Annular dynamical disorder of the rare earth ions in a $\text{La}_2\text{Zr}_2\text{O}_7$ pyrochlore via single crystal synchrotron X-ray diffraction

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Abstract. The reciprocal lattices of a range of rare earth titanate and zirconate pyrochlores have recently been shown to exhibit an extremely characteristic diffuse intensity distribution identical in form to that characteristic of β -cristobalite implying the existence of β -cristobalite-like orientational disorder of essentially rigid, $(\text{O}2)(\text{R}^{3+})_4$ tetrahedra within the pyrochlore structure type. A single crystal X-ray diffraction study of $\text{La}_2\text{Zr}_2\text{O}_7$ has been carried out utilizing synchrotron radiation in order to investigate this proposed orientational disorder and to determine an unknown oxygen atom fractional co-ordinate. An annular distribution of residual electron density is found around the average La ion positions in $\{111\}$ planes perpendicular to the local $\text{O}2\text{—La—O}2$ directions and interpreted as implying that the La ions never in fact occupy the average 16d positions but rather are dynamically disordered around an annulus perpendicular to that direction in an exactly analogous manner to that which occurs in β -cristobalite.

1. Introduction

Rare earth oxide pyrochlores have ideal stoichiometry $\text{R}_2\text{M}_2(\text{O}1)_6(\text{O}2)_1$ and crystallize in space group $Fd3m$ with four crystallographically independent atom sites (R^{3+} , a rare earth ion, in 16d at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, M^{4+} in 16c at 000, O1 in 48f at $x, \frac{1}{8}, \frac{1}{8}$ and O2 in 8b at $\frac{3}{8}, \frac{3}{8}, \frac{3}{8}$; origin choice 2). The one unknown oxygen atom fractional co-ordinate, x , determines the extent to which the six- and eight-fold co-ordination polyhedra surrounding the M and R cations are distorted from octahedral and cubic co-ordination respectively. For a regular octahedral oxygen environment around the quadrivalent M^{4+} cations, x should be 0.3125 whereas, for a regular cubic oxygen environment around the large trivalent rare earth ion, x should be 0.375. In practice, x tends to be smallest for the largest rare earth ions and ranges from 0.319 to 0.343 for rare earth oxide pyrochlores (Subramanian and Sleight, 1993).

The lower x values, as found for the largest rare earth oxide pyrochlores such as, for example, $\text{La}_2\text{Zr}_2\text{O}_7$, distort the rare earth ion co-ordination polyhedra away from cubic towards a puckered hexagonal bipyramidal co-ordination with two rather short $\text{R—O}2$ bonds and six rather longer $\text{R—O}1$ bonds. Subramanian and Sleight (1993) point out that these short $\text{R—O}2$ bonds are in fact among the shortest R—O bond lengths ever found and that such rare earth cations are in the highest electric field gradients ever observed. The short $\text{R—O}2$ bond lengths also lead to rather short R—R separation distances within $\text{O}2(\text{R})_4$ tetrahedra and to the O2 ion being considerably over-bonded (Tabira, Withers, Thompson and Schmid, 1999c).

The structure type can be described in a variety of different ways (Subramanian, Aravamudan and Subba Rao, 1983; Subramanian and Sleight, 1993; Hyde, Thompson and Withers, 1993). For the purposes of the current paper,

Fig. 1. Shows the two constituent network structures that together comprise the pyrochlore structure type. The first (top) is an $(\text{M}^{4+})_2(\text{O}1)_6$ array of corner-connected, cation-centred “octahedra” while the second (bottom) is an $\text{O}2(\text{R}^{3+})_2$ array of corner-connected, oxygen-centred tetrahedra (of ideal anti- β -cristobalite structure type).

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perhaps the most useful such description is in terms of two separate, interpenetrating network structures, as shown in Fig. 1. The first such interpenetrating structure (see Fig. 1(a)) is an $(M^{4+})_2(\text{O}1)_6$ array of corner-connected, cation-centred “octahedra” while the second (see Fig. 1(b)) is an $(\text{O}2)(R^{3+})_2$ array of corner-sharing, oxygen-centred tetrahedra (the anti-type to the ideal β -cristobalite structure type). While the R^{3+} -O1 distance of closest approach between the two network structure types (the rare earth ions of the latter structure are situated at the centres of puckered hexagonal rings of O1 ions in the former) is usually significantly longer than any intra-network bond distance, the distance is still sufficiently short that the two structures of Fig. 1 can not be thought of as being truly independent.

