

Electrical and Other Properties of $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, and $\text{Pb}(\text{NO}_3)_2$

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The temperature dependence of the dielectric constant and AC resistivity of polycrystalline samples of $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, and $\text{Pb}(\text{NO}_3)_2$ have been determined from -140 to $\sim 300^\circ\text{C}$, and the four-terminal DC resistivity of single crystals measured above room temperature. The energy parameters of ionic conductivity are deduced from the DC resistivity data. A solid state transition is detected in $\text{Ba}(\text{NO}_3)_2$, and anomalous temperature variations of the dielectric constant and resistivity of the three compounds are interpreted in terms of a threshold in the thermal activation of modes of vibration of the nitrate group.

Determinations of the unit cell dimensions by means of X-ray diffraction over the temperature range 4.2 to $\sim 700^\circ\text{K}$ show the expansion curves to include points of inflexion, the form of the curve for $\text{Ba}(\text{NO}_3)_2$ differing from the other two. There is no evidence of structural, order-disorder, or other energetic transformations in the experimental X-ray, DTA, or magnetic susceptibility data presented.

The work performed earlier in this laboratory on anhydrous univalent nitrates¹⁻⁷ has now been extended to include the divalent salts $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, and $\text{Pb}(\text{NO}_3)_2$, which were selected as examples of a class of compounds suitable for comparison with those already studied. In particular, possible variations in the role of the nitrate group in determining the properties of the crystalline solids were of interest in view of the differences in valence and crystal structure between the univalent and divalent nitrates.

The first, and superficial, investigation of the structures of $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, and $\text{Pb}(\text{NO}_3)_2$ was reported⁸ in 1917. Five years later Vegard⁹ showed the compounds to be isostructural and of cubic symmetry with four formula units per unit cell, the most probable space group being suggested as $Pa\bar{3}$. The nitrate group was deduced to be pyramidal in form. In later work, Vegard and Bilberg,¹⁰ and Vegard and Roer¹¹ found the nitrate group to be planar in all three compounds,* the preferred space group being maintained

* The positional parameters given for N and O in the structure of $\text{Pb}(\text{NO}_3)_2$ are not in precise agreement with the claimed planarity, however.

as $Pa3$. There was no evidence of rotation of the group about its threefold axis at room temperature. Vegard and coworkers thus introduced the three fundamental structural problems of correct space group, the symmetry properties of the nitrate group, and the possibility of its rotation within the crystal lattice.

Jaeger and van Melle,¹² who obtained single crystal X-ray data at room temperature, found $Pa3$ to be the most probable space group for the three compounds. X-Ray diffraction techniques have also been used in several determinations of unit cell dimensions.¹³⁻¹⁸ Thermal expansion above room temperature has been investigated by Vegard and Roer¹¹ and Srinivasan,¹⁹ while Bridgman²⁰ examined $Sr(NO_3)_2$ over a lesser temperature range. Below room temperature, Hülsmann and Biltz²¹ made pycnometric density determinations at three points down to -195°C for $Ba(NO_3)_2$, without noting any anomaly.

The question of the planarity of the nitrate group remains controversial some fifty years after the first investigations. Possibly of greater interest, however, is the nature of the thermal activity of the group as a function of temperature, since this is fundamental in accounting for many of the physical properties of the compounds. The possibility of rotation of the nitrate group was examined in neutron diffraction experiments by Hamilton²² and Lutz²³ on $Pb(NO_3)_2$ and $Ba(NO_3)_2$, respectively. Both authors interpreted their results in terms of space group $Pa3$, and held there to be no free rotation of the anion. Lutz suggested that in $Ba(NO_3)_2$ the group oscillates about its threefold axis with an amplitude of $\sim 9^\circ$ at room temperature, whereas Hamilton found evidence of some loss of order at $\sim 200^\circ\text{C}$ in $Pb(NO_3)_2$. On applying the neutron diffraction technique to $Ba(NO_3)_2$, Birnstock²⁴ obtained reflections which were inconsistent with the systematic extinctions appropriate to space group $Pa3$, and concluded $P2_13$ to be correct. The latter space group has no centre of symmetry, and implies the presence of two crystallographically distinct nitrate groups in the unit cell. Birnstock found both groups to be of pyramidal form, with the nitrogen atoms displaced $\sim 0.1 \text{ \AA}$ from the plane of the oxygen atoms, the latter defining an equilateral triangle. The structural arrangement of $Ba(NO_3)_2$ together with the form of the nitrate groups according to Birnstock is shown in Fig. 1.

The Raman and IR absorption spectra of the compounds have been fairly widely studied over the range 700 to 1500 cm^{-1} , without there being notable agreement as to the values of the frequencies concerned or their assignment to modes of vibration. For these data the reader is therefore referred to the individual publications (see Refs. 25-44), but it is relevant to note here that most of the authors find evidence of modification of the nitrate group compared with the relatively isolated singly charged planar ion. The departures are detected in the form of shifts in frequency value, and a splitting of degenerate vibrations. These effects have been attributed to distortion of the group as a result of an unbalanced crystal field at its site in the lattice, or a loss of symmetry caused by a degree of covalence in the anion-cation bonding. In general, only one of the two explanations is referred to, but it seems likely that a reduction of group symmetry arises from both causes. The IR absorption spectra of Schroeder *et al.*³⁶ at and below room temperature included a series

of maxima with a constant frequency difference of $\sim 20 \text{ cm}^{-1}$. These frequencies were interpreted as referring to an oscillation of the nitrate group about its threefold axis, and the authors suggested that rotation about this axis occurs at room temperature.

