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Synthesis and Characterization of $La_3NbSe_2O_4F_2$

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Crystals of the unusual oxyfluoroselenide $La_3NbSe_2O_4F_2$ were obtained during the exploration of the quaternary La/Nb/Cu/Se system. Oxygen was extracted from the silica tube, while fluorine was present as a minor impurity in the La powder. The compound crystallizes in space group D_{2h}^{16}–*Pnma* of the orthorhombic system with four formula units in a cell with dimensions: a = 11.290(4), b = 4.001(1), and c = 18.062(4) Å (T = 113 K). The structure has been determined by single-crystal X-ray methods. The presence of F in the crystals was confirmed by windowless EDAX measurements. The two F sites were distinguished from the four O sites from a combination of the X-ray refinement and a bond-valence parameter calculation made with the program EUTAX. In the structure the Nb atom is octahedrally coordinated while each of the three independent La atoms is in a tricapped trigonal prism. The Nb atom is bound to one Se atom and five O atoms while the three La sites are coordinated by various combinations of Se, O, and F atoms. The NbO_5Se octahedra corner share and the $LaSe_xO_yF_z$ tricapped trigonal prisms face share in the b direction. © 1993 Academic Press, Inc.

Introduction

Some oxyselenides and many oxyfluorides have been reported. Among the known oxyselenides are compounds in the *Ln*/*M*/Se/O system (*M* = Cu, Ag, Ga, In, Ge, Sn, As, Sb, Bi; *Ln* = lanthanide) whose structures consist of Ln_2O_2 and M_xSe_y slabs (*1*). Also, the series of compounds $Ln_2Ta_3Se_2O_8$ (*Ln* = La . . . Nd) are known; here the *Ln* atoms are in tricapped trigonal prismatic sites and the Ta atoms are in distorted octahedral sites (*2*). The known oxyfluorides include LaOF (*3*), SbOF (*4, 5*), and the *Ln*OF series (*6*). However, there appear to be no examples of solid state oxyfluoroselenides. There are, of course, the molecular compounds $SeOF_2$ (*7*), $SeOF_2 \cdot NbF_5$ (*8*), and $Xe(OSeF_5)_2$ (*9*). Here we describe the synthesis and structure of the first solid state oxyfluoroselenide, $La_3NbSe_2O_4F_2$.

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Experimental

Synthesis. The compound $La_3NbSe_2O_4F_2$ was synthesized during an exploration of the La/Nb/Cu/Se system. The binary sesquiselenide La_2Se_3 was prepared from the reaction of elemental powders of La (Reacton, 99.9%) and Se (Aldrich, 99.999+%) in stoichiometric amounts in an evacuated quartz tube at 1275 K. La_2Se_3, Nb (Alfa 99.8%), Cu (Alfa 99.5%), and Se were loaded into a quartz tube in the molar ratio 0.5 : 1 : 2 : 5, evacuated to 10^{-5} Torr, and sealed. The tube was heated in a furnace to 1475 K, held there for 4 days, and then quenched to room temperature. The major product of the reaction was Cu_3NbSe_4 (*10*), which formed as red prismatic crystals. Also present, however, were about a dozen small yellow needles. Analysis of eight of these yellow crystals with the microprobe of an EDAX (Energy Dispersive Analysis by X-rays)-equipped Hitachi S-570 scanning electron microscope confirmed the presence of

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La, Nb, and Se in approximately a 3 : 1 : 2 ratio. No significant amount of any other element with an atomic number greater than 10 was detected; the Be window on the standard EDAX detector filters out the soft X-rays from elements having $Z \leq 10$. Because of the low ratio of selenium to metal, we believed that the compound was a La/Nb/Se/O phase, the oxygen having been extracted from the silica tube (*2*).

