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Deep-ultraviolet nonlinear optical crystals by design: A computer-aided modeling blueprint from first principles

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ABSTRACT Deep-ultraviolet (DUV) nonlinear optical (NLO) crystal is indispensable in current DUV all-solid-state laser technology, which is the key device to generate DUV light by frequency conversion. Due to stringent criteria, DUV NLO crystals are scarce and their discovery faces a big challenge. Although $\text{KBe}_2\text{BO}_3\text{F}_2$ (KBBF) is already excellent for current uses, the development of DUV science requires the materials with shorter output wavelengths and larger NLO effects, so as to meet the needs of DUV lasers with higher precision and higher power. Therefore, how to efficiently design DUV NLO materials has always been the core issue in NLO materials science. Looking back on the development of NLO materials, it turns out that theoretical modeling and simulation is an effective and efficient method, not only for mechanism understandings, but also for experimental exploration. In this article, in order to accelerate the process of DUV materials discovery, we summarize and propose a powerful computer-aided modeling system and design blueprint that can be used to evaluate the DUV NLO performance in a faster way than pure experiments. With this in hand, we enrich the understanding of NLO structure-property correlation, and systematically prospect the DUV NLO properties on the basis of many existing and designed structures according to different structural types and chemical compositions. Seven novel structures are predicted for the first time to exhibit potential DUV NLO capabilities. All the results enable us to believe that the computer-aided modeling blueprint will play an important role in the exploration of new DUV NLO crystals.

Keywords: deep-ultraviolet, nonlinear optical crystal, first-principles calculation

INTRODUCTION

Nonlinear optical (NLO) crystals have an irreplaceable role in the field of laser technology due to the advantages of high beam quality, tunable wavelengths, miniaturization and high power [1–4]. They also have a wide variety of applications in the field of information technology, such as quantum optics, optical phase modulation, and optical information storage [5–9]. As such, NLO crystals are important fundamental materials for optoelectronic information technology today and in the future. Remarkably, in the deep-ultraviolet (DUV, $\lambda < 200$ nm) region, NLO crystals play a key role in developing the DUV lasers for photolithography, atto-second pulse generation, and advanced instrument development, etc. [10–14]. An important example is ultra-precision angular resolved photoelectron spectroscopy (ARPES) that adopts the 177.3 nm-laser, which has been widely used in the surface state measurements of high-temperature superconductors, topological insulators and two-dimensional (2D) materials [14–17].

The core and key issue in the field of NLO crystals is to improve the comprehensive performance of NLO crystals. For fulfilling the higher DUV conversion, they must comprise two stringent criteria, i.e., short phase-matching (PM) wavelength and high second-harmonic generation (SHG) efficiency [18–20]. In general, a qualified DUV NLO crystal must have (I) good DUV transparency, requiring optical bandgap $E_g \geq 6.3$ eV and preferably ≥ 7.1 eV for the practical 177.3 nm-laser; (II) sufficient PM capacity, usually requiring large DUV birefringence with $\Delta n > 0.08$ in the DUV region. The shortest PM wavelength λ_{PM} depends on the dispersion of respective re-

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fractive indices, e.g., $n_{\max}(2\lambda_{\text{PM}}) = n_{\min}(\lambda_{\text{PM}})$ for type-I PM process; and (III) effective SHG effect d_{eff} , determined by large SHG coefficient $|d_{ij}| \geq d_{36} = 0.39 \text{ pm V}^{-1}$ of KH_2PO_4 (KDP) in the PM direction, and in general, the larger d_{ij} , the higher conversion efficiency. Only meeting the criteria of (I), (II) and (III), can crystals realize PM DUV conversion. To date, few crystals can satisfy these criteria because of either small Δn (e.g., LiB_3O_5 (LBO)) or E_g (e.g., $\beta\text{-BaB}_2\text{O}_4$ (BBO)) [21–25]. In this sense, the realization of DUV conversion needs good balance of E_g vs. Δn with not only sufficiently wide DUV E_g but also sufficiently large DUV Δn . Under the premise of this balance, large SHG effects are then favorable.

In fact, for most structures it is difficult to achieve the rigorous balance, making DUV NLO crystals extremely scarce. As a rare exception, $\text{KBe}_2\text{BO}_3\text{F}_2$ (KBBF) has a structural feature beneficial for this balance [26], exhibiting a large birefringence ($\Delta n \approx 0.08$), strong SHG effect ($d_{22} \approx 0.5 \text{ pm V}^{-1}$), wide bandgap ($E_g \approx 8.3 \text{ eV}$) and good mechanical stability. For current uses, KBBF is already an excellent DUV NLO crystal, which has practically achieved the 177.3-nm laser with 200 mW and has played a very important impetus in the DUV laser fields [3,26,27]. It should be emphasized that, owing to the difficulty of crystal growth, the thickness of KBBF along the z -axis is limited to 2–3 mm, making the power improvement at 177.3 nm very small. The development of DUV field requires that NLO crystals have shorter PM wavelengths and stronger SHG effects, so as to meet the increasingly urgent needs for DUV lasers with higher precision and higher power [13]. Therefore, it is necessary to explore more promising DUV NLO crystals to achieve this goal.

However, no material was found to exceed the performance of KBBF before 2013 [22]. This is mainly because KBBF has pushed the DUV NLO performance to the extreme in borates based on the anionic group theory proposed by Prof. Chuangtian Chen [21]. This theory captures the essence of NLO origin and provides a concise structure-property law for UV/DUV NLO crystals, which has indeed achieved a great success in guiding the discovery of BBO, LBO and KBBF, but it is inefficient to evaluate the NLO performance in an *ab-initio* manner due to the approximation that ignores the contribution of A-site cations. Therefore, as the anionic group theory faces the challenge from the stringent criteria for accurate evaluation [28], the improvement of DUV NLO performance is an arduous task in NLO materials science.

With the in-depth understanding of NLO mechanisms, high-precision first-principles methods have been adop-

ted into the studies of NLO crystals in the past two decades [18]. A complete set of CASTEP-compatible programs based on density functional theory (DFT) calculations have been successfully developed, which have advanced the NLO crystal field and accelerated the experimental explorations [29–34]. The proposed first-principles method for NLO calculations is based on strict crystal band and perturbation theory, without empirical parameter settings. As such, it is more efficient to accurately obtain the NLO properties, and more reliable to *ab-initio* design new NLO structures [28].

It is worth noting that, combining theoretical predictions with experimental characterizations, some compounds have been obtained, which do exhibit DUV NLO properties comparable to that of KBBF. As the first breakthrough in 2013, our group proposed a series of DUV NLO fluoride carbonates [35], in which $\text{RbAlCO}_3\text{F}_2$ was predicted with wide E_g and large Δn so as to induce $\lambda_{\text{PM}} \approx 152 \text{ nm}$. This is the first time to predict possible DUV NLO structures beyond KBBF theoretically. In 2015, two novel DUV NLO structures, i.e., $\text{NH}_4\text{Be}_2\text{BO}_3\text{F}_2$ (ABBF) and $\gamma\text{-Be}_2\text{BO}_3\text{F}$ (γ -BBF), were theoretically predicted [36]. Both of them were synthesized experimentally in 2018 [37], with good agreement between experimental and predicted results. Other achievements were completed in 2017–2018 [38–43]. And especially, $\text{NH}_4\text{B}_4\text{O}_6\text{F}$ (ABF) series with excellent DUV NLO properties were synthesized [40]. These could originate from the first-principles studies for $\text{LiB}_6\text{O}_6\text{F}$ series from 2011 to 2013 [44]. And the experiments in 2017 awakened the research of the fluorooxoborates [38].

These new developments clearly demonstrate that the search for DUV materials has not approached to the extreme, but only encounters the “bottleneck”. Inspired by the Materials Genome Project [45], we believe that there still have room for the discovery of new DUV NLO structures by combining different NLO-active “genes” beyond $(\text{BO}_3)^{3-}$ and $(\text{BeO}_3\text{F})^{5-}$ in KBBF. The computer-aided simulations are playing an increasingly important role in the design and search for more promising DUV NLO materials other than KBBF, and the theoretical research on structure-property relations will become more efficient to promote to satisfy criteria (I), (II) and (III).

In this work, we design a computer-aided modeling system for DUV NLO crystals by adopting the KBBF structure as the starting point. By adopting first-principle methods and high-throughput proposal, this modeling system considers different structure types and chemical compositions, and comprehensively includes the contribution of anionic and cationic parts to DUV NLO

performance to accurately evaluate the DUV NLO properties of many existing and designed compounds. Using this system, we indeed find several new structures exhibiting potential DUV NLO capabilities, including wide energy bandgap, strong SHG effect, large birefringence and short PM output wavelength. Therefore, this computer-aided modeling system provides an efficient and effective guidance for exploring DUV NLO materials, by avoiding the waste of human and financial resources.

