Supplementary data. Ti^{4+}-, Sn^{4+}-, $^{VI}Ge^{4+}$-, ^{VI}Si-, $^{VI}Mn^{4+}$-, $^{VI}Pb^{4+}$-, $^{VI}Te^{4+}$-, Nb-, Ta-, Sb^{5+}-, Mo^{6+}-, W^{6+}-, U^{4+}, and Th-oxide minerals with the stoichiometry MO_2 which do not belong to the columbite supergroup

For the sake of completeness, we report in this section selected data on a number of mineral species which, although based on the MO_2 stoichiometry, do not meet the criteria for belonging to the wolframite-columbite supergroup.

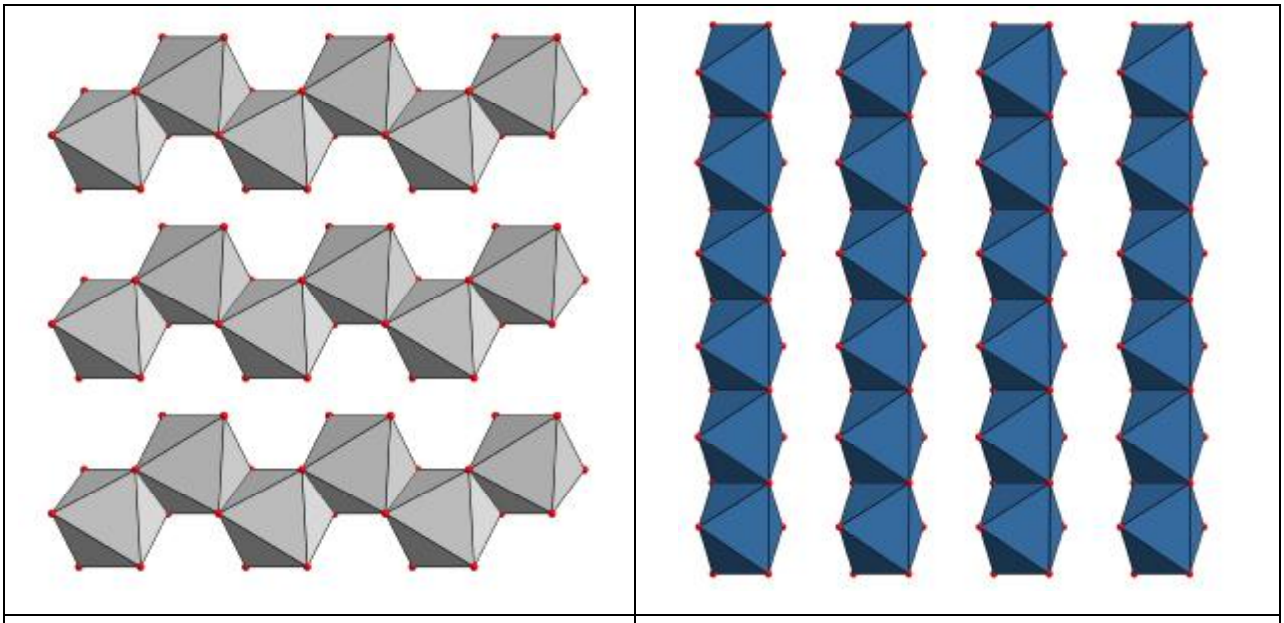
In *biehlite*, Sb_2MoO_6 (space group *C*2/*c*, *a* 18.08, *b* 5.92, *c* 5.08 Å, β 97.0°, *Z* = 4), MoO_6 octahedra share edges to form infinite *zig-zag* chains (Schlüter *et al*., 2000). However, generally the structure of biehlite is topologically different from those of columbite supergroup minerals.

In *alumotantite*, $AlTaO_4$ (space group *Pbcn*, *a* 4.47, *b* 11.31, *c* 4.775 Å; Z = 4), AlO_6 octahedra share edges to form infinite *zig-zag* chains. The octahedra TaO_6 share common vertices to form layers. The Al- and Ta-centered octahedra share common edges (Voloshin *et al*., 1981; Ercit *et al*., 1992).

Simpsonite (Kerr and Holmes, 1945), $Al_4Ta_3O_{13}(OH)$ (space group *P*3, *a* 7.39, *c* 4.52 Å; *Z* = 1), is remotely related to alumotantite: hexagonal closest-packing of oxygen atoms in simpsonite is preserved in its topotactic substitution with alumotantite (Ercit *et al*., 1992).

