Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

Structures of the ordered double perovskites Sr_2YTaO_6 and Sr_2YNbO_6

Christopher J. Howard,[a,b]* Paris W. Barnes,[c] Brendan J. Kennedy[d] and Patrick M. Woodward[e]

[a]Australian Nuclear Science and Technology Organisation, Private Mail Bag 1, Menai, NSW 2234, Australia, [b]School of Physics, The University of Sydney, Sydney, NSW 2006, Australia, [c]Materials Science Division, Argonne National Laboratory, Argonne, IL 60439, USA, [d]School of Chemistry, The University of Sydney, Sydney, NSW 2006, Australia, and [e]Department of Chemistry, Ohio State University, 100 West 18th Avenue, Columbus, OH 43210-1185, USA

Correspondence e-mail: cjh@ansto.gov.au

Received 11 January 2005
Accepted 20 April 2005

The ordered perovskite Sr_2YTaO_6, distrontium yttrium tantalum hexaoxide, has been reported as showing an unusual triclinic structure, at odds with the results from a recent group-theoretical analysis. A new investigation establishes that Sr_2YTaO_6 and the isostructural Sr_2YNbO_6, distrontium yttrium niobium hexaoxide, in fact both adopt the commonly occurring monoclinic structure, with the space-group symmetry $P2_1/n$.

1. Introduction

In a recent systematic group-theoretical analysis and review of the ordered double perovskites $A_2BB'X_6$ (Howard *et al.*, 2003), it was noted that the triclinic structure of Sr_2YTaO_6 as reported by Woodward (1997) did not conform to the group-theoretical results. Thus, Sr_2YTaO_6 was identified as a compound meriting further investigation. We have undertaken such an investigation and have also examined the isostructural compound Sr_2YNbO_6. This reinvestigation led to a revised structural model, which we report here.

Howard *et al.* (2003) used group-theoretical methods to list the structures arising from the rock-salt ordering of the B and B' cations in combination with the ubiquitous BX_6 (or $B'X_6$) octahedral tilting. There were 12 distinct structures found. Full details, including space-group symmetry, lattice vectors and the origin of the unit cell with respect to that of the simple cubic perovskite, and the pattern of octahedral tilting described using Glazer (1972) notation,[1] have been previously recorded by Howard *et al.* (2003). In considering structures involving both in-phase (Glazer's +) and out-of-phase (−) octahedral tilting, those showing both positive and negative tilting about the same axis (±) were excluded from the list, since in those structures the tilts in successive layers of octahedra would differ in magnitude, in addition to any difference of sign. This selection criterion was used not only in the case of ordered double perovskites (Howard *et al.*, 2003), but in several previous and subsequent group-theoretical analyses of octahedral tilting in perovskites (Howard & Stokes, 1998, 2002; Stokes *et al.*, 2002; Howard *et al.*, 2002; Howard & Zhang, 2004*a*,*b*; Howard & Stokes, 2004). The triclinic structure previously proposed for Sr_2YTaO_6 was assumed to belong to the tilt system $a^+b^-c^-$ (Woodward, 1997). However, this tilt system was not found in the group-theoretical analysis; the

---

[1] This is fully explained in Glazer's paper (Glazer, 1972) and in many subsequent publications (see, for example, Howard *et al.*, 2003, and references cited therein).

closest match being the tilt system $a^{\pm}b^{-}c^{-}$. As a structure exhibiting positive and negative tilting about the same axis, $a^{\pm}b^{-}c^{-}$ was culled from the list. The contradiction between the group-theoretical analysis and the report of $a^{+}b^{-}c^{-}$ tilting in Sr_2YTaO_6 raises some important questions. Is the structure of this compound really unique among ordered double perovskites and if so, why? In the symmetry analysis of distorted perovskites is it valid to discard structures that show both positive and negative tilting about the same axis? The results reported here describe our collection and analysis of new high-resolution neutron and X-ray powder diffraction patterns for the isostructural compound Sr_2YNbO_6 (Barnes, 2003), together with a reanalysis of the X-ray and neutron powder diffraction patterns that were used to make the initial structure assignment for Sr_2YTaO_6 (Woodward, 1997).