COMPUTATIONAL SECTION

Different from the experiments, the computer-aided modeling system can provide efficient benefits to evaluate the energy bandgap, SHG effect, birefringence and PM output by a reasonable, controllable and convenient program. Fig. 1 depicts the flowchart of probing DUV NLO crystals based on KBBF, which is basically the starting structure for most DUV modeling. Herein, KBBF can be divided into four components according to microscopic structure units and chemical compositions, i.e., A-site cation K^+ , B-site cation Be^{2+} , G(group)-site anionic group $(BO_3)^{3-}$, and H(halogen)-site halogen anion F^- .

The first step needs a new compound with the general chemical formula of $A_iB_jG_mH_n$ ($i, j, m, n = 0, 1, 2 \dots$) through rational substituents of A-site, B-site, G-site, and/or H-site ions or groups. The A-site cations mainly include those cations with strong ionic characteristics, such as alkali and alkaline earth metal cations; the B-site cations mainly include the center ions usually coordinated with oxygen atoms, such as Be^{2+} , Zn^{2+} , Al^{3+} , Sc^{3+} ; the G-site anionic groups mainly include covalent oxide units such as $(BO_3)^{3-}$, $(BO_4)^{5-}$, $(CO_3)^{3-}$, $(NO_3)^-$, $(SiO_4)^{4-}$, $(PO_4)^{3-}$, $(SO_4)^{2-}$ and their combinations; and the H-site halogen anions mainly refer to F^- , Cl^- , etc.

The second step needs to design initial structures based on the selection principles. To satisfy the criterion (I), oxides/halides are the first selection option since other compound systems are difficult to possess a DUV E_g . The ions should not include non-filling d or f electrons (e.g., Ce^{3+}), electronic lone pairs (e.g., Bi^{3+}), and large covalent radius (e.g., Cd^{2+}), and the nonbonding states should be removed as much as possible. For criterion (II), layer-structures are better than 3D frame-structures (e.g., BPO_4) due to larger anisotropy. Moreover, layer-structures usually have more moderate refractive dispersions, especially in the spectral region close to E_g , which are more suitable to achieve the PM condition compared with chain-structures (e.g., $NaBeB_3O_6$ and LiB_6O_9F) [46]. Criterion (III) is not harsh since many acentric compounds

Figure 1 Computer-aided modeling system and design blueprint of DUV NLO crystals based on the KBBF system.

with parallel polar units can have a relatively strong SHG effect ($\sim$ KDP). It is accordingly summarized that the structure-selection principles for DUV NLO materials comprise: (i) a layer-structure with polar-parallel alignment, (ii) active-groups without nonbonding orbitals, and (iii) suitable connections between active-groups. Taking $(BO_3)^{3-}$ as an example, (a) $(BO_3)^{3-}$ should remain coplanar; (b) three terminal oxygens should be attached to covalent atoms, e.g., Be^{2+} or Al^{3+} ; (c) anionic-group-density should be as high as possible [47]. This is actually the reason why KBBF exhibits such predominant DUV NLO performances by well satisfying these principles.

Once the initial structures of $A_iB_jG_mH_n$ are obtained, our targeted calculations can be employed to run the third step to determine whether the candidates are good or not. If the structure has already existed in the crystal database, e.g., ICSD (Inorganic Crystal Structures Database), its NLO results can be naturally obtained from references or calculations. If the structure is new, the following procedure is to perform the high-precision first-principles calculations for the structural optimization and electronic structures. In our first-principles calculations, the plane wave pseudopotential method implemented in CASTEP based on DFT was adopted [48,49]. The ion-electron interactions are modeled by the optimized norm-conserving pseudopotentials [50]. The crystal geometries are optimized using the quasi-Newton method [51], followed by the band structure and optical properties calculations. According to our examinations for DUV oxides, the hybrid PBE0 functional was used to determine E_g , while the scissors-corrected GGA method with PBE functional was used to calculate the optical properties, wherein the scissors-operator is the difference between PBE0 and GGA-PBE bandgaps [32,52,53]. After the determination of refractive indices n and birefringence Δn , the shortest PM wavelength λ_{PM} can be computed. Meanwhile, using the expressions developed by Lin *et al.* [30], the SHG coefficients d_{ij} can be simulated. As a self-consistent *ab initio* approach without introducing any experimental parameter, our computational method has been proven to be very suitable to study the NLO properties in DUV NLO materials [34].

In order to obtain the most favorable structures, necessary judgments must be performed. The first step is to determine whether $E_g \geq 6.3$ eV, i.e., $\lambda_{UV} \leq 200$ nm. If the result is “Yes”, it would be better to judge whether $E_g \geq 7.1$ eV, i.e., $\lambda_{UV} \leq 177.3$ nm for the sixth harmonic generation (6HG) of 1064 nm Nd:YAG lasers. The second step is to determine whether $\lambda_{PM} \leq 200$ or 177 nm, which is the most critical evaluation for the desired DUV output. The third step is to give the effective SHG coefficient d_{eff} under type I or II PM condition by using the obtained matrix of SHG coefficients d_{ij} , and to estimate the conversion efficiency under ideal conditions. If the structure exhibits good DUV NLO performance, the next step would be the evaluation of the prospect for single crystal growth and post-processing. The dynamic stability of the compound structure can be determined by the calculated phonon dispersion spectrum which has virtual frequency or not [54]. Meanwhile, the lattice stability under ambient temperature can be confirmed by molecular dynamics (MD) simulations [55]. If the structure is maintained after

a long-time MD simulation, it would exhibit practically stable properties. In addition, the elastic and thermal properties can be theoretically calculated if necessary. With the comprehensive DFT evaluation, it is anticipated that the experimental synthesis and characterizations would be significantly accelerated.

The present DFT calculations are sufficiently effective and can be more efficient than conventional experimental explorations, in which bulk crystals with suitable size and good quality are necessary for the measurements of DUV E_g (e.g., UV-vis diffuse reflection method), SHG coefficients (e.g., Maker fringes method) and refractive indices (e.g., polarizing microscope method). The large-size crystal growth is complicated and time-consuming, which hinders the rapid characterizations of practical NLO properties. Although some preliminary experiments can be employed for evaluation, the evidences are not adequate and the errors might be large. Following our extensive studies and testing, in a highly accuracy way, we can efficiently obtain the bandgap E_g , SHG coefficients d_{ij} , birefringence Δn , the shortest SHG output λ_{PM} and finally effective SHG effect d_{eff} , all of which are the most necessary index for determining DUV NLO performance. In addition, the mechanical and crystal growth property can be compared with KBBF based on the calculations, such as interlayer binding energy, thermodynamic properties, and mechanical-elastic constants. From the analysis, the structure-property relationships can be obtained to guide the consequent researches.

RESULTS AND DISCUSSION

The core step of searching for DUV NLO crystals is to produce a rational structure that fits the DUV criteria. Based on the modeling system and structure-selection principles, we attempt to design such kinds of NLO structures. We discuss almost-all kinds of possible compounds of $A_iB_jG_mH_n$, in which potential DUV NLO crystals might emerge from combined theoretical analysis and available experimental comparisons. These existing and designed compounds are mainly examined in five ways, i.e., reasonable *A*-site substitute, *B*-site substitute, *G*-site substitute, *H*-site substitutes, and without *A*-site cations, respectively. The five design strategies include both the cationic and anionic contributions to the NLO performance, which will provide a more comprehensive understanding on the structure-property correlation of DUV NLO crystals.

A-site cationic substitute

The *A*-site cations herein include alkali-metals (e.g., Li^+ ,

Na^+ , K^+ , Rb^+ , Cs^+), alkaline-earth-metals (e.g., Ca^{2+} , Sr^{2+} , Ba^{2+}), and some cationic groups (e.g., NH_4^+ , CH_3NH_3^+). Based on the anionic group theory, the d_{ij} or Δn is mainly derived from the anionic groups with large geometrical anisotropy. The spherical A-site cations have negligible contribution to the overall SHG effect. However, they can change the micro-arrangement and adjust the final cell-size, to some extent affecting the ultimate NLO properties.

$\text{ABe}_2\text{BO}_3\text{F}_2$ ($A = \text{K}, \text{Rb}, \text{Cs}; \text{Na}, \text{Li}, \text{Tl}; \text{NH}_4, \text{CH}_3\text{NH}_3$)

As typical KBBF-family members, $\text{RbBe}_2\text{BO}_3\text{F}_2$ (RBBF) and $\text{CsBe}_2\text{BO}_3\text{F}_2$ (CBBF) have similar topological structures as KBBF (Fig. 2a) [56–58]. Table 1 lists their crystallographic data with good agreement between experimental (exp.) and calculated (cal.) results. As the cationic size increases, $(\text{BO}_3)^{3-}$ remains the same size but $(\text{BeO}_3\text{F})^{5-}$ elongates along the c -axis. Compared with KBBF, the volumes of RBBF and CBBF expand by about 6% and 15%, respectively. Table 1 also lists their NLO properties, demonstrating that the choice of A-site cations from K^+ to Rb^+ and Cs^+ does not affect the E_g and d_{22} , but reduces the $\Delta n = n_o - n_e$, because the c -axis n_e increases while the a - b plane n_o keeps almost constant. This is so-called “NLO-size-effect” [56]. As such, the λ_{PM} of CBBF > 200 nm despite its $\lambda_{\text{UV}} \approx 150$ nm, and the d_{eff} of RBBF is only $0.5 \times \text{KBBF}$ despite its $d_{22} \approx \text{KBBF}$.

