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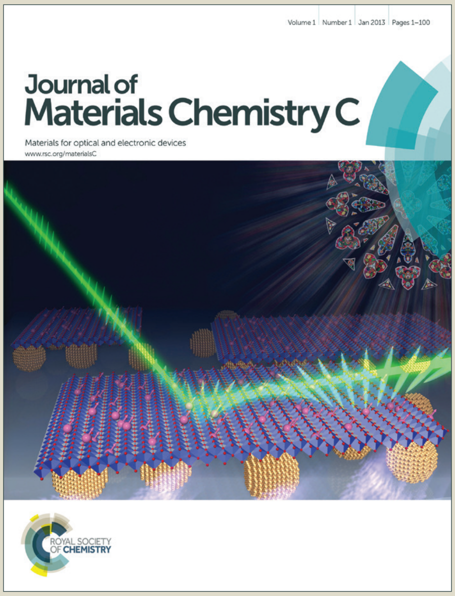

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Approaching the structure of *RE*BaB$_9$O$_{16}$ (*RE* = rare earth) by characterizations of its new analogue Ba$_6$Bi$_9$B$_{79}$O$_{138}$

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Understanding structure-property relationship is the key to rationally design superior materials. *RE*BaB$_9$O$_{16}$ (*RE* = La-Lu, Y) is a series of well-known photoluminescent hosts, which has been extensively studied but without any structure details reported. We prepared its new analogue Ba$_6$Bi$_9$B$_{79}$O$_{138}$ (**BBBO**) and proved the isomorphism by X-ray diffraction studies, in spite of the fact that they possess different cationic compositions. In addition, we successfully prepared complete solid solutions Ba$_6$(Bi$_{1-x}$Eu$_x$)$_9$B$_{79}$O$_{138}$ ($0 \le x \le 1$). Single crystal XRD characterizations on a qualified crystal of **BBBO** proposed an ordered structure model in the noncentrosymmetric space group *R*3. It possesses a layered-type structure composed of BO$_4$-BiO$_6$-BO$_4$ sandwiched layers and polyborate inter-layer groups. Ba^{2+} atoms locate in the inter-layer cavities. There are three and two independent Bi and Ba atoms, respectively. In other words, we took one more step forward in understanding the structure of *RE*BaB$_9$O$_{16}$ by analysing its new analogue. It is believed to be helpful for further interpreting and developing *RE*BaB$_9$O$_{16}$-based optical materials.

Introduction

Nowadays ternary borates have received great attention due to their promising optical performances, such as nonlinear optical (NLO) and photoluminescent (PL) properties.[1,2] Among rare earth or bismuth borates, there are lots of compounds with outstanding optical properties, for example, GdBaB$_9$O$_{16}$ and GdBa$_3$B$_9$O$_{18}$ are good phosphor hosts;[3-5] Bi$_2$ZnB$_2$O$_7$ and Cd$_4$BiO(BO$_3$)$_3$ are NLO materials.[6,7]

GdBaB$_9$O$_{16}$, which was reported by Saubat et al. as early as in 1980,[8] is the first member of a large family *REM*B$_9$O$_{16}$ (*RE* = La-Lu, Y, *M* = Sr or Ba).[9,10] This series of borates contains two types of cations, *RE*$^{3+}$ and *M*$^{2+}$. People obtained highly efficient blue, green, and red phosphors by doping rare-earth-type activators (such as Eu^{2+}, Tb^{3+}, and Eu^{3+}).[11] Massive efforts have been devoted to investigate the PL properties of *RE*BaB$_9$O$_{16}$, such as *REM*B$_9$O$_{16}$:Tb^{3+}, Ce^{3+} (*RE* = La, Gd, and Y, *M* = Sr or Ba),[9] *RE*BaB$_9$O$_{16}$:Eu^{3+},[4,10-12] GdBaB$_9$O$_{16}$:*RE* (*RE* = Gd, Sm, Dy, Pr, Nd),[3,13-15] and EuBaB$_9$O$_{16}$.[16,17] These materials have potential applications in white light-emitting diodes (WLED),[17] tricolor lamps,[11,18] plasma display panels (PLD) under VUV excitation[4,19] and as well as laser materials.[20] However, in contrast to the extensive studies on properties, the knowledge on the crystal structure of *RE*BaB$_9$O$_{16}$ was still in the primary stage. For example, several symmetrically correlated unit cells were proposed in different space groups, including hexagonal, *C*-centered monoclinic and rhombohedral.[9-11,20,21] No further structural detail was reported.