Structure Determination of $La_3NbSe_2O_4F_2$. The crystal used for data collection was a yellow needle 0.30 × 0.024 × 0.026 mm on edge bounded by {010}, {001}, and {102}. The unit cell constants were determined from a least-squares analysis of the setting angles of 16 reflections in the range $35° < 2\theta$ (Mo $K\alpha_1$) $< 42°$ that had been automatically centered at 113 K on a Picker FACS-1 diffractometer. Six representative standard reflections measured every 100 reflections during the course of the data collection showed no significant variation in intensity. Additional data collection parameters and crystallographic details are described in Table I. Intensity data were processed and corrected for absorption (*11*) on an IBM RS/6000 series computer with programs and methods standard in this laboratory.

The observed Laue symmetry and the systematic absences ($0kl$, $k + l = 2n + 1$; $hk0$, $h = 2n + 1$) are consistent with the orthorhombic space groups D_{2h}^{16}–*Pnma* and C_{2v}^{9}–$Pn2_1a$. Initially, the composition $La_3NbSe_2O_5$ was assumed and a correction for absorption was made. An R index of 0.048 resulted from the averaging of the hkl and $h\bar{k}l$ reflections; these are equivalent in *Pnma* but not in $Pn2_1a$. Consequently, the space group D_{2h}^{16}–*Pnma* was chosen; this choice was confirmed by the resultant satisfactory refinement. The initial La, Nb, and Se positions were determined from direct methods with the program SHELXS-86 (*12*). The O atoms were found from a subsequent electron density map. After the inclusion of oxygen the stoichiometry was $La_3NbSe_2O_6$. The structure was refined with the use of the program SHELXL92 (*13*) by full-matrix least-squares techniques, the function $\Sigma w(F_o^2 - F_c^2)^2$ being minimized. Anisotropic thermal motion and an extinction parameter were included. Given the stoichiometry $La_3NbSe_2O_6$, charge balance requires La(IV) or Nb(VII) as there are no short Se–Se interactions. Very small thermal parameters for two of the oxygen sites suggested to us that an element such as fluorine might be in those sites. Therefore a windowless EDAX experiment was undertaken to determine the presence of any elements lighter than Na. The windowless EDAX spectrum (Fig. 1) reveals the presence of oxygen and fluorine in the crystals. Carbon appears in the spectrum because the samples were mounted with colloidal graphite on a carbon disk. Subsequent elemental analyses of the starting materials indicated that the La powder contains 0.013% F. Fluorine was included in the refinement at the two oxygen sites that displayed small thermal parameters. This results in the stoichiometric formula $La_3NbSe_2O_4F_2$, with charge balance achieved with La(III), Nb(V), Se(-II), O(-II), and F(-I). The addition of fluorine had only a small effect on the refinement, resulting in an increase in the thermal parameters of the fluorine sites. The data were corrected again for absorption, with the linear absorption coefficient calculated from the composition $La_3NbSe_2O_4F_2$. The program STRUCTURE TIDY (*14*) was used to standardize the positional parameters. The final refinement led to a value of $R_w(F_o^2)$ of 0.084. The conventional R index (on F for $F_o^2 > 2\sigma(F_o^2)$) is 0.036. The final difference electron density map shows no feature with a height greater than 0.5% that of a La atom.

Final values of the atomic parameters and equivalent isotropic thermal parameters are given in Table II. Final anisotropic thermal parameters and structure amplitudes are available.[1]

[1] See NAPS Document No. 05024 for 11 pages of supplementary materials from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid.

