

Structural characterization of $\text{RE}_{10}\text{W}_{22}\text{O}_{81}$ rare-earth tungstates (RE = Ce, Nd)

Rosemary S. Barker and Ivana Radosavljevic Evans*

Department of Chemistry, Durham University,
Durham DH1 3HP, EnglandCorrespondence e-mail:
ivana.radosavljevic@durham.ac.uk

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The single-crystal diffraction study of $\text{Ce}_{10}\text{W}_{22}\text{O}_{81}$ and powder X-ray diffraction (XRD) experiments on $\text{Ce}_{10}\text{W}_{22}\text{O}_{81}$ and $\text{Nd}_{10}\text{W}_{22}\text{O}_{81}$ show that the true space group of these phases is *Pbnm*, contrary to the previous literature reports of the space groups *Pbcn* and *Pbcm* for the rare-earth tungstates (RE = La, Ce, Pr, Nd) with this general formula. The structure contains rare-earth cations in seven-, eight- and ninefold coordination. W atoms are found in corner-sharing WO_5 groups, and also in WO_6 and WO_7 polyhedra which share edges and corners to form W_6O_{17} units. The new model obtained from our single-crystal work gives better agreement with powder XRD data on both $\text{Ce}_{10}\text{W}_{22}\text{O}_{81}$ and $\text{Nd}_{10}\text{W}_{22}\text{O}_{81}$, and gives more plausible coordination environments and bond-valence sums.

1. Introduction

Four rare-earth tungstates in the $\text{RE}_{10}\text{W}_{22}\text{O}_{81}$ series have been reported in the literature. Compounds of this composition have been prepared for larger rare earths, RE = La, Ce, Pr and Nd. Yoshimura *et al.* (1975) reported the unit-cell dimensions and space group *Pbcn* (space group no. 60 in *International Tables for Crystallography*, 2005, Vol. A) for these four compositions, while Shimazaki *et al.* (1999) prepared the Pr analogue and determined its unit-cell parameters. The first full crystallographic determination of this structure type was performed by Grenthe *et al.* (2001), who studied $\text{Nd}_{10}\text{W}_{22}\text{O}_{81}$ by high-resolution electron microscopy and laboratory powder X-ray diffraction. They solved the structure in the space group *Pbcm* (space group no. 57 in *International Tables for Crystallography*, 2005, Vol. A), contrary to the symmetry reported previously (Yoshimura *et al.*, 1975).

We have grown crystals of $\text{Ce}_{10}\text{W}_{22}\text{O}_{81}$ and determined its structure from single-crystal X-ray diffraction in the space group *Pbnm* (non-standard setting¹ space group 62 in *International Tables for Crystallography*, 2005, Vol. A). Furthermore, our studies show that for both Ce and Nd compounds, this structure gives a better agreement to the powder XRD data than the previous literature model.

2. Experimental

2.1. Sample preparation

Preheated CeO_2 and WO_3 oxides were mixed in a 5:11 stoichiometric ratio in quantities to make *ca* 2 g of the $\text{Ce}_{10}\text{W}_{22}\text{O}_{81}$ product, thoroughly ground and fired overnight at

¹ Standard setting *Pnma*.

Table 1Experimental data for Ce₁₀W₂₂O₈₁.

Crystal data	
Chemical formula	Ce ₁₀ O ₈₁ W ₂₂
<i>M_r</i>	6741.85
Cell setting, space group	Orthorhombic, <i>Pbnm</i>
Temperature (K)	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	3.8891 (4), 36.080 (4), 21.901 (2)
<i>V</i> (Å ³)	3073.1 (5)
<i>Z</i>	2
<i>D_x</i> (Mg m ⁻³)	7.285
Radiation type	Mo <i>K</i> α
<i>μ</i> (mm ⁻¹)	48.34
Crystal form, colour	Elongated prism, brown
Crystal size (mm)	0.08 × 0.02 × 0.02
Data collection	
Diffractometer	Area
Data collection method	<i>ω</i>
Absorption correction	Multi-scan (based on symmetry-related measurements)
<i>T_{min}</i>	0.91
<i>T_{max}</i>	1.00
No. of measured, independent and observed reflections	32 374, 4244, 2524
Criterion for observed reflections	<i>I</i> > 3.0σ(<i>I</i>)
<i>R_{int}</i>	0.044
<i>θ_{max}</i> (°)	29.6
Refinement	
Refinement on	<i>F</i> ²
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.054, 0.101, 0.91
No. of reflections	2524
No. of parameters	166
Weighting scheme	Chebyshev polynomial†
(Δ/ <i>σ</i>) _{max}	0.0006
Δ <i>ρ</i> _{max} , Δ <i>ρ</i> _{min} (e Å ⁻³)	7.28, -7.55

