

The crystal structure of $\text{Tm}_5\text{Re}_2\text{O}_{12}$

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Abstract

The crystal structure of $\text{Tm}_5\text{Re}_2\text{O}_{12}$, pentathulium dirhenium dodecaoxide, was determined by synchrotron diffraction on a reticular merohedral twin, revealing space group $C2/m$ with $a = 12.3717$ (7), $b = 5.6744$ (3), $c = 7.4805$ (4) Å, $\beta = 107.816$ (2)° and $Z = 2$. Distorted ReO_6 octahedra form chains with alternating rhenium–rhenium distances of 2.455 (1) and 3.219 (1) Å. Early reports on Ln_2ReO_5 compounds are critically reviewed in the light of our results for $\text{Tm}_5\text{Re}_2\text{O}_{12}$.

1. Introduction

Crystalline phases of ternary oxides in the system $\text{Ln}_2\text{O}_3\text{--ReO}_2\text{--Re}_2\text{O}_7$, with Ln a lanthanide or yttrium, can be characterized by the Ln:Re ratio and the formal oxidation state of rhenium. The latter can vary from +4 to +7, so that a wide range of different compositions and structure types may occur. Of particular interest are those compounds with a non-integral value of the formal

oxidation state of rhenium as in that case some kind of metallic bond is expected. Structurally well characterized examples are the lanthanum compounds $\text{La}_3\text{Re}_2\text{O}_9$ (Besse *et al.*, 1978), $\text{La}_4\text{Re}_6\text{O}_{19}$ (Longo & Sleight, 1968; Morrow & Katz, 1968) and $\text{La}_3\text{Re}_2\text{O}_{10}$ (Torardi & Sleight, 1986). For all these compounds, rhenium–rhenium pairs with shorter bond lengths than in metallic rhenium (2.76 Å) are observed. The title compound belongs to the group of compounds with general composition $\text{Ln}_5\text{Re}_2\text{O}_{12}$ and is another example with rhenium in a formal oxidation state of +4.5. A structure model, assuming space group $P2_1/m$, has been reported for $\text{Dy}_5\text{Re}_2\text{O}_{12}$, but a correct refinement was prevented by twinning (Baud *et al.*, 1983). A better description is given for $\text{Ho}_5\text{Re}_2\text{O}_{12}$, based on a centred monoclinic cell with linear chains of edge-sharing distorted ReO_6 octahedra (Heumannskämper & Jeitschko, 1987). Within these chains, rhenium–rhenium pairs exist with bond lengths of 2.437 Å. Unfortunately, neither atomic parameters nor intensity data are reported, so that an isotopic relation between $\text{Ho}_5\text{Re}_2\text{O}_{12}$ and other

