# BRIEF COMMUNICATION

# Crystal Structure Refinement of $Mg_5Nb_4O_{15}$ and $Mg_5Ta_4O_{15}$ by Rietveld Analysis of Neutron Powder Diffraction Data

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The crystal structure of the isomorphous phases $Mg_5Nb_4O_{15}$ and $Mg_5Ta_4O_{15}$ was refined from neutron powder diffraction data. These compounds are isostructural with pseudobrookite, $Fe_2TiO_5$. The two kinds of metal sites of this structure are randomly occupied by Mg(II) and Nb(V) or Ta(V). The structure consists of double chains of $(Mg, M)O_6$ units (where $M =$ Nb or Ta), sharing edges on the $bc$ plane, interconnected through common oxygens along the $a$ axis to give a three-dimensional array. The $(Mg, M)O_6$ polyhedra at both metal positions can be described as very distorted octahedra, with $(Mg, M)-O$ distances ranging from 1.93 to 2.22 Å. The crystallographic formulas can be written as $(Mg_{0.73(2)}Nb_{0.27(2)})_{4c}(Mg_{0.94(2)}Nb_{1.06(2)})_{8f}O_5$ and $(Mg_{0.66(2)}Ta_{0.34(2)})_{4c}(Mg_{1.01(2)}Ta_{0.99(2)})_{8f}O_5$ respectively, where 4c and 8f are the Wyckoff sites of the two metal positions of the structure. The space group is Cmcm (orthorhombic) and $Z = 4$. Unit cell parameters, cell volume, $R_{wp}$ and $R_I$ values obtained were $a = 3.8068(1)$ Å, $b = 10.0561(1)$ Å, $c = 10.2566(1)$ Å, $V = 392.64(2)$ Å$^3$, and 6.72% and 2.94% for the niobium compound; and $a = 3.81884(6)$ Å, $b = 10.0574(2)$ Å, $c = 10.2343(2)$ Å, $V = 393.07(2)$ Å$^3$, and 4.46%, and 2.36% for the tantalum compound. © 1998 Academic press

## INTRODUCTION

Recently there has been a large increase in interest in Nb mixed oxides due to the report of some superconducting oxides containing Nb in a reduced oxidation state (1). We have previously studied the compounds $Ba_5Nb_4O_{15-x}$ (2, 3), which have a layered perovskite-related structure, and found interesting electrical properties which make these oxides good candidates in the search for new superconducting materials (2). Aiming to expand our research to the $MgO-M_2O_5$ ($M =$ Nb or Ta) systems, we first were

involved in the study of some phases containing Nb(V) or Ta(V).

The phase diagram of the $MgO-Nb_2O_5$ system was first reported by Tilloca and Perez Jorba (4) and later confirmed by Abbattista *et al.* (5) and Brück *et al.* (6). Four compounds were studied, namely $MgNb_2O_6$ with columbite structure (7), $Mg_4Nb_2O_9$ with corundum structure (8), $Mg_{2/3}Nb_{11\,1/3}O_{29}$ (9), and $Mg_5Nb_4O_{15}$ (10). In the $MgO-Ta_2O_5$ system some phases were reported by Baskin *et al.* (11): $MgTa_2O_6$ (trirutile), $Mg_4Ta_2O_9$ (corundum), and $Mg_3Ta_2O_8$. The X-ray powder diffraction data of the latter corresponds to the $Mg_5Ta_4O_{15}$ phase later identified by Kasper (10). That work was the first to report the existence of the isostructural phases $Mg_5Nb_4O_{15}$ and $Mg_5Ta_4O_{15}$, showing a crystal structure related to that of the mineral pseudobrookite, $Fe_2TiO_5$ (12). The powder diffraction patterns of $Mg_5Nb_4O_{15}$ and $Mg_5Ta_4O_{15}$ prepared above 1500°C were indexed assuming an ordering of Mg(II) and Nb(V) or Ta(V) cations making necessary the tripling of the $a$ unit cell parameters to obtain the so-called "tripseudobrookite" structure type. The lattice parameters of the orthorhombic unit cells were reported to be $a = 11.43(1)$ Å, $b = 10.06(1)$ Å, and $c = 10.26(1)$ Å for $Mg_5Nb_4O_{15}$ and $a = 11.46(1)$ Å, $b = 10.06(1)$ Å, and $c = 10.24(1)$ Å for $Mg_5Ta_4O_{15}$ (10). Later, Tilloca and Perez Jorba (4) reported the existence of a disordered $Mg_5Nb_4O_{15}$ phase, formed above 1200°C, with an X-ray powder diagram rigorously comparable to that of $Fe_2TiO_5$. They could not find any X-ray evidence for an ordering of Mg(II) and Nb(V) cations. Finally, Abbattista *et al.* (5) also reported the existence of this disordered phase above 1200°C with orthorhombic symmetry ($a = 3.799$ Å, $b = 10.066$ Å, and $c = 10.243$ Å) but again they could not find any evidence of a superstructure.

