

## Disordered structure of $\text{ZrW}_{1.8}\text{V}_{0.2}\text{O}_{7.9}$ from a combined X-ray and neutron powder diffraction study at 530 K

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A novel compound, vanadium aliovalent substituted zirconium tungstate,  $\text{ZrW}_{1.8}\text{V}_{0.2}\text{O}_{7.9}$ , was prepared with vanadium substituting tungsten rather than the common zirconium substitution. The structure of the high-temperature phase was refined from combined neutron and X-ray powder diffraction data gathered at 530 K. This phase is the disordered centric modification (space group  $P\bar{a}3$ ) and the average crystal structure is similar to that of  $\beta\text{-ZrW}_2\text{O}_8$ . The V atom occupies only a W2 site and charge compensation is achieved through oxygen vacancy, *i.e.* the oxygen vacancy occurs at only the O4 site. [Atom names follow the established scheme; Evans *et al.* (1996). *Chem. Mater.* **8**, 2809–2823.]

### Comment

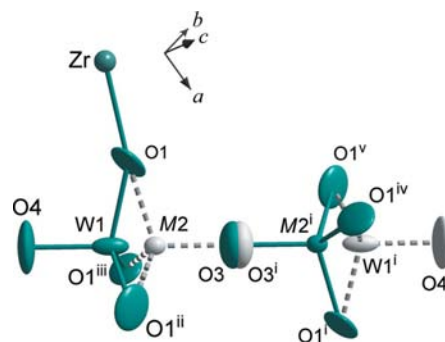
The remarkable observation of isotropic negative thermal expansion (NTE) for cubic  $\text{ZrW}_2\text{O}_8$  was described by Mary *et al.* (1996), who found that an order–disorder phase transition occurs at approximately 440 K. Below this temperature, a secondary bond along the threefold axis of the cubic unit cell links a pair of  $\text{WO}_4$  tetrahedra to form  $\text{W}_2\text{O}_8$  units, in which the W–O<sub>terminal</sub> bond of each  $\text{WO}_4$  unit in a given chain points in the same direction. Above the transition temperature, the structure becomes disordered, with the  $\text{WO}_4$  tetrahedra oriented in two opposite directions with equal probability (Fig. 1). The space group symmetry consequently gains an inversion center on the threefold axis and changes from  $P2_13$  to  $P\bar{a}3$  (Evans *et al.*, 1999).

To improve the material properties of NTE compounds with the cubic  $\text{ZrW}_2\text{O}_8$  structure, solid solutions have been prepared by substituting Zr with lower-valent ions to obtain  $\text{Zr}_{1-x}\text{M}_x\text{W}_2\text{O}_{8-x/2}$  ( $M = \text{Sc}^{3+}, \text{Y}^{3+}, \text{Yb}^{3+}, \text{Er}^{3+}, \text{Eu}^{3+}$  and  $\text{In}^{3+}$ ). Phase transition temperatures for these solid solutions are lower due to local structural features, including the introduc-

tion of local  $\text{WO}_4$  pair orientational disorder (Yamamura *et al.*, 2004, 2007), and an ionic conductivity increase derived from oxygen vacancy defects (Li, Han *et al.*, 2007; Li, Xia *et al.*, 2007). However, the work reported so far has been limited to Zr-site substitution. In the present work, we report the successful preparation of  $\text{ZrW}_{1.8}\text{V}_{0.2}\text{O}_{7.9}$ , an aliovalent tungsten-substituted solid solution. The crystal structure at 530 K was analyzed using Rietveld refinement of combined X-ray diffraction (XRD) and neutron powder diffraction (NPD) data.

