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# Crystal structure of $Sb_2MoO_6$

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*Crystal structure* / $Sb_2MoO_6$

**Abstract.** The molybdenum antimony oxide $Sb_2MoO_6$ crystallizes in the triclinic space group $P\bar{1}$. Cell parameters measured on an X-ray diffractometer CAD4 were $a=7.481(2)$ Å; $b=7.504(1)$ Å; $c=10.120(2)$ Å; $\alpha=70.43(2)°$; $\beta=70.91(2)°$; $\gamma=83.35(2)°$. From neutron diffraction the following parameters were obtained $a=7.4774(2)$ Å; $b=7.5017(2)^{\star}$; $c=10.1259(2)^{\star}$; $\alpha=70.374(1)°$; $\beta=70.889(1)°$; $\gamma=83.246(1)°$.

The structure determination is based on a single crystal X-ray diffraction study and a powder neutron diffraction profile refinement. 4124 independent reflections collected on an X-ray diffractometer lead to an $R$ factor of 7.4%, while neutron diffraction profile refinement gave an $R$ factor of 4.8%.

$MoO_6$ octahedra are distorted and the neighbourhoods of the Sb atoms are described up to the 5 closest oxygen atoms.

$MoO_6$ octahedra share corners and build sheets with the $MoO_4$ composition. $MoO_4$ sheets are separated by $Sb_2O_2$ layers. This arrangement is very similar to that of keochlinite $Bi_2MoO_6$ except that, due to centrosymmetry, the former compound is not ferroelectric.

## Introduction

The samples used in the present study were prepared in the following ways: the powder was prepared by heating a mixture of $Sb_2O_3$ valentinite and $MoO_3$ in a sealed quartz tube. The powder mixture was reheated for 24 hours under the same conditions.

The crystals of $Sb_2MoO_6$ were prepared by slowly pulling a sealed quartz tube containing the powder of $Sb_2MoO_6$ through a furnace at about 546 °C.

The whole operation took 50 hours and gave crystals approximatively 0.2 mm long.

$Sb_2MoO_6$ single crystals are very often twinned and the true system is rather difficult to discover. In a previous paper we demonstrated that $Sb_2MoO_6$ crystals were triclinic, not monoclinic. That result was based on several X-ray single crystal measurements and on powder neutron diffraction (A. Laarif, A. Hewat, F. Theobald and H.Vivier, 1983).

## X-ray single crystal study

The crystal used had the dimensions 0.23 mm × 0.05 mm × 0.016 mm. 4469 reflections were collected on a Nonius CAD4 diffractometer using radiation $MoK\alpha \lambda = 0.7107$ Å.

$1 < \theta < 34°$; $-11 \leq h \leq 11$; $0 \leq k \leq 11$; $-13 \leq l \leq 15$; $\mu(MoK\alpha) = 13622\, m^{-1}$; scan width $(0.5 + 0.2 \tan \theta)°$.

An attempt to solve the structure in the centrosymmetric space group $P\bar{1}$ using the MULTAN (Main, Lessinger, Woolfson, Germain, Declercq, 1977) program was unsuccessful; on the other hand MULTAN enabled us to locate all the heavy atoms in the cell using space group $P1$ with no symmetry.

Interpeak-distances were used to find which peaks could be taken as heavy atoms; the 11 first peaks in the list corresponded to heavy atoms; the 12th heavy atom corresponded to peak number 15 in the list; distances between peaks selected in that way ranged between 3.41 Å and 4.00 Å. For the refinements eighty six reflections with a null intensity were rejected; 4383 reflections remained for refinements with program SHELX (Sheldrick, 1976).

The next step was to define which atoms were antimony or molybdenum atoms. At the beginning all atoms were given an $U$ factor of 0.02 and all except one were assumed to be antimony atoms and gradually molybdenum atoms were identified by the behaviour of their $U$ factor during the refinements and by the observation of their neighbourhood on Fourier-difference maps.

At that point the structure appeared to be centrosymmetrical and even oxygen atoms respected that symmetry. Further calculations were performed in space group $P\bar{1}$. 4124 independent reflections lead to an $R$ factor of 11.5%.