† See Watkin (1994) and Prince (1982); [weight] = 1.0/[*A*₀**T*₀(*x*) + *A*₁**T*₁(*x*)... + *A*_{*n*} - 1]**T*_{*n*} - 1(*x*)], where *A_i* are the Chebyshev coefficients listed below and *x* = *F*/*F*_{max} method = robust weighting (Prince, 1982); *W* = [weight] * [1 - (Δ*F*/6*σ*F*)²]² *A_i* are: 5.48, 8.03, 4.81, 1.83 and 0.648.

1173 K in an evacuated silica tube. The polycrystalline material obtained was subsequently heated to 1323 K, slowly cooled to 873 K at a rate of 3 K h⁻¹ and then furnace-cooled to room temperature. Small crystals were isolated from the product. The same procedure was followed for the synthesis of polycrystalline Nd₁₀W₂₂O₈₁, except that the reaction was carried out at 923 K in an open alumina crucible.

2.2. X-ray diffraction

Single-crystal X-ray diffraction data were collected on a Bruker AXS SMART 6000 diffractometer with a CCD detector, using Mo *K*α radiation. An elongated prism-shaped crystal with the approximate dimensions 0.02 × 0.02 × 0.08 mm³ was selected for data collection. A full sphere of data was collected with a frame width of 0.3° and a counting time of 20 s per frame. Data reduction was carried out using the *SAINTE* software suite (Bruker, 2000). A multiscan absorption correction (Sheldrick, 1998) was applied to the raw data. The crystal structure was solved by direct methods using *SIR92* (Altomare *et al.*, 1994) and refined in the *CRYSTALS* software package (Betteridge *et al.*, 2003). A total of 166 parameters (fractional coordinates, anisotropic atomic

Table 2Average *M*—O bond lengths in Ce₁₀W₂₂O₈₁.

Atom	Coordination No.	<i>d_{av}</i> (Å)
W1	6	1.91
W2	5	1.85
W3	7	1.99
W4	6	1.93
W5	5	1.86
W6	5	1.83
W7	6	1.93
Ce8	9	2.54
Ce9	7	2.46
Ce10	8	2.51

displacement parameters for metals and isotropic for O atoms, an extinction parameter and scale) were refined. Full experimental details are given in Table 1.²

Room-temperature powder XRD data were collected on a Bruker AXS D8 advance diffractometer with a Solex detector, using Cu *K*α radiation. All powder XRD data were analysed using *TOPAS Academic* (Coelho, 2005).

3. Results

3.1. Initial Ce₁₀W₂₂O₈₁ phase identification by powder XRD

The initial attempt to identify the synthesized polycrystalline product as Ce₁₀W₂₂O₈₁ was carried out by fitting our powder XRD pattern recorded on this material to the structural model in the ICSD (Inorganic Crystal Structure Database, 2007) for the analogous Nd compound (space group *Pbcm*). Although there was no doubt about the identity of the material prepared, small discrepancies could be observed in the Rietveld plot (Fig. 1*a*); for example, for several low-angle peaks (below 2θ = 25°, marked with black arrows) very little intensity was calculated. The agreement factor obtained in the Rietveld refinement using the literature Nd₁₀W₂₂O₈₁ model was *R_{wp}* = 0.1302. It should be pointed out that these reflections are predicted by the unit-cell dimensions, as demonstrated by a satisfactory Pawley fit. We have also prepared polycrystalline Nd₁₀W₂₂O₈₁; the same discrepancies observed for Ce₁₀W₂₂O₈₁ exist in the fit to the Nd₁₀W₂₂O₈₁ powder data in the space group *Pbcm* (Fig. 1*b*). We note that similar discrepancies around the same 2θ values can be seen in the published Rietveld plot for Nd₁₀W₂₂O₈₁ (Grenthe *et al.*, 2001). This initial Rietveld analysis therefore suggested that the existing RE₁₀W₂₂O₈₁ structural model is slightly incorrect.

