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Short communication

$Li_{3.366}Mg_{0.317}B_2O_5$: The first pyroborate in the Li_2O-MgO-B_2O_3 system

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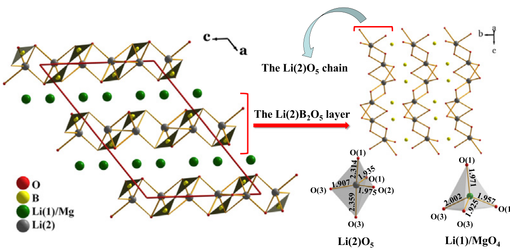
GRAPHICAL ABSTRACT

The first pyroborate in the Li_2O-MgO-B_2O_3 system featuring edge- and face-sharing LiO_5 polyhedra, $Li_{3.366}Mg_{0.317}B_2O_5$, has been synthesized *via* high temperature solution method.



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ABSTRACT

The first pyroborate in the Li_2O-MgO-B_2O_3 system, $Li_{3.366}Mg_{0.317}B_2O_5$, has been synthesized *via* high temperature solution method. The crystal structure can be described as isolated B_2O_5 units connecting with the Li(2) O_5 chains to generate the ${}^{2}_{\infty}[Li_2(2)B_2O_5]$ layers, which condense alone *a*-axis, and the co-occupied Li(1)/Mg atoms fill into the voids between the layers. Interestingly, edge- and face-sharing Li(2)O_5 polyhedra are rarely found in $Li_{3.366}Mg_{0.317}B_2O_5$ and its maternal compound β-$Li_4B_2O_5$. Moreover, torsion and dihedral angles between two BO_3 triangles of B_2O_5 in $Li_{4-2x}Mg_xB_2O_5$ (x = 0, 0.317, 2) are investigated to explore the structure regulation *via* introduction of the Mg^{2+} cation. The structure refinement, thermal stability and infrared spectrum are presented in detail.

During the last several decades, increasing attention has been focused on the design and synthesis of nonlinear optical materials, especially borates: one of the fascinating and practically important characteristics of the borate crystals is their wide variety of structure chemistry [1–16]. In general, the boron atoms can bond with oxygen atoms to form the BO_3 triangles or the BO_4 tetrahedra, then the BO_3 triangles or the BO_4 tetrahedra share corners (or edges) to create various B—O clusters as the fundamental building blocks (FBBs), such as B_2O_5, B_3O_6, B_5O_{11}, B_6O_{13}, *etc.*, which can further generate zero-dimensional (0D) clusters, rings and cages, or polymerize into 1D infinite chains, 2D layers, or 3D frameworks [17–30]. The diverse structures make borate own excellent properties for technical applications, some borates, such as LiB_3O_5 (LBO) [31], β-BaB_2O_4 (β-BBO) [32], CsB_3O_5 (CBO) [33], $CsLiB_6O_{10}$ (CLBO) [34] and $KBe_2BO_3F_2$ (KBBF) [35] have been reported and commercialized.

Over the past few decades, the Li_2O–B_2O_3 system gains extensive attention due to the excellent optical properties and abundant structures [36–44], such as LBO [31], $Li_2B_4O_7$ [37], Li_3BO_3 [40], $Li_4B_2O_5$ [43] and $Li_6B_4O_9$ [44] *etc.* According to the diagonal relationships of the periodic table of elements, the magnesium element is physically and chemically similar to lithium element [45], namely, both of them possess similar ionic radius (Li: 0.76 and Mg: 0.72) and low coordination (such as, 4, 5, 6). Hence, it is a feasible strategy to substitute the alkali-metal lithium by magnesium to synthesize a new class of

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Table 1
Crystal data and structure refinement for $Li_{3.366}Mg_{0.317}B_2O_5$.

Empirical formula	$Li_{3.366}Mg_{0.317}B_2O_5$
Crystal system	Monoclinic
Space group	C2/c (No. 15)
a (Å)	12.710(10)
b (Å)	4.796(4)
c (Å)	8.517(7)
β (°)	126.960(8)
Volume (Å^3)	414.9(6)
Z	4
Reflections collected/unique	1202/478 [*R*(int) = 0.0268]
GOF on F^2	1.0604
Final *R* indices [*I* > 2sigma(I)][a]	R_1 = 0.0424, wR_2 = 0.1019
R indices (all data)[a]	R_1 = 0.0562, wR_2 = 0.1106

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w\ F_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$.

compounds.

Based on the Inorganic Crystal Structure Database (ICSD 3.7.0), only the single crystal structure of $LiMgBO_3$ in $Li_2O–MgO–B_2O_3$ system [46] was reported. Moreover, powder X-ray diffraction data of $Li_{2.45}Mg_{0.3}BO_{3.025}$ [47] and $Li_2MgB_2O_5$ [48,49] have been previously characterized, while the crystal structure were failed to obtain. Hence, the research in the $Li_2O–MgO–B_2O_3$ system is under-investigation, which drives us to explore and anticipate to obtain new borate in this system.

Guided by the above ideas, extensive efforts performed led to a new crystal of $Li_{3.366}Mg_{0.317}B_2O_5$ (LMBO), which is the first pyroborate in the $Li_2O–MgO–B_2O_3$ system. In terms of the structure, the rarely found $Li(2)O_5$ chains in borate link with B_2O_5 to form the $^2_\infty[Li_2(2)B_2O_5]$ layers, then the layers condense alone *a*-axis, and distorted Li(1)/Mg atoms fill into the layers to generate a 3D framework. In addition, the configurations of B_2O_5 were investigated to explore the structure regulation *via* introduction of doped cation.

