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The effect of temperature and phase state on the infrared spectrum of $Ba(NO_3)_2$

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Abstract

The temperature dependence of the infrared spectra of $Ba(NO_3)_2$ is reported in the whole ordered–disordered phase, from about 25°C up to 400°C. The study includes the temperature dependence of the infrared-active lattice modes. The frequency ν_1 denotes the totally symmetric N–O stretching mode, ν_2 the bending mode, ν_3 the asymmetric stretching mode, ν_4 the asymmetric in-plane bending mode, $2\nu_1, 2\nu_3$ the first overtones, and $(\nu_1 + \nu_4)$ and $(\nu_1 + \nu_3)$ the combination modes. We have measured and interpreted the IR spectral band shapes, intensities and frequencies of the internal modes as a function of temperature. The results reveal that the transformation from the ordered state (phase II) to the disordered state (phase I) of $Ba(NO_3)_2$ is indicated by clear variations in the spectral parameters for $(\nu_1 + \nu_4)$, $2\nu_1$, $(\nu_1 + \nu_3)$ and $2\nu_3$. The temperature dependence of the relaxation parameters confirms the gradual transformation due to the growing of the disorder in the crystal structure which appears at about 300°C and is associated with a thermal energy of about 0.012 eV.

INTRODUCTION

Crystalline nitrate salts have been the subject of several recent infrared and Raman spectroscopic investigations. Pronounced variations in the observed spectra due to differences in crystal structure required treatment of data according to the selection rules in the appropriate factor group representation [1, 2]. An unperturbed nitrate ion with D_{3h} symmetry would generate the spectrum: symmetric stretch $\nu_1(A_1')$ Raman-active at about $1050\,cm^{-1}$; out-of-plane deformation $\nu_2(A_2'')$ infrared-active at about $825\,cm^{-1}$; and both antisymmetric stretch $\nu_3(E')$ and antisymmetric bend $\nu_4(E')$ which are Raman- and infrared-active at about 1380 and $720\,cm^{-1}$, respectively [3].

In the present study, the results of investigations on IR spectra of $Ba(NO_3)_2$ from room temperature (about 25°C) up to 400°C are reported.

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Isotropic cubic barium nitrate is reported in the literature to belong to the crystal class $2/m3$. X-ray investigations of $Ba(NO_3)_2$, however, suggested that it crystallizes in space group $Pa3$. The centrosymmetric symmetry was confirmed on the basis of new morphological studies. In powder neutron diffraction studies of $Ba(NO_3)_2$, the space group $Pa3$ was found, together with remarkably strong oscillations around the nitrogen atoms. The N–O bond lengths were determined as 1.27 and 1.23 Å [4].

The arrangement of the metal (M^{2+}) ions in the crystal structure of $Ba(NO_3)_2$ corresponds to a cubic face-centred Bravais lattice. These ions are connected by nitrate groups with the N atoms on the three-fold axes and are twelve-coordinated by O atoms [5].

Infrared and Raman spectra of isomorphous cubic crystals of $Ba(NO_3)_2$ have been recorded at room temperature. The observed vibrational spectra have been interpreted conveniently in terms of a factor group analysis [2].

Dielectric constant ε and d.c. resistivity measurements of the barium nitrate showed the existence of thermal hysteresis accompanying the phase transformation [6].

In addition, sharp peaks were obtained in both the differential thermal analysis (DTA) and thermomechanical analysis (TMA) curves. The TMA curve of $Ba(NO_3)_2$ showed a pronounced peak at about 300°C [7]. An examination of the infrared spectra of metallic nitrates has shown that in progressing from monovalent metallic nitrates to tetravalent metallic nitrates, there is a gradual lowering of the nitrate symmetry, with a transition from a D_{3h} to a C_{2v} point group symmetry. The degree of dissymmetry arising in these nitrates appears to be related in part to the ionic potential of the cation [8].

