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Preparation and Properties of Substituted Iron Tungstates

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Polycrystalline samples of members of the systems $Fe_{2-x}Cr_xWO_6$ and $Fe_{1-x}Mn_xWO_4$ were prepared and single crystals of $Fe_{1-x}Mn_xWO_4$ were grown by chemical vapor transport. Their crystallographic parameters and electrical properties were characterized. Fe_2WO_6 crystallizes with the tri-α-PbO_2 structure and is an *n*-type semiconductor. For $0.3 \leq x \leq 2$, the system $Fe_{2-x}Cr_xWO_6$ crystallizes with the inverse trirutile structure and is nonconducting due to blocking of iron(II)–iron(III) conduction paths by chromium(III). For $0 \leq x \leq 1$, the system $Fe_{1-x}Mn_xWO_4$ crystallizes with the wolframite structure and shows *p*-type semiconducting behavior. The nature of the variation of resistivity with x of $Fe_{1-x}Mn_xWO_4$ suggests that interchain electron transfer may occur in this structure.

Introduction

The use of iron(III) oxide as a potential photoanode for photoinduced electrolysis of water has been reported (*1–5*). The interest in this compound has been generated by its relatively narrow band gap (~2.2 eV) and its stability in aqueous solutions. It was found that pure α-Fe_2O_3 has a high resistivity ($>10^6 \Omega$ cm) and shows no detectable photocurrent (*6*). Although the phase boundary between α-Fe_2O_3 and Fe_3O_4 is sharp (*7*), α-Fe_2O_3 can be made conductive through the introduction of small amounts of Fe_3O_4 by exposure to a reducing atmosphere. The spinel Fe_3O_4 contains both iron(II) and iron(III) on octahedral sites, and conduction occurs via electron transfer from iron(II) to iron(III). However, iron(III) oxide itself crystallizes with the corundum structure which contains only trivalent iron, and cannot tolerate deviations from a metal-to-oxygen ratio of 2 : 3.

One of the problems in the search for new iron-containing oxide semiconductors for potential photoelectrodes is the relationship between electrical transport properties and structure. Compounds crystallizing with the α-PbO_2, wolframite, and rutile structures are potentially interesting materials because they can contain varying amounts of iron(II) and iron(III) on equivalent sites. In the following sections, the preparation of some iron-containing transition metal tungstates crystallizing with the tri-α-PbO_2, wolframite, and trirutile structures will be described, and the relationship between the observed electrical properties and certain structural features, such as cation distribution and geometry of octahedral linkages, will be discussed.

Experimental

The preparation of iron(III) tungstate Fe_2WO_6 has been described previously (*8*).

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Samples were prepared by a solid state reaction of Fe_2O_3 (obtained by decomposition of iron(II) oxalate in air) and WO_3 (obtained by heating 99.9% pure tungsten foil under flowing oxygen for 4 days at 1000°C). A finely ground mixture of the oxides was placed in a covered platinum crucible and heated in air at 950°C for 6 days. Polycrystalline samples of the solid solution $Fe_{2-x}Cr_xWO_6$ were prepared by heating finely ground mixtures of Fe_2O_3 (Mapico Red), Cr_2O_3 (obtained by thermal decomposition of $(NH_4)_2Cr_2O_7$ (Mallinkrodt, analytical reagent) at 600°C for 30 hr in air), and WO_3 for 6 days at 950°C in air in covered platinum crucibles.

Polycrystalline $FeWO_4$ was prepared by a solid state reaction of FeO and WO_3 (*9*). FeO was obtained by reacting freshly reduced iron metal (Leico) with Fe_2O_3 (Mapico Red) for 3 days at 900°C in sealed evacuated silica tubes and quenching the tubes rapidly into cold water to prevent disproportionation of FeO into Fe and Fe_3O_4. A finely ground mixture of FeO and WO_3 was heated at 900°C for 6 days in a sealed evacuated silica tube. Polycrystalline samples of the solid solution $Fe_{1-x}Mn_xWO_4$ were prepared by heating finely ground mixtures of FeO, MnO, and WO_3 for 6 days at 900°C in sealed evacuated silica tubes. MnO was prepared by hydrogen reduction at 650°C of manganese(III) hydroxides obtained from alkaline peroxide oxidation of a manganese(II) sulfate solution.

