Letters

X-ray determination of lattice parameters, thermal expansion and defect formation energy of sodium bromate

The lattice parameter a_T of sodium bromate has been measured in the temperature range 289 to 589 K using a 15 cm diameter symmetrically focusing back-reflection camera. a_T in Å is related to the temperature T by $a_T = 6.6528 + (170.8418 \times 10^{-6})T - (5.1430 \times 10^{-8})T^2 + (2.5883 \times 10^{-10}) T^3$. The linear thermal expansivity α is calculated by differentiation of a_T with respect to T and it varies anomalously with temperature above 400 K. The analysis of the anomalous expansion data gives the thermal defect formation energy a value of 0.85 ± 0.04 eV.

The thermal expansion coefficient (α) of sodium bromate ($NaBrO_3$) has been measured interferometrically both by Sharma [1] and Ganesan [2]. Their results indicate an anomalous behaviour for α; namely α increases quite rapidly at high temperatures. According to Lidiard [3] such an anomalous expansion is expected for ionic crystals in the intrinsic range of temperatures. Lawson [4], who studied the thermal expansions of silver halides, attributes such anomalous behaviour of α to the thermal generation of point defects.

The lattice parameter of $NaBrO_3$ has been determined only at room temperature (Swanson *et al.* [5]) and no data are available on the temperature variation of the lattice parameter either at low or at high temperatures. No X-ray determination of the coefficient of thermal expansion has so far been reported. Hence the investigation of sodium bromate was undertaken with the following objectives: (i) to determine the lattice parameter and thermal expansion as a function of temperature from 289 to 589 K, and (ii) to obtain information about thermally produced defects and to calculate the energies of formation of defects from the anomalous thermal expansion data.

The powder samples of $NaBrO_3$ with a specified purity of 99.99% were obtained from Riedel Dettaen Agseelze, Hannover, Germany. To obtain uniform particle size these powder samples were filtered through a 44 μm sieve.

A symmetrically focusing back-reflection camera of 15 cm diameter was used for obtaining powder photographs at elevated temperatures with filtered CuKα radiation. The specimen holder and heater were of such a design that the specimen could be heated to and maintained at any desired temperature. The temperature of the specimen could be measured to an accuracy of ± 0.8 K with the help of a Pt–13% Rh thermocouple and a commercial temperature controller.

The powder photographs were obtained at sixteen temperatures between 289 to 589 K. The X-ray powder photographs showed sixteen lines: $(8\,1\,0)_{\alpha_1\alpha_2}$, $(8\,1\,1)_{\alpha_1\alpha_2}$, $(7\,3\,3)_{\alpha_1\alpha_2}$, $(8\,2\,1)_{\alpha_1\alpha_2}$, $(6\,5\,3)_{\alpha_1\alpha_2}$, $(8\,2\,2)_{\alpha_1\alpha_2}$, $(8\,3\,1)_{\alpha_1\alpha_2}$, and $(7\,5\,1)_{\alpha_1\alpha_2}$. These lines were used in evaluating the lattice parameter at different temperatures using an extrapolation method [6] with an error function ϕ tan ϕ. Independent measurements and calculations were made on each film and the average values obtained from these are given in Table I. The standard errors calculated by the method of Jette and Foote [7] are also tabulated. The lattice parameter found in the present work at 298 K is 6.7058 Å, which compares excellently with the reported (Swanson *et al.* [5]) value of 6.705 Å at 298 K. The variation of lattice parameter with the temperature shown in Fig. 1 is

TABLE I Lattice parameter of sodium bromate at various temperatures

T (K)	Lattice parameter a (Å)
289	6.7041
299 (RT)	6.7061 ± 0.0002
309	6.7084
323	6.7114
336	6.7139
348	6.7169
381	6.7250
395	6.7280
435	6.7389
453	6.7437
473	6.7490
503	6.7587
509	6.7605
547	6.7732
571	6.7822
589	6.7881

© 1978 Chapman and Hall Ltd. Printed in Great Britain.

