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# Thermal stability and crystal structure of $\beta$ -Ba<sub>3</sub>YB<sub>3</sub>O<sub>9</sub>

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## Abstract

A new compound,  $\beta$ -Ba<sub>3</sub>YB<sub>3</sub>O<sub>9</sub>, has been attained through solid phase transition from  $\alpha$ -Ba<sub>3</sub>YB<sub>3</sub>O<sub>9</sub> at high temperatures. Differential thermal analysis (DTA) revealed the phase transition at about 1120°C, the melting temperature at about 1253°C. Its crystal structure has been determined from powder X-ray diffraction data. The refinement was carried out using the Rietveld method and the final refinement converged with  $R_p = 10.5\%$  and  $R_{wp} = 13.7\%$ . This compound belongs to the hexagonal space group *R*-3, with lattice parameters  $a = 13.0441(1) \text{ \AA}$  and  $c = 9.5291(1) \text{ \AA}$ . There are 6 formulas per unit cell and 7 atoms in the asymmetric unit. The structure of  $\beta$ -Ba<sub>3</sub>YB<sub>3</sub>O<sub>9</sub> is built up from Ba(Y)O<sub>8</sub>, BaO<sub>6</sub> and YB<sub>6</sub>O<sub>18</sub> units formed by one YO<sub>6</sub> octahedron and six BO<sub>3</sub> triangles with shared O atoms.

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**Keywords:**  $\beta$ -Ba<sub>3</sub>YB<sub>3</sub>O<sub>9</sub>; Structure determination; X-ray powder diffraction

## 1. Introduction

In the past decades much research interest has been focused on the synthesis and characterization of borate compounds of alkaline earth and rare earth elements for the exploration of nonlinear optical materials. A series of borate compounds such Ca<sub>4</sub>YO(BO<sub>3</sub>)<sub>3</sub> [1] and CaLa<sub>3</sub>(BO<sub>3</sub>)<sub>5</sub> [2] have been discovered in these systems.

Recently, with the advent of the Internet and optical fibers, the demand for birefringent crystals is soaring [3,4]. The rules of mineralogy indicate that the compounds including Y, Ti elements probably produce large birefringence. Consequently, in order to further search new ternary compounds with large birefringence and/or nonlinear optical properties, we investigated the phase relations in BaO–Y<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>, and found some new ternary compounds [5,6]. In this ternary system, we found the existence of  $\beta$ -Ba<sub>3</sub>YB<sub>3</sub>O<sub>9</sub> through solid state reaction from  $\alpha$ -Ba<sub>3</sub>YB<sub>3</sub>O<sub>9</sub> at high temperatures. In 1999, Khamaganova et al. [7] have reported the compounds Ba<sub>3</sub>Ln(BO<sub>3</sub>)<sub>3</sub> (*Ln* = La–Lu, Y),  $\alpha$ -Ba<sub>3</sub>YB<sub>3</sub>O<sub>9</sub> being one of them, but the  $\beta$ -phase of Ba<sub>3</sub>YB<sub>3</sub>O<sub>9</sub> was

not reported in his work. And they have determined the melting temperature at 1137°C of Ba<sub>3</sub>YB<sub>3</sub>O<sub>9</sub>, which is proved to be incorrect by the differential thermal analysis in our work. In this paper, we also determined the crystal structure of  $\beta$ -Ba<sub>3</sub>YB<sub>3</sub>O<sub>9</sub>. Ilyukhin and his coworkers [8] have reported the structure of Ba<sub>3</sub>DyB<sub>3</sub>O<sub>9</sub> ( $a = 13.041(3) \text{ \AA}$ ,  $c = 9.523(2) \text{ \AA}$ , *R*-3, *Z* = 6). Thompson et al. [9] also reported crystal structure of Sr<sub>3</sub>ScB<sub>3</sub>O<sub>9</sub> ( $a = 12.135(1) \text{ \AA}$ ,  $c = 9.184(1) \text{ \AA}$ , *R*-3, *Z* = 6). According to the crystal data,  $\beta$ -Ba<sub>3</sub>YB<sub>3</sub>O<sub>9</sub> is isostructural with Ba<sub>3</sub>DyB<sub>3</sub>O<sub>9</sub> and Sr<sub>3</sub>ScB<sub>3</sub>O<sub>9</sub>, however, the structure of Ba<sub>3</sub>DyB<sub>3</sub>O<sub>9</sub> is very different from that of Sr<sub>3</sub>ScB<sub>3</sub>O<sub>9</sub>. Compared with the X-ray powder diffraction pattern of the two compounds above [9,10] and similar ionic radius of Y and Dy, we found that it is reasonable that  $\beta$ -Ba<sub>3</sub>YB<sub>3</sub>O<sub>9</sub> is isostructural with Ba<sub>3</sub>DyB<sub>3</sub>O<sub>9</sub>. However, during the refinement, we could not get a satisfactory result based on the structure of Ba<sub>3</sub>DyB<sub>3</sub>O<sub>9</sub> and found the crystal structure of Ba<sub>3</sub>DyB<sub>3</sub>O<sub>9</sub> is probably unreasonable because the bond valence for boron calculated based on the coordinates given in their paper deviate substantially from its normal valence. Consequently, the structure of  $\beta$ -Ba<sub>3</sub>YB<sub>3</sub>O<sub>9</sub> was solved by direct methods from powder X-ray diffraction data combined with the structure of Ba<sub>3</sub>DyB<sub>3</sub>O<sub>9</sub> and with infrared spectroscopy to further characterize the B–O coordination.

