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## New Ternary Oxides of Pentavalent and Hexavalent Rhenium of the Type $\text{AReO}_4$ or $\text{A}_2\text{ReO}_6$

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Compounds of the type  $\text{AReO}_4$  where A is Mg, Mn, Fe, Co, Ni, Zn, Al, and Ga have been prepared. Most have structures related to that of rutile, but the wolframite structure is observed for A = Mg, Mn, and Zn.  $\text{MnReO}_4$  exhibits anisotropic electrical resistivity.  $\text{Cr}_2\text{ReO}_6$  was prepared in the trirutile structure, and  $\text{Fe}_2\text{ReO}_6$  has the tri- $\alpha$ - $\text{PbO}_2$  structure. All of these new oxides of rhenium appear to require high pressure for their synthesis. These compounds represent the first cases in all of these structure types where both cations have open d shells.

### Introduction

Rhenium oxides of the type  $\text{AReO}_4$  are well known where the A cation is univalent and Re is in its group oxidation state of VII. However,  $\text{AReO}_4$  compounds have not been reported where Re is in an oxidation state of less than VII. Compounds of the type  $\text{A}_2\text{ReO}_6$  have not been reported for any oxidation state of Re. If A were a first-row transition metal cation, an interesting combination of localized 3d electrons and delocalized 5d electrons might result. Thus, attempts were made to synthesize compounds of these types.

### Experimental Section

Rhenium trioxide was obtained from ROC/RIC. All other reactants were reagent grade or better. Syntheses were carried out in a tetrahedral anvil previously described.<sup>1</sup> The conditions were generally 58 kbars at 1200–1300° for 1–4 hr using platinum containers. Reactant ratios are given in Table I.

X-Ray powder patterns were recorded at 25° using a Hägg-Guinier camera with  $\text{CuK}\alpha_1$  radiation and an internal standard of high-purity KCl ( $a = 6.2931$  Å). Indexed powder patterns have been submitted to ASTM. Electrical data were obtained by the four-probe method using indium-solder contacts.

### Results

The new  $\text{AReO}_4$  and  $\text{A}_2\text{ReO}_6$  phases prepared are listed in Table I. These compounds are all black or dark violet. The pressure required for the syntheses of these phases was not determined, but 30 kbars was adequate to prepare  $\text{MnReO}_4$ . Synthesis attempts at 3 kbars were unsuccessful; thus, substantial pressure is apparently necessary. Therefore, these compounds all appear to be metastable, but they exist for years at ambient conditions without noticeable decomposition. Chemical analyses were not attempted in view of the very small sample size. However, closed containers were used for syntheses, and the products were single phase. Thus, the compositions of the products are determined by the reactants.

**MgReO<sub>4</sub>, MnReO<sub>4</sub>, and ZnReO<sub>4</sub>.** These compounds apparently have the wolframite structure. The cell dimensions are given in Table I. The intensities of reflections from powder patterns were compared to those from analogous tungstates, and they were qualitatively the same. Single-crystal X-ray photographs of  $\text{MnReO}_4$  were consistent with the wolframite structure.

Crystals of  $\text{MnReO}_4$  large enough for anisotropic resistivity measurements were obtained. At room temperature the resistivity parallel to the  $c$  axis was 0.39 ohm cm, and perpendicular to this axis the resistivity was 3.1 ohm cm. The activation energy was 0.4 eV in both directions. The magnetic susceptibility of  $\text{MnReO}_4$  was investigated from 78 to 298°K. The room-temperature molar susceptibility was  $23 \times 10^3$ . This smoothly decreased to  $17.5 \times 10^3$  at 210°K and then smoothly increased to  $19 \times 10^3$  at 78°K.

