Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

Preparation, crystal structure and magnetic properties of the high-pressure phase $MnReO_4$ with a wolframite-type structure

K. G. Bramnik,[a] H. Ehrenberg,[a]* S. Buhre[b] and H. Fuess[b]

[a]Institute for Materials Science, Darmstadt University of Technology, Petersenstrasse 23, D-64287 Darmstadt, Germany, and [b]Institute for Mineralogy, Johann-Wolfgang-Goethe University, Senckenberganlage 28, D-60054 Frankfurt, Germany

Correspondence e-mail:
ehrenberg@tu-darmstadt.de

Received 4 August 2004
Accepted 17 February 2005

The ternary oxide $MnReO_4$, manganese rhenium oxide, has been synthesized under a high pressure of 5.5 GPa at 1473 K and its crystal structure has been determined by single-crystal X-ray diffraction. $MnReO_4$ crystallizes in a wolframite-type structure with average bond lengths of $\langle Re-O\rangle = 1.935$ and $\langle Mn-O\rangle = 2.160$ Å that are in good agreement with the ionic radii of Re^{6+} and Mn^{2+}. The magnetic properties of $MnReO_4$ have been studied by SQUID measurements, revealing magnetic ordering below 275 (10) K and a weak ferromagnetic component of the ordered magnetic structure.

1. Introduction

Only a few ternary oxides of 3*d* transition metals and rhenium in a lower oxydation state than +7 have been reported in the literature (Sleight, 1975; Baur *et al.*, 1992; Bramnik, Ehrenberg, Theissmann *et al.*, 2003). Sleight (1975) described a series of 3*d* transition metal–rhenium–oxygen compounds with two different compositions: MReO$_4$ (M = Mn, Fe, Co, Ni, Zn) and M_2ReO_6 (M = Cr, Fe), synthesized at high pressure (5.8 GPa, 1473–1573 K; Sleight, 1975). The structural characterization in that work was restricted to the determination of cell parameters from powder diffraction, and structure types are proposed based on similarities in cell metrics and diffracted patterns from analogous tungsten compounds. Accordingly, four structure types with a different cation distribution in half of the octahedral interstices in a hexagonal-close packing of O atoms were considered:

(i) A rutile-type structure was suggested for $FeReO_4$, $NiReO_4$ and $CoReO_4$. In contrast to the tetragonal unit cell of $FeReO_4$ two different types of orthorhombic distortions were proposed for $NiReO_4$ and $CoReO_4$.

(ii) Monoclinic wolframite-type structures were suggested for $MnReO_4$ and $ZnReO_4$.

(iii) A trirutile-type structure was proposed for Cr_2ReO_6 with linear chains of edge-sharing octahedra.

(iv) A tri-α-PbO_2 structure with zigzag chains of edge-sharing octahedra was proposed for Fe_2ReO_6.

Complete structure analyses based on single-crystal X-ray diffraction have only been reported for $CoReO_4$ (Baur *et al.*, 1992) and $(V_{0.5}Re_{0.5})O_2$ (Bramnik, Ehrenberg, Theissmann *et al.*, 2003). In $CoReO_4$ the ReO_6 octahedra are linked by edge-sharing, forming infinite chains of ReO_4 in this structure. The Re—Re distance in these chains is 2.8923 (3) Å, which is larger than in metallic rhenium. The infinite chains of rhenium polyhedra are linked *via* common corners with similar infinite chains of edge-sharing CoO_6 octahedra, *i.e.* a rutile-related structure was confirmed. $(V_{0.5}Re_{0.5})O_2$ crystallizes in a rutile-type structure with V and Re randomly distributed on one

doi:10.1107/S0108768105005380

cation site. The substitution of 50% of the vanadium by rhenium has (*meta*-) stabilized the high-temperature form of VO_2 at ambient conditions (Bramnik, Ehrenberg, Theissmann *et al.*, 2003).

In this work we report on the high-pressure synthesis of the ternary rhenium manganese oxide $MnReO_4$, its detailed crystal structure and its magnetic properties.

