

Synthesis and Structure Determination of $\text{Sm}_3\text{NbSe}_3\text{O}_4$

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$\text{Sm}_3\text{NbSe}_3\text{O}_4$ has been synthesized and its structure determined. The following crystal data were obtained: $M_r = 844.84 \text{ g} \cdot \text{mol}^{-1}$, orthorhombic, $Pnma$, $a = 6.8943(4) \text{ \AA}$, $b = 7.7529(8) \text{ \AA}$, $c = 14.7644(12) \text{ \AA}$, $V = 789.2(1) \text{ \AA}^3$, $Z = 4$, $D_x = 7.111 \text{ g} \cdot \text{cm}^{-3}$, $\text{MoK}\alpha$, $\lambda = 0.71073 \text{ \AA}$, $\mu = 372 \text{ cm}^{-1}$, $F(000) = 1444$, $T = 295 \text{ K}$, $R = 0.035$ for 1466 unique reflections with $F_o > 4\sigma(F_o)$, 62 variables, $\text{GoF} = 0.818$. The structure of $\text{Sm}_3\text{NbSe}_3\text{O}_4$ was determined by single-crystal X-ray diffraction. Two distinct types of polyhedra can be distinguished: a very distorted one with eight surrounding atoms (four O and four Se atoms) around Sm1 and Nb, and a bicapped trigonal prismatic one around Sm2. The crystal structure of this new compound can be described on the basis of corrugated planes perpendicular to the c axis. These planes are built up from edge-sharing trigonal prismatic polyhedra (Sm2); connection between successive planes is achieved through the distorted polyhedra which surround atoms Sm1 and Nb. © 1998 Academic Press

INTRODUCTION

Compared to the very large number of reported ternary oxides or ternary chalcogenides of lanthanides and transition metals, relatively few corresponding oxychalcogenides are known. This latter class of compounds has to be distinguished from the sulfoxides or selenoxides which contain chalcogen–oxygen bonds; in oxychalcogenide compounds, X (S, Se) and O atoms are directly bonded to the metal atoms. The crystal chemistry of compounds with a low sulfur content (with respect to the oxygen content) is related to that of pure oxides, i.e., a strong ionic character leading in general to a more pronounced 3D structure type than in the corresponding pure chalcogenide homologues.

Focusing only on the quaternary La–Ti–S–O system, new compounds have been recently characterized. The more oxygen-rich oxysulfides are $\text{La}_4\text{Ti}_3\text{S}_4\text{O}_8$ and $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$ (1). Examples with a very low oxygen content include $\text{Sr}_{5.8}\text{La}_{4.4}\text{Ti}_{7.8}\text{S}_{24}\text{O}_4$ and $\text{La}_{14}\text{Ti}_8\text{S}_{33}\text{O}_4$ (2) as well as $\text{La}_{20}\text{Ti}_{11}\text{S}_{44}\text{O}_6$ (3), $\text{Ce}_{20}\text{Ti}_{11}\text{S}_{44}\text{O}_6$ (4), and $\text{La}_8\text{Ti}_{10}\text{S}_{24}\text{O}_4$ (5). The latter five phases, which have a much lower oxygen content than the first two, exhibit a common structural feature. Indeed, one can recognize a 2D array of rutile-like

(edge-sharing) chains which cross perpendicularly to form a $[\text{Ti}_4\text{S}_2\text{O}_4]$ cluster in all five of these compounds. No structural relationship exists between the oxygen-rich and oxygen-poor compounds.

Here, we present the synthesis and structure of $\text{Sm}_3\text{NbSe}_3\text{O}_4$, which corresponds to a situation with as much Se as O. This chemical composition is similar to that of $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$; i.e., they have an identical Ln/T ratio ($Ln = \text{La}, \text{Sm}$; $T = \text{Ti}, \text{Nb}$) and a comparable cation/anion ratio. However, as $\text{Sm}_3\text{NbSe}_3\text{O}_4$ and $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$ have very different chalcogen/oxygen ratios, no structural relationships exist between them.

