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The Synthesis of New Ilmenite-Type Derivatives, $CuVO_3$ and $CoVO_3$

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The compositions $CuVO_3$ and $CoVO_3$ were studied at high pressure in a tetrahedral anvil press. Reactions of CuO and V_2O_4 or Cu_2O and V_2O_5, as well as the conversion of $\alpha CuVO_3$ to a high-pressure phase, were investigated. Two related golden phases, a triclinic, distorted ilmenite, $CuVO_3$(I), and a rhombohedral ilmenite, $CuVO_3$(II), were isolated. Magnetic and resistivity measurements are reported for both high-pressure phases. These phases give the known $\alpha CuVO_3$ when heated above 340° at one atmosphere of pressure.

Triclinic, ilmenite-type $CoVO_3$, isostructural with $CuVO_3$(I), was prepared in the reaction of CoO and V_2O_4 at 65 kbars pressure. The magnetic properties show the composition to be ordered below a Néel temperature of 142°K.

Introduction

The compositions $CuVO_3$ and $CoVO_3$ have been studied little in the past even though the preparation and powder diffraction pattern of $CuVO_3$ have been reported (*1*, *2*). Several authors (*3*–*6*), however, have prepared a variety of semiconducting copper-vanadium "bronzes." Attempts to prepare $CoVO_3$ by Rüdorff *et al.* (*7*) were unsuccessful.

In this paper crystallographic, magnetic, and electrical properties of $CuVO_3$ and $CoVO_3$ phases prepared at high pressure are reported.

Experimental

Reactants

The following copper oxides were used without further purification: CuO (Spex Industries, Inc., 99.999%), CuO (Baker and Adamson, reagent grade), Cu_2O (Fisher Scientific Co., certified reagent, 98.7%), and Cu_2O (Baker and Adamson, reagent grade, 96.8%). V_2O_5 and V_2O_3 were obtained from the Vanadium Corporation of America, and V_2O_4 was prepared by the solid-state reaction of the two oxides at 800–900° in an evacuated, fused-silica tube for 24 hr. Purified CoO was obtained from City Chemical Corp. or prepared by the thermal decomposition of cobalt (II) carbonate *in vacuo*.

The nomenclature used in describing the various phases has been described previously (*8*). The low-pressure, low-temperature phases are prefixed with the letters of the Greek alphabet while the high-pressure phases are suffixed with Roman numerals.

The reactant, $\alpha CuVO_3$, was prepared by a previously reported method (*1*, *2*) (490° for 8.5 hr). The X-ray pattern of this product was identical to that reported (*1*, *2*).

Anal. Calcd. for $CuVO_3$: Cu, 39.1; V, 31.4; O, 29.5
Found: Cu, 38.2; V, 32.9; O, 30.3

Apparatus

The tetrahedral anvil press is of National Bureau of Standards design (*9*) and has previously been described (*10*).

The electrical measurements were made on single crystals using a four-probe method. For $CoVO_3$, obtained as a powder, electrical resistivity was measured using two probes with the powder compressed at 36 TSI. The magnetic data were obtained on powders with a Cahn microbalance.

The X-ray data were obtained at 25° with a Hägg–Guinier camera utilizing monochromated CuKα radiation and an internal standard on KCl ($a = 6.2931$ Å). Cell dimensions were refined by the least squares method. Single crystals were studied with an X-ray precession camera using MoKα radiation for the determination of symmetry, space group, and approximate cell dimensions.

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TABLE I

Powder Diffraction Data on the $CuVO_3$ and $CoVO_3$ Systems

	$\alpha CuVO_3$				$CuVO_3(II)$		
h k l	*I*	*d*(obs.)	*d*(calcd.)	*h k l*	*I*	*d*(obs.)	*d*(calcd.)
1 1 0	25	6.4370	6.4295	0 0 3	15[a]	(4.6861)[a]	4.6887
3 0 0	10	3.7114	3.7121	1 0 1	10[a]	(4.1076)	4.1042
2 1 1	10	3.6411	3.6319	0 1 2	20	3.6595	3.6630
2 2 0	40	3.2143	3.2147	1 0 4	100	2.7201	2.7198
2 0 2	25	3.0202	3.0190	1 1 0	80	2.4782	2.4773
1 3 1	100	2.8379	2.8376	1 1 3	2	2.1898	2.1904
1 2 2	90	2.7329	2.7328	0 2 1	5[a]	(2.1201)	2.1209
4 0 1	80	2.5961	2.5960	0 2 4	20	1.8308	1.8315
4 1 0	10	2.4298	2.4301	1 0 7	5[a]	(1.8212)	1.8198
3 2 1	10	2.4069	2.4072	1 1 6	20	1.7029	1.7028
3 1 2	30	2.3422	2.3422	0 1 8	2	1.6272	1.6270
1 1 3	60	2.2445	2.2446	2 1 1	2[a]	(1.6117)	1.6111
0 4 2	20	2.2017	2.2007	2 1 4	15	1.4725	1.4727
3 3 0	10	2.1420	2.1432	3 0 0	15	1.4306	1.4303
2 3 2	20	2.0820	2.0821	3 0 3	2[a]	(1.3676)	1.3681
2 4 1	10	2.0171	2.0197	10, 10	5	1.3370	1.3366
				1 1 9	2[a]	(1.3207)	1.3218

