

## Mg<sub>5</sub>TiO<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub>

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Single crystals of pentamagnesium titanium(IV) tetraoxide bis(borate), Mg<sub>5</sub>TiO<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub>, were prepared by slow cooling of the melt from 1623 K in air. The crystal is isostructural with the mineral ludwigite (Mg<sub>2</sub>FeO<sub>2</sub>BO<sub>3</sub>). The Mg and Ti atoms are coordinated by six O atoms and the B atom is coordinated by three O atoms. There are three Mg sites and one mixed site statistically occupied by Mg and Ti atoms. Atoms are at the following special positions: 2*a* (0, 0, 0) and 2*d* (0,  $\frac{1}{2}$ ,  $\frac{1}{2}$ ) for two Mg atoms, 4*g* (*x*, *y*, 0) for the mixed Ti/Mg site and the BO<sub>3</sub> group, and 4*h* (*x*, *y*,  $\frac{1}{2}$ ) for a third Mg and two oxide O atoms. MgO<sub>6</sub> and (Ti/Mg)O<sub>6</sub> octahedra are connected by sharing of edges to form zigzag folding layers along the *c* axis. Triangular prismatic tunnels are formed between the folding layers by sharing apical O atoms of the MgO<sub>6</sub> and (Ti/Mg)O<sub>6</sub> octahedra.

### Comment

Some oxyborates with a structural chemical formula of M<sub>5</sub>M<sup>IV</sup>O<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub> have been reported. The title compound, Mg<sub>5</sub>TiO<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub>, and Mg<sub>5</sub>SnO<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub> were synthesized by

Konijnendijk & Blasse (1985). They presumed that Mg<sub>5</sub>TiO<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub> and Mg<sub>5</sub>SnO<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub> were isostructural with ludwigite [Mg<sub>2</sub>FeO<sub>2</sub>BO<sub>3</sub> or Mg<sub>4</sub>Fe<sub>2</sub>O<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub>; Takéuchi *et al.*, 1950] and orthopinakiolite [Mg<sub>3</sub>Mn<sub>3</sub>O<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub>; Randmets, 1960; Takéuchi, 1978], respectively. They also synthesized solid solutions of Mg<sub>5</sub>Sn<sub>1-x</sub>Ti<sub>x</sub>O<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub> (0 ≤ *x* ≤ 1) and reported their photoluminescence properties. Crystal structure analysis of these compounds, however, was not carried out. Recently, the crystal structure of Mg<sub>5</sub>SnO<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub> has been found to be a novel ludwigite-type superstructure [triclinic, space group  $F\bar{1}$ , *a* = 6.1295 (8) Å, *b* = 18.714 (3) Å, *c* = 24.719 (3) Å, α = 90.021 (5)°, β = 90.032 (4)° and γ = 90.041 (5)°] by single-crystal X-ray diffraction (Kawano & Yamane, 2010). On the other hand, no information on the crystal structure of Mg<sub>5</sub>TiO<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub> has been reported. In the present study, we confirmed Mg<sub>5</sub>TiO<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub> as isostructural with the mineral ludwigite (Mg<sub>2</sub>FeO<sub>2</sub>BO<sub>3</sub>, orthorhombic, space group *Pbam*) and analysed its crystal structure. Synthetic oxyborates having the ludwigite structure are, for example, Ni<sub>5</sub>M<sup>IV</sup>O<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub> [M<sup>IV</sup> = Ti (Stenger *et al.*, 1973; Armbruster & Lager, 1985), V (Bluhm & Müller-Buschbaum, 1989*a*), Mn (Bluhm & Müller-Buschbaum, 1989*a*), Ge (Bluhm & Müller-Buschbaum, 1989*b*) and Zr (Bluhm & Müller-Buschbaum, 1989*b*)], Co<sub>5</sub>M<sup>IV</sup>O<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub> [M<sup>IV</sup> = Ti (Stenger *et al.*, 1973), Mn (Utzolino & Bluhm, 1996) and Sn (Utzolino & Bluhm, 1996)] and Zn<sub>5</sub>MnO<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub> (Busche & Bluhm, 1995).

