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Ba₇(BO₃)₃GeO₄X (X=Cl, Br): the borogermanate halides with rigid GeO₄ tetrahedra and flexible XBa₆ octahedra

Ming Wen, Zhipeng Lian, Hongping Wu, Xin Su, Qingfeng Yan, Juanjuan Lu, Zhihua Yang and Shilie Pan

The first borogermanate halides, Ba₇(BO₃)₃GeO₄X (X=Cl, Br) have been synthesized by high temperature solution method. Ba₇(BO₃)₃GeO₄X (X=Cl, Br) are isostructural and crystallize in the orthorhombic space group Pbam (no. 55). They feature a Ba−based 3D framework, while isolated GeO₄ tetrahedra and BO₃ triangles are filled in the space created by the framework. Significantly, Ba₇(BO₃)₃GeO₄X (X=Cl, Br) possess similar formula with the borosilicate halides, Ba₇(BO₃)₃SiO₄X (X=Cl, Br), while they are not isostructural. A interpretation for the structural transformation between them is demonstrated here considering rigid GeO₄ tetrahedra and flexible XBa₆ (X=Cl, Br) octahedra. IR spectrum, UV-Vis-NIR diffuse reflectance spectrum and first-principles calculations have been carried out on title compounds.

Introduction

Borates have been widely investigated owing to their rich chemistry structures. Especially the borates with planar BO₃ units have attracted considerable attention, because the delocalization of BO₃ groups is beneficial for strong second-harmonic generation (SHG) response and large birefringence based on anionic group theory. A statistical analysis of borate fundamental building blocks, carried out by P. Becker, indicates that the borates with isolated BO₃ groups will be found in the system with appropriate cations/boron ratios (>1). Thus, in the alkaline-earth borates the formula M₇(BO₃)₃F₃ (M=Ba or Sr) with a large cations/boron ratio have attracted scientists’ interests.

In the M₇(BO₃)₃F₃ (M=Ba or Sr) system, two compounds Ba₇(BO₃)₃F₃ and Ba₃Sr₄(BO₃)₃F₃ were first identified by Keszler et al in 1994. In 2008, Zhang’s group has reinvestigated the crystal structure of Ba₃Sr₄(BO₃)₃F₃ and grown large crystal by the top-seeded solution growth method, which shows an SHG intensity about 0.5 times as large as that of KH₂PO₄ (KDP). Then in 2012, Bekker et al has systematically studied the M₇(BO₃)₃F₃ (M=Ba or Sr) system. They found that the system exists disorders between (4F)⁺ and (BO₃F)⁺ and a series compounds of Ba₇(BO₃)₃F₂₋ₓ and Ba₄₋ₓSrₓ(BO₃)₃GeO₄ are identified. However, in the crystal structure, the existence of disorder in the crystal is not favorable for the excellent physical or chemistry properties.

The basic structural units SiO₄ have been introduced into borate to replace the (4F)⁺ or (BO₃F)⁺ owing to SiO₄ tetrahedra possessing the same charge with (4F)⁺ or (BO₃F)⁺, which may solve the disorders in the crystal structure and improve the properties. Inspired by this, the compounds Ba₇(BO₃)₃SiO₄X (X=Cl, Br) have been synthesized by our group, in which the structural disorder disappears. Ba₇(BO₃)₃SiO₄X (X=Cl, Br) crystallize in different space groups, centrosymmetric Pbam (no. 55) and polar P6₃mc (no. 186), respectively.

Thus, we have investigated the substitution of Ge for Si in other reported borates determined by single crystal X-ray diffraction structure. We found that most of the compounds are isostructural (Table S1 in the Supporting Information). In these borates, we define a parameter of R (O/M = Si or Ge), which represents the mole ratio of the...
O element and the substitution element. In general, a higher value of R means a lower mole ratio of the substituted element in the compounds, which causes smaller change from the substitution and more likely results in the isostructural substitution. Therefore when R is higher than 3, all the compounds are isostructural. It is unusual that Ba$_7$(BO$_3$)$_3$GeO$_4$X (X=Cl, Br) and Ba$_7$(BO$_3$)$_3$SiO$_4$X (X=Cl, Br) are not isostructural with a quite high R value of 13. The structural transformation between Ba$_7$(BO$_3$)$_3$GeO$_4$X (X=Cl, Br) and Ba$_7$(BO$_3$)$_3$SiO$_4$X (X=Cl, Br) have been discussed in detail in the paper. We have also reported the spectrum and the first-principles calculations of the title compounds.