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Table 1

Experimental details of X-ray powder diffraction and Rietveld refinement

Diffractometer used	Rigaku D/Max-2400
Radiation type	CuK $\alpha$
Wavelength	1.5418
Profile range	10–135°
Step size ( $2\theta$ )	0.02°
Step scan time (s)	1
Number of observation ( $N$ )	6251
Number of structure parameters ( $P_1$ )	30
Number of profile parameters ( $P_2$ )	14
$R_p$ (%)	10.5
$R_{wp}$ (%)	13.7
$R_{exp}$ (%)	5.95
$S$	2.3

Note:  $R_p = \sum |y_{io} - y_{ic}| / \sum |y_{io}|$ ,  $R_{wp} = \sqrt{\sum w_i (y_{io} - y_{ic})^2 / \sum w_i y_{io}^2}$ ,  $R_{exp} = [(N - P_1 - P_2) / \sum w_i y_{io}^2]^{1/2}$ ,  $S = \sum [w_i (y_{io} - y_{ic})^2 / (N - P_1 - P_2)]^{1/2}$ .

## 2. Experimental procedure

A mixture of high-purity  $Y_2O_3$  (A.R.),  $BaCO_3$  (A.R.),  $H_3BO_3$  (>99.99%) in stoichiometric proportion, 1:6:6, was finely ground and first heated in a platinum crucible at 700°C for 10 h to decompose  $H_3BO_3$  and  $BaCO_3$ , and then reground and heated in a platinum crucible at 1100°C for 48 h to obtain  $\alpha$ - $Ba_3YB_3O_9$  and at 1140°C for 40 h to obtain  $\beta$ - $Ba_3YB_3O_9$ . The two phases of the compound  $Ba_3YB_3O_9$  were cooled in a furnace to the room temperature. The diffraction data were collected on an X-ray Rigaku diffractometer D/Max-2400 with a power of 40 kV at 120 mA, employing CuK $\alpha$  radiation by using a graphite monochromator. More details on the X-ray diffraction experiment can be found in Table 1.

A CP-G differential thermal instrument was employed to perform DTA and TGA experiments. The heating and cooling rate was 10°C/min in the temperature range from room temperature to 1300°C. Infrared spectra were recorded with a Perkin-Elmer 983G infrared spectrophotometer in the 1500–250  $cm^{-1}$  wave-number range using KBr pellets.

## 3. Results and discussion

Figs. 1 and 2 present the DTA and TGA curves of  $\alpha$ - $Ba_3YB_3O_9$  and  $\beta$ - $Ba_3YB_3O_9$ , respectively. The results of TGA indicate no weight loss between room temperature and 1300°C. The results of DTA of the two phases are similar in course of heating and cooling. Two endothermic peaks are observed during heating and one exothermic peak during cooling. The peaks at about 1128°C are related to the phase transition from the  $\alpha$ - to  $\beta$ -phase and the ones at about 1253°C is the melting point of the compound  $Ba_3YB_3O_9$ . In the cooling curves, the peaks at about 1160°C are the freezing

