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Three New Mixed-Alkali- and Alkaline-Earth-Metal Borates: From 1D Chain to 2D Layer to 3D Framework

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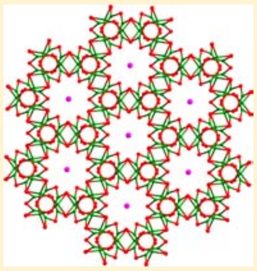
Supporting Information

ABSTRACT: Three new mixed-metal borates, $K_4Ba_2[B_{14}O_{20}(OH)_{10}]\cdot 3H_2O$ (**1**), $LiSr_2[B_{10}O_{16}(OH)_3]$ (**2**), and $LiBa[B_9O_{15}]$ (**3**), have been made under hydro(solvo)thermal conditions and characterized by means of IR, UV−vis−near-IR, thermogravimetric analysis, powder X-ray diffraction, and single-crystal X-ray diffraction, respectively. **1** is a 1D chain constructed from $B_{14}O_{21}(OH)_{10}{}^{10-}$ cluster units, **2** is of a 2D layer with nine-membered-ring windows built up of $B_{10}O_{19}(OH)_3{}^{9-}$ cluster units, while **3** exhibits a 3D framework with 12-membered-ring channels composed of B_3O_7 cluster units.



INTRODUCTION

Borates are of great interest because of their structural diversity and practical application in second-harmonic generation.[1] Generally, a B atom can covalently bond to three or four O atoms to form triangular or tetrahedral groups, which further connect to each other through common vertices to build different isolated B−O clusters, which can be used as the structural building units (SBUs) to further polymerize into infinite chains,[2] sheets,[3] and frameworks.[4] To date, a lot of borates have been made in which the largest SBU is up to 63 unique B atoms.[5] In order to better understand the structures of borates, Christ and Clark and also Burns have developed the B−O cluster description based on SBUs for the complex borates.[6]

So far, the borate system with alkali metals and alkaline-earth metals has been widely studied. β-BaB_2O_4 (BBO),[7] LiB_3O_5 (LBO),[8] and $CsLiB_6O_{10}$ (CLBO)[9] are well-known nonlinear-optical (NLO) materials. They have a variety of acentric structure types, good chemical and thermal stability, wide transparency ranges, and higher optical damage thresholds. These characteristics make them very useful in the NLO field. Recently, Pan et al. reported a series of alkali- and alkali-earth-metal borates under high-temperature solid-state conditions;[10] Kolis and co-workers also obtained alkali- and alkali-earth-metal borates by the high-temperature hydrothermal synthesis method.[11] With our group still focusing on mild temperature hydro(solvo)thermal synthesis, we successfully obtained a series of aluminoborates[12] and germanium borates[13] by using different organic amines or alkali metals. Here, we employed the hydro(solvo)thermal method under mild conditions to make three new metal polyborates of $K_4Ba_2[B_{14}O_{20}(OH)_{10}]\cdot 3H_2O$ (**1**), $LiSr_2[B_{10}O_{16}(OH)_3]$ (**2**), and $LiBa[B_9O_{15}]$ (**3**).

EXPERIMENTAL SECTION

Materials and Methods. IR spectra were obtained from a sample powder pelletized with KBr on a Nicolet iS10 FT-IR spectrophotometer over a range of 400−4000 cm^{-1}. The UV−vis−near-IR (NIR) transmittance spectra were recorded at room temperature by using a Shimadzu UV-3600 spectrophotometer in the wavelength range from 190 to 2000 nm. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA 1100 analyzer in an air atmosphere with a heating rate of 10 °C/min. Powder X-ray diffraction (PXRD) data were obtained using a Bruker D8 Advance X-ray diffractometer with Cu Kα (λ = 1.54056 Å).

Syntheses. Three compounds were made by the mild hydrothermal technique in a Teflon-lined stainless steel bomb.

$K_4Ba_2[B_{14}O_{20}(OH)_{10}]\cdot 3H_2O$ (1). A mixture of H_3BO_3 (0.927 g, 15 mmol), $Ba(OH)_2\cdot 8H_2O$ (0.316 g, 1 mmol), KOH (0.112 g, 2 mmol), and H_2O (5.0 mL) was sealed in a 23 mL stainless steel reactor at 170 °C for 7 days and then cooled to room temperature. Colorless blocked crystals of **1** were recycled by filtration, washed with deionized water, and dried at ambient conditions. Yield: 25% (based on Ba).

