

On the symmetry of wulfenite (Pb[MoO₄]) from Mežica (Slovenia)

Ildikó Cora,^{a*} Mátyás Czugler,^b István Dódoný^a and
Aleksander Rečnik^c

^aDepartment of Mineralogy, Eötvös Loránd University, Pázmány P. stny. 1/c, 1117 Budapest, Hungary, ^bInstitute of Structural Chemistry, Chemical Research Center, Hungarian Academy of Sciences, Pusztaszeri út 59–67, 1025 Budapest, Hungary, and ^cDepartment for Nanostructured Materials, Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia
Correspondence e-mail: coraildiko@gmail.com

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Wulfenite [lead(II) molybdate(VI)] is known as a scheelite structure in the $I4_1/a$ space group. The structure of the unusual ‘hemimorphic’ wulfenite crystals from the Mežica mine was refined in the noncentrosymmetric space group $\bar{I}\bar{4}$ using a Pb/Mo exchange disorder model with the approximate composition $\text{Pb}_{0.94}\text{Mo}_{0.06}[\text{MoO}_4]$. Pb atoms in the $2b$ positions are substituted by Mo at about 12%. The crystal is shown to be twinned by inversion. Hemimorphism may result from the short-range chemical ordering of the metal atoms at the $2b$ positions.

Comment

The mineral wulfenite ($\text{Pb}[\text{MoO}_4]$) is a member of the scheelite group of minerals with the general formula ABO_4 , where the most abundant cations in the A and B positions are Ca, Sr, Ba and Pb, and Mo and W, respectively. Structure determinations for scheelite using single-crystal X-ray and neutron diffraction techniques indicated the $I4_1/a$ space group (Zalkin & Templeton, 1964; Kay *et al.*, 1964). Gürmen *et al.* (1971) studied the structure of scheelite-type minerals, such as SrMoO_4 , SrWO_4 , CaMoO_4 and BaWO_4 , using neutron diffraction refinement and compared their O-atom positions. Arakcheeva & Chapuis (2008) gave a comprehensive study of scheelite-like structures with both commensurate and incommensurate modulations in the site occupations and with substitutions along the $\langle uv0 \rangle$ directions.

The first isotropic (Leciejewicz, 1965; neutron diffraction study) and anisotropic (Lugli *et al.*, 1999; X-ray diffraction data) structure refinements of wulfenite from various localities resulted in the same symmetry. Recently, Hibbs *et al.* (2000) studied ‘hemihedral’ (with polar symmetry along the c axis) tungstenian wulfenite crystals ($\text{Pb}[\text{Mo}_{0.64}\text{W}_{0.36}\text{O}_4]$) from Chillagoe (Australia) and found different W–Mo distributions over the $2a$ and $2c$ tetrahedral positions, responsible for the

reduced $\bar{I}\bar{4}$ symmetry. Hemihedrism was interpreted as a result of ordered substitution of Mo by W. Their conclusion may be subject to debate, since the difference in the R values resulting from isotropic structure refinement in the space group $I4_1/a$ ($R = 0.040$) and from anisotropic refinement in the space group $\bar{I}\bar{4}$ ($R = 0.038$) is not very significant.

Hurlbut (1955) first described two types of unusual ‘hemimorphic’ wulfenite crystals from the Mežica mine (Slovenia) showing two habits: (i) pyramidal crystals indicating polar character on the $[001]$ axis; and (ii) tabular crystals twinned on $\{00\bar{1}\}$. Based on their morphology and on etch and piezoelectric tests, he suggested that wulfenite from the Mežica mine crystallizes with tetragonal–pyramidal (4) symmetry. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) microdiffraction studies of these hemimorphic wulfenites from the Doroteja locality in the Mežica mine imply $I4$ (acentric tetragonal–pyramidal) symmetry (Zavašnik *et al.*, 2010). As a result of this lower symmetry, Rečnik (2010) explained a new law of basal inversion twinning, the so-called Doroteja Law, macroscopically observable in wulfenite crystals from this locality. These hemimorphic wulfenite crystals are the subject of this work.

Most of the previous structural studies indicated the space group $I4_1/a$ for wulfenite. In contrast, many intense reflections in our data set violate the extinction rules of this symmetry, *e.g.* for $00l$ the $l = 2n$ (with l values up to ± 22) reflections, and several $hk0$ reflections ($h, k \neq 2n$), are evident. Experimentally, only the I -centring is proven ($h + k + l = 2n$). The space groups $I4$, $I4/m$, $\bar{I}\bar{4}$, $Imm2$, $I4/mmm$ and $I2/m$ were checked in structure refinements, as well as $I4_1/a$. Except for $\bar{I}\bar{4}$, the best R values resulting from the refinements in the above space groups converged to only about $R = 0.07$ – 0.08 .

