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Characterization of $MnCrO_3$ and $CrMnO_4$

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Received May 12, 1976 AIC603495

The crystallographic, magnetic, and electrical transport data of two high-pressure phases, $MnCrO_3$ and $CrMnO_4$, are presented. Thermal treatment of these two phases yield the same spinel, $Mn_{1.5}Cr_{1.5}O_4$, which is also characterized. The triclinic, distorted-corundum phase $MnCrO_3$ is an antiferromagnetic semiconductor having a Weiss constant of −245 K and a magnetic moment consistent with the formulation $Mn^{III}Cr^{III}O_3$ possessing high-spin manganese(III). $CrMnO_4$ is ferrimagnetic having a Néel temperature of 187 K. From crystal chemistry data and magnetic properties, the orthorhombic, distorted-rutile compound is believed to have the formulation $Cr^{III}Mn^{V}O_4$.

Introduction

The corundum structure of Al_2O_3 consists of a close-packed hexagonal oxygen array that is distorted by electrostatic repulsions between pairs of Al^{3+} ions in face-shared octahedra. The metal atoms fill two-thirds of the available octahedral sites, and the octahedral-site pairs are ordered along the *c* axis of the unit cell. Disordered ABO_3 compounds, where A and B are trivalent metal ions of approximate ionic radii 0.50–0.80 Å, also have the corundum structure. If the A and B cations order into like-atom basal-plane layers that alternate along the hexagonal *c* axis, the structure becomes that of ilmenite, $Fe^{II}Ti^{IV}O_3$. The ilmenite structure is normally found for octahedral-site A^{2+} and B^{4+} cations.

Sawamoto[2a] has reported the high-pressure preparation of $MnCrO_3$. This compound was claimed to possess a distorted ilmenite structure and to contain low-spin Mn(III). We report here its synthesis by two different chemical routes and its magnetic and transport properties. A more complete characterization of the high-pressure $CrMnO_4$ phase is also presented. Some properties of this latter compound were presented in ref 2b.

Experimental Procedure

Reagents. Chromium(III) oxide was prepared in a reactive form by the low-temperature (400 °C) decomposition of Baker Analyzed chromium(III) oxalate. The black product was found to have a powder diffraction pattern identical with that given for Cr_2O_3 prepared at higher temperature. MnO and Mn_2O_3 obtained from the Diamond Shamrock Chemical Co. were used directly as received. Their respective powder patterns compared well with those reported in the literature. Chromium(IV) oxide was prepared from the hydrothermal reaction of Cr_2O_3 and CrO_3 at 400 °C and 3 kbars pressure in a sealed platinum capsule. The tetragonal cell parameters of the product, dried in O_2 at 300 °C for 1 h, were $a = 4.4199 \pm 6$ and $c = 2.9164 \pm 4$ Å. This ferromagnetic reagent had a Curie temperature of 125 °C. Anal. Calcd for CrO_2: O, 38.10; weight loss on reduction to Cr_2O_3, 9.54%. Found: O, 39.13; weight loss, 10.05%.

Manganese(IV) oxide was prepared by the thermal decomposition of $Mn(NO_3)_2 \cdot 6H_2O$ in an O_2 atmosphere at 500 °C for 15 h. The tetragonal cell parameters were $a = 4.3977 \pm 3$ and $c = 2.8728 \pm 3$ Å. Anal. Calcd for MnO_2: O, 36.81; weight loss on reduction to MnO, 18.40%. Found: O, 35.97; weight loss, 18.23%.

Apparatus. X-ray data were obtained on a 114.6-mm diameter Debye–Scherrer camera or on a GE XRD-5 powder diffractometer utilizing Cu Kα radiation. The cell parameters were refined from the powder data with a least-squares computer program.

Thermal analyses (DTA, TGA, and DSC) were performed on a Du Pont Model 990 thermal analyzer. The studies were performed in a gettered argon atmosphere at a heating rate of 20°/min or in a hydrogen/argon atmosphere at a heating rate of 15°/min.