The power of X-ray and neutron powder diffraction methods in structural studies of materials is well known. Joint refinement from NPD and XRD data, in addition to simply adding extra data points to the observables, provides two special advantages. Firstly, the neutron scattering length (analogous to the X-ray atomic scattering factor) does not fall off with  $\sin \theta/\lambda$ , significantly enhancing Debye–Waller sensitivity. Secondly, the peak shapes of NPD data are well behaved compared with those obtained using X-rays, giving a smoother refinement. The complementary nature of the two methods has been successfully utilized in the simultaneous determination of structural parameters for both O and heavy atoms (Carrio *et al.*, 2002) in structures in which a large contrast in neutron scattering lengths exists (Rodriguez *et al.*, 2004). NPD was previously used to distinguish V and Cr by Douglas & Anthony (1996); as vanadium is almost transparent to thermal neutrons, the combined XRD and NPD data analysis supplied sufficient information on vanadium to obtain a complete structure characterization.

In the present work, we combine XRD and NPD data to overcome the transparency of vanadium to thermal neutrons and to stabilize the refinement of O-atom structural parameters, especially the oxygen atomic displacement parameters (ADPs). The process began with refinement to preliminary XRD data, which provided nearly full parameter information for vanadium and the heavy atoms. However, the ADPs of the O atoms were not positive definite in this refinement, so the NPD data were included in order to stabilize the oxygen



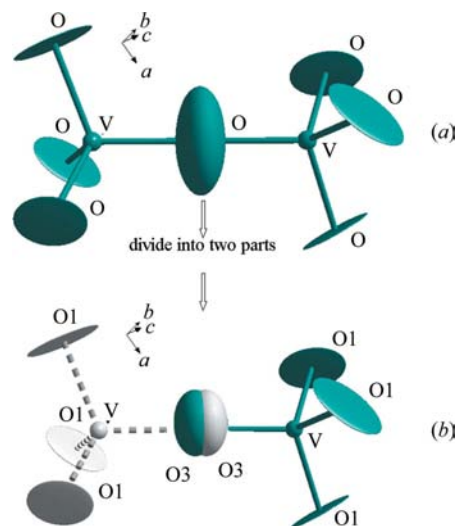
**Figure 1**

The structure of  $\text{ZrW}_{1.8}\text{V}_{0.2}\text{O}_{7.9}$ , which also serves as a schematic representation of the high-temperature disordered structure of  $\beta\text{-ZrW}_2\text{O}_8$ . Displacement ellipsoids are drawn at the 75% probability level. The basic asymmetric unit and its neighbor are dark-colored, while the second disorder group is light gray. Atoms on the threefold axis (W1, M2 and O3) have an occupancy fraction of 0.5, while that of O4 is 0.45. [Symmetry codes: (i)  $1-x, 1-y, 1-z$ ; (ii)  $z, x, y$ ; (iii)  $y, z, x$ ; (iv)  $1-y, 1-z, 1-x$ ; (v)  $1-z, 1-x, 1-y$ .]

ADPs. Although the NPD data have better resolution than the XRD data, in the actual refinement the structural parameters of the heavy atoms show large fluctuations and the  $R(F^2)$  value is large (0.86) when only NPD data are used. Therefore, for this structure and these data, the combination of XRD and NPD data is necessary. Equal weighting was used for both XRD and NPD data so that one type would not dominate the other.

