Structure determination of the intermediate tin oxide Sn_3O_4 by precession electron diffraction

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Abstract. The structure of an intermediate form of tin oxide was investigated by precession electron diffraction. The results support a revised version of a layered, vacancy-ordered structure for Sn_3O_4 proposed in the preceding literature. The lattice parameters were found to be consistent with a monoclinic cell which is a distorted superlattice of the cassiterite structure. Zero-order Laue zone (ZOLZ) Patterson maps, phased projections and phases measured from a [001] first-order Laue zone (FOLZ) conditional Patterson map all support the proposed modification to the tin coordinates over the unmodified form. The results of kinematical refinement were not satisfactory, although weak features found in the Patterson maps were consistent with the oxygen atoms being located close to the previously proposed positions.

1. Introduction

Two forms of tin oxide are known to exist, SnO and SnO_2 . Besides these, a metastable intermediate oxide has been reported to occur during the decomposition reaction of SnO ever since the first reports of the thermal instability of this compound [3]. This metastable phase has been found under a wide variety of atmospheres and conditions: vacuum, air and even in a chondritic interplanetary dust particle [20]. Additionally, the phase has been reported in thin films and more recently in a number of nanostructured materials.

The disproportionation reaction of SnO is consistent with the two step mechanism:

Quantitative kinetic studies [18, 8] support such a two step reaction mechanism. However, the intermediate oxide phase is always present in multiphasic samples – occurring as small crystals which remain attached to particles of

tin from which they grow (Fig. 1). To date, it has not been possible to separate or isolate the compound, and as a consequence the exact composition of the intermediate oxide remains controversial. The compositions Sn_5O_6 , Sn_3O_4 and Sn_2O_3 have all been mentioned in the literature.

Two difficult analytical methods have been attempted to determine the composition experimentally: Measurement of the quantity of metallic tin in the products of the disproportionation reaction [6], and indirect measurement of the Sn:O ratio in the intermediate oxide [19]. The two analyses yielded the compositions Sn_3O_4 and Sn_2O_3 respectively, and these two compositions have featured most prominently in the available literature. Attempts to determine the composition of the intermediate oxide by Mössbauer spectroscopy have been frustrated by the multiphasic nature of the samples.

Knowledge of the crystal structure of the compound similarly limited. Two different triclinic unit cells were proposed using a combination of electron diffraction and X-ray powder diffraction [13] or X-ray powder diffraction alone [19]. By consideration of the volume of the cell based on these results and comparison with the covalent radius of a single tin atom, is it most likely that the unit cell contains six tin atoms. This conclusion is supported by information from first-principles computer simulation and the consideration of comparable structures [21, 14].

Based on linewidth considerations, a Mossbauer study suggested that the intermediate compound has a limited range, or no range at all, of composition [17]. Electron

Fig. 1. A dark-field image showing a particle of intermediate tin oxide, attached to a globule of metallic tin.

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energy-loss spectroscopy has been applied to fingerprint this phase in order to differentiate the tin oxides phases by this technique [16].

Since single-crystal X-ray diffraction analysis on this compound is impossible due to the small size of the crystals, and powder diffraction has yielded only limited information, this specimen is a good subject for analysis using electron diffraction. However, the cylindrical shape of the particles makes it difficult to record data from a single well-defined thickness. Therefore, the diffracted intensities, even with precession, are unlikely to be of a very high quality so far as structure solution is concerned. Therefore, this specimen makes it possible to see how far a structure solution effort can be taken under conditions which are far from ideal.

2. Preliminary investigation

A specimen of the intermediate tin oxide was synthesised by the thermal decomposition of SnO (blue-black, Aldrich) for one hour at 723 K in a sealed glass tube containing an argon atmosphere. Precession diffraction patterns [23] were acquired at 300 keV from a specimen of tin oxide powder which contained particles similar to that shown in Fig. 1. A NanoMEGAS Spinning Star unit was used to perform the precession of the electron beam, enabling the acquisition of zone axis precession electron diffraction patterns to be undertaken. Suitable particles of the intermediate compound were located by searching for the characteristic “microphone” shape, and then positioning the probe on the cylindrical section of the particle. The patterns were recorded on photographic film.

All patterns were digitised and the images corrected for the non-linearity of the response of the film using results from a previous calibration experiment. A beam stop was used in many cases to avoid saturation and blooming of the film, the missing reflections being generated by the application of Friedel’s Law during later processing. The precession angle for the first three patterns was 25 mrad, and the precession angle for the fourth pattern was about 15 mrad.

Before the patterns could be indexed, the possible structures already discussed in previous literature were considered. The cell proposed by Lawson [13] cell was triclinic, having the parameters

$$\begin{aligned} a &= 0.486 \text{ nm} & b &= 0.588 \text{ nm} & c &= 0.820 \text{ nm} \\ \alpha &= 93.0^\circ & \beta &= 93.35^\circ & \gamma &= 91.0^\circ, \end{aligned}$$

while the cell derived by Seko *et al.* [21] from first-principles calculations for Sn₃O₄ was monoclinic, with

$$\begin{aligned} a &= 0.821 \text{ nm} & b &= 0.493 \text{ nm} & c &= 0.585 \text{ nm} \\ & & \beta &= 94.7^\circ. \end{aligned}$$