In the present work we report the refinement of the crystal structures of $Mg_5Nb_4O_{15}$ and $Mg_5Ta_4O_{15}$ by Rietveld analysis of high-resolution neutron powder

**TABLE 1**
**Atomic Positions and Occupation Factors in $Mg_5Nb_4O_{15}$**

| Atom | Wyckoff site | $x$ | $y$ | $z$ | Occupancy |
|---|---|---|---|---|---|
| Mg | 4c | 0.00 | 0.18772(20) | 0.25 | 0.182(6) |
| Nb | 4c | 0.00 | 0.18772(20) | 0.25 | 0.068(6) |
| Mg | 8f | 0.00 | 0.13649(13) | 0.56335(13) | 0.235(6) |
| Nb | 8f | 0.00 | 0.13649(13) | 0.56335(13) | 0.265(6) |
| O1 | 4c | 0.00 | 0.76178(22) | 0.25 | 0.25 |
| O2 | 8f | 0.00 | 0.04702(16) | 0.11737(13) | 0.50 |
| O3 | 8f | 0.00 | 0.30807(16) | 0.07224(14) | 0.50 |

**TABLE 3**
**Atomic Positions and Occupation Factors in $Mg_5Ta_4O_{15}$**

| Atom | Wyckoff site | $x$ | $y$ | $z$ | Occupancy |
|---|---|---|---|---|---|
| Mg | 4c | 0.00 | 0.18799(15) | 0.25 | 0.164(6) |
| Ta | 4c | 0.00 | 0.18799(15) | 0.25 | 0.086(6) |
| Mg | 8f | 0.00 | 0.13674(10) | 0.56323(10) | 0.252(6) |
| Ta | 8f | 0.00 | 0.13674(10) | 0.56323(10) | 0.248(6) |
| O1 | 4c | 0.00 | 0.76237(17) | 0.25 | 0.25 |
| O2 | 8f | 0.00 | 0.04806(12) | 0.11693(10) | 0.50 |
| O3 | 8f | 0.00 | 0.30893(12) | 0.07106(11) | 0.50 |

diffraction data, also showing evidence for the absence of superstructures in samples prepared at 1450 and 1550°C.

## EXPERIMENTAL

$Mg_5Nb_4O_{15}$ and $Mg_5Ta_4O_{15}$ were prepared as white polycrystalline powders from stoichiometric mixtures of analytical grade MgO and $Nb_2O_5$ or $Ta_2O_5$, respectively. $Mg_5Nb_4O_{15}$ was prepared by heating the sample two times at 1200°C for 24 h in an alumina crucible, then regrinding and heating again in a Pt crucible in air at a final temperature of 1450°C for 24 h. $Mg_5Ta_4O_{15}$ was prepared by heating the sample at 1550°C for 10 h in a Pt crucible in air, then regrinding and heating again.