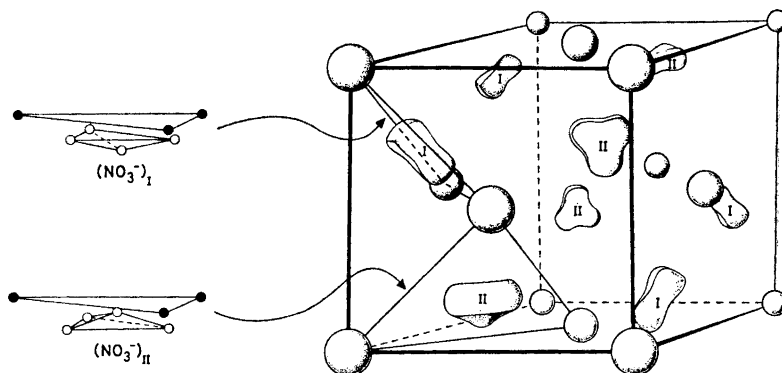


Fig. 1. Structural arrangement of $\text{Ba}(\text{NO}_3)_2$ according to Birnstock,²⁴ indicating the configuration of the nitrate groups I and II on the left-hand side of the diagram.

Birnstock²⁴ showed that birefringence in $\text{Ba}(\text{NO}_3)_2$, which would indicate other than cubic symmetry, arises from the presence of internal stress in the crystals. The possible influence of internal stress on other measurable parameters should also be borne in mind. There is an apparent absence of piezoelectricity in single crystals of the compounds, and this finding is in accordance with $Pa\bar{3}$ as the correct space group, whereas the morphological studies of Buckley,⁴⁵ Belyustin *et al.*,⁴⁶ and Birnstock²⁴ appear to indicate the lower symmetry of $P2_13$.

The low temperature calorimetric data for $\text{Ba}(\text{NO}_3)_2$ ^{47,48} show a satisfactory internal agreement, while the use of the "drop" method above room temperature⁴⁹ led to results of limited resolution. Sluggish phase transitions are not excluded, however, since they tend to escape detection by any calorimetric method. Results of DTA measurements above room temperature include no indications of solid state transformations at atmospheric pressure in any of the three compounds.⁵⁰⁻⁵² The upper temperature limits for such determinations are set by the decomposition properties of the compounds, and in these cases decomposition occurs below the melting points. There is little agreement on the relevant temperatures however,^{19,50-54} the lowest figure given in each case being 560°C for $\text{Sr}(\text{NO}_3)_2$, 525°C for $\text{Ba}(\text{NO}_3)_2$, and 425°C for $\text{Pb}(\text{NO}_3)_2$.

Measurements of dielectric constant (ϵ) for the compounds have hitherto been restricted to polycrystalline and powder samples, the published values falling within the following ranges: $\text{Sr}(\text{NO}_3)_2$ 5.3 – 5.6,^{55,56} $\text{Ba}(\text{NO}_3)_2$ 5.0 – 9.2,⁵⁵⁻⁶¹ and $\text{Pb}(\text{NO}_3)_2$ 14.0 – 16.0,^{56,58,59,61,62} from which it is seen that the value for $\text{Pb}(\text{NO}_3)_2$ is markedly higher than for the other two compounds. The refractive index of $\text{Pb}(\text{NO}_3)_2$ is also noticeably high, the values being $\text{Sr}(\text{NO}_3)_2$ 1.567,

$\text{Ba}(\text{NO}_3)_2$ 1.572, and $\text{Pb}(\text{NO}_3)_2$ 1.782.⁶³ Observation of ϵ for $\text{Ba}(\text{NO}_3)_2$ down to liquid hydrogen temperature has been stated to yield a decreasing value of the parameter.⁶⁴ An investigation of the influence of impurities on dielectric parameters has shown ϵ to be less sensitive to univalent than multivalent cationic impurities in $\text{Ba}(\text{NO}_3)_2$.⁶⁰

Electrical conductivity measurements were first performed on $\text{Ba}(\text{NO}_3)_2$ by Faraday⁶⁵ in 1834, when he found the melt to be conducting, but did not detect a passage of current through the solid. The measurement of conductivity (σ) then appears to have been neglected until 1969, when Khamskii and Freidin⁶⁶ obtained results for $\text{Ba}(\text{NO}_3)_2$ with small additions of LiNO_3 . Normal ionic conductivity was found, with $\log \sigma$ varying in inverse proportion with the reciprocal of the absolute temperature. It was suggested that intrinsic conduction occurs in this compound through the medium of Ba^{2+} ions moving between interstitial lattice positions. No corresponding data are available for $\text{Sr}(\text{NO}_3)_2$ or $\text{Pb}(\text{NO}_3)_2$.

Against this background of limited knowledge, several experimental methods of proven value were employed in the present investigation. In particular, carefully performed electrical measurements are known to provide a sensitive indication of conditions in the crystal lattice, especially in relation to structural phase transitions and the onset of various types of disorder. Measuring techniques developed in this laboratory, for obtaining such data were also supplemented by the measurement of related parameters.

EXPERIMENTAL

Preparation of samples. The commercially obtained starting materials used were a "Baker analyzed" $\text{Sr}(\text{NO}_3)_2$ reagent and *p.a.* grade $\text{Ba}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$ from E. Merck AG. The supplied materials were thrice recrystallized from aqueous solution, finely divided by crushing, and dried at 150°C. The impurity concentrations of various samples determined by the method of atomic absorption are shown together with the manufacturers' specifications of maximum impurity levels in Table 1. Samples for dielectric measurements were formed by pressing the powdered compound into the form of discs of 30 mm diameter and ~0.5 mm thickness. Conducting silver paint (Leitsilber 200, Degussa) was applied to both sides of the samples in order to provide electrodes. Additional samples of $\text{Ba}(\text{NO}_3)_2$ were formed by allowing the compound to solidify from the melt as a thin film on a silver plate 30 mm square. A second electrode was also formed from Leitsilber 200 in these cases. Samples for resistivity measurements were cut from single crystals grown slowly from aqueous solution by means of evaporation at 40°C.

