Synthesis and Characterization of the Rare-Earth Vanadium Oxyselenides $Ln_7VO_4Se_8$ ($Ln =$ Nd, Sm, Gd)

Olivier Tougait and James A. Ibers[1]

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113

The new compounds $Ln_7VO_4Se_8$ ($Ln =$ Nd, Sm, Gd) were each prepared by heating V, Se, and the corresponding rare-earth sesquioxide at 1223 K in a sealed fused-silica tube. Single crystals have been grown through the use of an antimony flux. They have been characterized by single-crystal and powder X-ray diffraction measurements and by energy dispersive X-ray analysis. These isostructural compounds crystallize with two formula units in the orthorhombic space group *Pbam* in cells (at 153 K) of dimensions: $Nd_7VO_4Se_8$, $a = 14.3419(9)$ Å, $b = 15.5528(10)$ Å, $c = 3.9948(3)$ Å; $Sm_7VO_4Se_8$, $a = 14.200(2)$ Å, $b = 15.451(2)$ Å, $c = 3.9511(6)$ Å; $Gd_7VO_4Se_8$, $a = 14.075(8)$ Å, $b = 15.424(6)$ Å, $c = 3.903(1)$ Å. The new structure type comprises four crystallographically independent Ln atoms with three different coordination geometries and one V atom in an octahedral environment. Magnetic measurements reveal that $Gd_7VO_4Se_8$ is paramagnetic down to 5 K. © 2000 Academic Press

Key Words: X-ray structure; neodymium; samarium; gadolinium; oxychalcogenide; magnetism.

INTRODUCTION

The majority of oxychalcogenide compounds reported to date contain a rare-earth element. Their crystal structures can be classified in two broad categories. In the first, the O^{2-} and Q^{2-} ions ($Q =$ chalcogen = S, Se, or Te) are separated in distinct sheets; in the second, there is a three-dimensional arrangement in which both O^{2-} and Q^{2-} anions pack in the same plane with the cations located in the interstitial sites to minimize the electrostatic repulsion between neighboring ions. Examples of the first category are legion. They include the ternary $(LnO)_2S_2$ phases $Ln =$ rare-earth (1), in which there are $(LnO)_2$ layers formed from corner-sharing of $[LnO_4]$ tetrahedra that are well separated by sheets of S_2^{2-} disulfide anions. Other striking examples are the layered oxychalcogenides formed by a rare-earth and a second metal (M) belonging to group 11,

13, 14, or 15 (2). Their structures are built from (LnO) and (M_xQ_y) layers that stack successively along a crystallographic axis with the cations specifically surrounded by one type of anion. In the second category are most of the quaternary $Ln/M/O/Q$ compounds, where the 3d-transition metal M belongs to group 4, 5, or 6. In such compounds the 3d cation is usually in an octahedral hole whereas the 4f element is usually in a trigonal prismatic hole and each may be surrounded by a combination of O^{2-} and Q^{2-} anions.

Among the latter quaternary systems that contain a group 5 transition metal are $Ln_5V_3O_7S_6$ ($Ln =$ La, Ce, Pr, Nd) (3, 4), $Ln_2Ta_3O_8Q_2$ ($Ln =$ La, Ce, Pr, Nd) (5–7), and $Sm_3NbO_4Se_3$ (8). We present here the synthesis and structural analysis of a new series of quaternary rare-earth vanadium oxyselenides, $Ln_7VO_4Se_8$ ($Ln =$ Nd, Sm, Gd). We also examine the close resemblance of their crystal structures to that of U_3ScS_6 (9).

EXPERIMENTAL

Syntheses

Syntheses were carried out in sealed fused-silica tubes. Materials used included Nd, Alfa, 40 mesh 99.9%; Sm, Alfa, 40 mesh 99.9%; Gd, Alfa, 40 mesh 99.9%; Nd_2O_3, Aldrich, 99.9%; Sm_2O_3, Aldrich, 99.9%; Gd_2O_3, Aldrich, 99.9%; Se, Alfa, 325 mesh, 99.99%; V, Alfa, 325 mesh, 99.99%; VCl_3, Aldrich, 99%; and Sb, Alfa, 325 mesh, 99.5%.