Depending on the “size-effect”, the A-site substitute of Na^+ or Li^+ with smaller radius is good choice for DUV PM. $\text{NaBe}_2\text{BO}_3\text{F}_2$ (i.e., α -phase) is an existing compound with similar layering structural feature as KBBF but dif-

ferent symmetry C2 [59]. Fig. 2b and Table 1 shows its structure and NLO properties. Due to the refractive dispersion caused by the sliding layers, the λ_{PM} is red-shifted by 13 nm than that of KBBF. It also shows a strong layering growth tendency. According to the KBBF structure, $\beta\text{-NaBe}_2\text{BO}_3\text{F}_2$ and $\text{LiBe}_2\text{BO}_3\text{F}_2$ with R32 symmetry were further designed. The calculated Δn are 0.064 and 0.067, both larger than that of KBBF, and their λ_{PM} are blue-shifted by 2 and 7 nm, respectively, due to the “size-effect”; however, phonon vibration analysis (Fig. S1) shows that they have instabilities owing to the presence of virtual frequencies. The interlayer slide of Na^+/Li^+ makes the framework not stable.

If the improvement of single-crystal growth property is paid attention to, a possible approach is to use covalent A-site cations (e.g., Tl^+ or Ag^+) instead of K^+ , Rb^+ or Cs^+ to enhance the interlayer connection. $\text{TlBe}_2\text{BO}_3\text{F}_2$ is a representative with similar structure as KBBF and exhibits possibly better growth performance in preliminary experiments [60]. However, it has relatively small E_g (~ 6.3 eV) and Δn (~ 0.045), so it cannot achieve effective SHG output below 200 nm. Another case is $\text{AgBe}_2\text{BO}_3\text{F}_2$, whose E_g is only 4.9 eV (cal.) and which has not been DUV transparent. This means that the substitution with covalent A-site cations is not a good choice for DUV NLO crystals.

Since small-radius and covalent substitutes for the A-site cations hardly enhance DUV capability and single crystal growth property, an effective method is to use some relatively isolated ionic groups with certain covalence. By replacing K^+ in KBBF with ammonium ion

Figure 2 Structures of $\text{ABe}_2\text{BO}_3\text{F}_2$ ($A = \text{K}, \text{Rb}, \text{Cs}, \text{Tl}, \text{NH}_4$) (a), $\text{NaBe}_2\text{BO}_3\text{F}_2$ (b), $\text{NaCaBe}_2\text{B}_2\text{O}_6\text{F}$ (c), $\text{NaSr}_3\text{Be}_3\text{B}_3\text{O}_9\text{F}_4$ (d) and $\text{BaBe}_2\text{BO}_3\text{F}_2$ (e).

Table 1 Calculated crystallographic data and NLO properties as compared to available experimental results

	Symmetry	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	<i>E_g</i> (eV)	<i>d_{ij}</i> (pm V ⁻¹)	Δ <i>n</i> at 400 nm	λ _{UV} (nm)	λ _{PM} (nm)	Refs
A-site substitute											
KBe ₂ BO ₃ F ₂	Cal.	<i>R</i> 32	4.279	4.279	19.520	309.537	8.31	<i>d</i> ₂₂ =0.41	0.059	150	172 [56]
	Exp.	<i>R</i> 32	4.427	4.427	18.744	318.135	8.45	<i>d</i> ₂₂ =0.47	0.088	147	161 [26]
RbBe ₂ BO ₃ F ₂	Cal.	<i>R</i> 32	4.296	4.296	20.548	328.356	8.21	<i>d</i> ₂₂ =0.40	0.057	151	185 [56]
	Exp.	<i>R</i> 32	4.439	4.439	19.820	338.178	8.18	<i>d</i> ₂₂ =0.45	0.078	152	174 [57]
CsBe ₂ BO ₃ F ₂	Cal.	<i>R</i> 32	4.315	4.315	22.012	354.959	8.23	<i>d</i> ₂₂ =0.38	0.055	151	210 [56]
	Exp.	<i>R</i> 32	4.458	4.458	21.310	366.688	8.23	<i>d</i> ₂₂ =0.50	0.064	151	202 [58]
α-NaBe ₂ BO ₃ F ₂	Cal.	<i>C</i> 2	7.723	7.723	7.341	372.459	8.26	<i>d</i> ₂₃ =0.44	0.059	151	185 This work
	Exp.	<i>C</i> 2	7.693	7.693	7.600	384.538	8.07	~KDP	-	154	- [59]
β-NaBe ₂ BO ₃ F ₂ ^a	Cal.	<i>R</i> 32	4.245	4.245	17.866	278.793	8.11	<i>d</i> ₂₂ =0.44	0.064	153	170 This work
LiBe ₂ BO ₃ F ₂ ^a	Cal.	<i>R</i> 32	4.228	4.228	17.023	263.537	8.38	<i>d</i> ₂₂ =0.46	0.067	149	165 This work
TlBe ₂ BO ₃ F ₂	Cal.	<i>R</i> 32	4.290	4.290	20.640	328.950	6.58	<i>d</i> ₂₂ =0.46	0.044	189	330 This work
	Exp.	<i>R</i> 32	4.439	4.439	19.942	340.260	≥6.30	~KDP	-	≤200	- [60]
NH ₄ Be ₂ BO ₃ F ₂	Cal.	<i>R</i> 3	4.299	4.299	20.658	330.642	8.37	<i>d</i> ₂₂ =0.40; <i>d</i> ₃₃ =0.23	0.053	148	188 [36]
	Exp.	<i>R</i> 32	4.442	4.442	19.909	340.170	8.12	~1.2×KDP	0.091	153	174 [37]
CH ₃ NH ₃ Be ₂ BO ₃ F ₂ ^a	Cal.	<i>R</i> 3	4.324	4.324	25.986	420.700	7.88	<i>d</i> ₂₂ =0.30; <i>d</i> ₃₃ =0.14	0.039	158	222 This work
NaCaBe ₂ B ₂ O ₆ F	Cal.	<i>Cc</i>	4.536	4.536	14.257	254.065	7.21	<i>d</i> ₂₂ =0.18	0.059	173	245 [62]
	Exp.	<i>Cc</i>	4.623	4.623	14.182	262.527	6.52	~0.5×KDP	-	191	- [62]
NaSr ₃ Be ₃ B ₃ O ₉ F ₄	Cal.	<i>R</i> 3 <i>m</i>	10.447	10.447	8.309	785.347	7.25	<i>d</i> ₁₂ =0.84	0.048	172	248 [63]
	Exp.	<i>R</i> 3 <i>m</i>	10.406	10.406	8.289	777.367	7.29	~2×KDP	-	171	- [63]
BaBe ₂ BO ₃ F ₃	Cal.	<i>P</i> 6 ₃	7.628	7.628	13.990	704.950	8.41	<i>d</i> ₁₅ =0.02	0.077	148	180 [65]
	Exp.	<i>P</i> 6 ₃	7.428	7.428	14.469	691.300	≥6.70	~0.3×KDP	-	≤186	- [65]
B-site substitute											
BaAlBO ₃ F ₂	Cal.	<i>P</i> 6̄	4.814	4.814	9.390	188.474	7.61	<i>d</i> ₂₂ =0.70	0.037	164	275 [66]
	Exp.	<i>P</i> 6̄	4.888	4.888	9.403	194.555	7.53	<i>d</i> ₂₂ =1.24	0.042	165	273 [66]
Rb ₃ Al ₃ B ₃ O ₁₀ F	Cal.	<i>P</i> 3 ₁ <i>c</i>	8.517	8.517	8.115	509.768	6.58	<i>d</i> ₂₂ =0.39	0.063	189	235 [67]
	Exp.	<i>P</i> 3 ₁ <i>c</i>	8.682	8.682	8.742	570.671	≥6.30	~1.2×KDP	-	≤200	- [67]
K ₃ Ba ₃ Li ₂ Al ₄ B ₆ O ₂₀ F	Cal.	<i>P</i> 6̄2 <i>c</i>	8.584	8.584	16.343	1042.817	5.97	<i>d</i> ₂₂ =0.48	0.053	209	248 [68]
	Exp.	<i>P</i> 6̄2 <i>c</i>	8.755	8.755	16.435	1090.868	6.54	~1.5×KDP	-	190	- [68]
KAlBO ₃ F ^a	Cal.	<i>P</i> 6̄	5.016	5.016	3.744	81.594	7.15	<i>d</i> ₁₁ =0.47; <i>d</i> ₂₂ =0.66	0.078	174	182 This work
KAl ₂ B ₂ O ₆ F ^a	Cal.	<i>R</i> 32	4.915	4.915	23.815	498.143	6.50	<i>d</i> ₂₂ =0.61	0.091	191	192 This work
BaZnBO ₃ F	Cal.	<i>P</i> 6̄	4.880	4.880	4.561	94.089	5.69	<i>d</i> ₁₁ =-0.67; <i>d</i> ₂₂ =1.76	0.081	219	269 [69]
	Exp.	<i>P</i> 6̄	5.066	5.066	4.280	95.119	5.57	~2.8×KDP	-	223	- [69]
KZn ₂ BO ₃ F ₂ ^a	Cal.	<i>R</i> 32	4.750	4.750	22.891	447.200	6.29	<i>d</i> ₂₂ =0.24	0.046	197	266 This work
KScBO ₃ F ^a	Cal.	<i>P</i> 6̄	5.199	5.199	4.232	99.074	6.81	<i>d</i> ₁₁ =2.03; <i>d</i> ₂₂ =2.01	0.186	183	183 This work
KYBO ₃ F ^a	Cal.	<i>P</i> 6̄	5.014	5.014	4.489	97.757	6.11	<i>d</i> ₁₁ =2.16; <i>d</i> ₂₂ =1.02	0.179	203	204 This work
KLaBO ₃ F ^a	Cal.	<i>P</i> 6̄	4.789	4.789	4.390	87.185	5.91	<i>d</i> ₁₁ =1.74; <i>d</i> ₂₂ =0.00	0.183	211	210 This work
G-site substitute											
KBe ₂ B ₃ O ₆ F ₂ ^a	Cal.	<i>R</i> 32	6.152	6.152	13.672	448.077	7.44	<i>d</i> ₂₂ =0.83	0.126	167	167 This work
BaAlB ₃ O ₆ F ₂ ^a	Cal.	<i>P</i> 6̄	6.475	6.475	7.787	282.752	7.86	<i>d</i> ₂₂ =1.01	0.086	158	200 This work

