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LETTER TO THE EDITOR

Synthesis, Structure, and Properties of $LiWN_2$[1]

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We report the synthesis of a new ternary nitride $LiWN_2$ by the reaction of Li_2WO_4 with NH_3 at 745°C. The compound crystallizes in a layered hexagonal structure with a = 2.863 and c = 15.608 Å. $LiWN_2$ is metallic, consistent with its structure with W(V) in trigonal prismatic coordination and Li^{1+} in octahedral coordination. © 1994 Academic Press, Inc.

Synthesis of new ternary nitrides is receiving increased attention of solid-state chemists because of their interesting structure and properties (1, 2). Synthesis of metal nitrides, especially the ternary and higher ones, is, however, not straightforward, mainly because the free energies of formation are small, precluding direct synthesis using elemental nitrogen at high temperatures (3). In recent times new transition metal nitrides were synthesized by low-temperature methods. Low-temperature synthetic routes to new nitrides include: (a) reaction of metal oxides with NH_3(4, 5), (b) decomposition of metal amides (6, 7), (c) reaction of transition metals with alkali metal/alkaline earth metal amides (8, 9), and (d) reaction of transition metal halides with alkali metal nitrides (10, 11). Among these, nitrides from oxide precursors with reaction of NH_3 are attractive since a large number of oxide precursors are known; this method is likely to give rise to a large number of new nitrides and oxynitrides. Thus, MWN_2 (M = Mn, Fe, Co, and Ni) was synthesized by heating the corresponding MWO_4 (12, 13). $LiMoN_2$ was the first ternary, metallic, layered nitride synthesized by the reaction of Li_2MoO_4 with NH_3. Since Li_2WO_4 and Li_2MoO_4 are similar in their structure and properties, we considered it possible to synthesize $LiWN_2$ from Li_2WO_4. The structure and electrical properties are expected to be similar to those of $LiMoN_2$. Here we report the first synthesis, structure, and properties of $LiWN_2$.

Li_2WO_4 was prepared by heating a 1 : 1 mixture of Li_2CO_3(99%) and WO_3(99%) at 700°C for 12 hr with one intermittent grinding. The obtained product was X-ray pure Li_2WO_4. The title compound $LiWN_2$ was synthesized by heating Li_2WO_4 in flowing NH_3 gas (1–2 g in an alumina boat with a flow rate ~160 cc/min) at 745°C for 12 hr in a quartz tube. The sample was quenched to room temperature, and the black product obtained was washed with dried ethanol four times. The product was examined by powder X-ray diffraction and transmission electron microscopy. Nitrogen estimation was done using TGA in an oxygen atmosphere (Fig. 1). The mass gain of 12.738% is close to the theoretical value of 12.777% for the decomposition of $LiWN_2$ to 1/2 Li_2O and WO_3. Lithium estimation was done using flame photometry, which led to the composition $Li_{0.99\pm0.2}WN_2$. Therefore, we conclude that the compound is nearly stoichiometric $LiWN_2$.

The indexed X-ray powder diffraction pattern of $LiWN_2$ is given in Fig. 2. All the lines in the powder pattern could be indexed in a hexagonal cell with lattice parameters a = 2.863 and c = 15.608 Å. Since the pattern is similar to that of $LiMoN_2$ (5) we assume the same structural model for $LiWN_2$, with $R3$ as the space group. The calculated and observed d spacing as well as intensities are given in Table 1. Intensity calculations were done using the Lazy Pulverix program; these match reasonably well with the observed values.

Electron diffraction and microscopy (TEM) were car-

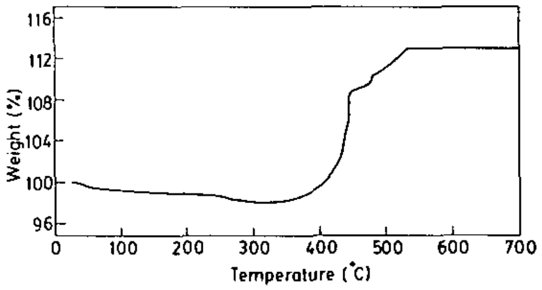

FIG. 1. TGA of $LiWN_2$ in O_2 (heating rate = 1°C/min).

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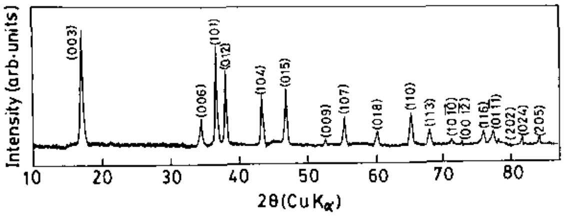

FIG. 2. Cu$K\alpha$ X-ray powder diffraction pattern of $LiWN_2$.

