



## Effect of Hydrostatic Pressure on the Phase Transitions in $K_2ZnCl_4$

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(Received October 27, 1983)

Effect of hydrostatic pressure on the normal(I)-incommensurate(II)-ferroelectric(III) phase transitions in  $K_2ZnCl_4$  was studied by differential thermal analysis and dielectric constant measurements. The I-II transition temperature (283°C at 0 GPa) increases with increasing pressure with a rate of 110 K GPa<sup>-1</sup>. The II-III transition temperature (the ferroelectric Curie temperature: 127°C at 0 GPa) decreases with an initial slope of -86.2 K GPa<sup>-1</sup> as pressure increases. The results were compared with previously reported pressure effects of other  $K_2SeO_4$ -group ferroelectrics.

Potassium tetrachlorozincate  $K_2ZnCl_4$  is a member of the  $K_2SeO_4$ -group ferroelectrics. Above room temperature it has two phase transitions at about 280°C and 130°C.<sup>1,2)</sup> The highest temperature phase (phase I) belongs to the normal structure of  $\beta$ - $K_2SO_4$  type with the space group of  $Pmcn$ .<sup>3)</sup> The intermediate phase (phase II) shows an incommensurate lattice modulation along the pseudo-hexagonal  $c$ -direction with the wave number of  $q_z \sim (1/3)c_0^*$ , where  $c_0^*$  denotes the reciprocal lattice parameter in phase I. The room temperature phase of III is ferroelectric along the  $a$ -direction (space group  $P2_1cn$ ).<sup>2)</sup> The ferroelectric structure is caused by locking-in of the incommensurate wave number at the commensurate value of  $(1/3)c_0^*$ .<sup>2)</sup> Such a series of normal-incommensurate-ferroelectric phase transitions was first observed in  $K_2SeO_4$ ,<sup>4)</sup> and then in  $Rb_2ZnBr_4$ ,<sup>5)</sup> and  $Rb_2ZnCl_4$ .<sup>2)</sup> The phase transitions in these compounds have attracted much interest, and many works have been done on the physical properties accompanied with them. Relatively little, however, seems to be known about the effects of external stresses. This letter reports the hydrostatic pressure effects on the phase transitions in  $K_2ZnCl_4$ . The results are compared with those of other  $K_2SeO_4$ -group ferroelectrics reported so far.

Single crystals of  $K_2ZnCl_4$  were prepared by slow evaporation of aqueous solution which contained an excess of  $ZnCl_2$ . The pressure effect on the I-II transition was

studied by differential thermal analysis (DTA). A thermocouple pile consisting of four pairs of chromel-constantan wires of 0.12 mm  $\phi$  was served for the detection of the DTA signal. Single crystals of  $K_2ZnCl_4$  (about 600 mg in weight) and LiF (about 300 mg) were used as the specimen and reference material for DTA measurements. Typical temperature changing rate was about 0.6 K s<sup>-1</sup>. The pressure effect on the ferroelectric Curie temperature (II-III transition) was studied by measurements of dielectric constant. The specimens used for the dielectric measurements were of  $a$ -plates with the dimension of 10 mm<sup>2</sup>  $\times$  0.7 mm. Since as grown crystals often showed a broad and small peak of dielectric constant at the Curie temperature probably due to certain imperfections included,<sup>1,3)</sup> the specimens were annealed at 300°C for 13 hours in vacuum prior to measurements. Carbon paste, Dotite XC-12, was attached on the specimen surface as the electrode. The dielectric constant was measured with an LCR-meter, YHP 4275A, at 1 MHz. The high pressure bomb used was an inner-furnace type one possessing seven electrical lead plugs. Silicone oils of Toshiba TSF 331 and TSF 333 were used as the pressure-transmitting fluids for the dielectric ( $T \lesssim 150^\circ\text{C}$ ) and DTA ( $T \gtrsim 250^\circ\text{C}$ ) measurements, respectively. Temperature and pressure were respectively measured with a chromel-alumel thermocouple and a manganin gauge.

