

Structural and Electronic Relationships between Conducting Iron Niobates and Iron Tungstates*

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Members of the system Fe-Nb-O and Fe-W-O were compared, and their electronic properties were correlated with the structural parameters. The compounds crystallize as ordered variants of the basic α -PbO₂ structure, and the nature of the ordering of the [FeO₆] and [NbO₆] or [WO₆] octahedra determines the conductivity which may be observed for these phases.

Introduction

The use of α -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 (6) that pure α -Fe₂O₃ has a high resistivity ($>10^6$ Ω cm) and shows no detectable photocurrent. Although the phase boundary between α -Fe₂O₃ and Fe₃O₄ is sharp (7), α -Fe₂O₃ can be made conducting by the introduction of small amounts of Fe₃O₄ on exposure to a reducing atmosphere. The spinel, Fe₃O₄, contains both Fe²⁺ and Fe³⁺ on octahedral sites and conduction occurs via electron transfer from Fe²⁺ to Fe³⁺. Iron(III) oxide itself crystallizes with the corundum structure which contains only trivalent iron and, in addition, cannot tolerate deviations from a metal-to-oxygen ratio of 2:3. Another difficulty which presents itself

in the use of iron(III) oxide as a photoanode is the large positive flat band potential reported by Kung *et al.* (5). Despite a reasonably favorable band gap for α -Fe₂O₃, the value of 0.7 V for V_{fb} (measured against H₂ at pH = 13.3) means that the actual efficiency of the electrode is low. The practical significance of V_{fb} is that this is numerically equal to the minimum applied voltage required to decompose water. It has also been shown by Kung *et al.* (5) that the use of oxide photoanodes having small band gaps, so as to utilize a large portion of the solar spectrum, requires too large an applied voltage. In order to develop a potentially useful electrode-containing iron, it is therefore necessary to obtain stable compounds having both Fe²⁺ and Fe³⁺ on equivalent sites, as well as to alter the composition sufficiently so as to maintain a relatively small band gap and a reduced applied voltage.

A number of potentially interesting iron compounds which crystallize with the rutile, wolframite, columbite, or tri- α -PbO₂ structures can be synthesized. These struc-

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ture types can accommodate varying amounts of both Fe(II) and Fe(III). In the following sections, each structure will be discussed, and the photoelectronic properties of a number of iron-containing compounds will be related to certain structural features.

The Properties of Iron(III) Niobate and Iron(II) Tungstate

The compound iron(III) niobate, FeNbO_4 , crystallizes below 1085°C with the monoclinic wolframite structure (space group $P2_1/C-C_{2h}^4$). Roth and Waring (8) and Laves *et al.* (9) have shown that between 1085 and 1380°C , a transition to orthorhombic $\alpha\text{-PbO}_2$ (space group $Pbcn-D_{2h}^{14}$) can occur which will further transform to the tetragonal rutile structure (space group $PA_2/mnm-D_{2h}^{14}$) above 1380°C and approximately 100° below the melting point.

The structural relationship of these phases can be discussed in terms of the variation in the linking of $[\text{MO}_6]$ octahedra and the nature of the cation distribution within the octahedra. In the most symmetrical form of rutile, the FeNbO_4 structure consists of a hexagonal close-packed arrangement of the anions in which the metal atoms, Fe or Nb, are in octahedral coordination.

In the rutile structure, shown in Fig. 1, it can be seen that each octahedron shares a pair of opposite edges as well as further linking by sharing of vertices, in such a way that straight chains are formed along the c direction. It is a structure of 6:3 coordination where every metal atom is surrounded by six oxygen atoms approximately at the corners of a regular octahedron, and every oxygen atom by three titanium atoms approximately at the corners of an equilateral triangle. As shown in Fig. 1b, there is a random distribution of Fe and Nb atoms in one-half of the available octahedral sites.

