DOI: 10.1002/zaac.200600176

Sm_2O_2I − A New Mixed-Valence Samarium(II,III) Oxide Halide

Mikhail Ryazanov, Constantin Hoch, Hansjürgen Mattausch and Arndt Simon*

Stuttgart, Max-Planck Institut für Festkörperforschung

Received June 27th, 2006.

Abstract. Dark red single crystals of Sm_2O_2I were obtained from a reaction of SmI_2 (in the presence of SmOI) and Na in a sealed tantalum ampoule at 650 °C. The title compound crystallizes in the monoclinic system ($C2/m$, $Z = 4$, $a = 12.639(2)$, $b = 4.100(1)$, $c = 9.762(3)$ Å, $\beta = 117.97(2)°$). The structure consists of corrugated $[Sm^{2+}Sm^{3+}(O^{2-})_2]^+$ layers of edge and vertex-connected Sm_4O tetrahedral units with I^- anions separating the layers.

Keywords: Samarium mixed-valence Samarium (II,III); Oxide halides; Crystal structure

Introduction

Although there has been great progress in the preparation of reduced halide phases of the lanthanide metals in low oxidation states during the past few decades [1−4], this field still remains a challenging topic in chemistry. In general, the metal atoms in such “reduced” compounds adopt either a mixed $4f^n5d^x$ electronic configuration as in metallic halides like LaI [5] and LnI_2 (La = La-Pr, Gd) [1], or a stable divalent $4f^n$ configuration especially for Eu^{2+} ($4f^7$) and Yb^{2+} ($4f^{14}$). Based on the relative stability of Ln ions with half-occupied and fully occupied 4f shells, our recent efforts were directed towards the preparation of monovalent samarium and thulium halides. The present contribution describes a new Sm_2O_2I oxide halide which has been obtained during the attempts to synthesize SmI via “metallothermic” reduction of SmI_2 with sodium.

So far, two ternary samarium phases, SmOI [6] and Sm_4OI_6 [7], are known in the system Sm-I-O. The first one crystallizes in the tetragonal PbFCl structure type as do other related lanthanide(III) oxide halides [6]. The second compound belongs to the family of divalent Sm_4OX_6 oxide halides (X = Cl [8]) whose structures are characterized by isolated O-centered $[Sm_4O]$ tetrahedra and halogen atoms forming one-dimensional anionic channels. The title compound is a new mixed-valence samarium oxide halide with a layered structure composed of edge and vertex-sharing $[Sm_4O]$ units.

Experimental Details

Sm metal pieces (99.99 %; Johnson Matthey, Germany), sodium (99 %; Cl < 0.01 %, K < 0.05 %; Merck) and iodine powder (99.8 %; Merck) were utilized as starting materials without further purification. All manipulations were handled under purified Ar either in a glovebox (H_2O < 0.2 ppm; O_2 < 0.8 ppm) or by employing standard Schlenk techniques. SmI_2 was prepared from the elements in an evacuated sealed silica tube by slowly heating to 800 °C [9]. For a reduction reaction, the resulting samarium diiodide sample that turned out to contain a minor amount of O-containing impurities[1] was mixed with bulk Na pieces in the 1:1 ratio and filled into a Ta container. The latter was then arc-welded under argon and sealed in an evacuated silica jacket to prevent oxidation of the container. The reaction mixture (*ca.* 0.5 g) was heated at 650 °C for 7 days, followed by cooling in air to room temperature.

Some of the dark red flat needle crystals of Sm_2O_2I with a metallic luster (~ 0.08 × 0.04 × 0.02 mm in size) were selected from the mixture of unreacted SmI_2, Sm, and NaI under a microscope inside a drybox and sealed in glass capillaries under Ar atmosphere for X-ray measurements. The diffraction data were collected at room temperature using a single-crystal Stoe IPDS (Image Plate Diffraction System) instrument with graphite monochromatized Ag $K\alpha$ radiation. Single-crystal lattice parameters were determined from 2958 reflections in the region $5.8° < 2\theta < 50.0°$. For the structure determination the intensity data set was corrected for Lorentz, polarization factors and absorption using the Stoe programs X-RED and X-SHAPE [10]. All relevant details concerning the data collection are listed in Table 1.