Due to the irregular shape of the crystal it proved impossible to measure the orientation of the faces. For that reason absorption corrections were performed using program DIFABS (Walker and Stuart, 1983): among 4383 reflections introduced in those calculations only 3617 were actually used for the definition of the correction parameters, those reflections having $F(0)/\sigma[F(0)] < 3$ (746 reflections and $F_{calc}/\sigma(F_o) < 3$ (20 reflections) being temporarily rejected. The minimum correction factor was 0.824 and the maximum 1.419.

Finally 4124 independent reflections were obtained and 625 reflections having $F/\sigma(F) < 1$ were suppressed from the refinement calculations. The

**Table 1.** Atomic coordinates of $Sb_2MoO_6$ X-ray single crystal study

| Atoms | *x* | *y* | *z* |
|---|---|---|---|
| Sb(1) | 0.1297(2) | 0.5591(2) | 0.1734(1) |
| Sb(2) | 0.0580(2) | 0.1217(2) | 0.1776(1) |
| Sb(3) | 0.5829(2) | 0.6272(2) | 0.1622(1) |
| Sb(4) | 0.6161(2) | 0.0835(2) | 0.1621(1) |
| Mo(1) | 0.7764(2) | 0.7232(2) | 0.4838(1) |
| Mo(2) | 0.2734(2) | 0.7812(2) | 0.4978(1) |
| O(1) | 0.398(2) | 0.756(2) | 0.317(1) |
| O(2) | 0.387(2) | 0.688(2) | 0.060(1) |
| O(3) | 0.919(2) | 0.275(2) | 0.313(1) |
| O(4) | 0.692(2) | 0.887(2) | 0.064(1) |
| O(5) | 0.739(2) | 0.532(2) | 0.433(1) |
| O(6) | 0.231(2) | 0.025(2) | 0.440(1) |
| O(7) | 0.757(2) | 0.919(2) | 0.318(1) |
| O(8) | 0.196(2) | 0.371(2) | 0.065(1) |
| O(9) | 0.723(2) | 0.600(2) | 0.688(1) |
| O(10) | 0.871(2) | 0.205(2) | 0.068(1) |
| O(11) | 0.532(2) | 0.231(2) | 0.439(1) |
| O(12) | 0.023(2) | 0.728(2) | 0.441(1) |

remaining 3499 reflections gave a conventional final *R*-factor of 7.4%. Slightly negative thermal factors were obtained for the 2 molybdenum atoms in the asymmetric unit and so we decided to confirm the results by neutron diffraction. Coordinates of atoms obtained from X-ray are given in Table 1[1].

## Neutron powder diffraction study

About 2 $cm^3$ of $Sb_2MoO_6$ powder was packed into a 15 mm diameter vanadium can and placed in a He gas flow cyrostat. A 20-hours scan was performed at 5 K to ensure that the true low temperature structure would be found: since the symmetry is triclinic but pseudo-orthorhombic, a phase transition might increase the symmetry at higher temperatures. The high resolution D1A diffractometer at the ILL in Grenoble was used (Hewat and Bailey, 1976). The ten separate patterns from the individual counters were intercalibrated and averaged to produce a single pattern extending from 6° to 160° in steps of 0.05° ($2\theta$); calculations were performed using the POWDER computer program (Hewat, 1980).

Profile refinement of the data was performed using a modified version of the Rietveld method (Rietveld, 1969; Hewat, 1973) and ORTEP (Johnson, 1964) plots and bond lengths and angle calculations performed with the X-

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[1] Additional material to this paper can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 50724, the names of the authors and the title of the paper

