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Abstract
The ferroelectric transition temperature T_c of $(NH_2CH_2COOH)_3 \cdot H_2SO_4$ (TGS), which is a typical order–disorder-type ferroelectric, was determined by dielectric constant and Raman scattering measurements under high pressure. T_c increased, passed through a maximum and then decreased slightly with increasing pressure, and then abruptly dropped at about 2.5 GPa, where a transition to a new high-pressure phase was confirmed to exist. A tentative p–T phase diagram was proposed for TGS.

1. Introduction

The effects of pressure on ferroelectrics have been actively studied by many investigators [1]. Their results regarding the pressure dependence of the ferroelectric transition temperature, T_c, clearly show that $\mathrm{d}T_c/\mathrm{d}p < 0$ for displacive-type ferroelectrics and $\mathrm{d}T_c/\mathrm{d}p > 0$ for order–disorder-type ones, although KDP and its family, belonging to the latter group, have $\mathrm{d}T_c/\mathrm{d}p < 0$, which is ascribed to the fact that their ferroelectricity is coupled with the configuration of H or D on the hydrogen bond connecting the PO_4 tetrahedra. These pressure effects—with the exception of those on KDP and its family—have been qualitatively explained to some degree. However, we felt strongly motivated to examine the validity of these empirical laws at higher pressure, where experiments have not been carried out yet.

As the ferroelectric for testing, we selected $(NH_2CH_2COOH)_3 \cdot H_2SO_4$ (abbreviated as TGS). The reasons that we selected it are as follows:

  (i) it is one of the most typical order–disorder-type ferroelectrics;
 (ii) T_c for this material at ambient pressure is about $49\,^\circ\mathrm{C}$, which is an appropriate temperature for high-pressure experiments; and
(iii) several investigators have already carried out high-pressure experiments.

The investigators mentioned in (iii) reported $\mathrm{d}T_c/\mathrm{d}p > 0$, and some of them [2], who carried out studies at relatively high pressure, obtained a gradual divergence from linearity with pressure,
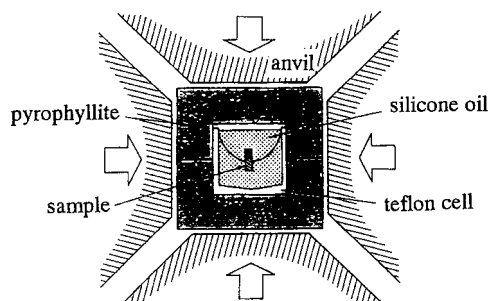
Figure 1. The cell with a liquid pressure medium, for the dielectric constant measurement using a cubic press.
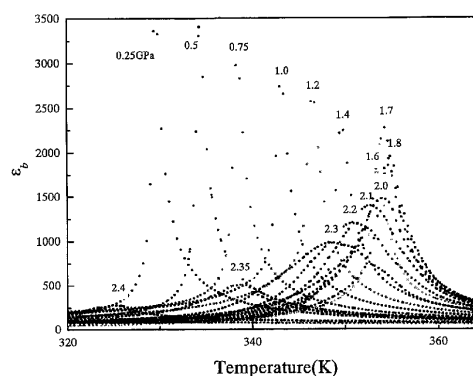
Figure 2. The dielectric constant ε_b of TGS as a function of temperature under various pressures.

which gives us every reason to expect $dT_c/dp < 0$ at higher pressure. Thus, we have made dielectric constant and Raman scattering measurements to determine T_c under high pressure.

2. Experimental method

The single crystal used in the present study was grown from an aqueous solution by a cooling method.

### 2.1. Dielectric constant measurement [3]

Pressure was generated with the so-called cubic-anvil apparatus, in which six anvils were driven by a hydraulic press. Simultaneously, the sample was cooled down to 77 K by immersing the whole anvil assemblage into liquid nitrogen, and then heated to 390 K by an electrical heater wound around the anvil assemblage. The sample, of $1.5 \times 1.5 \times 0.5$ mm^3, cut from a single crystal was compressed in a liquid pressure medium, silicone oil (SH510), in a Teflon cell, which was set in a cubic pyrophyllite cell (see figure 1). Two thin copper wires introduced into the Teflon cell were attached with silver paste to the gold-plated upper and lower surfaces of the sample. The dielectric constant along the crystallographic b-axis was measured by a YHP4192A impedance analyser operated at frequencies of 1–100 kHz. Measurements were made in two processes: a heating process under constant pressure and a compression process at constant temperature. Pressure was calibrated using the fixed points of Bi at room temperature, and was kept constant in the cooling or heating processes by automatically holding the press load constant during the experiment.

### 2.2. Raman scattering measurement

High pressure was generated by a DAC with a 4:1 mixture of methanol and ethanol as the pressure medium. Pressure was determined by the ruby fluorescence technique. As the excitation light source, an argon-ion laser (NEC GLG-3250) with an output of 100–200 mW at 514.5 nm was employed. The Raman spectra were recorded in the back-scattering geometry using a Jobin-Yvon triple monochromator (T64000) with a liquid-nitrogen-cooled CCD imaging detection system.

