Effects of hydrostatic pressure on the paraelectric - ferroelectric phase transition in deuterated glycinium phosphite crystals

LETTER TO THE EDITOR

Effects of hydrostatic pressure on the paraelectric–ferroelectric phase transition in deuterated glycinium phosphite crystals

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Abstract. The dielectric properties of the deuterated glycinium phosphite crystal were investigated under hydrostatic pressures up to 7 kbar. The paraelectric–ferroelectric phase transition temperature T_c^D decreases linearly with $dT_c^D/dp = -5.0\,°C\ kbar^{-1}$ with increasing hydrostatic pressure p. Pressure effects on its dielectric properties are due to the shift of T_c^D with pressure. A large isotope effect on the pressure coefficient of the ferroelectric transition temperature dT_c/dp as well as on the transition temperature was observed.

The glycine phosphite ((NH_3CH_2COOH)H_3PO_3, abbreviated as GPI) crystal exhibits a second-order paraelectric–ferroelectric transition at $-49.3\,°C$ ($= T_c^H$) at atmospheric pressure [1, 2]. GPI belongs to the space group $P2_1/a$ in a monoclinic system at room temperature [3]. The GPI compound is a representative hydrogen-bonded ferroelectric crystal characterized by infinite chains of hydrogen-bonded phosphite anions which are directed along the crystallographic c-axis perpendicular to the ferroelectric b-axis [1–3]. There is a large isotope effect on the transition temperature by substitution of deuterium for hydrogen [2, 4]. The transition temperature of deuterated GPI (abbreviated as DGPI), T_c^D, is $49\,°C$ at atmospheric pressure [2, 4]. The ratio of T_c^D/T_c^H is 1.44. Since the hydrogen bond is one of the mechanically weakest bonds in the crystal, the application of hydrostatic pressure to GPI and DGPI crystals is expected to significantly influence their ferroelectric phase transition. The transition temperature in GPI has recently been reported to decrease with increasing pressure with a slope $dT_c^H/dp = -11.0\,°C\ kbar^{-1}$ [5]. Both the strong isotope effect on T_c and the large negative sign of the pressure coefficient of T_c, dT_c/dp, indicate the essential role of the strong interphosphite hydrogen bonds in the paraelectric–ferroelectric phase transition mechanism of the GPI crystals [4, 5]. Two kinds of symmetrical hydrogen bond with a double potential well for protons exist in this crystal. Ordering of protons could be expected below T_c [1–3]. Betaine phosphite (BPI) consists of chains of hydrogen-bonded tetrahedra along the ferroelectric b-axis [6]. In BPI, the hydrogen-bonded chains of phosphite groups are parallel to the ferroelectric axis [6], $T_c^D/T_c^H = 1.43$, and $dT_c^H/dp = -11.8\,°C\ kbar^{-1}$ [7]. In KH_2PO_4 (KDP), the hydrogen-bonded chains are perpendicular to the ferroelectric c-axis [8], $T_c^D/T_c^H = 1.80$ [9], and $dT_c^H/dp = -4.6\,°C\ kbar^{-1}$ [10]. In CsH_2PO_4 (CDP), the hydrogen-bonded chains are parallel to the ferroelectric b-axis [11], $T_c^D/T_c^H = 1.71$ [12], and $dT_c^H/dp = -8.5\,°C\ kbar^{-1}$ [13]. Moreover, in KDP, there is a large isotope effect on
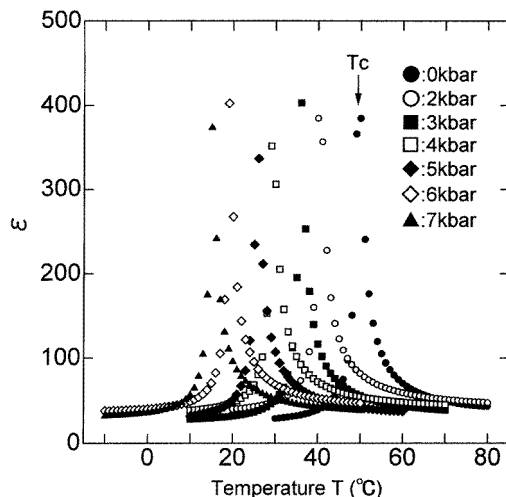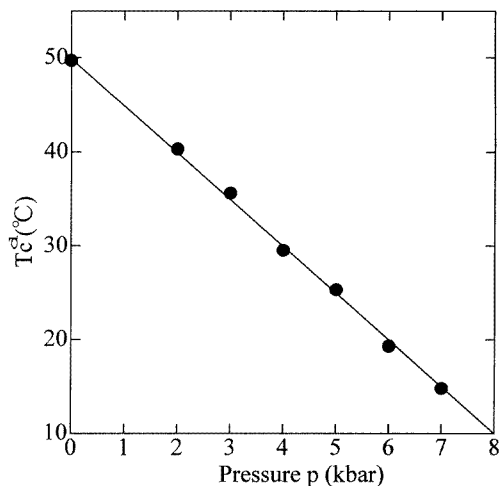
Figure 1. The temperature dependence of the relative permittivity ε at 1 kHz with different pressures along the b-axis of the DGPI crystal on heating.

