Pressure Effect on Phase Transition in Partially Deuterated $Cs(H_{1-x}D_x)_2PO_4$

Eisuke MAGOME^{*}, Satoshi TOMIOKA, Yusuke TAO, and Masaru KOMUKAE

Department of Applied Physics, Faculty of Science, Tokyo University of Science, Shinjuku, Tokyo 162-8601, Japan (Received November 16, 2009; accepted December 28, 2009; published February 10, 2010)

KEYWORDS: CsH₂PO₄, phase transition, pressure effect, dielectric constant, isotope effect DOI: 10.1143/JPSJ.79.025002

Hydrogen-bonded compounds, in which the hydrogen bonds are relatively weak intermolecular interactions, exhibit many unusual and important properties. Modification of the molecular potential by the application of a hydrostatic pressure changes the physical properties of a compound. Consequently, there has been great interest in hydrogenbonded ferroelectric and antiferroelectric crystals, particularly on studying the hydrostatic pressure effect in them. In AH_2BO_4 -type crystals [A = K, Rb, Cs, Tl, NH₄, (CH₃)₂NH₂; B = P, As], which constitute a large and important group of hydrogen-bonded ferroelectrics, the transition temperature $T_{\rm C}$ increases considerably on deuteration, indicating that the hydrogen bonds in these crystals play an important role in the phase transition. The crystals of KH₂PO₄, RbH₂PO₄, and NH₄H₂PO₄ belong to the tetragonal system, whereas the crystals of $C_{sH_2}PO_4$, $T_1H_2PO_4$, and $(CH_3)_2NH_2H_2PO_4$ belong to the monoclinic system. The tetragonal and monoclinic AH₂BO₄-type crystals have extremely different physical properties associated with the phase transition. Experimental results on the effects of hydrostatic pressure on the crystals of KH₂PO₄, RbH₂PO₄, and NH₄H₂PO₄ have shown large isotope effects on both the transition temperature and the pressure derivatives of the transition temperature dT_C/dp .¹⁻³⁾ As an example, the values of dT_C/dp are -46 and -25 K/GPa for KH₂PO₄ and KD₂PO₄, respectively.⁴⁾ Thus, the pressure derivative of the transition temperature of KH₂PO₄ decreases by about 50% on deuteration. However, Yasuda et al. have reported that the values of $dT_{\rm C}/dp$ for both undeuterated and deuterated CsH₂PO₄ crystals are the same, being -85 K/GPa.⁵⁾ On the other hand, Gesi *et al.* have reported that the values of dT_C/dp for undeuterated and deuterated CsH₂PO₄ crystals are -56 and -85 K/GPa, respectively.⁶⁾ These two results appear to be contradictory. It is interesting to consider whether the lack of an isotope effect on dT_C/dp is an intrinsic characteristic of CsH₂PO₄, in contrast with KH₂PO₄, RbH₂PO₄, and NH₄H₂PO₄. It is, therefore, necessary to investigate the effect of hydrostatic pressure on the transition temperature of $C_{s}(H_{1-x}D_{x})_{2}PO_{4}$ with deuterium concentration x.

Crystals of CsH_2PO_4 were grown by a slow evaporation method from an aqueous solution containing Cs_2CO_3 and H_3PO_4 in a molar ratio of 1 : 2. Partially deuterated $Cs(H_{1-x}D_x)_2PO_4$ crystals were grown from a H_2O and D_2O solution of CsH_2PO_4 . Single crystals of a solid solution



Fig. 1. Temperature dependence of the dielectric constant along the *b*-axis of CDP measured at 15.8 kHz. The vertical arrows indicate ferroelectric transitions and the values indicate the hydrostatic pressures at $T_{\rm C}$.

were grown by a slow evaporation method after performing recrystallization several times in order to obtain single crystals with the desired deuterium concentration. Measurement of the dielectric constants of CsH₂PO₄, $Cs(H_{0.78}D_{0.22})_2PO_4$, and $Cs(H_{0.15}D_{0.85})_2PO_4$ (abbreviated as CDP, 22%d-CDP, and 85%d-CDP, respectively) under a hydrostatic pressure was carried out along the *b*-axis with an LCR meter (HP4284A) at a frequency of 15.8 kHz. A Cu-Be high-pressure vessel containing Fluorinate as the pressure transmitting fluid was used to apply hydrostatic pressures to the sample. The value of pressure was obtained using a calibrated Manganin resistance gauge during the measurement. The temperature of sample was measured with a copper-constantan thermocouple placed near the sample, which was surrounded by the Manganin resistance gauge. The samples were about $2 \times 2 \text{ mm}^2$ in area and about 1 mm thick, and silver paste was used as electrodes. The sample temperature was changed at a rate of 0.25 K/min.