	$CuVO_3(I)$			$CoVO_3(I)$		
h k l	*I*	*d*(obs.)	*d*(calcd.)	*I*	*d*(obs.)	*d*(calcd.)
0 1 0	25[a]	(4.6845)	4.6850	10[a]	(4.6375)	4.6555
0 0 1	8[a]	(4.1423)	4.1436	—	—	—
1 1 0	10[a]	(4.0939)	4.0958	10[a]	(4.1219)	4.1265
1 0 0	10	3.7702	3.7642	30	3.7537	3.7558
1 1 −1	60	3.6204	3.6247	100	3.6281	3.6270
0 1 −1	40	2.7617	2.7630	90	2.7488	2.7492
−1 1 1	100	2.7231	2.7238	65	2.7105	2.7109
1 2 0	60	2.6745	2.6747	80	2.6838	2.6835
1 1 1	80	2.5012	2.5030	95	2.5214	2.5218
2 1 −1	70	2.4819	2.4816	65	2.4882	2.4883
1 0 −2	80	2.4565	2.4566	65	2.4629	2.4641
0 2 0	10	2.3419	2.3424	2[a]	(2.3249)	2.3277
2 0 −1	—	—	—	15	2.2161	2.2157
1 1 −2	2	2.1877	2.1868	—	—	—
1 2 1	—	—	—	30	2.1865	2.1869
2 2 −1	60	2.1661	2.1657	15	2.1738	2.1738
0 1 2	—	—	—	30	2.1301	2.1264
2 2 0	2	2.0483	2.0478	2[a]	(2.0606)	2.0633
−2 0 0	5	1.8840	1.8821	30	1.8781	1.8779
2 2 −2	10	1.8097	1.8123	—	—	—
0 2 2	10	1.8047	1.8063	—	—	—
−1 1 −1	—	—	—	25	1.7401	1.7398
−2 1 1	15	1.7292	1.7300	25	1.7195	1.7196
1 2 −2	40	1.7059	1.7059	30	1.7007	1.7006

[a] Observed with $CrK\alpha$ radiation; *d*(obs.), in parentheses, from Debye–Scherrer powder pattern.

A G. E. X-ray fluorescent unit and an Electron Microprobe were used to determine the Cu–V ratios in the products obtained. A Du Pont DTA apparatus was used to determine the melting points and decomposition temperatures for the various phases.

TABLE II

ELECTRICAL AND MAGNETIC PROPERTIES OF THE $CuVO_3$ PHASES

	Electrical properties		Magnetic properties		
Phases	$\rho_{298°K}$ (Ω-cm)	E_a (eV)	Magnetic type	$p_{\mathrm{eff}}^2(\mathrm{BM})^2$	θ(°K)
$\alpha CuVO_3$	1.3	0.08	Paramagnetic	1.31	−154
$CuVO_3$(I)	1.6×10^{-1}	0.03	Paramagnetic	1.26	−41
$CuVO_3$(II)	2×10^{-1}	0.05	VanVleck paramag.	—	—

Results

$\alpha CuVO_3$ Phase

Single crystals of $\alpha CuVO_3$ were prepared by the hydrothermal reaction (*11*) of Cu_2Cl_2 and $NaVO_3$ in a gold tube. The $\alpha CuVO_3$ prepared in the solid state reaction was found to be stoichiometric by X-ray fluorescence studies (Cu:V= 1.0:0.99) and by chemical analyses (c.f. reagents). Single-crystal precession studies indicated rhombohedral symmetry having the possible space groups: $R3$ or $R\bar{3}$. The Guinier data were refined on the basis of the following hexagonal cell: $a = 12.859 \pm 2$ and $c = 7.186 \pm 2$ Å. The rhombohedral cell is $a = 7.800 \pm 6$ Å and $\alpha = 111.02 \pm 1°$. The indexed powder data, based on the hexagonal cell, are given in Table I, the electrical and magnetic properties in Table II. DTA showed a melt endotherm at 536° and decomposition at 616°.

