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$Sr_8MgB_{18}O_{36}$: a New Alkaline-Earth Borate with a Novel Zero-Dimensional $(B_{18}O_{36})^{18-}$ Anion Ring

Wenjiao Yao,[†,‡] Xingxing Jiang,[†,‡] Hongwei Huang,[§] Tao Xu,[†,‡] Xiaoshan Wang,[†,‡] Zheshuai Lin,[*,†] and Chuangtian Chen[†]

[†]Beijing Center for Crystal R&D, Key Lab of Functional Crystals and Laser Technology of Chinese Academy of Sciences, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

[§]School of Materials Science and Technology, China University of Geosciences, Beijing 100083, People's Republic of China

[‡]University of the Chinese Academy of Sciences, Beijing 100049, People's Republic of China

Supporting Information

ABSTRACT: A new polyborate, $Sr_8MgB_{18}O_{36}$, has been synthesized. Its crystal structure was determined from single-crystal X-ray diffraction data, and characterizations were made by differential scanning calorimetry, Fourier transform IR, UV−vis−near-IR diffuse-reflectance, and first-principles calculations. The structure of $Sr_8MgB_{18}O_{36}$ contains a novel isolated anionic group—an 18-membered ring $(B_{18}O_{36})^{18-}$, which is the first found in borates.

Borates have been an important research focus for many years, and they have given rise to numerous applications because they possess many attractive properties, such as high electrical conductivity in ion conductors,[1] efficient frequency conversion capability in nonlinear optical crystals,[2] and large birefringence in controlling the polarization of illuminating lasers.[3] Therefore, it is of importance to explore new borate compounds with novel structural features. The structural diversity of the borates can be attributed to the coordination of boron as it bonds with either three or four O atoms to form a BO_3 triangle or BO_4 tetrahedron. These can be further linked by sharing O atoms to form isolated rings and cages or to construct infinite chains, sheets, or networks. In addition, the cations may significantly influence the packing patterns of anionic groups,[4,5] leading to new phases with interesting stoichiometries, structures, and properties. In this Communication, we report the synthesis and crystal structure of a new binary alkaline-earth-metal mixed borate, $Sr_8MgB_{18}O_{36}$. The structure of the new compound is built from isolated $(B_{18}O_{36})^{18-}$ rings, a MgO_6 octahedron, and SrO_n (n = 6, 7) polyhedra. The $(B_{18}O_{36})^{18-}$ building block is the first found in borates. The novel $(B_{18}O_{36})^{18-}$ group expands the structural diversity of borates. The properties of the crystal were characterized by a variety of experimental and computational methods.

Polycrystalline samples of $Sr_8MgB_{18}O_{36}$ were obtained by a traditional solid-state reaction with a stoichiometric mixture of $SrCO_3$, MgO, and H_3BO_3.[6] Single crystals were grown through spontaneous crystallization from different flux methods.[7] The powder X-ray diffraction (PXRD) patterns of polycrystalline samples display excellent agreement with the theoretical simulations from the single-crystal structure. The resulting colorless and transparent crystals from the flux method were chosen for further characterization. The FT-IR spectrum validates the existence of BO_3 and BO_4 groups in the $Sr_8MgB_{18}O_{36}$ structure, which are also commonly found in other borates.[8] Differential scanning calorimetric measurement reveals that this compound remains stable up to the phase transition temperature of 1052 °C. UV−vis−near-IR diffuse-reflectance data demonstrate that its UV cutoff wavelength is below 200 nm. All measured data are displayed in the Supporting Information.

The structure of the $Sr_8MgB_{18}O_{36}$ crystal was determined from single-crystal X-ray diffraction data.[9] The atomic coordinates, related anisotropic displacement parameters, and selected bond lengths (Å) and angles are summarized in Tables S2−S4 in the Supporting Information.

