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## Effect of pressure on the ferroelectric properties of telluric acid ammonium phosphate

M N Shashikala, H L Bhat and P S Narayanan

Department of Physics, Indian Institute of Science, Bangalore-560012, India

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**Abstract.** Telluric acid ammonium phosphate (TAAP) is a new class-m ferroelectric with a transition temperature of 45 °C. Recent Raman spectroscopy studies of this crystal suggest that the phase transition takes place predominantly by the order–disorder nature of the hydrogen bonds of the type N—H—O. The hydrogen-bonded ferroelectrics are known to be very sensitive to external pressure and deuteration. In view of this, the effect of hydrostatic pressure on ferroelectric properties of TAAP has been studied up to 6 kbar. It was found that  $T_C$  shifts to lower temperatures under the influence of external pressure. At low pressures,  $T_C$  decreases more rapidly than at high pressures. The pressure derivative evaluated from the linear portion of the curve is  $-2.69$  °C kbar $^{-1}$ . The effect of pressure on the spontaneous polarisation is to reduce its value although the continuous nature of the transition does not undergo any change up to the maximum pressure employed. These results and the shift of  $T_C$  to higher temperature upon deuteration support the order–disorder nature of the hydrogen bonds during the phase transition.

### 1. Introduction

Monoclinic telluric acid ammonium phosphate (TAAP) having the chemical formula  $\text{Te}(\text{OH})_6 \cdot 2\text{NH}_4\text{H}_2\text{PO}_4 \cdot (\text{NH}_4)_2\text{HPO}_4$  belongs to a new class-m ferroelectric [1]. It undergoes a second-order phase transition with a Curie temperature of 45 °C [2]. The room-temperature crystal structure of TAAP shows that the crystal belongs to space group  $Pn$  with  $Z = 2$ . A plausible assumption is that the high-temperature phase of TAAP belongs to class 2/m. The crystal structure and the vibrational spectroscopy studies [3, 4] of TAAP reveal the presence of N—H—O type of hydrogen bonds. A detailed Raman spectroscopy study carried out by us on this crystal [5] across the phase transition has suggested that the phase transition occurs predominantly through an order–disorder nature of the hydrogen bonds. The properties of hydrogen-bonded ferroelectrics are generally very sensitive to external pressure, deuteration, etc. Such studies have made significant contributions to the understanding of the nature of the ferroelectric (FE) phenomena involved [6]. In the present paper we report the effect of pressure on the FE properties of TAAP up to 6 kbar.

### 2. Experimental details

Optical quality single crystals of TAAP were grown at room temperature (25 °C) by water evaporation from the aqueous solution of telluric acid, ammonium hydrogen phosphate and diammonium hydrogen phosphate mixed in the required proportions [7]. The dielectric measurements of the crystal were carried out at 10 kHz using HP 4275 model

multifrequency *LCR* meter. The data were fed to an IBM personal computer to plot the dielectric constant versus temperature. An EN24 steel piston–cylinder type of pressure cell with liquid paraffin as pressure-transmitting medium was used to apply the hydrostatic pressure [8]. The temperature of the crystal was measured using a copper–constantan thermocouple set close to the crystal. The pressure was calibrated with a manganin gauge to an accuracy of  $\pm 2\%$ . The dielectric data were collected while the temperature was varied at a rate of  $0.1\text{ }^{\circ}\text{C min}^{-1}$  at various constant pressures. The spontaneous polarisation was measured with a modified Sawyer–Tower circuit at 50 Hz. All measurements were carried out on (101) crystal plates with air-drying silver paste as electrodes.