TABLE I

CRYSTAL DATA AND INTENSITY COLLECTION FOR $La_3NbSe_2O_4F_2$

Formula	$La_3NbSe_2O_4F_2$
Formula mass (amu)	769.6
Space group	D_{2h}^{16}–*Pnma*
a (Å)	11.290(4)[a]
b (Å)	4.001(1)
c (Å)	18.062(4)
V (Å^3)	815.8(4)
Z	4
ρ_c (g cm^{-3})	6.27
T of data collection (K)[b]	113
Crystal shape	Needle ≈ 0.30 × 0.024 × 0.026 mm bounded by {010}, {001}, {102}
Crystal volume (mm^3)	1.50×10^{-4}
Radiation	graphite monochromated Mo Kα ($\lambda(K\alpha_1)$ = 0.7093 Å
Linear abs. coeff. (cm^{-1})	255.96
Transmission factors[c]	0.454–0.635
Detector aperture (mm)	Horizontal, 5.5; vertical, 5.5; 32 cm from crystal
Scan type	θ–2θ
Scan speed (deg min^{-1})	2.0 in 2θ
Scan range (deg)	−0.6 to +1.0 in 2θ
Takeoff angle (degrees)	2.5
$\lambda^{-1} \sin\theta$, limits (Å^{-1})	0.052–0.810, $3° \le 2\theta(\text{Mo } K\alpha_1) \le 70°$
Background counts[d]	10 sec. at each end of scan with rescan option
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (0.04 \times F_o^2)^2$
Data collected	$+h, \pm k, +l$
No. of data collected	3618
No. of unique data, including $0 \ge F_o^2 \ge -3\sigma(F_o^2)$	2018
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	1691
No. of variables	74
R_{ave}	0.048
$R_w(F^2)$	0.084
R(on F for $F_o^2 > 2\sigma(F_o^2)$)	0.036
Error in observation of unit weight (e^2)	1.02

[a] Obtained from a refinement with the constraints $\alpha = \beta = \gamma = 90°$.

[b] The low-temperature system is based on a design by Huffman (*22*).

[c] The analytical method as employed in the Northwestern absorption program, AGNOST, was used for the absorption correction (*11*).

[d] The diffractometer was operated under the Vanderbilt disk-oriented system (*23*).

Bond-Valence Parameter Calculations. Bond-valence parameter calculations were performed with the use of the program EUTAX (*15*). The goal of the calculations was to distinguish between O and F sites through the computation of the total valency present at each site. The first calculation assumed six O sites and no F sites; it resulted in valence sums near 2.0 for four of the O sites and 1.59 and 1.39 for two others. In the second calculation these latter two sites were assigned as F atoms and valence sums of 1.16 and 1.02 resulted (Table III). The two sites assigned to F are the same as those derived from the X-ray refinement. The agreement between these two independent methods is good evidence for the correct placement of oxygen versus fluorine and for $La_3NbSe_2O_4F_2$ being the stoichiometry of the present compound.

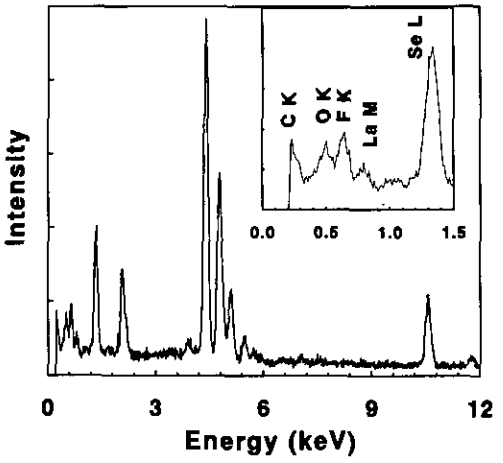

FIG. 1. Windowless EDAX spectrum of $La_3NbSe_2O_4F_2$.

TABLE III

BOND VALENCES FOR $La_3NbSe_2O_4F_2$

Atom	Total bond valence
La(1)	2.95
La(2)	3.21
La(3)	3.10
Nb	4.90
Se(1)	2.22
Se(2)	1.76
O(1)	1.97
O(2)	2.04
O(3)	2.08
O(4)	1.91
F(1)	1.16
F(2)	1.02

Results and Discussion

The crystal structure of $La_3NbSe_2O_4F_2$ contains a distorted NbO_5Se octahedron and three independent distorted $LaSe_xO_yF_z$ tricapped trigonal prisms. A view down the *b* axis is given in Fig. 2. Figure 3 shows the coordination spheres about the metal atoms, with atoms labeled. Selected bond distances and angles for $La_3NbSe_2O_4F_2$ are provided in Table IV. The La–O and La–F distances are comparable to those found in LaOF (La–O = 2.58; La–F = 2.42 Å) (*3*). The Nb–O distances fall within the range found in *H*–Nb_2O_5 (1.753(4) to 2.479(3) Å) (*16*), while the Nb–Se distance is longer than the average distances seen in both $NbSe_3$ (2.684 Å) (*17*) and Nb_2Se_9 (2.659 Å) (*18*).