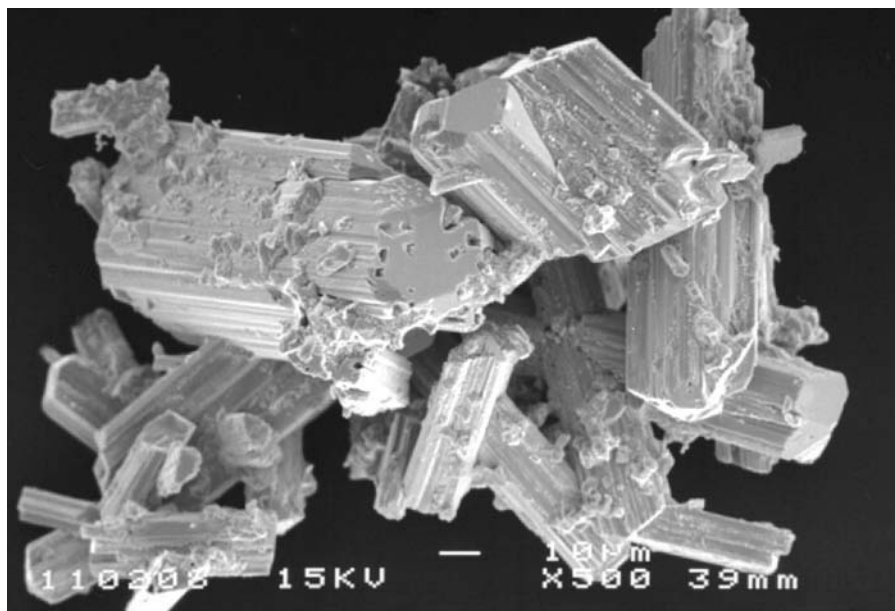


Fig. 1. Scanning electron micrograph of $\text{Tm}_5\text{Re}_2\text{O}_{12}$ crystals.

Ln₅Re₂O₁₂ compounds cannot be deduced from that work. In the present contribution, we report on the crystal structure of Tm₅Re₂O₁₂, determined from synchrotron diffraction data. Different structure types of rare earth rhenium oxides with compositions near Ln₂ReO₅ are proposed in the literature (Muller & Roy, 1969). However, deviations from this stoichiometry could not be excluded for Y₂ReO₅, γ-Gd₂ReO₅, Dy₂ReO₅, Er₂ReO₅ and Yb₂ReO₅. The suggested compositions and the interpretation of IR spectroscopy results (Savel'eva *et al.*, 1977) have to be reconsidered in the light of our results.

2. Experimental and analysis of data

The samples investigated have been synthesized by subsolidus reaction of 0.0005 mol Tm₂O₃ (Alfa, 99.99%) and 0.0005 mol ReO₂ (Aldrich, 99.9%). The reactants were intimately mixed in an agate mortar under acetone and sealed in welded Pt/Rh(90/10) tubes. After heating the tubes under argon atmosphere from room temperature to 1673 K at a rate of 300 K min⁻¹, the temperature was held for 12 h before cooling to room temperature at a rate of 180 K min⁻¹. The reaction product was analysed by scanning electron microscopy and contained small crystals with prismatic shape, as shown in Fig. 1. One crystal of 100 μm length and about 10–15 μm diameter was isolated and used for diffraction studies at room temperature (see Table 1). Data collection was performed using the κ diffractometer at beamline F1 of HASYLAB, Germany, which is situated at a bending magnet. The beam was monochromated to a wavelength of 0.4275 Å by a double-crystal Si(111) monochromator; higher harmonic rejection was achieved by detuning of the second monochromator crystal. The beam was unfocussed and defined by a slit system to a cross section of 0.12 × 0.12 mm. Its intensity was monitored by a polarimeter with NaI scintillation counters, and a feedback system on the second monochromator crystal ensured a constant incident beam intensity. Several data sets were collected with a crystal-to-detector distance of 4 cm using a 1K Smart detector from Bruker/AXS (Karlsruhe, Germany) with a 0.1° rotation per frame and exposure times of 2 and 5 s. The ω scans at six different φ settings in steps of 60° covered 90° in ω, ensuring a coverage of 100% and a redundancy higher than 12. The integration was performed with the *SAINT* program from Bruker/AXS, and diffracted-beam absorption was fitted by spherical harmonic functions using restrained full-matrix least squares following the method of Blessing (1995).

The observed reflections are compatible with the space groups *P2₁/m* and *P2₁*, with $a = 7.4805$ (4), $b = 5.6744$ (3), $c = 12.3717$ (7) Å and $\beta = 107.816$ (2)°. However, a structure solution based on either of these space groups was not successful. In both cases unrealistic short Re–O bonds of ~1 Å were derived and the