When FeNbO_4 crystallizes with the α -

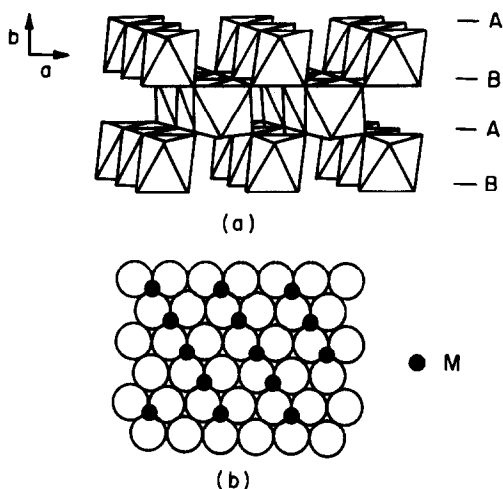


Fig. 1. Structure of rutile: (a) packing of MO_6 octahedra; (b) closest-packed layer of oxygen around M atoms.

PbO_2 structure, the edge-sharing is different from that found in rutile. Whereas in rutile the edge-sharing occurs at opposite edges in each octahedron, in $\alpha\text{-PbO}_2$ the shared edges of an octahedron are closer together. This leads to zig-zag chains (see Fig. 2) of octahedra along the c direction rather than the straight octahedral strings found in rutile. As with the rutile structure, only one-half of the octahedral sites are occupied, and random distribution of the Fe and Nb atoms in the zig-zag chains prevails.

The wolframite polymorph (Fig. 3) can be compared to the $\alpha\text{-PbO}_2$ structure as an ordered and slightly distorted variant. The two cations Fe and Nb are arranged in an ordered fashion over the cation positions in $\alpha\text{-PbO}_2$. Zig-zag chains of FeO_6 and NbO_6 octahedra form, as in $\alpha\text{-PbO}_2$, but every occupied chain contains either Fe or Nb atoms.

As indicated previously, FeNbO_4 undergoes two phase transitions at elevated temperatures, wolframite $\xrightarrow{1085} \alpha\text{-PbO}_2 \xrightarrow{1380}$ rutile.

The transformation of wolframite to α -

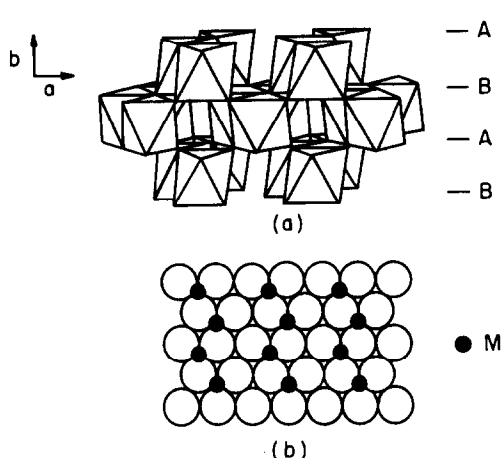


FIG. 2. Structure of α - PbO_2 : (a) packing of MO_6 octahedra; (b) closest-packed layer of oxygen around M atoms.

PbO_2 is considered to be essentially an order-disorder transition in which the separate chains of $[\text{FeO}_6]$ and $[\text{NbO}_6]$ octahedra become identical; i.e., there is a random distribution of Fe and Nb atoms within the structural array. White *et al.* (10) have observed that α - PbO_2 transformed on heating to the rutile polymorph. In this transforma-

