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Deep-Ultraviolet Nonlinear Optical Materials: $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$

Hongwei Huang,*[†] Lijuan Liu,[‡] Shifeng Jin,*[§] Wenjiao Yao,[‡] Yihe Zhang,[†] and Chuangtian Chen*[‡]

[†]School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China

[‡]Center for Crystal Research and Development and Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[§]Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

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 $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$ have been developed through cationic structural engineering. The most closely arranged $[Be_2BO_5]_\infty$ planar layers, connected by the flexible $[B_2O_5]$ 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 ~1.3 and 1.4 times that of KDP for $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$, respectively. The deep-UV optical transmittance spectra based on single crystals indicated their short-wavelength cut-offs are down to ~170 nm. These results demonstrated that $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$ 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), ultrahigh-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 $KBe_2BO_3F_2$ (KBBF).[1,9,10] The brilliant NLO properties mainly come from the infinite planar $[Be_2BO_3F_2]_\infty$ 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 $M_2Be_2B_2O_7$ (M = Sr, Ba)[11−13] consisting of planar $[Be_3B_3O_6]_\infty$ 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 $M_2Be_2B_2O_7$ 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 $[Be_2BO_3O_2]_\infty$, similar with $[Be_2BO_3F_2]_\infty$ in KBBF, was found in γ-$KBe_2B_3O_7$,[14] $Na_2CsBe_6B_5O_{15}$,[15] etc., in which the $[Be_2BO_5]_\infty$ layers are bridged via planar $[B_3O_6]$ and planar $[BO_3]$ 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 $[BO_3]$ perpendicular to the layer in $Na_2CsBe_6B_5O_{15}$ must be further twisted. Then, $[B_2O_5]$ group, a flexible unit suitable for structural design was taken into consideration. Compared with the rigid $[BO_3]$ and $[B_3O_6]$ groups, the $[B_2O_5]$ groups are more flexible as the two constitute $[BO_3]$ 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 $NaSr_3Be_3B_3O_9F_4$[16] and $MM'Be_2B_2O_6F$ sieries.[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 $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$ were successfully developed. In their structures, the linkage of distorted $[B_2O_5]$ groups between layers results in a much narrower spacing 5.97 Å in $Na_2Be_4B_4O_{11}$ and 5.94 Å in $LiNa_5Be_{12}B_{12}O_{33}$, and consequently, giving rise to the largest NLO effects in the layer beryllium borates. The short UV cutoff

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edges of $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$ 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 $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$ were grown from a high-temperature solution by spontaneous crystallization (Figures S1−2). The growth systems were $Na_2CO_3/BeO/B_2O_3$ and $Li_2CO_3/Na_2CO_3/BeO/B_2O_3$ with molar ratios 2:1:2 and 0.5:1.5:1:2, respectively. The powder XRD patterns of ground crystals for $Na_2Be_4B_4O_{11}$ (Figure S3) and $LiNa_5Be_{12}B_{12}O_{33}$ (Figure S4) exhibit good agreement with the calculated XRD patterns.

$Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$ 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 $[Be_2BO_5]_\infty$ layers along *a*−*c* plane, constructed by $[BO_3]$ and $[BO_4]$ groups with ratio 1:2, were found in their structures, as shown in Figure 1c. The adjacent $[Be_2BO_5]_\infty$ layers are further bridged together through distorted $[B_2O_5]$ groups by sharing O atoms (2-fold coordinated) to build a framework with tunnels running along the *b*-axis (Figure 1d).

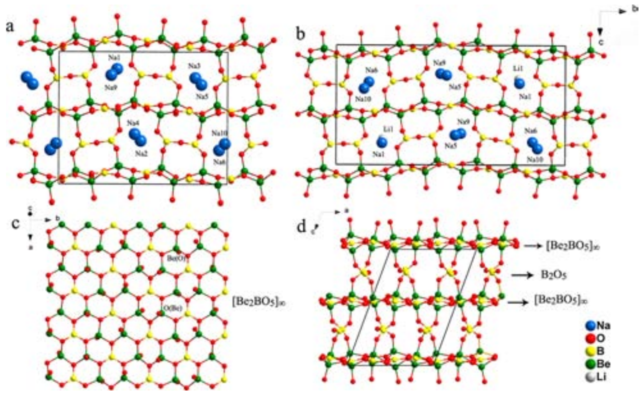

Figure 1. Crystal structures of $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$. Unit cells of (a) $Na_2Be_4B_4O_{11}$ and (b) $LiNa_5Be_{12}B_{12}O_{33}$ along *b*−*c* plane. (c) The 2D infinite planar $[Be_2BO_5]_\infty$ layer. (d) The $[Be_2BO_5]_\infty$ layers connected by B_2O_5 groups along *a*−*c* plane.

