THERMAL EXPANSION OF NITRATES OF LEAD, BARIUM AND STRONTIUM

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1. Introduction

Lead, barium and strontium nitrates form an isomorphous series of cubic crystals, which can be crystallised from aqueous solutions without water of hydration at ordinary temperatures. X-ray studies of these crystals carried out by Vegard (1922) indicate that they belong to the pentagon dodecahedral type of the tetrahedral class. The metal atoms are arranged in a face centred cubic lattice and the nitrate ions are situated on the diagonals of the elementary cubes into which the unit cell can be divided. There are four molecules per unit cell. These crystals belong to the same space group as sodium chlorate and the nitrate ions are not planar. The Raman effect in these crystals has been studied by B. L. Rao (1941), and Couture and Mathieu (1947, 1948). The stress optical coefficients for barium and lead nitrates were measured by Bhagavantam and Krishna Rao (1948, 1953). The elastic constants were determined by Bhimasenachar and Seshagiri Rao (1950).

The aim of the present work was to investigate the thermal expansion coefficients of single crystals of these nitrates and to find out the influence of the metallic ion on the coefficient of expansion.

2. Method of Measurement

The thermal expansion of these crystals above room temperature was measured by the interferometric method. The apparatus was the same as that set up by Press (1950) and used extensively by Sharma and Sridhar in this laboratory. The temperature was measured with a calibrated chromel-alumel thermocouple and a precision vernier potentiometer reading up to $\pm 1\,\mu v$. The rate of heating never exceeded 1° C. per minute. The thermo E.M.F. was read every minute and the heating current was regulated when necessary to maintain a uniform rate of heating. The time of transit of the fringe across a fixed mark was noted. The thermo E.M.F. exactly at the time a fringe crossed could be found by interpolation. Different rates of heating were also employed. The experiment was repeated after taking apart the interferometric arrangement and resetting it for a fresh run.

The crystals were grown by slow evaporation from saturated solutions of the salts. Transparent crystals of 4 to 5 mm. height were obtained. Three such pieces were ground to form pyramids of the same height and were used as the spacers between the interferometric plates. The interferometric arrangement was given a heat treatment before the commencement of each experiment.

RESULTS

A smooth curve is drawn passing evenly through the experimental points obtained in different runs and the value of the expansion coefficient $\bar{\alpha}$ read from the curve is given in Table I. The curves are exhibited in Fig. 1.

TABLE I

Mean expansion coefficient $\bar{\alpha}$ of barium, strontium and lead nitrates

Temperature °C.	$\bar{\alpha} \times 10^6$		
	$Ba(NO_3)_2$	$Sr(NO_3)_2$	$Pb(NO_3)_2$
75	18·3	32·1	32·9
100	19·1	32·6	33·4
125	19·9	33·2	33·8
150	20·8	34·0	34·4
175	21·6	34·4	34·8
200	22·4	34·8	..
225	23·2	35·4	..
250	..	35·8	..
275	..	36·6	..
300	..	37·2	..
325	..	38·2	..
350	..	39·2	..
375	..	40·2	..
400	..	41·0	..
425	..	42·2	..
450	..	45·0	..
475	..	47·8	..
500	..	48·2	..
525	..	46·6	..
Lattice const. in Å.U.	8·11	7·81	7·84
Radius of Metallic ion, in Å.U.	2·17	2·04	2·05

The maximum scatter of the experimental points obtained in different runs did not amount to more than 3%. In the majority of cases the agreement was much closer.

