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Synthesis of new transition metal nitrides, MWN_2 (M ≡ Mn, Co, Ni)

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Abstract

We report the synthesis of ternary transition metal nitrides of the formula MWN_2 for M ≡ Mn, Co, Ni by reaction of the corresponding MWO_4 with NH_3 gas at 600–700 °C. $MnWN_2$ is isostructural with the already-known $FeWN_2$, crystallizing in a hexagonal structure ($a = 2.901(2)$, $b = 16.48(5)$ Å) related to $LiMoN_2$. $CoWN_2$ and $NiWN_2$ (which are isostructural amongst themselves) adopt a different hexagonal structure with a smaller c parameter. While the Mn and Fe nitrides are semiconducting, the Co and Ni nitrides are semimetallic.

Keywords: Transition metal nitrides; Semimetallics; Semiconductors

1. Introduction

As compared with the large number of metal oxides known at present, metal nitrides constitute a small family consisting of at best a few hundred members. There is a growing interest in the synthesis of new metal nitrides because of the fascinating structure and properties exhibited by members of this family [1]. However, the synthesis of metal nitrides, especially the ternary and higher ones, is not straightforward, mainly because the free energies of formation are small, thus precluding direct synthesis using elemental nitrogen at high temperatures. Alternative strategies such as ammonolysis of metal oxide precursors [2,3] and decomposition of metal amides [4,5] have been employed for the synthesis of metal nitrides in recent times. The ammonolysis route is quite attractive because of the availability of a large number of ternary metal oxides which could be employed as precursors to nitrides. Thus, using Li_2MoO_4, $FeWO_4$, $FeMoO_4$ and Na_2WO_4 as precursors, $LiMoN_2$ [2], $FeWN_2$ [3], Fe_3Mo_3N [6] and Na_3WO_3N [7] respectively have been synthesized. Of these, $LiMoN_2$ is a novel metallic nitride crystallizing in a hexagonal structure where Mo(V) exists in trigonal prismatic coordination. $FeWN_2$ also possesses a similar hexagonal unit cell but the details of its structure and properties are not known [3].

In an attempt to understand the structure and properties of ternary transition metal nitrides of the general formula MWN_2 where M is a 3d transition metal, we investigated the formation of such phases by reaction of the corresponding MWO_4 with NH_3 gas. Here we report the successful synthesis and preliminary characterization of these nitrides for M ≡ Mn, Co, Ni.

2. Experimental details

MWN_2 (M ≡ Mn, Fe, Co, Ni) nitrides were prepared by reaction of freshly prepared MWO_4 with flowing NH_3 gas at temperatures ranging from 600 to 700 °C. The synthesis conditions are given in Table 1. In a typical synthesis the precursor oxide (about 1.5 g) in a ceramic boat was heated in a stream of NH_3 gas (about 120 cm^3 min^{-1}). After the reaction the samples

Table 1
Synthesis and characterization of MWN_2

Compound	Ammonolysis conditions	Lattice parameters (Å)		Electrical property
		a	c	
$MnWN_2$	700 °C, 14 h	2.901(2)	16.48(5)	Semiconducting
$FeWN_2$	700 °C, 15 h	2.870(2)	16.45(6)	Semiconducting
$CoWN_2$	600 °C, 20 h	2.878(3)	15.24(5)	Semimetallic
$NiWN_2$	600 °C, 20 h	2.869(3)	15.25(5)	Semimetallic

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were quenched to room temperature and the products examined by powder X-ray diffraction (Jeol JDX-8P X-ray diffractometer). While the synthesis of single-phase $MnWN_2$ and $FeWN_2$ was relatively straightforward, the synthesis of $CoWN_2$ and $NiWN_2$ required close control of the reaction temperature and duration. In many preparations metallic Co and Ni were found as impurities. Quantitative analysis of $MnWN_2$ (Mn and W by energy-dispersive X-ray analysis and N by a Heraeus CHN-O-RAPID combustion analyser) led to the composition $MnWN_{1.97\pm0.02}$. Electrical resistivity measurements were carried out on pressed pellets using a four-probe method and magnetic susceptibility measurements using a Lewis coil force magnetometer (field gradient 9.5 Oe cm^{-1} A^{-1}).

3. Results and discussion

The synthesis of $FeWN_2$ by ammonolysis of $FeWO_4$ was reported by Bem and Loye [3]. Employing this method, we could synthesize MWN_2 (M≡Mn, Co, Ni) together with $FeWN_2$ by reaction of MWO_4 with NH_3 gas at 600–700 °C. The X-ray powder diffraction patterns of all the metal nitrides (Fig. 1) are indexable on hexagonal cells similar to those of $LiMoN_2$ and $FeWN_2$. It is seen that the Mn and Fe compounds are isostructural amongst themselves, having similar unit cell dimensions. The X-ray diffraction (XRD) pattern of $MnWN_2$ (Table 2) is very similar to that of $LiMoN_2$. On the other hand, the Co and Ni compounds, which also seem to be isostructural amongst themselves, crystallize in a hexagonal structure with a smaller c parameter ($c=15.25$ Å; Table 1). This distinct decrease in the c parameter by about 1.2 Å on going from the Mn and Fe to the Co and Ni compounds probably signals a change in the anion stacking sequence or the cation coordination.