### 3. Results and discussion

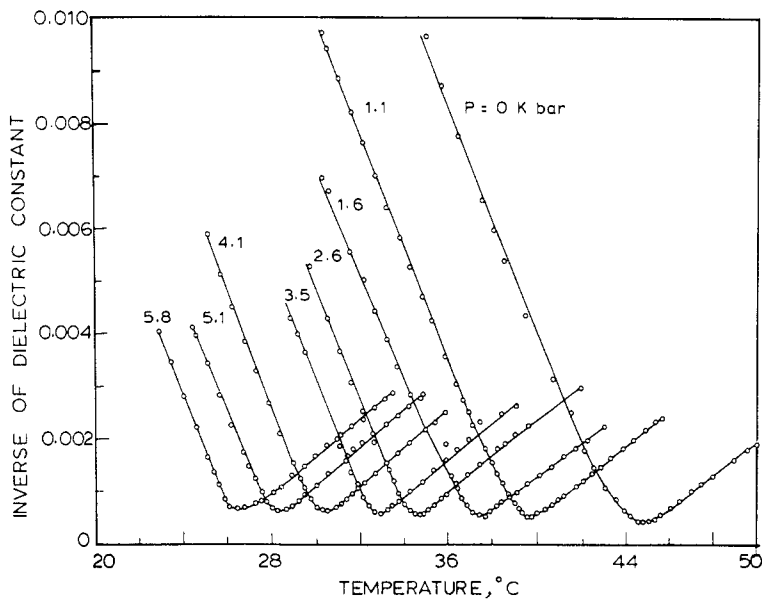
The temperature dependence of the dielectric constant measured at different pressures revealed that pressure displaces the whole dielectric constant curve to lower temperatures. Figure 1 shows the temperature dependence of the inverse of the dielectric constant for TAAP at different hydrostatic pressures. It can be seen that the Curie–Weiss law  $\epsilon = C^{(p)}/T - T_0^{(p)}$  is well obeyed in both paraelectric (PE) and FE phases over a wide range of temperatures at different pressures. Here the superscript (*p*) is introduced to emphasise that *C* and *T*<sub>0</sub> are functions of pressure.

Figure 2 shows the *p*–*T* phase diagram for TAAP. As can be seen, the transition temperature decreases with increasing pressure. Initially *T*<sub>C</sub> decreases rapidly even for small external pressures. However, as the external pressure increases, the transition temperature decreases less rapidly and is linear with pressure. The slope  $dT_C/dp$  evaluated from the linear part of curve is  $-2.69\text{ }^{\circ}\text{C kbar}^{-1}$ . This value is comparable with the pressure derivative of the transition temperature of well known hydrogen-bonded ferroelectrics KDP, ADP, etc [6].

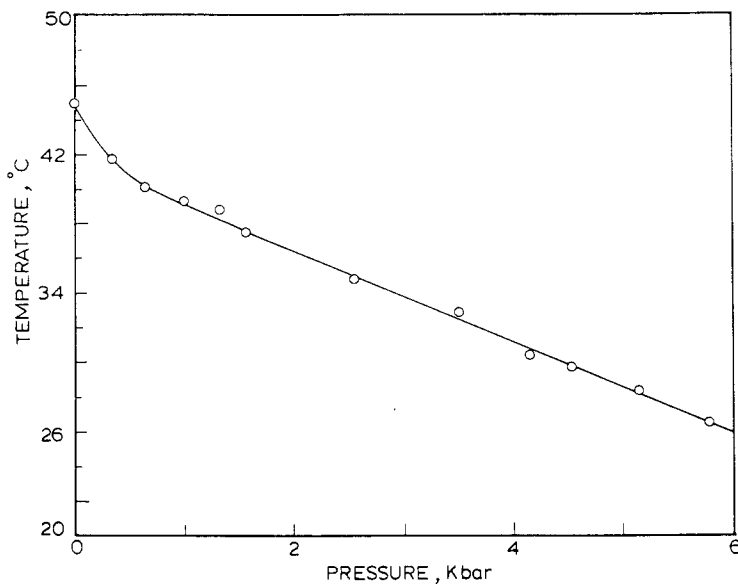
Haussuhl and Nicolau [9] have measured the variation in *T*<sub>C</sub> under the influence of hydrostatic pressure for TAAP by recording the pressure-induced shift of resonance frequencies of the pure longitudinal modes propagating in the direction [101]. They have measured the resonance frequencies at two fixed pressures, *p* = 0 and *p* = 1.58 kbar and reported a value of  $-3.8\text{ }^{\circ}\text{C kbar}^{-1}$  for the pressure derivative. From figure 2, one finds that the slightly higher value of  $dT_C/dp$  obtained by them may be due to the initial behaviour noticed by us.