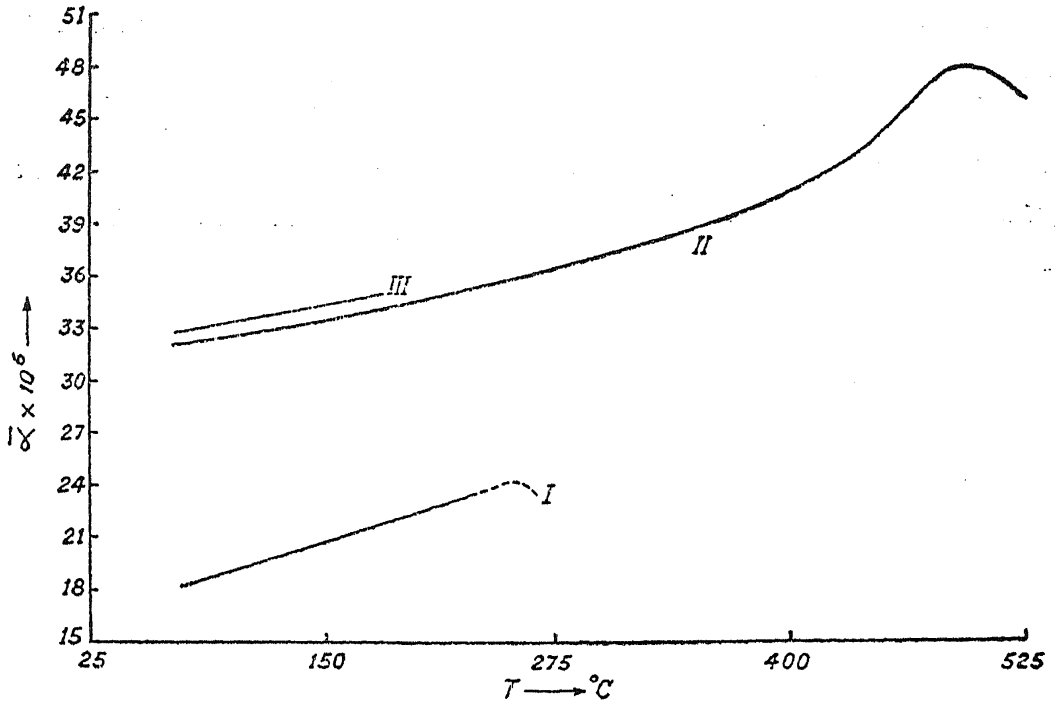

FIG. 1. Expansion Coefficient $\bar{\alpha}$ *vs.* Temperature Curve for (I) Barium Nitrate, (II) Strontium Nitrate and (III) Lead Nitrate.

Values near the room temperature were not obtained because the furnace took a certain time to reach thermal equilibrium.

The expansion coefficients are mean values over 20° C. temperature intervals.

Lead nitrate decomposes rapidly above 200° C. (Mellor, 1924). Crystals of barium nitrate cracked to pieces when they were heated beyond 270° C. But from 250° C. they gave anomalous results indicated by the dotted curve in Fig. 1. Crystals of strontium nitrate did not exhibit any such phenomena up to about 550° C.

The expansion coefficients of lead, barium and strontium nitrates could be expressed satisfactorily by the following equations:—

$Pb(NO_3)_2$: $\bar{\alpha}_t = 31{\cdot}5 \times 10^{-6} + 1{\cdot}9 \times 10^{-8} t°$ C. (Between 75–180° C.)

$Ba(NO_3)_2$: $\bar{\alpha}_t = 15{\cdot}8 \times 10^{-6} + 3{\cdot}3 \times 10^{-8} t°$ C. (Between 75–250° C.)

$Sr(NO_3)_2$: $\bar{\alpha}_t = 31{\cdot}6 \times 10^{-6} + 8{\cdot}0 \times 10^{-9} t°$ C. $+ 4{\cdot}0 \times 10^{-11} t^2$ (Between 75–425° C.)

radius of oxygen atom $= 0{\cdot}75$ Å.U.

radius of nitrogen atom $= 0{\cdot}75$ Å.U.

At the bottom of Table I are entered the lattice constants and radii of the ions of these nitrates. These values are taken from Vegard (1922).

In Table II are collected the elastic constants of the crystal. The values of C_{11} and C_{12} were determined by Bhimasenachar and Seshagiri Rao (1950). The values of S_{11}, S_{12} and $S_{11} + 2S_{12}$ are calculated from these measurements. The molar volumes V are taken from Vegard (1922). The specific heat of barium nitrate was measured between 13° C. and 98° C. by Regnault (1841). The specific heats of all the three nitrates were determined by Kopp (1865) between 16° and 48° C.

According to Gruneisen (1914) the linear expansion coefficient for a cubic crystal is given by

$$V\alpha = (S_{11} + 2S_{12})\,\gamma C_v$$

Here C_v is the molar specific heat and γ is the Gruneisen constant. The values of γ calculated using the above formula are given.