The *tapiolite-group minerals*, *tapiolite*-(*Fe*) and *tapiolite*-(*Mn*) are dimorphous with *columbite*-(*Fe*) and *columbite*-(*Fe*), respectively, but there are significant differences between the crystal structures of these minerals. Minerals of the tapiolite group (Wise and Černý, 1996) are tetragonal, space group *P*4/*mnm* or *P*4$_2$/*mnm*, with the general formula $M1M2_2O_6$ (*M*1 = Mg, Mn^{2+}, Fe^{2+}; *M*2 = Ta, Sb^{5+}) and unit-cell parameters *a* = 4.6 – 4.8, *c* = 9.1 – 9.3 Å (*Z* = 2). In tapiolite-(Fe) (Goldschmidt, 1926), both the Fe^{2+} and Ta cations occupy unique positions in the ordered structure (equivalent to the Ti sites in rutile) and have a distorted octahedral arrangement. Each oxygen atom is surrounded by three cations. Edge-sharing octahedra form chains parallel to [001], with an intrachain stacking sequence (*M*1-*M*2-*M*2)$_\infty$. Adjacent chains are linked by shared vertices of the octahedra. This structure has been termed the trirutile structure (Goldschmidt, 1926).

In tapiolite-group minerals and columbites/ixiolites, octahedra share different pairs of edges. This results in the formation of *zig-zag* and direct chains, respectively (Figs. S1 and S2).



Columbite and ixiolite	Tapiolite and rutile

Fig. S1. "Layers" of chains of octahedra in the structures of columbite/ixiolite and tapiolite/rutile

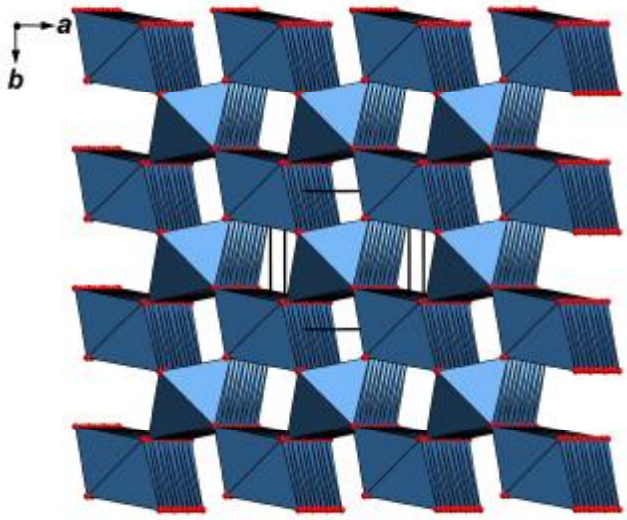


Fig. S2. Trirutile-type structure of tapiolite: a general view. The unit cell is outlined.

In the overwhelming majority of analysed tapiolite samples, Fe strongly dominates over Mn. Based on this fact as well as the fact that unit-cell parameters of tapiolite-Mn holotype are very close to those of tapiolite-(Fe) (Wise and Černý, 1996; Lahti *et al.*, 1983), the existence of natural tapiolite-(Mn) is questionable.

The other members of the tapiolite group are ***byströmite*** $MgSb^{5+}_2O_6$ (Mason and Vitaliano, 1952), ***ordoñesite*** $ZnSb^{5+}_2O_6$ (Switzer and Foshag, 1955), and ***tripuhyite*** $Fe^{2+}Sb^{5+}_2O_6$ (Mason and Vitaliano, 1953).

The *scheelite group* includes tetragonal (space group $I4_1/a$, a 5.09 – 5.24, c 11.37 – 11.69 Å; Z = 4) minerals with the general formula $M1M2O_4$ ($M1$ = Ca, Pb^{2+}, or Bi^{3+}; $M1$ = W^{6+}, Mo^{6+}, or As^{5+}). The minerals belonging to this group are scheelite, powellite, stolzite, wulfenite, and tetrarooseveltite. The crystal structures of these minerals are based on a quasi-framework formed by edge-sharing *zig-zag* chains of $M1O_8$ polyhedra; isolated $M2O_4$ tetrahedra share common vertices with the $M1$-polyhedra (Figs. S3 and S4).