EXPERIMENTAL

The apparatus used and the experimental techniques applied were essentially identical with those described previously [9]. The IR spectra were recorded using a Beckmann G.R. 7224 spectrophotometer. The material used was ultra pure $Ba(NO_3)_2$ (B.D.H.). The prepared $Ba(NO_3)_2$ samples were mixed with about 1 mg of KBr powder and placed in a cylindrical die of 10 mm diameter after shaking the mixture for about half a minute. The die was evacuated to ensure dryness and the sample was then pressed, giving a clear disc about 1 mm thick. The spectral measurements were recorded in the region from 4000 to 400 cm^{-1} with a scanning time of 30 min.

RESULTS

In the following IR results, Herzberg's notation was used for the internal fundamental normal vibrations of the NO_3^- ion [10].

Temperature dependence and phase state of the bands in $Ba(NO_3)_2$

In the present study, the observed room temperature spectrum of $Ba(NO_3)_2$ did not exhibit any bands which could be attributed to any mode other than those due to the ionic fundamentals of the NO_3^- group. The accuracy of the frequency measurements is estimated to be $\pm 1\ cm^{-1}$ for sharp peaks and about $\pm 10\ cm^{-1}$ for broad bands.

IR spectra were obtained at 25, 200 and 250°C for the ordered state II and at 310, 320, 330, 350 and 400°C for the disordered state I. The frequencies of each band of the NO_3^- ion and their assignments are shown in Table 1.

Figure 1 shows the effect of temperature on the infrared absorption spectra of $Ba(NO_3)_2$ during the phase transition. The combination mode $(\nu_1 + \nu_4)$ is a sharp peak at about $1775\ cm^{-1}$; however, the first overtone $2\nu_1$ is a broad band at about $2120\ cm^{-1}$. Also, there are very small changes in the frequency assignment as the temperature increases. But a clear increase in the areas of the modes $(\nu_1 + \nu_4)$ and $2\nu_1$ can be discerned with increasing temperature up to the transition point at about 300°C. After the transition, i.e. when barium nitrate is completely in the disordered state I, the areas of the modes $(\nu_1 + \nu_4)$ and $2\nu_1$ decrease with increasing temperature, as depicted in Fig. 2. These characterizations are similarly exhibited in Fig. 3 for the variation in the relative integrated intensity with temperature for the $2\nu_1$ mode, and for the relative peak height of the $(\nu_1 + \nu_4)$ mode.

The combination mode $(\nu_1 + \nu_3)$ and the first overtone $2\nu_3$, at about 2430 and $2780\ cm^{-1}$, respectively, are sensitive to the ordering and disordering of $Ba(NO_3)_2$. The peak heights and areas are reduced in the disordered phase I relative to the ordered phase II, as shown in Fig. 4. Large increases in the

TABLE 1

Infrared spectra of $Ba(NO_3)_2$

ν/cm^{-1}	Ordered state			Transition point	Disordered state				
	25°C	200°C	250°C	300°C	310°C	320°C	330°C	350°C	400°C
ν_4	730SP	728SP	728SP	728SP	728SP	728SP	728SP	728SP	728SP
ν_2	820W	815SP	815SP	815SP	815SP	815SP	815SP	815SP	818SP
ν_1	1030SH	1015W	1015W	1015W	1015W	1020W	1015W	1015W	1015W
ν_3	1375VB	1375VB	1380VE	1400VB	1375VB	1370VB	1370VB	1368VB	1400VB
$2\nu_4$	1425VW	1430SH	–	–	–	–	–	–	–
$2\nu_2$	–	1650SHS	–	–	–	–	–	–	–
$\nu_1 + \nu_4$	1775SP	1775SP	1775SP	1775SP	1775SP	1775SP	1772SP	1772SP	1772SP
$2\nu_1$	2120W	2120BB	2110BB	2110BB	2115BB	2110BB	2110BB	2110BB	2110BB
$\nu_1 + \nu_3$	2420BB	2430BB	2430BB	2420BB	2415BB	2430BB	2430BB	2440BB	2440BB
$2\nu_3$	2780B	2780B	2780BB	2780BB	2780BB	2780BB	2785BB	2780BB	2780BB

Key: SP, sharp; W, weak; VB, very broad; VW, very weak; BB, broad band; B, broad; SH, shoulder; SPS, sharp strong.

