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Preparation and Properties of the Oxyfluoride Systems $V_2O_{5-x}F_x$ and $VO_{2-x}F_x$*

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Partial substitution of fluorine for oxygen in VO_2 and V_2O_5 was achieved by reacting V and V_2O_5 under 1.33 kb pressure in the presence of concentrated or dilute solutions of HF. Two new phases having the composition $V_2O_{5-x}F_x$ $(0 < x < 0.025)$ and $VO_{2-x}F_x$ $(0 < x < 0.2)$ were prepared. X-Ray diffraction studies have been carried out on both phases and show the structure of $V_2O_{5-x}F_x$ to be orthorhombic and isostructural to V_2O_5, while $VO_{2-x}F_x$ has a tetragonal structure of the rutile type (for $x \geqslant 0.03$). Single-crystal-resistivity data show $V_2O_{5-x}F_x$ to be a semiconductor, whereas $VO_{2-x}F_x$ undergoes a metallic to semiconductor transition at a temperature solely dependent upon the value of x.

Introduction

In recent years, there have been numerous publications concerning the electrical properties of the vanadium oxides. V_2O_5 has been reported to be a semiconductor with an activation energy of ~0.2 eV (*1*–3), and VO_2 is known to undergo a semiconductor-metal transition at 340°K (*4*). This transition is accompanied by a crystallographic change from monoclinic (*5*, *6*) to tetragonal symmetry (*7*).

The structure of V_2O_5 was studied by Bachmann et al. (*8*), and the probable space group was reported to be *Pmnm*; the unit cell dimensions are $a = 11.150$ Å, $b = 4.369$ Å, $c = 3.563$ Å. The structure is built up from distorted trigonal bipyramids of oxygen and vanadium. The vanadium atoms are located in the centers of the deformed trigonal bipyramids and all the vanadium sites are equivalent. The bipyramids are joined along edges to form chains extending parallel to the *b* axis.

Pouchard et al. (*9*) have shown that the V–V nearest distance along these chains is approximately 3.05 Å. The electrical properties of V_2O_5 are consistent with the absence of any unpaired *d* electrons. Monovalent cation substitution has received considerable attention (*10*–*13*), and it is reported that the creation of V^{4+} lowers the activation energy. However, there does not appear to be any evidence for the creation of a conduction band, and, therefore, the V–V distance must be greater than the critical distance (R_c) calculated by Goodenough (*14*) as 2.94 Å for tetravalent vanadium.

The semiconductor-metallic transition observed for VO_2 has resulted in detailed studies of this compound (*4*, *15*–*17*). Below 340°K, VO_2 has been reported to show a distorted rutile-type structure with monoclinic symmetry ($P2_1/c$). The metal atoms are located within the strings of VO_6 octahedra occurring as doublets, as in the MoO_2 structure type. Heckingbottom and Linnett (*6*) have indicated that there is little evidence for direct metal–metal bonding along these chains. However, Goodenough (*18*) has proposed and Rogers (*19*) has utilized a band model in which the *d* electrons of t_{2g} symmetry are delocalized by both strong metal–metal interactions and strong covalent mixing with the oxygen p_π orbitals. Above the transition temperature these bands overlap and are each partially filled. The compound is tetragonal ($P4_2/mnm$) and all the V–V distances are equivalent (2.87 Å). Below the transition temperature the π^* bands due to covalent mixing are empty, and the remaining *d* band is split in two by the formation of V–V pairs along the *c* axis.

It has already been shown that fluorine may be

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substituted for oxygen in the compounds WO_3 and MoO_3 (*20–22*). Appreciable substitution of fluorine for oxygen resulted in a change from semiconductor to metallic behavior in both systems. It would, therefore, be most interesting to study the effect of fluorine substitution for oxygen on the electrical properties of both the V_2O_5 and VO_2 systems. The effect of the fluorine substitution would be evident both by the creation of additional *d* electrons and the influence of the t_{2g}–p_π overlap by the more electronegative anion.

Experimental

Preparation of Materials

Anion substituted compounds of the systems $V_2O_{5-x}F_x$ and $VO_{2-x}F_x$ were prepared during the course of this investigation. Single crystals were synthesized using hydrothermal techniques described by Pierce et al. (*21*). A mixture of reagent grade V_2O_5 (Johnson-Matthey), and high-purity vanadium (Gallard-Schlesinger Corp., N.Y.), in the proper ratio, were placed in thin-walled gold tubes 5 mm i.d. × 100 mm sealed at one end. After the addition of the proper amount of HF, the top of the tube was crimped shut and melt-sealed; the tube was then placed in a steel-pressure vessel. The temperature and pressure were continually monitored and, therefore, both of these parameters were controlled to ±5°C and ±0.01 kb, respectively.

