Structure of two new borates $YCa_3(AlO)_3(BO_3)_4$ and $YCa_3(GaO)_3(BO_3)_4$

Yi Yu[a], Q.S. Wu[a], R.K. Li[b],*

[a]*Department of Chemistry, Tongji University, Shanghai 200092, China*
[b]*Beijing Center for Crystal Research and Development, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100080, China*

Abstract

By replacing Mn in $YCa_3(MnO)_3(BO_3)_4$ with trivalent Al and Ga, two new borates with the compositions of $YCa_3(MO)_3(BO_3)_4$ (M = Al, Ga) were prepared by solid-state reaction. Structure refinements from X-ray powder diffraction data revealed that both of them are isostructural to gaudefroyite with a hexagonal space group $P6_3/m$. Cell parameters of $a = 10.38775(13)$Å, $c = 5.69198(10)$Å for the Al-containing compound and $a = 10.5167(3)$Å, $c = 5.8146(2)$Å for the Ga analog were obtained from the refinements. The structure is constituted of AlO_6 or GaO_6 octahedral chains interconnected by BO_3 groups in the ab plane to form a Kagomé-type lattice, leaving trigonal and apatite-like tunnels. It is found that most rare-earth and Cr, Mn ions can be substituted into the Y^{3+} and M^{3+} sites, respectively, and the preference of rare-earth ions to locate in the trigonal tunnel is correlated to the sizes of the M^{3+} ions.
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1. Introduction

Studies of borate compounds have attracted continuing attention in recent years. Because of the variety of their structure and their diverse properties, borates show comprehensive potential utility in fields of many aspects: nonlinear optical devices (BBO, LBO), phosphors (SrB_4O_7: Eu in UV-emitting lamps, $GdMgB_5O_{10}$: Ce, Tb in green fluorescence), self-frequency doubling laser systems (Nd: $YAl_3(BO_3)_4$), etc. [1]

The magnetic property is also an important part in the scientific research of borates. $FeBO_3$, found by Bernal et al. in 1963, is one of the extremely rare materials that combine transparency in the visible and spontaneous magnetization at room temperature [2–5]. Unusual magnetic behaviours, such as: one-dimensional (1D) magnetism in $PbMBO_4$ (M = Cr, Fe, Mn) [6], two-dimensional (2D) spin-gap

system in $SrCu_2(BO_3)_2$ [7] and frustrated triangular antiferromagnet in $LiMnBO_3$ [8] have also been reported.

Gaudefroyite, $Ca_4(MnO)_3(BO_3)_3CO_3$, is another compound with 1D ferromagnetic chains and triangular arrangement of magnetic ions [9]. It is constituted of MnO_6 octahedral chains running along c and the MnO chains are interlinked by BO_3 groups in the ab plane. Replacing the CO_3^{2-} group in graudefroyite with a BO_3^{3-} group and simultaneously superseding a Ca^{2+} with Y^{3+} to keep the charge balance, another borate compound $YCa_3(MnO)_3(BO_3)_4$ was found [10]. In an attempt to replace the Mn^{3+} in $YCa_3(MnO)_3(BO_3)_4$ with other trivalent metal ions, we obtain two new borates with the compositions of $YCa_3(AlO)_3(BO_3)_4$ and $YCa_3(GaO)_3$ $(BO_3)_4$.

2. Experimental

Samples of $YCa_3(AlO)_3(BO_3)_4$ and $YCa_3(GaO)_3(BO_3)_4$ were prepared from analytically pure starting materials of Y_2O_3, $CaCO_3$, Al_2O_3, Ga_2O_3 and H_3BO_3 by solid-state