Single crystals of $Sm_7VO_4Se_8$ were first obtained from the reaction of Sm, V, and Se in the ratio 3:1:6 together with a small amount of VCl_3 in an unprotected sealed fused-silica tube. The reaction tube was heated at a rate of 10 K/h to 1223 K and held there for 96 h. It was then cooled to 973 K at 3 K/h and then the furnace was turned off. The sample was washed with a mixture of CH_3OH/H_2O and dried with acetone. A few dark red needle-like crystals of what turned out to be $Sm_7VO_4Se_8$ were found.

Attempted quantitative syntheses (c.a. 0.5 g) at 1223 K of $Ln_7VO_4Se_8$ ($Ln =$ Nd, Sm, Gd) from stoichiometric amounts of Ln, Ln_2O_3, V, and Se (ratio 13:4:3:24, respectively) yielded poorly crystalline samples contaminated with

Ln_2Se_3 of the U_2S_3 structure type (10) and with Ln_2OSe_2 of the Dy_2OS_2 structure type (11), as determined from powder X-ray diagrams.

Improved yields of about 50% of crystalline $Ln_7VO_4Se_8$ (Ln = Nd, Sm, Gd) were obtained from the reaction of a mixture of 0.8 mmol of Ln, 0.4 mmol of Ln_2O_3, 0.4 mmol of V, and 2.4 mmol of Se, together with 0.4 to 0.8 mmol Sb to assist the crystallization. The reagents were loaded into fused-silica tubes, sealed under vacuum of 10^{-4} Torr, heated to 1223 K over a 48 h period, maintained there for 96 h, cooled to 923 K at 2.5 K/h, and then the furnace was turned off. The final products appeared as colored needle-like crystals on the surface of unreacted materials on the walls of the tube.

Energy-Dispersive X-Ray (EDX) Analysis

EDX analyses were carried out on three different single crystals from each preparation with the use of a 3500N Hitachi SEM. The presence of O was detected, but reasonable semi-quantitative analysis for this element could not be obtained. EDX results on the other elements gave the average atomic ratios: Nd(45(2)), V(5(1)), Se(50(2)); Sm(44(2)), V(6(1)), Se(50(2)), Gd(44.5(20)), V(5(1)), Se(50.5(15)) which can be compared with the calculated values for a composition $Ln_7VO_4Se_8$, Ln(43.7)V(6.3)Se(50) (Ln = Nd, Sm, Gd).

Crystal Structure Analyses

X-ray diffraction data were collected on a Bruker Smart 1000 CCD diffractometer at 153 K with the use of monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). The diffracted intensities generated by a scan of $0.3°$ in ω were recorded on 1878 and 1271 frames covering more than a hemisphere of the Ewald sphere for $Nd_7VO_4Se_8$ and $Sm_7VO_4Se_8$, respectively. The exposure times were 25 s/frame for $Sm_7VO_4Se_8$ and 15 s/frame for $Nd_7VO_4Se_8$. For both compounds, cell refinement and data reduction were carried out with the use of the program SAINT+ (12) and a face-indexed absorption correction was made with the use of the program XPREP (12). Then the program SADABS (12) was employed to make incident beam and decay corrections.

The crystal structures were solved in the centrosymmetric space group $Pbam$ of the orthorhombic system. The positions of Ln, Se, and V were located by direct methods with the program SHELXS of the SHELXTL-PC suite of programs (13) and the positions of the O atoms were located from successive difference electron density syntheses. Atomic positions were then standardized as recommended (14). The structures were refined by full-matrix least-squares techniques with the program SHELXL of the SHELXTL-PC suite of programs (13). Final refinements included anisotropic displacement parameters. Crystallographic details

are presented in Table 1. Atomic coordinates and equivalent atomic displacement parameters, with their standard deviations, are given in Tables 2 and 3. Selected bonds distances for both compounds are given in Table 4.

