

X-ray Determination of the Lattice Parameter and the Thermal Expansion of Lead Nitrate

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High-temperature X-ray diffractometer studies of lead nitrate in the temperature range 25–430°C indicate that it is thermally stable between 25 to 380°C and decomposes to lead oxide (red) at 430°C. The lattice parameter has been investigated at various temperatures between 25 and 348°C using a high-temperature X-ray diffractometer and 10 cm diameter symmetrically focusing back-reflexion camera. The lattice parameter is found to increase parabolically with temperature.

Introduction

Lead nitrate [Pb(NO₃)₂] crystallizes in space group *T* (*Pa*3) and is isomorphous with barium and strontium nitrates. Srinivasan (1955) has studied the thermal expansion in the temperature range 75–175°C by an interferometric method. He reports that it decomposes beyond 200°C. The thermal expansion has also been found by Haussühl (1963) using a dilatometric method. However, the lattice parameter of Pb(NO₃)₂ has been determined only at room temperature (Straumanis & Ievins, 1936; Vegard & Roer, 1941; Swanson, Gilfrich & Ugrinic, 1955) and no data are available on the temperature variation of the lattice parameter either at low or at high temperatures. Hence it was decided to study lead nitrate in order to find the range of temperature in which it is thermally stable and to determine the *a* parameter and thermal expansion as a function of temperature in the high-temperature range.

Experimental procedure

The powder samples of Pb(NO₃)₂ were obtained from British Drug Houses Ltd., London and had a specified purity of 99.99%. This powder sample was filtered through a 44 μm sieve to give fairly uniform particle size.

The high-temperature X-ray diffractometer studies were conducted at Bhabha Atomic Research Centre, Trombay. The experimental set up used to obtain the diffraction pattern has been described elsewhere (Momin, Matthews & Karkhanvala, 1971). All X-ray diffraction studies were made using filtered Cu *K*α radiation (36 kV 18 mA). A symmetrically focusing back-reflexion camera of 10 cm diameter was also used for obtaining powder photographs at elevated temperatures with filtered copper radiation.

Diffraction patterns were studied at elevated temperatures between 25 and 430°C. An interesting feature was observed in X-ray diffractometer study in the temperature range 380–420°C. No reflexions were observed in the X-ray diffraction pattern between 380 and 420°C. At 430°C an entirely new diffraction pattern compared with the pattern at 348°C was observed and the colour of the specimen changed to red. These preliminary observations indicate that Pb(NO₃)₂ decom-

posed into PbO (red) at 430°C. To confirm the observed decomposition of Pb(NO₃)₂, a fresh Pb(NO₃)₂ sample was taken and was heated to 430°C. Then it was cooled to room temperature (25°C) and the diffraction pattern was taken; it resembles that taken at 430°C. The above procedure was followed with four samples at the following elevated temperatures: 48, 80, 104, 154, 252, 305, 348 and 380 °C. The diffraction patterns observed with the samples at elevated temperatures (48–380°C) and with the cooled samples were the same. These patterns resembled the patterns taken at room temperature from a fresh sample. The present investigations suggest that the Pb(NO₃)₂ is thermally stable in the temperature range 25–380°C and that it decomposes at 430°C. The decomposition is irreversible.

Results and discussion

The high-temperature X-ray diffractometric automatically recorded patterns showed ten reflexions, (422)_{a₁a₂}, (511)_{a₁a₂}, (440)_{a₁a₂}, (531)_{a₁a₂} and (600)_{a₁a₂}. A typical diffraction pattern taken at room temperature (25°C) in the angular range 57° to 72°C is shown in Fig. 1. These reflexions were scanned at ½° 2θ/min at different temperatures in the range 25° to 348°C in air. The accurate determination of the lattice parameter was done using the Nelson & Riley (1945) function to an accuracy of ±0.0002 Å. The lattice parameter so obtained for each temperature is listed in column 3 of Table 1.