Once the discrepancy in the definition of the axes is taken into account, it is apparent that the parameters are similar, with the shortest repeat length differing by just over 7% between the two, and the other lengths being much closer to agreement. The cell found by Murken and Trömel [19] was similar apart from a substantial discrepancy in the

shortest lattice repeat, having

$$\begin{aligned} a &= 0.546 \text{ nm} & b &= 0.818 \text{ nm} & c &= 0.371 \text{ nm} \\ \alpha &= 93.8^\circ & \beta &= 92.3^\circ & \gamma &\approx 90^\circ. \end{aligned}$$

It did not escape the attention of early researchers that a supercell of the cassiterite unit cell could be constructed which agrees quite closely with the measurements of the lattice parameters of the intermediate phase [13]. The structure of SnO₂ (*stannic oxide*) is tetragonal with $a = b = 0.472$ and $c = 0.314$ nm and has the space group $P4_2/mnm$. The structure is known as the *rutile* structure, named after the mineral form of titanium dioxide, while the mineral form of SnO₂ is itself known as *cassiterite*. In this structure, tin atoms appear in a body-centered arrangement, within which the centre tin atom is surrounded by six oxygen atoms in a distorted octahedral coordination. The same octahedral arrangement surrounds the corner tin atoms, but rotated by 90° about the *c*-axis.

Although the algebraic relationship between the cassiterite unit cell and the supercell was not given in the early literature, it can be determined by drawing projections of the cassiterite structure and locating vectors which connect tin atoms separated by lengths which were close to the published lattice repeats of the intermediate structure. If the lattice vectors of the rutile structure are expressed in vector form as $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$, then the lattice vectors of a suitable supercell, $\mathbf{a}'$, $\mathbf{b}'$ and $\mathbf{c}'$, are given by:

$$\mathbf{a}' = \mathbf{b} - 2\mathbf{c} \quad \mathbf{b}' = \mathbf{a} \quad \mathbf{c}' = -\mathbf{b} - \mathbf{c}.$$

This transformation is shown graphically in Fig. 2, and produces a monoclinic unit cell with the lattice parameters

$$\begin{aligned} a' &= 0.786 \text{ nm} & b' &= 0.472 \text{ nm} & c' &= 0.567 \text{ nm} \\ & & \beta &= 93.29^\circ, \end{aligned}$$

which compare favourably with the unit cell proposed by Lawson [13] and the monoclinic cell of Seko *et al.* These parameters are all slightly smaller than the values given by both Seko and Lawson, by around 4%, which suggests that the metastable intermediate oxide structure has a more open nature probably brought about by vacant oxygen sites.

Fig. 2. A transformation of the cassiterite unit cell (outlined in grey) which produces a cell with parameters close to the cell parameters of Lawson and Seko *et al.* (outlined in black). Oxygen atoms are represented by small grey circles, while tin atoms are represented by larger black circles. Four oxygen atoms, marked by squares, can be removed to produce cell contents close to the vacancy-ordered structure of Seko *et al.*

It should be noted that the two unit cell definitions from the published literature do not agree on the definitions of the axes (*i.e.* which algebraic symbol should be assigned to which vector), and this can be a source of much confusion. In the work of Seko *et al.* the assignment of axes was constrained to match the conventional setting of a monoclinic unit cell. Therefore, in order to simplify discussions of symmetry existing in the structure, the unit cell definition of Seko *et al.* has been used above (apart from the statement of Lawson's original cell values), and will be used in all further discussion in this chapter. In addition, a right-handed coordinate system has been used to define the unit cell and atomic coordinates.

Examples of precession electron diffraction patterns acquired as described above are shown in Fig. 3. Several patterns were identified as coming from the $[010]$ and $[0\bar{1}1]$ zone axes. A smaller number were identified as the $[001]$ orientation, and none at all were identified as the $[100]$ orientation. From this, it can be speculated that the morphological form of the intermediate oxide crystals is related to their crystallographic structure, with the elusive $[100]$ direction being located parallel to the cylindrical 'axis' of the particles. This direction is the hardest to reach since the crystals tend to lie flat against the carbon support film and the tilt range of the specimen holder in the microscope is limited. Even if a crystal were to be found in this orientation, the thickness is likely to be large and the diffraction pattern from the intermediate phase likely to overlap with diffraction from the globule of elemental tin attached.

Reflection intensities were acquired in a roughly circular domain out to around 17 nm^{-1} , 13 nm^{-1} and 13 nm^{-1} for the $[001]$, $[010]$ and $[0\bar{1}1]$ zone axes respectively.

Fig. 3. Precession electron diffraction patterns from the intermediate oxide, recorded at 300 keV.