dT_c/dp $(d_T^D c/dp = -2.5\,°\text{C kbar}^{-1})$ [14]. On the other hand, ferroelectric crystals formed with glycine are known: triglycine sulphate (TGS) [15], triglycine selenate (TGSe) [15] and triglycine fluoroberyllate (TGFB) [16], where the protons are ordered at all temperatures and the transitions are of the order–disorder type and second order, and the pressure coefficients of T_c^H in the TGS family are positive $(dT_c^H/dp = +2.6, +3.7,$ and $+2.5\,°\text{C kbar}^{-1}$ for TGS [15], TGSe [15], and TGFB [16], respectively).

In this letter, the hydrostatic pressure effects on the paraelectric–ferroelectric phase transition in DGPI are presented.

GPI crystals were grown from saturated water solutions of stoichiometric quantities of glycine and phosphorous acid by the slow evaporation method at 301 K [1]. The deuterated crystals were obtained from a solution in D_2O (99.8%) by the recrystallization method [2, 4]. The value of deuterium concentration was estimated to be more than 95% for the protons attached to nitrogen (NH_3) and oxygen (OH) atoms and $\sim$65% for the P–H bonds from the IR and Raman powder spectra [2, 4]. A plate perpendicular to the ferroelectric b-axis was cut out using a beryllium wire cutter from a single crystal. After being mirror polished with No 1500 Al_2O_3 powder, a specimen was painted with silver paste on its surfaces for electrodes. The electrical capacitance was measured at the frequency of 1 kHz within a field of 10 V cm^{-1} using an HP4275A *LCR* meter. A high-pressure vessel with 1:1 mixture of normal pentane and isopentane as a pressure transmitting fluid was used in order to apply the hydrostatic pressure to the specimen [17]. The pressure and the temperature were measured with Manganin gauges to an accuracy of $\pm$1.5% and within $\pm$0.1 K with a potentiometer with a calibrated alumel–chromel thermocouple set close to one of the electrodes, respectively. All the dielectric data were gathered with temperature varying at a rate of 0.5 K min^{-1} under various constant pressures. All the observed data are reversible on lowering pressure with good reproducibility.

Figure 1 shows the temperature dependence of the relative permittivity ε along the b-axis of the DGPI crystal at 1 kHz with different pressures. ε has a peak at the paraelectric–ferroelectric transition temperature T_c^D of 49.7 °C at atmospheric pressure. It was reported that the dielectric dispersion in the DGPI crystals was not observed up to 1 MHz for either