Magnetic data were obtained on a Faraday-type magnetic system utilizing a Cahn microbalance. The samples were suspended in a helium atmosphere at a reduced pressure (100–200 Torr). The low-temperature cell was calibrated with a $HgCo(SCN)_4$ standard ($\chi_g(20\ ^\circ C) = 16.44 \times 10^{-6}$ emu/g and $\Theta = +4$ K). The high-temperature cell (300–620 K) was calibrated with high-purity Gd_2O_3 ($\chi_g(20\ ^\circ C) = 135 \times 10^{-6}$ emu/g and $\Theta = -18$ K).

The reactions were carried out in gold capsules in a belt-type apparatus at 60–65 kbars and 1000 °C. The reaction time was 2 h in each preparation. The samples were subsequently quenched to ambient temperature before the pressure was slowly released. A Heathkit vacuum-tube voltmeter was used to obtain electrical data from −196 to +300 °C by a two-probe method on dense polycrystalline chunks of the products.

$MnCrO_3$. The synthesis of $MnCrO_3$ was investigated according to two separate chemical routes

$$MnO + CrO_2 \rightarrow MnCrO_3 \quad \text{(method A)}$$

$$Mn_2O_3 + Cr_2O_3 \rightarrow 2MnCrO_3 \quad \text{(method B)}$$

The reactions were carried out at 60–65 kbars; the x-ray powder patterns of the two products were similar. The data indicated a triclinic distortion of the corundum or ilmenite structure. The products showed no traces of the reactants or other impurities. The powder pattern of the product prepared by method B was suitably indexed on a triclinic basis with the following cell dimensions: $a = 5.112 \pm 5$, $b = 5.381 \pm 6$, $c = 4.980 \pm 4$ Å; $\alpha = 89.67 \pm 4$, $\beta = 117.83 \pm 3$, $\gamma = 62.58 \pm 3°$. The unit-cell volume is 103.19 Å^3. The *d* values, intensities, and *hkl* indexing are similar to those reported by Sawamoto.[2a] The triclinic cell can be transposed to a pseudohexagonal (corundum) cell where $a \approx 5.05$ and $c \approx 13.75$ Å. The c/a ratio for such a cell is 2.72.

Magnetic measurements were made on the two products, and the susceptibilities of the two materials were within 2% of each other. The low-temperature data on the product prepared by method A gave $\mu_{eff} = 39.9^{1/2}\ \mu_B$ and $\Theta = -284$ K. The low- and high-temperature data for the product prepared by method B yielded $\mu_{eff} = (38.4 \pm 5)^{1/2}\ \mu_B$ and $\Theta = -245$ K (Figure 1). No field dependence was noted between 80 and 615 K.

A DSC experiment on the product from method A showed no trace of CrO_2, which would exhibit a transition at the Curie temperature, $T_C = 398$ K. DTA showed an irreversible exotherm at 950 °C. TGA showed a weight loss commencing at 690 °C and continuing to 1150 °C. The total weight loss was 3.45%, and the brownish black residue had the spinel structure.

The theoretical weight loss for the reaction

$$6MnCrO_3 \rightarrow 4Mn_{1.5}Cr_{1.5}O_4 + O_2\uparrow$$

is 3.44%. The spinel product presumably has the formal ion distribution $Mn^{II}[Mn^{III}_{0.5}Cr^{III}_{1.5}]O_4$, with high-spin Mn^{3+} ions in octahedral sites. Indexing of the powder pattern was consistent with the space group *Fd*3*m* and a cell dimension of 8.455 Å. This same spinel can be formed by heating a stoichiometric mixture of Cr_2O_3 and Mn_2O_3 to 1000 °C for 20 h, even in a sealed system. It was obtained previously[2b] from the thermal decomposition of $CrMnO_4$.