Single crystals of $Fe_{1-x}Mn_xWO_4$ were grown from single-phase polycrystalline samples by chemical vapor transport using tellurium(IV) chloride as a transport agent. A concentration of 2.3 mg $TeCl_4$/cc was used; the temperature of the charge zone was 985°C and that of the growth zone 900°C. Crystal growth proceeded for one week. All products were removed from the transport tube, washed immediately with dilute hydrochloric acid, then rinsed with water and dried with acetone. In all cases, crystals large enough for electrical measurements were formed.

X-ray diffraction patterns of the polycrystalline materials and ground single crystal powders were taken using a Philips Norelco diffractometer with monochromatic Cu$K\alpha_1$ radiation from a high-intensity copper source (λ = 1.5405 Å). Cell parameters were determined from slow-scan (0.25 degree 2θ/min) diffraction patterns over the range of $10 \leq 2\theta \leq 70°$; the reflections were indexed and precise lattice parameters were obtained using a least squares refinement.

Sintered disks of Fe_2WO_6 were prepared as described previously (*8*) by hotpressing aliquots of approximately 800 mg for 2 hr at 980°C at an applied pressure of 5000 psi. Dies and plungers of Diamonite (Al_2O_3) were used. The heating rate was about 12°C/hr, and at the end of the sintering process the disks were allowed to cool at nearly the same rate. The product was x-rayed with Fe$K\alpha$ radiation (λ = 1.9360 Å) using the Debye–Scherrer method, and its pattern was compared with those of the corresponding starting compounds to confirm that the phase did not undergo any change during the sintering process. Sintered disks of $Fe_{2-x}Cr_xWO_6$ were prepared by pressing aliquots of approximately 200 mg at 90,000 psi; 10 drops of Carbowax were added to the sample before pressing to facilitate the formation of a well-sintered disk. The pressed disks were placed on a bed of powder having the same composition, in an alumina crucible. The disks were heated at a rate of 50°C/hr to 950°C and maintained at that temperature for 7 hr. At the end of the sintering process, the disks were cooled at the same rate. The product was x-rayed with Fe$K\alpha$ radiation (λ = 1.9360 Å) using the Debye–Scherrer method, and its pattern was compared with those of the corresponding starting materials (as was described for Fe_2WO_6). Homogeneous single crystals of members of the