*Corresponding author. Fax: +86 10 82621890.
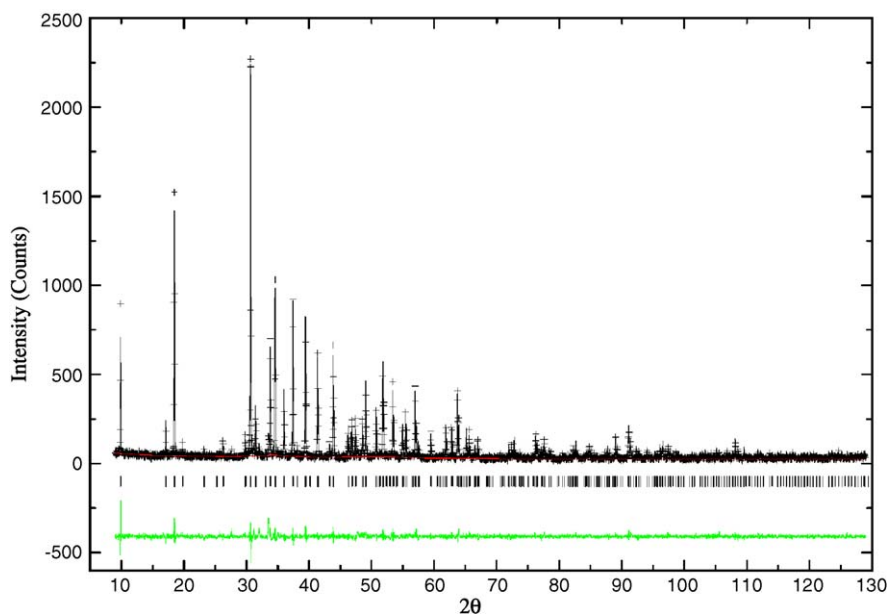*E-mail address:* rkli@cl.cryo.ac.cn (R.K. Li).

Fig. 1. The XRD patterns of $YCa_3(AlO)_3(BO_3)_4$ (the plus signs and tick marks represent observed data and peak positions, the lines are the calculated pattern and the difference plot).
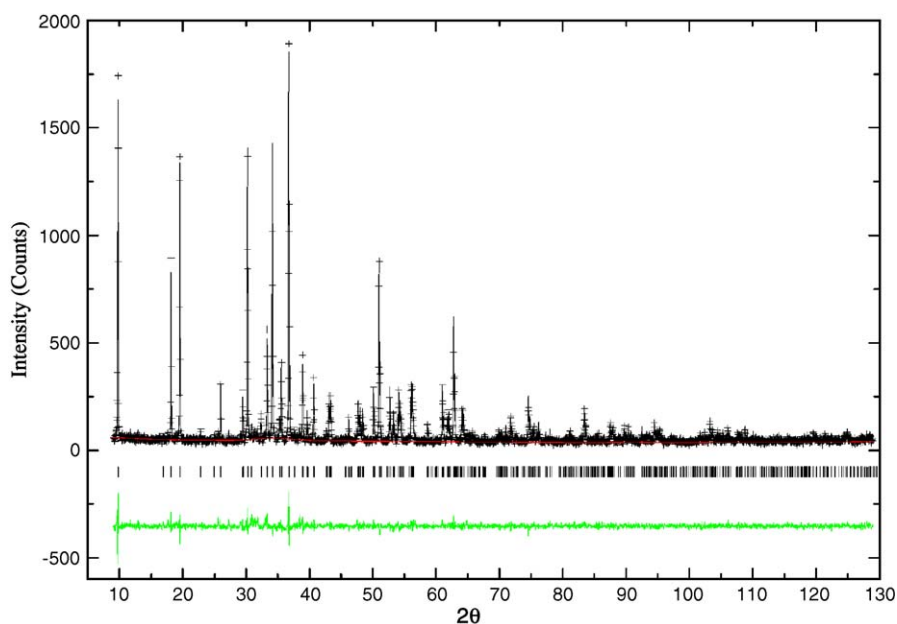

Fig. 2. The XRD patterns of $YCa_3(GaO)_3(BO_3)_4$ (see Fig. 1 for the legend).

reaction. The mixtures of the starting compounds were heated at 500 °C for 10 h and then sintered at 1000–1100 °C. Since the reaction proceeds very slowly, it is important to maintain the reaction time at 1000–1100 °C for about 3–4 weeks with several intermediate grindings. The X-ray diffraction (XRD) data were collected with a Bruker D8 diffractometer ($CuK\alpha$ radiation source, reflection mode, step size $0.03°(2\theta)$ and counting time 5 s per step with 2θ range of 9–129°). Structure refinements were carried out using the XRD data and the GSAS package [11] (Figs. 1 and 2).