Electrical resistivity data on high-density $MnCrO_3$ disks from both preparative methods showed semiconducting behavior between −193 and +300 °C. The linear region in the log (resistivity) vs. $1/T$ plot showed an activation energy of 0.47 eV between 250 and 290 K.

$CrMnO_4$. The synthesis of $CrMnO_4$ was carried out under high pressure by the reaction of stoichiometric amounts of MnO_2 and CrO_2. Only at this composition in the CrO_2–MnO_2 system does the resulting phase exist. The powder diffraction data are given in Table I. The orthorhombic cell dimensions are $a = 4.339 \pm 1$, $b = 4.441 \pm 3$, and $c = 2.888 \pm 1$ Å. The unit cell volume is 56.42 ± 3 Å^3.

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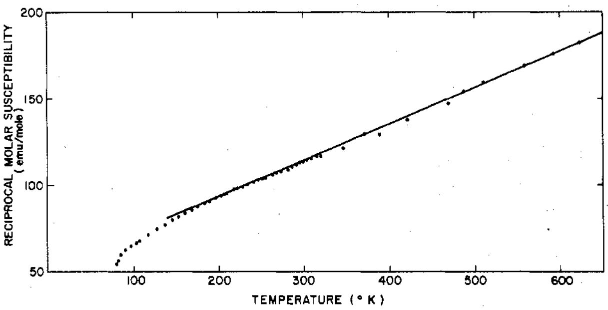

Figure 1. Reciprocal molar susceptibility of $MnCrO_3$ vs. absolute temperature.

Table I. Crystallographic Data for the Various Cr/Mn/O Derivatives

Orthorhombic $CrMnO_4$				Cubic $Mn_{1.5}Cr_{1.5}O_4$ spinel			
hkl	*I*	*d*(obsd), Å	*d*(calcd), Å	*hkl*	*I*	*d*(obsd), Å	*d*(calcd), Å
110	100	3.1253	3.1252	111	25	4.8754	4.8756
011	40	2.4233	2.4213	220	50	2.9850	2.9857
101	60	2.4162	2.4144	311	100	2.5454	2.5462
200	2	2.2017	2.1994	222	5	2.4375	2.4378
111	20	2.1210	2.1212	400	20	2.1098	2.1112
210	2	1.9722	1.9709	422	10	1.7234	1.7238
121	20	1.6350	1.6344	511	30	1.6252	1.6252
211	40	1.6284	1.6280	440	45	1.4932	1.4928
220	15	1.5617	1.5626	533	5	1.2880	1.2878
002	10	1.4436	1.4442	622	2	1.2734	1.2731
310	2	1.3934	1.3923	630	2	1.2592	1.2589
112	15	1.3109	1.3110				

The low-temperature magnetic data[2b] suggested a ferrimagnetic Néel temperature of 187 K in a magnetic field of 300 G. The saturation magnetization obtained from the reciprocal field vs. magnetization at 4.2 K was 21.8 emu/g, which corresponds to 0.66 μ_B per $CrMnO_4$ formula. Collinear ferrimagnetism with spin-only atomic moments would give 1.0 μ_B for the two possible ionic configurations Cr^{4+} (d^2)–Mn^{4+} (d^3) and Cr^{3+} (d^3)–Mn^{5+} (d^2). The compound was investigated in the paramagnetic region to 650 K in order to distinguish between these two possibilities. The data (Figure 2) show a small anomaly due to a trace of unreacted, ferromagnetic CrO_2 (T_C = 398 K). The dashed line in the figure shows a correction to the data if a 2.5% ferromagnetic impurity is subtracted from the susceptibility data. Such a correction yields an effective moment of $20.0^{1/2}$ μ_B and $\Theta = 52$ K.

The magnetic susceptibility was field dependent to about 385 K. On cooling from the highest temperatures (650 K), the susceptibility was reduced indicating slight decomposition of the sample.

