

Hydrostatic-Pressure Effects on the Dielectric Properties of Ferroelectric $\text{AgNa}(\text{NO}_2)_2$

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Dielectric constant of single crystals of $\text{AgNa}(\text{NO}_2)_2$ was measured along the ferroelectric b -axis as a function of temperature at various hydrostatic pressures up to 8 kbar. The Curie point T_c and the paraelectric Curie temperature θ vary linearly with pressure p with the coefficients of $dT_c/dp = (9.4 \pm 0.2)^\circ\text{C kbar}^{-1}$, and $d\theta/dp = (9.3 \pm 0.2)^\circ\text{C kbar}^{-1}$. The dielectric relaxation time at T_c decreases with increasing pressure. The pressure effect on the dielectric relaxation is discussed on the basis of a molecular field theory.

§ 1. Introduction

Silver sodium nitrite $\text{AgNa}(\text{NO}_2)_2$ is ferroelectric below the Curie point of about 38°C .^{1,2)} Recent X-ray diffraction study³⁾ showed that the space groups below and above the Curie point are C_{2v}^0 - $Fd2d$ and D_{2h}^4 - $Fddd$, respectively. The crystal structure in the ferroelectric state is a slight version of that of ferroelectric NaNO_2 . If one ignores the difference between Ag and Na atoms and slight canting of NO_2^- molecular plane in $\text{AgNa}(\text{NO}_2)_2$, the two structures are coincident with each other. In fact, the Curie constants and the spontaneous polarizations extrapolated to the completely ordered state are almost the same among the two ferroelectrics.^{2,4)} The mechanism of the ferroelectric process in $\text{AgNa}(\text{NO}_2)_2$ should be very close to that in NaNO_2 . However, there is a marked difference between the phase transitions in NaNO_2 and $\text{AgNa}(\text{NO}_2)_2$, that is, a long period antiferroelectric phase has been observed in a narrow temperature range of about 1°C above the Curie point of NaNO_2 whereas such an intermediate phase has not been found in $\text{AgNa}(\text{NO}_2)_2$.^{2,5)} The antiferroelectric phase in NaNO_2 is known to be expanded under hydrostatic pressure: It widens to about 50°C at 40 kbar.⁶⁾ The similarity of the transition mechanisms in $\text{AgNa}(\text{NO}_2)_2$ and in NaNO_2 would naturally raise a doubt whether or not an intermediate phase can be observed in $\text{AgNa}(\text{NO}_2)_2$ at high pressures.

On the other hand, $\text{AgNa}(\text{NO}_2)_2$ shows a dipolar dielectric relaxation in a low frequency region below 1 MHz. This will enable us to measure the hydrostatic-pressure effect on the dipolar dielectric relaxation in this material by using a conventional bridge technique. The present paper reports the effects of hydrostatic pressure on the dielectric

properties and the phase transition of $\text{AgNa}(\text{NO}_2)_2$. The results will be discussed in comparison with those of NaNO_2 .

§ 2. Experiments

Single crystals of $\text{AgNa}(\text{NO}_2)_2$ were grown from aqueous solution by slow evaporation around 25°C .⁷⁾ Several b -plates of which typical dimension was $0.7\text{ mm} \times 3\text{ mm}^2$ were cut with a wet thread saw by using saturated aqueous solution of NaNO_2 as the solvent. After polishing the specimen with 1,200 mesh carborundum powder, silver paint (Du Pont #4922) was attached as electrodes. The high pressure apparatus used was described elsewhere.⁸⁾ Kerosene was used as the pressure-transmitting fluid. The dielectric constant and the dielectric dispersion were measured with a transformer ratio arm bridge, TR-1B of Ando Denki Co., Ltd. The pressure dependence of the Curie point was determined from the temperature variation of the dielectric constant measured at 300 Hz. After passing through the transition point several times at high pressures, the dielectric properties and the Curie point were considerably changed probably due to increase of strains. Therefore, the measurements at different pressures were carried out by using virgin samples. At a constant pressure, temperature of the specimen was changed always from below. Temperature and pressure were measured with an alumel-chromel thermocouple to an accuracy of 0.05°C and with a manganin gauge to 50 bar, respectively.

