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LETTER TO THE EDITOR

Ultrasonic velocity and attenuation in ferroelectric TAAP

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Abstract. The longitudinal ultrasonic velocity and attenuation in ferroelectric telluric acid ammonium phosphate (TAAP) along the direction perpendicular to the (101) face has been measured across the Curie temperature at 10, 30 and 50 MHz. A pronounced anomaly in ultrasonic attenuation is observed at 50 MHz near the Curie temperature. The ultrasonic velocity exhibits a slope variation at the transition temperature.

It was pointed out by Landau and Khalatnikov that an anomalous increase in ultrasonic attenuation should be observed in systems undergoing second-order phase transition, owing to an increase in the relaxation time of the order parameter near T_c (Landau and Khalatnikov 1954). This has been confirmed in a number of crystals undergoing ferroelectric phase transitions (Garland 1970, Nettleton 1970, Rehwald 1973). Our earlier dielectric measurements in ferroelectric telluric acid ammonium phosphate (TAAP; chemical formula: $Te(OH)_6 \cdot 2NH_4H_2PO_4 \cdot (NH_4)_2HPO_4$) in the region 10–400 kHz indicated an anomalous increase in the relaxation time near the Curie temperature (Shashikala *et al* 1990). Hence it was thought desirable to study the ultrasonic attenuation behaviour in TAAP across the phase transition. In this letter we present the results of our measurements of the temperature dependence of the velocity and attenuation of the longitudinal ultrasonic waves propagating along the direction perpendicular to the (101) face across the Curie temperature.

TAAP is a room-temperature ferroelectric with many of its physical properties comparable to that of TGS (Guilliott Gauthier *et al* 1984). It undergoes a second-order phase transition from monoclinic *Pn* to a non-polar phase at the Curie temperature of 45 °C. The spontaneous polarization lies in the (010) plane and shows a maximum along the direction perpendicular to the (101) face. Raman spectroscopic studies of this crystal suggest that the phase transition takes place predominantly through the order–disorder nature of the hydrogen bonds of the type N—H——O (Shashikala 1990).

Large single crystals of TAAP weighing up to 50 g were grown from solution employing a recirculation technique (Nicolau 1984). The specimen for ultrasonic measurements was of size $\simeq$10 mm × 10 mm × 10 mm. It was cut from the grown crystal with the natural {101} faces as the active surfaces. These faces were polished to give a smooth surface. X-cut quartz transducers of fundamental frequency 10 MHz were bonded to {101} opposite faces using stopcock grease (Nonaq, Fisher Scientific Co.). The specimen

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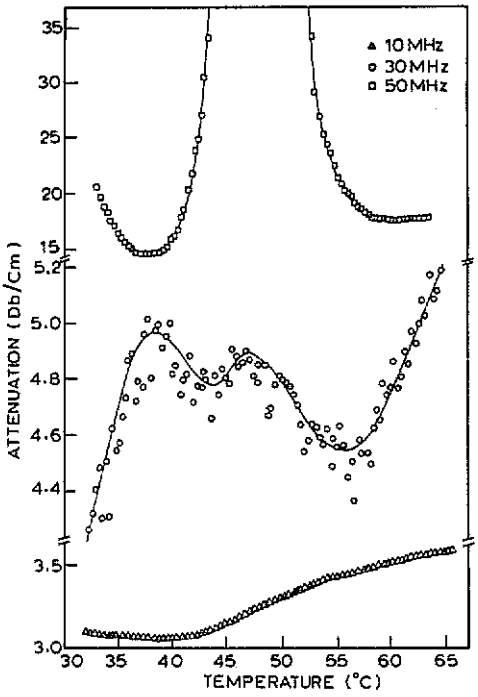

Figure 1. Ultrasonic velocity as a function of temperature at 10, 30 and 50 MHz.