For compounds of the system $V_2O_{5-x}F_x$, mixtures of reagent grade V_2O_5 and powdered V metal were weighed out in the desired mole ratio and placed in containers formed by sealing one end of a 10-cm length of 5 mm i.d. gold tubing. The desired amount of reagent-grade 48% hydrofluoric acid was added dropwise to the reaction mixture. In most cases the mole ratio of HF to vanadium in the reactants was approximately 15.

In order to grow single crystals, the reaction was carried out at 500°C under 1.33 kb pressure for 72 hr followed by slow cooling at a rate of 50°C/hr.

For preparation of compounds having the composition $VO_{2-x}F_x$, a mixture of reagent-grade V_2O_5 and powdered vanadium metal was weighed out in the desired mole ratio and placed in containers formed by sealing one end of a 170-mm length of 5 mm i.d. gold tubing. The desired amount of reagent-grade 6% hydrofluoric acid was added dropwise to the reaction mixture. In most cases the mole ratio of HF to vanadium in the reactants was approximately 20. The other end of the capsule was then sealed and the samples heated at the desired temperature and pressure. Polycrystalline samples were prepared by raising the temperature to 600°C while holding the pressure at 1.33 kb. The reaction was then allowed to proceed for 168 hr under these conditions before being quenched.

In order to grow single crystals, the method of preparation of the sample had to be changed; reagent-grade vanadium pentoxide and powdered vanadium metal were not mixed before the reaction. V_2O_5 was first introduced in the gold capsule, followed by the desired amount of reagent-grade 6% hydrofluoric acid added dropwise. The gold tube was then closed mechanically (by squeezing) and vanadium metal was added to the tube above the seal before the end of the capsule was sealed. The samples were placed in the pressure vessel and the reaction was carried out in a horizontal furnace at the desired temperature and pressure. Crystals were obtained at 600°C while holding the pressure at 1.33 kb for 100–300 hr, followed by slow cooling of the pressure vessel at an approximate rate of 50°C/hr.

Chemical Analysis

Products of the system $V_2O_{5-x}F_x$ were dissolved in concentrated hydrochloric acid. The solution was then brought to a pH of 5 with a solution of sodium acetate. An excess of EDTA was added to prevent complexing of the fluoride ions. final The volume of the solution was adjusted to 100 ml with distilled water. The fluoride ion concentration was then measured with an electrode (Fluoride Ion Activity Electrode, Model 94-09, Orion Research Inc., Cambridge, Mass.) specifically sensitive to this ion. The total reducing power of the products was confirmed by dissolving them in acid V^{5+} sulfate solution and titrating the resulting V^{4+} potentiometrically with ceric sulfate. The results are shown in Table I.

Samples of $VO_{2-x}F_x$ were dissolved in acid V^{5+} sulfate solution. The fluoride ion concentration determination was then carried out with the appropriate electrode. The total reducing power of the products was also confirmed. The values of *x* in

TABLE I

ANALYSIS OF $V_2O_{5-x}F_x$ COMPOUNDS

Values of x in $V_2O_{5-x}F_x$	
Fluorine analysis	Reducing power analysis
0.012 ± 2	0.014 ± 2
0.023	0.028

TABLE II

ANALYSIS OF $VO_{2-x}F_x$ COMPOUNDS

Values of x in $VO_{2-x}F_x$	
Fluorine analysis	Reducing power analysis
0.032 ± 2	0.032 ± 2
0.038	0.043
0.140	0.137
0.208	0.208

$VO_{2-x}F_x$ from both fluoride and reducing power analyses are shown in Table II.

The analysis of total vanadium present was carried out on a few samples by dissolving them in concentrated sulfuric acid. All the vanadium was then oxidized to V^{5+} with an excess of $KMnO_4$ solution. V^{5+} was reduced to V^{4+} by a stream of SO_2 and a standardized solution of $KMnO_4$ was used to oxidize the vanadium back to the plus five state in order to determine the total amount of vanadium present.