The $[0\bar{1}1]$ zone axis is difficult to differentiate from the $[011]$ zone axis, since the projected lattice parameters in both cases are very similar. The difference in lattice parameters is comparable with the accuracy in lattice parameter measurement which can be reasonably achieved using conventional transmission electron diffraction techniques, and therefore presents a problem. Instead of using the lattice repeat distances to distinguish between the projections, the ratios and angles between the principal lattice repeats were examined as possibilities to distinguish between the two projections. Although they are still subject to lens distortions and errors due to irregular shrinkage of photographic film, the ratios and angles are not subject to errors in camera length and should therefore be more reliable. According to Lawson's triclinic unit cell, in the $[0\bar{1}1]$ projection the ratio of the interplanar spacings d_{100}/d_{011} should be 2.12. For the $[011]$ projection, the ratio $d_{100}/d_{0\bar{1}1}$ would be 2.24. Using the Seko unit cell, the ratio d_{100}/d_{011} was calculated as 2.19 and the ratio $d_{100}/d_{0\bar{1}1}$ is 2.17. The mean measured value of the ratio from four measurements from separate negatives was 2.2 ± 0.1 . With the extreme similarity of the values, and the estimated error in the experimental measurement, it was decided that the ratios did not distinguish adequately between the two possibilities and so the interaxial angles were next investigated. The measured obtuse angle between the reciprocal axes in the patterns was $93.3^\circ \pm 0.5^\circ$. For the Seko unit cell, the angle in the $[0\bar{1}1]$ projection would be 96.9° , or 90.9° for the $[011]$ projection. For the Lawson cell, the angles would be 93.9° for the $[0\bar{1}1]$ projection, or 92.1° for the $[011]$ projection. If the Seko unit cell is used, then the measured value is approximately midway between the two calculated values. However, if the Lawson cell is used, then the $[0\bar{1}1]$ is more in agreement. Only the Lawson value for $[0\bar{1}1]$ comes close to the measured value. The patterns were therefore indexed as coming from this orientation, although it is acknowledged that the confidence in indexing these patterns was not high. A similar difficulty arises with indexing the $[001]$ zero-order Laue zone pattern, since the angle between the reciprocal axes in this projection is 90° within the accuracy of measurement (and indeed would be exactly 90° for a monoclinic unit cell). Therefore, there is a possibility that the maps shown for this axis appear mirrored in one or both principal axes.

The lattice was measured from multiple measurements of the $[001]$, $[0\bar{1}1]$ and $[010]$ zone axis diffraction patterns. The measurements, with their estimated standard errors, are as follows:

$$\begin{aligned} d_{100} &= 0.80 \pm 0.02 \text{ nm} & d_{010} &= 0.48 \pm 0.01 \text{ nm} \\ d_{001} &= 0.55 \pm 0.01 \text{ nm} & d_{0\bar{1}1} &= 0.38 \pm 0.01 \text{ nm} \\ \widehat{a^*b^*} &= 90.5^\circ \pm 0.5^\circ & \widehat{a^*c^*} &= 84.2^\circ \pm 0.5^\circ. \end{aligned}$$

These six values are sufficient to uniquely determine the lattice parameters a , b , c , α , β , γ , but to do so requires the simultaneous solution of the complicated equations for calculating interplanar spacings and angles in a triclinic cell, which is extremely difficult to perform algebraically. This solution was performed by using a least-squares fitting procedure based on a routine from the GNU Scientific

Library [5], yielding the following cell parameters:

$$\begin{aligned} a &= 0.80 \pm 0.02 \text{ nm} & \alpha &= 89.4^\circ \pm 0.5^\circ \\ b &= 0.55 \pm 0.01 \text{ nm} & \beta &= 95.9^\circ \pm 0.5^\circ \\ c &= 0.48 \pm 0.01 \text{ nm} & \gamma &= 89.6^\circ \pm 0.5^\circ, \end{aligned}$$

where the new error estimates have been taken as 2% of the quoted value for the distances, estimated from the repeatability of lattice parameter measurements and the accuracy of the camera length calibration. The error was estimated as 0.5° for the angles, in accordance with the accuracy expected for lattice parameter determination by electron diffraction from previous experience.

Seko *et al.* (2008) suggest the monoclinic space group $P2_1/c$ for their structure, but this symmetry is incompatible with the triclinic unit cell proposed by Lawson. It was found that the $[010]$ projection could be indexed consistently only by a doubling of the unit cell in the c direction, meaning the absence of all reflections of the form $h0l$ where l is odd. Since the measured lattice parameters are close to the monoclinic unit cell within the estimated accuracy of measurement, and forbidden reflections are present which are consistent with the proposed space group ($P2_1/c$), this provides evidence in support of a structure based on that proposed by Seko *et al.* Projections of this structure along principal crystallographic directions are shown in Fig. 4, and this figure will be referred to later.

A key feature of the Seko structure is that it can be formed from the cassiterite supercell structure described earlier by first applying a shift to the atomic coordinates of $1/2, 0, 1/2$ and then removing oxygen atoms with $-1/6 < x < 1/6$ from the structure to leave an empty region in the structure. The remaining atoms form a ‘layer’ in the $b-c$ plane. The oxygen atoms which must be removed are highlighted with square boxes in Fig. 2. The tin atoms in the middle of this layer, of which there are only two (since these atoms lie on the crystallographically special position denoted by the Wyckoff symbol $2d$), are octahedrally coordinated by six oxygen atoms with bond

Fig. 4. Key projections from Seko's predicted structure for Sn_3O_4 . Large grey spheres represent tin atoms, and smaller green spheres represent oxygen.

