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LETTER TO THE EDITOR

Effects of hydrostatic pressure on the paraelectric–ferroelectric phase transition in glycine phosphite (Gly·H₃PO₃)

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Abstract. The dielectric properties of the Gly·H₃PO₃ crystal were investigated under hydrostatic pressure. Pressure effects on its dielectric properties are due to the shift of the paraelectric–ferroelectric transition temperature T_C with pressure. With increasing pressure p , T_C decreases greatly with $dT_C/dp = -11.0^\circ\text{C kbar}^{-1}$.

The glycine phosphite (Gly·H₃PO₃, abbreviated as GPI) crystal exhibits a paraelectric–ferroelectric transition at -49.3°C at atmospheric pressure [1]. GPI belongs to the space group $P2_1/a$ in a monoclinic system at room temperature [2]. The spontaneous polarization appears along the b -axis [1]. 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, 2]. Two kinds of symmetrical hydrogen bond with a double potential well for protons exist in this crystal. Ordering of protons could be expected below room temperature [1, 2]. Betaine phosphite (BPI) consists of chains of hydrogen-bonded tetrahedra along the ferroelectric b -axis [3]. The ferroelectric phase transition is connected with the ordering of protons in hydrogen-bonded phosphite anions. In BPI, the hydrogen-bonded chains of phosphite groups are parallel to the ferroelectric axis [3]. In KH₂PO₄ (KDP), the hydrogen-bonded chains are perpendicular to the ferroelectric c -axis [4]. In CsH₂PO₄ (CDP), the hydrogen-bonded chains are parallel to the ferroelectric b -axis [5]. On the other hand, the following ferroelectric crystals formed with glycine are known: betriglycine sulphate (TGS) [6], triglycine selenate (TGSe) [6] and triglycine-fluoberyllate (TGFB) [7], where the protons are ordered at all temperatures, and the transitions are of the order–disorder type and second order. Since the hydrogen bond is one of the mechanically weakest bonds in the crystal, the application of hydrostatic pressure to GPI crystals is expected to significantly influence its ferroelectric phase transition. It is well known that in KDP type ferroelectric crystals the pressure coefficients of the Curie temperature T_C are negative ($dT_C/dp = -4.6$ and $-8.5^\circ\text{C kbar}^{-1}$ for KDP [8] and CDP [9], respectively), whereas the pressure coefficients of T_C in the TGS family are positive ($dT_C/dp = +2.6$, $+3.7$ and $+2.5^\circ\text{C kbar}^{-1}$ for TGS [6], TGSe [6] and TGFB [7], respectively).

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

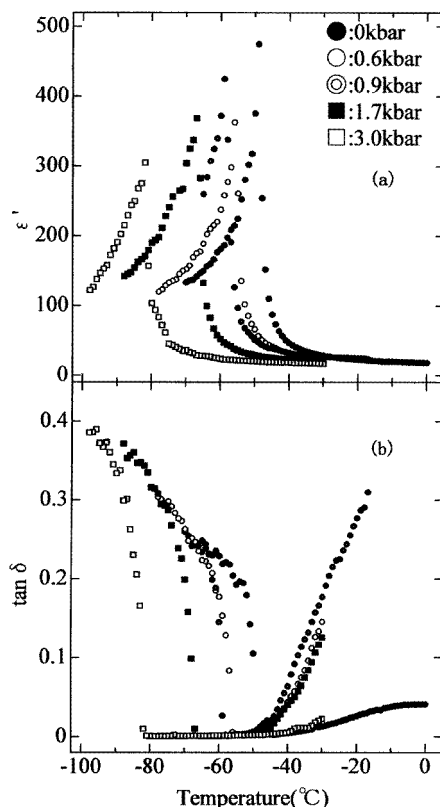


Figure 1. The temperature dependence of (a) the relative permittivity ϵ' and (b) the dielectric loss tangent $\tan \delta$ at 10 kHz with different pressures along the b -axis of the GPI crystal.

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]. A plate perpendicular to the ferroelectric b -axis was cut out by 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 and the dielectric loss tangent were measured at 10 kHz within a field of 10 V cm^{-1} using an HP4275A LCR meter. A Cu-Be high-pressure vessel with 1:1 mixture of normal and isopentane as a pressure transmitting fluid was used in order to apply the hydrostatic pressure to the specimen [10]. The pressure vessel was placed in a conventional low-temperature Dewar. The pressure was measured with Manganin gauges to an accuracy of $\pm 1.5\%$. The temperature was varied by positioning the vessel in the vapour above the liquid nitrogen in the Dewar. The temperature of the specimen was measured with a potentiometer with a calibrated Cu-constantan thermocouple set closely to one of the electrodes. All the dielectric data were gathered for temperature varying at a rate of 0.3 K min^{-1} under various constant pressures. All the observed data are reversible on lowering pressure with good reproducibility.