**AlReO<sub>4</sub>, GaReO<sub>4</sub>, and FeReO<sub>4</sub>.** These phases presumably have the rutile structure with a statistical distribution of the cations. A single crystal of  $\text{FeReO}_4$  showed a room tem-

Table I. Synthesis and Crystallographic Data<sup>a</sup>

Compd	$a$ , Å	$b$ , Å	$c$ , Å	$\beta$ , deg	Reactants
$\text{MgReO}_4$	4.690	5.573	5.066	92.03	$\text{MgO-ReO}_3$
$\text{MnReO}_4$	4.802	5.630	5.076	92.73	$3\text{MnO}_2-2\text{ReO}_3-\text{Re}$
$\text{ZnReO}_4$	4.695	5.605	5.026	91.27	$\text{ZnO-ReO}_3$
$\text{AlReO}_4$	4.636		2.803		$3\text{Al}_2\text{O}_3-5\text{ReO}_3-\text{Re}$
$\text{GaReO}_4$	4.692		2.850		$3\text{Ga}_2\text{O}_3-5\text{ReO}_3-\text{Re}$
$\text{FeReO}_4$	4.668		2.927		$3\text{Fe}_2\text{O}_3-5\text{ReO}_3-\text{Re}$
$\text{NiReO}_4$	4.625	4.678	2.893		$\text{NiO-ReO}_3$
$\text{CoReO}_4$	6.503	6.732	2.881		$\text{Co}_3\text{O}_4-\text{Co}-4\text{ReO}_3$
$\text{Cr}_2\text{ReO}_6$	4.551		8.907		$\text{Cr}_2\text{O}_3-\text{ReO}_3$
$\text{Fe}_2\text{ReO}_6$	4.541	16.629	4.974		$\text{Fe}_2\text{O}_3-\text{ReO}_3$

<sup>a</sup> Errors in cell edges are estimated to be  $\pm 0.05\%$ .

perature electrical resistivity of  $8 \times 10^{-4}$  ohm cm which decreased slightly on cooling. Magnetic measurements indicated antiferromagnetism with a Neel temperature of 194°K.

**NiReO<sub>4</sub> and CoReO<sub>4</sub>.** These phases also appear to have structures related to that of rutile. However, they are definitely not tetragonal. A simple orthorhombic distortion was indicated for  $\text{NiReO}_4$  (Table I). A different type of orthorhombic distortion was indicated for  $\text{CoReO}_4$ . This is a C-centered orthorhombic cell where  $a$  and  $b$  are larger by a factor of  $2^{1/2}$ . This cell for  $\text{CoReO}_4$  was confirmed by single-crystal X-ray studies.

**Cr<sub>2</sub>ReO<sub>6</sub> and Fe<sub>2</sub>ReO<sub>6</sub>.** The powder pattern of  $\text{Cr}_2\text{ReO}_6$  was readily indexed on the basis of the trirutile structure. A comparison of intensities with those from  $\text{Cr}_2\text{WO}_6$  confirmed that  $\text{Cr}_2\text{ReO}_6$  and  $\text{Cr}_2\text{WO}_6$  are essentially isostructural.  $\text{Fe}_2\text{ReO}_6$  is isostructural with  $\text{Fe}_2\text{WO}_6$  which has been described<sup>2</sup> as having a tri- $\alpha$ - $\text{PbO}_2$  structure.

### Discussion

All of the new compounds reported here have structures based on hexagonal close-packed oxygen layers with all cations in octahedral sites. Since the oxygen-to-total metal ratio is 2 in all cases, half of the octahedral sites are occupied. Two fundamentally different ways of filling these sites are relevant to this discussion. In the rutile structure, there are linear chains of edge-shared octahedra. The  $\alpha$ - $\text{PbO}_2$  structure also has chains of edge-shared octahedra, but here the chains are zigzagged. Substitutions of the type  $\text{A}^{\text{III}}\text{M}^{\text{VO}}_4$  in the rutile structure (e.g.,  $\text{FeTaO}_4$ ) have never led to a long-range ordering of the cations.<sup>3</sup> (Actually, there may be a very high degree of order along a chain; but due to the particular geometry, there is essentially no electrostatic incentive for such chains to order with respect to one another. Thus, there is no long-range order in three dimensions). Substitutions of the type  $\text{A}^{\text{III}}\text{M}^{\text{VO}}_4$  are not known in the rutile structure. However, substitutions of the types  $\text{A}^{\text{II}}\text{M}^{\text{V}}_2\text{O}_6$  and  $\text{A}^{\text{III}}_2\text{M}^{\text{VI}}\text{O}_6$  in the rutile structure (e.g.,  $\text{MgTa}_2\text{O}_6$  and  $\text{Cr}_2\text{WO}_6$ ) are accompanied by long-range ordering of A and M in three dimensions.<sup>4,5</sup> The resulting structure is referred to as the trirutile structure. Ordering of cations in the  $\alpha$ - $\text{PbO}_2$  structure can occur for either the  $\text{AMO}_4$