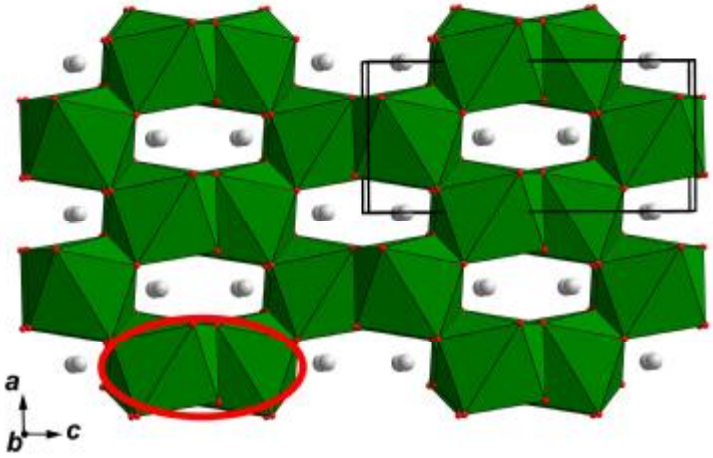


Fig. S3. The crystal structure of scheelite-group minerals. A *zig-zag* chain of $M1O_8$ polyhedra is shown with the ellips.

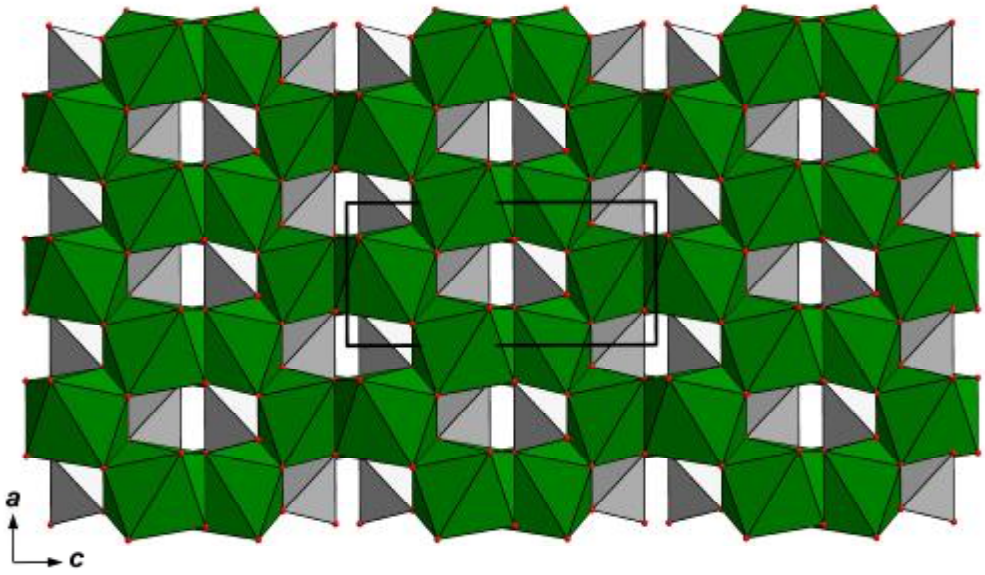
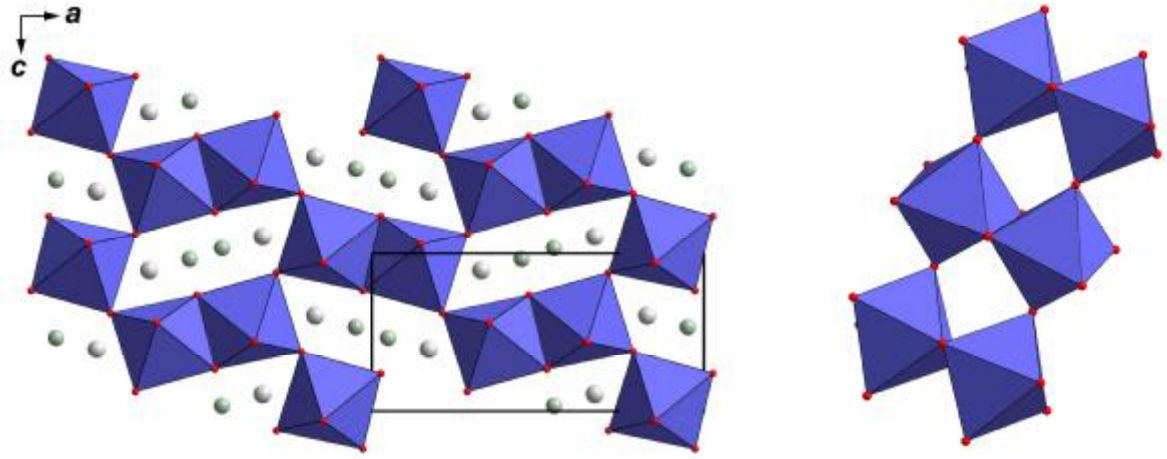