Table 1. Comparison of the atomic coordinates for the Seko and cassiterite supercell structures.

			x/a	y/b	z/c
Seko	Sn-1	$2d$	$1/2$	0	$1/2$
	Sn-2	$4e$	0.826	0	0.707
	O-1	$4e$	0.733	0.675	0.503
	O-2	$4e$	0.403	0.698	0.774
Cassiterite Supercell	Sn-1	$2d$	$1/2$	0	$1/2$
	Sn-2	$4e$	$1/2 + 1/3$	0	$1/2 + 1/3$
	O-1	$4e$	0.732	0.805	0.537
	O-2	$4e$	0.398	0.695	0.704
	O-3	$4e$	0.935	0.305	0.630

angles of approximately 90° . The remaining tin atoms, of which there are four (being the multiplicity of the general position in the space group $P2_1/c$), form the outer surface of the ‘layer’. The gap between the layers is ‘filled’ for by lone pair electrons on these ‘outer’ tin atoms, as is the case for the SnO romarchite structure. Two symmetrically unique oxygen atoms exist, both of which are found on general crystallographic positions, to produce a total of eight oxygen atoms and hence give the formula $2\text{Sn}_3\text{O}_4$ for the monoclinic unit cell.

To better understand the symmetry of the relationship between the two structures, the cassiterite supercell structure itself can also be cast into the same space group as the Seko structure. In this case, two unique tin atoms and three unique oxygen atoms are found. Again, one tin atom lies on the special Wyckoff position $2d$ and the others on the general position ($4e$) such that the unit cell contains six tin atoms in total. All three oxygen atoms lie on general positions to produce a total of 12 oxygen atoms in the unit cell and hence the overall formula 6SnO_2 . If one of the symmetrically unique oxygen atoms is removed from the structure, then a row of oxygen atoms is eliminated from the structure in the way just mentioned, and the structure becomes very similar to that proposed by Seko. This can be seen by comparing the coordinates from both structures, which are shown in Table 1. In this Table, Sn-1 is in the middle of the ‘layer’, and Sn-2 is at the ‘surface’. O-3 is the oxygen atom which is removed to produce the layered structure. It is relevant to note that all the oxygen atoms which must be removed to give the required vacancy ordering are produced by symmetry from a single unique atom, and also that the relatively large shift in the z -coordinate of Sn-2 causes the direction of the line of closely spaced tin atoms seen in the $[010]$ projection, to reverse. This can be seen by comparing Figs. 2 and 4.

3. ZOLZ Patterson maps

The fidelity of the diffraction intensities from such a thick crystal of a metal oxide is likely to be reduced by the combined effects of dynamical interactions, inelastic scattering, incoherent multiple scattering arising from defects in the crystals and thickness averaging. Accordingly, it was decided not to go straight for a structure solution

Fig. 5. Left column: Patterson maps calculated from the precession patterns shown in Fig. 3. Solid contours represents positive values, dashed contours negative values. Negative values arise primarily through Fourier truncation and dynamical effects. Right column: Simulated maps using the Seko structure for Sn_3O_4 .

using direct methods via an automated pieces of software. Instead, a more cautious approach was followed, investigating first the information seen in Patterson transforms to determine Sn–Sn and Sn–O interatomic vectors. Patterson maps formed from ZOLZ intensities in the $[001]$, $[010]$ and $[0\bar{1}1]$ zone axes are shown in Fig. 5. Fourier truncation and possible dynamical effects were seen to lead to negative values in the maps, as seen in Fig. 5.

In the $[001]$ orientation, six strong peaks appear in a 3×2 repeating pattern, and between them there is a background ripple. It was assumed that the strong peaks could be attributed entirely to scattering from the tin atoms, and that the background ripple may contain information about the oxygen atom positions. The interatomic vectors seen in this orientation are consistent with the tin atom positions of the cassiterite supercell, whose positions are themselves very close to those proposed by Seko *et al.*

In the $[010]$ orientation, strong peaks appear in a diagonal line which crosses the map, and it can be seen that this line acts to bisect the obtuse angle of the projected unit cell rather than the acute angle. This orientation of the tin atoms in relation to the obtuse angle is in agreement with the proposed structure of Seko *et al.*, rather than that of the cassiterite supercell described earlier. Additionally, a distortion of some of the peaks can be seen. To investigate this further, the map was sharpened by performing a normalisation using a method similar to the Wilson method [24], except that the falloff of intensity with increasing resolution was fitted using a different function

$$I_g = A \exp(-Bs_g) + C, \quad (1)$$

where I_g and s_g represent the intensity and value of $\sin \theta/\lambda$ for the reflection $\mathbf{g}$ respectively. θ is the Bragg angle and λ is the wavelength of the incident electrons. A , B and C

Fig. 6. Sharpened $[010]$ ZOLZ Patterson map from the intermediate oxide, created using $E^{4/5}/F^{1/5}$.

are constants determined by the fitting procedure. This form was found to fit the observed falloff more closely than the conventional Debye-Waller equation. The normalisation procedure increases the sharpness of the map, but at the expense of increasing the amount of Fourier ripple and noise. To mitigate this, the Fourier moduli used to synthesise the final map were $E^{4/5}I^{1/5}$, where E is the normalised intensity and I was the original measured intensity. This produced a ‘partially normalised’ map, with reduced Fourier ripple.

In the sharpened map, shown in Fig. 6, a clear division of these peaks was seen, each one being split into a large peak and a neighbouring smaller peak. Such a splitting is not consistent with the cassiterite supercell structure, which predicts that the tin atoms should fall exactly along a straight line in this projection. However, this splitting is again consistent with the proposed structure from Seko *et al.* Vectors have been drawn on the $[010]$ projection in Fig. 4 to show that two separate Sn–Sn vectors exist per unit cell, numbered 1 and 2, with vector 2 occurring twice as many times as vector 1. It can be seen from the sharpened Patterson map that the peaks corresponding to the two vectors, also numbered in Fig. 6, occur with heights in a similar ratio. Therefore, evidence from this Patterson map supports the Seko structure.

