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# Preparation and Characterization of Conducting Iron Tungstates

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Several iron(III) tungstates have been prepared, and their crystallographic, magnetic, electric, and photoelectronic properties have been characterized. The compounds crystallize with the tri-α-$PbO_2$ structure, and the actual ordering of the $MO_6$ octahedra ($M$ = Fe or W) appears to determine these properties. Under illumination, $Fe_2WO_6$ photoanodes show a photoresponse intermediate between those of conducting α-$Fe_2O_3$ and $WO_3$, although the flat-band potential is still too positive.

## Introduction

Since the discovery by Fujishima and Honda (*1*) that an *n*-type $TiO_2$ electrode could be used for the photoinduced electrolysis of water, there has been a large effort spent in the search for more efficient photoanodes. Several studies (*2–10*) have reported the use of iron(III) oxide and tungsten(VI) oxide as potential candidates as photoanodes. These compounds have been found to be stable in aqueous solutions and possess optical band gaps of about 2.2 eV ($Fe_2O_3$) and 2.7 eV ($WO_3$). Although these band gaps allow for greater utilization of the solar spectrum than $TiO_2$ (e.g., ~3.1 eV), their flat-band potentials of 0.7 V ($Fe_2O_3$) and 0.5 V ($WO_3$) (referred to a reversible hydrogen electrode at pH 13.3) (*6*) require a large applied bias before photoinduced electrolysis occurs. In the search for other oxides having relatively small band gaps and also small flat-band potentials, some iron-containing ternary systems have been investigated (*11*). It was found, by comparison with the alkaline-earth niobates, that $FeNbO_4$, which crystallizes with the wolframite structure, showed the highest photoresponse, which was due to $[FeO_6]$ active centers. Since $[WO_6]$ octahedra must be responsible for the quantum efficiency observed in $WO_3$ photoanodes, compounds containing both $[FeO_6]$ and $[WO_6]$ octahedra may be expected to show improved photoresponse.

In this study, $Fe_2WO_6$ and several other iron tungstates fulfilling these structural criteria have been prepared, and some of their photoelectronic as well as their crystallographic, magnetic, and electric properties have been characterized.

## Experimental

*Synthesis.* All of the iron(III) tungstates were prepared from the solid-state reactions between $Fe_2O_3$ (formed by decomposition in air of iron(II) oxalate) and $WO_3$ (prepared by heating 99.99% pure tungsten foil under flowing oxygen for 80 hr at 1000°C). A finely ground mixture of appropriate amounts of the starting materials was

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placed in a covered platinum crucible and heated in air at 950°C for 92–126 hr. $FeWO_4$ was prepared at 925°C in sealed evacuated silica tubes by reacting $WO_3$ and FeO, which was obtained by reacting $Fe_2O_3$ and iron metal. Each sample was x-rayed, reground, and then reheated. After the last heating, the product was removed rapidly from the furnace, allowed to cool to room temperature, and reexamined by x-ray analysis. This was done in order to confirm the formation of a single phase, as well as to determine cell parameters. A Philips–Norelco diffractometer with $CuK\alpha_1$ radiation ($\lambda$ = 1.5405 Å) was used at a scan rate of 0.25° $2\theta$/min and a chart speed of 30 in./hr. Cell parameters were obtained from refinement of the data with the aid of a computer.

Disks were formed by hot-pressing aliquots of approximately 800 mg for 2 hr at 980°C at an applied pressure of 5000 psi. For this purpose, 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. Under these conditions, disks with a surface of about 1.3 cm$^2$ and a thickness of 0.09 cm were obtained. They were x-rayed with $FeK\alpha$ radiation (1.9360 Å), using the Debye–Scherrer method, and their films were compared to those of the corresponding polycrystalline starting compounds to confirm that the phases did not undergo any changes during the sintering process.

*Magnetic measurements.* Magnetic susceptibilities were measured using a Faraday balance (*12, 13*) at a field strength of 10.4 kOe. The data then were corrected for core diamagnetism (*14*).

*Electrical measurements.* The resistivities of the samples were measured using the van der Pauw technique (*15*). Contacts were made by the ultrasonic soldering of indium directly 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 measurements of the Seebeck effect.