3.2. Crystal structure of Ce₁₀W₂₂O₈₁

Ce₁₀W₂₂O₈₁ crystallizes in the orthorhombic space group *Pbnm* (Table 1), which is a non-standard setting of *Pnma*. The non-standard setting for this space group is used throughout

² Supplementary data for this paper are available from the IUCr electronic archives (Reference: ZB5001). Services for accessing these data are described at the back of the journal.

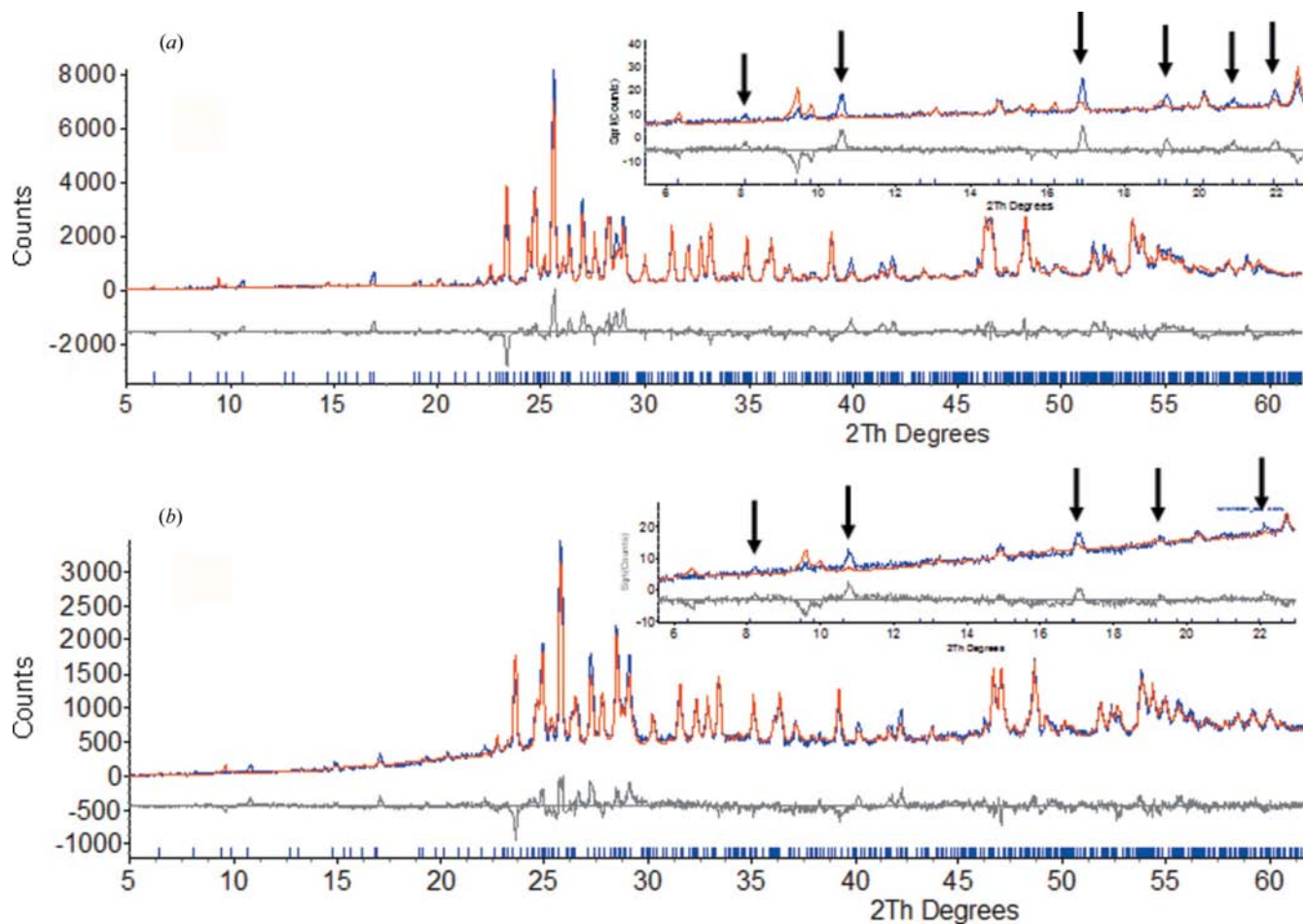


Figure 1 Rietveld plots for: (a) $Ce_{10}W_{22}O_{81}$ and (b) $Nd_{10}W_{22}O_{81}$, based on the published $Nd_{10}W_{22}O_{81}$ structural model in the space group *Pbcm* (Grenthe *et al.*, 2001). Black arrows indicate some of the reflections for which virtually no intensity is calculated in *Pbcm*. Inserts represent low-angle regions of the powder patterns shown on a square-root scale.

