

Preparation and Properties of Tetragonal Tungsten Oxyfluoride Bronzes*

T. G. REYNOLDS AND A. WOLD

*Department of Chemistry and Division of Engineering,
Brown University, Providence, Rhode Island 02912*

Received July 13, 1972

Reaction of tungsten(VI) oxide and tungsten metal in the presence of dilute solutions of hydrofluoric acid under hydrothermal conditions has resulted in the formation of a series of tetragonal oxyfluoride bronzes having the composition $\text{WO}_{3-x}\text{F}_x$ ($0.03 \leq x \leq 0.09$). These compounds are isostructural with the tetragonal bronze $\text{Na}_{0.10}\text{WO}_3$. The material appears to exhibit metallic conductivity.

Introduction

The transition metal oxides MoO_3 , WO_3 and ReO_3 exist with the cation in its highest oxidation state. The substitution of fluoride ion ($r_{\text{F}^-} = 1.36 \text{ \AA}$) for the oxide ion ($r_{\text{O}^{2-}} = 1.40 \text{ \AA}$) should be feasible from size considerations. The resultant change in oxidation state caused by the need to preserve electrical neutrality leads to stabilization of the transition metal cation with mixed valences on the same site. It has been shown by Goodenough (1) that similar materials can exhibit metallic behavior if partially occupied delocalized π^* bands result from the overlap of cation t_{2g} and oxygen p_π orbitals.

Hydrothermal techniques have been developed (2, 3) which permit oxyfluorides of many transition metals to be synthesized. In the $\text{VO}_{2-x}\text{F}_x$ system, it has been shown by Bayard *et al.* (4) that incorporation of fluoride ion into the lattice leads to stabilization of the higher symmetry tetragonal form. This results in a linear decrease of the semiconductor-metallic transition temperature from 340 K to 65 K as the fluoride content, x , goes from 0 to 0.21. This observation has been independently verified by Chamberland (3).

Preparation of oxyfluorides in the MoO_3 system by Pierce *et al.* (5) has led to the formation of two new phases. The $\text{Mo}_4\text{O}_{11.2}\text{F}_{0.8}$ phase is orthorhombic and exhibits semiconductor behavior while the $\text{MoO}_{2.4}\text{F}_{0.6}$ compound has a

cubic, ReO_3 type structure (space group $Pm3m$) similar to that of the tungsten bronzes. Sleight (2) independently studied the oxyfluoride bronzes of molybdenum and also reported the existence of cubic tungsten oxyfluoride bronzes. The $\text{WO}_{3-x}\text{F}_x$ system for $0.17 \leq x \leq 0.66$ studied by Sleight using hydrothermal techniques was reported to be metallic and crystallized with the ReO_3 structure.

The existence of lower-symmetry alkali metal bronzes has been demonstrated by Hagg and Magneli (6). The tetragonal phase which exists in the sodium and lithium-tungsten-bronze systems for low alkali content ($x = 0.10$) is made up of corner-shared octahedra and bears a close resemblance to the perovskite bronzes. Thus, it appears to occupy an intermediate position in the development of the structure between WO_3 (distorted ReO_3) and the cubic tungsten bronzes.

The analogous tetragonal tungsten bronze oxyfluorides have not been synthesized and this paper presents an extension of hydrothermal techniques to the preparation and characterization of such materials.

Experimental

Preparation of Materials

Compositions in the system $\text{WO}_{3-x}\text{F}_x$ were prepared by the reaction of tungsten(VI) oxide and powdered tungsten under hydrothermal conditions in the presence of hydrofluoric acid. Reagent grade tungsten(VI) oxide (Gallard-Schlesinger

* This research has been supported by NSF Grant No. GP-26617.

and powdered tungsten (Sylvania, 0.76 μm) were weighed out in the proper ratio and mixed together in an agate mortar until a uniform colored mixture was obtained. The mixture was transferred to a thin-walled gold tube, 5 mm by approximately 10 cm long, which had been crimped and melt sealed at the bottom. The desired amount of hydrofluoric acid was added dropwise and the gold tube crimped and melt sealed at the top. The sample tube was weighed several times during the loading procedure so that the amount of charge, amount of hydrofluoric acid and final weight would be accurately determined.

