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Synthesis and Characterization of New Double Tungstates $Li_2M^{II}(WO_4)_2$ (M = Co, Ni, and Cu)

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Received February 13, 2001. Revised Manuscript Received June 25, 2001

Two new double tungstates, $Li_2Co(WO_4)_2$ and $Li_2Ni(WO_4)_2$, have been prepared by solid-state reaction and characterized. The structures of these isostructural compounds (triclinic, space group $P\bar{1}$) have been determined from X-ray and neutron diffraction data and found to be built up of alternating layers of zigzag rows of edge-sharing WO_6 octahedra and MO_6 octahedra (M = Co^{2+} or Ni^{2+}) as in wolframite-like phases. However, the MO_6 octahedra are arranged in columns but not connected to each other; perpendicular to these columns there are rows of edge-sharing LiO_6 octahedra which also connect the different MO_6 octahedra. The structure of a previously reported lithium−copper(II) double tungstate with the same stoichiometry, $Li_2Cu(WO_4)_2$, has also been determined and found to be similar to that proposed for these new double tungstates. The three compounds melt incongruently at temperatures between 750 and 770 °C. Conductivity measurements revealed that these compounds are not good ionic conductors probably because of the full occupancy of lithium positions which hinders the motion of the ions along the $(LiO_6)_\infty$ columns.

Introduction

A large number of double tungstates and molybdates have been studied in recent years, basically because of their interesting luminescence properties and possible application in the field of solid-state lasers.[1–3] Many of these double tungstates have the general formula $A^IM^{III}(WO_4)_2$, where A is an alkali metal and M is a trivalent cation such as Bi^{3+}, In^{3+}, or Cr^{3+} or a rare earth element such as Sm^{3+}, Eu^{3+}, Gd^{3+}, and so forth. As in the MWO_4 family of compounds, two different coordinations have also been found for tungsten in these phases, either tetrahedral for the scheelite-like double tungstates as in $NaLa(WO_4)_2$[4] or octahedral for those adopting the wolframite type of structure as in $LiFe(WO_4)_2$.[5] However, only a few double tungstates of divalent elements have been structurally investigated and not much has been said about their chemical and/or physical properties. In fact, to our knowledge, only four elements (cop-

per, iron, magnesium, and zinc) have been found to form this type of compound. Thus, Russian authors described lithium double tungstates of Cu(II) and Fe(II), with the general formula $Li_2M^{II}(WO_4)_2$ ($Li_2O/MO/2WO_3$, 1:1:2).[6,7] Although the structures were not fully investigated at the time, a wolframite-like structure was proposed for both compounds. The wolframite ((Fe,Mn)WO_4)-type structure is very common among MWO_4 compounds (where M^{2+} is a 3d transition metal ion with a radius smaller than 1 Å), and it can be described as made up of hexagonal close-packed oxygens with certain octahedral sites filled by M^{2+} and W^{6+} cations in an ordered way.[8] Magnesium has been reported to form two double tungstates though with different stoichiometry than that proposed for Fe(II) and Cu(II): $Li_2Mg_2(WO_4)_3$ (1:2:3)[9] and $Na_4Mg(WO_4)_3$ (2:1:3).[10] While no structural data have been given for the sodium−magnesium double tungstate, the crystal structure of $Li_2Mg_2(WO_4)_3$ was considered to be similar to that of $Li_2Fe_2(MoO_4)_3$ and $Li_3Fe(MoO_4)_3$,[11] with W^{6+} tetrahedrally coordinated to four oxygen atoms. Finally, three double tungstates of divalent zinc have been reported, though none with lithium: $Na_{2.4}Zn_{0.8}(WO_4)_2$,[7] $Na_4Zn(WO_4)_3$,[10] and $K_4Zn(WO_4)_3$.[12] From these, structural data have been given

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Table 1. Conditions of Synthesis of Li$_2$M(WO$_4$)$_2$ (M = Co, Ni, and Cu)

sample	synthesis	color
Li$_2$Co(WO$_4$)$_2$	650 °C/146 h	purple
Li$_2$Ni(WO$_4$)$_2$	650 °C/60 h, 700 °C/160 h	yellow
Li$_2$Cu(WO$_4$)$_2$	680 °C/60 h, 700 °C/160 h	green-yellow

only for K$_4$Zn(WO$_4$)$_3$ which also presents the W^{6+} ions tetrahedrally coordinated to four oxygen atoms.