Fig. S4. The crystal structure of scheelite in polyhedral presentation. W-centered tetrahedra are grey.

The fergusonite group contains monoclinic or tetragonal minerals with the general formula $M1M2O_4$ (*M*1 = *REE*, *M*2 = Nb, Ta), which are topologically similar to members of the scheelite-group. The M2 cation may have tetragonal or strongly distorted octahedral coordination.

The crystal structures of *aeschynite-group minerals* (orthorhombic, space group *Pnmb*, *a* 7.4 – 7.5, *b* 10.9 – 11.1, *c* 5.2 – 5.4 Å; *Z* = 4) with the general formula $M1M2_2(O,OH)_6$ (*M*1 = Ca, *REE*; *M*2 = Ti, Nb, Ta) is based on a quasi-framework composed by double chains of pairs of edge-sharing $M2O_6$ octahedra (Fig. S5). The chains are connected with each other *via* common vertices of the octahedra.



a b

Fig. S5. General view of the aeschynite crystal structure (a), and double chain of Ti-centered octahedra in aeschynite (b).

Cervantite-group minerals with the general formula $M1^{3+}M2^{5+}O_4$ (*M*1 = Sb, Bi; *M*2 = Nb, Ta, Sb) are characterized by orthorhombic symmetry (space group $Pna2_1$ or *Pnan*, *a* ~ 5.6, *b* ~ 4.9 *c* ~ 11.8 Å; *Z* = 4). The crystal structures are based on layers of corner-sharing $M2^{5+}O_6$ octahedra alternating with the rows built by $M1^{3+}O_4$ polyhedra, that could be considered as a tetragonal pyramids with four basal oxygen atoms and the apical vertex at which the non-bonded electron pair is pointing. The rows and the layers are linked *via* common oxygen vertices.

The *koechlinite group* includes koechlinite $Bi^{3+}{}_2Mo^{6+}O_6$ and russellite $Bi^{3+}{}_2W^{6+}O_6$. Both minerals are orthorhombic (space group $Pca2_1$, *a* ~ 5.4 – 5.5, *b* ~ 16.2 – 16.4, *c* ~ 5.5 Å; *Z* = 4). The structure is based on the layers of corner-sharing distorted $M2O_6$ octahedra (with four short *M*2–O bonds and two elongate bonds) sandwiched between layers of bismuth and oxygen where Bi has six-fold coordination. Presumably, tungstibite $Sb^{3+}{}_2W^{6+}O_6$ is related to the koechlinite group.

The *thoreaulite-group minerals*, *thoreaulite* $Sn^{2+}Ta_2O_6$ and foordite $Sn^{2+}Nb_2O_6$ form solid-solution series. The minerals are monoclinic (space group *C*2/*c*, *a* ~ 17.1, *b* ~ 4.9, *c* ~ 5.5 – 5.6 Å, β

~ 90.9°; *Z* = 4). Their structures are based on the two-octahedron-thick, perforated sheets of Ta/Nb-centred octahedra alternating with the layers of edge-sharing SnO_8 polyhedra.

The crystal structure of ***brannerite-group minerals*** (brannerite $U^{4+}Ti_2O_6$ and thorutite $ThTi_2O_6$, both monoclinic, space group *C*2, *Cm*, or *C*2/*m*, *a* ~ 9.8, *b* ~ 3.8, *c* ~ 7.0 Å, β ~ 119°; *Z* = 2) contains layers of edge-sharing ***zig-zag*** chains of TiO_6 octahedra. Isolated direct chains of edge-sharing UO_2 or ThO_2 octahedra occur between the layers.