EXPERIMENTAL

Synthesis

The compound $\text{Sm}_3\text{NbSe}_3\text{O}_4$ was synthesized as a side product in an attempt to prepare the $(\text{SmSe})_{1+x}\text{NbSe}_2$ misfit derivative (6). A mixture of elemental powders of Sm, Nb, and Se, weighted in stoichiometric amounts to get the misfit phase, was sealed in a quartz ampoule under vacuum ($p = 2 \times 10^{-2} \text{ atm}$). The silica tube was not protected against reaction with the Sm by a carbon coating. The tube was progressively heated in a furnace to 1000°C and maintained at this temperature for 10 days. The intermediate product of the reaction was ground before a reheating at 1000°C with a small amount of I_2 ($< 5 \text{ mg} \cdot \text{cm}^{-3}$) to promote crystallization. The tube was then air-quenched. The reaction yielded a mixture of black platelets of the misfit derivative and easily distinguishable orange-colored needles of this new phase. The source of oxygen is unknown but is most likely the reaction of Sm with the silica tube.

Semiquantitative chemical analyses on these crystals were carried out using an EDS-equipped scanning electron microscope. The EDS results from three distinct crystals (averaged atomic percentages) confirm the presence of oxygen and corroborate the structure composition of non-oxygen atoms as follows: Sm, 43.0 (42.85); Nb, 16.3 (14.3); Se, 40.7 (42.85) (calculated values are in parentheses). The oxygen content was indirectly deduced from the interatomic distances where typical Nb–O ($\approx 1.90 \text{ \AA}$) and Sm–O ($\approx 2.35 \text{ \AA}$) distances are occurring.

Symmetry and Unit Cell Parameters

Preliminary investigation with the use of precession and Weissenberg X-ray photographic techniques indicated that this compound crystallizes with orthorhombic symmetry. A needle-shaped crystal with dimensions $0.22 \times 0.054 \times 0.030$ mm³ was mounted on an Enraf-Nonius CAD4 diffractometer using MoK α radiation. The crystal orientation matrix was determined from 25 reflections in the

range $5.52^\circ < \theta < 19.65^\circ$. Table 1 lists the experimental conditions for data collection. The unit cell parameters were refined from 25 arbitrarily chosen higher order reflections ($26.70^\circ < 2\theta < 55.88^\circ$) using the CELDIM program. From a refinement with the constraints $\alpha = \beta = \gamma = 90^\circ$, one obtains $a = 6.8943(4)$ Å, and $b = 7.7529(8)$ Å, $c = 14.7644(12)$ Å.

Structure Refinement

A total of 7081 reflections were collected in the range $1.5^\circ < \theta < 35^\circ$ ($-11 < h < 11$, $-12 < k < 12$, and $0 < l < 23$). The data were corrected for Lorentz-polarization effects and for absorption (faces indexed). The observed systematic conditions ($0kl$, $k + l = 2n$; $hk0$, $h = 2n$) are compatible with the space groups $Pnma$ (No. 62) and $Pn2_1a$ (No. 33). Intensity statistics favored the centrosymmetric space group $Pnma$. An R index of 0.0683 resulted from the averaging of reflections; a total of 1727 unique reflections ($F_o > 0$) were used for the refinements.

The structure was solved by direct methods (and subsequent difference-Fourier analyses) and refined by full-matrix least-squares techniques from the SHELXTL program (7). All atoms were refined anisotropically and a secondary extinction parameter was included. The final cycle of the least-squares refinement gave agreement factors of $R = 0.035$ for 1466 $F_o > 4\sigma(F_o)$ and 0.045 for all 1727 data, $wR = 0.111$, and GoF = 0.818. The final electron density map with coefficients $F_o - F_c$ shows maximum and minimum peaks at 4.46 and -3.84 e Å⁻³, respectively; the highest peaks are found within 0.8 Å of the samarium atoms. Atomic coordinates and anisotropic thermal parameters are listed in Tables 2 and 3, respectively.