§ 3. Results

a) Pressure effect on the Curie point

Figure 1 shows the temperature dependence of the real dielectric constant ϵ' at 300 Hz at various

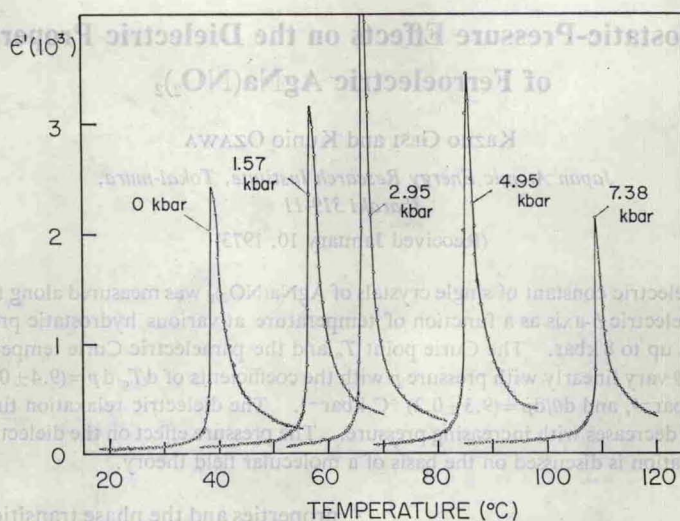


Fig. 1. Temperature dependence of the real dielectric constant ϵ' of $\text{AgNa}(\text{NO}_2)_2$ at various hydrostatic pressures. Frequency: 300 Hz.

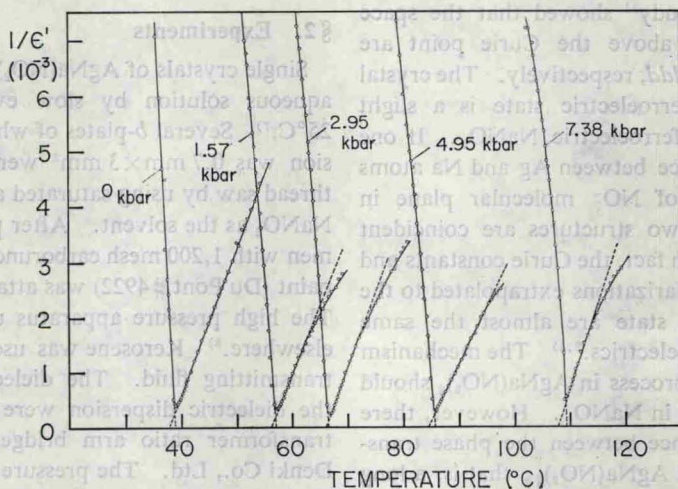


Fig. 2. Temperature dependence of the reciprocal of the real dielectric constant $1/\epsilon'$ of $\text{AgNa}(\text{NO}_2)_2$ at various hydrostatic pressures. Frequency: 300 Hz.

hydrostatic pressures. The Curie point T_c shifts towards higher temperature with increasing pressure. Any pressure-induced intermediate phase just above the Curie point was not found up to 8 kbar. In Fig. 2, the reciprocal of the real dielectric constant is indicated as a function of temperature at different pressures. A Curie-Weiss relation holds in a temperature range of several degrees above the Curie point. At higher temperatures, a deviation from the Curie-Weiss relation which is probably due to the increase of electrical conductivity of the specimen is seen. The paraelectric Curie temperature θ also increases with increasing pressure. Figures 3 and 4 represent the hydrostatic-pressure dependences of the Curie