From X-ray diffraction powder patterns, collected on a Rigaku diffractometer equipped with monochromatized Cu$K\alpha_1$ radiation, $Gd_7VO_4Se_8$ was found to be isostructural with $Nd_7VO_4Se_8$ and $Sm_7VO_4Se_8$. Accurate lattice constants of $a = 14.075(8)$ Å, $b = 15.424(6)$ Å, $c = 3.903(1)$ Å

TABLE 1
X-Ray Crystallographic Details

	$Nd_7VO_4Se_8$	$Sm_7VO_4Se_8$
Crystal symmetry	Orthorhombic	
Space group	$Pbam$	
a (Å)	14.3419(9)	14.200(2)
b (Å)	15.5528(10)	15.451(2)
c (Å)	3.9948(3)	3.9511(6)
V (Å^3)	891.1(1)	866.9(2)
T (K)	153	153
Z	2	2
ρ_{cal} (g cm^{-3})	6.55	6.98
μ (cm^{-1})	368.3	406.1
Min and max transmission factors	0.060/0.468	0.206/0.729
Crystal color and habit	Plum needle	Dark red needle
Crystal size (mm)	$0.304 \times 0.026 \times 0.022$	$0.390 \times 0.012 \times 0.008$
No. measured reflections	7736	5362
R_{int}	0.0451	0.0309
No. unique reflections	1248	1200
$R(F)^a$	0.0267	0.0306
$Rw(F_o^2)^b$	0.0618	0.0630

$^a R(F) = \Sigma ||F_o| - |F_c||/\Sigma |F_c|$,
$^b Rw(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$, where $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$ for $F_o^2 \geq 0$ and $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 < 0$.

TABLE 2
Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $Nd_7VO_4Se_8$

Atom	Wyckoff position	x	y	z	$U_{eq} \cdot (Å^2)^a$
Nd(1)	4h	0.00602(3)	0.18989(2)	0.5	0.0063(1)
Nd(2)	4h	0.21991(3)	0.33653(2)	0.5	0.0071(1)
Nd(3)	4g	0.21022(3)	0.11717(2)	0	0.0066(1)
Nd(4)	2c	0	0.5	0	0.0084(2)
Se(1)	4h	0.35456(5)	0.02889(4)	0.5	0.0085(2)
Se(2)	4h	0.38152(5)	0.46902(4)	0.5	0.0070(2)
Se(3)	4g	0.07038(5)	0.32776(4)	0	0.0079(2)
Se(4)	4g	0.34458(5)	0.26479(4)	0	0.0073(2)
V(1)	2a	0	0	0	0.0066(3)
O(1)	4h	0.1726(4)	0.1884(3)	0.5	0.008(1)
O(2)	4g	0.0434(4)	0.1178(3)	0	0.007(1)

$^a U_{eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3
Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $Sm_7VO_4Se_8$

Atom	Wyckoff position	x	y	z	U_{eq} (Å²)
Sm(1)	4h	0.00661(3)	0.19011(3)	0.5	0.0067(1)
Sm(2)	4h	0.21969(3)	0.33605(3)	0.5	0.0077(1)
Sm(3)	4g	0.21038(3)	0.11778(3)	0	0.0072(1)
Sm(4)	2c	0	0.5	0	0.0092(2)
Se(1)	4h	0.35454(7)	0.02887(6)	0.5	0.0092(2)
Se(2)	4h	0.38045(6)	0.46812(5)	0.5	0.0076(2)
Se(3)	4g	0.06986(7)	0.32837(5)	0	0.0083(2)
Se(4)	4g	0.34482(7)	0.26442(6)	0	0.0077(2)
V(1)	2a	0	0	0	0.0064(4)
O(1)	4h	0.1731(5)	0.1887(4)	0.5	0.008(1)
O(2)	4g	0.0448(4)	0.1184(4)	0	0.006(1)

were obtained at 153 K from a single crystal with the use of the Bruker diffractometer.