2. Experimental

MnO (Aldrich, 99%) and ReO_3 (STREM Chemicals, 99.9%) were chosen as starting materials. MnO and ReO_3 were ground together in an agate mortar in a molar ratio of 1:1 with acetone, placed in a platinum container and heated under pressure. The high-pressure synthesis was performed in a Girdle–Belt apparatus with pyrophyllite and graphite as the pressure-transmitting and heating mediums. The sample holder was squeezed by the application of 5.5 GPa before the temperature was raised to 1473 K over 20 min. This temperature was held for 120 min before the current for heating was disconnected and, after room temperature was reached, the pressure was released to ambient conditions. Black crystals with edges of up to 50 µm were obtained by this technique. The crystal structure of $MnReO_4$ was solved by single-crystal X-ray diffraction using the Xcalibur system from Oxford Diffraction. The software packages *SHELXS* (Sheldrick, 1990) and *SHELXL* (Sheldrick, 1997) were used for structure solution and refinement, as included in *X-STEP*32 (Stoe & Cie, 2000). Complementary X-ray powder diffraction was performed on a Stoe Stadi/P powder diffractometer [Co $K\alpha_1$ radiation, curved Ge monochromator, transmission mode, step 0.02^0 (2θ), linear PSD counter] for phase analysis and the crystal structure was confirmed by Rietveld's method, using the software package *Winplotr* (Roisnel & Rodriguez-Carvajal, 2001). The temperature dependence of magnetization was measured with a superconducting quantum interference device (SQUID) from Quantum Design on a 13.3 mg powder sample at a constant field strength of 100 G, both in zero-field cooled (ZFC) and field-cooled (FC) mode.

Table 1
Experimental details.

Crystal data	
Chemical formula	MnO_4Re
M_r	305.14
Cell setting, space group	Monoclinic, $P2/c$
a, b, c (Å)	4.8022 (5), 5.6318 (6), 5.0803 (6)
β (°)	92.762 (9)
V (Å^3)	137.24 (3)
Z	2
D_x (Mg m^{-3})	7.384
Radiation type	Mo $K\alpha$
No. of reflections for cell parameters	664
θ range (°)	3.6–32.4
μ (mm^{-1})	48.46
Temperature (K)	304 (1)
Crystal form, colour	Prism, black
Crystal size (mm)	0.05 × 0.04 × 0.03
Data collection	
Diffractometer	Oxford Diffraction Xcalibur (TM); single-crystal X-ray diffractometer with sapphire CCD detector
Data collection method	Rotation method data acquisition using ω and φ scans(s)
Absorption correction	Numerical
T_{min}	0.257
T_{max}	0.401
No. of measured, independent and observed reflections	823, 272, 263
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.038
θ_{max} (°)	26.3
Range of h, k, l	$-5 \Rightarrow h \Rightarrow 5$ $-6 \Rightarrow k \Rightarrow 7$ $-6 \Rightarrow l \Rightarrow 6$
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.066, 1.17
No. of reflections	272
No. of parameters	30
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0383P)^2 + 2.3979P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.28, −2.38
Extinction method	*SHELXL*
Extinction coefficient	0.003 (2)

Computer programs used: *CrysAlis CCD*, *CrysAlis RED* (Oxford Diffraction Ltd, 2003), *SHELXS*97 (Sheldrick, 1990), *SHELXL*97 (Sheldrick, 1997), *Diamond* (Crystal Impact GbR, 2001).

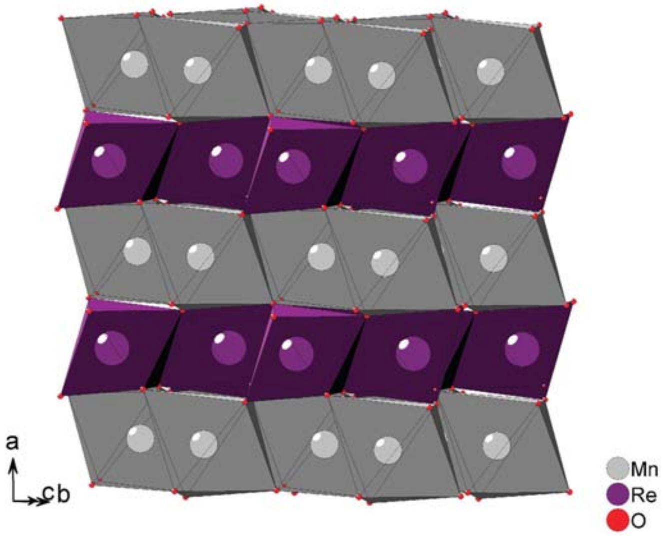

Figure 1
Crystal structure of $MnReO_4$.

3. Results and discussion

X-ray single-crystal structure analysis confirmed the wolframite-type structure of $MnReO_4$ as proposed by Sleight (1975), see Fig. 1. A monoclinic unit cell with a = 4.8025 (2), b = 5.6290 (2), c = 5.0748 (2) Å and β = 92.731 (2)° was determined (see Table 1), and the structure was solved and refined based on the space group $P2/c$.[1] X-ray powder diffraction

---

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: WS5018). Services for accessing these data are described at the back of the journal.

revealed an almost pure sample with only very weak contributions from β-ReO_2 (2 wt %) and β-Mn_2O_3 (1.5 wt %). The reflection positions of these impurity phases are indicated by the two lower lines of reflection marks in Fig. 2.

