kbar) and II-III (27.0 kbar) of bismuth and I-II (37.0 kbar) of thallium.

3. Experimental Results

The capacitance C and loss tangent $\tan \delta$ was measured by Q-meter at 100 kHz in the pressure range of 0 to 40 kbar. The spontaneous polarization was measured by the improved Sawyer-Tower circuit [9]. The type-a apparatus was used for the measurement of the phases I and II of $CaCO_3$ and type-b for other measurements.

3.1 Dielectric properties of KNO_2

Previously, we reported that KNO_2 is not ferroelectric at room temperature and its permittivity is invariant of the pressure at phase II [7]. Figure A1 shows the temperature-pressure phase diagrams [10] of KNO_2. Figure 4 shows the pressure dependence of logarithmic dielectric conductivity ($\log_e \omega_\varepsilon \tan \delta$) at $\omega = 2\pi \times 10^5$. At a constant temperature, $\log_\varepsilon \sigma$ decreases linearly with p

$$\log_e \sigma = -\alpha p + \log_e \sigma_0 \qquad (1)$$

where $\alpha = d \log \cdot \sigma / dp$ represents a gradient of the linear portion and is a constant independently of the pressure, and σ_0 is the dielectric conductivity at zero pressure.

At the temperature T(K), electrical conductivity σ of ionic crystal is given by

$$\log_e \sigma = -E/kT + \log_e \phi/kT \qquad (2)$$

where E is the activation energy, U is energy in the diffusion of lattice defects in the crystal and W is the energy in the generation of lattice defects, where E = U + W/2 (intrinsic region) and E = U (extrinsic region), k is the Boltzmann constant, and ϕ is a constant which is determined by the crystal itself.

Recently, Samara reported that logarithmic dielectric conductivity of thallium halogenide decreases with an inverse of the absolute temperature at low frequencies of 1 to 100 kHz under constant pressure. In addition, he pointed out that Eq. (2) holds even at the dc and low frequencies; activation energy obtained from the straight portion of the characteristic curves agrees with that obtained from the measurement of ionic conduction [11].

Substituting empirical Eq. (1) into Eq. (2), we obtain

$$E = \beta p + E_0 \qquad (3)$$

where

$$\beta = \alpha kT, \quad E_0 = kT \log_e(\phi/kT \sigma_0)$$
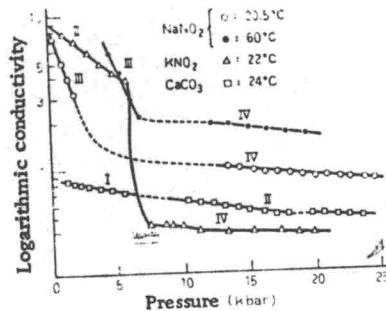

Fig. 4. Pressure dependence of logarithmic dielectric conductivity ($\log_e \sigma$) of a c-plate $CaCO_3$ (24°C), powdered KNO_2 (22°C) and a b-plate $NaNO_2$ (20.5°C, 60°C). $\varepsilon_r = 12.7$ and $\tan \delta = 0.55$ under atmospheric conditions for KNO_2 (100 kHz).

Therefore, activation energy increases in proportion to the pressure at a constant temperature. From the mark Δ in Fig. 4, we obtain $\beta = dt/dp = 4.1 \times 10^{-3}$ eV/kbar in phase II at the transition pressure less than 6.4 kbar. Electrical conductivity of KNO_2 at room temperature under normal pressure is in the intrinsic region and its activation energy is 0.63 eV [12]. Therefore at high pressure, the activation energy exceeds 0.63 eV.

The above-mentioned facts can be explained as follows; under high pressure, crystals are pressurized and the diffusion and generation of lattice defects cease. As a result, both U and W/2 increase and electrical conductivity decreases. Therefore, the effect of the pressure increase on electrical conduction is similar to the effect of the temperature reduction on the electrical conduction. In Samara's experiment under normal pressure, the temperature dependence of $\log_e \sigma$ is very small below 290 K. In Fig. 4 the pressure dependence of $\log_e \sigma$ is small at high pressure.

3.2 Dielectric properties of $NaNO_3$

Since Sawada's discovery of ferroelectric properties of $NaNO_2$ in 1958 [13], a number of researchers has reported that the phase I is ordinarily dielectric, phase II is anti-ferroelectric, and phase III is ferroelectric. The phase diagram is shown in Fig. 7 A2 [10]. However, no one has reported the phase transition from the phase III to IV and the dielectric properties at the phase IV.

Figure 5 shows the pressure dependence of permittivity and loss tangent of b-plate $NaNO_2$ at 100 kHz.

(i) The pressure corresponding to the III-IV phase transition is 8.7 kbar at 20.5°C and 11.0 kbar at 60°C. The relative permittivity is constant at the phase III, and decreases rapidly by