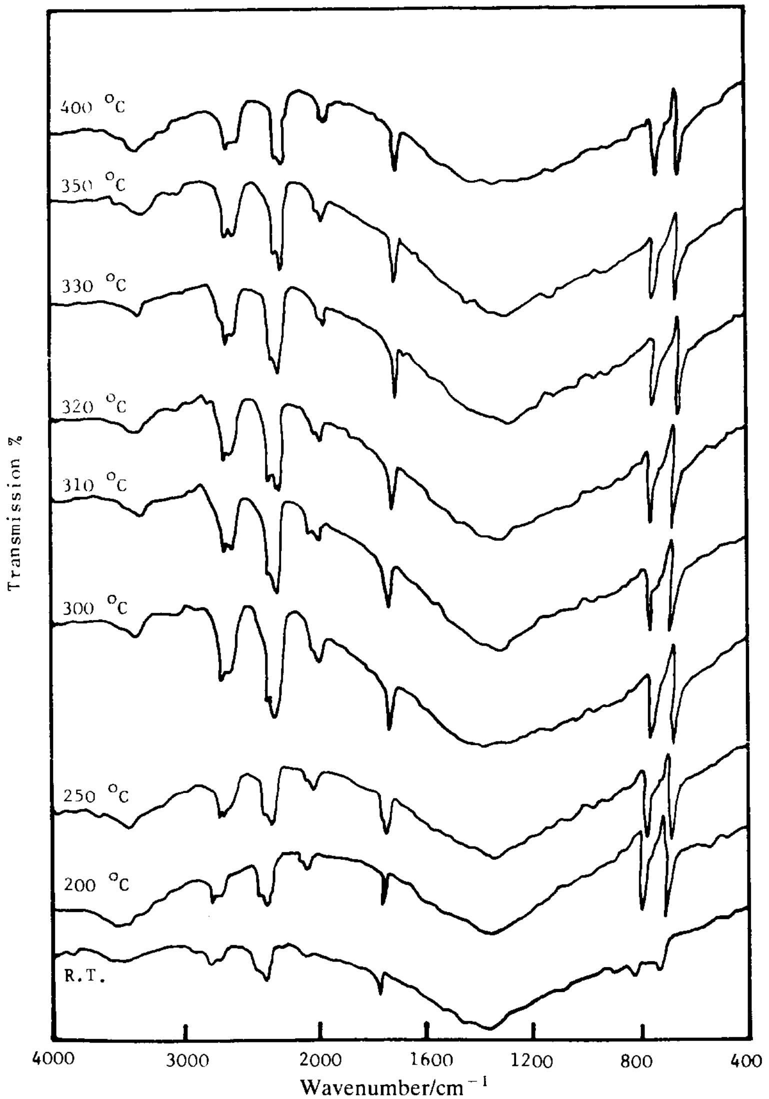

Fig. 1. The effect of temperature on the infrared absorption spectrum of $Ba(NO_3)_2$.

relative integrated intensities of the $(\nu_1 + \nu_3)$ and $2\nu_3$ modes occur with increasing temperature up to the transition point (about 300°C), followed by a gradual decrease in these intensities during the transformation of $Ba(NO_3)_2$ to the disordered state I, as shown in Fig. 5.

The gradual change in the curves of relative integrated intensities versus temperature, Figs. 3 and 5, near the phase transition point could be taken to indicate the beginning of an orientation motion of the NO_3^- ions in the lattice. Consequently, this could be considered as a simple indication of the start of the disordering of $Ba(NO_3)_2$.

