

The wulfenite–stolzite series: centric or acentric structures?

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ABSTRACT

Three natural crystals of the wulfenite (PbMoO₄)–stolzite (PbWO₄) series were investigated by single-crystal X-ray diffraction. The results indicate that the symmetry is $I4_1/a$ from nearly pure wulfenite to intermediate compositions, in contrast to previous work which claimed a symmetry change to $\bar{I}4$ symmetry (acentric) for intermediate compositions compared with $I4_1/a$ (centric space group) for the end-members. The results reported here show that the reflections violating $I4_1/a$ symmetry observed in this work and in a previous study are related primarily to $\lambda/2$ effects, even if Renninger effects are not excluded. Consequently, we find that the $I4_1/a$ symmetry is retained throughout the wulfenite–stolzite series.

KEYWORDS: wulfenite, stolzite, single-crystal, X-ray diffraction.

Introduction

It is well known that acentric crystals show technologically important properties such as piezoelectricity and pyroelectricity. Therefore, testing the presence or the absence of a centre of symmetry is essential for determining the technological potential of a material. A recent structural study of the wulfenite (Wu, PbMoO₄)–stolzite (St, PbWO₄) join, Hibbs *et al.*, (2000) concluded that intermediate compositions have $\bar{I}4$ symmetry and are, therefore, acentric and contrasting with the centric $I4_1/a$ symmetry of the end-member structures (Moreiras *et al.*, 1991; Moreau *et al.*, 1996; Lugli *et al.*, 1999). Hibbs *et al.* (2000) studied two crystals with compositions PbMo_{0.90}W_{0.10}O₄ (Wu₉₀St₁₀) and PbMo_{0.60}W_{0.40}O₄ (Wu₆₀St₄₀), and from the presence of a number of reflections violating $I4_1/a$ symmetry, inferred space group $\bar{I}4$ for Wu₆₀St₄₀. In particular, they found nine forbidden reflections in $hk0$ zone and three in $00l$ zone. As the change from $I4_1/a$ to $\bar{I}4$ space group is accompanied by the loss of centres of symmetry and the compounds belonging to the wulfenite–stolzite join could represent important technolo-

gical materials and so it would seem that the possible $I4_1/a \rightarrow \bar{I}4$ transformation warrants further investigation, paying special attention to the reflections violating $I4_1/a$ symmetry. The aim of the study reported here was to determine if the $I4_1/a \rightarrow \bar{I}4$ transition actually occurs along the wulfenite–stolzite join, focussing the study on presence of the critical reflections. We investigated three natural crystals, covering a wide compositional range, by means of single-crystal X-ray diffraction using a CCD detector.

Sample and experimental

Three natural crystals along the wulfenite–stolzite join were selected on the basis of their optical extinction, absence of twinning and crystal size. The samples come from hydrothermal veins in the Valle del Cervo granite, Biella, Italy, and were previously analysed by Secco *et al.* (2005). The three samples have the following compositions:

Sample 137: Pb(Mo_{0.99}W_{0.01})O₄, (Wu₉₉St₁).

Sample 08: Pb(Mo_{0.84}W_{0.16})O₄, (Wu₈₄St₁₆) - composition near Sonora wulfenite (Hibbs *et al.*, 2000).

Sample 07: Pb(Mo_{0.54}W_{0.46})O₄, (Wu₅₄St₄₆) - composition near Chillagoe wulfenite (Hibbs *et al.*, 2000).

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Intensity data were collected at ambient conditions using a STOE STADI4 single-crystal diffractometer equipped with graphite-monochromated Mo- $K\alpha$ radiation (50 kV, 40 mA $\lambda = 0.71073$ Å) using a CCD detector (Oxford Diffraction) in the range $5 \leq 2\theta \leq 85^\circ$ and a 0.2° ω -scan with an exposure time of 10 s. The sample-to-detector distance was 60 mm. The CrysAlis Red program (Oxford Diffraction) was used to integrate the intensity data and applying a Lorentz-polarization correction, while *X-RED* and *X-SHAPE* programs (Stoe and Cie, 1999) were used to correct for absorption. Anisotropic refinements with reflection weighting were performed using the *SHELX-97* package (Sheldrick, 1997) in space group $I4_1/a$ for all samples, using the atom coordinates of Hibbs *et al.* (2000) as a starting model. The distribution statistics of E values together with Sheldrick's criterion (Sheldrick, 1997) for the full data of each crystal investigated were used to check the space group assignment. Ionized scattering curves were used for Pb, Mo and W, whereas a partly-ionized scattering curve was used for oxygen