$LiSr_2[B_{10}O_{16}(OH)_3]$ (2). A mixture of H_3BO_3 (0.309 g, 5 mmol), $SrCO_3$ (0.147 g, 1 mmol), $KHCO_3$ (0.100 g, 1 mmol), and H_2O (5.0 mL) was sealed in a 23 mL stainless steel reactor at 170 °C for 7 days and then cooled to room temperature. Colorless needlelike crystals of **2** were obtained by the same recycle method. Yield: 34% (based on Sr).

$LiBa[B_9O_{15}]$ (3). A mixture of H_3BO_3 (0.494 g, 8 mmol), $Ba(OH)_2\cdot 8H_2O$ (0.158 g, 0.5 mmol), Li_2CO_3 (0.074 g, 1 mmol), H_2O (0.5 mL), and pyridine (5.0 mL) was also sealed in a 23 mL stainless steel reactor at 200 °C for 7 days and then cooled to room temperature. Colorless blocked crystals of **3** were obtained by the same recycle method. Yield: 75% (based on Ba).

Determination of Crystal Structures. The crystals of three compounds were centered on a Gemini A Ultra diffractometer with a Atlas CCD area detector and an X-ray source using graphite-

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monochromated Mo Kα (λ = 0.71073 Å) in the ω scanning mode at room temperature. The structures were all solved by direct methods using the *SHELXS-97* program package.[14] The H atoms of the H_2O molecules and hydroxyls were added geometrically and refined using a riding model. The structures were solved by direct methods using the *SHELXL-97* program package.[14] All non-H atoms were refined anisotropically. The structure was checked for missing symmetry elements by the program *PLATON*.[15] Crystal data and structure refinement information for three compounds are given in Table 1. The ICSD numbers for the three compounds are 426108, 426109, and 426110.

Table 1. Crystal Data and Structure Refinement for 1−3

	1	2	3
formula	$K_4Ba_2B_{14}O_{33}H_{16}$	$LiSr_2B_{10}O_{19}H_3$	$LiBaB_9O_{15}$
fw	1126.55	597.30	482.58
cryst syst	triclinic	triclinic	hexagonal
space group	$P\bar{1}$	$P\bar{1}$	$R\bar{3}c$
a (Å)	9.0768(3)	6.6427(16)	10.9642(3)
b (Å)	12.9220(8)	11.005(3)	10.9642(3)
c (Å)	13.3452(9)	11.330(5)	17.0330(7)
α (deg)	106.889(6)	61.42(3)	90
β (deg)	95.075(4)	72.954(19)	90
γ (deg)	105.890(4)	72.434(14)	120
V (Å^3)	1416.32(14)	682.4(4)	1773.27(10)
Z	2	2	6
D_c (g/cm^3)	2.642	2.907	2.711
μ(Mo Kα)/mm^{-1}	3.484	7.939	3.451
GOF on F^2	1.026	0.990	1.050
R1/wR2 [$I > 2\sigma(I)$]	0.0231/0.0528	0.0332/0.0614	0.0145/0.0344
R1/wR2 (all data)	0.0308/0.0554	0.0455/0.0645	0.0196/0.0351
largest diff peak and hole (e/Å^3)	0.58 and −0.57	0.67 and −0.70	0.28 and −0.34