A DSC experiment with $CrMnO_4$ showed no transition on heating to 530 °C. This supports the fact that the CrO_2 concentration in the product is exceedingly small. The DTA plot shows a strong irreversible transition commencing at 653 °C (maximum at 715 °C). A TGA experiment was carried out to measure the effect of heating $CrMnO_4$ to 1000 °C. A weight loss of 12.0% was noted between 600 and 970 °C. A theoretical weight loss of 12.5% is calculated for the reaction

$$3CrMnO_4 \rightarrow 2Mn_{1.5}Cr_{1.5}O_4 + 2O_2\uparrow$$

The dark brown residue in the TGA experiment was a spinel with a unit cell dimension 8.455 Å.

The electrical resistivity of a polycrystalline chunk of the $CrMnO_4$ derivative showed semiconducting behavior (decrease in resistance as the temperature was increased) throughout the temperature range studied. An activation energy of 0.15 eV was calculated from the linear portion (200–300 K) in the log (resistivity) vs. reciprocal temperature plot of the data.

$Mn[Mn_{0.5}Cr_{1.5}]O_4$ Spinel. The spinel residues formed by the thermal decomposition of $MnCrO_3$ and $CrMnO_4$ exhibit no tetragonal distortion at room temperature. A listing of the calculated and observed *d* values is given in Table I. This same product was obtained by Speidel and Muan,[3] who studied the solid-solution formation between Mn_2O_3 and Cr_2O_3. They noted the production of a spinel phase above 700 °C for the equimolar composition.

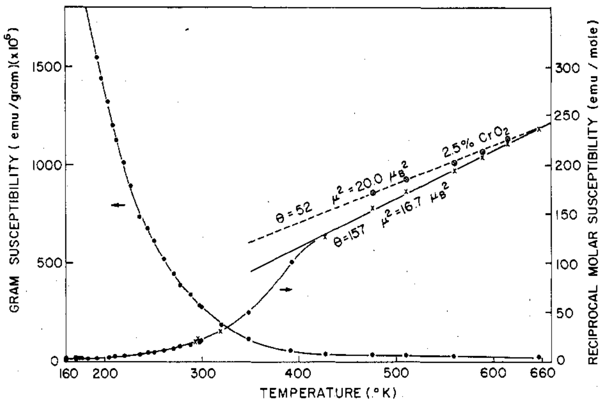

Figure 2. Magnetic properties of $CrMnO_4$ as a function of absolute temperature. The solid line in the molar susceptibility plot represents the observed data. The dotted line represents the data corrected by subtraction of a 2.5% impurity of ferromagnetic CrO_2 from the observed data.

High-temperature magnetic susceptibility measurements gave $\Theta = -317$ K and $\mu_{eff} = 62.1^{1/2}$ μ_B. No field dependence was noted between room temperature and 657 K.

Discussion

The magnetic data for $MnCrO_3$ are consistent with the ionic configuration $Mn^{III}Cr^{III}O_3$ and high-spin ionic moments, which would give a spin-only $\mu_{eff} = 39.0^{1/2}$ μ_B compared to the observed $\mu_{eff} = (38.4 \pm 5)^{1/2}$ μ_B. Octahedral high-spin Mn^{3+} ($t_{2g}{}^3e_g{}^1$) is commonly found in oxides, but a cooperative Jahn–Teller distortion of the octahedral polyhedra occurs when the Mn^{3+} ion concentration is high, as in Mn_2O_3, Mn_3O_4, MnO(OH), and $LaMnO_3$.[4]

The formal oxidation states Cr^{3+} and Mn^{3+} are compatible with a disordered corundum structure, and the distortion from hexagonal to triclinic symmetry probably is due to a cooperative Jahn–Teller distortion associated with the Mn^{3+} ions.