X-Ray Data

Cell parameters and X-ray-diffraction powder-intensity data were determined using a Norelco diffractometer with monochromatic radiation (AMR-202 Focusing Monochromator) and a high-intensity copper source (Cu $K_{\alpha 1}$) = 1.5405 Å. These are reported in Tables III and IV. Cell parameters and space group were also determined by the single-crystal-precession technique using molybdenum radiation (Mo $K_{\alpha 1}$) = 0.70926 Å.

Electrical Measurements

Resistance measurements were made on single crystals having the composition $V_2O_{5-x}F_x$ using the conventional four-probe technique. The samples used for these measurements were needles 5 × 0.5 × 0.5 mm. Four indium leads were attached to the crystals by means of ultrasonic soldering. The samples were mounted on alumina plates and the leads were attached to indium terminals.

TABLE III

CELL PARAMETERS OF $V_2O_{5-x}F_x$ COMPOUNDS

Compound	Cell parameters (Å)			Activation energy (eV)
	a	b	c	
V_2O_5	11.510 ± 5	3.563 ± 3	4.369 ± 4	~0.2
$V_2O_{4.987}F_{0.013}$	11.530	3.568	4.377	0.23
$V_2O_{4.975}F_{0.025}$	11.460	3.554	4.368	0.18

TABLE IV

CELL PARAMETERS OF $VO_{2-x}F_x$ COMPOUNDS

Compound	Cell parameters (Å)		Activation energy (eV)	T_t (°K)
	a	c		
VO_2	4.530 ± 4	2.869 ± 3	0.5 just below T_t	340
$VO_{1.97}F_{0.03}$	4.552 ± 4	2.853 ± 3	0.07	298
$VO_{1.96}F_{0.04}$	4.554 ± 4	2.854 ± 3	0.06	282
$VO_{1.86}F_{0.14}$	4.562 ± 4	2.876 ± 5	<0.01	155
$VO_{1.79}F_{0.21}$	4.569 ± 4	2.886 ± 3	<0.01	65

For crystals of the composition $VO_{2-x}F_x$ resistance measurements were made on single crystals using the van der Pauw (*23*) technique. The samples used for these measurements were irregularly shaped crystals and it was not possible to orient them along a definite axis. These crystals were ground to a thickness of about 0.2 mm. Four indium leads were attached to the crystals by means of ultrasonic soldering. The samples were then mounted on alumina plates and the leads were attached to silver solder terminals that were bonded to the alumina plates. Resistivity measurements were made as a function of temperature from liquid helium to room temperature.

Results and Discussion

The composition of the products obtained when these mixtures of V_2O_5 and V were fired at 500°C under 1.33 kb pressure for 72 hr are shown in Table I.

The powder-diffraction pattern of $V_2O_{5-x}F_x$ (with $x = 0.013$ and $x = 0.025$) was similar to that observed for V_2O_5 and was indexed on the basis of an orthorhombic cell. The cell parameters were refined by least squares and are shown in Table III. Single-crystal X-ray precession photographs showed the space group of $V_2O_{5-x}F_x$ to be identical to the space group of V_2O_5, that is *Pmmn* (D_{2h}^{13}). There is very little structure change with the introduction of fluoride, except for small shifts in the cell dimensions.

Activation energies were calculated from the resistivity data and are shown in Fig. 1. The crystals used for electrical measurements were of good quality and it can be reasonably assumed that those values are correct. The activation energy for V_2O_5 was recently calculated (*1–3*) and found to be

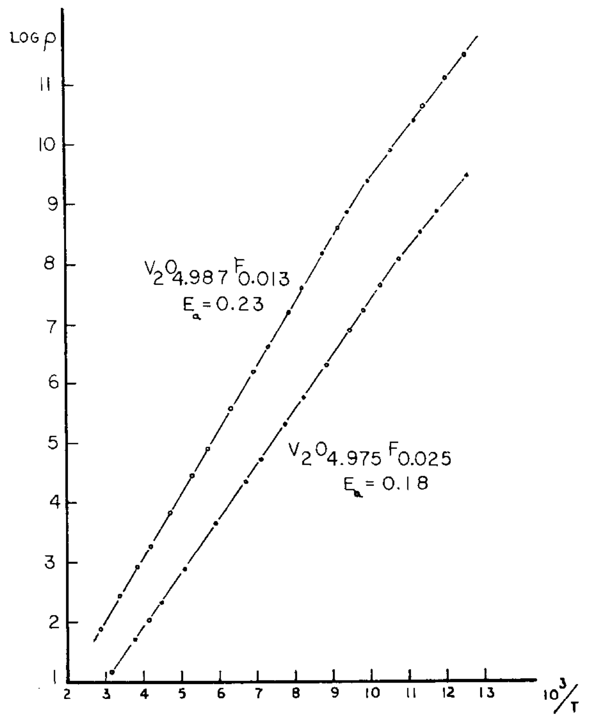

FIG. 1. Log resistivity vs $10^3/T$ for $V_2O_{5-x}F_x$ compounds.