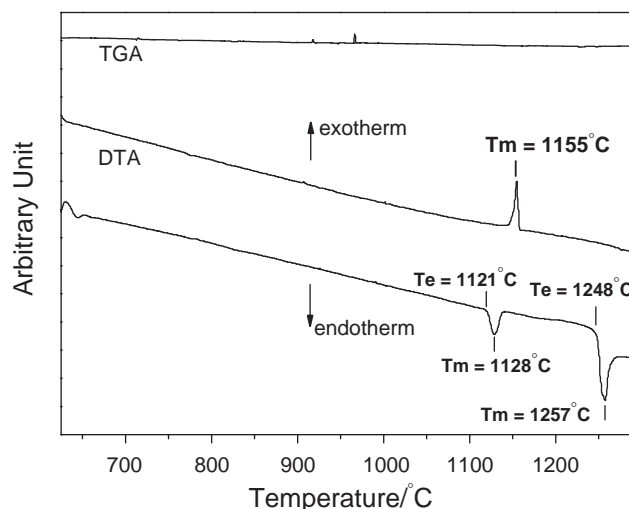


Fig. 1. DTA and TGA curves of  $\alpha$ - $Ba_3YB_3O_9$ . The lower DTA curve represents increasing temperature measurements, the upper DTA trace decreasing temperature measurements.

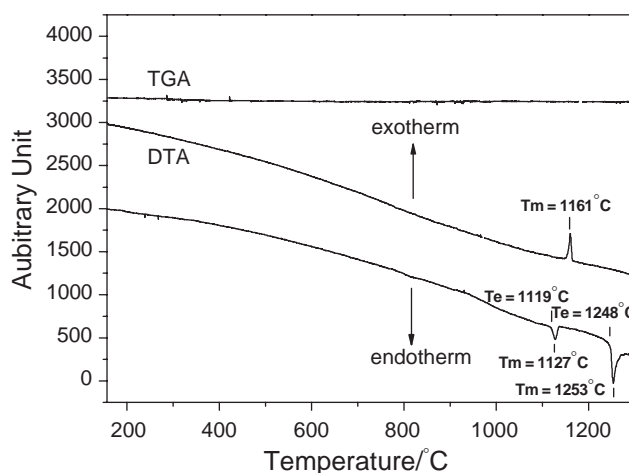


Fig. 2. DTA and TGA curves of  $\beta$ - $Ba_3YB_3O_9$ . The lower DTA curve represents increasing temperature measurements, the upper DTA trace decreasing temperature measurements.

points of both  $\alpha$ - $Ba_3YB_3O_9$  and  $\beta$ - $Ba_3YB_3O_9$ . The DTA curves of the two phases also confirm that the phase transition from the  $\alpha$ - to the  $\beta$ -phase proceeds at about 1140°C and the opposite process easily reacts by annealing at any temperature below 1110°C. The result is in good agreement with that of our experiments.

The powder diffraction pattern of  $\beta$ - $Ba_3YB_3O_9$  could be indexed using the Dcvol91 program [11] based on a hexagonal cell with the lattice parameters  $a = 13.0528(8)$  Å and  $c = 9.5358(8)$  Å. Systematic absence of  $hkl$  with  $-h+k+l = 3n$  suggests that its space group is  $R\bar{3}$  or  $R3$ ,  $R\bar{3}m$ ,  $R3m$ . According to the results above, we compared the X-ray diffraction pattern of  $\beta$ - $Ba_3YB_3O_9$  to that of known  $Ba_3DyB_3O_9$ , and found that their X-ray patterns are similar. The space group of  $Ba_3DyB_3O_9$  is  $R\bar{3}$  with lattice

parameters  $a = 13.041(3) \text{ \AA}$  and  $c = 9.523(2) \text{ \AA}$  [8]. Therefore the space group of  $\beta\text{-Ba}_3\text{YB}_3\text{O}_9$  is probably  $R\bar{3}$ .

In order to confirm the coordination surroundings of B–O in  $\beta\text{-Ba}_3\text{YB}_3\text{O}_9$  structure, IR spectrum of  $\beta\text{-Ba}_3\text{YB}_3\text{O}_9$  was measured at room temperature and given in Fig. 3. In the IR absorption wavenumbers smaller than  $800 \text{ cm}^{-1}$  originate mainly from the lattice dynamic modes and will not be considered due to its complexity. According to previous work See, e.g., [12], the strong bands above  $1100 \text{ cm}^{-1}$  should be assigned to the B–O asymmetric stretching of triangular  $[\text{BO}_3]^{3-}$  groups.