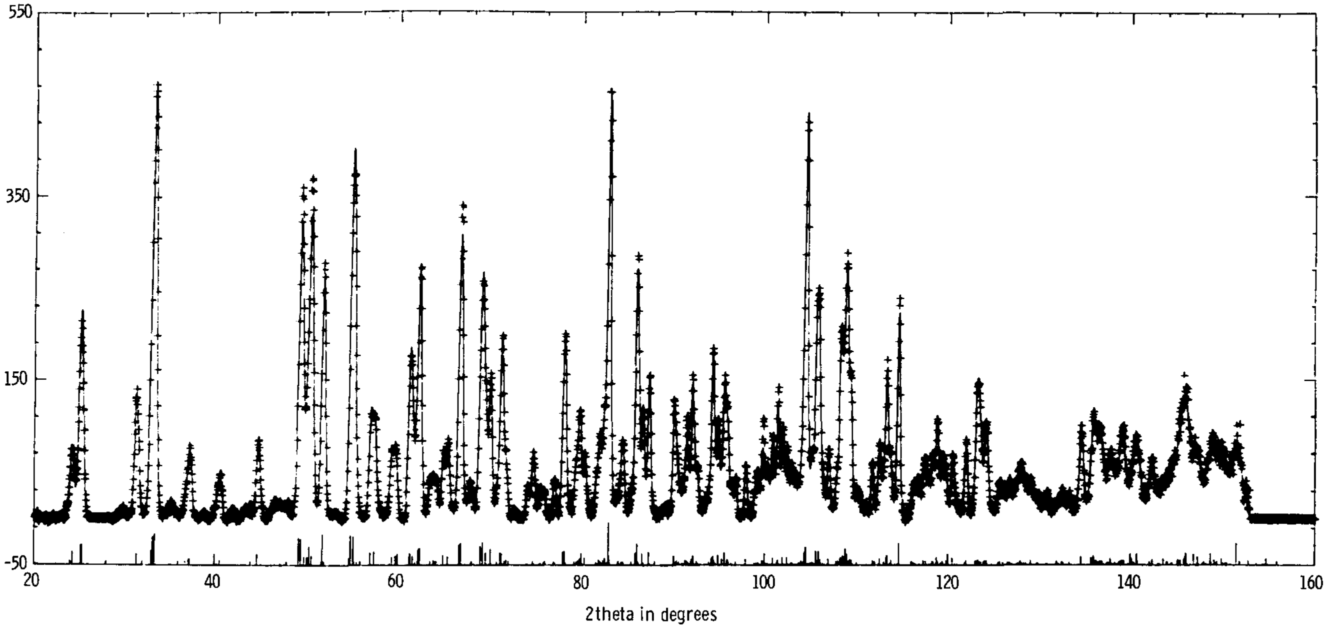

**Fig. 1.** Observed and calculated neutron profiles of $Sb_2MoO_6$ at 5 K

**Table 2.** Atomic coordinates of $Sb_2MoO_6$ from neutron diffraction profile refinement

| Atoms | $x$ | $y$ | $z$ |
|---|---|---|---|
| Sb(1) | 0.129(1) | 0.557(1) | 0.1722(8) |
| Sb(2) | 0.057(1) | 0.1269(1) | 0.1792(8) |
| Sb(3) | 0.586(1) | 0.618(1) | 0.1613(8) |
| Sb(4) | 0.618(1) | 0.085(1) | 0.1639(8) |
| Mo(1) | 0.7739(8) | 0.7217(8) | 0.4859(6) |
| Mo(2) | 0.2699(8) | 0.7793(7) | 0.5010(7) |
| O(1) | 0.406(1) | 0.762(1) | 0.3098(7) |
| O(2) | 0.387(1) | 0.689(1) | 0.0585(8) |
| O(3) | 0.917(1) | 0.2694(1) | 0.3186(7) |
| O(4) | 0.694(1) | 0.887(1) | 0.0665(8) |
| O(5) | 0.741(1) | 0.5355(9) | 0.4267(8) |
| O(6) | 0.229(1) | 0.0242(9) | 0.4455(7) |
| O(7) | 0.7553(8) | 0.9262(9) | 0.3144(8) |
| O(8) | 0.1992(9) | 0.3715(9) | 0.0606(8) |
| O(9) | 0.7229(8) | 0.5041(9) | 0.6840(7) |
| O(10) | 0.870(1) | 0.2060(9) | 0.0704(7) |
| O(11) | 0.5376(1) | 0.2359(9) | 0.4395(9) |
| O(12) | 0.0199(9) | 0.7257(9) | 0.4395(9) |

RAY 76 program system. Coordinates obtained from X-rays were used as a starting set. Thermal factors $B$ for the different atoms of a given element were constrained to be the same; so all together there were 54 coordinate parameters, 3 isotropic temperature factors, 6 cell dimensions or angles, 3 half-width parameters (called $u$, $v$ and $w$), the asymmetry parameter, the zero point and the scale factor – a total of 69 parameters, all of which were refined simultaneously.