3. Results and discussion

Inspection of the XRD patterns of the title compounds revealed that they all resemble that of $YCa_3(MnO)_3(BO_3)_4$, therefore an initial structure model and atomic positions of $YCa_3(MnO)_3(BO_3)_4$ were adopted for the structure refinement. In the refinements for both compounds, the total Y/Ca ratios were fixed to their starting composition of 1:3 and the relative site occupancies ($n1$, $n2$) at Ca/Y1 and Ca/Y2 sites were refined using linear constraints of $n1 = 3(1 - n2)$ for Ca and $1 - n1 = 3n2$ for Y, respectively. The

Table 1
Refined crystallographic parameters for $YCa_3(AlO)_3(BO_3)_4$[a] and $YCa_3(GaO)_3(BO_3)_4$[b]

Atoms	Sites	x	y	z	U_{iso}	n	BVS
Ca/Y1	2c	1/3	2/3	1/4	0.0123(13)	0.203/0.797(14)	2.733+/3.153+
Ca/Y2	6h	0.1295(5)	0.8428(5)	1/4	0.018(2)	0.932/0.068(5)	2.173+/2.500+
Al	6g	0	1/2	0	0.0163(15)	1	2.778+
B1	6h	0.221(3)	0.763(3)	3/4	0.005(5)	1	2.751+
B2	4e	0	0	0.102(12)	0.05(2)	1/2	3.099+
O1	6h	0.0915(13)	0.4736(12)	1/4	0.017(4)	1	2.012−
O2	6h	0.342(2)	0.9210(14)	3/4	0.020(4)	1	1.663−
O3	12i	0.3044(9)	0.4749(8)	0.5369(12)	0.011(2)	1	2.032−
O4	12i	0.068(3)	0.917(3)	0.599(3)	0.017(4)	1/2	2.030−
Ca/Y1	2c	1/3	2/3	1/4	0.011(2)	0.29/0.71(2)	2.727+/3.141+
Ca/Y2	6h	0.1264(7)	0.8414(6)	1/4	0.014(2)	0.905/0.095(6)	2.000+/2.301
Ga	6g	0	1/2	0	0.0120(9)	1	3.086+
B1	6h	0.228(5)	0.772(5)	3/4	0.02[c]	1	2.883+
B2	4e	0	0	0.117(10)	0.02[c]	1/2	3.081+
O1	6h	0.098(2)	0.4769(15)	1/4	0.003(4)	1	2.179−
O2	6h	0.331(2)	0.915(2)	3/4	0.018(5)	1	2.023−
O3	12i	0.3021(10)	0.4770(12)	0.539(2)	0.012(4)	1	1.919−
O4	12i	0.053(3)	0.907(3)	0.587(3)	0.005(6)	1/2	1.977−

[a]Space group $P6_3/m$: $a = 10.38775(13)$Å, $c = 5.69198(10)$Å, $wR_p = 15.00\%$, $\chi^2 = 1.326$.
[b]Space group $P6_3/m$: $a = 10.5167(3)$Å, $c = 5.8146(2)$Å, $wR_p = 13.93\%$, $\chi^2 = 1.332$.
[c]Fixed.

refinements quickly converged to the agreement indices of $wR_p = 15.00\%$, $\chi^2 = 1.326$ for the Al-containing compound and $wR_p = 13.93\%$, $\chi^2 = 1.332$ for the Ga analog. The final refinements of these two new borates confirmed that they belong to an analog structure of $YCa_3(MnO)_3(BO_3)_4$. Refined crystallographic structure details are listed in Table 1.

Since Al^{3+} and Ga^{3+} ions can combine with oxygen to form six coordinated AlO_6 and GaO_6 octahedra just as Mn^{3+} ion does, in the title compounds, Al^{3+} and Ga^{3+} substitute Mn^{3+} and form the gaudefroyite lattice. The unit cell dimensions of the $YCa_3(MO)_3(BO_3)_4$ with $a = 10.38775(13)$Å, $c = 5.69198(10)$Å for $M = Al$, $a = 10.5167(3)$Å, $c = 5.8146(2)$Å for $M = Ga$ and $a = 10.5726(5)$Å, $c = 5.8576(3)$Å for $M = Mn$ reflect their difference in the M^{3+} ionic radii [12] (for Al^{3+}—0.535 Å, Ga^{3+}—0.62 Å and Mn^{3+}—0.645 Å). Although Al^{3+} and Ga^{3+} are not Jahn–Teller ions, it is found that the AlO_6 and GaO_6 octahedra are still distorted though in less extents compared to MnO_6 with the observed differences between longest and shortest M–O bonds of 0.202 Å for Al, 0.252 Å for Ga and 0.32 Å for Mn, respectively (Table 2).

