

Effect of Hydrostatic Pressure on the Phase Transitions in Ferroelectric $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{COO})_6$ and $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$

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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