RESULTS AND DISCUSSION

Structure of 1. **1** crystallizes in triclinic space group $P\bar{1}$ with Z = 2. In the asymmetric unit, there are four K atoms, two Ba atoms, a $B_{14}O_{21}(OH)_{10}$ cluster, and three lattice water molecules, respectively (Figure 1a). The SBU is an unusual $B_{14}O_{21}(OH)_{10}$ cluster, which could be considered as two $B_7O_{11}(OH)_5$ half-units linked by a common O16 atom. Each $B_7O_{11}(OH)_5$ half-unit is composed of four B−O tetrahedra [a $BO_3(OH)$, a $BO_2(OH)_2$, and two BO_4] and three B−O triangles [two $BO_2(OH)$ and a BO_3], which forms three classic B_3O_3 cycles linked by two common BO_4 tetrahedra. According to the classification of polyborate anions proposed by Christ and Clark,[6] the shorthand notation for the $B_{14}O_{21}(OH)_{10}$ cluster is 14:[2(7:3Δ+4T)]. The B−O distances range from 1.350(4) to 1.397(4) Å, and the O−B−O bond angles are 115.1(3)−124.7(3)° for BO_3 triangles. The B−O distances range from 1.445(5) to 1.503(4) Å, and the O−B−O bond angles are 105.0(2)−113.4(3)° for BO_4 tetrahedra. It is worth noting that the SBU here is quite different from that of the known isolated cyclic tetradecaborate $[(C_4H_{15}N_3)]_2[B_{14}O_{20}(OH)_6]$.[16] The $B_{14}O_{21}(OH)_{10}{}^{10-}$ clusters are further connected via O8 atoms, forming a novel 1D chain structure along the c axis (Figure 1b).

In the structure of **1**, K and Ba atoms are located in the channels formed via the hydrogen-bonding interactions between the B−O chains (Figure 1c). K atoms occupy four different crystallographic sites, which are all coordinated with eight O atoms with distances of 2.615(3)−3.297(3) Å. Two distinct Ba atoms are all bonded to nine O atoms with distances of 2.689(2)−3.059(2) Å. At the same time, there are O−H···O weak hydrogen bonds not only between adjacent B−O chains but also between the B−O chains and H_2O molecules, with O···O from 2.696 to 3.180 Å.

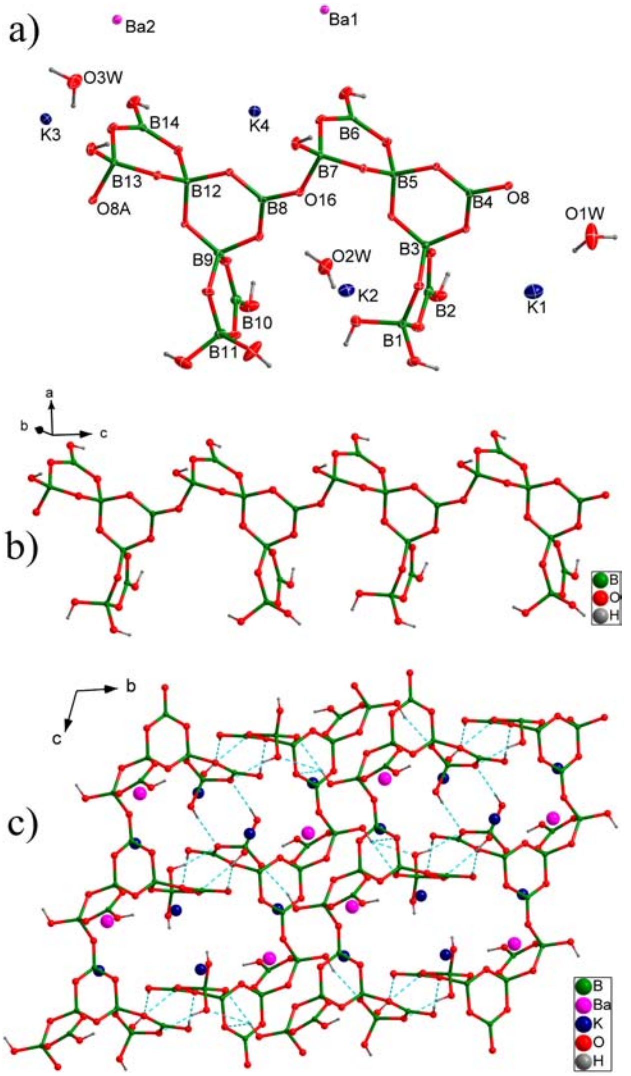

Figure 1. (a) ORTEP plot of the asymmetric unit of **1** (thermal ellipsoids of 50% probability). Symmetry code: A, x, y, $-1 + z$. (b) View of the 1D B−O chain constructed from $[B_{14}O_{21}(OH)_{10}]$ SBUs. (c) View of the packing structure of **1** along the c axis. The water molecules are omitted for clarity.

