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$Li_{0.8}Mg_{2.1}B_2O_5F$:the First Borate Fluoride with Magnesium-oxygen-fluorine Octahedral Chains

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We have claimed that the fluoride atom exists in LMBF by solving the crystal structure and by the powder synthesis experiment (we are unable to synthesize the LMBF compound without fluoride precursors) and by the EDS experiment. And in order to further confirm that our structural mode is correct, we have also tried other possibilities as follows: (a) LMBF was synthesized by high temperature solution method and it is less possible to contain OH which can also be proved by IR spectrum and the TG curve (Fig. 6 and 7) since there is no OH absorption peak on IR spectrum and there is no weight loss on the TG curve. (b) We attempt to refine the "doubtful" F atom position with half occupied O atom (and 50% vacancy to ensure the charge balance), but the refined results are GooF = 2.642, *R1* = 0.1567, *wR2* = 0.5343, which means that it is impossible for the position of F atom to have half occupied O atom. (c) The possible F atom position in the structure is located in a general position. We also try to refine the site with disordered O/F; the value of third FVAR is 1.129 which means that the disorder between the O and F atom is inappropriate. From the above discussion, we can draw the conclusion that the site is indeed occupied by F atom only. Therefore, the above paragraph has been added in the supporting information.

References:

[1] Husheng Liu, Hongxiang Shao, ICP-MS analysis technique and applications, BeiJing, 2005. (Chinese)

[2] Datong Zhang, Scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS) analysis technique, GuangZhou, 2009. (Chinese)

Table S1 Selected bond lengths (Å) and angles (deg) for LMBF[a].

Mg(1)-F(1)	1.9754(1)	Li(2)-O(5)	1.8880(1)
Mg(1)-O(4)	2.0325(2)	Li(2)-O(3)#10	1.9875(1)
Mg(1)-O(4)#1	2.0795(2)	Li(2)-O(3)#12	2.0394(1)
Mg(1)-O(2)	2.0891(1)	Li(2)-O(5)#11	2.1204(9)
Mg(1)-O(1)#2	2.0958(1)	Li(2)-O(5)#9	2.1287(1)
Mg(1)-O(2)#3	2.1154(1)	Mean	2.033
Mean	2.065	B(1)-O(2)#3	1.3673(3)
Mg(2)-F(1)	2.0008(1)	B(1)-O(1)	1.3712(3)
Mg(2)-O(3)#3	2.0577(1)	B(1)-O(5)	1.4076(3)
Mg(2)-O(3)	2.0681(1)	Mean	1.382
Mg(2)-O(1)	2.1134(1)	B(2)-O(4)	1.3356(3)
Mg(2)-O(1)#1	2.1665(1)	B(2)-O(3)#6	1.3638(3)
Mg(2)-O(2)#5	2.2038(1)	B(2)-O(5)#2	1.4230(3)
Mean	2.102	Mean	1.374
Li(1)/ Mg(3)-O(4)	1.9643(1)	O(2)#3-B(1)-O(1)	124.8(2)
Li(1)/Mg(3)-O(4)#8	1.9643(1)	O(2)#3-B(1)-O(5)	115.4(2)
Li(1)/ Mg(3)-F(1)	2.1165(1)	O(1)-B(1)-O(5)	119.8(2)
Li(1)/Mg(3)-F(1)#8	2.1165(1)	O(4)-B(2)-O(3)#6	126.6(2)
Li(1)/Mg(3)-F(1)#3	2.1329(1)	O(4)-B(2)-O(5)#2	120.7(2)
Li(1)/Mg(3)-F(1)#6	2.1329(1)	O(3)#6-B(2)-O(5)#2	112.6(2)
Mean	2.071		