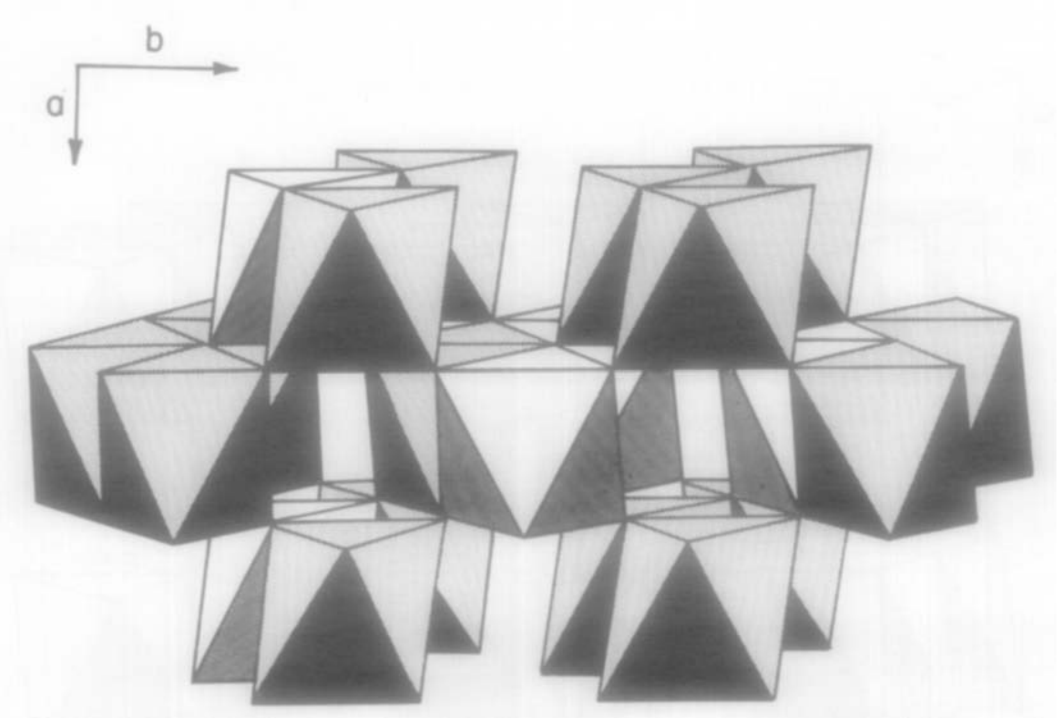

FIG. 1. The tri-α-PbO_2 structure with c-axis perspective of linked octahedra; light-shaded octahedra represent $[WO_6]$ units.

system $Fe_{2-x}Cr_xWO_6$ could not be grown by chemical vapor transport because of the large difference in the transport rates of Fe_2WO_6 and Cr_2WO_6.

The resistivities of both single crystals and sintered disks were measured using the van der Pauw technique (*10*). Contacts were made by the ultrasonic soldering of indium onto the samples, and their ohmic behaviors were established by measuring their current-voltage characteristics. The sign of the majority carriers was determined from qualitative measurement of the Seebeck effect.

Results and Discussion

The structure of Fe_2WO_6 has been described by Senegas and Galy (*11*). Fe_2WO_6 crystallizes with the tri-α-PbO_2 structure, an ordered variant of the α-PbO_2 structure. It consists of a distorted hexagonal close-packed array of oxygen anions in which one half the octahedral interstices are occupied by iron and tungsten in an ordered manner. The cations are distributed in such a way as to give rise to skew-edge linked chains of octahedra extending along the c direction as shown in Fig. 1. Separate chains are corner linked to each other. Senegas and Galy have indicated that, ideally, one third of these puckered chains contains only iron atoms (denoted by dark octahedra), and two thirds show a one-to-one ordering of iron and tungsten atoms (alternating dark and light octahedra). The 2 : 1 cation ordering causes a tripling of the b axis relative to the normal α-PbO_2 unit cell. The space group is *Pbcn* and the lattice parameters for the orthorhombic cell are

$$a = 4.557(1)\ \text{Å} \qquad b = 16.750(1)\ \text{Å} \qquad c = 4.965(1)\ \text{Å}.$$

