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A High-Pressure Modification of $MgVO_3$

B. L. CHAMBERLAND, P. S. DANIELSON, AND C. W. MOELLER

Department of Chemistry and Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06268

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The preparation of a high-pressure form of $MgVO_3$ has been accomplished utilizing two independent synthesis methods. The triclinic, ilmenite-type phase has been characterized by its crystallographic, magnetic, and electrical properties. Its structure is believed to be similar to that previously observed for other ilmenite-type AVO_3 derivatives ($CoVO_3$, $NiVO_3$, and $MnVO_3$). The properties of $MgVO_3$ appear to be intermediate between the localized electron model found in $MnVO_3$, $CoVO_3$, and $NiVO_3$, and the delocalized electron regime observed in $CuVO_3$.

Introduction

The ambient pressure form of $MgVO_3$ was first reported by Rüdorff and Reuter (*1*) who also presented some magnetic properties. The structure of $MgVO_3$ has recently been described by Cros, *et al.* (*2*), and by Bouloux *et al.* (*3*) from independent single crystal studies. In both structural determinations the V^{4+} and Mg^{2+} ions occupy square pyramidal sites but Bouloux *et al.* (*3*) assign the structure to the *Cmc*2_1 space group while Cros *et al.* (*2*) refined their crystallographic data in the more symmetrical *Cmmm* space group.

A study of the magnetic properties for the ambient pressure phase and the preparation and characterization of the high-pressure $MgVO_3$ phase is presented. The structural relationship between the high-pressure $MgVO_3$ and other isostructural AVO_3 derivatives is described.

Reactants and Preparation

High-purity VO_2 was prepared by the symproportionation reaction of V_2O_3 and V_2O_5 in a sealed, evacuated, fused silica tube at 1000° for 24 hr. The blue-black product was shown to be VO_2 by its X-ray powder pattern and its crystallographic transition at 68°C. Ambient pressure $MgVO_3$ (designated in this paper as $MgVO_3$, whereas $MgVO_3$(I) denotes the high-pressure form) was prepared by the reaction of reagent grade MgO with VO_2 in an evacuated fused silica tube at 1000° for 24 hr. The dark brown product was characterized by its X-ray powder pattern as pure $MgVO_3$.

High-pressure $MgVO_3$(I) was prepared by two different preparative methods, expressed by the following equations:

$$MgO + VO_2 \xrightarrow{P} MgVO_3(I) \qquad \text{Method A}$$

$$MgVO_3 \xrightarrow{P} MgVO_3(I) \qquad \text{Method B}$$

Both reactions were carried out at 1000° and 60–65 kbar pressure for 1 hr. The reactants were placed in gold capsules (to maintain the oxygen stoichiometry) and, after the prescribed thermal treatment at the applied pressure, was then rapidly quenched to room temperature prior to the release of pressure.

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TABLE I

CRYSTALLOGRAPHIC DATA FOR THE AMBIENT PRESSURE FORM OF $MgVO_3$

a (Å)	b (Å)	c (Å)	Vol. (Å^3)	Reference
5.291(3)	10.018(5)	5.239(3)	277.7	(*2*)
5.243(2)	10.028(2)	5.293(2)	278.3	(*3*)
5.240(4)	10.012(12)	5.288(4)	277.4(4)	This work

The high-pressure reactions were conducted in a belt-type apparatus in a 500-ton press. The temperature and pressure calibrations were carried out in separate experiments and are believed to be accurate to within 10% of the conditions reported.

Characterization

Crystallographic studies utilized a G.E. XRD-5 powder diffractometer or a Guinier–deWolff camera with Ni-filtered, Cu$K\alpha_1$ radiation. Thermal analyses were performed with a du Pont Model 990 thermal analyzer equipped with DSC, DTA and TGA modules. All thermal analyses were performed in a gettered argon atmosphere to prevent oxidation of the products.

The magnetic properties were obtained by the Faraday method using a 7-in. magnet and a Cahn microbalance. The calibration of the system has been previously described (*4*).

Two-probe electrical measurement of the resistivity on a dense cylindrical disk (1 mm thick × 3.8 mm diameter) of $MgVO_3$(I) showed high resistance, semiconductivity behavior at low temperature and moderate resistance at room temperature. The resistance vs reciprocal temperature plot showed two linear regions with a discontinuity at 300°K. The activation energies calculated from the two linear regions were 0.61 eV (at low temperature) and 0.41 eV above 300°K.

