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Effect of Hydrostatic Pressure on the Phase Transitions in Ferroelectric Ca₂Sr(C₂H₅COO)₆ and Ca₂Pb(C₂H₅COO)₆

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Effects of hydrostatic pressure on the phase transitions in ferroelectric $Ca_2Sr(C_2H_5COO)_6$ and $Ca_2Pb(C_2H_5COO)_6$ were studied by dielectric constant measurements in a temperature range of $-100 \sim +200^{\circ}C$ 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 deg kbar⁻¹ for the Sr-salt and 23.4 deg kbar⁻¹ for the Pb-salt, respectively. The II-III transition temperatures ($-173^{\circ}C$ in the Sr-salt, $-88^{\circ}C$ in the Pb-salt at 1 atm) increase with increasing pressure, and the first order II-III phase boundaries terminate at critical points of $p_{crit}=3.35$ kbar; $T_{crit}=-35^{\circ}C$ in the Sr-salt, and $p_{crit}=1.73$ kbar; $T_{crit}=-41^{\circ}C$ 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 Ca2Sr(C2H5COO)6 and in $Ca_2Pb(C_2H_5COO)_6$.¹⁾ In $Ca_2Sr(C_2H_5COO)_6$, 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 $D_4^8 - P4_82_12)^{3,4}$ 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 $Ca_2Pb(C_2H_5COO)_6$, similar transitions to those in Ca2Sr(C2H5COO)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 Ca2Pb(C2H5COO), 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 $Ca_2Pb(C_2H_5COO)_6$ is non-polar $D_4^4 - P4_12_12$ (or $D_4^8 - P4_{3}2_{1}2$). However, one of the present authors (KG) recently revealed that Phase II and III of Ca₂Pb(C₂H₅COO)₈ are pyroelectric.⁸⁾ Very recently Takashige et al.9) found ferroelectric activity of Phase II of well annealed crystal of $Ca_2Pb(C_2H_5COO)_6$. 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 $Ca_2Sr(C_2H_5COO)_6$ and Ca_2Pb $(C_2H_5COO)_6$ 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