Fe_2WO_6 prepared from stoichiometric

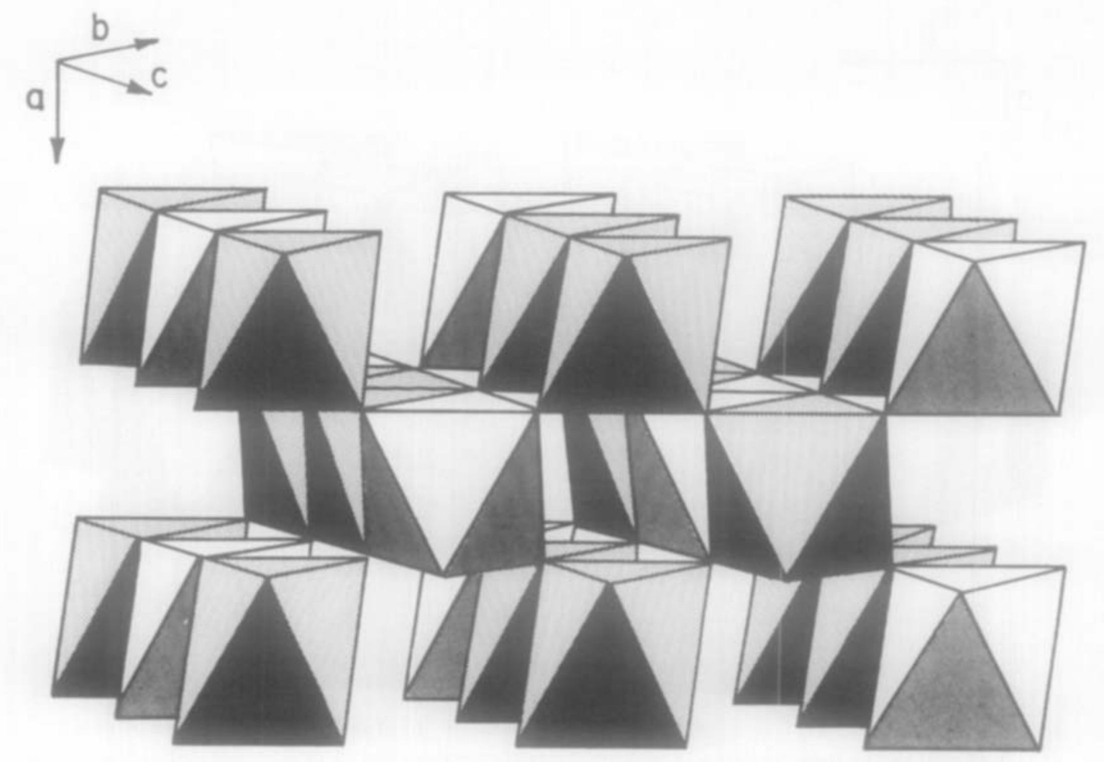

FIG. 2. The AB_2O_6 trirutile structure showing cation ordering in straight chains of octahedra; light-shaded octahedra represent $[WO_6]$ units.

mixtures of the appropriate oxides always shows trace amounts of α-Fe_2O_3 in the product, as indicated by the presence of some of the strongest reflections of this oxide (012, 110, 024, 116, 214) near the limit of detection. This material has been reported (*8*) to be an *n*-type semiconductor with an activation energy of .17 eV and a room temperature resistivity of ~50 Ω cm. The presence of trace amounts of α-Fe_2O_3 can be accounted for on the basis of a solid solution of small amounts of $FeWO_4$ in Fe_2WO_6 as shown by Leiva (*8*). Thus, the extrinsic *n*-type semiconducting behavior of Fe_2WO_6 is consistent with the solid solution of $FeWO_4$ in Fe_2WO_6, thereby introducing iron(II) and iron(III) on equivalent sites so that conduction may occur along the chains of the tri-α-PbO_2 structure by electron hopping.

The solid solution $Fe_{2-x}Cr_xWO_6$ is single phase in the region $.3 \leq x \leq 2$ and crystallizes with the inverse trirutile structure, an ordered variant of the rutile structure, which has been described by Bayer (*12*) for Cr_2WO_6. The inverse trirutile structure (space group *P*4/2*mnm*) can be described as a hexagonal close-packed array of oxygen anions in which one half of the octahedral

TABLE I

CRYSTALLOGRAPHIC DATA FOR $Fe_{2-x}Cr_xWO_6$ (SPACE GROUP *P*4/2*mnm*)

x	*a*(Å)	*c*(Å)	*V*(Å³)
2	4.580(1)	8.865(1)	186.0
1	4.607(1)	8.916(1)	189.2
0.5	4.619(1)	8.941(1)	190.8
0.3	4.627(1)	8.964(1)	192.0

