

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

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Effect of hydrostatic pressure on the phase transitions in ferroelectric $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_2\text{COO})_6$ and $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_2\text{COO})_6$ were studied by dielectric loss measurements in a temperature range of -100°C to 100°C . The II-III transition temperature range up to about 100°C was studied. The II-III transition temperature of the Sr salt, 60.4°C , decreased with increasing pressure. The dielectric loss peaks of the Sr salt and Pb salt were observed at 100°C and 110°C , respectively, at atmospheric pressure. The dielectric loss peaks shifted to lower temperatures with increasing pressure. The transition temperature of the Sr salt at the critical pressure, 1.75 kbar , was 33.4°C . The transition temperature of the Pb salt at the critical pressure, 2.35 kbar , was 32.1°C . A sharp maximum in the dielectric loss frequency shift was observed at the critical point of the transition.

1. Introduction

At atmospheric pressure, two transitions were observed both in $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_2\text{COO})_6$ and in $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_2\text{COO})_6$. In $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_2\text{COO})_6$, the room temperature phase (Phase I) transforms to Phase II at about 9°C , then Phase II transforms to Phase III at about -169°C . The space groups of Phase I and II are determined as A_2^2 ($P4_2/m$) for $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_2\text{COO})_6$ and C_2h ($P2_1/m$) for $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_2\text{COO})_6$, respectively. Ferroelectricity has been found in Phase II. A discontinuous change in spontaneous polarization was reported in the transition temperature.¹ The transition is of the second order, while the II-III transition is of the first order. In $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_2\text{COO})_6$, one transition to Phase II and another transition to Phase III have been observed. The highest temperature of the transition to Phase II at atmospheric pressure is 60.4°C . The dielectric loss peak of the grown crystals of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_2\text{COO})_6$ shows a rather broad peak at the II-III transition temperature. The dielectric loss peak shows a discontinuous change at the II-III transition temperature. Earlier structure analysis² showed that the space group of Phase II ($\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_2\text{COO})_6$) is non-polar D_2^+ ($P2_1$). However, one of the present authors (K.O.) recently revealed that Phase II and III of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_2\text{COO})_6$ are ferroelectric. Recently, Katsube et al.³ found ferroelectricity of Phase II of well annealed crystal of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_2\text{COO})_6$. Then, the point groups of

Phase I and II should be D_2^+ and C_2h , respectively. Taking into account the results of optical dielectric loss measurements together with the pyroelectric results, the changes in the physical properties of the ferroelectric phase II with the hydrostatic pressure have been studied. It has been found that the II-III transition temperature decreases with the effect of hydrostatic pressure. The results of pressure effects and provide a piece of information about the transition mechanism. A part of the present study was preliminarily reported elsewhere.⁴

2. Experimental

Single crystals of $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_2\text{COO})_6$ and $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_2\text{COO})_6$ 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 the Pb salt and strontium hydroxide, calcium propionate, and propionic acid for the Sr salt. Several epiplates were cut out of single crystals. After annealed with electric discharge, the specimen was set in a pressure bomb which had seven electrical terminals. 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 type for measurements above room temperature, another was a Cu-Be bomb for low

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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