

Cubic $\text{ZrW}_{1.75}\text{Mo}_{0.25}\text{O}_8$ from a Rietveld refinement based on neutron powder diffraction data

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Key indicators: powder neutron study; $T = 298$ K; mean $\sigma(\text{Zr}-\text{O}) = 0.003$ Å; disorder in main residue; R factor = 0.032; wR factor = 0.044; data-to-parameter ratio = 32.6.

The solid solution in the system Zr–Mo–W–O with composition $\text{ZrW}_{1.75}\text{Mo}_{0.25}\text{O}_8$ (zirconium tungsten molybdenum octoxide) was prepared by solid-state reactions as a polycrystalline material. Its structure has cubic symmetry (space group $P2_13$) at room temperature. The structure contains a network of corner-sharing ZrO_6 octahedra (.3. symmetry) and MO_4 ($M = \text{W}, \text{Mo}$) tetrahedra (.3. symmetry). Along the main threefold axis of the cubic unit cell, the MO_4 tetrahedra are arranged in pairs forming $M_2\text{O}_8$ units in which the $M1\text{O}_4$ tetrahedra have larger distortions in terms of bond distances and angles than the $M2\text{O}_4$ tetrahedra. These units are disordered over two possible orientations, with the $M-\text{O}_{\text{terminal}}$ vectors pointing to the $[111]$ or $[\bar{1}\bar{1}\bar{1}]$ directions. The reversal of the orientations of the $M_2\text{O}_8$ units results from the concerted flips of these units. The time-averaged proportions of flipped and unflipped $M_2\text{O}_8$ units were determined and the fraction of unflipped $M_2\text{O}_8$ units is about 0.95. The order degree of the $M_2\text{O}_8$ unit orientation is about 0.9. During the reversal process, the M -atom site has a migration about 0.93 Å, one of the O-atom sites has a 0.25 Å migration distance, whereas two other O-atom sites migrate marginally (≈ 0.08 Å). The results prove the constraint strategy to be a reasonable approach based on the ratcheting mechanism.

Related literature

For a general description of the structures and properties of unsubstituted ZrW_2O_8 , see: Mary *et al.* (1996); Evans *et al.* (1996, 1999). Details on the ratcheting mechanism have been described by Hampson *et al.* (2004, 2005). For the synthesis of the title compound, see: Zhao *et al.* (2007). For a detailed description of polyhedral distortion parameters, see: Baur (1974); Robinson *et al.* (1971). For isomorphism and polymorphism in cubic ZrW_2O_8 type compounds, see: Evans *et al.*

(2000); Lind *et al.* (1998); Huang *et al.* (2005); Deng *et al.* (2008). For their unusual isotropic negative thermal expansion properties, see: Mary *et al.* (1996).

Experimental

Crystal data

$\text{ZrW}_{1.75}\text{Mo}_{0.25}\text{O}_8$
 $M_r = 564.93$
Cubic, $P2_13$
 $a = 9.156880$ (17) Å
 $V = 767.79$ (1) Å³
 $Z = 4$

Time-of-flight radiation
 $\lambda = 0.5\text{--}4.4$ Å
 $T = 298$ K
Specimen shape: cylinder
 $30 \times 10 \times 10$ mm

Data collection

GPPD diffractometer
Specimen mounting: standard cylindrical vanadium sample holder

Scan method: time of flight
 $2\theta_{\text{min}} = 53$, $2\theta_{\text{max}} = 145^\circ$

Refinement

$R_p = 0.032$
 $R_{wp} = 0.044$

1893 reflections
58 parameters

Table 1

Selected geometric parameters (Å, °).

Zr1—O1 ⁱ	2.0384 (21)	M1—O4	1.7105 (32)
Zr1—O2 ⁱⁱ	2.0915 (20)	M1—M2-1	0.9294 (23)
Zr1—O1-1 ⁱⁱⁱ	2.0261 (21)	M2—O2	1.7933 (16)
Zr1—O2-1 ⁱ	2.1037 (19)	M2—O3	1.729 (4)
M1—O1	1.8069 (18)	O1—O2-1	0.084 (4)
M1—O3	2.405 (4)	O3—O3-1	0.254 (7)
O1—M1—O1 ⁱⁱⁱ	115.82 (6)	O2—M2—O2 ⁱⁱⁱ	109.66 (9)
O1—M1—O4	101.96 (9)	O2—M2—O3	109.28 (9)

$M = \text{Mo}, \text{W}$. Symmetry codes: (i) $-z + \frac{1}{2}, -x, y - \frac{1}{2}$; (ii) $-z + \frac{1}{2}, -x + 1, y - \frac{1}{2}$; (iii) z, x, y .

Data collection: IPNS local software (Worlton *et al.*, 2006); cell refinement: GSAS (Larson & von Dreele (2000)); data reduction: IPNS local software; program(s) used to solve structure: GSAS; program(s) used to refine structure: GSAS; molecular graphics: VICS-II (Izumi & Dilanian, 2005); software used to prepare material for publication: GSAS.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2222).