In ***rosiaite***, $PbSb^{5+}{}_2O_6$, layers of isolated PbO_6 octahedra alternate with layers formed by six-membered rings of edge-sharing SbO_6 octahedra (Fig. S6).

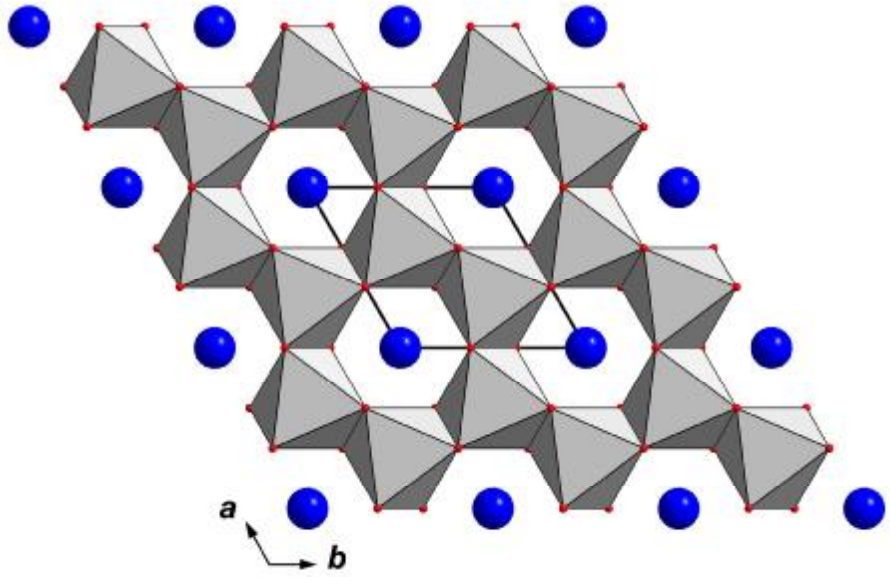


Fig. S6. The crystal structure of rosiaite. Pb atoms are shown with blue balls.

Data on these and some other minerals with the stoichiometry MO_2 which do not belong to the columbite supergroup are given in Table S1.

Table S1. Some Ti^{4+}-, Sn^{4+}-, $^{VI}Ge^{4+}$-, ^{VI}Si-, $^{VI}Mn^{4+}$-, $^{VI}Pb^{4+}$-, $^{VI}Te^{4+}$-, Nb-, Ta-, Sb^{5+}-, Mo^{6+}- and W^{6+}-oxide minerals with the stoichiometry MO_2 which do not belong to the columbite supergroup.

Name	Endmember formula	Comments
Tapiolite group (all tetragonal)		
Tapiolite-(Fe)	$Fe^{2+}Ta_2O_6$	
Tapiolite-(Mn)	$Mn^{2+}Ta_2O_6$	
Byströmite	$MgSb^{5+}{}_2O_6$	
Ordoñesite	$ZnSb^{5+}{}_2O_6$	
Tripuhyite	$Fe^{2+}Sb^{5+}{}_2O_6$	
Rutile group (all tetragonal)		
Rutile	TiO_2	
Argutite	GeO_2	
Cassiterite	SnO_2	
Paratellurite	TeO_2	
Plattnerite	PbO_2	
Pyrolusite	MnO_2	
Stishovite	SiO_2	
Cervantite group (all orthorhombic)		
Bismutocolumbite	$BiNbO_4$	
Bismutotantalite	$BiTaO_4$	
Stibiocolumbite	$SbNbO_4$	
Stibiotantalite	$SbTaO_4$	
Cervantite	$Sb^{3+}Sb^{5+}O_4$	
Scheelite group (all tetragonal)		
Scheelite	$CaMoO_4$	
Powellite	$PbWO_4$	
Stolzite	$CaMoO_4$	
Wulfenite	$PbMoO_4$	
Tetrarooseveltite	$Bi^{3+}AsO_4$	
Fergusonite group (tetragonal and monoclinic)		
Fergusonite-(Ce)	$CeNbO_4$	Tetragonal; in the IMA List of Minerals the formula is given as $CeNbO_4 \cdot 0.3H_2O$
Fergusonite-(Y)	$YNbO_4$	Tetragonal
Formanite-(Y)	$YTaO_4$	Tetragonal
Fergusonite-(Ce)-β	$CeNbO_4$	Monoclinic
Fergusonite-(Nd)-β	$NdNbO_4$	Monoclinic
Fergusonite-(Y)-β	$YNbO_4$	Monoclinic
Aeschynite group (all orthorhombic)		
Aeschynite-(Ce)	$CeTi_2O_5(OH)$	In the IMA List of Mineral the formula is given as$(Ce,Ca,Fe,Th)(Ti,Nb)_2(O,OH)_6$