Figs. 1 and 2 show the coordination environments for the Mg, Ti, B and O atoms, and the crystal structure of Mg<sub>5</sub>TiO<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub>, respectively. In the asymmetric unit, there are three Mg sites and one mixed site statistically occupied by Mg and Ti atoms with an occupancy of 0.5. Atoms in the crystal structure are at the following special positions: 2*a* (0, 0, 0) for Mg<sub>3</sub>, 2*d* (0,  $\frac{1}{2}$ ,  $\frac{1}{2}$ ) for Mg<sub>4</sub>, 4*g* (*x*, *y*, 0) for Ti<sub>1</sub>/Mg<sub>1</sub>, B<sub>1</sub>, O<sub>1</sub>, O<sub>2</sub> and O<sub>3</sub>, and 4*h* (*x*, *y*,  $\frac{1}{2}$ ) for Mg<sub>2</sub>, O<sub>4</sub> and O<sub>5</sub>. The formula of Mg<sub>4</sub>(MgTi)O<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub> is obtained by replacing two Fe atoms

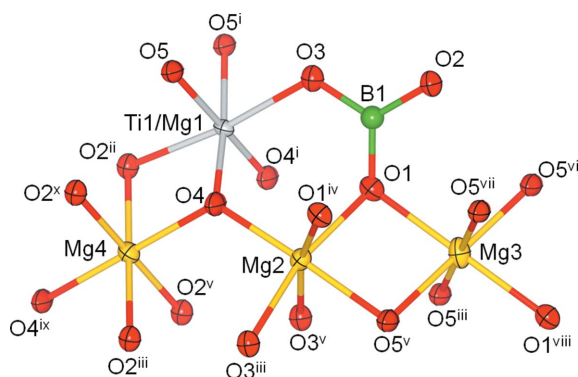


Figure 1

The atomic arrangement around Mg, Ti, B and O atoms in the structure of Mg<sub>5</sub>TiO<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub>. Displacement ellipsoids are drawn at the 90% probability level. [Symmetry codes: (i) *x*, *y*, *z* - 1; (ii) -*x* +  $\frac{1}{2}$ , *y* +  $\frac{1}{2}$ , *z*; (iii) *x* -  $\frac{1}{2}$ , -*y* +  $\frac{1}{2}$ , -*z* + 1; (iv) *x*, *y*, *z* + 1; (v) *x* -  $\frac{1}{2}$ , -*y* +  $\frac{1}{2}$ , -*z*; (vi) -*x* +  $\frac{1}{2}$ , *y* -  $\frac{1}{2}$ , *z*; (vii) -*x* +  $\frac{1}{2}$ , *y* -  $\frac{1}{2}$ , *z* - 1; (viii) -*x*, -*y*, -*z*; (ix) -*x*, -*y* + 1, -*z* + 1; (x) -*x* +  $\frac{1}{2}$ , *y* +  $\frac{1}{2}$ , *z* + 1.]

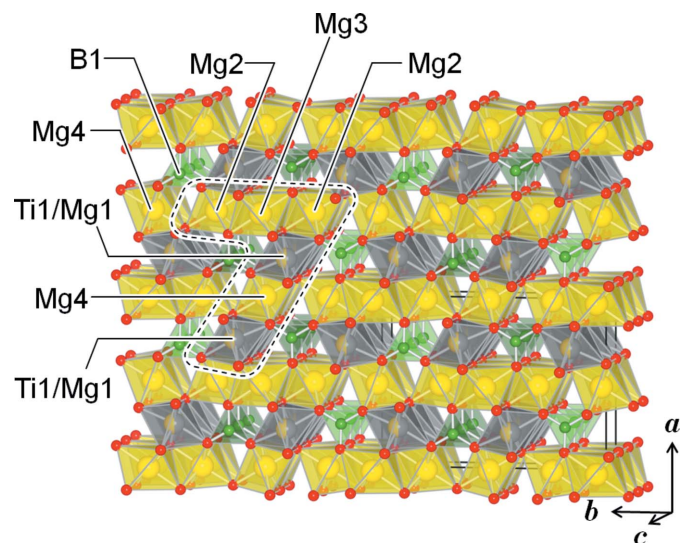


Figure 2

The crystal structure of Mg<sub>5</sub>TiO<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub> in a representation using cation-centred oxygen polyhedra. The area surrounded by the dashed line represents the repeating unit of the zigzag folding layers.

