

layer (Fig. 2) but the formula has changed because O(3) atoms also belong to the coordination sphere of Bi; the formula of the layer of the corner-sharing VO<sub>6</sub> octahedra is thus VO<sub>2.75</sub><sup>0.5-</sup>.

According to Zhou (1988), in the Bi<sub>2</sub>VO<sub>5.5</sub> structure there are no Bi<sub>2</sub>O<sub>2</sub><sup>2+</sup> layers and this compound cannot be included in the Aurivillius family of oxides. The structure of Bi<sub>2</sub>VO<sub>5.5</sub> contains alternating Bi<sub>2</sub>O<sub>2</sub><sup>2+</sup> layers formed by very irregular corner-sharing BiO<sub>4</sub> tetrahedra and VO<sub>2.75</sub><sup>0.5-</sup> layers of corner-sharing distorted VO<sub>6</sub> octahedra.

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*Acta Cryst.* (1992). **C48**, 1179–1182

## Structure of Sn<sub>0.854</sub>Mo<sub>6</sub>S<sub>8</sub>

BY L. LE LAY

*Applied Superconductivity Center, University of Wisconsin-Madison, Madison, WI 53706, USA*

D. R. POWELL

*Chemistry Department, University of Wisconsin-Madison, Madison, WI 53706, USA*

AND T. C. WILLIS

*Applied Superconductivity Center and Materials Science and Engineering Department, University of Wisconsin-Madison, Madison, WI 53706, USA*

(Received 11 June 1991; accepted 9 December 1991)

**Abstract.** Molybdenum tin sulfide, Sn<sub>0.854</sub>Mo<sub>6</sub>S<sub>8</sub>,  $M_r = 933.5$ , trigonal,  $R\bar{3}$ ,  $a_R = 6.5100(10)$  Å,  $\alpha_R = 89.47(2)^\circ$ ,  $V_R = 275.86(7)$  Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 5.619$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 9.777$  mm<sup>-1</sup>,  $F(000) = 422.70$ ,  $T = 295$  K,  $R = 0.0401$  for 517 observed reflections. The title compound is isostructural to SnMo<sub>6</sub>S<sub>8</sub>, but displays a cation non-stoichiometry.

**Introduction.** In the series of large-cation sulfide Chevrel phases (MMo<sub>6</sub>S<sub>8</sub> where  $M$  is a metallic cation), it is generally believed that non-stoichiometry, if any, occurs on the 2(c) sulfur sites along the rhombohedral axis. This issue has been addressed previously, theoretically (Hughbanks & Hoffmann, 1983) and experimentally – powder neutron diffraction showed that partial S-atom substitution by O

atoms can occur (Hinks, Jorgensen & Li, 1983) and this was confirmed by single-crystal characterization (Chang, Tao, Swinnea & Steinfink, 1987). Evidence for missing S atoms on the 2(c) special positions has also been shown for a PbMo<sub>6</sub>S<sub>8</sub> single crystal (Marezio, Dernier, Remeika, Corenzwit & Matthias, 1973). In the case of superconducting Chevrel phases, such as PbMo<sub>6</sub>S<sub>8</sub> and SnMo<sub>6</sub>S<sub>8</sub>, depressed physical properties have been linked to such defects – the greater the deviation from ideal stoichiometry, the lower the critical temperature ( $T_c$ ) and the upper critical field ( $H_{c2}$ ) (Foner, McNiff & Hinks, 1985).

We report here the first crystal data showing non-stoichiometry on the metallic cation site in SnMo<sub>6</sub>S<sub>8</sub>.