Table 1. *Experimental details*

Crystal data	
Chemical formula	Tm ₅ Re ₂ O ₁₂
Chemical formula weight	1409.05
Cell setting	Monoclinic
Space group	<i>C2/m</i>
a (Å)	12.3717 (7)
b (Å)	5.6744 (3)
c (Å)	7.4805 (4)
β (°)	107.816 (2)
V (Å ³)	499.96 (5)
Z	2
D_x (Mg m ⁻³)	9.360
Radiation type	Synchrotron
Wavelength (Å)	0.42750
No. of reflections for cell parameters	460
θ range (°)	3.43–38.89
μ (mm ⁻¹)	16.587
Temperature (K)	293 (2)
Crystal form	Needle
Crystal colour	Black
Data collection	
Diffractometer	CCD
Data collection method	ω scans
Absorption correction	Empirical (Blessing, 1995)
T_{\min}	0.19
T_{\max}	0.85
No. of measured reflections	8671
No. of independent reflections	4961
No. of observed reflections	4165
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.0532
θ_{\max} (°)	38.89
Range of h, k, l	–36 → h → 36 –11 → k → 16 –21 → l → 20
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0682
$wR(F^2)$	0.1518
S	1.246
No. of reflections used in refinement	4961
No. of parameters used	52
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0103P)^2 + 1.6684P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	<0.0001
$\Delta\rho_{\max}$ (e Å ⁻³)	14.225
$\Delta\rho_{\min}$ (e Å ⁻³)	–12.324
Extinction method	None
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C)
Computer programs	
Structure solution	<i>SHELXS97</i> (Sheldrick, 1990)
Structure refinement	<i>SHELXL97</i> (Sheldrick, 1997)

reliability values remained as high as about 15%. Therefore, the possibility of twinning was taken into account, which was further supported by unusual extinction rules: all reflections with h even and $k + l$ odd are systematically absent. This can be explained by

centring and a twinning law based on two domains, linked to each other by a rotation through 180° about the c^* axis. To transform to the standard setting, the a and c axes are interchanged, resulting in C symmetry with $a = 12.3717$ (7), $b = 5.6744$ (3), $c = 7.4805$ (4) Å and $\beta = 107.816$ (2)°. A ratio of 3.4:1 between domains 1 and 2 was refined from the intensities of the non-overlapping reflections and allowed for the separation of the intensities of overlapping reflections. The hkl set for the dominant domain with 4961 unique reflections and $R_{\text{int}} = 5.32\%$ was further used for structure solution and refinement with *SHELXS97* (Sheldrick, 1990) and *SHELXL97* (Sheldrick, 1997), respectively.

3. Results and discussion

The atomic parameters of $\text{Tm}_5\text{Re}_2\text{O}_{12}$ are summarized in Table 2. This structure model gives $R_1 = 0.682$ for 4165 reflections with $F_o > 4\sigma(F_o)$ and 0.817 for all 4961 reflections. Distorted ReO_6 octahedra form chains along $[010]$ by common edges with alternating rhenium–rhenium distances of 2.455 (1) and 3.219 (1) Å (see Fig. 2). These chains are interconnected along $[001]$ by TmO_6 octahedra, linked by the O atoms, which form a common edge between the short rhenium–rhenium bonds. Following the notation of Table 2, Tm1 has octahedral coordination and the TmO_6 octahedra are not linked to one another. On the other hand, Tm2 and Tm3 form monocapped trigonal prisms. Prisms of each type (either Tm2 or Tm3) form zigzag chains parallel to $[010]$, with alternating orientation of the prisms within one chain, *i.e.* ‘up’ and ‘down’ with respect to the

