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Study of dielectric properties of $RbNO_3$ single crystals

A. SADANANDA CHARY, S. NARENDER REDDY, T. CHIRANJIVI
Department of Physics, University College of Science, Osmania University,
Hyderabad 500 007, India

Dielectric properties, dielectric constant (k), dielectric loss (tan δ) and a.c. conductivity (σ) in the solution-grown single crystals of $RbNO_3$ are presented from room temperature to about 200° C covering the frequency range 10^2 to 10^5 Hz. A broad peak observed in tan δ-frequency data between 10^3 and 10^5 Hz is thought to be due to impurity–vacancy dipoles. The sudden rise of three parameters near 160° C is attributed to the known phase transition from trigonal to CsCl structure.

1. Introduction

Of the alkali nitrate crystals, $RbNO_3$ has a structure isomorphous with $CsNO_3$ at room temperature [1–4]. $RbNO_3$ is known to have three distinct phase transformations at higher temperatures [4–6]. At low temperature and high pressure, yet a different phase is known to be present [7, 8].

There have been some studies reported on the variation of dielectric constant (k) and dielectric loss (tan δ) with temperature [5, 8–10], but none of the investigations studied the variation of dielectric constant, dielectric loss and a.c. conductivity with both frequency and temperature and correlated the three. Our study of these transformations by measuring the d.c. conductivity with temperature [11] shows that the transition IV to III at about 160° C is predominant, associated with the maximum variation of conductivity. Our studies on thermal analysis [12], show that all three transitions are endothermic.

In this paper we report our studies of dielectric constant (k), dielectric loss (tan δ) and a.c. conductivity (σ) in single crystals of $RbNO_3$ both with frequency and temperature.

2. Experimental procedure

Single crystals used in this study were grown by the slow evaporation method at room temperature. The starting material was obtained from Fluka AG, Chem. Fabrik CH 9470 Buchs. The salt was dissolved in double distilled water, filtered and allowed to evaporate slowly. After about 10 d, needle-shaped crystals were obtained with the length along the trigonal c-axis. Good crystals of approximate size $2 \times 2 \times 1\,\text{mm}^3$ were silver painted and mounted in a spring-loaded crystal holder. Measurements were made along the direction perpendicular to the c-axis. Data were recorded on a GR-716 type Capacitance bridge. The accuracy of measurement was about 3% in k and 5% in loss (tan δ). A constant heating rate of about $1.5^\circ\text{C}\,\text{min}^{-1}$ was maintained and the temperature was recorded using a chromel–alumel thermocouple.

3. The different phases

$RbNO_3$ has four stable forms between room temperature and its melting point:

$$\underset{\text{Trigonal}}{\text{IV}} \xrightleftharpoons{164^\circ\text{C}} \underset{\text{Cubic (CsCl)}}{\text{III}} \xrightleftharpoons{219^\circ\text{C}}$$

$$\times\ \underset{\text{Rhombohedral}}{\text{II}} \xrightleftharpoons{285^\circ\text{C}} \underset{\text{Cubic (NaCl)}}{\text{I}}$$

All these are reversible transformations.

3.1. IV to III

X-ray studies [6] revealed that when heated up to 164° C the room-temperature phase IV (trigonal) transforms to cubic (CsCl) phase III. The trigonal triad (0 0 0 1) of IV phase transforms to cubic triad (1 1 1) of III phase with the trigonal $(1\,0\,\bar{1}\,1)$ direction becoming (1 0 0), which is the cube edge direction as shown in Fig. 1. If cooled, any one of the four cube diagonals can give rise to the trigonal c-axis in the reversible transformation, III to IV. In the trigonal phase $a = 1.048$ nm and $c = 0.745$ nm, and in the cubic CsCl phase $a = 0.437$ nm.

3.2. III to II

According to Salhotra *et al.* [13] the cube, shown in Fig. 2a, is pulled along the body diagonal to change over to the rhombohedral cell of Fig. 2b. In the cubic phase $a = 0.437$ nm, and in the rhombohedral phase $a = 0.48$ nm.