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supplementary materials

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Cubic $\text{ZrW}_{1.75}\text{Mo}_{0.25}\text{O}_8$ from a Rietveld refinement based on neutron powder diffraction data

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Comment

Cubic ZrW_2O_8 type compounds have been attracting considerable interests due to their unusual isotropic negative thermal expansion properties (Mary *et al.*, 1996). Many research groups have been studying isomorphism and polymorphism behaviors of this family (Evans *et al.*, 2000; Deng *et al.*, 2008; Huang *et al.*, 2005; Lind *et al.*, 1998), to investigate the structure-property relationships in detail, and to explore procedures for improving the properties of such materials. By means of Mo atoms partially substituting W atoms to form a cubic solid solution of the type $\text{ZrW}_{2-x}\text{Mo}_x\text{O}_8$, we were able to extend the thermal stability range of cubic ZrW_2O_8 type compounds. Recently, we have reported the high-temperature synthesis of the solid solution $\text{ZrW}_{2-x}\text{Mo}_x\text{O}_8$ series (Zhao *et al.*, 2007), and found that the order-disorder phase transition temperature (T_{tr}) and the order degree of the $\text{ZrW}_{2-x}\text{Mo}_x\text{O}_8$ series decrease with the increase of the Mo concentration. According to the X-ray diffraction patterns, these compounds ($x < 0.9$) adopt the ordered α - ZrW_2O_8 structure at room temperature. However, the detailed average crystal structures are not reported.

In this paper, we describe the synthesis of cubic $\text{ZrW}_{1.75}\text{Mo}_{0.25}\text{O}_8$ and the average crystal structure as determined from neutron powder diffraction data using the Rietveld method. The crystal structure is presented in Fig. 1 and plot of the Rietveld refinement is shown in Fig. 2.

The structure of $\text{ZrW}_{1.75}\text{Mo}_{0.25}\text{O}_8$ contains a network of corner-sharing ZrO_6 octahedra and MO_4 tetrahedra. Each octahedron shares all six corners with six separate MO_4 tetrahedra, but each MO_4 tetrahedron shares only three of its four oxygen corners with adjacent octahedra. In other words, each MO_4 tetrahedron has a 'terminal' oxygen atom. Along the main 3-fold axis of the cubic unit cell, the MO_4 tetrahedra are arranged in pairs forming condensed M_2O_8 units. The 'terminal' O atom of each MO_4 tetrahedron points in the same direction in the M_2O_8 unit, leading to an O4-M1...O3-M2 arrangement (Fig. 3). The M -O_{terminal} bond lengths are significantly shorter than the other M -O bond lengths. The second nearest M atom to terminal O4 atom lies at a distance of about 3.6 Å, so O4 atom is strictly one-coordinate. However, the distance to the terminal O3 atom is about 2.4 Å, indicating that it has one short and one long bond to the M atom. The existence of some interaction between M1 and the terminal O3 atom of the adjacent M_2O_4 tetrahedron is proved by larger distortions in terms of bond angles and distances of M_1O_4 tetrahedra than that of M_2O_4 tetrahedra. The values of the bond length distortion index D (Baur, 1974), 0.02028, and of the bond angle variance σ^2 (Robinson *et al.*, 1971), 58.12 °², of M_1O_4 tetrahedra are both larger than that of M_2O_4 tetrahedra in which D is 0.01355 and σ^2 is 0.0445. Moreover, the O1—O3 distance of 2.69 Å is shorter than all other O—O distances, indicating there is a weak repulsive interaction between these two atoms. This is supported by bond angle values; O1—M1—O1 is larger than O2—M2—O2 and O1—M1—O4 is smaller than O2—M2—O3.

Based on the structure model of α - ZrW_2O_8 (Evans *et al.*, 1996, 1999), some special conditions were constrained to match the 'ratcheting mechanism' described by Hampson *et al.* (2004, 2005) that considers the static (averaged) crystal structure determined by X-ray diffraction and the NMR observation of oxygen dynamics. The refinement results indicate that before

supplementary materials

and after the reversal process, the M atom site has a migration about a 0.93 Å, the O3 atom site has a 0.25 Å migration, whereas the O1/O2 atom site migrate only a little (0.08 Å). The time-averaged proportion of flipped and unflipped M_2O_8 units was determined. The fraction of unflipped M_2O_8 units is about 0.95 and the order degree (defined as $2f-1$, in which f is the site occupancy value of the unflipped part) is about 0.9.

Experimental

Cubic $ZrW_{1.75}Mo_{0.25}O_8$ was prepared using a similar procedure described previously (Zhao *et al.*, 2007). Analytical-grade reagents $ZrOCl_2 \cdot 8H_2O$, $(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were dissolved in water and the solutions of Zr(IV) and Mo(VI) were simultaneously dropped into the slurry of the W(VI) compound to obtain a white precipitate. The precipitate was dried together with the mother liquor at 373 K and subsequently ground in an agate mortar to obtain a homogeneous powder. Then the powder was sintered at 873 K for 3 h. and then pressed into a pellet under a pressure of 4 MPa. Then the pellet was again sintered at 1403 K for 1 h and then quenched to room temperature to yield cubic $ZrW_{1.7}Mo_{0.3}O_8$. During the sintering process, the weight loss of this sample, which is attributed to the volatility of MoO_3 , is 1.4 wt %, so the exact formula is $ZrW_{1.75}Mo_{0.25}O_8$. The trace of ZrO_2 as an impurity in the powder is undetectable by neutron diffraction.

