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TECHNICAL REPORT NO. 20

Preparation and Photoelectronic Properties of $FeWO_4$

by

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ABSTRACT Single crystals and polycrystalline samples of $FeWO_4$ were prepared and characterized. From high temperature paramagnetic data, the presence of high spin state $Fe^{II}(3d^6)$ was confirmed. Qualitative Seebeck measurements indicated p-type conductivity. The measured room temperature resistivity of single crystals was $\sim 100\,\Omega$-cm with an activation energy of .16(2) eV. No appreciable photocurrents were found in 0.2M NaAc at pH = 8.3.

Introduction

Iron oxide, α-Fe_2O_3, has a relatively narrow band gap of 2.2 eV which makes it a potential candidate for use as an n-type photoanode. Unfortunately, pure α-Fe_2O_3 is not a photoconductor because of its high resistivity, which results from the presence of iron in only a single valence state. Whereas it has been reported that the electrical conductivity of pure α-Fe_2O_3 can be increased by heating it at high temperatures, the actual phase formed is a surface layer of Fe_3O_4 rather than a non-stoichiometric oxide (1).

Sanchez has shown (2) that α-Fe_2O_3 can be made conducting by the formation of members of the series $Fe_{2-x}Ge_xO_3$ $(0.05 > x > 0)$. He concluded that the polycrystalline iron oxide doped with Si or Ge could be used as a photoanode in a photoelectrochemical cell, but that the photocurrents obtained are too small for practical applications.

In the search for other oxides having relatively small band gaps and also small flat-band potentials, several iron-containing ternary systems have been investigated (3,4). $FeNbO_4$, which crystallizes with the α-PbO_2 structure above 1085°C, showed an appreciable photoresponse, but its flat-band potential of between 0.1 and 0.4V versus SCE at a pH of 8.5 is still too positive. Another ternary iron compound, crystallizing with the wolframite structure, is $FeWO_4$. In this material, iron is divalent ($3d^6$), and hence it may be possible to prepare a p-type electrode by introducing acceptor levels above the valence band. Conduction in $FeWO_4$ is possible since a certain miscibility between $Fe^{II}WO_4$ and $Fe^{III}{}_2WO_6$ is possible (5).

Experimental Procedure

Synthesis

Polycrystalline $FeWO_4$ was prepared by the direct combination of FeO and WO_3. The reaction was carried out in a sealed evacuated silica tube at 900°C for 3 days with two intermediate grindings. The FeO was obtained by reacting iron powder (Leico) with Fe_2O_3 (Mapico Red) in sealed evacuated silica tubes for 3 days at 900°C and quenching the tube rapidly in cold water in order to prevent disproportionation of the FeO into Fe and Fe_3O_4.

Single crystals of $FeWO_4$ were grown by chemical vapor transport using tellurium(IV) chloride as the 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. The thick, irregularly shaped black plates which formed were up to 7 mm on a side. All products were removed from the transport tube, washed immediately with dilute hydrochloric acid, and then rinsed with water and dried with acetone.

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

The density of polycrystalline $FeWO_4$ was determined using the hydrostatic technique (5). Perfluoro (1-methyldecalin) was used as the liquid, and its density was calibrated before each measurement with a silicon crystal ($d = 2.328\ g/cm^3$ at 22°C).

Stability of $FeWO_4$ towards oxidation was determined by means of thermogravimetric analysis using a Cahn electrobalance (Model RG). The analysis was carried out with an oxygen flow rate of 20 cc/min, over a temperature range of room temperature to 900°C. The rate of heating was maintained at 25°C/hr.

Magnetic measurements were performed using the Faraday balance previously described by Morris and Wold (6). The magnetic susceptibilities of ground single crystal powders were measured from 300 to 800K at a field strength of 10.4 kOe. No corrections were made for core diamagnetism.

The resistivities of the samples were measured using the van der Pauw technique (7). 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 measurements of the Seebeck effect.

Results and Discussion

The commonly accepted space group for the wolframite structure is P2/c, and the parameters obtained from x-ray diffraction patterns of $FeWO_4$ given in Table I are found to be in reasonable agreement with earlier reported values. There was reasonably good agreement (within 3%) between the measured density of polycrystalline $FeWO_4$ (7.75 g/cm^3 at 22°C) and the value calculated from the cell parameters ($d = 7.52\ g/cm^3$).

The stability of $FeWO_4$ towards oxidation was determined by means of thermogravimetric analysis. The products obtained after heating a powdered sample under an oxygen atmosphere to a temperature of 860°C were Fe_2WO_6 and WO_3, as identified by x-ray analysis. These results confirm the studies of the oxidation of $FeWO_4$, as reported by Berman and Campbell (8).