The sealed samples were then loaded into a $\frac{1}{2}$ -in. i.d. hydrothermal pressure vessel fabricated of René 41 steel. The vessel was filled with water, the degree of fill being adjusted to yield the desired pressure at the operating temperature, and then sealed. A Chromel–Alumel thermocouple was attached to the outside of the pressure vessel allowing the temperature to be measured and controlled to $\pm 3^\circ\text{C}$. The assembled pressure vessel was attached to a Tem-Pres Model HR-2C-2 hydrothermal bench.

Reactions were carried out in a horizontal furnace at 700°C and 2 kbar pressure for periods of 50–300 hr. At the completion of the synthesis the vessel was removed and allowed to cool to 300°C (time required approximately 10 min) and then quenched in water.

Chemical Analysis

The samples were analyzed for fluorine content using an electrode¹ specifically sensitive to this ion. Samples for analysis (20–40 mg) were dissolved in hot 2 *N* NaOH. Once the solution had cooled, the pH was adjusted to 6.0(2) using 2 *N* hydrochloric acid. The pH adjustment was necessary to eliminate the formation of HF and HF_2^- which occur in strongly acidic solutions. The possibility of polyvalent tungsten complexing the fluoride ion was removed by adding an excess of EDTA (ethylenediaminetetraacetic acid). The solutions were then brought to 100 ml and the electrode potential measured against the output of a standard calomel electrode using a Keithley Model 610 BR electrometer.

The electrode output was calibrated against a series of standard solutions of known fluoride ion concentration. The fluoride activity coefficient depends on the total ionic strength and conse-

quently the standard solutions were prepared by dissolving 25 mg of WO_3 in hot 2 *N* NaOH, adding the proper amount of NaF standard solution, and EDTA. The pH was then adjusted to 6.0(2) with 2 *N* hydrochloric acid. The solutions were brought to 100 ml and the potential measured as indicated above. The resultant log-linear electrode potential versus F^- concentration curve was used to determine F^- in the unknowns.

X-Ray Data

Cell dimensions and phase identification were determined using a Norelco diffractometer with monochromatic radiation (AMR-202 focusing monochromator) and a high intensity copper source $\lambda\text{CuK}\alpha_1 = 1.5405 \text{ \AA}$. Additional data for determining cell dimensions were obtained using a Guinier-type focusing camera Model XDC 7000 (Incentive Research and Development AB, Stockholm, Sweden) employing $\text{CuK}\alpha_1$ radiation. Potassium chloride, $a_0 = 6.2931 \text{ \AA}$, was employed as an internal standard and cell dimensions were refined using a least-squares fit of the data.

Electrical Measurements

Resistivity measurements were made as a function of temperature on single crystals over the temperature range 77–320 K using the van der Pauw technique (7). The samples employed were approximately 0.5–1.0 mm on an edge and four indium leads were attached using an ultrasonic soldering technique reported previously (8). The soldered crystal was mounted on an alumina plate and connections were made from it to solder pads using indium. The alumina plate was attached to a copper block to insure good temperature uniformity and a copper constantan thermocouple was glued to the alumina close to the sample. The resistivity was measured using a Keithley 503 Milliohmmeter and the thermocouple output was read with a Hewlett–Packard Model 3450A Digital Multifunction Meter.

Results and Discussion

Blue-black crystals were synthesized in the $\text{WO}_{3-x}\text{F}_x$ system for $x = 0.03\text{--}0.09$. Their X-ray patterns may be indexed on the basis of a tetragonal cell in the manner first reported by Magneli (9) for $\text{Na}_{0.1}\text{WO}_3$ ($a = 5.248$, $c = 3.895 \text{ \AA}$). Refinement of unit cell dimensions for a typical material in this series is shown in Table I.

It was found that although the ratio of W/WO_3 in the reactants had some effect in determining

¹ Fluoride Ion Activity Electrode Model 94-09, Orion Research Inc., Cambridge, Mass.