(Continued)

	Symmetry		a (Å)	b (Å)	c (Å)	V (Å ³)	E_g (eV)	d_{ij} (pm V ⁻¹)	Δn at 400 nm	λ_{UV} (nm)	λ_{PM} (nm)	Refs
NH ₄ B ₄ O ₆ F	Cal.	$Pna2_1$	8.450	10.838	6.495	594.858	7.87	$d_{32}=0.72$; $d_{33}=-0.91$	0.112	158	164	[40]
	Exp.	$Pna2_1$	7.602	11.197	6.595	561.400	7.97	~3×KDP	0.130	156	158	[40]
BaB ₄ O ₆ F ₂ ^a	Cal.	Cc	6.542	11.496	10.374	752.922	7.80	$d_{11}=-0.42$; $d_{12}=0.57$	0.065	160	180	[74]
KB ₂ O ₃ F ^a	Cal.	$P3$	4.360	4.360	4.976	81.911	7.46	$d_{22}=0.76$; $d_{33}=-0.55$	0.064	167	180	This work
KB ₄ O ₆ F ^a	Cal.	$R32$	4.365	4.365	23.983	395.650	7.53	$d_{22}=1.00$	0.083	165	176	This work
KCaCO ₃ F	Cal.	$P\bar{6}m2$	5.097	5.097	4.455	100.231	6.31	$d_{11}=1.33$	0.112	197	197	[75]
	Exp.	$P\bar{6}m2$	5.063	5.063	4.576	101.577	≥6.30	~3.3×KDP	-	≤200	-	[35]
KBeCO ₃ F ^a	Cal.	$Amm2$	5.444	5.444	2.970	83.875	7.61	$d_{11}=-0.70$; $d_{12}=0.94$	0.129	164	163	[35]
KAlCO ₃ F ₂ ^a	Cal.	$P\bar{6}2c$	4.699	4.699	10.473	200.289	8.41	$d_{22}=0.73$	0.108	148	147	[35]
AlNO ₃ F ₂ ^a	Cal.	$P\bar{6}2c$	4.773	4.773	8.672	171.088	7.18	$d_{22}=1.63$	0.178	174	174	[77]
KSIBO ₃ F ₂ ^a	Cal.	$P\bar{6}$	4.749	4.749	10.302	201.195	8.47	$d_{16}=0.48$	0.060	147	178	This work
KSIB ₃ O ₆ F ₂ ^a	Cal.	$P\bar{6}$	6.820	6.820	8.663	348.944	7.75	$d_{16}=0.53$	0.100	161	161	This work
PBO ₃ F ₂ ^a	Cal.	$P\bar{6}2c$	4.683	4.683	9.575	181.817	9.21	$d_{16}=0.61$	0.076	135	155	[81]
PB ₃ O ₆ F ₂ ^a	Cal.	$P\bar{6}2c$	6.862	6.862	9.089	370.619	9.10	$d_{16}=0.45$	0.099	137	137	[81]
H-site substitute												
KBe ₂ BO ₃ Cl ₂ ^a	Cal.	$R32$	4.304	4.304	26.162	419.682	7.63	$d_{22}=0.39$	0.005	163	N/A	This work
KBe ₂ BO ₃ H ₂ ^a	Cal.	$R32$	4.264	4.264	16.863	265.562	6.70	$d_{22}=0.59$	0.016	186	N/A	This work
KBe ₂ BO ₃ (OH) ₂ ^a	Cal.	$R32$	4.321	4.321	21.269	343.903	6.63	$d_{22}=0.46$	0.057	188	250	This work
Without A-site												
α-Be ₂ BO ₃ F	Cal.	$C2$	4.283	4.283	8.559	130.169	8.40	$d_{15}=0.02$	0.077	148	180	[82]
	Exp.	$C2$	4.438	4.438	8.699	141.870	≥6.70	~0.3×KDP	-	≤186	-	[82]
γ-Be ₂ BO ₃ F	Cal.	$R32$	4.283	4.283	12.288	195.176	8.88	$d_{12}=0.63$	0.094	140	149	[36]
	Exp.	$R32$	4.440	4.440	12.470	212.870	≥6.30	~2.3×KDP	-	≤200	-	[37]
YCO ₃ F ^a	Cal.	$P\bar{6}2c$	4.747	4.747	4.395	85.761	7.40	$d_{11}=2.62$	0.197	168	168	[77]
AlCO ₃ F ^a	Cal.	$P\bar{6}2c$	4.793	4.793	3.414	67.920	8.51	$d_{22}=0.98$	0.153	146	146	[77]
Be ₂ CO ₃ F ₂ ^a	Cal.	$R32$	4.215	4.215	14.180	218.167	8.46	$d_{22}=0.87$	0.111	147	155	[77]
SiCO ₃ F ₂ ^a	Cal.	$P\bar{6}2c$	4.658	4.658	9.434	177.261	9.64	$d_{22}=0.96$	0.135	129	129	[77]

a) represents that the compounds are theoretically designed.

(NH₄⁺), we directly obtained NH₄Be₂BO₃F₂ (ABBF) with *R*3 symmetry by selecting the same polar-axis of NH₄⁺ [36]. Clearly, ABBF is analogous to KBBF, and its size is between those of KBBF and RBBF (Table 1) because the radius of NH₄⁺ is between those of K⁺ and Rb⁺. Based on the “NLO-size effect, ABBF’s Δ*n* is expected to be smaller than that of KBBF while larger than that of RBBF/CBBF.

Calculations show that ABBF has close λ_{UV} (~150 nm) and *d*₂₂ (~1.2×KDP) to those of KBBF, RBBF and CBBF. However, the λ_{PM} is red-shifted from KBBF to ABBF, RBBF and CBBF. ABBF exhibits comparable DUV NLO properties with RBBF, demonstrating it could theoretically achieve the DUV 193.7 nm-output like RBBF. The

dynamical stability of ABBF was further verified by phonon calculations. The phonon spectra of ABBF and KBBF are similar, with no imaginary phonon mode observed (Fig. S1), indicating that ABBF is dynamically stable as KBBF. In fact, the compound has been obtained in recent experiments [37]. The calculated bulk and Young moduli revealed that ABBF has more favorable mechanical properties than KBBF, especially in the *c*-direction [36].

In short, ABBF is a newly obtained KBBF-family member using our proposed modeling system. In addition to NH₄⁺, some other groups, e.g., CH₃NH₃⁺, HC(NH₂)₂⁺, CH₃C(NH₂)₂⁺, C(NH₂)₃⁺, (CH₃)₃NH⁺, and (CH₃)₂C(H)-

NH_3^+ , may be used as the *A*-site cationic candidates to form the ABBF analogues. For example, we have also designed $\text{CH}_3\text{NH}_3\text{Be}_2\text{BO}_3\text{F}_2$ (MABBF) to show the related NLO properties. The size of the MA is larger than that of NH_4^+ especially along the *c*-axis, so its Δn becomes smaller than that of ABBF. Table 1 lists its NLO properties, demonstrating that it cannot achieve the DUV output ($\lambda_{\text{PM}} > 200$ nm) although its E_g is large enough (~ 7.9 eV).

