15,16)} A simple phenomenological treatment of an improper ferroelectric¹⁶⁾ shows that a relation between Q_{13}^d and Q_{13}^d

$$Q_{13}^d = Q_{13} + (\zeta/\chi_{33}) \quad (2)$$

is held, where ζ is a parameter which measures the strength of the coupling between the polarization and the transition parameter. If one assumes the parameter ζ being temperature independent, $Q_{13}^d = Q_{13}$ when $1/\chi_{33}$ goes to zero. According to Hamano's results,¹⁸⁾ Q_{13}^d and Q_{33}^d just below the Curie temperature where $1/\chi_{33}$ is considerably small are given as 0.26×10^{-9} cgs esu and -2.1×10^{-9} cgs esu, respectively. Putting these values into eq. (1) one gets $dT_c/dp = 40$ deg kbar⁻¹. The value is about twice as large as the observed one but gives the correct order of magnitude.

Recently, Takashige *et al.*⁹⁾ showed that as grown crystals of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$ are strongly biased, and that the bias field can be removed by annealing at 250°C . The rather broad dielectric constant peak¹⁾ and very small anomaly in specific heat reported in earlier works are due to the bias field. Our preliminary measurements on the dielectric constant of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$ which was annealed at 250°C for 48 hr showed that there is a very sharp λ -type peak of dielectric constant at the I-II transition, and at the same time the temperature at which the dielectric constant shows maximum is lowered by about 5°C . The value of the Curie constant of the annealed $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$ is estimated as $C = 40 \text{ K}$. Influence of the bias field on the pressure coefficient of the I-II transition temperature would not be so serious, since the shape of the dielectric constant peak does not change appreciably with pressure. Then, the volume electrostrictive coefficient Q_h of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$ is given from eq. (1) as -3.7×10^{-9} cgs esu by using the Curie constant and observed pressure coefficient. The value of Q_h is about five times as large as the one obtained for the Sr-salt.

The volume change at the II-III transitions in $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{COO})_6$ and $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$ at 1 atm can be evaluated from the specific heat data¹⁾ and the initial pressure coefficient of the transition temperature by using the Clausius-Clapeyron relation $\Delta v = Q_L \cdot (d \ln \theta_{\text{II-III}}/dp)_{p=0}$. If one puts the measured transition heats of 255 cal mol⁻¹ for the Sr-salt and 1160 cal mol⁻¹ for the Pb-salt into the place of the latent heat Q_L , one gets $\Delta v = 1.1\%$ for the Sr-salt and $\Delta v = 1.9\%$ for the Pb-salt. The relatively large volume change at the II-III transition at 1 atm would cause crashing of a single crystal by passing the transition.

The results shown in Figs. 1, 3, and 4 indicate the first order II-III transition lines in $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{COO})_6$ and $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$ terminate at the critical points. Generally saying, a first order phase boundary curve can terminate in the pressure-temperature plane (a) at a triple point where three phase boundaries meet together, (b) at a critical point through which the first order nature of the transition passes into the second order one; such a critical point may be called as the Curie critical point according to the terminology of Ginzburg,²⁰⁾ and (c) at a liquid-vapor type critical point where the transition terminates, and above the critical point no phase transition exists.¹⁰⁾ The case (c) can occur only if the crystal symmetry does not change through the transition.¹⁰⁾ Such a transition which may be called as an isomorphous transition is unquestionably seldom among the solid state transitions. So far the liquid-vapor type critical points have been observed only for the γ - α transition in Ce²¹⁾ and for the Mott transition in Cr-doped V_2O_5 .²²⁾ So far as the dielectric property was concerned, no evidence for existence of a triple point was obtained for the II-III transitions in the present materials. On the other hand, the pressure and temperature dependence of the low frequency dielectric constant above the critical point shows a resemblance to that of the temperature coefficient of the electrical conductance and the volume thermal expansion coefficient around the liquid-vapor type critical point of the γ - α transition in Ce.^{21, 23)} Up to date, no detailed structure analysis has been published for Phase III of $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{COO})_6$ and $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$. However, at least Phases II and III of the both salts are polar, and unpublished x-ray data¹⁾ showed that Phase III of the Pb-salt is isomorphous

with Phase II of the Sr-salt. Recent experimental results⁸⁻¹⁰⁾ seem to suggest that Phase II of the Pb-salt is isomorphous with Phase II of the Sr-salt. Then, it is possible that Phases II and III of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$ are isomorphous with each other. Although the final conclusion should be postponed until the structure analysis of Phase III of the two propionates is completed, it is tempting to speculate that the II-III transitions in $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{COO})_6$ and $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$ are isomorphous transitions, and the II-III phase boundaries terminate at the liquid-vapor type critical points just alike the γ - α transition in Ce. Such an isomorphous transition can take place in a ferroelectric through a displacement of ions between general positions which belong same site symmetry of the crystal space group. A simple phenomenological theory²⁴⁾ based upon the above assumption gives a semi-quantitative agreement with the pressure and temperature dependence of low frequency dielectric constant of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$ in the critical region and in the supercritical region.

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