On the other hand, a larger number of double molybdates with divalent elements have been described in the literature. Thus, Fe, Co, Ni, and Cu form lithium double molybdates with the (1:2:3) stoichiometry, Li$_2$M$_2$-(MoO$_4$)$_3$,[11,13−15] similar to that proposed for the magnesium double tungstate but different from that of the iron and copper double tungstates. The coordination around the Mo(VI) ions in these compounds is also tetrahedral as for tungsten in Li$_2$Mg$_2$(WO$_4$)$_3$ and K$_4$Zn(WO$_4$)$_3$.

Since the available information about this type of double tungstates remains scarce and somehow confusing, we decided to explore the existence of new lithium−metal(II) double tungstates and to reinvestigate the structure of the lithium−copper compound for which the previously published information was incomplete.

Experimental Section

The synthesis of these compounds was carried out by solid-state reaction of Li$_2$CO$_3$ (Aldrich Chem. Co., 99+%), WO$_3$ (Aldrich Chem. Co., 99+%), and MO (CuO, Aldrich Chem. Co., 99+%; NiO, J. T. Baker Chemical, 99+%). Instead of the metal oxide, hydrated cobalt nitrate (Co(NO$_3$)$_2$·6H$_2$O, J. T. Baker Chemical, 99+%) was used for the preparation of the lithium−cobalt double tungstate. Stoichiometric amounts of the starting reagents were mixed and intimately ground in an agate mortar under acetone and then fired (in air) in high alumina crucibles (Adolph Coors, Co). Initially the samples were fired at 600 °C for a few hours, to allow decarbonation, and then between 650 and 700 °C, as summarized in Table 1. After firing, samples were reground and reheated to ensure homogeneity.

X-ray powder diffraction (XRD), performed on a Siemens D-5000 diffractometer (Ni-filtered Cu Kα radiation, λ = 1.5418 Å), was used to follow the evolution of the chemical reaction; the final samples were confirmed to be single phase by this technique. For the structure determination and refinement, data were collected using a step width of 0.02° over the range 15° < 2θ < 75° with a total collection time of about 12 h.

The structures of the Li$_2$M^{II}(WO$_4$)$_2$ (M = Co, Ni, and Cu) tungstates were solved in different steps from the X-ray diffraction patterns:

(1) The unit cell parameters were determined using the TREOR program.[16]

(2) A pattern matching—without structural model—allowed us to extract the integrate intensities of the Bragg peaks. This was done using the FULLPROF program.[17]

(3) The starting structural model was obtained by direct methods and from the Patterson function calculated from the integrate intensities using the SHELXS-86 program.[18] Thus, the heavy atoms (W and transition metal) were located.

(4) The light atoms (oxygen and lithium) were located by Fourier synthesis, using SHELXL-92.[19] Thus, the structural model was completed.

(5) The structural model developed in this way was refined by the Rietveld method by fitting the powder X-ray diffraction patterns using the FULLPROF program.[17]

Since X-ray diffraction is not the best technique to study structural features due to light atoms, such as oxygen and lithium, neutron diffraction experiments were performed at room temperature on the diffractometer G4.2 of the Orphée Reactor at Laboratoire Léon Brillouin. A monochromatic beam of wavelength 2.3433 Å was selected with a Ge(004) monochromator; for this radiation the instrumental resolution is within the range $2.7 \times 10^{-3} \leq (\Delta Q/Q) \leq 0.022$.

Thus, the initial structural models developed from the X-ray diffraction patterns were refined against the neutron diffraction data.