approximately 0.2 eV. It can be seen that the oxyfluorides have about the same activation energies as reported for V_2O_5.

The resistivity curves, shown in Fig. 1, are those of specimens held under growth conditions for 72 hr before slow cooling. These curves indicate semiconducting behavior.

Four different compositions corresponding to the formula $VO_{2-x}F_x$ with $x = 0.032, 0.038, 0.140, 0.208$ were prepared. The corresponding powder-diffraction patterns were indexed on the basis of a tetragonal cell (see Fig. 2) and are shown in Table IV. Single-crystal diffraction photographs revealed the Laue group $4/mmm$ and the systematic extinction $0kl{:}k + l = 2n$ which is consistent with the space group $P4_2/mnm$, and is identical to the space group reported for the high temperature phase of VO_2 (*7*). Low temperature X-ray experiments indicate that crystallographic transitions occur at temperatures depending on the value of x in the system $VO_{2-x}F_x$.

Activation energies were calculated from the resistivity data (see Fig. 3). The values are given in Table IV for different values of x in $VO_{2-x}F_x$. It can be seen from these curves that a metallic to semiconductor transition occurs at a temperature which decreases with increasing values of x. This change in the electrical properties of $VO_{2-x}F_x$ can be explained by the corresponding crystallographic transition from the monoclinic phase to the tetragonal phase which has been observed by means of low-temperature X-ray analysis. A linear relationship exists between the value of x and the transition temperature (T_t) as shown in Fig. 4; this extrapolates to the correct transition temperature for pure VO_2. For

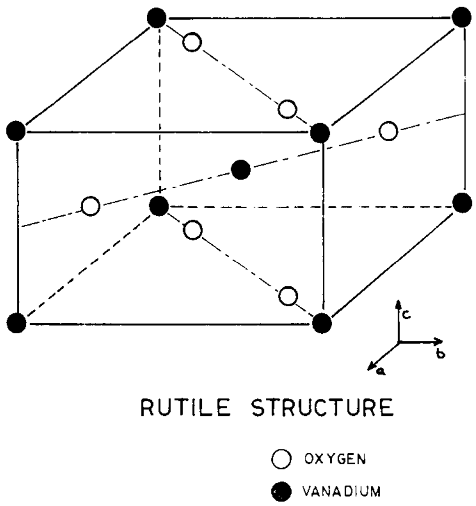

FIG. 2. Rutile structure.

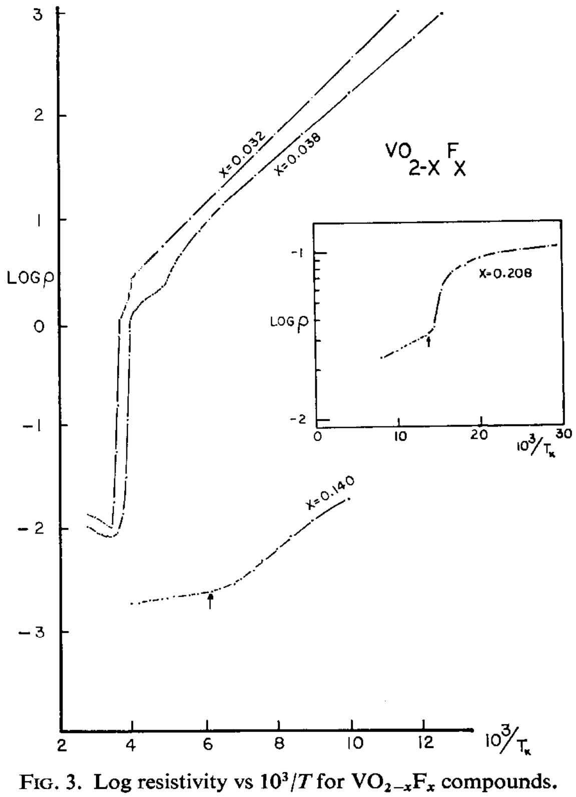

FIG. 3. Log resistivity vs $10^3/T$ for $VO_{2-x}F_x$ compounds.

