Dielectric Study on Ionic Orientational Disorder in the Low-Temperature Phases of Ionic Plastic Crystal KNO_2

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The complex dielectric permittivity of ionic plastic crystal KNO_2 was measured in the frequency range 20–10^6 Hz and the temperature range 22–300 K. A small step-like anomaly of the static dielectric permittivity appeared at the rhombohedral (phase II) to monoclinic (phase III) transition ($T_{tr2} = 264.1$ K). In phase III, the static dielectric permittivity decreased gradually on cooling over a wide temperature range 50–264 K. These results indicate that the orientation of the NO_2^- ion is still disordered at high temperatures in phase III and becomes ordered gradually with decreasing temperature. The dielectric dispersion associated with this motion occurred in the temperature range 70–150 K. From these data and the previously reported ^{15}N NMR data, we propose a model of the motion of NO_2^- in phase III in which the anion undergoes 180°-flip motion about the axes perpendicular to the molecular C_2 axis in an asymmetric double-minimum potential.

1. Introduction

Alkali metal nitrites MNO_2 (M = K, Rb, Cs) and $TlNO_2$ crystallize into a plastic phase around room temperature [1–8]. Our nitrogen and alkali metal nuclei NMR studies [9–12] have revealed isotropic reorientation of the NO_2^- ion and self-diffusion of the cations in the plastic phase of these compounds. The entropy of fusion of the plastic phases [2] is smaller than $20\ J\ K^{-1}\ mol^{-1}$ satisfying the Timmermans criterion of the plastic crystal [13].

KNO_2 undergoes two structural phase transitions at 314.7 K ($= T_{tr1}$) and 264.1 K ($= T_{tr2}$) [1]. We hereafter call the plastic phase stable between 314.7 and 710 K (melting point) phase I, the intermediate phase between 264.1 and 314.7 K phase II, and the low-temperature phase below 264.1 K phase III. Phase I has a NaCl-type cubic lattice with space group $Fm\bar{3}m$, $Z = 4$, and $a = 666$ pm (at 318 K) [14]. The orientation of the NO_2^- ion is highly disordered as described above. Phase II has a rhombohedral lattice with space group $R\bar{3}m$, $Z = 1$, $a = 446.8$ pm, and $\alpha = 68.8°$ (at 298 K) [14]. The orientation of NO_2^- ion is disordered about the $\bar{3}$ axis. A monoclinic structure has been reported for phase III with space group $P2_1/c$, $Z = 4$, $a = 416$, $b = 962$, $c = 619$ pm, and $\beta = 113°$ (at 253 K) [14].

One expects the NO_2^- ions to be orientationally ordered in phase III from the low symmetry of the crystal structure [15], even though the atomic positions of K^+ and NO_2^- ions have not been determined. The heat capactiy exceeds the normal vibration value at temperatures as low as 50 K and increases with increasing temperature toward the III-II transition [1]. The excess entropy ($15.1\ J\ K^{-1}$ mol) due to this anomaly is comparable with the first order component of the III-II transition entropy ($10.8\ J\ K^{-1}$ mol). This result suggests that the orientation of the NO_2^- ion becomes disordered gradually with increasing temperature over an extremely wide temperature range in phase III. Our ^{15}N and ^{39}K NMR study [9] also supported the existence of the orientational disorder of the NO_2^- ions; i.e., a minimum of spin-lattice relaxation time T_1 appeared at about 160 K (in phase III) in both ^{15}N and ^{39}K data. We tentatively assigned this minimum to the NO_2^- 180°-flip considering the temperature dependence of the ^{15}N NMR spectra but it is also possible to explain the NMR data with a small-angle reorientation of the whole anion about one of the three principal axes of the chemical shift tensor.

As described above, there exists a confusion on the orientation of the NO_2^- ion in phase III; i.e., the structural study suggests orientational ordering of the NO_2^- ions while the calorimetric and NMR studies suggest an orientational disorder of the NO_2^- ions. The main purpose of the present study is to examine the existence of the orientational disorder of NO_2^- ions in phase III. Because of the net negative charge, one cannot assign a unique dipole moment to a nitrite ion. But reorientation of a nitrite ion is accompanied by reorientation of the polarization. This gives rise to an effective dipole moment associated with the ionic motion. Thus the dielectric study can provide conclusive information on the reorientational motion of the NO_2^- ions. It is also of interest to investigate the temperature and frequency dependence of the reorientational motions (if any) of the NO_2^- ions as functions of both temperature and frequency.