Figure 1 indicates the temperature dependence of the dielectric constant along the  $a$ -

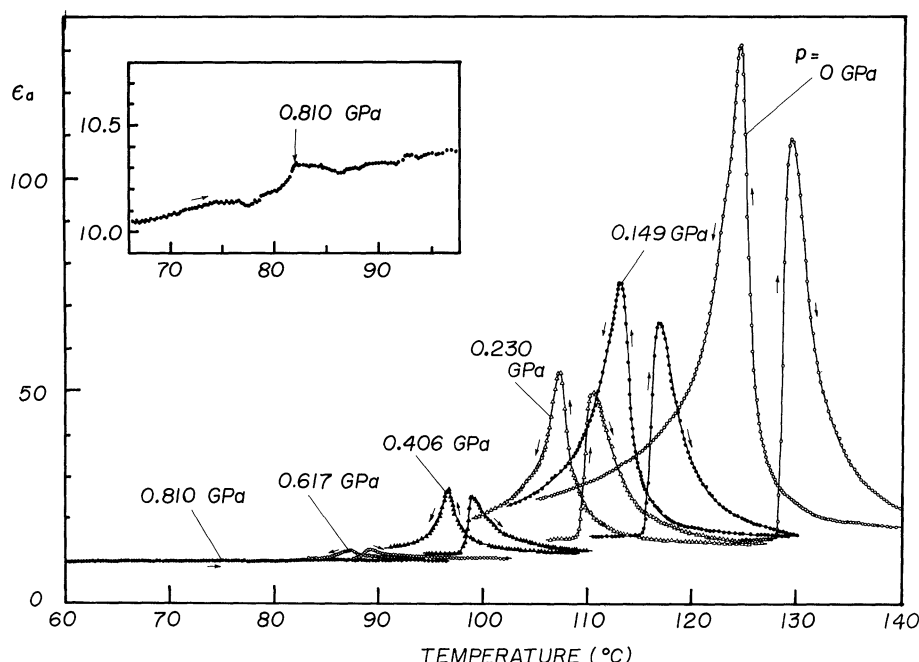


Fig. 1. Temperature dependence of the dielectric constant along the  $a$ -direction of  $K_2ZnCl_4$ ,  $\epsilon_a$ , at various hydrostatic pressures. Frequency: 1 MHz.

direction at various hydrostatic pressures. At 0 GPa, the dielectric constant shows a  $\lambda$ -type peak at the Curie temperature with the peak value of 110~140. The Curie temperature shows a thermal hysteresis of about 5 K during heating and cooling processes. As pressure increases the Curie temperature monotonically decreases accompanied with a marked depression of the dielectric constant peak. Finally at 0.81 GPa the dielectric constant anomaly becomes only a slight break on the dielectric constant vs temperature curve as shown in the inset of Fig. 1. However, the initial value of dielectric constant peak was recovered when pressure was removed. So that, the depression should not be caused by structural damages induced by high-pressure application.

Figure 2 shows the DTA anomaly at the I-II transition at a hydrostatic pressure of 0.308 GPa. A thermal anomaly is seen at the I-II transition temperature as indicated by an arrow. Taking into account possible temperature lag between the specimen and the thermocouple, we determine the I-II transition temperature as the average of the anomaly

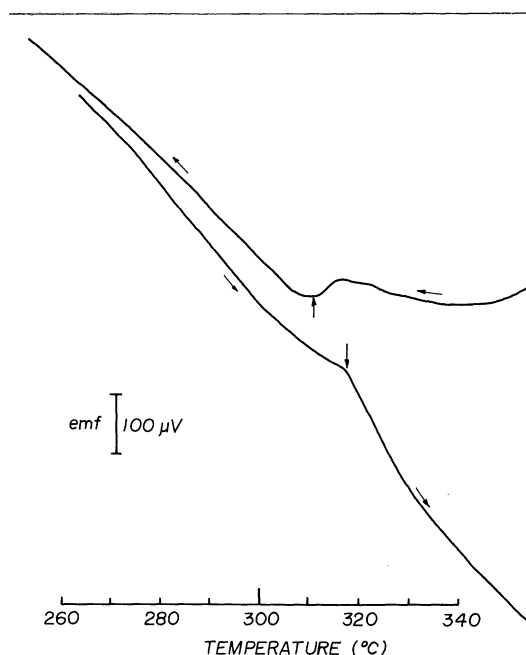


Fig. 2. DTA anomaly at the I-II transition in  $K_2ZnCl_4$  at 0.308 GPa.

temperatures observed on heating and cooling runs.