The neutron diffraction diagrams were collected in the high-resolution D2B powder diffractometer of the Institut Laue Langevin, at Grenoble. The high-intensity mode was used to collect the spectra at 295 K. The wavelength, 1.594 Å, was selected from the (533)-plane of a Ge monochromator. About 8 g of each sample was enclosed in a vanadium 8-mm-diameter can. The 64 counters, spaced at 2.5 intervals, were moved by steps of 0.05 in the range $2.5° \leq 2\theta \leq 162.5°$. The counting time was about 3 h.

Both neutron diffraction patterns were analyzed by the Rietveld method (13), using the FULLPROF program (14), a strongly modified version of the Young and Wiles refinement program (15). A pseudo-Voigt function was chosen to generate the lineshape of the diffraction peaks.

The profile refinements were performed in the space group $Cmcm$, taking as a starting model that of $Fe_2TiO_5$ with pseudobrookite structure (12,16). This structure contains two positions for metal atoms, which have been described (12) as octahedral positions (Wyckoff site 4c) and tetrahedral positions (Wyckoff site 8f). The formula $Mg_5M_4O_{15}$ ($M$ = Nb or Ta) can be rewritten as $Mg_{5/3}M_{4/3}O_5$ in order to be compared with the stoichiometry of the pseudobrookite $Fe_2TiO_5$. Necessarily there must be a mixed occupancy of one or both of the metal positions: the simplest cases can be written as $(Mg)_{4c}(Mg_{2/3}M_{4/3})_{8f}O_5$ and $(M)_{4c}(Mg_{5/3}M_{1/3})_{8f}O_5$. The most general formula is $(Mg_{1-m}M_m)_{4c}(Mg_{2/3+m}M_{4/3-m})_{8f}O_5$, in which both 4c and 8f positions are occupied by both cations Mg(II) and Nb(V) or Ta(V), randomly distributed. The mixing parameters ($m$) for both compounds were obtained by refining the occupancy factors.

No regions were excluded in the refinements. As small amounts of $MgNb_2O_6$ (columbite) or $MgTa_2O_6$ (trirutile) and $Mg_4Ta_2O_9$ (corundum) were detected in the patterns of $Mg_5Nb_4O_{15}$ and $Mg_5Ta_4O_{15}$, respectively, the profile refinements of the mixtures were performed. In the final runs, the following parameters were refined: six background coefficients, zero-point, half-width, pseudo-Voigt, and asymmetry parameters for the peak shape; unit cell parameters, scale factors; and positional, occupancy, and thermal anisotropic factors. In the final refinement cycles, the shifts in the atomic parameters were zero up to the fourth decimal place.

**TABLE 2**
**Anisotropic Thermal Factors in $Mg_5Nb_4O_{15}$**

| Atom | Wyckoff site | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|
| (Mg, Nb) | 4c | 0.0068(6) | 0.0015(1) | 0.0012(1) | 0.00 | 0.00 | 0.00 |
| (Mg, Nb) | 8f | 0.0082(4) | 0.0019(1) | 0.0028(1) | 0.00 | 0.00 | 0.0004(1) |
| O1 | 4c | 0.0173(6) | 0.0038(1) | 0.0019(1) | 0.00 | 0.00 | 0.00 |
| O2 | 8f | 0.0205(4) | 0.0024(1) | 0.0019(1) | 0.00 | 0.00 | −0.0005(1) |
| O3 | 8f | 0.0100(4) | 0.0026(1) | 0.0023(1) | 0.00 | 0.00 | 0.0000(1) |

