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New Defect Vanadium Dioxide Phases

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Two new monoclinic V_2O_4 phases were prepared at high pressure from the regular monoclinic (M_1) form of V_2O_4. The unit cell dimensions for the unmodified monoclinic (M_2) phase are: $a = 9.083$, $b = 5.763$, $c = 4.532$ Å, and $\beta = 91.30°$. The space group $C\,2/m$ is consistent with the crystallographic data. The new vanadium dioxide exhibited a structural transition and an abrupt, reversible change in resistivity (approx. 4 orders of magnitude) at 66°C similar to that observed in M_1–type V_2O_4. This new form of V_2O_4 is believed to be stabilized by chemical and structural defects. Controlled substitution of V^{5+} for V^{4+} in the structure led to yet another monoclinic (M_3) phase. This phase is closely related to the M_2 phase. The M_3 unit cell dimensions are: $a = 4.506$, $b = 2.899$, $c = 4.617$ Å, and $\beta = 91.79°$, having the space group $P\,2/m$. The substitution of V^{3+} yielded only monoclinic (M_1) derivatives. The modified products have varied semiconductor to metal transition temperatures which depend on the type and amount of substitution and defect structure.

Introduction

The crystallographic, electrical, and magnetic properties of monoclinic-type (M_1) V_2O_4 have been investigated extensively in the past decade. Vanadium dioxide is of theoretical and practical interest because of its reversible crystallographic and electronic transition at 68°C. The physical properties of V_2O_4 have recently been reviewed (*1*, *2*).

Attempts to prepare crystals of V_2O_4 at high pressure yielded a new phase of vanadium dioxide having similar physical properties to those of the regular monoclinic (M_1) form of V_2O_4 but possessed a different crystallographic powder diffraction pattern. The properties of this new phase and the phases prepared by the substitution of V^{5+} and V^{3+} ions into the V_2O_4 structure at high pressure were investigated.

Experimental

Reagents

High purity oxides of vanadium, V_2O_5 and V_2O_3, obtained from the Vanadium Corporation of America, were used in all the reactions. Monoclinic V_2O_4 was prepared by heating stoichiometric amounts of V_2O_3 and V_2O_5 to 1000° for 24hr in a sealed, evacuated silica tube. The V_2O_4 product prepared in this manner had the monoclinic (M_1) MoO_2-type structure. The powder pattern and cell dimensions of this product were in good agreement with those published in the literature.The product exhibited a strong crystallographic transition at 67°C to the rutile-type structure.

Anal. of V_2O_4. Calc. Weight gain on oxidation to V_2O_5: 9.65%; Weight loss on reduction to V_2O_3: 9.65%. Found. Weight gain: 9.20 ± .05%; Weight loss: 9.99 ± .10%.

Apparatus

A tetrahedral-anvil press of NBS design (*3*) was used in all the experiments. The reactants were heated in platinum or gold capsules surrounded by a BN sleeve and a graphite heater. A du Pont DTA and TGA (Model 900 and 950) thermal analyzer was used to determine the endothermic crystallographic transition and the stoichiometry of the products. X-ray powder diffraction data were obtained with a Hägg–Guinier camera using monochromatized Cu $K\alpha_1$ radiation and a KCl internal standard. The films were read on a Mann film reader; d values were calculated using (Cu $K\alpha_1$) = 1.54051 and a(KCl) = 6.2931 Å. Accurate cell dimensions were obtained by least-squares refinement of the

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TABLE I

VANADIUM DIOXIDE PHASES OBTAINED AT VARIOUS TEMPERATURES AND PRESSURES IN THE TETRAHEDRAL-ANVIL PRESS (PLATINUM CAPSULES)