2. Experimental

KNO_2 crystals were prepared from $NaNO_2$ (Wako Pure Chemical Ind., Ltd.) using the cation exchange method

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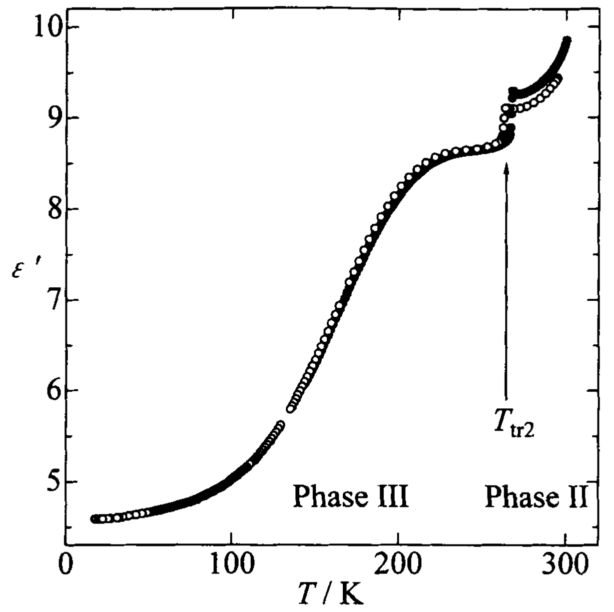

Fig. 1
The temperature dependence of the real part of the dielectric permittivity ε' of KNO_2 observed at 1 kHz in the heating (●) and cooling (○) directions. T_{tr2} denotes the reported II-III phase transition temperature [1]

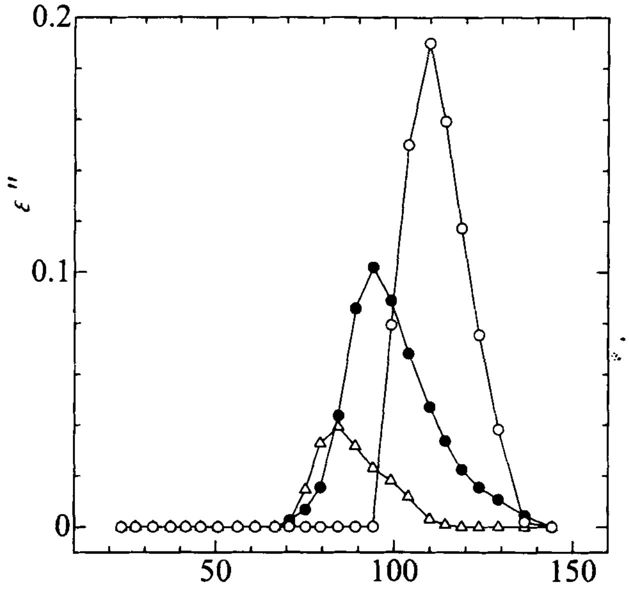

Fig. 2
Temperature dependence of the imaginary part of the dielectric permittivity ε' of KNO_2 observed at 1 kHz (△), 10 kHz (●) and 100 kHz (○)

(Diaion SK-1 resin, Mitsubishi Kasei Corp.). Concentration of the eluent under N_2 gas atmosphere yielded KNO_2 crystals. These crystals were purified by recrystallization from water. The purified crystals were dried in a desiccator over P_2O_5 for a week. Analyses by ICP emission spectrometry (Ash ICAP-757V, Nippon Jarrell) and ion chromatography (IC 100, Yokogawa) demonstrated excellent purity of the sample crystal; i.e., K^+: 99.9%, Na^+: 0.1%, NO_2^-: 100%.

Powdered crystals were shaped into a disc by applying a pressure of about 400 MPa. The diameter and thickness of the disk were 2 cm and 0.642 mm, respectively. For electrodes, two circular pieces of gold foil with diameter of about 18 mm were attached with a small amount of Apiezon N grease on both sides of the sample disk. All of these operations were carried out under dry N_2 gas atmosphere since KNO_2 crystals are very hygroscopic. The disk was then mounted on a double thermostated environment in a cryostat. The capacitance was measured with an LCR meter (HP4284A, Hewlett Packard). The dielectric permittivity was measured at 1 kHz as a function of temperature in the range between 22 and 300 K. The temperature was changed continuously at the rates of 0.5–1 K min^{-1} for both cooling and heating directions. The frequency dependence of the dielectric permittivity was measured at 48 frequencies between 20 and 10^6 Hz and at every 5 K in the temperature range 22–144 K. The sample temperature was stabilized to 0.03 K with an accuracy of 0.1 K.

