CALORIMETRIC AND DIELECTRIC STUDIES OF PHASE TRANSITION IN TlNO$_2$ CRYSTAL

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The molar heat capacity of TlNO$_2$ crystal has been measured between 14 and 355 K with an adiabatic calorimeter.  A heat capacity anomaly due to a phase transition was found at (282.4±0.5) K.  The enthalpy and entropy changes of the transition are 6400 J mol$^{-1}$ and 23.6 J K$^{-1}$mol$^{-1}$, respectively.  The complex dielectric permittivity was measured in the frequency range between 200 Hz and 100 kHz.  Dielectric dispersion and relaxation were found between 80 and 180 K.  The activation enthalpy derived from the dielectric measurement is 19 kJ mol$^{-1}$ and is possibly related to the reorientation of the NO$_2^-$ ion.

Thallium(I) nitrite, TlNO$_2$, crystallizes in the cesium chloride structure at room temperature.[1]  The V-shaped NO$_2^-$ ion must be in an orientationally disordered state in the crystal in view of the octahedral symmetry of the anion site.  A phase transition is thus expected at a lower temperature.  This offers a possibility of studying orientational order-disorder transition and ionic reorientation in a structurally simple crystal.  In this letter we report new finding and preliminary study of phase transition in thallium(I) nitrite crystal by means of calorimetric and dielectric measurements.

The thallium(I) nitrite crystal was prepared by the double decomposition of Ba(NO$_2$)$_2$ and Tl$_2$CO$_3$ aqueous solutions.  The Ba(NO$_2$)$_2\cdot$H$_2$O crystal was prepared from extra-pure grade reagents of NaNO$_2$ and BaCl$_2\cdot$2H$_2$O (both from Wako Pure Chemicals).  Commercial Tl$_2$CO$_3$ (from Mitsuwa Pure Chemicals) was recrystallized from aqueous solution before use.  Rose-orange TlNO$_2$ crystal was obtained by slow evaporation of the double decomposition mixture at 25°C.  The sample for calorimetry was recrystallized from aqueous solution.  The elemental analysis for Tl gave (81.7±0.4)% by Tl$_2$CrO$_4$ gravimetric method in agreement with the calculated value of 81.63 %.
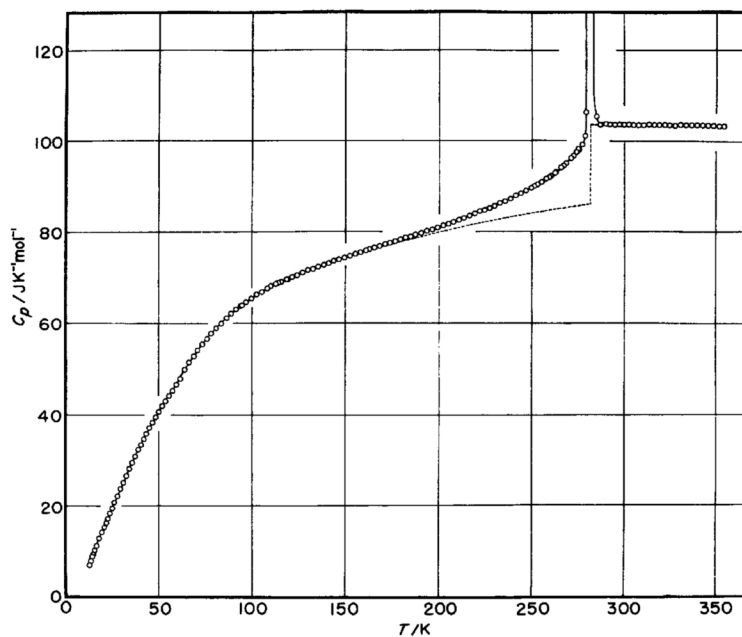
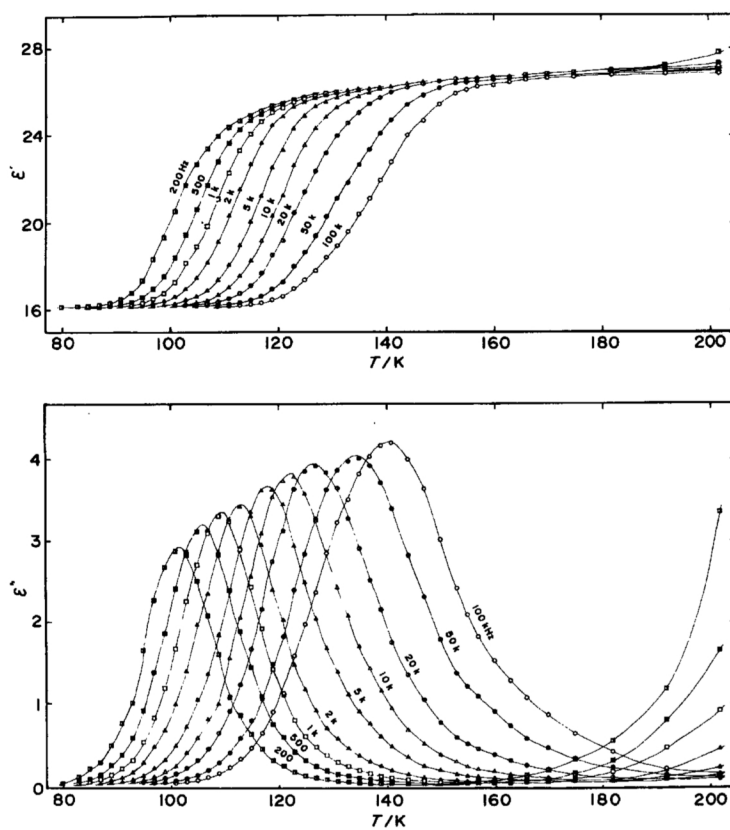Figure 1. Molar heat capacity of $TlNO_2$ crystal.



