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X-ray Debye temperature of sodium bromate

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The X-ray Debye temperature, θ_M, of sodium bromate has been determined by measuring integrated intensities of selected Bragg reflections at the following temperatures: 298, 381, 453, 503 and 571 K. It is found that θ_M varies anomalously with temperature above 381 K. The analysis of the anomalous Debye temperature data gives a value for the thermal defect formation of value 0.80 ± 0.04 eV.

1. Introduction

The Debye temperature plays a vital role in the understanding of a large number of solid state problems connected with lattice vibrations. A number of physical parameters such as mean-square atomic displacements [1] and elastic constants [2] are known to depend upon the Debye temperature of a solid. Salter [3] has shown that Debye temperatures obtained from different physical properties will not, in general, be equal. No data on X-ray Debye temperatures for the isomorphic structures of sodium bromate ($NaBrO_3$) and sodium chlorate ($NaClO_3$) are reported in the literature.

In the present work, measurements of X-ray diffracted intensities at various temperatures were carried out with the object of extracting the X-ray Debye temperature, θ_M, for sodium bromate. The θ_M obtained in the present investigation was compared with the Debye temperature obtained from elastic constants [4]. An attempt has also been made to study the variation of θ_M with temperature.

2. Theory

The method, which depends upon the principle of measuring the integrated intensities of a large number of Bragg reflections at a fixed temperature, was first outlined by Buerger [5]. This method was described in detail by Walford and Schoeffel [6] and has been used here to determine the X-ray Debye temperature, θ_M. Recently, Kulkarni and Bichile [7] used this method to obtain X-ray Debye temperatures of $Ba(NO_3)_2$ and $Sr(NO_3)_2$ assuming a single Debye–Waller factor (M) for all three atoms in the compounds.

The average vibrational amplitudes are related to the Bragg intensities, within quasi-harmonic approximation, through the Debye–Waller theory. The integrated intensity (I) from a cubic powder sample can be expressed as follows [8]:

$$I = KL_PP\,|F|^2 \qquad (1)$$

where K is a constant; L_P is a function of the Bragg angle only known as the Lorentz–Polarization factor; P is multiplicity; and F is the modulus of the structure factor.

The structure factor for sodium bromate (space group T^4) can be written as

$$F(h\,k\,l) = f_{Na}F_{Na}e^{-M_{Na}} + f_{Br}F_{Br}e^{-M_{Br}} + 3f_OF_O\,e^{-M_O}. \qquad (2)$$

The exponential terms in Equation 2 represent the Debye–Waller factors for the three constituent atoms, i.e. sodium, bromine, and oxygen, respectively; f_{Na}, f_{Br} and f_O are the respective atomic scattering factors; F_{Na}, F_{Br} and F_O are the respective structure factors which are sine and cosine functions of $h\,k\,l$ values; all other terms have the usual meaning, as defined in [9]. According to James [8], the Debye–Waller factor is defined as

$$M(T) = \frac{6h^2T}{mk\theta_M^2}\left(\phi(X) + \frac{X}{4}\right)\sin^2\phi/\lambda^2$$

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$$= B\sin^2\theta/\lambda^2 \qquad (3)$$

with

$$B = \frac{6h^2T}{mk\theta_M^2}\left(\phi(X) + \frac{X}{4}\right). \qquad (4)$$

Here m is the mass of the atom (taken as the mean mass), h is Planck's constant, K is Boltzman's constant, θ_M is the X-ray Debye temperature, T is the temperature, θ is the Bragg angle, $X = \theta_M/T$, and λ is the wavelength of the X-rays; the function $[\phi(X) + X/4]$ is tabulated by James [8].

As the masses of sodium, bromine and oxygen atoms are different, the respective Debye–Waller factors (M_{Na}, M_{Br} and M_O) will also be different in $NaBrO_3$. To a first approximation let the M_{Na}, M_{Br} and M_O be equal to each other in accordance with Kulkarni and Bichile [7]. To this effect Equation 2 becomes

$$F(h\,k\,l) = [f_{Na}F_{Na} + f_{Br}F_{Br} + 3f_OF_O]\,e^{-M}$$

$$= \Sigma f e^{-M}, \qquad (5)$$

where

$$\Sigma f = f_{Na}F_{Na} + f_{Br}F_{Br} + 3f_OF_O.$$

Equation 1 may be written with the help of Equations 3 and 5 as

$$I = KL_PP|\Sigma f|^2\,e^{-2B\sin^2\theta/\lambda^2}. \qquad (6)$$

The experimental structure factor (F_{corr}) may be obtained from Equation 6 using measured integrated intensity (I) as shown below:

$$|F_{corr}|^2 = \frac{I}{L_PP} = K|\Sigma f|^2\,e^{-2B\sin^2\theta/\lambda^2}. \qquad (7)$$