RESULTS

The needle axis for any investigated crystal of this phase corresponds to the b axis. The Bragg photograph taken for

TABLE 1
Experimental Conditions

Crystal Data	
Chemical formula	Sm ₃ NbSe ₃ O ₄
Chemical formula weight	844.84
Cell setting	Orthorhombic
Space group	<i>Pnma</i>
a (Å)	6.8943(4)
b (Å)	7.7529(8)
c (Å)	14.7644(12)
V (Å ³)	789.17(11)
Z	4
Temperature (K)	293
ρ_{cal} (g/cm ³)	7.111(1)
μ (mm ⁻¹)	37.2
Crystal shape	Needle
Crystal color	Orange
Crystal size (mm ³)	$\approx 0.054 \times 0.22 \times 0.030$, bounded by faces {100}, {010}, and {001}
Data Collection	
Diffractometer	Enraf-Nonius CAD4
Radiation type	MoK α
Wavelength (Å)	0.71073
Monochromator	Graphite
θ range (deg)	1.5–35
Scan type	ω/θ
ω	$1.0 + 0.35 \tan \theta$
Range of h, k, l	$-11 \leq h \leq 11$ $-12 \leq k \leq 12$ $0 \leq l \leq 23$
No. of indpt reflections $F_o > 0$	1727
No. of reflections $F_o > 4\sigma(F_o)$	1466
Refinement	
For 1466 data with $F_o > 4\sigma(F_o)$	
R^a	0.035
wR^a	0.101
For all 1727 data	
R	0.045
wR	0.111
No. of parameters	62
GoF ^a	0.818
Extinction parameter	0.0022(2)
Residual electron density [max, min (e Å ⁻³)]	4.46, -3.84

^a $R = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR = (\sum w(F_o^2 - F_c^2)^2/\sum(w(F_o^2)^2))^{1/2}$; $w = 1/(\sigma^2(F_o^2) + (0.1P)^2)$; $P = (\max(F_o^2, 0) + 2F_c^2)/3$; GoF = $(\sum(w(F_o^2 - F_c^2)^2)/(n - p))^{1/2}$.

TABLE 2
Positional Parameters and Equivalent Isotropic Displacement Parameters for Sm₃NbSe₃O₄

Atom	Site	x	y	z	U_{eq}^a (Å ²)
Sm1	4c	0.78130(7)	$\frac{1}{4}$	0.58276(3)	0.00562(13)
Sm2	8d	0.21486(5)	$-0.00680(4)$	0.65383(3)	0.00679(12)
Nb	4c	0.82588(13)	$\frac{3}{4}$	0.56850(6)	0.0058(2)
Se1	4c	0.49523(15)	$\frac{1}{4}$	0.72884(7)	0.0074(2)
Se2	4c	0.55039(14)	$\frac{3}{4}$	0.70307(7)	0.0073(2)
Se3	4a	$\frac{1}{2}$	0	$\frac{1}{2}$	0.0223(3)
O1	4c	0.8575(10)	$\frac{3}{4}$	0.4394(5)	0.0057(12)
O2	8d	0.8854(8)	$-0.0287(7)$	0.6132(4)	0.0120(10)
O3	4c	0.1323(10)	$\frac{3}{4}$	0.5694(5)	0.0083(13)

^a $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

TABLE 3
Anisotropic Thermal Parameters for $\text{Sm}_3\text{NbSe}_3\text{O}_4$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sm1	0.0050(2)	0.0059(2)	0.0059(2)	0	0.00038(15)	0
Sm2	0.0055(2)	0.0065(2)	0.0084(2)	-0.00025(10)	0.00039(10)	-0.00004(10)
Nb	0.0059(3)	0.0068(4)	0.0047(3)	0	0.0004(3)	0
Se1	0.0055(4)	0.0096(4)	0.0070(4)	0	-0.0008(3)	0
Se2	0.0057(4)	0.0086(4)	0.0074(4)	0	-0.0004(3)	0
Se3	0.0190(6)	0.0371(8)	0.0107(5)	-0.0101(5)	0.0069(4)	-0.0208(5)
O1	0.009(3)	0.004(3)	0.005(3)	0	-0.002(2)	0
O2	0.006(2)	0.014(3)	0.017(3)	0.000(2)	-0.004(2)	0.001(2)
O3	0.004(3)	0.010(3)	0.011(3)	0	-0.001(2)	0

