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Crystal Structure and Magnetic Properties of Sm_3ReO_7

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Crystals of a new ternary samarium rhenium oxide, Sm_3ReO_7 were obtained by subsolidus reaction of samariumsesquioxide and rheniumdioxide (ratio 1.5 : 1) in sealed Pt–10Rh-tubes at 1673 K. The structure was determined by single-crystal X-ray diffraction. Sm_3ReO_7 crystallizes in the orthorhombic system with unit cell dimensions a = 10.736(5), b = 7.392(3), and c = 7.519(3) in space group *Cmcm* (No. 63) with Z = 4. The structure consists of ReO_6 octahedra, distorted SmO_6 octahedra, and SmO_8 prisms that are interconnected to each other to form a three-dimensional network. Rhenium has the formal oxidation state of +5 but no metal–metal bond is observed in this compound. The observed magnetization in the temperature range 4 K $< T <$ 52 K is explained by a Curie–Weiss law modified by a temperature independent Van Vleck paramagnetism of samarium (3+). © 1996 Academic Press, Inc.

INTRODUCTION

Ternary oxides of rare-earth elements (lanthanum to lutetium including yttrium) and rhenium in an oxidation state below (+7) have been reported by several authors. Only a few compounds have been characterized by single crystal structure determination: $La_3Re_2O_{10}$ (1), $La_4[Re_2]O_{10}$ (2), $Nd_4Re_2O_{11}$ (3), $La_4Re_6O_{19}$ (4, 5), $La_6Re_4O_{18}$ (6), $Dy_5Re_2O_{12}$ (7), $Ho_5Re_2O_{12}$ (8). Muller and Roy (9) and Baud and Capestan (10) reported extensive studies of several lanthanoid rich lanthanoid rhenium oxides. In this paper the structural and magnetic characterisation of a new samarium rhenium oxide Sm_3ReO_7 with a formal rhenium oxidation state of +5 is described.

EXPERIMENTAL

The synthesis of Sm_3ReO_7 single crystals was carried out by subsolidus reaction of a stoichiometric mixture of reagent grade samariumsesquioxide (Sm_2O_3, Aldrich 99.99%) and rheniumdioxide (ReO_2, Alfa 99.99%) in the ratio 1.5 : 1. All reactants were intimately mixed in an agate mortar under acetone and sealed into an Pt–10Rh-tube with 20 vol% of residual oxygen. The sample was heated in a tube furnace in argon atmosphere with a ramping rate of 300 K/h to 1673 K for 12 h. Afterward it was cooled down with 120 K/h to room temperature. Argon atmosphere was used as a protection measure.

On opening the tube a single phase of prismatic dark black crystals was obtained. Most of the crystals had well developed faces. The mean diameter of a crystal was as large as 0.1 to 0.15 mm. The sample itself was checked microscopically (optical and REM) as well as by EDX (Sm : Re ratio = 3 : 1) and X-ray examination. The details of the X-ray single-crystal data collection and structure refinement are summarized in Table 1. In order to deter-

TABLE 1
Details of X-Ray Single-Crystal Data Collection and Structure Refinement

Diffractometer: CAD4	Radiation: Mo$K\alpha$, λ = 0.71069 Å
Fine-focus sealed tube	Graphite monochromator
Detector: Scintillation counter	Pulse-height-discrimination
Scan: $\omega/2\theta$	Cell parameters from 48 reflections (46.1° $\leq 2\theta \geq$ 53.5°)
Crystal size: 0.05 × 0.06 × 0.16 mm^3	Crystal habit: prism
Crystal color: black	Temperature: 300 K
$h = -13 \rightarrow 13$	2636 measured reflections (3.35° $\leq \theta \leq$ 27.42°)
$k = -9 \rightarrow 9$	388 independent reflections [$R_{(int)}$ = 0.044]
$l = -9 \rightarrow 9$	
Absorption correction: Psi-scan	
Refinement method (35 parameters)	Full-matrix least-squares on F^2
GooF = S = 1.145	$\Delta\rho_{max}$ = 3.445 $eÅ^{-3}$, $\Delta\rho_{min}$ = −2.311 $eÅ^{-3}$
Final R indices 388 [$F > 2\sigma(F)$]	R_1 = 0.0303, wR_2 = 0.0721
R indices 388 (all data)	R_1 = 0.0312, wR_2 = 0.0727
Extinction correction: Zachariasen	Extinction coefficient: 0.0067(4)
Atomic scattering factors from:	Int. Tables Vol. IV Tables 2.2B and 2.3.1
Structure refinement: SHELXS-86 (11), SHELX-93 (12)	