[a] Note. Symmetry transformations used to generate equivalent atoms: #1 x+1,y,z; #2 x+1/2,-y+1/2,z+1/2; #3 x-1,y,z; #4 x-1/2,-y+1/2,z+1/2; #5 x-1/2,-y+1/2,z-1/2; #6 -x+2,-y+1,-z+2; #7 x+1/2,-y+1/2,z-1/2; #8 -x+1,-y+1,-z+2; #9 -x,-y,-z+2; #10 -x+3/2,y-1/2,-z+3/2; #11-x+1,-y,-z+2;#12 x-3/2,-y+1/2,z+1/2; #13 -x+1/2,y-1/2,-z+5/2; #14 -x+1/2,y+1/2,-z+5/2; #15 -x+3/2,y+1/2,-z+3/2; #16 x+3/2,-y+1/2,z-1/2

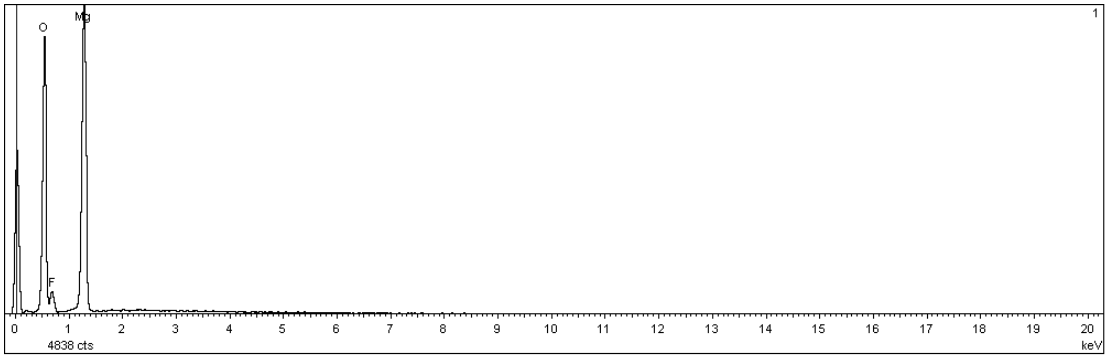

Fig. S1 The EDS spectrum of the LMBF crystal. (The molar ratio: Mg:O:F=1.7:3.8:1)

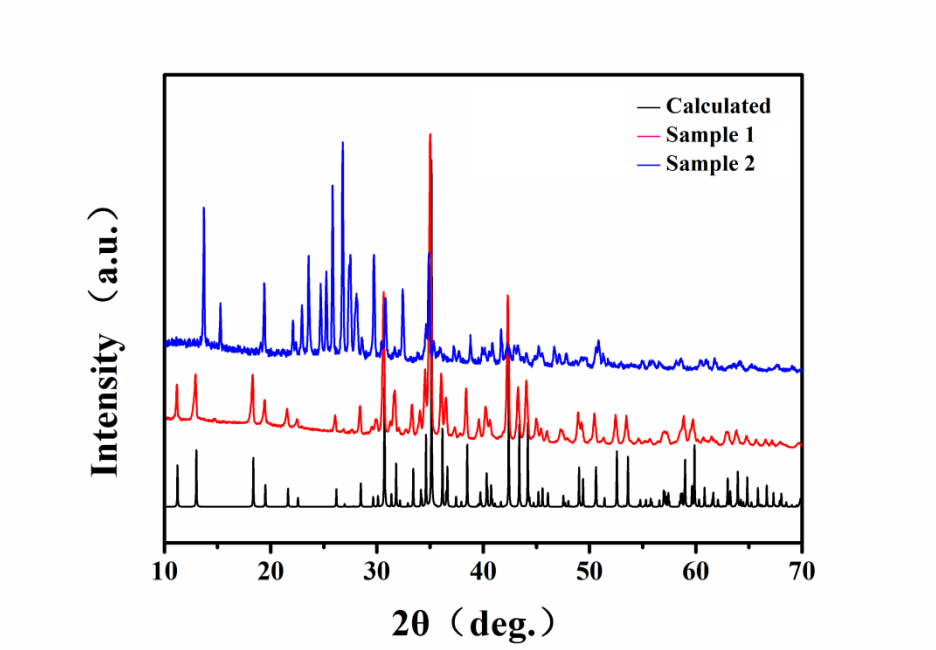

Fig. S2 XRD patterns of the LMBF: sample **1** containing F element; sample **2** without F element.