It is well known that Bi^{3+} has the same valence state, comparable cationic radius (1.03 Å for six-coordinated Bi^{3+} and La^{3+}) and therefore similar coordination behavior with rare earth cations (*RE*$^{3+}$) in many cases. For example, γ- and δ-BiB$_3$O$_6$ are isostructural with δ- and γ-*RE*B$_3$O$_6$, respectively;[22,23] Ba$_3$BiB$_9$O$_{18}$ possesses the same structure type with Ba$_3$*RE*B$_9$O$_{18}$.[24] Inspired by these reports, we initially attempted to replace *RE*$^{3+}$ in *RE*BaB$_9$O$_{16}$ by Bi^{3+}, thus to prepare a presumably existed phase "BaBiB$_9$O$_{16}$". And probably with such a plan, it is possible to obtain a single crystal because the Bi^{3+}-containing compound usually has a low melting point. In fact, we sintered a powder sample with the composition Ba : Bi : B =1 : 1 : 9, and the powder X-ray diffraction pattern presented a very similar profile with that of *RE*BaB$_9$O$_{16}$, however this sample contained other impurities like Ba$_2$B$_{10}$O$_{17}$ and Bi$_3$B$_5$O$_{12}$. This result proved our assumption that the isomorphism truly exists but the actual composition of Ba-Bi-B-O somehow deviated from "BaBiB$_9$O$_{16}$".

In the next step, the phase-pure sample was obtained when applying the starting cationic ratio of Ba : Bi : B = 2 : 3 : 28 in this quasi-ternary phase diagram. We define this ternary phase to be **BBBO** hereafter in this work. Its powder XRD pattern is very similar with that of *RE*BaB$_9$O$_{16}$ as shown in Fig. 1. Moreover, the crystallography parameters for both compounds are closely related (i.e. GdBaB$_9$O$_{16}$, *a* = 7.809 Å, *c* = 46.47 Å,[11] **BBBO**, *a* = 7.84 Å, *c* = 46.56 Å, and the possible space groups are *R*3, *R*32, or *R*3*m*). This discovery motivated us to further investigate the relationship between **BBBO** and *RE*BaB$_9$O$_{16}$, though the cationic compositions may be different.

Herein, we carefully performed the single crystal XRD on a qualified **BBBO** crystal at room temperature. Our crystallographic study proposes an ordered structure model in the noncentrosymmetric space group *R*3. The coordination for cations and the connections of the framework are chemically reasonable. The final composition for **BBBO** is determined to be Ba$_6$Bi$_9$B$_{79}$O$_{138}$. We also successfully prepared complete solid solutions of $Ba_6(Bi_{1-x}Eu_x)_9B_{79}O_{138}$ ($0 \leq x \leq 1$) by high temperature solid state reactions. Then it is evident about the isomorphism. We believe our work will help people deeply understand and rationally optimize the optical properties of "*RE*BaB_9O_{16}". At last, it also becomes very interesting to figure out why **BBBO** and "*RE*BaB_9O_{16}" share the same structure type but have different cationic ratio. The possible reason is also proposed in our study.

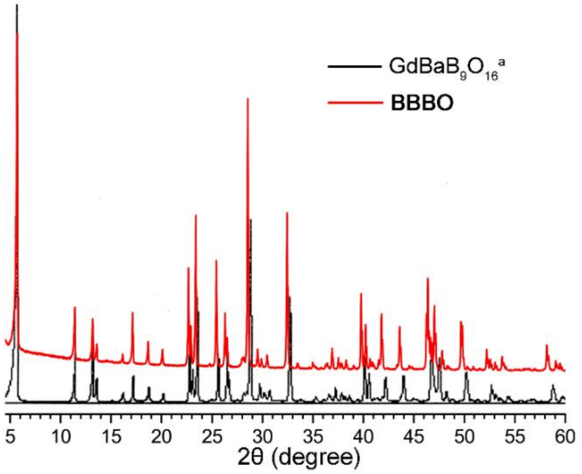

Fig. 1 Comparison of XRD patterns for $Ba_2Bi_3B_{25}O_{44}$ (synthesized in this work) and $GdBaB_9O_{16}$ (cited from ref. 11).