(Ibers and Hamilton, 1974, International Tables for X-ray Crystallography). Final refined site occupancies are in excellent agreement with the analysed compositions of each sample. Details of the crystal-structure refinements (unit-cell parameters, atomic coordinates, polyhedral volumes, distortion parameters and bond lengths) are reported in Table 1. Finally, sample 07 has an almost identical composition to the Chillagoe wulfenite sample studied by Hibbs *et al.* (2000), who proposed the $I\bar{4}$ space group. This was tested on a newly installed STOE STADI4 single-crystal diffractometer equipped with a point detector in order to confirm the data collected on the CCD detector.

Results and Discussion

The aim of this work was to establish whether or not intermediate wulfenite–stolzite intermediate compositions have centric ($I4_1/a$) or acentric ($I\bar{4}$) structures, by investigating the origin of reflections that violate $I4_1/a$ symmetry. The crystal structure refinement results relative to our

TABLE 1. Detail on the crystal-structure refinements performed in this work. The unit-cell parameters, atomic coordinates, polyhedral volumes, distortion parameters and bond lengths are reported. Standard deviations are reported in parentheses.

	Sample 137 ($I4_1/a$)	Sample 08 ($I4_1/a$)	Sample 07 ($I4_1/a$)
a (Å)	5.433(1)	5.434(2)	5.442(1)
c (Å)	12.098(1)	12.106(2)	12.078(1)
V (Å ³)	357.1(1)	357.5(1)	357.7(1)
$N(\text{obs refl})$	386	258	245
$R1_{\text{obs}}$ (%)	4.3	5.4	3.9
Pb $x y z$	0 0 $\frac{1}{2}$	0 0 $\frac{1}{2}$	0 0 $\frac{1}{2}$
Mo $x y z$	0 0 0	0 0 0	0 0 0
electrons	43.5	47.6	55.8
O x	0.2356(12)	0.2366(20)	0.2327(18)
y	0.1359(12)	0.1374(20)	0.1362(18)
z	0.0815(6)	0.0810(8)	0.0815(8)
Pb–O (Å)	2.636(6) $\times 4$	2.626(10)	2.647(10)
	2.601(7) $\times 4$	2.606(11)	2.609(9)
V_{Pb} (Å ³)	31.98(4)	31.87(7)	31.66(5)
Mo–O (Å)	1.776(6) $\times 4$	1.781(11)	1.767(10)
V_{M} (Å ³)	2.871(12)	2.890(18)	2.826(12)
$\# \sigma_{\text{oct}}^2$	5.72	8.19	4.72
$\# \lambda_{\text{oct}}$	1.0015	1.0021	1.0012

* Electron density calculated on the basis of two tetrahedral sites
 # after Robinson *et al.* (1971)

CRYSTAL STRUCTURES OF WULFENITE–STOLZITE

TABLE 2. List of the forbidden reflections with the integrated intensity and standard deviations as % relative to the strongest reflection 112 in the samples investigated in this work.

Reflection	Sample 137	Sample 008	Sample 007
0 1 0	0.42(4)	0.51(7)	0.67(5)
1 1 0	0.39(5)	0.36(6)	0.91(8)
1 2 0			0.38(8)
0 0 2	0.67(6)	0.42(3)	0.61(4)
0 1 2	0.42(4)	0.50(8)	0.82(7)
1 2 2			0.28(7)
0 1 4			0.48(8)
0 0 6			0.32(7)

samples show a general good agreement with those from Hibbs *et al.* (2000), and so the only differences relate to the number and type of the reflections violating $I4_1/a$ symmetry, which for our samples are reported in Table 2. All samples here studied show the same four forbidden reflections, of which three violate the I lattice and a glide plane (reflections 010, 012 and 110) and one violates the 4_1 screw axis (reflection 002). However, the most stolzite-rich sample (07) also shows an additional four forbidden reflections of which three violate the I lattice and the a glide plane (reflections 120, 122 and 014) and one violates the 4_1 screw axis (006). The most intense

reflection for the 07 sample (110) corresponds to just 0.9 % of the intensity of the most intense reflection measured for this crystal (112).

