Measurement of the Static Disorder Contribution to the Temperature Factor in Cubic Stabilized ZrO₂

BY D. N. ARGYRIOU

Australian Nuclear Science and Technology Organisation, Private Mail Bag 1, Menai, NSW 2234, Australia, and Department of Applied Physics, University of Technology, Sydney, PO Box 123, Broadway, NSW 2007, Australia

(Received 30 April 1992; accepted 27 July 1993)

Abstract

Neutron powder diffraction has been used to measure the temperature factors of both the cation and the anion atoms in 10 mol% Y₂O₃–ZrO₂ over the temperature range 15 to 1323 K. The Housley–Hess approach has been used to determine the static disorder term of the temperature factors for both the Zr/Y and O atoms. The static contribution was determined to be 1.04 (6) Å² for Zr/Y and 2.2 (1) Å² for O. From these results, a Debye temperature of 527 (20) K was calculated for this sample.

1. Introduction

In its pure form, zirconia is monoclinic at room temperature, tetragonal between ~1440 and 2640 K and cubic from 2640 K up to the melting point at ~2950 K. The cubic form of zirconia is stabilized to room temperature by the incorporation of trivalent or divalent oxides (Y₂O₃, CaO, MgO) to form cubic stabilized zirconias (CSZ). The incorporation of stabilizer atoms into the lattice introduces oxygen vacancies to maintain charge balance. CSZs are known electrolytes and exhibit excellent ionic conductivity at high temperatures (Green, Hannink & Swain, 1989).

Powder and single-crystal diffraction experiments on a variety of CSZs have consistently measured large temperature factors for both the anion and the cations. This has been explained as significant static displacements from the ideal cubic zirconia structure (fluorite) appearing as a static component in the observed temperature factor. A number of workers have attempted to determine the directions of the static displacements but, although the indications of static disorder are always clear, there appears to be some confusion over their precise directions. The early work of Carter & Roth (1963) and subsequent investigations by Horiuchi, Schultz, Leung & Williams (1984) and Howard, Hill & Reichert (1988) have claimed that O atoms are displaced in the [111] direction. On the other hand, Morinaga, Cohen & Faber (1979) and Steele & Fender (1974) argue that O atoms are displaced in the [100] direction. Although there is little doubt that CSZ is a defect fluorite structure, there has not been a thorough investigation of the temperature factor as a function of temperature or an attempt to measure the static disorder component at low temperatures where the true thermal parameter will be at a minimum.

In this paper, a measurement of the temperature factor for both the cations and the anion is reported over the temperature range 15 to 1323 K using neutron powder diffraction. The results show that even at 15 K the temperature factors are large and the static disorder component is significant. With the Housley–Hess approach, the static disorder component of the temperature factor is calculated for both atoms. Temperature factors corrected for static disorder are used to calculate the Debye temperature.

2. Experimental procedure

Neutron diffraction patterns* were recorded using the high-resolution powder diffractometer (HRPD) at the Australian Nuclear Science and Technology Organisation’s (Ansto) HIFAR research reactor (Howard, Ball, Davis & Elcombe, 1982). Diffraction patterns were collected from a 10 mol% Y₂O₃–ZrO₂ powder sample at 15, 300, 673, 1073 and 1323 K. A neutron wavelength of 1.377 Å was used for the 15 and 300 K patterns while a wavelength of 1.493 Å was used for the 673, 1073 and 1323 K patterns. Diffraction patterns were recorded over a 2θ range of 0 to 155°, with a step size of 0.05°. The diffraction pattern at 15 K was collected using an APD cryorefrigerator, while high-temperature (T > 300 K) diffraction patterns were collected using Ansto’s 1100 high-temperature powder diffraction furnace. In this furnace, the powder sample is placed in a stainless steel can and lowered into a vertical thin-wall sintered-alumina tube furnace. The heating elements are wound around the alumina tube and positioned above and below the neutron beam path. The sample is attached onto the thermocouple, providing close monitoring of sample

* The observed step-scan neutron diffraction data collected for all temperatures have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71558 (on diskette). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
temperature. The furnace is microprocessor controlled, which ensures that temperatures remain within 2 K of the desired temperature over the course of the experiment. Diffraction lines from the stainless steel can were observed: f.c.c. steel at 673 and 1073 K; and b.c.c. and f.c.c. steel for the 1323 K pattern. For the 15 and 300 K experiments, the sample was contained in a vanadium can.