In Fig. 3, the observed pressure-temperature

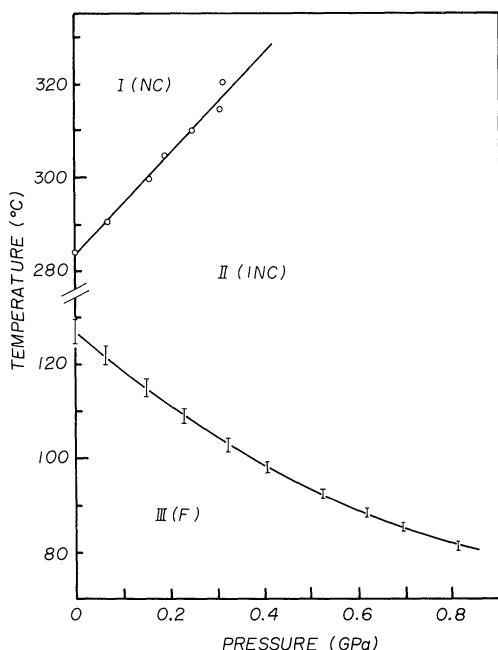


Fig. 3. Pressure-temperature phase diagram of  $\text{K}_2\text{ZnCl}_4$ . NC, INC, F denote the normal, incommensurate, and ferroelectric phases, respectively. Thermal hysteresis of II-III transition is represented by vertical bars.

phase diagram of  $\text{K}_2\text{ZnCl}_4$  is shown. The I-II transition temperature at 0 GPa is  $283 \pm 2^\circ\text{C}$ . It increases nearly linearly with increasing pressure with a slope of  $110 \pm 10 \text{ K GPa}^{-1}$ . On the other hand, the Curie temperature (II-III transition temperature) decreases as pressure increases. In Fig. 3, the thermal hysteresis of the Curie temperature is represented by short vertical bars. We assume the Curie temperature  $T_c$  in thermal equilibrium as the middle point of the thermal hysteresis bar. Then, the relation between  $T_c$  and pressure  $p$  is well represented by a quadric function of  $T_c = T_c^0 + Kp + \gamma p^2$  with the parameters of  $T_c^0 = 127 \pm 0.2^\circ\text{C}$ ,  $K = -(86.2 \pm 0.9) \text{ K GPa}^{-1}$ , and  $\gamma = (3.7 \pm 0.1) \times 10 \text{ K GPa}^{-2}$  as is shown by a thick curve in Fig. 3.

We can estimate the specific heat anomaly at the I-II transition of  $\text{K}_2\text{ZnCl}_4$  from thermal expansion data and pressure coefficient of transition temperature  $dT_i/dp$  using the Ehrenfest relation of

$$dT_i/dp = (\Delta\alpha/\Delta C_p) \cdot (T_i/\rho), \quad (1)$$

where  $\Delta\alpha$  and  $\Delta C_p$  are changes in the volume

thermal expansion coefficient and the specific heat at constant pressure at the transition, respectively,  $\rho$  the density. Kucharczuk *et al.*<sup>3)</sup> recently gave the volume thermal expansion coefficients of  $\text{K}_2\text{ZnCl}_4$  as  $19 \times 10^{-5} \text{ K}^{-1}$  at  $297^\circ\text{C}$  and  $21.5 \times 10^{-5} \text{ K}^{-1}$  at  $297^\circ\text{C}$ , below and above the I-II transition temperature. Inserting their difference into  $\Delta\alpha$  in eq. (1) and using the value of  $dT_i/dp = 110 \text{ K GPa}^{-1}$ , we can get an estimation of  $\Delta C_p = -6 \text{ J mol}^{-1} \text{ K}^{-1}$  (the calculated density of  $\text{K}_2\text{ZnCl}_4$  is  $2.36 \times 10^3 \text{ kg m}^{-3}$ <sup>6)</sup>). The value is comparable with those observed for the normal-incommensurate phase transitions in  $\text{K}_2\text{SeO}_4$  ( $\Delta C_p = -8.5 \text{ J mol}^{-1} \text{ K}^{-1}$ <sup>7)</sup>) and  $\text{Rb}_2\text{ZnCl}_4$  ( $\Delta C_p \sim -10 \text{ J mol}^{-1} \text{ K}^{-1}$ <sup>8)</sup>).