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or the  $A_2MO_6$  compositions. The structure of the ordered  $\alpha$ - $PbO_2$  arrangement is known as the wolframite structure for the  $AMoO_4$  composition. There are two different possibilities for the  $A_2MO_6$  (or  $AM_2O_6$ ) composition. These are referred to as the tri- $\alpha$ - $PbO_2$  or the columbite structure.<sup>2,3</sup>

The oxidation state of the A cation is definite in  $Mg^{II}ReO_4$ ,  $Zn^{II}ReO_4$ ,  $Al^{III}ReO_4$ , and  $Ga^{III}ReO_4$ . Thus, it is certain that  $AREO_4$  compounds have been prepared where rhenium is formally pentavalent and where it is formally hexavalent. The wolframite structure is found for the definite  $A^{II}Re^{VI}O_4$  situation, and the statistical rutile structure is found for the definite  $A^{III}Re^{VO}_4$  combination.

The oxidation states in  $FeReO_4$  might be  $Fe^{II}-Re^{VI}$  or  $Fe^{III}-Re^V$ . This is a particularly interesting problem since the oxidation states in  $Ba_2FeMoO_6$  are  $Fe^{III}-Mo^V$ ,<sup>6,7</sup> while in all three forms of  $FeMoO_4$  the  $Fe^{II}-Mo^{VI}$  combination prevails.<sup>8</sup> In  $Ba_2FeReO_6$  the oxidation states are  $Fe^{III}-Re^V$ , but it is proposed that this combination is nearly degenerate with the  $Fe^{II}-Re^{VI}$  situation.<sup>9</sup> Thus, the oxidation states in  $FeReO_4$  could not be predicted. The fact that  $FeReO_4$  is isostructural with  $Al^{III}Re^{VO}_4$  and  $Ga^{III}Re^{VO}_4$  rather than  $Mg^{II}Re^{VI}O_4$  and  $Zn^{II}Re^{VI}O_4$  strongly suggests that the oxidation states are  $Fe^{III}-Re^V$  in  $FeReO_4$ . This is an especially strong argument since no  $A^{II}M^{VI}O_4$  compounds are known to have the rutile structure. A  $Fe^{III}Re^{VO}_4$  combination is further supported by the cell volume of  $FeReO_4$  relative to the cell volumes of  $AlReO_4$  and  $GaReO_4$ . The volume for  $GaReO_4$  is slightly less than that of  $FeReO_4$  which is expected if the iron is trivalent. A  $Fe^{II}Re^{VI}O_4$  combination would be expected to give a significantly larger cell volume.

The oxidation states in  $CoReO_4$  and  $NiReO_4$  are less certain. In  $Ba_2CoReO_6$  and  $Ba_2NiReO_6$ , the oxidation states are  $A^{II}-Re^{VI}$ ,<sup>9</sup> and there is no suggestion of valence degeneracy as indicated for  $Ba_2FeReO_6$ . Thus, an  $A^{II}-Re^{VI}$  combination might be expected for both  $NiReO_4$  and  $CoReO_4$ . However, it then becomes somewhat surprising that these compounds do not have the wolframite structure. The answer may be that  $CoReO_4$  and  $NiReO_4$  are  $A^{III}Re^{VO}_4$  at high pressure where they adopt a rutile-type structure. High pressure would tend to favor  $A^{III}-Re^V$  over  $A^{II}-Re^{VI}$  since the former would have a higher density. This is true because whereas  $Re^V$  is slightly larger than  $Re^{VI}$ ,  $A^{II}$  is considerably larger than  $A^{III}$ . On release of the pressure, the valence situation might go from  $A^{III}-Re^V$  to  $A^{II}-Re^{VI}$ . However, the disorder and delocalization in  $NiReO_4$  and  $CoReO_4$  may lead to a situation where neither  $A^{II}-Re^{VI}$  nor  $A^{III}-Re^V$  applies.