The advantage of the “independent” network structure description is that it highlights the existence of the β -cristobalite-like $(\text{O}2)(R^{3+})_2$ array of essentially rigid, oxygen-centred tetrahedra. This is important because the reciprocal lattices of a range of rare earth titanate and zirconate pyrochlores have recently been shown to exhibit an extremely characteristic diffuse intensity distribution (see Fig. 2) which is identical in form to that characteristic of β -cristobalite itself (Tabira *et al.*, 1999c; Tabira, Withers, Miniverni and Grimes, 2000; Withers, Thompson and Welberry, 1989). As described in more detail in Tabira *et al.* (1999c, 2000), this distribution takes the form of transverse polar-

ized $\{110\}^*$ sheets of diffuse intensity perpendicular to each of the six $\langle 110 \rangle$ directions of real space. At any one zone axis orientation, this gives rise to polarized diffuse streaking along any excited $\langle hhl \rangle^*$ direction of reciprocal space (see, for example, the (a) $\langle 111 \rangle$ and (b) close to $\langle 001 \rangle$ zone axis electron diffraction patterns (EDP's) of Fig. 2). The presence of such a diffuse distribution implies the existence of characteristic β -cristobalite-like orientational disorder of the constituent $(\text{O}2)(R^{3+})_4$ tetrahedra (see, for example, Fig. 3 of Tabira *et al.*, 1999c). In the case of β -cristobalite itself, this orientational disorder is due to the existence of low (essentially zero) frequency phonon modes (RUM's) which have been shown to give rise to anular dynamical disorder of the oxygen ions (isomorphous to the rare earth ions in the current case) in local $\langle 111 \rangle$ planes perpendicular to the two short Si—O bonds (Welberry, Hua and Withers, 1989; Swainson and Dove, 1993; Dove, Heine, Hammonds, Gambhir and Pryde, 1998). We therefore focus primarily on the disorder behaviour of the La ions in what follows. By analogy with β -cristobalite, we believe the $(\text{O}2)(R^{3+})_4$ tetrahedral orientational disorder is most likely also dynamic in the current case. Proof of this contention, however, requires some sort of spectroscopic probe. Whether static or dynamic, however, the observed characteristic diffuse distribution requires β -cristobalite-like $(\text{O}2)(R^{3+})_4$ tetrahedral orientational disorder.

Whilst considerable experimental evidence for rare earth lattice vibrational anisotropy exists, both indirectly in the form of a strong Goldanskii-Karyagin effect in quadrupole Mössbauer spectra (Armon *et al.*, 1974; Chien and Sleight, 1978) as well as directly in the form of conventional anisotropic thermal parameters (see, for example, Kennedy, Hunter and Howard, 1997), there has been little direct systematic structural investigation as to the form of this lattice vibrational anisotropy. The difficulty in growing large enough, high quality single crystals of most rare earth oxide pyrochlores (as a result of their melting points being too high $\sim 2000^\circ\text{C}$) has to date precluded such an investigation. This paper aims to investigate this anisotropy via a high quality synchrotron single crystal study of a $\text{La}_2\text{Zr}_2\text{O}_7$ single crystal synthesized using a high temperature solar furnace.

2. Experimental

2.1 Synthesis

The rare earth sesquioxide $\text{LaO}_{1.5}$ (Research Organic/Inorganic Chemical Corp. 99.9%) and ZrO_2 (Z-Tech > 99.9%, including 2.57% HfO_2) as starting materials were fired at 1000°C for a day before weighing. (The nominal rare earth sesquioxides were found to be extremely hygroscopic so that pre-firing before weighing was found to be essential (Tabira *et al.*, 1999c)). The resultant component oxide, made up to the stoichiometry $\text{La}_2\text{Zr}_2\text{O}_7$, was then thoroughly mixed mechanically with ethanol before being pressed into pellets. The pellets were placed on alumina tiles and heated at 1500°C for three days followed by re-pelleting before heating again at 1500°C for a further ten days. The pellets were subsequently quenched in water

Fig. 2. $\langle 111 \rangle$ (a) and close to $\langle 001 \rangle$ (b) zone axis diffraction patterns of $\text{La}_2\text{Zr}_2\text{O}_7$ showing the characteristic β -cristobalite-like polarized $\{110\}^*$ sheets of diffuse intensity. At any one orientation these $\{110\}^*$ sheets of diffuse intensity give rise to polarized diffuse streaking along $\langle hhl \rangle^*$ directions of reciprocal space.