for easier direct comparison with the previously published structural model. The asymmetric unit contains three Ce atoms, seven W atoms and 23 O atoms. Both cation types exist in variable coordination environments (Table 2).

The larger Ce atoms are seven-, eight- and nine-coordinate (Fig. 2), with the average bond lengths of 2.54, 2.46 and 2.51 Å for the three unique sites Ce8, Ce9 and Ce10, respectively.

W atoms are found in five-, six- and sevenfold coordination (Table 2), forming WO_5 , WO_6 and WO_7 polyhedra. A polyhedral representation of the $Ce_{10}W_{22}O_{81}$ structure, with the O atoms omitted for clarity, is shown in Fig. 3.

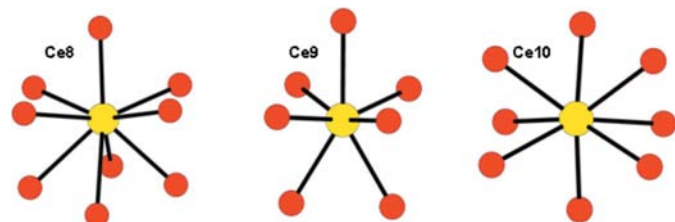


Figure 2 Coordination environment of Ce atoms in $Ce_{10}W_{22}O_{81}$.

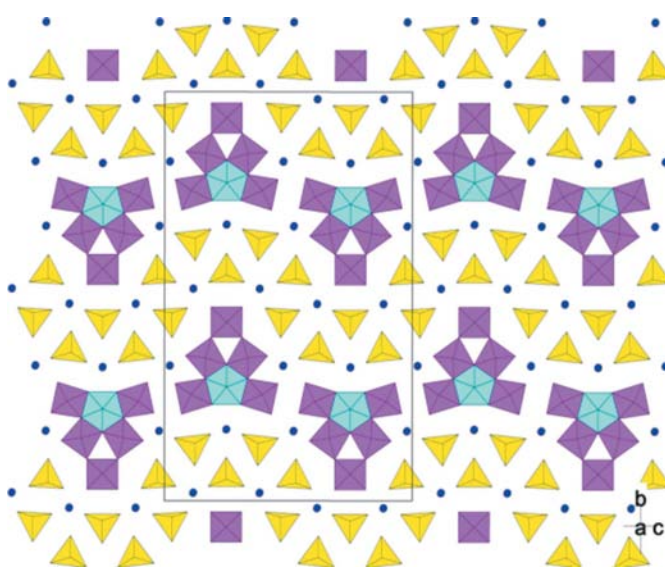


Figure 3 Polyhedral representation of $Ce_{10}W_{22}O_{81}$: Ce – small dark spheres; WO_5 groups – yellow polyhedra; WO_6 groups – pink polyhedra; WO_7 groups – light blue polyhedra.

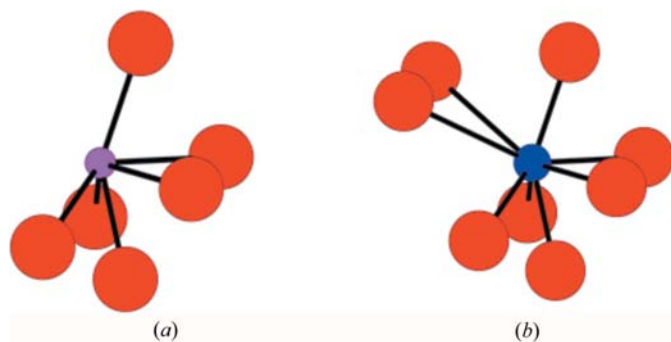


Figure 4
 (a) Coordination environment of the octahedral W5 site in the $\text{Nd}_{10}\text{W}_{22}\text{O}_{81}$ model (Grenthe *et al.*, 2001); (b) a more plausible coordination environment achieved when this site is assigned as Nd.