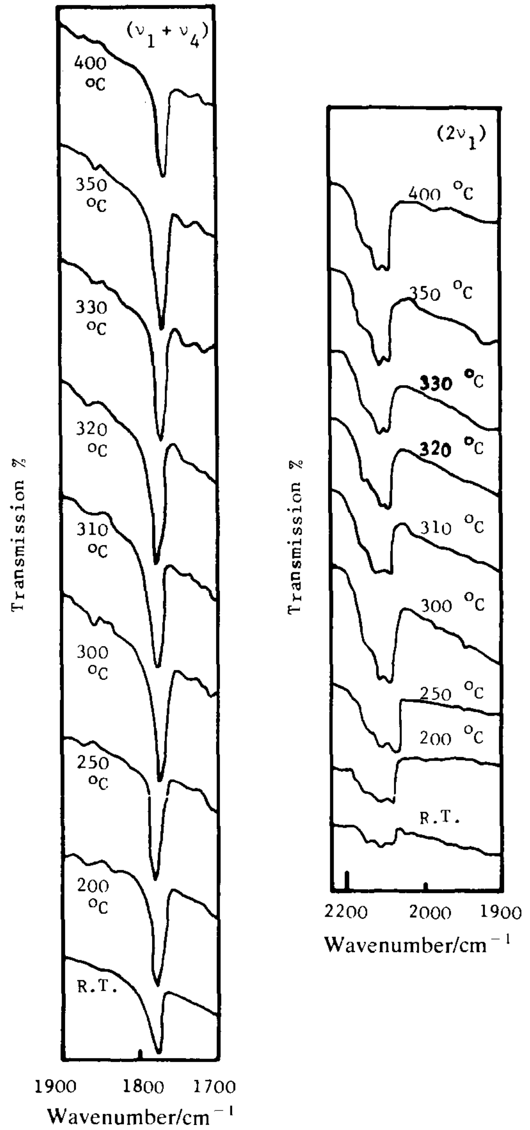

Fig. 2. Temperature dependence of the ($\nu_1 + \nu_4$) and $2\nu_1$ bands of the nitrate group of $Ba(NO_3)_2$.

The spectra of the disordered phase I of $Ba(NO_3)_2$ show a loss in detailed structure relative to those of the ordered phase II. This is due to the fact that the environment of a molecule or an ion at a particular site in the unit cell in the ordered crystal should be uniform, and a variation in this environment from molecule to molecule is to be expected in the disordered crystal [11].