*Photoelectrolytic measurements.* Photoanodes were prepared by evaporating thin films of gold on the backs of the sintered disks to provide good electrical contact. The gold face of each disk was attached to the electrode by means of indium solder, and all but the front surfaces were coated with an electrically insulating resin (Miccrostop, Michigan Chrome Chemical Corp.). The photoelectrolysis measurements were carried out with a 150-W xenon lamp, a monochromator (Oriel Model 7240), a glass cell with a quartz window, and a current amplifier as described previously (*16*). A platinized platinum electrode of large surface area served as the cathode. All voltage measurements were made with reference to a saturated calomel electrode (SCE). The electrolyte, 0.2 *M* sodium acetate (pH 7.8), was purged of dissolved oxygen by continuous bubbling of 85% argon/15% hydrogen gas.

## Results and Discussion

*Structure and crystallography.* Several reports exist concerning the structure of $Fe_2WO_6$ (*17–21*). Basically, this compound has been reported to crystallize with the columbite structure when prepared below 800°C (*20*), and with the tri-$\alpha$-$PbO_2$ structure when prepared at higher temperatures (*19, 21*). Both of these structures may be regarded as superlattice variants of the fundamental $\alpha$-$PbO_2$ structure. They consist of hexagonal close-packed planes of $O^{2-}$ anions in which only half of the octahedral sites are occupied by the metal atoms, Fe or W. The fundamental difference between both structures is in the nature of the 2:1 cation ordering. As shown in Fig. 1, for $Fe_2WO_6$ with the tri-$\alpha$-$PbO_2$ structure, each of the resulting octahedra shares a pair of

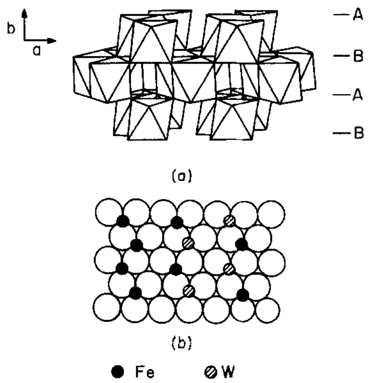

FIG. 1. Tri-α-$PbO_2$ structure of $Fe_2WO_6$: (a) packing of $MO_6$ octahedra; (b) closest-packed layer of oxygen around Fe and W atoms.

skew edges in such a way that zig-zag chains are formed parallel to the *c* direction. Senegas and Galy (*21*) have indicated that ideally one-third of these zig-zag chains contain only iron atoms, and two-thirds of the chains show a 1 : 1 ordering of iron and tungsten atoms. In the columbite structure, the ordering is such that each zig-zag chain contains only one type of metal (either iron or tungsten), and so there are twice as many zig-zag chains with iron atoms as with tungsten atoms. When compared to the α-$PbO_2$ structure, the 2 : 1 cation order causes a tripling of the *b* parameter in the tri-α-$PbO_2$ structure, and of the *a* parameter in the columbite.

In this study, it was not possible to obtain the columbite variant of $Fe_2WO_6$ as a pure single phase, since the tri-α-$PbO_2$ variant also appears to form at low temperatures. Once the tri-α-$PbO_2$ structure forms, long anneals even at temperatures below 800°C are unsuccessful in changing the structural ordering. When these samples were heated up to about 800°C in a differential scanning calorimeter, there was no indication of any phase transition. Consequently, $Fe_2WO_6$ samples were prepared at 950°C, since at this temperature the tri-α-$PbO_2$ structure is well crystallized.

It also was determined by x-ray diffraction that $Fe_2WO_6$ cannot be prepared without the appearance of a small amount 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. These small peaks could be observed in products prepared at temperatures lower than 950°C. Analogous results were also observed when the preparations were attempted in a sealed silica tube. Similar observations have been reported for other iron-containing ternary systems where the compounds crystallize with the wolframite and columbite structures (*11*). In these studies, the iron(III)-containing phase forms a solid solution with a phase containing iron(II), and both structures can be derived from the α-$PbO_2$ framework, and are closely related to the tri-α-$PbO_2$ structure. Hence, the presence of trace quantities of α-$Fe_2O_3$ in the attempted preparation of pure $Fe_2WO_6$ is consistent with the solid solution of small amounts of $FeWO_4$. Further evidence for the existence of a solid solution between $Fe_2WO_6$ and $FeWO_4$ was obtained by preparing a product having the nominal composition $Fe_{1.97}W_{1.03}O_6$. The resulting material maintained the tri-α-$PbO_2$ structure.

In addition, the disappearance of the small peaks of α-$Fe_2O_3$ could be achieved when iron(III)-deficient compounds were prepared, corresponding to members of the system $Fe_{2-2x}W_{1+x}O_6$. On increasing the value of $x$, the α-$Fe_2O_3$ peaks decreased in intensity, and for the composition $Fe_{1.92}W_{1.04}O_6$, a phase free of detectable α-$Fe_2O_3$ was obtained. All compounds belonging to this system also crystallized in the tri-α-$PbO_2$ structure.