Fig. 3. (a) $(\bar{1}10)$ and (b) $(11\bar{1})$ sections of the residual electron density map based on the isotropic thermal vibration refinement. Both (orthogonal) sections show the unusual form of the residual electron density around the La ion at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$. The pair of positive and negative dumbbell densities apparent in (a) can be interpreted as simply resulting from a cut through the donut shaped region of positive electron density shown in (b).

from 1500 °C. XRD patterns using a Guinier-Hägg camera (monochromated $\text{CuK}\alpha_1$ radiation – 25 mA $\times$ 40 kV) confirmed the appropriate pyrochlore product was obtained and gave resultant pyrochlore unit cell dimensions $a_0 = 10.802(1)$ Å for 2θ angles of 11 reflections – in good agreement with previously reported results (Deiseroth and Müller-Buschbaum, 1970; Subramaniam and Sleight, 1993).

This polycrystalline powder specimen was then shaped into a rod so that it was suitable to be set in a solar furnace. Details about the synthetic process via a solar furnace are described elsewhere (Yamada and Noguchi, 1976; Yamada, Mizuno and Ishizuka, 1988; Yamada, Mizuno and Traverce, 1992–3). XRD patterns of the product thus obtained gave $a_0 = 10.799(1)$ Å.

2.2 X-ray diffraction

Grains of the lightly crushed resultant specimen were picked up under an optical microscope, mounted on glass capillaries and their crystal quality checked. The single crystal chosen for the synchrotron X-ray diffraction experiment had the average shape of an obtuse-angle (c.a. 120°) isosceles trigonal prism ($0.024 \times 0.024 \times 0.042$ mm³) with a thickness of 0.006 mm. The crystal volume was esti-

mated to be 1.5×10^{-6} mm³. The 2θ angles of 19 reflections measured on the diffractometer gave a cell constant $a_0 = 10.7997(3)$ Å.

The unique face of the trigonal prism was determined to correspond to a $(11\bar{1})$ crystal plane by looking at crystal orientation on a four-circle diffractometer. The crystal planes of the three faces perpendicular to this unique $(11\bar{1})$ face were too small to be determined by the same method. However, given that they are of necessity perpendicular to $(11\bar{1})$ and that two of them subtend an angle of 60°, it was assumed that these latter two faces belong to the $\{110\}$ family of crystal planes. Under this assumption, there are three possibilities for the crystal orientation. Setting A: the two $\{110\}$ type planes are $(\bar{1}10)$ and (101) , hence the remaining face is $(2\bar{1}1)$. B: the two $\{110\}$ type planes are $(\bar{1}10)$ and (011) , and the remaining face is $(\bar{1}21)$. C: the two $\{110\}$ type planes are (011) and (101) , while the remaining face is (112) . These settings gave internal R factor, R_{int} , values of 0.0344, 0.0354 and 0.0342, respectively. Setting C was employed in the subsequent refinement procedure. Minimum and maximum transmission factors estimated in this case were 0.853 for $g = 2\bar{2}0$ and 0.951 for $g = 199$, respectively.

Data was collected over a hemisphere ($l \geq 0$) of reciprocal space at room temperature (299 K), using a hori-

zontal-type four-circle diffractometer at the vertically-polarized X-ray wiggler beam line, BL14A, of the Photon Factory (PF), Tsukuba, Japan. A fast Avalanche Photodiode Detector (APD) installed at this station was used to measure the integrated diffraction intensities. The wavelength of the X-ray beam was tuned by a double Si(111) crystal monochromator to 0.74688(7) Å, as determined from the 2θ angles of the $\{16, 0, 0^*\}$ reflections. This wavelength was chosen so as to maximize photon flux while avoiding the excitation of Zr 1s electrons. The six $\{16, 0, 0\}^*$ equivalent reflections were monitored every 200 reflections measured. The integrated intensities of 8,748 reflections in total were measured. The reflections with $F_0 < 3\sigma F_0$ were omitted from the data set in light of counting statistics, giving rise to 5,802 significant reflections. Observed structure factors were averaged over the equivalent reflections of the space group of $Fd\bar{3}m$. Eventually 294 independent reflections were used in the subsequent structure refinement. Selected experimental and crystal data can be found in Tables 1 and 2, respectively.