Rietveld refinements of the neutron data were carried out using the program LHPM (Hill & Howard, 1986). In the refinement, the background was fitted using the polynomial function

\[ y = \frac{a}{(2\theta) + b + c(2\theta)^2 + d(2\theta)^3}, \]

while diffraction peak profiles were modelled using a Voigt function including an asymmetry correction (Howard, 1982). In the case where stainless steel diffraction lines were observed, the f.c.c. or b.c.c. phase or both were included in the refinement. For stainless steel, the only variables that were refined were a scale factor, lattice parameter and the thermal parameter for Fe. There was some overlap between CSZ diffraction lines and b.c.c. and f.c.c. Fe. The strongest overlap was between the 022 fluorite peak (2\(\theta\) = 48.21°) and the 002 b.c.c. Fe (2\(\theta\) = 48.73°). The advantage of using Rietveld refinement is that such strong overlaps can be modelled accurately.

As mentioned earlier, a number of authors have attempted to model the direction of the static displacements and have refined diffraction data by displacing the anion from the \(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\) site in either [111] and/or [100] directions. In this work, our objective is to demonstrate that deviations from the fluorite structure in CSZ are static, hence all refinements were carried out in space group \(Fm\bar{3}m\), with Zr/Y at (0,0,0) and O at \(\frac{1}{4}, \frac{1}{4}, \frac{3}{4}\). Together with lattice parameters, isotropic temperature factors were refined for Zr/Y and O atoms at all temperatures. Although zirconia is a weak neutron absorber, thermal parameters were corrected for absorption using the method outlined by Hewat (1979) (\(\mu_r = 0.132, \Delta B = 0.01 \text{ Å}^2\)). A typical diffraction pattern collected is shown in Fig. 1. The results of the refinements are shown in Table 1.

### Table 1. Experimental results: lattice parameters and temperature factors as determined from Rietveld profile refinement as a function of temperature from a 10 mol% \(Y_2\text{O}_3-Zr\text{O}_2\) powder sample

<table>
<thead>
<tr>
<th>(T (K))</th>
<th>(a (\text{Å}))</th>
<th>(B_{\text{Zr/Y}} (\text{Å}^2))</th>
<th>(B_0 (\text{Å}^2))</th>
<th>(R_w (%))</th>
<th>(R_B (%))</th>
</tr>
</thead>
<tbody>
<tr>
<td>15*</td>
<td>5.1420 (3)</td>
<td>1.16 (3)</td>
<td>2.55 (4)</td>
<td>7.0</td>
<td>1.4</td>
</tr>
<tr>
<td>300*</td>
<td>5.1478 (3)</td>
<td>1.33 (3)</td>
<td>2.79 (4)</td>
<td>6.8</td>
<td>1.8</td>
</tr>
<tr>
<td>673†</td>
<td>5.1672 (2)</td>
<td>1.48 (3)</td>
<td>3.28 (6)</td>
<td>7.2</td>
<td>1.5</td>
</tr>
<tr>
<td>1073†</td>
<td>5.1900 (3)</td>
<td>2.15 (5)</td>
<td>3.79 (7)</td>
<td>7.8</td>
<td>1.5</td>
</tr>
<tr>
<td>1323†</td>
<td>5.2039 (3)</td>
<td>2.12 (5)</td>
<td>3.90 (7)</td>
<td>8.9</td>
<td>1.9</td>
</tr>
</tbody>
</table>

* Measured with a neutron wavelength of \(\lambda = 1.377 \text{ Å}\).
† Measured with a neutron wavelength of \(\lambda = 1.493 \text{ Å}\).

### 3. Experimental results and analysis

Fig. 2 shows that the temperature factor increases with temperature as expected for both cation and anion atoms and the change in the temperature factor from 300 to 15 K is small. The temperature factor is still relatively large, even at 15 K, especially for the O atom. This clearly indicates that there is significant static disorder in the structure on both sites. The contribution of the static disorder to the temperature factor can be estimated by extrapolating the experimental \(B\) values for both atoms to 0 K. With the assumption that the thermal contribution is negligible at low temperatures, the static component of the temperature factor is found to be 2.5 Å\(^2\) for O and 1.08 Å\(^2\) for Zr/Y. Although this approach is attractive because of its simplicity, it is not accurate because the

![Fig. 1. Rietveld fit to the observed cubic zirconia diffraction pattern collected at a temperature of 673 K. The top series of peak markers shows the calculated positions for the fluorite peaks of 10 mol% \(Y_2\text{O}_3-Zr\text{O}_2\) while the bottom series indicate the peak positions due to the stainless steel can. The difference between observed and calculated diffraction patterns is shown below the peak markers.](image1)

![Fig. 2. The observed temperature factors for Zr/Y and O over the temperature range of 15 to 1373 K as determined from Rietveld fitting.](image2)
relationship between mean-square thermal displacement and temperature is not linear and thermal vibrations persist even at 0 K.