**Experimental**

**Solid-State synthesis**

Polycrystalline samples of Ba$_7$(BO$_3$)$_3$GeO$_4$X (X=Cl, Br) were synthesized via conventional solid-state reactions. Stoichiometric mixtures of BaCO$_3$, BaCl$_2$, GeO$_2$, and B$_2$O$_3$ at a molar ratio 6.5:0.5:1:1.5 for Ba$_7$(BO$_3$)$_3$GeO$_4$Cl and BaCO$_3$, BaBr$_2$, GeO$_2$, and B$_2$O$_3$ at a molar ratio 6.5:0.5:1:1.5 for Ba$_7$(BO$_3$)$_3$GeO$_4$Br have been ground and packed into alumina crucibles. Raw materials were preheated at 600 °C for 14 h. The mixtures were heated to 900°C for Ba$_7$(BO$_3$)$_3$GeO$_4$Cl and 950 °C for Ba$_7$(BO$_3$)$_3$GeO$_4$Br, then held for 4 days, and finally cooled to room temperature. During the sintering processes the samples have been ground thoroughly. The purity of the samples was confirmed by a powder X-ray diffraction (XRD), which agree well with the theoretical patterns of the compounds (Figure S1 in the Supporting Information).

**Crystal growth**

The single crystals of Ba$_7$(BO$_3$)$_3$GeO$_4$X (X=Cl, Br) were grown from the high temperature solutions using NaCl–LiCl, NaBr–LiBr and B$_2$O$_3$ as the flux systems. The solutions were obtained in platinum crucibles by melting mixtures of BaCO$_3$, GeO$_2$, B$_2$O$_3$, NaCl and LiCl at a molar ratio of 7:1:2.5:2:5 for Ba$_7$Ge$_3$O$_4$Cl and BaCO$_3$, GeO$_2$, B$_2$O$_3$, NaBr and LiBr at a molar ratio of 7:1:2.5:1:4 for Ba$_7$Ge$_3$O$_4$Br. The solutions were heated to 900 °C, dwell at this temperature for 10 h, then slowly cooled to 700 °C at a rate of 3 °C·h$^{-1}$ and finally cooled down to room temperature at a rate of 10 °C·h$^{-1}$. The crystals of Ba$_7$(BO$_3$)$_3$GeO$_4$X (X=Cl, Br) have been obtained, which were used for the single-crystal X-ray diffraction analysis.

**Structure determination**

The crystal structures of Ba$_7$(BO$_3$)$_3$GeO$_4$X (X=Cl, Br) were collected by a Bruker SMART APEX II CCD diffractometer with monochromatic Mo Kα radiation at 293(2) K, which were further integrated with the SAINT program. The calculations were completed by programs from the SHELXTL crystallographic software package, while their structures were determined by direct methods with SHELXS-97. Final least-squares refinements are on F$^2$ with data having F$^2 > 2\sigma$(F$^2$).

PLATON has been used to check for missing symmetry. Crystal data and structure refinement information are shown in Table 1. And final refined atomic positions and isotropic thermal parameters are displayed in Table S2 in the Supporting Information.

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<th>Temperature</th>
<th>Ba$_7$(BO$_3$)$_3$GeO$_4$Cl</th>
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<td>296(2) K</td>
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<td>b (Å)</td>
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**Infrared and UV–vis–NIR diffuse reflectance spectroscopy**

The infrared spectra with the range of 400−4000 cm$^{-1}$ have been performed on Shimadzu IR Affinity-1 Fourier transform infrared spectrometer. UV–vis–NIR diffuse reflectance data have been performed on the Solid Spec-3700DUV spectrophotometer with a range from 190 to 2600 nm. Then Polytetrafluoroethylene is used as a standard. Finally we converted the reflectance spectra to absorbance by the function, F(R) = (1 − R)$^2$/2R. R represents the reflectance while F(R) represents the Kubelka–Munk remission function.

