Change in the Order of the Phase Transition in Ferroelectric Triglycine Selenate at High Pressures

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Dielectric constant of ferroelectric triglycine selenate was measured at hydrostatic pressures around 5 kbar in the vicinity of the Curie temperature. A discontinuous change of the dielectric constant at the Curie temperature and a thermal hysteresis of the transition (typically about 0.2°C at 5.28 kbar) were found. The result indicates that the order of the ferroelectric transition changes from second to first order by application of hydrostatic pressure. Unusual dielectric properties of TGSe at high pressures so far reported can be interpreted on the basis of the order-change in the transition.

Triglycine selenate (TGSe) is a ferroelectric having an isomorphous structure with triglycine sulfate and fluoroberyllate.[1] The Curie temperature of TGSe at 1 atm is about 22°C. The effect of hydrostatic pressure on the dielectric properties of TGSe has been widely investigated by several authors.[2-5] A unusual effect of hydrostatic pressure on the dielectric properties of TGSe is that the peak value of the dielectric constant at the Curie temperature is markedly depressed by pressure.[3,5] Samara[6] interpreted this phenomenon in terms of clamping due to the viscosity of the pressure-transmitting-fluid. However, this seems not to be realistic since the material is not piezoelectric in the paraelectric phase. Recently Leonidova *et al.*[5] measured the effect of electric field E on the temperature shift ΔT for the maximum dielectric constant, and found that ΔT does not obey the 2/3 law, $\Delta T \propto E^{2/3}$, which is expected from the thermodynamics of a second order phase transition of ferroelectrics.

These anomalous behaviors of the dielectric properties of TGSe at high pressures are interpretable by assuming that the order of the transition changes from second to first by application of pressure. Up to date no evidences have reported for the order change explicitly; discontinuous changes in the spontaneous polarization and dielectric constant were not noticed in the experiment of Polandov *et al.*[3] nor was the double hysteresis loop. If a first order phase transition is very close to a second order in nature, it is rather difficult to observe double hysteresis loops and discontinuous change in spontaneous polarization. Observation of the discontinuous change and the thermal hysteresis

in the dielectric constant at the Curie temperature is more convenient to check the order of transition.

In the present letter, we describe an evidence of the first order phase transition in TGSe at high pressures. A *b*-plate which was pre-annealed at 100°C for 35 hr was set in a Cu-Be pressure bomb and the dielectric constant was measured with a three terminal capacitance bridge at 50 kHz in a hydrostatic pressure region of 5~6 kbar. The pressure-transmitting-fluid used was kerosene. The temperature was controlled with a water-bath in accuracy of ±0.005°C. During the measurement the temperature of the specimen was changed in a
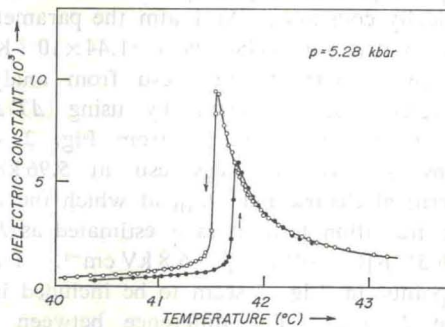

Fig. 1. Temperature dependence of the dielectric constant of TGSe along the *b*-axis at 5.28 kbar. Frequency: 50 kHz.

slow rate of about 0.05°C min⁻¹.

Figure 1 shows a result at a pressure of 5.28 kbar. There are a clear discontinuity at the Curie temperature and a thermal hysteresis of about 0.2°C in the dielectric constant vs temperature curve. A weak double hysteresis loop was also found for the present specimen just

above the Curie temperature. The difference between the Curie temperature T_c and the Curie-Weiss temperature T_0 was about 0.4°C for the heating run.

The critical point at which the first order phase boundary curve passes into the second order one in the pressure-temperature plane is denoted as the Curie critical point after the nomenclature of Ginzburg.[7] The critical nature of the transition at the Curie critical point qualitatively differs from that of the second order one. In the case of TGSe the Curie critical point exists at a low pressure since the transition even at 1 atm shows to be very close to what should be expected for the Curie critical point.[8]

On the basis of the order change at high pressures, the break of 2/3 law reported by Leonidova et al.[5] can be interpreted as follows; in Fig. 2, the value of log ΔT reported by Leonidova et al. are replotted against log E instead of the original plot of ΔT vs $E^{2/3}$. A good proportionality is held between ΔT and E; this is a characteristic of a first order phase transition.[9] A simple phenomenological theory of ferroelectrics shows that for a first order transition $(\Delta T/\Delta E)_{E=0} = (\sqrt{2}/\eta)\cdot(\zeta/-\xi)^{1/2}$, where η, ξ, and ζ are the coefficients of the power series expansion of the free energy G by the polarization P; $G = G_0 + \eta(T-T_0)P^2 + \xi P^4 + \zeta P^6$. A simple assumption is that the parameters T_0 and ξ are pressure dependent while η and ζ are practically constants. At 1 atm the parameters are estimated for TGSe as $\eta = 1.44 \times 10^{-8}\,\mathrm{K}^{-1}$, $\xi \cong 0$, and $\zeta = 3.45 \times 10^{-18}$ cgs esu from analysis of dielectric data.[8] Then, by using $(\Delta T/\Delta E) = 0.44$°C kV^{-1} cm evaluated from Fig. 2, one obtains $\xi = -1.9 \times 10^{-10}$ cgs esu at 5.96 kbar. The critical electric field E_{crit} at which the first order transition terminates is estimated as $E_{crit} = (16/5^{5/2})\cdot[(-\xi)^{5/2}/\zeta^{3/2}] = 6.8$ kV cm^{-1}. Then, the points in Fig. 2 seem to be included in a region $E \leq E_{crit}$. The difference between the Curie temperature and the Curie-Weiss temperature is estimated as $T_c - T_0 = \xi^2/(4\eta\zeta) = 1.8$°C,

which is comparable to 1.5°C at 4.5 kbar reported by Leonidova et al.[5] The values of $T_c - T_0$ reported by different authors somewhat differ from each other. Thus the pressure dependence of ξ varies with impurities or internal stresses in the specimen used.
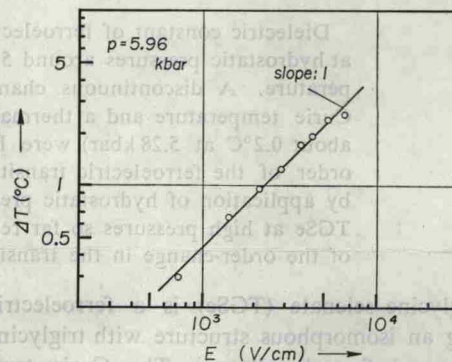

Fig. 2. Log-log plot of the temperature shift ΔT of the maximum dielectric constant against electric field E at 5.96 kbar. The figure is replotted from the diagram of ΔT vs $E^{2/3}$ given by Leonidova et al.[9]

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