**Experimental.** The single crystal was grown by a technique previously reported (Rossel, Sandvold, Sergent, Chevrel & Potel, 1990). About 2 g of a mixture of SnS, MoS<sub>2</sub> and Mo, whose nominal composition was Sn<sub>0.66</sub>Mo<sub>6</sub>S<sub>6</sub>, were placed in an alumina crucible. This ensemble was then put into an out-gassed Mo container which was sealed in a 250 kPa argon atmosphere. The container was then heated in a tungsten-wire resistance furnace, in a  $1.3 \times 10^{-4}$  kPa vacuum. The technique used ensures minimum oxygen contamination. The sample was heated from 293 to 1573 K in 40 min, then heated to 1873 K in 1 h, held at 1873 K for 5 min, cooled from 1873 to 873 K in 16.7 h, and finally furnace cooled to 293 K. The crystal, extracted from the matrix, was a  $0.27 \times 0.27 \times 0.20$  mm parallelepiped.

The diffractometer used for the intensity data collection was a Siemens P3f; the radiation was Mo K $\alpha$  and the monochromator was a highly oriented graphite crystal. Cell parameters were determined by refinement of 24 reflections with  $32 \leq 2\theta \leq 40^\circ$ . 1600 reflections were collected in the range  $4.0 \leq 2\theta \leq 60.0^\circ$  with index ranges  $-9 \leq h \leq 9$ ,  $-5 \leq k \leq 9$  and  $-9 \leq l \leq 6$ . Three standard reflections were checked every 100 reflections with a maximum variation of 0.03. The scan speed varied from 2 to  $12^\circ \text{ min}^{-1}$  in  $\omega$  and the scan range ( $\omega$ ) was  $0.60^\circ$ . 537 reflections were found to be independent ( $R_{\text{int}} = 5.92\%$ ), and were used to solve the structure. 517 of them had  $F > 4.0\sigma(F)$ . An analytical absorption correction was applied (minimum and maximum transmission were 0.0837 and 0.2797 respectively).

Previously published atomic coordinates of SnMo<sub>6</sub>S<sub>8</sub> were used as first values to initiate the structure refinement (Chevrel, Rossel & Sergent, 1980). Anisotropic displacement parameters, as well as an extinction correction parameter, were eventually used in the full-matrix least-squares refinement of  $F$ . The extinction correction factor was  $\chi = 0.019(2)$ , where  $F_c^* = F_c [1 + 0.002\chi F^2/\sin(2\theta)]^{-0.25}$  (Larsen, 1970). Final  $R$  and  $wR$  values (observed data) were 0.0401 and 0.0746, respectively, with  $w^{-1}$

$= \sigma^2(F) + 0.0008F^2$ . Goodness of fit was 2.06. The largest shift/e.s.d. was 0.014. The largest difference peak was  $4.00 \text{ e } \text{\AA}^{-3}$  and occurred at  $1 \text{ \AA}$  from the metal site. The largest difference hole was  $-1.71 \text{ e } \text{\AA}^{-3}$ . Neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1). Computing was performed using the Siemens *SHELXTL-Plus* (VMS) system with version 4.2 programs (Sheldrick, 1990). Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 1 and a selection of bond lengths and structural distances is given in Table 2. The S-atom site-occupancy factors were not varied because thermal parameters for these positions are comparable to that of the Mo site, suggesting complete occupancy by S atoms.\*

**Discussion.** A projection of the structure is shown in Fig. 1. Sn<sub>0.854</sub>Mo<sub>6</sub>S<sub>8</sub> expectedly displays features close to that of the fully occupied SnMo<sub>6</sub>S<sub>8</sub>. It can be described in the same way: the Mo<sub>6</sub>S<sub>8</sub> comprises a distorted Mo<sub>6</sub> octahedron inscribed in a pseudo-cube S<sub>8</sub>. Sn atoms are located in channels created by the Mo<sub>6</sub>S<sub>8</sub> network and are surrounded by eight S atoms forming a distorted cube – six in 6(*f*) positions and two in 2(*c*) positions along the ternary axis [see, for instance, Chevrel & Sergent (1982)].