The symmetry information, the unit cell dimensions, and the data were then input to Fullprof program [13] to decompose the pattern. Total 569 values of  $|F_{\text{obs}}|$  were extracted. The agreement indices converged to the values  $R_{\text{wp}} = 9.39\%$  and  $R_{\text{exp}} = 5.94\%$ . Direct methods were applied with Shelxs-86 program [14] to  $|F_{\text{obs}}|$  obtained by using the program Fullprof program [13]. The list of interatomic distances showed that 5 of the 10 peaks listed in the E-map were likely to correspond to the possible positions of atoms (two Ba, two Y, one O and one B). The last two independent atomic positions, two O, were found by difference Fourier synthesis with Shelxl-93 [15] and approximate  $|F_{\text{obs}}|$  values derived by the pattern decomposition method. Rough structure obtained by using direct method combined with the structural model of  $\text{Ba}_3\text{DyB}_3\text{O}_9$  was refined with the Rietveld method by the program DBW9411 [16] and FullProf2000 See, e.g., [17]. All atomic positions were refined isotropically. Because of the scattering factor of boron atom is much smaller than that of Ba and Y, constrains on the B–O bond length and B–O–B angle were placed on the boron atom to prevent it from going away during the refinement. The final residual factors of the refinement are  $R_p = 10.5\%$ ,  $R_{\text{wp}} = 13.7\%$  and  $R_{\text{exp}} = 5.95\%$ .

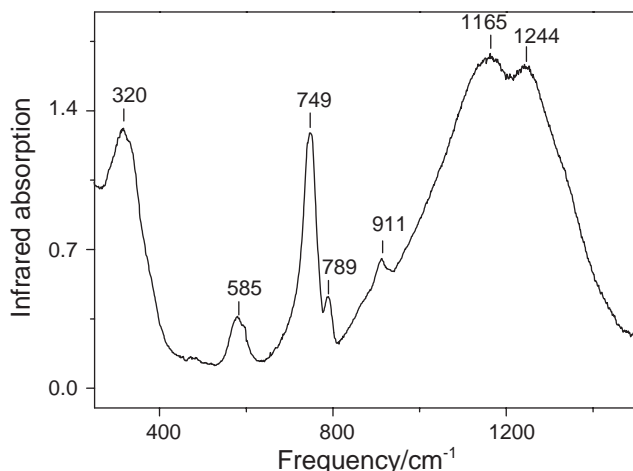


Fig. 3. Infrared spectra of  $\beta\text{-Ba}_3\text{YB}_3\text{O}_9$ .

Crystallographic details are summarized in Table 2. The final positional parameters are listed in Table 3. A list of selected bond lengths and angles is given in Table 4. Final refinement results are presented in Fig. 4.

The unit cell of  $\beta\text{-Ba}_3\text{YB}_3\text{O}_9$  consists of 2 Ba, 2 Y (one Ba and one Y occupy the same position), 1 B and 3 O, all are located on the general Wyckoff positions. Fig. 5 shows the projection of the structure of  $\beta\text{-Ba}_3\text{YB}_3\text{O}_9$  along the  $c$ -axis. The structure is built up from  $\text{YB}_6\text{O}_{18}$  units,  $\text{BaO}_6$  octahedra and  $\text{Ba(Y)O}_8$  polyhedra. The  $\text{YB}_6\text{O}_{18}$  groups are formed by one  $\text{YO}_6$  octahedron and six  $\text{BO}_3$  triangles with shared O1 atoms (Fig. 6).

