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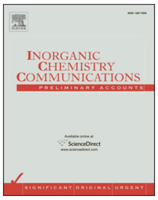

Short communication

A new alkaline-earth metal borate $SrB_3O_4(OH)_3 \cdot H_2O$ with UV cutoff edge below 190 nm

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ABSTRACT

A new alkaline-earth metal borate $SrB_3O_4(OH)_3 \cdot H_2O$, has been successfully synthesized using the hydrothermal method. Single-crystal X-ray diffraction analysis reveals that it crystallizes in the centrosymmetric space group $P2_1/c$, $a = 6.249(4)$ Å, $b = 11.459(6)$ Å, $c = 8.749(5)$ Å, $\beta = 108.493(6)°$, $Z = 4$. $SrB_3O_4(OH)_3 \cdot H_2O$ contains infinite $[B_3O_4(OH)_3]^{2-}$ chains along the *c* axis direction extended by the B_3O_8 units with Sr^{2+} cations filling the space between these chains. There are inter-chain hydrogen-bonds leading to a compact 3D structure. $SrB_3O_4(OH)_3 \cdot H_2O$ possesses a large experimental band gap of 6.15 eV and a short wavelength cutoff edge lower than 190 nm (183 nm) as found by the UV–vis-NIR diffuse reflectance spectrum. The calculated band structure and the density of states of $SrB_3O_4(OH)_3 \cdot H_2O$ suggest that its indirect energy gap is 5.76 eV which agrees with the experimental result. The thermal behavior and the IR spectrum of $SrB_3O_4(OH)_3 \cdot H_2O$ are also reported in this work.

Deep-ultraviolet (DUV) birefringent crystals with cutoff edges below 200 nm have important applications in fields of 193 nm immersion lithography, photo fragment translational spectroscopy, DUV Raman spectrometers, and fluorescence spectrometers, etc. [1–4]. Inorganic borate crystals have been widely explored for these applications since the boron atom may adopt triangular or tetrahedral oxygen coordination to form the BO_3 triangles or BO_4 tetrahedra, and then these groups may be further linked by sharing bridging oxygen atoms to form isolated rings and cages or infinite chains, layers and 3D networks, for instance, $[B_3O_6]$, $[B_3O_7]$, $[B_5O_{10}]$ and so on, which determines the diversity of the borate family [5]. In particular, due to the large electronegativity difference between the B atom and the O atom, borate material may have a wide optical transmission window. Metal cations, such as the alkali/alkaline-earth metal cations, often contribute to the cutoff edge shift to the UV region, because the d-d or f-f electronic transitions in the closed d or f orbits have negative influences on the energy band gap [6]. The rational combination of the above multiple types of units in the same compound is an effective synthetic route for new inorganic borates with deep-UV cutoff edge. During the past several decades, continuous efforts have led to significant discoveries of a number of important alkaline-earth metal borate with a deep-UV cutoff edge, such as α-BaB_2O_4 (189 nm) [7], β-BaB_2O_4 (185 nm) [8], $Ba_2B_6O_9(OH)_4$ (below 190 nm) [9], $Sr_4B_{10}O_{18}(OH)_2 \cdot 2H_2O$ (below 190 nm) [10], etc. [11–12]. Based on this idea, we have started to explore alkaline-earth metal borate having deep-UV cutoff edge. In this paper, a new centrosymmetric alkaline-earth metal borate $SrB_3O_4(OH)_3 \cdot H_2O$ were grown using hydrothermal method for the first time. $SrB_3O_4(OH)_3 \cdot H_2O$ possesses a large experimental band gap of 6.15 eV and a short cutoff edge lower than 190 nm measured by UV–vis-NIR diffuse reflectance spectrum. The synthesis, crystal structure, thermal behavior, IR and electron structure calculations of $SrB_3O_4(OH)_3 \cdot H_2O$ are reported in this work.

The $SrB_3O_4(OH)_3 \cdot H_2O$ single crystal was synthesized by hydrothermal reaction. A mixture of H_3BO_3 (0.309 g, 5 mmol), $SrCl_2 \cdot 6H_2O$ (0.266 g, 1 mmol), KOH (0.112 g, 2 mmol), and distilled water (8 mL) were placed into a 23 mL autoclave with a Teflon liner. The autoclave was heated at 160 °C for 24 h and naturally cooled to about 25 °C. The product was repeatedly washed with deionized water, then large quantities of crystalline bulk crystals had been obtained. The yield of $SrB_3O_4(OH)_3 \cdot H_2O$ was 62% based on Sr.