NaCaBe₂B₂O₆F, *NaSr₃Be₃B₃O₉F₄* and *BaBe₂BO₃F₃*

If some oxygen-bridged bonds are added instead of ionic interactions between layers, the growth property would be improved, which can be shown from the single-layered KBBF-type structures and double-layered $\text{Sr}_2\text{Be}_2\text{B}_2\text{O}_7$ -type structures [61]. However, the dangling orbitals of the O^{2-} -bridge atoms reduce the E_g . In order to improve the interlayer connection with few nonbonding states, using F-bridge bonds instead of O-bridge bonds is considered as a good strategy, e.g., in $\text{NaCaBe}_2\text{B}_2\text{O}_6\text{F}$ and $\text{NaSr}_3\text{Be}_3\text{B}_3\text{O}_9\text{F}_4$ [62,63]. For $\text{NaCaBe}_2\text{B}_2\text{O}_6\text{F}$, the SHG effect is only $0.5\times\text{KDP}$ because of the non-parallel alignment of $(\text{BO}_3)^{3-}$ (Fig. 2c). For $\text{NaSr}_3\text{Be}_3\text{B}_3\text{O}_9\text{F}_4$, the layer-structure declines to an umbrella shape but not an ideal plane, so Δn becomes smaller than that of KBBF (Fig. 2d). This crystal cannot produce the DUV SHG output although it has strong SHG effect ($\sim 2\times\text{KDP}$) and large-size crystal ($\sim 13\text{ mm} \times 14\text{ mm} \times 20\text{ mm}$) [64].

In addition, using alkaline earth metals, e.g., Ca^{2+} , Sr^{2+} , Ba^{2+} , as the *A*-site cations might enhance the interlayer interaction. $\text{BaBe}_2\text{BO}_3\text{F}_3$ (BBBF) is an example with layer-structures as shown in Fig. 2e [65]. Unfortunately, this structure exhibits too small SHG effect because of the anti-parallel arrangement of $(\text{BO}_3)^{3-}$. If $(\text{BO}_3)^{3-}$ can be aligned in a parallel pattern, BBBF would exhibit large SHG effect and achieve the DUV PM output.

From the above discussion, one may conclude that the *A*-site cationic substitute, one of the most important ways to enrich the KBBF-like system, can be used to modulate the NLO response of active anionic units for achieving the DUV NLO balance. In the practical design strategies, basically, K^+ is the first choice of *A*-site cations for $A_iB_jG_mH_n$ -type compounds. Meanwhile, NH_4^+ can be a candidate for improving the interlayer connection. In addition, Ba^{2+} is also suitable to be the *A*-site cation when the charge should be balanced, which can still maintain an effective DUV NLO capability.

B-site cationic substitute

The *B*-site cations include Be^{2+} , Al^{3+} , Zn^{2+} , Sc^{3+} , etc., which are usually attached to the anionic groups to

constitute the skeleton structures. The primary role of *B*-site cations in DUV NLO crystals is to saturate the nonbonding states and keep an anisotropic NLO-active structure.

BaAlBO₃F₂, *Rb₃Al₃B₃O₁₀F* and *KAlBO₃F*

$\text{BaAlBO}_3\text{F}_2$ (BABF) is a typical NLO crystal with $E_g \approx 7.5$ eV and $d_{22} \approx 3\times\text{KDP}$ [66]. Fig. 3a shows its KBBF-like structure composed by $(\text{AlBO}_3\text{F}_2)_\infty^{5-}$ layers. Due to the low structural anisotropy of $(\text{AlO}_3\text{F}_2)^{5-}$, it has too small Δn (~ 0.04) to satisfy the DUV PM requirement. Even if we introduce Ca^{2+} instead of Ba^{2+} to reduce the size according to the “size-effect”, the Δn just increases from 0.04 to 0.05, still insufficiently large. Introducing alkali-metal cations instead of Ba^{2+} and interlayer F-bridged bond instead of F–Ba ionic bond are feasible to enlarge Δn . This can be shown by experimental $\text{Rb}_3\text{Al}_3\text{B}_3\text{O}_{10}\text{F}$ [67], which features a framework composed by $(\text{Al}_3(\text{BO}_3)_3\text{OF})_\infty$ layers and Al–F bridged bonds (Fig. 3b). However, calculations show that $\Delta n \approx 0.06$ and $E_g \approx 6.6$ eV are still not large enough, which result in inapplicable $\lambda_{\text{PM}} \approx 235$ nm. Similar case includes another experimental $\text{K}_3\text{Ba}_3\text{Li}_2\text{Al}_4\text{B}_6\text{O}_{20}\text{F}$ [68].

To enlarge the DUV E_g and Δn , we designed two structures, KAlBO_3F and $\text{KAl}_2\text{B}_2\text{O}_6\text{F}$, as shown in Fig. 3c and d. Note that $(\text{AlO}_3\text{F}_2)^{5-}$ bipyramids are connected by $(\text{BO}_3)^{3-}$ triangles to form the $(\text{Al}_3\text{B}_3\text{O}_6\text{F}_6)$ -rings, which are further linked by the apical F to form 3D framework. Such a structure makes these compounds exhibit larger E_g (~ 7.2 and 6.5 eV) and Δn (~ 0.08 and 0.09) than those of $\text{Rb}_3\text{Al}_3\text{B}_3\text{O}_{10}\text{F}$, so both can achieve the PM SHG output below 200 nm ($\lambda_{\text{PM}} \approx 182$ and 192 nm). Although they cannot output the practical 177.3-nm laser through 6HG, they are at least available for 193.7 nm-laser output. Moreover, they are dynamically stable from the analysis of phonon spectra (Fig. S1), indicating the synthesis possibility in the experiments.

BaZnBO₃F, *KZn₂BO₃F₂* and *KREBO₃F* (*RE* = Sc, Y, La)

One can also consider Zn^{2+} as a possible *B*-site cation due to its chemical similarity as Be^{2+} . BaZnBO_3F belongs to this NLO crystal with $E_g \approx 5.6$ eV and $d_{ij} \approx 3\times\text{KDP}$ [69]. Obviously, its E_g becomes too small to be transparent to DUV light due to relatively weak Zn–O coupling. For $\text{KZn}_2\text{BO}_3\text{F}_2$ with designed KBBF-like structure, its $E_g \approx 6.3$ eV is also not suitable. Basically, small E_g is the reason why Zn-based KBBF-like structures cannot be applied as DUV NLO materials.

As an alternative to *B*-site cation, rare-earth-metal-based compounds greatly enrich the NLO borate field,

Figure 3 Structures of $\text{BaAlBO}_3\text{F}_2$ (a), $\text{Rb}_3\text{Al}_3\text{B}_3\text{O}_{10}\text{F}$ (b), KAlBO_3F (c), $\text{KAl}_2\text{B}_2\text{O}_6\text{F}$ (d), $\text{KBe}_2\text{B}_3\text{O}_6\text{F}_2$ (e) and $\text{BaAlB}_3\text{O}_6\text{F}_2$ (f).

including $\text{YAl}_3(\text{BO}_3)_4$ [31], LaBeB_3O_7 [70], $\text{REBe}_2\text{B}_5\text{O}_{11}$ ($\text{RE}=\text{Y}, \text{Gd}$) [71], which exhibit potential DUV NLO capabilities. The RE-site atoms usually include Sc^{3+} , Y^{3+} and La^{3+} . Accordingly, we designed a series of KBBF-like RE-based borates of KREBO_3F ($\text{RE}=\text{Sc}, \text{Y}, \text{La}$) similar to KAlBO_3F . Their NLO properties show that only KScBO_3F can achieve the DUV output whereas KYBO_3F and KLaBO_3F cannot because of their relatively small E_g . Note that KScBO_3F exhibits much larger SHG effect ($\sim 5\times\text{KDP}$) than most of the DUV materials ($1\text{--}3\times\text{KDP}$), so it can achieve much higher conversion efficiency, which is an advantage of this NLO class.

From the discussion of this section, the B-site cationic substitute is an effective way for balancing E_g and Δn . Al^{3+} and Sc^{3+} can be used as two B-site candidates. If we choose NH_4^+ (or Li^+) instead of K^+ in KAlBO_3F , $\text{KAl}_2\text{B}_2\text{O}_6\text{F}$ or KREBO_3F , the DUV NLO properties would be tunable and well maintained based on the NLO size-effect.

G-site anionic group substitute

Anionic group theory tells us covalent borate anionic groups play a dominant role in the NLO responses. There are four main anionic groups in borates, i.e., $(\text{B}_3\text{O}_6)^{3-}$ (e.g., in BBO), $(\text{B}_3\text{O}_7)^{5-}$ (e.g., in LBO), $(\text{BO}_3)^{3-}$ (e.g., in

KBBF) and $(\text{BO}_4)^{5-}$ (e.g., in SrB_4O_7) [72], which are considered as four NLO material genomes (of course, it is also reasonable to consider that BO_3 and BO_4 are two basic units in borates, while B_3O_6 and B_3O_7 or B_2O_5 , B_5O_{10} , etc. are composite building blocks), exhibiting exciting structural chemistry with a great variety of connection and arrangement patterns [73].