Structure factors were evaluated using the spherical atomic scattering factors for the relevant ions taken from the *International Tables for Crystallography* (Vol. C, 1999) except in the case of O²⁻ where they were taken from Tokonami (1965). The anomalous dispersion terms were taken by interpolation from tabulated values (Sasaki, 1989) at a wavelength of 0.74688 Å to give $\Delta f'$ and $\Delta f''$

values of -0.5249 , 2.6788 for La; -2.2212 , 0.6132 for Zr; 0.0092 , 0.0067 for O. The mass absorption coefficients for the wave length were also obtained by interpolation of tabulated values (Sasaki, 1990).

3. Results

The first determination of the unknown fractional coordinate x of O1 in La₂Zr₂O₇ was made by Deiseroth and Müller-Buschbaum (1970) based on single crystal Weissenberg and precession photograph intensity data. They reported a value of 0.295 ($=X$) for origin choice 1 (the non-centrosymmetric setting) of $Fd\bar{3}m$, resulting in a conventional R between 0.05 and 0.12 for their individual two-dimensional data set. (No values were given for thermal parameters, however, either isotropic or anisotropic). X can be converted into the equivalent $x = 0.330$ for the current choice of origin by the relation $x = \frac{5}{8} - X$. This value for x was used as a starting point for refinement.

At the initial stage of refinement, isotropic thermal vibration for all constituent atom species in the structure was assumed along with a value for x of 0.330 as mentioned above. An appropriate isotropic secondary extinction correction was then applied. The structural parameters converged to the following values: $x = 0.3309(5)$ with isotropic U 's of $0.00606(9)$ Å² for La, $0.0042(1)$ Å² for Zr, $0.0078(6)$ Å² for O1 and $0.005(1)$ Å² for O2, giving conventional reliability factors $R/wR = 0.038/0.030$. The x value altered little from the starting value.

A ($\bar{1}10$) section of a difference Fourier map at this stage revealed a distinctive pair of positive residual density peaks around the positions of each of the La ions with a maximum height of $4.4 e\text{Å}^{-3}$ (see Fig. 3a). In this figure, positive and negative density is drawn in warm and cool colours, respectively. The numbers in the scale bar on the right hand side of the figure are given in units of one hundredths of an electron per cubic ångström. This section contains a double infinite zigzag chain of ... -O1-La-O2-La- ... ions connecting with each other at the positions of the La ions. Whilst the positive regions of residual electron density appear along the La-O1 bond directions, an equally distinctive pair of negative residual density peaks (with a maximum depth of $10.1 e\text{Å}^{-3}$) occur along the La-O2 bond directions. This residual electron density map is consistent with the notion that the La ions vibrate quite anisotropically and move rather more towards the neighbouring O1 oxygen ions than the neighbouring O2 oxygen ions as a result of the La-O2 bond length being too short.

In the next stage of the refinement, the La ions were thus allowed to vibrate anisotropically. All parameters included in the refinement again rapidly converged, giving rise to R/wR factors of 0.016/0.014. The only unknown positional parameter, the x parameter of O1, converged to 0.3307(2). This value is in good accord with that predicted from apparent valence calculations and also with a value recently experimentally determined via a Wide-Angle CBED technique (Tabira and Withers, 1999a, b; Tabira *et al.*, 2000). The refined parameters of this average structure model are given in Table 3. Although both the Zr and O2 ions vibrate rather isotropically, the La and O1 ions

Table 1. Experimental and refinement data for La₂Zr₂O₇.