2. Experimental

Sr_2YNbO_6 was synthesized by standard high-temperature solid-state methods. The compound was prepared by reacting stoichiometric quantities of $YNbO_4$ and $SrCO_3$ at 1573 K (Barnes, 2003). This route was favoured over the direct reaction of $SrCO_3$, Y_2O_3 and Nb_2O_5 in order to avoid the presence of unreacted Y_2O_3. X-ray powder diffraction patterns from this compound were recorded on image plates using the Debye–Scherrer camera installed on BL-02B2 at SPring-8, Hyogo, Japan (Nishibori *et al.*, 2001). The sample was contained in a 0.2 mm glass capillary and the X-ray wavelength was 0.4973 Å. X-ray patterns were recorded at sample temperatures 100, 150, 200, 250 and 300 K. The 300 K pattern is displayed here in Fig. 1. Room-temperature neutron diffraction data were recorded using the high-resolution powder diffractometer, HRPD, at the ISIS neutron facility, Rutherford Appleton Laboratories, UK (Ibberson *et al.*, 1992). For this experiment the sample was housed in an 11 mm diameter vanadium can. Diffraction patterns were recorded over the time-of-flight range 30–130 ms in both back-scattering and 90° detector banks, corresponding to *d* spacings from 0.6 to 2.6 Å and from 0.9 to 3.7 Å, respectively. The patterns were normalized to the incident beam spectrum as recorded in the upstream monitor and corrected for detector efficiency according to prior calibration with a vanadium scan.

3. Results

The room-temperature X-ray pattern was successfully indexed assuming a monoclinic unit cell with the dimensions a = 5.81174 (5), b = 5.86444 (5), c = 8.24541 (7) Å, β = 90.166 (1)°. There was no suggestion even at the resolution of the synchrotron-based instrument that lower (triclinic) symmetry should be invoked. Indeed the pattern was well fitted using the Rietveld (1969) method, as implemented in the program *RIETICA* (Howard & Hunter, 1998), assuming the commonly occurring $P2_1/n$ monoclinic structure corresponding to the tilt system $a^{-}a^{-}c^{+}$ (Howard *et al.*, 2003). The fit obtained is displayed in Fig. 1. The neutron patterns were quite well fitted with the same structural model (Fig. 2), using the EXP-GUI version of the *GSAS* Rietveld package (Larson & Von Dreele, 2000; Toby, 2001). Details of the room-temperature structure obtained from fitting the neutron data are recorded in Table 1. Visual inspection shows the structure (Fig. 3) to be as expected for the combination of *B*-site cation ordering and $a^{-}a^{-}c^{+}$ octahedral tilting. X-ray patterns recorded at lower temperatures closely resembled the room-temperature pattern, indicating that the structure remains monoclinic with $P2_1/n$ symmetry down to 100 K.

In light of the result that Sr_2YNbO_6 adopts the often observed $a^{-}a^{-}c^{+}$ tilting instead of the more exotic and

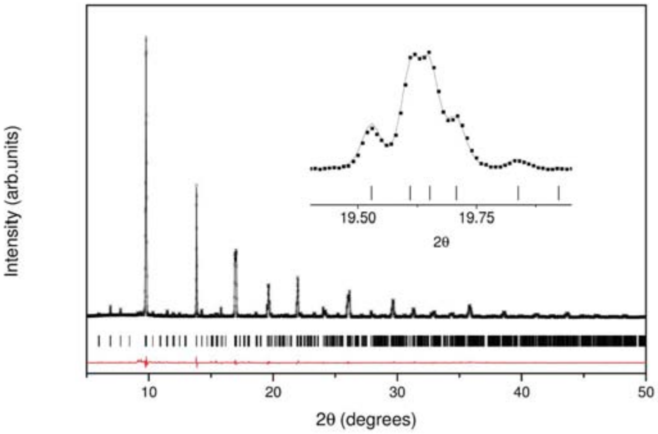

Figure 1
Synchrotron X-ray diffraction pattern (crosses) recorded from Sr_2YNbO_6 at BL-02B2, SPring-8, Japan. The X-ray wavelength was 0.4973 Å. The pattern was fitted (continuous line) assuming a monoclinic structure with $P2_1/n$ space-group symmetry. The markers below the pattern indicate the expected peak positions and the line below these the difference between the observed and calculated patterns. The inset shows detail of the fit at the group of reflections indexing as 440 on the doubled (~ 8.25 Å) perovskite cell.

