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## *X-ray Debye temperature of sodium chlorate*

The Debye temperature plays an important role in the study of a large number of solid-state problems involving lattice vibrations. A number of physical parameters such as mean square atomic displacements, Herbstein [1], and elastic constants, Gazzara and Middleton [2], are known to depend upon the Debye temperature of a solid. It has been shown by Salter, [3], that Debye temperatures obtained by different physical properties will not, in general, be equal. The survey of the literature shows that there is a scarcity of adequate data on X-ray Debye temperatures for the isomorphic structures of sodium bromate ($NaBrO_3$) and sodium chlorate ($NaClO_3$). The X-ray Debye temperature of sodium bromate has been determined by Kulkanri and Wathore [4] but, to our knowledge, no results have yet been published on the X-ray Debye temperature of sodium chlorate.

In the present work, measurements of X-ray diffracted intensities at various temperatures were carried out with the object of extracting X-ray Debye temperature $\theta_M$ for sodium chlorate. The $\theta_M$ obtained in the present investigation was compared with the Debye temperature obtained from elastic constants, Mason [5].

A method which depends on the principle of measuring the integrated intensities of a large number of Bragg reflections at a fixed temperature was first outlined by Buerger [6]. This method has been described in detail by Walford and Schoeffel [7] and has been used here to determine the X-ray Debye temperature $\theta_M$. Recently Kulkarni and Bichile [8] used this method to obtain X-ray Debye temperatures of $Ba(NO_3)_2$ assuming a single Debye–Waller factor ($M$) for all three atoms in the compound.

The average vibrational amplitudes are related to the Bragg intensities, within the quasi-harmonic approximation, through the Debye–Waller theory. The integrated intensity, $I$, from a cubic powder sample can be expressed as follows, James [9]

$$I = KL_\mathrm{p}P|F|^2, \tag{1}$$

where $K$ is a constant; $L_\mathrm{p}$ is a function of the Bragg angle known as the Lorentz-polarization factor; $P$ is multiplicity; and $|F|$ is the modulus of the structure factor.

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

$$F(h\,k\,l) = f_\mathrm{Na}F_\mathrm{Na}\mathrm{e}^{-M_\mathrm{Na}} + f_\mathrm{cl}F_\mathrm{cl}\mathrm{e}^{-M_\mathrm{cl}} + 3f_\mathrm{O}F_\mathrm{O}\mathrm{e}^{-M_\mathrm{O}}. \tag{2}$$

The exponential terms in Equation 2 represent the Debye–Waller factors for the three constituent atoms of sodium, chlorine and oxygen; $f_\mathrm{Na}$, $f_\mathrm{Cl}$ and $f_\mathrm{O}$ are their respective atomic scattering factors; $F_\mathrm{Na}$, $F_\mathrm{Cl}$ and $F_\mathrm{O}$ are their respective structure factors which are sine and cosine functions of $hkl$ values; all other terms have standard meanings (as defined in the International Tables for crystallography, 1969, [10]). According to James [9], the Debye–Waller factor is defined as

$$M(T) = \frac{6h^2T}{mK\theta_M^2}\left\{\phi(x) + \frac{x}{4}\right\}\frac{\sin^2\theta}{\lambda^2} \tag{3}$$

or

$$M(T) = B\frac{\sin^2\theta}{\lambda^2} \qquad (4)$$

where

$$B = \frac{6h^2T}{mK\theta_M^2}\left(\phi(x) + \frac{x}{4}\right) \qquad (5)$$

Here $m$ is the mass of the atom (taken as the mean mass), $h$ is Planck's constant, $K$ is Boltzman's constant, $\theta_M$ is the X-ray Debye temperature, $T$ is the temperature, $\theta$ is the Bragg angle, $x = \theta_M/T$, and $\lambda$ is the wavelength of the X-rays; the function $(\phi(x) + x/4)$ is tabulated by James [9].