Figure 3 shows the variation in spontaneous polarisation with temperature at different hydrostatic pressures. As can be seen from the figure the spontaneous polarisation decreases with increasing pressure. The continuous decrease in *P*<sub>s</sub> with increasing temperature reflects the second-order nature of the transition. Further, the persistence of spontaneous polarisation up to 6 kbar indicates that the nature of the transition continues to be of the second order until the maximum pressure that we have employed. The change in the value of *P*<sub>s</sub> with pressure at constant temperature is mostly associated with the shift of the Curie point. This is illustrated in figure 4 which shows five isobars of *P*<sub>s</sub> versus reduced temperature, *T* – *T*<sub>C</sub>, derived from figure 3. This shows that there is no pronounced change in the magnitude of *P*<sub>s</sub> with pressure. Similar behaviour has been observed for other ferroelectrics also [10, 11].

From the above experimental results, it can be established that the dielectric properties of TAAP obeys the predictions of the thermodynamic theory. In the case of second-order transitions, one needs to consider in the free-energy expansion only up to fourth power (to a good approximation) in the polarisation. Then, the free energy expressed



**Figure 1.** Variation in inverse  $1/\epsilon$  of dielectric constant with temperature at different pressures.



**Figure 2.** Hydrostatic pressure dependence of transition temperature of TAAP.

in terms of hydrostatic pressure  $p$ , polarisation  $P$  and temperature  $T$  is given by

$$A(p, P, T) = \Lambda p^2 + \frac{1}{2}(\gamma + \Omega p)P^2 + \frac{1}{4}\xi P^4. \tag{1}$$

Here  $\Lambda$  and  $\Omega$  are functions of elastic and electrostrictive constants, and coefficients  $\gamma$  and  $\xi$  are, in general, functions of temperature.

The above equation yields, for the dielectric constant in the PE phase,

$$\begin{aligned} (1/\epsilon)_{T > T_0^{(p)}} &= (1/4\pi)(\gamma + \Omega p) = (T - T_0^{(p)})/C^{(p)} \\ &= (T - T_0)/C^{(p)} + kp/C^{(p)} \end{aligned} \tag{2}$$

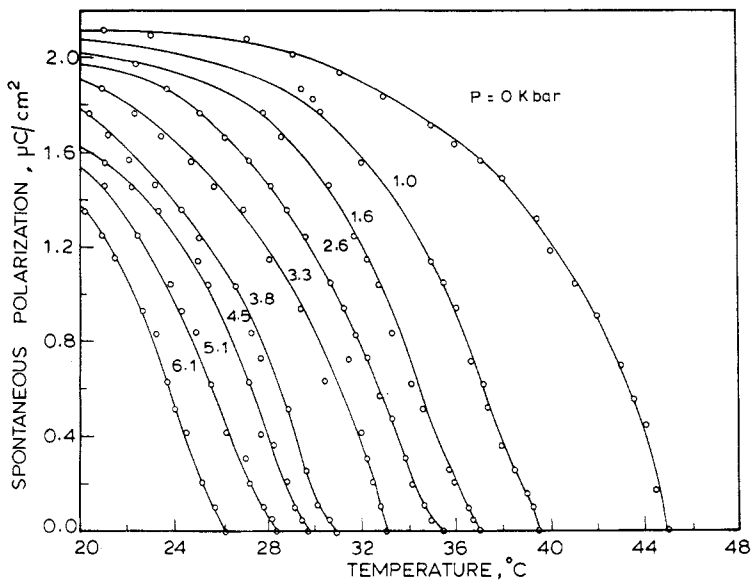


Figure 3. Spontaneous polarisation as a function of temperature at different pressures.