Finally, the Patterson map from the $[0\bar{1}1]$ intensities has a similar appearance to the maps shown previously for the $[010]$ orientation, containing two principal peaks besides the self-correlation peak, approximately forming a diagonal line across the projected unit cell. The map would appear at first glance to be consistent with the projected Seko structure for this orientation. However, on closer inspection, the line of stronger peaks is seen to be in the opposite orientation compared to the origin of the unit cell: in the Seko structure, the line of three tin atoms bisects the obtuse angle of the oblique projected unit cell, whereas in the observed Patterson map, the line of stronger peaks bisects the acute angle. The workflow used to create the Patterson map was carefully checked to verify this observation.¹

¹ The described property of the Seko structure occurs in both the $[011]$ and $[0\bar{1}1]$ zone axes, and so the conclusion is unaffected by the lack of confidence in distinguishing between these two orientations.

Fig. 7. Key projections from the modified form of Seko's predicted structure for Sn_3O_4 . Large grey spheres represent tin atoms, and smaller green spheres represent oxygen.

By visualisation of ways of modifying the Seko structure, it became apparent that the structure could be made consistent with the Patterson maps by applying a shift of $\frac{1}{2}\mathbf{b}$ to Sn-2. Key projections of the modified structure so formed are shown in Fig. 7. It can immediately be seen that the two projections already analysed in this section (and found to be consistent with the previous Seko structure) are unchanged, while the orientation of the line formed by closely spaced tin atoms in the $[0\bar{1}1]$ projection is reversed. Additionally, a large discontinuity visible in this line with the Seko structure (Fig. 4) is reduced almost to nothing, and this is also consistent with the observations.

4. FOLZ conditional Patterson maps

Maps were synthesised from the FOLZ intensities. A two-dimensional projected potential synthesised from HOLZ intensities alone is typically not real-valued [22]. In such a map, each atomic peak will appear multiplied by an associated phase factor which represents its coordinate in the out-of-plane direction [2]. The 'conventional' Patterson map, $P(\mathbf{r})$ is expressed as

$$P(\mathbf{r}) = \frac{1}{\Omega} \int U(\mathbf{r}') U(\mathbf{r} + \mathbf{r}') d\mathbf{r}', \quad (2)$$

where $\mathbf{r}$ and $\mathbf{r}'$ are three-dimensional vectors in real space, Ω is the volume of the unit cell, $U(\mathbf{r})$ is the crystal potential. Using this form, the HOLZ conditional Patterson map from intensities in the n -th Laue zone of the $[001]$ zone axis can be defined as [15]:

$$P^n(\mathbf{R}) = \int_0^1 P(\mathbf{r}) \exp(-2\pi i n z) dz, \quad (3)$$

where $\mathbf{R}$ is a two-dimensional vector in the plane perpendicular to the zone axis, and z is a coordinate in the direction parallel to the zone axis.

Fig. 8. FOLZ Patterson map from the intermediate oxide, with the corresponding colour wheel indicating shown to the left. The colours as shown in the colour wheel represent phase, while the saturation represents modulus of the complex-valued function.

In addition, the curvature of the Ewald sphere means that the sampling of Fourier components will lead to an annulus of data rather than a filled circle. This leads to severe ripple in the Patterson map which makes weaker peaks very difficult to see. Fig. 8 shows a $[001]$ zone axis FOLZ Patterson map from the intermediate tin oxide structure. In this map, the saturation of colour at a particular point indicates the magnitude of the complex value at that point, and the hue indicates the phase, according to the colour wheel shown to the right of the map. In the colour wheel, the dark line indicates the position of zero phase, with phase increasing anticlockwise around the wheel and magnitude increasing from the centre to the rim. The FOLZ Patterson map shows five main peaks in addition to the self-correlation peak, in the same positions as they were observed in the ZOLZ maps, as expected. The phases of these peaks encode some information about the out-of-plane components of the sums of the interatomic vectors matching that particular two-dimensional coordinate, as described by the above equation.

The phases at the summits of the six large peaks were measured from the map, and the values compared to those calculated using both the unmodified and modified Seko structures. The errors in the values were estimated as the mean of moduli of the differences between the quoted value and the values at the four nearest neighbouring elements in the Fourier transform array, and therefore gives an estimate of how quickly the phase value is changing across the peak. As expected, the errors measured in this way are larger for the experimental measurements because

Table 2. Phase values, in radians, at the summits of the principal peaks in the conditional Patterson map. The quoted errors represent the rate at which the phase was changing across the summit of the peak as described in the text. Errors measured in this way for both sets of calculated values were negligibly small.

Peak number	measured	Seko	modified Seko
1	0.00 ± 0.04	0.00	0.00
2	-1.85 ± 0.05	-1.60	2.03
3	-1.81 ± 0.06	1.62	-2.03
4	-3.13 ± 0.05	0.00	0.00
5	-1.48 ± 0.07	1.54	-1.12
6	1.48 ± 0.07	-1.54	1.12

the experimental maps are subject to errors in phase due to contributions from the oxygen atoms, incorrect Fourier moduli and Fourier truncation, none of which were included in the simulation. Table 2 shows these values, with the definitions of the peak numbers found below the Patterson map in Fig. 8. It can immediately be seen that the unmodified Seko structure provides phases for many of the peaks which differ from the measured values by around π radians. Although the values calculated for the modified structure do not match exactly the measured values, they are very much closer, differing from them only by around 0.2–0.3 radians. The FOLZ conditional Patterson map in this orientation therefore provides further evidence for the modified Seko structure described earlier versus the unmodified structure.