Magnetic Measurements

Magnetic measurements were carried out with a SQUID magnetometer (MPMS5, Quantum Design). The sample, 7.8 mg of selected single crystals of $Gd_7VO_4Se_8$ ground to a fine powder, was loaded in a gelatin capsule. Zero-field cooled measurements were performed with a 5 kG applied field in the temperature range 5–300 K. All data were corrected for electron core diamagnetism (15).

RESULTS AND DISCUSSION

The new compounds $Ln_7VO_4Se_8$ (Ln = Nd, Sm, Gd) are isostructural and crystallize in a new structure type. These phases are perhaps most readily obtained for the intermediate Ln^{3+} cations as attempts to prepare the Ce analogue afforded $Ce_5V_3O_7Se_6$, which is isostructural with the series of oxysulfides $Ln_5V_3O_7S_6$ (Ln = La, Ce, Pr, Nd) (3, 4). In

the present compounds the four independent Ln atoms per asymmetric unit are found in three different coordination polyhedra: $Ln(1)$ and $Ln(3)$ are in bicapped trigonal prisms (LnO_3Se_5) as shown in Fig. 1a; $Ln(2)$ is in a 7-octahedron ($LnOSe_6$) as shown in Fig. 1b; $Ln(4)$ is in an octahedron ($LnSe_6$) as shown in Fig. 1c. Such octahedral $LnSe_6$ moieties have been found in the ternary selenides $BaLn_2Se_4$ (Ln = Nd, Sm, Gd) crystallizing with the $CaFe_2O_4$ structure type (16) and in $ALnSe_2$ compounds (A = alkali metal) crystallizing with the α-$NaFeO_2$ structure type (17). In the present structure the coordination geometry of the unique V atom per asymmetric unit is also octahedral, with four Se atoms forming the pseudo equatorial plane and two O atoms in *trans* positions.

The main building units of the structure are motifs derived from trigonal prisms and octahedra. The heights of these moieties correspond to the length of the c-parameter, and thus interconnection in the [001] direction occurs by the face sharing of trigonal prisms and Se–Se edge sharing of octahedra. A projection on the a–b plane of the three-dimensional structure of $Sm_7VO_4Se_8$ is displayed in Fig. 2.

The structure can be viewed as a succession of alternating slabs along the b-axis of single slabs of octahedra centered by V(1) and Sm(4) and slabs of joined polyhedra centered by Sm(1), Sm(2), and Sm(3). Within the Sm layers, the three different polyhedra pack by edge sharing and face sharing. Along the b-direction, they are separated by single slabs of octahedra. Within this second slab, the two different species, namely $Sm(4)Se_6$ and VO_2Se_4, are bridged by $Sm(1)O_3Se_5$ and $Sm(3)O_3Se_5$ trigonal prisms, which also bring about by edge sharing the interconnection between the adjacent slabs.

The three-dimensional structure of $Ln_7VO_4Se_8$ (Ln = Nd, Sm, Gd) results in the following coordination geometries about O and Se. Atoms O(1) and O(2) are tetrahedrally coordinated: O(1) is surrounded by four Ln atoms, whereas O(2) is surrounded by three Ln atoms and one V atom; atoms Se(1), Se(3), and Se(4) are surrounded by five Ln atoms in a square pyramid; atom Se(2) adopts an