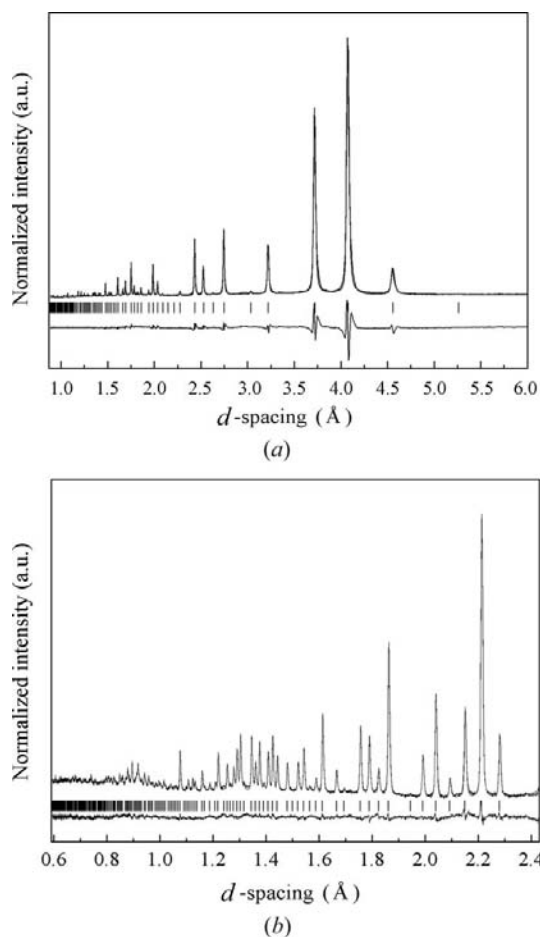
Comparing the structure of  $\beta$ -ZrW<sub>2</sub>O<sub>8</sub> with that of the vanadate ZrV<sub>2</sub>O<sub>7</sub>, we find that both structures contain AO<sub>6</sub> octahedra and MO<sub>4</sub> tetrahedra linked by shared corners only (Evans *et al.*, 1998). The configuration of [VO<sub>3</sub>O<sub>1/2</sub>]<sub>2</sub> in ZrV<sub>2</sub>O<sub>7</sub> (Fig. 2a) is analogous to that of [W<sub>2</sub>(O<sub>1</sub>)<sub>3</sub>O<sub>3</sub>]<sub>2</sub>, except that in the case of the vanadate, a single bridging O atom on the center of symmetry completes the tetrahedral coordination of each V atom, forming a pyrovanadate group, while in  $\beta$ -ZrW<sub>2</sub>O<sub>8</sub>, atoms O3 are terminal, completing the W<sub>2</sub>O<sub>4</sub> tetrahedra (Fig. 1) (Evans *et al.*, 1996). The distance of the O3 atomic site from the symmetry center is 0.011 Å in  $\beta$ -ZrW<sub>2</sub>O<sub>8</sub>, so in interpreting the present structure we assume that what was the O-atom site on the symmetry center in ZrV<sub>2</sub>O<sub>7</sub> is here superposed with the two congeners of O3 from the W-containing structure. (We maintain the name O3 for the combined site; our O3 site is half-occupied.) The structural unit [V(O<sub>1</sub>)<sub>3</sub>O<sub>3</sub>]<sub>2</sub> is comparable in shape with [W<sub>2</sub>(O<sub>1</sub>)<sub>3</sub>O<sub>3</sub>]<sub>2</sub> (Fig. 2b). The disordered average structure for ZrW<sub>1.8</sub>V<sub>0.2</sub>O<sub>7.9</sub> is thus modeled as 0.45 units of W<sub>2</sub>O<sub>8</sub> in either of the centrosymmetrically related positions (black or gray in Fig. 1) and 0.1 units of [V(O<sub>1</sub>)<sub>3</sub>O<sub>3</sub>]<sub>2</sub> (Fig. 2), superimposed on each other to give a composite pattern that could be illustrated by the superposition of the atomic sites represented in Figs. 1 and 2(b). The M2 site is occupied by W and V atoms with a stoichiometric ratio because they have compatible coordination numbers and ionic radii [ $r(W^{6+}) = 0.42$  Å and  $r(V^{5+}) = 0.355$  Å; Shannon, 1976]. The [V(O<sub>1</sub>)<sub>3</sub>O<sub>3</sub>]<sub>2</sub> group substitutes [W<sub>2</sub>(O<sub>1</sub>)<sub>3</sub>O<sub>3</sub>]<sub>2</sub> tetrahedra. The resulting occupancy fractions of the O1 and O3 sites have contributions from the atoms of the [W<sub>2</sub>(O<sub>1</sub>)<sub>3</sub>(O<sub>3</sub>)<sub>2</sub>] and [V(O<sub>1</sub>)<sub>3</sub>O<sub>3</sub>]<sub>2</sub> units (in which the bridging O atom is split into equal parts and equivalent to O3 in the parent ZrW<sub>2</sub>O<sub>8</sub> structure) in addition to the [W<sub>1</sub>(O<sub>1</sub>)<sub>3</sub>]<sub>2</sub> unit, leaving a partial (0.05) O-atom vacancy at each of the O4 sites. The site O3 in the present structure is a superposition of O3 from [W<sub>2</sub>(O<sub>1</sub>)<sub>3</sub>O<sub>3</sub>]<sub>2</sub> and O3 from [V(O<sub>1</sub>)<sub>3</sub>O<sub>3</sub>]<sub>2</sub>. The atomic coordinates of O3 represent a mean position. The results thus describe an average crystal structure of a vanadium aliovalent substituted solid solution ZrW<sub>1.8</sub>V<sub>0.2</sub>O<sub>7.9</sub> with the structure of  $\beta$ -ZrW<sub>2</sub>O<sub>8</sub>, as shown in Fig. 1, where M2 = W/V.