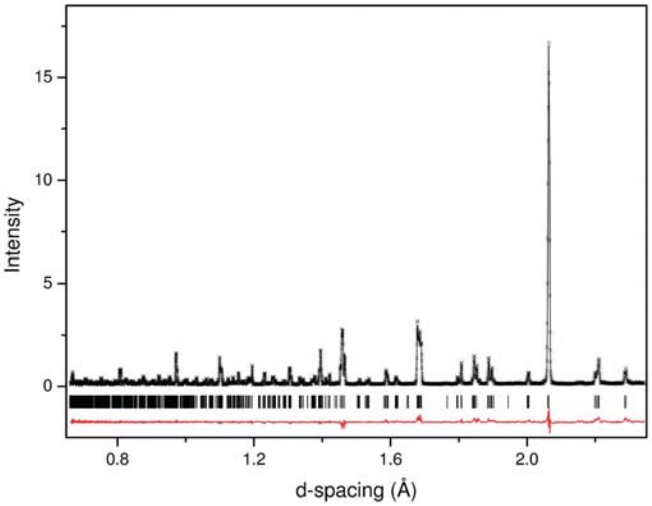

Figure 2
Neutron diffraction pattern recorded from Sr_2YNbO_6 in the back-scattering detector bank of the high-resolution powder diffractometer, HRPD, at the ISIS facility, UK. Again the crosses represent the observed pattern and the continuous line through them the pattern calculated assuming a monoclinic structure with $P2_1/n$ space-group symmetry.

Table 1
The room-temperature structure of Sr_2YNbO_6 as refined from ISIS neutron powder diffraction data.

The unit-cell dimensions are: $a = 5.81174$ (5), $b = 5.86444$ (5), $c = 8.24541$ (7) Å; $\beta = 90.166$ (1)°; space-group symmetry $P2_1/n$. The goodness-of-fit parameters are $\chi^2 = 3.3$, $R_{wp} = 0.065$.

	x	y	z	U_{iso} (Å^2) × 10^2
Sr	−0.0065 (3)	0.4675 (2)	0.2512 (3)	1.66 (3)
Y	0	0	0	1.08 (5)
Nb	0	0	1/2	1.21 (6)
O1	0.0768 (3)	0.0204 (3)	0.2646 (3)	1.65 (4)
O2	0.2266 (3)	0.3030 (4)	−0.0382 (3)	1.51 (6)
O3	0.3054 (3)	0.7736 (4)	−0.0424 (3)	1.73 (6)

Table 2
The room-temperature structure of Sr_2YTaO_6 as refined from constant wavelength neutron powder diffraction data collected at the High Flux Beam Reactor, Brookhaven National Laboratory (Woodward, 1997).

The unit-cell dimensions are: $a = 5.81216$ (5), $b = 5.85937$ (6), $c = 8.24479$ (8) Å; $\beta = 90.1479$ (7)°; space-group symmetry $P2_1/n$. The measures-of-fit are $\chi^2 = 1.03$, $R_{wp} = 0.063$.

	x	y	z	U_{iso} (Å^2) × 10^2
Sr	−0.0060 (3)	0.4705 (2)	0.2497 (3)	0.95 (2)
Y	0	0	0	0.47 (5)
Ta	0	0	1/2	0.05 (5)
O1	0.0752 (3)	0.0196 (3)	0.2635 (3)	0.93 (4)
O2	0.2274 (3)	0.3016 (3)	−0.0384 (2)	0.87 (5)
O3	0.3031 (3)	0.7741 (3)	−0.0412 (2)	0.74 (5)

controversial $a^-b^-c^+$ tilting, we resolved to reinvestigate the structure of Sr_2YTaO_6. The investigation amounted to a reanalysis of the laboratory X-ray diffraction data and the high-resolution neutron powder diffraction data (from the High Flux Beam Reactor, Brookhaven National Laboratory) recorded earlier by Woodward (1997). It soon became apparent that the patterns could be successfully fitted assuming the same structural model as described above for Sr_2YNbO_6. That is the same $P2_1/n$ monoclinic structure, tilt system $a^-a^-c^+$, as tabulated by Howard *et al.* (2003). The crystal structure obtained by refinement (Rietica) from the neutron data is given in Table 2.[2] Note the close correspondence with the values given for Sr_2YNbO_6.