3. Results and Discussion

Temperature Dependence of Dielectric Permittivity

The real part of the dielectric permittivity ε' measured at 1 kHz is plotted as a function of temperature in Fig. 1. The open and closed circles denote the data measured on cooling and heating directions, respectively. These data correspond to the temperature dependence of static dielectric permittivity above 110 K since dielectric relaxation at 1 kHz was observed at as low as 110 K as shown below. A step-like anomaly appeared at 262 K on cooling and at 267 K on heating. This anomaly is attributed to the II-III phase transition ($T_{tr2} = 264.1$ K). The hysteresis effect may be related to the first order nature of the transition [1]. Fairly large ε' in phase II (rhombohedral) reflects the orientational disorder of NO_2^- ions around the $\bar{3}$ axis reported by the X-ray diffraction study [14]. It is of interest that ε' of phase III (monoclinic) was still large even below T_{tr2} and gradually decreased with decreasing temperature. This suggests that the orientation of an NO_2^- dipole is still partly disordered in phase III and the number of the reorienting NO_2^- dipoles decreases with decreasing temperature.

Dielectric Relaxation

Fig. 2 shows the temperature dependence of the imaginary part of the dielectric permittivity ε'' at three selected frequencies. This data clearly shows the occurrence of the dielectric relaxation due to the NO_2^- dipoles in the frequency range examined. The temperature dependence of the maximum value of ε'', decreasing upon cooling, corresponds to that of ε' shown in Fig. 1.

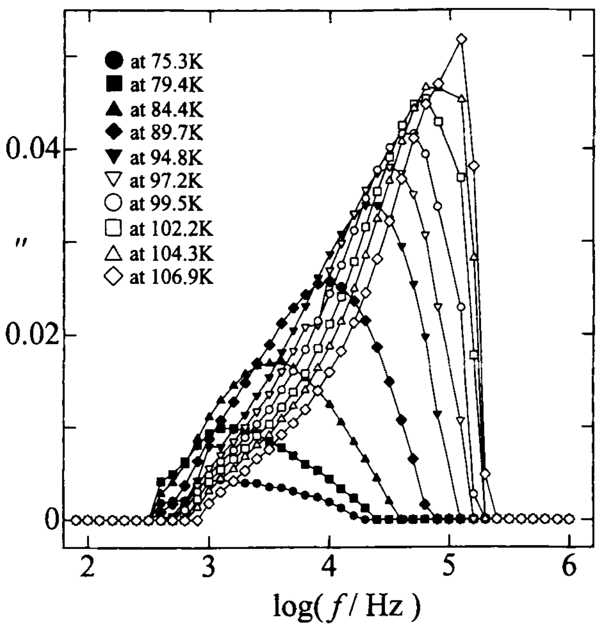

Fig. 3
Frequency dependence of the imaginary part of the dielectric permittivity ε'' of KNO_2 observed at 75.3 (●), 79.4 (■), 84.4 (▲), 89.7 (◆), 94.8 (▼), 97.2 (▽), 99.5 (○), 102.2 (□), 104.3 (△), and 106.9 K (◇)

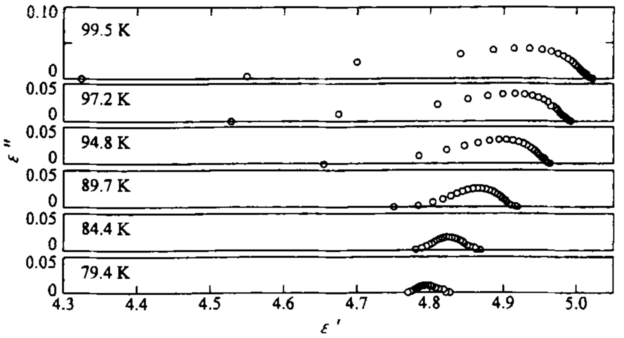

Fig. 4
Complex permittivity loci of KNO_2

The log (f/Hz) vs. ε'' plots and ε' vs. ε'' plots (Cole-Cole plot) are shown in Figs. 3 and 4, respectively. An interesting feature of the dielectric loss is found in its frequency dependence at different temperatures. At higher temperatures, the frequency dependence of ε'' (Fig. 3) is more gradual on the left side (i.e., at low frequencies) of the maximum than the right side (high frequencies), while the asymmetry is reversed at lower temperatures. At the intermediate temperature (84.4 K), the line shape is symmetric. Thus the relaxation is of a non-Debye type and the non-Debye character changes with the temperature. These relaxation data could not be reproduced by well-known relaxation functions (Cole-Cole [15], Cole-Davidson [16], Williams-Watts [17], and Havriliak-Negami functions [18]). The non-Debye relaxation is probably related with the ordering of the orientation of NO_2^- ions, Such cooperative ordering involves orientational interaction among the ions as an essential ingredient. This interaction introduces a factor not included in the single τ relaxation and may be responsible for the heavily deformed Cole-Cole semicircle plotted in Fig. 4.

