Deep-Ultraviolet Nonlinear Optical Materials: $\text{Na}_2\text{Be}_4\text{B}_4\text{O}_{11}$ and $\text{LiNa}_5\text{Be}_{12}\text{B}_{12}\text{O}_{33}$

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Supporting Information

ABSTRACT: Deep-UV coherent light generated by nonlinear optical (NLO) materials possesses highly important applications in photonic technologies. Beryllium borates comprising anionic planar layers have been shown to be the most promising deep UV NLO materials. Here, two novel NLO beryllium borates $\text{Na}_2\text{Be}_4\text{B}_4\text{O}_{11}$ and $\text{LiNa}_5\text{Be}_{12}\text{B}_{12}\text{O}_{33}$ have been developed through cationic structural engineering. The most closely arranged $[\text{Be}_4\text{BO}_{11}]_{\infty}$ planar layers, connected by the flexible $[\text{B}_2\text{O}_3]_{\infty}$ groups, have been found in their structures. This structural regulation strategy successfully resulted in the largest second harmonic generation (SHG) effects in the layered beryllium borates, which is $\sim$1.3 and 1.4 times that of KDP for $\text{Na}_2\text{Be}_4\text{B}_4\text{O}_{11}$ and $\text{LiNa}_5\text{Be}_{12}\text{B}_{12}\text{O}_{33}$, respectively. The deep-UV optical transmittance spectra based on single crystals indicated their short-wavelength cut-offs are down to $\sim$170 nm. These results demonstrated that $\text{Na}_2\text{Be}_4\text{B}_4\text{O}_{11}$ and $\text{LiNa}_5\text{Be}_{12}\text{B}_{12}\text{O}_{33}$ possess very promising application as deep-UV NLO crystals.

Deep-ultraviolet (deep-UV, $\lambda < 200$ nm) nonlinear optical (NLO) materials have become increasingly important because of their unique ability for deep-UV coherent light generation, which are of interest in laser micromachining, photochemical synthesis, and especially many advanced scientific instruments, e.g., deep-UV photoemission electron microscopy (DUV-PEEM), ultra-high-resolution and angle-resolved photoemission spectrometer (URPES and ARPES, respectively), and so forth.1–5 However, it is difficult to find suitable materials that possess high NLO coefficients, sufficient birefringence, and especially the short absorption edge.6

Beryllium borates have been shown to be one of the most promising deep UV NLO materials as they are supposed to possess very large energy gap.7,8 Up to now, the sole NLO crystal which can practically generate the deep-UV lasers is KBe$_2$BO$_3$F$_2$ (KBBF).9,10 The brilliant NLO properties mainly come from the infinite planar $[\text{Be}_2\text{BO}_3\text{F}_2]_{\infty}$ layers, which can provide relatively large SHG coefficients and sufficient birefringence. However, it is very difficult to grow in thickness because of its strong layering tendency, which severely limits its application. In order to overcome this problem, some well-known NLO crystals $\text{M}_2\text{Be}_2\text{B}_2\text{O}_7$ ($\text{M} = \text{Sr}, \text{Ba}$)11–13 consisting of planar $[\text{Be}_2\text{B}_2\text{O}_6]_{\infty}$ network have been designed by our group, in which the layers are bridged by O atoms bound to Be atoms. Nevertheless, the high-quality crystals and the fine structures of $\text{M}_2\text{Be}_2\text{B}_2\text{O}_7$ have not been obtained yet because of their structural polymorphism problem. Recently, new progress has been made in the layered beryllium borates. A novel planar layer $[\text{Be}_2\text{BO}_3\text{O}_2]_{\infty}$, similar with $[\text{Be}_2\text{BO}_2\text{F}_2]_{\infty}$ in KBBF, was found in $\gamma$-$\text{KBe}_2\text{B}_3\text{O}_7$,14 $\text{Na}_2\text{CsBe}_6\text{B}_5\text{O}_{15}$15 etc., in which the $[\text{Be}_2\text{BO}_3]_{\infty}$ layers are bridged via planar $[\text{B}_4\text{O}_6]_{\infty}$ and planar $[\text{BO}_3]_{\infty}$ groups, respectively. The strong connections provided by the covalent bonds between layers may alleviate layering growth habit that hindered the applications of KBBF crystal. Moreover, the findings facilitate feasible designing of new deep-UV NLO crystals by connecting the planar layers with various boron–oxygen anionic groups. To maximize the NLO effects and construct the most compact structure in the layered beryllium borates, an effective strategy is reducing the interlayer spacing to increase the density of the NLO active structural units. For that purpose, the smallest boron–oxygen unit $[\text{BO}_4]$ perpendicular to the layer in $\text{Na}_2\text{CsBe}_6\text{B}_5\text{O}_{15}$ must be further twisted. Then, $[\text{B}_2\text{O}_3]_{\infty}$ group, a flexible unit suitable for structural design was taken into consideration. Compared with the rigid $[\text{BO}_4]$ and $[\text{B}_3\text{O}_5]$ groups, the $[\text{B}_2\text{O}_3]_{\infty}$ groups are more flexible as the two constitute $[\text{BO}_4]$ groups are easier to bend and rotate around their O atom junction. By introducing of lighter cations to accompany with the flexible interlayer groups, the NLO properties and UV transparency of the layered beryllium borates could be improved simultaneously, as we have demonstrated in $\text{NaSr}_2\text{Be}_2\text{B}_2\text{O}_7 \cdot \text{F}_4$16 and $\text{MM'}\text{Be}_2\text{B}_2\text{O}_7\cdot \text{F}$ series.17