4. Discussion

The most relevant bond distances and angles are given in Table 3, along with the bond-valence sums (Brown, 1978; Brown & Altermatt, 1985) for each atom. The observed values of the bond distances within the octahedra are in good agreement with the values predicted from ionic radii (Shannon, 1976): 1.99 Å for Nb—O, 1.99 Å for Ta—O and 2.25 Å for Y—O. The bond-valence sums show that the coordination environment for strontium and oxygen are perfectly reasonable. For perovskites a further check of the accuracy of the structure can be obtained by examining the O—B—O angles, which should all be reasonably close to 90°. The observed values are all within ±2° of 90°. On all counts the structures appear to be chemically reasonable. This fact combined with the high quality of the fit leaves little doubt that the structures reported here are accurate.

This result raises a practical question. How did it come to pass that Sr_2YTaO_6 was previously incorrectly assigned triclinic symmetry (Woodward, 1997)? A brief analysis of the missteps made in making the incorrect assignment is of practical use for others working in the area of perovskite structure determination. In the same work 12 compounds were reported with $a^-a^-c^+$ tilting and $P2_1/n$ symmetry (Woodward, 1997). It is worth noting that among these 12 the deviation of the monoclinic β angle from 90° was reported to be less than 0.05° in all but two cases, and less than 0.09° in the two outliers (Ca_2FeTaO_6 and Ca_2AlTaO_6). These distortions are considerably smaller than the 90.15° value seen in Sr_2YTaO_6. Such small deviations from 90° are difficult to observe unless one is working with (*a*) very high resolution data and (*b*) samples that show very little intrinsic peak broadening. Thus, Sr_2YTaO_6 exhibits a peak-splitting pattern that can only be fit with a monoclinic unit cell, whereas the other $P2_1/n$ compounds can be fit with a pseudo-orthorhombic unit cell. This fact sets Sr_2YTaO_6 apart from the other $P2_1/n$ perovskites studied. Nonetheless, the reported cell parameters ($a = 5.855$, $b = 5.809$, $c = 8.240$ Å, $\alpha = 89.85$, $\beta = 90.02$, $\gamma = 89.97$°) are quite close to a monoclinic cell and, as shown here, the pattern can be fit with a monoclinic cell. The incorrect assumption of triclinic symmetry was based on the observation that α rather than β is distinctly different from 90°. This apparent contradiction can be easily rectified if the lengths of the a and b axes are inverted, thereby exchanging the values of α and β. Since the values of a and b are quite close to begin with, one might assume that this would naturally happen during the refinement process. This assumption was tested using *GSAS*. It was found that unless the initial value of the a axis was chosen to be smaller than that of the b axis the program became trapped in a local minimum and did not converge to the correct values. The problem of local minima is one that is particularly problematic in many distorted perovskites because of the high degree of pseudo-symmetry that they possess. For perovskites one tool that can be used to avoid this pitfall is the program *SPuDS* (Lufaso & Woodward, 2001), which can be used to generate a starting model for the refinement process. For Sr_2YTaO_6 with $a^-a^-c^+$ tilting *SPuDS* predicts the following unit-cell dimensions: $a = 5.744$, $b = 5.935$, $c = 8.251$ Å and $\beta = 90.03$°. *SPuDS* predicts Ta—O distances of ~ 1.99 Å, Y—O distances of ~ 2.27 Å and Ta—O—Y angles of ~ 151°. These values compare favourably with the values observed (see Table 3). Careful comparison shows that the predicted lengths of the a and b axes are more different than the observed values, and the predicted value of β is closer to 90° than is observed. These minor discrepancies can largely be attributed to small distortions of the octahedra. Bear in mind that *SPuDS* calculates a structure based on the assumption that the octahedra remain regular, whereas Table 3 shows this assumption is not perfectly met. Nonetheless, the fact that $a <$

---

[2] Supplementary data for this paper are available from the IUCr electronic archives (Reference: WS5023). Services for accessing these data are described at the back of the journal.

Table 3
Relevant bond distances, bond angles and bond-valence sums for Sr_2YNbO_6.