3.3. II to I

Near 285° C, II rhombohedral phase changes over to I cubic (NaCl) phase. According to Salhotra *et al.* [13] the pulling mentioned above continues as the temperature is increased to attain finally the NaCl structure, shown in Fig. 2c. It can be seen that, of the eight rubidium ions on the corners of the cube in II phase, six rubidium ions fall on the face centres of the NaCl structure during this process of pulling, leaving the two ions that lie on the body diagonal. In the

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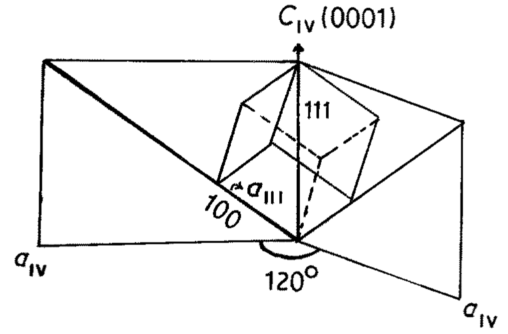

Figure 1 Structural relationship between the unit cells of IV phase and III phase of $RbNO_3$.

rhombohedral II phase $a = 0.48$ nm, and in the cubic (NaCl) I phase $a = 0.725$ nm.

4. Observations and discussion

4.1. Variation with frequency at room temperature

Fig. 3 shows the variation of dielectric constant (k) with frequency at room temperature. It can be seen that the value of k which is about 110 at 100 Hz falls with frequency until about 30 kHz and then reaches a near constant value of about 22. At frequencies near ultraviolet, the contribution to polarization is mainly electronic where $k = n^2$ (n is refractive index). As the frequency is lowered the contribution to polarization from atomic or ionic polarization becomes significant. Finally, at lower frequencies near microwave and lower dipolar, the contribution becomes significant. It is reasonable to suggest that there is a contribution from all sources to the polarization measured in our experiments, where the maximum value of frequency is only 300 kHz. Thus the large value of dielectric constant at low frequency suggests that there is a contribution from all four known sources of polarization, namely electronic, ionic, dipolar and space charge polarization of which the latter is known to contribute strongly at low frequencies [14].

Fig. 4 shows the variation of dielectric loss (tan δ) with frequency at room temperature. From a value of 6.1×10^{-1} at 100 Hz it decreases and reaches a minimum of 1.75×10^{-1} which then gradually increases until 10 kHz giving a broad peak between 1 and 100 kHz. The value of tan δ generally decreases exponentially with frequency. Any peak, if it appears, corresponds to the presence of dipoles. The broad peak seen in our results could be due to impurity–vacancy (I–V) dipoles [15] produced by the unavoidable bivalent metal impurities present in the starting material, these being copper, lead, cadmium, zinc and iron. The frequency 10 kHz, where tan δ is maximum, corresponds to the ratio between the period of applied external field and the period of relaxation of dipoles at which the dipoles have greatest loss of energy to overcome the resistance of the viscous medium.

4.2. Variation with temperature at 10 kHz

Fig. 5 shows the variation of dielectric constant (k) with temperature at a frequency of 10 kHz. From room temperature, k decreases up to 110° C which then increases slowly with temperature, increasing rapidly at about 160° C, after which the rise once again becomes slow. The sudden increase of k at 160° C obviously corresponds to the known phase transition from trigonal to CsCl-type cubic. This result is in accordance with Kawashima *et al.* results [5] measured at 1 kHz and Fujimoto *et al.* results [10] at 1 MHz. The slow increase of k up to 160° C implies that there are no significant changes in the crystal lattice but a slight release of bonds through volume dilatation [13, 16]. At the transition temperature the relaxational motion of NO_3 groups causes a sudden rise of k because in addition to the usual contribution, from electronic and ionic, orientational polarization becomes considerably more.

Fig. 6 shows the variation of dielectric loss (tan δ) with temperature at a frequency of 10 kHz. From room temperature it gradually falls up to 110° C and then starts to increase up to 160° C, where there is a sudden rise near the transition temperature. In the work of Dikant *et al.* [9], a certain amount of scattering was noticed in place of a sudden increase of tan δ at this transition temperature, which they attributed to the instabilities occurring during the transition. No further comparison can be made unfortunately, because we have not come across any other published work in this regard.

Fig. 7 shows the variation of a.c. conductivity, calculated from the data of k and tan δ, with temperature at a frequency of 10 kHz. There is a slow decrease of conductivity up to 110° C, 2.61 on the x-axis, and then a gradual increase up to 160° C, 2.31 on the x-axis, which becomes sudden near the phase transition IV to III. The sudden increase in conductivity is obvious because the room-temperature trigonal phase which is of low symmetry, changes over to CsCl (cubic) phase of higher symmetry [6].