	Conditions			Products		
Reactants	Temp. (°C)	Pressure (k bar)	Time (hr)	Space Group	Cell Vol.	T_t (°C)
V_2O_4 M_1	900	65	2	$C2/m$	237.67 ± 10	66
V_2O_4 M_1	1000	65	2	$C2/m$	237.20 ± 1	68
V_2O_4 M_1	1100	65	2	$C2/m$	237.33 ± 8	69
V_2O_4 M_1	1200	65	1	$C2/m$	237.41 ± 11	71
V_2O_4 M_1	1000	40	1	*mix*[a]	—	—
V_2O_4 M_1	1000	20	1	$P2_1/c$	117.97 ± 6	66.5
$V_2O_4 + 2\%\ V^{5+}$	1000	65	1	$P2/m$	60.27 ± 13	80
$V_2O_4 + 4\%\ V^{5+}$	1000	65	1	$P2/m$	60.28 ± 12	86
$V_2O_4 + 10\%\ V^{5+}$	1000	65	1	$P2/m$	60.30 ± 11	88
$V_2O_4 + 2\%\ V^{3+}$	1000	65	1	*mix*[a]	—	56.5
$V_2O_4 + 4\%\ V^{3+}$	1000	65	1	$P2_1/c$	118.25 ± 20	52
$V_2O_4 + 10\%\ V^{3+}$	1000	65	1	$P2_1/c$	118.52 ± 28	47

[a] Mixture of monoclinic phases.

powder data. A four-probe, van der Pauw technique was used to measure electrical resistivity on crystals of the new phases at various temperatures.

Results

Preparation

Under certain conditions of pressure and temperature, monoclinic (M_1) V_2O_4 was converted to a new monoclinic (M_2) or pseudo-orthorhombic phase. Small additions of V_2O_5 to the initial reactant charge led to a different monoclinic (M_3) or pseudo-orthorhombic product. The results are summarized in Table I. A preparative P vs T diagram for the formation of the monoclinic (M_2) phase is given in Fig. 1. Although pressure was used to produce both monoclinic (M_2 and M_3) phases, they presumably are not true high-pressure phases since both undergo reversible transitions below 100°C and similar metal-modified phases have been isolated at atmospheric pressure. Therefore, Fig. 1 should not be construed to represent a

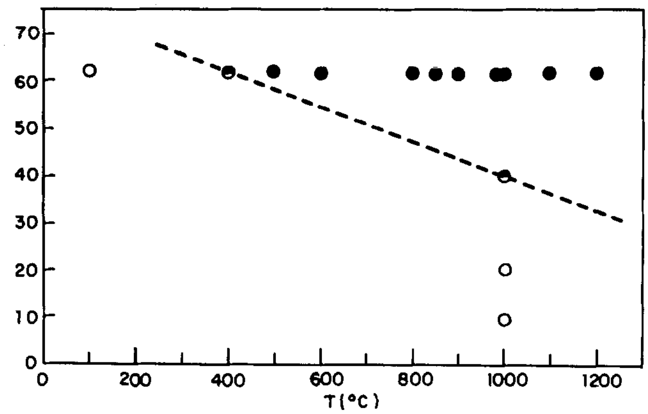

FIG. 1. Stability Field of Monoclinic V_2O_4 (M_1 and M_2 structural types). All experiments conducted in platinum reaction vessels. ○ Monoclinic M_1; ● monoclinic M_2; ⊖ two phases.

field of thermodynamic stability. The monoclinic phases reported in the table and figure were all prepared in platinum capsules. Some experiments (with M_1-type V_2O_4) performed in gold capsules produced only the monoclinic (M_1) form of V_2O_4 and the new M_2 or M_3 phases were never obtained in such capsules. Platinum was not detected in the M_2 phase and attempts to prepare platinum-modified V_2O_4 by the reaction of VO_2 with PtO_2 at high pressure yielded only the M_3 phase and elemental platinum.

Crystallographic Properties

Monoclinic (M_2) Phase

Single crystal studies on the crystals prepared in the high-pressure experiments with (M_2) V_2O_4 showed pseudo-orthorhombic symmetry. A suitable single crystal for structure determination could not be found. The majority of crystals investigated were observed to be twinned or highly distorted. Attempts to determine the actual symmetry and structure were therefore abandoned. The powder patterns could be indexed on a large orthorhombic cell ($a = 12.677$, $b = 12.969$, and $c = 5.764$ Å). Indexing on a monoclinic basis, however, appears more reasonable. The monoclinic unit cell dimensions are: $a = 9.083$, $b = 5.763$, $c = 4.532$ Å, and $\beta = 91.30°$. The unit cell volume is 237.20 Å^3 and $Z = 8$ with an X-ray density of 4.64 g/cc. Two determinations of density by the water-immersion method gave 4.61 and 4.62 g/cc, in excellent agreement with the theoretical value. The $C2/m$ space group is consistent with the indexed powder data and other crystallographic data. The powder pattern, with observed and calculated interplanar spacings, is given in Table II.