Diffractometer	Rigaku
Monochromator	Silicon(111)-double crystal
Scan type	$\omega - 2\theta$
Scan width in ω [deg]	0.5
Scan speed in ω [$^\circ \text{ min}^{-1}$]	16
Maximum $\sin \theta/\lambda$ [Å ⁻¹]	1.24
Range of h, k and l	$-26 \leq h, k \leq 26, 0 \leq l \leq 26$
Standard reflections	six $\{16, 0, 0\}^*$ equivalents
Number of reflections measured	8748
$F = 0$	1102
$F \leq 3\sigma(F)$	1844
Significant	5802
Independent	294
Transmission range	0.853–0.951
Rint before absorption correction	0.037
after absorption correction	0.034
Extinction correction g [arcsec]	0.080(7)
Minimum extinction y^a for (hkl)	0.91 for (222)
No. of variables	11
R/wR	0.017/0.015
Maximum $\Delta\rho$ [$e\text{Å}^{-3}$]	+1.6
Minimum $\Delta\rho$ [$e\text{Å}^{-3}$]	-1.6
Maximum $\Delta\rho/\sigma$	0.000000

a: $F_{\text{obs}} = yF_{\text{calc}}$ where F_{calc} is the value of the kinematical structure factor calculated.

Table 2. Crystal data of La₂Zr₂O₇.

Crystal system	cubic
Space group	$Fd\bar{3}m$ (No. 227)
a [Å]	10.7997(3)
V [Å ³]	1259.60(7)
Z	8
M	572.25
d_x [g cm^{-3}]	6.035
μ [mm^{-1}]	17.838 for $\lambda = 0.74688$ Å

Table 3. Atomic parameters of $\text{La}_2\text{Zr}_2\text{O}_7$ in the average structure model.

positional			
Atom	<i>x</i>	<i>y</i>	<i>z</i>
La	$1/2$	$1/2$	$1/2$
Zr	0	0	0
O1	0.3307(2)	$1/8$	$1/8$
O2	$3/8$	$3/8$	$3/8$

Thermal ($\text{\AA}^2$)							
Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq}
La	0.00648(4)	U_{11}	U_{11}	−0.00159(4)	U_{12}	U_{12}	0.512(1)
Zr	0.00382(5)	U_{11}	U_{11}	0.00013(8)	U_{12}	U_{12}	0.302(1)
O1	0.0086(7)	0.0070(4)	U_{22}	0	0	0.0036(6)	0.60(2)
O2	0.0073(7)	U_{11}	U_{11}	0	0	0	0.58(2)

vibrate quite anisotropically. Table 4 shows the resultant root-mean-square (r.m.s.) amplitudes of vibration along the individual principal axes of the thermal ellipsoids of vibration for the constituent ions. As expected, the ellipsoid of the La ion is significantly compressed along the $\langle 111 \rangle$ direction.

The anisotropy of the thermal ellipsoid found for the La ion in this study is consistent with a similar anisotropy experimentally deduced for the Gd ion in $\text{Gd}_2\text{Ti}_2\text{O}_7$ by ^{156}Gd quadrupole Mössbauer spectra (Armon *et al.*, 1974). In the average structure of this pyrochlore, the electric field gradient at the Gd nuclei was considered to be axially symmetric with respect to the local O2–Gd–O2 direction (corresponding to the $\bar{3}$ axis). Squared displacement parameters, $\langle x_{\perp}^2 \rangle$ and $\langle x_{\parallel}^2 \rangle$, representing shifts perpendicular and parallel to this local symmetry axis, were then derived under the condition of axial local symmetry for three different temperatures 4.2, 36 and 70 K. Based on the results at 70 K, they gave $\langle x_{\perp}^2 \rangle = 2.15(8) \times 10^{-19} \text{ cm}^2$ and $\langle x_{\parallel}^2 \rangle = 0.45(10) \times 10^{-19} \text{ cm}^2$. These values are comparable with the corresponding values of $8.1 \times 10^{-19} \text{ cm}^2$ and $3.3 \times 10^{-19} \text{ cm}^2$, respectively, found in this room temperature study at 299 K.

