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The ressure Dependence of the Dielectric Properties of Potassium Nitrite

Sanji FUJIMOTO, Naohiko YASUDA, Mitsue KOIZUMI† and Masahiko SHIMADA†

Electrical Engineering Department, Gifu University, Gifu

†*Institute of Scientific and Industrial Research, Osaka University, Osaka*

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The dielectric properties of potassium nitrite (KNO_2) have been investigated by the use of X-ray techniques and by the measurement of dielectric characteristics, but it has never been made to decide whether the room temperature phase of KNO_2 under atmospheric pressure is ferroelectric or not.

In 1964, Parry *et al.* pointed out the possibility of the ferroelectricity in the room temperature phase of KNO_2.[1] Later, it was reported by Tanisaki *et al.* in 1965 that KNO_2 has a possibility to show ferroelectricity or antiferroelectricity below room temperature,[2] and by Rao *et al.* in 1966 that KNO_2 is ferroelectric at room temperature and has a ferroelectric-paraelectric transition at 40°C,[3] while in 1969 Mitsui *et al.* listed a transition at 47°C which may be a ferroelectric-paraelectric one.[4]

On the contrary, in 1969 Solbakk *et al.* suggested that the room temperature phase is nonferroelectric on account of belonging to the space group $R\bar{3}m$ and centro-symmetrical structure.[5] In 1971, Mansingh *et al.* reported that the phase transition observed at the frequency of both 100 kHz and 3.6 GHz at 40°C under atmospheric pressure was not ferroelectric-paraelectric, therefore the room temperature phase under atmospheric pressure does not seem to be ferroelectric.[6]

However, this determination by them cannot be recognized unconditionally, for the measuring frequency may be higher than that of dielectric relaxation as well as in $AgNa(NO_2)_2$.[7] Then the authors tried to check it by the measurements of spontaneous polarization and electrical capacitance & dielectric loss tangent at lower frequency of both 1 kHz and 100 kHz over a range of pressure ($0\sim20$ kbar) at room temperature. The apparatus applying the quasi-hydrostatic high pressure to the KNO_2 samples was a piston-cylinder type press with pyrophillite filled with vaseline as a pressure transmitting medium. For calibration of oil pressure, the bismuth I-II and II-III phase transitions which occur at 25.5 kbar and 27.0 kbar respectively were adopted. Each sample was prepared by compressing powdered KNO_2 obtained from KNO_2 (85% pure) by recrystallization, and was a disk which was 10 mm in diameter and 0.7 mm in thickness. After each surface of the sample was coated with silver paste as a electrode, the sample was dried up for a day at about 120°C and was covered with beeswax to prevent it from hygroscopicity.

The phase diagram of KNO_2 given by Rapoport is shown in Fig. 1.[8]

Now, the capacitance C & the dielectric loss tangent $\tan\delta$ of samples were measured under various pressures along a dot-dash line in Fig. 1 at both 1 kHz and 100 kHz with a conventional ac-bridge and Q-meter respectively, and the existence of the spontaneous polarization was examined by the improved Sawyer-Tower's circuit.[9,10]

The pressure dependences of capacitance and dielectric loss tangent are shown in Fig. 2. The value of 6.3 kbar in Fig. 2 is the transition pressure which corresponds to the 6.4 kbar in Fig. 1, but the phase transition seems to be not ferroelectric-paraelectric one, since the capacitance C has no peak.

Furthermore, the relative dielectric constant ε_r and the dielectric loss tangent $\tan\delta$ of

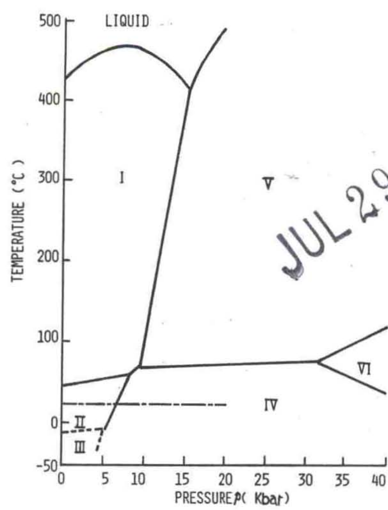

Fig. 1. Temperature-pressure phase diagram for potassium nitrite (after Rapoport.)

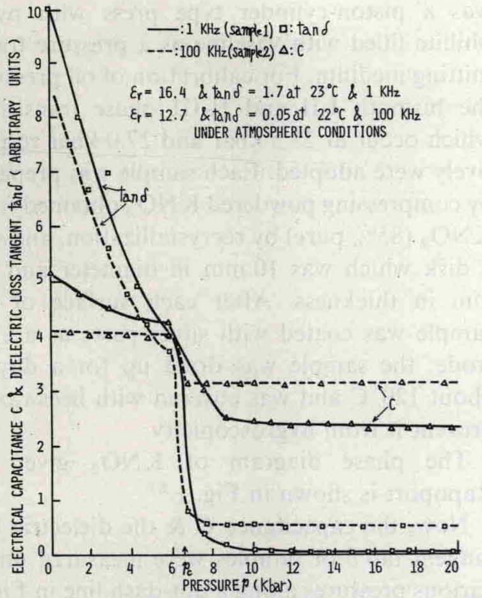

Fig. 2. The pressure dependence of electrical capacitance C and dielectric loss tangent $\tan\delta$ of powdered potassium nitrite at room temperature.

powdered KNO_2 at 1 kHz and 100 kHz under atmospheric conditions are $\varepsilon_r = 16.4$ & $\tan\delta = 1.7$ and $\varepsilon_r = 12.7$ & $\tan\delta = 0.05$ respectively. The values of ε_r and $\tan\delta$ at 1 kHz are larger than those at 100 kHz because of the contribution of dc-conductivity.[6] And the value of $\tan\delta$ at the pressure below the transition pressure p_c is larger than that at the pressure above p_c, because the mobility of ions which contribute to $\tan\delta$ at the pressure below p_c is larger than that at the pressure above p_c.

Moreover, by the fact that the hysteresis loop in dielectric flux density vs. electric field is not observed under $0 \sim 20$ kbar at room temperature, it is determined that the spontaneous polarization does not exist.

From these facts mentioned above, it can be stated that the room temperature phase under atmospheric pressure (phase II shown in Fig. 1) of potassium nitrite (KNO_2) is not ferroelectric.

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