Dielectric measurements. Measurements of parallel sample capacitance C_p and electrical dissipation D were obtained in the temperature range -140 to 30°C with the sample situated within the cryostat described in a previous publication.² The measurements were performed at 1 kHz using an impedance bridge (General Radio, type 1650-A). More precise values of the parameters were determined at room temperature for considerably larger samples, and these values were used to normalize the results obtained as functions of temperature. Measurements at higher temperatures were obtained using a suitable sample holder,³ a dry atmosphere being secured by the use of P_2O_5 at temperatures < 100°C.

Resistance determination by four-terminal DC method. Four-terminal DC resistance measurements on suitably shaped single crystals were performed between 20 and 300°C using an electrometer bridge which has been described in another publication.⁶⁷ The sample was mounted in a special holder,⁶ and its temperature automatically controlled by means of electronic equipment.⁶

Table 1. (a) Manufacturers' specification of maximum impurity contents (in ppm) of compounds supplied.

Impurity	Sr(NO ₃) ₂	Ba(NO ₃) ₂	Pb(NO ₃) ₂
Ca		≦ 20	
Fe	1	≦ 5	≦ 10
Cu			≦ 10
Sr		≦ 100	
Ba	80		
Pb	1	≦ 5	
NH ₄		≦ 10	
Alkalies	1500		
Cl	10	≦ 5	≦ 5
SO ₄	10		

(b) Impurity contents of (i) starting material, (ii) thrice recrystallized material, (iii) single crystals grown from material (ii).

Impurity	Sr(NO ₃) ₂			Ba(NO ₃) ₂			Pb(NO ₃) ₂		
	(i)	(ii)	(iii)	(i)	(ii)	(iii)	(i)	(ii)	(iii)
Li	210	170	160	50	30	30	40	30	30
Na	170	170	170	110	100	110	150	130	130
K	120	100	100	140	130	120	170	160	150
Al	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10

X-Ray diffraction. All samples were crushed and X-ray photographs were taken in a Guinier type camera of 80 mm diameter with monochromatized CuK α -radiation ($\lambda = 1.54050 \text{ \AA}$) using KCl as internal standard. A General Electric powder diffractometer with cryostat attachment (CuK α -radiation, diamond powder as internal standard) was used to collect X-ray data below room temperature. High temperature X-ray powder photographs were obtained in a 190 mm diameter Unicam camera with the samples sealed in thin-walled quartz capillaries. The temperature of the furnace surrounding the specimen was kept constant to within $\pm 3^\circ\text{C}$ during the exposures. The Pt/Pt-Rh thermocouples of the furnace were calibrated with a standard couple located at the position of the specimen. In the latter case, lattice dimensions were determined from the high-angle reflections, utilizing the Nelson-Riley⁶⁸ type extrapolation.

Differential thermal analysis. DTA measurements were performed over the temperature range 20 to $\sim 300^\circ\text{C}$ using a Du Pont (type 900) thermoanalyzer. The heating rate was $5^\circ\text{C}/\text{min}$ in air, with aluminium oxide as reference material. Approximately 100 mg samples were used.

Proton magnetic resonance. PMR spectra of powder samples of Ba(NO₃)₂ were recorded on a DP-60 Varian Associate NMR Spectrometer operating at a frequency of 60 MHz. The sample holder was of the LP-4331 type and field sweep was carried out with a Varian field-dial unit.

Density measurements on samples of $\sim 2 \text{ g}$ were carried out pycnometrically at 25°C with kerosene as displacement liquid.

Magnetic susceptibilities were measured between 90 and 680°K by the Faraday method (maximum field $\sim 8000 \text{ O}$), using 100–150 mg samples. The magnetic field was calibrated with the aid of a known mass of HgCo(SCN)₄.