The crystal structure of $SrB_3O_4(OH)_3 \cdot H_2O$ was determined by single-crystal XRD on an APEX II CCD diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 296 (2) K and plates were integrated with the SAINT program [13]. The SHELXTL crystallographic software package was used to perform all the calculations [14]. The structure was solved by the direct methods and refined by full matrix least-squares fitting on F^2 using SHELXTL, and all non hydrogen atoms were refined by means of the least squares of anisotropic thermal parameters. All the hydrogen atoms were located from subsequent difference Fourier maps and their positional and isotropic displacement parameters were freely refined. The structure was checked using Addsym routine of PLATON [15] and no higher symmetry

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was found. CSD-434218 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the ICSD database via https://www.fiz-karlsruhe.de/leistungen/kristallographie/kristallstrukturdepot.html. Crystal data and structure refinement information for $SrB_3O_4(OH)_3 \cdot H_2O$ are given in Table 1; The final atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) of non hydrogen atoms for $SrB_3O_4(OH)_3 \cdot H_2O$. U_{eq} is defined as one-third of the trace of the orthogonal zed U_{ij} tensor is listed in Table S1. The selected bond distances and bond angles are listed in Table S2.

n order to further determine the purity of $SrB_3O_4(OH)_3 \cdot H_2O$, powder X-ray diffraction (PXRD) pattern of $SrB_3O_4(OH)_3 \cdot H_2O$ was obtained on a IBruker D8 ADVANCE X-ray diffractometer using Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). Diffraction patterns were taken from 10 to 70° with a scan step width of 0.02° and a fixed counting time of 1 s/step. The experimental powder XRD pattern is in agreement with the calculated one based on the single-crystal crystallographic data (Fig. 1).

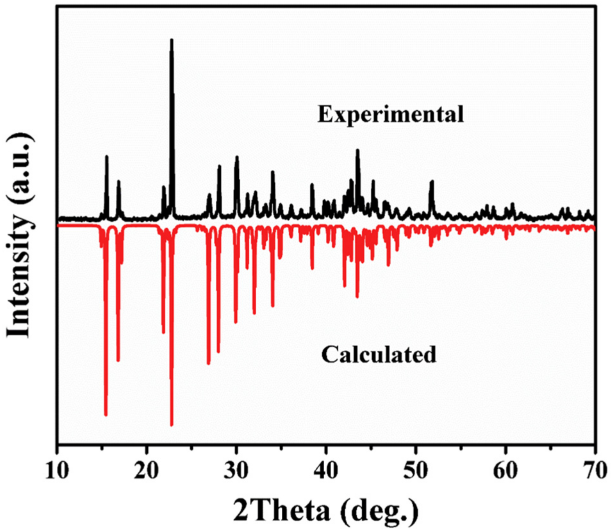

Fig. 1. The calculated (red) and experimental (black) XRD patterns of $SrB_3O_4(OH)_3 \cdot H_2O$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$SrB_3O_4(OH)_3 \cdot H_2O$ crystallizes in centrosymmetric space group $P2_1/c$ of the monoclinic system with an asymmetric unit consisting of one Sr, three B, eight O, and five H atoms (Fig. 2). $SrB_3O_4(OH)_3 \cdot H_2O$ contains infinite $[B_3O_4(OH)_3]^{2-}$ chains along the c axis direction extended by the B_3O_8 units made up of one BO_3 triangle (Δ) and two BO_4 tetrahedra (T) with vertex-sharing O atoms along the ab plane (Fig. 3a). The BO_3 triangles have B—O distances in the range of 1.347–1.388 Å, and the BO_4 tetrahedra have longer B—O distances in the range of 1.452–1.510 Å. The O—B—O angles are in the range of 115.1–125.5° for the BO_3 triangles and 106.1–113.7° for the BO_4 tetrahedra, which are in agreement with other borate compounds reported previously [16]. As the fundamental building blocks (FBB), B_3O_8 ring connect with each other by sharing O5 atoms to form an infinite one-dimensional polymer borate chiral $[B_3O_4(OH)_3]^{2-}$ chains along the c axis direction. Of particular interest is that adjacent 1D right-handed infinite helical chains are antiparallel when viewed along the c axis (Fig. 3b). The Sr^{2+} cations filling the space between these chains will balance the charge and hold the chains together by the connection with O atoms (Fig. 4a). IIn this structure, the Sr atoms are bonded to eight O atoms, seven O atoms from three $[B_3O_4(OH)_3]^{2-}$ chains, one O atom from coordinated H_2O molecules, forming the SrO_8 polyhedron with Sr—O distances in the range of 2.527 to 2.865 Å (Fig. 4b). At the same time, there are inter-chain hydrogen-bonds O6-H2···O4 [2.705 Å], O7-H3···O5 [3.191 Å] and O7-H3···O5 [2.995 Å], which lead to a compact 3D structure.