Monoclinic (M_3) Phase

The powder diffraction data for the 2% V_2O_5–98% V_2O_4 product could suitably be indexed with the pseudo-orthorhombic unit cell dimensions: $a = 6.340$, $b = 6.588$, and $c = 2.883$ Å. This cell is a sub-unit of that given for the monoclinic (M_2) product above. The

TABLE II

Powder Diffraction Data for the Different V_2O_4 Defect Phases

Monolinic II[a]				Monoclinic III[b]			
I_{obs}	$h\,k\,l$	d_{obs}	d_{calc}	I_{obs}	$h\,k\,l$	d_{obs}	d_{calc}
2	−1 1 1	3.3360	3.3363				
75	−2 0 1	3.2428	3.2442	90	−1 0 1	3.2677	3.2747
100	2 0 1	3.1712	3.1716	100	1 0 1	3.1707	3.1739
10	3 1 0	2.6816	2.6798				
95	0 2 1	2.4319	2.4315	90	1 1 0	2.4353	2.4375
10	0 0 2	2.2676	2.2656	10	2 0 0	2.2743	2.2517
15	−2 2 1	2.1534	2.1544	20	−1 1 1	2.1621	2.1706
15	2 2 1	2.1319	2.1328	30	1 1 1	2.1327	2.1404
2	−2 0 2	2.0453	2.0458				
2	2 0 2	2.0092	2.0092	5	2 0 1	2.0080	2.0000
2	1 3 0	1.8807	1.8794				
25	−2 2 2	1.6682	1.6681	40	−2 1 1	1.6764	1.6733
40	2 2 2	1.6481	1.6481	50	2 1 1	1.6497	1.6458
10	−4 0 2	1.6209	1.6221	20	−2 0 2	1.6345	1.6374
15	4 0 2	1.5858	1.5858	20	2 0 2	1.5856	1.5869
2	−1 3 2	1.4497	1.4498				
20	0 4 0	1.4405	1.4408	20	−3 0 1	1.4413	1.4408
2	2 0 3	1.4237	1.4236	10	−2 1 2	1.4262	1.4256
35	0 2 3	1.3379	1.3378	30	3 1 0	1.3425	1.3330
5	−2 4 1	1.3169	1.3168	10	1 2 1	1.3188	1.3184
2	3 3 2	1.3112	1.3113	5	−1 1 3	1.3126	1.3106

[a] Monolinic (M2) $C\,2/m$, $a = 9.083 \pm 3$, $b = 5.7631 \pm 8$, $c = 4.5323 \pm 7$ Å; $\beta = 91.30 \pm 2°$.

[b] Monoclinic (M3) $P\,2/m$, $a = 4.506 \pm 10$, $b = 2.899 \pm 5$, $c = 4.617 \pm 10$ Å; $\beta = 91.79 \pm 11°$.

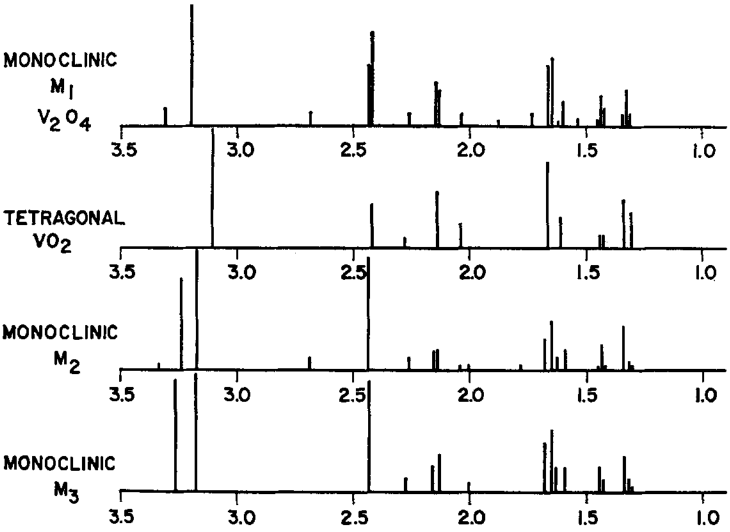

FIG. 2. Powder diffraction patterns for the various forms of V_2O_4.