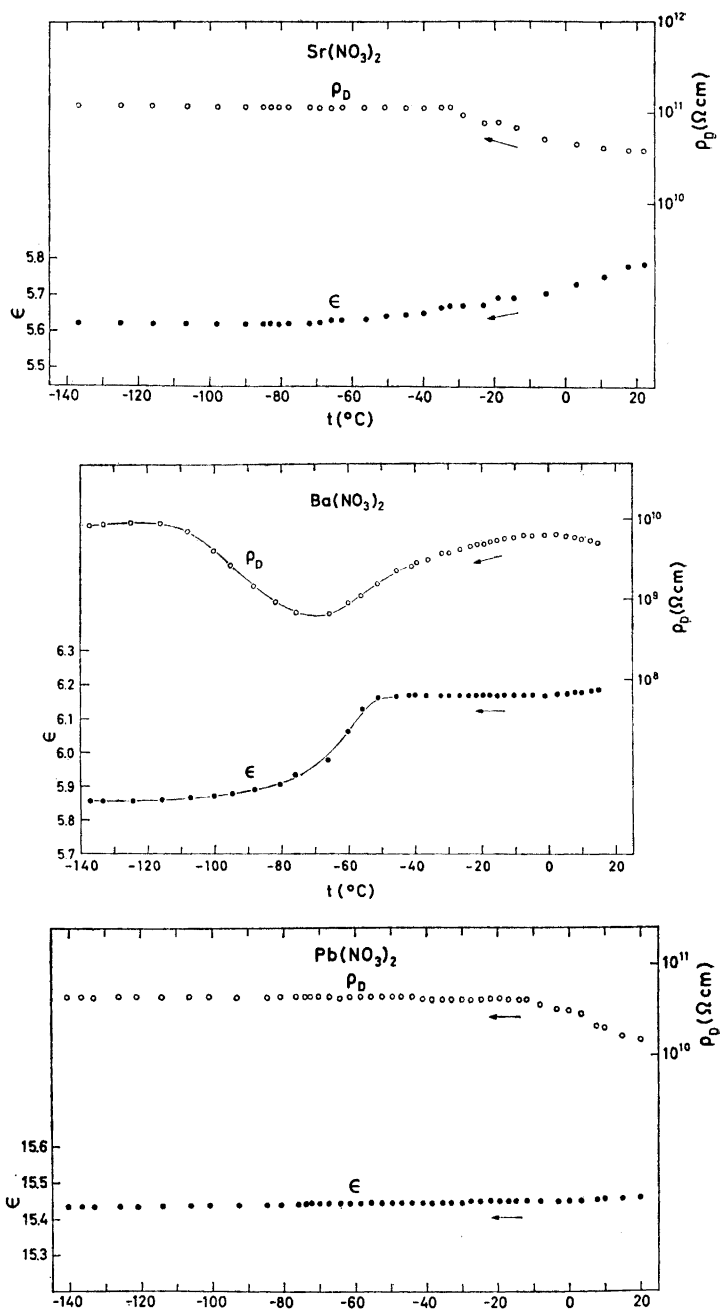


Fig. 2. Dielectric constant ϵ and resistivity ρ_D below room temperature for (a) $\text{Sr}(\text{NO}_3)_2$, (b) $\text{Ba}(\text{NO}_3)_2$, and (c) $\text{Pb}(\text{NO}_3)_2$.

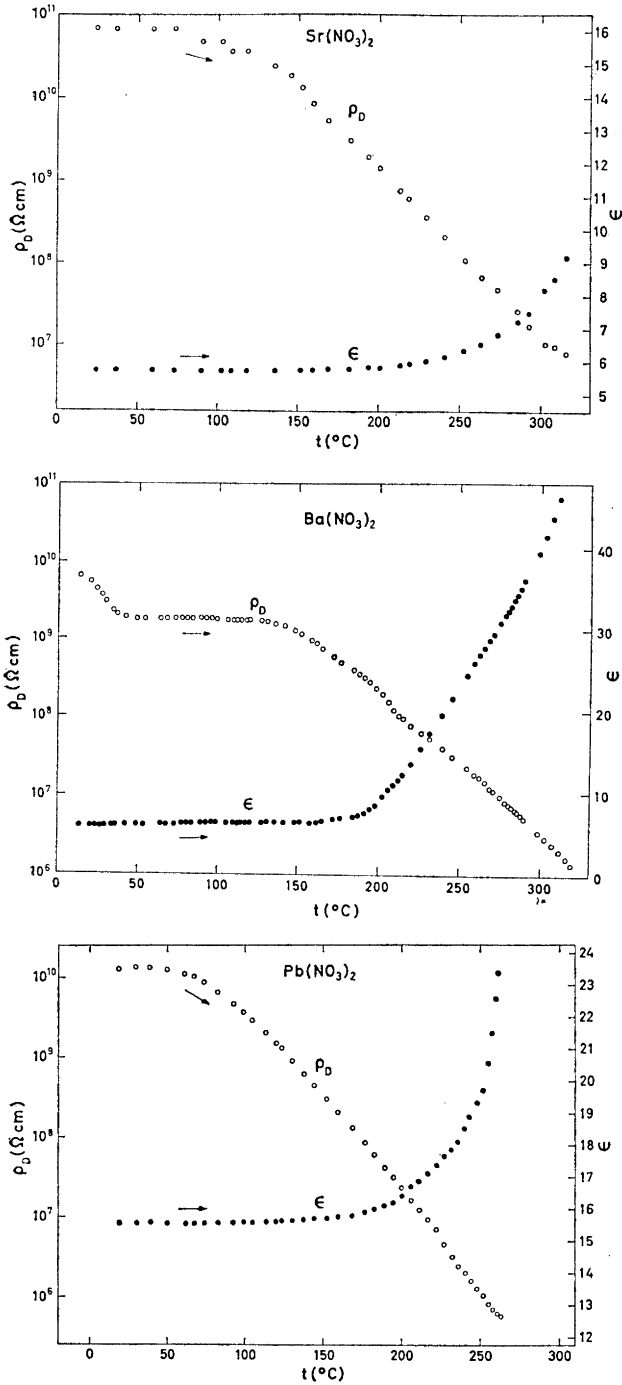


Fig. 3. Dielectric constant ϵ and resistivity ρ_D above room temperature for (a) $\text{Sr}(\text{NO}_3)_2$, (b) $\text{Ba}(\text{NO}_3)_2$, and (c) $\text{Pb}(\text{NO}_3)_2$.

RESULTS

(i) *Dielectric data.* The variation of the dielectric constant ϵ and resistivity $\rho_D (=S/(\omega C_p D t))$ where ω is the angular frequency of the applied emf, C_p the equivalent parallel capacitance of the sample, D the dissipation, t the sample thickness, and S the electrode area) with temperature for $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, and $\text{Pb}(\text{NO}_3)_2$ below room temperature are shown in Fig. 2a – c, and at higher temperatures in Fig. 3a – c. The curves, which are in each case typical of the three or more samples investigated, were obtained in the direction of temperature change indicated on the diagrams. At room temperature, where the sets of readings overlap, good agreement was obtained between the various samples and methods of measurement employed, and the results were found to show good reproducibility.