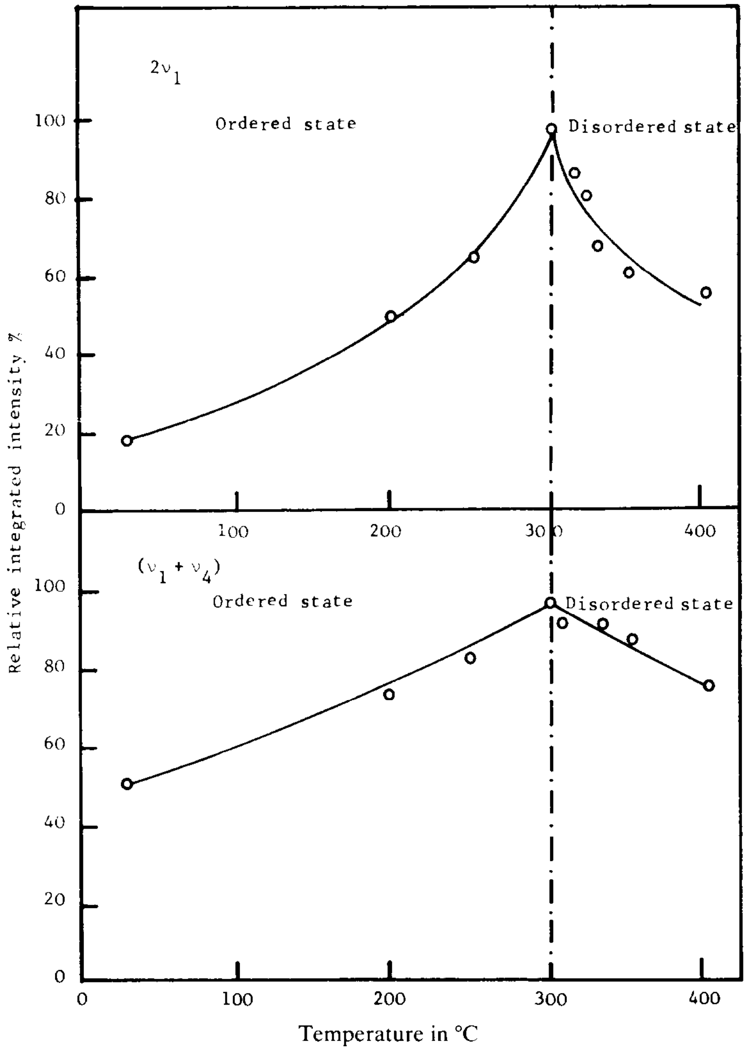

Fig. 3. Temperature dependence of the relative intensities of the $2\nu_1$ overtone mode and the $(\nu_1 + \nu_4)$ combination mode.

Determination of the rotational energy barrier

The energy barrier separating the different orientations of the NO_3^- group in the two phases I and II can be determined using the relaxation time equation [12]

$$\tau = \tau_0 \exp(U/KT) \tag{1}$$

where U is the rotational barrier energy. The relaxation time [13] was determined using the equation

$$\tau = \frac{1}{\pi \, \Delta\nu c} \tag{2}$$

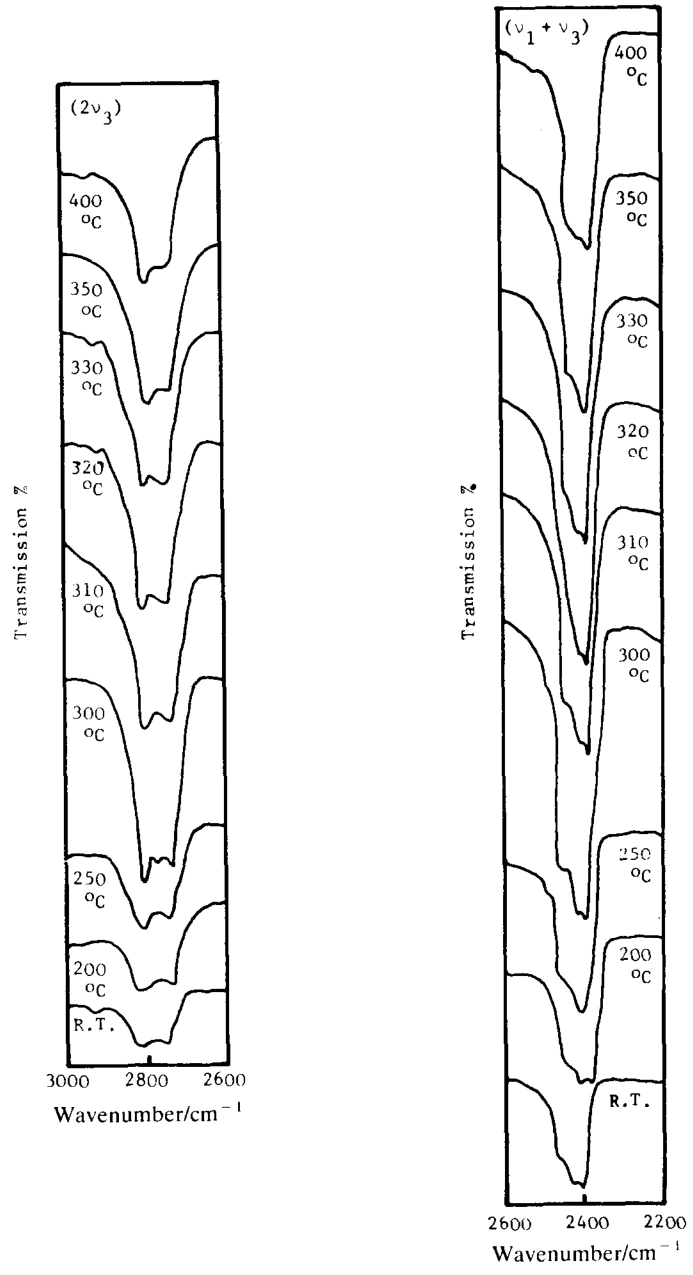

Fig. 4. Temperature dependence of the $(\nu_1 + \nu_3)$ and $2\nu_3$ bands of the nitrate group of $Ba(NO_3)_2$.