A better approach is first to express the experimental thermal parameter as a combination of the true thermal parameter and a static term, i.e.

$$B_k^{\text{exp}} = B_k^{\text{thermal}} + B_k^{\text{static}}.$$  \hspace{1cm} (1)

The approach devised by Housley & Hess (1966) can then be utilized to estimate the thermal contribution at 0 K and therefore determine the static component of the experimental temperature factor. This approach was recently used successfully by Cheary (1991) in the measurement of static disorder in Cs hollandites. A brief outline of the procedure is given here.

The mean-square displacement $B$ of atom $k$ is given by (Willis & Pryor, 1975, pp. 117–118; Housley & Hess, 1966)

$$B_k = (4\pi h/m_k) \times \sum_i \left( \frac{1}{2} + \frac{\exp \left( \hbar \omega_i/k_BT \right) - 1}{\omega_i^{-1}} \right) \omega_i^{-1},$$ \hspace{1cm} (2)

where $\omega_i$ is the frequency of the $i$th normal mode, $k_B$ is Boltzmann's constant and $T$ is the absolute temperature. From the form of (2), we can see that at $T = 0$ the slope will be zero and at the limit where $T \to \infty$ the slope will reach a constant. By obtaining the low- and high-temperature forms of (2), we can see that at low temperatures $B_k$ is proportional to $1/\omega$, while at high temperatures $B_k$ is proportional to $1/\omega^2$. Assuming that the mean weighted frequencies $\omega_i^2(-1) \geq \omega_i^2(-2)$ [where $\omega_i^2(-1)$ and $\omega_i^2(-2)$ are averages based on $1/\omega$ and $1/\omega^2$, respectively], we can obtain the inequality

$$B_k^2(0) \leq \left( \frac{\hbar^2}{2m_k k_BT} \right) B_k(T).$$  \hspace{1cm} (3)

Equation (3) is analogous to the Heisenberg uncertainty relation and is extremely useful since it sets the upper limit for the mean-square thermal vibration at $T = 0$ K [$B_k^{\text{thermal}}(0)_{\text{max.}}$] in terms of the mean-square vibration at some temperature $T$. At high temperatures, the thermal contribution to the experimental temperature factor becomes significant and (3) will tend towards an equality.

The values of $B_k^{\text{thermal}}(0)_{\text{max.}}$ shown in Table 2 were determined by plotting $B_k(0)$ calculated using (3) for each measurement at temperature $T$ against $1/T$ and extrapolating to the condition $1/T = 0$ (Cheary, 1991). The minimum value of the static disorder component, $B_k^{\text{static}}_{\text{min.}}$, was then obtained by subtracting $B_k^{\text{thermal}}(0)_{\text{max.}}$ from experimental measurements closest to $T = 0$ (in this case 15 K). Values of $B_k^{\text{static}}_{\text{min.}}$ determined using this method for both anion and cations are 2.2 (1) Å$^2$ for the O atom and 1.04 (6) Å$^2$ for Zr/Y (see Table 2).

### Table 2. Estimated maximum thermal contribution and minimum static displacement components of the observed temperature factor

<table>
<thead>
<tr>
<th></th>
<th>Zr/Y</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_k^{\text{thermal}}(0)_{\text{max.}}$ (Å$^2$)</td>
<td>0.11 (3)</td>
<td>0.34 (7)</td>
</tr>
<tr>
<td>$B_k^{\text{static}}_{\text{min.}}$ (Å$^2$)</td>
<td>1.04 (6)</td>
<td>2.2 (1)</td>
</tr>
</tbody>
</table>

If the mean-square thermal displacements are assumed to follow the Debye model, the Debye temperature $\theta_D$ can be calculated from the experimental thermal parameter corrected for static disorder [i.e. $B_k^{\text{thermal}}(T) = B_k^{\text{exp}}(T) - B_k^{\text{static}}_{\text{min.}}$]. The Debye model for a cubic monoatomic solid is adapted to a multiatom solid by using the mass-weighted thermal parameter $B_M$ (Willis & Pryor, 1975), so that

$$B_M^{\text{thermal}} = \frac{6\hbar^2}{M k_B \theta_D} \left[ \frac{\varphi(x)}{x} + \frac{1}{4} \right], \hspace{1cm} x = \theta_D/T,$$ \hspace{1cm} (4)

where $B_M = (1/M) \sum m_k B_k$; the summation is done over the unit cell, $M$ is the mass of the unit cell, $g$ is the number of atoms in the unit cell and $\varphi(x)$ is the Debye function, which is given by the relation

$$\varphi(x) = (1/x) \int_0^x \left[ y/(e^y - 1) \right] dy.$$  \hspace{1cm} (5)

The Debye temperature was obtained by a least-squares fit of $B_M(T)$ calculated from the corrected $B_k(T)$ values to (4). The only refineable parameter was $\theta_D$. Fig. 3 shows the corrected $B_M(T)$ values plotted against temperature, while the continuous line represents the calculated $B_M(T)$ values corresponding to a Debye temperature of 527 (20) K.