$\text{KBe}_2\text{B}_3\text{O}_6\text{F}_2$, $\text{BaAlB}_3\text{O}_6\text{F}_2$, $\text{NH}_4\text{B}_4\text{O}_6\text{F}$ and $\text{BaB}_4\text{O}_6\text{F}_2$

As an important NLO unit, $(\text{B}_3\text{O}_6)^{3-}$ in BBO exhibits wide E_g ($\sim 6.7\text{ eV}$), strong d_{ij} ($\sim 2\times\text{KDP}$) and large Δn (~ 0.10). Although it seems to achieve the DUV NLO balance, it cannot be used for DUV due to its unavailable $\lambda_{\text{PM}} \approx 204\text{ nm}$, mainly originating from relatively small E_g [25]. Note that the refractive dispersion of BBO is not as good as that of KBBF, which is another important reason why its PM ability is lower than that of KBBF. If the non-bonding states could be removed by coordinating covalent elements such as Be^{2+} or Al^{3+} with $(\text{B}_3\text{O}_6)^{3-}$, the system may become a DUV NLO material. Accordingly, based on KBBF and BABF, we designed two compounds $\text{KBe}_2\text{B}_3\text{O}_6\text{F}_2$ and $\text{BaAlB}_3\text{O}_6\text{F}_2$, respectively, using $(\text{B}_3\text{O}_6)^{3-}$ instead of $(\text{BO}_3)^{3-}$ and $\text{Be}^{2+}/\text{Al}^{3+}$ as the B-site cations. Fig. 3e, f display their structures, in which the sizes within

the *a-b* plane are expanded by about 50% and squeezed by about 30% along the *c*-axis. As a result, the structural anisotropy is greatly enlarged from KBBF to $\text{KBe}_2\text{B}_3\text{O}_6\text{F}_2$ and $\text{BaAlB}_3\text{O}_6\text{F}_2$ to $\text{BaAlB}_3\text{O}_6\text{F}_2$, making their Δn and SHG effect greatly enhanced. Table 1 shows that Δn and d_{22} (0.12 and 0.83 pm V^{-1} for $\text{KBe}_2\text{B}_3\text{O}_6\text{F}_2$; 0.086 and 1.01 pm V^{-1} for $\text{BaAlB}_3\text{O}_6\text{F}_2$) are much larger than those of KBBF (0.059 and 0.41 pm V^{-1}) and BABF (0.037 and 0.70 pm V^{-1}). Thus, their λ_{PM} are blue-shifted from 172 to 167 nm and 235 to 200 nm.

Unfortunately, they are not dynamically stable due to the heavy virtual frequencies in phonon spectra (Fig. S1), which are mainly caused by the vibration modes from $\text{BeO}_3\text{F}-\text{B}_3\text{O}_6$ and $\text{AlO}_3\text{F}_2-\text{B}_3\text{O}_6$ groups. It is why similar structures are rare in ICSD. If we introduce $(\text{BO}_3\text{F})^{4-}$ to replace $(\text{BeO}_3\text{F})^{5-}$ in the structure to form $(\text{B}_4\text{O}_7\text{F})^-$ group, the instabilities may be eliminated and the DUV capability would be improved. A typical example from recent experiments is $\text{NH}_4\text{B}_4\text{O}_6\text{F}$ (ABF) with a wave-like layer-framework linked by NH_4^+ as shown in Fig. 4a [40]. Its NLO properties are excellent, including $E_g \approx 8.0 \text{ eV}$, $d_{ij} \approx 3 \times \text{KDP}$, $\Delta n \approx 0.13$ and $\lambda_{\text{PM}} \approx 158 \text{ nm}$. Another example is $\text{BaB}_4\text{O}_6\text{F}_2$, which is designed theoretically and can achieve the DUV PM output of 180 nm [74]. Herein, we have also designed two novel structures, i.e., $\text{KB}_2\text{O}_3\text{F}$ and $\text{KB}_4\text{O}_6\text{F}$, with single-layer structure and double-layer structure as shown in Fig. 4b, c. Table 1 shows that they exhibit large $E_g \approx 7.5 \text{ eV}$, $d_{22} \approx 2\text{--}2.5 \times \text{KDP}$ and $\Delta n \approx 0.06\text{--}0.08$, so they can achieve DUV PM output of 180 and 176 nm. Once obtained in experiments, they could be applied for the 193.7 nm/177.3 nm laser.

KCaCO_3F , KBeCO_3F , KAlCO_3F_2 and AlNO_3F_2

Similar to $(\text{BO}_3)^{3-}$, $(\text{CO}_3)^{2-}$ and $(\text{NO}_3)^-$ units exhibit planar triangle structures, so they are good units beneficial to

large d_{ij} and Δn . KCaCO_3F is a typical NLO carbonate with strong d_{11} ($\sim 3 \times \text{KDP}$) and Δn (~ 0.11) but small E_g ($\sim 6.3 \text{ eV}$) because Ca^{2+} cannot remove the nonbonding states of $(\text{CO}_3)^{2-}$ (Fig. 4d) [75]. Similar cases include other ABCO_3F -type ($A = \text{K, Rb, Cs}$; $B = \text{Mg, Ca, Sr}$) carbonates [76]. For improving E_g while keeping d_{ij} and Δn suitable, we found an existing compound $\text{Sr}_2\text{AlCO}_3\text{F}_5$ exhibiting larger E_g ($\sim 7.8 \text{ eV}$) than KCaCO_3F because Al^{3+} partially removed the nonbonding states of $(\text{CO}_3)^{2-}$. Accordingly, we designed two series of ABeCO_3F and AAlCO_3F_2 ($A = \text{Li, Na, K, Rb, Cs}$) to evaluate the possible DUV NLO capabilities [35]. KBeCO_3F and KAlCO_3F_2 as two representatives (Fig. 4e, f), have achieved the balance with $E_g \approx 7.6$ and 8.4 eV and $\Delta n \approx 0.13$ and 0.11 , so they can output the DUV PM cutoff wavelength of 163 and 147 nm. Moreover, their SHG effects are larger than that of KBBF. As dynamically stable phases, AAlCO_3F_2 were the first series predicted to break the limit of KBBF with superior PM capabilities, although they have not been obtained in the follow-up experiments.

AlNO_3F_2 is a typical NLO nitrate (Fig. 4g) with the balance of $E_g \approx 7.0 \text{ eV}$ and $\Delta n \approx 0.22$ [77]. It can output a 178 nm-output theoretically. It is the first possible nitrate that we have predicted as a DUV NLO compound. Similar to $(\text{B}_3\text{O}_6)^{3-}$, there is additionally a $(\text{C}_3\text{N}_3\text{O}_3)^{3-}$ unit that exhibits similar structure and NLO properties as BBO [78]. For example, $\text{Ca}_3(\text{C}_3\text{N}_3\text{O}_3)_2$ has large SHG effect ($\sim 3.46 \text{ pm V}^{-1}$) and Δn (~ 0.35) but small E_g ($\sim 5.6 \text{ eV}$). If its nonbonding states can be eliminated as discussed in the case of $(\text{B}_3\text{O}_6)^{3-}$, then it could be used as possible DUV material.

KSiBO_3F_2 , $\text{KSiB}_3\text{O}_6\text{F}_2$, PBO_3F_2 and $\text{PB}_3\text{O}_6\text{F}_2$

In general, the *B*-site elements e.g., Be, Al, Sc, exhibit relatively weaker covalence than B, and tend to form the

Figure 4 Structures of $\text{NH}_4\text{B}_4\text{O}_6\text{F}$ (a), $\text{KB}_2\text{O}_3\text{F}$ (b), $\text{KB}_4\text{O}_6\text{F}$ (c), KCaCO_3F (d), KBeCO_3F (e), KAlCO_3F_2 (f), AlNO_3F_2 (g), KSiBO_3F_2 (h) and $\text{KSiB}_3\text{O}_6\text{F}_2$ (i).

coordination bonds with borate groups. As the increase of covalence, the *B*-site elements will share more electrons with adjacent oxygen atoms to form the covalent bonds. Then these elements are no longer general *B*-site whereas should be defined as *G*-site. Such elements mainly include C, N, Si and P. According to Pauling rules of the chemical formation, C and N are difficult to coordinate with borate groups, so there are almost no known borocarbonates or boronitrates found in the experiments. However, once the covalent *G*-site elements (e.g., Si or P) are coordinated with the borate units, they would remove much more nonbonding states than the coordinated *B*-site elements (e.g., Be or Al). Therefore, it is necessary to evaluate the DUV NLO properties of Si-based and P-based systems since borosilicates and borophosphates are relatively abundant in ICSD. Unfortunately, most of the known borosilicates and borophosphates exhibit small structural anisotropy, so the Δn is not sufficiently large. This is mainly because Si^{4+} and P^{5+} tend to form tetrahedral units such as $(\text{SiO}_4)^{4-}$ and $(\text{PO}_4)^{3-}$, which usually share the vertex-oxygen atoms to form 3D framework structures with low spatial anisotropy.