Alternatively, one could interpret the residual density map as implying that the La ions never actually occupy the average 16d position but rather are displaced from the refined average position in directions essentially perpendicular to the local O2–La–O2 direction. This suggestion

is best investigated via an orthogonal $(11\bar{1})$ section of the difference Fourier map going through the central La in Fig. 3a (and hence through the origin), and depicted as a dashed line therein. The resultant map (see Fig. 3b) shows an annular or circularly distributed region of positive electron density (with a maximum of $3.5 \text{ e}\text{\AA}^{-3}$) surrounding each La ion. The pair of positive residual density peaks found in Fig. 3a can thus be interpreted as simply resulting from a cut through this donut shaped region of positive electron density. (Note that there is also evidence in the above difference density plots that not only are the La and O2 positions split but that the Zr and O1 ions are probably also split. This would not be surprising given a β -cristobalite-like distortion of the $\text{O2}(\text{La})_2$ sub-lattice. Unfortunately, however, it has not proved possible to directly interpret the apparently split Zr and O1 positions in terms of a correlated pattern of atomic shifts because we cannot validly assume that the individual $\text{Zr}(\text{O1})_6$ octahedra are rigid. We have therefore focused on the $\text{O2}(\text{La})_2$ sub-lattice and on the La ions in particular when interpreting the observed difference density plots).

Moving away from the $(11\bar{1})$ plane (through the central La ion) shown in Fig. 3b along the projection direction, the donut-shaped distribution decreases in density, and changes its shape from circular to one containing three peaks away from the La position in the average structure along the $\langle 112 \rangle$ equivalent directions. However, overwhelmingly the density remains situated on or very close to the $(11\bar{1})$ plane which goes through the origin as shown in Fig. 3b. At the final stage of refinement, in an attempt to refine the radius of the circle, La was assumed to statistically shift from the $16d$ ($1/2, 1/2, 1/2$) positions towards the neighbouring $96h$, ($1/2 + \epsilon, 1/2 - \epsilon, 1/2$), positions. Of the six $96h$ positions surrounding any one $16d$ position, only one can of course be occupied at any one time so that the average occupancy of these $96h$ positions is taken to be $1/6$. For the local atomic arrangement envisaged, see Fig. 1 of Hua, Welberry, Withers and Thompson (1988).

Because of the strong correlation between ϵ and the thermal vibration parameters of the La ions, the latter were initially constrained to be isotropic. This refinement again converged rapidly. The value of the parameter ϵ defin-

Table 4. Root-mean square (r.m.s.) amplitude along three principal axes of the thermal ellipsoids.

Atom	r.m.s. ($\text{\AA}$)	Direction
La	0.090	$\langle 1\bar{1}0 \rangle$
	0.090	$\langle 1\bar{1}2 \rangle$
	0.057	$\langle 111 \rangle$
Zr	0.064	$\langle 111 \rangle$
	0.061	$\langle \bar{1}10 \rangle$
	0.061	$\langle \bar{1}12 \rangle$
O1	0.103	$\langle 01\bar{1} \rangle$
	0.093	$\langle 100 \rangle$
	0.059	$\langle 011 \rangle$
O2	0.086	isotropic

Table 5. Atomic parameters of La₂Zr₂O₇ in the final model.

positional			
Atom	<i>x</i>	<i>y</i>	<i>z</i>
La	$1/2 + \varepsilon$	$1/2 - \varepsilon$	$1/2$
occupancy = $1/6$, $\varepsilon = 0.00606(9)$			
Zr	0	0	0
O1	$0.3306(2)$	$1/8$	$1/8$
O2	$3/8$	$3/8$	$3/8$

thermal ($\text{\AA}^2$)							
Atom	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃	<i>B</i> _{eq}
La	0.00334(7)	<i>U</i> ₁₁	<i>U</i> ₁₁	0	0	0	0.263(2)
Zr	0.00374(6)	<i>U</i> ₁₁	<i>U</i> ₁₁	0.00015(8)	<i>U</i> ₁₂	<i>U</i> ₁₂	0.295(1)
O1	0.0083(8)	0.0070(4)	<i>U</i> ₂₂	0	0	0.0036(6)	0.59(2)
O2	0.0073(7)	<i>U</i> ₁₁	<i>U</i> ₁₁	0	0	0	0.57(2)

Table 6. Selected bond lengths ($\text{\AA}$) based on the parameters of the average structure and the statistically split La on 96h site model.