Experimental

Synthesis

All samples in this series were synthesized by high temperature solid state reaction. The starting materials, H_3BO_3 and Bi_2O_3, were of analytical grade and used as obtained from commercial sources without further purification; $BaCO_3$ and Eu_2O_3, were used after a pre-calcination at 800 ℃. Typically, for the synthesis of **BBBO**, a powder mixture of a stoichiometric composition of $BaCO_3$ and Bi_2O_3 was ground thoroughly together with appropriate excessive H_3BO_3 (Ba : Bi : B = 2 : 3 : 28) in an agate mortar and pressed into a small pellet. The pellet was first heated slowly (0.5 ℃/min) up to 550 ℃ and kept for 15 hours to decompose the carbonate and boric acid. The resultant mixture was extensively re-ground and pressed into a small pellet. It was further heated at 650 and 700 ℃ for 15 hours, respectively, with an intermediate grinding. The synthesis of Eu^{3+} doped samples were performed with a similar procedure. The final reaction temperature increased from 700 to 830 ℃ along with the increase of Eu^{3+} content.

In order to make clear the structure detail of this large family, single crystals of **BBBO** were grown because it has a relatively low melting point at 800 ℃ as shown in the DSC curve (see Fig. S1 in the Electronic Supplementary Information, ESI). The evaporation problem of B_2O_3 and the large difference in the density of the melting components (such as Bi_2O_3 and B_2O_3) make it difficult to obtain a homogeneous flux. Therefore, we first prepared pure **BBBO** powder by solid state reaction, and then used it as the raw material for crystal growth. The specific procedure is as below: **BBBO** powder was loaded into a Pt crucible and heated to 820 ℃. It was kept for 10 hours to obtain a homogeneous flux, which was then cooled down to 770 ℃ at a rate of 0.33 ℃/h, and followed by cooling to the room temperature naturally. Colourless block crystals of **BBBO** were obtained, which were cracked into small pieces for single crystal X-ray diffraction.

Structure determination

Single-crystal XRD data were collection at 293 K on a Bruker SMART X-ray diffractometer equipped with an APEX-CCD area detector and using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A total of 7268 reflections were collected in the region of $2.62° < \theta < 33.59°$, with $-6 \leq h \leq 12$, $-12 \leq k \leq 10$, $-63 \leq l \leq 69$, of which 3905 were independent and 3489 were observed ($I > 2\sigma$). Empirical absorption correction was applied.[25] The crystal structure was solved by direct method (SHELXS-97) and refined by full-matrix least-squares refinement.[26] All the Ba, Bi atoms were refined anisotropically, while B and O atoms were refined isotropically. Detailed crystallographic information is given in Table 1. The atomic coordinates and selected bond lengths are listed in Tables S1 and S2, respectively. CIF file and details of the structure are provided in the Supporting Information.

Table 1. X-ray data collection conditions, crystallographic and structure refinement parameters for **BBBO.**

Chemical formula	$Ba_6Bi_9B_{79}O_{138}$
Deposition No.	CCDC 1037340
M_r (g/mol)	5766.85
Space group (number)	*R*3 (146)
Lattice parameters (Å)	*a* = 7.841(1), *c* = 46.557(9)
V (Å^3)	2478.6(7)
Z	1
Density (g/cm^3)	3.86
Radiation type, λ (Å)	Mo $K\alpha 1$, 0.71073
Diffractometer	Bruker Smart Apex-CCD
Temperature (K)	293
*F*000	3771
μ(Mo Kα) (mm-1)	27.65
2θ range (deg)	5.24-67.18
Number of reflections measured	7268
Number of independent reflections	3905
Number of observed reflections	3489
Number of parameters	235
Structure determination	Direct method
Structure refinement	Shelx97
R_{int}	0.0500
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0415$
R indices (all data)	$R1 = 0.0455$
GOF	0.908

Characterizations

Powder X-ray diffraction data for the refinements of cell parameters were collected at room temperature on a PANalytical X'pert diffractometer equipped with a PIXcel 1D detector (Cu

Kα, 40 kV and 40 mA). Le Bail refinements were performed to obtain the cell parameters using TOPAS software package.[27] The thermal stability was analyzed with differential scan caloric (DSC) and thermogravimetric analysis (TGA) on a Mettler-Toledo TGA/DSC1 instrument under a N_2 flow with a heating rate of 10 ℃/min. FT-IR spectrum was measured on a NICOLET In10 MX spectrum instrument. Solid-state ^{11}B MAS NMR data was recorded on a Varian Unity Plus-400 spectrometer under a spinning speed of 20 kHz, using $BF_3{\bullet}OEt_2$ as the reference.