TABLE 4
Interatomic Distances (Å) for $Ln_7VO_4Se_8$ (Ln = Nd, Sm)

|		Ln = Nd	Ln = Sm			Ln = Nd	Ln = Sm
Ln(1)	O(2) × 2	2.352(2)	2.329(3)	Ln(3)	O(1) × 2	2.347(3)	2.320(3)
Ln(1)	O(1)	2.389(5)	2.364(7)	Ln(3)	O(2)	2.392(5)	2.351(6)
Ln(1)	Se(2)	3.0491(8)	3.031(1)	Ln(3)	Se(4)	2.9974(8)	2.963(1)
Ln(1)	Se(3) × 2	3.0724(6)	3.0452(8)	Ln(3)	Se(1) × 2	3.1876(6)	3.1592(9)
Ln(1)	Se(4) × 2	3.1380(6)	3.1104(9)	Ln(3)	Se(2) × 2	3.3211(6)	3.3036(8)
Ln(2)	O(1)	2.401(5)	2.371(6)	Ln(4)	Se(3) × 2	2.8627(7)	2.8314(9)
Ln(2)	Se(4) × 2	2.9037(6)	2.8784(8)	Ln(4)	Se(1) × 4	2.9227(5)	2.8928(8)
Ln(2)	Se(3) × 2	2.9337(6)	2.9058(8)				
Ln(2)	Se(2)	3.1014(8)	3.062(1)	V(1)	O(2) × 2	1.936(5)	1.937(6)
Ln(2)	Se(1)	3.1767(8)	3.160(1)	V(1)	Se(2) × 4	2.6663(5)	2.6510(7)
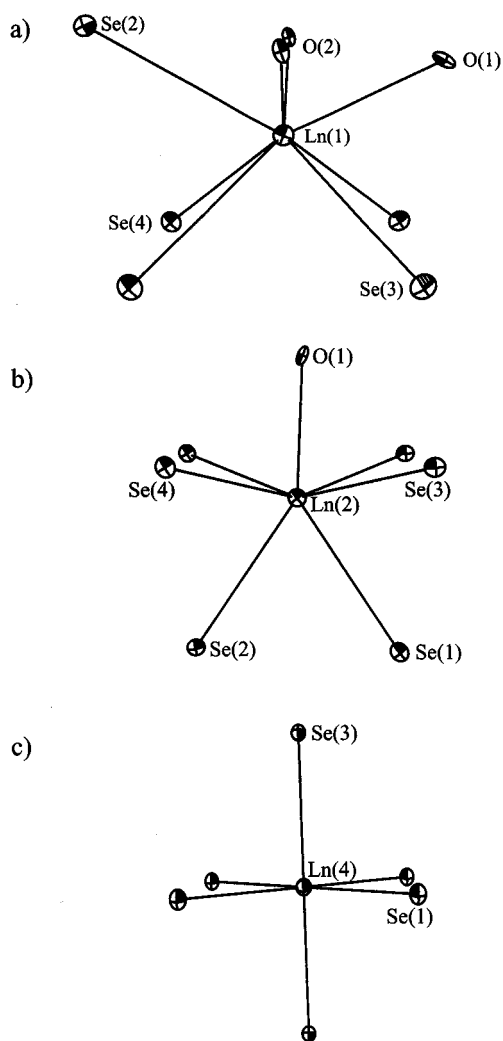
FIG. 1. View of the environment of (a) $Ln(1)$, (b) $Ln(2)$, and (c) $Ln(4)$ in $Ln_7VO_4Se_8$. Displacement ellipsoids are drawn at the 60% probability level.
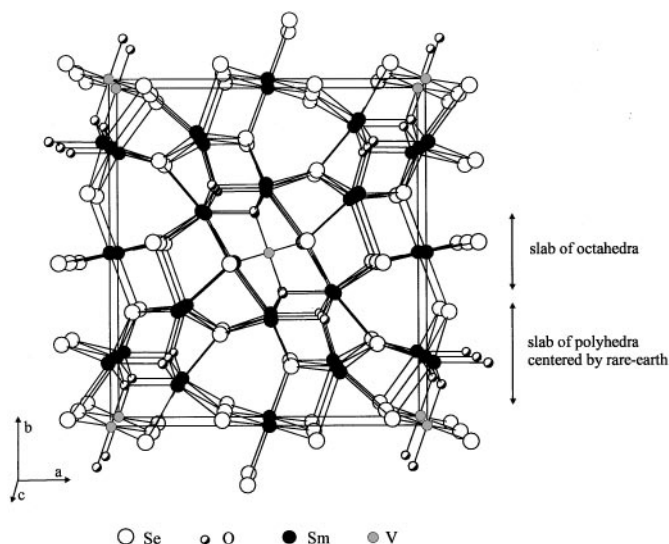

