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Synthesis and crystal structure of a new cesium barium borate, $CsBaB_3O_6$

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Abstract

A new ternary borate oxide, cesium barium borate, $CsBaB_3O_6$, has been synthesized by solid-state reaction at 700 °C, and the single crystals were grown using CsF as a flux. The crystal structure has been determined by X-ray diffraction. It crystallizes in the trigonal space group $P321$ with a cell of dimensions $a = 12.469(3)$ Å, $c = 7.444(3)$ Å, $\alpha = 90.00^\circ$, $\gamma = 120.00^\circ$, $V = 1002.3(5)$ Å^3, $Z = 6$. The fundamental building units of $CsBaB_3O_6$ are the B_3O_6 plane hexagonal rings, which are parallel to each other and stack along the *c*-axis, and the Cs and Ba atoms alternately occupy sites between the B_3O_6 sheets. A comparison of the structures of $CsBaB_3O_6$, β-BaB_2O_4 and $CsBO_2$ is presented.

Keyword: Cesium barium borate; $CsBaB_3O_6$; Crystal structure; Nonlinear optical (NLO) materials

1. Introduction

In the past two decades, many nonlinear optical (NLO) materials have been discovered in borates [1]. Among these, mixed borates grabbed much attention from many research groups. For example, $CsLiB_6O_{10}$ [2,3], $LiKB_4O_7$ [4], and $LiRbB_4O_7$ [4], etc. which have good NLO properties. This induced a considerable interest in search for new promising compounds for nonlinear optics in ternary borate systems such M_2O–$M'O$–B_2O_3 (M = alkali-metal, M' = alkaline-metal).

In these systems, M_2O–$M'O$–B_2O_3 (M = Li, Na, K; M' = Ca, Sr, Ba) have been investigated by several groups [5–15], and many compounds which some are non-centrosymmetric and may be candidates for NLO materials were synthesized. However, to our knowledge, there is no report on the mixed borates in M_2O–$M'O$–B_2O_3 (M = Rb, Cs, M' = Mg, Ca, Sr, Ba) systems until now. We have, therefore, started investigating these systems.

This paper describes the synthesis, growth and crystal structure of a novel cesium barium borate, $CsBaB_3O_6$. The compound crystallizes in the trigonal space group $P321$ and the fundamental building units are B_3O_6 groups, which do not exist in any of the known mixed alkaline and alkaline-earth metal borates, but exist in some metaborates ($CsBO_2$ [16], β-BaB_2O_4 [17,18]). The comparison of the structures of these compounds is discussed here.

2. Experimental

2.1. Solid-state synthesis and crystal growth

Polycrystalline samples of $CsBaB_3O_6$ were synthesized by solid-state reactions of stoichiometric amounts of Cs_2CO_3 (99.99%), $BaCO_3$ (99%) and H_3BO_3 (99%). After dehydration of boric acid by slow heating to 500 °C, the temperature was raised to 700 °C for several days with several intermediate remixing. The reaction products were analyzed by powder X-ray diffraction (XRD) (Brucker D8 advance X-ray diffractometer, Cu$K\alpha$ radiation). In all syntheses, a minor or trace amount of β-BaB_2O_4 was identified in the products, even after prolonged heating of a sample for 10 days at 700 °C. This was likely the result

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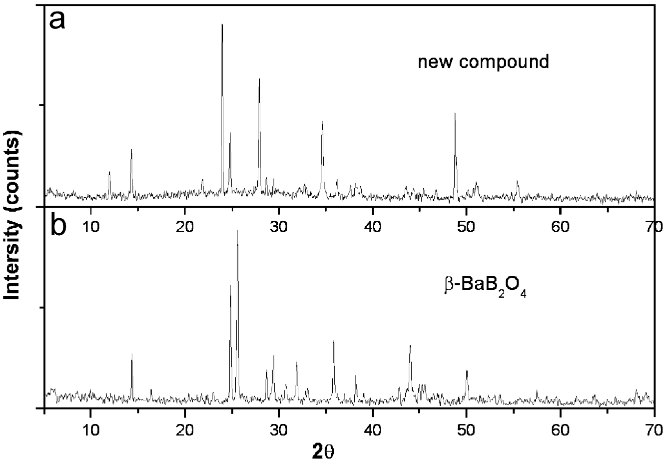

Fig. 1. X-ray powder diffraction patterns.

of a slight loss of Cs_2O and B_2O_3 by evaporation at high temperature.

We added a small excess of Cs_2O (10%) and B_2O_3 (10%) to the starting mixture, and repeated the above reactions. The XRD shows β-BaB_2O_4 is eliminated from the products. Fig. 1a shows the XRD pattern of synthesized polycrystalline $CsBaB_3O_6$.