Results and Discussion

Crystal structure of $Ba_6Bi_9B_{79}O_{138}$

The BaO-Bi_2O_3-B_2O_3 diagram has already been reported in literature since it contains the well-known NLO compounds β-BaB_2O_4 and α-BiB_3O_6.[28,29] The phase equilibrium in this ternary system was first reported by Egorysheva and his co-workers in the temperature range of 600-700 ℃ in 2006, and four ternary compounds were reported as $Ba_3BiB_3O_9$, $BaBiBO_4$, $BaBi_2B_4O_{10}$, and "$BaBiB_{11}O_{19}$".[28] When raising the temperature to > 730 ℃, there is an additional ternary compound $Ba_3BiB_9O_{18}$.[24] In 2012, the composition of "$BaBiB_{11}O_{19}$" was corrected to be "$Ba_2Bi_3B_{25}O_{44}$" according to the single crystal X-ray diffraction.[29] In ref. 29, it crystallizes in *R*-3*m* with cell parameters of a = 7.851(2) Å and c = 46.20(1) Å. It adopts a complicated borate layered structure with Bi^{3+} ions occupying the interlayer octahedral cavities, and the Ba^{2+} ions are located in the cavities within the borate layers. It should be mentioned that the borate layer is very complex, which was described in a disordered manner.[29]

It seems that "$Ba_2Bi_3B_{25}O_{44}$" is the right formula for **BBBO**. However, when we checked the structural details in ref. 29, a chemically unreasonable fragment was observed. Fig. 2a shows a part of proposed structure model in ref. 29, where the occupancies for O8 and B3 are not equal (1/3 and 1/2, respectively). If it was true, the atomic arrangement in the real space would be unrealistic as schemed in Fig. 2b (the occupancy for B4 is reported as 1/6), where vertical oxygen atoms were missing for some $B3O_3$ triangles. We speculate this previously reported crystal symmetry is too high and this is the reason why a disordered structure model was established and led to an unreasonable structure fragment (see Fig. 2).

In our work, a qualified single crystal was selected for crystallographic study, and a relatively ordered structure model in the space group *R*3 has been established with a fine convergence during the refinements. There are 30 crystallographically independent atoms, including 2 Ba, 3 Bi, 16 O, and 9 B. Among them, 2 Ba, 3 Bi and O1 atoms are located on the three-fold axis (3*a* site). Other O and B atoms are all located in general positions (9*b* site).

Three unique Bi atoms are all coordinated by six oxygen atoms in octahedral environment with regular bond lengths and angles, as shown in Table S2. Two unique Ba atoms are both nine-coordinated with the Ba-O distances in the range of 2.89(1)-2.93(2) Å. B atoms are either three- or four-coordinated, forming BO_3 triangular or BO_4 tetrahedra. The different coordination environments of boron are confirmed by IR and ^{11}B MAS-NMR spectra as shown in Fig. S2 in ESI.

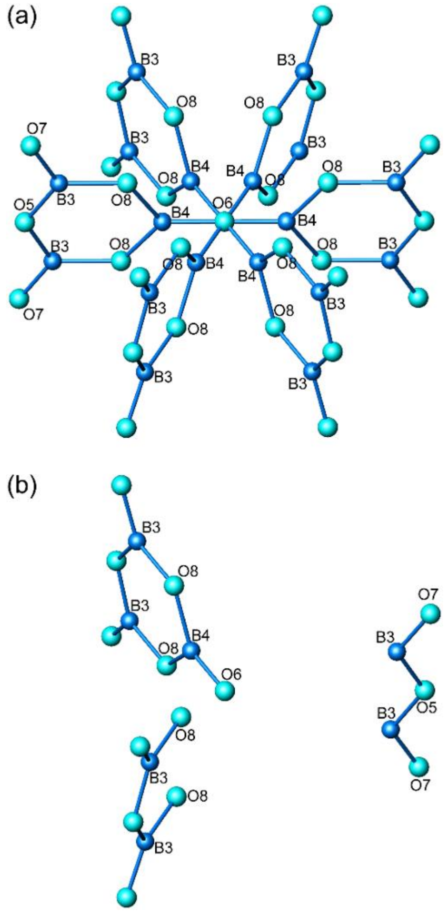

Fig. 2 (a) Structure fragment of the disordering model in *R*-3*m* proposed in ref. 29; (b) the real structural connections if the occupancy factors of B3, O8 and B4 are 1/2, 1/3 and 1/6, respectively as proposed in ref. 29. Apparently it is not chemically reasonable, because some of the B3 atoms are two-coordinated.