**Numerical calculation details**

The electronic structure calculations were performed using a plane-wave basis set and pseudopotentials within density functional theory (DFT) implemented in the total-energy module CASTEP. The exchange and correlation effects were treated by Perdew–Burke–Ernzerhof (PBE) in the generalized gradient approximation (GGA). The interactions between the ionic cores and the electrons were described by ultrasoft pseudopotentials. The following orbital electrons were treated as valence electrons: Ba 5s$^2$5p$^6$6s$^2$, Ge 4s$^2$4p$^2$, B 2s$^2$2p$^1$, O 2s$^2$2p$^4$, Cl 3s$^2$3p$^5$, Br 5s$^2$5p$^7$. The calculations were performed on Shimadzu IR Affinity-1 Fourier transform infrared spectrometer. UV–vis–NIR diffuse reflectance data have been performed on the Solid Spec-3700DUV spectrophotometer with a range from 190 to 2600 nm. Then Polytetrafluoroethylene is used as a standard. Finally we converted the reflectance spectra to absorbance by the function, F(R) = (1 − R)$^2$/2R. R represents the reflectance while F(R) represents the Kubelka–Munk remission function.
$2s^22p^4$, $Cl$ $3s^23p^5$ and $Br$ $4s^24p^5$. The number of plane waves included in the basis were determined by a cutoff energy of 340 eV, and the numerical integration of the Brillouin zone was performed using a $4 \times 4 \times 3$ Monkhorst–Pack scheme\textsuperscript{36} k-point grid sampling for $Ba_4(BO_3)_3GeO_2Cl$ and $Ba_4(BO_3)_3GeO_2Br$. Our test showed that these computational parameters ensure a good convergence in the present studies.

The linear optical response properties of the $Ba_4(BO_3)_3GeO_2X$ ($X=Cl, Br$) were examined through calculating the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The imaginary part of the dielectric function $\varepsilon_2$ is given in the following equation:\textsuperscript{37}

$$\varepsilon_1(q \to \infty, \hbar\omega) = \frac{2e^2}{\Omega} \sum_{\mathbf{k}} \left| \langle \phi_{\mathbf{k}} | \mathbf{r} | \phi_{\mathbf{k}}' \rangle \right|^2 \delta \left[ E_{\mathbf{k}}^r - E_{\mathbf{k}}^i - E \right]$$

The real part $\varepsilon_1(\omega)$ can be obtained from the imaginary part $\varepsilon_2(\omega)$ by the Kramers–Kronig transformation. All the other constant optical constants, such as the absorption spectrum, refractive index, and reflectivity are derived from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$.

Results and discussion

Structure

Both of the title compounds crystallize in an orthorhombic space group, $Pbam$ (no. 55). As $Ba_4(BO_3)_3GeO_2X$ ($X=Cl, Br$) are isostructural, only the structure of $Ba_4(BO_3)_3GeO_2Br$ is described in detail here. There are six unique Ba sites, two unique B sites, one unique Ge site, one unique Br site and eight unique O sites in the asymmetric unit (Table S2 in the Supporting Information). In the structure of $Ba_4(BO_3)_3GeO_2Br$, $BaO_6$ (n=8, 9) and $BaO-Br_2$ polyhedra are interconnected by shared oxygen atoms to form the 3D framework (Figure 1a), while isolated $GeO_4$ tetrahedra and $BO_3$ triangles are filled in the space created by the framework. (Figure 1b).

Selected bond distances and angles for $Ba_4(BO_3)_3GeO_2X$ ($X=Cl, Br$) are presented in Figure S3 in the Supporting Information. The $Ba-O$, $B-O$, $Ge-O$ and $Ba-Br$ distances varying $2.567(7)$–$3.217(5)$ Å, $1.362(12)$–$1.391(9)$ Å, $1.737(7)$–$1.766(5)$ Å and $3.1424(15)$–$3.7463(13)$ Å, respectively. These values are observed in other reported compounds.\textsuperscript{16a, 38}

Comparing the structure of $Ba_4(BO_3)_3GeO_2X$ ($X=Cl, Br$) with $Ba_4(BO_3)_3SiO_4X$ ($X=Cl, Br$).

$Ba_4(BO_3)_3SiO_4X$ ($X=Cl, Br$) are isostructural and crystallize in the hexagonal $P6_3mc$ space group, while $Ba_4(BO_3)_3GeO_2X$ ($X=Cl, Br$) crystallize in orthorhombic $Pbam$. Three unique Ba atoms, one unique B atom, one unique Si atom, four unique Ge atoms and one unique Br atom are in the asymmetric unit of $Ba_4(BO_3)_3SiO_4Br$. The structure of $Ba_4(BO_3)_3SiO_4Br$ are composed of a 3D $Ba(3)$-based framework with tunnels viewing along $c$ axis, in which the $BrBa(2)$ chains are resides (Figure 2a). In addition, $[Ba(1)O_6Si(Oi)O]$ single chains and isolate $BO_3$ triangles are filled in the framework to form its 3D network structure (Figures 2b and 2c). In the structure, the $[Ba(1)O_6Si(Oi)O]$ single chain consists of isolated $SiO_4$ tetrahedra and $Ba(1)O_{10}$ polyhedra.