Lattice parameters and bond lengths are also remarkably close to that of the stoichiometric SnMo<sub>6</sub>S<sub>8</sub>, where  $a_R$  is reported to lie between 6.513 and 6.527 Å,  $\alpha_R$  between 89.52 and 89.70°,  $V_R$  between 274.7 and 278 Å<sup>3</sup> (Chevrel *et al.*, 1980; Yvon, 1979). Additionally, in the Mo<sub>6</sub> cluster of SnMo<sub>6</sub>S<sub>8</sub>, the intra-triangle [Mo(1)—Mo(1)] <sub>$\Delta$</sub>  distance is 2.688 Å and the inter-triangle Mo(1) <sub>$\Delta$</sub> —Mo(1) <sub>$\Delta$</sub>  distance is 2.737 Å (Chevrel *et al.*, 1980). Although the largest-difference electron density map peak was  $4.00 \text{ e } \text{\AA}^{-3}$ , its location,  $1 \text{ \AA}$  away from the Sn site, makes the possibility of Sn displacement along the ternary axis unlikely – the corresponding hypothetical chalcogen–metal distance would then be about  $1.7 \text{ \AA}$ , which is too short to be ascribed even an Sn—O distance.

Two important observations arise from the present study. First, this non-stoichiometric compound exists and is stable. This is expected since the empty-channel structure Mo<sub>6</sub>S<sub>8</sub> also exists and is stable in the same conditions (room pressure and temperature). The second point relates to the nature of the

\* Lists of structure factors, anisotropic thermal parameters and bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54948 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0368]

Table 1. *Positional parameters, equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) and metal occupancy*

Equivalent isotropic  $U$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	$x$	$y$	$z$	$U_{eq}$	Occupancy
Sn(1)	0	0	0	0.0318 (4)	0.854 (2)
Mo(1)	0.22508 (8)	0.41614 (7)	0.56111 (8)	0.0067 (2)	
S(1)	0.3791 (2)	0.1262 (2)	0.7443 (2)	0.0095 (4)	
S(2)	0.2408 (2)	0.2408 (2)	0.2408 (2)	0.0107 (3)	

Table 2. *Selected bond lengths and structural distances ( $\text{\AA}$ )*

$[\text{Mo}(1) - \text{Mo}(1)]_{\Delta}$  is the distance between Mo atoms belonging to an  $\text{Mo}_3$  triangle perpendicular to the threefold axis;  $\text{Mo}(1)_{\Delta} - \text{Mo}(1)_{\Delta}$  is the shortest distance between Mo atoms belonging to two different such triangles;  $\Delta - \Delta$  is the distance between two such triangles.

$[\text{Mo}(1) - \text{Mo}(1)]_{\Delta}$	2.675 (1)	$\text{Mo}(1) - \text{S}(1)$	2.515 (2)
$\text{Mo}(1)_{\Delta} - \text{Mo}(1)_{\Delta}$	2.736 (1)	$\text{Mo}(1) - \text{S}(1)$	2.548 (2)
$\Delta - \Delta$	2.258 (1)	$\text{Mo}(1) - \text{S}(2)$	2.386 (2)
$\text{Mo}(1) - \text{S}(1)$	2.437 (2)	$\text{Sn}(1) - \text{S}(2)$	2.741 (3)
$\text{Mo}(1) - \text{S}(1)$	2.454 (2)		

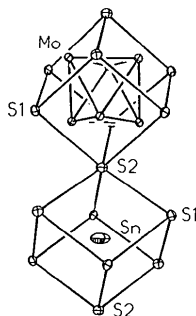


Fig. 1. Projection of the structure of  $\text{Sn}_{0.854}\text{Mo}_6\text{S}_8$ . The thermal ellipsoids are shown on a 70% probability scale.

stoichiometry. Several previous studies ascribed depressed physical properties in this compound and the similar compound  $\text{PbMo}_6\text{S}_8$  to either S-atom deficiencies or partial O-atom substitution on the S 2(c) sites. Indeed, the existence of such defects has been theoretically calculated for the entire series of Chevrel phases (Hughbanks & Hoffmann, 1983) and experimentally observed on both powders and single crystals (Hinks *et al.*, 1983; Chang *et al.*, 1987). On the other hand, a study of a  $\text{PbMo}_6\text{S}_8$  single crystal showed evidence for cation non-stoichiometry, along with S-atom deficiency (Marezio *et al.*, 1973). These authors did not, however, correlate physical properties to such defects.