The cell dimensions for all  $A^{II}M^{VI}O_4$  compounds with the wolframite structure are plotted in Figure 1 as a function of the radius<sup>10</sup> of  $A^{II}$ . All compounds with this structure show essentially the same behavior with respect to the  $a$  dimension. However,  $MgTeO_4$ <sup>11</sup> and the  $AREO_4$  compounds show a larger  $c$  and a smaller  $b$  dimension than the analogous molybdates and tungstates. The wolframite structure consists of edge-shared octahedra chains which are parallel to the  $c$  axis. Thus, for  $MgTeO_4$  and the  $AREO_4$  compounds, the cation-cation distances within the chains are probably longer but the chains are closer together relative to the analogous tungstates and molybdates. However, this is not a firm conclusion since the positional parameters in these phases have not been refined.

In tungstates and molybdates with the wolframite structure, there is considerable distortion of the octahedra surrounding Mo and W. This distortion is almost certainly related to multiple-bond formation between Mo or W and oxygen using the empty d orbitals of Mo or W. Such bonding is impossible for Te with its closed d shell. Such bonding is also unlikely for  $Re^{VI}$ , especially if its antibonding 5d electron is delocalized. Thus, the octahedra around  $Re^{VI}$  and  $Te^{VI}$  are almost certain to be more regular, and this is probably the primary reason

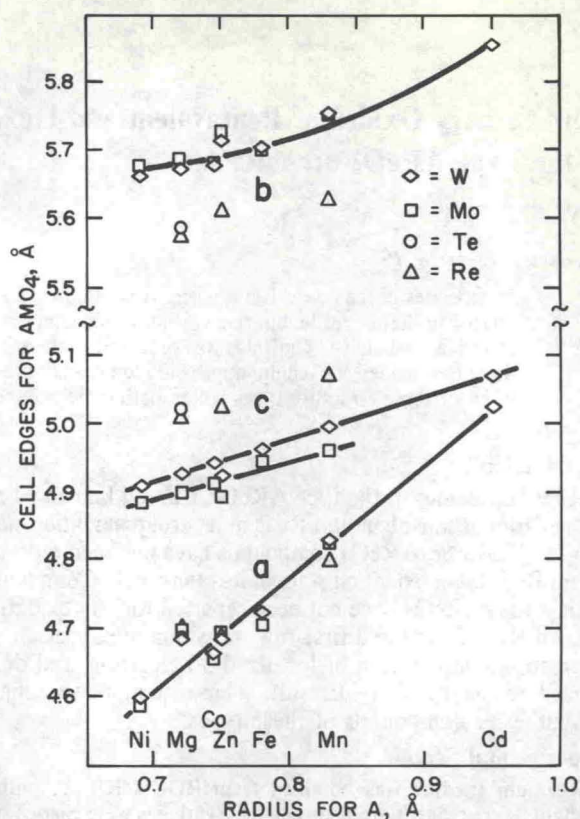


Figure 1. Cell edges vs. radius of A for  $AMO_4$  compounds with the wolframite structure.

for their different behavior in Figure 1. The points for  $MnReO_4$  in Figure 1 offer good support for a  $Mn^{II}-Re^{VI}$  valence combination.

$MnReO_4$  is the first compound to be prepared with the wolframite structure where both cations have partially filled d shells. The d electrons of  $Re^{VI}$  should be very delocalized relative to those of  $Mn^{II}$ . Since there are infinite  $Re-O-Re-O$  and  $Re-Re-Re$  linkages along the  $c$  axis but not perpendicular to it, anisotropic electrical resistivity might well be expected. In fact, metallic behavior might be expected along  $c$  with semiconducting behavior perpendicular to  $c$ . However, defects will generally preclude one-dimensional metals. Thus, it may be that the  $Re$  edge-shared octahedra do result in one-dimensional metallic behavior over a finite distance. However, an activation energy is required for a conduction electron to pass through a defect in a chain, and an activation energy is also required for an electron to pass from one chain to another. In fact, the easiest path for a conduction electron encountering a defect might be to jump to a neighboring chain. Thus, it is entirely reasonable that the activation energy in the two directions is the same but that the conductivity is somewhat better along the  $c$  axis.

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**Registry No.**  $MgReO_4$ , 53849-95-9;  $MnReO_4$ , 53849-96-0;  $ZnReO_4$ , 53849-97-1;  $AlReO_4$ , 53906-75-5;  $GaReO_4$ , 53906-76-6;  $FeReO_4$ , 53906-77-7;  $NiReO_4$ , 53906-78-8;  $CoReO_4$ , 53906-79-9;  $Cr_2ReO_6$ , 53849-98-2;  $Fe_2ReO_6$ , 53849-99-3.

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