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Preparation and Characterization of $MgMnO_3$ and $ZnMnO_3$

B. L. CHAMBERLAND†, A. W. SLEIGHT, AND J. F. WEIHER

Central Research Department,‡ E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898

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Two new ilmenites of tetravalent manganese have been prepared at high pressures: $MgMnO_3$: $a = 4.945$ Å, $c = 13.73$ Å; and $ZnMnO_3$: $a = 4.965$ Å, $c = 13.80$ Å. The compounds were found to be antiferromagnetic, and $MgMnO_3$ possessed semiconducting electrical properties.

Introduction

Ilmenite-type compounds of formula $AMn^{IV}O_3$ have been reported where A is Ni (*1*), (*2*) and Co (*2*). These particular compositions are ferrimagnetic and semiconducting (*2*), (*3*). Other compounds where A is Ca, Ba, or Sr have been found to possess the cubic perovskite structure or a closely related hexagonal layer-type structure (*4–6*).

The objective of this work was to prepare and characterize other possible $AMn^{IV}O_3$ compositions having the ilmenite-type structure.

Experimental

The reactants were reagent grade or better. Manganese dioxide was prepared by the thermal decomposition of $Mn(NO_3)_2 \cdot 6H_2O$ in oxygen at 500°C. $MgMnO_3$ was prepared either by the hydrothermal reaction of $MgCl_2 \cdot 6H_2O$, Li_2MnO_3, and $KClO_3$ or by the solid state reaction of MgO and MnO_2 at high pressure. Pure $ZnMnO_3$ was formed by the high-pressure reaction of ZnO and MnO_2 mixtures containing small amounts of $KClO_3$.

Hydrothermal reactions were carried out in collapsible gold ampoules held at 700°C and 3000 atm for about six hours. High-pressure experiments were performed in a tetrahedral anvil press (*7*) at 900–1000°C and 65 kbars in platinum or gold capsules.

X-ray powder patterns were obtained on the ilmenite products at 25°C with a Hägg-Guinier camera using strictly monochromatic $CuK\alpha_1$ radiation and an internal standard of KCl ($a = 6.2931$ Å). The cell dimensions were refined by least squares.

Electrical resistivities were measured on single crystals of $MgMnO_3$ by the conventional four-probe method (*7*). Magnetic susceptibility data were obtained on powdered samples of the ilmenites by the Faraday method using a Cahn RG microbalance (*4*).

Differential thermal and thermogravimetric analyses were performed on a Du Pont 900 thermal analyzer.

Results

Analytical and crystallographic data on $MgMnO_3$ and $ZnMnO_3$ are presented in Table I. The magnetic susceptibility results are shown in Fig. 1.

$MgMnO_3$

This compound was isolated with the ilmenite-type structure whether prepared hydrothermally or at high pressure. Attempts to prepare $MgMnO_3$ at atmospheric pressure produced a cubic phase that was found to be oxygen deficient with the approximate composition $MgMnO_{2.9}$. Differential thermal analysis on pure $MgMnO_3$ indicated decomposition at 580°C with the loss of small amounts of oxygen. The residue from the dta experiment was found to be identical to the $MgMnO_{2.9}$ phase obtained from reactions carried out at 600–1000°C in 1 atm of O_2.

Electrical resistivity data showed semiconducting behavior in the region 4.2–298°K. The activation energy was 1 eV, and the room-temperature resistivity was approximately 10^9 Ω cm.

The slope of the line for $MgMnO_3$ in Fig. 1 indicates an effective moment of 3.48 μB per Mn, and the intercept of this line, θ, is −36°K. Although no well-defined Néel temperature was observed, departure from Curie–Weiss behavior begins at about 40°K.

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† Present address: Department of Chemistry, University of Connecticut, Storrs, Connecticut.

‡ Contribution No. 1610.

TABLE I

	Hexagonal Cell Dimensions		Analytical Results		
Compound	a (Å)	c (Å)	% A	% Mn	% O
$MgMnO_3$	4.945	13.73	18.9(19.1)[a]	42.7(43.2)	37.8(37.7)
$ZnMnO_3$	4.965	13.80			28.4(28.5)

[a] Numbers in parentheses denote theoretical values for the given composition.

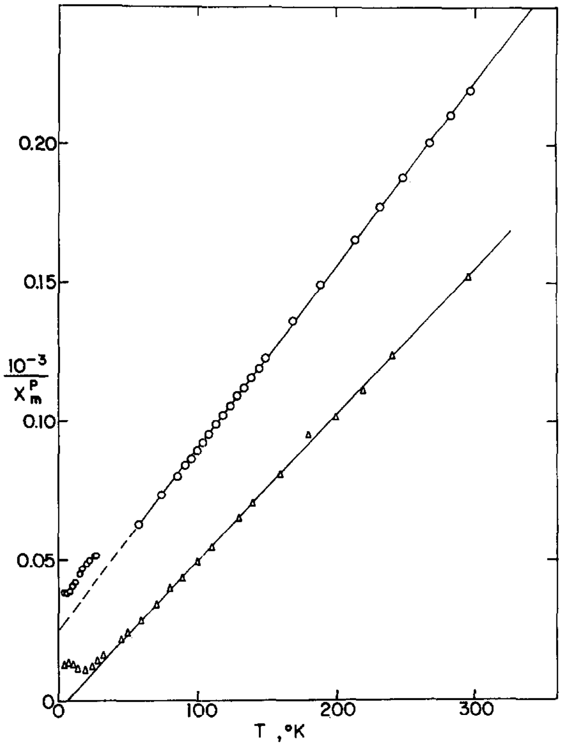

FIG. 1. Magnetic susceptibility data from $MgMnO_3$ (circles) and $ZnMnO_3$ (triangles).

