1. Introduction

With the development of laser micromachining, laser communication, and modern scientific instruments, the requirement for NLO crystals is growing rapidly. So far, commercialized optical crystals such as β-BaB₂O₄ (BBO), LiB₃O₅ (LBO) and CsLiB₆O₁₀ (CLBO) have been used for these applications, and potential candidates such as PbₓOₓClₓ (POC), Ba₃Ga₈Sb₂S₃, Ba₄B₁₁O₂₀F (BBOF), and K₃B₆O₁₀Cl (KBOC) are emerging, but it is still challenging to get “wanted” NLO materials with conditions satisfying a “large SHG response”, “laser damage threshold”, and “short UV cut-off”. According to anionic group theory, the main non-linearity of a crystal is the geometrical superposition of the microscopic second-order susceptibility of the constituent NLO-active anionic groups. Some well-known NLO-active anion groups, such as BO₃, CO₃, and NO₃ triangles with π-conjugation configurations, MO₆ octahedra (M = Mo⁶⁺, W⁶⁺, Nb⁵⁺, and V⁵⁺) with d⁰ transition metal ions, and TO₆ distorted polyhedra (T = Pb²⁺, Bi³⁺) with active lone pairs have been explored as feasible NLO candidates. A crystal containing one or more NLO active groups may possess a stronger NLO effect, typical examples are Pb₂B₅O₁₄I with 13.5 × KDP and Pb₂(BO₃)(NO₃) with 9 × KDP. However, the BO₃ group, possessing both wide transparency and large SHG effects, is still one of the best structural units for deep-UV NLO materials.

Ge/Si-containing alkaline, alkaline earth and rare earth metal borates are representative because of the rich structures involved in combining groups of Ge/Si–O tetrahedra and B–O groups, and such borates have fascinated many material scientists to study their optical properties due to their promising uses in optical equipment. Studies show that Ge/Si-containing borate crystals have the properties of deep-UV cut-off edges. Up to now, a series of Ge/Si-containing borates have been synthesized, such as Cs₂GeB₄O₉, Cs₂B₂SiO₅, and LaBGeO₅, which all have potential for application in deep-UV second-order nonlinear-optical crystalline materials based on their moderate SHG responses and short cut-off edges under 200 nm. In addition to this, various frameworks built of B–O and R–O (R = Si, Ge) are potent factors to obtain excellent materials. Some investigators reported that the molar ratio of B/R can affect the structural type of such composite borates. In B-rich R-containing borates where B/R > 1, the basic B–O units tend to condense into rings and then connect with RO₄, such as in Rb₂GeB₄O₉ with a B/Ge ratio of 3/1 and Rb₂GeB₄O₉ with a B/Ge ratio of 4/1, in which the B₂O₇ or B₂O₈ BBUs combined with GeO₄ by sharing the vertices of oxygen atoms to form a B–Ge–O connection mode. BO₄ and RO₄ structural motifs are found in low polymer borosilicate LaBRO₅ with a B/Si ratio

As potential candidates for deep-UV nonlinear optical (NLO) crystals, borosilicates and borogermanates, which contain NLO-active groups such as B–O, Si–O and Ge–O, have fascinated many scientists. The crystal structures, electronic structures and optical properties of seven borates in different B/R (R = Si, Ge) ratios have been studied using DFT methods. Through the SHG-density, we find that besides the recognized contribution of the π-conjugation configuration of BO₃ to second harmonic generation (SHG), the tetrahedra have a non-negligible influence. This is because the non-bonding p orbitals of the bridging oxygen in the tetrahedra are observably closer to the Fermi level than those in BO₃, which is observed in the PDOS of RbGeB₄O₉ and RbGeB₄O₉. This conclusion would be very meaningful in the understanding of the relationship between the crystal structure and nonlinear optical properties.