The high-temperature paramagnetic data for $FeWO_4$ are shown in Fig. 1, and indicate ideal Curie behavior. The molar Curie constant obtained from Fig. 2 was $C_M = 3.33$, with $\mu_{eff} = 5.16\mu_B$. This compares with a calculated value of $\mu_{eff} = 4.9\mu_B$ assuming a spin-only moment for high spin state $Fe^{II}(3d^6)$. These results are in agreement with those reported by Ülkü (9) from neutron diffraction measurements. His results indicated an effective moment of $5.29\mu_B$ per iron atom.

Electrical conductivity was measured on single crystals of $FeWO_4$ from liquid nitrogen to room temperature, and the results are shown in Fig. 2.

FIG. 1
Temperature dependence of the molar magnetic susceptibility of $FeWO_4$, giving $\mu_{eff} = 5.16\mu_B$.

FIG. 2
Temperature dependence of the electrical conductivity of $FeWO_4$, giving an activation energy of 0.16(2) eV.

The activation energy (Ea) was determined to be .16(2) eV and is in good agreement with previously reported results (10). From qualitative Seebeck measurements, the crystals were shown to be p-type so that photoelectrodes of this material should act as photocathodes. However, it was found that no appreciable photocurrents were produced in 0.2M NaAc at pH = 8.3. This raises the question as to whether compounds containing only Fe^{2+} are capable of acting as p-type photocathodes for the photodecomposition of water.

TABLE I

CRYSTALLOGRAPHIC PARAMETERS FOR $FeWO_4$

Sample	a (Å)	b (Å)	c (Å)	β	V (Å^3)
Synth. polycryst.	4.734(1)	5.709(1)	4.963(1)	90	134.1
Synth. ground crystals	4.730(1)	5.708(1)	4.963(1)	90	134.0
Synth. polycryst. (11)	4.733(2)	5.709(2)	4.964(3)	90	134.1
Synth. polycryst. (12)	4.724	5.705	4.961	90	133.7
Synth. polycryst. (10)	4.71	5.70	4.97	90	133.4
Nat. ground crystal (9)	4.730(3)	5.703(2)	4.952(2)	90	133.6
Nat. single crystal (13)	4.750	5.720	4.97	90°10'	135