in  $\text{Mg}_4\text{Fe}_2\text{O}_4(\text{BO}_3)_2$  (Takéuchi *et al.*, 1950) by Mg and Ti atoms, *i.e.*  $2\text{Fe}^{3+} \rightarrow \text{Mg}^{2+} + \text{Ti}^{4+}$ .

Mg and Ti atoms are situated in six-coordinated oxygen octahedra.  $\text{MgO}_6$  and  $(\text{Ti}/\text{Mg})\text{O}_6$  octahedra are connected by sharing of edges to form zigzag folding layers along the *c* axis. As shown in Fig. 2, a repeating unit of the folding layers is composed of  $\text{Mg}_2\text{O}_6$ – $\text{Mg}_3\text{O}_6$ – $\text{Mg}_2\text{O}_6$  stacking along the *b* axis and  $(\text{Ti}/\text{Mg})\text{O}_6$ – $\text{Mg}_4\text{O}_6$ – $(\text{Ti}/\text{Mg})\text{O}_6$  stacking along the *a* axis. The folding layers are connected by sharing the apical O4 atoms of the  $\text{Mg}_2\text{O}_6$ ,  $\text{Mg}_4\text{O}_6$  and  $(\text{Ti}/\text{Mg})\text{O}_6$  octahedra. Triangular prismatic tunnels are formed between the folding layers. The B1 atoms in the tunnels are coordinated by the O1, O2 and O3 atoms, forming isolated triangular borate groups of  $\text{B}_1\text{O}_3$ . O4 and O5 belonging to the  $\text{Mg}_2\text{O}_6$ ,  $\text{Mg}_4\text{O}_6$  and  $(\text{Ti}/\text{Mg})\text{O}_6$  octahedra make no bond with the B1 atoms.

Bond valence sums (BVS; Brown & Altermatt, 1985) of the Mg, Ti and B atoms were calculated with the bond valence parameters  $l_0(\text{Mg}^{2+}) = 1.693 \text{ \AA}$ ,  $l_0(\text{Ti}^{4+}) = 1.815 \text{ \AA}$  and  $l_0(\text{B}^{3+}) = 1.371 \text{ \AA}$  (Brese & O'Keeffe, 1991). The BVS values of the Mg2, Mg3 and Mg4 atoms were 2.1, 2.0 and 2.1, respectively. Those of the Ti1 and Mg1 atoms at the Ti1/Mg1 site were 3.33 and 2.39, respectively. The average of these values is 2.86 and close to the mean valence (+3) of  $\text{Mg}^{2+}$  and  $\text{Ti}^{4+}$ . The B1–O distances are in the range 1.377 (4)–1.388 (4)  $\text{ \AA}$ , and these values are consistent with those of  $M_5^{\text{II}}M^{\text{IV}}\text{O}_4(\text{BO}_3)_2$  [1.32 (3)–1.43 (3)  $\text{ \AA}$ ] mentioned above (Stenger *et al.*, 1973; Armbruster & Lager, 1985; Bluhm & Müller-Buschbaum, 1989*a,b*; Stenger *et al.*, 1973; Utzolino & Bluhm, 1996; Busche & Bluhm, 1995). The O–B1–O angles of 119.0 (3)–121.9 (3)° indicate an almost trigonal planar geometry for  $\text{B}_1\text{O}_3$ .