Structure of 2. **2** crystallizes in triclinic space group $P\bar{1}$ with Z = 2. As shown in Figure 2a, there are two Li atoms, two Sr atoms, and a $B_{10}O_{19}(OH)_3$ cluster in the asymmetric unit. The SBU in **2** is a $B_{10}O_{19}(OH)_3$ cluster that consists of two different $B_5O_{10}(OH)$ and $B_5O_{10}(OH)_2$ units. The $B_5O_{10}(OH)_2$ unit comprises two B−O triangles [$BO_2(OH)$ and BO_3] and three B−O tetrahedra [a $BO_3(OH)$ and two BO_4], whereas the $B_5O_{10}(OH)$ unit is formed by three B−O triangles [a $BO_2(OH)$ and two BO_3] and two BO_4 tetrahedra. The $B_5O_{10}(OH)$ and $B_5O_{10}(OH)_2$ units are linked by an O11 atom to form the $B_{10}O_{19}(OH)_3$ cluster, which can be written as 10:[(2Δ+3T)(3Δ+2T)]. The B−O distances range from 1.349(5) to 1.402(5) Å, and the O−B−O bond angles are 114.0(3)−124.9(4)° for BO_3 triangles. The B−O distances range from 1.433(3) to 1.537(5) Å, and the O−B−O bond angles are

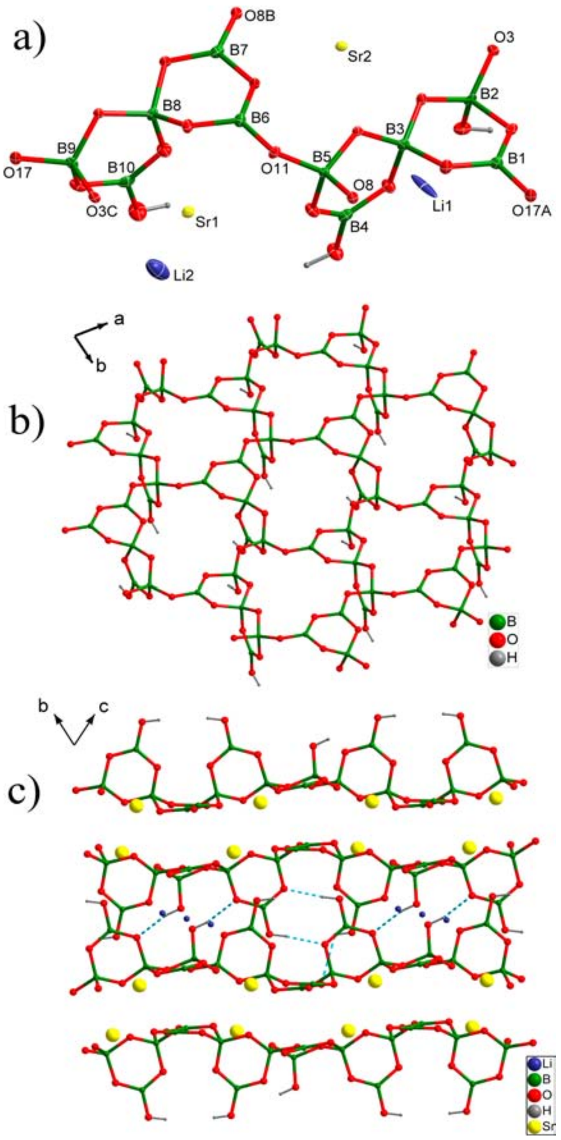

Figure 2. (a) ORTEP plot of the asymmetric unit of **2** (thermal ellipsoids of 50% probability). Symmetry codes: A, 1 + *x*, 1 + *y*, −1 + *z*; B, −1 + *x*, *y*, *z*; C, *x*, −1 + *y*, 1 + *z*. (b) View of the 2D B−O layer constructed from $B_{10}O_{16}(OH)_3$ clusters. (c) View of the packing structure of **2** along the *a* axis.