Thermal analyses were carried out to assess the chemical stability of the single-phase samples up to 900 °C on a Thermal Analyst 2100 (TA Instruments). Experiments were run using a heating rate of 10 °C min^{-1} (Pt/Pt−Rh thermocouple) and an air stream flowing at 100 mL min^{-1} (typical specimen weight 10−12 mg).

Lithium ionic conductivity was measured on pellets of the samples by ac impedance spectroscopy using a Solartron 160 impedance analyzer over a frequency range from 20 Hz to 20 MHz and a temperature range from room temperature to 700 K. Both opposite faces of the pellets were pasted with platinum as the electrodes.

Results and Discussion

Structure. X-ray diffraction patterns, depicted in Figure 1a−c, corresponding to Li$_2$M^{II}(WO$_4$)$_2$ for cobalt, nickel, and copper, respectively, show that the samples are single phase, since all the peaks can be indexed with a unique triclinic unit cell. The patterns of Li$_2$Co(WO$_4$)$_2$ and Li$_2$Ni(WO$_4$)$_2$ are very similar, suggesting that both compounds are isostructural.

Parts a−c of Figure 2 show the neutron diffraction patterns—experimental, calculated, and their difference—corresponding to Li$_2$M^{II}(WO$_4$)$_2$ (M = cobalt, nickel, and copper, respectively). The calculated patterns were obtained using the final structural model refined from the starting one developed from the integrate intensities of the X-ray patterns, as described in the Experimental Section. The final structural parameters, obtained by fitting the neutron diffraction data, are collected in Table 2. Table 3 shows the main interatomic distances together with the bond valence sum (BVS) calculations[20] of every atom and the global instability index (GII).[21] The former parameters reproduce quite well the values expected of the oxidation states of the different ions, whereas the latter suggest that the bonds in these tungstates are mainly of ionic nature.[22] At this point it must be recalled that the bond valence sum method works properly for structures in which the ions can relax without constraints[23] such as high symmetry requirements, a high degree of covalence of the bonds, metastable character of the phases, and so forth.

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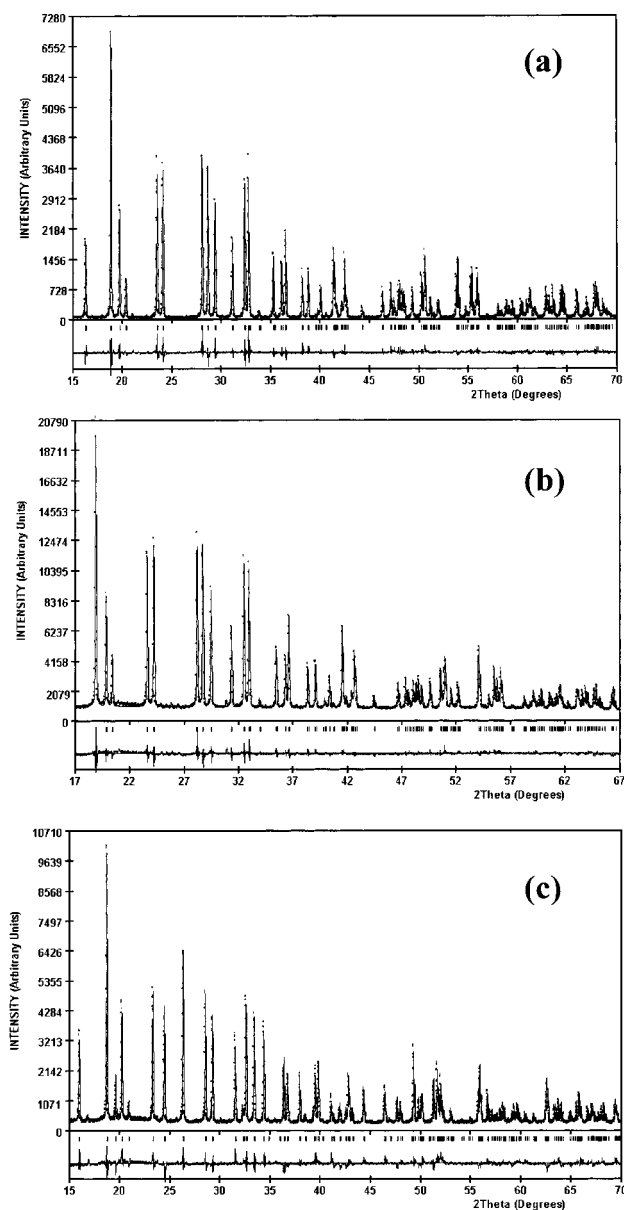(23) Brown, I. D. *J. Solid State Chem.* **1991**, *90*, 155.

