

## On the Frequency Dependence of the Dielectric Properties of $\text{NaNO}_3$

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The influence of the frequency of measurement and the inclusion of the divalent impurity  $\text{Ba}^{2+}$  on the dielectric properties of polycrystalline  $\text{NaNO}_3$  has been determined. Samples of zone refined  $\text{NaNO}_3$  were investigated at frequencies in the range  $2 \times 10^2$  to  $10^5$  Hz and at temperatures of 21 to 224°C. Values of dielectric constant and a.c. resistivity show that the lattice disorder introduced by the phase transformation occurring over the temperature range  $\sim 150$  to  $\sim 275^\circ\text{C}$  is characterized by relaxation frequencies of  $10^3$  to  $10^4$  Hz.

The study of atomic, molecular, and ionic group disorder in crystals is of considerable theoretical and practical interest, and the subject has been discussed by many authors in relation to  $\text{NaNO}_3$  and other compounds. A fundamental problem in this connection lies in the development of a good lattice dynamical model for each compound, together with details of changes which are required at phase transformations and other anomalies occurring within the ranges of temperature and pressure over which the compound exists as a crystalline solid. The nature and scope of the model depend inherently on the kind of experimental investigations upon which it is based. Experimental data involving averages over large numbers of atoms and considerable periods of time, as occur for example in calorimetry and X-ray diffraction, have played an important role in the historical development of the subject. Such experiments have often led to the discovery of disorder phenomena, and have provided the fundamental energetic and spatial parameters upon which the lattice models are based. Information of this type is, however, insufficient for a complete understanding of events, and it is desirable to include in the model some of the parameters of motion for individual atoms as functions of time.

The various experimental techniques which depend on, or are influenced by, resonance effects at the atomic level are of special value in this connection. At high frequencies, infrared and ultraviolet spectroscopic methods yield valuable information, while at low frequencies one depends mainly upon magnetic resonance and dielectric measurements. Of the experimental work

which has been performed hitherto on  $\text{NaNO}_3$ , there appears to be only one study which is indicative of low frequency effects. The quadrupole-split NMR spectrum obtained by Eades *et al.*,<sup>1</sup> showed an unusually rapid variation in the value of the quadrupole coupling constant with temperature for the  $^{23}\text{Na}$  nuclei, which was suggested as being due to diffusion through the lattice of  $\text{Na}^+$  ions at a jump rate of  $\geq 10^3 \text{ s}^{-1}$  in the disordered phase. According to this interpretation, the transformation over the range  $\sim 150$  to  $\sim 275^\circ\text{C}$ , which is known to involve orientational disorder of nitrate groups, also produces positional disorder of the cations.

In the absence of an externally applied electric field, such movements of ions can occur in the ideal ordered lattice as cooperative interchanges involving two or more closely situated members of the sublattice; and the possibilities for movement in a real crystal will be greatly increased by the presence of defects such as vacancies. On application of an electric field to the crystal the translations are more likely to occur in the direction favoured by the field, thus constituting an electric current. Providing a sufficiently small proportion of the total number of ions possess the increased energy required to effect the transitional jump at any instant, the total amount of energy associated with this degree of freedom will not be great, since there is no disorder entropy attached to distributions of metastable positions of the ions.

It is thought that the positional jumping of cations in  $\text{NaNO}_3$  is related to the reorientations of the anions through the medium of fluctuations in lattice potential. An implication of this correlation is that anion reorientations do not occur in negligibly short time intervals, during which the bulk of the lattice would remain unresponsive owing to inertia. Instead, the jumping process appears to occupy a time interval which is comparable with the periods of normal lattice modes of oscillation. Consistent with this view, anion reorientations are regarded as being cooperative over small distances. This interpretation of the situation in  $\text{NaNO}_3$  represents a departure from the general model proposed by Darmon and Brot,<sup>2</sup> in which group reorientations occur sufficiently fast to leave the surrounding ions undisturbed.