As the whole structure is very complex (see Fig. 3a), we need to describe the structure in a layered manner along the *c*-axis. As show in Fig. 3b, the BiO_6 octahedra aligned within the *ab*-plane sandwiched by two BO_4 layers. In detail, $B1O_4$ and $B2O_4$ share three corners (O6, O7 and O9) to form a 6_3 net parallel to *ab*-plane (see Fig. 3c); similarly, $B3O_4$ and $B4O_4$ share corners (O14, O15 and O16) and graft on the other side of BiO_6-layer. These oxygen atoms, including O6, O7, O9, O14, O15 and O16, are in fact stacked in the closed-packing fashion, and the Bi^{3+} ions occupied 1/3 of the octahedral cavities (see Fig. 3d). In other words, each BiO_6 links to 12 BO_4 tetrahedra, forming a sandwiched layer.

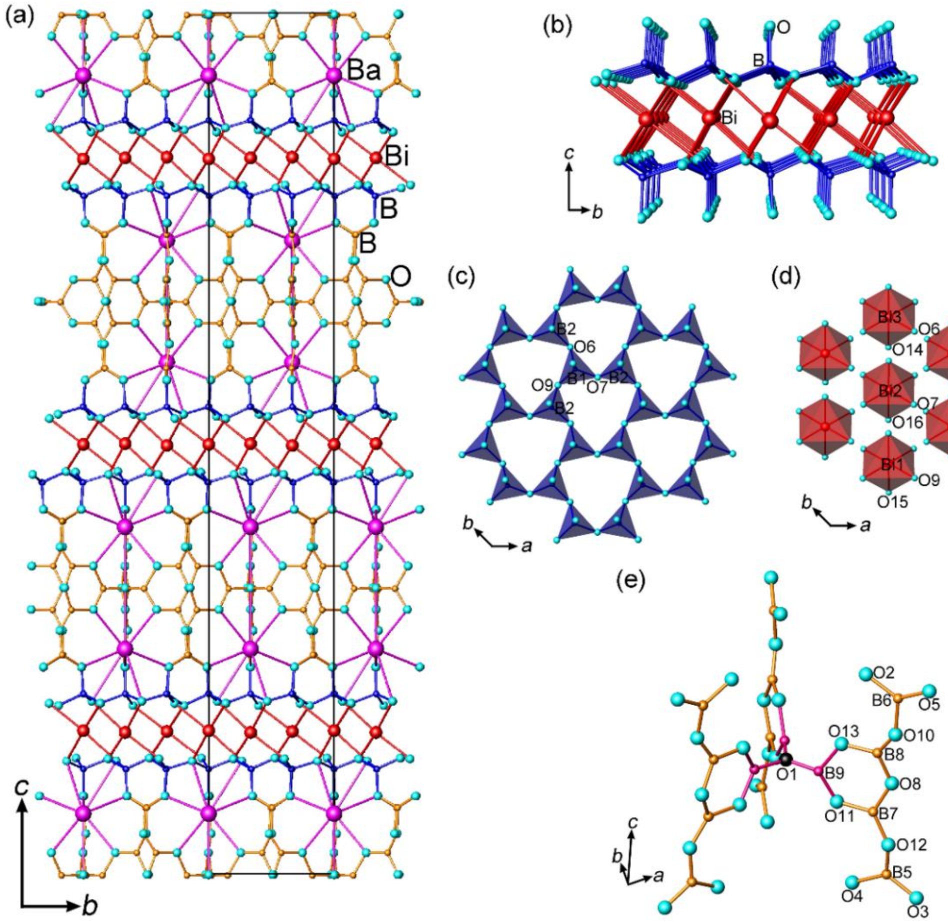

Fig. 3 (a) the whole structure of **BBBO** in the space group *R*3 determined in this work; (b) a representative view of the sandwiched layer; (c) BO_4 tetrahedra share corners to form a 6_3 net, which graft to the both sides of BiO_6-octahedra layer; (d) an arrangement of BiO_6 octahedra within the *ab*-plane; (e) an enlargement of the inter-layer polyborate species which are linked with each other through O1 atom. All the atoms are fully occupied except that B9 has an occupancy factor of 7/9 to balance the charge neutrality.