Figure 2. Above: dielectric constant of $TlNO_2$
crystal at various frequencies.
Below: dielectric loss of $TlNO_2$ crystal.

Heat capacity was measured with an adiabatic calorimeter between 14 and 355 K. The calorimetric apparatus was described elsewhere.[2),3),4),5)] The sample crystal was 102.074g in weight corresponding to 0.40764 mol. The crystal contributed about 75 % of the observed total heat capacity at room temperatures.

The complex dielectric permittivity was measured with a capacitance bridge (General Radio Co. type 1615-A) in the frequency range from 200 Hz to 100 kHz. The cryostat was described briefly elsewhere.[6)] The powder crystal of $TlNO_2$ was pressed to form a disc of 1 cm diameter and 1 mm thickness. Conducting silver paint was applied to the circular faces.

Figure 1 shows the molar heat capacity of $TlNO_2$ crystal. A large heat-capacity anomaly was found at $(282.4\pm0.5)$ K. The enthalpy and entropy of the transition, determined by use of the normal heat capacity given as dotted line in Fig. 1, are 6400 $J\,mol^{-1}$ and 23.6 $J\,K^{-1}mol^{-1}$, respectively. It is to be noted that the high temperature phase has larger heat capacity than the low temperature phase.

The real($\varepsilon'$) and imaginary($\varepsilon''$) parts of the relative dielectric permittivity are shown in Fig. 2. The dielectric dispersion was observed between 80 and 180 K. The magnitude($\Delta\varepsilon'\simeq10$) of the dispersion suggests that reorientation of $NO_2^-$ ion is responsible for the relaxation. The dielectric relaxation time $\tau=(2\pi f_{max})^{-1}$ caluculated by assuming a single relaxation process is plotted versus inverse temperature in Fig. 3 where $f_{max}$ is the maximum loss frequency. The activation enthalpy is 19 $kJ\,mol^{-1}$. Another dispersion which was caused by the phase transition at 282.4 K becomes significant above 180 K. The dielectric loss increased rapidly as the temperature approached the phase transition point and high electric conductivity($\simeq2.0\times10^{-3}\Omega^{-1}m^{-1}$ at 301 K) was observed in the high temperature phase.



Figure 3. Arrhenius plot of the relaxation time determined dielectrically.

The dielectric dispersion suggests that the low temperature phase of this crystal has some orientational disorder. The magnitude of the dielectric absorption increases with increasing temperature. With the assumption of two state model, this
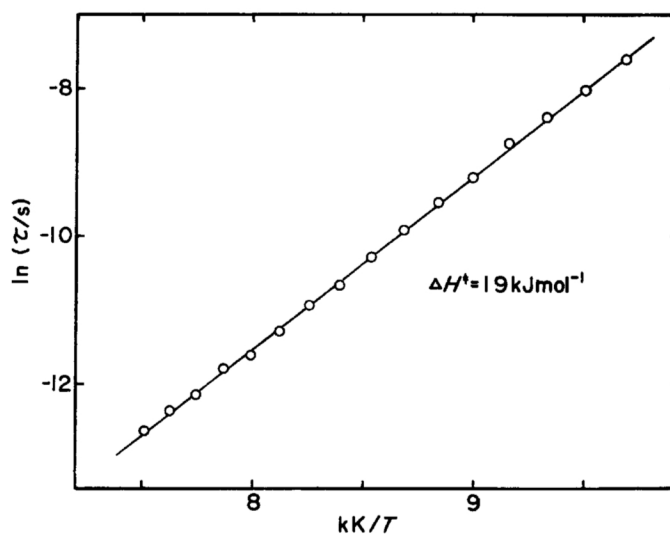
indicates that energy difference between the two minima separated by the activation enthalpy 19 kJ mol$^{-1}$ is larger than $RT$.[7] The prolonged relaxation time for the reorientational motion on cooling will hinder the crystal to reach the equilibrium state. Thus we can expect a heat capacity anomaly at a temperature where the dielectric relaxation time becomes about $10^{-4}$ Hz, the inverse of the "calorimetric" time scale. The detailed calorimetric study on this subject is now going on.

The simplest disorder compatible with the cubic symmetry of the high temperature phase is one which allows 4 x 3 = 12 orientations for the nitrite ion. The entropy due to this orientational disorder is equal to 20.7 J K$^{-1}$mol$^{-1}$ and explains the most part of the observed transition entropy. However, the low temperature phase of the crystal retains orientational disorder as mentioned above. The disorder in the high temperature phase appears thus more extensive than is expected from the 12-fold degeneracy. The larger heat capacity of the high temperature phase supports this view. Large excess heat capacity whose origin is not well understood at present has been found in the orientationally disordered phases of substances composed of globular molecules such as cyclohexane[8],[9] and 2,3-dimethylbutane.[10] Interestingly the present crystal has high plasticity[1],[11] as these organic "plastic" crystals do. High plasticity and the excess heat capacity may thus be characteristic of highly disordered crystals irrespective of their molecular or ionic nature. Mechanical measurement of TlNO$_2$ crystal is in progress.

### References

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