preferred indexing on a monoclinic (M_3) basis yields the cell dimensions: $a = 4.506$, $b = 2.899$, $c = 4.617$ Å, and $\beta = 91.79°$. The unit cell volume is 60.28 Å^3 and $Z = 2$. These data are consistent with the space group $P2/m$. The indexed powder pattern of the M_3 product is given in Table II with the calculated and observed interplanar spacings with relative intensities.

High-temperature Crystallographic Data

A sample of the M_2 phase was heated to 100°C in a Tem-Press, high-temperature diffractometer. The powder diffraction pattern appeared to have a tetragonal, rutile-type structure with unit cell parameters $a = 4.552$ and $c = 2.852$ Å, and vol. = 59.09 Å^3. On cooling the sample to room temperature (after a 4 hour heat treatment at 100°C), the original M_2 powder diffraction pattern was regenerated, Heat treatment at higher temperature (800–900°C under argon) yielded the original M_1 form of V_2O_4 as the room-temperature product. The M_3 phase showed a similar tetragonal, rutile-type powder pattern at high temperature.

Electrical Properties

Results of four-probe resistivity measurements on crystals of monoclinic (M_2) V_2O_4, and a V^{5+}-doped V_2O_4 are shown in Figs. 3 and 4. Both crystals show semiconductivity behavior below the transition temperature (T_t), a sharp discontinuity, and metallic conductivity above the transition temperature. The V^{5+}-doped crystal cracked on cycling through the transition and the resistivity differed on return to room temperature (Fig. 4).

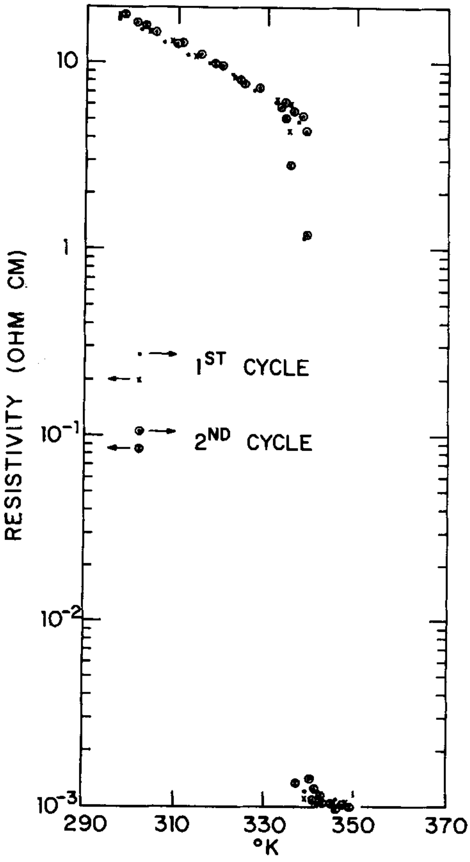

FIG. 3. Resistivity data for monoclinic (M_2–type) V_2O_4

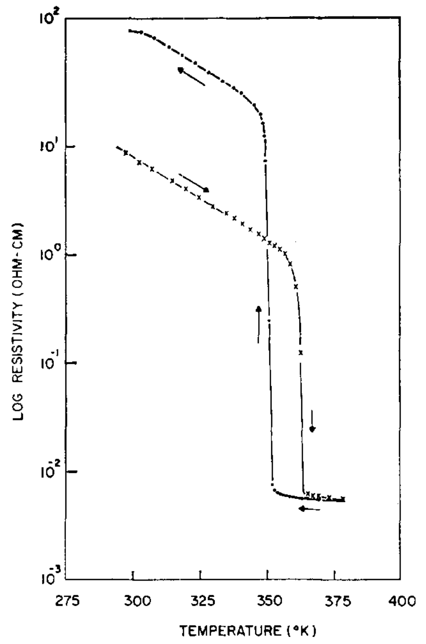

FIG. 4. Resistivity data for monoclinic (M_3–type) V_2O_4. The composition of the crystal is $V^{4+}_{.95}V^{5+}_{.04}\square_{.01}O_2$. The crystal cracked on cooling through the transition.