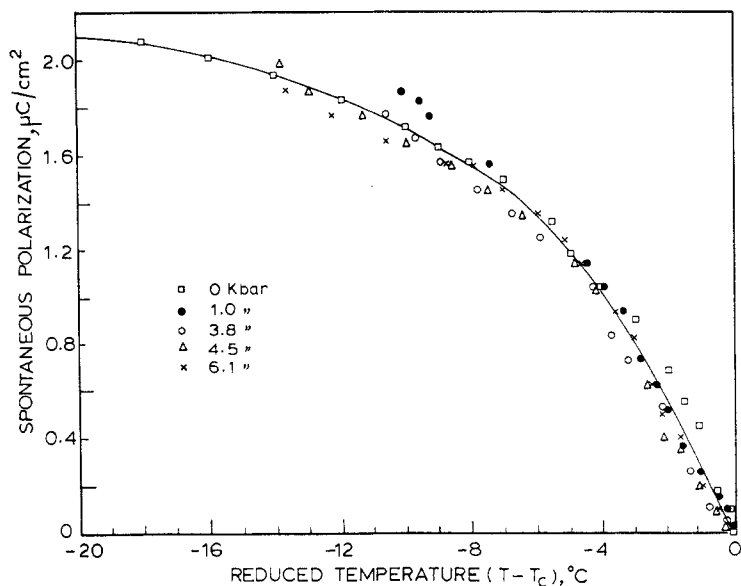
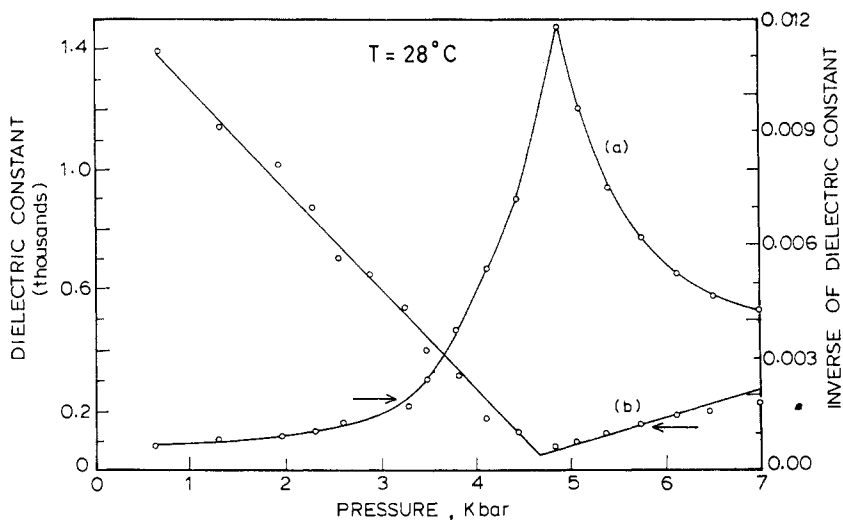
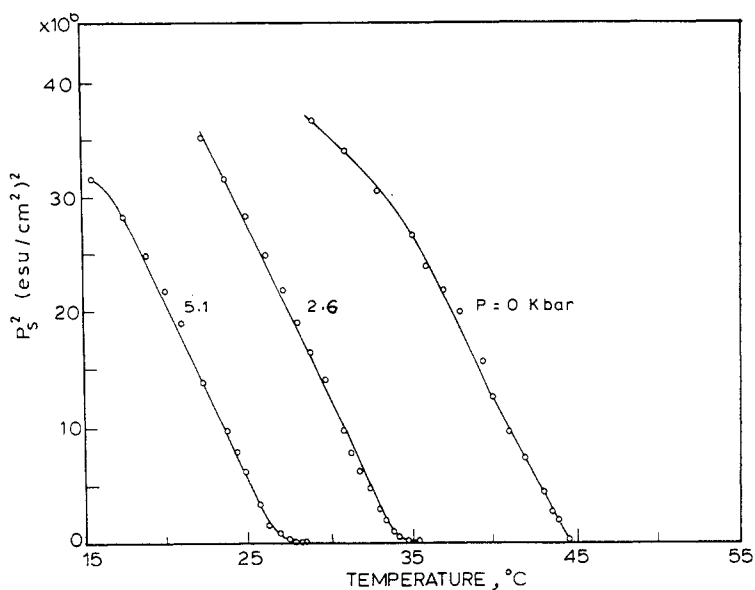


Figure 4. Spontaneous polarisation as a function of reduced temperature at different pressures  $p$ :  $\square$ , 0 kbar;  $\bullet$ , 1.0 kbar;  $\circ$ , 3.8 kbar;  $\Delta$ , 4.5 kbar;  $\times$ , 6.1 kbar.