Figure 1. Graphic results of the profile fitting—without a structural model—of the X-ray powder diffraction data corresponding to **(a)** Li$_2$Co(WO$_4$)$_2$, **(b)** Li$_2$Ni(WO$_4$)$_2$, and **(c)** Li$_2$Cu-(WO$_4$)$_2$.

In Figures 3 and 4 schematic representations of the structures of Li$_2$M(WO$_4$)$_2$ (M = Co and Ni, isostructural) and Li$_2$Cu(WO$_4$)$_2$, respectively, are depicted. Both structures are very similar; they are built up by alternating layers of WO$_6$ and MO$_6$ octahedra lying on the *ac* plane. The WO$_6$ octahedra are linked by edge-sharing, giving rise to nonconnected zigzag rows running along the *a*-axis. On the other hand, the MO$_6$ octahedra are not connected. The connection between them is reached by corner sharing with WO$_6$ octahedra in such a way that every MO$_6$ octahedron shares three corners with three different WO$_6$ octahedra in the same tungsten layer: two with WO$_6$ octahedra of the same row and one corner with an octahedron of a neighboring row (Figure 5a). The three remaining corners of the MO$_6$ polyhedron are shared in a similar manner with two rows of a second (WO$_4$)$_\infty$ layer (see Figure 5b).

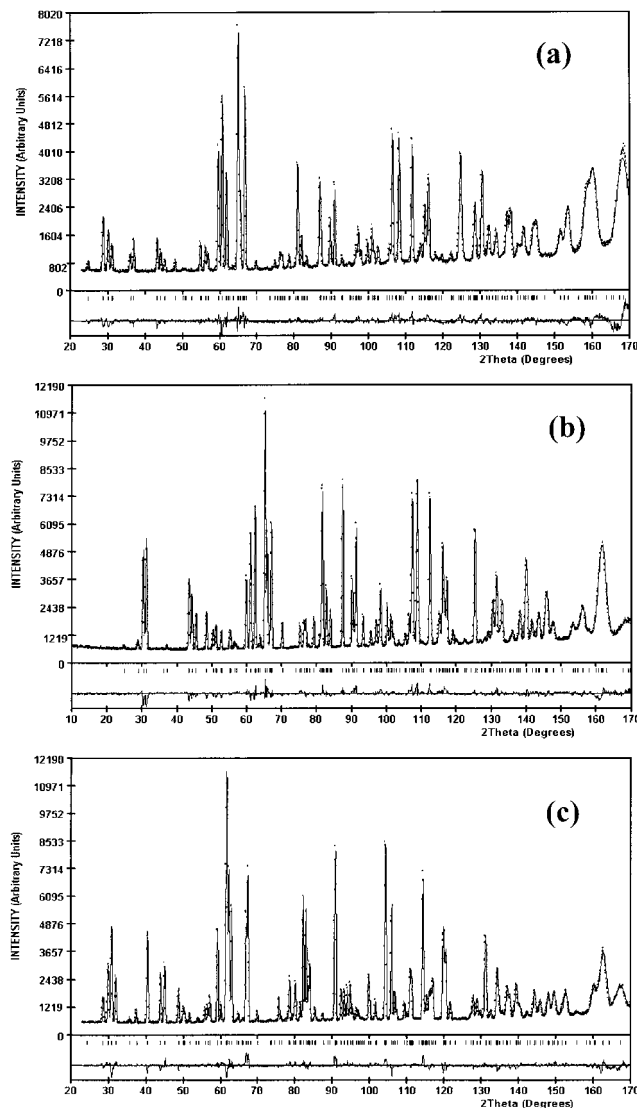Unlike some other double tungstates of divalent elements previously described in the literature such as