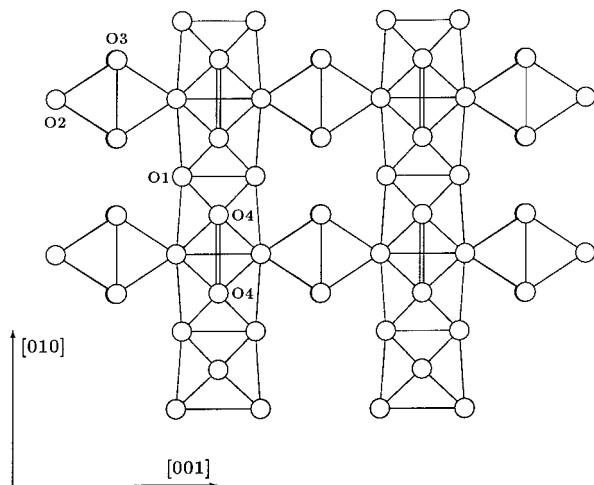


Fig. 2. View on the bc plane, displaying the chains of ReO_6 octahedra along $[010]$ and the short rhenium–rhenium bonds within. These chains are interconnected along $[001]$ by TmO_6 octahedra (Tm1 in the notation of Table 1). In reciprocal space, the reflections of the two domains in the crystal are linked by a 180° rotation about the a^* axis. As a twofold rotation about an axis perpendicular to the bc plane is a pseudo-symmetry, the observed twinning is consistent with the atomic arrangement.

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

$$U_{\text{eq}} = (1/3)\Sigma_i \Sigma_j U^{ij} a^i a^j a_j$$

Site	Wyckoff notation)	x	y	z	U_{eq}
Re1	4(g)	0	0.28367 (4)	0	0.00224 (3)
Tm1	2(d)	1/2	0	1/2	0.00381 (5)
Tm2	4(i)	0.31373 (2)	1/2	0.17505 (5)	0.00319 (4)
Tm3	4(i)	0.19638 (2)	0	0.35973 (5)	0.00313 (4)
O1	4(i)	0.0012 (4)	0	0.1787 (8)	0.0057 (5)
O2	4(i)	0.4989 (5)	0	0.2053 (9)	0.0076 (6)
O3	8(j)	0.3459 (3)	0.2520 (8)	0.4265 (7)	0.0060 (4)
O4	8(j)	0.1655 (3)	0.2461 (8)	0.0833 (8)	0.0063 (4)

overcapped face (see Fig. 3). The capping oxygen is O1 for both TmO_7 prisms, but shifted in opposite directions for Tm2 and Tm3. This results in significantly elongated edges O1–O3 (3.361 Å for Tm2 and 3.296 Å for Tm3) compared with the corresponding edges O1–O4 (2.752 Å for Tm2 and 2.734 Å for Tm3). The zigzag chains are interconnected along $[001]$ by sharing edges O3–O3 and O4–O4.

The zigzag chains of TmO_7 prisms containing Tm2 and Tm3 are of very similar geometry, but differ with

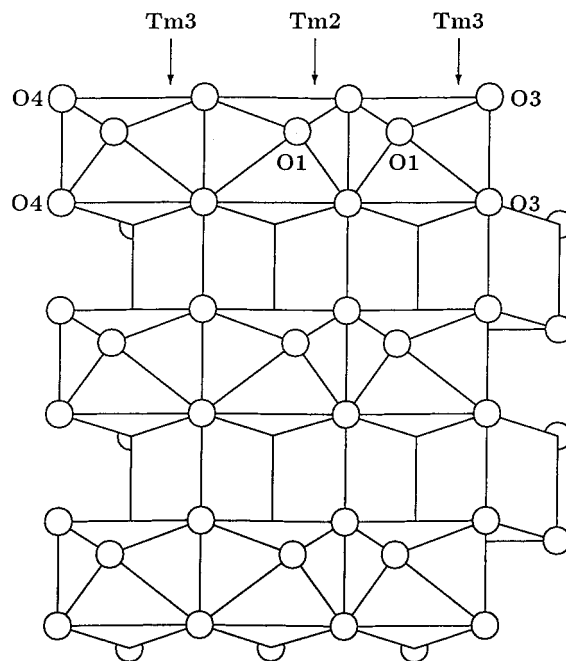


Fig. 3. Zigzag chains of monocapped, trigonal prisms of TmO_7 , running parallel to $[010]$. Chains with either Tm2 or Tm3 ions are linked to each other by common edges, O3–O3 ($d = 2.809$ Å) or O4–O4 ($d = 2.799$ Å), respectively. Within one zigzag chain, the prisms are also interconnected by sharing edges, *i.e.* O4–O4 ($d = 2.876$ Å) for Tm2 and O3–O3 ($d = 2.922$ Å) for Tm3. The orientations of the prisms alternate along $[010]$ for both the Tm2 and Tm3 chains in phase. For clarity, the viewing direction on the bc plane has been slightly tilted, through 15° , along the horizontal c axis.