In the $\bar{I}\bar{4}$ space group, racemic twinning by merohedry was indicated as early as the isotropic refinement stage. The

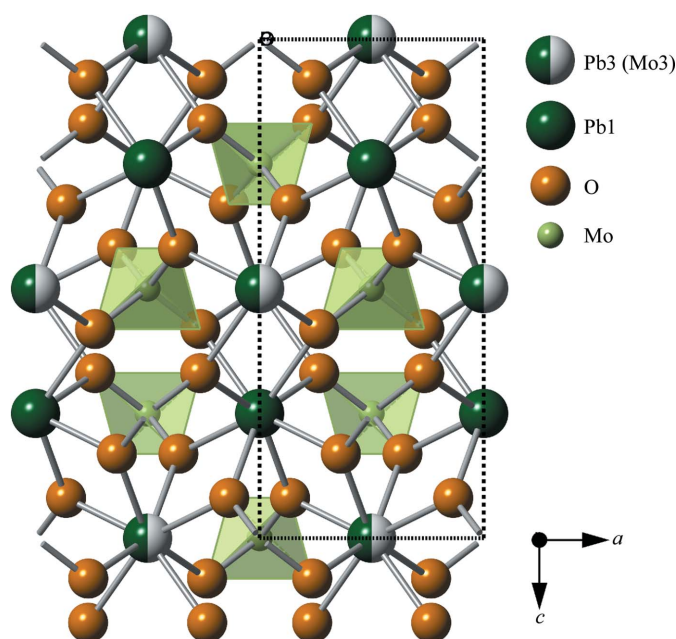


Figure 1
Polyhedral representation of Mežica wulfenite, projected along the b axis.

volume ratio of the twinned pair refined to 0.50 (6). The Pb and Mo cations were both allocated to two Wyckoff sites (Table 1). The Pb sites at the 2*b* positions proved to be substituted by ~12% Mo, which corresponds to the composition Pb_{0.94}Mo_{0.06}[MoO₄]. The final anisotropic refinement converged to acceptably low *R* values for 30 parameters and no restraints. The resulting Pb:Mo ratio is within the range of the quantified energy-dispersive X-ray spectroscopy (EDS) data, the considered uncertainties and the different sample volumes. Final atomic parameters are listed in Table 1.

Besides the explanation of Pb/Mo substitution, the difference between the occupancy of the 2*b* and 2*d* Pb positions (and the potentially minor difference between the 2*a* and 2*c* Mo positions) could also be regarded as vacancies, which would also be in line with the Pb > Mo content observed from the EDS analyses. However, our X-ray model refinement, based on Pb/Mo substitution at the 2*b* site, resulted in consistently lower *R*, *wR*² and *S* values (by about 0.005–0.01%) and also in lower residual densities at the metal sites.

Relevant bond distances for both *I*4₁/*a* Monte Cengio wulfenite (Lugli *et al.*, 1999) and $\bar{I}4$ Mežica wulfenite are listed for comparison in Table 2. Although the degree of freedom in the space group $\bar{I}4$ is higher than that in *I*4₁/*a*, the corresponding atomic distances and bond angles in the MoO₄ and PbO₈ groups in both the Mežica wulfenite and wulfenites with *I*4₁/*a* symmetry are identical within the known s.u. criteria. The hemimorphism of the Mežica wulfenite (*cf.* Fig. 1) may be interpreted as a result of ordering.

Experimental

A small single-crystal chip was carefully selected as a good scattering sample for experiments at *T* = 294 K. EDS analyses were measured on 100–200 nm sized wulfenite crystals using a Technai G² X-Twin 200 kV analytical TEM. Besides Pb and Mo, the O content was also measured. The measured Pb:Mo ratios were close to 1 [atoms per formula unit (apfu) for Pb = 0.98 (4)]. These values are consistent with the ~12% substitution in the 2*b* Pb site. A slight correlation was observed between the resolution of the data and the refined substitution at the 2*b* Pb site (at 0.6 Å resolution the substitution at the 2*b* site is ~4%, while at 0.83 Å resolution it is ~12%). Such virtual resolution dependence of the composition might be easily interpreted in terms of the clearly deficient scattering model at a higher than usual (0.6 Å) resolution. Here, the dominant scattering of the core electrons and the use of spherical scattering factors yield an

Table 1

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Pb1	2 <i>d</i>	0.5000	0.0000	0.2500	0.0213 (13)
Mo1	2 <i>c</i>	0.0000	0.5000	0.2500	0.018 (3)
Mo2	2 <i>a</i>	0.0000	0.0000	0.0000	0.022 (4)
Pb3†	2 <i>b</i>	0.5000	0.5000	0.0000	0.025 (2)
Mo3‡	2 <i>b</i>	0.5000	0.5000	0.0000	0.025 (2)
O1	8 <i>g</i>	0.2344 (13)	−0.1372 (14)	0.0806 (6)	0.0302 (17)
O2	8 <i>g</i>	0.2338 (14)	0.3648 (14)	0.1697 (6)	0.0307 (17)

† Occupancy = 0.881 (8). ‡ Occupancy = 0.119 (8).

