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Preparation and Characterization of Rare Earth Rhenium Oxides Ln_6ReO_{12}, Ln = Ho, Er, Tm, Yb, Lu

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Compounds of the series Ln_6ReO_{12}, Ln = Ho, Er, Tm, Yb, and Lu, have been prepared by subsolidus reaction and are isotypic with Ln_6MoO_{12}, Ln_6WO_{12}, and Ln_6UO_{12}, crystallizing in space group $R\bar{3}$ with $Z = 3$ for the R-centered setting. The magnetic moment per rhenium ion in Lu_6ReO_{12} is $0.74(1)\mu_B$, and Yb_6ReO_{12} orders antiferromagnetically below 2.15(10) K.

Key Words: **crystal structure; magnetic susceptibilities; rhenium (+VI) compounds.**

INTRODUCTION

Mixed oxides of composition $MeO_3 \cdot Ln_2O_3$, with Ln a rare earth element or yttrium, are known for the hexavalent metals Me = Mo, W, and U (1). They crystallize in a rhombohedral structure related to the ordered Ln_7O_{12} phases. Furthermore, the stability ranges of this structure type in the ternary phase systems MeO_2–MeO_3–Ln_2O_3 have been discussed, revealing a significant dependence on the specific cations (2). Accordingly, the formation of this structure type requires a minimum cation size ratio Me/Ln of 0.67. Based on this empirical criterion the same crystal structure was predicted for all the fictitious compounds Ln_6ReO_{12}, but the assumed ionic radius for Re^{6+} has not been reported. Only the existence of $ReO_3 \cdot 3Y_2O_3$ is mentioned in the literature (3).

In this contribution we report on the synthesis of Ln_6ReO_{12} compounds with Ln = Ho, Er, Tm, Yb, and Lu, which is essentially different from the preparation of the Mo, W, and U compounds due to the high volatility of Re_2O_7 and the multivalence of rhenium. In addition to the structures determined from X-ray powder data the magnetic properties of these compounds will be reported.

EXPERIMENTAL

All compounds have been synthesized by subsolidus reaction. For this purpose the sesquioxides Ln_2O_3 have been mixed with ReO_2 in the ratio 2:1, i.e., a ratio Ln:Re = 4:1. The reactants were intimately ground in an agate mortar under acetone and filled in a Pt/Rh(90/10%) tube under argon atmosphere. The tubes were welded to ensure that they were properly closed. The furnace was flushed with argon before heating the samples to 1200°C at a rate of 300°/h, tempering for 12 h, cooling to room temperature at a rate of 180°/h and afterward tempering again at 1200°C for 24 h at the same rates. A green-blackish powder was obtained which showed two distinct phases under a light microscope. Both kinds of specimen have further been investigated by X-ray powder diffraction, using a STOE STADI P diffractometer with germanium-monochromatized Cu $K\alpha_1$ radiation and a position-sensitive detector with 6° aperture in transmission mode. The temperature dependence of magnetization at field strength of 0.01 T for Ln = Ho, Er, Tm, Yb and 0.25 T for Lu was measured down to 1.8 K with a superconducting quantum interference device (SQUID) from Quantum Design.

RESULTS AND DISCUSSION

Crystal Structure

All compounds Ln_6ReO_{12}, Ln = Ho, ..., Lu, gave very similar diffraction patterns, which could be indexed on the basis of a trigonal cell. The structure solution from powder data revealed the space group $R\bar{3}$ with $Z = 3$ for the R-centered setting. The structural parameters have been refined by the Rietveld method using FULLPROF (5), resulting in the lattice constants listed in Table 1. Atomic parameters in Table 2 and the corresponding observed and calculated profiles together with the difference curve in Fig. 1 are given for Tm_6ReO_{12} as a representative. Isotropic temperature factors have been applied for the oxygen atoms, but anisotropic ones for the Ln and Re atoms, for the latter restricted by local site symmetry to only two independent parameters. In the case of Ln = Lu the Lu:Re ratio was confirmed to be 6.0(1) by EDX. $[ReO_6]$-octahedra are connected with 12 $[LnO_7]$-units by common oxygens, to six of

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TABLE 1
Cell Parameters for the Compounds Ln_6ReO_{12} as Determined from Powder X-Ray Diffraction Data by Rietveld Refinement

Ln	*a* (Å)	*c* (Å)
Ho	9.7621 (3)	9.3016 (3)
Er	9.7291 (2)	9.2553 (2)
Tm	9.6953 (3)	9.2084 (3)
Yb	9.6425 (3)	9.1672 (3)
Lu	9.6269 (2)	9.1316 (2)

Note. The sigmas are in agreement with (4).

them by sharing edges and to six others by sharing corners. The crystal structure is shown in Fig. 2. The second phase in the reaction mixture was identified to be Ln_3ReO_8 with fluorite-type structure (6).