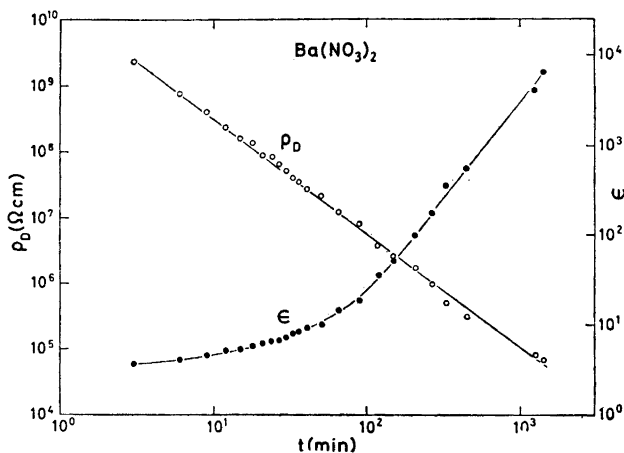


Fig. 4. Variation of ϵ and ρ_D for $\text{Ba}(\text{NO}_3)_2$ with time on exposure to humid air.

Although handled with a view to keeping the samples dry, they were not sealed against the ingress of moisture, and it was therefore of interest to investigate the influence of water vapour upon the measured parameters. It was found that only $\text{Ba}(\text{NO}_3)_2$ was appreciably affected by the presence of a saturated atmosphere of water vapour and the influence of the time of exposure ϵ and ρ_D is shown in Fig. 4. Samples of the compound exposed to a saturated atmosphere at room temperature were found to increase in weight by an average of 0.3 %.

In order to investigate the possible effect of exposure to water vapour upon the unit cell dimensions, Guinier photographic data were collected for the following samples:

- (a) Polycrystalline $\text{Ba}(\text{NO}_3)_2$ cooled from the melt.
- (b) Crystals from aqueous solution dried at $> 100^\circ\text{C}$.
- (c) As under (b), but dried at room temperature by means of P_2O_5 .
- (d) As under (b), but exposed to the laboratory atmosphere.

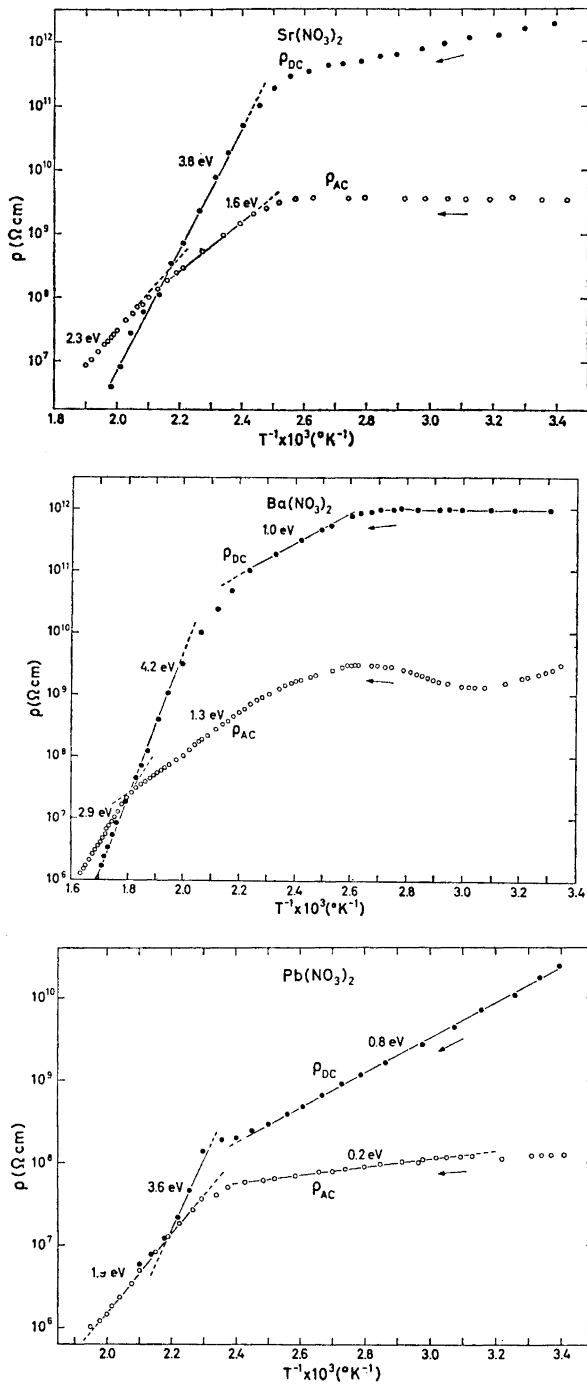


Fig. 5. Four-terminal DC resistivity ρ_{DC} and ρ_{AC} at 1 kHz above room temperature for (a) $\text{Sr}(\text{NO}_3)_2$, (b) $\text{Ba}(\text{NO}_3)_2$, and (c) $\text{Pb}(\text{NO}_3)_2$.

The values of a for the various samples were found to be in agreement within the experimental error.

As a means of investigating adsorbed water in $\text{Ba}(\text{NO}_3)_2$ crystals at reduced temperature, PMR spectra were obtained for samples exposed to an atmosphere of water vapour at room temperature. Signals characteristic of highly mobile protons were found at room temperature, and their amplitudes fell sharply between -4 and -8°C , becoming almost eliminated at -15°C .