The temperature dependence of inverse magnetic susceptibility reveals paramagnetic behaviour above $T_N = 275$ (10) K, see Fig. 3, with a Curie–Weiss temperature of $\theta = 67$ (7) K and a paramagnetic moment of 5.35 (7) μ_B per formula unit of $MnReO_4$. This value is in very good agreement with the paramagnetic moments obtained for $Ba_{2-x}Sr_xMnReO_6$ (x = 0–2), 5.33–5.44 μ_B (Popov *et al.*, 2003). The observed temperature dependence of $MnReO_4$ is in good agreement with the reported local minimum of magnetic susceptibility between 78 and 298 K at *ca* 210 K (Sleight, 1975), appearing as a local maximum for the inverse magnetic susceptibility in Fig. 3. The differences between FC and ZFC data indicate a weak ferromagnetic component below $T_C \simeq 225$ K in agreement with the positive Curie–Weiss temperature. The magnetization *versus* applied field loops confirmed hysteresis behaviour with remanent magnetizations per formula unit of 2.2×10^{-3} μ_B (5 K), 1.5×10^{-4} μ_B (50 K) and 2.4×10^{-5} μ_B (150 K). Compounds with Re^{6+} are known for their unusual magnetic properties with very weak but significant ferromagnetic components, even above room temperature (*e.g.* Bramnik *et al.*, 2001; Bramnik, Ehrenberg, Dehn & Fuess, 2003). The underlying mechanism is not yet clear. A combined investigation of the electronic configurations of the Mn and Re ions on one hand, and the determination of magnetization density using the diffraction of polarized neutrons on the other, is needed to elucidate the magnetic interactions. The localized electron configurations in Mn^{2+} and Re^{6+} should result in a larger paramagnetic moment than that observed. An Re^{7+} core and an itinerant electron coupling with Mn^{2+} might be proposed, supported by the rather good electronic conductivity of $MnReO_4$ (Sleight, 1975). However, the average Re—O bond distance is 1.935 Å, which is in good agreement with the Re—O bond distances observed in other compounds with a formal rhenium oxidation state of +6: in Ba_2MnReO_6 1.921 Å (Khattak *et al.*, 1975; even larger value of 1.984 Å reported in Popov *et al.*, 2003), in $Sr_7Re_4O_{19}$ 1.930 and 1.940 Å (Bramnik *et al.*, 2001); in the $Sr_{11}Re_4O_{24}$ compound with Re in two different oxidation states (+6 and +7) ordered in the crystal structure; 1.947 Å for Re^{6+} octahedra (Bramnik *et al.*, 2000). The delocalization of an electron leads to the average Re—O bond distance of 1.875 Å, as in the case of the metallic conductor ReO_3 with octahedral coordinated Re in the formal oxidation state of +6 (Jorgensen *et al.*, 1986). This bond length is close to those of the octahedrally coordinated Re^{7+}: in $Sr_5Re_2O_{12}$ the bond lengths are 1.897, 1.880 and 1.877 Å (Mons *et al.*, 1992), but they are much shorter than the observed value in $MnReO_4$. The average bond length for Mn—O is 2.160 Å, which is slightly smaller than the value of 2.23 Å for Mn^{2+} in its high-spin state, but larger than 2.07 Å for the low-spin state or any other formal oxidation state of Mn. In summary, bond-length considerations favour a basically localized Re^{6+}–Mn^{2+} configuration (*i.e.* a d^5–d^1 system) as in $Ba_{2-x}Sr_xMnReO_6$, where additional EXAFS data have been taken into account (Popov *et al.*, 2003). Therefore, $MnReO_4$ might be the first example of a high-pressure synthesized phase with rhenium in the formal oxidation state of +6. Note the formal oxidation state of rhenium is +5.2 in $Sr_{0.4}ReO_3$ (Baud *et al.*, 1979), +5 in $CoReO_4$ (Baur *et al.*, 1992) and +4 in $(V_{0.5}Re_{0.5})O_2$ (Bramnik, Ehrenberg, Theissmann *et al.*, 2003).