TABLE 2
Atomic Parameters for Tm_6ReO_{12} as Representatives for the Series of Isotypic Compounds Ln_6ReO_{12}, Ln = Ho, ..., Lu

Atom	Site	*x*	*y*	*z*	B_{eff}
Re	3*a*	0	0	0	0.47(7)
Tm	18*f*	0.2527(3)	0.0411(5)	0.3543(3)	0.55(2)
O1	18*f*	0.185(3)	0.042(4)	0.113(2)	1.3(6)
O2	18*f*	0.226(3)	0.031(4)	0.599(2)	1.2(5)

Note. The uncertainties are calculated in agreement with (4). Only isotropic temperature factors have been refined for the oxygen atoms, while one third of the trace of the anisotropic tensor is given for the Tm and Re atoms.

The compounds Ln_6ReO_{12}, Ln = Ho, ..., Lu, are the first examples of rare earth rhenium oxides with a formal oxidation state of rhenium + VI. This series offers a suitable test

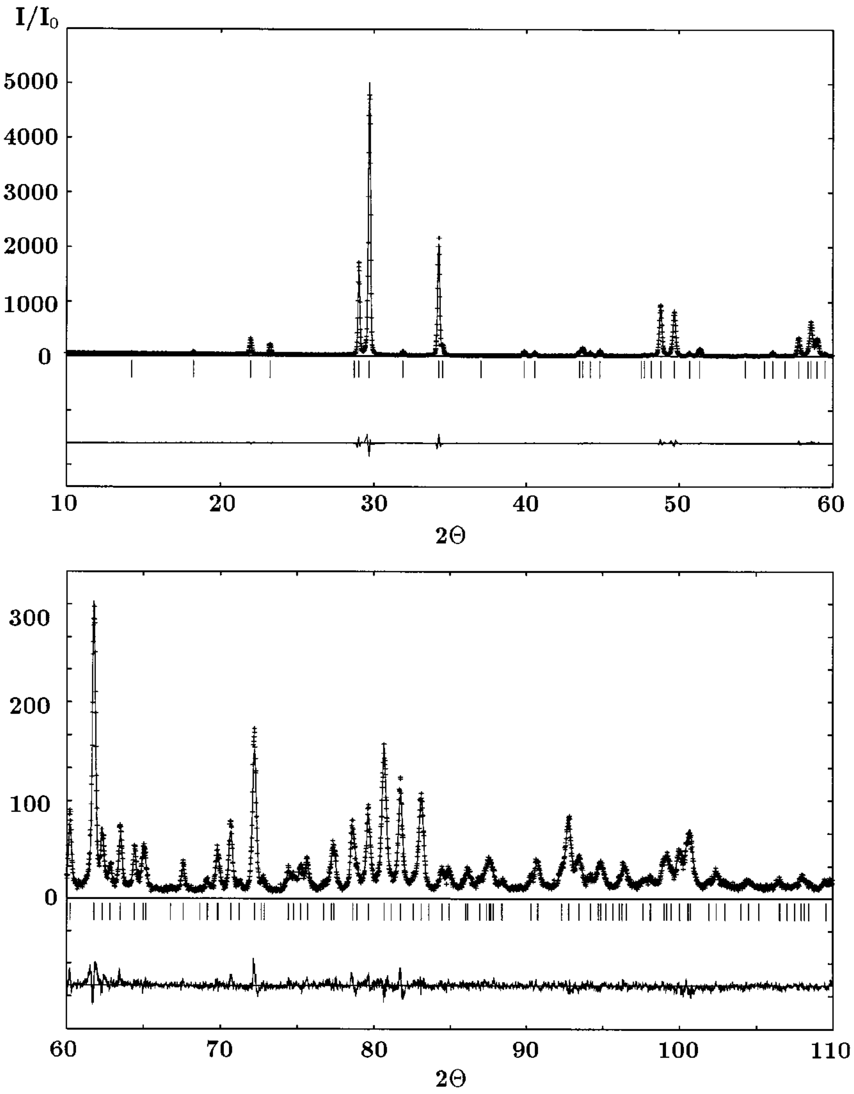

FIG. 1. The observed and fitted profiles for Tm_6ReO_{12} and the corresponding difference curve (Cu$K\alpha_1$). The powder pattern has been split into two parts with different scales for clarity.