**TABLE 4**
**Anisotropic Thermal Factors in $Mg_5Ta_4O_{15}$**

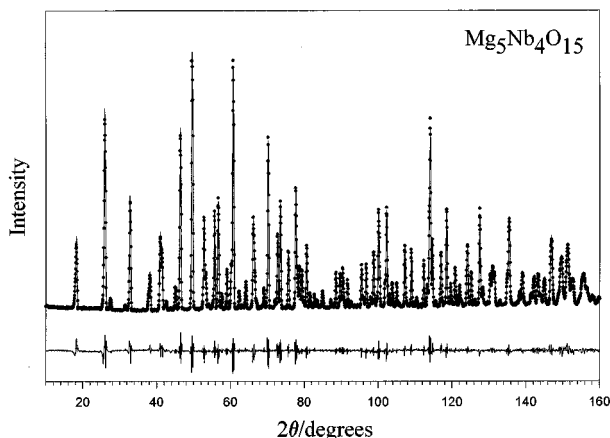| Atom | Wyckoff site | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|
| (Mg, Ta) | 4c | 0.0080(5) | 0.0010(1) | 0.0010(1) | 0.00 | 0.00 | 0.00 |
| (Mg, Ta) | 8f | 0.0084(3) | 0.0013(1) | 0.0016(1) | 0.00 | 0.00 | −0.00002(8) |
| O1 | 4c | 0.0140(5) | 0.0032(1) | 0.0019(1) | 0.00 | 0.00 | 0.00 |
| O2 | 8f | 0.0230(4) | 0.0015(1) | 0.0018(1) | 0.00 | 0.00 | −0.0007(1) |
| O3 | 8f | 0.0057(3) | 0.0022(1) | 0.0023(1) | 0.00 | 0.00 | 0.00004(9) |

**FIG. 1.** Observed (circles), calculated (solid line), and difference (bottom) neutron diffraction profiles for $Mg_5Nb_4O_{15}$ at 295 K.



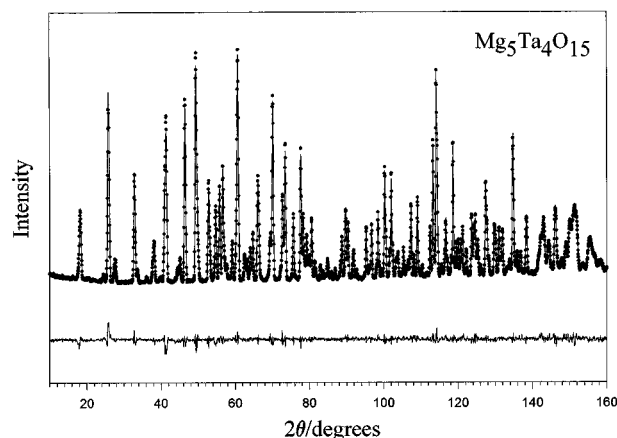**FIG. 2.** Observed (circles), calculated (solid line), and difference (bottom) neutron diffraction profiles for $Mg_5Ta_4O_{15}$ at 295 K.

## RESULTS AND DISCUSSION

The final atomic coordinates and anisotropic thermal factors after the refinements of the neutron powder diffraction data are listed in Tables 1, 2, 3, and 4. The excellent agreement between the observed and calculated profile of the patterns is shown in Figs. 1 and 2. Final bonding distances are given in Tables 5 and 6. From the refined scale factors of the pseudobrookite and columbite phases in the Nb compound, the weight fraction of columbite was estimated as 2.78%, whereas in the Ta compound the weight fraction of $MgTa_2O_6$ and $Mg_4Ta_2O_9$ were 7.03% and 8.05%, respectively.