High-Pressure $CuVO_3$ Phases

Three reactions, expressed by the following equations, were studied at 65 kbars in the preparation of high-pressure $CuVO_3$ phases.

$$Cu_2O + V_2O_5 \rightarrow 2\,CuVO_3 \tag{1}$$

$$2CuO + V_2O_4 \rightarrow 2\,CuVO_3 \tag{2}$$

$$\alpha CuVO_3 \rightarrow CuVO_3 \tag{3}$$

Results of these reactions are given in Table III.

Two different products were formed depending upon the reactants and the reaction conditions. These two phases are distinguished by the Cu:V ratio or stoichiometry. Electron microprobe and X-ray fluorescence studies indicate that $CuVO_3$ (II) is slightly nonstoichiometric (V-deficient), $CuV_{\sim 0.9}O_3$, while $CuVO_3$(I) is nearer to stoichiometry (Cu:V = 1.0:0.95). Trace amounts of a second phase were often observed in these high-pressure products. This impurity was an orthorhombic form of V_2O_4 (*12*) that appeared as a black crystalline band surrounding the golden $CuVO_3$ products in 2–5% concentrations.

TABLE III

RESULTS OF HIGH-PRESSURE REACTIONS (65 KBARS)

Reaction (equation)	Copper oxide source[a]	Temp. (°C)	Time (hr)	Product
1	F	900	1	$CuVO_3$(II)
1	F	600	1	$CuVO_3$(I)
1	B & A	900	1	$CuVO_3$(I)
2	S or B & A	1000	1–2	$CuVO_3$(II)
3	H or B & A	600–1000	2	$CuVO_3$(I)
3	H or SS	600	2	$CuVO_3$(I)

[a] F = Fisher, S = Spex, B & A = Baker and Adamson, H = hydrothermal $\alpha CuVO_3$ product, SS = solid-state $\alpha CuVO_3$ product.

Attempts to prepare nonstoichiometric, high-pressure forms of $CuVO_3$ directly yielded multiphase products.

$CuVO_3$(I)

Single-crystal precession data on crystals of $CuVO_3$(I) indicated triclinic symmetry. The powder pattern of this phase strongly resembles that of $CuVO_3$(II) except that each reflection at high 2 θ values is split into multiplets giving a triclinic pattern (Table I). The Guinier powder data were refined with the following cell dimensions: $a = 4.967 \pm 3$; $b = 5.404 \pm 3$; $c = 4.914 \pm 2$ Å, $\alpha = 90.32 \pm 2$; $\beta = 119.05 \pm 2$; and $\gamma = 65.00 \pm 2°$. The volume of the unit cell is 99.95 ± 17 Å^3 with two formula weights per unit cell.

Anal. Calcd. for $CuVO_3$: 0, 29.5
Found: 0, 30.6

The electrical and magnetic properties of $CuVO_3(I)$ are given in Table II. The DTA showed an irreversible exotherm at 342° with the formation of $\alpha CuVO_3$.

$CuVO_3(II)$

$CuVO_3(II)$ apparently has an ilmenite-type structure. Single-crystal studies indicated the space group $R\bar{3}m$. The refined hexagonal lattice parameters are: $a = 4.9547 \pm 6$, and $c = 14.066 \pm 4$ Å. The indexed powder pattern is given in Table I, while the electrical and magnetic properties are reported in Table II. It should be noted that some *hkl* ordering reflections [viz. (003), (101), etc.] are not observed in powder patterns obtained with CuKα radiation. These reflections are observed, however, when CrKα radiation is used. The calculated density of the ilmenite form is slightly greater than that of the triclinic form assuming the same formula weight (5.411 vs. 5.404 g/cm^3, respectively).

Anal. Calcd. for $CuVO_3$: O, 29.5
Found: O, 30.5

The DTA on $CuVO_3(II)$ showed an irreversible exotherm at 322°, a melt endotherm at 550°, and a decomposition at 615°. The residue of $CuVO_3(II)$ heated to 400° gave a powder diffraction pattern of $\alpha CuVO_3$ and the original golden color of the high-pressure product had changed to black.

$CoVO_3(I)$

The $CoVO_3$ phase could be prepared at 65 kbars and 900–1000° for 1–2 hr from either the reaction of CoO and V_2O_4 or from a preheated mixture of CoO and V_2O_4 (sealed tube reaction). The black, crystalline product was found to have a similar powder diffraction pattern to that of $CuVO_3(I)$ and the two compositions apparently are isostructural.

The Guinier data were refined with the following triclinic cell dimensions: $a = 4.980 \pm 1$; $b = 5.411 \pm 1$; $c = 4.929 \pm 1$ Å; $\alpha = 90.04 \pm 1$; $\beta = 118.76 \pm 1$; and $\gamma = 63.44 \pm 1°$. The cell volume is 100.17 ± 5 Å^3. The indexed powder pattern is given in Table I.