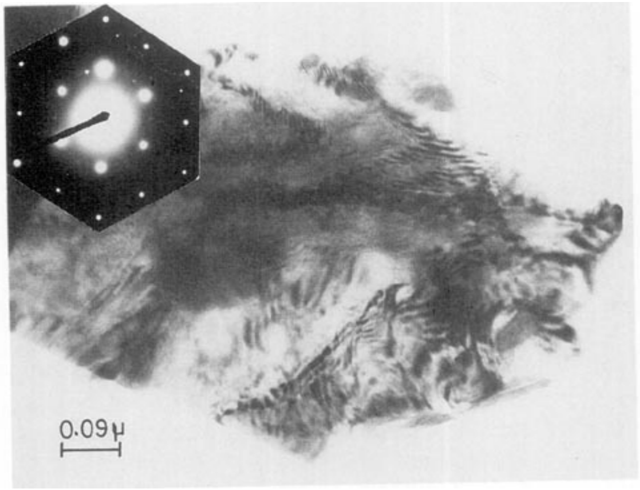

FIG. 3. TEM pictures of platelets. Inset shows diffraction pattern in [0001] zone direction from the platelet.

ried out to confirm the structure and morphology of powder particles. Figure 3 shows a bright field image of a crystal showing layered morphology. The electron diffraction pattern from such a platelet (shown in the inset of Fig. 3) corresponds to the [0001] zone direction. Since the crystal easily cleaves to (0001) planes we could not readily obtain crystals with c-axis stacking perpendicular to the electron beam direction. In Fig. 4 we show a lattice image of one of the crystals showing 5.20-Å lattice fringes along the c direction. In the crystal structure this corresponds to the expected W–W layer distance along the c axis. The selected-area diffraction pattern shown in the inset clearly shows spots corresponding to (0003) planes with d spacing close to 5.20 Å. The high-resolution image therefore confirms the ordering of W within the layer. In the structure refinement of $LiMoN_2$, mixing of Mo(V) and Li^{1+} sites to the extent of 15% was proposed (5). However, such mixing in $LiWN_2$ was not directly evident from high-resolution images. A detailed structure investigation of both $LiMoN_2$ and $LiWN_2$ by transmission electron microscopy is in progress.

TABLE 1
X-Ray Powder Diffraction Pattern of $LiWN_2$[a]

h	k	l	d_{obs} (Å)	d_{cal} (Å)	I_{obs}	I_{cal}
0	0	3	5.215	5.212	100	100
0	0	6	2.603	2.601	19	14
1	0	1	2.448	2.448	62	45
0	1	2	2.362	2.363	42	39
1	0	4	2.094	2.092	32	32
0	1	5	1.941	1.941	42	29
0	0	9	1.733	1.734	6	5
1	0	7	1.658	1.657	22	18
0	1	8	1.532	1.534	10	11
1	1	0	1.430	1.431	22	13
1	1	3	1.380	1.380	12	8
1	0	10	1.321	1.320	6	6
0	0	12	1.300	1.300	3	2
1	1	6	1.255	1.255	12	6
0	1	11	1.231	1.231	11	7
2	0	2	1.225	1.224	4	6
0	2	4	1.181	1.181	8	9
2	0	5	1.1521	1.152	8	8
1	1	9	1.103	1.104	7	6

[a] Unit cell parameters $a = 2.863(3)$ and $c = 15.608(5)$ Å.

Magnetic susceptibility of $LiWN_2$ was measured using a Lewis coil force magnetometer; nearly temperature-independent susceptibility of $LiWN_2$ down to 100 K, with $\chi = 0.45 \times 10^{-6}$ emu/g, is indicative of the Pauli paramagnetic nature of the material. Since in $LiWN_2$, W(V) is in trigonal prismatic coordination, we expect the metallic properties to arise from the half-filled d_z^2 band (14). Electrical resistivity measurements were carried out on pressed pellets using a four-probe method. The R vs T curve is shown in Fig. 5. The room temperature resistivity of 40×10^{-3} ohm cm is indicative of the metallic nature of the material. However, nearly temperature-independent re-

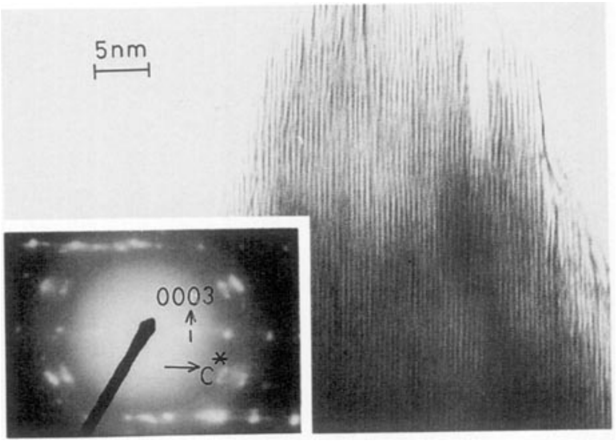

FIG. 4. HREM image of $LiWN_2$ along the [0001] zone axis. Inset shows the diffraction pattern in the c^* direction, and the spots correspond to (0003) reflection.

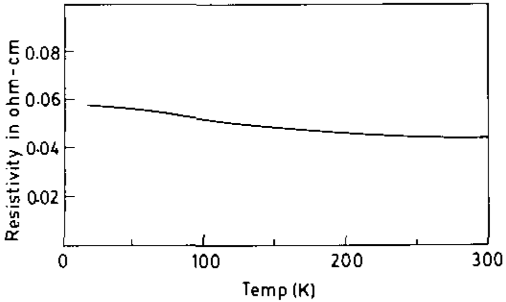

FIG. 5. R vs T of $LiWN_2$.

sistance from 300 to 20 K is probably due to grain boundary effects in pressed pellets.

In conclusion, we have synthesized $LiWN_2$, a new layered ternary nitride crystallizing in a hexagonal structure with $a = 2.863$ and $c = 15.608$ Å. The morphology and structure were determined using TEM. The magnetic susceptibility and metallic electrical properties are consistent with its structure.

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