The starting atomic parameters derived via direct methods using the program SHELXS-97 [11] were subsequently refined with the program SHELXL-97 [11] (full-matrix least-squares on F^2) with anisotropic atomic displacements for all non-oxygen atoms. The atomic coordinates and equivalent isotropic thermal parameters are reported in Table 2. Selected interatomic distances and bond angles are given in Table 3. Further details on the crystal structure determination are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany

---

* Prof. Dr. Dr.h.c. mult. Arndt Simon
Max-Planck-Institut für Festkörperforschung
Heisenbergstr. 1
D-70569 Stuttgart, Deutschland
FAX: 0711/689/1091
E-mail: A.Simon@fkf.mpg.de

[1] An unambiguous assignment of the X-ray powder diffraction data is hampered due to peak overlap between the diffraction patterns of SmI_2 and SmIO.

Table 1 Crystal data and structure refinement for Sm_2O_2I

Formula weight	459.60
Lattice dimensions	
a /Å	12.639(2)
b /Å	4.100(1)
c /Å	9.762(3)
β /°	117.97(2)
Unit cell volume/Å^3	446.8(2)
Crystal system	monoclinic
Space group	*C*2/*m* (No. 12)
Z	4
Calculated density/g·cm^{-3}	6.833
Diffractometer	Stoe IPDS I
Radiation	Ag $K\alpha$, λ = 0.56086 Å
Temperature/K	293(2)
Absorption correction	Numerical, program X-Shape [10]
μ/mm^{-1}	17.45
Scan width	$5.8° < 2\theta < 50.0°$
Indices h, k, l	$-17 < h < 17$, $-6 < k < 6$, $-14 < l < 14$
Structure determination and refinement	Programs SHELXS-97 and SHELXL-97 [11]
Reflections measured	3935
Independent reflections, Parameters	841, 25
R_{int}	0.086
R_1 [$I > 2\sigma I$)]	0.056
R_1 (all data)	0.075
wR_2 (all data)	0.161
Goodness-of-fit on F^2	1.200

Table 2 Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for Sm_2O_2I

Atom	Site	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
Sm1	4*i*	0.3478(1)	0	0.4575(2)	0.0078(5)
Sm2	4*i*	0.0303(1)	0	0.7948(2)	0.0104(5)
I	4*i*	0.6735(2)	0	0.1316(2)	0.0151(5)
O1	4*i*	0.156(2)	0	0.441(3)	0.014(4)
O2	4*i*	0.460(2)	0	0.333(2)	0.011(4)

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

Table 3 Selected structural parameters (Å, °) in Sm_2O_2I

Sm1-O1	2.29(1)	Sm1-Sm2^{ii}	3.639(2)
Sm1-O1^{i}	2.35(2)	Sm1-Sm2^{iii}	4.226(4)
Sm1-O2	2.26(2)	Sm2-O1^{iv}	2.40(2)
Sm1-O2^{ii}	2.33(2)	Sm2-O2	2.435(15)
Sm1-I1	3.550(2)	Sm2-I1	3.464(3)
Sm1-Sm1^{i}	3.595(2)	Sm2-I1^{i}	3.564(2)
Sm1-Sm1^{ii}	3.535(3)	Sm2-I1^{v}	3.619(2)
Sm1-Sm2	4.025(2)	Sm2-Sm2	4.100(1)
Sm1-O1-Sm1^{vi}	127(1)	Sm1^{ii}-O2-Sm1	100.9(8)
Sm2^{iv}-O1-Sm1^{i}	126(1)	Sm2-O2-Sm2	114.7(8)
Sm1^{ii}-Sm1-Sm1^{i}	137.41(5)	Sm1^{i}-Sm1-Sm1^{i}	69.53(5)

Symmetry codes: (i) −1/2−x, 1/2+y, 1−z; (ii) −x, y, 1−z; (iii) 1/2+x, 1/2+y, z; (iv) −x, 1+y, 1−z; (v) 1/2+x, −1/2+y, z; (vi) x, −1+y, z;

(**crysdata@fiz-karlsruhe.de**), referring to the depositary number CSD-416706.