105.4(3)−115.7(3)° for BO_4 tetrahedra. The $B_{10}O_{19}(OH)_3$ clusters are further connected through O3, O8, and O17 atoms to form a 2D-layered structure with nine-membered-boron-ring windows at the *ab* plane (Figure 2b). Moreover, the adjacent layers are related by 2-fold axes and two kinds of the terminals (hydroxyls) exist in the layers and point out of the layers: the hydroxyls of the $BO_2(OH)$ triangles of each layer point into the same side of the layer with different orientations, while the hydroxyls of the $BO_3(OH)$ tetrahedra of each layer point into the same sides with the same orientations (Figure 2c).

Two unique Sr atoms are located in the cavity surrounded by the nine-membered boron rings within the layer, while two Li atoms are located between two adjacent layers (Figure 2c). The 9- and 10-coordinate Sr−O bond distances vary from 2.570(6) to 2.888(5) Å and from 2.474(5) to 2.964(5) Å, respectively. The 5- and 6-coordinate Li−O bond distances vary from 1.778(6) to 2.537(5) Å and from 2.022(5) to 2.615(5) Å, respectively. There are weak hydrogen bonds between adjacent layers with O···O from 2.739 to 3.047 Å.

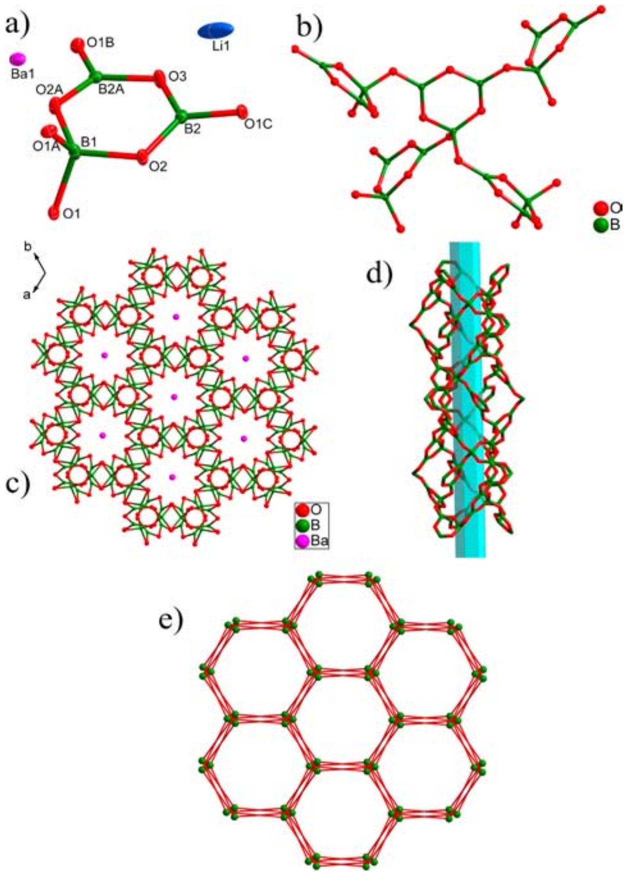

Figure 3. (a) ORTEP plot of the asymmetric unit of **3** (thermal ellipsoids of 50% probability). Symmetry codes: A, $^{2}/_{3} - x$, $^{1}/_{3} - x + y$, $^{11}/_{6} - z$; B, $^{4}/_{3} + x - y$, $^{2}/_{3} + x$, $^{5}/_{3} - z$; C, $-^{2}/_{3} - x + y$, $-^{1}/_{3} + y$, $^{5}/_{3} + z$. (b) View of the linkage of B_3O_7 SBUs. (c) View of the 3D B−O framework made of the B_3O_7 SBUs along the *c* axis. (d) View of the 12-membered-boron-ring channels in **3**. (e) Topological view of the framework **3**.