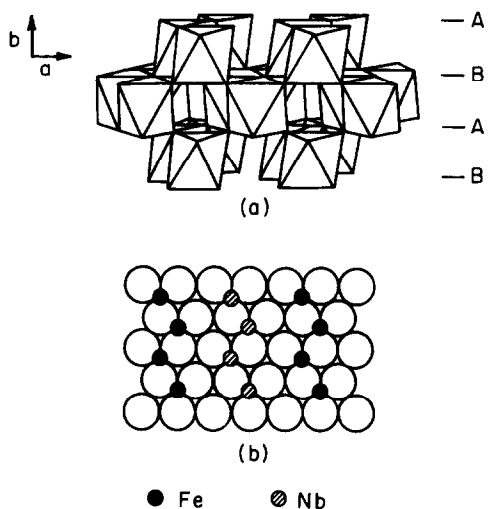


FIG. 3. Structure of wolframite: (a) packing of MO_6 octahedra; (b) closest-packed layer of oxygen around Fe and Nb atoms.

tion, the chains of $[\text{Fe,Nb}]_6\text{O}_6$ octahedra change from a zig-zag configuration found in the α - PbO_2 structure to straight chains in the rutile structure. Anderson and Galy (11) have indicated that such transformations may occur by the movement of cations in adjoining layers along the edge of an octahedron to a previously unoccupied site. This is shown in Fig. 4.

The room-temperature resistivity of a well-sintered FeNbO_4 disk was reported to be $40 \pm 1 \Omega\text{-cm}$ (12). It would be anticipated that the resistivity of intrinsic FeNbO_4 would be much higher than $40 \Omega\text{-cm}$ if all of the iron were in the trivalent state. The disks were shown to be *n*-type, and the mobility was less than $0.1 \text{ cm}^2/\text{V}$.

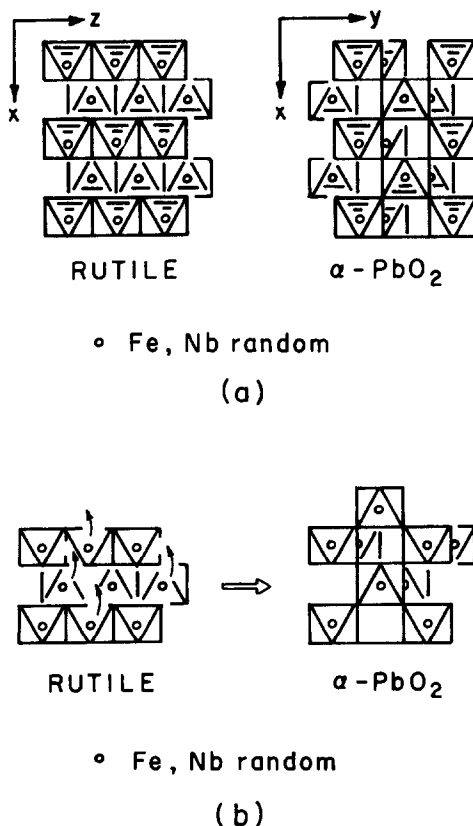


FIG. 4. (a) Relative positions of cations in rutile and α - PbO_2 . (b) Movement of cations during phase transformation.

sec, as would be expected for a hopping conductor (13).

These properties are consistent with the structural studies of Turnock (14), which indicated that FeNb_2O_6 may be incorporated in solid solution with FeNbO_4 . The formation of such a solid solution would be consistent with relatively high conductivity and the phase separation of a few percent of $\alpha\text{-Fe}_2\text{O}_3$. It was observed (12) that careful examination of X-ray patterns obtained from sintered disks of FeNbO_4 indicated the presence of the strongest peak of $\alpha\text{-Fe}_2\text{O}_3$. Measurement of the photoresponse of FeNbO_4 (12) indicated a flat-band potential between 0.1 and 0.4 V versus SCE in a pH of 8.5, and an optical band gap of 2.08(2) eV. It was also indicated (12) that there was probably an additive superposition of multiple photoactive centers, rather than the "averaging" process suggested by conventional band theory.

The compound FeWO_4 also crystallizes with the wolframite structure. For this composition, the $[\text{FeO}_6]$ octahedra should contain only divalent iron. Single crystals of FeWO_4 can be grown by chemical vapor transport, using TeCl_4 as a transport agent (15). It was observed that the resistivity of the crystals grown were related to the degree of oxidation, i.e., the trivalent iron content of the charge. This is consistent with other studies (16, 17) which indicated that the wolframite structure can accommodate both divalent and trivalent iron simultaneously.