Refinement

The starting structure model for refinement is based on the crystal structure of α - ZrW_2O_8 (Evans *et al.* 1999). The schematic representation of the starting structure model is shown in Fig. 3. During the refinement sets of constraints of structure parameters were used to match the 'ratcheting mechanism' (Hampson *et al.*, 2004, 2005). The W sites of the original model are statistically occupied by W and Mo atoms (denoted with M). The corresponding atomic coordinates of flipped and unflipped M_2O_8 units are set to be centrosymmetric through the imaginary inversion center of the unit cell. The corresponding anisotropic atomic displacement parameters are constrained to be equal for each site. The initial occupancy fractions of the original atomic sites were set to 1 (the occupancy fraction sum of $M1$ and $M2$ were set to unity) while those of the derived atomic sites were set to 0. During the refinement process, the occupancy fraction of the atoms as a parameter in either unflipped or flipped part is constrained to maintain the chemical composition. Two histograms (bank 1 and bank 5) of data from GPPD were used in the refinement. The given reliability factors (see Tables) are the result of the combined refinement based on bank 1 and bank 5 data.

Figures

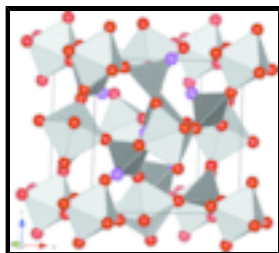


Fig. 1. Polyhedral representation of cubic $ZrW_{1.75}Mo_{0.25}O_8$. ZrO_6 octahedra and MO_4 tetrahedra are shown as light-gray and dark-gray polyhedra. The bridging oxygen atoms and the terminal oxygen atoms are shown as red and pink balls, respectively. For clarity, the atoms related to the flipped part are removed from the figure.

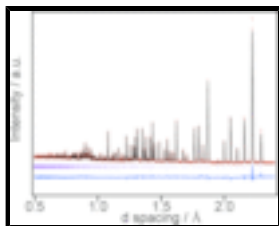


Fig. 2. Final Rietveld refinement neutron powder data plot and difference plot for cubic $\text{ZrW}_{1.75}\text{Mo}_{0.25}\text{O}_8$. The crosses are the observed data, the solid line is the calculated pattern, and the tick marks indicate the calculated reflection positions. The difference curve is plotted below. Only the 145° bank data is shown.

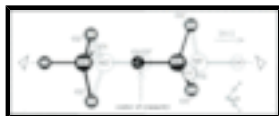


Fig. 3. The schematic representation of the starting structural model for cubic $\text{ZrW}_{1.75}\text{Mo}_{0.25}\text{O}_8$. Black balls and circles represent 'unflipped' and 'flipped' atoms, respectively.

Zirconium tungsten molybdenum octaoxide

Crystal data

$\text{ZrW}_{1.75}\text{Mo}_{0.25}\text{O}_8$	$V = 767.790(4) \text{ \AA}^3$
$M_r = 564.93$	$Z = 4$
Cubic, $P2_13$	$D_x = 4.887 \text{ Mg m}^{-3}$
$a = 9.156880(17) \text{ \AA}$	Time-of-flight radiation
$b = 9.156880(17) \text{ \AA}$	$\lambda = 0.5\text{-}4.4 \text{ \AA}$
$c = 9.156880(17) \text{ \AA}$	$T = 298 \text{ K}$
$\alpha = 90^\circ$	Specimen shape: cylinder
$\beta = 90^\circ$	$30 \times 10 \times 10 \text{ mm}$
$\gamma = 90^\circ$	white

Data collection

GPPD diffractometer	Scan method: time of flight
Specimen mounting: standard cylindrical vanadium sample holder	$T = 298 \text{ K}$

Refinement

Least-squares matrix: full	55 constraints
$R_p = 0.032$?
$R_{wp} = 0.044$	$(\Delta/\sigma)_{\max} = 0.02$
$S = 1.53$	Extinction coefficient: ?
58 parameters	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Zr1	0.00068 (14)	0.00068 (14)	0.00068 (14)	0.01044	
W1	0.34038 (14)	0.34038 (14)	0.34038 (14)	0.01449	0.8339 (22)
W2	0.60102 (13)	0.60102 (13)	0.60102 (13)	0.01048	0.8339 (22)
O1	0.20648 (18)	0.4373 (2)	0.4482 (2)	0.02634	0.9530 (26)