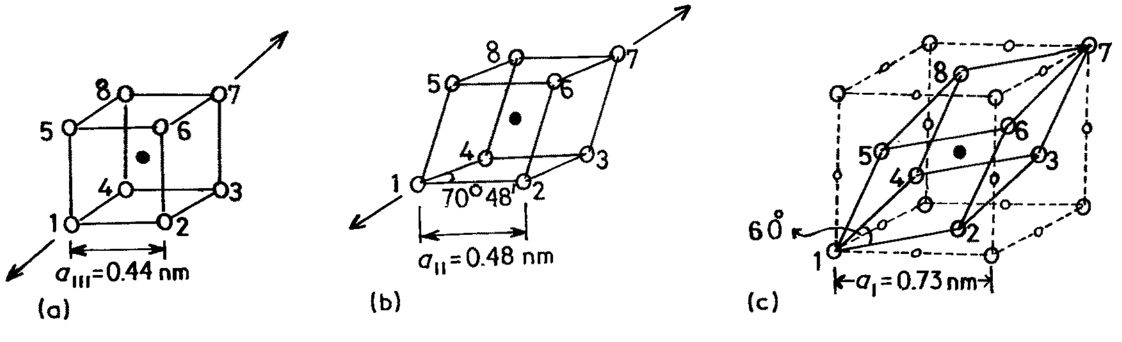

Figure 2 Structural relationships of $RbNO_3$ in III, II and I phases: (a) III cubic (CsCl) phase, (b) II rhombohedral phase, (c) I cubic (NaCl) phase.

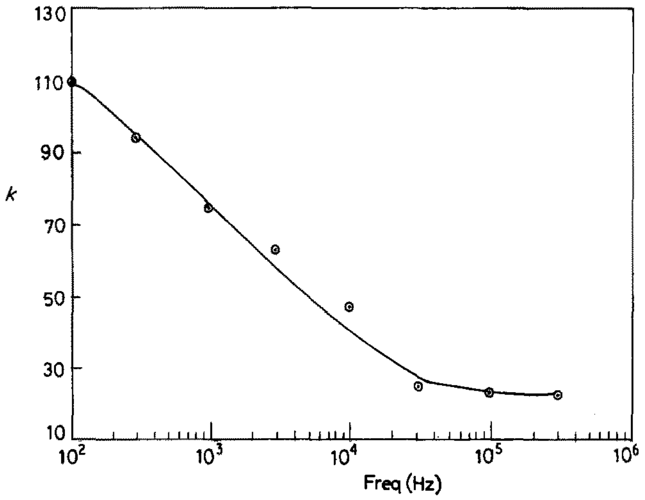

Figure 3 Variation of dielectric constant (k) with frequency at room temperature, for $RbNO_3$.

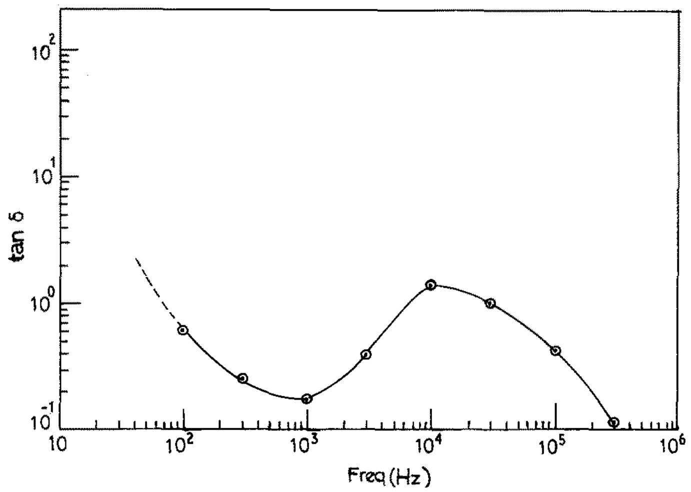

Figure 4 Variation of dielectric loss (tan δ) with frequency at room temperature, for $RbNO_3$.