Table 2  
Crystal data for  $\beta\text{-Ba}_3\text{YB}_3\text{O}_9$

Molecular formula	$\beta\text{-Ba}_3\text{YB}_3\text{O}_9$
Formula weight	677.33
Crystal system	Hexagonal
Space group	$R\bar{3}$
$a$ (Å)	13.0441(1)
$c$ (Å)	9.5291(1)
Volume (Å <sup>3</sup> )	1403.71(2)
$Z$	6
Density (g cm <sup>-3</sup> )	4.805
Color	White

Table 3  
Selected inter-atomic distances (Å) and angles (deg) in  $\beta\text{-Ba}_3\text{YB}_3\text{O}_9$

Ba1–O1	2.721(18)	Y2–O1	2.343(18)
Ba1–O1	2.987(24)	Y2–O1	2.343(23)
Ba1–O1	3.029(21)	Y2–O1	2.343(21)
Ba1–O2	2.693(18)	Y2–O1	2.343(18)
Ba1–O2	2.838(19)	Y2–O1	2.343(23)
Ba1–O2	2.562(20)	Y2–O1	2.343(21)
Ba1–O3	2.519(17)	B1–O1	1.344(67)
Ba1–O3	2.790(17)	B1–O2	1.316(62)
Ba2–O3	2.749(16)	B1–O3	1.339(61)
Ba2–O3	2.749(17)	O1–B1–O2	121.2(5)
Ba2–O3	2.749(18)	O1–B1–O3	116.2(5)
Ba2–O3	2.749(16)	O2–B1–O3	119.6(6)
Ba2–O3	2.749(17)		
Ba2–O3	2.749(18)		

Table 4  
Atomic coordinates, thermal, and occupancy parameters for  $\beta\text{-Ba}_3\text{YB}_3\text{O}_9$

Atom	Site	$x$	$y$	$z$	$B$ (Å <sup>2</sup> )	$N^a$
Ba1	18f	0.3720(1)	0.2480(1)	0.4743(2)	1.63(4)	5/6
Y1	18f	0.3720(1)	0.2480(1)	0.4743(2)	1.63(4)	1/6
Y2	3a	0.0	0.0	0.0	0.9(1)	1.0
Ba2	3b	0.0	0.0	0.5	1.9(1)	1.0
O1	18f	0.1298(17)	0.1804(16)	−0.1085(16)	1.4(4)	1.0
O2	18f	0.2626(16)	0.2558(16)	−0.2896(16)	1.1(4)	1.0
O3	18f	0.0710(13)	0.1922(13)	−0.3264(17)	1.0(4)	1.0
B1	18f	0.1552(60)	0.2000(55)	−0.2461(67)	1.4(4)	1.0

<sup>a</sup> Not refined.

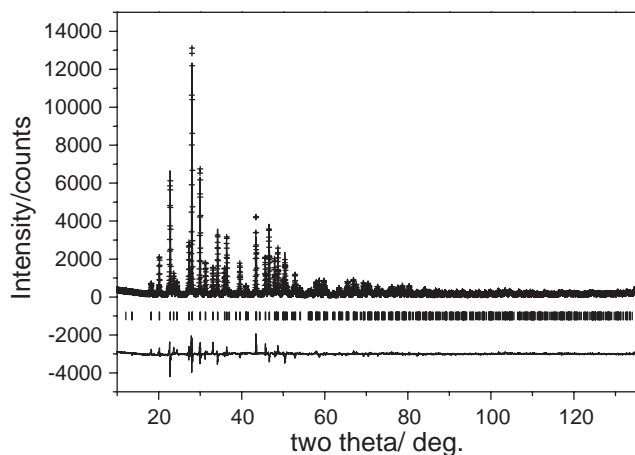


Fig. 4. The final Rietveld refinement plots of the  $\beta$ - $\text{Ba}_3\text{YB}_3\text{O}_9$ . Small black crosses (+) represent the experimental values and the continuous lines the calculated pattern. The solid line at the bottom is the difference between the experimental and calculated values. The vertical bars (|) show the positions of the calculated values for the Bragg reflections.

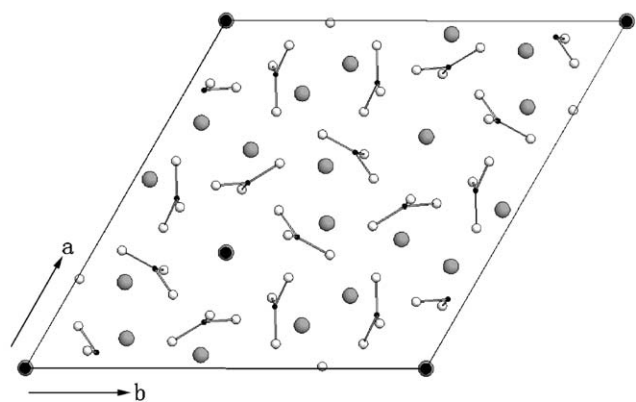


Fig. 5. Projection of the structure of  $\beta$ - $\text{Ba}_3\text{YB}_3\text{O}_9$  along [001], small black circles stand for B atoms and large black ones stand for Y atoms; small white circles stand for O atoms and the gray ones stand for Ba atoms.