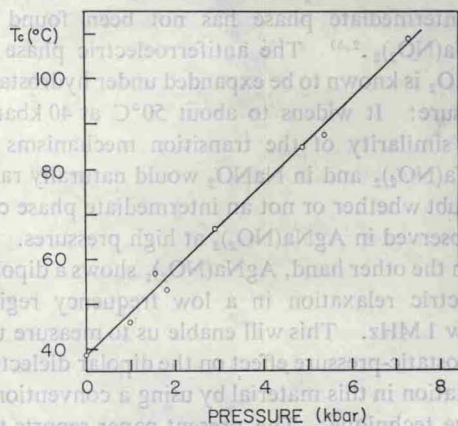


Fig. 3. Hydrostatic-pressure dependence of the Curie point T_c of $\text{AgNa}(\text{NO}_2)_2$.

point T_c and the paraelectric Curie temperature θ , respectively. In the pressure region studied here, both T_c and θ depend linearly on pressure. The pressure coefficients are given as

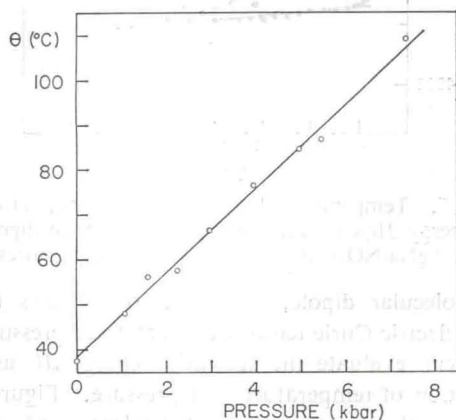


Fig. 4. Hydrostatic-pressure dependence of the paraelectric Curie temperature θ of $\text{AgNa}(\text{NO}_2)_2$.

$$dT_c/dp = 9.4 \pm 0.2^\circ\text{C kbar}^{-1},$$

and

$$d\theta/dp = 9.3 \pm 0.2^\circ\text{C kbar}^{-1}.$$

That is, the two coefficients coincide with each other in the limit of experimental errors. The observed pressure coefficient of the Curie point satisfactorily agrees with $dT_c/dp = 9.1^\circ\text{C kbar}^{-1}$ reported by Belyaev *et al.*¹²⁾ In the present work, any systematic pressure variation of the Curie constant was not detected because of uncertainty in dimension measurement of the specimen.

b) Dielectric dispersion at high pressures

Figure 5 (a) and (b) shows the temperature dependence of real dielectric constant for various

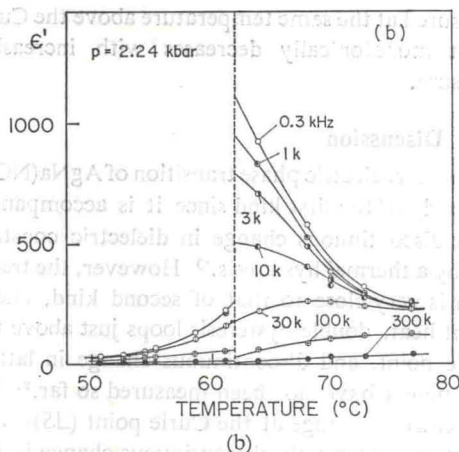
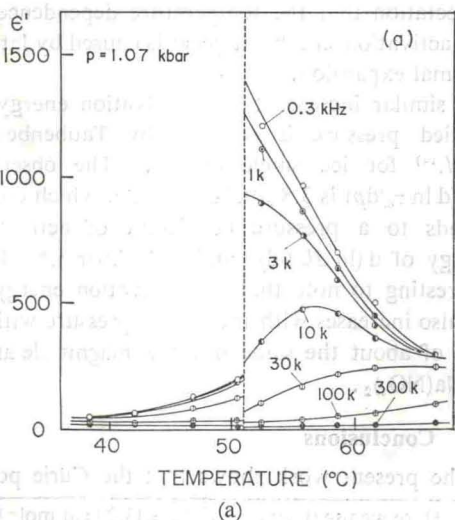


Fig. 5. Temperature dependence of the real dielectric constant of $\text{AgNa}(\text{NO}_2)_2$ for various frequencies (a) $p = 1.07$ kbar, (b) $p = 2.24$ kbar.