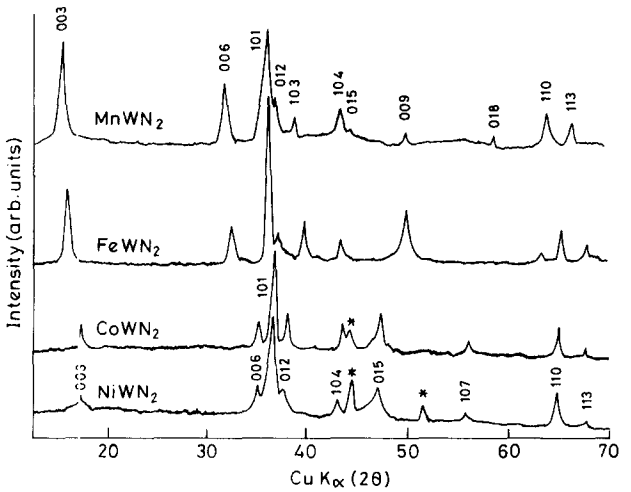

Fig. 1. Cu Kα X-ray diffraction patterns of MWN_2 (M≡Mn, Fe, Co, Ni). The asterisks indicate Co and Ni metal impurities.

Table 2
X-Ray powder diffraction data for $MnWN_2$ (unit cell parameters $a=2.901(2)$, $c=16.48(5)$ Å)

$h\ k\ l$	d_{obs} (Å)	d_{cal} (Å)	I/I_0
0 0 3	5.471	5.465	97
0 0 6	2.754	2.743	53
1 0 1	2.474	2.483	100
0 1 2	2.410	2.409	37
1 0 3	2.292	2.290	15
1 0 4	2.136	2.138	21
1 0 5	2.001	2.004	6
0 0 9	1.824	1.822	8
0 1 8	1.582	1.585	7
1 1 0	1.450	1.450	29
1 1 3	1.402	1.401	22

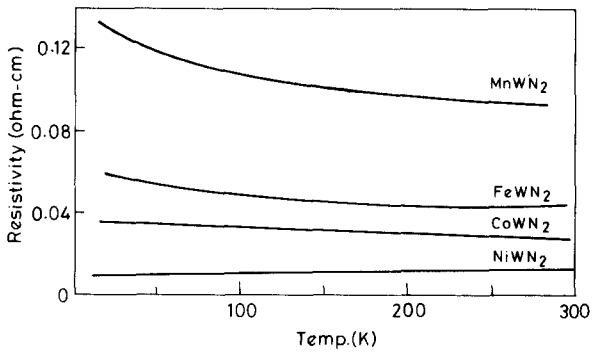

Fig. 2. Resistivity vs. temperature for MWN_2 (M≡Mn, Fe, Co, Ni).

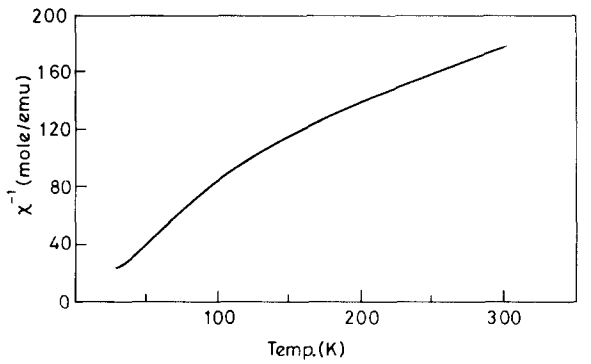

Fig. 3. Inverse magnetic susceptibility vs. temperature for $MnWN_2$.

In the ideal $LiMoN_2$ structure where nitride ions are in the AABB... sequence, Mo(V) is in trigonal prismatic coordination. In view of the close similarity of the XRD patterns of $MnWN_2$ and $FeWN_2$ to that of $LiMoN_2$, we believe that both $MnWN_2$ and $FeWN_2$ are isostructural with $LiMoN_2$. Accordingly, W(IV) would be in trigonal prismatic coordination and Mn and Fe in octahedral coordination in these nitrides. The electrical and magnetic properties of $MnWN_2$ are consistent with this structural model. The material is semiconducting (Fig. 2) and Curie–Weiss paramagnetic (Fig. 3). The magnetic moment of 5.58 μ_B obtained from the linear region of the χ_m^{-1}–T plot is consistent with octahedral