Figure 1 shows the temperature dependence of the dielectric constant measured for CDP during heating at various pressures below 0.24 GPa. The dielectric constant shows a maximum at the transition temperature. The transition temperature decreases monotonically with increasing pressure. The pressure within the vessel diminishes at a rate of about $1.08 \times 10^{-3} \,\text{GPa/K}$ with decreasing temperature. The vertical arrows in Fig. 1 indicate the transition temperatures under various hydrostatic pressures and the values indicate the hydrostatic pressures at the transition temperatures. The effect of pressure on the ferroelectric transition temperatures of 22%d-CDP and 85%d-CDP was also measured at various pressures, in order to compare with the results for CDP shown in Fig. 1. The transition temperatures of both 22%d-CDP and 85%d-CDP decrease monotonically with increasing pressure, as shown in Fig. 2. The hydrostatic pressure dependences of the transition temperature of CDP, 22%d-CDP, and 85%d-CDP are shown in Fig. 3. The plots in Fig. 3 indicate the results obtained from Figs. 1 and 2. The transition temperatures of CDP, 22%d-CDP, and 85%d-CDP are 156, 180, and 253 K at atmospheric pressure, respectively. The obtained transition temperatures agree well with those reported by Deguchi et al.⁷⁾ This result indicates a

^{*}E-mail: magome@rs.kagu.tus.ac.jp



Fig. 2. Temperature dependence of the dielectric constants along the *b*-axis of 22%d-CDP and 85%d-CDP measured at 15.8 kHz. The vertical arrows indicate ferroelectric transitions and the values indicate the hydrostatic pressure at $T_{\rm C}$.

relatively large isotope effect on the transition temperature, which is well known. The transition temperatures generally decrease almost linearly with increasing pressure. The transition temperatures at high pressures, however, deviate somewhat from linearity with decreasing deuterium concentration. The obtained results are in good agreement with the lines that represent the expansion equations obtained by a least-squares method. The transition temperature $T_{\rm C}$ of CDP can be well described by the expression $T_{\rm C} = -200p^2 - 100p^2$ 68p + 156, where p denotes pressure. The value of dT_C/dp near zero pressure was estimated to be -68 ± 11 K/GPa for CDP. In a similar way to CDP, the values of dT_C/dp near zero pressure for 22%d-CDP and 85%d-CDP were estimated to be -67 ± 8 and -67 ± 2 K/GPa by using $T_{\rm C} =$ $-130p^2 - 67p + 180$ and $T_{\rm C} = -35p^2 - 67p + 253$, respectively. In order to assess the isotope effect on dT_C/dp , it is convenient to introduce the ratio $\xi = (dT_C^D/dp)/(dT_C^H/dp)$, where T_C^H and T_C^D represent the transition temperatures of undeuterated and deuterated crystals, re-



Fig. 3. Pressure dependence of the ferroelectric transition temperatures T_C for CDP, 22%d-CDP, and 85%d-CDP.

spectively. In tetragonal AH₂BO₄-type crystals, the ratios for KH_2PO_4 and $NH_4H_2PO_4$ are 0.54 and 0.41, respectively.⁴⁾ These ratios mean that dT_C/dp is considerably affected by deuteration in the tetragonal AH₂BO₄-type crystals. From the present investigation, the ratio was estimated to be $0.99 \cong 1$ for CDP. The ratio $\xi \cong 1$ in the case of CDP is a striking contrast to the results for tetragonal AH₂BO₄-type crystals. CDP crystals show a lack of an isotope effect on dT_C/dp . The obtained results are consistent with those for (CH₃)₂- $NH_2H_2BO_4$ (B = P, As) crystals belonging to the monoclinic system in AH₂BO₄-type crystals.^{8,9)} The deuteration effect on dT_C/dp in the tetragonal AH_2BO_4 -type crystals is large, but it is hardly observed in the monoclinic AH₂BO₄type crystals. The reason for this difference in the effects of deuteration on dT_C/dp for tetragonal and monoclinic AH₂BO₄-type crystals is not clear. Therefore, in order to clarify the origin of the isotope effect on $T_{\rm C}$ and $dT_{\rm C}/dp$ in AH₂BO₄-type crystals, it is necessary to investigate differences in the hydrogen bonds and changes in crystal structure caused by applying hydrostatic pressure to tetragonal and monoclinic AH₂BO₄-type crystals.

- 1) G. A. Samara: Ferroelectrics 7 (1974) 221.
- 2) P. S. Peercy and G. A. Samara: Phys. Rev. B 8 (1973) 2033.
- 3) G. A. Samara: Phys. Rev. Lett. 27 (1971) 103.
- 4) G. A. Samara: Ferroelectrics 20 (1978) 87.
- N. Yasuda, S. Fujimoto, M. Okamoto, H. Shimizu, K. Yoshino, and Y. Inuishi: Phys. Rev. B 20 (1979) 2755.
- 6) K. Gesi and K. Ozawa: Jpn. J. Appl. Phys. 17 (1978) 435.
- K. Deguchi, E. Okaue, and E. Nakamura: J. Phys. Soc. Jpn. 51 (1982) 3569.
- T. Yamada, J. Hatori, F. Shikanai, M. Komukae, and T. Osaka: J. Phys. Soc. Jpn. 69 (2000) 288.
- T. Yamada, F. Shikanai, J. Hatori, M. Komukae, and T. Osaka: J. Phys. Soc. Jpn. 68 (1999) 3911.