From the refined mixing parameters ($m$), giving the relative occupation of the metal sites by Mg(II) and Nb(V) or Ta(V), the crystallographic formulas of $Mg_5Nb_4O_{15}$ and $Mg_5Ta_4O_{15}$ can be written as $(Mg_{0.73(2)}Nb_{0.27(2)})_{4c}(Mg_{0.94(2)}Nb_{1.06(2)})_{8f}O_5$ and $(Mg_{0.66(2)}Ta_{0.34(2)})_{4c}(Mg_{1.01(2)}Ta_{0.99(2)})_{8f}O_5$, respectively. It is interesting to note that the relative magnesium and tantalum occupancies in the tantalum compound would permit, in principle, the formation of a superstructure with formula $(Mg_2Ta)_{4c}(Mg_3Ta_3)_{8f}O_{15}$, but there are no additional lines in the diffraction pattern that confirm this possibility, at least in the sample prepared at 1550°C. However, we suggest that quenching from synthesis temperature to room temperature would increase the possibility of obtaining an ordered structure. The differences found in the $m$
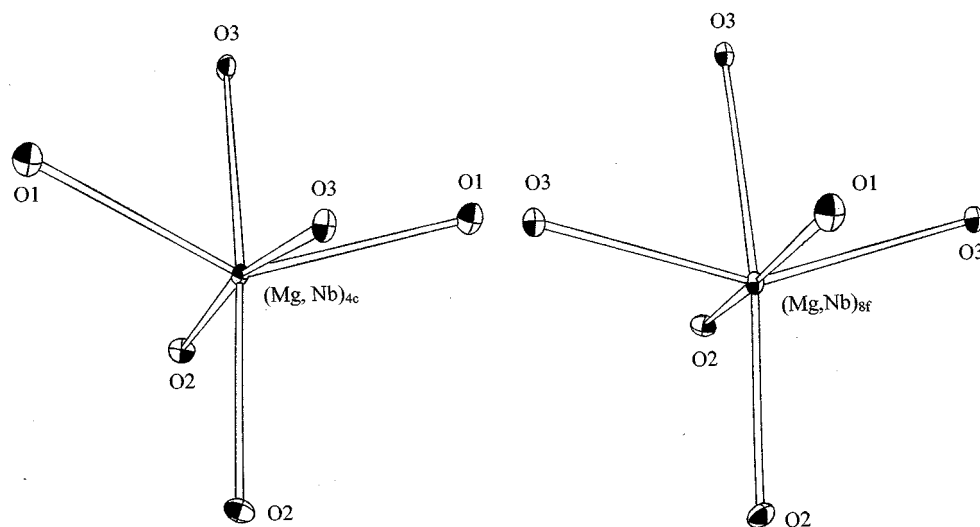


**FIG. 3.** View of the oxygen coordination polyhedra of the two different metal sites, 4c and 8f, in $Mg_5Nb_4O_{15}$.

occupancy factors for both compounds cannot be explained in terms of ionic radii, since hexacoordinated Ta(V) and Nb(V) both have the same ionic radii (0.64 Å) (17); likewise the average interatomic distances $\langle (Mg, M)_{8f} \, O \rangle$ and $\langle (Mg, M)_{4c}–O \rangle$ for $M = Nb$ or Ta are coincident within the experimental error (Tables 5 and 6).

The mixed occupancy of both metal positions by different cations has already been described for disordered pseudo-brookite phases. For instance, Tiedemann and Müeller-Buscbaum (18) reported a crystallographic formula $(Fe_{0.667} Ti_{0.333})_{4c}(Ti_{0.667}Fe_{1.333})_{8f}O_5$ for disordered $Fe_2TiO_5$.