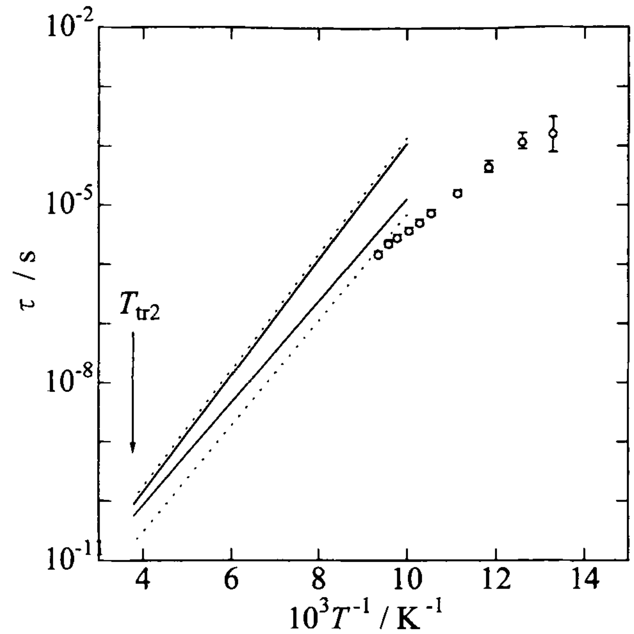

Fig. 5
Arrhenius plot of the relaxation times of KNO_2 obtained from this work (○) and the motional correlation times of ^{39}K (solid lines) and ^{15}N (broken lines) derived from NMR spin-lattice relaxation times [9]. T_{tr2} denotes the II-III phase transition temperature

Relaxation Time

The (averaged) dielectric relaxation times at respective temperatures were evaluated from the maximum frequencies (f_{max}) in Fig. 3 by using the relation:

$$\tau = 1/2\pi f_{max} ,$$

and plotted in Fig. 5. The motional correlation times obtained from ^{39}K (solid lines) and ^{15}N (broken lines) NMR [9] are also plotted for comparison. Each of the ^{39}K and ^{15}N data has two lines since the spin-lattice relaxation times were fitted to a combination of two BPP equations [19] with different activation energies. In the temperature region 100-110 K, where both dielectric and NMR data are available, they agree reasonably well with each other. This result suggests that the same motion (the reorientation of a NO_2^- ion) was observed by these two different techniques. Disagreement for the slope of each data may be caused by differences in data analysis; i.e., the NMR data were analyzed by assuming two Debye relaxation processes while the dielectric relaxation times are mean values over an unspecified distribution.

Motion of Nitrite Ions in Phase III

In the present dielectric study, we found the dielectric relaxation due to the reorientational motion of the NO_2^-

electric dipole in phase III. In our previous ^{15}N NMR study [9], no marked change in the chemical shift anisotropy was observed in phase III. The motion compatible with both dielectric and NMR data is the 180°-flip about the axes perpendicular to the molecular C_2 axis. The temperature dependence of the static dielectric permittivity indicates that this flipping motion takes place in an asymmetric double minimum potential and the population of the orientation with the lower energy increases with decreasing temperature. This is consistent with the previous calorimetric [1] and structural [14] data; the former indicated that the NO_2^- ions are orientationally disordered at higher temperatures and become ordered gradually with decreasing temperature and the latter (the structural data) indicated that two energetically-equivalent orientations of NO_2^- ion are unacceptable. The strange temperature dependence of the relaxation function shown in Figs. 3 and 4 is still an open question though it may be related to the gradual ordering of NO_2^- ions. In order to clarify the mechanism of this effect, it is necessary to analyze the dielectric data by quantitative models based on the temperature dependence of the structure of phase III. We are now analyzing the neutron diffraction data recently collected at several temperatures in phase III. Complete explanation of the dielectric and NMR data will be reported with the results of the neutron diffraction study in a near future [20].

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