Similarly, in KBBF, *β*-$KBe_2B_3O_7$, *γ*-$KBe_2B_3O_7$ and $Na_2CsBe_6B_5O_{15}$, the 2D beryllium borate $[Be_2BO_3O_2]_\infty$ or $[Be_2BO_3F_2]_\infty$ layers are also the fundamental building components. However, it is important to note the connections between the adjacent $[Be_2BO_3O_2]_\infty$ or $[Be_2BO_3F_2]_\infty$ layers are very different in these beryllium borates. In structure of KBBF, the adjacent $[Be_2BO_3F_2]_\infty$ layers are held together via ionic bond of K and F atoms, while the neighboring $[Be_2BO_3O_2]_\infty$ layers are bridged by basic boron−oxygen groups in other structures, for instance, by $[B_3O_6]$ group in *γ*-$KBe_2B_3O_7$ and by BO_3 group in $Na_2CsBe_6B_5O_{15}$. Since the NLO-active planar layers $[Be_2BO_3F/O_2]_\infty$ 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 $[Be_2BO_3F_2]_\infty$ layers results in a relatively small interlayer spacing of 6.25 Å. When $[B_3O_6]$ group with height 4.11 Å was incorperated in to the $[Be_2BO_3O_2]_\infty$ interlayers as a connecting unit, a large spacing 8.7 Å has been formed in *γ*-$KBe_2B_3O_7$ (Figure 2b). Instead, the linkage by $[BO_3]$ group with height 1.98 Å shrinks the distance to 6.23 Å, which is smaller than that in KBBF, as shown in $Na_2CsBe_6B_5O_{15}$ in Figure 2c.

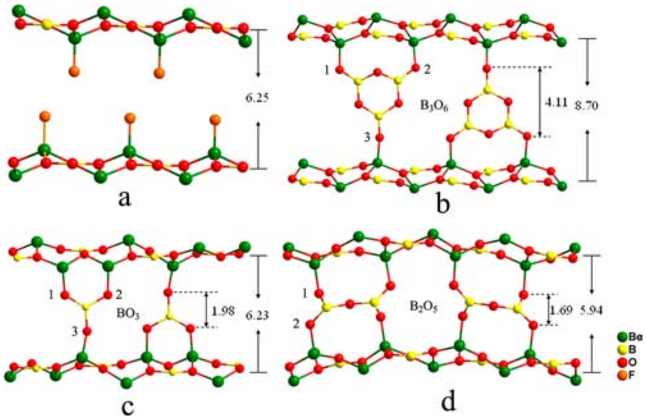

Figure 2. Comparison of connecting units between $[Be_2BO_3O_2]_\infty$ or $[Be_2BO_3F_2]_\infty$ layers. (a) The adjacent $[Be_2BO_3F_2]_\infty$ layers held together via ionic forces of K and F atoms in structure of KBBF. (b) $[B_3O_6]$ group as the connecting unit between $[Be_2BO_3O_2]_\infty$ in *γ*-$KBe_2B_3O_7$. (c) $[BO_3]$ group as the connecting unit between $[Be_2BO_5]_\infty$ in $Na_2CsBe_6B_5O_{15}$. (d) $[B_2O_5]$ group as the connecting unit between $[Be_2BO_5]_\infty$ in $LiNa_5Be_{12}B_{12}O_{33}$.

In view of small cation may result in a more compact layered structure,[8] new beryllium borates comprising $[Be_2BO_3F_2]_\infty$ layers connected by ideal units i.g. $[B_2O_5]$ groups, may be obtained via using the cation with small size. Through the utilization of Na^+ as single cation, we successfully developed the qualified beryllium borate $Na_2Be_4B_4O_{11}$, which also possesses a $[Be_2BO_3O_2]_\infty$ planar layer in its structure. To accompany the smaller Na cations, the $[B_2O_5]$ groups between the $[Be_2BO_5]_\infty$ layers have been largely bended and distorted, with an reduced average height of only 1.72 Å along the piling direction of $[Be_2BO_5]_\infty$ layers, which successfully lead to a much narrower spacing of 5.97 Å in $Na_2Be_4B_4O_{11}$ than 6.23 Å in $Na_2CsBe_6B_5O_{15}$. 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 $LiNa_5Be_{12}B_{12}O_{33}$, with the same $[Be_2BO_3O_2]_\infty$ planar layers, was obtained. Because of the introduction of Li^+ ion, the flexible $[B_2O_5]$ group was further distorted. In $LiNa_5Be_{12}B_{12}O_{33}$, the average height of $[B_2O_5]$ 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 $[B_2O_5]$ groups and cations has also been analyzed. As layer connectors, the size of B−O anionic groups and the distance between the two adjacent Be−O bonds on one side of the layer should be matched. As the distance between Be13 and Be21 is 4.33 Å, it requires that the B−O anionic groups possess the similar value. Thus, the more flexible $[B_2O_5]$ group is distorted to accommodate to the rigid $[Be_2BO_3O_2]_\infty$ layers, in which the two $[BO_3]$ groups keep an angle of 76.37°, and the distances between two terminal O atoms are 4.1−4.2 Å, as shown in Figure 3a. Subsequently, the front (F) and back (B) Be−O bonds in $[Be_2BO_5]_\infty$ layers were arranged alternately to allow the bonding to the distorted