5. Conclusion

From the study of k and tan δ with frequency it is felt that some I–V dipoles exist which would give rise to a broad peak, and from the study of k, tan δ and a.c. conductivity with temperature it is understood that the known IV–III phase transition is due to increasing disorder of nitrate ions. First-order transitions are associated with change of volume and entropy. This IV–III transition which is associated with a change of entropy of 1.07 R [17] and change of volume [13] is a first-order transition. In our earlier study of d.c. conductivity we observed temperature hysteresis during the transition. It should be noted that the phase transitions associated with temperature and pressure hystereses are of first order [17].

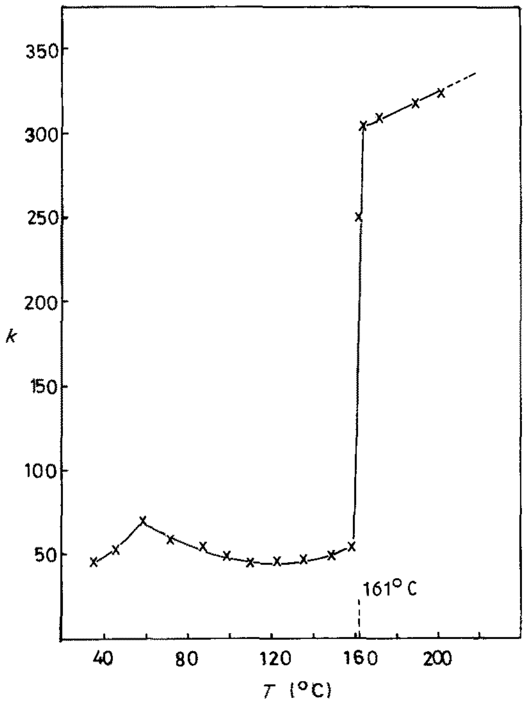

Figure 5 Variation of dielectric constant (k) with temperature at 10 kHz, for $RbNO_3$.

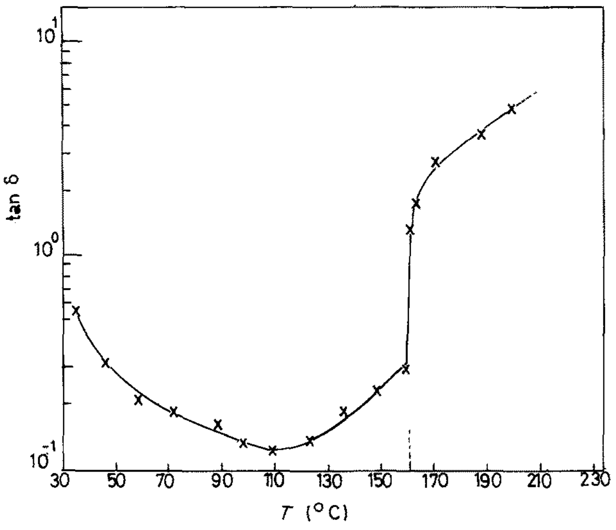

Figure 6 Variation of dielectric loss (tan δ) with temperature at 10 kHz, for $RbNO_3$.

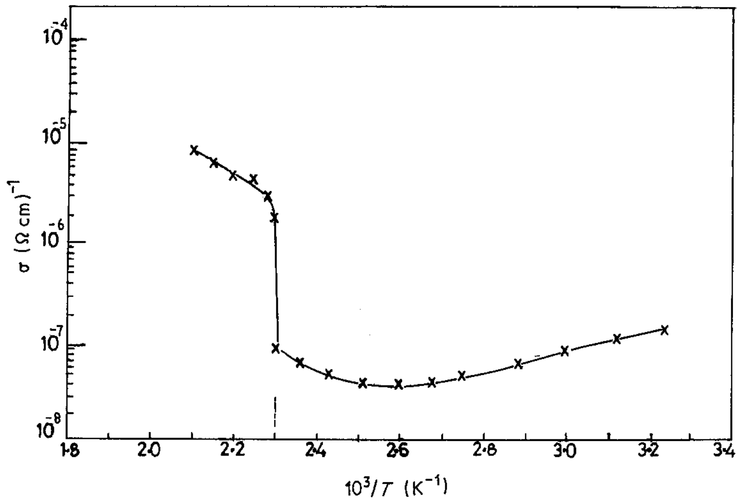

Figure 7 Variation of a.c. conductivity with $10^3/T$ at 10 kHz, for $RbNO_3$.

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