Results and Discussion

Metallothermic reduction of SmI_2 in a Na melt at 650 °C yields NaI and metallic samarium, suggesting no stable intermediate SmI_x ($x < 2$) phases in the binary Sm-I system.

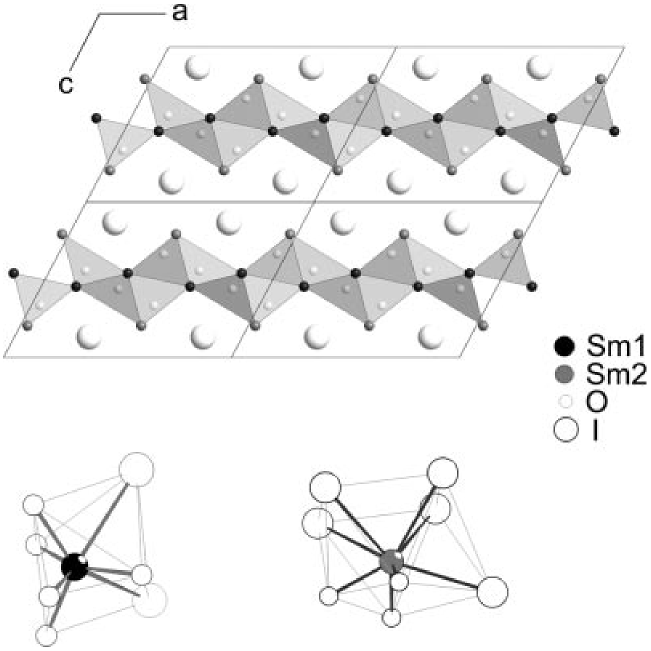

Fig. 1 Projection of the crystal structure of Sm_2O_2I down the *b* axis, with the unit cells outlined (Top). The bottom part shows coordination polyhedra around the metal atoms Sm1 and Sm2, respectively.

Among the reaction products, dark red needle-like crystals of composition Sm_2O_2I were obtained as a by-product due to oxygen contamination of the starting materials. As a bulk yet microcrystalline product, Sm_2O_2I can be prepared by the metallothermic reaction with sodium at 650 °C in high yield (approx. 50-60 %) when incorporating a stoichiometric amount of Sm_2O_3 and excess of NaI as flux.

The crystal structure of Sm_2O_2I comprises a new structure type[2] which, however, is closely related to the structures of known oxide halides Ln_4OI_6 (Ln = Sm [7], Eu [13]) Eu_2OI_2 [14] in that it contains oxygen-centered {Sm_4O} units as basic building blocks. These are connected via *cis*-edges and vertices to form corrugated layers parallel (001), which are separated from each other by I atoms (Fig. 1).

According to the chemical composition, Sm_2O_2I is a mixed valence compound. In fact, the metal atoms occupy two crystallographically distinct sites with different coordinations. The trivalent Sm1 atoms are surrounded by 5 O^{2-} and 2 I^- ions (monocapped trigonal prism), whereas the divalent Sm2 atoms are eight-coordinated ($3O^{2-}+5I^-$) in a bicapped trigonal prismatic environment (Fig. 1). The Sm1-O distances range from 2.26(2) to 2.35(2) Å close to the sum of ionic radii (r(Sm^{3+}) = 1.02 Å for CN = 7, r(O^{2-}) = 1.38 Å) [15]. The Sm2-O bonds are somewhat longer with an average of 2.42 Å being similar to the Sm^{II}-O distances

---

[2] After submission of our publication a report on the isotypic compound Eu_2O_2Br appeared [12], however, described with the different setting *I*2/*m*.

in Sm_4OI_6 (2.39(2) and 2.436(7) Å, respectively) [7]. A similar change in bond lengths is found for the Sm1-I and Sm2-I distances (cf. Table 3.). Based on the concept of bond valence and using the tabulated bond valence parameters for the Sm^{III}-O (R_o = 2.088 Å) and Sm^{III}-I bonds (R_o = 2.84 Å) [16], the empirical valence of atoms Sm1 was calculated to be 3.1. As there is no data on bond valence parameters for Sm^{II}-I and Sm^{II}-O, we estimated these values (2.88 and 2.15 Å, respectively) from the crystal data for SmI_2 [17] and from the relation[3] between R values for Eu^{III}-O (2.076 Å) and Eu^{II}-O (2.147 Å) [16]. The summation of all bond valences for atoms Sm2 leads to an empirical valence of 2.2, thus proving a structural model according to the ionic description $[(Sm^{3+})(Sm^{2+})(O^{2-})_2]^+I^-$.