Metal atoms in both 4c and 8f positions are hexacoordinated to oxygens as shown in Fig. 3. From bond distances and angles, the coordination polyhedra for both positions can be described as distorted tetrahedra (with $(Mg, M)$–O distances between 1.93 and 1.98 Å), with two additional longer bonds to oxygen (with distances ranging from 2.17 to 2.22 Å) giving rise to very distorted octahedra.
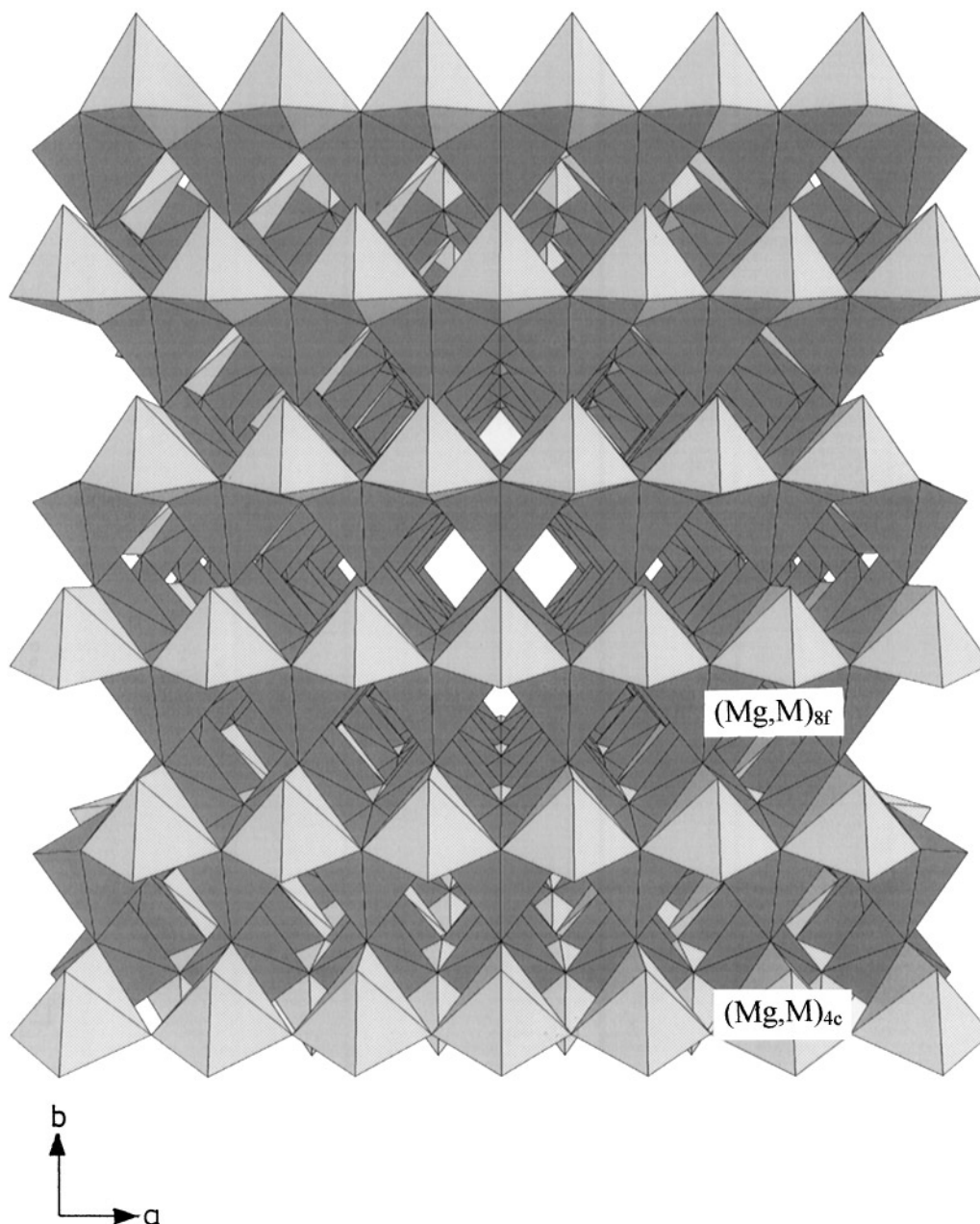


**FIG. 4.** Overall view of the $Mg_5M_4O_{15}$ ($M = Nb$ or Ta) structure. Dark octahedra represent the $(Mg, M)_{4c}O_6$ units and light octahedra represent the $(Mg, M)_{8f}O_6$ units.