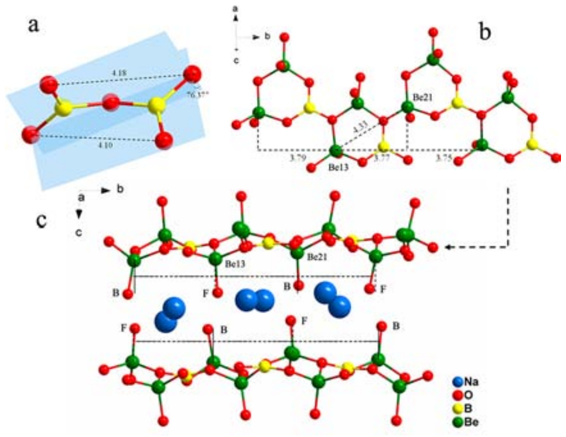

Figure 3. Correlation between $[B_2O_5]$ groups and cations. (a) The distorted $[B_2O_5]$ group. (b) $[Be_2BO_5]_\infty$ layer that shows the direction and arrangement of B−O bond. (c) The caves between $[Be_2BO_5]_\infty$ layer with the filling of Na^+ cations in $Na_2Be_4B_4O_{11}$. F and B represent front and back, respectively.

$[B_2O_5]$ group. In addition, this configuration results in roughly the same size of the caves to accommodate sodium cations, as displayed in Figure 3b,c. That is the reason that cations are single Na^+ or Na^+-Li^+ mixed cation, in which the content of Li^+ could not be very high. In other words, the upper limit of Li we achieved in layered beryllium borates was $LiNa_5Be_{12}B_{12}O_{33}$.

The deep-UV and UV optical transmittance spectra of $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$ crystals with size 2.5 × 2.5 × 0.1 mm^3 were recorded at room temperature using a spectrophotometer (VUVas2000, McPherson) in the wavelength range 120−380 nm. Due to the absence of large and qualified single crystals, the accurate UV cutoff edges of the beryllium borates featuring $[Be_2BO_3O_2]_\infty$ layers have not been determined yet.[14,15] Here, we give the first deep-UV and UV optical transmittance spectrum obtained on large single crystals of this kind in the deep-UV region. As shown in Figure 4a, the UV short-wavelength absorption edges of $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$ are located at 171 and 169 nm, respectively, and the transmittance percent of $LiNa_5Be_{12}B_{12}O_{33}$ is above 70% from 180 nm. These UV cutoff edges are comparable to that of $NaSr_3Be_3B_3O_9F_4$ (170 nm)[16] and shorter than those of $K_3B_6O_{10}Cl$ (180 nm)[18] and $NaCaBe_2B_2O_6F$ (190 nm),[17] which are potential deep-UV NLO materials newly found. The short cutoff edges of $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$ indicate their promising prospects for applications in deep-UV range as NLO materials.

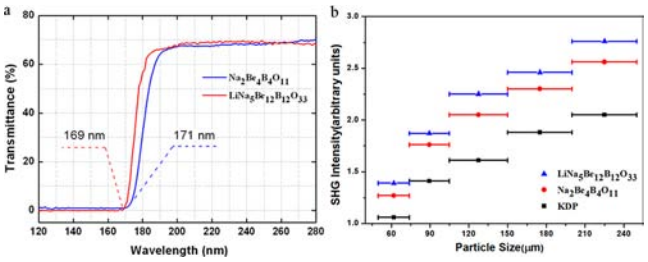

Figure 4. (a) Transmittance spectra and (b) SHG measurements of $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$ crystals.