Within the metal atom substructure, the trivalent Sm1 atoms form slightly corrugated layers of six-membered rings in the chair conformation like in α-arsenic. These layers are surrounded on both sides by the divalent Sm2 atoms capping the square faces of the $(Sm1)_6$ rings. The resulting metal atom framework comprises alternating chains of distorted *trans*-edge connected $\{(Sm1)_4(Sm2)_2\}$ octahedra and *cis*-edge sharing $\{(Sm1)_3Sm2\}$ units which are condensed into corrugated layers parallel (001) (see Fig. 2). The shortest Sm-Sm distances are 3.535(3) and 3.595(2) Å between the Sm1 atoms, similar to those in elemental Sm (3.59-3.62 Å) [18].

Figure 2 shows a single layer in the *ab* plane of the crystal structure. In the corrugated layer one distinguishes two types of $\{Sm_4O\}$ units which differ in their geometrical details. The first one is a distorted $\{(Sm1)_2(Sm2)_2O\}$ tetrahedron. As the Sm^{III} ions form one edge of the tetrahedron opposite to the other formed by Sm^{II}, the edge lengths are different, however, the *trans*-edges remain orthogonal. The other structural unit, $\{(Sm1)_3(Sm2)O\}$, is better described as a trigonal pyramid with the Sm1 atoms forming the basal plane and the Sm2 atom occupying the apical position. Both units are connected into infinite corrugated layers according to $^2_\infty[\{(Sm^{III}1)_{2/5}(Sm^{II}2)_{2/3}O^{2-}\}\{(Sm^{III}1)_{3/5}(Sm^{II}2)_{1/3}O^{2-}\}]^+$ in the *ab* plane. The $\{(Sm1)_3(Sm2)O\}$ units are connected only via *cis*-edges, whereas the $\{(Sm1)_2(Sm2)_2O\}$ tetrahedra share both common edges and vertices. As a consequence, the $[Sm_2O_2]$ layers are not completely compact but contain trigonal antiprismatic voids in the [101] direction (Fig. 3). In each layer, such voids formed by 4 Sm1 + 2 Sm2 atoms are face-capped from both sides by I atoms, which, in turn, line up into alternating yet slightly distorted linear strings parallel to [101] with a shortest I-I contact of 3.97 Å.

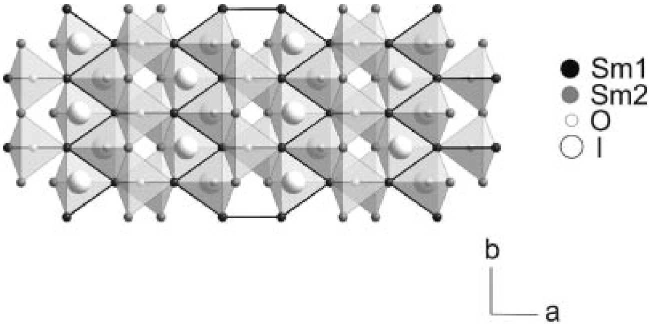

Fig. 2 View of a corrugated layer of *cis*-edges and vertex connected $\{Sm_4O\}$ clusters and and arrangement of iodide ions in the (001) plane.

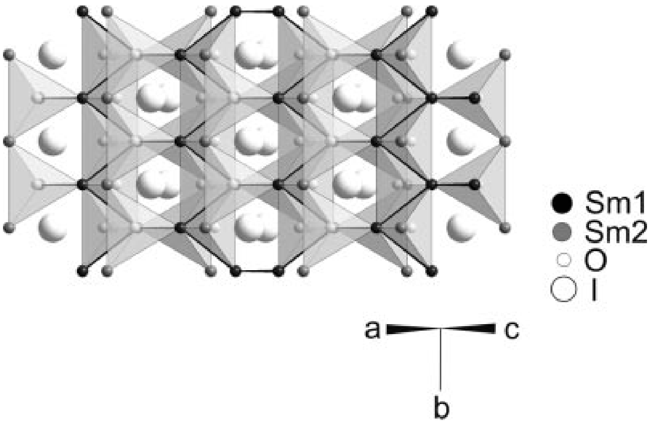

Fig. 3 Projection of the crystal structure of Sm_2O_2I along [101].