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TABLE 2
Atomic and Thermal Parameters for Sm_3ReO_7 at 300 K as Derived from Single-Crystal X-ray Diffraction

Space group	a [Å]	b [Å]	c [Å]	V [$Å^3$]	Z
Cmcm	10.736(5)	7.392(3)	7.519(3)	596.67(5)	4

Atom	Position	x	y	z	u_{eq} [$Å^2$]
Sm(1)	8(g)	0.2746(1)	0.2990(1)	0.25	0.014(1)
Sm(2)	4(b)	0	0.5	0	0.023(1)
Re	4(a)	0	0	0	0.012(1)
O(1)	4(c)	0.5	0.4238(3)	0.25	0.015(3)
O(2)	16(h)	0.1257(1)	0.1850(2)	0.0356(2)	0.026(2)
O(3)	8(g)	0.3680(1)	0.0241(2)	0.25	0.017(2)

Atom	$U11$	$U22$	$U33$	$U12$	$U13$	$U23$
Sm(1)	0.015(1)	0.010(1)	0.018(1)	0.001(1)	0.000	0.000
Sm(2)	0.017(1)	0.034(1)	0.017(1)	0.000	0.000	−0.004(1)
Re	0.014(1)	0.008(1)	0.015(1)	0.000	0.000	0.000(1)
O(1)	0.018(6)	0.010(6)	0.016(6)	0.000	0.000	0.000
O(2)	0.031(4)	0.026(4)	0.021(4)	−0.010(4)	0.003(3)	−0.002(3)
O(3)	0.018(5)	0.007(4)	0.026(5)	−0.004(4)	0.000	0.000