5. Direct methods

Many of the algorithms described in the previous chapter were applied to data from the intermediate oxide. Particular success was experienced with the tangent formula [12], an implementation of which was created for the purposes of experimentation. This implementation allowed the numerical parameters for selection of strong reflections, selection of concentrated triplets and criteria for assigning phases to be varied freely, and the resulting map inspected by eye. After selecting the reflections with the strongest normalised structure factors and finding the strongest triplets amongst them, the convergence procedure [7] was applied to determine the best reflections to which to assign the initial ‘seed’ phases. Initial phases could either be assigned randomly or different sets of values systematically iterated through, and the implementation was able to store and re-use the lists of phase relationships to vastly increase the speed with which different trial phase ‘seeds’ could be attempted. The implementation also allows *tangent refinement* to occur, meaning that the phases of structure factors which were phased previously could be updated if a new phase was later calculated with a larger value of the parameter α , which represents the reliability of the calculated phase value, than the previous assignment [7]. The final map was synthesised only from the reflections to which phases had been assigned.

Projected potentials obtained in this way are shown in Fig. 9. All the maps are consistent with the proposed structure. A ‘kink’ can be seen in the $[010]$ map, supporting the distortion noted earlier in the Patterson map for this orientation. A dashed line has been marked on the diagram as a guide to the eye to show this more clearly. The $[0\bar{1}1]$ projection is seen to show lines of closely-spaced tin atoms which bisect the acute angle of the projected unit cell, consistent with the the proposed revision to the previous structural model for Sn_3O_4 . A 2×2 array of unit cells has been shown for the $[0\bar{1}1]$ projection to show more clearly that the lines are not ‘kinked’ in the manner of those in the $[010]$ projection. For the $[001]$ projection, it is apparent that the connectivity between reflections established by the direct methods procedure was unable to create strong phase relationships to provide useful

Fig. 9. Projected potential maps determined using the tangent formula from the precession electron diffraction data.

phase values for the superlattice reflections. As a result of this, the map is constructed only from the stronger reflections, leading to a projected potential which appears in an exact 3×2 repeat.

Coordinates for the tin atoms were measured from the potential maps, and mean values taken where more than one value was available for a particular coordinate (such as the x -coordinates), and the results combined to produce a three-dimensional structure model. In order to render the coordinates compatible with the space group of the Seko structure (which is unchanged by the modification of the tin coordinates), the means of coordinates were used where atoms were in symmetrically equivalent positions. The coordinates after this modification are shown in Table 3. The coordinates of the independent atoms are shown in bold.

Table 3. Tin atoms measured from the phased projections. Above: The raw values measured from the phased projections. Below: The same coordinates after enforcing the symmetry of the space group $P2_1/c$, compared to those of the modified Seko structure. Bold numbers indicate atoms belonging to the asymmetric unit cell.

Values as measured from potential map			
	x/a	y/b	z/c
Sn-1	0.5	0.0	0.5
Sn-1	0.50 ± 0.04	0.49 ± 0.02	0.00 ± 0.03
Sn-2	0.82 ± 0.04	0.49 ± 0.02	0.71 ± 0.03
Sn-2	0.16 ± 0.04	0.49 ± 0.02	0.29 ± 0.03
Sn-2	0.16 ± 0.04	0.00 ± 0.02	0.79 ± 0.03
Sn-2	0.82 ± 0.04	0.00 ± 0.02	0.21 ± 0.03

Symmetry adjusted values			Modified Seko structure			
	x/a	y/b	z/c	x/a	y/b	z/c
Sn-1	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$
Sn-1	$\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	0
Sn-2	0.83 ± 0.04	0.50 ± 0.02	0.71 ± 0.03	0.826	0.500	0.707
Sn-2	0.17 ± 0.04	0.50 ± 0.02	0.29 ± 0.03	0.174	0.500	0.293
Sn-2	0.17 ± 0.04	0.00 ± 0.02	0.79 ± 0.03	0.174	0.000	0.793
Sn-2	0.83 ± 0.04	0.00 ± 0.02	0.21 ± 0.03	0.826	0.000	0.207

6. Oxygen atoms

The next step in the structure solution process is to attempt to locate the oxygen atoms. It must first be determined whether a modification in coordinates – like the one applied to the tin atoms – must also be applied to the oxygen atoms in order to produce a structure consistent with the expected bond lengths and angles. If the formula is assumed to be Sn_3O_4 with the space group $P2_1/c$, then there are two oxygen atoms in the structure which are symmetrically independent, both in positions with a multiplicity of four, producing a total of eight tin atoms and hence achieving the correct stoichiometry. In the Seko structure, the tin atoms Sn-1 and Sn-2 are coordinated by six oxygen atoms, in a distorted octahedral coordination. It was found that shifting either one of the two independent oxygen atoms in the same way as the tin atoms, by $b/2$, produced an unreasonable structure with some very short Sn–O bonds and large empty regions. If neither atom was shifted, then the structure appeared to remain very similar to that of the Seko structure. This was also found to be the case if both oxygen atoms were shifted. Table 4 shows the coordinates of the two symmetrically independent oxygen atoms for the Seko structure, the modified structure with the oxygen coordinates also modified, and the cassiterite supercell for comparison.