Structure of 3. **3** crystallizes in hexagonal space group $R\bar{3}c$ with *Z* = 6. There are one Li atom, one Ba atom, two B atoms, and three O atoms in the asymmetric unit (Figure 3a). Of the two B atoms, B1 adopts tetrahedral oxygen coordination (BO_4) with B−O bond lengths varying from 1.460(2) to 1.477(2) Å and O−B−O bond angles from 104.9(1) to 116.1(1)°. B2 adopts triangular oxygen coordination (BO_3) with B−O bond lengths varying from 1.348(3) to 1.349(3) Å and O−B−O bond angles from 117.7(2) to 122.6(2)°. Two BO_3 units and one BO_4 unit link together to form a ring-shaped B_3O_7 SBU, and then each B_3O_7 SBU links the same four adjacent ones through common O atoms (Figure 3b). The alternate connectivity of the B_3O_7 SBUs through their vertices gives rise to a novel 3D B−O framework with 12-membered-boron-ring channels (Figure 3c,d). To better understand the connection mode of the B_3O_7 SBUs, the topology of **3** has been investigated, which can be described as a four-connected net if each B_3O_7 SBU acts as a four-connected node. As shown in Figure 3e, the network has a NbO topology.

The Ba and Li atoms are located in the 12-membered-boron-ring channels. The Ba1 atom is situated in the 6-fold axis and coordinated to 12 O atoms with 6 Ba−O bond lengths of

2.901(1) Å and another length of 3.046(1) Å. The Li1 atom is also situated in the 6-fold axis and coordinated to three O atoms with a Li–O length of 1.882(2) Å.

The bond valence sums (BVSs)[17] of B and metal atoms in three compounds were calculated and are listed in Tables S1–S3 in the Supporting Information (SI). These results agree with the expected oxidation states 3+, 1+, and 2+ for B, Li/K, and Sr/Ba, respectively.

Structure Comparison. Of the three compounds, they have three types of SBUs and display very different structures. In compound **1**, the SBU is $B_{14}O_{21}(OH)_{10}$, in which 10 terminal OH groups prevent further connection of the B–O clusters and two deprotonated O atoms act as bridging atoms (Figure 1a) to link two adjacent SBUs along one direction, forming a 1D chain (Figure 1b). In compound **2**, the $B_{10}O_{19}(OH)_3$ SBU has three terminal OH groups and six deprotonated O atoms that act as the bridging atoms (Figure 2a); thus, each SBU links six other ones along two directions, resulting in a 2D layer (Figure 2b). In **3**, however, there is no hydroxyl in the B_3O_7 SBU (Figure 3a), so each SBU connects four other ones along three directions to form a 3D open framework. Therefore, the numbers of hydroxyls in the SBU play a key role in formation of the different dimensional structures: the more hydroxyls in the SBU, the lower the structural dimension. In addition, three types of SBUs have a common characteristic; i.e., they all consist of a B_3O_3 six-membered ring. From a synthetic point of view, both compounds **1** and **2** were made under the same conditions (170 °C and 5 mL of distilled water). The OH groups exist in the SBUs of compounds **1** and **2** because the solvent is water, which influences the condensation of H_3BO_3. Furthermore, the average radius of the metal atoms (K and Ba) in **1** is large than that (Li and Sr) in **2**; this may be why the polymerization of H_3BO_3 is weakened in **1**. In compound **3**, under a higher temperature (200 °C) and less water (0.5 mL of distilled water and 5 mL of pyridine) as the solvent, no OH group exists in the SBU, thus forming a high polymeric B–O framework. In order to further understand the influence of the solvent and temperature on the syntheses of the three compounds, we use the conditions of **3** to synthesize **1** and **2**, but we failed to make **1** so no crystal was obtained, while for the synthesis of **2**, we only got a reported compound $Li_3[B_5O_8(OH)_2]$[18] with a 3D B–O framework. We also take the conditions of **1** and **2** to make **3** but only obtain a known $Ba_2[B_6O_9(OH)_4]$[19] with a 2D B–O layer. In general, under mild hydro(solvo)thermal conditions, the high temperature and less water will make the H_3BO_3 polymerization degree largely increase. From that mentioned above, these differences indicate that the mild hydrothermal technique is an effective method for making novel borates.

PXRD. The PXRD patterns of as-synthesized samples and the simulated patterns on the basis of single-crystal structures of **1**–**3** have been carried out on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 1.54056 Å). The diffraction peaks corresponded well in positions, indicating the phase purity of the three as-synthesized samples. The difference in the reflection intensities between the simulated and experimental patterns was due to variation in the crystal orientation for the powder samples (Figures S1–S3 in the SI). However, the experimental PXRD pattern of compound **1** shows very weak peak intensities and possible amorphous products and/or a secondary crystalline phase (Figure S1 in the SI). This may simply be due to decomposition following dehydration in air.