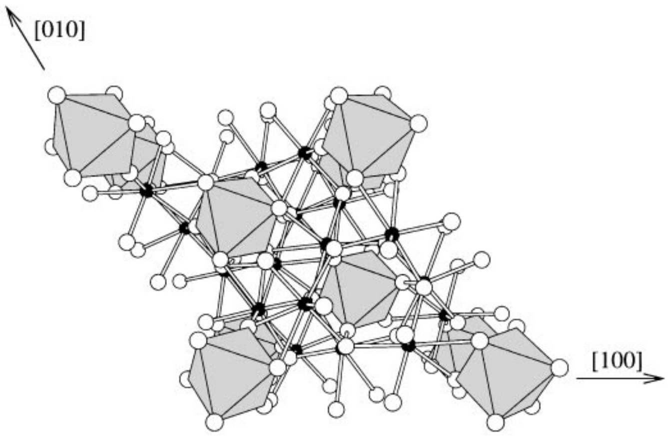

FIG. 2. The crystal structure of Ln_6ReO_{12}, view along the [001] direction. $[ReO_6]$ octahedra and Ln–O bonds are shown for all cations in one unit cell, including all Re ions on the corners. Some oxygen atoms outside the unit cell are also shown to complete the coordination polyhedra for all Re and Ln ions.

TABLE 3
Magnetic Properties of the Compounds Ln_6ReO_{12}

Ln	$\mu(Ln^{3+})/\mu_B$	Θ/K	M_0/(emu/g)	T range
Ho	8.91(4)	-0.21	$1.2 \cdot 10^{-4}$	10–180 K
Er	9.25(8)	-11.5	$4.2 \cdot 10^{-6}$	25–180 K
Tm	7.15(6)	-12.7	$9.6 \cdot 10^{-7}$	20–50 K
Yb	3.19(3)	-2.03	$1.8 \cdot 10^{-5}$	10–100 K
Lu	—	-1.29	$2.4 \cdot 10^{-4}$	1.8–80 K

Note. The same magnetic moment per Re^{6+} ion of $0.74\mu_B$ was assumed for all compounds as deduced from the temperature dependence of magnetization in Lu_6ReO_{12} with only diamagnetic rare earth ions. Only data within the given temperature range have been used to determine the Curie–Weiss parameters.

for the empirical stability criterion for this structure type, previously deduced for the Mo, W, and U series (2). Accordingly, this rhombohedral structure type should only be formed if the ratio between the ionic radii of the hexavalent metal ions and the trivalent rare-earth ion is at least 0.67. Using a consistent set of ionic radii for sixfold coordination of the metal ions (7), slightly different ratios are obtained. The relevant values are summarized in Table 4. Although the Re^{6+} ion is much smaller than W^{6+} and Mo^{6+}, the stability edge of Ln_6ReO_{12} is not shifted to smaller rare earth elements, but just in between those of W and Mo. The largest rare earth element forming the Ln_6MeO_{12} structure type is Er for Me = Mo, Dy for Me = W, and Ho for Me = Re. The U^{6+} ion is sufficiently large to build up this structure type for all rare earth elements and for yttrium. The stability limit can be given by a common critical ratio Me/Ln of 0.655 for Me = Mo, W, or U, but a value of 0.605 is deduced for the case of Me = Re. Nevertheless, it is confirmed that the stability range is limited by a critical size of the rare earth ion, even if this critical size cannot be related to the size of the hexavalent ion as proposed. In particular for the case of rhenium, which occurs in the formal oxidation states +4, +5, +6, and +7 with calculated ionic radii varying from 0.63 to 0.53 Å for sixfold coordination, it is questionable which value should be applied to the above mentioned stability criterion. As we start with rheniumdioxide, i.e., Re^{+4} and end up with Re^{+6}, an intermediate ionic radius of 0.605 Å can fit the analogy to the Mo, W, and U series.

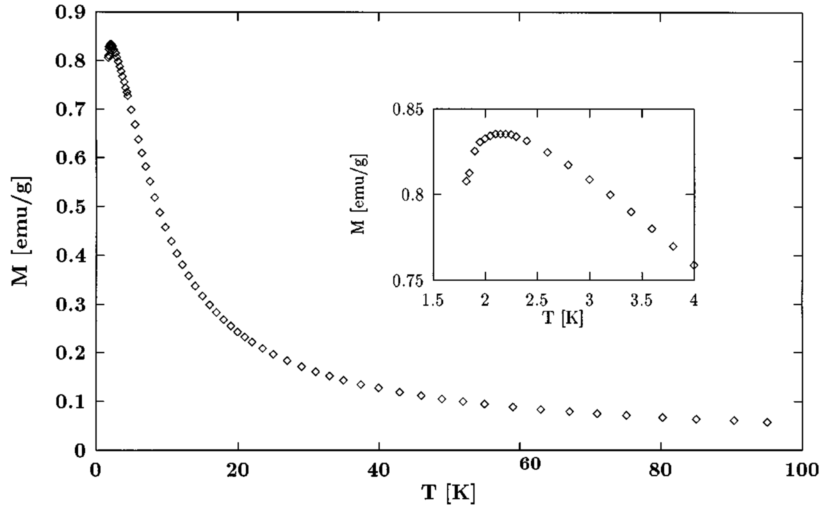

FIG. 3. Temperature dependence of magnetization for Yb_6ReO_{12}. The low temperature behavior is exposed in the inset.