The SHG response of $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$ was measured by the Kurtz−Perry method[19] using a Q-switched Nd:YAG laser (1064 nm). It was consistent with the phase-matching behavior according to the rule proposed by Kurtz and Perry. The second harmonic signals of $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$ were found to be ∼1.3 and 1.4 times as large as that of KDP standard (Figure 4b). Based on the anionic group theory of NLO activity in borates,[20,21] the BO_3 units are responsible for the large SHG effects. As the two $[BO_3]$ units of the $[B_2O_5]$ group almost arranged in opposite direction, they contribute less to the total NLO contribution. Thus, the $[BO_3]$ groups in the $[Be_2BO_5]_\infty$ planar layer determine the SHG effects of $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$.

The density of $[BO_3]$ groups in $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$ is 0.00994 and 0.010 per $Å^3$, which is about 1.05 and 1.06 times that of KBBF (0.00946), respectively. Since the SHG signal is proportional to the square of the nonlinear d_{eff} coefficient and the nonlinearity of KBBF determined to be 1.12 × d_{36} (KDP), the SHG intensities of $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$ were calculated to be 1.38 and 1.42 times that of KDP, which is in good agreement with the experimental values. Besides, the SHG effects of $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$ are also larger than all other layered beryllium borates, including $NaCaBe_2B_2O_6F$, γ-$KBe_2B_3O_7$, β-$KBe_2B_3O_7$, $RbBe_2B_3O_7$, KBBF, and $Na_2CsBe_6B_5O_{15}$ with SHG effects of 0.3, 0.68, 0.75, 0.79, 1.12, and 1.17 times that of KDP, respectively.[14,15,17] The relationship between SHG intensity and the layer spacing in all these $[Be_2BO_3F/O_2]_\infty$ contained beryllium borates is shown in Figure S5. It can be seen that the maximized NLO effect has been achieved in $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$ through cationic structural design, in which the flexible $[B_2O_5]$ groups used as a connection construct the compact crystal structure.

Aside from the already mentioned layered beryllium borates, another kind of beryllium borates of current interest is those consisting of big rings. Some recent progress in this field includes the synthesis of $M_3Be_2B_5O_{12}(OH)$ (M = Sr, Ba)[22] and $NaSr_3Be_3B_3O_9F$,[16] whose structural units are $[Be_3B_3O_{12}(OH)]$ and $[Be_2B_4O_{12}F]$ 12-membered rings built by three hexatomic rings, respectively. Similar ring-structure was also found in a halogen borate $K_3B_6O_{10}Cl$,[18] in which the 12-membered rings are $[B_6O_{13}]$ groups. However, the major problem for those materials is that the BO_3 groups in these big rings keep relatively large angles with each other (>25°), so that they could not afford sufficient birefringence to achieve the phase matching below 200 nm. Similarly, the big layer spacing for many reported layered beryllium borates is also unfavorable for large birefringence. As revealed in $CsBe_2BO_3F_2$(CBBF),[23,24] a new UV NLO material belonging to KBBF family, the larger layer spacing compared with KBBF results in decreased birefringence, and thus the shortest wavelength it achieved is only 201 nm. In comparsion with the previous reported KBBF analogue beryllium borates, $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$ feature the significantly reduced layer spacing and the presence of lighter cations, so that the high NLO coefficients, short absorption edge, and especially the large birefringence could be simultaneously improved.

In addition, the differential scanning calorimetry (DSC) curves of $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$ exhibit only one endothermic peak starting on the heating curves at 910 and 890 °C, respectively (Figures S6 and S7). The XRD patterns of melted residues reveal that they decompose into BeO, which indicates the compounds melt incongruently. Therefore, large crystals of $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$ must be grown at lower temperature by flux methods. As the flux systems contain 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 $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$ with $[Be_2BO_5]_\infty$ layers have been developed through cationic structural engineering. The introduction of Na^+ cation and Na^+, Li^+ as mixed cation successfully constructs the most compact layered structures in $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$, in which the flexible $[B_2O_5]$ groups act as novel connecting units between layers. This structural design strategy successfully resulted in the largest SHG effects in the layered beryllium borates, which is ∼1.3 and 1.4 times that of KDP for $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$, respectively. The deep-UV optical transmittance spectra of single crystals indicated their short wavelength cut-offs are located at ∼170 nm, which is the first accurate result in the $[Be_2BO_3O_2]_\infty$ layered material family. These results demonstrated that $Na_2Be_4B_4O_{11}$ and $LiNa_5Be_{12}B_{12}O_{33}$ possess 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.

■ AUTHOR INFORMATION

Corresponding Authors

hhw@cugb.edu.cn
shifengjin@iphy.ac.cn
cct@mail.ipc.ac.cn

Notes

The authors declare no competing financial interest.

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