Fig. 5. Pressure dependence of relative permittivity (ε_{rb}) and loss tangent (tan δ) of a b-plate NaNO$_2$ at 100 kHz (20.5°C, 50°C).
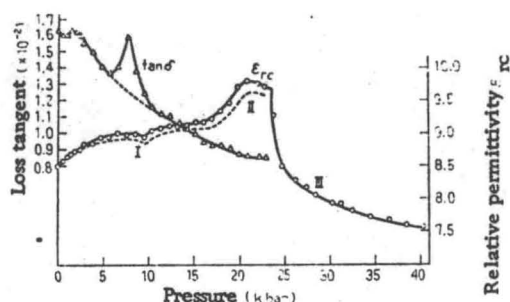

Fig. 6. Pressure dependence of relative permittivity (ε_{rc}) and loss tangent (tan δ) of a c-plate CaCO$_3$ at 100 kHz (24°C).

68% at the III-IV phase-transition pressure and then becomes constant at the phase IV.

(ii) The loss tangent exhibits small peaks at the III-IV phase transition pressure.

(iii) With increasing temperature, the pressure versus permittivity curve and the pressure versus loss tangent curve shift toward the high-pressure side.

A set of the transition pressures (8.7 kbar, 11.0 kbar) shown in Fig. 6 agrees with the transition pressure obtained by Rapoport [10] and Bridgman [14] by the volume-discontinuity method [see Fig. 7 (A2)].

The reduction of permittivity and the occurrence of small peaks of loss tangent at the transition pressure may be due to dispersion effect caused by jumping of ions to empty lattices under electric field.

The marks O and ● represent the pressure dependence of log$_e$ σ which are obtained from ε_{rb} and tan δ in Fig. 5. As seen in these curves at low pressures (below 2 kbar at 20.5°C and below 7.0 kbar at 60°C) and in the phase IV, the value

of log$_e$ σ decreases with the pressure p according to Eq. (1). Its pressure dependence is expressed as $\beta = 1.30 \times 10^{-2}$ eV/kbar (20.5°C) and 1.35×10^{-2} eV/kbar (60°C) in phase III and 6.0×10^{-4} eV/kbar (20.5°C) and 6.3×10^{-4} eV/kbar (60°C) in the phase IV. The pressure dependences of activation energy in both phases differ, but activation energy increases with the pressure. The electrical conduction of NaNO$_2$ is in the intrinsic region at room temperature under normal pressure.

When electric field of 1.1×10^6 V/m was applied to the sample under the pressure of 15 kbar, hysteresis loops were observed in the field vs. flux density characteristic curves at the temperature above 123°C. This indicates that the sample is ferroelectric in phase III above 123°C and its spontaneous polarization is 0.3 μC/cm^2.

3.3 Dielectric properties of CaCO$_3$

The physical properties of CaCO$_3$ under high pressure have been investigated by Bridgman's volume-discontinuity method [15], Davis' X-ray diffraction method [16] and Bell's D.T.A. method [17]. Figure 7 (A3) shows the phase diagram of CaCO$_3$ [18].

Figure 6 shows the pressure dependence of permittivity and loss tangent of a c-plate CaCO$_3$. From this figure, we conclude that:

(i) The permittivity increases gradually with the pressure in the pressure range from 0 to 18 kbar and increases rapidly near 18 kbar and becomes constant in the region II (19 to 23 kbar) and then decreases in the region III (above 23 kbar).

(ii) The loss tangent curves exhibit peaks at 8 kbar.

The above regions I, II and III correspond to the phases I, II and III of CaCO$_3$. The transition pressure (19 kbar, 23 kbar) obtained in this experiment at room temperature is slightly higher than the transition pressures (14.6 kbar, 17.7 kbar) obtained by the volume-discontinuity method [15] and (15.5 kbar, 18.7 kbar) obtained by X-ray diffraction method [16].

According to the conventional studies on the pressure dependence of the permittivity of solid materials at low frequencies, the permittivity decreases with the pressure. Mayburg reported that the permittivity of ionic crystals, such as MgO, LiF, NaCl, KCl, etc., decrease with the pressure at 1 kHz. He stated that this permittivity reduction is due to an increase of repulsion among ions which decreases the polarization coefficient and also due to overlapping of neighboring ions which decreases an internal electric field [19].

Unlike Mayburg's results, the permittivity of CaCO$_3$ in the phase I obtained in this measurement increases with the pressure. This may be due to the following reasons: with an increase of