3. Results and discussion

The temperature dependences of the dielectric constant ε_b of TGS are given at various pressures in figure 2. The temperature where ε_b attains a maximum is defined as T_c. As shown by dots in figure 3, it increased monotonically with increasing pressure up to about 1.8 GPa, and then, after passing through a maximum, gradually decreased to about 2.4 GPa, at which point it
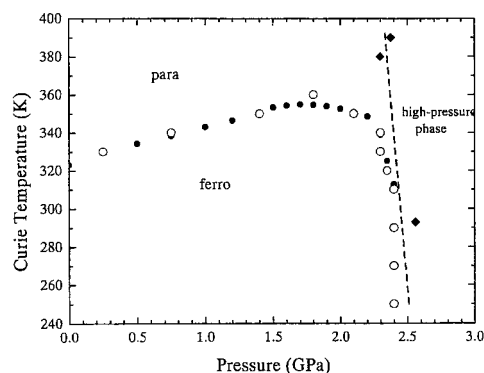
Figure 3. The ferroelectric transition temperature T_c determined in the heating process under various pressures and the anomaly points of the dielectric constant-pressure curves shown in figure 4 (see the text). A dashed line indicates a tentative phase boundary.
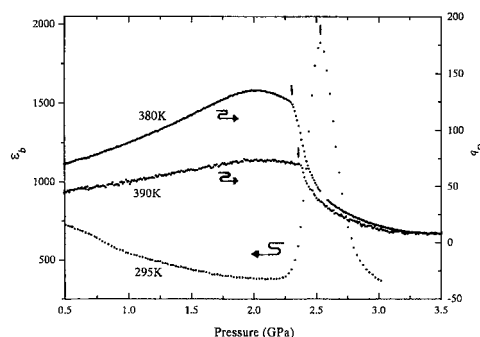
Figure 4. The dielectric constant ε_b of TGS as a function of pressure at constant temperatures. Arrows indicate anomalies probably corresponding to phase transition.

suddenly dropped. We also plotted the values of ε_b for various (p, T) conditions in figure 2, as a function of pressure at several constant temperatures. They also gave the peak indicating T_c, which was plotted using open circles in figure 3. The agreement between the dots and the open circles for the T_c–p relation is very good. It seems that T_c abruptly decreased at around 2.4 GPa. If so, the dielectric state at pressures higher than 2.4 GPa must be the same paraelectric phase as at high temperatures at ambient pressure.

In order to examine this, we measured the dielectric constant directly as a function of pressure at several constant temperatures up to 390 K. The results are plotted in figure 4. The values at 295 K formed almost the same peak as those marked by open circles in figure 3— that is, a peak symmetric about the pressure axis. But the values at 380 and 390 K are very different—that is, there is an asymmetric change with a sharp shoulder on the right-hand side. These pressures, corresponding to the maximum or the shoulder, are plotted as diamonds in figure 3. Thus, we can roughly draw the phase boundary—at pressures around 2.5 GPa— which separates the ferroelectric phase and the paraelectric phase, both of which are stable at ambient pressure, from the high-pressure phase newly found in the present study. The dielectric constants of the new phase are much smaller than those of the ferroelectric phase, but comparable with those of the paraelectric phase, as seen in figure 4. The new phase is probably paraelectric at temperatures higher than, at least, 100 K.

Figure 5 shows the Raman spectra obtained in the compression process at room temperature. Several new peaks marked by arrows appeared at 2.7 GPa, although none of them appeared at 2.2 GPa. The transition to the high-pressure phase took place at a pressure between 2.2 and 2.7 GPa. This pressure range includes the transition pressure of about 2.5 GPa determined by the above-mentioned dielectric constant measurement. These new Raman peaks diminished at pressures between 2.2 and 1.6 GPa in the decompression process, which indicates the hysteresis of the transition pressure.

The Raman spectra were also obtained in the stable region of the paraelectric phase at 0.6 GPa, 339 K and 1.4 GPa, 361 K. They were apparently different from that of the high-pressure phase, which supports the phase diagram of figure 3.

In statistical mechanics, the Ising model for order–disorder-type ferroelectrics gives the relation $k_B T_c = \mu^2 J$, where k_B is the Boltzmann constant, μ a dipole moment, and J the dipole–dipole interaction. The gradual decrease of T_c with pressure observed at pressures between 1.8 and 2.4 GPa must be ascribed to the decrease of μ with pressure, because J is proportional
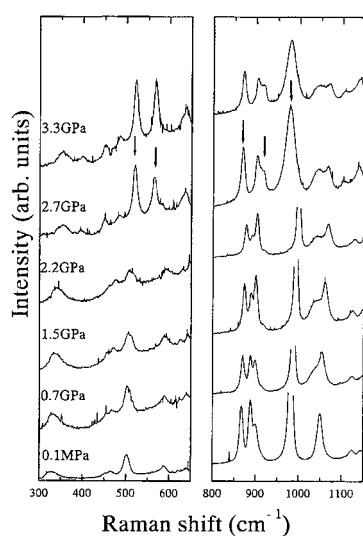
Figure 5. Raman spectra of TGS obtained in the compression process at room temperature.

to r^{-3}, where r denotes the distance between the two dipoles, and increases with pressure. An experiment to estimate μ for TGS under pressure is indispensable to further discussion.

4. Conclusions

By the dielectric constant and Raman scattering measurements under high pressure, the following results were obtained:

(i) The ferroelectric transition temperature T_c had a maximum. The decrease of T_c with pressure is a phenomenon that was first observed for typical order–disorder-type ferroelectrics; we must re-examine our results using various hydrostatic pressure media to confirm this finding.

(ii) A new high-pressure phase was found above about 2.5 GPa, which is not one of the ferroelectric and paraelectric phases stable at ambient pressure.

Very recently, Suzuki *et al* [4] have made x-ray diffraction experiments on TGS using an alcohol mixture medium at high pressure and room temperature, and successfully observed a crystallographic transition at pressures between 2.43 and 2.60 GPa, which is also consistent with the present results.

References

[1] See, for example,
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