The bonding environment of the tin atoms was compared for the four cases discussed: the Seko structure, the modified Seko structure with the oxygen atoms unchanged, the same with the oxygen atoms also moved, and the cassiterite supercell. Schematic diagrams of the bonding environments of the two symmetrically unique tin atoms are shown in Fig. 10. In this diagram, the orientation indications at the bottom, common to all diagrams in each column, are approximate. Dashed lines indicate bonds leading into the paper, and wedged lines indicate bonds leading out of the plane of the paper. When visualising the bonding, it must be kept in mind that the structure is three dimensional. In the case of Sn-2, the diagrams have been drawn such that the lone pair extends out of the plane of the paper. The coordinates of the atom which was inspected are shown in each cell. It can be seen that the environment of either Sn-1 or Sn-2 is preserved, depending on whether the oxygen positions are left unmodified or changed, respectively.

In cassiterite, all tin-oxygen bonds have lengths of 0.204 nm; the bonds in the romarchite structure are slightly longer at 0.222 nm. The bonds for Sn-1 are seen to create an approximately octahedral coordination of the tin atom in all cases, with two angles close to 90° and one differing by around 10° . The environment of Sn-1 in the case of altered oxygen positions is very similar to that of

Table 4. Proposed oxygen atom positions.

	Seko structure			Oxygen positions altered			Cassiterite supercell		
	x/a	y/b	z/c	x/a	y/b	z/c	x/a	y/b	z/c
O-1	0.733	0.675	0.503	0.733	0.175	0.503	0.732	0.805	0.537
O-2	0.403	0.698	0.774	0.403	0.198	0.774	0.398	0.695	0.704
O-3	–	–	–	–	–	–	0.935	0.305	0.630

Fig. 10. Schematic diagrams showing the bonding of the two symmetrically independent tin atoms, compared between the four structures discussed in the text. The top row shows the environment of Sn-1, and the bottom row shows the environment of Sn-2. Further details are found in the text.

the cassiterite structure, with more uniform bond lengths, closer to the cassiterite bond length, and very similar bond angles. The Seko structure produces two longer bonds of 0.249 nm and 0.237 nm, and one shorter bond at 0.178 nm. The bond angles and lengths for Sn-2 in the 'altered oxygen' structure are also very close to those for the cassiterite structure, differing only by around 0.01 nm and 3° at most.

Meanwhile, the proposed structure with unaltered oxygen atom positions displays the same non-uniform bond lengths for Sn-1, along with a similar non-uniformity for the bond lengths around Sn-2, which were measured at 0.241 nm, 0.252 nm and 0.161 nm. The bond angles for Sn-2 also differ from both the cassiterite structure and the Seko structure, by having all three bonds within 5° of 90°. The more uniform distribution of angles would seem to be preferable on the grounds of even distribution of electron density around that atom, and it is noted that such a uniform distribution of angles also appears in the romarchite structure — although in that case the angles are smaller, at 74°.

As with the modification to the tin coordinates described earlier, the modification to the coordinates of the oxygen atoms does not affect either the [010] or [001] projections of the structure. From the available data, only the [011] projection can show the alteration. Therefore, although the modification to the oxygen positions is favoured on the grounds of bonding considerations, experimental information which distinguishes between the two cases is sparse.

Close inspection of the Patterson maps was undertaken to attempt to find evidence of the oxygen atoms. Simulated maps from the Seko structure were shown earlier, next to the experimental maps, in Fig. 5, and it should be

recalled that the proposed revision to the Seko structure does not alter the [010] or [001] projections. Circles have been marked on the maps to show peaks which qualitatively agree between pairs of maps. A good correspondence was seen for the [010] zone axis, with the three strongest peaks in the simulated Patterson map also being present in the experimental map.

No evidence for oxygen atoms in positions consistent with the models could be found in the [001] Patterson map, with many peaks and ripples being visible which do not match the simulated map.

The experimental [011] Patterson map was compared with simulated maps for maps generated with the two oxygen sublattice possibilities described above. However, the correspondence with either map was very weak. Some agreement was found with the 'unaltered oxygen' structure, and a very tenuous correspondence of only one peak with the 'altered oxygen' structure.

Fourier difference maps were constructed in an attempt to reveal the weakly scattering oxygen atoms, however the resulting maps contained large amounts of ripple. This was attributed to the poor correspondence between the measured intensities and the kinematical model. Inspection of the maps for extra peaks was inconclusive.

7. Refinement

Although the quality of Fourier difference maps suggested that least-squares refinement was not justified given the quality of the data, data sets were presented to the refinement program SHELXL-97 in order to determine whether any useful results could be obtained. Refinement was al-

ways performed in the space group $P2_1/c$, and the coordinates of Sn-1, which lies on a special crystallographic position, were automatically fixed by the program. SHELXL-97's default behaviour, to refine against the intensities, was used. The starting coordinates for the tin atoms were those from Table 3 after adjustment for the symmetry of the space group. Both sets of possibilities for the oxygen coordinates were attempted, where appropriate, to attempt to determine if the figures of merit were lower for one sublattice than the other. Refinement was performed with zonal diffraction data, without merging the individual lists of intensities together. For each zone axis, all measured intensities were included in the refinement. The default weighting scheme of SHELXL-97 was used, with the standard deviations of the intensities being taken as the square roots of the intensities.