Thermal Analyses

DTA on the monoclinic phases showed a strong endotherm on heating at a rate of 5 to 15 deg/min and an exotherm on cooling through the transition. The transition temperatures, T_t, are given in Table I. These data are within $a \pm 2°$ deviation. Analytical data were obtained by TGA oxidation to V_2O_5 and also by reduction to V_2O_3 in O_2/Ar and H_2/Ar atmospheres, respectively.

Anal. Calc. for V_2O_4: Weight gain on oxid.: 9.65%; Weight loss on reduc.: 9.65%. Found for M_2 phase: Weight gain on oxid.: 9.38%; Weight loss on reduc.: 9.75%. Found for M_3 phase (2% V_2O_5): Weight gain on oxid.: 8.10%; weight loss on reduc.: 11.07%. Found for V^{3+}-M_2 phase (5% V_2O_3): Weight gain on oxid.: 10.13%; weight loss on reduc.: 9.02%.

Discussion

The presence of homopolar V^{4+} pairs and an unsymmetrical arrangement of oxygen about V^{4+} appear to be responsible for most of the unusual crystallographic and physical properties of V_2O_4. As the pairs are broken, a tetragonal structure is formed and metallic conduction via t_{2g} bands occurs. The monoclinic M_1 cell of V_2O_4 is related to the rutile-type tetragonal cell as shown by Westman (*4*) and Goodenough (*2*). In the new monoclinic structures (M_2 and M_3) some of the V^{4+} pairs must still be present at room temperature to account for the DTA endotherms and electrical characteristics observed. The symmetry and structure of the high-temperature phases (at 100°C) are not known with certainty but the powder patterns appear to be tetragonal, similar to the rutile-type structure, but this phase can not be identical to the tetragonal rutile-type VO_2 since reversibility of the phases has been demonstrated. It should be noted that the "tetragonal" volume obtained from the high-temperature experiment on M_2-type V_2O_4 is 59.09 Å³ while that of pure VO_2 at 96°C is 59.13 Å³ (*5*). The smaller volume is probably due to cation vacancies which are still ordered above the transition temperature. These defects are lost or randomized at higher temperature and the products obtained from such a heat treatment then revert to the regular M_1-structure of V_2O_4 at room temperature. The M_2 phase, therefore, is believed to be formed and stabilized by the long range ordering of defects within the crystal structure under the high-pressure and high-temperature conditions. The M_2 products appear to be oxidized slightly and might contain cation vacancies which would give rise to the smaller unit cell volumes observed. The formation of (M_2) V_2O_4 and its relation to the (M_1) V_2O_4 phase are represented by the following equations:

$$\underset{M_1}{V_2O_4} \xleftrightarrow{65°C} \underset{T_1}{VO_2} \xrightarrow{\text{high pressure}} \underset{\substack{M_2 \\ \text{(defect structure)}}}{V_{2-x}O_4}$$

$$\underset{M_2}{V_{2-x}O_4}\ \text{(defect struc.)} \xleftrightarrow{70°C}$$

$$\underset{T_2}{V_{1-x}O_2} \xrightarrow[-O_2]{800\text{-}900°C} \underset{T_1}{VO_2} \xleftrightarrow{65°C} \underset{M_1}{V_2O_4}$$

