EFFECT OF HYDROSTATIC PRESSURE ON THE DIELECTRIC PERMITTIVITY OF $NaNbO_3$ SINGLE CRYSTALS

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(Received August 16, 1979)

Investigations of electric permittivity, $\varepsilon(T)$, near the phase transition $P \rightleftarrows R$ were done. The results indicated that for the $NaNbO_3$ monocrystals investigated: $dT'_a/dp = 14.5$–22.3 K/10^{-1} GPa† (heating process) and $dT''_a/dp = 8.5$–19.3 K/10^{-1} GPa (cooling process). A strong "broadening" of $\varepsilon(T)$ in the surroundings of temperature, T_a, was observed under pressure $p \geqslant 0.4$ GPa. This is evidence of the decay of the $P \rightleftarrows R$ transition. The anomaly of electric permeability existing at the temperature range 250°–320°C suggests that the ferroelectric phase, Q, is induced under the action of pressure $\leqslant 0.3$ GPa in the region of antiferroelectric phase, P. Investigations of spontaneous polarization in the phase, Q, using the hysteresis loop method, at a field of about 7 kV/cm, did not give the expected results. However, it did not give evidence for the non-existence of the phase, Q.

1. Introduction

Sodium niobiate is a material having ferro-, antiferro- or paraelectric properties dependent on temperature. Based X-ray investigations, the existence of 6 phase transitions and 7 different phases between them was stated in this material [1–4]. These authors have stated, that a series of transitions, at temperatures of 360°C, 480°C, 520°C, 575°C and 640°C was observed at temperatures higher than room temperature. One of these transitions is very interesting for dielectric investigations. It is the transition from the antiferroelectric phase (P) to the antiferroelectric phase (R) $P \rightleftharpoons R$ near the temperature $T_a = 350$°C. The electric permeability, $\varepsilon(T)$, attains a sharp maximum at this temperature. Based on works concerning other materials having antiferroelectric properties [5, 6], it seemed of interest to investigate the influence of hydrostatic pressure on this maximum and also on the dynamics of transition $P \rightleftharpoons R$. Many authors suggest that the ferroelectric phase, Q, exists in $NaNbO_3$ between the P and R phases. The existence of phase, Q, is dependent on external factors like stress and the electric field [1, 7]. This was a reason for these investigations.

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† 1 kbar = 10^8 Pa = 10^{-1} GPa.

2. *Experimental and results*

The $NaNbO_3$ monocrystals, investigated in this work, were obtained by the author of [8], accordingly to Wood [9] from a solution of melted compounds: Na_2CO_3-Nb_2O_5-NaF using suitable weight proportions.

The platinum electrodes were deposited at temperatures of 650°C–700°C on the bright--yellow monocrystals having sizes of $1.5 \times 2 \times 0.5$ mm. Then, the monocrystals were placed in the prepared holder with a heater. The whole apparatus was placed in a high-pressure gas chamber using high purity helium as a medium. The investigations of $\varepsilon(T)$ were carried at a measuring field frequency of 1 kHz at a field strength of 0.05 kV/cm with the temperature rate $dT/dt = 2$ K/min. Individual $\varepsilon(T)$ curves were obtained for the selected values which were constant for a given measurement run of gas pressure.

In order to obtain the $\varepsilon(T)$ dependence the series of samples having a sharp maximum of electric permeability (ε_{max}) at temperatures $T_a = 350°$–370°C under normal pressure, was tested. For increasing values of pressure, the shift of T_a towards higher temperatures, a developing "broadening" in the maximum of $\varepsilon(T)$, and a simultaneous decrease of

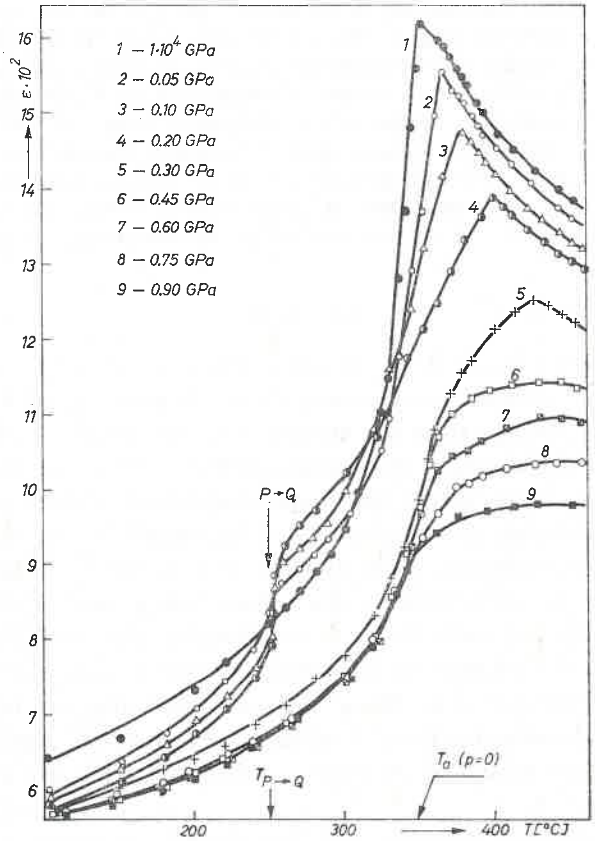

Fig. 1. Isobaric changes in electric permittivity, ε, as a function of temperature for $NaNbO_3$ monocrystals

ε_{max}, were observed. For pressures higher than 0.4 GPa the $\varepsilon(T)$ curves are diametrically opposed to the $\varepsilon(T)$ curves for a normal pressure.