a crystal rotating along this axis shows layer lines of strong intensities (for $k = 0, 2, \dots$) and of very weak intensities (for $k = 1, 3, \dots$). The atomic coordinates (Table 2) show that the y coordinates for all atoms are either around 0, $\frac{1}{2}$ or strictly $\frac{1}{4}$, $\frac{3}{4}$. Thus, along the b direction, several of the same atoms are separated by approximately $b/2$ (≈ 3.8 Å) because of symmetry (for instance, x, y, z and $x, \frac{1}{2} - y, z$ when $y \approx 0$), a condition that occurs for sites $8d$ (Sm2, O2) and $4a$ (Se3). Otherwise, for $y = \frac{1}{4}$ and $\frac{3}{4}$, other pairs of atoms not related by symmetry are roughly juxtaposed along this b direction, for example, Sm1/Nb, Se1/Se2, and O1/O3. The crystal structure of $\text{Sm}_3\text{NbSe}_3\text{O}_4$ viewed down the b axis is shown in Fig. 1.

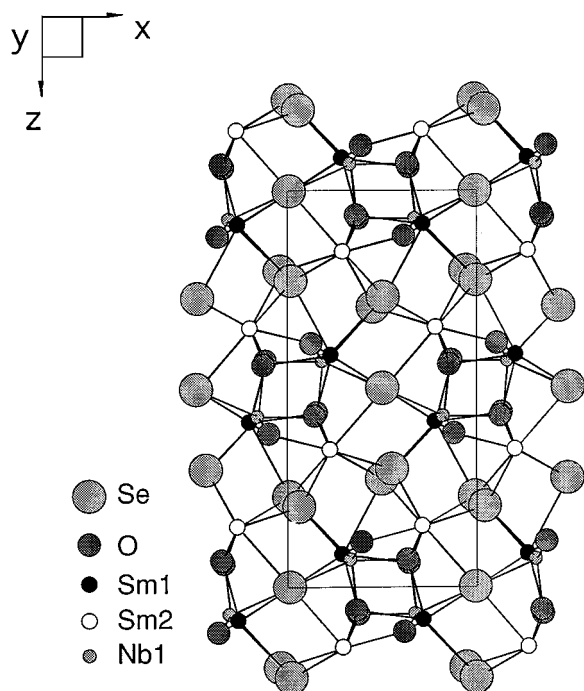


FIG. 1. Projection of the structure of $\text{Sm}_3\text{NbSe}_3\text{O}_4$ onto the (a, c) plane; all atoms have $0 \leq y \leq 1$.

Interatomic distances are given in Table 4 for distinct polyhedra around the metal atoms Sm1, Nb, and Sm2.

The Sm atoms in $\text{Sm}_3\text{NbSe}_3\text{O}_4$ are eight-coordinate. Atom Sm1 is surrounded by four O atoms and four Se atoms: two O atoms (O1 and O3) and two Se atoms (Se1, Se1'), all at $y = \frac{1}{4}$, describe a quadrilateral base with Sm1 also at $y = \frac{1}{4}$ in a very excentered position; two Se [$2 \times \text{Se3}$ ($y = 0, \frac{1}{2}$)] and two O [$2 \times \text{O2}$ ($y = 0, \frac{1}{2}$)] atoms lie in a perpendicular plane (see Fig. 2a).

As the Nb atom is found at about the same x, z coordinates as Sm1, but shifted by $b/2$, the coordination around Nb is quite similar to that of Sm1 since all its surrounding atoms have also an "equivalent" one shifted by $b/2$ (see Fig. 2b). The only difference within this polyhedron is a much longer Nb1-Se2 distance (3.711 Å) than the corresponding Sm1-Se1 distance (3.148 Å) within the Sm1 polyhedron. Thus, Nb is seven-coordinate rather than eight-coordinate.

The Sm2 atom is in a trigonal prism of four Se (two Se1, two Se2) and two O (O1, O3) atoms which is bicapped by O2 and Se3 (Fig. 2c). Adjacent bicapped trigonal prisms around Sm2 atoms are bridged via a common edge (Se1, Se2) to form "corrugated planes" of polyhedra perpendicular to the c direction (Fig. 3). Sm1/Nb atoms connect these successive planes through the four atoms (Se1, Se1', O1, and O3)/(Se2, Se2', O1, and O3) that constitute the quadrilateral base of the Sm1/Nb polyhedron, respectively. The Se3 atom plays a particular role in the connection between both types of polyhedra [Sm1 (or Nb) and Sm2]. The Se3 atoms are at the center of an octahedron of metal atoms, with Sm2 as the vertices, the "square plane" being constituted with two Sm1 and two Nb atoms.