In order to obtain the single crystals, we heated the polycrystalline samples of $CsBaB_3O_6$ to 900 °C, and obtained the colorless transparent melt, then reduced the temperature at the rate of 30 °C/h to 600 °C, the colorless transparent hexagonal crystals were obtained. The result of XRD (Fig. 1b) shows that the obtained crystals are β-BaB_2O_4, which implies $CsBaB_3O_6$ melts incongruently. The crystallization experiments were carried out by high-temperature solution method using CsF as a flux. The initial materials of Cs_2CO_3 (0.3 mol), BaO (0.6 mol), H_3BO_3 (1.8 mol), and CsF (0.68 mol) were weighed, heated to thoroughly melt in a Φ 40 mm × 40 mm Pt crucible, and a Pt thread was dipped into the solution. Then the temperature was cooled slowly from 750 to 660 °C at a rate of 1 °C/h. The crystals grew on the Pt thread, and were pulled out of the solution, then were cooled down to the room temperature at rate 20 °C/h.

2.2. Structure determination

A colorless crystal with dimensions of 0.10 mm × 0.10 mm × 0.08 mm was selected for XRD analysis. Data collection was performed on a Bruker SMART CCD diffractometer equipped with graphite monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) at 293(2)k in the range $1.89° < \theta < 26.41°$. A total of 4609 reflections were collected with 1386 unique ones ($R_{int} = 0.0594$), of which 1115 with $I > 2\sigma(I)$ were observed and used in the succeeding refinements. The structure was solved by direct methods with SHELXS-97 program [19] and the SADABS absorption corrections were applied to all intensity data. The absolute structure was refined by the TWIN/BASF commands and all atoms were refined anisotropically. The final cycle of refinement converged to $R = 0.0591$ and w$R = 0.1531$ ($w = 1/[\sigma^2(F_o^2) + (0.0000P)^2 + 77.4862P]$, where $P = (F_o^2 + 2F_c^2)/3$). $S = 1.204$, $(\Delta/\sigma)_{max} = 0.000$, $(\Delta\rho)_{max} = 2.755$ and $(\Delta\rho)_{min} = -2.576$ e/Å^3. Details of crystal parameters, data collection and structure refinement are given in Table 1. The atomic positions and equivalent isotropic temperature parameters for $CsBaB_3O_6$ are given in Table 2, and the selected bond distances and angles are listed in Table 3.

Table 1
Crystallographic data and structure refinement parameters for $CsBaB_3O_6$

Molecular formula	$CsBaB_3O_6$
Molecular weight	398.67
Crystal system	Trigonal
Space group	$P321$ (no. 150)
Unit cell parameters	$a = 12.469(3)$ Å $\alpha = 90°$ $b = 12.469(3)$ Å $\beta = 90°$ $c = 7.444(3)$ Å $\gamma = 120°$ $V = 1002.3(5)$ Å^3 $Z = 6$
Density (calcd)	3.963 mg/m^3
Crystal size	0.12 × 0.10 × 0.08 mm^3
Diffractometer	Bruker SMART CCD
Radiation	(Mo $K\alpha$,) $\lambda = 0.71073$ Å
Temperature	294(2) K
Scan type	π and ω scans
θ range	1.89–26.41°
Unique reflections, R_{int}	1386, 0.0594
Limiting indices	$-10 \leqslant h \leqslant 15$, $-15 \leqslant k \leqslant 8$, $-9 \leqslant l \leqslant 7$
$F(0\,0\,0)$	1044
Absorption coefficient	11.281 mm^{-1}
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.204
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0591$, w$R2 = 0.1531$
R indices (all data)	$R1 = 0.0700$, w$R2 = 0.1583$
Absolute structure parameter	0.43(18)
Extinction coefficient	0.0038(4)
Largest diff. peak and hole	2.755 and −2.576 eÅ^{-3}

2.3. Physical property measurements

The SHG property of $CsBaB_3O_6$ was evaluated by Kurtz's method [20]. The measurement was referred to a sample of KH_2PO_4 (KDP) powder, which was sieved to about 100 μm in size. The powder samples were prepared and hand pressed into a 1 cm diameter round box with two glass windows, which was irradiated by a Nd:YAG laser. Infrared spectra were recorded with a vector22 (BRUKER) Fourier transform infrared spectrometer in the 300–1500 cm^{-1} wave number range using KBr pellets. The transmission spectrum of $CsBaB_3O_6$ crystals was recorded on Lambda 900 UV/vis/NIR (Perkin-Elmer) spectrophotometer which can operate over 185–3000 nm at room temperature. The sample was cut from the grown crystal with thickness 1.5 mm. The melting behaviors of $CsBaB_3O_6$ were investigated by differential thermal analysis (DTA) using a Labsys TMTG-DTA16(SETARAM) thermal

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors[a] ($Å^2 \times 10^3$)

	x	y	z	U (eq)
Ba(1)	2981(1)	2981(1)	5000	16(1)
Cs(1)	3042(2)	3042(2)	0	26(1)
Ba(2)	0	3668(2)	5000	17(1)
Cs(2)	0	3636(2)	0	24(1)
B(1)	2050(20)	6240(20)	2830(30)	10(5)
B(2)	440(20)	1300(20)	2830(30)	6(4)
B(3)	5370(20)	2710(20)	2850(30)	9(4)
O(1)	866(13)	5835(15)	2950(20)	16(3)
O(2)	2495(13)	5410(14)	2810(20)	12(3)
O(3)	860(15)	2463(15)	2950(30)	18(4)
O(4)	1243(15)	811(16)	2790(20)	23(4)
O(5)	4157(19)	2079(17)	2980(30)	27(4)
O(6)	6067(15)	4009(15)	2800(20)	18(3)