BPO_4 is a typical borophosphate with tetrahedral $(\text{BO}_4)^{5-}$ and $(\text{PO}_4)^{3-}$ [79]. It has strong SHG effect ($\sim 0.76 \text{ pm V}^{-1}$) and extremely short DUV edge ($\sim 134 \text{ nm}$). However, due to its small Δn (< 0.01), BPO_4 cannot produce the UV PM output. A similar example in borosilicates is LiBSiO_4 with tetrahedral $(\text{BO}_4)^{5-}$ and $(\text{SiO}_4)^{4-}$ [80]. It also exhibits strong SHG effect ($\sim 0.70 \text{ pm V}^{-1}$) and wide E_g ($\sim 8.8 \text{ eV}$) but small Δn (< 0.01), and it cannot satisfy the DUV NLO requirements. If BPO_4 and LiBSiO_4 are expected as DUV NLO materials, they need to expand the structural anisotropy. To achieve this goal, the coplanar $(\text{BO}_3)^{3-}$ or $(\text{B}_3\text{O}_6)^{3-}$ units are introduced to replace $(\text{BO}_4)^{5-}$ and to coordinate with $(\text{PO}_4)^{3-}$ in BPO_4 or $(\text{SiO}_4)^{5-}$ in LiBSiO_4 , thus to form a layered structural topology, which is favorable to exhibiting large E_g since the terminal O^{2-} of $(\text{BO}_3)^{3-}$ or $(\text{B}_3\text{O}_6)^{3-}$ are bonded by P or Si. Meanwhile, new structural units such as (PO_mF_n) or (SiO_mF_n) can be formed by incorporating fluorine into the lattice, which can further remove the dangling bonds and tune the pattern of anionic groups.

Accordingly, KSiBO_3F_2 , $\text{KSiB}_3\text{O}_6\text{F}_2$, PBO_3F_2 and $\text{PB}_3\text{O}_6\text{F}_2$ were designed as the representative KBBF-like borosilicates and borophosphates (Figs 4h, i and 5a, b) [81]. Since the nonbonding states are eliminated, KSiBO_3F_2 , $\text{KSiB}_3\text{O}_6\text{F}_2$, PBO_3F_2 and $\text{PB}_3\text{O}_6\text{F}_2$ can be transparent in the DUV region. Table 1 lists their calculated E_g , d_{ij} , Δn and λ_{PM} . Compared with LiBSiO_4 ,

KSiBO_3F_2 and $\text{KSiB}_3\text{O}_6\text{F}_2$ exhibit slightly smaller E_g (~ 8.5 and 7.7 eV), weaker d_{ij} (~ 0.48 and 0.53 pm V^{-1}), larger Δn (~ 0.06 and 0.10) and shorter λ_{PM} (~ 178 and 161 nm), thus exhibiting superior DUV PM abilities. Compared with BPO_4 , PBO_3F_2 and $\text{PB}_3\text{O}_6\text{F}_2$ have comparable E_g (~ 9.2 and 9.1 eV), weaker d_{ij} (~ 0.61 and 0.45 pm V^{-1}), larger Δn (~ 0.08 and 0.10) and shorter λ_{PM} (~ 155 and 137 nm), also exhibiting superior DUV PM abilities.

From the discussion of this section, the *G*-site substitute is important to expand the systems with potential DUV NLO properties. In general, $(\text{BO}_3)^{3-}$ exhibits a relatively large E_g but small Δn , $(\text{NO}_3)^-$ exhibits a relatively large Δn but small E_g , and $(\text{CO}_3)^{2-}$ can achieve large E_g and Δn . However, borate-based anionic groups are more favorable to form some complex framework groups with other groups such as borate, silicate and phosphate groups than nitride or carbonate groups, which still play a dominant role in the DUV NLO field.

H-site anionic substitute

The *H*-site anions are important for DUV NLO structures, which can eliminate the nonbonding states, adjust the NLO structure and balance the electronic charge. As the most effective *H*-site choice, fluoride possesses larger electronegativity and smaller atomic radius than oxygen. Therefore, fluoride oxides usually exhibit larger E_g than other kinds of oxides.

In addition, F can be introduced into some basic anionic units such as $(\text{BeO}_4)^{6-}$ or $(\text{BO}_4)^{5-}$ tetrahedral groups to form $(\text{BeO}_3\text{F})^{5-}$ or $(\text{BO}_3\text{F})^{4-}$ quasi-plane groups. As a result, the fluoride-oxide groups may exhibit relatively large structural anisotropy for large Δn . If F is replaced by other *H*-site anions such as Cl^- , H^- , and OH^- , the resulting $\text{KBe}_2\text{BO}_3\text{X}_2$ ($\text{X} = \text{Cl}, \text{H}, \text{OH}$) may not exhibit available DUV NLO properties as shown in Table 1.

Without A-site cations

As an important supplement of *A*-site substitute, reducing the *A*-site cationic size to zero will further enhance the DUV NLO properties in the KBBF system based on the “NLO size-effect”. If some kinds of 2D layers can be formed by introducing the planar anionic units (e.g., $(\text{BO}_3)^{3-}$ or $(\text{CO}_3)^{3-}$), the structural anisotropy will be enlarged and the DUV PM conditions are possibly satisfied, which can be successfully shown in the following cases from $\alpha\text{-Be}_2\text{BO}_3\text{F}$ in Fig. 5c to $\gamma\text{-Be}_2\text{BO}_3\text{F}$ in Fig. 5d.

Bridge-bonded layer-structures and $\text{Be}_2\text{BO}_3\text{F}$

$\text{Be}_2\text{BO}_3\text{F}$ has an existing α -phase derived from KBBF by removing one K^+ and F^- . It has large Δn (~ 0.08) and short

Figure 5 Structures of PBO_3F_2 (a), $\text{PB}_3\text{O}_6\text{F}_2$ (b), $\alpha\text{-Be}_2\text{BO}_3\text{F}$ (c), $\gamma\text{-Be}_2\text{BO}_3\text{F}$ (d), $\text{Y/AlCO}_3\text{F}$ (e) and $\text{Be}_2\text{CO}_3\text{F}_2$ (f).

λ_{PM} (~ 180 nm), but small SHG effect ($\sim 0.2 \times \text{KBBF}$) [82]. The adjacent $(\text{Be}_2\text{BO}_3\text{F}_2)_\infty$ layers are interconnected by the bridge F^- anions, resulting in densely stacked layers. If the borate groups are parallel-aligned as illustrated in Fig. 5d, the total SHG response will be strengthened. From our calculations in Table 1, the Δn and d_{12} of the designed γ -phase are 0.10 and $1.5 \times \text{KBBF}$, respectively [36]. Its λ_{PM} can reach 149 nm, blue-shifted by about 12 nm than that of KBBF. Fortunately, this sample was obtained in the experiments and reported recently [37]. The available experimental measurements are consistent with our predictions, guaranteeing our modeling system suitable to some extent.

Some similar F-bridge layer-framework systems can be also designed theoretically, e.g., YCO_3F and AlCO_3F as shown in Fig. 5e. Based on the existing NLO carbonate YCO_3OH with $E_g \approx 7.2$ eV, $d_{36} \approx \text{KDP}$, $\Delta n \approx 0.06$ and $\lambda_{\text{PM}} \approx 255$ nm, we have constructed a layer YCO_3F structure by introducing F instead of OH to enlarge the polarity and anisotropy [83]. From the DFT calculations as listed in Table 1, indeed the NLO response and Δn are greatly enlarged, respectively from 0.5 to 2.6 pm V^{-1} and 0.06 to 0.20 pm V^{-1} . Accordingly, YCO_3F can realize the practical DUV 177.3 nm SHG output since its $\lambda_{\text{PM}} \approx 168$ nm. In order to further enlarge E_g , we can introduce Al^{3+} to replace Y^{3+} to coordinate with $(\text{CO}_3)^{2-}$. The results show that E_g of AlCO_3F is actually increased while maintaining Δn sufficiently large (~ 0.15). Thus, λ_{PM} of AlCO_3F is blue-shifted from 168 to 146 nm. Meanwhile, the NLO coefficient is $2.5 \times \text{KDP}$, available for the sufficient DUV conversion. All the analysis indicates that the polar F-bridge layer-frameworks without A-site cations are indeed beneficial to the DUV PM output with sufficient

NLO effect.

vdW-connected layer-structures and $\text{Be}_2\text{CO}_3\text{F}_2$

The dense-stacking layer-frameworks without A-site cations belong to another kind of DUV NLO structures. The key strategy is to use the interlayer van der Waals (vdW) interaction instead of conversational ionic interaction to make the adjacent layers connected densely. The kind of vdW layers is demonstrated in Fig. 5f, in which we introduce the $(\text{Be}_2\text{CO}_3\text{F}_2)_\infty$ carbonate layers to replace the $(\text{Be}_2\text{BO}_3\text{F}_2)_\infty$ borate layers in KBBF [77]. Note that $(\text{Be}_2\text{CO}_3\text{F}_2)_\infty$ itself is an NLO-active layer structure with large anisotropy, polar alignment and few nonbonding states. As the produced crystal, $\text{Be}_2\text{CO}_3\text{F}_2$ can exhibit large $\Delta n \approx 0.11$, strong $d_{11} \approx 2 \times \text{KBBF}$, and short $\lambda_{\text{PM}} \approx 155$ nm (Table 1), which is expected to be a possible DUV NLO system. Moreover, its type-I (o+o $\rightarrow$ a) PM angle θ at 177.3 nm is about 56° , so its d_{eff} is about 3.3 times larger than that of KBBF. Under the same laser and crystal conditions, its output power would be about 10 times larger than that of KBBF.