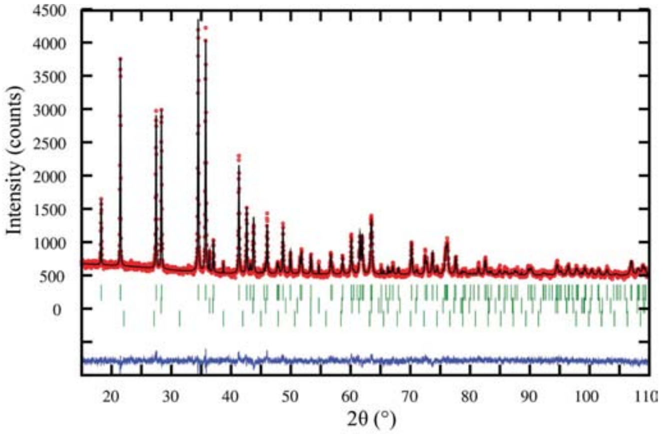

Figure 2
Observed, calculated and difference X-ray powder diffraction pattern of $MnReO_4$.

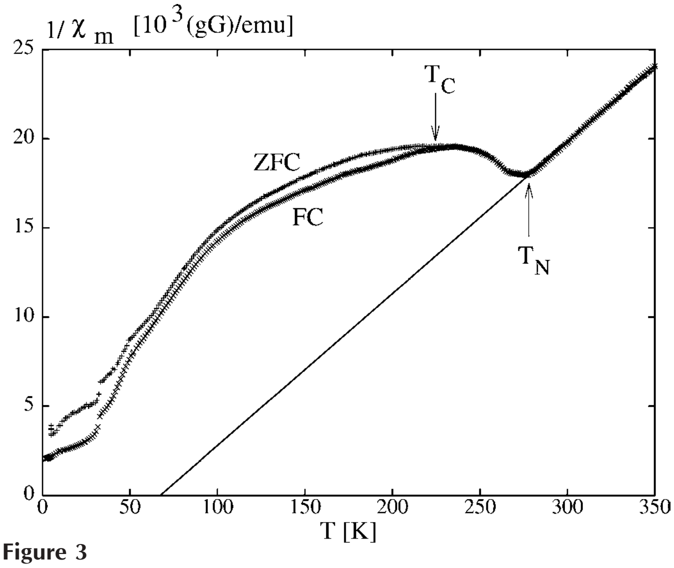

Figure 3
Temperature dependence of the inverse specific magnetic susceptibility for a powder sample of $MnReO_4$, calculated from magnetization data in zero-field cooled and field-cooled modes. The line corresponds to a Curie–Weiss fit to the data in the paramagnetic region between 280 and 350 K.

Financial support from the Deutsche Forschungsgemeinschaft (DFG FU125/42) is gratefully acknowledged.

References

Baud, G., Besse, J. P., Chevalier, R. & Chamberland, B. L. (1979). *J. Solid State Chem.* **28**, 157–162.

Baur, W. H., Joswig, W., Pieper, G. & Kassner, D. (1992). *J. Solid State Chem.* **99**, 207–211.

Bramnik, K. G., Ehrenberg, H., Dehn, J. K. & Fuess, H. (2003). *Solid State Sci.* **5**, 235–241.

Bramnik, K. G., Ehrenberg, H. & Fuess, H. (2001). *J. Solid State Chem.* **160**, 45–49.

Bramnik, K. G., Ehrenberg, H., Theissmann, R., Fuess, H. & Morán, E. (2003). *Z. Kristallogr.* **218**, 455–457.

Bramnik, K. G., Miehe, G., Ehrenberg, H., Fuess, H., Abakumov, A. M., Shpanchenko, R. V., Pomjakushin, V. Yu & Balagurov, A. M. (2000). *J. Solid State Chem.* **149**, 49–55.

Crystal Impact GbR (2001). *Diamond*. Version 2.1e. Crystal Impact GbR, Postfach 1251, 53002 Bonn, Germany.

Jorgensen, J.-E., Jorgensen, D. J., Batlogg, B., Remeika, J. P. & Axe, J. D. (1986). *Phys. Rev. B*, **33**, 4793–4798.

Khattak, C. P., Cox, D. E. & Wang, F. F. Y. (1975). *J. Solid State Chem.* **13**, 77–83.

Mons, H. A., Schriewer, M. S. & Jeitschko, W. (1992). *J. Solid State Chem.* **99**, 149–157.

Oxford Diffraction Ltd (2003). *XCalibur*, *CrysAlis Software System*, Version 1.170. Oxford Diffraction Ltd, Abingdon, Oxfordshire.

Popov, G., Greenblatt, M. & Croft, M. (2003). *Phys. Rev. B*, **67**, 024406.

Roisnel, T. & Rodriguez-Carvajal, J. (2001). *Mater. Sci. Forum*, **378–381**, 118–123.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Sleight A. W. (1975). *Inorg. Chem.* **14**, 597–599.

Stoe & Cie (2000). *X-STEP*32. Stoe & Cie, GmbH Darmstadt, Germany.