Figure 2. Experimental (points), calculated (solid line), and difference (bottom) neutron powder diffraction patterns for **(a)** Li$_2$Co(WO$_4$)$_2$, **(b)** Li$_2$Ni(WO$_4$)$_2$, and **(c)** Li$_2$Cu(WO$_4$)$_2$.

Li$_2$Mg$_2$(WO$_4$)$_3$ and K$_4$Zn(WO$_4$)$_3$, which feature tungsten ions tetrahedrally coordinated to four oxygen atoms, in the title compounds tungsten ions are located in octahedral positions. The same octahedral coordination has been proposed for tungsten in the lithium−iron(II) double tungstate,[7] Li$_2$Fe(WO$_4$)$_2$, although neither the symmetry nor the unit cell reported in this case seems to be correct, and also in some double tungstates LiMWO$_4$ of trivalent elements (M = Fe(III), Cr(III), In(III), and so forth).[5]

Interestingly enough, the structure of the title compounds can be seen as derived from the wolframite one. In Figure 6a−c views of wolframite, LiFe(WO$_4$)$_2$, and Li$_2$Ni(WO$_4$)$_2$, respectively, are depicted; the three structures have in common the presence of zigzag rows of edge-sharing WO$_6$ octahedra running parallel and giving rise to layers of composition (WO$_4$)$_\infty$. Between two consecutive layers of this type the metals (Fe + Mn, Li + Fe, or Li + Ni) are located in octahedral positions. Thus, the MO$_6$ polyhedra define infinite layers, which differ from one structure to another both in the composition [(MO$_4$)$_\infty$ in wolframite and LiFe(WO$_4$)$_2$ (with M = Fe + Mn and Li + Fe, respectively) and ((Li$_2$ +

Table 2. Structure Parameters of Li₂M(WO₄)₂ As Refined from Neutron Diffraction Data

atom	site[d]	$M = Co$[a] x/a	y/b	z/c	B_{iso} (A²)	$M = Ni$[b] x/a	y/b	z/c	B_{iso} (A²)	site[d]	$M = Cu$[c] x/a	y/b	z/c	B_{iso} (A²)
W	2i	0.2709(9)	0.5335(9)	0.6644(9)	0.04(1)	0.2643(7)	0.5337(6)	0.6649(5)	0.05(1)	2i	0.2732(6)	0.9619(6)	0.3385(5)	1.06(7)
M	1d	1/2	0	0	0.13(1)	1/2	0	0	0.12(1)	1e	1/2	1/2	0	0.80(6)
O(1)	2i	−0.1725(8)	0.2783(7)	0.6668(6)	0.16(1)	−0.0322(6)	0.2421(5)	0.9231(4)	0.15(1)	2i	−0.1521(5)	0.2218(4)	0.3494(4)	1.08(4)
O(2)	2i	0.2374(8)	0.7506(8)	0.8065(7)	0.16(1)	0.5136(5)	0.7499(5)	0.8100(5)	0.15(1)	2i	0.2377(5)	0.7505(5)	0.1810(5)	1.08(4)
O(3)	2i	0.6814(8)	0.7260(9)	0.5409(7)	0.16(1)	0.5482(6)	0.7218(5)	0.3299(4)	0.15(1)	2i	0.6640(5)	0.7878(5)	0.4381(4)	1.08(4)
O(4)	2i	0.2743(8)	0.2413(8)	0.9237(6)	0.16(1)	0.0437(4)	0.7276(5)	0.5430(4)	0.15(1)	2i	0.2779(5)	0.2686(5)	0.0890(4)	1.08(4)
Li	2i	0.051(2)	0.074(2)	0.257(2)	1.63(1)	0.027(2)	0.072(2)	0.254(1)	1.40(1)	2i	−0.057(2)	0.573(2)	0.236(2)	1.9(2)