There are no interlayer atoms in $\text{Be}_2\text{CO}_3\text{F}_2$, resulting in the more densely stacked layers. We can also design similar vdW layers such as SiCO_3F_2 , which consists of polar $(\text{SiCO}_3\text{F}_2)_\infty$ layers formed by $(\text{SiO}_3\text{F}_2)^{4-}$ and $(\text{CO}_3)^{2-}$. Its NLO properties are listed in Table 1, including short $\lambda_{\text{UV}} (\sim 129 \text{ nm})$, strong $d_{ij} (\sim 1 \text{ pm V}^{-1})$ and large $\Delta n (\sim 0.13)$. Compared with $\text{Be}_2\text{CO}_3\text{F}_2$, SiCO_3F_2 exhibits a larger E_g due to the stronger covalence of Si than Be. Considering the close d_{ij} and Δn , it can realize a shorter DUV output ($\lambda_{\text{PM}} \approx 129 \text{ nm}$), which is the theoretically shortest wavelength in the DUV NLO crystal field. Other structures include AlNO_3F_2 , PBO_3F_2 and $\text{PB}_3\text{O}_6\text{F}_2$ as listed in

Table 1, indicating the possible DUV NLO properties induced by polar vdW layer structures without A-site cations [77].

CONCLUSIONS

In summary, we systematically evaluated the DUV NLO capabilities induced by the A-site, B-site, G-site and H-site parts in the KBBF-type structures. These studies are mainly based on our developed computer-aided modeling system, which are efficiently accurate and can serve as a blueprint for DUV NLO materials exploration and design. Importantly, high-throughput calculations can also be performed in other broader systems according to our proposed modeling and evaluation flowchart. In the current stage, finding a compound with possible DUV NLO properties from ICSD is of great difficulty. Therefore, the comprehensive materials design and analysis using effective theoretical modeling proposal is urgently necessary for current and future DUV NLO researches [84,85].

As summarized in Fig. 6, dozens of typical KBBF-type structures, regardless existing or hypothetical, are evaluated based on the structure-selections and first-principles calculations (for details see Table S1). The evaluation standard of DUV NLO crystals is finalized and further illustrated by the coordinate of the shortest SHG wavelength λ_{PM} and SHG effect d_{ij} . As the practical laser sources, 193.7 and 177.3 nm are selected as two important redlines for DUV generation. Moreover, KBBF is marked by black stars as the benchmark DUV NLO crystal ($d_{22} = 0.45 \text{ pm V}^{-1}$ vs. $\lambda_{\text{PM}} = 161 \text{ nm}$). BBO and $\text{YAl}_3(\text{BO}_3)_4$ (YAB), which are two typical NLO materials in the DUV region, are used as two referenced NLO crystals with $2 \times \text{KBBF}$ vs. 204 nm and $3.9 \times \text{KBBF}$ vs. 210 nm, respectively.

Circular dots are those experimentally obtained crystal structures. Among them, 14 compounds including RBBF [57], CBBF [58], NBBF [59], ABBF [37], $\text{BaBe}_2\text{BO}_3\text{F}_3$ [65], $\text{MB}_5\text{O}_7\text{F}_3$ (M = Ca, Sr) [43], $\text{NaB}_4\text{O}_6\text{F}$ [86], $\text{RbB}_4\text{O}_6\text{F}$ [41], $\text{CsB}_4\text{O}_6\text{F}$ [39], $\text{CsKB}_8\text{O}_{12}\text{F}_2$ [41], $\alpha\text{-BBF}$ [82], $\gamma\text{-BBF}$ [37] and ABF [40] exhibit possible DUV NLO properties from available experimental and calculated results. In particular, $\gamma\text{-BBF}$ and ABF are expected to have superior DUV SHG capabilities than KBBF. Therein, both of them are located at the preferred area of DUV NLO materials with shorter λ_{PM} ($< 161 \text{ nm}$) and larger $|d_{ij}|_{\text{max}}$ ($> \text{KBBF}$) in the green shadow of Fig. 6. Red pentagrams are our designed systems, including 12 compounds proposed in the previous studies and 18 new structures predicted in this work. Among them, 20 crystals exhibit possible DUV NLO output properties with six located in the preferred

Figure 6 Evaluation standard of DUV NLO crystals by the coordination of d_{ij} and λ_{PM} . DUV NLO properties of the typical existing and designed structures are evaluated. The preferred area is shown as the green shadow.

area. In particular, ABBF and $\gamma\text{-BBF}$ are two successful systems that were first predicted theoretically and then obtained experimentally. It should be pointed out that quasi-phase matching technique is also a very promising method for the DUV generation, especially for those NLO crystals with small birefringence but large optical non-linearity (e.g., SrB_4O_7 or BPO_4) [72,79]. Although it may have higher requirements for the engineering and design of NLO materials, once realized, it will promote the development of DUV laser field [87].

Depending on the computer-aided modeling system, we predict seven novel structures for the first time including KAlBO_3F , $\text{KAl}_2\text{B}_2\text{O}_6\text{F}$, KScBO_3F , $\text{KB}_2\text{O}_3\text{F}$, $\text{KB}_4\text{O}_6\text{F}$, KSiBO_3F_2 and $\text{KSiB}_3\text{O}_6\text{F}_2$ that can exhibit good DUV NLO properties as shown in Table 1. If we further perform cationic replacement using Rb, Cs, NH_4 instead of K, more NLO compounds with similar properties could be found according to the NLO size-effect. Together with some other systems that we studied previously, e.g., $\text{RbAlCO}_3\text{F}_2$, $\text{BaB}_4\text{O}_6\text{F}_2$, AlNO_3F_2 , PBO_3F_2 , $\text{PB}_3\text{O}_6\text{F}_2$, YCO_3F , $\text{Be}_2\text{CO}_3\text{F}_2$ and SiCO_3F_2 [35,74,77,81], we have acquired several series of possible DUV NLO crystals by the design blueprint, looking forward to further exploration in the experiments. Based on the findings of more DUV NLO structural types, we believe that our proposed first-principles-based modeling system and design blueprint will play a more positive role in the exploration for new DUV NLO materials.

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Author contributions Kang L performed the theoretical calculations. Kang L, Lin Z and Huang B supervised the theoretical analysis and wrote the paper. Liang F gave the academic suggestion. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Phonon vibration spectra of $\text{NaBe}_2\text{BO}_3\text{F}_2$, $\text{LiBe}_2\text{BO}_3\text{F}_2$, KAlBO_3F_2 , $\text{KAl}_2\text{B}_2\text{O}_6\text{F}_2$, $\text{KBe}_2\text{B}_3\text{O}_6\text{F}_2$, $\text{BaAlB}_3\text{O}_6\text{F}_2$, AlCO_3F , SiCO_3F_2 , AlNO_3F_2 , PBO_3F_2 , and $\text{PB}_3\text{O}_6\text{F}_2$, and NLO properties including d_{ij} and λ_{PM} of the compounds in Fig. 6 are available in the online version of the paper.

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深紫外非线性光学晶体设计：基于第一性原理的计算机辅助设计蓝图

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摘要 深紫外非线性光学晶体在当前深紫外全固态激光技术中是不可或缺的，它是通过频率转换产生深紫外相干光的核心元件。由于严苛的性能标准，深紫外非线性光学晶体非常稀少，其新型材料的发现面临巨大挑战。尽管 $\text{KBe}_2\text{BO}_3\text{F}_2$ (KBBF) 晶体对于许多当前的用途已经非常出色，但是深紫外科学的发展需要深紫外非线性光学晶体具有更短的输出波长和更大的倍频效应，以满足更高精度和更高功率的深紫外激光需求。因此，如何有效地设计深紫外非线性光学晶体一直是非线性材料科学领域的一个核心问题。回顾非线性材料的发展，理论设计和模拟对非线性光学机理的理解和非线性材料的探索都是一种有效且高效的方案。为了进一步加速深紫外非线性材料的探索进程，在本文中，我们总结并提出了一套功能全面的计算机辅助建模系统和设计蓝图，该系统可用于高效且严格地评估候选材料的深紫外非线性光学性能。依靠此建模系统，我们不仅可以丰富对非线性光学结构与性能关系的理解，而且能够从许多已知的和设计的结构出发，根据不同的结构类型和化学组分，系统研究其深紫外非线性光学的具体特性。基于此设计蓝图，我们总结了二十多种可能的深紫外非线性光学晶体结构，并首次预言了能够呈现出潜在的深紫外非线性光学性能的七种新颖结构。我们相信，这套计算机辅助建模系统和设计蓝图将会在探索新型深紫外非线性光学材料的进程中发挥重要作用。