In $YCa_3(MO)_3(BO_3)_4$, MO_6 octahedra share edges to form chains along c, and in ab plane the MO_6 chains are connected by triangular BO_3 groups forming a Kagomé-type lattice (Fig. 3). Two kinds of tunnels exist in the Kagomé lattice, a smaller trigonal tunnel which is occupied by a mixture of Y/Ca ions and a larger apatite-like hexagonal tunnel which hosts Ca/Y ions and isolated BO_3 groups. There is a much pronounced tendency for the Y^{3+} ion to reside in the smaller trigonal tunnel and the relative ratio of Y/Ca in this tunnel is also correlated to the M^{3+} ion size: with the highest Y content 80% for the smallest

Table 2
Selected bond lengths of $YCa_3(AlO)_3(BO_3)_4$ and $YCa_3(GaO)_3(BO_3)_4$

$YCa_3(AlO)_3(BO_3)_4$	$YCa_3(GaO)_3(BO_3)_4$
Ca/Y1–O1: 2.301(11) Å × 3	Ca/Y1–O1: 2.273(14) Å × 3
Ca/Y1–O3: 2.475(7) Å × 6	Ca/Y1–O3: 2.501(10) Å × 6
Ca/Y2–O1: 2.358(11) Å × 1	Ca/Y2–O1: 2.401(14) Å × 1
Ca/Y2–O2: 2.505(11) Å × 1	Ca/Y2–O2: 2.50(2) Å × 1
Ca/Y2–O3: 2.416(8) Å × 2	Ca/Y2–O3: 2.476(10) Å × 2
Ca/Y2–O4: 2.33(2) Å × 1	Ca/Y2–O4: 2.33(2) Å × 1
Ca/Y2–O4: 2.39(3) Å × 1	Ca/Y2–O4: 2.33(3) Å × 1
Ca/Y2–O4: 2.40(3) Å × 1	Ca/Y2–O4: 2.56(3) Å × 1
Al–O1: 1.807(7) Å × 2	Ga–O1: 1.867(8) Å × 2
Al–O2: 2.009(10) Å × 2	Ga–O2: 2.119(12) Å × 2
Al–O3: 1.926(8) Å × 2	Ga–O3: 1.984(9) Å × 2
B1–O2: 1.49(3) Å × 1	B1–O2: 1.34(5) Å × 1
B1–O3: 1.37(2) Å × 2	B1–O3: 1.41(2) Å × 2
B2–O4: 1.359(13) Å × 3	B2–O4: 1.36(2) Å × 3

Al^{3+} ion, a medium 71% Y content for Ga^{3+} ion and lowest 51% Y occupation for the largest Mn^{3+} ion. The trigonal tunnel is formed by M–O–B–O six-membered ring; its size is dictated by the M–O bond lengths since the B–O bond lengths in the BO_3 planar group among different compounds are relatively constant. Smaller tunnel means the negative charges from the surrounding oxygen atoms are more concentrative, for the charge balance, ions with higher charge prefer to sit in, thus Y^{3+} ion with a higher valence than Ca^{2+} tends to occupy the site in the trigonal tunnel. The above viewpoint is also confirmed by bond valence sums (BVS) [13] of Ca^{2+}/Y^{3+} in the hexagonal and trigonal tunnels. BVS of Ca^{2+} in trigonal tunnel is much higher (2.73+, for both $M = Al$ and Ga, well above the ideal value of 2+) than it in hexagonal one (2.18+ for