Intentional substitution of V^{5+} into the V_2O_4 matrix yielded a related but different monoclinic (M_3) phase. The M_3 products are formed at several compositions in the $V^{4+}_{2-x}V^{5+}_{x}O_{4+y}$ series. Since these compositions are prepared at high pressure it could be assumed that V^{5+} ions would occupy octahedral sites instead of their regular tetrahedral or pyramidal coordination. The orthorhombic, ambient-pressure form of $CrVO_4$ containing tetrahedral V^{5+} ions undergoes a crystallographic transformation to the rutile-type structure at high pressure in which the V^{5+} ions occupy octahedral sites (*6*). Further, it might be more fitting to consider the oxygen-rich system V_2O_{4+y} in terms of a metal deficient or a defect system of general formula $V^{4+}_{1-(x+y)}V^{5+}_x\square_yO_2$, where $y = x/4$, having a completely close-packed structure based on anions. The normalized cell volumes of these derivatives are relatively much larger than that of stoichiometric V_2O_4 with the M_1 structure. If the structure were based entirely on the presence of octahedral V^{5+} ions one would predict a smaller unit cell volume since V^{5+} is much smaller than V^{4+}, which is contrary to our observations. As the defect concentration in the M_3 structure increases, the unit cell volume also increases. The superstructure lines in the M_2 powder diffraction pattern are not observed in the patterns of the M_3 derivatives. The two structures are obviously related as can be observed from a comparison of their powder patterns (Fig. 2) and unit cell dimensions.

Recent studies on the metal-modified derivatives of V_2O_4 have yielded a variety of products which have been claimed to possess monoclinic, orthorhombic, triclinic, or (a super-structural, tri-rutile) tetragonal symmetry. In the VO_2–WO_2 studies by Israelsson and Kihlborg (*7*), a careful examination of the crystallographic properties of products indicated a variety of structures for the various $V_{1-x}W_xO_2$ phases. In the region $0.785 \leqslant x \leqslant 0.673$, monoclinic ($M_3$-type or pseudo-orthorhombic) phases were observed. These phases were believed to possess a deformed rultile-type structure.

A structural investigation on twinned crystals of $V_{.975}Cr_{.025}O_2$ (M_2 phase) by Marezio, McWhan, Remeika, and Dernier (*8*) showed two types of vanadium atoms located in edge-shared octahedra forming chains. One chain was linear along the b_m axis and contained V–V pairs with alternating short and long interatomic metal distances (2.538 and 3.259 Å, respectively). The metal atoms in the other (zig-zag) chain were equidistant (2.933 Å). This distance is approximately that of the R_c value calculated as the critical separation of V^{4+}-V^{4+} ions for localized *vs* itinerant 3*d* electron behavior in oxides (R_c for $V^{4+} = 2.94$ Å). The homopolar pairs in the M_2 structure probably break up at the transition temperature and the added metallic nature of the zig-zag chain explains the increased metallic nature of the M_2 phase at the onset of the electrical transition

In the M_3 structure of $V_{.975}Cr_{.025}O_2$ the zig-zag chains contained V–V atoms at distances of 2.913 Å, a value much smaller than R_c, indicative of metallic or delocalized electrons in these V^{4+}–V^{4+} columns as found in the metallic (tetragonal) form of stoichiometric VO_2. The other chain in the structure still contains homopolar pairs as in the monoclinic (M_1) form of V_2O_4. The M_3 phase therefore, can be considered as an intermediate in the $M_1 \leftrightarrow T_1$ equilibrium. The electrical properties of $V^{4+}_{.96}V^{5+}_{.04}\square_{.01}O_2$ (Fig. 4) are in good accord with these postulates since the change in resistivity at the transition is half that found in high purity, stoichiometric V_2O_4, where the change in resistivity at T_t is 5 orders of magnitude (*9*).

Israelsson and Kihlborg (*7*) were the first to report and recognize the M_3 structure for a metal-modified V_2O_4 derivative even though several workers observed anomalies in the physical and crystallographic properties of such derivatives. Kosuge (*10*) noted a distorted rutile-type phase when Fe^{3+} was substituted in V_2O_4, but this phase was not characterized crystallographically. Two distinct magnetic transitions were observed on these iron-modified compositions. Mitsuishi (*11*) similarly observed two transitions in iron-doped V_2O_4 from resistivity and powder diffraction studies. A triclinic structure for aluminum-modified V_2O_4 was reported by Mitsuishi (*11*), but his diffraction data are strikingly similar to that of the M_2 phase. Everhart and MacChesney (*12*) reported the electrical resistivity of Fe-modified V_2O_4 showing anisotropic behavior and a single, strong transition at approximately 69.5°C. The increased transition temperature, composition, and resistivity behavior would indicate that they have also prepared a monoclinic (M_2 or M_3) form of $Fe^{3+}_xV_{2-x}O_4$. The substitution of trivalent metal ions in the V_2O_4 matrix gives rise to structures of the type $V^{4+}_{1-2x}V^{5+}_x M^{3+}_x O_2$ and the presence of these two foreign ions (V^{5+} and M^{3+}) act in a similar way to the defects introduced in the V_2O_4 structure by slight oxidation or substituting V^{5+} into the structure at high pressure.