It follows from Equation 7 that the slope of the plot of $\ln(|F_{corr}|^2/|\Sigma f|^2)$ versus $\sin^2\theta/\lambda^2$ yields the temperature factor B and hence θ_M can be obtained from it.

3. Experimental procedure

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. The experimental apparatus of Bhabha Atomic Research centre (BARC) used in this work for high-temperature measurements has been described elsewhere [10] and a brief account of the same is given here. MRC model X-36-N3 high temperature X-ray diffractometer attachment mounted on the Philips Norleco wide-angle diffractormeter was used for high-temperature X-ray diffraction studies. The temperature of the specimen can be varied from 150 to 1500 K with the aid of this attachment. For high-temperature work, the powder specimens were mounted on the strip-type resistive heating element (platinum 40% rhodium alloy), which works as a specimen holder.

Integrated intensities were measured using 20 scans, β-filtered Cu$K\alpha$ radiation and a pulse-height discriminator. The scan rates were adjusted such that they gave relatively large net counts ($\sim 8 \times 10^3$) from the low-intensity high-order reflections. Scanning rates and background counting times were adjusted so that the statistical counting errors were less than 2%. The integrated intensities of eight to eleven reflections were measured at the following fixed temperatures: 298, 381, 453, 503 and 571 K. These measurements were repeated several times. Precaution was taken to minimize the extinction by using very fine powder samples. The temperature of the sample was measured with Pt–13% Rh thermocouple with an estimated precision of ± 1 K.

In addition, the integrated intensities of nine reflections were measured at room temperature (309 K) with the help of a simple diffractometer [11] fabricated in our laboratory. These measurements were repeated at least six times.

4. Results and discussion

The data were collected at 298, 381, 453, 503 and 571 K. The measured intensities were corrected for thermal diffuse scattering (TDS) using the correction factor for cubic powders given by Chipman and Paskin [12]. In addition to TDS correction, intensities were also corrected for Lorentz–Polarization (L_P) and absorption. The corrected structure factors, F_{corr}, were determined from the corrected intensities for each reflection using Equation 7. The plots of $\ln(|F_{corr}|^2/|\Sigma f|^2)$ versus $\sin^2\theta/\lambda^2$ for different temperatures are shown in Figs. 1 to 3. Here the symbol $|\Sigma f|^2$ stands for the calculated value of the square of the structure factor for $NaBrO_3$. In calculating Σf, the reliable positional parameters from Wyckoff [13] and atomic scattering factors from the International tables [9] were used. It is apparent from Figs. 1 to 3 that the even–even ($h + k = 2n$, $l + k = 2n$), even–odd ($h + k = 2n$, $l + k = 2n + 1$), odd–even ($h + k = 2n + 1$, $l + k = 2n$) and odd–odd ($h + k = 2n + 1$, $l + k = 2n + 1$) reflections lie on the same straight line. The solid lines in Figs. 1 to 3 are least-squares fit to the experimental data points. The Debye

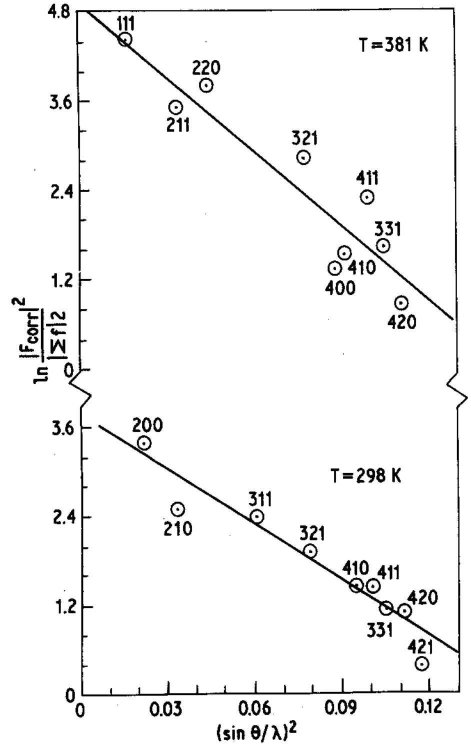

Figure 1 Plot of ln $(|F_{\text{corr}}|^2/|\Sigma f|^2)$ versus $\sin^2\theta/\lambda^2$.