FIG. 2. View of the unit cell of $Sm_7VO_4Se_8$ along the c axis.

structure of U_3ScS_6 comprises layers of octahedra centered by Sc^{3+} cations and layers of trigonal prisms centered by Ln cations that stack successively along a crystallographic axis of an orthorhombic unit-cell. The obvious differences between the U_3ScS_6 and $Ln_7VO_4Se_8$ structures are in the substitution of two S or Se atoms by two O atoms and the substitution of one $3d$ cation within the layer of octahedra by a Ln cation. It is useful in this regard to think of $Ln_7VO_4Se_8$ as $Ln_6[LnV]Q_{12}$. There are also structural differences in the packing mode within the Ln slab. In the U_3ScS_6 type structure, the three different polyhedra centered by f elements lie in the same a–b plane and pack by sharing triangular faces, whereas in the $Ln_7VO_4Se_8$ structure type, one polyhedron, namely $Ln(3)O_3Se_5$, is shifted by $b/2$, increasing the close-packing among the three nonequivalent polyhedra. Consequently, the interatomic
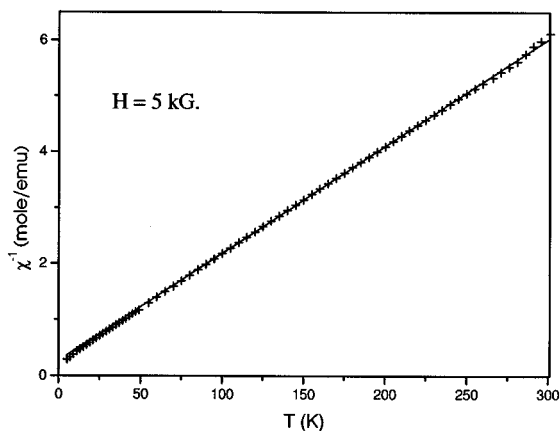
irregular octahedral geometry constructed from four Ln atoms and two V atoms.

The charge balance is achieved in the phases $Ln_7VO_4Se_8$ (Ln = Nd, Sm, Gd) with the metals in their expected trivalent oxidation states. The V–O(2) bonds (see Table 4) are 0.06 Å shorter than an expected V^{III}–O contact of about 2.0 Å (18, 19). On the other hand, the V–Se(4) bonds are approximately 0.08 Å longer than the average values reported for the V^{III} compounds TlV_5Se_8 (20) and $AgVP_2Se_6$ (21). Such differences may result from the oxyphilic nature of V^{III}.

The crystal structure of these new compounds is closely related to that of U_3ScS_6 (9), which is also commonly adopted by rare-earth and trivalent cations, for example, Sm_3InS_6 (22), Ln_3InSe_6 (Ln = Pr, Sm, Gd) (23, 24), and Ln_3CrSe_6 (Ln = Sm, Gd, Tb, Dy, Y) (24, 25). The crystal

FIG. 3. χ^{-1} versus T for $Gd_7VO_4Se_8$. The solid line is the Curie–Weiss fit.

distances between *Ln* cations shrink significantly; for example, the shortest Sm–Sm contact decreases from 3.929(1) Å in Sm_3CrSe_6 to 3.678(1) Å in $Sm_7VO_4Se_8$.