As the masses of sodium, chlorine and oxygen atoms are different, the respective Debye–Waller factors ($M_{\mathrm{Na}}$, $M_{\mathrm{Cl}}$ and $M_{\mathrm{O}}$) will also be different in $\mathrm{NaClO_3}$. The mean mass of $\mathrm{NaClO_3}$ is 21.4 which is close to the mass of the sodium atom and lies midway between the masses of chlorine and oxygen atoms. To a first approximation let $M_{\mathrm{Na}}$, $M_{\mathrm{Cl}}$ and $M_{\mathrm{O}}$ be equal to each other in accordance with Kulkarni and Bichile [8]. Equation 2 therefore becomes

$$\begin{aligned} F(h\,k\,l) &= (f_{\mathrm{Na}}F_{\mathrm{Na}} + f_{\mathrm{Cl}}F_{\mathrm{Cl}} + 3f_{\mathrm{O}}F_{\mathrm{O}})\,\mathrm{e}^{-M} \\ &= \Sigma f\,\mathrm{e}^{-M} \qquad (6) \end{aligned}$$

where

$$\Sigma f = f_{\mathrm{Na}}F_{\mathrm{Na}} + f_{\mathrm{Cl}}F_{\mathrm{Cl}} + 3f_{\mathrm{O}}F_{\mathrm{O}}.$$

Equation 1 may be written, using Equations 4 and 6, as

$$I = KL_{\mathrm{P}}P|\Sigma f|^2\,\mathrm{e}^{-2B\sin^2\theta/\lambda^2} \qquad (7)$$

The experimental structure factor, $F_{\mathrm{corr}}$, may be obtained from Equation 7 using measured integrated intensity, $I$, as

$$|F_{\mathrm{corr}}|^2 = \frac{I}{L_{\mathrm{P}}P} = K|\Sigma f|^2\,\mathrm{e}^{-2B\sin^2\theta/\lambda^2} \qquad (8)$$

It follows from Equation 8, that the slope $\ln(|F_{\mathrm{corr}}|^2/|\Sigma f|^2)$ against $\sin^2\theta/\lambda^2$ yields the temperature factor $B$ and hence $\theta_M$ can be obtained.

The powder samples of $\mathrm{NaClO_3}$ with a specified purity of 99.99% were obtained from Reidel Agseelze, Hannover, Germany, To obtain a uniform particle size these powder samples were filtered through a 44 $\mu$m sieve. The experimental set-up of Bhabha Atomic Research Centre (BARC), used in this work for high temperature measurements, has been described elsewhere (Momin, Mathews and Karkhanavala, [11]).

Integrated intensities were measured using $2\theta$ scans, $\beta$-filtered Cu$K\alpha$ radiation and a pulse height discriminator. The scan rates were adjusted such that they give 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 four to eight reflections were measured at the following fixed temperatures: 298, 376, 430 and 479 K. These measurements were repeated several times. Precautions were taken to minimize the extinction by using very fine powder samples. The temperature of the sample was measured with a Pt/13% Rh thermocouple with an estimated precision of ± 1 K.

The data were collected at 298, 376, 430 and 479 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 ($L_{\mathrm{p}}$) and absorption. The corrected structure factors $F_{\mathrm{corr}}$ were determined from the corrected intensities for each reflection using Equation 8. The plots of $\ln|F_{\mathrm{corr}}|^2/|\Sigma f|^2$ against $\sin^2\theta/\lambda^2$ for different temperatures are shown in Fig. 1a and b. Here the symbol $|\Sigma f|$ stands for the calculated value of the square of the structure factor for $\mathrm{NaClO_3}$. In calculating $\Sigma f$, the reliable positional parameters from Wyckoff [13] and atomic scattering factors from the International Tables for X-ray crystallography [10] were used. It is apparent from Fig. 1a and b 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 and 2 are least squares fit to the experimental data points. The Debye temperature derived from the slopes of Fig. 1a and b are given in Table I.