where $\Delta\nu$ is the half-band width of the IR absorption band, and c is the velocity of light. In the region of ν_2, Fig. 6 shows the results of these calculations which indicate that phase I is associated with an energy barrier of 0.279 eV, while phase II has an energy barrier of 0.291 eV.

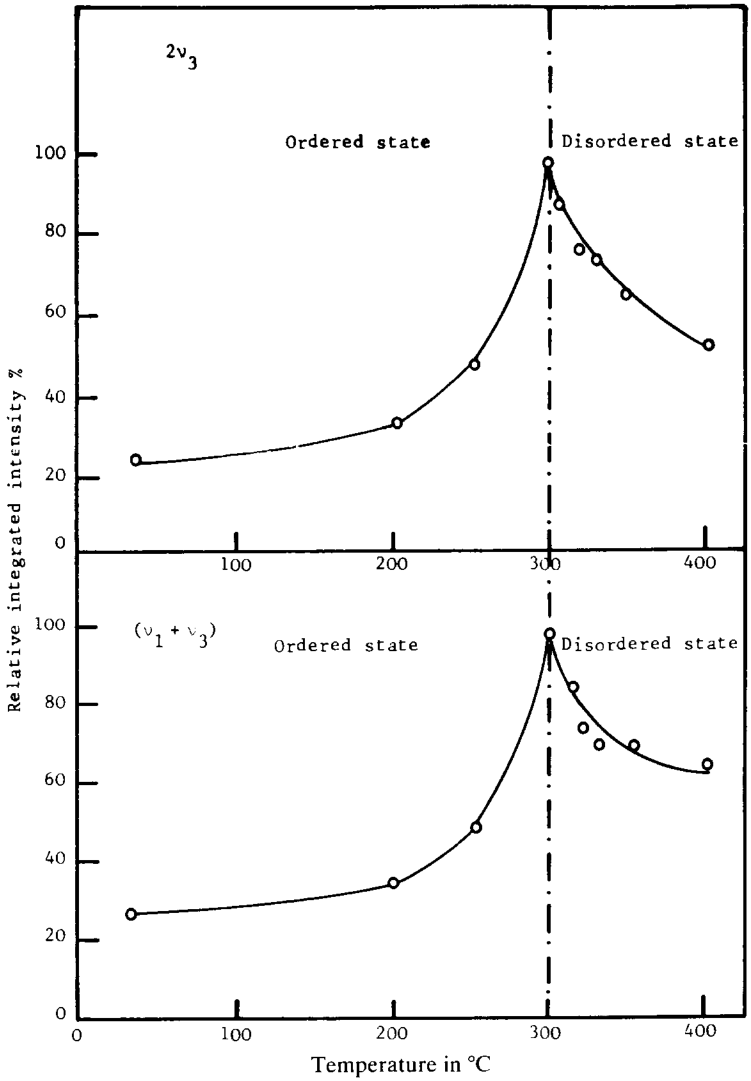

Fig. 5. Temperature dependence of the relative intensity for the $2\nu_3$ overtone mode and the $(\nu_1 + \nu_3)$ combination mode.

DISCUSSION

The order–disorder phenomenon of molecules in crystals may be observed experimentally by studying the temperature dependence of the vibrational spectra in the region of the internal vibrations of the molecule, as well as in the region of the external lattice vibrations.