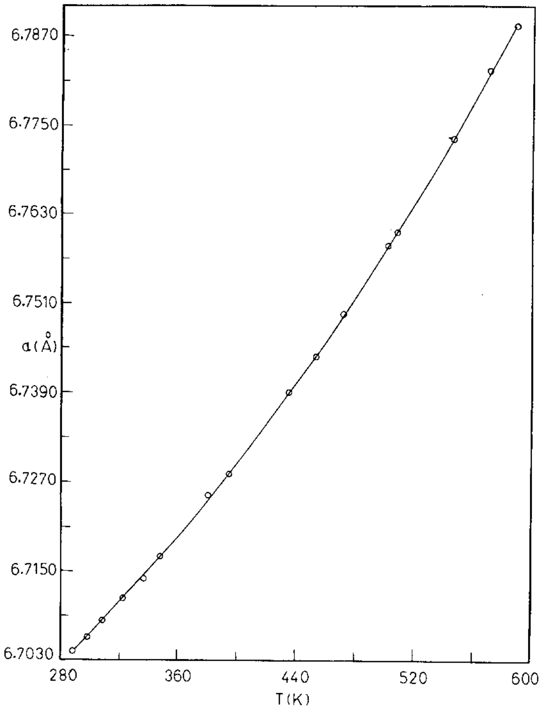

Figure 1 Plot of a versus T.

non-linear and the least squares fitting to these data points gives the following equation:

$$a_T = 6.6528 + (170.8418 \times 10^{-6})T - (5.1430 \times 10^{-8})T^2 + (2.5883 \times 10^{-10})T^3, \quad (1)$$

where a and T are expressed in Å and K respectively. The corresponding equation for the coefficient of thermal expansion obtained by differentiation of a_T with respect to temperature is

$$\alpha_T = (25.68 \times 10^{-6}) - (1.55 \times 10^{-8})T + (1.17 \times 10^{-10})T^2 \quad (2)$$

where α and T are expressed in K^{-1} and K respectively. The error in α is estimated to be less than 2.5% per 10 K.

The variation of α_T with temperature of this work, of Sharma [1] and of Ganesan [2] are presented in Table II. A comparative study of the coefficients of expansion at different temperatures given by previous workers (Sharma [1] and Ganesan [2]) and the present work shows that the values of Sharma near room temperature are higher by about 21.9% than our values; whereas Ganesan's values are higher by about 15.6% than the present values. The gradient of the α–T curve of this work agrees reasonably with that of Ganesan [2]. On the contrary, the present work gives a higher gradient for the α–T curve than that of Sharma [1] so that at higher temperatures (above 480 K) the microscopic X-ray values are much larger than the macroscopic values of Sharma [1]. We have found from differential thermal analysis (DTA) measurements that $NaBrO_3$ decomposes around 610 K and melts at 654 K. It is possible that the thermal expansion will increase rapidly as the melting point is approached. Although it is not possible to give any exact reason for the discrepancy between the α_T values of this investigation and of the previous work (Sharma [1] and Ganesan [2]), it may be attributed to point defects in crystals.

The thermal expansion data obtained in this work by an X-ray diffraction technique and by Sharma [1] by an interferometric method both show an anomalous behaviour at higher temperatures (above 400 K). The above anomalous expansion data were used in evaluating defect formation energy. According to Lidiard [3] the presence of defects produce a fractional change in volume

$$\delta = \Delta V/V = A \exp(-E/2kT), \quad (3)$$

where A is a constant and E is the formation

TABLE II Thermal expansion coefficient of sodium bromate at various temperatures

T(K)	$\alpha(10^6\,K^{-1})$ Present work	$\alpha(10^6\,K^{-1})$ Sharma (1950)	$\alpha(10^6\,K^{-1})$ Ganesan (1959)
289	30.97	39.02	35.90
299	31.50	39.25	36.80
309	32.06	39.50	37.80
323	32.88	39.85	39.00
336	33.68	40.19	40.20
348	34.45	40.51	41.20
381	36.76	41.45	44.00
395	37.81	41.85	45.10
435	41.08	43.12	49.00
453	42.67	43.70	–
473	44.52	44.41	–
503	47.48	45.45	–
509	48.10	45.72	–
547	52.21	47.15	–
571	54.97	–	–
589	57.14	–	–

energy of the defect. The additional expansion $\Delta\alpha$ due to this change in volume is

$$\Delta\alpha = \frac{1}{V}\frac{\mathrm{d}}{\mathrm{d}T}(\Delta V) = \frac{A}{2kT^2}\exp(-E/2kT), \tag{4}$$