frequencies at $p = 1.07$ kbar and 2.24 kbar, respectively. A remarkable dielectric dispersion is recognized below 300 kHz. The dielectric relaxation time τ_0 is estimated by $\tau_0 = 1/\omega_m$, where ω_m is the angular frequency at which the imaginary dielectric constant shows the maximum. The temperature dependences of the dielectric relaxation time at several hydrostatic pressures are indicated in Fig. 6. The curve for $p = 0$ is cited from ref. 9. The dielectric relaxation time

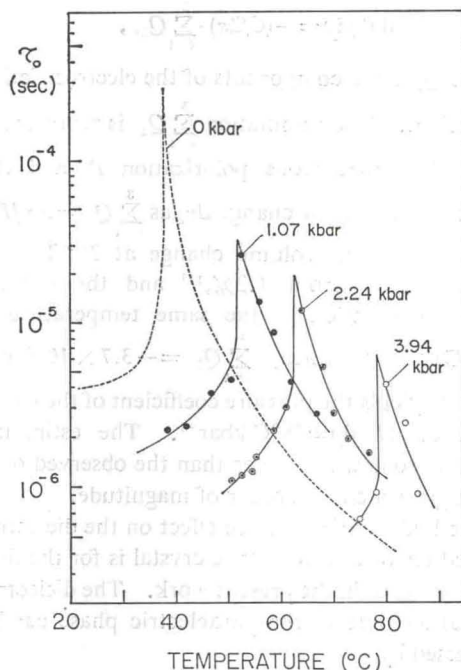


Fig. 6. Temperature dependence of the dielectric relaxation time τ_0 of $\text{AgNa}(\text{NO}_2)_2$ at different hydrostatic pressures.

measured at the same temperature above the Curie point monotonically decreases with increasing pressure.

§ 4. Discussion

The ferroelectric phase transition of $\text{AgNa}(\text{NO}_2)_2$ is clearly of the first kind since it is accompanied by a discontinuous change in dielectric constant and by a thermal hysteresis.²⁾ However, the transition is very close to that of second kind, and a latent heat, double hysteresis loops just above the Curie point, and discontinuous change in lattice parameters have not been measured so far.^{2,10,11)} The entropy change at the Curie point $(\Delta S)_{T_c}$ can be estimated from the discontinuous change in the spontaneous polarization $(P_s)_{T_c} \simeq 2 \mu\text{C cm}^{-2}$ ⁴⁾ as $(\Delta S)_{T_c} \simeq -0.08 \text{ cal K}^{-1} \text{ mol}^{-1}$ by using a thermodynamical relation of $(\Delta S)_{T_c} = -(2\pi P_s^2/C)_{T_c}$ together with the observed Curie constant $C = 4.63 \times 10^3 \text{ K}$.⁹⁾ Then, the volume change Δv at the Curie point should be 0.046% from the Clausius-Clapeyron relation of $\Delta v = (dT_c/dp) \cdot (\Delta S)_{T_c}$ together with the observed value of dT_c/dp . The estimation of the volume change is about the same as is observed in NaNO_2 .¹³⁾

The hydrostatic-pressure coefficient of the Curie point is represented in terms of the electrostriction by a formula;

$$dT_c/dp = -(C/2\pi) \cdot \sum_{i=1}^3 Q_{2i},$$

where Q_{2i} 's are components of the electrostrictive coefficient. The summation $\sum_{i=1}^3 Q_{2i}$ is represented from the spontaneous polarization P_s and the spontaneous volume change Δv_s as $\sum_{i=1}^3 Q_{2i} = \Delta v_s/P_s^2$. The spontaneous volume change at 25°C is reported to be about 1.2%,¹¹⁾ and the spontaneous polarization at the same temperature is $6.0 \mu\text{C cm}^{-2}$.⁴⁾ Then, $\sum_{i=1}^3 Q_{2i} = -3.7 \times 10^{-11} \text{ cgs esu}$. It yields the pressure coefficient of the Curie point of $dT_c/dp = 28^\circ\text{C kbar}^{-1}$. The estimated value is somewhat larger than the observed one, but it gives a correct order of magnitude.