The Properties of Diiron(III) Tungstate

The wolframite structure represents only one ordered variant of the more fundamental $\alpha\text{-PbO}_2$ structure. Fe_2WO_6 has been reported to crystallize with the columbite structure when prepared below 800°C (18), and with the tri- $\alpha\text{-PbO}_2$ structure when prepared at higher temperatures (18). Both of

these structures may be regarded as superlattice variants of the $\alpha\text{-PbO}_2$ type. In the columbite structure (Fig. 5), a 2:1 cation ordering occurs, rather than the 1:1 ordering observed in the wolframite structure. This 2:1 cation order causes a tripling of the a parameter, but the orthorhombic space group ($Pbcn$) of $\alpha\text{-PbO}_2$ is preserved. Leiva *et al.* (19) have shown that the columbite variant of Fe_2WO_6 is difficult to obtain as a single phase since the tri- $\alpha\text{-PbO}_2$ variant also appears to form at low temperatures. The fundamental difference between the columbite and the tri- $\alpha\text{-PbO}_2$ structures is in the nature of the 2:1 cation ordering which occurs in these structures. Senegas and Galy (20) have indicated that for the tri- $\alpha\text{-PbO}_2$, one-third of the zig-zag chains along the c direction contain only iron atoms, and two-thirds of the chains show a 1:1 ordering of iron and tungsten atoms (Fig. 6). As a result of the differences in the ordering of the $[\text{FeO}_6]$ and $[\text{WO}_6]$ octahedra, the cell parameters of the three structure types $\alpha\text{-PbO}_2$, tri- $\alpha\text{-PbO}_2$, and columbite have the following relationships:

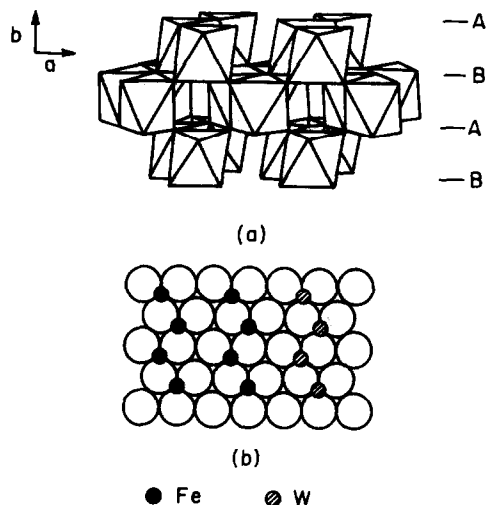


FIG. 5. Structure of columbite: (a) packing of MO_6 octahedra; (b) closest-packed layer of oxygen around Fe and W atoms.

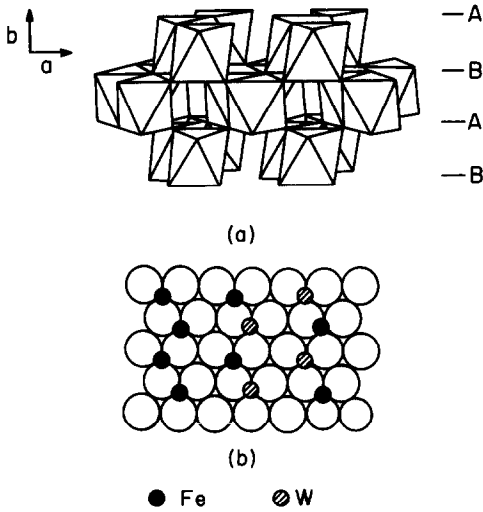


FIG. 6. Structure of tri- α - PbO_2 : (a) packing of MO_6 octahedra; (b) closest-packed layer of oxygen around Fe and W atoms.