supplementary materials

O2	0.78912 (16)	0.5691 (2)	0.55685 (18)	0.01893	0.9530 (26)
O3	0.4920 (2)	0.4920 (2)	0.4920 (2)	0.02679	0.9530 (26)
O4	0.23253 (13)	0.23253 (13)	0.23253 (13)	0.03851	0.9530 (26)
Mo1	0.34038 (14)	0.34038 (14)	0.34038 (14)	0.01449	0.11913 (32)
Mo2	0.60102 (13)	0.60102 (13)	0.60102 (13)	0.01048	0.11913 (32)
W1-1	0.65963 (14)	0.65963 (14)	0.65963 (14)	0.01449	0.0411 (22)
W2-1	0.39898 (13)	0.39898 (13)	0.39898 (13)	0.01048	0.0411 (22)
Mo1-1	0.65963 (14)	0.65963 (14)	0.65963 (14)	0.01449	0.00587 (32)
Mo2-1	0.39898 (13)	0.39898 (13)	0.39898 (13)	0.01048	0.00587 (32)
O3-1	0.5080 (2)	0.5080 (2)	0.5080 (2)	0.02679	0.0470 (26)
O4-1	0.76747 (13)	0.76747 (13)	0.76747 (13)	0.03851	0.0470 (26)
O1-1	0.79352 (18)	0.5627 (2)	0.5518 (2)	0.02634	0.0470 (26)
O2-1	0.21088 (16)	0.4309 (2)	0.44315 (18)	0.01893	0.0470 (26)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zr1	0.0104 (2)	0.0104 (2)	0.0104 (2)	-0.0002 (3)	-0.0002 (3)	-0.0002 (3)
W1	0.0145 (5)	0.0145 (5)	0.0145 (5)	0.0080 (6)	0.0080 (6)	0.0080 (6)
W2	0.0105 (5)	0.0105 (5)	0.0105 (5)	0.0006 (4)	0.0006 (4)	0.0006 (4)
O1	0.0198 (9)	0.0272 (12)	0.0320 (11)	0.0083 (8)	0.0142 (8)	-0.0013 (8)
O2	0.0054 (7)	0.0272 (10)	0.0242 (10)	0.0057 (6)	0.0016 (7)	0.0058 (7)
O3	0.0268 (5)	0.0268 (5)	0.0268 (5)	-0.0090 (6)	-0.0090 (6)	-0.0090 (6)
O4	0.0385 (6)	0.0385 (6)	0.0385 (6)	-0.0119 (6)	-0.0119 (6)	-0.0119 (6)
Mo1	0.0145 (5)	0.0145 (5)	0.0145 (5)	0.0080 (6)	0.0080 (6)	0.0080 (6)
Mo2	0.0105 (5)	0.0105 (5)	0.0105 (5)	0.0006 (4)	0.0006 (4)	0.0006 (4)
W1-1	0.0145 (5)	0.0145 (5)	0.0145 (5)	0.0080 (6)	0.0080 (6)	0.0080 (6)
W2-1	0.0105 (5)	0.0105 (5)	0.0105 (5)	0.0006 (4)	0.0006 (4)	0.0006 (4)
Mo1-1	0.0145 (5)	0.0145 (5)	0.0145 (5)	0.0080 (6)	0.0080 (6)	0.0080 (6)
Mo2-1	0.0105 (5)	0.0105 (5)	0.0105 (5)	0.0006 (4)	0.0006 (4)	0.0006 (4)
O3-1	0.0268 (5)	0.0268 (5)	0.0268 (5)	-0.0090 (6)	-0.0090 (6)	-0.0090 (6)
O4-1	0.0385 (6)	0.0385 (6)	0.0385 (6)	-0.0119 (6)	-0.0119 (6)	-0.0119 (6)
O1-1	0.0198 (9)	0.0272 (12)	0.0320 (11)	0.0083 (8)	0.0142 (8)	-0.0013 (8)
O2-1	0.0054 (7)	0.0272 (10)	0.0242 (10)	0.0057 (6)	0.0016 (7)	0.0058 (7)

Geometric parameters (\AA , $^\circ$)

Zr1—O1 ⁱ	2.0384 (21)	O3—M2	1.729 (4)
Zr1—O1 ⁱⁱ	2.0384 (21)	O3—M1-1	2.659 (4)
Zr1—O1 ⁱⁱⁱ	2.0384 (21)	O3—M2-1	1.475 (4)
Zr1—O2 ^{iv}	2.0915 (20)	O3—O3-1	0.254 (7)
Zr1—O2 ^v	2.0915 (20)	O4—M1	1.7105 (32)
Zr1—O2 ^{vi}	2.0915 (20)	O4—M2-1	2.6400 (29)
Zr1—O1-1 ^{iv}	2.0261 (21)	M1-1—M2	0.9295 (23)
Zr1—O1-1 ^v	2.0261 (21)	M1-1—O2	1.7261 (18)
Zr1—O1-1 ^{vi}	2.0261 (21)	M1-1—O2 ^{vii}	1.7261 (18)
Zr1—O2-1 ⁱ	2.1037 (19)	M1-1—O2 ^{viii}	1.7261 (18)