Given the chemical composition $\text{Sm}_3\text{NbSe}_3\text{O}_4$, charge balance requires Sm(III) and Nb(V) to compensate Se(II) and O(II) as no short Se-Se bonding is present. Bond valence calculations roughly confirm these assumptions. The bond valence method is a semiempirical method that relates the valence for any atom to its coordination. Each bond is assigned a valence according to the equation

TABLE 4
Interatomic Distances and Bond Valences

Atom 1	Atom 2	Distance (Å)	Symmetry codes ^a	Bond valence	Atom 1	Atom 2	Distance (Å)	Symmetry codes	Bond valence					
Sm1	O2	2.321(6)	8	0.533	Sm2	Se1	3.0426(9)	4	0.365					
	O2	2.321(6)				Se2	3.0504(9)			10	0.358			
	O3	2.325(8)				Se2	3.0717(9)							
	O1	2.511(7)				7	0.408			Nb	O2	1.883(6)	13	1.08
	Se1	2.9226(12)									O2	1.883(6)		
	Se3	3.0018(4)									O1	1.919(7)		
	Se3	3.0018(4)									O3	2.113(7)		
	Sm2	Se1				3.1485(12)	6			0.275	Se2	2.7485(13)	5	0.52
total = 3.506				Se2	3.7108(14)	6		0.04						
O3		2.330(5)	9	0.520	Se2				3.1349(7)					
O2		2.355(5)	1	0.486	Se3	3.1349(7)		11	0.18					
O1		2.471(4)	2	0.355	Se3	3.1349(7)								
Se1		2.9878(8)	2	0.423	total = 4.648									
Se3	3.0043(4)	0.405			Sm1	Nb	3.5103(10)	3						

^aSymmetry transformations used to generate equivalent atoms: (1) $x - 1, y, z$; (2) $-x + 1, -y + 1, -z + 1$; (3) $-x + 2, -y + 1, -z + 1$; (4) $x - \frac{1}{2}, y, -z + \frac{3}{2}$; (5) $x + 1, y, z$; (6) $x + \frac{1}{2}, y, -z + \frac{3}{2}$; (7) $-x + 1, y + \frac{1}{2}, -z + 1$; (8) $x, -y + \frac{1}{2}, z$; (9) $x, y - 1, z$; (10) $x - \frac{1}{2}, y - 1, -z + \frac{3}{2}$; (11) $1 - x, y + \frac{1}{2}, 1 - z$; (12) $x, y + 1, z$.

$v_{ij} = \exp[(R_{ij} - d_{ij})/b]$, where $b = 0.37$ is a universal constant, d_{ij} is the interatomic distance, and R_{ij} is the bond valence parameter tabulated by Brese and O'Keeffe (8). The valence of atom i is defined as the summation over all the interatomic bonds; i.e., $V_i = \sum v_{ij}$.

The lack of crystallographic data for this kind of structure with two cations (Sm and Nb) and two anions (O and Se) has probably led to bad estimated values of the tabulated R_{ij} parameters for these bonds. This can explain the somewhat different results obtained for Sm1 and Nb, 3.5 and 4.65, respectively (see Table 4), compared with the expected ones, i.e., 3 and 5, respectively. We can also notice that Sm1 and Nb atoms have about the same environment (just

shifted by $b/2$); therefore, a hypothetical Sm/Nb mixing within these sites could occur, which in turn should give bad calculations. However, such a mixing was not demonstrated through X-ray structure refinement.