[a] U (eq) defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected bond lengths (Å) and angles (deg)

Ba(1)–O(1) × 2	2.698(16)	Cs(1)–O(1) × 2	3.074(17)
Ba(1)–O(5) × 2	2.71(2)	Cs(1)–O(5) × 2	3.16(2)
Ba(1)–O(3) × 2	2.835(18)	Cs(1)–O(3) × 2	3.282(18)
Ba(1)–O(4) × 2	2.976(17)	Cs(1)–O(4) × 2	3.293(17)
Ba(2)–O(3) × 2	2.712(17)	Cs(2)–O(3) × 2	3.110(19)
Ba(2)–O(5) × 2	2.787(19)	Cs(2)–O(5) × 2	3.22(2)
Ba(2)–O(1) × 2	2.807(17)	Cs(2)–O(1) × 2	3.245(16)
Ba(2)–O(6) × 2	3.197(16)	Cs(2)–O(6) × 2	3.467(16)
Ba(2)–O(2) × 2	3.209(15)	Cs(2)–O(2) × 2	3.474(15)
B(1)–O(1)	1.31(3)	B(2)–O(4)	1.41(3)
B(1)–O(2)	1.39(3)	B(3)–O(5)	1.31(3)
B(1)–O(2)	1.40(3)	B(3)–O(6)	1.37(3)
B(2)–O(3)	1.27(3)	B(3)–O(6)	1.41(3)
B(2)–O(4)	1.39(3)		
O(1)–B(1)–O(2)	121.6(19)	O(4)–B(2)–O(4)	115.3(18)
O(1)–B(1)–O(2)	120.1(19)	O(5)–B(3)–O(6)	118(2)
O(2)–B(1)–O(2)	118.2(19)	O(5)–B(3)–O(6)	124(2)
O(3)–B(2)–O(4)	123.4(18)	O(6)–B(3)–O(6)	118.3(19)
O(3)–B(2)–O(4)	121.3(19)		

analyzer in air. The heating rate was 20 °C/min from room temperature to 900 °C.

3. Results and discussion

3.1. Crystal structure

3.1.1. Anion

The anion in the structure is a nearly planar $[B_3O_6]^{3-}$ group constructed of three BO_3 triangles with two of the three corners shared. There are three types of B atoms and formed three classes of B_3O_6 groups (Fig. 2). The B–O bond lengths vary from 1.27(3) to 1.41(3) Å with an average value of 1.37 Å, and the O–B–O angles are between 115.3(18)° and 124(2)°. These values indicate the B_3O_6 groups deviate slightly from hexagonal symmetry, but are normal in a B_3O_6 plane hexagon. The discrete B_3O_6 rings are perpendicular to the three-fold axis and are parallel arrangement of the (001) plane. From Table 2, the atoms in B_3O_6 rings are not absolutely in one plane, each terminal O atom is a small deviation from the corresponding plane. From results of calculation, the O(1) atom is deviated from $B(1)_3O(2)_3$ hexagon about at 0.089 Å, the O(3) atom is deviated from $B(2)_3O(4)_3$ hexagon by 0.089 Å, and the O(5) atom is deviated from $B(3)_3O(6)_3$ hexagon by 0.093 Å. The B_3O_6 rings, which in the same layers nearly point in same direction, and which in the two neighborhood layers point almost opposite directions with the small angle between them from (001) direction.

3.1.2. Cations

The cations in the structure are Ba atoms and Cs atoms which alternately locate between the B_3O_6 sheets and form Ba atom layers and Cs atom layers. The Ba(1) atom is bonded to eight O atoms and exhibits distorted dodecahedral coordination, with two shorter Ba–O distances 2.698(16) Å, two pairs of longer distances 2.71(2) and 2.835(18) Å, two the longest 2.976(17) Å (Fig. 3a). The Ba(2) atom is bonded to 10 O atoms and forms the $Ba(2)O_{10}$ polyhedron, with two shorter Ba(2)–O distances 2.712(17) Å, two pairs of longer distances 2.787(19) and 2.807(17) Å, two pairs of the longest distances 3.197(16) and3.209(15) Å (Fig. 3b). Similarly, the coordination polyhedra of Cs atoms have two types: $Cs(1)O_8$ dodecahedron (Fig. 3c) and $Cs(2)O_{10}$ polyhedra (Fig. 3d); the distances are ranging from 3.074(17) to 3.293(17) Å for Cs(1)–O, and from 3.110(19) to 3.474(15) Å for Cs(2)–O.