WO_5 trigonal bipyramids share two corners each with two adjacent WO_5 polyhedra, thus connecting into chains which run along the crystallographic a axis. WO_6 and WO_7 polyhedra form W_6O_{17} units. Each of these units is formed by a central WO_7 polyhedron sharing four of its edges in the equatorial plane with four different WO_6 octahedra; this motif is capped by a fifth WO_6 group *via* two shared corners. W_6O_{17} units link up in the a direction by corner sharing. The short unit-cell

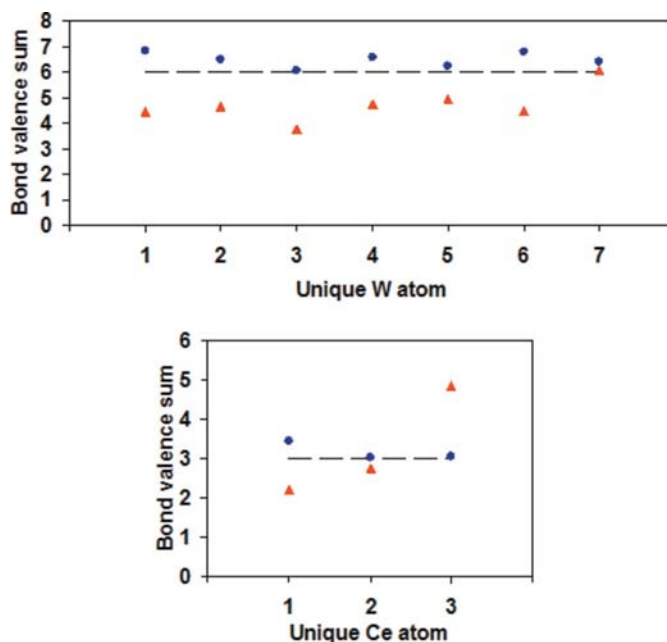


Figure 5
 Bond-valence sums for W and Ce cations in $\text{Ce}_{10}\text{W}_{22}\text{O}_{81}$ based on the structural model in the space groups $Pbnm$ (blue circles) and $Pbcm$ (red triangles). Expected values for each cation are shown in dashed lines.