Table 2

Pb—O and Mo—O bond lengths (Å).

	This work	Lugli <i>et al.</i> (1999)
Pb1—O1	2.619 (7)	2.611 (3)
Pb1—O2	2.643 (8)	2.636 (3)
Mo2—O1	1.772 (7)	1.769 (3)
Pb3—O2	2.620 (7)	2.611 (3)
Pb3—O1 [†]	2.635 (8)	2.636 (3)
Mo1—O2	1.763 (8)	1.769 (3)

Symmetry code: (i) *x*, *y* + 1, *z*.

over-weighted spherical scattering model. The disorder-dependent smearing of the electron densities, as well as the deformation density due to valence and higher-orbital electron densities, thus logically provide somewhat lower populations than at a lower (0.83 Å) resolution.

Finally, we note that this model describes a twinned and disordered crystal using a discrete substitution site. This disorder model itself is only an approximation, as other Wyckoff sites might also contain minute contamination of, for example, chalcogenide elements.

Crystal data

Pb _{0.94} Mo _{0.06} [MoO ₄]	<i>Z</i> = 4
<i>M_r</i> = 360.42	Mo <i>K</i> α radiation
Tetragonal, $\bar{I}4$	<i>μ</i> = 47.59 mm ^{−1}
<i>a</i> = 5.442 (1) Å	<i>T</i> = 294 K
<i>c</i> = 12.1177 (14) Å	0.10 × 0.10 × 0.05 mm
<i>V</i> = 358.87 (5) Å ³	

Data collection

Rigaku R-AXIS RAPID diffractometer	6322 measured reflections
Absorption correction: numerical (<i>NUMABS</i> ; Higashi, 2002)	335 independent reflections
<i>T</i> _{min} = 0.064, <i>T</i> _{max} = 0.336	333 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.120

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.025	Δρ _{max} = 0.71 e Å ^{−3}
<i>wR</i> (<i>F</i> ²) = 0.061	Δρ _{min} = −0.86 e Å ^{−3}
<i>S</i> = 1.16	Absolute structure: Flack (1983),
335 reflections	with 156 Friedel pairs
30 parameters	Flack parameter: 0.50 (6)

Racemic twinning was indicated during the isotropic refinement and the volume ratio of the twin pairs was refined to 0.50 (6). All atoms were treated anisotropically. An extinction parameter was also refined, and an occupancy constraint was applied for the 2*b* site.

Data collection: *CrystalClear* (Rigaku, 2008); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KU3043). Services for accessing these data are described at the back of the journal.

References

- Arakcheeva, A. & Chapuis, G. (2008). *Acta Cryst.* **B64**, 12–25.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Gürmen, E., Daniels, E. & King, J. S. (1971). *J. Chem. Phys.* **55**, 1093–1097.
- Hibbs, D. E., Jury, C. M., Leverett, P., Plimer, I. R. & Williams, P. A. (2000). *Mineral. Mag.* **64**, 1057–1062.
- Higashi, T. (2002). *NUMABS*. Rigaku Corporation, Tokyo, Japan.
- Hurlbut, C. S. (1955). *Am. Mineral.* **40**, 857–860.
- Kay, M. I., Frazer, B. C. & Almodovar, I. (1964). *J. Chem. Phys.* **40**, 504.
- Leciejewicz, J. (1965). *Z. Kristallogr.* **121**, 158–164.
- Lugli, C., Medici, L. & Saccardo, D. (1999). *Neues Jahrb. Mineral. Monatsh.* **6**, 281–288.
- Rečnik, A. (2010). In *Minerals of the Lead and Zinc Ore Deposit Mežica*. Ljubljana: Bode Vlg.
- Rigaku (2008). *CrystalStructure*. Rigaku Corporation, The Woodlands, Texas, USA.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Zalkin, A. & Templeton, D. H. (1964). *J. Chem. Phys.* **40**, 501–504.
- Zavašnik, J., Rečnik, A., Samardžija, Z., Meden, A. & Đódoný, I. (2010). *Acta Mineral. Petrogr. Abstr. Ser.* **6**, 727.