The LMBO was obtained *via* high temperature solution method with spontaneous crystallization method (all experimental details are presented in the Supporting information). The detailed information of crystal structure is listed in Table 1, Table S1 and Table S2 in the Supporting information. The polycrystalline sample of LMBO was synthesized by solid-state reaction method (Fig. 1). For comparison, the polycrystalline samples of $Li_4B_2O_5$ and $Mg_2B_2O_5$ were synthesized with the similar method.

LMBO crystallizes in a monoclinic system with space group of C2/c. There are one crystallographically unique O(2) atom with 4*e* site symmetry and other all atoms with 8*f* site symmetry in the asymmetric unit of LMBO. All B atoms are coordinated to three oxygen atoms to create the BO_3 triangles, then two BO_3 triangles vertex-share one O atom to form the isolated B_2O_5 polyhedra (FBBs). The Li(2) atoms form $Li(2)O_5$ chains through edge- and face-sharing of five O atoms, which

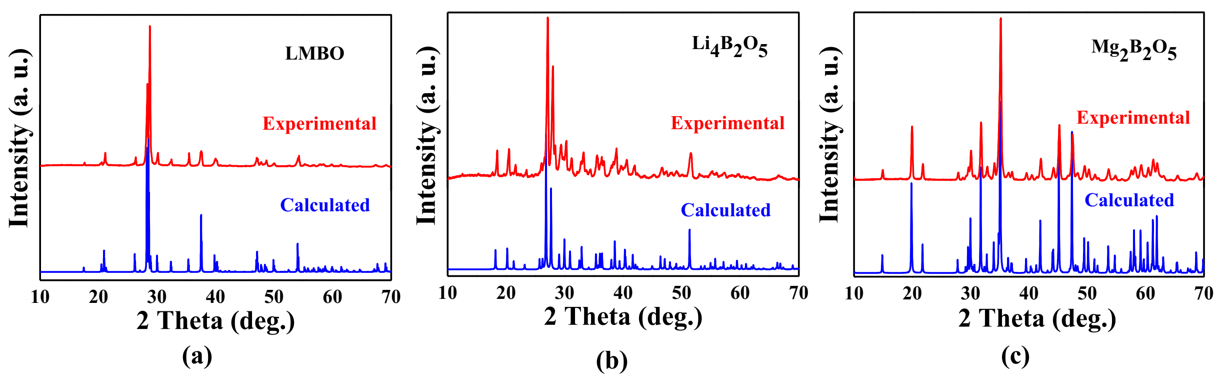

Fig. 1. Experimental and calculated XRD patterns of (a) LMBO, (b) $Li_4B_2O_5$, (c) $Mg_2B_2O_5$.

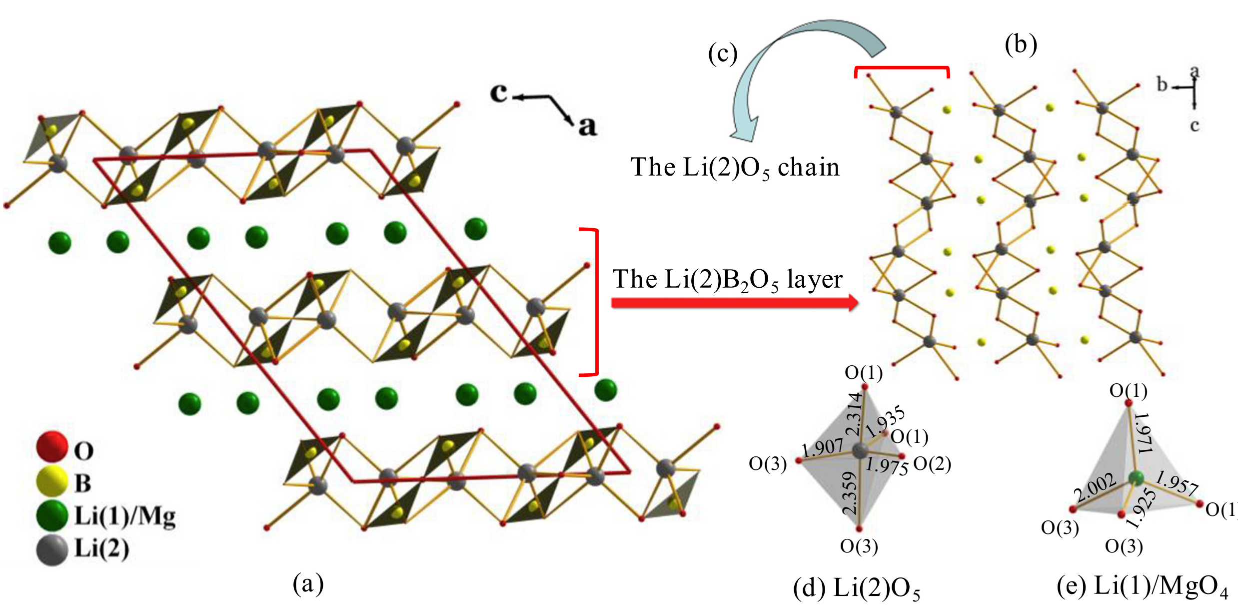

Fig. 2. (a) The overall structure of LMBO. (b) The $Li(2)B_2O_5$ infinite layer. (c) The $Li(2)O_5$ chain. (d) The $Li(2)O_5$ polyhedron. (e) The $(Li(1)/Mg)O_4$ tetrahedron.