Zr1—O2-1 ⁱⁱ	2.1037 (19)	M1-1—O3	2.659 (4)
Zr1—O2-1 ⁱⁱⁱ	2.1037 (19)	M1-1—O3-1	2.405 (4)
M1—O1	1.8069 (18)	M1-1—O4-1	1.7105 (32)
M1—O1 ^{vii}	1.8069 (18)	M1-1—O1-1	1.8069 (18)
M1—O1 ^{viii}	1.8069 (18)	M1-1—O1-1 ^{vii}	1.8069 (18)
M1—O3	2.405 (4)	M1-1—O1-1 ^{viii}	1.8069 (18)
M1—O4	1.7105 (32)	M2-1—M1	0.9294 (23)
M1—M2-1	0.9294 (23)	M2-1—M2	3.204 (4)
M1—O3-1	2.659 (4)	M2-1—O1	1.8528 (18)
M1—O2-1	1.7260 (18)	M2-1—O1 ^{vii}	1.8528 (18)
M1—O2-1 ^{vii}	1.7260 (18)	M2-1—O1 ^{viii}	1.8528 (18)
M1—O2-1 ^{viii}	1.7260 (18)	M2-1—O3	1.475 (4)
M2—O2	1.7933 (16)	M2-1—O4	2.6400 (29)
M2—O2 ^{vii}	1.7933 (16)	M2-1—O3-1	1.729 (4)
M2—O2 ^{viii}	1.7933 (16)	M2-1—O2-1	1.7933 (16)
M2—O3	1.729 (4)	M2-1—O2-1 ^{vii}	1.7933 (16)
M2—M1-1	0.9295 (23)	M2-1—O2-1 ^{viii}	1.7933 (16)
M2—M2-1	3.204 (4)	O3-1—M1	2.659 (4)
M2—O3-1	1.475 (4)	O3-1—M2	1.475 (4)
M2—O4-1	2.6399 (29)	O3-1—O3	0.254 (7)
M2—O1-1	1.8528 (18)	O3-1—M1-1	2.405 (4)
M2—O1-1 ^{vii}	1.8528 (18)	O3-1—M2-1	1.729 (4)
M2—O1-1 ^{viii}	1.8528 (18)	O4-1—M2	2.6399 (29)
O1—Zr1 ^{ix}	2.0384 (21)	O4-1—M1-1	1.7105 (32)
O1—M1	1.8069 (18)	O1-1—Zr1 ^x	2.0261 (21)
O1—M2-1	1.8528 (18)	O1-1—M2	1.8528 (18)
O1—O2-1	0.084 (4)	O1-1—O2	0.084 (4)
O2—Zr1 ^x	2.0915 (20)	O1-1—M1-1	1.8069 (18)
O2—M2	1.7933 (16)	O2-1—Zr1 ^{ix}	2.1037 (19)
O2—M1-1	1.7261 (18)	O2-1—M1	1.7260 (18)
O2—O1-1	0.084 (4)	O2-1—O1	0.084 (4)
O3—M1	2.405 (4)	O2-1—M2-1	1.7933 (16)
O1 ⁱ —Zr1—O1 ⁱⁱ	90.82 (10)	O2 ^{viii} —M2—O3	109.28 (9)
O1 ⁱ —Zr1—O1 ⁱⁱⁱ	90.82 (10)	O2 ^{viii} —M2—M1-1	70.72 (9)
O1 ⁱ —Zr1—O2 ^{iv}	178.37 (10)	O2 ^{viii} —M2—O3-1	109.28 (9)
O1 ⁱ —Zr1—O2 ^v	87.64 (8)	O2 ^{viii} —M2—O1-1	110.24 (11)
O1 ⁱ —Zr1—O2 ^{vi}	89.74 (8)	O2 ^{viii} —M2—O1-1 ^{vii}	110.90 (10)
O1 ⁱ —Zr1—O1-1 ^{iv}	179.4968 (9)	O2 ^{viii} —M2—O1-1 ^{viii}	1.88 (12)
O1 ⁱ —Zr1—O1-1 ^v	88.83 (7)	O3—M2—M1-1	180.0
O1 ⁱ —Zr1—O1-1 ^{vi}	88.83 (7)	O3—M2—O1-1	107.43 (8)
O1 ⁱ —Zr1—O2-1 ⁱⁱ	92.01 (12)	O3—M2—O1-1 ^{vii}	107.43 (8)
O1 ⁱ —Zr1—O2-1 ⁱⁱⁱ	89.92 (10)	O3—M2—O1-1 ^{viii}	107.43 (8)
O1 ⁱⁱ —Zr1—O1 ⁱⁱⁱ	90.82 (10)	M1-1—M2—O3-1	180.0