Hysteresis was observed in the investigations of $\varepsilon(T)$ at temperatures of transitions P $\rightleftharpoons$ R. In the processes of heating (T_a') and cooling (T_a'') increases with pressure from a value of about 30°C for the normal pressure up to about 42°C for $p = 0.45$ GPa were observed.

Fig. 2 shows the dependence of critical temperatures T_a', T_a'' (curves *1*, *2*) and $\Delta T_a = T_a' - T_a''$ (curve *3*) as a function of pressure. The slopes dT_a/dp and $d(\Delta T_a)/dp$ were calculated from straight lines seen in Fig. 2. For the series of samples studied the rate of pressure changes T_a', T_a'' and ΔT_a varies within the limits: $dT_a'/dp = 14.5$–22.3 K/10^{-1} GPa, $dT_a''/dp = 8.5$–19.3 K/10^{-1} GPa and $d(\Delta T_a)/dp = 2.0$–3.1 K/10^{-1} GPa.

Fig. 3 shows the dependence of ε and $1/\varepsilon$ as a function of pressure at temperature of 700°C for the sample (curves *1*, *2*). This demonstrates the largest changes in values of $T_a(p)$ and $\varepsilon(T)$ with respect to the whole series studied. The dependence $1/\varepsilon$ is a linear function of pressure having the formula:

$$\varepsilon = \frac{C^*}{P - P_0}, \quad \text{for } p > p_0 \tag{1}$$

where C^* and p_0 are constants. The calculated C^* and p_0 have values from $C^* = 1.6 \times 10^3$ GPa up to $C^* = 2.72 \times 10^3$ GPa and $p_0 = -1.6$ GPa. Curve *3* shows changes in $1/\varepsilon_{max}$.

Apart from the above changes in ε in the surroundings of T_a (Fig. 1), the sharp rise in ε is observed for increasing pressure near a temperature of 250°C. This effect is observed only up to a pressure of about 0.2–0.3 GPa. Anomalous changes in ε occur at a temperature range from 250°C to about 320°C.

3. Discussion

The investigations of electric permeability for $NaNbO_3$ monocrystals as a function of hydrostatic pressure and temperature were concentrated on the most distinct phase transition, that is, P $\rightleftharpoons$ R. In the R phase, the electric permeability of $NaNbO_3$, measured at constanst pressure (10^{-4} GPa — 0.2 GPa) in the same samples, obeys the Curie–Weiss Law. At constant temperature, the pressure variation of ε in the R phase can be represented approximately by expression (1) (Fig. 3). Equation (1) is found to hold [5] over a wide pressure range for most ferroelectrics in their PE phases. Over the range of the measurements T_a increases linearly with pressure (Fig. 2). The temperature dependence of the frequency (ω_a) of this AF mode can be written as:

$$\omega_a^2 \propto K'(T - T_a), \tag{2}$$

where T_a is the AF transition temperature and K' is a constant. According to expression (2) the increase in the AF transition temperature, T_a, with pressure shows that the AF mode "softens" with decreasing volume. In the absence of experimental data on the phonon dispersion relations and their temperature dependence in $NaNbO_3$, some insight into

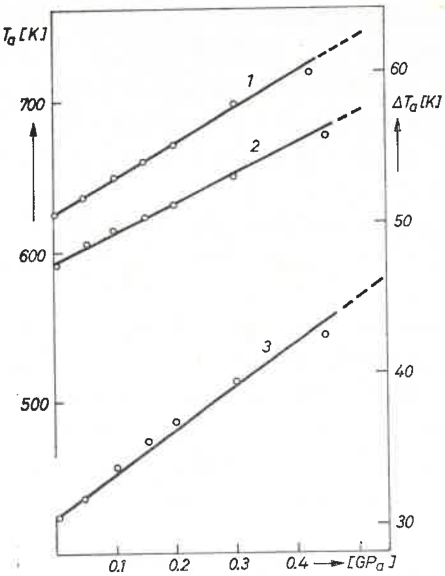

Fig. 2. Changes in the critical temperatures T_a', T_a'' and of ΔT_a (curve *3*) for the phase transition $P \rightleftarrows R$ as a function of pressure in the process of heating (curve *1*) and cooling (curve *2*)