Figure 1 The structure of $Ba_4(BO_3)_3GeO_2Br$. (a) Ba–based 3D framework. (b) 3D network of $Ba_4(BO_3)_3GeO_2Br$. All the Ba–O and Ba–Br bonds have been omitted for clarity.

Figure 2 The structure of $Ba_4(BO_3)_3SiO_4Br$. (a) $[BrBa]_n$. (b) $Ba(3)$-based 3D framework. (c) 3D network of $Ba_4(BO_3)_3SiO_4Br$. All the Ba–O bonds have been omitted for clarity.

Similarly, the structure of $Ba_4(BO_3)_3GeO_2Br$ composes of a 3D $Ba(1, 4, 5)$-based framework with tunnels viewing along $b$ axis, in which the $BrBa(2, 6)$ chains are located (Figure 2a). In
addition, $\{[\text{Ba}(3)\text{O}_4(\text{GeO}_2)]\}$ double chains and isolate BO$_3$ triangles are filled in the framework to form its 3D network structure (Figures 2b and 2c). The $\{[\text{Ba}(3)\text{O}_4(\text{GeO}_2)]\}$ double chain are built of isolated GeO$_4$ tetrahedra and Ba(3)O$_6$ polyhedra.

Accordingly, the structural transformation between Ba$_2$(BO$_3$)$_3$SiO$_4$Br and Ba$_2$(BO$_3$)$_3$GeO$_4$Br will be discussed from the following two parts: (A) the arrangements of chains and (B) the Ba-based 3D frameworks.

(A) The transformation from $\{[\text{Ba}(1)\text{O}_4(\text{SiO}_2)]\}$ single chains to $\{[\text{Ba}(3)\text{O}_4(\text{GeO}_2)]\}$ double chains. In the structure of Ba$_2$(BO$_3$)$_3$SiO$_4$Br, the parallel single chains of $\{[\text{Ba}(1)\text{O}_4(\text{SiO}_2)]\}$ are linked by Ba(3)O$_6$ polyhedra (Figure 4a). When the Si atoms are replaced by the Ge atoms, it causes a weak squeeze between GeO$_4$ tetrahedra and Ba(3)O$_6$ polyhedra owing to the dimensional effect (the average bond lengths of Si–O is 0.155 Å smaller than that of Ge–O). In addition, as we know, the rigid units are hard to be compressed and squeezed while the flexible ones are easy. In the structure, the SiO$_4$ and GeO$_4$ tetrahedra can be regarded as rigid due to their small bond distance variations comparing to that of Ba–O polyhedra. However, comparing with Ba–O polyhedra, the BrBa$_6$ octahedra can be regarded as flexible units for their largest bond distance variations in the structures. Thus, the Ba(3)O$_6$ polyhedra are squeezed by the rigid GeO$_4$ tetrahedra to the flexible BrBa$_6$ octahedra (Figure 4b). As a result, the Ba(3)O$_6$ polyhedra have been squeezed out of the chains, which leads to the single chains connect each other to form the double chains (Figures 4c and 4d).

Figure 3 The structure of Ba$_2$(BO$_3$)$_3$GeO$_4$Br. (a) $\{[\text{BrBa}_6]\}$, (b) Ba–based 3D framework, (c) 3D network of Ba$_2$(BO$_3$)$_3$GeO$_4$Br. All the Ba–O bonds have been omitted for clarity.

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The peaks in the region of 860–900 cm\(^{-1}\) can be assigned to the asymmetric stretching vibration of BO\(_3\) groups (Figure S2 in the Supporting Information). The peaks observed in the region of 733–641 cm\(^{-1}\) are attributed to the out-of-bending of BO\(_3\). The peaks in the region of 860–900 cm\(^{-1}\) can be assigned to an asymmetrical stretch of Ge–O of the tetrahedral germanium. The absorption bands in the range of 450–600 cm\(^{-1}\) correspond to the bending vibrations of the Ge–O bonds. Infrared spectra further confirm the existence of BO\(_3\) triangles and GeO\(_4\) tetrahedra, which is consistent with the results obtained from single crystal X-ray structural analyses.

The UV−vis−NIR diffuse reflectance spectra of Ba\(_2\)(BO\(_3\))\(_2\)GeO\(_4\)X (X=Cl, Br) are deposited in Figure S3 in the Supporting Information. It indicates that the experimental optical band gap of Ba\(_2\)(BO\(_3\))\(_2\)GeO\(_4\)Cl and Ba\(_2\)(BO\(_3\))\(_2\)GeO\(_4\)Br are 5.28 and 5.31 eV, respectively. The large band gaps of the title compounds suggest that they may be used as the optical window materials.