TABLE I
WO_{2.91}F_{0.09}

<i>d</i> _{obs}	<i>d</i> _{calc}	<i>h k l</i>
3.8417	3.8435	0 0 1
3.7372	3.7336	1 1 0
2.6800	2.6778	1 1 1
2.6418	2.6401	2 0 0
2.1758	2.1760	2 0 1
2.0110	2.0118	2 1 1
1.9215	1.9215	0 0 2
1.8673	1.8668	2 2 0
1.8054	1.8056	1 0 2
1.7083	1.7085	1 1 2
1.6796	1.6791	2 2 1
1.6704	1.6697	3 1 0
1.5531	1.5535	2 0 2
1.5314	1.5314	3 1 1
1.4912	1.4904	2 1 2
1.2602	1.2603	3 1 2
1.2482	1.2484	4 0 1
<i>a</i> ₀ = 5.280 Å	<i>c</i> ₀ = 3.843 Å	

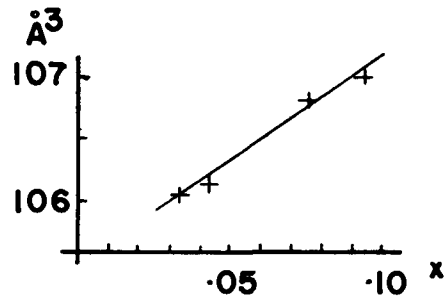


FIG. 1. Cell volume vs ψ .

the structure and fluorine content of the products, the mole ratio of F/W played a more important role. For a constant value of W/WO₃ = 0.10, the products varied from tetragonal to cubic with increasing F/W (Table II). For a value of F/W = 1.9, the tetragonal phase with a fluorine content of *x* = 0.087 was obtained. For the two higher values of F/W = 6.9 and 13.7, the products were primitive, cubic materials with properties similar to the compounds reported by Sleight (2). The

TABLE 2
EFFECT OF F/W RATIO ON *x* IN WO_{3-x}F_x

Lot	Synth.	W/WO ₃	F/W	<i>x</i>	X-ray data
301	700°C 2kbar	0.10	1.9	0.087	Tetragonal <i>a</i> = 5.280 <i>c</i> = 3.843
302	700°C 2kbar	0.10	6.9	0.405	Cubic <i>a</i> = 3.810 Å
303	700°C 2kbar	0.10	13.7	0.438	Cubic <i>a</i> = 3.816 Å

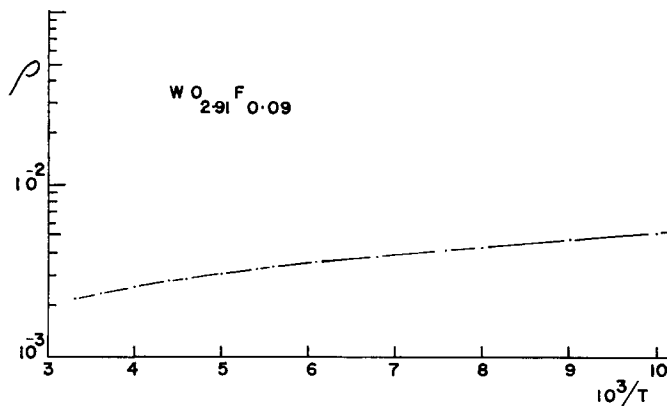


FIG. 2. ρ vs $10^3/T$.

tetragonal phase could only be obtained when F/W remained less than two. Within this tetragonal region, the change in cell volume is small but shows linear behavior (Fig. 1).

The results of electrical measurements on a crystal taken from the preparation for which $x = 0.09$ are shown in Fig. 2. The calculated activation energy in the high-temperature region is 0.018 eV, whereas at low temperatures it approaches 0.009 eV. This behavior is quite similar to that reported by Pierce (5) for the molybdenum bronze $\text{MoO}_{2.4}\text{F}_{0.6}$ and Sleight (2) for the cubic ReO_3 type molybdenum oxyfluorides. Although these materials have a very low activation energy, they are believed to be metallic. The small observed activation energy is probably caused by imperfections in the crystals.

As indicated by Magneli (9) the tetragonal structure is built up of corner-shared WO_6 octahedra. The tungsten atoms form networks in the a - b plane which are slightly displaced (0.25 Å) in the c direction above and below the plane. This structure is similar to the deformed ReO_3 -type

tungsten(VI) oxide. Thus, it would appear that the tungsten oxyfluorides $\text{WO}_{3-x}\text{F}_x$ $0.03 \leq x \leq 0.09$ exist as an intermediate tetragonal structure between WO_3 and the cubic ReO_3 oxyfluorides reported by Sleight. It also appears that the orbital interactions in the substantially octahedral BX_6 units have not been altered.

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