Results

The dark brown $MgVO_3$ product was indexed on an orthorhombic basis and its unit cell parameters compare favorably with those of other authors (see Table I). The magnetic properties for the $MgVO_3$ show a Curie–Weiss behavior with a Weiss constant of -120°K and an effective magnetic moment μ_{eff} of 1.67 μ_B (see Fig. 1).

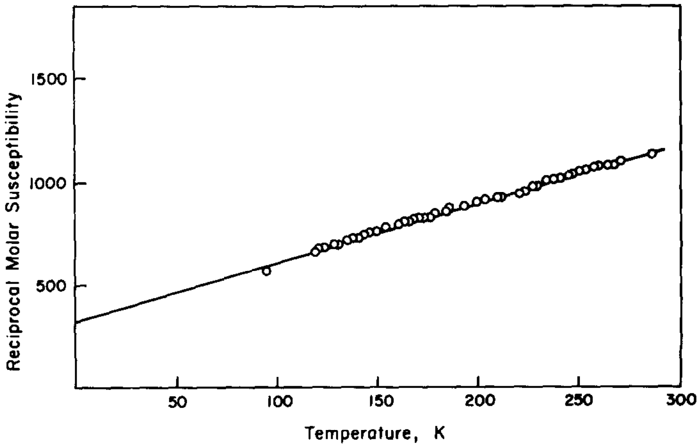

FIG. 1. Reciprocal molar susceptibility of ambient pressure $MgVO_3$ as a function of absolute temperature.

The environment of ligands about V^{4+} in $MgVO_3$ was found to be (*2*, *3*) square pyramidal with a short apical V–O distance of 1.65 Å. The four basal vanadium oxygen bond distances are: 2 at 1.92 Å and 2 at 1.97 Å. The vanadium atom is above the plane of the four basal oxygen atoms. The basal bond angle (O–V–O) is approximately 140°.

The crystal field for a square pyramidal environment predicts two low-lying degenerate orbitals (d_{xz} and d_{yz}). For π ligands, such as oxygen, approximate molecular orbital calculations (*5*) show that the energy of these particular orbitals increase while that of the d_{xy} decreases and with a bond angle of about 140° the three orbitals are strongly interacting. The unpaired electron (in a $3d^1$ system) should therefore show a reduced effective moment compared to the spin-only moment (somewhat less than 1.73 μ_B) and this is experimentally observed.

The VO_5 pyramid in $MgVO_3$ is joined by two basal edges and its apical vertex to other VO_5 square pyramids forming a two-dimensional network of joined pyramids along the *ab* plane in the structure. The V–V distance along the shared edge is 2.96 Å. This distance is very near to that given by Goodenough (*6*) for a delocalized electron regime in V^{4+} oxides ($R_c = 2.94$ Å).

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR $MgVO_3(I)$[a]

h	*k*	*l*	I_{obs}	d_{obs}	d_{calc}
0	1	0	100	4.636	4.628
0	0	1	100	4.136	4.134
1	1	0	40	4.071	4.077
1	0	0	30	3.735	3.738
1	1	−1	100	3.616	3.620
0	1	−1	30	2.755	2.755
−1	1	1	20	2.689	2.686
1	1	1	70	2.491	2.492
2	1	−1	70	2.469	2.469
1	0	−2	70	2.444	2.444
1	0	1	30	2.243	2.241
1	1	−2	30	2.184	2.185
2	2	−1	30	2.161	2.159
2	0	0	30	1.869	1.869
2	2	−2	10	1.810	1.810
−2	1	1	30	1.709	1.710
2	3	0	30	1.674	1.673
3	3	−1	30	1.453	1.454
2	0	1	30	1.439	1.439
0	1	3	30	1.423	1.424

[a] Guinier–deWolff camera utilizing Cu$K\alpha_1$ radiation.