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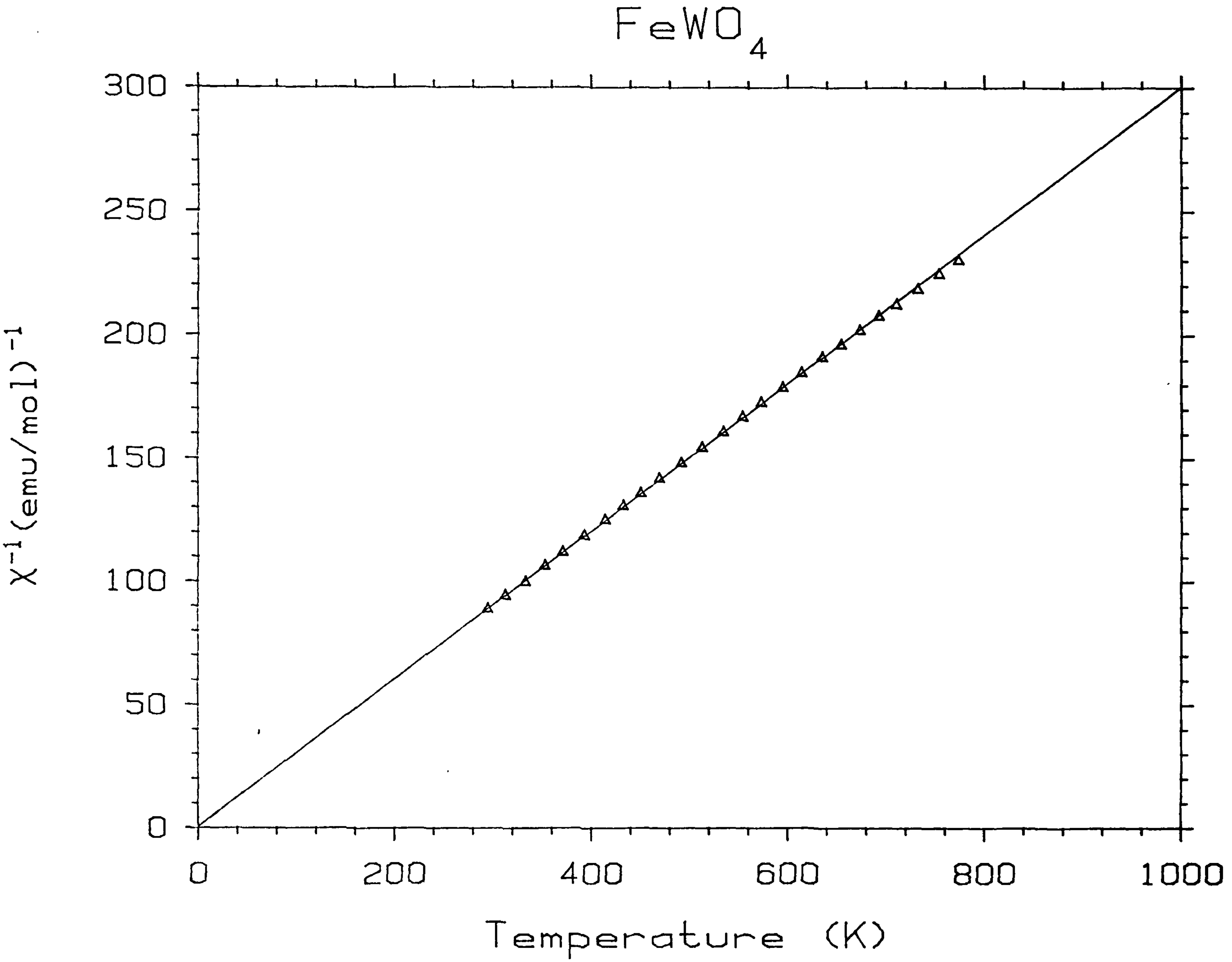
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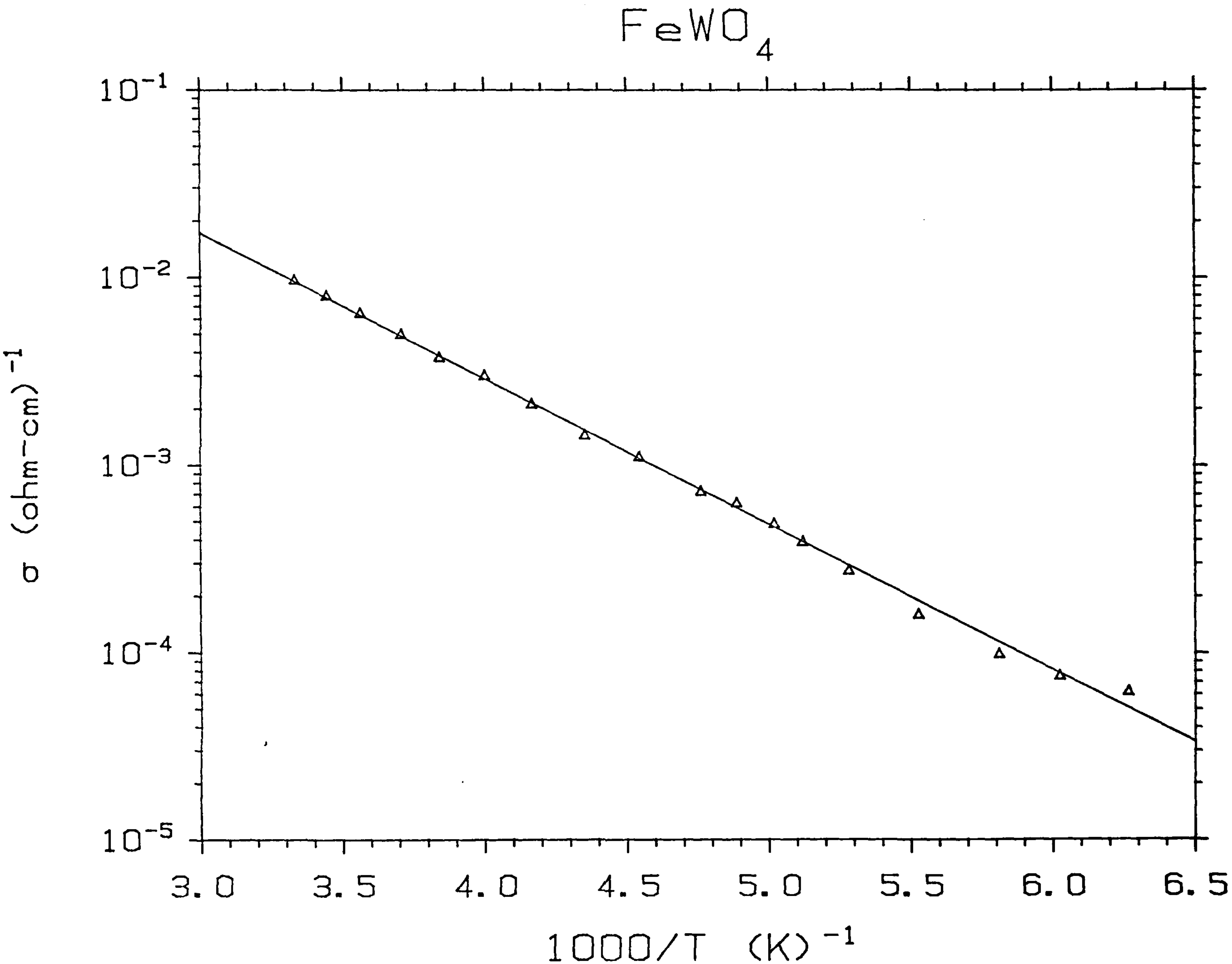
250
200
150
100
50
0
0
200
400
600
800
1000
Temperature (K)


FeWO$_4$
σ (ohm-cm)$^{-1}$
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
1000/T (K)$^{-1}$

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