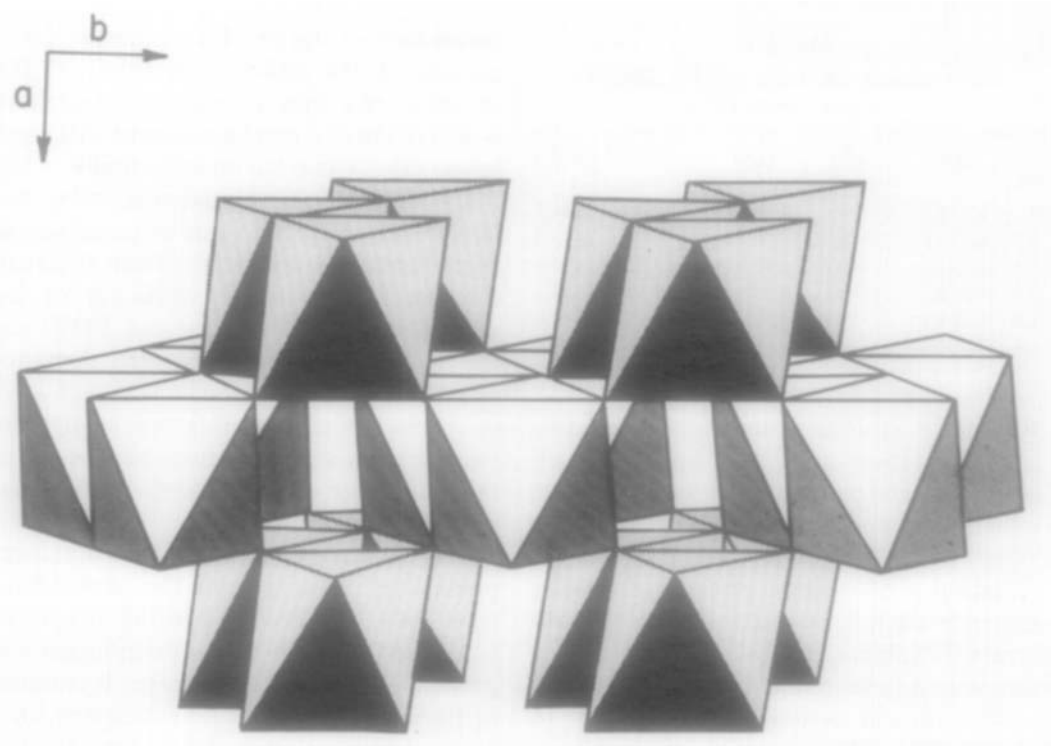

FIG. 3. The wolframite structure with c-axis perspective of skewed chains of octahedra; light-shaded octahedra represent $[WO_6]$ units.

interstices are occupied so as to give rise to straight chains of edge linked octahedra. There is a 2 : 1 cation ordering within the chains of the inverse trirutile structure, as shown in Fig. 2. The variation of cell parameters with composition (shown in Table I) and the variation of cell volume with composition are consistent with Végard's law. The decrease in cell volume with increasing chromium content is consistent with the decrease in ionic radius between iron(III) and chromium(III).

All single-phase materials $Fe_{2-x}Cr_xWO_6$ for $.3 \leq x \leq 2$ were found to be nonconducting. This is consistent with chromium(III) effectively blocking any possible conduction pathways involving iron(II) and iron(III) in the straight chains of the inverse trirutile structure. Thus, substitution of chromium(III) in Fe_2WO_6 changes the structure from tri-α-PbO_2 to inverse trirutile, and electron hopping involving iron(II) and iron(III) in the straight chains of the inverse trirutile structure is effectively blocked.

$FeWO_4$ crystallizes with the monoclinic wolframite structure ($P2/c$), another ordered variant of the α-PbO_2 structure, which has been described by Ülkü (*13*) and Cid-Dresdner (*14*). It consists of a distorted hexagonally close-packed array of oxygen anions in which one half of the octahedral interstices are filled, giving rise to puckered skew-edge linked chains of octahedra along the c direction, as shown in Fig. 3. The cation distribution within these chains differs from that of the tri-α-PbO_2 structure; in the wolframite structure, the puckered chains are occupied entirely by either iron(II) or tungsten(VI) (represented by dark or light octahedra, respectively) in alternate layers. There are no mixed chains in the

TABLE II

CRYSTALLOGRAPHIC DATA FOR $Fe_{1-x}Mn_xWO_4$ (SPACE GROUP $P2/c$)

x	a(Å)	b(Å)	c(Å)	β	V(Å^3)
0	4.734(1)	5.709(1)	4.963(1)	~90°	134.1
0.2	4.751(1)	5.718(1)	4.969(1)	~90°	135.0
0.5	4.782(1)	5.733(1)	4.984(1)	90.57(2)°	136.6
0.8	4.811(1)	5.749(1)	4.992(1)	90.90(2)°	138.1
1.0	4.829(1)	5.759(1)	4.998(1)	91.16(2)°	139.0