The high-pressure $MgVO_3(I)$ modification was observed to have a triclinic distortion of the ilmenite structure and the powder diffraction data were suitably indexed on this basis (see Table II). The unit cell parameters are: $a = 4.941(2)$, $b = 5.363(4)$, $c = 4.890(3)$ Å; $\alpha = 90.95(5)$, $\beta = 118.99(4)$, and $\gamma = 63.48(3)°$. The volume of the triclinic cell is 98.0(2) Å^3. This cell can be reduced to a pseudo-rhombohedral cell of $a = 5.450$ and $\alpha = 53.89°$. This corresponds to the pseudohexagonal cell $a = 4.939$ and $c = 13.93$ Å having an axial ratio of 2.82(1).

$MgVO_3(I)$ is isostructural with several other AVO_3 derivatives which have also been prepared under high-pressure conditions. The proposed structure of $MgVO_3(I)$ is shown in Fig. 2. The octahedral VO_6 groups are face-shared, edge-shared, and vertex-shared as in the corundum and the ilmenite structures.

An ordering of metal atoms, different from that observed in the ilmenite structure, has been proposed (*7*) for $NiVO_3$ and this same

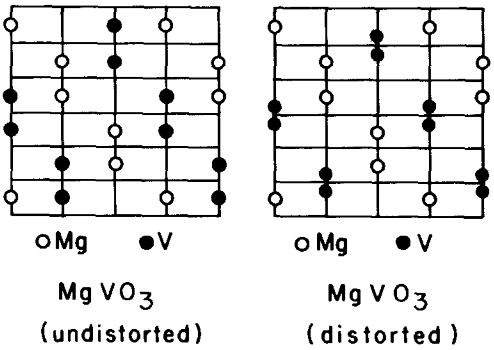

FIG. 2. The proposed structural model for the cationic distribution of metallic ions in the oxygen layer sequence. The diagram on left represents the undistorted arrangement of cations, whereas the figure on the right shows the homopolar bonding in the V–V face-shared position which leads to distortion of the structure.

TABLE III

CRYSTALLOGRAPHIC DATA FOR DISTORTED ILMENITES

	Triclinic cell						Pseudo-hexagonal cell			
Composition	*a*	*b*	*c*	*α*	*β*	*γ*	a	c	c/a (±0.01)	References
$CoVO_3$	4.980	5.411	4.929	90.04	118.76	63.44	4.985	13.97	2.80	(*8*)
$NiVO_3$	4.935	5.377	4.903	90.72	119.13	63.00	4.940	13.85	2.80	(*7*)
$MnVO_3$	5.072	5.550	5.023	90.00	118.23	63.24	5.092	14.32	2.81	(*9*)
$MgVO_3$(I)	4.941	5.363	4.890	90.95	118.99	63.48	4.939	13.93	2.82	This work
$CuVO_3$(I)	4.967	5.404	4.914	90.32	119.05	64.00	4.964	14.07	2.83	(*8*, *10*)
$CuVO_3$(II)	—	—	—	—	—	—	4.955	14.07	2.84	(*8*, *11*)

ordering is believed to be present in $MgVO_3$(I). In $MgVO_3$(I) the vanadium atoms occupy the face-shared positions with other vanadium atoms along the pseudohexagonal *c* axis. In this structure, homopolar (face-shared) V^{4+}–V^{4+} pairs are formed which distort the structure from hexagonal to triclinic symmetry. The magnetic and electrical conductivity experiments support this structural model.

Discussion

The unit cell parameters for all the high-pressure AVO_3 derivatives are given in Table III. The pseudohexagonal parameters derived from the triclinic cells are listed with corresponding axial ratios. The latter values are a measure of the interactions between V^{4+} ions in the distorted *hk*0 plane of the pseudohexagonal structure. A high *c*/*a* ratio is indicative of strong M–M interactions (*12*). $MgVO_3$(I) is intermediate between the localized electronic systems (such as $NiVO_3$, $MnVO_3$, and $CoVO_3$) and the delocalized electronic behavior found in $CuVO_3$. This suggests that the electronic interactions in $MgVO_3$(I) can possibly be probed by a temperature study of the magnetic and electrical conduction properties.