A similar sandwiched layer structure built of metal-centered octahedra and two BO_4 layers has been reported in $H_2InB_5O_{10}$,[30] while the inter-layer connections are different. As shown in Fig. S3 in ESI, the inter-layer distance in $H_2InB_5O_{10}$ is short and allows the insertion of BO_4 monolayer.[30] The inter-layer distance in **BBBO** is much longer, which is probably the longest one in layered-type metal borates. Polyborate anions interconnect the adjacent sandwiched layers into a three-dimensional structure (see Fig. 3a and 3e), where all boron atoms are exclusively three-coordinated and Ba^{2+} ions locate in large cavities within the polyborate framework. As shown in Fig. 3e, every three pentaborate anions are linked by O1, which is a three-coordinated bridge oxygen. Here, O1 was fully occupied and B9 was treated as partially occupied (7/9) in order to keep the charge neutrality. Note that B9 is the only atom with a partial occupancy factor. The occupancy factors for O11 and O13 are consistent with those of B7 and B8, thus all the species are chemically reasonable. According to the above analyses, the deduced formula for **BBBO** is $Ba_6Bi_9B_{79}O_{138}$.

Structure relationship between $Ba_6Bi_9B_{79}O_{138}$ and $REBaB_9O_{16}$

REBaB_9O_{16} has been studied for decades due to its outstanding PL performance,[8-20] however, an exact crystal structure has yet been determined. The latest structure characterization of this series was reported in 2000, and a rhombohedral structure with cell parameters of a = 7.785(2) Å and c = 46.21(1) Å for $GdBaB_9O_{16}$ (the possible space group *R*3, *R*32, and *R*3*m*) was suggested base on the analyses of XRD and electron diffraction.[11] As discussed above, the structure of $Ba_6Bi_9B_{79}O_{138}$ was established in the space group of *R*3 with a = 7.841(1) Å and c = 46.557(9) Å. The cell parameters are very similar with those of $GdBaB_9O_{16}$. Furthermore, remarkably similar powder XRD patterns for $Ba_6Bi_9B_{79}O_{138}$ and $GdBaB_9O_{16}$ were observed (see Fig. 1). These findings suggest $Ba_6Bi_9B_{79}O_{138}$ is a new analogue to *RE*BaB_9O_{16}.

It is known that Bi^{3+} and Eu^{3+} have similar ionic radii, coordination characteristic and even physical-chemistry properties. Complete solid solutions of $Ba_6(Bi_{1-x}Eu_x)_9B_{79}O_{138}$ (0

$\leq x \leq 1$) were indeed prepared successfully by high temperature solid state reactions. As shown in Fig. 4a, no observable impurity peaks were found in powder XRD patterns, where the refection peaks show a slight shift. It is understandable due to the close ionic radii for Bi^{3+} and Eu^{3+}. The slight difference in cell lattice parameters, including *a*, *c* and *V*, can be verified by Le Bail refinements as summarized in Table S3 in ESI, and the unit cell volumes along with the increase of *x* is shown in Fig. 4b, which shrinks linearly. The similarity between these XRD patterns of $Ba_6(Bi_{1-x}Eu_x)_9B_{79}O_{138}$ (especially for the fully Eu-concentrated $Ba_6Eu_9B_{79}O_{138}$) with that of REBaB$_9$O$_{16}$ confirms our assumption of isomorphism. It therefore makes sense to interpret the structure of REBaB$_9$O$_{16}$ as below. There are two and three crystallographically independent sites for Ba and rare earth ions, respectively. The framework is established by alternating staking of BO$_4$-REO$_6$-BO$_4$ sandwiched layers and polyborate layers with Ba^{2+} filled in the intervals.