TABLE 4
Ionic Radii in Å of Selected Ions in Sixfold Coordination as Taken from (7) and Ratios, Relevant for the Stability Criterion

Mo^{+6}	0.59	Y^{3+}	0.900	Dy^{3+}	0.912
W^{+6}	0.60	La^{3+}	1.032	Ho^{3+}	0.901
Re^{+6}	0.55	Gd^{3+}	0.938	Er^{3+}	0.890
U^{+6}	0.73	Tb^{3+}	0.923	Lu^{3+}	0.861

Mo:Y	0.656	W:Y	0.667	Re:Y	0.611	U:Y	0.811
Mo:Ho	0.655	W:Gd	0.640	Re:Dy	0.603	U:La	0.707
Mo:Er	0.663	W:Dy	0.658	Re:Ho	0.610		

Magnetic Properties

The observed temperature dependences of magnetization have been fitted by a Curie–Weiss law, modified by an additional temperature independent contribution M_0,

$$M(T) = \frac{C}{T - \Theta} + M_0. \quad [1]$$

A magnetic moment of 0.74(1) μ_B per Re^{6+} ion was deduced from the Curie constant for $Ln = Lu$. The magnetic moments for the rare earth elements are given in Table 3, based on the same rhenium contribution in all compounds. Re^{+6} is one of the very rare examples of a $5d^1$ electron configuration. In a crystal field of octahedral symmetry the five $L = 2$ states split into a low-lying triplet and a doublet. In the limiting case of infinite crystal field splitting and ideal cubic symmetry, the ground state with effective angular momentum $\tilde{J} = 3/2$ has the Landé factor $g(\tilde{J}) = 0$. The observed magnetic moment of Re^{+6} has an anisotropic contribution from further splittings of the triplet due to crystal field effects of lower symmetry and an isotropic contribution due to the finite splitting between doublet and triplet. Both effects can be distinguished based on the anisotropy of the g-tensor, but the experimental determination of its matrix elements requires a single crystal of sufficient size for paramagnetic resonance spectroscopy, which could not be prepared so far. Down to 1.85 K antiferromagnetic ordering is only suggested for $Ln = Yb$ from the pronounced maximum of magnetization at $T = 2.15(10)$ K; see Fig. 3. Nevertheless, deviations from the Curie–Weiss law are also observed at low temperatures for $Ln = Ho$, Er, and Tm as shown for the inverse magnetization in Fig. 4.

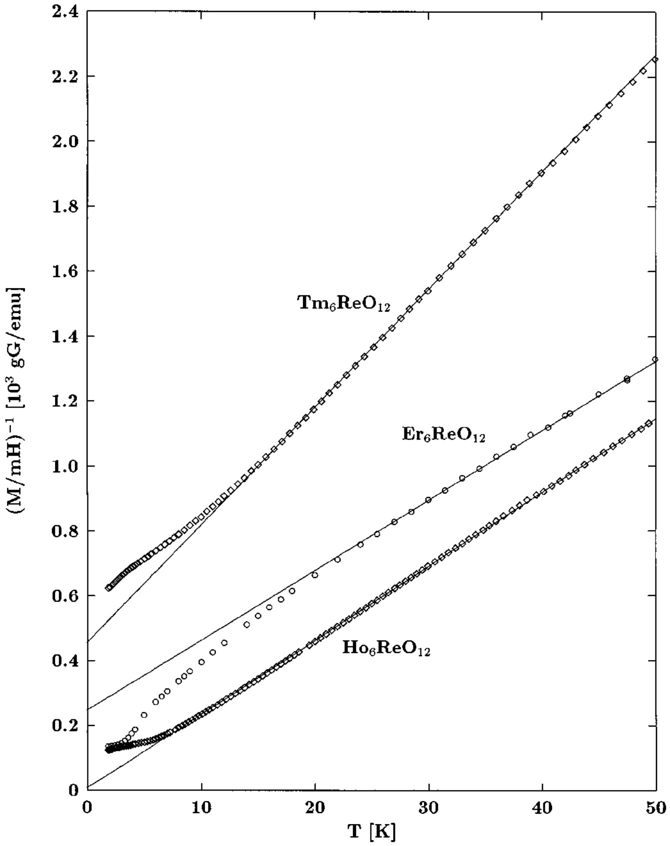

FIG. 4. Temperature dependence of the inverse magnetization for Ho_6ReO_{12}, Er_6ReO_{12}, and Tm_6ReO_{12}. The drawn lines belong to modified Curie–Weiss fits with the parameters of Table 3.

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