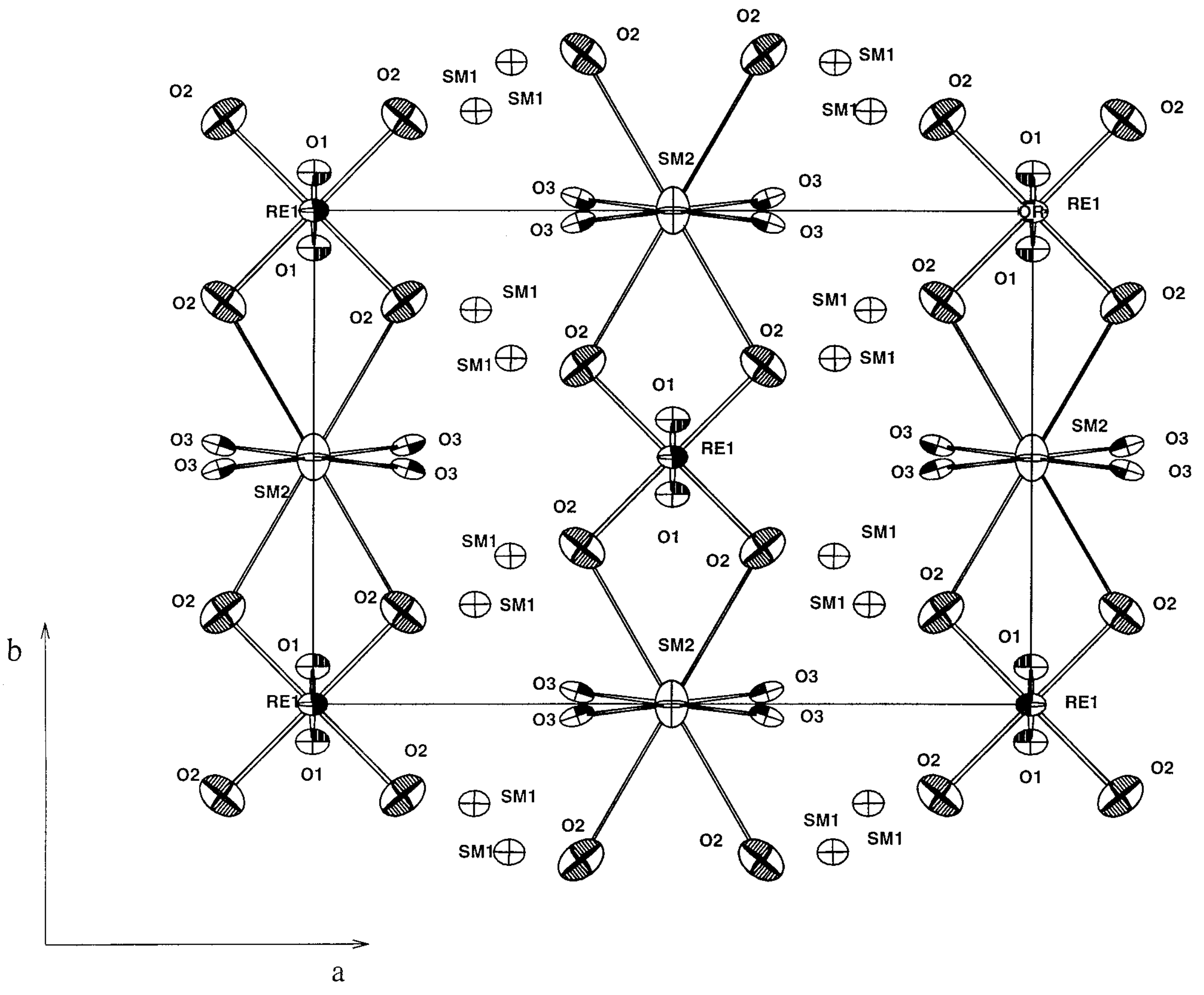

FIG. 1. Crystal structure of Sm_3ReO_7, view along the [0 0 1] direction.

TABLE 3
Bond Lengths [Å] for the ReO_6, SmO_6, and SmO_8 Units in Sm_3ReO_7

Sm(1)–O(1)	2.287(5)
Sm(1)–O(2)	2.400(2), 2.419(8)
Sm(1)–O(2)	2.259(9), 2.62(10)
Sm(1)–Re	3.4019(7)
Sm(1)–Sm(1)	3.7284(5)
Sm(1)–Sm(2)	3.7738(7)
Sm(2)–O(2)	2.701(9)
Sm(2)–O(3)	2.359(6)
Sm(2)–Sm(2)	3.7557(4)
Re–O(1)	1.960(4)
Re–O(2)	1.938(8)

mine the magnetic properties magnetization measurements were performed in the temperature range from 4 to 52 K using a SQUID with a field strength of 0.1 T.

RESULTS

Positional parameters for Sm_3ReO_7 are summarized in Table 2. The main interatomic distances are listed in Table 3. The crystal structure of Sm_3ReO_7 is presented in Fig. 1. The formal oxidation state of rhenium in this compound is +5.

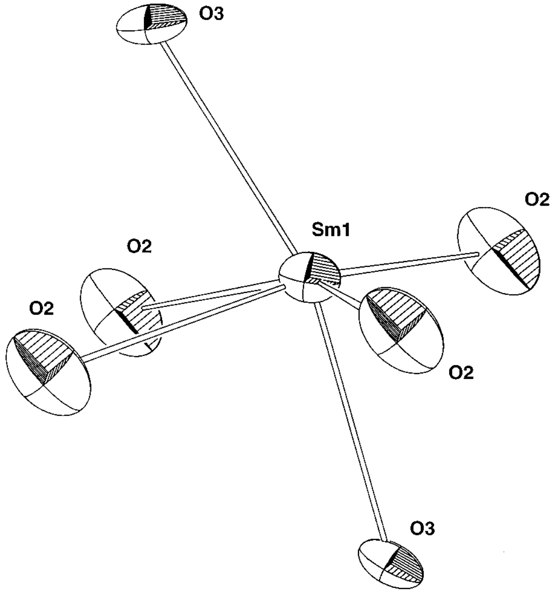

FIG. 2. The sixfold oxygen coordination around the samarium-(1) atom in Sm_3ReO_7.

The structure of Sm_3ReO_7 consists of slightly distorted rhenium–oxygen octahedra which build up corner sharing chains in the [0 0 1] direction. Two crystallographic independent samarium sites, six and eightfold coordinated, exist in this structure type. The arrangement of samarium-