To further understand the structure, we compared the structure $SrB_3O_4(OH)_3 \cdot H_2O$ with that of $Sr_2[B_6O_9(OH)_4]$ reported by G.-Y. Yang [17]. Though these two structures are built by the same FBB of B_3O_8 units made up of one BO_3 triangle and two BO_4 tetrahedra with vertex-sharing O atoms, the $SrB_3O_4(OH)_3 \cdot H_2O$ crystallizes in centrosymmetric space group $P2_1/c$ of the monoclinic system while $Sr_2[B_6O_9(OH)_4]$ crystallizes in noncentrosymmetric space group $P2_1$. $SrB_3O_4(OH)_3 \cdot H_2O$ contains infinite $[B_3O_4(OH)_3]^{2-}$ chains along the c axis direction extended by the B_3O_8 units, adjacent 1D right-handed infinite helical chains are antiparallel when viewed along the c axis which negates any remnant polarization effects (Fig. 5a). $Sr_2[B_6O_9(OH)_4]$ features a two-dimensional network with $[B_6O_9(OH)_4]^{4-}$ cluster where each $[B_6O_9(OH)_4]^{4-}$ cluster is connected to four neighboring ones, forming a wave-like 2D borate layer parallel to the bc plane. Of particular interest

Table 1
Crystal data and structure refinement information for $SrB_3O_4(OH)_3 \cdot H_2O$.

Empirical formula	$SrB_3O_4(OH)_3 \cdot H_2O$
Formula weight	253.09
Temperature	296.15 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group, Z	$P2_1/c$, 4
Unit cell dimensions	$a = 6.249(4)$ Å
	$b = 11.459(6)$ Å
	$c = 8.749(5)$ Å
	$\beta = 108.493(6)°$
Volume	594.2(6) $Å^3$
Density (calculated)	2.829 Mg/m^3
Absorption coefficient	9.077 mm^{-1}
$F(000)$	488
Crystal size	0.155 mm × 0.126 mm × 0.104 mm
Theta range for data collection	3.031° to 27.479°
Limiting indices	$-8 \le h \le 8, -14 \le k \le 14, -11 \le l \le 10$
Reflections collected/unique	3540/1355 [$R(\text{int}) = 0.0248$]
Completeness to theta = 25.24	99.9%
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.085
Final R indices [$F_o^2 > 2\sigma(F_o^2)$][a]	$R_1 = 0.0251$, $wR_2 = 0.0642$
R indices (all data)[a]	$R_1 = 0.0303$, $wR_2 = 0.0661$
Largest diff. peak and hole	0.585 and −0.555 e $Å^{-3}$

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w F_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$.

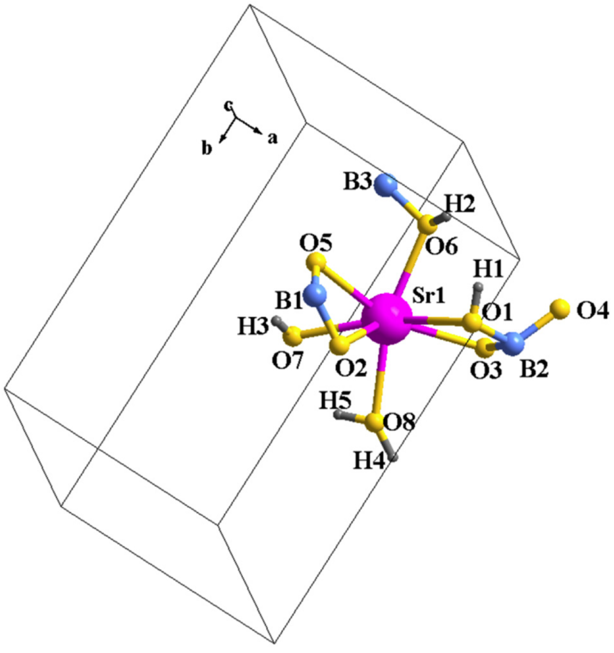

Fig. 2. The asymmetric unit of $SrB_3O_4(OH)_3 \cdot H_2O$.