so that

$$T^2(\Delta\alpha) = \frac{A}{2k}\exp(-E/2kT). \tag{5}$$

The α_T values obtained from the present X-ray data shown in Fig. 2, were used to plot graphs of $\ln(T^2\Delta\alpha)$ versus $1/T$ (Fig. 3). The graph (Fig. 3) exhibits essentially straight line behaviour, and so least-squares fitting was used to calculate the slope. The defect formation energy derived from this slope is 0.85 ± 0.04 eV. The defect formation energy of value 0.70 ± 0.04 eV was also obtained from the macroscopic data of Sharma [1] using a similar procedure. Both these values are far smaller than the formation energy of 1.40 eV obtained from the electrical conductivity measurements of Ramsastry *et al.* [8]. Such disagreement is not unknown. There is some controversy in the literature as to whether there should be agreement between the formation energies obtained from the electrical conductivity data and those calculated from the anomalous thermal expansion. It appears to us that the present day understanding of the anomalous thermal expansion of ionic crystals at temperatures approaching the melting point is not quite satisfactory, and all that can be said is that point defects do contribute to the thermal expansion to some extent.

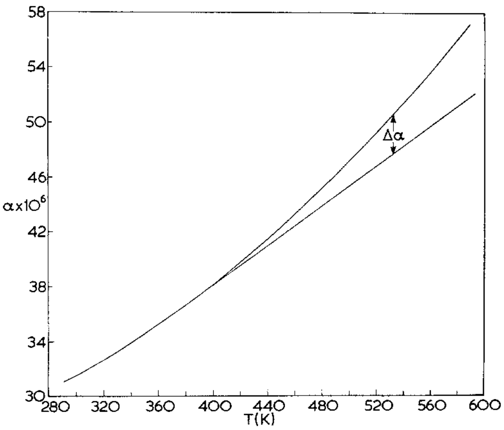

Figure 2 Plot of α versus T.

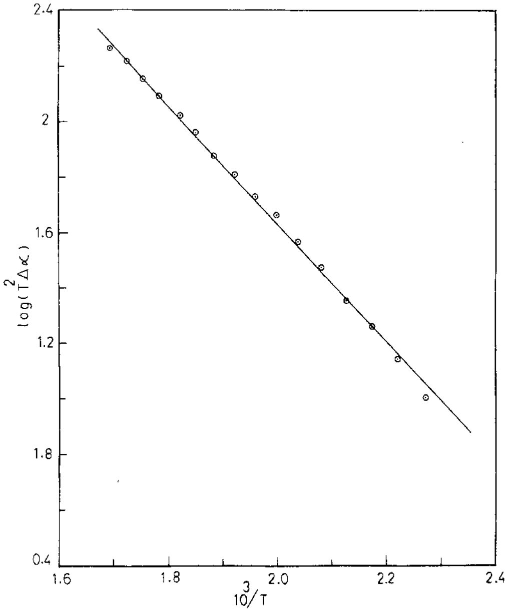

Figure 3 Plot of log $(T^2\,\Delta\alpha)$ versus $1/T$.

References

1. S. S. SHARMA, *Proc. Ind. Acad. Sci.* **A31** (1950a) 83.
2. S. GANESAN, *J. Ind. Inst. Sci. Bangalore* **41A** (1959) 9.
3. A. B. LIDIARD, *Handbook Phys.* **20** (1957) 246.
4. A. W. LAWSON, *Phys. Rev.* 78 (1950) 185.
5. H. E. SWANSON, N. T. GILFRICH and G. M. UGRINIC, Standard X-ray diffraction Patterns, NBS Circular 539 (1955) 5.
6. H. P. KLUG and L. E. ALEXANDER, "X-ray diffraction procedures" (John Wiley, New York, 1954) p. 474.
7. E. R. JETTE and F. FOOTE, *J. Chem. Phys.* 3 (1935) 605.
8. C. RAMASASTRY and Y. V. G. S. MURTI, *J. Phys. Chem. Solids* 24 (1963) 1384.

Received 25 October 1977
and accepted 17 January 1978.

T. N. WATHORE*
R. G. KULKARNI
Department of Physics, Marathwada University,
Aurangabad, Maharashtra, India

---

*Present address: Department of Physics, Government Arts and Science College, Aurangabad (Maharashtra), India.