Further support for a distorted corundum structure rather than a distorted ilmenite structure comes from the volume vs. radii plot of Figure 3. The mixed corundum compounds of composition $A^{III}B^{III}O_3$ seem to possess larger unit cell volumes than the normal corundum derivatives and the ordered $A^{II}B^{IV}O_3$ ilmenite phases. This is most certainly due to the random packing of A^{3+} and B^{3+} ions within layers of the corundum structure. Solid solutions between A_2O_3 and B_2O_3 corundum phases have volumes that increase to a maximum as the 1:1 stoichiometry is approached.[5] The packing of large A^{2+} ions and small B^{4+} ions in alternate layers (allowing no random mixing within a layer) leads to more efficient packing and smaller unit cell volumes. The ilmenite compositions, therefore, lie below the normal corundum curve in Figure 3.

The line in Figure 3 represents the corundum field as published in ref 6; it shows slight curvature at large volumes and high average ionic radii.[7] The compounds of Figure 3, arranged in order of increasing volumes, and with high-pressure phases in italics, are as follows: for ilmenite, $NiMnO_3$, $CoMnO_3$, *$MgMnO_3$*, *$NiVO_3$*, *$MgVO_3$*, *$ZnMnO_3$*, *$CuVO_3$*, *$CoVO_3$*, $NiTiO_3$, $MgTiO_3$, $CoTiO_3$, $ZnTiO_3$, $FeTiO_3$, *$MnVO_3$*, $MnTiO_3$, $CdTiO_3$; for corundum, Al_2O_3, Ga_2O_3, Cr_2O_3, V_2O_3, Fe_2O_3, Rh_2O_3, Ti_2O_3; for mixed corundum, $Cr_{1.9}V_{0.09}Fe_{0.01}O_3$, *$NiCrO_3$*, $VCrO_3$, $FeCrO_3$, *$GaFeO_3$*, $CrRhO_3$, $FeVO_3$, $FeRhO_3$, *$MnCrO_3$*.

From its unit cell volume, $MnCrO_3$ falls further above the corundum line than any of the known mixed-corundum phases displayed in Figure 3. Therefore, $MnCrO_3$ appears to be a distorted-corundum and not a distorted-ilmenite product as previously reported by Sawamoto.[2a]

The structure of $CrMnO_4$ is unusual; it adopts a distorted rutile structure similar to that observed for $CaCl_2$ and the

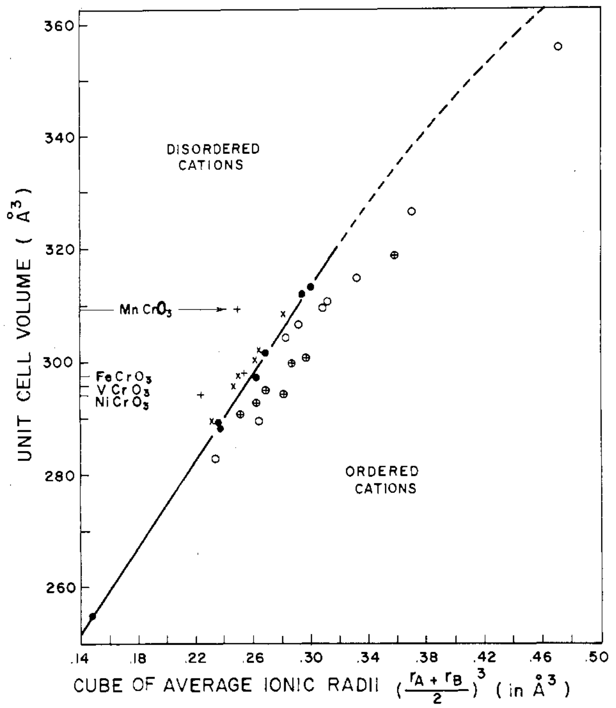

Figure 3. Plot of unit cell volumes vs. the cube of the average ionic radii for various A_2O_3 (corundum) and ABO_3 (mixed corundum and ilmenite) phases. The line and solid circles represent the pure corundum field. The mixed corundum compounds are represented by X (ambient pressure compounds) and by + (high-pressure phases). The ilmenite derivatives are represented by ○ (ambient-pressure phases) and by ⊕ (high-pressure phases).

high-pressure form of PtO_2. The high-temperature $\mu_{eff} = 20^{1/2}$ μ_B is consistent with the ionic configuration $Cr^{III}Mn^{V}O_4$, which would have a spin-only $\mu_{eff} = 23^{1/2}$ μ_B.