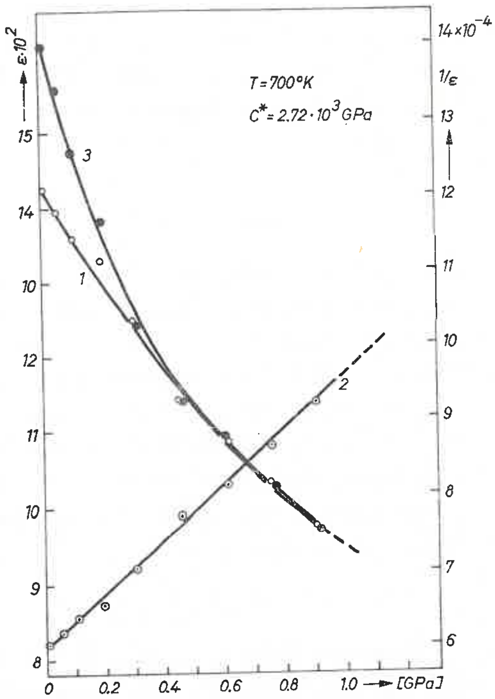

Fig. 3. Isothermal changes in electric permittivity (curve *1*) and $1/\varepsilon$ (curve *2*) as a function of pressure, for $T > T_a$. Curve *3* presents the dependence $1/\varepsilon_{max}(p)$

the nature of the AF mode can be gained by examining the displacements of the various ions which occur at the AF $\rightleftharpoons$ PE transition.

For the series of samples tested the determined values of dT_a/dp and $d(\Delta T_a)/dp$ change within the limits given above. The cause for the large differences in the values of dT_a/dp and $d(\Delta T_a)/dp$ for samples investigated is probably the intrinsic imperfections and stresses produced during the process of crystal growing. Using the Clausius–Clapeyron equation [5] we obtain:

$$\frac{dT_a}{dp} = T_a \frac{\Delta V}{Q}, \tag{3}$$

where ΔV is the change in the volume during phase transition and Q is the heat of transition. The quantity $(dT_a/dp)_{calc}$ can be estimated. It was calculated, that $dT_a/dp = 13\,K/10^{-1}$ GPa at a temperature ~360°C, determining that heat, $Q = 108.5$ cal/mole [8] from the DTa measurements and taking the change of volume $V = 485.95$ Å^3/cell from the X-ray investigations of $NaNbO_3$ [3]. The value $(dT_a/dp)_{calc}$ corresponds to the experimental data.

The temperature dependence, $\varepsilon(T)$, shows the sharp maximum at the temperature of transition P $\rightleftharpoons$ R, while it is expected to be at the transition to paraelectric phase ~480°C. This suggests the temperature of about 350°C. It seems that the observed linear dependences $1/\varepsilon(T)$ and $1/\varepsilon(p)$, for temperatures higher than T_a, confirm this conclusion.

Anomalies in the dependences $\varepsilon(T)$, observed at temperatures of 250°–320°C for pressures higher than a normal ones but lower than 0.2–0.3 GPa, are interesting from the point of considerations on the possibility of the coexistence of two phases: antiferroelectric, P, and ferroelectric, Q, [1] below temperature of about 350°C. The proximetry of the values of free energy in the P and Q phases at temperatures of 20°–360°C and the transitions P → Q and Q → P, stated at temperatures 20°–260°C by X-ray investigations [1] confirm the existence of the ferroelectric phase Q. This temperature range can shift up or down dependent on the value intrinsic stresses [1]. Then the changes of these stresses upon the action of external hydrostatic pressure can influence substantially the existence of the phase Q and also temperature range of occurrence. Therefore, the observed anomalies in $\varepsilon(T)$ at temperature of about 250°C (Fig. 1) can be connected with the occurrence of P → Q transition.

Hitherto, the phase, Q, was forced by strong electric fields [10–12]. Then, the electric hysteresis loop was observed, which was the explicit evidence of the occurrence of the ferroelectric phase. The investigations of the electric hysteresis loop, carried by the author, using a Sawyer–Tower method in the field ~7 kV/cm did not fully give the expected results. However, some non-linearity of $P(E)$ was obtained, but it was not a fully saturated hysteresis loop and the measured polarization was very low.

An application of fields higher than 7 kV/cm to the sample caused its breakdown at a temperature range higher than 250°C. The $NaNbO_3$ crystals investigated have a rather high electric conductivity [13]. A substantial concentration of free changes can lead to the screening of the spontaneous polarization.

4. *Summary and conclusions*

In this work the effects of temperature and hydrostatic pressure on the dielectric properties and phase transitions of $NaNbO_3$ were investigated. The results show that in $NaNbO_3$ monocrystals there are two independent low-frequency temperature-dependent lattice vibrational modes FE mode which determines the Curie–Weiss behaviour of the electric permeability, ε, in the PE phase, and an AF mode which causes the AF $\rightleftharpoons$ PE transition. The frequency of the FE mode increases with increasing pressure. However the frequency of the AF mode decreases, corresponding to an increase in the AF $\rightarrow$ PE transition temperature, T_a. As a result, the large anomaly in ε, at the transition decreases and a strong "broadening" at $\varepsilon(T)$ is observed under pressure of 0.4 GPa. At the temperature range of 250°–320°C the observed intermediate FE phase, Q, was induced in $NaNbO_3$ by the application of pressure.

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