$$a \alpha\text{-PbO}_2 \approx a \text{ tri-}\alpha\text{-PbO}_2 \approx a/3 \text{ columbite,}$$

$$3b \alpha\text{-PbO}_2 \approx b \text{ tri-}\alpha\text{-PbO}_2 \approx 3b \text{ columbite,}$$

$$c \alpha\text{-PbO}_2 \approx c \text{ tri-}\alpha\text{-PbO}_2 \approx c \text{ columbite.}$$

A comparison of the ordering sequences and consequent changes in the cell parameters is shown in Fig. 7. It can be readily seen that the idealized occupancy of the octahedra along the zig-zag chains in the tri- α - PbO_2 structure is such as to give one chain containing only iron atoms for every two chains containing an ordered arrangement of iron and tungsten atoms. The iron in pure Fe_2WO_6 is all trivalent, and hence disks prepared from this composition should give a high resistivity. However, Leiva *et al.* have shown (19) that Fe_2WO_6 cannot be prepared without the appearance of a small amount of $\alpha\text{-Fe}_2\text{O}_3$ in the product. Such samples also show a higher conductivity than would be expected for pure Fe_2WO_6 . In addition, Leiva showed that a solid solution of Fe_2WO_6 and FeWO_4 can be prepared and still maintain the tri- α - PbO_2 structure. The electrical properties of these phases indicate that there may be some degree of disorder between the Fe and W atoms

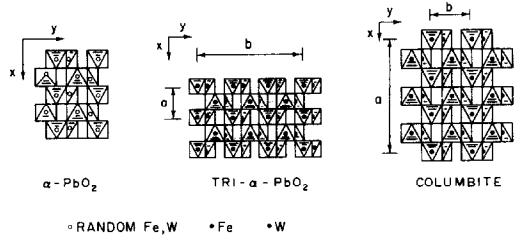


FIG. 7. Relative positions of cations in $\alpha\text{-PbO}_2$, tri- $\alpha\text{-PbO}_2$, and columbite.

within the chains (19). However, if all of the chains contained a considerable number of W atoms, no conductivity would be observed.

Both iron(III) niobate (12) and diiron(III) tungstate (19) show photoresponses, although their flat-band potentials are positive, and hence these materials show low efficiencies as photoanodes. Pure iron(II) tungstate does not appear to yield a photoresponse (15), which would seem to indicate that trivalent iron must be present for a response to be observed.

Summary

The wolframite, tri- α - PbO_2 , and columbite structures represent ordered variants of the basic $\alpha\text{-PbO}_2$ type. When FeNbO_4 crystallizes with the wolframite structure, the Fe and Nb cations are arranged in an ordered manner which results in the lowering of the symmetry from orthorhombic to monoclinic. As in $\alpha\text{-PbO}_2$, zig-zag chains of $[\text{FeO}_6]$ and $[\text{NbO}_6]$ octahedra, are formed, but each chain contains only either Fe or Nb. The same structural features were observed for the composition FeWO_4 . These compounds can accommodate both divalent and trivalent iron in the zig-zag chains of $[\text{FeO}_6]$ octahedra, which results in high conductivity because of electron transfer within these chains. Two other variants of the $\alpha\text{-PbO}_2$ type are the tri- $\alpha\text{-PbO}_2$ and the columbite structures. For these variants, there is a 2:1 cation ordering rather than

the 1:1 order observed in the wolframite structure. FeNb_2O_6 has the columbite structure, and Fe_2WO_6 can be prepared as a single phase with the tri- α - PbO_2 structure. The existence of mixed iron valencies in the Fe-Nb-O phases was shown to be due to the solid solution of FeNbO_4 and FeNb_2O_6 . There is also evidence for the solid solution between FeWO_4 and Fe_2WO_6 . Undoubtedly, the existence of both Fe^{2+} and Fe^{3+} in these structures is the basis for the observed conductivity.

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