(ii) *Four-terminal DC resistivity*. Reproducible results for single crystal samples of each compound are plotted as functions of the reciprocal of the absolute temperature in Fig. 5a – c. Also shown in the diagrams are the values of ρ_{AC} for polycrystalline samples obtained at 1 kHz.

For $\text{Ba}(\text{NO}_3)_2$, the $\log \rho_{\text{DC}}$ versus T^{-1} curve can be represented to a first approximation by three linear sections having junctions at ~ 380 and $\sim 485^\circ\text{K}$; while the corresponding curves for $\text{Sr}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$ include two linear sections each, the temperatures of intersection being ~ 400 and $\sim 435^\circ\text{K}$, respectively. The values of energy parameter which are given in electron volts on the diagrams are the corrected values as deduced by making allowance for the regions of overlap following a method described previously.¹

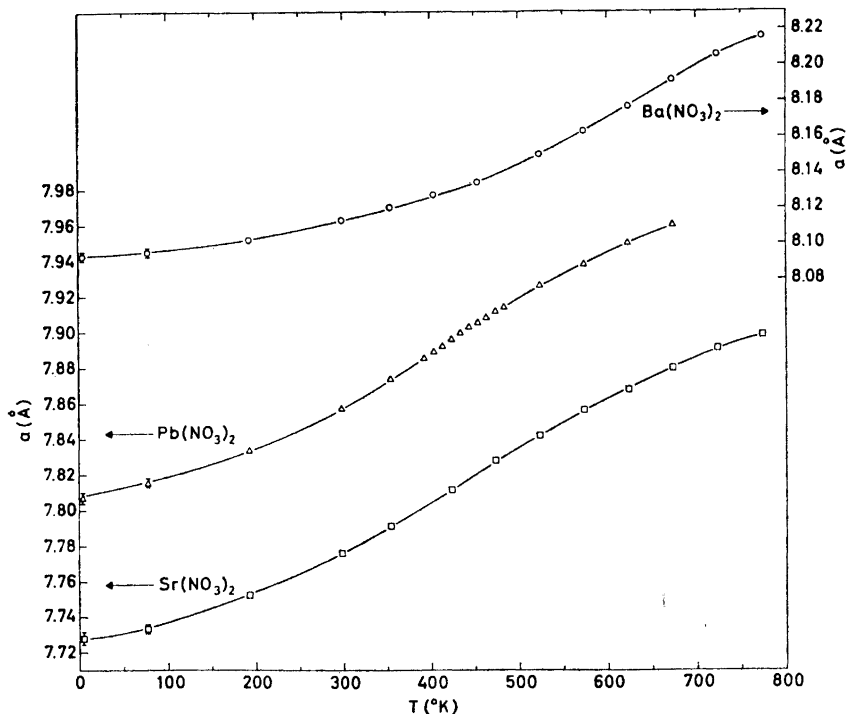


Fig. 6. Unit cell dimensions for $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, and $\text{Pb}(\text{NO}_3)_2$ as functions of temperature. Experimental error limits are indicated by vertical bars, where these exceed the size of the symbols.

(iii) *Differential thermal analysis.* The DTA data obtained in the temperature region from 20 to 300°C for the compounds are in good agreement with those published by Gordon and Campbell,⁵⁰ and it would therefore be superfluous to present them here. Thus there is no thermal evidence of structural transitions within the stated temperature range.

(iv) *Temperature dependence of the unit cell dimensions.* In order to gain a more detailed view of the temperature dependent structural properties of the compounds, X-ray powder diffraction data were collected in the range 4.2 – ~800°K. Throughout this temperature range there is no indication of changes in lattice symmetry for any of the compounds and the almost invariable relative intensities of the reflections show that the positional parameters are approximately independent of temperature. The data suggest, furthermore, that no drastic alterations take place in the harmonicity of the lattice oscillations, and disorder.

The thermal expansion, due to anharmonic terms in the potential energy of the interatomic displacements, shows a distinctly non-linear behaviour for all three compounds (Fig. 6). The non-linear expansion curves yield values of slope corresponding to expansion coefficients ($\alpha = \frac{1}{a_{273}} \frac{\partial a}{\partial T}$ referred to the unit cell dimension at 273°K (a_{273})) as follows,

$$\begin{aligned} \text{Sr}(\text{NO}_3)_2 : 14.0 \times 10^{-6} &\leq \alpha \leq 41.2 \times 10^{-6} \text{C}^{-1} \\ \text{Ba}(\text{NO}_3)_2 : 2.1 \times 10^{-6} &\leq \alpha \leq 37.0 \times 10^{-6} \text{C}^{-1} \\ \text{Pb}(\text{NO}_3)_2 : 13.8 \times 10^{-6} &\leq \alpha \leq 40.7 \times 10^{-6} \text{C}^{-1} \end{aligned}$$

(v) *Magnetic susceptibility.* The measured susceptibilities of the compounds (uncorrected for induced diamagnetism) were found to be temperature independent within the limits of experimental accuracy over the range 78 to 670°K. The values (in e.m.u./mol $\times 10^6$) obtained are as follows: -71.5 ± 0.9 for $\text{Sr}(\text{NO}_3)_2$, -68.3 ± 0.7 for $\text{Ba}(\text{NO}_3)_2$, and -80.0 ± 1.0 for $\text{Pb}(\text{NO}_3)_2$.

(vi) *Density.* The X-ray and pycnometrically determined densities (in g cm^{-3}) of the compounds under consideration are as follows: $\text{Sr}(\text{NO}_3)_2$ 2.989 and 2.986, $\text{Ba}(\text{NO}_3)_2$ 3.241 and 3.235, and $\text{Pb}(\text{NO}_3)_2$ 4.534 and 4.528, respectively.