$Ba(1)O_8$ and $Ba(2)O_{10}$ polyhedra arrange alternately between the two sheets of B_3O_6 in the (0 0 1) direction and connect each other by sharing two edge O atoms. $Ba(1)O_8$ dodecahedron are sharing edge O atoms with B_3O_6 rings and $Ba(2)O_{10}$ polyhedra share the edge and ring-on O atoms with B_3O_6 rings. At the same time, $Ba(1)O_8$ dodecahedron connect $Cs(1)O_8$ dodecahedron through sharing four edge O atoms, and $Ba(2)O_{10}$ polyhedra connect $Cs(2)O_{10}$ polyhedra through sharing six edge O atoms. $Cs(1)O_8$ and $Cs(2)O_{10}$ polyhedra connect adjacent B_3O_6 and Ba–O polyhedra in the above way.

3.1.3. Bond-valence analysis

To examine the validity of the determined structure, Brown's bond-valence theory [21] was used to calculate the valence sum for the ions. The results of the calculations are given in Table 4. It can be seen that the calculated valence sums are in good agreement with their normal valences.

3.1.4. Structure description

A perspective view of the $CsBaB_3O_6$ structure along the (0 0 1) direction is shown in Fig. 4. The crystallographic structure of $CsBaB_3O_6$ can be described as a layer-like structure, since there is stacking along the c-axis of B_3O_6 plane hexagonal rings with the Cs and Ba atoms alternately occupying sites between the B_3O_6, sheets and these layers

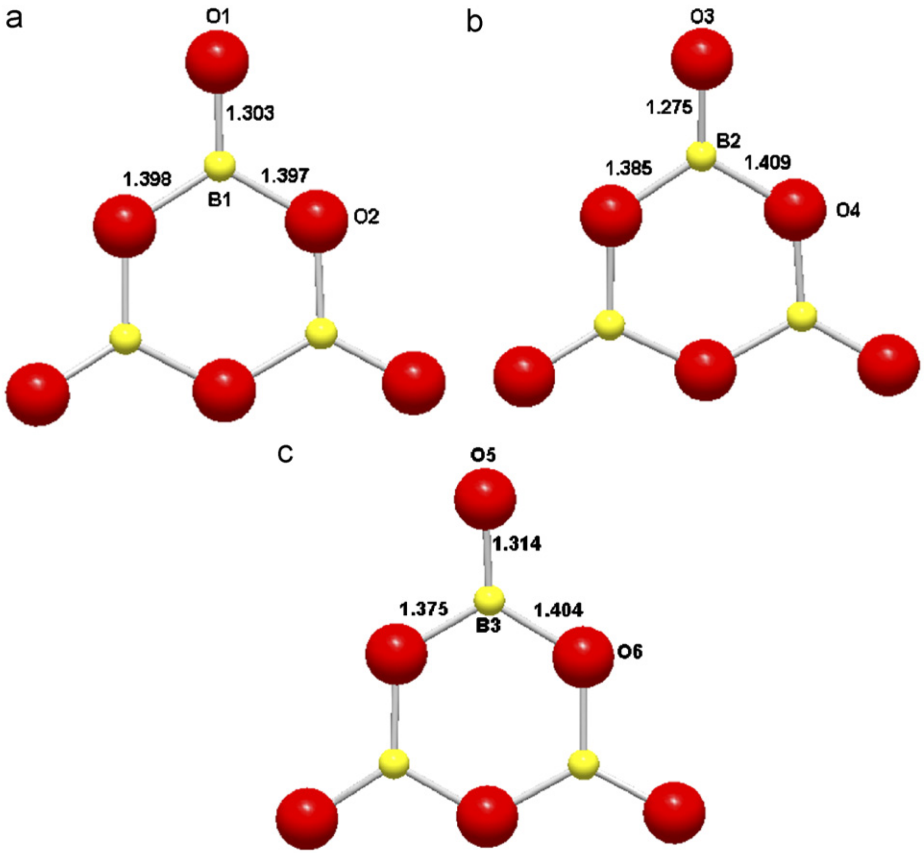

Fig. 2. The different B_3O_6 groups. Distances are in Å.

of Cs ($z = 0$), B(O)6 ($z = 0.283$), Ba ($z = 0.5$) form in the sequence ABCABC… stack.

Another description of this framework can be done using the Cs–O and Ba–O polyhedra. They are connected with each other by edge O atoms to form a three-dimensional irregular polygonal hole framework that are interposed by B_3O_6 rings (Fig. 5).