A detailed analysis of the CCD images was undertaken for all the violating reflections reported in Table 2. In particular, it appears that such reflections are related to a $\lambda/2$ effects, as is evident in Fig. 1. It is well known that $\lambda/2$ reflections for a Mo X-ray tube and a graphite monochromator are easily identified by decreasing the voltage of the X-ray tube below 34.9 kV, whereupon reflections originating from the $\lambda/2$ effect suddenly disappear (Kirschbaum *et al.*, 1997): for Mo- $K\alpha$ radiation $\lambda/2 = 0.3554 \text{ \AA}$ and the corresponding accelerating voltage is 34.9 kV. In Fig. 1 we show how the intensity of the 110 reflection (the most intense violating reflection for the 07 sample) suddenly disappears going from 38 to 34 kV. If this reflection was genuine, rather than an experimental artefact, going from 50 kV to 34 kV we could expect a decrease in intensity by about 70% and not a zero intensity (Kirschbaum *et al.*, 1997). The same test was performed for the other violating reflections, which gave the same result.

We infer that the violation of $I4_1/a$ symmetry observed in W-rich sample 07 and in W-poorer 08 and 137 wulfenites investigated in this work are, therefore, not due to a phase transition, but to $\lambda/2$ effects. Finally, the E statistics and Sheldrick's criterion were used to provide additional confir-

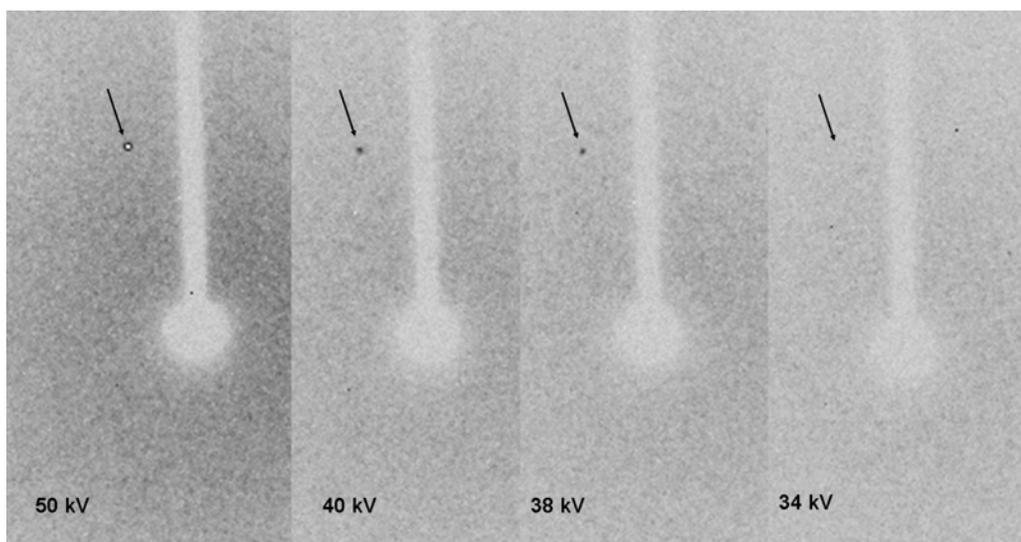


FIG. 1. CCD image showing the 110 reflection for different X-ray tube operating voltages. Each image was collected for 30 s.

mation of our space group assignment. The values of $|E^2-1|$ for samples 137, 08 and 07 were 0.590, 0.633, and 0.638, respectively. These values could indicate that all the samples studied in this work are acentric (Sheldrick, 1997). However, it is well known that $|E^2-1|$ statistics may be unreliable if heavy atoms are present in a structure, especially if they lie on special positions or if there are very few reflections in $0kl$, $h0l$ and $hk0$ projections (SHELX-97 manual, section 13-3, Sheldrick, 1997). As our samples have heavy atoms (Pb, W and Mo) lying on special positions, statistical tests of space group assignment cannot be relied upon. A final test on the 110 reflection, the strongest violator in all three samples, was done using a diffractometer equipped with a point detector (see Experimental section) and, as observed for the data collected on the CCD detector, at 34 kV the reflection suddenly disappears. Thus, we conclude that intermediate compositions of the wulfenite-stolzite series have the same $I4_1/a$ symmetry as the end-members.

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