wolframite structure, and separate chains of unlike cations are corner linked to each other. The cell parameters of $FeWO_4$ determined from polycrystalline powders are $a = 4.734(1)$ Å, $b = 5.708(1)$ Å, $c = 4.963(1)$ Å, and $\beta \sim 90°$. Single crystals of $FeWO_4$ grown by chemical vapor transport with tellurium(IV) chloride are p-type semiconductors with a room temperature resistivity of $\sim 100\Omega$ cm and an activation energy of .16 eV (*9*). The extrinsic p-type semiconducting behavior of $FeWO_4$ is consistent with the presence of a small amount of iron(III) introduced by solid solution of some Fe_2WO_6. Iron(II) and iron(III) would then be present on equivalent sites, allowing conduction to occur along the chains of the wolframite structure by electron hopping.

The solid solution $Fe_{1-x}Mn_xWO_4$ is single phase where $0 \leq x \leq 1$ and crystallizes with the wolframite structure. The variation of cell parameters with composition is shown in Table II, and the variation of cell volume with composition is consistent with Végard's law. The increase in cell volume with increasing manganese content is consistent with the slightly larger ionic radius of manganese(II) high spin, compared with that of iron(II) high spin.

The electrical properties of $Fe_{1-x}Mn_xWO_4$ were measured on single crystals grown by chemical vapor transport with $TeCl_4$. The stoichiometry of each crystal measured was checked by grinding part of the crystal and determining the lattice parameters of the resulting powder. Comparison of the lattice parameters of the crystals with that of the polycrystalline powders showed good agreement. All crystals in this system having measurable resistivity showed p-type semiconducting behavior; however, the value of resistivity at room temperature increases from 100Ω cm for pure $FeWO_4$ to only 400Ω cm for the composition $Fe_{.8}Mn_{.2}WO_4$, and 5000Ω cm for $Fe_{.5}Mn_{.5}WO_4$. Manganese(II) does not effectively block the conduction pathways in the structure, and this result suggests that electron delocalization may occur in the wolframite structure to give rise to interchain electron transfer.

The resistivity of these iron-containing phases crystallizing with the wolframite, tri-α-PbO_2, and inverse trirutile structures is affected by both cation distribution and geometry of octahedral linkage. It is found in Fe_2WO_6 that when the octahedral linkages are changed from skew-edge linked to straight-edge linked, the conduction pathways are blocked effectively by chromium(III). Similar results were reported by Khazai *et al.* (*15*) for the system $Fe_{1-x}Cr_xNbO_4$, where substitution of chromium(III) resulted in a structural change from wolframite to rutile with a large increase in resistivity. In manganese-substituted $FeWO_4$, the wolframite structure with its skew-edge linked chains is maintained. It is found that the conduction pathways in this system are not blocked effectively by manganese(II), possibly because of interchain electron delocalization. Thus, it appears that not only the cation distribution but also the structure type is important in determining the electrical properties of these phases.

Conclusions

Fe_2WO_6 is an n-type semiconductor crystallizing with the tri-α-PbO_2 structure, an ordered variant of the more basic α-PbO_2

structure. The extrinsic semiconducting behavior is consistent with the presence of both iron(II) and iron(III) in the puckered chains of the structure. The presence of the two valence states of iron is due to a solid solution of a small amount of $FeWO_4$ in Fe_2WO_6. Substitution of chromium(III) into Fe_2WO_6 changes the structure type to inverse trirutile, and it is found that chromium(III) effectively blocks any electron hopping between iron(II) and iron(III) in this structure.

$FeWO_4$, on the other hand, is a *p*-type semiconductor crystallizing with the wolframite structure. The extrinsic semiconducting behavior of $FeWO_4$ is consistent with the presence of both iron(II) and iron(III) in the puckered chains produced by solid solution with a small amount of Fe_2WO_6. Substitution of manganese(II) into $FeWO_4$ maintains the wolframite structure; however, the room temperature resistivity does not vary as markedly as anticipated for electron hopping between iron(II) and iron(III) along the puckered chains. This suggests that contributions to the electrical conductivity may occur by interchain electron transfer via $[WO_6]$ octahedra in the $FeWO_4$ structure.

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