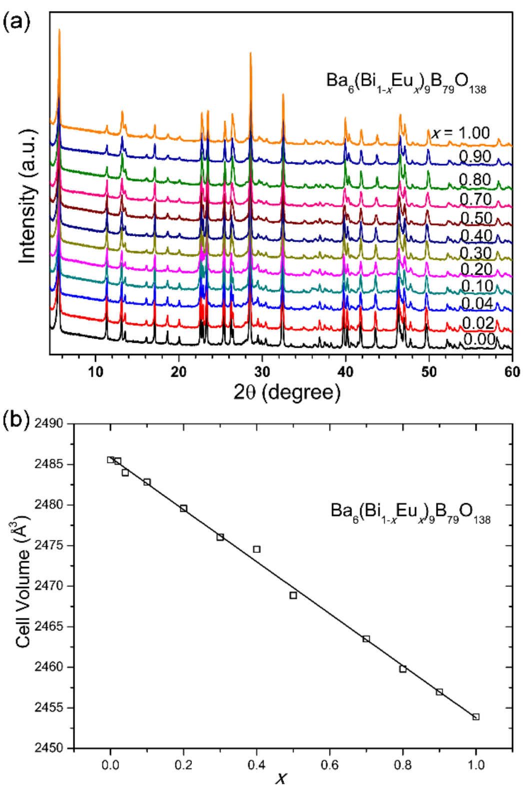

Fig. 4 (a) XRD patterns for $Ba_6(Bi_{1-x}Eu_x)_9B_{79}O_{138}$ ($0 \leq x \leq 1$) synthesized by solid state reactions; (b) change of unit cell volumes for $Ba_6(Bi_{1-x}Eu_x)_9B_{79}O_{138}$ along with the doping content of Eu^{3+}.

Actually, in spite of the missing of the exact structure, the PL studies of REBaB$_9$O$_{16}$ have been always active for decades.[9-17] Especially, the local coordination environment of RE^{3+} ions have been investigated by using Eu^{3+}-luminescence as a structural probe.[11,16,17] For example, the presence of a strong $^5D_0 \rightarrow {}^7F_2$ emission usually indicates that the coordination environment of Eu^{3+} is deviated from inversion symmetry.[11,16] Moreover, the non-degenerate $^5D_0$-$^7F_0$ emission lines of Eu^{3+} are relevant with the number of the crystallographically independent sites in a given host matrix.[31] For EuBaB$_9$O$_{16}$, three $^7F_0 \rightarrow {}^5D_0$ emission peaks were observed in a site-selective laser excitation spectrum, indicating at least three different crystallographic sites for Eu^{3+} in the structure.[16] It supports the proper symmetry of EuBaB$_9$O$_{16}$ and $Ba_6Bi_9B_{79}O_{138}$ is *R*3 rather than *R*-3*m*. Usually, people can measure the NLO property to verify whether the crystal structure is centrosymmetric or noncentrosymmetric. Here in our case of **BBBO**, the real structure is just slightly derivate from centrosymmetric and no observable powder second harmonic generation was detected.

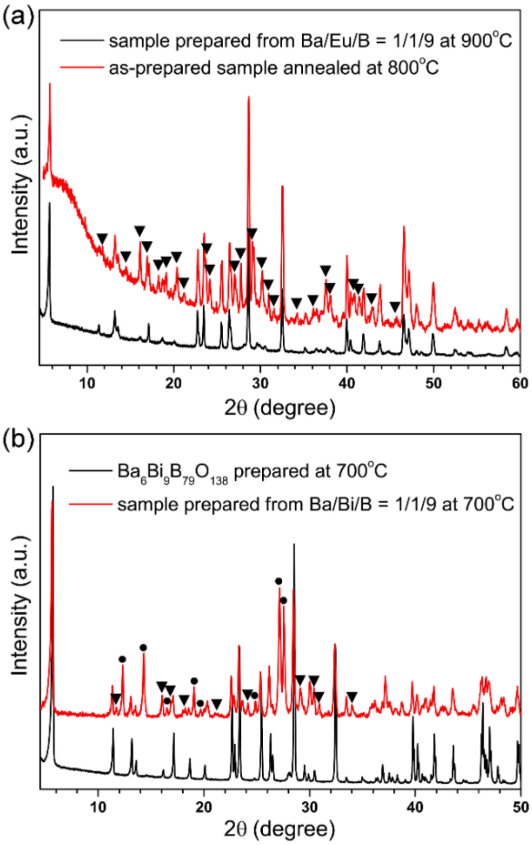

Fig. 5 (a) XRD for as-prepared sample using the composition Ba : Eu : B = 1 : 1 : 9 at 900 ºC, which was further annealed at 800 ºC; (b) XRD for phase-pure $Ba_6Bi_9B_{79}O_{138}$ prepared at 700 ºC and for as-prepared sample using the composition Ba : Bi : B = 1 : 1 : 9 at 700 ºC. The reflections marked as ▼ and ● belong to $Ba_2B_{10}O_{17}$ and $Bi_3B_5O_{12}$, respectively.