(where  $T_0^{(p)} = T^0 - kp$ ). Here the last two equalities follow from the observed Curie-Weiss temperature dependence of  $\epsilon$  at constant pressure and the linear dependence of transition temperature on pressure. Since  $C^{(p)}$  is found to be pressure independent in the linear region of the  $p$ - $T$  phase diagram, at any given temperature, equation (2) indicates that  $1/\epsilon$  is a linear function of pressure with slope  $k/C$ . Figure 5 shows the plot of  $\epsilon$  versus pressure at a constant temperature. It can be seen that, in the PE phase,  $\epsilon$  obeys the relation  $\epsilon = C^*/p - p_0$  (at any given temperature,  $C^*$  and  $p_0$  are constants corresponding to  $C$  and  $T_0$ , respectively). Comparison of this with equation (2) shows



**Figure 5.** Variation in dielectric constant (curve A) and inverse of dielectric constant (curve B) with pressure at a constant temperature of 28 °C.



**Figure 6.** Variation in square of the spontaneous polarisation with temperature at different pressures.

that

$$k/C = 1/C^* \quad (3)$$

for TAAP,  $k = -2.69 \text{ }^\circ\text{C kbar}^{-1}$  and  $C = 3000 \text{ K}$ . The theoretical slope then is  $k/C = 8.96 \times 10^{-4} \text{ kbar}^{-1}$  close to the experimental value of  $7.5 \times 10^{-4} \text{ kbar}^{-1}$ .

From equations (1) and (2) it also follows that the spontaneous polarisation near  $T_C$  is given by

$$P_s^2 = -4\pi/C^p \xi [T - (T_0 - kp)] \quad (4)$$

With  $C^{(p)}$  independent of pressure and assuming that  $\xi$  is independent of temperature and pressure the above equation shows that  $P_s^2$  is a linear function of temperature at

constant pressure. Figure 6 shows the plot of  $P_s^2$  versus temperature for different pressures. It can be seen that  $P_s^2$  varies linearly with temperature close to transition temperature. It is found that the values of  $C$  and  $\xi$  nearly remain constant above 0.5 kbar, suggesting that the product  $C\xi$  remains constant at different pressures as predicted by the theory.

#### 4. Conclusions

The transition temperature of TAAP decreases significantly with increasing external pressure similar to the behaviour of the ferroelectrics in which the hydrogen bond plays an important role in the phase transition. The behaviour of dielectric properties at high pressures could be explained successfully using thermodynamic theory. As was mentioned earlier, the Raman spectroscopy studies of TAAP suggest that FE-PE transition occurs predominantly by the order-disorder nature of the hydrogen bonds. Further it has been observed that the deuteration of TAAP shifts the transition temperature from 318 K to 361 K, i.e.  $T_C^D/T_C^H = 1.13$  [12]. This type of behaviour is well known in hydrogen-bonded ferroelectrics such as KDP and LHS [13] wherein the deuteration causes a marked expansion of the hydrogen bond length by increasing the  $T_C$ . This effect is then opposite to that of the pressure effect wherein the bond length decreases. The negative sign of the pressure derivative obtained by us is consistent with this explanation. The mechanism of FE-PE transition in these crystals has been explained as due to the ordering of hydrogen atoms in the double-minimum potential well in the FE phase. On the basis of this model, the decrease in the Curie point with increasing pressure was explained to result from either a thermal activation of the protons across a lower barrier or an increase in the tunnelling probability of the protons through the lower and narrower barrier. Although the FE-PE transition in TAAP may not be exactly similar to the above-mentioned mechanism the present studies confirm that the phase transition in TAAP takes place by ordering of the hydrogen atoms in the FE phase.

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