Magnetic susceptibility measurements as a function of temperature (Fig. 3) indicate that $Gd_7VO_4Se_8$ is paramagnetic down to 5 K. The inverse susceptibility obeys the Curie–Weiss law $\chi^{-1} = (T - \theta)/C$. The fit of the data in the temperature range 50–300 K results in a Curie constant $C = 52.3(2)$ emu K^{-1} mol^{-1} and a paramagnetic temperature $\theta = -14.3(7)$ K. The value of C agrees with that of 58.0 emu K^{-1} mol^{-1} calculated from $7 C(Gd^{3+}) + C$(spin-only V^{3+}) (26).

REFERENCES

1. W. Wichelhaus, *Naturwissenschaften* **65,** 593–594 (1978).
2. M. Guittard, S. Benazeth, J. Dugué, S. Jaulmes, M. Palazzi, P. Laruelle, and J. Flahaut, *J. Solid State Chem.* **51,** 227–238 (1984).
3. T. Vovan, J. Dugué, and M. Guittard, *C. R. Acad. Sci., Sér. 2* **292,** 957–959 (1981).
4. J. Dugué, T. Vovan, and P. Laruelle, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **41,** 1146–1148 (1985).
5. T. D. Brennan, L. E. Aleandri, and J. A. Ibers, *J. Solid State Chem.* **91,** 312–322 (1991).
6. T. D. Brennan and J. A. Ibers, *J. Solid State Chem.* **98,** 82–89 (1992).
7. G. Guo, Y. Wang, J. Chen, H. Zhuang, J. Huang, and Q. Zhang, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **51,** 1964–1966 (1995).
8. A. Meerschaut, C. Boyer, A. Lafond, L. Cario, and J. Rouxel, *J. Solid State Chem.* **137,** 122–126 (1998).
9. N. Rodier and V. Tien, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **32,** 2705–2707 (1976).
10. J. Flahaut, *in* "Handbook on the Physics and Chemistry of Rare Earths" (K. A. Gschneidner Jr. and L. R. Eyring, Eds.), Vol. 4, pp. 1–88, North-Holland, New York, 1979.
11. T. Schleid, *Z. Anorg. Allg. Chem.* **602,** 39–47 (1991).
12. SMART Version 5.054 Data Collection and SAINT-Plus Version 6.02A Data Processing Software for the SMART System, Bruker Analytical X-Ray Instruments, Inc., Madison, WI, 2000.
13. G. M. Sheldrick, SHELXTL DOS/Windows/NT Version 5.10, Bruker Analytical X-Ray Instruments, Inc., Madison, WI, 1997.
14. L. M. Gelato and E. Parthé, *J. Appl. Crystallogr.* **20,** 139–143 (1987).
15. L. N. Mulay and E. A. Boudreaux, Eds., "Theory and Applications of Molecular Diamagnetism," Wiley-Interscience, New York, 1976.
16. J. Dugué, D. Carré, and M. Guittard, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **34,** 3564–3568 (1978).
17. W. Bronger, W. Brüggemann, M. von der Ahe, and D. Schmitz, *J. Alloys Compd.* **200,** 205–210 (1993).
18. W. R. Robinson, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **31,** 1153–1160 (1975).
19. P. Bordet, C. Chaillout, M. Marezio, Q. Huang, A. Santoro, S.-W. Cheong, H. Takagi, C. S. Oglesby, and B. Batlogg, *J. Solid State Chem.* **106,** 253–270 (1993).
20. K. Klepp and H. Boller, *J. Solid State Chem.* **48,** 388–395 (1983).
21. G. Ouvrard and R. Brec, *Mater. Res. Bull.* **23,** 1199–1209 (1988).
22. D. Messain, D. Carré, and P. Laruelle, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **33,** 2540–2542 (1977).
23. L. E. Aleandri and J. A. Ibers, *J. Solid State Chem.* **79,** 107–111 (1989).
24. O. Tougait and J. A. Ibers, *Inorg. Chem.* **39,** 1790–1794 (2000).
25. O. Tougait and J.A. Ibers, manuscript in preparation.
26. C. Kittel, "Introduction to Solid State Physics," 6th ed., Wiley, New York, 1986.