DISCUSSION

On examination of the values of ϵ and ρ_D for $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, and $\text{Pb}(\text{NO}_3)_2$ at reduced temperatures (Fig. 2a–c), it is clear that $\text{Ba}(\text{NO}_3)_2$ has an anomalous variation of both parameters with temperature. The anomaly in ϵ occurs for $t < -52^\circ\text{C}$, whereas ρ_D shows a minimum of ~100°C width, centred at -70°C . Over the low temperature regions investigated for the compounds, fairly constant values of ρ_D reflect a lattice situation in which only small variations occur in the number and mobility of charge carriers, and in the dielectric loss. In samples of compressed powder it may be supposed that at the high levels of resistivity recorded, a comparatively small number of carriers with a negligible activation energy, move along paths (which may include grain boundaries) having a rather constant resistance. The minimum

in ρ_D for $\text{Ba}(\text{NO}_3)_2$ therefore indicates an increase in the carrier density and/or their mobility, as could result from a reduction of potential barriers due to disorder accompanying a gradual structural transition. This explanation of the results is supported by the form of the variation of ϵ in the compound, from which it is seen that the transformation occurs at $-52 \pm 3^\circ\text{C}$. The change of 0.3 in ϵ across the transition (*i.e.* $\sim 5\%$) reflects a cooperative change in the polarizability of structural units in the lattice. The alteration may be restricted to the unit cell, a constituent ionic sublattice, or refer to long range cooperative effects; the underlying increment being modified by interactions between various contributions to the total polarizability.

The temperature dependence of the unit cell dimension for $\text{Ba}(\text{NO}_3)_2$ (Fig. 6), does not imply an appreciable alteration to the structure in the region of the anomaly, and in this respect the transformation differs from that discovered in KNO_3 ,² where a correlated deviation was found in the unit cell dimensions. In the present case, the change in polarizability probably results from the internal or mutual properties of the nitrate groups. A change in the torsional rigidity or clamping of a permanent dipole associated with the nitrate group may apparently be excluded since it would be likely to affect also the value of α . The absence of a corresponding transition reflected in the electrical data for the other two compounds over the same temperature range (*i.e.* $t > -140^\circ\text{C}$) may be related to the distinct differences in the temperature development of the anharmonic part of the oscillational spectrum as reflected in the expansion curves of Fig. 6. The above transformation in $\text{Ba}(\text{NO}_3)_2$ has also been detected by Rao⁶⁹ using paramagnetic resonance, the temperature of the transition being given as $\sim -80^\circ\text{C}$.

The influence of adsorbed water on the values of ϵ and ρ_D for $\text{Ba}(\text{NO}_3)_2$ (Fig. 4) shows a marked dependence upon the time of exposure. The form of these curves is compatible with a predominantly superficial adsorption, as suggested by the X-ray data and the weight change experiments. A possibility that the low temperature dielectric anomaly in this compound could be due to the presence of water in the samples is excluded by reason of the PMR data. The effect of adsorbed water is, on the other hand, apparent in the values of ρ_D for $\text{Ba}(\text{NO}_3)_2$ at temperatures up to $\sim 30^\circ\text{C}$ (Fig. 3b).

From the low temperature data (Fig. 2a-c), it is noticeable that the value of ϵ for $\text{Pb}(\text{NO}_3)_2$ is considerably greater than for the other two compounds. Similarly, the refractive index $n = 1.782$ for $\text{Pb}(\text{NO}_3)_2$ is to be compared with 1.567 and 1.572 for $\text{Sr}(\text{NO}_3)_2$ and $\text{Ba}(\text{NO}_3)_2$, respectively. Since the electronic contribution to ϵ equals n^2 , it is clear that this component and its interaction with the ionic and molecular polarizabilities, is at least partly responsible for the difference between the values.

On comparing ϵ and ρ_D for the compounds above room temperature (Fig. 3a-c), it is seen that the plotted curves are of essentially similar form. The regions of decreasing values of ρ_D are typical of conductivity governed by non-zero energy parameters of an intrinsic or extrinsic nature, while ϵ exhibits anomalous increases over temperature regions where ρ_D is essentially linearly dependent on temperature. This point will be returned to in conjunction with the single crystal resistivity data.

Accelerated increases in the values of ϵ occur at approximately 200, 180, and 160°C in $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, and $\text{Pb}(\text{NO}_3)_2$, respectively, and similar effects have been observed earlier for LiNO_3 ⁵ and NaNO_3 .³ Taking into consideration the lack of any observed anomaly in DTA, magnetic susceptibility, or thermal expansion data for the present compounds, any discussion of the phenomena will be tentative.

Examination of the ϵ and q_D curves suggests that the polarizability anomalies reflect a characteristic property of the nitrate group, such as an enhanced rotation of an electric dipole associated with the group. A rotation of this kind would, however, be expected to show also in an increase in the expansion coefficient, and no such increase is found (see Fig. 6). It is also difficult to regard the effect as being due to increased amplitudes of thermal oscillation of the ions if these are regarded as rigid entities, although reduced cohesive forces, and closer approach of the ions will both tend to increase ϵ .