	Sr_2YNbO_6	Sr_2YTaO_6
Bond distances (Å)		
Sr—O1	2.520 (2), 2.669 (2)	2.523 (2), 2.686 (2)
Sr—O2	2.553 (3), 2.820 (3), 2.912 (3)	2.542 (3), 2.830 (3), 2.912 (3)
Sr—O3	2.531 (3), 2.822 (3), 2.900 (3)	2.540 (3), 2.824 (3), 2.911 (3)
Y—O1 (×2)	2.229 (2)	2.218 (2)
Y—O2 (×2)	2.235 (2)	2.230 (2)
Y—O3 (×2)	2.245 (2)	2.230 (2)
B′—O1 (×2)	1.996 (2)	2.003 (2)
B′—O2 (×2)	1.989 (2)	2.001 (2)
B′—O3 (×2)	1.993 (2)	1.990 (2)
Bond angles (°)		
O1—Y—O2	88.79 (8)	89.01 (5)
O1—Y—O3	88.39 (8)	88.50 (6)
O2—Y—O3	88.96 (8)	88.85 (7)
O1—*B*′—O2	89.54 (9)	89.27 (6)
O1—*B*′—O3	89.65 (9)	89.60 (6)
O2—*B*′—O3	89.27 (9)	89.26 (8)
Y—O1—*B*′	154.7 (1)	155.2 (1)
Y—O2—*B*′	155.6 (1)	155.8 (1)
Y—O3—*B*′	153.8 (1)	154.5 (1)
Bond-valence sums		
Sr	1.84	1.85
Y	3.34	3.43
B′	4.81	4.86
O1	2.01	2.02
O2	1.97	2.00
O3	1.97	1.98

b and $\beta > 90°$ in the *SPuDS* starting model allows the refinement to quickly proceed to the correct structure. It is also worth noting that $P2_1/n$ structures generated in *SPuDS* always possess β angles very close to 90°. From this we conclude that the deviation of β from 90° can largely be attributed to small, but not insignificant, distortions of the YO_6 octahedron. A search of the ICSD (Inorganic Crystal Structure Database) for double perovskites with $P2_1/n$ symmetry reveals that in general the deviations of β from 90° are somewhat larger (90.1–90.3°) in compounds where at least one of the octahedral cations, such as a rare-earth or an alkaline-earth cation, has a fairly large radius. These types of cations are more prone to tolerate small distortions of their immediate octahedral environment than smaller more highly charged cations. Hence, it is reasonable to expect that such compositions will have a more distinctly monoclinic unit cell, rather than the pseudo-orthorhombic cell that is often observed.

5. Conclusions

The double perovskites Sr_2YTaO_6 and Sr_2YNbO_6 have structures with $P2_1/n$ space-group symmetry, resulting from Y/Ta(Nb) ordering and $a^-a^-c^+$ tilting. This type of distortion is very commonly seen among double perovskites and, furthermore, it is in line with the expectations for compounds with a tolerance factor (Goldschmidt, 1926) of 0.92 (as calculated by *SPuDS*). These compounds do not represent examples of structures with complex ± tilt systems that were rejected in the group theoretical analysis (Howard *et al.*, 2003), so to this extent the practice of discarding such tilt systems is vindicated.

The authors thank Kevin Knight, ISIS facility, for his assistance in collecting the HRPD neutron patterns, and Dr Y. Kubota from Osaka Women's University for help in recording