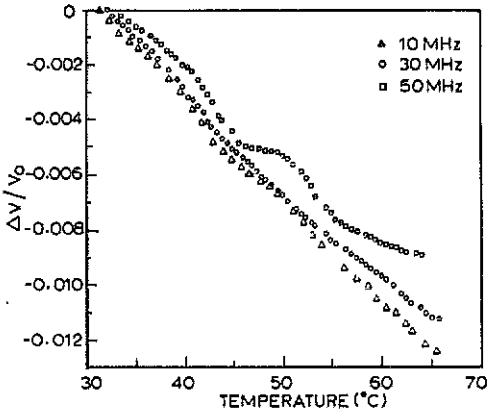

Figure 2. Ultrasonic attenuation as a function of temperature at 10, 30 and 50 MHz.

was mounted on a copper block and housed in a copper chamber which was submerged into a bath of paraffin oil. The ultrasonic data were collected while the temperature of the bath was varied slowly at the rate of 6 K h^{-1}. The velocity and attenuation were measured simultaneously as functions of temperature employing a phase-sensitive superheterodyne spectrometer, the details of which have been published elsewhere (Banerjee *et al* 1990). The apparatus was interfaced with a PC for data acquisition. While we could get good echo patterns at 10 MHz, we had to work with only a single echo at 30 and 50 MHz due to high attenuation.

The plots of relative changes in ultrasonic velocity and ultrasonic attenuation as functions of temperature are shown in figures 1 and 2 respectively. The ultrasonic velocity does not exhibit any discontinuity at the transition temperature, which is expected in a second-order phase transition. However, there is a distinct feature with a change in slope near the Curie temperature. An earlier study of the temperature dependence of elastic constants has also not revealed any discontinuity at T_c (Haussuhl and Nicolau 1985). It should be noted here that the value of attenuation shown in figure 2 is absolute only for 10 MHz. At 30 and 50 MHz only relative changes in attenuation are given since we could observe only a single echo. The results on ultrasonic attenuation clearly indicate the importance of the probe frequency in observing anomalies in ultrasonic attenuation. Whereas in TGS the anomaly could be observed at 5 MHz, for TAAP it is practically absent even at 10 MHz (Minaeva *et al* 1966). At 30 MHz a slight anomaly appears which becomes very much more pronounced at 50 MHz. Interestingly, at 30 MHz, there are two distinct peaks in attenuation close to T_c, the origin of which is not understood. The magnitude of the anomaly observed at 50 MHz is comparable to that in KDP (Litov and Uehling 1968).

In the case of ferroelectric crystals, depending on the nature of the phase, there are essentially two contributions to ultrasonic attenuation: one due to a 'piezoelectric–relaxational' mechanism and the other due to an 'electrostrictive–fluctuation' mechanism. The former arises because of the linear coupling between spontaneous polarization and strain, which exists in the ferroelectric phase. In crystals that are non-centrosymmetric even in the paraelectric phase, the same mechanism is operative. If, on the other hand, the crystal is centrosymmetric in the paraelectric phase, the ultrasonic attenuation is due to an 'electrostrictive–fluctuation' mechanism which arises because of the coupling between the strain and the spatially inhomogeneous thermal fluctuations in polarization. These fluctuations scatter the ultrasonic waves like a random distribution of inhomogeneities and thus give rise to ultrasonic attenuation (Levanyuk 1966). Even though the high-temperature crystal structure of TAAP is not known, various physical investigations suggest that the phase above T_c is likely to be centrosymmetric with the point group $P2/m$ (Shashikala 1990). Hence in this phase the ultrasonic attenuation is essentially due to an 'electrostrictive–fluctuation' mechanism. In addition, ultrasonic attenuation in the centrosymmetric paraelectric phase could also be produced through three-phonon processes (Tani and Tsuda 1967, 1969, Pytte 1970) and through domains that seem to persist even in the paraelectric phase (O'Brien and Litovitz 1964). The pyroelectric measurements for TAAP indicate that some residual polarization persists even above the Curie temperature, and hence attenuation due to the presence of domains above the Curie temperature is a distinct possibility (Shashikala 1990).

In conclusion, we have observed anomalous ultrasonic attenuation near the Curie temperature of ferroelectric TAAP as expected from the theory of Landau and Khalatnikov. The 'piezoelectric–relaxation' mechanism depends on the direction of propagation of the ultrasonic waves unlike the 'electrostrictive–fluctuation' mechanism (Minaeva *et al* 1969). A thorough study of the propagation of both longitudinal and transverse ultrasonic waves along other crystallographic directions across the Curie temperature is in progress and the results will be presented in a future publication.

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