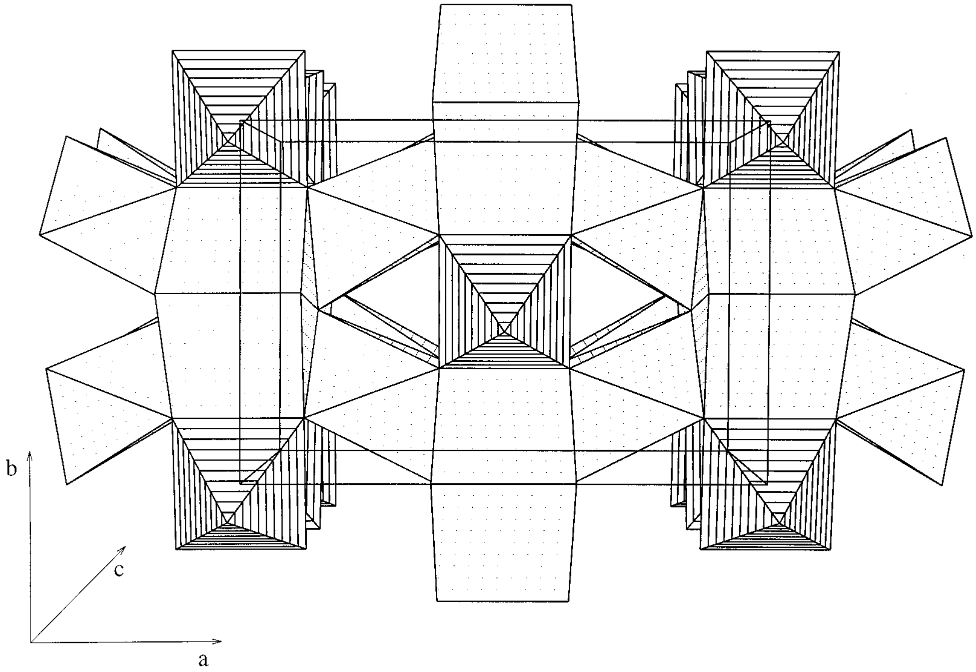

FIG. 3. The three-dimensional network of ReO_6, SmO_6, and SmO_8 polyhedra in Sm_3ReO_7: view along the [0 0 1] direction.

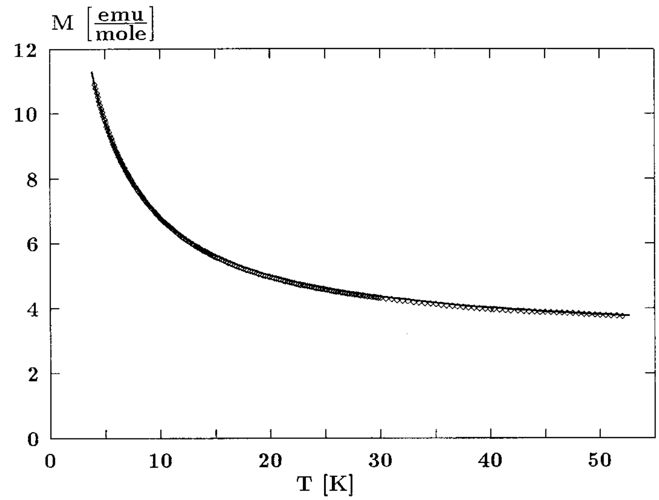

FIG. 4. Magnetization as a function of *T* with an applied field of 0.1 *T* of Sm_3ReO_7.

(1) and oxygen can be described as a highly distorted octahedron (Fig. 2) which builds up edge-sharing chains extended in the [0 0 1] direction. Two of these chains are interconnected in the [0 1 0] direction and form zigzag layers of corner-sharing SmO_6 octahedra. In addition the bridging oxygen, O(3), is also bonded to samarium-(2). The samarium-(2) environment is presented in Fig. 1. Samarium-(2) and eight oxygen atoms build up a rhombic prism. Two of these prisms are further linked together by sharing a common corner to form chains in the [0 0 1] direction.

The rhenium octahedra are interconnected by O(1). In addition they are also linked to the SmO_8 prism by bridging with O(2) to form edge sharing units. These Sm(2)–Re–O "layers" in the *bc*-plane are interconnected to the next layer in the [1 0 0] direction by parallel samarium-(1) atom layers. Furthermore the samarium-(1)–oxygen octahedra are linked to the samarium-(2) units by bridging with O(3) atoms sharing a common corner while the rhenium octahedra are connected by bonding with O(2). The three-dimensional network of Sm_3ReO_7 is given in Fig. 3.

The observed magnetization per mole is shown in Fig. 4 together with a fitted Curie–Weiss law modified by an additional temperature independent contribution M_0. The best fitting parameters are determined to $\Theta = -1.4(1)$ K and $M_0 = 2.95$ emu/mol. The large temperature independent contribution arises from the Van Vleck paramagnetism of Sm(3+). With the assumption that the temperature dependence of magnetization is only due to the rhenium ions, an effective magnetic moment of $|\boldsymbol{\mu}| = 0.6\ \mu_B$ is derived from the Curie constant for each rhenium (5+) ion.

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