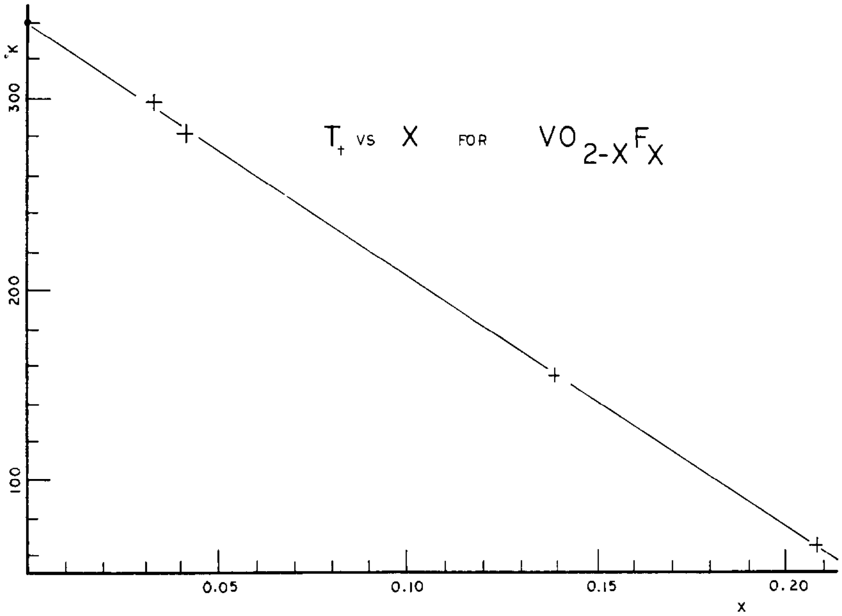

FIG. 4. Transition temperature (T_t) vs x for $VO_{2-x}F_x$ compounds.

the higher fluorine compounds, the transition region is considerably broadened and the transition point was chosen as the first deviation from log-linear behavior. A similar linear relationship exists between the volume of the tetragonal cell and the value of x, again extrapolating to the value of the pure VO_2 phase at $x = 0$ (see Fig. 5). The same behavior has been observed in compounds corresponding to the formula $V_{1-x}W_xO_2$ $(0 \leqslant x \leqslant 0.067)$ by Nygren and Israelsson (*24*).

It is seen, therefore, that the addition of fluorine tends to stabilize the high temperature, higher symmetry, rutile phase. The compositions containing larger amounts of substituted fluorine show primarily metallic behavior. However, for all compositions studied there still appears to be a discontinuity in the resistivity at the expected transition temperature (T_t).

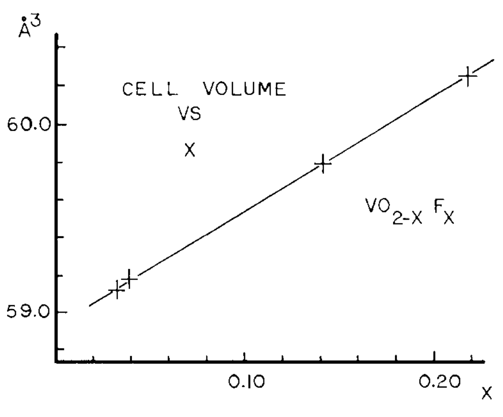

FIG. 5. Tetragonal cell volume vs x for $VO_{2-x}F_x$ compounds.

The metallic behavior observed in these materials may be explained on the model presented by Goodenough (*18*) and Rogers (*19*). In their model the band formed between the overlap of the $t_{2g}\sigma$ orbitals parallel to the crystallographic c direction splits into a more stable, pair-localized, bonding V–V state and a higher less stable σ^* state. The lower lying V–V level is filled with one electron per vanadium and hence the semiconducting properties of the monoclinic VO_2 may be explained. The substitution of fluorine for oxygen in VO_2 results in the creation of additional unpaired d electrons. Despite the tendency for the more electronegative anion to localize d electrons, it is apparent that for the amount of fluorine which has been substituted, the conduction paths have not been substantially altered.

Acknowledgment

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