In addition, in order to get the good result, we also refined the structure of  $\beta$ - $\text{Ba}_3\text{YB}_3\text{O}_9$  by using the structure of  $\text{Sr}_3\text{ScB}_3\text{O}_9$  as the initial structure. The refinement finally converged to agreement factors of  $R_p = 11.94\%$ ,  $R_{wp} = 15.75\%$  and  $R_{exp} = 5.96\%$  which is higher than that of the structure we obtained above. On the other hand, no  $\text{BO}_3$  triangles were found in the final structure refined by using the structure of  $\text{Sr}_3\text{ScB}_3\text{O}_9$ , though the bond lengths of B–O in  $\text{BO}_3$  triangles were also restricted. It is unreasonable according to the result of IR spectrum in which the observed frequencies at  $1100\text{ cm}^{-1}$  are characteristic of triangle  $\text{BO}_3$  units (see in Fig. 3).

To further provide a check on the consistency of the structure solution, the bond valences  $S$  have been calculated according to the Brown and Altermatt parameters [18] and are listed in Table 5. It can be seen

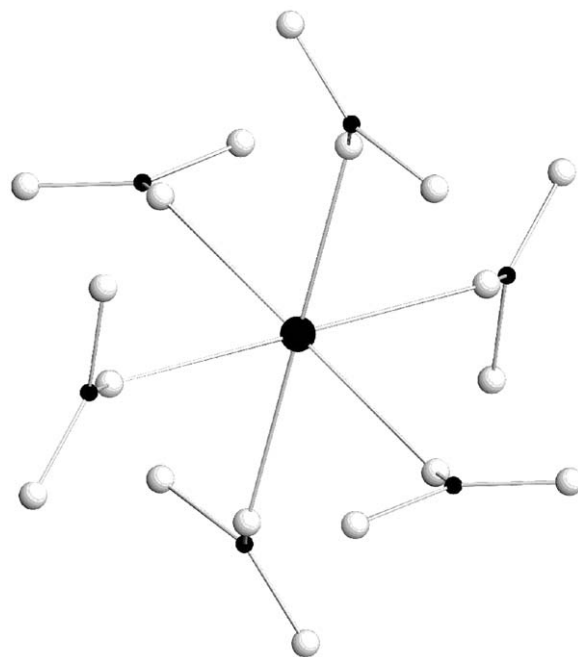


Fig. 6. Projection of the  $\text{YB}_6\text{O}_{18}$  group along [001], big black circles stand for Y atoms, small black ones stand for B atoms and the white ones stand for O atoms.

Table 5  
Calculated results for the bond valence sum of the compound  $\beta$ - $\text{Ba}_3\text{YB}_3\text{O}_9$

Cation	C.N.	Bond valence sum
Ba1	8	2.01
Ba2	6	1.96
Y2	6	2.82
B1	3	3.16

that the bond valence sum of each cation is in good agreement with the normal valence.

#### 4. Conclusion

In this work a new compound,  $\beta$ - $\text{Ba}_3\text{YB}_3\text{O}_9$ , has been synthesized by solid state reaction. Differential thermal analysis (DTA) revealed the phase transition and thermal stability of  $\beta$ - $\text{Ba}_3\text{YB}_3\text{O}_9$ . The DTA curves of the two phases also confirm that the phase transition from the  $\alpha$ - to the  $\beta$ -phase proceeds at about  $1140^\circ\text{C}$  and the opposite process easily reacts by annealing at any temperature below  $1110^\circ\text{C}$ . The crystal structure has been studied by means of powder X-ray diffraction techniques. The structure of  $\beta$ - $\text{Ba}_3\text{YB}_3\text{O}_9$  is built up from  $\text{BaO}_6$  octahedra,  $\text{Ba}(\text{Y})\text{O}_8$  polyhedra and  $\text{YB}_6\text{O}_{18}$  units formed by one  $\text{YO}_6$  octahedron and six  $\text{BO}_3$  triangles with shared O atoms. The result of IR spectrum confirmed the existence of  $[\text{BO}_3]^{3-}$  triangular groups.

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