3.1.5. *Comparison of the structures $CsBaB_3O_6$, $CsBO_2$ and β-BaB_2O_4*

It is known that B_3O_6 groups exist in some metaborates, for example, MBO_2 ($M =$ Na [22], K [23], Cs [16]), β-BaB_2O_4, etc. we choose $CsBO_2$ and β-BaB_2O_4 to compare the structures with that of $CsBaB_3O_6$. It is interesting that the three compounds all stack three-dimensional layer-like structure in (0 0 1) direction with basic unit of plane B_3O_6 groups. According to the previous study, B_3O_6 group can yield big microscopic second-order susceptibility [24]. But the arrangement of B_3O_6 groups in compounds lead to different SHG effect. In $CsBO_2$ [16], the planar B_3O_6 rings are parallel to each other, distributed layer upon layer along the (0 0 1) direction and the B_3O_6 rings in the neighborhood layers point in exactly opposite directions (Fig. 6a) which makes their contributions to the SHG effect cancel off. The B_3O_6 rings share common vertices with irregular CsO_7 polyhedra to form a three-dimensional layer framework. In β-BaB_2O_4 [17,18], all the B_3O_6 rings are parallel to the (0 0 1) plane, and in different layers the B_3O_6 rings rotate a little (Fig. 6c), which is of great benefit to produce large SHG effect. The Ba atom is coordinated to seven O atoms they and form BaO_7 polyhedra with sharing edge O atoms with B_3O_6 groups. In $CsBaB_3O_6$, the B_3O_6 rings in two neighborhood layers point in almost opposite directions. There are a small torsion angle in the opposite direction with the positions of O atoms slightly changing (Fig. 6b). The contribution of this arrangement to the SHG effect is nearly zero. As a whole, it is the variation in the radii and the coordination environments of the metal cations that is mainly responsible for the structural differences between $CsBaB_3O_6$, $CsBO_2$ and β-BaB_2O_4.

3.2. *SHG test*

$CsBaB_3O_6$ crystallizes in space group $P321$ and is non-centrosymmetric. However, in our SHG test, no second harmonic signal was detected. This is because the SHG signal is too small to be detected and it is consistent with our analysis in Section 3.1.5.

3.3. *Infrared spectroscopy*

In order to further confirm the coordination surroundings of B–O in the $CsBaB_3O_6$ structure, infrared absorption

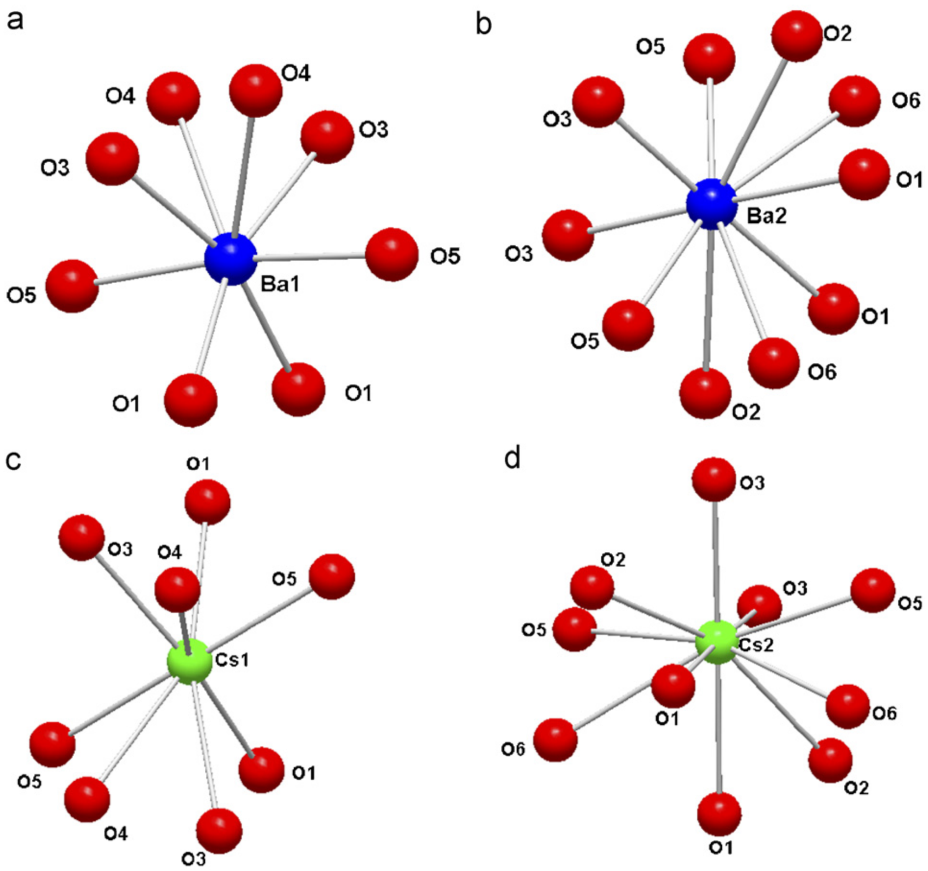

Fig. 3. Coordination polyhedra of the Ba(1), Ba(2), Cs(1), Cs(2) atoms.