The magnetic and crystallographic data for the spinel, $Mn_{1.5}Cr_{1.5}O_4$, are consistent with the ionic configuration $Mn^{II}[Mn^{III}_{0.5}Cr^{III}_{1.5}]O_4$, the observed $\mu_{eff} = 62.1^{1/2}$ μ_B being in good agreement with the corresponding spin-only $\mu_{eff} = 69.5^{1/2}$ μ_B.

Acknowledgment. B.L.C. wishes to thank the University of Connecticut Research Foundation for the financial assistance in obtaining high-pressure equipment and for the support given in establishing a high-pressure program. The manganese oxides were kindly donated by the Diamond Shamrock Chemical Co.

Registry No. $MnCrO_3$, 37267-30-4; $CrMnO_4$, 60645-63-8; $Mn_{1.5}Cr_{1.5}O_4$, 60645-62-7; CrO_2, 12018-01-8; MnO_2, 1313-13-9; Cr_2O_3, 1308-38-9; MnO, 1344-43-0.

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(7) Private communication with R. D. Shannon indicates that the curvature at high ionic radii is a better representation of the relationship of volume vs. radii for the corundum structures.

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Kinetics of Isotopic Oxygen Exchange between Water and Vanadium(V) in Basic Media

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Received June 1, 1976 AIC60406U

The exchange between ^{18}O-labeled solvent water and vanadium(V) in basic media ($[OH^-] \geq 0.1$ M) has a half-time of ~20 s at 0 °C and is measurable by conventional sampling methods. Under selected conditions it has been shown that there are 4.0 ± 0.1 equivalent oxygens associated with aqueous vanadium(V) with half-times of exchange as great as 30 s at 0 °C. This supports the orthovanadate (VO_4^{3-}) structure as the predominant species in water at high pH. The rate of exchange follows the equation $R = k[VO_4^{3-}]$ and is essentially independent of $[OH^-]$ and of the nature of other ions in the medium. The rate is an inverse function of ionic strength and has activation parameters of $\Delta H^\ddagger = 22.0 \pm 0.8$ kcal/mol and $\Delta S^\ddagger = 14.4 \pm 1$ cal deg^{-1} mol^{-1} ($\mu = 1.4$). The reaction mechanism for water exchange is discussed.

Introduction

Progress in understanding the composition of aqueous vanadium(V) solutions, the structure of the oxo-polyanions present, and the kinetics of their interconversion has been hindered by the lack of well-characterized ions of "known" aqueous structure which could be used as "tie-points" in studies of the oligomerization process. An excellent review was presented by Pope and Dale in 1971.[1] In most studies it has been assumed that tetrahedral VO_4^{3-} in strongly alkaline solution and linear VO_2^+(aq) in strongly acidic media are the species present. It has been generally found that the experimental facts are consistent with these assumptions. In alkaline media, for example, investigations of rates of diffusion,[2] emf,[3] ^{51}V NMR,[4] Raman spectra,[5] and light scattering[6] are consistent with tetrahedral VO_4^{3-} in solution as is found in the solid state. Because of the well-established tendency of vanadium(V) to expand its coordination sphere from 4 to 5 or 6 as seen in solid structures,[7] a concern remains that vanadium(V) may exist, for example, as 5- or 6-coordinate $VO_2(OH)_3^{2-}$ or $VO_2(OH)_4^{3-}$ which certain types of studies seem to favor.[8]

This isotopic water-exchange study was undertaken with the hope of finding a slow enough rate of exchange to allow the number of oxygens around vanadium(V) to be counted in dilute water solution. We were encouraged along these lines by the recent observations[9] which showed $V_{10}O_{28}^{6-}$ to ex-