Some of the metal-modified V_2O_4 derivatives reported in the literature are listed in Table III with their respective unit cell dimensions and cell volumes. Some of the literature values were converted from the pseudo-orthorhombic dimen-

TABLE III

CELL DIMENSIONS FOR METAL MODIFIED V_2O_4 COMPOSITIONS (M_3)

Composition	a (Å)	b (Å)	c (Å)	β (°)	Vol. (Å^3)	Reference
$V_{.3}W_{.7}O_2$	4.772	2.850	4.764	90.64	64.79	7
$V_{.82}Ti_{.18}O_2$	4.541	2.906	4.543	90.62	59.95	7
$V_{.80}Cr_{.20}O_2$	4.550	2.898	4.550	92.18	59.95	7
$V_{.965}Al_{.035}O_2$	4.498	2.916	4.617	91.73	60.53	13
$V_{.965}Cr_{.035}O_2$	4.521	2.907	4.528	91.82	59.49	13
$V_{.965}Fe_{.035}O_2$	4.519	2.895	4.542	91.90	59.38	13
$V^{4+}_{.95}V^{5+}_{.04}\square_{.01}O_2$	4.506	2.899	4.617	91.79	60.28	This work
$V_{1-x}O_2$ (Pt)	4.518	2.890	4.610	91.63	60.15	This work
$V_{1-x}O_2$ (Ni)	4.538	2.894	4.529	91.72	59.45	This work
$V_{1-x}O_2$ (Cu)	4.576	2.891	4.576	92.18	60.48	This work

sions by the relation: $\underline{a}_m = \sqrt{2}\ \underline{a}_o$, $\underline{b}_m = \underline{c}_o$, and $\underline{c}_m = \sqrt{2}\ \underline{b}_o$, or by the least-squares refinement of powder diffraction data. The elements in parentheses may or may not be present in the structure.

The transition temperature in the M_2 phases occurs in the region 65–72°C, and increases with increasing volume. The unit cell volume also increases with temperature and time in the tetrahedral anvil experiment indicating that the defect structure giving rise to the phase stabilization of the M_2 structure is time and temperature dependent (in addition to the pressure dependency).

The transition temperatures for the products with the M_3 structure are higher, in the region 80–92°C. A linear relationship between T_t and volume also exists in this series. This would indicate that as the defects (cation vacancies) increase, giving rise to larger volumes, the transition temperature increases (+6°C per a/o V^{5+}).

The substitution of V^{3+} for V^{4+} in the VO_2 structure yielded quite different results. Firstly, the M_2 or M_3 structure was not stabilized, and secondly, the increase in monoclinic (M_1) volume with increasing V^{3+} content exhibited a decrease in T_t (−2.5°C per a/o V^{3+}). The decrease in T_t by the substitution of a larger ion for V^{4+} in the V_2O_4 matrix has been noted previously, particularly for Cr^{3+}, Ti^{4+}, Ru^{4+}, etc. (*2*). In the V^{3+}–V_2O_4 system, the octahedral sites are filled but the additional cations must occupy interstitial sites. Therefore, the system can be expressed by the general formula $V^{4+}_{1-x}V^{3+}_{x}\,{}_iV^{4+}_{y}O_2$, where $y = x/4$ and ${}_iV^{4+}$ represent the interstitial atoms.

This system is closely related to the $V_2O_{4-x}F_x$ series reported previously (*14*, *15*) in which V^{3+} and F^- substitution caused a rapid decrease in T_t (−14°C per a/o F).

The complete structure determination of the M_2 and M_3 derivatives would be of special interest in order to accurately determine the V^{4+}–V^{4+} interatomic distances in the low- and high-temperature structures. These data are necessary to support the postulates concerning the electrical transport properties at the transition temperature.

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