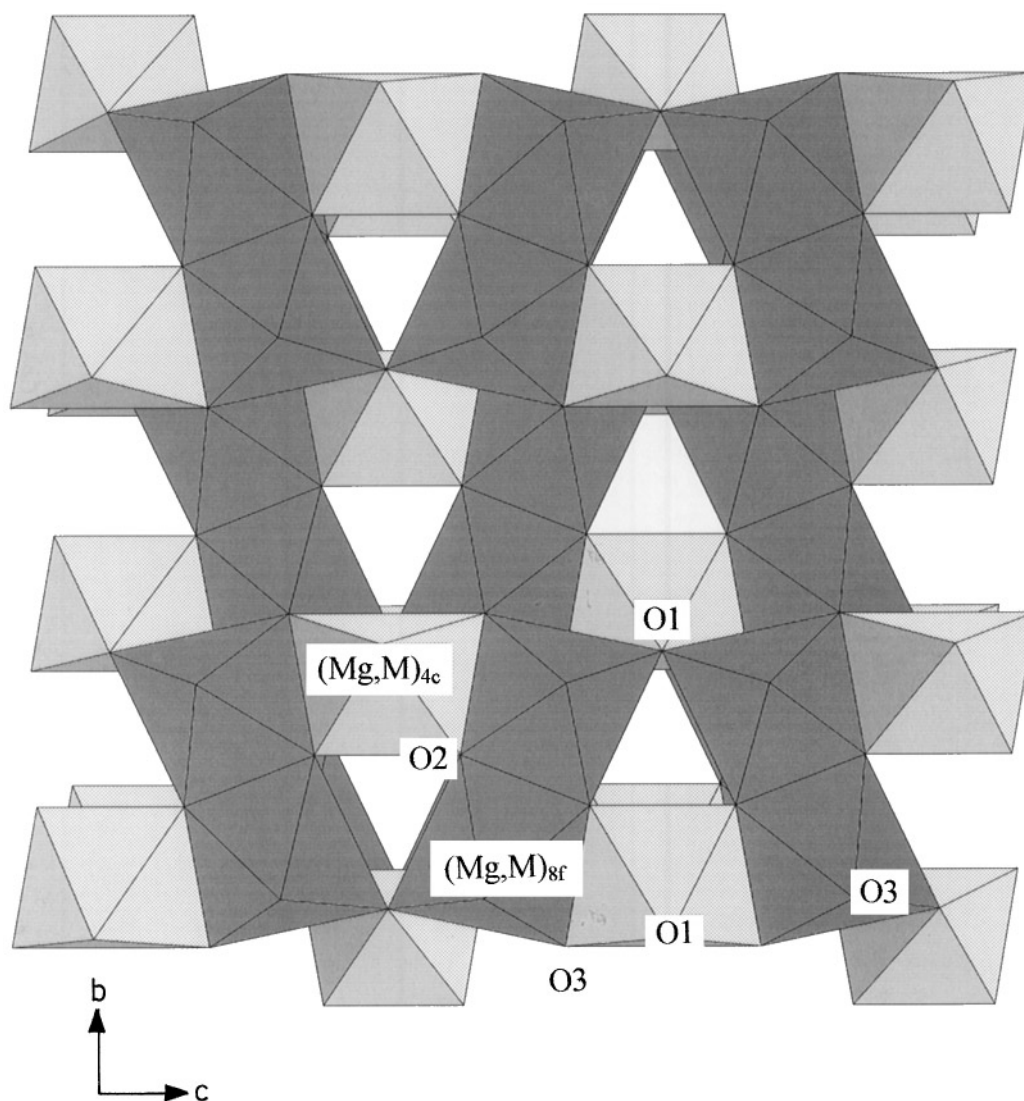**FIG. 5.** Projection showing a partial aspect of the crystal structure: the double chains of $(Mg, M)O_6$ ($M$ = Nb or Ta) units on the $bc$ plane.