The Nb atom is coordinated to one Se atom and five O atoms. The NbO_5Se octahedra corner share in the *b* direction through an O(4) atom. The three La atoms are coor-

TABLE II

POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS FOR $La_3NbSe_2O_4F_2$

Atom	*x*	*y*	*z*	U_{eq}[a] (Å^2)
La(1)	0.00371(4)	¼	0.39328(3)	0.0046(2)
La(2)	0.06683(4)	¼	0.80152(2)	0.0044(2)
La(3)	0.29432(4)	¼	0.53168(3)	0.0046(2)
Nb	0.19222(6)	¼	0.19491(4)	0.0040(3)
Se(1)	0.00718(7)	¼	0.07969(4)	0.0049(3)
Se(2)	0.28429(7)	¼	0.90836(5)	0.0054(3)
F(1)	0.0627(5)	¼	0.6683(3)	0.007(2)
F(2)	0.0702(5)	¼	0.5266(3)	0.009(2)
O(1)	0.0543(6)	¼	0.2549(3)	0.007(3)
O(2)	0.2812(6)	¼	0.1001(3)	0.007(3)
O(3)	0.3132(5)	¼	0.2607(3)	0.006(2)
O(4)	0.3303(5)	¼	0.6791(3)	0.005(2)

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

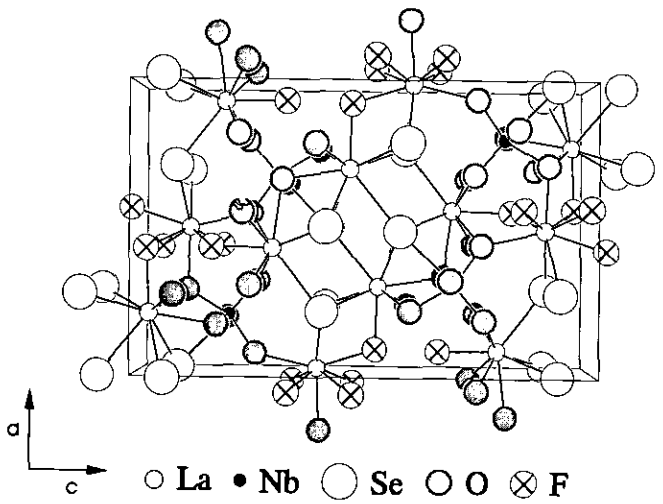

FIG. 2. View of the $La_3NbSe_2O_4F_2$ structure down [010]. The sizes of the atoms are arbitrary.

dinated variously to Se, O, and F atoms in tricapped trigonal prisms. These polyhedra face share in the *b* direction. Atom La(1) is coordinated to two Se, two O, and five F atoms with the capping atoms being O, O, and F. Atom La(2) is coordinated to three Se, five O, and one F atom with the capping atoms being Se, O, and F. Atom La(3) is coordinated to five Se, three O, and one F atom with the capping atoms being Se, O, and F. The NbO_5Se octahedron face shares with the polyhedron about atom La(2) through atoms O(2), O(4), and Se(1) and with the polyhedron about atom La(3) through atoms O(1), O(4), and Se(1). The NbO_5Se octahedron also shares three of its vertices with the polyhedra about atoms La(1), La(2), and La(3) through atoms O(1), O(3), and Se(1), respectively. The polyhedron about atom La(1) edge shares with the one about atom La(2) through atoms O(1) and F(1) and it shares a vertex with another polyhedron about atom La(2) through an Se(2) atom. The polyhedron about atom La(1) also shares an edge with the one about atom La(3) through atoms O(2) and F(2) and face shares with the one about La(3) through two Se(2) and one F(2) atom. Finally, the polyhedra about atoms La(2) and La(3) face share through two Se(1) and one O(4) atom.