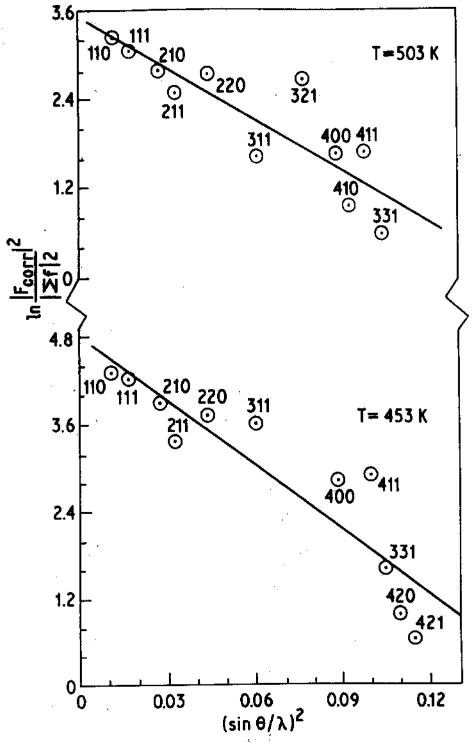

Figure 2 Plot of ln $(|F_{\text{corr}}|^2/|\Sigma f|^2)$ versus $\sin^2\theta/\lambda^2$.

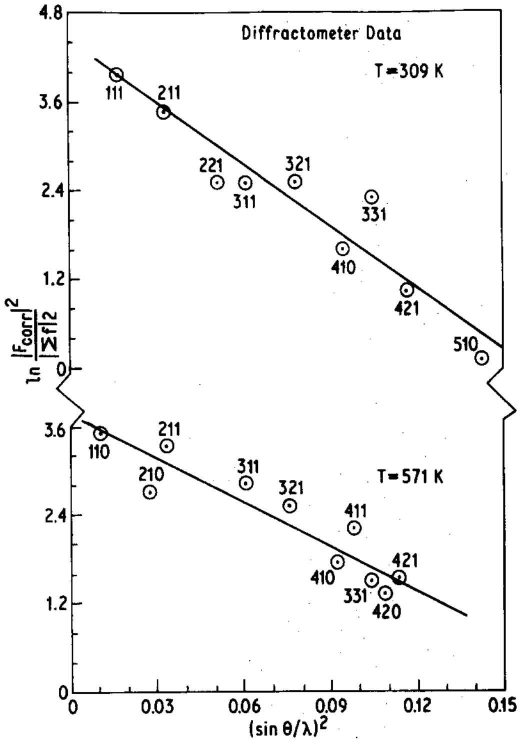

Figure 3 Plot of ln $(|F_{\text{corr}}|^2/|\Sigma f|^2)$ versus $\sin^2\theta/\lambda^2$.

temperatures derived from the slopes of Figs. 1 to 3 are given in Table I.

The data (Fig. 3) taken at 309 K is from our diffractometer, which has a slightly different 2θ scan range compared with the BARC diffractometer. Thus some of the reflections seen in the BARC data may not be present in our data (e.g. 1 1 0 absent at 309 K, 5 1 0 present only at 309 K). We have taken selected Bragg reflections in obtaining least-squares fitting of the data. Those reflections which deviate too much from the least-squares fitted line, are not shown in the figures (e.g. 3 2 1 at 453 K). As per theory, ln $(|F_{\text{corr}}|^2/|\Sigma f|^2)$ should decrease with increasing temperature for a particular reflection, but this is not so for some reflections (e.g. 4 2 1 at 298 and

TABLE I Debye temperatures calculated at various temperatures

T (K)	θ_M (K)	Diffractometer used
298	94 ± 6	BARC
309	94 ± 6	Ours
381	94 ± 6	BARC
453	107 ± 6	BARC
503	130 ± 6	BARC
571	149 ± 6	BARC

