Order and twining in Sb$_2$W$_{0.75}$Mo$_{0.25}$O$_6$

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Abstract

Synthesis, X-rays, TEM and HREM studies of the composition $x = 0.25$ of the solid solution Sb$_2$W$_{1-x}$Mo$_x$O$_5$ are reported. The phase crystallises in the monoclinic system, space group C2 and the cell parameters of its average structure are $a = 11.1296(6)$ Å, $b = 9.8868(9)$ Å, $c = 18.501(2)$ Å and $\beta = 96.951(9)^\circ$. Mo and W atoms are ordered in the 1/3 ratio. Twining and extended defects have been studied by TEM and HREM.

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1. Introduction

Several papers have been devoted to the syntheses and crystal structures of Sb$_2$MO$_6$ with M = W and Mo compounds [1–4]. They are described as an antimony-based analogue to the $\alpha$-Sb$_2$O$_3$ related structures are built up by alternate stacking of single layer slabs of tetragonal PbO type {$Bi_2O_2$}$_{2n+m}$ and slabs, $m$ layers thick, of perovskite {$Am_{-1}BmO_{3m+1}$}$_{2n}$ and {$BmO_{4}$}$_{2n}$ layers. Such type compounds owing to their peculiar structural organisation exhibit interesting ferroelectric or ferroelastic properties. Antiferroelectric modulations have also been demonstrated in both W and Mo compounds [3]. In order to organise a modulation of these properties, a solid solution Sb$_2$W$_{1-x}$Mo$_x$O$_6$ has been considered (0 $\leq x \leq 1$). Single crystals for particular values have been isolated and studied by X-ray (XRD) and transmission electron diffraction (TEM) as well as by high resolution electron microscopy (HREM). A super-cell was observed for the composition Sb$_2$W$_{0.75}$Mo$_{0.25}$O$_6$. Its structural study is reported in the present paper.

2. Experimental

Single crystals of the representative composition $x = 0.25$, Sb$_2$W$_{0.75}$Mo$_{0.25}$O$_6$, compound were grown from a stoichiometric mixture of Sb$_2$O$_3$, WO$_3$ and MoO$_3$ analytical grade reagents (Aldrich, 99.99%). The oxides were mixed in an agate mortar and placed in a quartz ampoule, which was evacuated and sealed, in order to avoid the oxidation of Sb$^{3+}$ to Sb$^{5+}$. The thermal treatment consists in two identical accumulative steps: heating from room temperature to 650 $^\circ$C at 5 $^\circ$/min, stabilization at 650$^\circ$C for 24 h and cooling to room temperature at 1 $^\circ$/min.

A small, dark green, plate-like crystal of 0.025 $\times$ 0.0063 $\times$ 0.175 mm$^{-3}$ in size was selected and isolated for X-ray investigations using a Nonius kappa CCD diffractometer (Mo $K_\alpha$ radiation). The full set of $I_{hkl}$ data collected for $\theta \leq 30^\circ$ was corrected for Lorentz-polarisation and absorption factors. The X-ray powder pattern of part of the remaining sample, carefully ground, was collected up to 2$\theta$ $\leq$ 80$^\circ$ using a Seifert XRD 3000 TT diffractometer equipped with a back graphite monochromator (Cu $K_\alpha$ radiation: $\lambda = 1.5418$ Å).
Some crystals were crushed and studied by electron microscopy using a Jeol 4000 and a Philips EM430 transmission electron microscopes.

3. Results

A preliminary single crystal study shows that this Sb\textsubscript{2}W\textsubscript{0.75}Mo\textsubscript{0.25}O\textsubscript{6} phase crystallizes in the monoclinic system. The crystal is twinned and shows a number of parallel planar defects located in the (001) plane as demonstrated in Fig. 1.

The cell parameters are \(a = 11.130(1) \text{ Å} \), \(b = 9.894(1) \text{ Å} \), \(c = 10.183(1) \text{ Å} \), \(\beta = 115.84(1)^\circ \) and \(V = 1009.3 \text{ Å}^3 \). Systematic extinction \(h + k = 2n + 1\) is observed for all reflections \(hkl\); this led to the three possible space groups \(C2/m, C2\) and \(Cm\). According statistical tests performed on \(I_{hkl}\) the non-centric \(Cm\) or \(C2\) space groups were privileged. The presence of a mirror plane being less probable in such structure type, a former structure determination run was performed in the \(C2\) space group. The structure was found to be analogous to \(\text{Sb}_2\text{WO}_6\).

A transformation matrix \(\left| \begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{array} \right| \) was then applied in order to have a \(\beta\) angle directly comparable with the data of Ling et al. [3]. The new cell parameters are reported in Table 1 together with the previous parameters of both \(\text{Sb}_2\text{WO}_6\) and \(\text{Sb}_2\text{MoO}_6\) for comparison.