A merely topological description of the structure can be obtained by considering in the first place the positions of Sm and I atoms. They form slightly corrugated 6^3 nets extending parallel to the (101) plane. The stacking of the layers reminds of a closest packing in which all octahedral voids are left empty and those tetrahedral voids only composed of Sm atoms are filled with oxygen atoms.

References

[1] J. E. Mee, J. D. Corbett, *Inorg. Chem.* **1965**, *4*, 88; J. D. Corbett, R. A. Sallach, D. A. Lokken, *Adv. Chem. Ser.* **1967**, *71*, 56.

[2] A. Simon, N. Holzer, Hj. Mattausch, *Z. Anorg. Allg. Chem.* **1979**, *456*, 207; Hj. Mattausch, W. Schramm, R. Eger, A. Simon, *Z. Anorg. Allg. Chem.* **1985**, *530*, 43.

[3] G. Meyer, Th. Schleid, *Inorg. Chem.* **1987**, *26*, 217; G. Meyer, *Chem. Rev.* **1988**, *88*, 93.

[4] A. Simon, Hj. Mattausch, G. J. Miller, W. Bauhofer, R. K. Kremer, *Handbook on the Physics and Chemistry of Rare Earths*, (K. A. Gschneidner Jr., L. Eyring, eds.) Vol. 15, North-Holland Publisher, Amsterdam-London-New York-Tokyo **1991**, 191.

[5] J. D. Martin, J. D. Corbett, *Angew. Chem.* **1995**, *107*, 234; M. Ryazanov, L. Kienle, A. Simon, Hj. Mattausch, *Inorg. Chem.* **2006**, *45*, 2068.

[6] F. H. Kruse, L. B. Asprey, B. Morosin, *Acta Crystallogr.* **1961**, *14*, 541.

---

[3] As Sm(II) and Eu(II) atoms exhibit very similar ionic radii (1.27 and 1.25 Å for C.N. = 8, respectively) [15], the estimation of the bond valence parameter (R) for Sm-O on the basis of related values for the Eu-O pairs is thought to be reliable.

[7] S. Hammerich, I. Pantenburg, G. Meyer, *Acta Crystallogr.* **2005**, *E61*, i234.

[8] Th. Schleid, G. Meyer, *Z. Anorg. Allg. Chem.* **1987**, *553*, 231.

[9] A. A. Yarovoi, G. E. Revzin, L. M. Petrova, *Neorgan. Mater.* (*Russ.*) **1971**, *7*, 437.

[10] X-RED 1.22, Stoe Data Reduction Program, Stoe & Cie GmbH, Darmstadt, **2001**; X-SHAPE 1.06, Crystal Optimization for Numerical Absorption Correction, Stoe & Cie GmbH, Darmstadt, **1999**.

[11] G.M. Sheldrick, SHELXS-97 and SHELXL-97, Programs for the Solution and Refinement of Crystal Structures, Göttingen, **1997**.

[12] S. Hammerich, I. Pantenburg, G. Meyer, *Z. Anorg. Allg. Chem.* **2006**, *632*, 1487.

[13] W. Liao, R. Dronskowski, *Acta Crystallogr.* **2004**, *C60*, i23.

[14] S. Hammerich, G. Meyer, *Z. Anorg. Allg. Chem.* **2006**, *632*, 1244.

[15] R. D. Shannon, *Acta Crystallogr.* **1976**, *A32*, 751.

[16] N. E. Brese, M. O'Keeffe, *Acta Crystallogr.* **1991**, *B47*, 192.

[17] H. Bärnighausen, W. Kuhn, unpublished results; cited from the *Gmelin Handbuch*, Vol. 23 C6, Springer Verlag, Berlin, **1978**, 148.

[18] A. H. Daane, R. E. Rundle, H. G. Smith, F. H. Spedding, *Acta Crystallogr.* **1954**, *7*, 532.