Figure 2. The pressure dependence of the paraelectric–ferroelectric phase transition temperature T_c^D of the DGPI crystal.
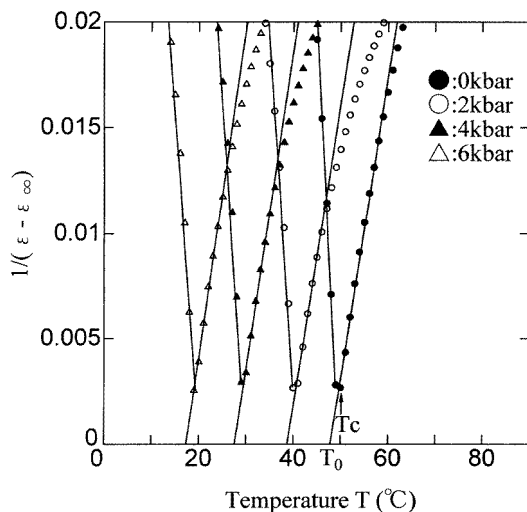
Figure 3. The temperature dependence of the reciprocal relative permittivity $1/(\varepsilon - \varepsilon_\infty)$ for different pressures at 1 kHz in the DGPI crystal on heating.

the paraelectric or the ferroelectric phase [4], whereas in the GPI crystals a low-frequency dispersion due to the domain wall motion was observed in the ferroelectric phase [1, 5]. With increasing hydrostatic pressure, the ε–T curve shifts towards lower temperatures. Pressure displaces the ferroelectric transition to lower temperatures. The shift of the Curie point (T_c^D) of DGPI with pressure is shown in figure 2. T_c^D decreases linearly with a slope of $dT_c^D/dp = -5.0\,°C$ kbar^{-1} with increasing pressure. This value of dT_c^D/dp is compared with $dT_c^H/dp = -11.0\,°C$ kbar^{-1} for GPI reported recently [5]. There is a large isotope effect on dT_c/dp. The temperature dependence of the reciprocal relative permittivity $1/\varepsilon$ along the b-axis in DGPI is shown for different pressures at 1 kHz in figure 3. The Curie–

Table 1. The Curie–Weiss temperature T_0, the temperature difference, $T_c^D - T_0$, between Curie temperature T_c^D and T_0, the Curie constants (C_+ and C_-) against pressure for DGPI.

Pressure (kbar)	T_0 (°C)	$T_c^D - T_0$ (K)	C_+ (K)	C_- (K)
0	47.9	1.8	684	277
2	38.7	1.6	666	263
3	34.2	1.4	647	275
4	27.7	1.7	666	280
5	23.7	1.6	639	268
6	17.5	1.8	643	282
7	13.0	1.8	627	285

Weiss law is well obeyed under various hydrostatic pressures. In a temperature range of about 10 K in the paraelectric phase above T_c, ε is well represented by the Curie–Weiss relationship of $\varepsilon = \varepsilon_\infty + C_+/(T - T_0)$, where C_+ is the Curie constant (below T_c^D, C_-), ε_∞ a constant (10), and T_0 the Curie–Weiss temperature. The values of T_0, the temperature difference, $T_c^D - T_0$, between T_c^D and T_0, and Curie constants C_+ and C_- are given against pressure in table 1. These values of T_c^D, T_0, ε_∞, C_+, and C_- are compared with $T_c^D = 49\,°C$, $T_0 = 47\,°C$, $\varepsilon_\infty = 10$, $C_+ = 705$ K, and $C_- = 265$ K reported previously [4]. The values of Curie constants ($C_+ = 684$ K, $C_- = 277$ K) are characteristic of ferroelectrics with the order–disorder type of phase transition and the value of the ratio of Curie constant above T_c^D to that below T_c^D, $C_+/C_- = 2.5$, is typical for ferroelectric crystals with a second-order transition, as pointed out previously [4]. Both Curie constants, C_+ and C_-, and the temperature difference, $T_c^D - T_0$, are found to be nearly independent of pressure. The main effect of pressure is to displace the Curie point to lower temperatures. Such behaviour of the ferroelectric phase transion with increasing hydrostatic pressure was also observed for GPI [5]. There are large isotope effects on both T_c and $\mathrm{d}T_c/\mathrm{d}p$ in GPI, as well known in KDP [9, 10, 14].

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