Active performance of tetrahedral groups to SHG response: theoretical interpretations of Ge/Si-containing borate crystals†

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As potential candidates for deep-UV nonlinear optical (NLO) crystals, borosilicates and borogermanates, which contain NLO-active groups such as B–O, Si–O and Ge–O, have fascinated many scientists. The crystal structures, electronic structures and optical properties of seven borates in different B/R (R = Si, Ge) ratios have been studied using DFT methods. Through the SHG-density, we find that besides the recognized contribution of the π-conjugation configuration of BO₃ to second harmonic generation (SHG), the tetrahedra have a non-negligible influence. This is because the non-bonding p orbitals of the bridging oxygen in the tetrahedra are observably closer to the Fermi level than those in BO₃, which is observed in the PDOS of RbGeB₄O₉ and RbGeB₄O₉. This conclusion would be very meaningful in the understanding of the relationship between the crystal structure and nonlinear optical properties.
of 1, and they form B–O–R six-membered rings which are formed by sharing the vertices of oxygen atoms. Meanwhile, in the R-rich case, the basic R–O units are in a chain instead of a ring, and the neighbouring R–O chains or clusters share terminal O atoms with BO₄ groups and cations to form the 3D framework, typical examples of this are Li₄B₄Si₈O₂₄, and KBGe₂O₆. Recently, only tetrahedral basic building unit (BBU) containing materials, such as BPO₄, LiBGeO₄ and Ba₃P₃O₁₀X (X = Cl, Br), have been reported to have considerable SHG.¹²,³⁵ implying that tetrahedral materials could also have a SHG response comparable with that of compounds that contain BO₄ groups. It is well known that tetrahedral structures possess shorter UV cut-off edges than BO₃, such as the cut-off edges of BPO₄ and LaGeO₃, which are below 134 nm and 193 nm, respectively. These characteristics make this kind of material a potential NLO material for deep-UV wavelengths. Furthermore, the relations between the B–R ratio and the crystal structures, electronic properties, energy bands, and especially the optical properties are studied systematically. The SHG-density method is used to characterise the SHG response of the electrons in compounds and atoms. The results show that RO₄ and BO₄ also take important roles in the SHG effect in compounds containing BO₄, particularly the oxygen between tetrahedra. This is because the non-bonding π orbitals of the bridging oxygens in the tetraheda are closer to the Fermi level than the conjugated π orbital in BO₄, which was observed from analyzing the PDOS.

2. Computational conditions

and theories

2.1. Electronic structures and linear optical properties

The electronic and band structures of Rb₂GeB₄O₉, RbGeB₂O₅, Rb₂Ge₂B₄O₇, LaB₃O₆, LaGeO₃, and KB₃Ge₃O₇ are studied. The relationship between the B–R ratio and the crystal structures, electronic properties, energy bands, and especially the optical properties are studied systematically. The SHG-density method is used to characterise the SHG response of the electrons in compounds and atoms. The results show that RO₄ and BO₄ also take important roles in the SHG effect in compounds containing BO₄, particularly the oxygen between tetrahedra. This is because the non-bonding π orbitals of the bridging oxygens in the tetrahedra are closer to the Fermi level than the conjugated π orbital in BO₄, which was observed from analyzing the PDOS.

2.2. Methods for calculating non-linear optical properties

At a zero frequency limit, the SHG coefficients are calculated using the so-called length-gauge formalism derived by Aversa and Sipe.⁴⁵ The static second order susceptibilities (Z) can be written as,⁴

\[ Z^{(2)}_{\text{ph}} = Z^{(2)}_{\text{ph}}(\text{VE}) + Z^{(2)}_{\text{ph}}(\text{VH}), \]

Virtual-electrons (VEs) can be ascribed as,

\[ Z^{(2)}_{\text{ph}}(\text{VE}) = \frac{e^3}{2\hbar m^2} \sum_{\nu \nu'} \int \frac{d^3k}{4\pi} P(\nu|\nu') \text{Im} \left[ P^o_{\nu''} P^o_{\nu'} P^o_{\nu''} \right] \]

\[ \times \left( \frac{1}{4\omega_{\nu''}\omega_{\nu'}} + \frac{2}{4\omega_{\nu''}\omega_{\nu'}^2} \right). \]