The present measurements were undertaken with the aim of detecting frequency effects which might reflect time dependent lattice parameters. Previous electrical studies on pure and doped samples were restricted to the use of d.c., or a.c. measuring frequencies of a single value.<sup>3-15</sup> On the basis of the separation of oxygen atoms found in recent X-ray investigations on  $\text{NaNO}_3$ ,<sup>16,17</sup> a hard sphere model of the nitrate group (assumed planar) gives  $2.20 \times 3.53 \text{ \AA}^2$  as the overall dimensions of the minimum cross section of the group, and the effective radius for translation perpendicular to its three-fold axis is thus  $1.57 \text{ \AA}$ . Since the nitrate groups are situated in planes, with their three-fold axes parallel to the crystallographic  $c$  axis, migration is most probable within these planes. The considerably smaller radius of the cation,  $0.95 \text{ \AA}$ , suggests, however, that it will normally be the dominant charge carrier.

Both interstitial ion and vacancy transport are *a priori* consistent with the known features of both the ordered and disordered lattice states. Ramasastry and Murti<sup>11</sup> have obtained evidence of conduction by interstitial cations in both states. Measurements of  $\sigma_{\text{d.c.}}$  on single crystals grown from the melt, and for two other samples containing  $\text{Ba}^{2+}$  as impurity showed the

addition of the divalent ions to decrease the conductivity. The reductions in conductivity were approximately proportional to the impurity concentrations used, implying that cation vacancies introduced into the lattice trap the normal carriers which, in the absence of any information regarding other cation impurities (*e.g.*  $\text{Li}^+$ ), may be tentatively assumed to be interstitial  $\text{Na}^+$  ions. More recently, Cerisier<sup>15</sup> measured the conductivities of compressed powder samples of  $\text{NaNO}_3$ , using pure compound, and samples with added  $\text{Ca}^{2+}$  or  $\text{Ba}^{2+}$ . A d.c. technique was used for  $\sigma > 10^{-6} \Omega^{-1} \text{cm}^{-1}$ , and 1 kHz a.c. at higher conductivities. The results for samples containing  $\text{Ba}^{2+}$  were inconclusive, but those with  $\text{Ca}^{2+}$  showed increases in  $\sigma$  with increasing impurity concentration; thus indicating the cation vacancy transport mechanism.

The contradictory nature of these results merits comment in view of the interest in ascertaining the correct nature of intrinsic charge transfer mechanism. Both of the above studies employ only two electrical connections to the sample and are therefore hampered by polarization potentials at the electrodes. Comparison of the results given by Cerisier<sup>15</sup> for a compressed sample of pure compound with those for single crystals<sup>11,14</sup> shows that at 500 K the conductivity of the compressed sample is greater by more than 1.5 orders of magnitude. This comparatively high value is indicative of the controlling effect of inter-grain boundaries and/or impurities in these samples, the results for which also differ markedly in form from those of single crystals. It therefore appears difficult to deduce properties of the crystal lattice from the effects of added impurities or increased pressure in such samples.

## EXPERIMENTAL

Samples of zone refined  $\text{NaNO}_3$  yielding the mass spectrographic analysis (in ppm) Li 8, Mg 1, Si 6, P < 1, Cl 4, K 3, and Ca 1.5, were recrystallized from the melt between parallel silver plates separated by 0.3 mm quartz spacers. Impure samples were prepared by adding to the melt weighed amounts of  $\text{Ba}(\text{NO}_3)_2$  which had been recrystallized from an aqueous solution of p.a. grade material.

The temperature of samples undergoing measurement was controlled by means of equipment described previously.<sup>14</sup> Values of sample capacitance and dissipation were obtained as functions of frequency using an impedance bridge (General Radio, type 1650-A) in conjunction with a signal generator (Oltronix RCO-6K).