Table 4
Ba–O, Cs–O and B–O bond valence in $CsBaB_3O_6$

	O1	O2	O3	O4	O5	O6	$\sum s$
Ba1	0.328 × 2		0.226 × 2	0.154 × 2	0.317 × 2		2.050
Ba2	0.244 × 2	0.082 × 2	0.315 × 2		0.257 × 2	0.085 × 2	1.966
Cs1	0.169 × 2		0.097 × 2	0.094 × 2	0.134 × 2		0.988
Cs2	0.107 × 2	0.057 × 2	0.154 × 2		0.114 × 2	0.059 × 2	0.982
B1	1.179	0.950 0.925			3.054		
B2			1.314	0.950 0.900			3.164
B3					1.179	1.003 0.900	3.082
$\sum s$	2.027	2.014	2.106	2.098	2.001	2.047	

spectrum of $CsBaB_3O_6$ was recorded. The absorption at wave numbers below 800 cm^{-1} originates mainly from the lattice dynamic modes and will not be considered due to its complexity. According to previous work [25], the strong bands above 1194 cm^{-1} should be assigned to the triangular B_3O_6 groups. The frequencies range from 1368 to 1458 cm^{-1} is corresponding to stretching vibration of extra-ring B–O bonds and the bands from 1194 to 1271 cm^{-1} are mainly characteristic of the stretching vibration of intra-ring B–O bonds.

3.4. Transmittance spectrum

The transmission spectrum of $CsBaB_3O_6$ crystals was recorded at room temperature. A wide transmission range

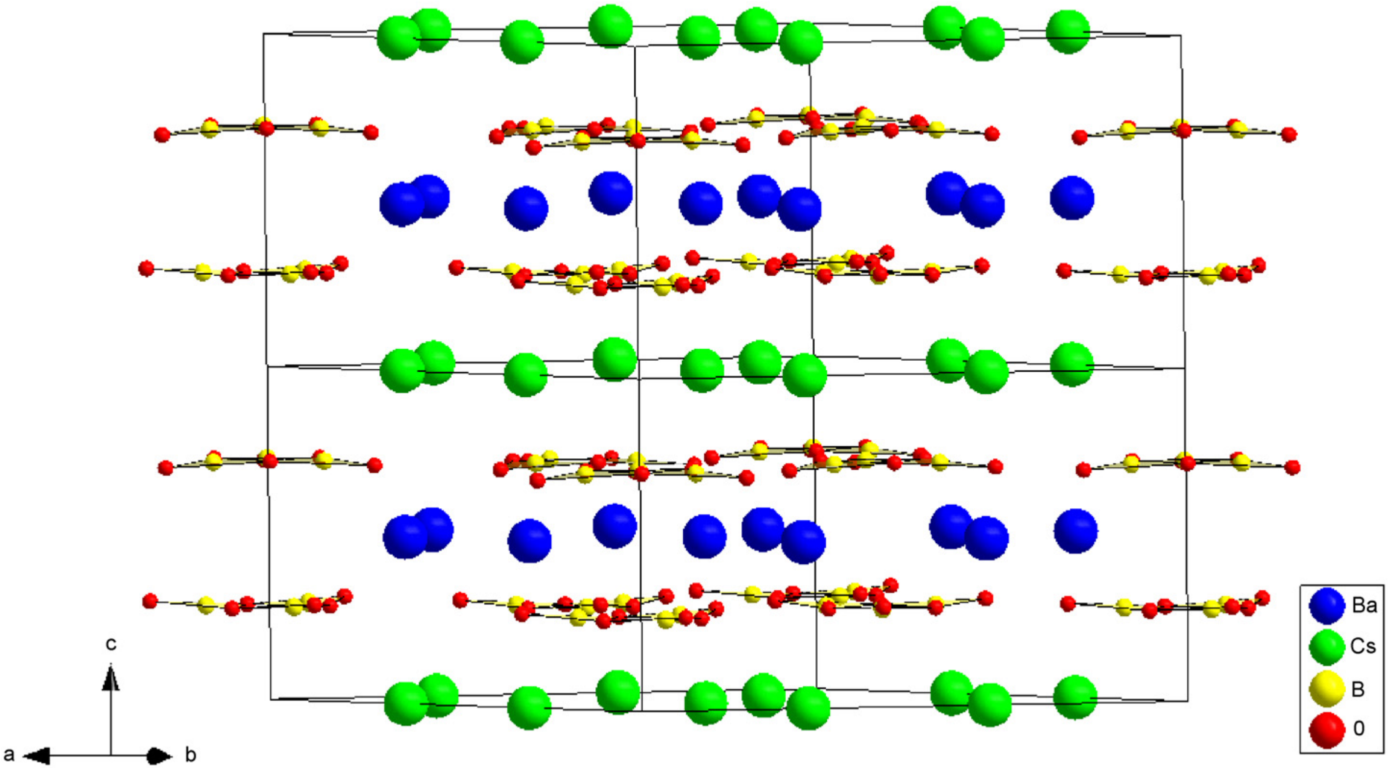

Fig. 4. The layer-like structure of $CsBaB_3O_6$.