![Fig. 3. $B_M^{\text{thermal}}$ (determined using $B_M^{\text{thermal}}$ values) versus temperature. The straight line shows the calculated temperature dependence of $B_M$ for a Debye temperature ($\theta_D$) of 527 K. In the fitting of equations (4) and (5), the low-temperature limit of the Debye function was taken to be $\varphi(x) = 1 - (1 - x) \exp (-x)$ (for the 15 K measurement), while the high-temperature limit was given by $\varphi(x) = 1 - x/4 + x^2/36$ (for $T \geq 300$ K).](image-url)
To confirm these results, we can use an alternative approach to determine \( B_M^{\text{static}} \) and \( \theta_D \). In this method, we combine (1) and (4) so we express the experimental \( B_M \) as

\[
B_M^{\text{exp}} = \frac{6g\hbar^2}{Mk_B\theta_D} \left[ \frac{\varphi(x)}{x} + \frac{1}{4} \right] + B_M^{\text{static}}. \tag{5}
\]

Using (5) and fitting \( \theta_D \) and \( B_M^{\text{static}} \) to the experimental data, we obtain a Debye temperature of 533 (20) K and a value for \( B_M^{\text{static}} \) of 3.3 (5) \( \text{Å}^2 \). The values of the Debye temperature obtained using both methods are very similar and within estimated errors. The static disorder components determined by using the Housley–Hess approach give a \( B_M^{\text{static}} \) of 3.28 \( \text{Å}^2 \), which agree very well with the \( B_M^{\text{static}} \) value determined from (5). The agreement therefore for the static disorder component and \( \theta_D \) between the two methods is extremely good and adds confidence to the approach taken. Of course, the Housley–Hess method has the advantage that one obtains \( B_M^{\text{static}} \) rather than \( B_M^{\text{static}} \) as in the latter method.

### 4. Discussion

Reported values for the temperature factor in CSZs vary dramatically. Observed temperature factors for the cation at room temperature range from 0.6 to 1.24 \( \text{Å}^2 \), while for the O atom they range from 1.9 to 2.89 \( \text{Å}^2 \). These measurements have been taken from a variety of compositions of CSZ and the wide range of measured values is probably due to the extent of disorder in different samples.

From the results of Table 2, the r.m.s. displacement \( \langle u \rangle \) over all directions for the cations and the O atom are 0.11 (3) and 0.17 (4) \( \text{Å} \), respectively. These results show that there is significant static disorder in both sites. Most of the previous work on this subject has concentrated on the displacements of O atoms from the fluorite positions; however, as shown here, there is an appreciable static disorder in the cation site as well. This measurement agrees well with the results of Steele & Fender (1974), which showed that the cations were displaced from the (0,0,0) site in the [110] direction by 0.1 Å in Zr(Yb)O\(_i\)87. Other evidence of static disorder in the cation atoms is given by Welberry, Butler, Thompson & Withers (1992) from X-ray diffuse scattering measurements.

It is interesting to compare the r.m.s. displacement of the O atom measured in this work with the displacements O atoms undergo in the cubic-to-tetragonal phase transformation. In this phase transition, O atoms are displaced by 0.21 Å (Howard, Hill & Reichert, 1988) in the [100] direction from the fluorite site. Our measured value for the magnitude of the oxygen static displacements compares quite well, particularly for this composition which is close to the cubic–tetragonal phase boundary. Values measured of the O-atom displacements in CSZ by previous workers are higher than 0.21 Å although comparable. Morinaga, Cohen & Faber (1979) conclude that O atoms are displaced by 0.25 Å in the [100] direction, while Steele & Fender (1974) claim they are displaced by 0.36 Å in the same direction. The reason for this anomaly is not clear, however there may be a compositional dependence on the extent and direction of relaxations in CSZ which would make comparisons difficult.

The author acknowledges the experimental assistance of Dr S. L. Town, and Drs M. M. Elcombe and C. J. Howard are thanked for helpful discussions on the theory and suggestions on this manuscript. This work received financial support from the Australian Government, Department of Industry Technology and Commerce, through Generic Technology Grant no. 15042.

### References