Figure 1(a) and (b) shows the temperature dependence of the relative permittivity ϵ' and the dielectric loss tangent $\tan \delta$ respectively at 10 kHz along the b -axis of the GPI crystal with different pressures. ϵ' has a peak at the ferroelectric transition temperature

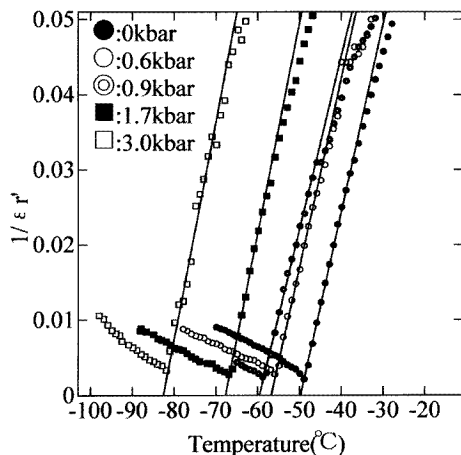


Figure 2. The temperature dependence of the reciprocal relative permittivity $1/\varepsilon'$ for different pressures at 10 kHz in the GPI crystal.

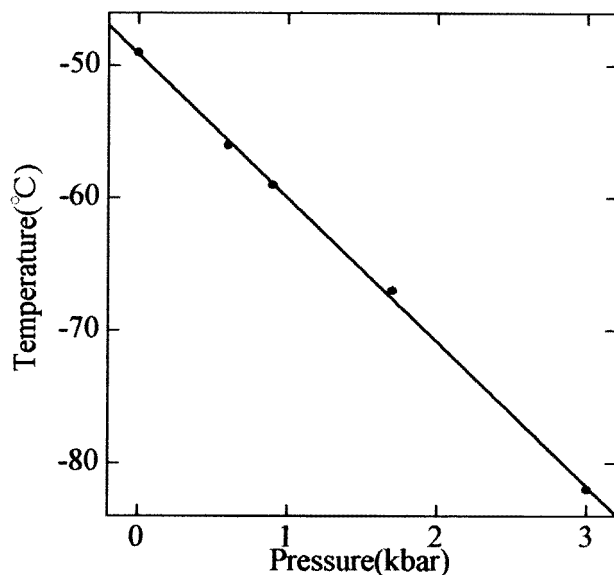


Figure 3. The pressure dependence of the paraelectric-ferroelectric phase transition temperature T_C of the GPI crystal.

T_C of -49.0°C at atmospheric pressure. In the paraelectric phase above T_C , ε' obeys the Curie-Weiss law: $\varepsilon' = \varepsilon'_0 + C/(T - T_0)$, where the Curie constant $C = 641$ K, a constant $\varepsilon'_0 = 6$, and the Curie-Weiss temperature $T_0 = -49.7^\circ\text{C}$. These values are compared with $C = 260$ K, $\varepsilon'_0 = 6.5$, and $T_0 = -48.45^\circ\text{C}$ reported previously [1]. With increasing hydrostatic pressure, the ε' and the $\tan\delta$ curves shift towards lower temperatures. The temperature dependence of the reciprocal relative permittivity $1/\varepsilon'$ is shown for different pressures at 10 kHz in figure 2. ε' obeys the Curie-Weiss law under hydrostatic pressures in the paraelectric phase. The values of T_0 , the temperature difference $T_C - T_0$, between T_0 and

Table 1. The Curie–Weiss temperature T_0 , the temperature difference, $T_C - T_0$, between Curie temperature T_C and T_0 , the Curie constant C against pressures for GPI.

Pressure (kbar)	T_0 ($^{\circ}\text{C}$)	$T_C - T_0$ (K)	C (K)
0	-49.7	0.74	641
0.6	-56.8	0.76	478
0.9	-59.6	0.59	720
1.7	-67.7	0.70	527
3.0	-82.6	0.59	517

T_C , and Curie constant C are given against pressure in table 1. The paraelectric–ferroelectric phase transition temperature T_C decreases linearly with $dT_C/dp = -11.0^{\circ}\text{C kbar}^{-1}$ with increasing pressure, as shown in figure 3. The main effect of pressure is to displace the Curie point to lower temperatures. This large value of dT_C/dp for GPI is compared with $dT_C/dp = -11.8^{\circ}\text{C kbar}^{-1}$ reported for BPI [11]. There is a steep increase at T_C in the $\tan \delta - T$ curves in the ferroelectric phase. Such an increase in $\tan \delta$ in the ferroelectric phase is due to the domain wall motion. At higher pressures, a steeper increase in $\tan \delta$ is seen near T_C , due to the change in the domain wall motion with pressure. Such behaviour in $\tan \delta$ with increasing pressure in the ferroelectric phase has also been reported in BPI [11].

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