supplementary materials

O1 ⁱⁱ —Zr1—O2 ^{iv}	89.74 (8)	M1-1—M2—O1-1	72.57 (8)
O1 ⁱⁱ —Zr1—O2 ^v	178.37 (10)	M1-1—M2—O1-1 ^{vii}	72.57 (8)
O1 ⁱⁱ —Zr1—O2 ^{vi}	87.64 (8)	M1-1—M2—O1-1 ^{viii}	72.57 (8)
O1 ⁱⁱ —Zr1—O1-1 ^{iv}	88.83 (7)	O3-1—M2—O1-1	107.43 (8)
O1 ⁱⁱ —Zr1—O1-1 ^v	179.4968 (9)	O3-1—M2—O1-1 ^{vii}	107.43 (8)
O1 ⁱⁱ —Zr1—O1-1 ^{vi}	88.83 (7)	O3-1—M2—O1-1 ^{viii}	107.43 (8)
O1 ⁱⁱ —Zr1—O2-1 ⁱ	89.92 (10)	O1-1—M2—O1-1 ^{vii}	111.43 (8)
O1 ⁱⁱ —Zr1—O2-1 ⁱⁱⁱ	92.01 (12)	O1-1—M2—O1-1 ^{viii}	111.43 (8)
O1 ⁱⁱⁱ —Zr1—O2 ^{iv}	87.64 (8)	O1-1 ^{vii} —M2—O1-1 ^{viii}	111.43 (8)
O1 ⁱⁱⁱ —Zr1—O2 ^v	89.74 (8)	Zr1 ^{ix} —O1—M1	153.75 (12)
O1 ⁱⁱⁱ —Zr1—O2 ^{vi}	178.37 (10)	Zr1 ^{ix} —O1—M2-1	174.36 (12)
O1 ⁱⁱⁱ —Zr1—O1-1 ^{iv}	88.83 (7)	Zr1 ^{ix} —O1—O2-1	139.9 (22)
O1 ⁱⁱⁱ —Zr1—O1-1 ^v	88.83 (7)	M1—O1—M2-1	29.39 (8)
O1 ⁱⁱⁱ —Zr1—O1-1 ^{vi}	179.4984 (9)	M2-1—O1—O2-1	44.3 (21)
O1 ⁱⁱⁱ —Zr1—O2-1 ⁱ	92.01 (12)	Zr1 ^x —O2—M2	171.71 (13)
O1 ⁱⁱⁱ —Zr1—O2-1 ⁱⁱ	89.92 (10)	Zr1 ^x —O2—M1-1	155.98 (13)
O2 ^{iv} —Zr1—O2 ^v	91.81 (10)	M2—O2—O1-1	133.9 (22)
O2 ^{iv} —Zr1—O2 ^{vi}	91.81 (10)	M2—O2—M1-1	30.55 (8)
O2 ^{iv} —Zr1—O1-1 ^v	90.60 (12)	M1-1—O2—O1-1	162.9 (23)
O2 ^{iv} —Zr1—O1-1 ^{vi}	92.72 (10)	M2—O3—M2-1	179.972
O2 ^{iv} —Zr1—O2-1 ⁱ	179.5134 (9)	M2-1—O3—O3-1	179.972
O2 ^{iv} —Zr1—O2-1 ⁱⁱ	88.52 (6)	M2—M1-1—O2	78.73 (10)
O2 ^{iv} —Zr1—O2-1 ⁱⁱⁱ	88.53 (6)	M2—M1-1—O2 ^{vii}	78.73 (10)
O2 ^v —Zr1—O2 ^{vi}	91.81 (10)	M2—M1-1—O2 ^{viii}	78.73 (10)
O2 ^v —Zr1—O1-1 ^{iv}	92.72 (10)	M2—M1-1—O4-1	179.972
O2 ^v —Zr1—O1-1 ^{vi}	90.60 (12)	M2—M1-1—O1-1	78.04 (9)
O2 ^v —Zr1—O2-1 ⁱ	88.53 (6)	M2—M1-1—O1-1 ^{vii}	78.04 (9)
O2 ^v —Zr1—O2-1 ⁱⁱ	179.5134 (9)	M2—M1-1—O1-1 ^{viii}	78.04 (9)
O2 ^v —Zr1—O2-1 ⁱⁱⁱ	88.52 (6)	O2—M1-1—O2 ^{vii}	116.27 (6)
O2 ^{vi} —Zr1—O1-1 ^{iv}	90.60 (12)	O2—M1-1—O2 ^{viii}	116.27 (6)
O2 ^{vi} —Zr1—O1-1 ^v	92.72 (10)	O2—M1-1—O4-1	101.27 (10)
O2 ^{vi} —Zr1—O2-1 ⁱ	88.52 (6)	O2—M1-1—O1-1 ^{vii}	115.68 (10)
O2 ^{vi} —Zr1—O2-1 ⁱⁱ	88.53 (6)	O2—M1-1—O1-1 ^{viii}	116.42 (11)
O2 ^{vi} —Zr1—O2-1 ⁱⁱⁱ	179.5122 (9)	O2 ^{vii} —M1-1—O2 ^{viii}	116.27 (6)
O1-1 ^{iv} —Zr1—O1-1 ^v	91.52 (10)	O2 ^{vii} —M1-1—O4-1	101.27 (10)
O1-1 ^{iv} —Zr1—O1-1 ^{vi}	91.52 (10)	O2 ^{vii} —M1-1—O1-1	116.42 (11)
O1-1 ^{iv} —Zr1—O2-1 ⁱ	178.51 (10)	O2 ^{vii} —M1-1—O1-1 ^{viii}	115.68 (10)
O1-1 ^{iv} —Zr1—O2-1 ⁱⁱ	87.63 (8)	O2 ^{viii} —M1-1—O4-1	101.27 (10)
O1-1 ^{iv} —Zr1—O2-1 ⁱⁱⁱ	89.73 (9)	O2 ^{viii} —M1-1—O1-1	115.68 (10)
O1-1 ^v —Zr1—O1-1 ^{vi}	91.52 (10)	O2 ^{viii} —M1-1—O1-1 ^{vii}	116.42 (11)
O1-1 ^v —Zr1—O2-1 ⁱ	89.73 (9)	O4-1—M1-1—O1-1	101.96 (9)