TABLE II

Elastic constants, molar volume, molar specific heat, and Gruneisen constant of barium, strontium and lead nitrates

Substance	$C_{11}\times10^{-11}$ dynes/sq. cm.	$C_{12}\times10^{-11}$ dynes/sq. cm.	$S_{11}\times10^{13}$ cm.²/dyne	$S_{12}\times10^{13}$ cm.²/dyne	$(S_{11}+2S_{12})\times10^{13}$	$\bar{\alpha}\times10^{6}$ at 75° C.	Molar volume V	Molar sp. heat C_v	γ
$Ba(NO_3)_2$	5·93	1·89	20·0	− 4·8	10·4	18·3	80·9	40	0·85
$Sr(NO_3)_2$	4·73	2·18	29·8	− 9·4	11·4	32·1	72·2	38	1·28
$Pb(NO_3)_2$	4·56	3·09	48·4	−19·5	9·4	32·9	73·1	36	1·70

DISCUSSION

The expansion coefficients of strontium and lead nitrates do not differ much till 200° C.; the difference between the coefficients is small and within the limits of experimental error (3%) (see Table I).

The expansion coefficient of barium nitrate is much smaller than the coefficients for the other two isomorphous salts.

Up to the highest temperatures studied (180° for lead and 250° C. for barium nitrates) the coefficients of expansion of barium and lead nitrates increase linearly with temperature. The rate of increase is greater for barium nitrate than for the other two salts.

The expansion coefficient of strontium nitrate exhibits a parabolic increase with temperature. While up to 200° C. its rate of increase is almost the same as that of lead nitrate, at higher temperatures the rate also goes up.

Near 425° C. the expansion coefficient exhibits a sharp rise. After 500° C., the curve exhibits a fall. The melting point of strontium nitrate is at 570° C.

The strontium and lead salts possess identical lattice constants and radius of the metallic ion. Hence a substitution of strontium for lead cannot be expected to cause any great change in the forces binding the different units in the lattice. This conclusion is in agreement with the fact that these two salts possess identical expansion coefficients (see Table I).

Barium ion has a larger radius than strontium or lead and hence a substitution of barium for the other ions might be expected to loosen up the lattice. So we should expect barium nitrate to have a slightly larger expansion coefficient than the other two salts. The contrary is the case. The expansion coefficient of barium nitrate is considerably smaller than that of the other two salts. This indicates that in spite of the larger radius, the binding in barium nitrate is tighter than in the other two. The melting point of barium nitrate, 592° C., is the highest among the three salts. Also a comparison of the solubilities of the three nitrates in water is interesting. The solubilities at 30° C. of barium, strontium and lead nitrates are 11·6, 88·6 and 60·7 gm. per 100 c.c. of water. The very small solubility of barium nitrate indicates a stronger binding in the crystal. This is also supported by the following facts. The lattice lines appearing in the Raman spectrum of barium nitrate are found to be more intense than those of strontium or lead nitrates (Couture and Mathieu, 1948). A study of the magneto-optic anomaly of aqueous solutions of these salts (Ramaseshan, 1950) shows that the anomaly factor is 0·651 for barium, 0·433 for strontium and 0·503 for lead nitrates. The higher value in barium nitrate solution definitely points to a stronger binding in this salt.

In Table II the values of Gruneisen's constant have been calculated for the three crystals. We find γ for barium nitrate is much less than 1 while the γ values of strontium and lead nitrates are of the order to be expected for truly ionic crystals. Small values of γ are typical for homopolar crystals. Probably the binding in barium nitrate is not truly ionic but partly homopolar. A study of the magneto-optic anomaly in these crystals may be expected to throw some light on this point.

In conclusion the author wishes to thank Prof. R. S. Krishnan for his continued interest and encouragement throughout the course of this work.

Abstract

The expansion coefficients of barium, strontium and lead nitrates have been studied above room temperatures. Lead nitrate decomposes rapidly

beyond 200° C. while crystals of barium nitrate crack above 270° C. Strontium nitrate exhibited no such phenomena till 550° C.

These crystals are isomorphous. The expansion coefficients of lead and strontium nitrates are nearly equal; they also possess the same ionic radii. Barium nitrate has a considerably smaller expansion coefficient though its ionic radius is larger than for the other two. This peculiar behaviour of barium nitrate indicates a stronger binding in this crystal—a fact which is supported by measurements on the elastic constants, Raman effect, solubilities of these salts and a study of the magneto-optic anomaly of aqueous solutions of these salts.

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