$Fe_2WO_6$ prepared in this study was orthorhombic (space group *Pbcn*) and the following cell constants were determined: $a = 4.577$ Å, $b = 16.75$ Å, $c = 4.965$ Å. These results are in good agreement with those previously reported (*21*).

*Magnetic properties.* The magnetic

structure of $Fe_2WO_6$ from 4.2 to 300 K has been studied by Pinto and Melamud (*22*). They reported an antiferromagnetic ordering at 4.2 K and a Neél temperature of approximately 240 K. Thus, it is not surprising that the dependence of inverse magnetic susceptibility with temperature for $Fe_2WO_6$, as shown in Fig. 2, is not completely linear at high temperature. However, above 600 K the susceptibility does approach linear behavior, and can be interpreted to yield a Curie–Weiss constant of about −450 K and an effective molar Curie constant of 7.7 (emu mole$^{-1}$ K). This value corresponds to a spin-only moment of about 5.6 $\mu_B$, which is in close agreement with the spin-only value of 5.9 $\mu_B$ for $Fe^{3+}$ ($S = 5/2$). The higher slope observed below 600 K indicates the presence of both ferro- and antiferromagnetic interactions in $Fe_2WO_6$, which would be consistent with the reported magnetic structure (*22*).

*Electrical properties.* A recent report (*23*) has indicated that $Fe_2WO_6$ is a *p*-type semiconductor. However, this study indicates that $Fe_2WO_6$, $Fe_{1.96}W_{1.02}O_6$, and $Fe_{1.92}W_{1.04}O_6$, as well as $Fe_{1.97}W_{1.03}O_6$, are all *n*-type semiconductors. Pure samples of $Fe_2WO_6$, $Fe_{1.96}W_{1.02}O_6$, and $Fe_{1.92}W_{1.04}O_6$ would be expected to have high electrical resistivities. However, the measured resistivities at room temperature ranged between 41 and 59 ohm-cm. This observed conductivity is consistent with the presence of Fe(III) and some Fe(II) on equivalent sites. The conductivity of an iron tungstate containing relatively large amounts of Fe(II), i.e., the composition $Fe_{1.97}W_{1.03}O_6$, gave a measured resistivity value in the same range as those of the other tungstates. This result seems to indicate the existence of some degree of disorder between the iron and tungsten atoms within the chains of the tri-$\alpha$-$PbO_2$ structure when the 2 : 1 ratio of these atoms is changed.

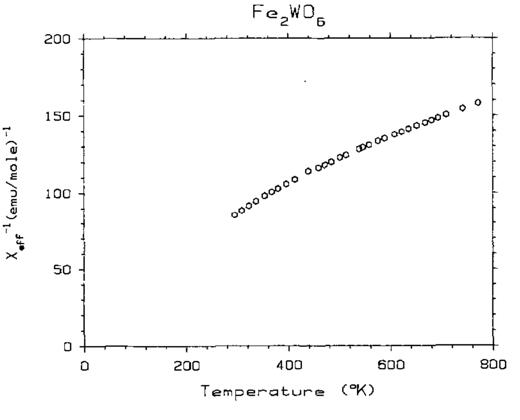

FIG. 2. Thermal variation of the inverse molar magnetic susceptibility of iron tungstate. The high-temperature slope corresponds to a $\mu_{eff}$ of 5.6 $\mu_B$.

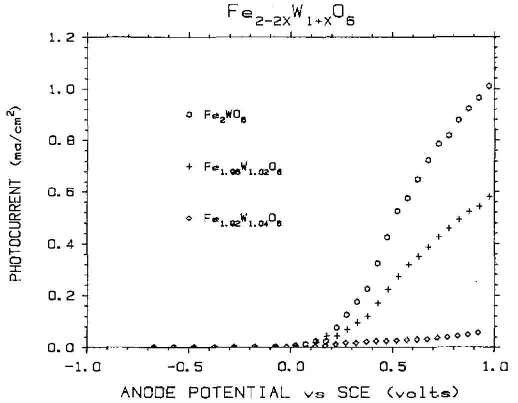

FIG. 3. Variation of photocurrent with anode potential for members of the system $Fe_{2-2x}W_{1+x}O_6$ in 0.2 *M* sodium acetate (pH 7.8) under "white" xenon arc irradiation of 1.0 W/cm$^2$.