The Debye temperature, $\theta_M$, obtained at room temperature from X-rays is 96 ± 10 K, while the Debye temperature $\theta_{\mathrm{E}}$ from elastic constant data (Mason [5]) is 133 K. This suggests that the Debye temperature obtained from elastic constants is higher than that of the present X-ray values which is in accordance with the assertion of Salter [3]. The discrepancy between the two may be explained on the basis of vibrational spectra.

TABLE I Debye temperatures calculated at various temperatures

| $T$ (K) | $\theta_M$ (K) |
|---|---|
| 298 | 96 ± 10 |
| 376 | 78 ± 10 |
| 430 | 86 ± 10 |
| 479 | 101 ± 10 |

Possibly the elastic constant value $\theta_E$ is higher than the X-ray $\theta_M$ value mainly due to the existence of peaks in the vibrational spectra at low frequencies. The fact that the even–even, even–odd, odd–even, and odd–odd reflections lie on the same straight line (Fig. 1a and b) indicates that $M_{Na} \approx M_{Cl} \approx M_O$. Thus, the experiment has not distinguished between the individual Debye temperatures or mean square atomic displacements appropriate to the atoms of sodium, chlorine and oxygen in $NaClO_3$. It is clear from Table I that $\theta_M$ remains practically constant over the temperature range 298 to 479 K.

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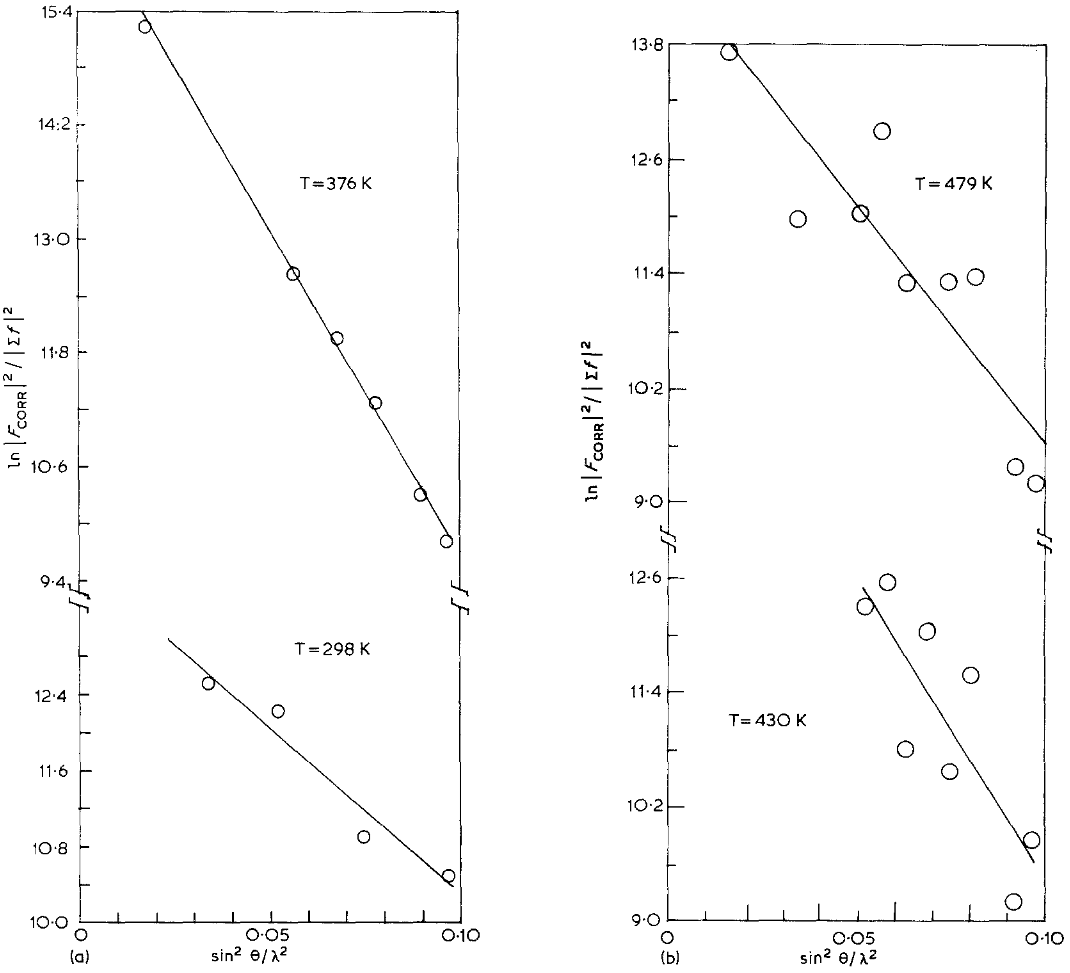