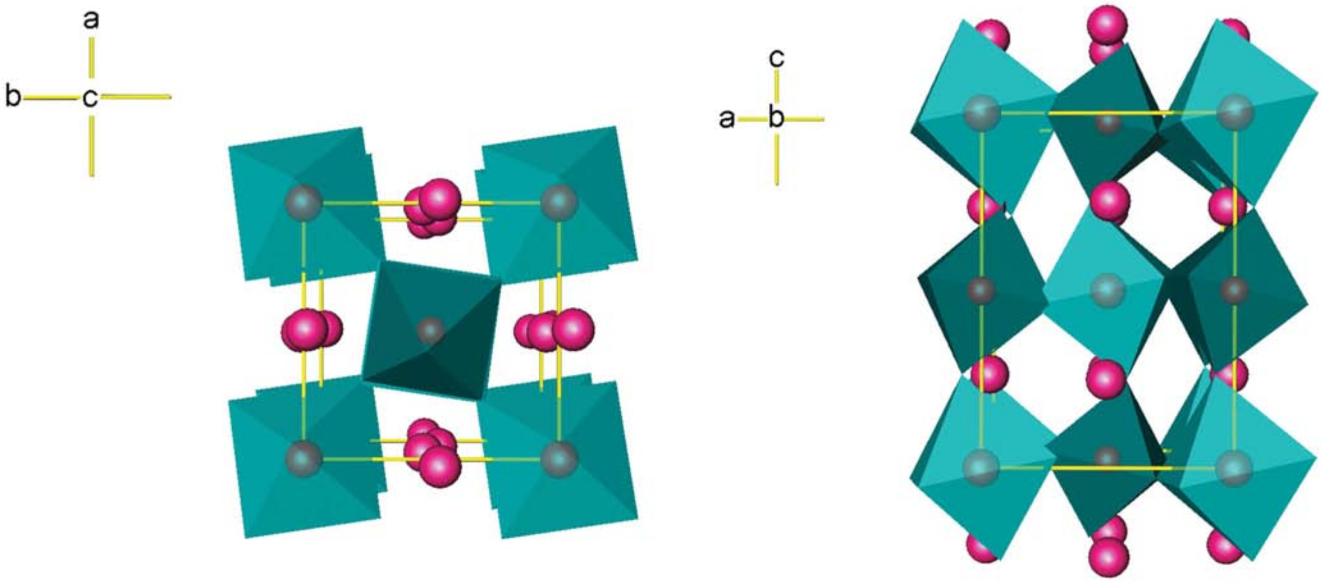

Figure 3
Two views of the structure of Sr_2YNbO_6. YO_6 and NbO_6 are shown as the lighter and darker octahedra, the Y and Nb ions being visible within them, and the Sr ions are located in the cavities. The in-phase tilting is evident in the view down the *c* direction, [001] of the parent perovskite. The equal out-of-phase tilts along the other two directions of the parent structure combine to produce a tilting around the monoclinic *b* axis, corresponding to $[\bar{1}10]$ in the parent structure.

the synchrotron X-ray patterns. The SPring-8 synchrotron facility is supported by JASRI, while the neutron facilities at ISIS are operated by the Council for the Central Laboratory of the Research Councils (CCLRC), with a contribution from the Australian Research Council. Travel funding to ISIS and SPring-8 was provided by the Access to Major Research Facilities Program. The studies of perovskites have been partly supported by the Australian Research Council.

References

Barnes, P. (2003). PhD Thesis. Ohio State University, USA.

Brown, I. D. (1978). *Chem. Soc. Rev.* **7**, 359–376.

Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.

Glazer, A. M. (1972). *Acta Cryst.* B**28**, 3384–3392.

Goldschmidt, V. M. (1926). *Naturwissenschaften*, **14**, 477–485.

Howard, C. J. & Hunter, B. A. (1998). *RIETICA*. Lucas Heights Research Laboratories.

Howard, C. J., Kennedy, B. J. & Woodward, P. M. (2003). *Acta Cryst.* B**59**, 463–471.

Howard, C. J., Luca, V. & Knight, K. S. (2002). *J. Phys. Condens. Matter*, **14**, 377–387.

Howard, C. J. & Stokes, H. T. (1998). *Acta Cryst.* B**54**, 782–789.

Howard, C. J. & Stokes, H. T. (2002). *Acta Cryst.* B**58**, 565.

Howard, C. J. & Stokes, H. T. (2004). *Acta Cryst.* B**60**, 674–684.

Howard, C. J. & Zhang, Z. (2004*a*). *Acta Cryst.* B**60**, 249–251.

Howard, C. J. & Zhang, Z. (2004*b*). *Acta Cryst.* B**60**, 763.

Ibberson, R. M., David, W. I. F. & Knight, K. S. (1992). Report RAL 92-031. Rutherford Appleton Laboratory, UK.

Larson, A. C. & Von Dreele, R. B. (2000) *GSAS*. Report LAUR 86–748. Los Alamos National Laboratory, New Mexico, USA.

Lufaso, M. W. & Woodward, P. M. (2001). *Acta Cryst.* B**57**, 725–738.

Nishibori, E., Takata, M., Kato, K., Sakata, M., Kubota, Y., Aoyagi, S., Kuroiwa, Y., Yamakata, M. & Ikeda, N. (2001). *Nucl. Instrum. Methods A*, **467–468**, 1045–1048.

Rietveld, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.

Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.

Stokes, H. T., Kisi, E. H., Hatch, D. M. & Howard, C. J. (2002). *Acta Cryst.* B**58**, 934–938.

Toby, B. H. (2001). *J. Appl. Cryst.* **34**, 210–213.

Woodward, P. M. (1997). PhD Thesis. Oregon State University, USA.