In most cases, it has been assumed that defects on S-atom sites alone were responsible for changes in the superconducting critical parameters. For instance, O-atom substitution has been shown to

alter the superconducting properties  $T_c$  and  $H_{c2}$  in the case of  $\text{SnMo}_6\text{S}_8$  and  $\text{PbMo}_6\text{S}_8$  (Foner *et al.*, 1985). This might be explained by the fact that most studies deal with powders, using lattice parameters as tracers for non-stoichiometry: if defects exist on the S sites, the hexagonal-parameters ratio  $c/a$  varies noticeably enough to allow a significant quantitative estimation of the defects (Hinks, Jorgensen & Li, 1984). The present study shows *a contrario* that a 15 at.% cation deficiency alters the lattice parameters with the same magnitude ( $c/a$  variation of about 0.6%) as a 15 at.% deficiency on the 2(c) S-atom sites (Hinks *et al.*, 1984), making it difficult to evaluate contributions of the two effects through powder diffraction analysis alone. This might be why cation deficiency has not been assumed to be responsible for changes in physical properties. The present study proves that although our crystal does not display the expected physical features (Le Lay, Willis & Larbaestier, 1992), it still possesses a fully stoichiometric  $\text{Mo}_6\text{S}_8$  unit, ruling out any excess Mo or S defect as factors influencing physical properties. It is therefore reasonable to link its low  $T_c$  (10.2 K instead of the expected 14 K) to the Sn defects alone. More generally, lowered superconducting properties of  $\text{SnMo}_6\text{S}_8$  (and presumably  $\text{PbMo}_6\text{S}_8$ ) observed in the literature could also partly be ascribed to such cation defects, along with O substitution. This shows that even if care is taken to keep oxygen from contaminating the sample, adequate metal stoichiometry and thorough homogenization are still needed to obtain the expected physical properties.

The US Department of Energy supports LLL under contract No. DE-AC02-82ER4007 and TCW under contract No. DE-FG02-86ER52131. The X-ray instruments were partially funded by the US National Science Foundation.

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*Acta Cryst.* (1992). **C48**, 1182–1185

## The Synthesis and Crystal Structure of LaHSe<sub>2</sub>O<sub>6</sub>, a Layered Anhydrous Selenite

BY RUSSELL MORRIS

*Department of Materials, University of California, Santa Barbara, CA 93106-9510, USA*

WILLIAM T. A. HARRISON AND GALEN D. STUCKY

*Department of Chemistry, University of California, Santa Barbara, CA 93106-9510, USA*

AND ANTHONY K. CHEETHAM

*Department of Materials, University of California, Santa Barbara, CA 93106-9510, USA*

(Received 14 April 1991; accepted 2 December 1991)

**Abstract.** Lanthanum hydrogenselenite, LaHSe<sub>2</sub>O<sub>6</sub>,  $M_r = 393.83$ , orthorhombic,  $Pc2_1b$ ,  $a = 7.139$  (6),  $b = 19.008$  (9),  $c = 8.469$  (9) Å,  $V = 1149.24$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 4.55$  g cm<sup>-3</sup>,  $\mu = 199.7$  cm<sup>-1</sup>,  $\lambda(\text{Mo } K\alpha, \text{ graphite monochromator}) = 0.71073$  Å,  $F(000) = 1392$ , room temperature [298 (2) K]. Final  $R = 3.61\%$ ,  $wR = 4.21\%$  for 1701 observed reflections [ $> 3\sigma(I)$ ]. LaHSe<sub>2</sub>O<sub>6</sub> has been prepared using hydrothermal synthetic techniques and its crystal structure elucidated by single-crystal X-ray diffraction. This new structure consists of layers of LaO<sub>10</sub>, HSeO<sub>3</sub> and SeO<sub>3</sub> polyhedra parallel to the  $ac$  plane; the layers are interconnected by Se—OH $\cdots$ O—(Se,La) hydrogen bonds.