**Band structures, density of states and optical properties**

The band structures of Ba\(_2\)(BO\(_3\))\(_2\)GeO\(_4\)X (X=Cl, Br) are presented in Figure S4 in the Supporting Information. The valence band maximum (VBM) and the conduction band minimum (CBM) are located at Γ point of the Brillouin zone indicating both of the two compounds belong to direct band-gap semiconductors. The extrapolated experimental optical gaps of 5.28 eV for Ba\(_2\)(BO\(_3\))\(_2\)GeO\(_4\)Cl and 5.31 eV for Ba\(_2\)(BO\(_3\))\(_2\)GeO\(_4\)Br are slightly larger than the calculated values 4.93 eV and 4.91 eV respectively, the underestimation of the band gap is generally due to insufficiently accuracy of exchange correlation energy under DFT methods. We can see that the results of our calculation are good and give reasonable explanations for the optical absorption spectra. The highest occupied and lowest unoccupied orbitals determine the way of electronic transitions and the absorption edge. It is shown in Figure S5 in the Supporting Information that the absorption edges of Ba\(_2\)(BO\(_3\))\(_2\)GeO\(_4\)Cl and Ba\(_2\)(BO\(_3\))\(_2\)GeO\(_4\)Br are mainly decided by O 2\p states in BO\(_3\) units.

The total and partial densities of states (DOS and PDOS) are shown in Figure 6. The top region of VBs extends wide range from -6.7 eV to VBM. This bands mostly originate from Ge 4s4p, B 2s2p and O 2s2p states with the mixings of Ba 5s5p and Cl 3p/Br 4p states, especially near the Fermi level. It is worthy to note that strong hybridizations occur among the Ge 4s4p, B 2s2p and O 2s2p states in the range of -6.7 eV to -0.7 eV. For Ba\(_2\)(BO\(_3\))\(_2\)GeO\(_4\)Cl and Ba\(_2\)(BO\(_3\))\(_2\)GeO\(_4\)Br, the conduction bands from CBM to 8.5 eV are derived from Ba 5s, Ge 4s4p and B 2p states with mixings of Ba 5s5p, B 2s and O 2s2p states, implying strong interactions in Ge−O and B−O bonds for the compounds. The valence bands and conduction bands near the gap are dominated by O 2p and Ba 5d states respectively. Accordingly, the absorption spectrum near the UV-Visible cut-off wavelength can be assigned as the charge transfers from O 2p states to the Ba 5d states.
On the basis of the electronic structures, the linear optical properties can be estimated. The imaginary part of dielectric birefringence (∆n) versus wavelength is shown in Figure S6 in the Supporting Information. It can be seen that the birefringences of Ba$_7$(BO$_3$)$_3$GeO$_3$Cl and Ba$_7$(BO$_3$)$_3$GeO$_3$Br are about 0.03 with the wavelength at 1064 nm.

Conclusion

The first borogermanate halides, Ba$_7$(BO$_3$)$_3$GeO$_3$X (X=Cl, Br) have been obtained by high temperature solution method. We have discussed the structural transformation from Ba$_7$(BO$_3$)$_3$SiO$_3$X (X=Cl, Br) to Ba$_7$(BO$_3$)$_3$GeO$_3$X (X=Cl, Br). The unusual structural transformation mainly originates from rigid GeO$_4$ tetrahedra and flexible XBa$_6$ (X=Cl, Br) octahedra. We believe that this interpretation can give new insights into structural transformation. The first-principles calculations show that the calculated band gaps (4.93 eV for Ba$_7$(BO$_3$)$_3$GeO$_3$Cl and 4.91 eV for Ba$_7$(BO$_3$)$_3$GeO$_3$Br) agree well with the experimental ones (5.28 and 5.31 eV). The top of the valence band is dominated by the mixture of B 2p and O 2p states, while the Ba 5d, Ge 4d, and O 2s ×2p states dominate the bottom of the conduction band.

Acknowledgements

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Notes and references

1. Electronic supplementary information (ESI) available: Calculated and observed XRD patterns, IR and UV-vis-NIR diffuse transmittance spectra, the substitution of Ge for Si in borates, final refined atomic positions and isotropic thermal parameters, selected bond distances and angles and first-principles calculations in Ba$_7$(BO$_3$)$_3$GeO$_3$X (X=Cl, Br). CCDC 1058752 for Ba$_7$(BO$_3$)$_3$GeO$_3$Cl and CCDC 1058753 for Ba$_7$(BO$_3$)$_3$GeO$_3$Br. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x