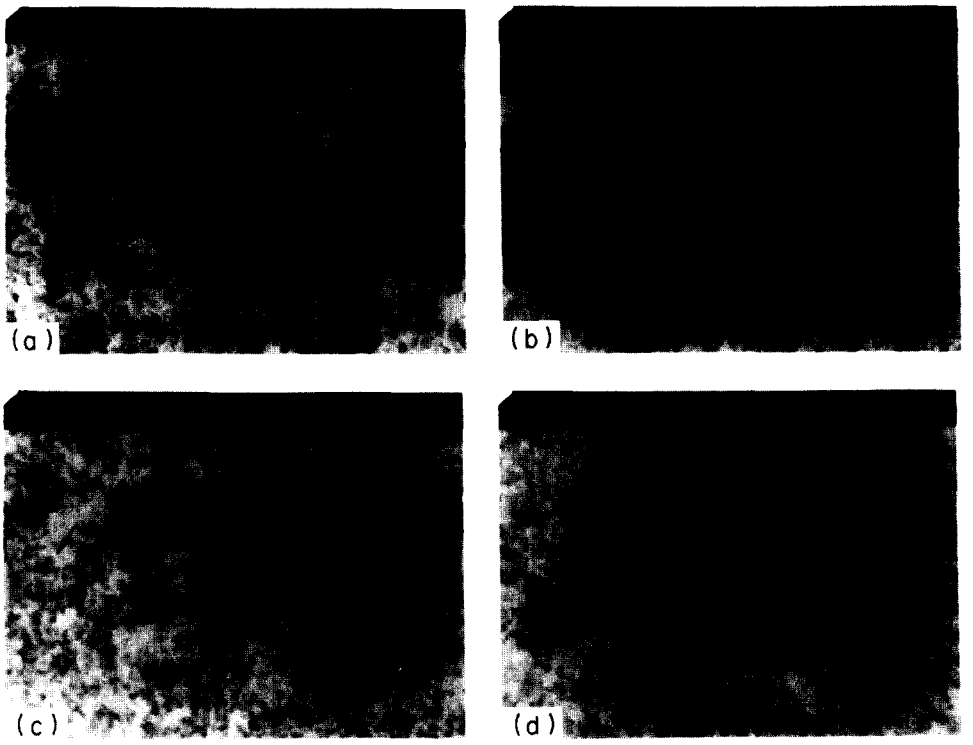

Fig. 4. Scanning electron micrographs of (a) $MnWN_2$, (b) $FeWN_2$, (c) $CoWN_2$ and (d) $NiWN_2$. The black dots marked with arrows in (c) and (d) represent metallic Co and Ni respectively.

Mn^{2+}:$3d^5$. $FeWN_2$ is also semiconducting (Fig. 2), indicating its likely formulation to be $Fe^{2+}W^{4+}N_2$. We could not measure the intrinsic magnetic property of this material, however, because the samples contained small amounts of iron as an impurity. The semiconducting behaviour of $MnWN_2$ and $FeWN_2$ is most likely due to W(IV):$5d^2$ in trigonal prismatic coordination, which would give rise to a filled d_z^2 band similar to MoS_2 and WS_2 [8]; the 3d electrons of Mn^{2+} and Fe^{2+} would, however, remain localized in the structure.

The Co and Ni compounds, on the other hand, showed a semimetallic behaviour with much lower resistivity (Fig. 2). Unfortunately, the magnetic properties of these materials could not be characterized because of the presence of metallic Co and Ni impurities in the preparations. The semimetallic behaviour is, however, not due to the metallic Co and Ni impurities. Scanning electron micrographs of the MWN_2 (M ≡ Mn, Fe, Co, Ni) samples (Fig. 4) clearly show that the metallic impurity phases in the Co and Ni nitrides (black dots in Figs. 4(c) and 4(d)) are too few and far between to account for the semimetallic conductivity. Accordingly, we believe that the observed conductivity of the Co and Ni nitrides represents the intrinsic electrical property of the nitrides. The semimetallic nature together with the smaller *c* parameter of these compounds suggests an octahedral geometry for W(IV) in these materials. Further investigations using pure $CoWN_2$ and $NiWN_2$ samples are essential to establish the structure and properties of these new phases.

4. Conclusions

In conclusion, we have synthesized three new ternary transition metal nitrides, MWN_2 (M ≡ Mn, Co, Ni), by reaction of the corresponding tungstate precursors with NH_3 gas. $MnWN_2$ and $FeWN_2$ (the latter has already been reported in the literature) crystallize in a hexagonal structure related to $LiMoN_2$. The electrical and magnetic properties of $MnWN_2$ are consistent with this structural model. The Co and Ni nitrides, which are isostructural amongst themselves, adopt a slightly different hexagonal structure.

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