Here, the designing for largest NLO effects in the layer beryllium borates was realized. Through the introduction of small Na$^+$ cation and Na$^+$, Li$^+$ mixed cations, two novel NLO beryllium borates $\text{Na}_2\text{Be}_2\text{B}_2\text{O}_7$ and $\text{LiNa}_2\text{Be}_2\text{B}_2\text{O}_7$ were successfully developed. In their structures, the linkage of distorted $[\text{B}_2\text{O}_3]_{\infty}$ groups between layers results in a much narrower spacing $5.97$ Å in $\text{Na}_2\text{Be}_2\text{B}_2\text{O}_7$ and $5.94$ Å in $\text{LiNa}_2\text{Be}_2\text{B}_2\text{O}_7$, respectively. The deep-UV optical transmittance spectra based on single crystals indicated their short-wavelength cut-offs are down to $\sim$170 nm. These results demonstrated that $\text{Na}_2\text{Be}_2\text{B}_2\text{O}_7$ and $\text{LiNa}_2\text{Be}_2\text{B}_2\text{O}_7$ possess very promising application as deep-UV NLO crystals.

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edges of \( \text{Na}_2\text{Be}_6\text{B}_5\text{O}_{15} \) and \( \text{LiNa}_5\text{Be}_{12}\text{B}_{12}\text{O}_{33} \) indicated that they could be used as deep UV NLO materials.

Due to the high toxicity of the BeO powders, all the experiments were performed under sufficient ventilation. Single crystals of \( \text{Na}_2\text{Be}_6\text{B}_5\text{O}_{15} \) and \( \text{LiNa}_5\text{Be}_{12}\text{B}_{12}\text{O}_{33} \) were grown from a high-temperature solution by spontaneous crystallization (Figures S1–2). The growth systems were \( \text{Na}_2\text{CO}_3/\text{BeO}/\text{B}_2\text{O}_3 \) and \( \text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3/\text{BeO}/\text{B}_2\text{O}_3 \) with molar ratios 2:1:2 and 0.5:1:5:1:2, respectively. The powder XRD patterns of ground crystals for \( \text{Na}_2\text{Be}_6\text{B}_5\text{O}_{15} \) (Figure S3) and \( \text{LiNa}_5\text{Be}_{12}\text{B}_{12}\text{O}_{33} \) (Figure S4) exhibit good agreement with the calculated XRD patterns.