Virtual-holes (VHs) can be ascribed as,

\[ Z^{(2)}_{\text{ph}}(\text{VH}) = \frac{e^3}{2\hbar m^2} \sum_{\nu \nu'} \int \frac{d^3k}{4\pi} P(\nu|\nu') \text{Im} \left[ P^o_{\nu''} F^o_{\nu'} P^o_{\nu''} \right] \]

\[ \times \left( \frac{1}{4\omega_{\nu''}\omega_{\nu'}} + \frac{2}{4\omega_{\nu''}\omega_{\nu'}^2} \right). \]

where \( \alpha, \beta, \) and \( \gamma \) are Cartesian components, \( \nu \) and \( \nu' \) denote valence bands, \( c \) and \( c' \) refer to conduction bands, and \( P(\nu|\nu') \) denotes full permutation. The band energy difference and momentum matrix elements are denoted as \( h_{\nu\nu'} \) and \( P^o_{\nu''} \), respectively. The two-band process was proved to be exactly zero which can be neglected in earlier work.⁴⁶

The band-resolved method⁴⁷,⁴⁸ is used. By using this method, the effective values of individual electronic states in the SHG coefficients can be divided into occupied and unoccupied bands, and the orbital contributions of total \( Z^{(2)} \) can be calculated. Furthermore, the integral SHG contribution of the corresponding energy region and the contribution of the valence bands and conduction bands can be obtained. The SHG-density method⁴⁹ is
performed using the effective SHG of each band (occupied and unoccupied) as the weighting coefficient (after being normalized with the total VE or VH \( \gamma^3 \) value) by summing together all of the probability densities of the occupied or unoccupied states. The SHG density can hence ensure that the quantum states irrelevant to SHG will not be shown in the occupied or unoccupied SHG-density, and the resulting distribution of such density highlights the origin of SHG.

3. Anionic group frameworks with different B/R ratios

The B–R connection patterns of KBGe\(_2\)O\(_6\) (ICSD281258), Li\(_4\)B\(_4\)Si\(_8\)O\(_{24}\) (ICSD90849), LaBRO\(_3\) (ICSD83397, ICSD39262), RbGeB\(_3\)O\(_7\) (ICSD261334), RbGeB\(_3\)O\(_7\) (ICSD261332), and Rb\(_2\)GeB\(_4\)O\(_9\) (ICSD261333) are shown in Fig. 1. It is obvious that the BBUs of the B-rich structures Rb\(_4\)Ge\(_3\)B\(_6\)O\(_{17}\), RbGeB\(_3\)O\(_7\) and Rb\(_2\)GeB\(_4\)O\(_9\) are BO\(_3\), BO\(_4\) and RO\(_4\), and B–O forms B\(_3\)O\(_8\), B\(_3\)O\(_7\) and B\(_4\)O\(_9\) rings, respectively. The B–O rings and RO\(_4\) are interlinked through sharing the vertices of oxygen atoms to form the B–O–R frameworks. In the R-rich case with a B/R ratio of 1/2, the BBUs of KBGe\(_2\)O\(_6\) and Li\(_4\)B\(_4\)Si\(_8\)O\(_{24}\) are BO\(_4\) and RO\(_4\), no BO\(_3\) exists. Although the two compounds have the same B/R ratio, their R–O patterns are different. For KBGe\(_2\)O\(_6\), the [Ge\(_2\)O\(_7\)]\(^-\) dimers formed by the condensation of [GeO\(_4\)]\(^2-\) units are linked by the topmost O atoms to form a chain along the \( a \) axis. While there are eight different possible coordination surroundings, the Si–O groups form four diverse [SiO\(_3\)]\(^-\) chains along the \( a \) axis in Li\(_4\)B\(_2\)Si\(_3\)O\(_{24}\), as described in Fig. S1 (ESI†). The neighbouring chains in the R-rich KBGe\(_2\)O\(_6\) and Li\(_4\)B\(_2\)Si\(_3\)O\(_{24}\) compounds are all connected by BO\(_4\) groups through sharing vertical oxygens to form frameworks of anionic groups. The difference in BBUs results in diverse symmetries of these two compounds, these are orthorhombic \( P2_12_12_1 \) for KBGe\(_2\)O\(_6\) and monoclinic \( P2_1 \) for Li\(_4\)B\(_2\)Si\(_3\)O\(_{24}\). This may be due to the larger radius of K\(^+\) and Ge\(^{4+}\) cations, and the different coordination environments of K\(^+\) and Li\(^+\). For the case of a B/R ratio of 1, the compound LaBRO\(_3\) shows a [BO\(_3\)]\(\infty\) spiral chain type formed by BO\(_4\) groups, in which the R atoms are connected with two neighbouring BO\(_4\) groups, and the neighbouring chains are linked by La\(^{3+}\) along the \( z \) axis to form 3D frameworks. From this we see that there is a close relationship between the B–R ratio and the BBUs, the B–O groups change from a three-coordination to four-coordination along with a change from B-rich to R-rich.

4. Results and discussion

4.1. Electronic structures

The calculated band gaps are shown in Fig. S2 (ESI†), KBGe\(_2\)O\(_6\), LaB GeO\(_3\), Rb\(_4\)Ge\(_3\)B\(_6\)O\(_{17}\), and RbGeB\(_3\)O\(_7\) are indirect band gap crystals with band gaps of 3.769, 4.185, 4.330 and 4.269 eV, respectively. Li\(_4\)B\(_2\)Si\(_3\)O\(_{24}\), LaBSiO\(_3\) and RbGeB\(_3\)O\(_7\) are direct
band gap crystals with band gaps of 5.509, 5.158 and 4.770 eV, respectively. The PDOS of KBGeO₆, Li₄B₂SiO₄, LaBSiO₅, LaBGeO₅, Rb₂Ge₂B₄O₁₇, RbGe₂O₂ and Rb₂GeB₅O₁₇ is demonstrated in Fig. S3 (ESI†), from which we can figure out the respective contributions of the cations and anionic groups in the near Fermi surface. In the case of the B-rich structures Rb₂Ge₂B₄O₁₇, RbGe₂B₇ and Rb₂GeB₅O₁₇, the conduction bands mainly come from the 4s 4p of Ge⁴⁺, 2p of B⁺, or s 4p of Rb⁺ and 2p of O²⁻. For the R-rich structures KBGeO₆ or Li₄B₂SiO₄, the p of K⁺ or 2s of Li⁺, 4s 4p of Ge⁴⁺ or 3s, 3p of Si⁺ and 2p of O²⁻ make the main contribution to the bottom of the conduction bands. At the top of the valence bands of the seven studied compounds, the dominating positions are all occupied by the 2p orbitals of O²⁻. Generally speaking, for the seven compounds discussed above, the interaction of the K⁺, Li⁺, Rb⁺ and La⁺ cations and the 2p orbital of O²⁻ control the near Fermi level. Furthermore, one can see that the orbitals of B and R have changed based on different B–R ratios at the top of the valence band.

4.2. Origin of the SHG response

Both GW and hybrid functionals have been adopted to study the band structures of nonlinear optic crystals,²³,²⁴,⁵⁰ but usually DFT will underestimate the band gap comparing the experimental value. The scissors operation is used to calculate the optical properties. For the seven studied compounds, the scissors operators are chosen as the difference between the calculated band gap and the experimental one or the PBE0 results, these are 2.301 eV for KBGeO₆, 2.619 eV for Li₄B₂SiO₄, 2.375 eV for LaBSiO₅, 2.415 eV for LaBGeO₅, 1.09 eV for Rb₂Ge₂B₄O₁₇, 2.149 eV for RbGe₂B₇ and 1.271 eV for Rb₂GeB₅O₁₇. Taking into account the scissors operator, the calculated linear and non-linear optical properties of the seven compounds are shown in Table 1, where the calculated efficient tensors are in good agreement with the SHG response in experiments. In this table, we can see that a larger B/R ratio tends to have a stronger SHG response. According to earlier work on the origin of birefringence values⁵¹ and SHG responses⁴⁴,⁵², BO₃ may be the main source of both the large birefringence and the SHG response.

In this work, the SHG-density method is employed to analyze the electron states in three of the B-rich compounds Rb₂Ge₂B₄O₁₇, RbGe₂B₇ and Rb₂GeB₅O₁₇ to study the mechanism of the SHG response. The virtual-electron (VE) contributions to the total SHG coefficients are obtained using the band-resolved method, these contributions are 74.63% (d₁₁), 94.06% (d₁₃) and 86.00% (d₂₄) for Rb₂Ge₂B₄O₁₇, RbGe₂B₇ and Rb₂GeB₅O₁₇, respectively. For the compound Rb₂GeB₅O₁₇, the occupied state of VEs is occupied by bridging oxygen O₉ and O₁₀, which are the bridging oxygens of the two neighbouring BO₄ groups (shown in Fig. 2). The unoccupied state of VEs is taken up by the BO₄ groups and the bridging oxygens of GeO₂ and BO₄ (Fig. 2a). For Rb₂Ge₂B₄O₁₇, the non-bonding 2p orbitals of the bridging oxygens of GeO₂ and BO₄ or BO₃, instead of those in the π-conjugation configuration of the BO₃ groups (Fig. 2b), have a considerable contribution to SHG. In the case of Rb₂GeB₅O₁₇, the contributions to SHG come from BO₄, BO₂ and GeO₂, as shown in Fig. 2c. That is to say, the π-conjugation configuration of the BO₃ group is not the only contributor to the SHG response in the B-rich structures, especially in Rb₂GeB₅O₁₇. Why do the tetrahedra such as BO₄, SiO₄ or GeO₂ make a significant contribution to the SHG response? To clear up this question, we have analysed the electron states in the near Fermi surface.

The PDOS of B, Si and Ge are shown in Fig. 3, from which one can see that from the most R-rich case changing to the most B-rich one, the state percentage of B-p orbitals at the top of valence bands tends to grow. The larger percentage of B-p orbitals indicates that, in the region of −5 to 0 eV, the interaction between B/R and O has changed along with the B/R ratio. That is to say, the contributor to the SHG response may be changed with the B/R ratio. From Table 1 we can see that for the B-rich compounds Rb₂Ge₂B₄O₁₇, RbGe₂B₇ and Rb₂GeB₅O₁₇, the SHG coefficients are obviously larger than those of the most R-rich ones of KBGeO₆ and Li₄B₂SiO₄, Fig. 2 shows the obvious SHG densities of the BO₄ or RO₄ tetrahedra, which imply that the π-conjugation configuration of BO₃ is not the only contributor to the SHG response, especially in the compounds Rb₂Ge₂B₄O₁₇ and Rb₂GeB₅O₁₇.

The PDOS of the O atoms for Rb₂Ge₂B₄O₁₇ is shown in Fig. 4a, in which the p orbitals of O₉ and O₁₀ (the bridging oxygens of two neighbouring BO₄ groups) occupy the valence-band maximum, meaning that O₉ and O₁₀ do contribute to the SHG response. For RbGe₂B₇ the PDOS of B, O and Ge,

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Space group</th>
<th>Experimental band gap (eV)</th>
<th>Calculated band gap (eV)</th>
<th>Calculated SHG coefficients (pm V⁻¹)</th>
<th>Experimental SHG response</th>
<th>Calculated birefringence</th>
</tr>
</thead>
<tbody>
<tr>
<td>KBGeO₆</td>
<td>P₂₁2₁₂₁</td>
<td>—</td>
<td>3.77</td>
<td>d₁₁ = −0.340 (0.87 KDP)</td>
<td>—</td>
<td>0.0050</td>
</tr>
<tr>
<td>Li₄B₂SiO₄</td>
<td>P₂₁</td>
<td>—</td>
<td>5.51</td>
<td>d₁₁ = −0.017, d₁₆ = −0.012, d₁₃ = 0.205, d₁₄ = 0.028 (0.07 KDP)</td>
<td>—</td>
<td>0.0083</td>
</tr>
<tr>
<td>LaBSiO₅</td>
<td>P₃₁</td>
<td>—</td>
<td>5.16</td>
<td>d₁₁ = 0.027, d₁₆ = 0.002, d₁₃ = −0.385 (0.99 KDP), d₁₄ = −0.029</td>
<td>≈1 KDP²⁶ 0.33 KDP²⁹ 1.3 KDP²⁰</td>
<td>0.015 0.034 0.0178</td>
</tr>
<tr>
<td>LaBGeO₅</td>
<td>P₃₁</td>
<td>6.41</td>
<td>4.19</td>
<td>d₁₁ = 0.142, d₁₆ = 0.236, d₁₃ = −0.179, d₁₄ = −0.310 (0.79 KDP)</td>
<td>1.3 KDP²⁰ 0.0210</td>
<td>0.017 0.021</td>
</tr>
<tr>
<td>Rb₂Ge₂B₄O₁₇</td>
<td>Cc</td>
<td>5.42</td>
<td>4.33</td>
<td>d₁₁ = −0.634 (1.63 KDP), d₁₆ = 0.390, d₁₃ = 0.467, d₁₄ = 0.443, d₁₅ = 0.694, d₁₆ = −0.95 (2.44 KDP)</td>
<td>1.3 KDP²⁰ 2.0 KDP²⁰</td>
<td>0.0227</td>
</tr>
<tr>
<td>RbGe₂B₇</td>
<td>Pnca₁</td>
<td>5.38</td>
<td>4.77</td>
<td>d₁₁ = 0.232, d₁₆ = 0.064, d₁₃ = −0.95 (2.44 KDP), d₁₄ = 0.056, d₁₅ = −0.173</td>
<td>2.0 KDP²⁰ 0.0227</td>
<td>0.017 0.021</td>
</tr>
</tbody>
</table>
Fig. 2  SHG densities of Rb$_4$Ge$_3$B$_6$O$_{17}$, RbGeB$_5$O$_7$ and Rb$_2$GeB$_4$O$_9$. The rainbow represents the activities of the veecc state and veeunocc state SHG.
corresponding to the integral of VE + VH, are given in Fig. 4b. The integral of the band-resolved $\mathcal{J}^{(2)}$ increases, corresponding to positive contributions to SHG. One can see that the $p$ orbitals of O1 and O3 (the bridging oxygens of BO$_4$ and BO$_3$), O4 and O5 (the bridging oxygens of GeO$_4$ and BO$_3$), and O6 and O7 (the bridging oxygens of BO$_4$ and GeO$_4$), but not that of O2 (the bridging oxygen of two neighbour BO$_3$ groups), occupy the main region within $-1.30$ to 0 eV. That is to say, the non-bonding $p$ orbitals of bridging oxygens occupy the valence-band maximum, which leads to the SHG response of RO$_4$. Why does the conjugate $\pi$ orbital in BO$_3$ not dominate the top of the valence band as previously expected?

For the trigonal planar BO$_3$ group, the overlapping $p$ orbitals tend to form $\pi$ bonds and the amount of non-bonding $p$ orbitals decreases, especially in the two BO$_3$ groups connected by sharing a vertical oxygen. So the valence-band maximum is mainly occupied by non-bonding $p$ orbitals of tetrahedra, such as BO$_4$ or RO$_4$, which results in the $\pi$-conjugated BO$_3$ group not being the only contributor to SHG, as BO$_4$ and RO$_4$ make apparent contributions to SHG (as in the compound RbGeBO$_3$).

In the structures where BO$_3$ connects with the BO$_4$ or RO$_4$ groups (as in the compounds Rb$_2$Ge$_2$BO$_7$ and Rb$_2$GeBO$_3$), the BO$_4$ and RO$_4$ along with the $\pi$-conjugated BO$_3$ group make equally important contributions to SHG. This implies that, in a structural unit, while the $\pi$-conjugated BO$_3$ group contributes to a larger part of SHG, the contributions of tetrahedral BO$_4$ and RO$_4$ cannot be neglected. Furthermore, it also shows that the connection pattern of the anionic group framework is quite important.

5. Conclusions

Using a DFT method, band structure, PDOS and SHG density are analyzed to study the influence of the BBUs on the linear and non-linear optical properties of compounds with different B–R ratios. Based on the SHG density of the seven studied compounds, in the B-rich structures Rb$_4$Ge$_3$B$_6$O$_{17}$, RbGeBO$_3$, and Rb$_2$GeBO$_3$, BO$_3$ is not the only contributor to SHG response. This is because the valence-band maximum is not
occupied only by orbitals of the $\pi$-conjugated BO$_3$ group, as the non-bonding $p$ orbitals of the bridging oxygens in BO$_4$ and RO$_4$ are closer to the Fermi level than that of BO$_3$ and tetrahedral BO$_4$ and RO$_4$ noticeably contribute to the SHG response. In summary, the tetrahedra may make a significant contribution to the SHG response of Ge/Si-containing borate crystals, which makes it necessary to study this kind of tetrahedral borate and is meaningful for the design and synthesis of NLO materials with varied structures.

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Notes and references