$Sr_8MgB_{18}O_{36}$ crystallizes in the centrosymmetric uniaxal trigonal system with space group $R\bar{3}c$, and its structure is illustrated in Figure 1. It features a complicated three-

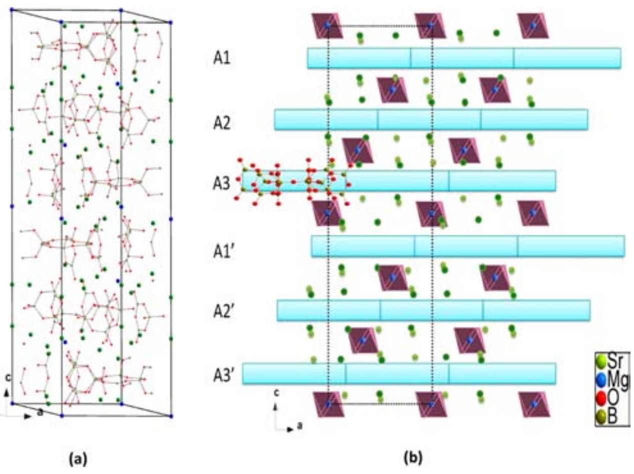

Figure 1. Structure of $Sr_8MgB_{18}O_{36}$ viewed along the *b* axis: (a) unit cell; (b) schematic diagram. Blue boxes are the basic $[B_{18}O_{36}]^{18-}$ building blocks, purple octahedra are MgO_6 groups, and dark- and light-green balls in part b indicate the Sr atoms in the different *ac* planes.

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dimensional framework that is built up of zero-dimensional $(B_{18}O_{36})^{18-}$ anion rings, MgO_6 octahedra, and SrO_n (n = 6, 7) distorted polyhedra. Sr, Mg, B, and O each occupy two, one, three, and seven crystallographically unique positions, respectively. In the $(B_{18}O_{36})^{18-}$ group, the bond lengths and angles in a BO_4 tetrahedron range from 1.466 to 1.522 Å and from 107.0° to 111.1°, respectively, while in a BO_3 triangle, they range from 1.326 to 1.398 Å, and 118.9° to 121.5°. The mean bond lengths in the BO_4 tetrahedron and BO_3 triangle are 1.4704 and 1.3815 Å, respectively. The MgO_6 octahedron is almost regular; the Mg−O bond lengths are all equal to 2.0628 Å, and the O−Mg−O angles are very close to 90°. In the SrO_n (n = 6, 7) polyhedra, the bond lengths vary from 2.399 to 2.7183 Å, with O−Sr−O bond angles from 51.58° to 137.89°. These bond lengths and angles in $Sr_8MgB_{18}O_{36}$ are comparable with those in other borates.[10] Because the bond lengths display large variations, the bond valence sums for all atoms were calculated (see Table S2 in the Supporting Information), which are in good agreement with the formal atom charges.

A notable feature in the structure of $Sr_8MgB_{18}O_{36}$ is the $(B_{18}O_{36})^{18-}$ fundamental building block, as illustrated in Figure 2, and is the first time to be observed in borates. It has a 12-membered (B_6O_6) circle, constructed from six B tetrahedra ($3[2\Delta + T]$) by sharing the common O vertex atoms. So, the $(B_{18}O_{36})^{18-}$ group can be condensed into complex polyborate (megaborate) circles described as $18(6 \times 3[2\Delta + T])$ according to the Christ and Clark notation.[11] The orientations of the B_3O_7 subgroups fall into three series, where every two B_3O_7 rings are arranged parallel, and the dihedral angles between the series are nearly 120°. The polyborate anion with 18 B atoms has never been found in any known borates. The topology-symmetry approach[12] further demonstrates that the $(B_{18}O_{36})^{18-}$ block belongs to the noncentrosymmetric D_3 (32) point group. However, it is a local symmetry and inconsistent with the symmetry of the overall $Sr_8MgB_{18}O_{36}$ structure, which belongs to the centrosymmetric point group $\bar{3}m$.

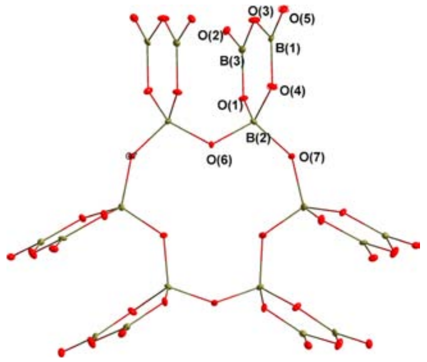

Figure 2. $[B_{18}O_{36}]^{18-}$ fundamental building block in which the central 12-membered (B_6O_6) circle is constructed from six B tetrahedra.