The best results were found using the $[010]$ zone axis ZOLZ intensities. In this case, the final figures of merit were $R_1 = 40\%$ and $wR_2 = 68\%$, with 327 reflections being included in the refinement. However, these figures of merit remain very high, even in comparison to other structure determinations from electron diffraction data. In this refinement attempt, the y coordinates of the atoms were fixed, because the zonal intensity data could not provide information about these values.

No geometrical correction had been applied to the intensities in the previous work, and it was suspected that this might be partially responsible for the high figures of merit. Therefore, the refinement was repeated after applying the correction factor from [9], in the form incorporating beam divergence. However, the refinement produced much higher figures of merit ($R_1 = 61\%$ and $wR_2 = 82\%$).

Refinement was attempted against the $[0\bar{1}1]$ intensities in the hope that the figures of merit would be able to distinguish between the two proposed oxygen structures. Starting from the model with the unaltered oxygen sublattice, the final figures of merit were $R_1 = 39\%$ and $wR_2 = 67\%$ with 232 reflections included. For the altered sublattice, the equivalent values were $R_1 = 46\%$ and $wR_2 = 73\%$. Therefore, the figures of merit support marginally the unaltered sublattice. However, the final atomic coordinates were, in both cases, dissimilar to the initial model. Applying a geometrical correction in the same way as before was again found to increase the figures of merit in both cases: to $R_1 = 57\%$ and $wR_2 = 69\%$ for the unaltered case, and $R_1 = 72\%$ and $wR_2 = 84\%$ for the altered case. In all four cases of refinement, it could be seen that the refined tin atom locations no longer formed the regular arrangement in the $[001]$ projection consistent with the Patterson map.

In order to restrict the refinement to small deviations from the starting structure during refinement with the $[0\bar{1}1]$ zone axis intensities, restraints were applied to keep the bond lengths and angles close to their starting values. As expected, if the standard deviation of the specified bond length (with is the way in which the weighting factor for a restraint is expressed in SHELXL-97) was made very small – around 0.0001 – then the refined structure was found to be very close to the starting structure. With the standard deviations set at the default values provided by SHELXL-97 of 0.02, the situation was similar to the unrestrained case just described.

All of the figures of merit encountered above are high, even in comparison to other refinements against electron diffraction intensities. Refinement against the $[001]$ FOLZ intensities did not produce much greater success, despite the knowledge that higher-order intensities should be less affected by dynamical effects due to their long extinction lengths. All atomic coordinates were allowed to vary, since the higher-order data provides information in three dimensions. However, no figures of merit below 70% could be found by any refinement attempt with these intensities.

Finally, refinement was attempted against the $[001]$ zone axis intensities. Unrestrained refinement gave $R_1 = 47\%$ and $wR_2 = 80\%$ with 382 reflections, and was found to produce a large deviation in the positions of one of the oxygen atoms. Recalling that initial doubt existed over the indexing of the $[001]$ ZOLZ diffraction pattern, further refinements were attempted in which the h or k indices inverted. The figures of merit did not vary by more than 1%, which suggests either that this data set is not of sufficient quality to distinguish between the two possible oxygen sublattices, or that this projection of the structure falls into the plane group $p2mm$. However, this symmetry is not consistent with any of the proposed models.

Overall, the very high figures of merit obtained during refinement, combined with the observation of the refinement process producing structures which are inconsistent with the Patterson maps (such as in the $[0\bar{1}1]$ case) and requiring tight restraints to keep under control, suggests that the fidelity of data is not sufficient for reliable refinement in this case. Methods for refinement of dynamical intensities have been proposed [11, 4] and will be investigated in the future.

8. Conclusion

The structure of an intermediate form of tin oxide was investigated. The results support a revised version of the layered, vacancy-ordered structure for Sn_3O_4 proposed by Seko [21], summarised in Table 5. The lattice parameters

Table 5. Structural details for the intermediate oxide which are consistent with the observations. The oxygen coordinates are those from the Seko structure; the y -coordinates are marked with parentheses to indicate that they were not directly observed.

Structural Parameters for SnO_{2-x}					
Crystal system	Monoclinic				
Space group	$P2_1/c$				
Lattice parameters	$a =$	$0.80 \pm 0.02 \text{ nm}$			
	$b =$	$0.55 \pm 0.01 \text{ nm}$			
	$c =$	$0.48 \pm 0.01 \text{ nm}$			
	$\beta =$	$95.9^\circ \pm 0.5^\circ$			
Atomic coordinates		x	y	z	
	Sn-1	$2d$	$\frac{1}{2}$	0	$\frac{1}{2}$
	Sn-2	$4e$	0.83	0.50	0.71
	O-1	$4e$	0.73	(0.68)	0.50
	O-2	$4e$	0.40	(0.70)	0.77

were found to be consistent with Seko *et al.*'s proposed monoclinic cell, which is based on a superlattice form of the cassiterite structure. ZOLZ Patterson maps, projected potentials and phases measured from a [001] FOLZ conditional Patterson map all support the proposed modification to the tin coordinates over the unmodified form. The results of kinematical refinement were not satisfactory, although weak features found in the [010] Patterson map were consistent with the oxygen atoms being located very close to the positions proposed by Seko *et al.* The bonding environment of the sixfold coordinated tin atom is unchanged by the proposed revision to the Seko structure.

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