A fundamental characteristic of the anomalies is the common threshold effect with temperature, and it is suggested that this is related to internal properties of the group as modified by the remainder of the lattice. The modes of oscillation of the group, as studied by IR techniques, are thermally activated in the way described by quantum mechanics, and the development of this activity with temperature is conveniently studied by means of the partition function $q(T)$ for the simple harmonic oscillator,⁷⁰ where

$$q(T) = \{1 - \exp(h\nu/kT)\}^{-1}$$

The partition function is related to the energy of an assembly of N oscillators by the expression

$$E_{\text{vib.}} = NkT^2 \frac{\partial}{\partial T} \log q(T)$$

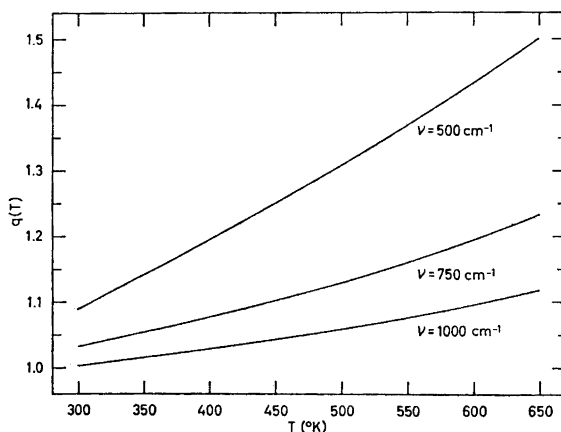


Fig. 7. Partition functions *versus* temperature for simple harmonic internal modes of oscillation of the nitrate group.

The temperature dependence of the partition function for three values of frequency which are typical of those determined experimentally for the nitrate group²⁵⁻⁴⁴ are plotted in Fig. 7, where it is seen that the low frequency oscillator shows a temperature threshold corresponding to that sought. According to this hypothesis, the observed decrease in threshold temperature with increasing cation mass results from decreases in the nitrate mode frequencies. The deduced thermal activation of the group is accompanied by a weakening of bonds, which may promote the formation of dipoles whose partial rotation is permissible without the need for further expansion of the lattice.

In accounting for the values of the four-terminal DC resistivity of single crystals of the compounds (Fig. 5a - c), two effects must be separated. These are transitions between various conduction mechanisms, and the influence of such inherent structural factors as the deduced temperature dependence of thermal activity of the nitrate group. The values of ρ_{AC} for polycrystalline samples, which are included in the diagrams, aid in the interpretation, because of the greater influence of grain boundaries, impurities, and polarization effects at the electrodes in the case of the two-terminal AC method.

The results for $\text{Ba}(\text{NO}_3)_2$ (Fig. 5b) include a transition between extrinsic and intrinsic modes of conduction in ρ_{AC} at $\sim 550^\circ\text{K}$. This interpretation of the change in slope is suggested by the intersection of the ρ_{AC} and ρ_{DC} curves around this temperature. The difference between the energy parameter values for ρ_{AC} and ρ_{DC} at higher temperatures reflects the difference in sample form, means of measurement, and especially, polarization effects at the electrodes in the two-terminal determination of the values of ρ_{AC} . The curved portion of ρ_{DC} in the vicinity of 470°K , for this compound, probably reflects the onset of thermal activation of the nitrate group in this region. It is interesting to note that the influence appears only in the activation of intrinsic carriers, since the impurity region of the ρ_{AC} curve shows no such correlation, and this applies also to the ρ_D values discussed earlier. According to this interpretation, intrinsic conduction is evident at temperatures down to $\sim 400^\circ\text{K}$, and the apparent value of energy parameter $W = 1.0$ eV refers to a transitional region of increasing nitrate group activity, although the charge carriers are probably interstitial cations in both cases. Geometrical considerations show that there are favourable interstitial sites of nearly tetrahedral symmetry for the Ba^{2+} ions. A similar explanation of results may be applied to $\text{Sr}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$, allowing for an apparent overlapping of structural and impurity effects.

Similarities between the electrical properties of $\text{Ba}(\text{NO}_3)_2$ at the transformation and those found in the univalent nitrates,⁴ cause one to seek a common origin in the properties of the nitrate group as modified by the individual lattice environment, since neither crystal structure nor cation valence can be the determining factor. This raises the question of planarity of the nitrate group, or rather, the possibility of small deviations from planarity. As seen from the introductory section, the experimental evidence is ambiguous on this point, and the small displacements of the nitrogen atoms deduced by Birnstock²⁴ were obtained on the possibly unjustified basis of isotropic temperature factors.

Experimental and theoretical studies have indicated that the weakly bonded or free NO_3^- ion is planar. For experimental evidence of this, one may refer to Herzberg,⁷¹ while Walsh⁷² has provided convincing quantum mechanical arguments in favour of a planar group. It is reasonable, therefore, to regard any departure from planarity as a distortion imposed by the lattice environment through the medium of an unbalanced electric field at the group site, or a peculiarity of bonding.

In the case of the present compounds, modifications due to an unbalanced field must result from a cooperative coordination of the groups, since the nitrogen atom displacements according to Birnstock²⁴ appear incompatible with the influence of the cations alone (cf. Fig. 1). This cooperative model is consistent with the experimental data presented here, and suggests in addition that the transformation in $\text{Ba}(\text{NO}_3)_2$ with increasing temperature is a cooperative one between a planar and a non-planar state. Partial rotation of the dipoles associated with the nitrate groups in the higher temperature phase would account for the 5 % increase in ϵ observed across the transition seen in Fig. 2b.

With regard to the tentative nature of this hypothesis, only two of the many implications will be mentioned here. Firstly, it may be supposed that $\text{Sr}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$ contain pyramidal nitrate groups at all temperatures. This would follow from the form of the expansion curves, and may result from the tighter coupling between groups in the smaller unit cells. Secondly, the low temperature transformations in the univalent nitrates are likely to be of the same kind, and although not free of attendant difficulties, this explanation appears to be worthy of further consideration.

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