O1-1 ^v —Zr1—O2-1 ⁱⁱ	178.51 (10)	O4-1—M1-1—O1-1 ^{vii}	101.96 (9)
O1-1 ^v —Zr1—O2-1 ⁱⁱⁱ	87.63 (8)	O4-1—M1-1—O1-1 ^{viii}	101.96 (9)
O1-1 ^{vi} —Zr1—O2-1 ⁱ	87.63 (8)	O1-1—M1-1—O1-1 ^{vii}	115.82 (6)
O1-1 ^{vi} —Zr1—O2-1 ⁱⁱ	89.73 (9)	O1-1—M1-1—O1-1 ^{viii}	115.82 (6)
O1-1 ^{vi} —Zr1—O2-1 ⁱⁱⁱ	178.51 (10)	O1-1 ^{vii} —M1-1—O1-1 ^{viii}	115.82 (6)
O2-1 ⁱ —Zr1—O2-1 ⁱⁱ	91.13 (9)	M1—M2-1—O1	72.57 (8)
O2-1 ⁱ —Zr1—O2-1 ⁱⁱⁱ	91.13 (9)	M1—M2-1—O1 ^{vii}	72.57 (8)
O2-1 ⁱⁱ —Zr1—O2-1 ⁱⁱⁱ	91.13 (9)	M1—M2-1—O1 ^{viii}	72.57 (8)
O1—M1—O1 ^{vii}	115.82 (6)	M1—M2-1—O3	179.9802
O1—M1—O1 ^{viii}	115.82 (6)	M1—M2-1—O3-1	179.972
O1—M1—O4	101.96 (9)	M1—M2-1—O2-1	70.72 (9)
O1—M1—M2-1	78.04 (9)	M1—M2-1—O2-1 ^{vii}	70.72 (9)
O1—M1—O2-1 ^{vii}	116.42 (11)	M1—M2-1—O2-1 ^{viii}	70.72 (9)
O1—M1—O2-1 ^{viii}	115.68 (10)	O1—M2-1—O1 ^{vii}	111.43 (8)
O1 ^{vii} —M1—O1 ^{viii}	115.82 (6)	O1—M2-1—O1 ^{viii}	111.43 (8)
O1 ^{vii} —M1—O4	101.96 (9)	O1—M2-1—O3	107.43 (8)
O1 ^{vii} —M1—M2-1	78.04 (9)	O1—M2-1—O3-1	107.43 (8)
O1 ^{vii} —M1—O2-1	115.68 (10)	O1—M2-1—O2-1 ^{vii}	110.90 (10)
O1 ^{vii} —M1—O2-1 ^{viii}	116.42 (11)	O1—M2-1—O2-1 ^{viii}	110.24 (11)
O1 ^{viii} —M1—O4	101.96 (9)	O1 ^{vii} —M2-1—O1 ^{viii}	111.43 (8)
O1 ^{viii} —M1—M2-1	78.04 (9)	O1 ^{vii} —M2-1—O3	107.43 (8)
O1 ^{viii} —M1—O2-1	116.42 (11)	O1 ^{vii} —M2-1—O3-1	107.43 (8)
O1 ^{viii} —M1—O2-1 ^{vii}	115.68 (10)	O1 ^{vii} —M2-1—O2-1	110.24 (11)
O4—M1—M2-1	179.9802	O1 ^{vii} —M2-1—O2-1 ^{viii}	110.90 (10)
O4—M1—O2-1	101.27 (10)	O1 ^{viii} —M2-1—O3	107.43 (8)
O4—M1—O2-1 ^{vii}	101.27 (10)	O1 ^{viii} —M2-1—O3-1	107.43 (8)
O4—M1—O2-1 ^{viii}	101.27 (10)	O1 ^{viii} —M2-1—O2-1	110.90 (10)
M2-1—M1—O2-1	78.73 (10)	O1 ^{viii} —M2-1—O2-1 ^{vii}	110.24 (11)
M2-1—M1—O2-1 ^{vii}	78.73 (10)	O3—M2-1—O2-1	109.28 (9)
M2-1—M1—O2-1 ^{viii}	78.73 (10)	O3—M2-1—O2-1 ^{vii}	109.28 (9)
O2-1—M1—O2-1 ^{vii}	116.28 (6)	O3—M2-1—O2-1 ^{viii}	109.28 (9)
O2-1—M1—O2-1 ^{viii}	116.28 (6)	O3-1—M2-1—O2-1	109.28 (9)
O2-1 ^{vii} —M1—O2-1 ^{viii}	116.28 (6)	O3-1—M2-1—O2-1 ^{vii}	109.28 (9)
O2—M2—O2 ^{vii}	109.66 (9)	O3-1—M2-1—O2-1 ^{viii}	109.28 (9)
O2—M2—O2 ^{viii}	109.66 (9)	O2-1—M2-1—O2-1 ^{vii}	109.66 (9)
O2—M2—O3	109.28 (9)	O2-1—M2-1—O2-1 ^{viii}	109.66 (9)
O2—M2—M1-1	70.72 (9)	O2-1 ^{vii} —M2-1—O2-1 ^{viii}	109.66 (9)
O2—M2—O3-1	109.28 (9)	M2—O3-1—O3	179.972
O2—M2—O1-1 ^{vii}	110.24 (11)	M2—O3-1—M2-1	179.972
O2—M2—O1-1 ^{viii}	110.90 (10)	Zr1 ^x —O1-1—M2	174.64 (11)
O2 ^{vii} —M2—O2 ^{viii}	109.66 (9)	Zr1 ^x —O1-1—O2	140.0 (22)

supplementary materials

O2 ^{vii} —M2—O3	109.28 (9)	Zr1 ^x —O1-1—M1-1	153.95 (13)
O2 ^{vii} —M2—M1-1	70.72 (9)	Zr1 ^{ix} —O2-1—M1	155.76 (13)
O2 ^{vii} —M2—O3-1	109.28 (9)	Zr1 ^{ix} —O2-1—M2-1	171.56 (13)
O2 ^{vii} —M2—O1-1	110.90 (10)	M1—O2-1—O1	162.9 (23)
O2 ^{vii} —M2—O1-1 ^{viii}	110.24 (11)	O1—O2-1—M2-1	133.9 (22)

Symmetry codes: (i) $-z+1/2, -x, y-1/2$; (ii) $y-1/2, -z+1/2, -x$; (iii) $-x, y-1/2, -z+1/2$; (iv) $-z+1/2, -x+1, y-1/2$; (v) $y-1/2, -z+1/2, -x+1$; (vi) $-x+1, y-1/2, -z+1/2$; (vii) z, x, y ; (viii) y, z, x ; (ix) $-z, x+1/2, -y+1/2$; (x) $-z+1, x+1/2, -y+1/2$.