$ZnMnO_3$

The zinc derivative could only be prepared at 65 kbars and 900°C. Attempts to prepare an ilmenite phase at atmospheric or 3 kbars yielded only spinel phases. From the data shown in Fig. 1, $ZnMnO_3$ has an effective moment of 3.90 μB, a θ of +6°K, and a Néel temperature of 18°K.

TABLE II

CRYSTALLOGRAPHIC DATA FOR $MgMnO_3$ AND $ZnMnO_3$

	$MgMnO_3$			$ZnMnO_3$		
h k l	$d_{(obs)}$	$d_{(calc)}$	I/I_o	$d_{(obs)}$	$d_{(calc)}$	I/I_o
0 0 3	4.5775	4.5769	40	—	—	—
1 0 1	4.0892	4.0884	20	4.1062	4.1059	5
0 1 2	3.6335	3.6336	35	3.6511	3.6501	50
1 0 4	2.6778	2.6785	80	2.6919	2.6918	85
1 1 0	2.4725	2.4726	80	2.4830	2.4828	100
0 1 5	2.3106	2.3117	5	2.3234	3.3236	20
0 0 6	—	—	—	2.3007	2.3011	5
1 1 3	2.1752	2.1754	80	2.1848	2.1851	30
0 2 1	—	—	—	2.1241	2.1246	5
2 0 2	—	—	—	2.0528	2.0529	5
0 2 4	—	—	—	1.8248	1.8250	45
1 0 7	—	—	—	1.7920	1.7928	5
2 0 5	—	—	—	1.6963	1.6965	10
1 1 6	1.6795	1.6795	100	1.6876	1.6877	40
2 1 1	1.6083	1.6076	5	1.6150	1.6143	2
2 1 4	1.4641	1.4641	40	1.4705	1.4705	40
3 0 0	1.4276	1.4276	50	1.4336	1.4335	60
1 2 5	1.3949	1.3945	5	1.4013	1.4008	5
2 0 8	—	—	—	1.3460	1.3459	5
0 3 3	1.3642	1.3628	20	—	—	—
1 0 10	1.3076	1.3075	20	1.3145	1.3146	10
1 1 9	1.2985	1.2984	20	1.3053	1.3050	15
2 2 0	1.2364	1.2363	10	—	—	—

Discussion

Ilmenite-type compounds of the formula ABO_3 are well-known where the B ion is Ti^{4+}. The A cation for the titanate ilmenites includes Mg, Fe, Ni, Co, Mn, Cd, and Zn (*8*), (*9*). All these compositions can be prepared at atmospheric pressure. Other ilmenite compounds possessing the ABO_3 formula have to be prepared under special conditions. $MgSnO_3$, $CdSnO_3$, and $NiMnO_3$ have been reported (*10*)–(*12*) by the low-temperature decomposition of mixed metal hydroxides, oxalates, or carbonates. Ilmenites of the type $CuVO_3$, $MgGeO_3$, $ZnGeO_3$, $MnGeO_3$, and $CoMnO_3$ have only been prepared (*13*)–(*17*) under high pressure conditions.

It has been shown that $MgMnO_3$ can be prepared at 3000 atm, but $ZnMnO_3$ was only made at 65 kbars. Zn^{2+} normally prefers tetrahedral coordination but has been found to exist in octahedral coordination especially in compounds prepared at high pressure. Both divalent ions, Mg^{2+} and Zn^{2+}, are found in octahedral sites in the titanate ilmenites.

The crystallographic data (Table II) show the ilmenite ordering lines, and the indices are consistent with the rhombohedral absence rule $-h + k + l = 3n$ and the space group $R\bar{3}$.

The magnetic data for both $ZnMnO_3$ and $MgMnO_3$ show an observed μ_{eff} close to that for Mn^{4+} free-spin value of 3.88 μB. The slight deviation from the theoretical value can be accounted for by possible disordering of *A* and *B* sites in the ilmenite structure. This defect would create near neighbor Mn^{4+}–O–Mn^{4+} linkages along the *c* axis which would affect the moment. The amount of disorder could be quite small to account for the slight deviation. Another possible reason for the observed decreased moment in $MgMnO_3$ could be the spin-orbit coupling that tends to lower the moments in some tetravalent manganese derivatives. These two ilmenites are the first examples in which the magnetic moment originates only from the transition metal B^{4+} ion.

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