[a] For M = Co, a = 4.9218(1) Å, b = 5.6675(1) Å, c = 5.8826(1) Å, α = 69.49(1)°, β = 91.46(1)°, γ = 116.14(1)°, V = 136.3(1) Å³, R_B = 0.051, R_W = 0.046, R_{exp} = 0.14, χ^2 = 0.10. [b] For M = Ni, a = 4.9070(1) Å, b = 5.6020(1) Å, c = 5.4803(1) Å, α = 70.92(1)°, β = 88.52(1)°, γ = 115.45(1)°, V = 134.4(1) Å³, R_B = 0.045, R_W = 0.044, R_{exp} = 0.13, χ^2 = 0.12. [c] For M = Cu, a = 4.9669(1) Å, b = 5.4969(1) Å, c = 5.8883(1) Å, α = 70.72(1)°, β = 85.99(1)°, γ = 66.04(1)°, V = 138.3(1) Å³, R_B = 0.052, R_W = 0.047, R_{exp} = 0.14, χ^2 = 0.11. [d] Space group = $P\bar{1}$ (2).
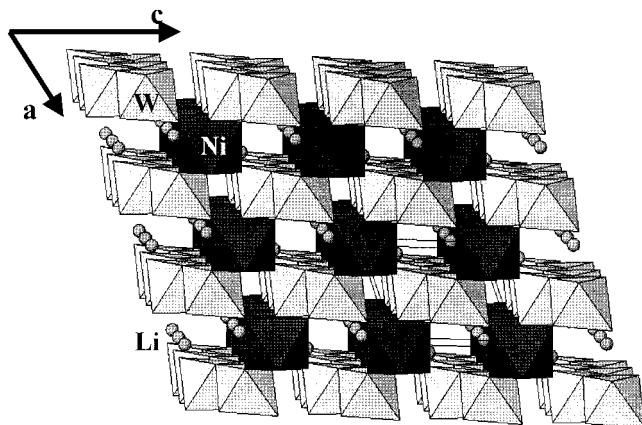
Figure 3. Schematic representation of the structure of Li₂M-(WO₄)₂ (M = Co, Ni).

Table 3. Selected Structural Information for Li₂M(WO₄)₂ (Distances in Angstroms)

M = Co		M = Ni		M = Cu	
Co−O(1)	2.164(4) ×2	Ni−O(1)	2.045(3) ×2	Cu−O(1)	2.415(2) ×2
Co−O(2)	2.099(4) ×2	Ni−O(2)	2.072(3) ×2	Cu−O(2)	2.012(3) ×2
Co−O(4)	2.047(4) ×2	Ni−O(3)	2.139(2) ×2	Cu−O(4)	1.931(3) ×2
W−O(1)	2.015(6)	W−O(1)	1.815(4)	W−O(1)	2.024(4)
W−O(1)′	2.030(5)	W−O(2)	1.770(4)	W−O(1)′	1.968(4)
W−O(2)	1.774(6)	W−O(3)	2.000(5)	W−O(2)	1.773(4)
W−O(3)	1.838(7)	W−O(3)′	2.032(4)	W−O(3)	1.819(4)
W−O(3)′	2.289(6)	W−O(4)	1.845(4)	W−O(3)′	2.307(4)
W−O(4)	1.82(1)	W−O(4)′	2.293(1)	W−O(4)	1.842(1)
Li−O(1)	2.23(1)	Li−O(1)	1.949(8)	Li−O(1)	2.060(9)
Li−O(2)	2.02(1)	Li−O(1)′	2.327(9)	Li−O(2)	2.020(9)
Li−O(3)	2.16(1)	Li−O(2)	1.998(9)	Li−O(3)	2.026(9)
Li−O(3)′	2.00(1)	Li−O(3)	2.234(9)	Li−O(3)′	2.509(9)
Li−O(4)	1.96(1)	Li−O(4)	2.143(8)	Li−O(4)	2.192(9)
Li−O(4)′	2.37(1)	Li−O(4)′	1.988(9)	Li−O(4)′	2.009(9)