Fig. 1

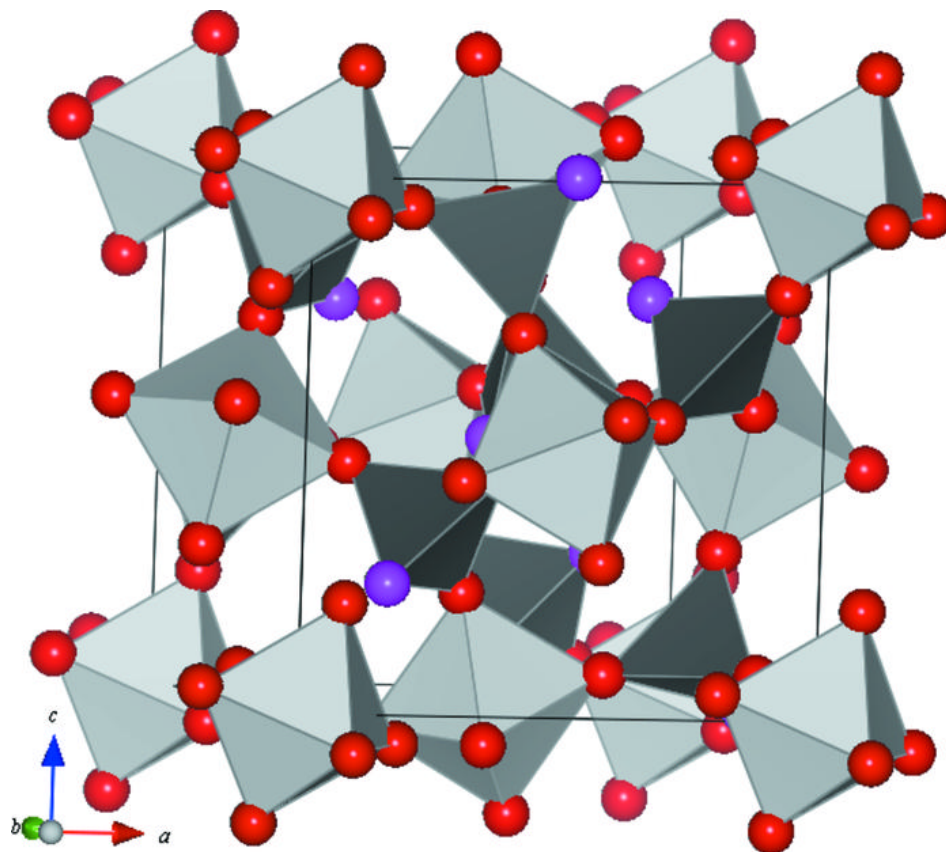


Fig. 2

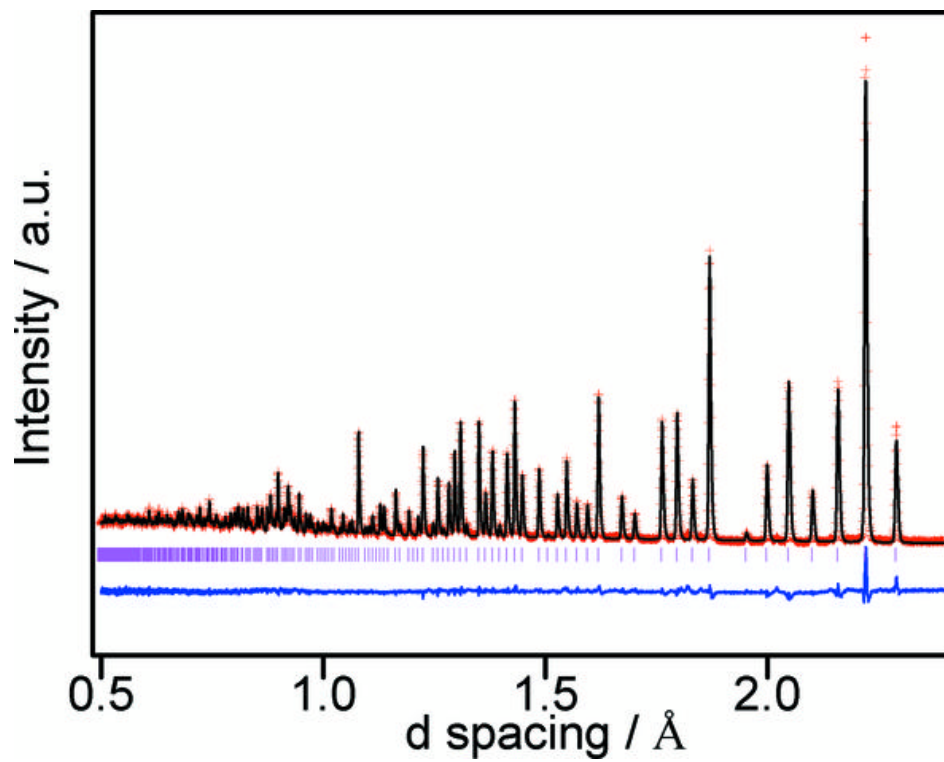


Fig. 3