The magnetic data for $MgVO_3$(I) are shown in Fig. 3. The low temperature region is

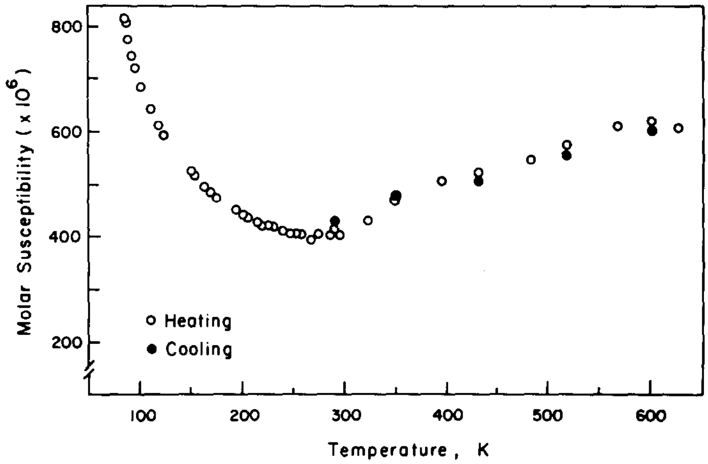

FIG. 3. The observed molar susceptibility of $MgVO_3$(I) as a function of absolute temperature.

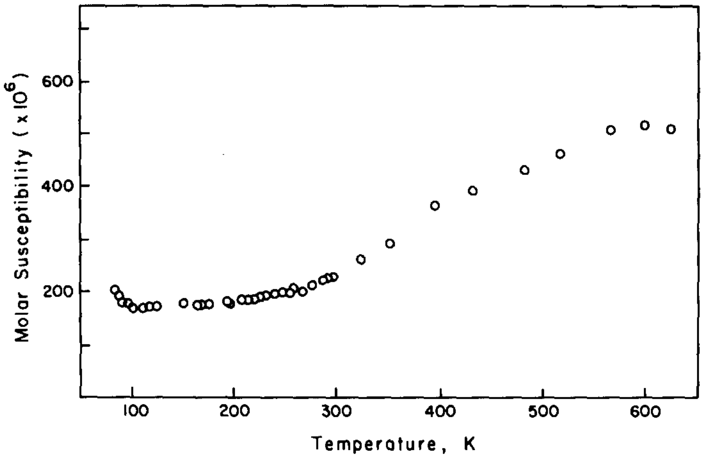

FIG. 4. The corrected molar susceptibility (removal of a 15% paramagnetic contribution from unpaired spins in Mg–V pairs) as a function of absolute temperature.

suggestive of some paramagnetic impurity (previously noted (*13*) in the magnetic data of metal-modified or nonstoichiometric VO_2). The lowest temperature portion of the $1/\chi$ vs T plot suggests about 15% unpaired electrons (free-spin calculation). This most probably results from the formation of Mg^{2+}–V^{4+} pairs (in face-shared octahedral positions) due to some random mixing of metal ions in octahedral sites. These mixed-metal pairs give rise to the increased susceptibility at low temperature. When this paramagnetic contribution is removed from the data, one obtains the data presented in Fig. 4. The low-temperature region now shows a TIP susceptibility of approximately 190×10^{-6} cgs. At 300°K an increase in molar susceptibility is indicative of delocalization of electrons in the face-shared octahedra as the homopolar bonds are broken. A similar but sharper transition is observed (*13*) in the magnetic susceptibility of monoclinic $VO_2 \rightarrow$ tetragonal VO_2. In $MgVO_3$(I) the transition does not appear to be first order and no structural transition has been observed in this temperature region.

The electrical conductivity data also suggest poor conduction at low temperature (homopolar pairs) and relatively good conduction at higher temperature (delocalization of electrons). These data are consistent with the proposed structure and the magnetic data.

It is concluded that $MgVO_3$(I) is intermediate in properties between the localized electron regime observed in $CoVO_3$, $MnVO_3$, and $NiVO_3$—whose c/a ratio are less than 2.82, and the delocalized electron picture presented for $CuVO_3$ whose c/a ratio is 2.84(1) and which has been shown to possess continuous chains of V–V atoms at 2.92 Å. The predicted critical radius for delocalized electrons in V^{4+} oxides is 2.94 Å.

Attempts are presently being made to isolate single crystals of $MgVO_3$(I) to determine its structure and the various bond distances. More precise measurement of the electrical resistivity will be performed on such crystals to confirm the localized → delocalized electronic phenomena already observed in the powdered samples.

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