Cation	Anions	Bond lengths
Average structure model		
La	O2 ⁱ	$2.33820(3) \times 2$
	O1 ⁱⁱ	$2.643(1) \times 6$
Average		2.567
Zr	O1 ⁱⁱⁱ	$2.0987(9) \times 6$
Split La model on 96h site		
La	O2 ⁱ	$2.3400(8) \times 2$
	O1 ^{iv}	$2.566(2) \times 2$
	O1 ^v	$2.646(2) \times 2$
	O1 ⁱⁱ	$2.723(2) \times 2$
Average		2.569
Zr	O1 ⁱⁱⁱ	$2.0982(9) \times 6$

Symmetry operators: (i) *x*, *y*, *z*; (ii) *x*, *y* + $1/2$, *z* + $1/2$; (iii) $\bar{x}$, *x* + $1/4$, $\bar{y}$, *y* + $1/4$, *z*; (iv) *z* + $1/2$, *x*, *y* + $1/2$; (v) *y* + $1/2$, *z* + $1/2$, *x*.

ing the magnitude of the La ion shift from the average structure position converged to 0.00606(9) associated with a reduced *U*_{iso} of 0.00334(7) $\text{\AA}^2$. The isotropic extinction parameter refined to 0.080(7). Full details of the refined parameters of this final structure model and selected bond lengths are given in Table 5 and 6, respectively. At this stage, the obtained refinement statistics were *R*/*wR* = 0.017/0.015. The above value for ε implies that La ions shift by $\sim 0.093 \text{ \AA}$ ($= a_0 \times \varepsilon \times \sqrt{2}$) from the average position, in other words, the O2–La–O2 bond is never linear but rather deviates from 180° by $\sim 4\text{--}5^\circ$.

4. Discussion and conclusions

The existence of an annular distribution of density in the {111} planes perpendicular to the local O2–La–O2 directions is rather striking and strongly reminiscent of β -cristobalite itself where it is now clear that the oxygen ions therein (analogous to the La ions in Fig. 1b) also never occupy the 16d sites of the average structure but rather are distributed uniformly around an annulus perpendicular to the local Si–O–Si direction and encircling these 16d sites (Welberry *et al.*, 1989; Swainson and Dove, 1993; Dove

et al., 1998; Keen, 1998). In the case of β -cristobalite itself, the radius of this annulus is quite large and such that the local Si–O bond length and Si–O–Si angle are altered from the crystal chemically unreasonable values of the average structure to values characteristic of almost all forms of silica.

In the current case, the radius of the annulus is rather smaller, perhaps constrained by the presence of the other Zr(O1)₆ network structure. Nonetheless we believe the above refinement provides clear evidence that the La ions likewise never actually occupy the average 16d positions but rather are dynamically disordered around an annulus perpendicular to the local O2–La–O2 direction in an exactly analogous manner to that which occurs in β -cristobalite itself. The effect of this distortion is to locally increase the magnitude of the rather short La–O2 bond lengths thereby reducing the over-bonding of the O2 ions, expanding the size of the (O2)La₄ tetrahedra and improving the local crystal chemistry. The existence of a weak but highly structured and quite reproducible diffuse intensity distribution in the form of {110}* polarized sheets of diffuse intensity (see Fig. 2), exactly analogous to an isomorphous diffuse distribution which occurs in β -cristobalite itself (Withers *et al.*, 1989), confirms that this increase in the local La–O2 bond lengths takes place in a correlated fashion involving {110} tetrahedral edge rotation of essentially rigid (O2)La₄ tetrahedra.

The above results appear to suggest that the β -cristobalite-type (O2)La₂ array of corner-sharing, oxygen-centred tetrahedra (see Fig. 1(b)) acts reasonably independently of the other network structure (the Zr(O1)₆ network structure (see Fig. 1(a)) comprising the pyrochlore structure type. Given that the La–O1 distance of closest approach between the two network structure types is significantly longer than any intra-network bond distance (consistent with a rather weaker bonding interaction between the two network structure types), this may not be such a surprising result. The situation is perhaps reminiscent of the effect of interstitial stuffing cations upon so-called “stuffed cristobalite” phases (Thompson, Withers, Palethorpe and Melnichenko, 1998). Nonetheless the question of how the Zr(O1)₆ network responds to the β -cristobalite-like distor-

tion of the (O2)La₂ array of corner-sharing, oxygen-centred tetrahedra (see Fig. 1(b)), while beyond the scope of the current contribution, remains an intriguing question to consider.

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