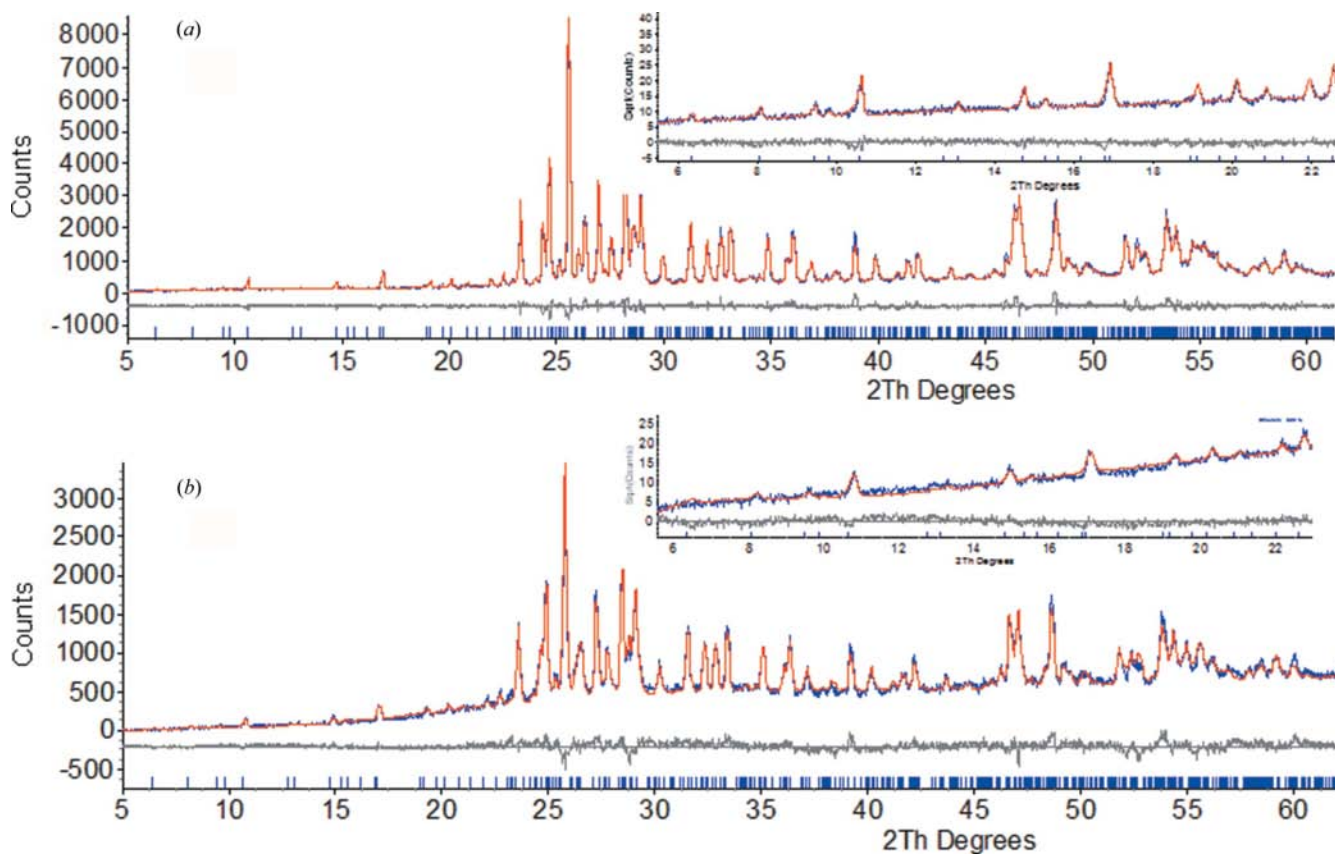


Figure 6
 Rietveld plot for (a) $\text{Ce}_{10}\text{W}_{22}\text{O}_{81}$ and (b) $\text{Nd}_{10}\text{W}_{22}\text{O}_{81}$ using our structural model in space group $Pbnm$, derived from the single-crystal study. Insert represents low-angle regions of the powder patterns shown on a square-root scale.

edge, $a = 3.8891(4) \text{ \AA}$, reflects the thickness of this structural building block.

This arrangement is clearly different from the one containing pentagonal columns, proposed by Grenthe *et al.* (2001). A close comparison of the two models shows that the metal positions in the two are essentially the same. However, on some of the metal sites the cation type seems to have been incorrectly assigned. In addition to the incorrect intensities calculated for some of the reflections in the powder XRD pattern, as seen in the Rietveld plot and discussed above, another suggestion of problematic cation-type assignment is manifested in implausible coordination environments found for some of the sites. For example, the W5 atom is described as octahedral; however, its coordination environment (Fig. 4*a*) does not have a satisfactory octahedral geometry. When this site is assigned a larger Nd cation and its coordination sphere considered accordingly, this atom becomes eight-coordinate with bond lengths between 1.8 and 2.7 Å – a plausible environment for a rare-earth cation (Fig. 4*b*).

Another way to assess the plausibility of a structural model is through calculation of bond-valence sums (Brown & Altermatt, 1985). Plots given in Fig. 5 show the bond-valence sums for Ce and W cations in $\text{Ce}_{10}\text{W}_{22}\text{O}_{81}$, derived from the two structural models considered. Again, the agreement with the expected bond-valence sum values is much better for the space group *Pbnm*.

Finally, in order to characterize bulk $\text{Ce}_{10}\text{W}_{22}\text{O}_{81}$, we have analysed its powder pattern by Rietveld refinement using our single-crystal structural model in the space group *Pbnm*. Much better agreement factors than in *Pbcm* are achieved ($R_{\text{wp}} = 0.0649$, Rietveld plot in Fig. 6*a*, versus $R_{\text{wp}} = 0.1302$ and the plot in Fig. 1). A similar improvement is achieved for the Nd analogue (Fig. 6*b*).

In summary, we present here a new structural model for rare-earth tungstates of the $\text{RE}_{10}\text{W}_{22}\text{O}_{81}$ series. It should be

noted, however, that inorganic oxide structure determination from X-ray powder diffraction and HRTEM – methods used for $\text{Nd}_{10}\text{W}_{22}\text{O}_{81}$ – is far from trivial and that Grenthe *et al.* (2001) commented on these limitations by suggesting that the structure they presented could be used ‘as a good starting point for a more accurate structure determination if single-crystal diffraction data become available in the future’.

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