## Experimental

The starting materials were powders of MgO (99.9%, Rare Metallic),  $\text{TiO}_2$  (99.9%, Rare Metallic) and  $\text{H}_3\text{BO}_3$  (99.99%, Sigma-Aldrich). MgO was heated at 1173–1273 K for 6–12 h in air before weighing. The powders were weighed with a  $\text{MgO}:\text{TiO}_2:\text{H}_3\text{BO}_3$  molar ratio of 5:1:2.7 and mixed in an agate mortar with a pestle. The mixture was pressed into a pellet, placed in a platinum boat and heated at 1623 K for 6 h in air. The heating and cooling rates were 200 and 15 K  $\text{h}^{-1}$ , respectively. The pellet partially melted, and single crystals were formed on its edge. A colourless and transparent single crystal showing blue emission under 254 nm ultraviolet excitation was selected.

### Crystal data

$\text{Mg}_5\text{TiO}_4(\text{BO}_3)_2$	$V = 343.29 (3) \text{ \AA}^3$
$M_r = 351.07$	$Z = 2$
Orthorhombic, <i>Pbam</i>	Mo $K\alpha$ radiation
$a = 9.2636 (5) \text{ \AA}$	$\mu = 1.76 \text{ mm}^{-1}$
$b = 12.2989 (5) \text{ \AA}$	$T = 298 \text{ K}$
$c = 3.01309 (15) \text{ \AA}$	$0.13 \times 0.09 \times 0.08 \text{ mm}$

### Data collection

Rigaku R-AXIS RAPID II diffractometer	3166 measured reflections
Absorption correction: numerical (NUMABS; Higashi, 1999)	463 independent reflections
$T_{\text{min}} = 0.864$ , $T_{\text{max}} = 0.925$	413 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.027$

**Table 1**

Selected geometric parameters ( $\text{ \AA}$ , °).

Ti1/Mg1–O4	1.9528 (11)	Mg3–O5 <sup>ii</sup>	2.0872 (11)
Ti1/Mg1–O5	2.0643 (11)	Mg3–O1	2.1047 (15)
Ti1/Mg1–O3	2.0829 (16)	Mg4–O4	2.0326 (15)
Ti1/Mg1–O2 <sup>i</sup>	2.1172 (16)	Mg4–O2 <sup>i</sup>	2.1142 (11)
Mg2–O4	1.9778 (16)	O1–B1	1.379 (3)
Mg2–O5 <sup>ii</sup>	2.0645 (17)	O2–B1	1.385 (3)
Mg2–O1	2.1110 (12)	O3–B1	1.387 (3)
Mg2–O3 <sup>ii</sup>	2.1296 (12)		
O1–B1–O2	121.8 (2)	O2–B1–O3	119.2 (2)
O1–B1–O3	119.00 (19)		

Symmetry codes: (i)  $-x + \frac{1}{2}, y + \frac{1}{2}, z$ ; (ii)  $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ .

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$	54 parameters
$wR(F^2) = 0.070$	$\Delta\rho_{\text{max}} = 0.41 \text{ e \AA}^{-3}$
$S = 1.29$	$\Delta\rho_{\text{min}} = -0.42 \text{ e \AA}^{-3}$
463 reflections	

Anisotropic displacement parameters were refined for Mg, Ti and O atoms. The site-occupation factors (SOFs) of the Ti and Mg atoms at the Ti1/Mg1, Mg2, Mg3 and Mg4 sites were fixed to 0.5/0.5, 1.0, 1.0 and 1.0, respectively, in the final refinement, because the refined SOF values of the Ti and Mg atoms at the Ti1/Mg1 site were close to 0.5, and those of the Mg atoms at the Mg2, Mg3 and Mg4 sites were around 1.0. The highest peak ( $0.41 \text{ e \AA}^{-3}$ ) and the deepest hole ( $-0.42 \text{ e \AA}^{-3}$ ) in the final difference map were observed at (0.2108, 0.1396, 0), 0.59  $\text{ \AA}$  from B1, and at (0.0030, 0.7446,  $\frac{1}{2}$ ), 0.46  $\text{ \AA}$  from Mg2, respectively.

Data collection: *PROCESS-AUTO* (Rigaku/MSC, 2005); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2005); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *VESTA* (Momma & Izumi, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KU3033). Services for accessing these data are described at the back of the journal.

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