571 K). This is mainly due to the temperature variation of θ_M (Table I).

The Debye temperature θ_M, obtained at room temperature from X-rays is 94 ± 6 K, while the Debye temperature θ_E from elastic constant data [4] is 127 K. It is obvious that the Debye temperatures obtained from X-rays (present work) and elastic constants [4] differ from each other in accordance with the assertion of Salter [3]. Possibly the elastic constant value of θ_E is higher than the X-ray θ_M value mainly due to the existence of peaks in the vibrational spectrum at low frequencies. The fact that the even–even, even–odd, odd–even and odd–odd reflections lie on the same straight line (Figs. 1 to 3) indicates that $M_{Na} \approx M_{Br} \approx M_O$. Thus, the experiment has not distinguished between the individual Debye temperatures or mean square atomic displacements appropriate to the atoms of sodium, bromine and oxygen in $NaBrO_3$.

It is clear from Table I that θ_M varies with temperature. The variations of θ_M with temperature shown in Fig. 4a are non-linear and a quadratic fit to these points by the method of least squares gives the following equation

$$\theta_M = 1.83 \times 10^2 - 0.55T + 0.09 \times 10^{-2} T^2$$

where θ_M and T are expressed in K. According to the Debye theory for $T \gg \theta_M$, C_v should be almost constant in the temperature range of our experiment. Using an expression of Kittel [14] for C_v, for $T \gg \theta_M$, it can be shown that $C_v = 3R[1 + \frac{3}{4}(\theta_M/T)]$, which gives a linear variation of θ_M with respect to T. But the present experimental results show a non-linear variation of θ_M with T (Fig. 4a). This fact suggests that θ_M varies anomalously with temperature above 381 K It is interesting to note that similar anomalous behaviour has been observed for thermal expansion above 400 K by Wathore and Kulharni [15] for $NaBrO_3$. Thus the present results agree with previous thermal expansion work [15].

An attempt has been made to obtain defect formation energy with the aid of anomalous Debye temperature data. Foreman and Lidiard [16] have shown that the excess specific heat, ΔC_v, due to vacancy formation is given by $\Delta C_v = (A/KT^2)e^{-E/2KT}$, where A is a constant and E is the defect formation energy. As C_V is directly related to θ_M, we can express $\Delta\theta_M$ similar to ΔC_v as

$$\Delta\theta_M = \frac{B}{KT^2} e^{-E/2KT},$$

where B is a constant and E is the defect formation energy. Experimentally, the excess Debye temperature $\Delta\theta_M$ due to vacancy formation is seen as an "anomalous" upward curvature in plots of θ_M versus T (Fig. 4a). $\Delta\theta_M$ is determined by extrapolating the linear behaviour of θ_M and subtracting the extrapolated values from the measured θ_M. A plot of $\ln(T^2\Delta\theta_M)$ versus $1/T$ (Fig. 4b) yields a straight line of slope $-E/2K$. The least-squares fitting procedure was used to calculate the slope of the graph (Fig. 4b). The defect formation energy derived from this slope is 0.80 ± 0.04 eV. This value agrees with the value 0.85 ± 0.04 eV obtained by thermal expansion data [15].

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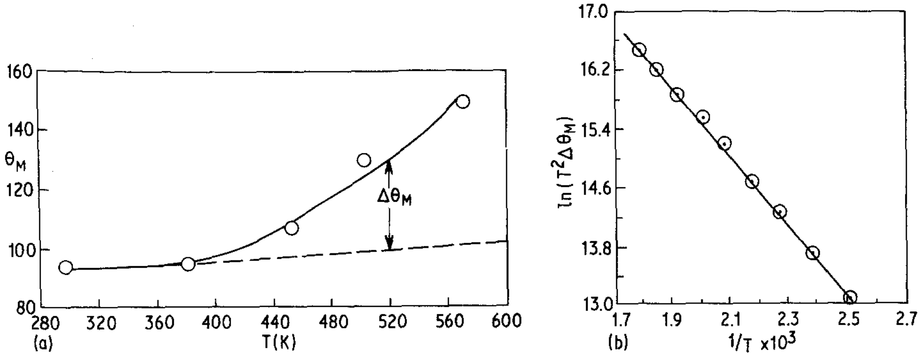

Figure 4 (a) Plot of θ_M versus T. (b) Plot of $\ln(T^2\Delta\theta_M)$ versus $1/T$.

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