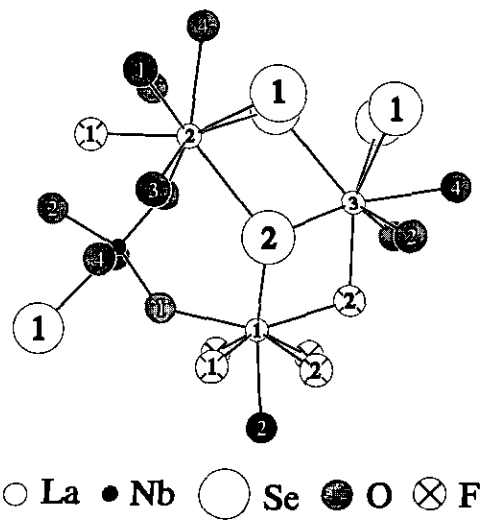

FIG. 3. View of the metal coordination spheres in the $La_3NbSe_2O_4F_2$ structure.

In known rare-earth oxychalcogenides the *Ln* atoms are in tricapped trigonal prisms, being coordinated to various combinations of O and *Q* atoms (*Q* = S, Se). In the $Ln_2Ta_3Se_2O_8$ structures (*2*) both *Ln* sites are coordinated by two Se and seven O atoms; in the $La_5V_3O_7S_6$ structure one unique La atom is coordinated to four O and