The effects of temperature and phase state on the internal fundamental normal vibrations of an NO_3^- ion provide a deeper understanding of the nature of the phase transition in $Ba(NO_3)_2$ and the associated changes in

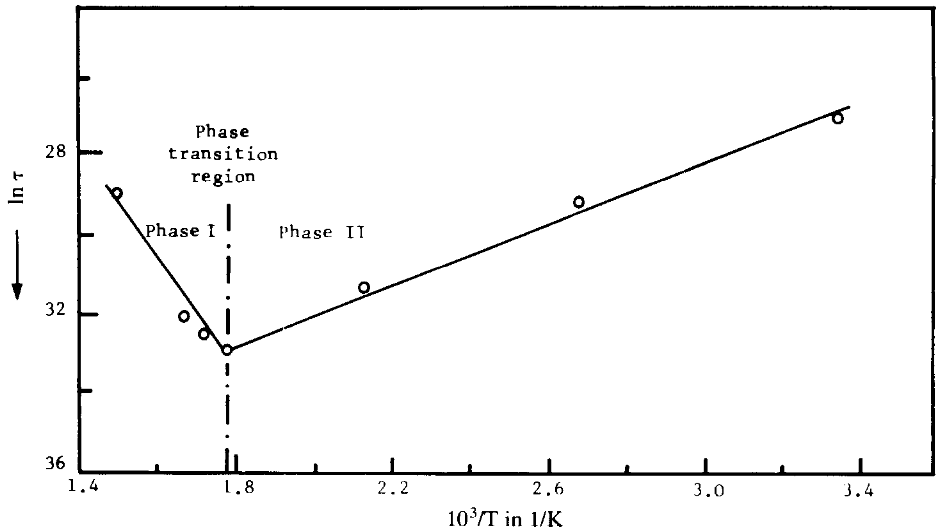

Fig. 6. Temperature dependence of the rotational energy barrier in the region of ν_2.

the interaction potential of the atoms in the NO_3^- ion during the phase conversions.

Near the transition point, the probability of reorientations of the molecules considerably increases with increasing temperature. But at the transition point the nature of the reorientations changes qualitatively, which should lead to a change in the characteristics of the vibrational spectrum of the crystal [9].

With increasing temperature, thermally activated reorientation processes are accompanied by weakening of the ionic bonds which may promote the formation of dipoles whose partial rotation is permissible and is associated with further expansion of the lattice [7]. This effect increases with temperature and the expansion reaches its maximum value at about 300°C, Figs. 3 and 5.

The IR bands of the ionic compounds arise from lattice vibrations of the individual ions. Because the vibrations occur through the lattice and are not concerned with a single unit, they are often observed as broad peaks which represent a composite band of several vibrations. For such compounds, the mass of the ion concerned plays an important role in determining the frequency of absorption. Because a regular decrease in frequency is observed with increasing size and mass, and decreasing polarizing power of the cation [14], the shifts in the infrared frequencies of barium nitrate are very small, see Table 1. This leads to thermal hysteresis, which gets narrower until a limiting condition is reached. This may be interpreted as a progressive break-up of the crystal structure [6]. The deviation in the planar nature of the nitrate groups must be very small owing to an anisotropic temperature factor for the O atom, with the longest axis of the ellipsoid of vibration being perpendicular to the N-O bond within the plane of the nitrate group [4].

Also, the variation in the intensity of each line depends on the number of ions undergoing a certain energy transition. Here, the band envelope as a whole is a representation of the total number of ions involved [15].

The lattice modes in solids may also be of a localized nature; although the crystal has long-range periodicity, the intermolecular potentials that determine the field at any ion site are known to be essentially determined by near-neighbour interactions. The effect of local and correlation crystal fields gives rise to characteristic peculiarities in the vibrational spectra of molecular crystals. The local crystal field causes a shift of the molecular energy levels and may result in a splitting of the degenerate states [1].

The results of the measurements show that temperature and, particularly, the phase state of NO_3^- exert a considerable effect on the anharmonicity of the internal vibration modes of the NO_3^- ion [16]. This indicates changes in the potential energy of interaction of the atoms in the NO_3^- ion during temperature-induced phase conversion in $Ba(NO_3)_2$. The change in the potential energy ΔU between the ordered phase II ($U = 0.291$ eV) and the disordered phase I ($U' \approx 0.279$ eV) is estimated as 0.012 eV.

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