The arrangement of the $(B_{18}O_{36})^{18-}$ rings in the ab plane (e.g., the A1 layer in Figure 1b) exhibits the same orientation, as shown in Figure 3a. From one layer to the next, the $(B_{18}O_{36})^{18-}$ groups rotate by 60° about the c axis and translate by $1/3(A + B)$, where A and B are the lattice constants along the a and b axes, respectively. Therefore, the (B_6O_6) circles are in a completely staggered arrangement in the neighboring layers, while they are overlapped but in the different orientations in every three layers, e.g., A1 and A1′ layers [the same as (A2 and A2′) and (A3 and A3′)] in Figure 1b, as viewed along the c axis. The MgO_6 octahedra and SrO_n (n = 6, 7) polyhedra are located between layers and connect the isolated $(B_{18}O_{36})^{18-}$ rings together. It is interesting to observe that as viewed along the c axis the MgO_6 and $Sr(2)O_7$ polyhedra are encircled by the (B_6O_6) rings, with the Mg/Sr(2) atoms right at the center point of the rings, as displayed in Figure 3b.

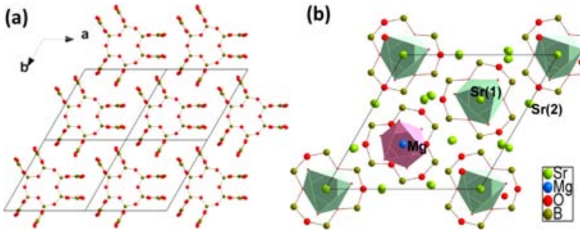

Figure 3. Structure of $Sr_8MgB_{18}O_{36}$ viewed along the c axis. (a) Schematic diagram of $[B_{18}O_{36}]^{18-}$ groups in the A1 plane. (b) Arrangement of Mg/SrO_n (n = 6, 7) groups and $[B_6O_6]$ rings. The pink and green polyhedra represent MgO_6 and $Sr(1)O_7$, respectively.

The first-principles electronic structure calculation shows that the $Sr_6MgB_{18}O_{36}$ crystal possesses the very large band gap of 7.32 eV (details given in the Supporting Information). Figure 4 shows the partial density of states (PDOS) projected on the constituent elements. Clearly, the PDOS can be divided into four regions, and some characteristics can be deduced: (1) The Sr 4s electrons are strongly localized at −31.0 eV and would be difficult to stimulate by external perturbations. (2) The energy states ranging from −20 to −12 eV mainly consist of Sr 4p, B 2s2p, and O 2s orbitals, and the large hybridization between B 2s2p and O 2s confirms the formation of strong covalent B−O bonds. (3) The orbitals of B and O dominate the upper part of the valence band (−10−0 eV), but the O 2p orbitals exclusively occupy the valence-band maximum. (4) The orbitals of almost all of the elements contribute to the bottom of the conduction band, among which the Sr 4d orbitals directly determine the conduction-band minimum. It is seen that the optical properties of $Sr_6MgB_{18}O_{36}$ mainly result from the electronic transition across forbidden bands in the $(B_{18}O_{36})^{18-}$ groups. The calculated refractive index dispersion curves (see Figure S4 in the Supporting Information) predict that $Sr_6MgB_{18}O_{36}$ is a negative uniaxial crystal and its birefringence is rather small (0.03 at λ = 1064 nm), originating from the relatively small anisotropy of the $(B_{18}O_{36})^{18-}$ group.

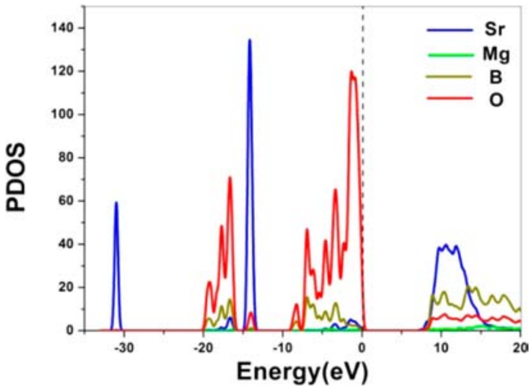

Figure 4. PDOS of $Sr_8MgB_{18}O_{36}$.