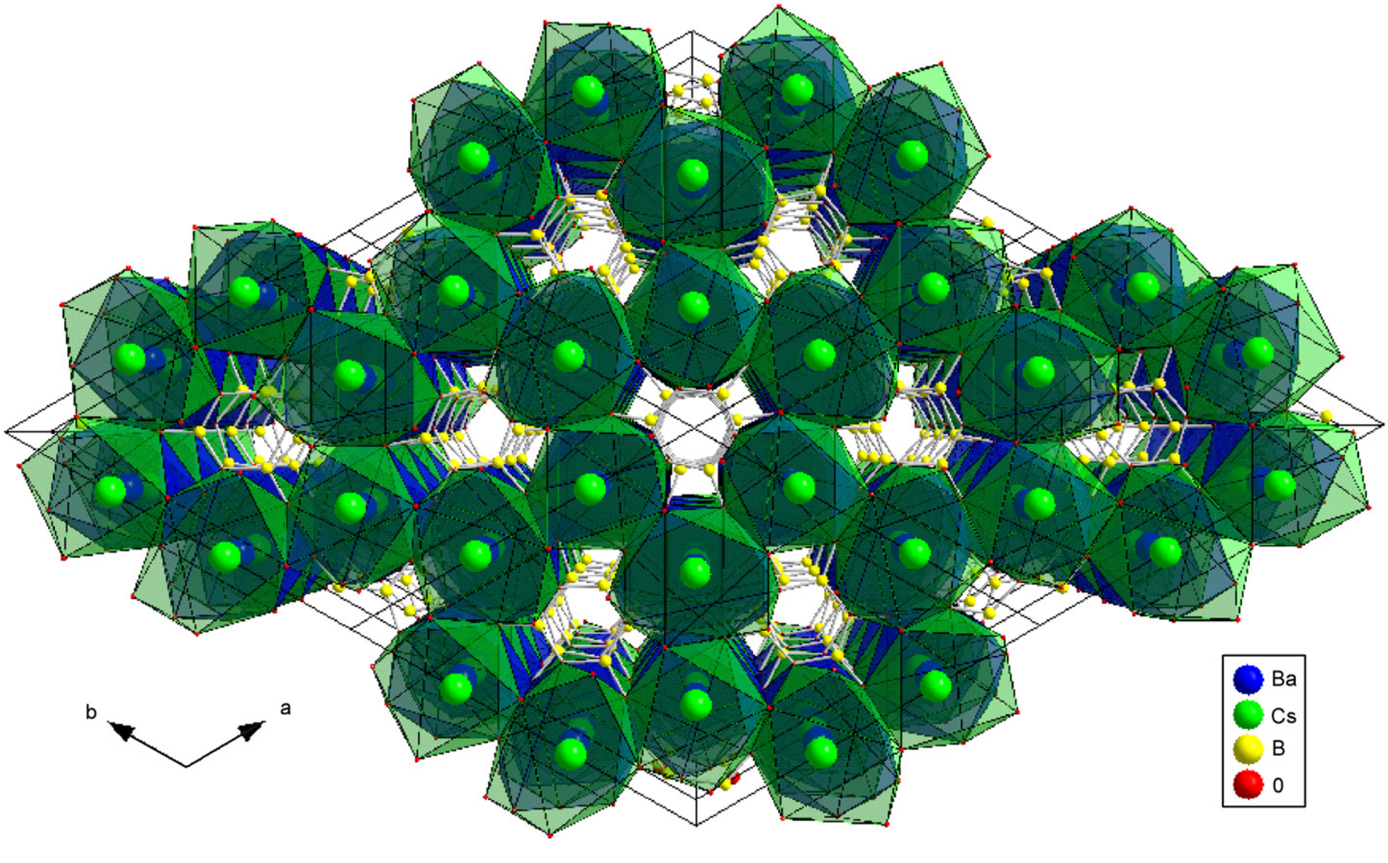

Fig. 5. Irregular polygonal hole resulting from condensation of Cs–O and Ba–O polyhedra.