\( \text{Na}_2\text{Be}_6\text{B}_5\text{O}_{15} \) and \( \text{LiNa}_5\text{Be}_{12}\text{B}_{12}\text{O}_{33} \) all crystallize in the noncentrosymmetric structures with chiral space groups \( P1 \) and \( Pc \), respectively. They possess similar crystal structures as illustrated in Figure 1a,b. The 2D beryllium borate \( [\text{Be}_2\text{BO}_3]_{\infty} \) layers along \( a-c \) plane, constructed by \( [\text{BO}_3] \) and \( [\text{BO}_4] \) groups with ratio 1:2, were found in their structures, as shown in Figure 1c. The adjacent \( [\text{Be}_2\text{BO}_3]_{\infty} \) layers are further bridged together through distorted \( [\text{BO}_3] \) groups by sharing O atoms (2-fold coordinated) to build a framework with tunnels running along the \( b \)-axis (Figure 1d).

Similarly, in KBBF, \( \beta-\text{KBe}_2\text{B}_3\text{O}_{7} \), \( \gamma-\text{KBe}_2\text{B}_3\text{O}_{7} \) and \( \text{Na}_2\text{CsBe}_6\text{B}_5\text{O}_{15} \), the 2D beryllium borate \( [\text{Be}_2\text{BO}_3]_{\infty} \) or \( [\text{Be}_2\text{BO}_3\text{F}_2]_{\infty} \) layers are also the fundamental building components. However, it is important to note the connections between the adjacent \( [\text{Be}_2\text{BO}_3]_{\infty} \) or \( [\text{Be}_2\text{BO}_3\text{F}_2]_{\infty} \) layers are very different in these beryllium borates. In structure of KBBF, the adjacent \( [\text{Be}_2\text{BO}_3\text{F}_2]_{\infty} \) layers are held together via ionic bond of \( K \) and \( F \) atoms, while the neighboring \( [\text{Be}_2\text{BO}_3]_{\infty} \) layers are bridged by basic boron–oxygen groups in other structures, for instance, by \( [\text{BO}_3] \) group in \( \gamma-\text{KBe}_2\text{B}_3\text{O}_{7} \) and by \( \text{BO}_3 \) group in \( \text{Na}_2\text{CsBe}_6\text{B}_5\text{O}_{15} \). Since the NLO-active planar layers \( [\text{Be}_2\text{BO}_3\text{F}/\text{O}]_{\infty} \) are almost the same in these beryllium borates, the density of layers has been the critical factor to determine the macro SHG effects. The interlayer spacing can be controlled by diverse connections. In KBBF, the ionic bond between nonbonding \( [\text{Be}_2\text{BO}_3\text{F}]_{\infty} \) layers results in a relatively small interlayer spacing of 6.25 Å. When \( [\text{BO}_3] \) group with height 4.11 Å was incorporated in to the \( [\text{Be}_2\text{BO}_3]_{\infty} \) interlayers as a connecting unit, a large spacing 8.7 Å has been formed in \( \gamma-\text{KBe}_2\text{B}_3\text{O}_{7} \) (Figure 2b). Instead, the linkage by \( [\text{BO}_3] \) group with height 1.98 Å shrinks the distance to 6.23 Å, which is smaller than that in KBBF, as shown in Na2CsBe2B3O15 in Figure 2c.