Intermetallic Distances (Å)

Co−Co	4.9218(1)	Ni−Ni	4.9070(1)	Cu−Cu	4.9669(1)
W−W	3.218(6)	W−W	3.194(5)	W−W	3.168(4)
Li−Li	2.67(2)	Li−Li	2.68(2)	Li−Li	2.98(2)
Co−W	3.08(5)	Ni−W	3.585(3)	Cu−W	3.520(3)
Co−Li	2.96(1)	Ni−Li	2.96(1)	Cu−Li	2.906(9)
W−Li	2.95(1)	W−Li	2.92(1)	W−Li	2.943(9)

Bond Valence Sums

Co	1.97(1)	Ni	1.88(5)	Cu	2.10(2)
W	5.94(4)	W	5.99(3)	W	6.03(4)
O(1)	1.93(2)	O(1)	2.04(2)	O(1)	1.98(2)
O(2)	2.07(2)	O(2)	2.08(2)	O(2)	2.12(2)
O(3)	1.98(2)	O(3)	1.95(2)	O(3)	1.95(2)
O(4)	2.04(2)	O(4)	2.00(2)	O(4)	2.12(2)
Li	1.10(1)	Li	1.13(1)	Li	1.08(2)
GII	0.061		0.078		0.083

Figure 4. Schematic view of the structure of Li₂Cu(WO₄)₂.
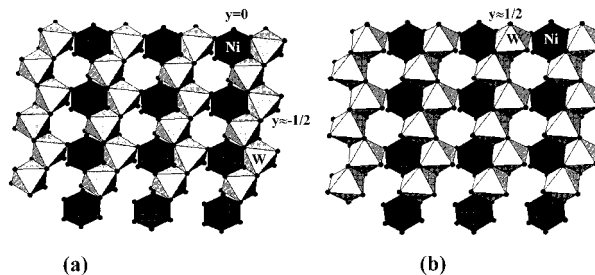
Figure 5. Schematic representation of the stacking sequence of WO₆ and MO₆ layers in Li₂M(WO₄)₂ (M = Co, Ni, and Cu) (see text).

rows are formed by alternating LiO₆ and FeO₆ polyhedra. A different arrangement of lithium and iron polyhedra has been suggested[5] in LiFe(WO₄)₂ as a function of temperature: when the material is quenched from high temperature, mixed rows are formed (as shown in Figure 6b); however, if the compound is treated for some time at moderate temperature, homogeneous rows of composition (FeO₆)∞ and (LiO₆)∞ are obtained. The transition from the latter to the former phase is produced on heating around 300 °C; however, it is not observed by TDA, since this is a second-order transition.

On the other hand, in the title compounds the layers defined by metals show a different structure: as depicted in Figure 6c one of these layers is built up by MO₆ octahedra, which are not connected to each other, arranged in columns; perpendicular to these columns there are rows of edge-sharing LiO₆ octahedra.
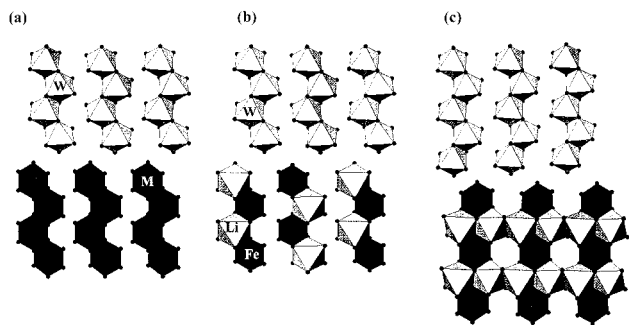
M)O₄)∞ (M = Co, Ni, and Cu) in the title compounds] and in the structure, as well. In wolframite the (Mn + Fe)O₆ octahedra are arranged in zigzag rows similar to that formed by WO₆ while in LiFe(WO₄)₂ similar zigzag

Figure 6. Representation of the layers present in **(a)** wolframite (Fe,Mn)WO₄, **(b)** LiFe(WO₄)₂, and **(c)** Li₂M(WO₄)₂ (M = Co, Ni, and Cu).