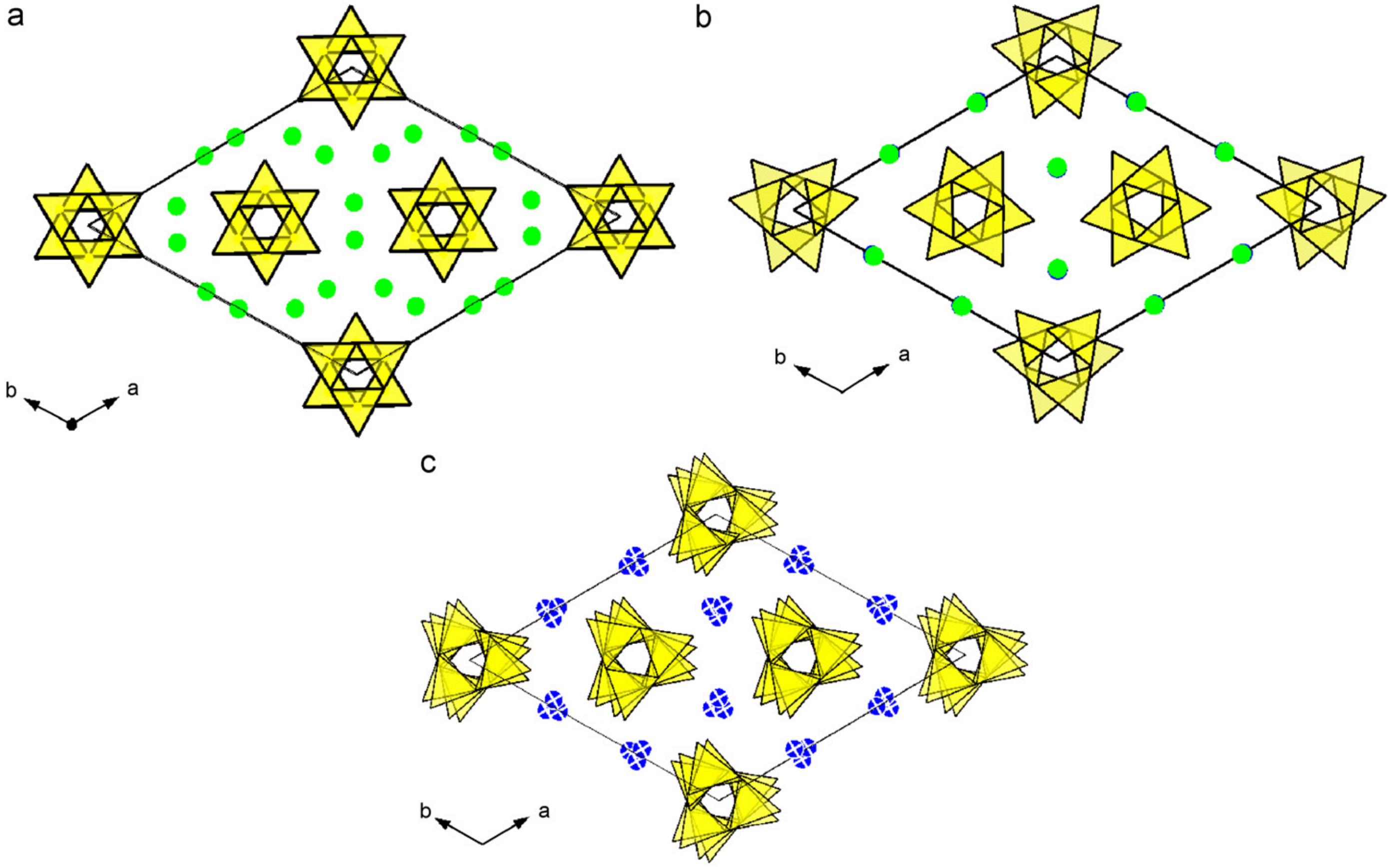

Fig. 6. Arrangement of B_3O_6 rings along (0 0 1) direction (a) $CsBO_2$, (b) $CsBaB_3O_6$ and (c) β-BaB_2O_4. The little yellow triangles are for BO_3 groups.

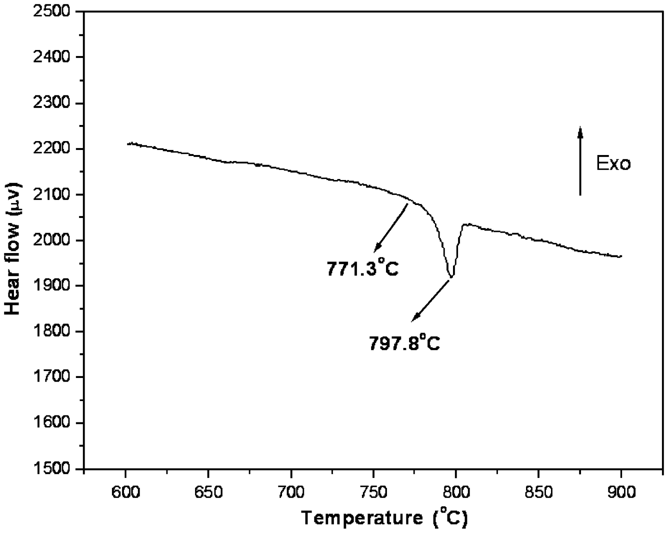

Fig. 7. DTA curve of $CsBaB_3O_6$.

is observed with the UV cutoff wavelength about 190 nm, which is similar to that of β-BaB_2O_4.

3.5. *Differential thermal analysis*

The melting behaviors of $CsBaB_3O_6$ were investigated by differential thermal and the resulting data are shown in Fig. 7. There is single apparent endothermic peak in the DTA curve, the onset point is 771.3 °C and the peak top is 797.8 °C. According to the experiment of Section 2, the endothermic peak is corresponding to incongruent melting behavior.

4. Conclusion

A novel mixed-borate cesium barium borate, $CsBaB_3O_6$ has been synthesized, and single crystals were grown using CsF as a flux due to incongruent melting behavior of $CsBaB_3O_6$. The crystal structure has been determined by single-crystal X-ray methods. It is a layer-type structure composed of plane B_3O_6 rings, which are parallel to each other and distributed layer upon layer along the (0 0 1) direction. The Cs and Ba atoms alternately occupy sites between the B_3O_6 sheets. The structures of $CsBaB_3O_6$, $CsBO_2$ and β-BaB_2O_4 are similar, and the difference among these compounds is the arrangement directions of B_3O_6 groups and the coordination of cations.

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Appendix A. Electronic Supplementary Material

The online version of this article contains additional supplementary data. Please visit doi:10.1016/j.jssc.2007.05.014.

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