The hydrostatic-pressure effect on the dielectric relaxation of a ferroelectric crystal is for the first time observed in the present work. The dielectric relaxation time in the paraelectric phase can be expressed by

$$\tau_0 = \frac{h}{k(T-\theta)} \exp(\Delta U/kT),$$

where ΔU is the activation energy for flip-flop of

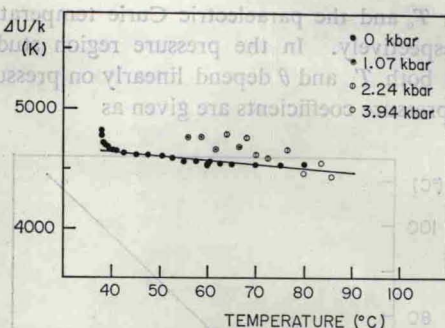


Fig. 7. Temperature dependence of the activation energy $\Delta U/k$ for the flip-flop of a molecular dipole of $\text{AgNa}(\text{NO}_2)_2$ at different hydrostatic pressures.

a molecular dipole. Then, if one knows the paraelectric Curie temperature at a fixed pressure, one can evaluate the activation energy ΔU as a function of temperature and pressure. Figure 7 shows the temperature dependence of the activation energy ΔU at different pressures. At atmospheric pressure, ΔU decreases with increasing temperature. Except a sudden increase just above the Curie point, the temperature variation of ΔU can be approximated by a linear relation of

$$\Delta U(T, 0) = \Delta U(T_0, 0)[1 + \alpha(T - T_0)],$$

with a temperature coefficient $\alpha = -(7.2 \pm 0.8) \times 10^{-4} \text{ K}^{-1}$.⁹⁾ The temperature coefficient of the activation energy is the same order of magnitude of the linear thermal expansion coefficients.¹¹⁾ If the temperature variation of the activation energy ΔU is caused as a result of lattice thermal expansions, ΔU will increase with pressure. It is seen that from Fig. 7, the difference $\Delta U(T, p) - \Delta U(T, 0)$ increases with increasing pressure up to about 2 kbar with a coefficient $d(\ln \Delta U)/dp \simeq 2 \times 10^{-2} \text{ kbar}^{-1}$. This seems to be consistent with the expectation that the temperature dependence of the activation energy at $p=0$ is caused by lattice thermal expansion.

A similar increase of the activation energy by applied pressure is reported by Taubenberger *et al.*¹⁴⁾ for ice single crystal. The observed $RT(d \ln \tau_0/dp)$ is $3.8 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$, which corresponds to a pressure coefficient of activation energy of $d(\ln \Delta U)/dp = 0.7 \times 10^{-2} \text{ kbar}^{-1}$.* It is interesting to note that the activation energy of ice also increases with increasing pressure with a rate of about the same order of magnitude as in $\text{AgNa}(\text{NO}_2)_2$.

§ 5. Conclusions

The present work shows that the Curie point

* Here we use the value of $\Delta U = 13.2 \text{ kcal mol}^{-1}$.¹⁵⁾

T_c and the paraelectric Curie temperature θ of $\text{AgNa}(\text{NO}_2)_2$ linearly depend on hydrostatic pressure up to about 8 kbar. The pressure coefficients of T_c and θ coincide with each other within the experimental errors. Any intermediate phase between the ferroelectric and the paraelectric phases is not found up to 8 kbar. The dielectric relaxation time measured at the same temperature above the Curie point considerably decreases with increasing pressure. The phenomena can be interpreted from the increase of the Curie point. Slight variation of the activation energy of the flip-flop of a molecular dipole with temperature and pressure is somewhat complicated, but the initial increase of the activation energy with increasing pressure seems to be consistent with the temperature variation of the activation energy at $p=0$.

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