*Photoelectronic properties.* The photoresponse observed for several iron tungstates is represented in Fig. 3, where the photocurrents obtained in the "white" light are plotted against the anode potential. For $Fe_2WO_6$ and $Fe_{1.92}W_{1.04}O_6$, transient photocurrents were observed between 0.05 and 0.5 V, and only the instantaneous responses were recorded in the plot. As can be seen, the largest photocurrents are reached for $Fe_2WO_6$ and decrease on increasing the tungsten and vacancy concentration. The resistivities of these compounds were shown to be similar, and the

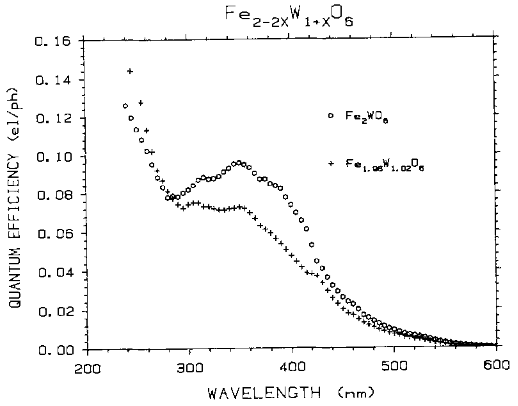

FIG. 4. Spectral variation of the quantum efficiency (in electrons/photon) obtained for members of the system $Fe_{2-2x}W_{1+x}O_6$ in 0.2 *M* sodium acetate (pH 7.8) at an anode potential of 0.8 V with respect to SCE.

observed difference of photoresponse between $Fe_2WO_6$ and the tungsten-rich compounds might be due to the introduction either of vacancies, which can act as recombination centers, or of tungsten ions into the predominantly iron chains. Thus, the existence of either vacancies or disorder between iron and tungsten atoms within the zig-zag chains would result in a decrease in the photoresponse. Thus, for the composition $Fe_{1.97}W_{1.03}O_6$, the observed photocurrents were low. The general shape of the curves observed for $Fe_2WO_6$ and $Fe_{1.96}W_{1.02}O_6$ is similar to that reported for other iron compounds (*11*). The onset of photocurrents is not sufficiently abrupt for a reliable determination of the flat-band potentials. The photoresponse cannot be obtained below an anode potential ranging from 0.1 to 0.4 V versus SCE at pH 7.8. These values appear to be similar to the potentials reported for conducting $Fe_2O_3$ and $WO_3$ samples (*3, 8*).

The quantum efficiency (in electrons/photon) of $Fe_2WO_6$ and $Fe_{1.96}W_{1.02}O_6$, as measured at an anode potential of 0.8 V versus SCE, is plotted in Fig. 4 against the wavelength of the incident light. For both compounds, the shape of the curves is similar, but the $Fe_2WO_6$ sample has a higher response at longer wavelengths. The photoresponse observed for these iron tungstates is nearly ten times greater than those reported for conducting $\alpha$-$Fe_2O_3$, but not as large as the maximum response obtained for conducting $WO_3$ electrodes (*7, 10*).

## Conclusions

$Fe_2WO_6$ and other related iron(III)-deficient tungstates corresponding to members of the ternary system $Fe_{2-2x}W_{1+x}O_6$ have been prepared, and crystallize with the tri-$\alpha$-$PbO_2$ structure. The building blocks on this framework are $MO_6$ octahedra ($M$ = Fe or W), and the ordering of these units appears to affect significantly the magnetic, electric, and photoelectronic properties of these compounds. Any deviation from the ideal ordering of these $MO_6$ octahedra may introduce [$WO_6$] octahedra into the zig-zag chains expected to contain only $FeO_6$ units. This disorder must affect any electron transfer process occurring within these chains, and hence the magnitude of the electrical resistivities and, together with any vacancies present, the quantum efficiencies.

The best photoresponse to "white" irradiation is obtained when the anode is made of $Fe_2WO_6$; its magnitude is larger than the values obtained from electrodes made of conducting $\alpha$-$Fe_2O_3$, but lower than the maximum reported for $WO_3$. Although the efficiency of $Fe_2WO_6$ photoanodes is enhanced at long wavelengths, the flat-band potential remains too positive for any practical application.

Measurement of the magnetic susceptibilities at high temperatures above 600 K yields an effective molar Curie constant whose value corresponds closely to that expected for spin-only $Fe^{3+}$ ions. In addition, the large, negative Curie–Weiss constant indicates the existence of strong antiferromagnetic interactions in $Fe_2WO_6$.

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