## RESULTS AND DISCUSSION

Values of the dielectric constant  $\epsilon$  as a function of the measuring frequency  $f$ , at various temperatures, are shown in Fig. 1 for a polycrystalline sample of  $\text{NaNO}_3$ , and another containing a mol fraction of  $5.0 \times 10^{-3} \text{Ba}^{2+}$ . The divalent impurity content of the latter sample was chosen to be close to the upper limit of  $3.4 \times 10^{-3}$  employed by Ramasastry and Murti.<sup>11</sup>

For the pure sample at 21°C,  $\epsilon$  is seen to decrease slightly from 7.2 with increasing frequency. The value of  $\epsilon$  obtained at 1 kHz for p.a. grade  $\text{NaNO}_3$  is 9.9.<sup>14</sup> The sample containing added  $\text{Ba}^{2+}$  is seen to have a value of  $\epsilon = 15.0$  at 300 Hz and 21°C; and this is decreased to 8.3 at  $5 \times 10^4$  Hz. The observed frequency dependence of the impurity component of dielectric constant suggests the presence of a relaxation effect which is probably due to the hindered

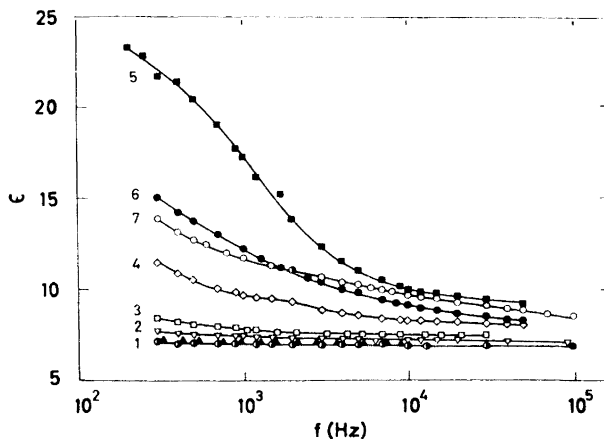


Fig. 1. Dielectric constant  $\epsilon$  versus measuring frequency  $f$ . Zone refined  $\text{NaNO}_3$ : Curve No. 1,  $\bullet$  21°C,  $\circ$  37°C,  $\triangle$  62.5°C; No. 2, 83°C; No. 3, 127°C; No. 4, 179°C; No. 5, 224°C. Zone refined  $\text{NaNO}_3$  with  $5.0 \times 10^{-3}$  mol fraction  $\text{Ba}(\text{NO}_3)_2$  added: No. 6, 21°C; No. 7, 39.2°C. The symbol  $\bullet$  represents coincident readings.

reorientation of dipoles formed by the  $\text{Ba}^{2+}$  ions and associated vacancies. The effect of increasing the temperature of this sample to 39.2°C is seen to be slight.

Increasing the temperature of the pure sample to 37 and 62.5°C has little effect on  $\epsilon$ , but over the sequence of temperatures 83, 127, 179, and 224°C, a rapid increase is evident in the low frequency values of this parameter. The values of  $\epsilon$  obtained at 224°C show a dependence on frequency which clearly demonstrates the presence of time dependent restraints on charge displacements in the crystal. The asymptotic form of the curve towards constant values above  $f \approx 10^4$  Hz shows that a limiting time constant of  $\sim 0.5 \times 10^{-4}$  s is associated with the displacements. This finding is interpreted as showing in a direct way that the limiting rate of positional jumping of the cations, and probably also of the orientational jumping of the anions, has an upper frequency limit of  $\sim 10^4$  Hz at 224°C. This temperature was chosen within the range of the thermal transformation in order to examine a crystal with a substantial degree of disorder. The result is consistent with the finding by Eades *et al.*<sup>1</sup> referred to earlier.

Values of a.c. resistivity  $\rho_D$ , calculated from the equivalent parallel resistance of the sample, are shown in Fig. 2. The curves for zone refined samples show little variation over the temperatures 21, 37, and 62.5°C; as was found previously for *p.a.* grade samples at 1 kHz.<sup>14</sup> Over the frequency range  $10^3$  to  $10^5$  Hz, the curve has values of slope which correspond approximately to  $\rho_D \propto f^{-1}$ , as is typical of dissipation by bound rather than mobile charge carriers. The values of  $\rho_D$  at these temperatures for  $f = 1$  kHz lie between those for *p.a.* samples and  $\rho_{d.c.}$  for single crystals at the same temperatures,<sup>14</sup> reflecting the greater purity of the zone refined samples compared with the *p.a.* material.