Aeschynite-(Nd)	$NdTi_2O_5(OH)$	In the IMA List of Mineral the formula is given as $(Nd,\textit{Ln},Ca)(Ti,Nb)_2(O,OH)_6$
Aeschynite-(Y)	$YTi_2O_5(OH)$	In the IMA List of Mineral the formula is given as $(Y,\textit{Ln},Ca,Th)(Ti,Nb)_2(O,OH)_6$
Nioboaeschynite-(Ce)	$Ce(NbTi)O_6$	In the IMA List of Mineral the formula is given as $(Ce,Ca)(Nb,Ti)_2(O,OH)_6$
Nioboaeschynite-(Y)	$Y(NbTi)O_6$	In the IMA List of Mineral the formula is given as $(Y,REE,Ca,Th,Fe)(Nb,Ti,Ta)_2(O,OH)_6$
Tantaloaeschynite-(Y)	$Y(TaTi)O_6$	In the IMA List of Mineral the formula is given as $Y(Ta,Ti,Nb)_2O_6$
Vigezzite	$CaNb_2O_6$	In the IMA List of Mineral the formula is given as $(Ca,Ce)(Nb,Ta,Ti)_2O_6$
Rynersonite	$CaTa_2O_6$	
Koechlinite group (all orthorhombic)		
Russellite	Bi_2WO_6	
Koechlinite	Bi_2MoO_6	
Tungstibite	Sb_2WO_6	Belonging to the koechlinite group is questionable
Thoreaulite group (both monoclinic)		
Foordite	$Sn^{2+}Nb_2O_6$	
Thoreaulite	$Sn^{2+}Ta_2O_6$	
Brannerite group (both monoclinic)		
Thorutite	$ThTi_2O_6$	In the IMA List of Mineral the formula is given as $(Th,U,Ca)Ti_2(O,OH)_6$
Brannerite	$U^{4+}Ti_2O_6$	
Baddeleyite group (both monoclinic)		
Baddeleyite	ZrO_2	
Akaogiite	TiO_2	
Uraninite group (all cubic)		
Uraninite	UO_2	
Thorianite	ThO_2	
Cerianite-(Ce)	CeO_2	
Tazheranite	ZrO_2	In the IMA List of Mineral the formula is given as $(Zr,Ti,Ca)(O,\square)_2$. Ca is considered as a component stabilizing the cubic structure.
Zirkelite	TiO_2	In the IMA List of Mineral the formula is given as $(Ti,Zr,Ca)O_{2-x}$. Ca is considered as a component stabilizing the cubic structure.

Vorlanite	$(Ca_{0.5}U^{6+}_{0.5})O_2$	
Ungrouped minerals		
Rosiaite	$PbSb^{5+}_2O_6$	Trigonal
Petscheckite	$U^{4+}Fe^{2+}Nb_2O_8$	Trigonal? Metamict. Related to liandratite?
Alumotantite	$AlTaO_4$	Orthorhombic
Simpsonite	$Al_4Ta_3O_{13}(OH)$	Trigonal
Pisekite-(Y)	$YNbO_4$?	Monoclinic? In the IMA List of Mineral the formula is given as $(Y,As,Ca,Fe,U)(Nb,Ti,Ta)O_4$
Brookite	TiO_2	Orthorhombic
Anatase	TiO_2	Tetragonal
Biehlite	Sb_2MoO_6	Monoclinic
Ramsdellite	MnO_2	Orthorhombic. Forms solid-solution series with groutite MnO(OH).
Akhtenskite	MnO_2	Hexagonal
Plattnerite	PbO_2	Tetragonal
Tellurite	TeO_2	Orthorhombic
Koragoite	$Mn^{2+}_3Nb_3(NbMn)W_2O_{20}$	Monoclinic. In the IMA List of Mineral the formula is given as $Mn^{2+}_2Mn^{3+}Nb_2(Nb,Ta)_3W_2O_{20}$

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