In view of small cation may result in a more compact layered structure, new beryllium borates comprising \( [\text{Be}_2\text{BO}_3\text{F}_2]_{\infty} \) layers connected by ideal units i.e. \( [\text{BO}_3] \) groups, may be obtained via using the cation with small size. Through the utilization of \( \text{Na}^+ \) as single cation, we successfully developed the qualified beryllium borate \( \text{Na}_2\text{Be}_6\text{B}_5\text{O}_{15} \), which also possesses a \( [\text{Be}_2\text{BO}_3]_{\infty} \) planar layer in its structure. To accompany the smaller \( \text{Na} \) cations, the \( [\text{BO}_3] \) groups between the \( [\text{Be}_2\text{BO}_3]_{\infty} \) layers have been largely bended and distorted, with an reduced average height of only 1.72 Å along the piling direction of \( [\text{Be}_2\text{BO}_3]_{\infty} \) layers, which successfully lead to a much narrower spacing of 5.97 Å in \( \text{Na}_2\text{Be}_6\text{B}_5\text{O}_{15} \) than 6.23 Å in \( \text{Na}_2\text{CsBe}_6\text{B}_5\text{O}_{15} \). This implies the density of anionic layers can truly be regulated by adjusting the cations. In order to further decrease lattice spacing to maximize the NLO effects, the smallest alkali metal Li+ ion was introduced. It is found that although no new phase with similar configuration has been found when using single Li+ ion as cation, a new beryllium borate \( \text{LiNa}_5\text{Be}_{12}\text{B}_{12}\text{O}_{33} \), with the same \( [\text{Be}_2\text{BO}_3]_{\infty} \) planar layers, was obtained. Because of the introduction of Li+ ion, the flexible \( [\text{BO}_3] \) group was further distorted. In \( \text{LiNa}_5\text{Be}_{12}\text{B}_{12}\text{O}_{33} \), the average height of \( [\text{BO}_3] \) group was 1.69 Å, and consequently the layer spacing was successfully reduced to 5.94 Å. That is, the minimum of the layer spacing has been reached.

The correlation between \( [\text{BO}_3] \) groups and cations has also been analyzed. As layer connectors, the size of \( B-O \) anionic groups and the distance between the two adjacent \( \text{Be}−\text{O} \) bonds on one side of the layer should be matched. As the distance between \( \text{Be}13 \) and \( \text{Be}21 \) is 4.33 Å, it requires that the \( B \) cation to one side of the layer should be matched. As the distance
0.1 mm 3 were recorded at room temperature using a quali
Na2Be4B4O11 and LiNa5Be12B12O33 crystals with size 2.5
K3B6O10Cl (180 nm), 18 and NaCaBe2B2O6F (190 nm), 17
determined yet.14,15 Here, we give the
NaSr3Be3B3O9F4 (170 nm) 16 and shorter than those of
of this kind in the deep-UV region. As shown in Figure 4a, the
UV short-wavelength absorption edges of Na2Be4B4O11 and
LiNaBe12B12O33 are located at 171 and 169 nm, respectively, and the transmittance percent of LiNaBe12B12O33 is above 70% from 180 nm. These UV cutoff edges are comparable to that of NaSrBe2B3O12Cl (170 nm)16 and shorter than those of K3B6O10Cl (180 nm)18 and NaCaBe2B2O6F (190 nm),17 which are potential deep-UV NLO materials newly found. The short cutoff edges of Na2Be4B4O11 and LiNaBe12B12O33 indicate their promising prospects for applications in deep-UV range as NLO materials.

Figure 3. Correlation between [B2O5] groups and cations. (a) The distorted [B2O5] group. (b) [Be2BO5] layer that shows the direction and arrangement of B−O bond. (c) The caves between [Be2BO5] layer with the filling of Na+ cations in Na2Be4B4O11. F and B represent front and back, respectively.

Figure 4. (a) Transmittance spectra and (b) SHG measurements of Na2Be4B4O11 and LiNa3Be12B12O33 crystals.
no volatile component, e.g., K, Rb, Cs, it will facilitate the crystal growth for large size, which is on the way.

In summary, the new alkaline beryllium borates Na$_2$Be$_4$B$_4$O$_{11}$ and LiNa$_5$Be$_{12}$B$_{12}$O$_{33}$, respectively. The deep-UV optical transmittance spectra of single crystals indicated their short wavelength cut-offs are located at $\sim$170 nm, which is the first accurate result in the [Be$_2$BO$_3$O$_2$]$_{\infty}$ layered material family. These results demonstrated that Na$_5$Be$_{12}$B$_{12}$O$_{33}$ possesses very promising application as deep-UV NLO crystals. In addition, this work also provides insights into structural design and exploration of new NLO crystals, especially in the deep-UV spectral region.

**ASSOCIATED CONTENT**

§ Supporting Information

XRD patterns, DSC traces, photos of as-grown crystals, high-quality structure figures and crystal data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

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