The final refinement plots for the XRD and NPD data are shown in Fig. 3. Total Rietveld refinement residual factors for the combined NPD and XRD data are  $R_p = 0.0385$  and  $wR_p = 0.0577$ , which are comparable with those for ZrW<sub>2</sub>O<sub>8</sub> at 483 K ( $R_p = 0.0431$  and  $wR_p = 0.0569$ ; Evans *et al.*, 1996). The cell parameter [9.11787 (6) Å] of ZrW<sub>1.8</sub>V<sub>0.2</sub>O<sub>7.9</sub> at 530 K is slightly smaller than that of ZrW<sub>2</sub>O<sub>8</sub> at 483 K [9.1371 (5) Å], which is attributed to two factors: (i) the radius of V<sup>5+</sup> is smaller than that of W<sup>6+</sup>, and (ii) V<sup>5+</sup> substituting a W<sup>6+</sup> atom introduces oxygen vacancy defects.



**Figure 2**

(a) A generic representation of the V<sub>2</sub>O<sub>7</sub> unit in the ZrV<sub>2</sub>O<sub>7</sub> structure and (b) its breakdown for structural model building. V<sub>2</sub>O<sub>7</sub> is divided into two equal parts [V(O<sub>1</sub>)<sub>3</sub>O<sub>3</sub>]<sub>2</sub> (denoted with different colors) from part (a) to part (b), in order to be consistent with the [W<sub>2</sub>(O<sub>1</sub>)<sub>3</sub>O<sub>3</sub>]<sub>2</sub> unit in ZrW<sub>2</sub>O<sub>8</sub>. The occupancy fraction of each O3 congener in [V(O<sub>1</sub>)<sub>3</sub>O<sub>3</sub>]<sub>2</sub> is half that of V. Displacement ellipsoids are drawn at the 75% probability level.



**Figure 3**

Fitted (a) X-ray and (b) neutron powder diffractograms for ZrW<sub>1.8</sub>V<sub>0.2</sub>O<sub>7.9</sub>.

The refinement yields structural parameters for  $ZrW_{1.8}V_{0.2}O_{7.9}$ , including ADPs and atomic coordinates, which are similar to those of  $\beta$ - $ZrW_2O_8$  at 483 K (Mary *et al.*, 1996), except that the ADP of atom O4 is slightly smaller than that in the matrix. The distortion indices  $D$  (bond length; Baur, 1974) of the  $W1O_4$  and  $(W2/V)O_4$  tetrahedra are 0.042 and 0.016, respectively, while they are 0.045 and 0.013, respectively, in  $\beta$ - $ZrW_2O_8$ . Thus, V substitution at the W2 site causes little distortion in the crystal structure.