The presence of Nb(V) was not expected in an oxyselenide derivative. However, in the search for parent compounds in the literature, we found mention of a compound with about the same chemical composition, $\text{La}_3\text{NbSe}_2\text{O}_4\text{F}_2$ (9). Charge balance is achieved with the substitution of one Se atom by two F atoms. A careful examination of the reported structure, despite the fact that the space group is also $Pnma$ and that the cell volume is about two times larger than that of $\text{Sm}_3\text{NbSe}_3\text{O}_4$, does not show clear evidence of some

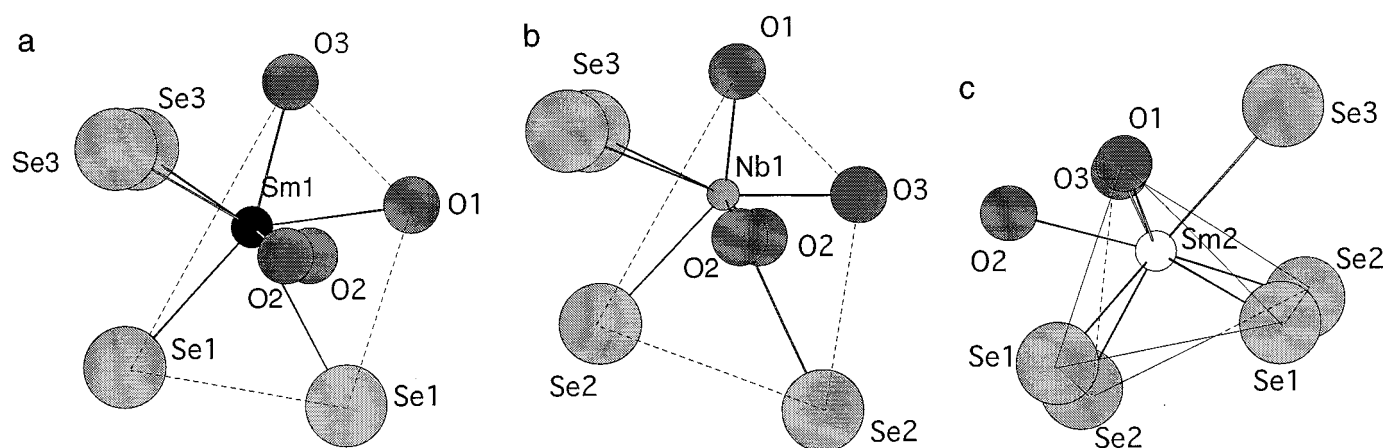


FIG. 2. View, projected along **b**, of the coordination environment of atoms (a) Sm1, (b) Nb1, and (c) Sm2 found in $\text{Sm}_3\text{NbSe}_3\text{O}_4$ (cation coordinates as in Table 2).

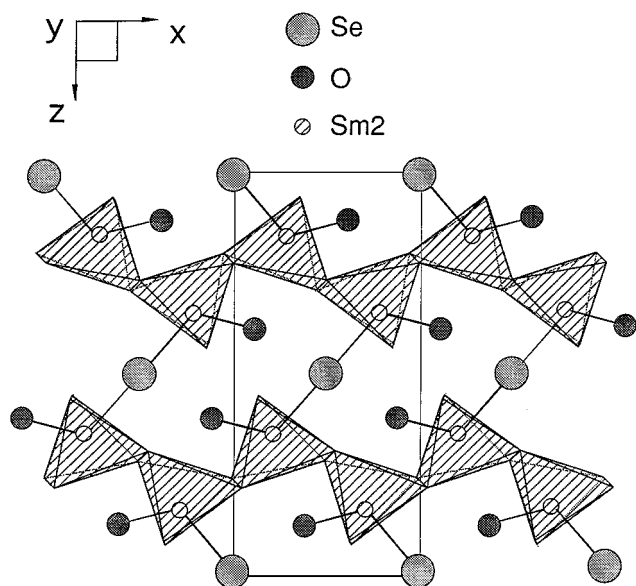


FIG. 3. Polyhedral representation of the "corrugated planes" of Sm²⁺-centered polyhedra stacked along *c*.

structural relationship. Indeed, the crystal structure of $\text{La}_3\text{NbSe}_2\text{O}_4\text{F}_2$ contains a distorted NbO_5Se octahedron and three independent distorted $\text{LaSe}_x\text{O}_y\text{F}_z$ tricapped trigonal prisms. Nothing comparable can be found in $\text{Sm}_3\text{NbSe}_3\text{O}_4$.

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