Absorption correction was performed by adding an isotropic term $\Delta B = 0.3$ to all the $B$-factors (Hewat, 1979). The neutron scattering lengths were b(Sb) = 0.564; b(Mo) = 0.640; b(O) = 0.580. The b-factor for Mo was determined recently (Koester, 1977) by the Christensen filter technique to be somewhat larger ($0.695 \pm 0.007$) but our results favour the earlier lower value: the Christensen filter technique is a bulk measurement and may have been affected by adsorbed gases. It would be necessary to measure b(Mo) by diffraction from a simple Mo oxide at known stoichiometry if this question was to be settled.

Very good agreement was obtained with the observed profile at 5 K, with only small shifts to the X-ray coordinates ($R_p = 7.7$). For comparison $R_I = 4.8$ should be approximately halved for comparison with $R_F$, the usual crystallographic $R$-factor for structure factors. Figure 1 shows the observed (+) and calculated profiles with the vertical bars marking the positions and strengths of the contributing reflections. Table 2 shows the neutron coordinates at 5 K.

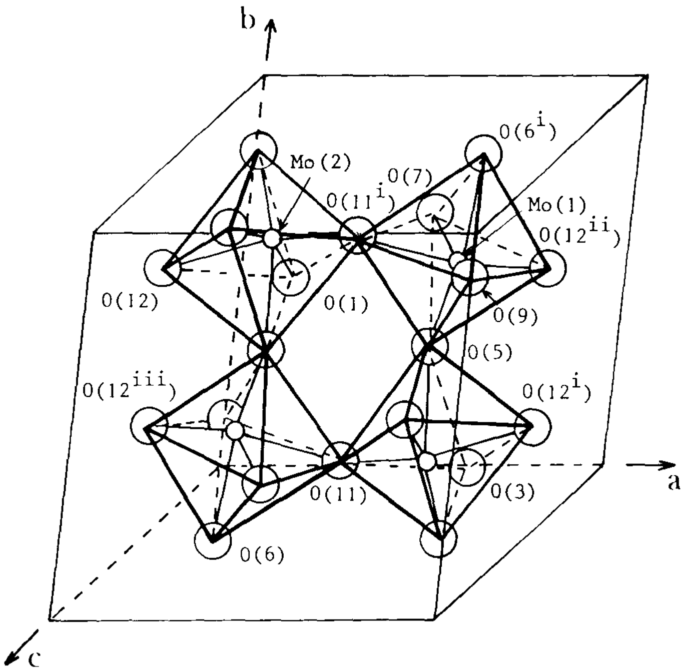

**Fig. 2.** Projection of a $MoO_4$ layer onto (001)

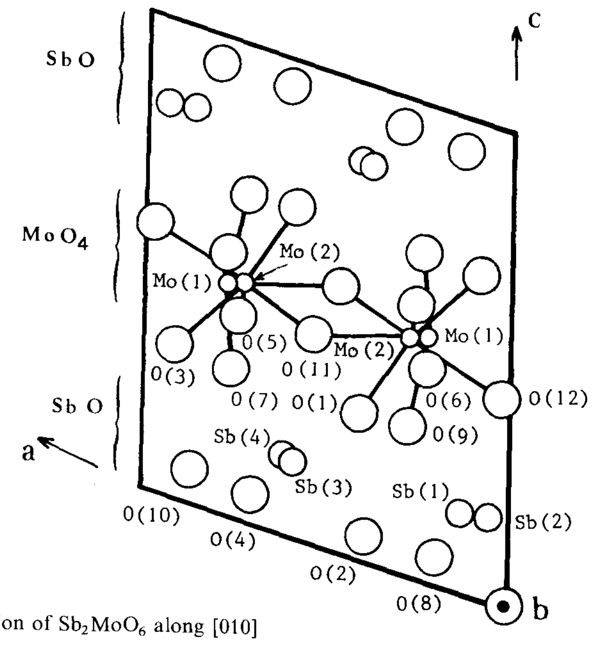

**Fig. 3.** Projection of $Sb_2MoO_6$ along [010]

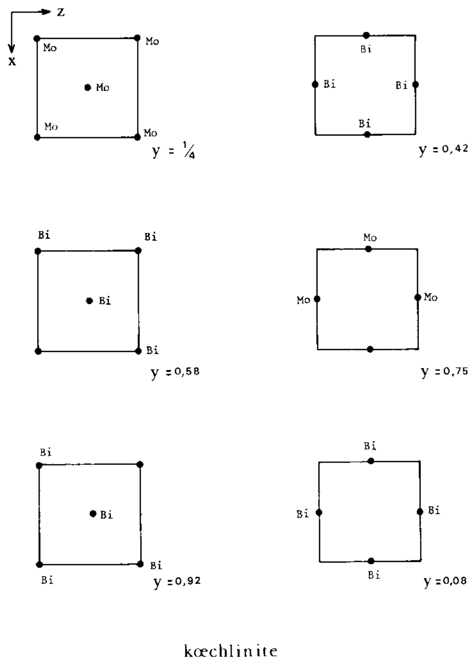

**Fig. 4.** Disposition of heavy atoms in $Bi_2MoO_6$ koechlinite, showing the fluorite-related structure

## Description of the structure

Mo atoms are hexacoordinated by O atoms: there are four short bonds (1.71 – 1.93 Å) and two longer bonds (2.22 – 2.27). This is due to the displacement of the molybdenum atom from the center of the octahedron towards edge O(5) – O(12) for Mo(1), and towards edge O(6) – O(11) for Mo(2).

Sb atoms may be considered as 5-coordinated: Sb(1), Sb(2) and Sb(4) have 3 short bonds (1.97 – 2.09) and 2 longer bonds ($> 2.32$ Å). For Sb(3) that distinction is still valid but not so clear.

The effective valence charge has been calculated according to the empirical formula and parameters given by Brown and Shannon (1973) and Brown and Wu (1976); values are close to those expected (+3 for $Sb^{3+}$ and +6 for $Mo^{6+}$).