IR Spectroscopy. The IR spectra (KBr pellets) of the three compounds were recorded on a Nicolet iS10 FTIR spectrophotometer (Figure S4 in the SI). For **1**, the existence of BO_3 triangles and BO_4 tetrahedra is confirmed by the presence of strong bands in the regions of 1410–1335 and 1030–940 cm^{-1}, respectively. The band near 3440 cm^{-1} is attributed to O–H stretching of H_2O molecules and OH groups. For **2**, the bands in the ranges of 1350–1270 and 1020–920 cm^{-1} are characteristic for BO_3 triangles and BO_4 tetrahedra, respectively. The band at 3340 cm^{-1} is assigned to the O–H stretch. For **3**, the existence of BO_3 triangles and BO_4 tetrahedra is confirmed by the presence of strong bands in the regions of 1440–1320 and 1080–920 cm^{-1}, respectively.

UV Transmittance Spectroscopy. The UV–vis–NIR transmittance spectra of the three compounds in the region of 190–2000 nm are obtained by a Shimadzu UV-3600 spectrophotometer (Figure S5 in the SI). The absorption spectral measurements indicate that from 400 to 2000 nm the transmittance rate of the three compounds is above 80%, but absorption at the NIR region indicates that the H_2O and –OH groups exist in the structures **1** and **2**. In addition, the transmission rate from 400 to 190 nm sharply decreases for the three compounds.

Thermal Stability Analysis. TGA was performed on a Mettler Toledo TGA/DSC 1100 analyzer in a flowing air atmosphere with a heating rate of 10 °C/min from 30 to 800 °C (Figure S6 in the SI). TGA shows that **1** has a two-step weight loss at about 95–650 °C, corresponding to the loss of three H_2O molecules (found, 4.58%; calcd, 4.79%) and dehydration of the hydroxyl groups (found, 7.99%; calcd, 8.36%). For **2**, only a step weight loss at 310 and 600 °C arises from the dehydration process of the –OH groups (found, 4.61%; calcd, 4.52%). For **3**, there is no obvious weight loss in the range of 40–800 °C.

■ CONCLUSION

In summary, three novel alkali-metal and alkaline-earth-metal mixed borates, **1**–**3**, have been synthesized under hydro(solvo)thermal conditions and exhibit chain, layer, and framework structures, respectively. Compound **1** contains the $B_{14}O_{21}(OH)_{10}$ SBUs, which further connect to each other through a common O atom to form a novel 1D chainlike structure. In the structure of **1**, the K and Ba atoms are located in the channels formed by the chains via hydrogen-bonding interactions. To compound **2**, the SBUs are the $B_{10}O_{16}(OH)_3$ clusters, which are further linked together through six common O atoms, forming a 2D-layered structure; the Sr atoms locate in the cavity within the layer, while the Li atoms locate in the channels formed by the adjacent layers via hydrogen-bonding interactions. In compound **3**, the B_3O_7 SBU as the four-connected node links four of the same ones through six vertices and gives rise to a novel 3D framework with 12-membered-boron-ring channels, in which the Li and Ba atoms are located. Notice that more hydroxyls in the SBU of the $B_{14}O_{21}(OH)_{10}$ cluster prevent the SBUs from further extending the 2D or 3D structure in **1**, only forming a 1D chain by one shared vertex. To compound **2**, the fewer hydroxyls and six available bridging oxygen vertices in the SBU of the $B_{10}O_{16}(OH)_3$ cluster result in a 2D network. In the structure of **3**, the B_3O_7 SBU without hydroxyls link four SBUs by its all four bridging oxygen vertices to produce a 3D framework. Therefore, the number of hydroxyls in the SBUs plays a key role in the formation of different dimensional structures: the more hydroxyls in the SBU, the lower the structural dimension. Additionally, in the synthesis of new metal borates, except solid-state synthesis, the mild hydro(solvo)thermal technique is also an effective method. Further work is in progress for making new borate materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystal data in CIF format of **1−3** (ICSD 426108−426110), selected bond distances and BVSs of the compounds, and additional figures of PXRD, IR spectroscopy, TGA, and transmittance spectroscopy. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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