TABLE IV

SELECTED DISTANCES (Å) AND ANGLES (DEG) FOR $La_3NbSe_2O_4F_2$

La(1)–Se(2)	2×	3.131(2)	F(1)–La(2)–O(1)	66.57(14)
La(2)–Se(1)	2×	3.050(2)	O(3)–La(2)–O(1)	64.1(2)
La(2)–Se(2)		3.123(2)	O(3)–La(2)–O(1)	140.2(2)
La(3)–Se(1)	2×	3.127(2)	O(1)–La(2)–O(1)	99.1(2)
La(3)–Se(1)		3.134(2)	F(1)–La(2)–O(4)	96.4(2)
La(3)–Se(2)	2×	3.123(2)	O(3)–La(2)–O(4)	124.73(11)
La(1)–O(1)		2.564(6)	O(1)–La(2)–O(4)	62.26(14)
La(1)–O(2)		2.515(6)	F(1)–La(2)–Se(1)	134.27(6)
La(2)–O(1)	2×	2.629(4)	O(3)–La(2)–Se(1)	80.37(12)
La(2)–O(3)	2×	2.526(4)	O(3)–La(2)–Se(1)	150.64(14)
La(2)–O(4)		2.693(6)	O(1)–La(2)–Se(1)	129.00(13)
La(3)–O(2)	2×	2.501(4)	O(1)–La(2)–Se(1)	68.36(12)
La(3)–O(4)		2.694(6)	O(4)–La(2)–Se(1)	68.72(9)
La(1)–F(1)	2×	2.409(3)	Se(1)–La(2)–Se(1)	81.97(3)
La(1)–F(2)		2.522(5)	F(1)–La(2)–Se(2)	129.27(13)
La(1)–F(2)	2×	2.607(4)	O(3)–La(2)–Se(2)	76.03(13)
La(2)–F(1)		2.406(5)	O(1)–La(2)–Se(2)	130.44(11)
La(3)–F(2)		2.532(6)	O(4)–La(2)–Se(2)	134.38(13)
La(1)–La(1)	2×	4.001(2)	Se(1)–La(2)–Se(2)	77.33(3)
La(1)–La(3)		4.125(2)	O(2)–La(3)–O(2)	106.2(2)
La(2)–La(2)		4.001(2)	O(2)–La(3)–F(2)	71.2(2)
La(3)–La(3)		4.001(2)	O(2)–La(3)–O(4)	64.06(14)
La(2)–Nb	2×	3.544(2)	F(2)–La(3)–O(4)	100.8(2)
La(3)–Nb	2×	3.566(2)	O(2)–La(3)–Se(2)	140.18(15)
Nb–O(1)		1.897(6)	F(2)–La(3)–Se(2)	71.93(9)
Nb–O(2)		1.984(6)	O(4)–La(3)–Se(2)	138.42(4)
Nb–O(3)		1.811(6)	O(2)–La(3)–Se(2)	75.14(12)
Nb–O(4)	2×	2.036(2)	Se(2)–La(3)–Se(2)	79.67(3)
Nb–Se(1)		2.949(2)	O(2)–La(3)–Se(1)	66.14(14)
F(1)–La(1)–F(1)		112.3(2)	O(2)–La(3)–Se(1)	128.22(14)
F(1)–La(1)–O(2)		73.18(14)	F(2)–La(3)–Se(1)	136.59(5)
F(1)–La(1)–F(2)		122.26(11)	O(4)–La(3)–Se(1)	67.53(10)
O(2)–La(1)–F(2)		104.6(2)	Se(2)–La(3)–Se(1)	144.23(3)
F(1)–La(1)–O(1)		67.61(13)	Se(2)–La(3)–Se(1)	89.53(3)
O(2)–La(1)–O(1)		105.6(2)	Se(1)–La(3)–Se(1)	79.55(3)
F(2)–La(1)–O(1)		149.8(2)	O(2)–La(3)–Se(1)	125.35(11)
F(1)–La(1)–F(2)		142.6(2)	F(2)–La(3)–Se(1)	137.97(12)
F(1)–La(1)–F(2)		61.29(14)	O(4)–La(3)–Se(1)	121.26(13)
O(2)–La(1)–F(2)		69.76(14)	Se(2)–La(3)–Se(1)	76.12(3)
F(2)–La(1)–F(2)		64.22(14)	Se(1)–La(3)–Se(1)	68.18(3)
O(1)–La(1)–F(2)		127.80(10)	O(3)–Nb–O(1)	104.1(3)
F(2)–La(1)–F(2)		100.2(2)	O(3)–Nb–O(2)	100.6(3)
F(1)–La(1)–Se(2)		143.97(12)	O(1)–Nb–O(2)	155.2(3)
F(2)–La(1)–Se(2)		71.90(10)	O(3)–Nb–O(4)	100.7(2)
O(1)–La(1)–Se(2)		85.09(11)	O(1)–Nb–O(4)	88.7(2)
F(2)–La(1)–Se(2)		72.91(11)	O(2)–Nb–O(4)	86.7(2)
F(2)–La(1)–Se(2)		133.37(12)	O(4)–Nb–O(4)	158.4(3)
F(1)–La(1)–Se(2)		75.39(12)	O(3)–Nb–Se(1)	176.2(2)
O(2)–La(1)–Se(2)		139.42(3)	O(1)–Nb–Se(1)	79.7(2)
Se(2)–La(1)–Se(2)		79.41(3)	O(2)–Nb–Se(1)	75.5(2)
F(1)–La(2)–O(3)		73.7(2)	O(4)–Nb–Se(1)	79.2(2)
O(3)–La(2)–O(3)		104.7(2)		

five S atoms while the other unique La atom is coordinated to five O and four S atoms (*19*); in both the $LaCrOS_2$ (*20*) and $CeCrOS_2$ (*21*) structures the *Ln* atoms are coordinated to three O and six S atoms. The addition of F to the coordination sphere clearly increases the complexity of the polyhedra, as exemplified by those in the present structure of $La_3NbSe_2O_4F_2$.

Attempts to find a rational synthesis for $La_3NbSe_2O_4F_2$ have been unsuccessful.

Acknowledgments

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