**Introduction.** Until recently there has been very little work, structural or otherwise, reported on phases containing rare-earth elements in combination with selenite (SeO<sub>3</sub><sup>2-</sup>) anions. The structures of PrH<sub>3</sub>·(SeO<sub>3</sub>)<sub>2</sub>(Se<sub>2</sub>O<sub>5</sub>) (Koskenlinna & Valkonen, 1977), CeSe<sub>2</sub>O<sub>6</sub> (Delage, Carpy, H'Naifi & Gourselle, 1986) and NaLa(SeO<sub>3</sub>)<sub>2</sub> (Morris, Hriljac & Cheetham, 1990) have been reported in the recent literature, these being the only anhydrous examples to date. These phases consist of the lanthanide atom in typical high coordination to oxygen, the coordination number depending on its ionic radius {eightfold for cerium [ $r(\text{Ce}^{4+}) = 1.28$  Å], ninefold for praseodymium [ $r(\text{Pr}^{3+}) = 1.32$  Å] and tenfold for lanthanum [ $r(\text{La}^{3+}) = 1.40$  Å]}, linked into a three-dimensional structure *via* the sharing of faces and/or edges with other Ln—O (Ln = lanthanide) poly-

hedra, and vertices with the trigonal-pyramidal SeO<sub>3</sub> units. This paper reports the synthesis, using hydrothermal techniques, and structure of a new layered lanthanum selenite, LaHSe<sub>2</sub>O<sub>6</sub>.

**Experimental.** LaHSe<sub>2</sub>O<sub>6</sub> was prepared from lanthanum nitrate, La(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (2 g), selenium dioxide, SeO<sub>2</sub> (5 g), and 15 cm<sup>3</sup> of water in a Teflon-lined steel autoclave. The autoclave was heated to 473 K for 48 h and then allowed to cool to room temperature. Colorless, plate-like crystals (maximum dimensions 3 × 1 × 0.5 mm) were recovered from the autoclave by suction filtration. A small crystal (0.5 × 0.1 × 0.05 mm) was mounted on a glass fibre using cyano-acrylate glue, and intensity data were collected on an Enraf-Nonius CAD-4 diffractometer (graphite-monochromated Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å). The unit-cell constants were determined from 25 centered reflections ( $12 < \theta < 18^\circ$ ) and then refined by the method of least squares. 3750 intensity data were collected in the range  $0 < 2\theta < 60^\circ$ , using the  $\omega$ - $2\theta$  scan mode [scan width =  $(1.0 + 0.35\tan\theta)^\circ$ , minimum scan speed =  $1.3^\circ \text{ min}^{-1}$ , maximum scan speed =  $6.7^\circ \text{ min}^{-1}$ ,  $0 \leq h \leq 10$ ,  $0 \leq k \leq 28$ ,  $0 \leq l \leq 12$ ]. The systematic absences ( $0kl$ ,  $l$ ;  $hk0$ ,  $k$ ) were consistent with the space groups  $Pcmb$  (No. 57; standard setting  $Pbcm$ ) and  $Pc2_1b$  (non-standard setting of  $Pca2_1$ , No. 29). No model could be established in the centrosymmetric space group, and all subsequent calculations assumed the structure was noncentrosymmetric, as confirmed by the successful course of the refinement.  $\psi$ -scan data on 2 reflections