3.1. Structure refinement

It appears possible to have an order between Mo and W corresponding to a \(\text{Mo}/\text{W} = 1/3\) ratio. W atoms are situated on two Wyckoff positions \(4c\) (\(x, y, z\)) and \(2a\) (0, 0, 0) while Mo are only on \(2a\) (0, 0, 0), with \(y_{\text{Mo}}\) roughly shifted by \(\frac{1}{3}\) from \(y_{\text{W}}\) value. In spite of a real improvement the \(R\) factor remains too high (around 26%). A refinement has been carried on using JANA software.

The refinement was again performed in the \(C2\) space group using SHELXL software. The heavy atoms are reasonably settled but the difference Fourier reveals a complex electron density map making an oxygen localization difficult (see Fig. 2).

New calculations were performed with the JANA software; even better reliability factors were obtained some discrepancies not acceptable remained in the bonding scheme.

It was decided to keep the average structure which gave the most important result about the Mo–W atom ordering. The ‘smearing’ behavior of the heavy atoms around their crystallographic site did not allow to show via difference Fourier calculations clear maxima for oxygen atoms. A refinement, even if it drops down the \(R\) factor was to our judgement meaningful.

3.2. Electron microscopy

Fig. 3 shows (a) (1\text{0\text{0\text{0}}}), (b) (0\text{1\text{0}}) and (c) (1\text{1\text{1}}) zone axis electron diffraction patterns typical of \(\text{Sb}_2\text{W}_{0.75}\text{Mo}_{0.25}\text{O}_6\). The presence of weak alternate rows of reflections (such as that containing the reflection labelled 1 1 1) in Fig. 3c requires the \(c\) axis reported for \(\text{Sb}_2\text{W}_{0.75}\text{Mo}_{0.25}\text{O}_6\) in Table 1 to be doubled from 9.250 to 18.501 Å. The size of the unit cell thus becomes essentially isomorphous to that already reported for the end-member \(\text{Sb}_2\text{WO}_6\) and \(\text{Sb}_2\text{MoO}_6\) phases [2,3]. That this resultant cell must be \(\text{F}\overline{1}\) centered is also clear from Fig. 3. It would thus seem most probable that the structure is isomorphous to the \(\text{F}\overline{1}\) structure of \(\text{Sb}_2\text{WO}_6\) reported by Ling et al. [3], and shown in projection down a (1\text{1\text{0}}) orientation in Fig. 4. Note that at this zone axis orientation the heavy metal atoms (Sb in green and Mo and

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<td>Crystal data of (\text{Sb}_2\text{WO}_6), (\text{Sb}_2\text{MoO}<em>6) and (\text{Sb}<em>2\text{W}</em>{0.75}\text{Mo}</em>{0.25}\text{O}_6)</td>
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W in the center of the blue octahedra) project into well-defined and well-separated atomic columns.

Extensive planar faulting on the a–b plane is apparent in low magnification images (see Fig. 3) and gives to the ubiquitous streaking along c* apparent in all three edp’s of Fig. 3. In addition, (001) twinning on the a–b plane (giving to twin variants whose reciprocal lattices are related by a mirror plane perpendicular to c*) is usually also apparent (see, for example, Fig. 3c). HREM images taken down a (110) zone axis orientation confirm such an interpretation (cf. the positions of the heavy metal atom columns in Fig. 2 with the positions of the black columns of ‘atoms’ in Fig. 5. This (001) twinning appears to be a rather finer scale version of the ferroelastic twinning already reported for Sb$_2$WO$_6$ by Castro et al. (see Figs. 1 and 2a of [1]). The positions of two such twins are labelled with arrows in Fig. 5. Note that in this particular case the first twin is followed almost immediately by the second twin so that the upper and lower crystalline slabs have the same orientational relationship although they have been displaced with respect to one another as is apparent from the HREM image. In such a case the reflections corresponding to the second twin orientation will not appear in the corresponding electron diffraction pattern although the streaking along c* will.

4. Conclusion

The possibility to get an order between Mo and W atoms in the solid solution Sb$_2$W$_{1-x}$Mo$_x$O$_6$ has been demonstrated, such solid solution being synthesized in the further scope to study ferroelectric and/or ferroelastic
properties. Anyhow, several crystallization tentatives did not allow to get single crystals of high quality, all of them being systematically and drastically altered by twining problems. Based on the average structure determine single crystal X-ray techniques which allowed to establish the Mo/W sequence order, the twining have been thoroughly investigated by TEM and HREM with the aim to understand the atomic architecture of these Sb$_2$W$_{1-x}$Mo$_x$O$_6$ phases and therefore to master their physical properties.

Fig. 3. Zone axis diffraction patterns along: (a) $\langle 100 \rangle$, (b) $\langle 010 \rangle$ and (c) $\langle 001 \rangle$.

Fig. 4. Projection along [110] direction of the Sb$_2$W$_{0.75}$Mo$_{0.25}$O$_6$ structure.

Fig. 5. HREM image taken down a $\langle 110 \rangle$ zone axis.

References