In conclusion, a new mixed alkaline-earth borate compound $Sr_8MgB_{18}O_{36}$ has been discovered in the SrO−MgO−B_2O_3 ternary system. The fundamental building block of this compound is the $(B_{18}O_{36})^{18-}$ anion ring in which a 12-membered (B_6O_6) circle is constructed from six (B_3O_7) groups. It is the first time that this ring has been seen in borates. These anionic groups are zero-dimensional, with the (B_6O_6) circles contained in the $(B_{18}O_{36})^{18-}$ rings being parallel to each other. The MgO_6 octahedra and SrO_n ($n = 6, 7$) polyhedra connect the isolated $[B_{18}O_{36}]^{18-}$ anionic groups, producing the infinite three-dimensional framework. The crystal exhibits incongruent melting inherency, and the UV cutoff edge is lower than 200 nm. The first-principles studies reveal that the direct energy band gap is 7.32 eV (∼170 nm), so this crystal might serve as a UV and a deep-UV optical material. Further investigations to grow large crystals and measure related physical properties are underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

[Experimental details, specified physical characterization, anisotropic displacement parameters, selected bond lengths and angles, first-principles calculations, and crystallographic data in CIF for $Sr_8MgB_{18}O_{36}$. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: zslin@ipc.ac.cn. Tel: 86-010-82543718. Fax: 86-010-82543709.

Notes

The authors declare no competing financial interest.

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(6) $SrCO_3$ (analytical reagent, AR), MgO (AR), H_3BO_3 (AR), B_2O_3 (99.5%), Li_2CO_3 (AR), $SrCl_2 \cdot 6H_2O$ (AR), NaF (AR), and LiF (AR) from commercial sources were used as received. The raw materials were carefully weighed and ground in an agate mortar until the mixture appeared homogeneous. Then the mixture was packed into platinum crucibles, which were then heated in a muffle furnace to about 600 K in the first round to ensure decomposition of H_3BO_3 and $SrCO_3$. After that, the mixture was ground adequately, heated gradually to 1223 K, and kept for 6 days with several interval grindings. PXRD analysis was performed until monophasic powders with white color were obtained, and the patterns show no difference.

(7) The raw materials and flux at various proportions were homogeneously mixed, placed in a platinum crucible, and gradually heated in a self-made furnace to 1253 K. In the melt cases, the samples were kept at that temperature for at least 24 h and stirred at regular intervals by a platinum plate to ensure homogeneity. The temperature was then lowered at a rate of 10 K/day until the mixture was frozen to the solid state. The crucible was then taken out of the furnace and cooled to room temperature in air. Many colorless, transparent block crystals were obtained for later tests. The temperature was controlled by a Shimaden FP23 controller with precision of ±0.1 K. (See the results of different growing schemes in the Supporting Information.)

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(9) Single-crystal X-ray diffraction data for $Sr_8MgB_{18}O_{36}$ were collected at 143 K on a Rigaku AFC10 single-crystal diffractometer from 2.1307° to 31.4970° with graphite-monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å) and a Saturn CCD detector. A colorless, transparent crystal with dimensions of $0.205 \times 0.19 \times 0.15$ mm^3 was selected for structure determination. *The CrystalClear* program was run to record the intensity data and perform cell refinement and data reduction. The structure was solved with *Shelxtl-97* by direct methods and refined by full-matrix least-squares techniques with anisotropic thermal parameters. Crystal data for $Sr_8MgB_{18}O_{36}$: $M = 1495.82$ g/mol, trigonal, $a = 11.4271(16)$ Å, $c = 36.913(7)$ Å, $V = 4174.2(12)$ Å^3, $T = 170$ K, $Z = 6$, space group $R\bar{3}c$ (No. 167), 13169 reflections measured. The final R1 values were 0.0331 $[I > 2\sigma(I)]$. The final wR(F^2) values were 0.0618 $[I > 2\ \sigma(I)]$. The final R1 values were 0.0363 (all data). The final wR(F^2) values were 0.0627 (all data). GOF on $F^2 = 1.293$.

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