After the isomorphism was confirmed, it becomes interesting to think about the true composition of REBaB$_9$O$_{16}$. In literature,[8-17] people prepared REBaB$_9$O$_{16}$ phosphors with the composition of *RE* : Ba : B = 1 : 1 : 9, and the XRD patterns does not show any impurity. Of course, it is possible that the excess Ba^{2+} partially occupy the Bi^{3+} position, for instance, forming "Ba$_6$($RE_{7.5}$Ba$_{1.5}$)B$_{79}$O$_{137.25}$". Experimentally, we heated a powder mixture with Eu : Ba : B = 1 : 1 : 9 at 900 ℃ with the XRD pattern shown in Fig. 5a, which indeed looks like a pure phase of "EuBaB$_9$O$_{16}$". We notice that the melting points for BaB_4O_7 and $Ba_2B_{10}O_{17}$ are 865 and 892 ℃, respectively.[32,33] So the reaction temperature of 900 ℃ is probably too high. Therefore, we further annealed the above sample at 800 ℃ for 10 hours in order to identify if there was any amorphous component. A series of new reflections occurred (see Fig. 5a), which can be assigned to $Ba_2B_{10}O_{17}$. Accordingly, we believe that the excess Ba^{2+} presents as a binary barium borate, and turns to an amorphous phase which cannot be detected by powder XRD.

Moreover, the attempt of synthesizing a sample starting from Ba : Bi : B = 1 : 1 : 9 was also performed at 700 ℃, which leads to a mixture of $Ba_6Bi_9B_{79}O_{138}$ together with $Ba_2B_{10}O_{17}$ and $Bi_3B_5O_{12}$ (see Fig. 5b). Looking at the Ba-Bi-B-O phase diagram, the composition of Ba : Bi : B = 1 : 1 : 9 indeed falls into the three-phase region of $Ba_6Bi_9B_{79}O_{138}$, $Ba_2B_{10}O_{17}$ and $Bi_3B_5O_{12}$. Our experimental results suggest that the real composition for REBaB$_9$O$_{16}$ might be Ba$_6$$RE_9B_{79}O_{138}$. Further and detailed experiments are needed to pin down this assumption.

Conclusions

We performed a single crystal XRD study on a qualified crystal of **BBBO** and determined its structure in the noncentrosymmetric space group *R*3, which gives a complex composition of $Ba_6Bi_9B_{79}O_{138}$. It possesses a layered-type structure composed of BO_4-BiO_6-BO_4 sandwiched layers and polyborate inter-layer groups. Ba^{2+} atoms locate within the polyborate intervals. Our structural model is basically consistent with the previously reported model in Ref. 29. We here proposed a relatively ordered structure, which contains three and two independent Bi and Ba atoms, respectively. More importantly, the isomorphism between **BBBO** and REBaB$_9$O$_{16}$ (*RE* = rare earth) was proved through the successful preparation of complete solid solutions $Ba_6(Bi_{1-x}Eu_x)_9B_{79}O_{138}$ ($0 \leq x \leq 1$). In other words, we took one more step forward in understanding the structure of REBaB$_9$O$_{16}$ by analysing its new analogue $Ba_6Bi_9B_{79}O_{138}$. It is believed to be helpful for further interpreting and developing REBaB$_9$O$_{16}$-based PL materials.

Acknowledgements

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Notes and references

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Electronic Supplementary Information (ESI) available: Tables of the atomic coordinates, selected bond distance for **BBBO**, unit cell parameters for $Ba_6(Bi_{1-x}Eu_x)_9B_{79}O_{138}$, DSC, IR, ^{11}B MAS-NMR for **BBBO**, crystal structure views of $H_2InB_5O_{10}$, CIF file. See DOI: 10.1039/b000000x/

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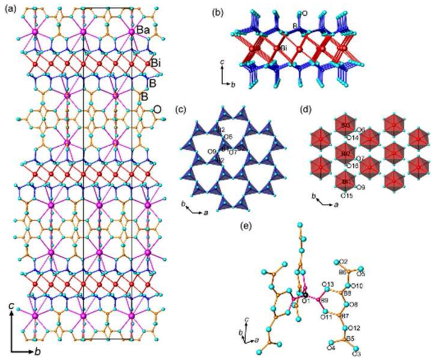
Graphic Abstract



The structure determination of $Ba_6Bi_9B_{79}O_{138}$ uncovers the mystery on crystallography of the well-known phosphors $\mathit{RE}BaB_9O_{16}$ (RE = Rare earth).