The pressure-temperature phase diagrams of the  $\text{K}_2\text{SeO}_4$ -group ferroelectrics were reported for  $\text{K}_2\text{SeO}_4$ <sup>9-11)</sup> and  $\text{Rb}_2\text{ZnCl}_4$ .<sup>12)</sup> The initial pressure coefficient of the Curie temperature of  $-86.2 \text{ K GPa}^{-1}$  in  $\text{K}_2\text{ZnCl}_4$  obtained in this work is comparable with  $-96.0 \text{ K GPa}^{-1}$  in  $\text{K}_2\text{SeO}_4$ <sup>11)</sup> and  $-48 \text{ K GPa}^{-1}$  in  $\text{Rb}_2\text{ZnCl}_4$ .<sup>12)</sup> Our preliminary study on  $\text{Rb}_2\text{ZnBr}_4$  showed that the Curie temperature of  $\text{Rb}_2\text{ZnBr}_4$  also decreases with increasing pressure with a little smaller rate of about  $-10 \text{ K GPa}^{-1}$ . So that, in all these  $\text{K}_2\text{SeO}_4$ -group ferroelectrics the Curie temperatures have negative pressure coefficients. On the other hand, the normal-incommensurate phase transition of I-II shows different pressure dependence among the  $\text{K}_2\text{SeO}_4$ -group compounds; namely, as pressure increases the I-II transition temperature decreases in  $\text{K}_2\text{SeO}_4$  with a rate of  $-65.5 \text{ K GPa}^{-1}$ ,<sup>11)</sup> while it increases in  $\text{K}_2\text{ZnCl}_4$ ,  $\text{Rb}_2\text{ZnCl}_4$ , and  $\text{Rb}_2\text{ZnBr}_4$ .\* Up to date clear soft phonon behavior in phase I has been observed only for  $\text{K}_2\text{SeO}_4$  by neutron scattering.<sup>4)</sup> The fact indicates displacive nature of the I-II transition in  $\text{K}_2\text{SeO}_4$ . On the other hand, in  $\text{Rb}_2\text{ZnBr}_4$  and  $\text{Rb}_2\text{ZnCl}_4$  soft phonons have not been confirmed above the I-II transition,<sup>13-15)</sup> instead diffuse scattering develops as temperature approaches to the I-II transition suggesting that the transitions in these Rb-

\* Preliminary measurements showed that the pressure coefficients of the I-II transition temperatures are about  $+59 \text{ K GPa}^{-1}$  and  $+3.5 \text{ K GPa}^{-1}$  in  $\text{Rb}_2\text{ZnBr}_4$  and  $\text{Rb}_2\text{ZnCl}_4$ , respectively.

compounds are rather of order-disorder type in nature. Samara<sup>16)</sup> pointed out that the displacive type ferroelectrics usually show negative pressure coefficients of the Curie temperature while the order-disorder type ones positive. The negative pressure coefficient of the I-II transition in  $\text{K}_2\text{SeO}_4$ , therefore, would relate to the displacive nature of the transition. Neutron inelastic scattering study will provide an answer to the question whether or not the large positive pressure coefficient really corresponds to the order-disorder character of the I-II transition in  $\text{K}_2\text{ZnCl}_4$ .

The marked depression of the dielectric constant peak at the Curie temperature is a characteristic pressure effect on  $\text{K}_2\text{ZnCl}_4$ . It should be noted that there is a similarity between the effects of hydrostatic pressure and of impurity on the dielectric properties around the Curie temperature of  $\text{K}_2\text{ZnCl}_4$ . Hamano *et al.*<sup>17)</sup> found that addition of  $\text{Rb}_2\text{ZnCl}_4$  as an impurity to  $\text{K}_2\text{ZnCl}_4$  markedly lowers the Curie temperature accompanied with depression of the dielectric constant peak. The specimen which contains only about 1.4 mol% of  $\text{Rb}_2\text{ZnCl}_4$  does not show a peak of dielectric constant at the Curie temperature, but there is a break on the dielectric constant vs temperature curve alike to the application of hydrostatic pressure of  $\sim 0.8$  GPa as shown in Fig. 1. These results suggest that both hydrostatic pressure and impurity such as  $\text{Rb}_2\text{ZnCl}_4$  prevent the incommensurate wave number from locking-in at the commensurate value of  $(1/3)c_0^*$ . Hamano *et al.*<sup>17)</sup> interpreted the impurity effect by assuming pinning of the incommensurate wave by impurities. On the other hand, the reduction of locking-in energy by pressure is probably caused by change in relative strength of short-range and long-

range interactions of dipole units through the reduction of lattice parameters.

### Acknowledgement

The author thanks Dr. K. Ozawa for his help in operation of high pressure instruments.

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