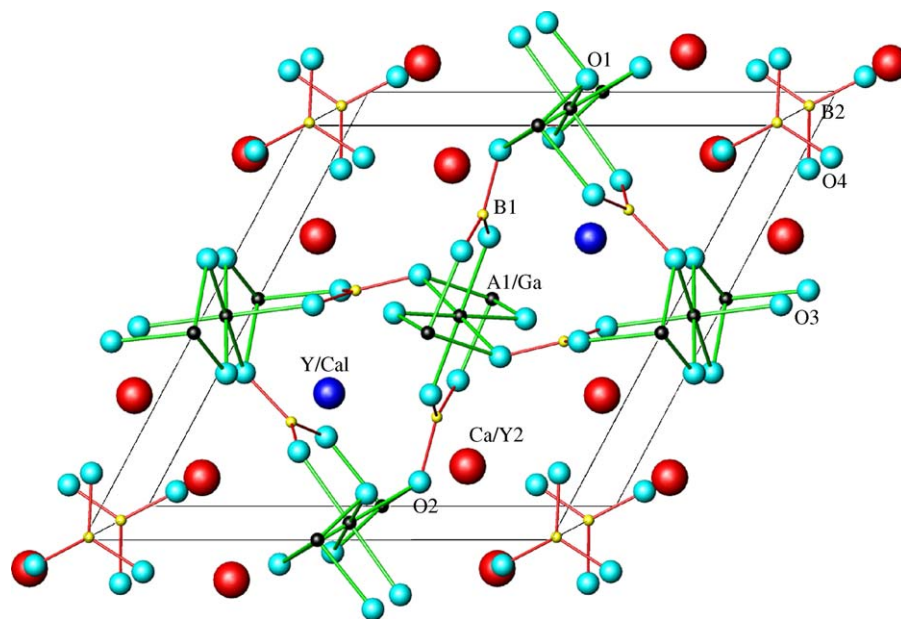Fig. 3. The structure of $YCa_3(AlO)_3(BO_3)_4$ and $YCa_3(GaO)_3(BO_3)_4$ (As B2 and O4 are half occupied, for clarity half of the B2 and O4 atoms are skipped).

$M = Al$, $2.00+$ for $M = Ga$, much closer to $2+$), so Ca^{2+} ions prefer to reside in the hexagonal tunnel. This ion selected occupation in certain sites will also affect other rare earth substitution, hence their luminescence properties.

4. Conclusion

Two new borate compounds $YCa_3(MO)_3(BO_3)_4$ ($M = Al$, Ga) were prepared by solid-state reaction at 1000–$1100\,^{\circ}C$ from substituting the Mn^{3+} ions in $YCa_3(MnO)_3(BO_3)_4$ with Al^{3+} or Ga^{3+} ions and their structures were determined by the X-ray powder diffraction data and the GSAS package. Their structures belong to space group $P6_3/m$ which are isostructural to gaudefroyite $Ca_4(MnO)_3(BO_3)_3CO_3$ and $YCa_3(MnO)_3(BO_3)_4$, composing of AlO_6 and GaO_6 octahedra along c and AlO and GaO chains linked by BO_3 groups forming an analogy Kagomé lattice in the ab plane. Ca^{2+}/Y^{3+} ions occupy the sites in the trigonal and hexagonal tunnels of the lattice. The ratio of Y^{3+} ions that reside in the trigonal tunnels depend on the sizes of the M^{3+} ions; the smaller the M^{3+} ions the more Y^{3+} ions will reside in the trigonal tunnel. Preliminary study shows that Cr, Mn and most rare-earth elements can substitute to the M^{3+} and Y^{3+} sites respectively, potential applications of the title compounds as phosphors and laser materials are under investigation.

References

[1] D.A. Keszler, Curr. Opin. Solid State Mater. Sci. 4 (1999) 155–162.
[2] I. Bernal, C.W. Struck, J.G. White, Acta Cryst. 16 (1963) 849–850.
[3] R. Diehl, Solid State Commun. 17 (1975) 743–745.
[4] V.P. Glazkov, S.E. Kichanov, D.P. Kozlenko, et al., J. Magn. Magn. Mater. 258–259 (2003) 543–544.
[5] R. Diehl, A. Räuber, F. Friedrich, J. Crystal Growth 29 (1975) 225–233.
[6] H. Park, R. Lam, J.E. Greedan, J. Barbier, Chem. Mater. 15 (2003) 1703–1712.
[7] H. Kageyama, K. Yoshimura, R. Stern, et al., Phys. Rev. Lett. 82 (1999) 3168–3171.
[8] R.K. Li, C.T. Chen, C. Greaves, Phys. Rev. B 66 (2002) 052405.
[9] R.K. Li, C. Greaves, Phys. Rev. B 70 (2004) 132411.
[10] R.K. Li, C. Greaves, Phys. Rev. B 68 (2003) 172403.
[11] A.C. Larson, R.B. von Dreele, General Structure Analysis System, Los Alamos National Lab, 1994.
[12] R.D. Shannon, Acta Cryst. A 32 (1976) 751–767.
[13] I.D. Brown, D. Altermatt, Acta Cryst. B 41 (1985) 244–247.