$MoO_6$ octahedra share corners as shown on Figure 2, which is a projection of atoms with $0.25 < z < 0.75$ onto a plane parallel to (001), building sheets with atoms Mo(1), Mo(2) and "equatorial" atoms O(5), O(6), O(11) and O(12). Apical atoms O(1) and O(3) complete the octahedra. Sheets $MoO_4$, infinite in two dimensions, are separated by sheets with composition $Sb_2O_2$ built by atoms Sb(1) to Sb(4), O(2), O(4), O(8) and O(10). (Fig. 3).

This arrangement exhibits similarities to that of several $Bi_2MoO_6$ compounds as described by Aurivillius (1952) and Wells (1975). The structure may be related to a series consisting of $Bi_2O_2$ layers interleaved with perovskite-like layers having the formula $Bi_{n-1}M_nX_{3n+1}$ (see Figure 2). For $M = \mathrm{Mo}$ and $X = \mathrm{O}$ the perovskite layer is simply $MoO_4$, which corresponds to the actual composition of the koechlinite $Bi_2MoO_6$. Deviations from tetragonal symmetry are due to $MoO_6$ octahedra tilts (Theobald, Laarif, Hewat, 1983).

*Koechlinite and $Sb_2MoO_6$ are fluorite related structures.* Heavy atoms in koechlinite and $Sb_2MoO_6$ occupy cationic positions close to those of a face-centered orthorhombic subcell similar to $CaF_2$. For koechlinite this may be seen from an observation of the superimposition of the heavy atoms as shown on Figure 4. The average distance between layers is $16.226/6 = 2.704$ Å. If doubled that distance equals 5.41 Å while $a = 5.506$ Å and $b = 5.487$ Å (for $CaF_2$: $a = 5.46$ Å).

For $Sb_2MoO_6$ the fluorite subcell is very distorted and so more difficult to demonstrate: projected on (001) layers of molybdenum and antimony layers appear stacked and the relation of every layer to the next one shows that the arrangement of the cation types has indeed a distorted face-centered subcell regardless of the element type of the heavy atoms.

The structure obviously may be twinned with (001) as a twin plane and this explains all the difficulties met in solving the structure.

A noteworthy difference between koechlinite and $Sb_2MoO_6$ is that koechlinite has no inversion center (space group $Pca2_1$).

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