## Experimental

Aqueous solutions of analytical grade  $ZrOCl_2 \cdot 8H_2O$ ,  $(NH_4)_6W_7O_{24} \cdot 6H_2O$  and  $NH_4VO_3 \cdot 6H_2O$  in a 1:1.8:0.2 molar ratio were used as starting materials. They were mixed under continuous stirring for 3 h and then concentrated at about 350 K for 3–5 h to yield a buff-colored powder. After grinding with an agate mortar, the powder was placed in a Teflon container, sealed in a stainless steel autoclave and heated at 473 K for 20 h with 6 M hydrochloric acid (10 ml) as an acidic steam source to prepare the hydrated precursor; this process is called the acidic steam hydrothermal (ASH) route (Guo *et al.*, 2007). The precursor was then heated for 2 h at 873 K and then quenched in air to produce a yellow crystalline powder of the title compound. No notable mass loss occurred for this final sample.

### Crystal data

$ZrW_{1.8}V_{0.2}O_{7.9}$	$V = 758.02 (2) \text{ \AA}^3$
$M_r = 558.73$	$Z = 4$
Cubic, $Pa\bar{3}$	$T = 530 \text{ K}$
$a = 9.11787 (6) \text{ \AA}$	Powder, yellow

### Data collection for XRD data

Philips XPert MPD diffractometer	Cu $K\alpha$ radiation
380 independent reflections	$\lambda = 1.54960 \text{ \AA}$
Specimen shape: flat sheet	$d_{\min} = 0.894 \text{ \AA}$ , $d_{\max} = 5.264 \text{ \AA}$
Specimen mounted in reflection mode	$2\theta_{\min} = 9.909^\circ$ , $2\theta_{\max} = 119.882^\circ$
Scan method: step	Increment in $2\theta = 0.017^\circ$

### Data collection for NPD data

GPPD at IPNS	Scan method: time of flight
627 independent reflections	Neutron radiation
Specimen shape: cylinder	$d_{\min} = 0.595 \text{ \AA}$ , $d_{\max} = 2.279 \text{ \AA}$
Specimen mounted in transmission mode	

### Refinement

$R_p = 0.0385$	Profile function (NPD): pseudo-Voigt
$R_{wp} = 0.0577$	51 parameters
$S = 2.49$	Preferred orientation correction: none
Excluded region(s): none	
Profile function (XRD): pseudo-Voigt	

The coordinates and displacement parameters reported in the supplementary material are the final results of the combined refinement from the XRD and NPD data. For the refinement, the initial structural model was based on the assumptions described in the *Comment*, and the initial cell-dimension and structural parameters were taken from  $\beta$ - $ZrW_2O_8$  (Evans *et al.*, 1996). During the refinement, the atomic coordinates and anisotropic displacement parameters (ADPs) of atoms V2 and W2 were constrained to be the same. The O4 site-occupancy fraction was fixed at 0.45 to maintain charge

neutrality. The occupancy fraction of each O3 position in  $[V(O1)_3O3]_2$  is 0.05. The ADP of O3 was also fixed to the value found for  $\beta$ - $ZrW_2O_8$  (Evans *et al.*, 1996) during the combined refinement of the XRD and NPD data. In all, 21 structural parameters were refined, including a lattice parameter, seven atomic coordinates and 13 ADPs. The conditions in the parallel refinement only using the NPD data (results available in the supplementary material) are the same as those for the combined refinement of the XRD and NPD data, except that the ADP of atom O3 was refined and the atomic coordinate of atom O3 was fixed to the value found for  $\beta$ - $ZrW_2O_8$  (Evans *et al.*, 1996).

Data collection: *GSAS* (Larson & Von Dreele, 2000); cell refinement: *GSAS*; data reduction: *GSAS*; program(s) used to refine structure: *GSAS*; molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *GSAS*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3187). Services for accessing these data are described at the back of the journal.

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