Finally, it is worth pointing out that the main difference between the structures of $Li_2M(WO_4)_2$ (M = Co and Ni) and $Li_2Cu(WO_4)_2$ is the relative positions of the atoms and the symmetry elements (in these cases the inversion centers). This seems to be due, most likely, to the strong Jahn−Teller effect found in the CuO_6 octahedra in which an important elongation (about 20%) is produced (see Table 3). The same effect has been observed in $CuWO_4$ (triclinic, space group $P\bar{1}$) where Cu(II) also has octahedral coordination with four oxygens in an approximately square planar configuration (Cu−O distance: 1.98 Å) and the remaining two at a longer distance (Cu−O: 2.40 Å) completing an elongated CuO_6 octahedra.[24] These distances are similar to the Cu−O distances found in $Li_2Cu(WO_4)_2$.

Thermal Analysis. Thermal analysis carried out on the title compounds up to 900 °C showed no evidence of phase transitions with a single endothermic event observed between 750 and 800 °C. X-ray powder diffraction experiments showed these peaks to be related with the peritectic decomposition of the three double tungstates into a liquid (Li_2WO_4 melts around 730 °C) and the corresponding wolframite structure, MWO_4 (M = Co, Cu, Ni). The event takes place at the following temperatures: 758 °C for $Li_2Ni(WO_4)_2$; 751 °C for $Li_2Co(WO_4)_2$; and 770 °C for $Li_2Cu(WO_4)_2$.

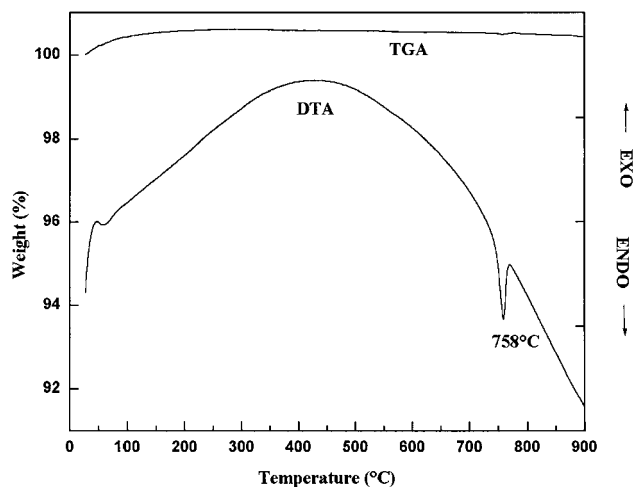(24) Kihlborg, L.; Gebert, E. *Acta Crystallogr. B* **1970**, *26*, 1020.

Figure 7. Thermal analysis traces for a $Li_2Ni(WO_4)_2$ sample heated in air at a rate of 10 °C/min.

Figure 7 shows the DTA and TG curves obtained for $Li_2Ni(WO_4)_2$.

Conductivity Measurements. Regarding the physical properties, the title materials were expected to be good ionic conductors, since they present rows of LiO_6 octahedra which share edges, suggesting that lithium ions might diffuse along these rows. However, the measured conductivity of these materials is very low; at room temperature the values of conductivity are $\sigma^{RT} = 1.2 \times 10^{-7}$ (Ω^{-1} cm^{-1}) and $\sigma^{RT} = 9.9 \times 10^{-8}$ (Ω^{-1} cm^{-1}) for $Li_2Ni(WO_4)_2$ and $Li_2Co(WO_4)_2$, respectively. These low values of conductivity are most likely due to the full occupancy of the lithium positions, which hinders the motion of the ions along the $(LiO_6)_\infty$ columns.