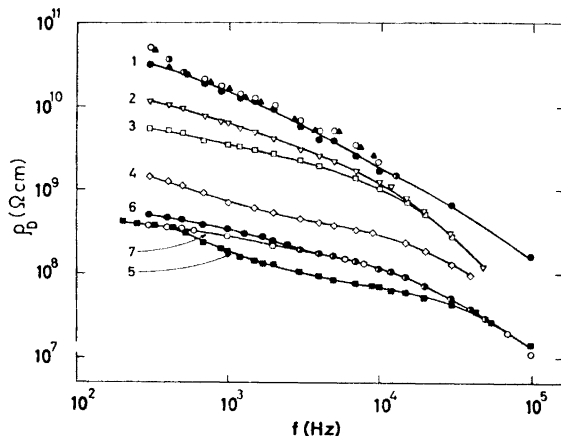


Fig. 2. Resistivity  $\rho_D$  versus measuring frequency  $f$ . Labelling of data as in Fig. 2.

In comparing the a.c. and d.c. resistivities for relatively pure and impure samples, the following factors have to be taken into consideration. In a pure sample the four-terminal d.c. and low frequency a.c. values of resistivity will, ideally, differ only by the amount of the dissipation caused by reorientation of hindered dipoles, which contribute to the alternating sample current in phase with the applied voltage. On the introduction of divalent cation impurities to crystals exhibiting conduction by interstitial cations, two alternatives arise. If the corresponding vacancies remain associated with the impurities at the temperature of measurement, the a.c. conductivity will be increased owing to relaxation of dipole reorientation; while the concentration of interstitial cations will be decreased, thereby reducing their contribution to the current. The latter effect is the only one detected using d.c. On the other hand, dissociated vacancies will contribute to both alternating and direct currents, without necessarily being majority carriers. From these considerations it is seen that only in exceptional cases will d.c. and a.c. values of resistivity be equal. This is demonstrated by the values of  $\rho_D$  for the pure sample at 21, 37, and 62.5°C (curve No. 1, Fig. 2) which shows a rate of variation of approximately one order of magnitude in resistivity for each order of magnitude change in frequency.

On increasing the temperature of pure samples above 62.5°C, the curves fall to progressively lower levels of resistivity and show a tendency to produce a minimum in the range  $10^3$  to  $10^4$  Hz. The latter effect is caused by relaxation losses associated with the charge jumping discussed in relation to the corresponding value of  $\epsilon$ . In comparing the relative magnitudes of the effects shown by the two parameters, it is noted that in the case of  $\rho_D$  both translation and relaxation losses are recorded, whereas  $\epsilon$  is little influenced by the former. The broad nature of the depression in  $\rho_D$  reflects the rather wide range of frequencies involved in the jump processes, and this prevents a deduction of

the height of the relevant energy barrier by observation of the change in the frequency of the minimum in  $\rho_D$  with temperature.

The resistivities of crystals containing added  $Ba^{2+}$  (curves Nos. 6 and 7, Fig. 2) are approximately two orders of magnitude lower than those for the pure compound at the same temperatures. Although being close to the curve for pure material at 224°C they show no tendency to form relaxation minima. The reduction in a.c. resistivity of impure compared with pure samples is not necessarily incompatible with the finding of increased d.c. resistivity for similar samples by Ramasastry and Murti,<sup>11</sup> as outlined in the foregoing arguments. The purpose of obtaining such data was to include sufficient divalent impurity in the sample to swamp the normal intrinsic and extrinsic carriers, and thereby to detect any relaxation effects analogous to those seen in pure crystals at higher temperatures. In fact, such phenomena are absent in the frequency range covered, thus demonstrating an inherent difference between the two mechanisms.

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