Electrical measurements made on powders of $CoVO_3(I)$ indicate semiconductor behavior with a resistivity of 8 ohm–cm at room temperature and an activation energy, E_a, of 0.15 eV. The magnetic data indicated antiferromagnetic behavior with $T_N = 142$°K. The observed p^2_{eff} is 28.5 (BM)^2, while the calculated moment for $Co^{2+}V^{4+}O_3$ [free spin $Co^{2+} = 26$ (BM)^2 ($g = 2.79$), and $V^{4+} = 3$ (BM)^2] is 29 (BM)^2. The observed Weiss constant is –9°K.

DTA showed a reversible transition at approximately 250°. This would indicate that $CoVO_3(I)$ is not a true high-pressure phase, but our attempts and those of Rüdorff *et al.* (*7*) to prepare this phase at lower pressures have been unsuccessful.

Discussion

Three different $CuVO_3$ phases and a related $CoVO_3$ phase have been prepared and characterized. For low-pressure $\alpha CuVO_3$ the observed moment of 1.31 (BM)^2 suggests that mixed valences of both Cu and V may occur, i.e.

$$\begin{array}{ccc} Cu^{+}V^{5+}O_3 & \rightleftharpoons & Cu^{2+}V^{4+}O_3 \\ \text{diamagnetic} & & \text{paramagnetic} \end{array}$$

The low value of the moment would further suggest that the phase is predominantly $Cu^{+}V^{5+}O_3$ [calc. $p^2_{\text{eff}} = O(\text{BM})^2$] rather than $Cu^{2+}V^{4+}O_3$ [calc. spin moment ~6 (BM)^2]. The large negative Weiss constant is consistent with this postulate.

Magnetic measurements indicate $CoVO_3(I)$ to be $Co^{2+}V^{4+}O_3$. This phase appears to be isostructural with $CuVO_3(I)$, but the latter does not exhibit the large, high-temperature paramagnetic moment that would be expected for $Cu^{2+}V^{4+}O_3$. An equilibrium between two valence states, similar to that proposed for $\alpha CuVO_3$, may also account for the low moment of $CuVO_3(I)$. Such an equilibrium is not probable in the cobalt-vanadium system since monovalent cobalt is not a stable valence state.

$CuVO_3(I)$ and $CoVO_3(I)$ are the first examples of a triclinic distortion of the ilmenite structure. The crystallographic relationship between $CuVO_3(I)$ and $CuVO_3(II)$ is sufficiently close to account for the similar chemical and physical properties of these two phases, i.e., the same golden color, similar electrical resistivities, small activation energies, and irreversible transition temperatures with the formation of $\alpha CuVO_3$.

Stoichiometry is important in the $CuVO_3$ system. Raveau (*1*) has demonstrated that reaction temperature is a critical parameter in the oxygen content of $\alpha CuVO_3$ prepared at autogenous pressure. This phase readily loses oxygen above 525° to yield $CuVO_{3-\delta}$ ($0.07 \leqslant \delta \leqslant 0.20$). Above 535° and at autogenous pressure, the $CuVO_{3-\delta}$ further decomposes to yield a mixture of Cu_3VO_4 and V_2O_4 with the loss of oxygen. At 700° or above, complete decomposition to Cu, O_2, and V_2O_4 occurs in a sealed system.

The tetrahedral anvil experiments were carried out in the temperature range 600 to 1000°, much above the decomposition temperature of $\alpha CuVO_3$ (at autogenous pressure). The high pressure in the anvil press prevented much of the decomposition, but trace amounts of V_2O_4 were observed as black crystalline bands in the reaction products. Decomposition may have proceeded according to the following equation to yield a nonstoichiometric phase:

$$CuVO_3 \rightleftharpoons CuV_{1-x}O_{3-2x} + x/2\, V_2O_4 \qquad [4]$$

In this reaction x is quite small since the amounts of V_2O_4 detected were only 2–5% of the total product. Copper-vanadium "bronzes" (*1–3*), reactants, or Cu_3VO_4 were never detected in the products investigated. Nonstoichiometry of this $CuV_{1-x}O_{3-2x}$ type has been demonstrated by electron microprobe, X-ray fluorescence, and elemental analyses. The deviations in the Cu:V ratio and cation:anion ratio from the $CuVO_3$ composition were small, but measurable. On the other hand, the new $CoVO_3$(I) phase appears to be stoichiometric from magnetic measurements and by the homogeneous nature of the product. A stoichiometric high-pressure $CuVO_3$ phase might also be expected to have the same structure as $CoVO_3$(I). It has been shown that $CuVO_3$(I), which is isostructural with $CoVO_3$(I), is indeed nearly stoichiometric and that $CuVO_3$(II), the ilmenite-type product, is significantly off stoichiometry.

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