| TABLE 5 | |
|---|---|
| Some Interatomic Distances in $Mg_5Nb_4O_{15}$ | |
| Atoms | Distance (Å) |
| $(Mg, Nb)_{4c}$–O1 | 2.044(1) $\times 2$ |
| $(Mg, Nb)_{4c}$–O2 | 1.963(2) $\times 2$ |
| $(Mg, Nb)_{4c}$–O3 | 2.188(2) $\times 2$ |
| $\langle(Mg, Nb)_{4c}$–O$\rangle$ | 2.065(2) |
| | |
| $(Mg, Nb)_{8f}$–O1 | 2.171(2) |
| $(Mg, Nb)_{8f}$–O2 | 1.927(2) |
| $(Mg, Nb)_{8f}$–O2 | 2.060(2) |
| $(Mg, Nb)_{8f}$–O3 | 1.9855(6) $\times 2$ |
| $(Mg, Nb)_{8f}$–O3 | 2.216(2) |
| $\langle(Mg, Nb)_{8f}$–O$\rangle$ | 2.057(2) |

| TABLE 6 | |
|---|---|
| Some Interatomic Distances in $Mg_5Ta_4O_{15}$ | |
| Atoms | Distance (Å) |
| $(Mg, Ta)_{4c}$–O1 | 2.0507(9) $\times 2$ |
| $(Mg, Ta)_{4c}$–O2 | 1.958(2) $\times 2$ |
| $(Mg, Ta)_{4c}$–O3 | 2.198(2) $\times 2$ |
| $\langle(Mg, Ta)_{4c}$–O$\rangle$ | 2.069(2) |
| | |
| $(Mg, Ta)_{8f}$–O1 | 2.164(1) |
| $(Mg, Ta)_{8f}$–O2 | 1.938(2) |
| $(Mg, Ta)_{8f}$–O2 | 2.048(2) |
| $(Mg, Ta)_{8f}$–O3 | 1.9877(5) $\times 2$ |
| $(Mg, Ta)_{8f}$–O3 | 2.211(2) |
| $\langle(Mg, Ta)_{8f}$–O$\rangle$ | 2.056(2) |

Figure 4 shows an overall view of the structure. It can be described as follows: $(Mg, M)_{4c}O_6$ octahedra ($M$ = Nb or Ta) share edges on the $bc$ plane with $(Mg, M)_{8f}O_6$ units to form double chains, parallel to the $c$ axis, as shown in Fig. 5. Within these double chains, adjacent $(Mg, M)_{8f}O_6$ polyhedra also share corners through O1 oxygens. The double chains are linked together along the [100] direction through O1 and O3 oxygens, giving rise to a three-dimensional array. Another important feature of this structure, shown in Fig. 4, is the presence of infinite chains of corner-sharing $(Mg, M)_{4c}O_6$ octahedra running along the $a$ axis. The rather bent $(Mg, M)_{4c}$–O1–$(Mg, M)_{4c}$ angle along the chains is 137.26(5) ($M$ = Nb) and 137.21(3) ($M$ = Ta). These chains are linked together by $(Mg, M)_{8f}O_6$ units sharing edges.

The oxidation states of both metal cations, Mg(II) and Nb(V) or Ta(V), allow us to presume the insulating behavior of $Mg_5M_4O_{15}$ ($M$ = Nb or Ta). In $Mg_5Nb_4O_{15}$, the fact that Nb(V) cations can be rather easily reduced to Nb(IV), with an ionic radius (0.68 Å) very close to that of Mg(II) (0.72 Å) (17), suggests the possibility of formation of reduced compounds in which Mg(II) is partially substituted by Nb(IV), giving rise to phases of stoichiometry $Mg_{5-x}Nb_{4+x}O_{15-y}$, with the Nb(IV)/Nb(V) ratio increasing with $x$ and $y$. The mixed-valence Nb(IV)/Nb(V) in the hypothetical intermediate phases suggests interesting electrical and magnetic properties for these compounds, based on the structure of pseudobrookite. Such phases with a pseudobrookite-type structure have been identified in the X-ray powder diffraction patterns of some reduction products of $MgNb_2O_6$ (columbite) (19), and they are being studied at present.

## ACKNOWLEDGMENTS

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