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

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(Received January 10, 1973)

Dielectric constant of single crystals of AgNa(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 $dT_c/dp = (9.4 \pm 0.2)$ °C kbar^{-1}, and $d\theta/dp = (9.3 \pm 0.2)$ °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 AgNa(NO$_2$)$_2$ is ferroelectric below the Curie point of about 38°C.[1,2] Recent X-ray diffraction study[3] showed that the space groups below and above the Curie point are C_{2v}^{10}-$Fd2d$ and D_{2h}^{24}-$Fddd$, 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 AgNa(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 AgNa(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 AgNa(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 AgNa(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 AgNa(NO$_2$)$_2$ and in NaNO$_2$ would naturally raise a doubt whether or not an intermediate phase can be observed in AgNa(NO$_2$)$_2$ at high pressures.

On the other hand, AgNa(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 AgNa(NO$_2$)$_2$. The results will be discussed in comparison with those of NaNO$_2$.

§2. Experiments

Single crystals of AgNa(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 mm $\times$ 3 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
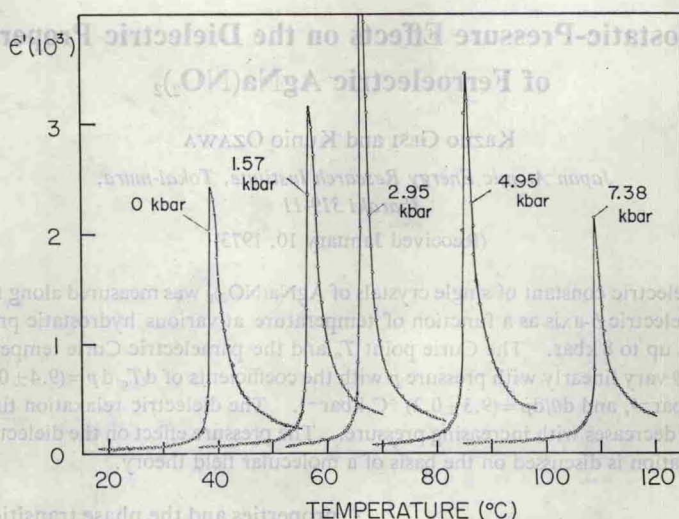
Fig. 1. Temperature dependence of the real dielectric constant ε' of $AgNa(NO_2)_2$ at various hydrostatic pressures. Frequency: 300 Hz.

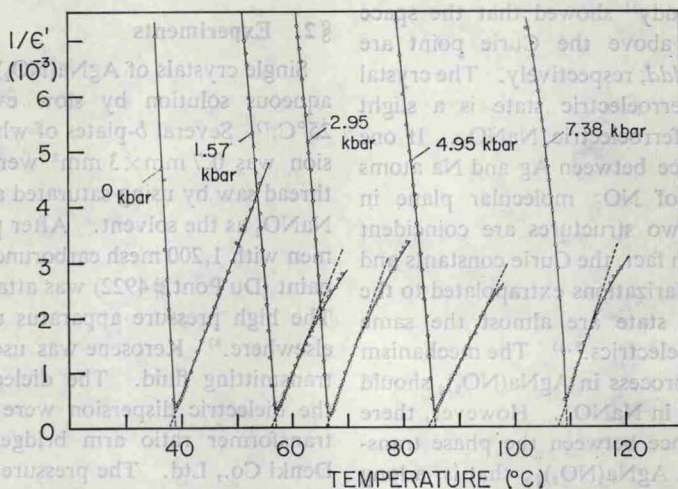Fig. 2. Temperature dependence of the reciprocal of the real dielectric constant $1/\varepsilon'$ of $AgNa(NO_2)_2$ at various hydrostatic pressures. Frequency: 300 Hz.

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
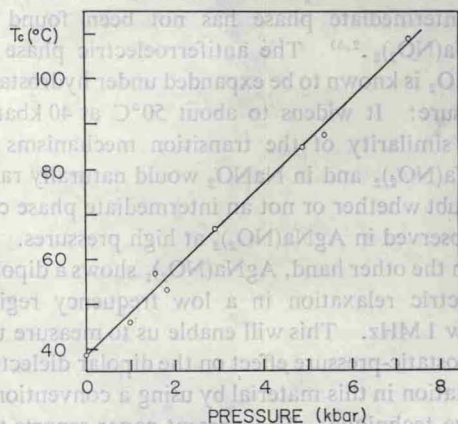

Fig. 3. Hydrostatic-pressure dependence of the Curie point T_c of $AgNa(NO_2)_2$.