Table 1. *Lattice parameter of Pb(NO₃)₂ at various temperatures*

<i>T</i> (°C)	X-ray photographic <i>a</i> (Å)	X-ray diffractometric <i>a</i> (Å)	Lattice parameter <i>a</i> (Å)
25	7.8596 ± 0.0002	7.8596 ± 0.0002	7.8596 ± 0.0002
48	–	7.8656	7.8656
55	7.8661	–	7.8661
80	7.8722	–	7.8722
104	–	7.8785	7.8785
145	7.8892	–	7.8892
154	–	7.8910	7.8910
185	7.8986	–	7.8986
230	7.9100	–	7.9100
252	–	7.9156	7.9156
275	7.9214	–	7.9214
305	–	7.9350	7.9350
348	–	7.9491	7.9491

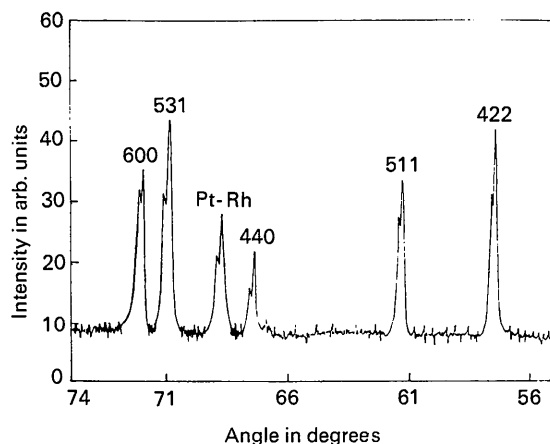


Fig. 1. X-ray diffraction pattern obtained at 25°C in the angular range 57° to 72°.

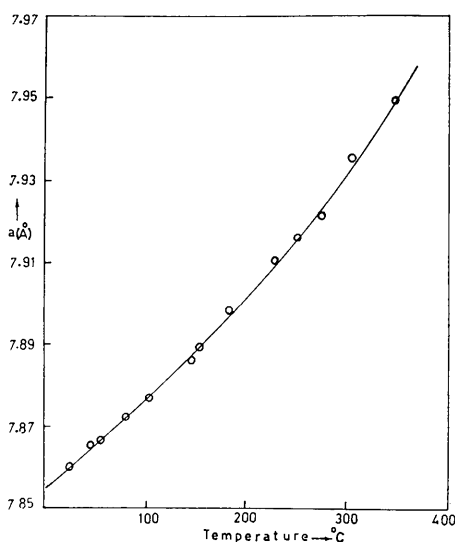


Fig. 2. The variation of the lattice parameter with the temperature.

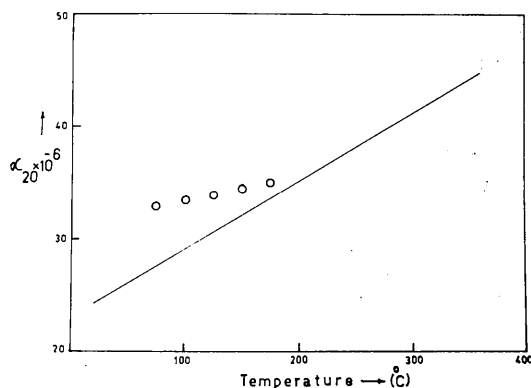


Fig. 3. The variation of thermal expansion coefficient with temperature. The line represents the results of the present study and circles that of Srinivasan (1955).

The powder photographs were obtained at seven temperatures between 25 and 275°C. The X-ray powder photographs taken with the back-reflexion focusing camera showed eight lines $(931)_{a_1 a_2}$, $(844)_{a_1 a_2}$, $(933)_{a_1 a_2}$ and $(10,0,0)_{a_1 a_2}$. These lines were used in evaluating the lattice parameter at different temperatures using the extrapolation method (Klug & Alexander, 1954) with an error function $\varphi \tan \varphi$. Independent measurements and calculations were made on each film and the average values obtained from these are given in column 2 of Table 1. The standard errors calculated by the method of Jette & Foote (1935) are also tabulated.