Table 3. Comparison between the observed relative integrated intensities of reflections in powder diffraction experiments on 'Yb₂ReO₅' (Muller & Roy, 1969), assumed to be actually Yb₅Re₂O₁₂, and on Tm₅Re₂O₁₂

(hkl)	'Yb ₂ ReO ₅ ' I/I _{max} (%)	Tm ₅ Re ₂ O ₁₂ I/I _{max} (%)
(001)	4	10
(20 $\bar{1}$)	5	6
(201)	7	5
(002), (20 $\bar{2}$)	20	18
(310)	90	100
(11 $\bar{2}$)	100	98
(400)	21	17
(020)	8	17
(112), (31 $\bar{2}$)	14	10
(40 $\bar{2}$), (202)	84	58
(021)	20	21
(220)	19	31
(221)	10	12
(20 $\bar{3}$)	2	2
(221)	3	5
(22 $\bar{2}$), (022)	28	33
(510)	9	7
(51 $\bar{2}$), (312)	9	8
(421)	5	6
(600), (42 $\bar{2}$), (222)	43	35
(204)	48	22
(023)	8	6
(131)	2	3
(42 $\bar{3}$)	5	5
(331), (330)	7	9
(13 $\bar{2}$)	6	8
(71 $\bar{2}$), (512)	16	11
(223), (62 $\bar{2}$), (422)	50	30
(514), (132), (114)	50	26

respect to the connectivity scheme to TmO₆ and ReO₆ octahedra: each coordination polyhedron of Tm2 is linked to four ReO₆ octahedra, to two of them by common edges and to the other two by sharing corners. For Tm3, only two links to ReO₆ octahedra exist, both by common edges and resulting in layers of TmO₇ and ReO₆ units parallel to the plane [201]. Each TmO₆ octahedron has common edges with two TmO₇ prisms for Tm3, interconnecting them along [100].

All structural aspects reported for Ho₅Re₂O₁₂ (Heumannskämper & Jeitschko, 1987) are in agreement with the structure of Tm₅Re₂O₁₂, so that an isotopic relation is strongly supported. Furthermore, the same crystal structure has been reported for Y₅Mo₂O₁₂ and Gd₅Mo₂O₁₂ (Torardi *et al.*, 1985).

The similarity of lattice parameters and the proposed centred monoclinic symmetry give rise to the specula-

tion that the assumed stoichiometries Y₂ReO₅, γ-Gd₂ReO₅, Dy₂ReO₅, Er₂ReO₅ and Yb₂ReO₅ (Muller & Roy, 1969) are erroneous and should be Ln₅Re₂O₁₂, Ln = Y, Gd, Dy, Er and Yb, crystallizing in the Y₅Mo₂O₁₂ structure type described above. This assumption is further supported by the reported uncertainties in the estimation of the Ln₂ReO₅ stoichiometry, as the investigated samples were the result of an unsuccessful attempt to synthesize Ln₂Re₂O₇ compounds and the twinning of all isolated crystals. However, the striking point is the similarity of reflection intensities given for a powder sample of 'Yb₂ReO₅' as compared to our results on Tm₅Re₂O₁₂ (see Table 3). The same conclusions hold for the samples 'Ln₂ReO₅' studied by IR spectroscopy and X-ray diffraction (Savel'eva *et al.*, 1977). Especially the interpretation of the absorption spectra, based on the assumption that the investigated compounds are of similar crystal structure as the alkaline earth metal uranates M₂UO₅, are challenged by our results and should be reconsidered by taking structural details and the existence of metallic rhenium-rhenium bonds into account.

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