*Figure 1* Plots of ln $|F_{corr}|^2/|\Sigma f|^2$ against $\sin^2\theta/\lambda^2$ for different temperatures.

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# *Thermal decomposition of a $Si_3N_4$–22 wt% $Al_2O_3$ alloy*

Materials near the $Si_3N_4$ corner of the $Si_3N_4$–AlN–$Al_2O_3$–$SiO_2$ quarternary, termed sialons, are candidate materials for high performance applications [1]. Hot pressed alloys in this system are useful because they possess high flexure strengths and good oxidation and creep resistance. However, since hot pressing reduces the ease with which these materials can be fabricated into complex shapes, procedures for sintering these materials to high density are required. A number of sintering studies performed on alloys within this system indicate that weight loss limits the density of the sintered product [2–4]. Thermal decomposition during sintering is undesirable because it competes against the densification process, enlarging pores that sintering tends to close. Nevertheless, despite the important effects it has on sintering $Si_3N_4$ based ceramics, the thermal decomposition reactions are not yet understood.

Mitomo and co-workers [3, 4], who examined the thermal decomposition of a $\beta'$-sialon, $Si_4Al_2O_2N_6$, noted that the dissociating species was SiO, and calculated the minimum SiO pressure required to inhibit weight loss. To maintain this pressure, they used a packing powder composed of $Si_3N_4$ and $SiO_2$. If this pressure was not maintained, the sample lost weight and its composition tended toward the AlN corner of the Si–Al–O–N system.

In this report, thermal decomposition studies of a $Si_3N_4$–22 wt% $Al_2O_3$ alloy are presented. When the $SiO_2$ in the $Si_3N_4$ powder is considered, the composition of this alloy falls within the $\beta'$–O′–X phase field in the phase diagram proposed by Jack [1].

The material was sintered under a variety of conditions designed to inhibit the weight loss. They are: (1) $N_2$ overpressure, (2) Reaction-bonded silicon nitride (RBSN) crucible liner, and (3) Buffered packing powder. The $N_2$ overpressure

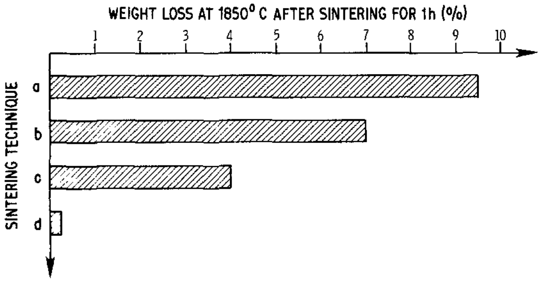

*Figure 1* Comparison of the effectiveness of four different techniques used to inhibit the weight loss reactions. (a) Buffered powder, no crucible liner, $P_{N_2} = 2$ atm; (b) unbuffered poweder, no crucible liner, $P_{N_2} = 14$ atm; (c) unbuffered powder, RBSN liner, $P_{N_2} = 14$ atm; (d) buffered powder, no crucible liner, $P_{N_2} = 14$ atm.

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