The lattice parameter measured in the present work at room temperature is in excellent agreement with those of Straumanis & Ievins (1936), Vegard & Roer (1941), and Swanson *et al.* (1955). The lattice parameter at various temperatures is given in column 4 of Table 1. The variation of the a parameter with temperature shown in Fig. 2 is non-linear and a quadratic fitted to these points by the method of least squares gave the following equation:

$$a_t = 7.8590 + 1.8962 \times 10^{-4}(t - 20) + 24.3026 \times 10^{-8}(t - 20)^2 \quad (1)$$

Here a and t are expressed in Å and °C respectively. The corresponding equation for the coefficient of thermal expansion obtained by differentiation of a_t with respect to temperature is

$$\alpha_t = 23.01 \times 10^{-6} + 6.02 \times 10^{-8}t \quad (2)$$

where α and t are expressed in °C⁻¹ and °C respectively. The error in the coefficient was estimated to be less than 2%. The variation of the thermal expansion with temperature calculated from equation (2) is shown in Fig. 3.

Srinivasan (1955) suggested that the expansion coefficient varies linearly with temperature. Our results agree with the above findings. It is apparent from Fig. 3 that the present results show more anharmonic effects than that of Srinivasan (1955). The present values of thermal expansion coefficients are rather lower than those given by Srinivasan (1955) and Haussühl (1963). These results are summarized in Table 2.

Table 2. Comparison of the present thermal expansion coefficient with previous measurements

Investigator	Thermal expansion at room temperature	
	(10 ⁻⁶ /°C)	Method
Present work	24.50	X-ray studies
Haussühl (1963)	30.00	Dilatometric studies
Srinivasan (1955)	31.9	Interferometric studies

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Theoretical Evaluation of the Intermolecular Interaction Energy of a Crystal: Application to the Analysis of Crystal Geometry

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Simple formulae for the interaction energy between two molecules have been used for writing a program which evaluates the total interaction energy of the molecules in a crystal. These formulae appear as sums of atom–atom and, eventually, atom–bond and bond–bond contributions. The non-additivity of the polarization energy is taken into account, and a rough estimate of the third-order non-additive terms ('triple dipole') is introduced. A suitable modification of the formulae for short interatomic distances allows us to treat hydrogen-bond interactions as well. We present results for the crystals of CH₄, CO₂, C₆H₆, and C₆H₅NO₂. The energies calculated for the experimental geometry are in good agreement with experiment. For CO₂ and C₆H₅NO₂ minimizations of the computed energy (with respect to unit cell parameters and orientation and position of one molecule in the cell) were performed and it was found that the experimental configuration actually was very close to a minimum. The configurations of neighbour molecules in the crystal are compared with the optimal configuration of a binary complex, and it appears that, for non-hydrogen-bonded molecules, significant differences between these configurations may occur. Finally, for nitrobenzene several local minima seem to exist on the energy hypersurface; the minimum corresponding to the known experimental geometry appears to be the lowest, but only by a small amount.

1. Introduction

An extensive compilation of the stacking patterns observed in the crystalline state for nucleic bases, either isolated or in combined form (nucleosides and nucleotides) was recently given by Bugg, Thomas, Sundaralingam & Rao (1971). Stacked configurations of the purine or pyrimidine rings appear in all these crystals, but the overlap is almost always partial. Trying to explain this partial stacking in terms of binary interactions only (*i.e.* the interaction between the two partially stacked bases), Bugg *et al.* were led to suggest that these partially stacked patterns could be understood only in terms of the polarization contribution [indeed, by using the dipole approximation (see *e.g.* Claverie & Rein, 1969) for the electrostatic and dispersion energy, they found that these two contributions could not explain the observed pattern]. However, when actual computations of the various contributions to the intermolecular interaction energy are performed,

the polarization contribution never appears as the prominent one [as concerns stacked configurations, see *e.g.* Claverie, Pullman & Caillet (1966) (stacked purines and pyrimidines); Caillet & Pullman (1968) (tetramethyl uric acid and aromatic hydrocarbons); Manton (1968, 1969 *a,b*) (charge transfer complexes: tetracyanoethylene and aromatic hydrocarbons)]. In all these cases several stacked configurations were tried (by moving the molecules in parallel planes) in order to explore roughly the energy surface: not only the *absolute magnitude* of the polarization contribution appeared markedly smaller than the magnitude of the other contributions, but the same property appeared to hold also for the *variations* of the different contributions: therefore, it may not be argued that the polarization term, although small by itself, could play a prominent role (by its variation) in the determination of the minimum-energy configuration.

Two other features, relevant for the present problem, appeared in these calculations of binary complexes: