1. Introduction

In the field of optical functional crystals, birefringence plays an important role in material processing, laser phase-matching, optical measurements, photolithography, and polarizing microscopic observation.1-21 Standing out from the discovered birefringent crystal materials, CaCO₃,14 YVO₄,15 and α-BaB₂O₄,16,17 are widely applied in optical devices such as polarizers, optical isolators, and compensators.18-20

Nowadays, many studies about birefringent crystals with large optical anisotropy have been carried out. For instance, Ca(BO₃)₂ (ref. 21) with the largest reported birefringence (0.247 at 193 nm) in the deep-ultraviolet (DUV) region is regarded as the most promising DUV birefringent material, while (NH₄)₂-C₂O₄-H₂O²² has also been identified as a promising UV birefringent material with a large birefringence (0.248 at 546 nm). Meanwhile, introducing F atoms into micro groups (e.g. from PO₄ to PO₃F and from SO₄ to SO₃F) can enhance the polarizability anisotropy significantly, and subsequently increase the birefringence to a certain extent.23 The original difference in the birefringence of Ba₄BP₃O₁₁ and Ba₄BP₃O₇F (from 0.013 to 0.034) mainly comes from the BO₄F tetrahedra.24 Introducing different numbers of fluorine atoms into B=O groups can modulate the polarizability anisotropy.25-28 Consequently, the introduction of the F atom has become a feasible strategy to enhance the polarizability anisotropy and enhance the birefringence.

Generally speaking, crystal structures and the corresponding microscopic groups are inextricably linked with the optical properties of materials, for instance, the arrangement of anionic frameworks or diverse combinations with metal cation polyhedrons will influence the birefringence in significant ways.28-32 Consequently, a feasible strategy to enhance the birefringence is introducing some functional modules with large optical anisotropy such as coplanar groups with π-conjugation systems (CO₃, BO₃, B₂O₆, C₂N₂O₃, etc.).25,33-37 At the same time, the isolated parallel distribution, quasi-one dimensional (1D) chain, and quasi-2D plane of anionic groups are proper arrangement modes that contribute to the microscopic effects in FMs. The current research on π-conjugated microscopic groups mainly focuses on the B=O unit (BO₃, BO₃, B₂O₅ and...
B₃O₅)\(^{18}\) and C–O unit (CO₃, C₂O₄, C₂O₆, C₄O₄, and C₆O₆)\(^{22}\) which make great contributions to the birefringence due to their large anisotropy of polarizabilities. Despite the enormous promise in their chemical and physical functionalities, the sheer amounts of boron nitrides are much smaller than those of the oxides, for reasons well known to chemists,\(^{29,48}\) and the units containing N have rarely been utilized in the optical functional crystals field. To explore the optically anisotropic hierarchy and the functionality of the B–N units on birefringence, we investigated their polarizability anisotropy characteristics using the DFT method. The B–N units were obtained from primary crystal information without structure optimization. The polarization anisotropy was acquired from static polarization according to the following formula:

\[
\Delta \alpha = \frac{1}{2} \left[ (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2 + 6(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2) \right]
\]

Nevertheless, it does not mean that the units containing N cannot make a contribution to the optical properties. To the best of our knowledge, there are only a few systematic studies that unveil the contribution of B–N groups towards enhancing birefringence. Based on the analysis of B–O groups, we propose an idea that BN₂ is a linear group containing sp orbital hybridization that contributes greatly to birefringence. Through the investigation of the BN₂ unit based on the Inorganic Crystal Structure Database (Version 4.7.1 build 20211220-1548, ICSD), seven ternary nitride borates with the formulas A₃BN₂ (A = Li, Na), A₃BN₄ (A = Mg, Ca), and Ba₃(BN₂)₂ were screened out.\(^{41–47}\) In order to explore the origin of the optical properties of the selected compounds, multiple analytical methods have been applied. The birefringence was calculated from the dielectric functions by the first-principles method, along with polarizability anisotropy and REDA analysis to further prove the contribution of the BN₂ unit to birefringence. Essentially, a new birefringent-enhanced FM was screened.

2. Computational details

The electronic structures and optical properties of the target compounds were calculated by first-principles calculations based on the density functional theory (DFT) method\(^{48}\) implemented in the CASTEP package.\(^{49}\) The exchange-correlation functional\(^{50}\) was Perdew–Burke–Ernzerhof (PBE) within the generalized gradient approximation (GGA). The norm-conserving pseudopotentials (NCP)\(^{51}\) were selected for structural optimization and calculating the electronic and optical properties. The electronic configurations were treated as follows: Li 2s\(^1\), B 2s\(^2\) 2p\(^2\), N 2s\(^2\) 2p\(^3\), Na 2s\(^2\) 2p\(^6\) 3s\(^1\), Mg 2s\(^2\) 2p\(^6\) 3s\(^2\), Ca 3s\(^2\) 3p\(^6\) 4s\(^2\), and Ba 5s\(^2\) 5p\(^6\) 6s\(^2\), the cutoff energy was set at 880 eV for Ca₃(BN₂)N, 990 eV for Mg₃BN₄, and 770 eV for Li₃BN₂ (P2₁/c), Li₃BN₄ (P4/mmm), Li₃BN₅ (I₄/madm), Na₃BN₂, and Ba₃(BN₂)₂. The scissor operators of 1.18 eV for Li₃BN₂ (P2₁/c), 1.21 eV for Li₃BN₄ (P4/mmm), 1.22 eV for Li₃BN₅ (I₄/madm), 1.24 eV for Na₃BN₂, 1.18 eV for Mg₃BN₂, 0.61 eV for Ca₃(BN₂)N and 1.00 eV for Ba₃(BN₂)₂ were applied to move the simulated conduction bands to the right place. Furthermore, to reach the convergence of this calculation, the Brillouin zone comprised 3 × 3 × 3 Monkhorst–Pack k-point sampling with a separation of 0.04 Å\(^{-1}\). The other calculation parameters and convergent criteria were employed as the default values of the CASTEP code.

3. Results and discussion

3.1. Crystal and electronic structure

To accelerate the process of advanced material discovery, computer-aided material design and prediction have recently emerged as particularly useful techniques and have exhibited various successful cases.\(^{55,56}\) In this work, in order to find the target compounds, the nitride borates with alkali and alkaline earth metal cations were screened in terms of the type of FMs with the BN₂ units by investigating the ICSD. In total, 7 structures were screened out, as listed in Table 1.

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As we can see, Fig. 1 shows the structure and arrangement of the seven compounds. Obviously, the BN2 units are all short straight linear groups. The two of Li3BN2 and Na3BN2, crystallize in the P21/c and P42/mnm space groups, and are composed of isolated and parallel BN2 units in opposite directions and A-site Li and Na cations (Fig. 1a, c and d). Mg3BN3 and Ca3(BN2)N belong to the space groups of P63/mcm and P4/mmmm, respectively, and the BN2 units are parallel to each other along the c axis, while the Mg and Ca cations show symmetric distribution. Li3BN2 and Ba3(BN2)2 belong to the I41/amd and P212121 space groups, respectively, and the BN2 units are not only aligned in a parallel manner but also have angles of 172.8° and 170.1°, as shown in Fig. 1c and g.

Since there is no data about the experimental bandgap, we employed the HSE06 hybrid functional to accurately predict the bandgaps of these compounds. Most of the title compounds possess a direct bandgap, while Li3BN2 (P21/c), Li3BN2 (P42/mnm) and Ba3(BN2)2 possess indirect ones. The calculated bandgaps using the GGA and HSE06 methods are shown in Table 1. The results from the HSE06 hybrid functional are 4.58 eV for Li3BN2 (P21/c), 4.57 eV for Li3BN2 (P42/mnm), 4.38 eV for Li3BN2 (I41/amd),

| Compounds       | Space group | Group | Eg-GGA (eV) | Eg-HSE06 (eV) | Birefringence (@1064 nm) |
|-----------------|-------------|-------|-------------|---------------|--------------------------|
| Li3BN2         | P21/c       | BN2   | 3.4         | 4.58          | 0.198                    |
| Li3BN2         | P42/mnm     | BN2   | 3.36        | 4.57          | 0.103                    |
| Li3BN2         | I41/amd     | BN2   | 3.16        | 4.38          | 0.116                    |
| Na3BN2         | P21/c       | BN2   | 1.52        | 2.76          | 0.157                    |
| Mg3BN3         | P63/mcm     | BN2   | 1.5         | 2.55          | 0.244                    |
| Ca3(BN2)N      | P4/mmmm     | BN2   | 0.55        | 1.16          | 0.411                    |
| Ba3(BN2)2      | P212121     | BN2   | 2.46        | 3.46          | 0.185                    |

Fig. 1 The arrangements of BN2 in the compounds (a) Li3BN2-14, (b) Li3BN2-136, (c) Li3BN2-141, (d) Na3BN2, (e) Mg3BN3, (f) Ca3(BN2)N and (g) Ba3(BN2)2.
2.76 eV for Na3BN2, 2.55 eV for Mg3BN3, 1.16 eV for Ca3(BN2)N, and 3.46 eV for Ba3(BN2)2, which are larger than those from GGA because of the discontinuity of the derivative on the exchange-correlation energy within the GGA functional. The GGA bandgaps of those compounds are listed in Fig. S1.†

The partial density of states (PDOS) as well as the orbitals near the Fermi level show the electronic states that are related to the optical properties. The total and partial density of states with the respective atoms were analyzed to clearly understand the electronic structures of the title compounds, and calculated to analyze the distribution of atomic orbitals in the energy range from −15 to 15 eV, as shown in Fig. S2.† Similar electronic structures demonstrated for the target compounds. It clear to see that the bands of the title compounds near the bandgap are mainly determined by the 2p orbital of the N at the valence bands (VBs) maximum, and the bottom of the conduction bands (CBs) primarily dominated by the B 2p orbital, which means that the B–N group will play an important role in the optical properties of the title compounds.

To reveal the birefringence-related functions of the BN2 anionic group, we performed an intensive comparison with BN3, BO2 and BO3. In order to explore these anionic groups, we investigated the electronic structure and optical properties of the BN2, BN3, BO2 and BO3 anionic groups using DFT implemented by the Gaussian 09 package.27 The electronic structures demonstrated for the target compounds contained the BN2 units near the bandgap are mainly determined by the 2p orbital of the N at the valence bands (VBs) maximum, and the bottom of the conduction bands (CBs) primarily dominated by the B 2p orbital, which means that the B–N group will play an important role in the optical properties of the title compounds.

Fig. 2 shows the corresponding polarizability anisotropy and highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO–LUMO) gaps of the four anionic groups. The polarizability anisotropy Δα values are 23.7, 13.7, 14.4, 7.0 for BN2, BN3, BO2 and BO3, respectively. It is obvious that the BN2 unit possesses the highest polarizability anisotropy among them. For BN2, BN3, BO2 and BO3, the HOMO–LUMO gaps are 5.1, 3.1, 9.2 and 8.5 eV, respectively. In particular, the BO3 unit has been recognized as a birefringence-preferential group, such as in Ca3(BN3)2 ref. (58) with a large birefringence of 0.104 (at 1064 nm). It was also confirmed that Δα increases with the π-electron population of the conjugated system, which indicates the possibility of large birefringence for the corresponding compounds with B–N units. These calculated results suggest that the BN2 unit possesses a larger polarizability anisotropy and maintains a moderate HOMO–LUMO gap as well. Thus, we investigated the compounds with BN2 units and analyzed their optical properties.

3.2. Optical properties

Using the GGA approach and scissors operator via the calculations with the CASTEP code, the birefringence Δn (Δn = nmax − nmin), which depends on the difference of the maximum and minimum values of the refractive index along the different optical principal axes, was obtained, and the title compounds possessed a large birefringence of about 0.1–0.4 (at 1064 nm). The birefringence values of Li3BN2 in different space groups are 0.198 (P21/c), 0.103 (P42/mnm), and 0.116 (I41/amd). For Na3BN2, Mg3BN3 and Ba3(BN2)2, their birefringence values are 0.157, 0.244, 0.185, respectively. The bandgap was calculated by GGA, and the birefringence of the compounds with BN2 units is shown in Fig. 3. Simultaneously, the results indicate that the birefringence of the title compounds is much larger than that of the birefringent materials. Ca3(BN2)N especially exhibits a gigantic birefringence of about 0.411 at 1064 nm, which is 3.5, 2.5, and 2.0 times those of the most commercially used birefringent crystals BaB2O4 (Δn = 0.116 at 1064 nm), CaCO3 (Δn = 0.164 at 1064 nm), and YVO4 (Δn = 0.208 at 1064 nm), respectively. Meanwhile, in comparison with the chain CNO,59 which possesses a birefringence of 0.3–0.4, and the compounds with planar Ca3N2O3, such as β-Str(Ca3N2O3)2 (Δn = 0.36 at 1064 nm) and Ca3(Ca3N2O3)2 (Δn = 0.35 at 1064 nm), the birefringence of Ca3(BN2)N is also larger than theirs, which indicates that the proposed compounds containing BN2 units such as Ca3(BN2)N are promising candidates for optical applications.

Since Ba3(BN2)2 belongs to a non-centrosymmetric group, the NLO coefficients were obtained with ab initio electronic structure calculations. Owing to the Kleinman symmetry, the P212121 space group for the investigated compounds yields three non-zero NLO coefficients. Similar to the calculation of linear optical properties, the same scissors were used to generate the NLO coefficients. At the zero-frequency limit, the...
calculated largest NLO coefficient $d_{14}$ is 0.174 pm V$^{-1}$ (≈0.44 × KDP) for Ba$_3$(BN$_2$)$_2$, and B–N interactions contribute the most to the SHG coefficients (Fig. S4†).

As a post-processing tool, SHG-density (SHG stands for second harmonic generation) was performed to further explore the contribution of atoms or groups to the SHG response through the CASTEP package. SHG-density is divided into occupied and unoccupied states of virtual-electron (VE) and virtual-hole (VH), respectively. Then, the distribution of density can be visualized by highlighting the map of SHG-density in the occupied and unoccupied states. For the Ba$_3$(BN$_2$)$_2$ VE and VH processes, VE occupies 57% in the SHG process for $d_{14}$. Therefore, both of the SHG processes of VE and VH with the occupied and unoccupied states were examined, as shown in Fig. S4.† In Ba$_3$(BN$_2$)$_2$, the density of SHG in the VE occupied and unoccupied states originate from B–N interaction and a small contribution from Ba–N interaction, respectively, while Ba–N interaction plays an important role in the VH process. The result indicates that the atoms in the asymmetric sublattice have an important contribution to the SHG response. 64

### 3.3. Optical properties analysis

To the best of our knowledge, the methods of analysis and birefringence estimation can also be employed to evaluate the ability of the functional units, such as the response electron distribution anisotropy (REDA) model,65,66 real-space atom-cutting (RSAC) technique,67 Born effective charge analysis method,68 Bader charge integration and the sum of polarizability anisotropy (SPA).70

The optical anisotropy of a crystal depends on the direction of the covalent bond in the anionic groups. Therefore, birefringence is sensitive to the anisotropy of the response electron distribution, corresponding to the REDA index $\Delta \rho^b = \rho^b_{\text{max}} - \rho^b_{\text{min}}$, $\rho^b_{\text{max}}$ and $\rho^b_{\text{min}}$ are the maximum and minimum of the covalent electron density of the covalent bond on the optical principal axes of a crystal, and $n_1$ is the minimum refractive index. Pan et al. proved the rationality of the REDA method, and that the birefringence is proportional to the REDA index. To check the above analysis and quantification, we employed the REDA method to calculate the bonding electron density difference ($\Delta \rho^b$) of the covalent bonds along the optical principal axes in Li$_3$BN$_2$ ($P_{2_1}/c$, $P4_2/mnm$, $I4_1/amd$), Na$_3$BN$_2$, Mg$_3$BN$_3$, Ca$_3$(BN$_2$)$_N$ and Ba$_3$(BN$_2$)$_2$. The $\Delta \rho^b$ values of BN$_2$ are 2.12–4.49 (×10$^{-2}$), and we calculated the $\Delta \rho^b$ values of the remaining anionic groups (Li–N, Na–N, Mg–N, Ca–N and Ba–N), as shown in Table 2. As a result, the BN$_2$ units contribute the most to $\Delta \rho^b$, which

### Table 2  Bonding electron density difference ($\Delta \rho^b$) for anionic groups in compounds calculated by the REDA method

| Compounds          | Group | $\Delta \rho^b$ (×10$^{-2}$) of BN$_2$ | $\Delta \rho^b$ (×10$^{-2}$) of A (Li, Na, Mg, Ca, Ba) N$_n$ | Birefringence ($\Delta 1064$ nm) |
|--------------------|-------|--------------------------------------|----------------------------------------------------------|---------------------------------|
| Li$_3$BN$_2$       | BN$_2$| 3.07                                 | 0.09                                                     | 0.198                           |
| Li$_3$BN$_2$       | BN$_2$| 2.51                                 | 0.09                                                     | 0.103                           |
| Li$_3$BN$_2$       | BN$_2$| 4.49                                 | 0.16                                                     | 0.116                           |
| Na$_3$BN$_2$       | BN$_2$| 2.15                                 | 0.09                                                     | 0.157                           |
| Mg$_3$BN$_3$       | BN$_2$| 3.28                                 | 0.09                                                     | 0.244                           |
| Ca$_3$(BN$_2$)$_N$ | BN$_2$| 2.65                                 | 0.09                                                     | 0.411                           |
| Ba$_3$(BN$_2$)$_2$ | BN$_2$| 2.12                                 | 0.09                                                     | 0.185                           |

Fig. 4 (a) A comparison of $\Delta \rho^b$(BN$_2$)/$E_g$ (HSE06) with the birefringence of the selected BN$_2$ compounds. (b) The structural comparison of Mg$_3$BN$_3$ and Ca$_3$(BN$_2$)$_N$. © 2022 The Author(s). Published by the Royal Society of Chemistry RSC Adv., 2022, 12, 14757–14764 | 14761
indicates that the BN$_2$ units are the main sources of birefringence in the title compounds. As is well known, the $\Delta \rho$ value obtained by the REDA method contains the arrangement of anionic groups, and the arrangement of BN$_2$ units in the title compounds are aligned in a parallel manner; the parallel or antiparallel arrangement is beneficial to the superposition of micro polarizability anisotropy. These results are generally in agreement with the increase of the macro birefringence.

Particularly, comparing Mg$_3$BN$_3$ and Ca$_3$(BN$_2$)$_2$N, we find that the birefringence of Ca$_3$(BN$_2$)$_2$N is about 1.7 times that of Mg$_3$BN$_3$, while the values of $\Delta \rho$ of BN$_2$ in Mg$_3$BN$_3$ and Ca$_3$(BN$_2$)$_2$N are 3.28 and 2.65, respectively. Therefore, the BN$_2$ units contribute about 130% in Mg$_3$BN$_3$ and 110% in Ca$_3$(BN$_2$)$_2$N, which are roughly in agreement. According to the formula of REDA approximation, except for the values of the bandgap, the other indicators in the formula of the two compounds are very close to each other. Consequently, we performed a comparison of $\Delta \rho$ of BN$_2$ with the birefringence, as shown in Fig. 4. As we can see, the proportion of $\Delta \rho$(BN$_2$)/$E_g$ is 2.284 in Ca$_3$(BN$_2$)$_2$N, almost 1.7 times that in Mg$_3$BN$_3$ (1.286), which indicates that the tendency is consistent with the variation of the birefringence. Simultaneously, there exists a significant difference between the bandgap of the two compounds, which is the main reason that Ca$_3$(BN$_2$)$_2$N exhibits an extraordinarily larger birefringence than Mg$_3$BN$_3$ while they have a similar contribution of BN$_2$ units.

4. Conclusion

In summary, we investigated the birefringence-enhanced FMs in a B–N system, and a linear group BN$_2$ unit was proposed. Through the investigation based on the Inorganic Crystal Structure Database, seven ternary boron nitrides with the formulas A$_3$BN$_3$ (A = Li, Na), A$_2$BN$_4$ (A = Mg, Ca), and Ba$_3$(BN$_2$)$_2$ were screened. Their birefringence values are in the range of 0.1–0.4 at 1064 nm, especially the birefringence of Ca$_3$(BN$_2$)$_2$N, which is 0.411 at 1064 nm, exceeding that of the commercial birefringent materials α-BaB$_2$O$_4$, CaCO$_3$ and YVO$_4$. Based on the analysis of the REDA and polarizability anisotropy, it was concluded that the large birefringence mainly originates from the BN$_2$ unit. Hence, the functionality of the BN$_2$ unit could be utilized in birefringence-enhanced FMs, which exhibits the possibility of applying B–N modules to the birefringent field. This study provides a feasible way to design optical materials with enlarged birefringence.

Conflicts of interest

The authors declare that they have no conflict of interest.

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