Unbiased screening of deep-ultraviolet and mid-infrared nonlinear optical crystals: Long-neglected covalent and mixed-cation motifs

Jizhang Wang ,^{1,2} Meng Ye,^{3,*} Xiaomi Guo,¹ Yang Li,¹ Nianlong Zou,¹ He Li,^{1,4} Zetao Zhang,¹ Sibo Zhao,¹

Zhiming Xu[®],¹ Haowei Chen,¹ Dezhao Wu[®],¹ Ting Bao[®],¹ Yong Xu[®],^{1,5,6,†} and Wenhui Duan^{®1,5,4}

¹State Key Laboratory of Low Dimensional Quantum Physics and Department of Physics, Tsinghua University, Beijing 100084, China ²School of Physics, Peking University, Beijing 100871, China

³Graduate School of China Academy of Engineering Physics, Beijing 100193, China

⁴Institute for Advanced Study, Tsinghua University, Beijing 100084, China

⁵Frontier Science Center for Quantum Information, Beijing, China

⁶RIKEN Center for Emergent Matter Science (CEMS), Wako, Saitama 351-0198, Japan

(Received 12 March 2024; revised 15 June 2024; accepted 30 July 2024; published 19 August 2024)

One of the most important nonlinear optical (NLO) effects is the second-harmonic generation (SHG), and crystals with strong SHG effects are called NLO crystals. The traditional anion group theory has guided the early discovery of NLO crystals, but the variety of NLO-active motifs discovered so far is limited. In this study, material-type unbiased high-throughput first-principles calculations are performed to screen thousands of materials in a materials database for NLO crystals at target frequencies. The electronic, linear, and nonlinear optical properties of these materials are calculated. Among them, 40 NLO crystals suitable for mid-infrared (MIR) frequencies and 5 for deep-ultraviolet (DUV) frequencies are identified, from 229 materials to which scissors correction is applied. As an extension, several NLO-active motifs that dominate the SHG response are identified, and they all show good transferability among similar materials. Furthermore, for materials where scissors correction cannot be applied due to the lack of accurate bandgap value in the database, a recommendation list of NLO crystals based on the scaling law of bandgap and SHG susceptibility is presented. The discovery of new NLO crystals at DUV and MIR frequencies and enrich our understanding in the search and design of new NLO crystals.

DOI: 10.1103/PhysRevMaterials.8.085202

I. INTRODUCTION

Nonlinear optical (NLO) crystals, known for their strong second-harmonic generation (SHG) effect, play essential roles in both fundamental science and optical applications [1,2]. The SHG effect doubles the light frequency as it passes through an NLO crystal. This frequency doubling greatly broadens the range of laser frequencies, and can be used in photodetectors [3], optical modulators [4], and pulsed lasers [5]. Additionally, SHG serves as a noncontact probe for structure characterization with high spatial and time resolution [6].

Until now, commonly used NLO crystals, such as β -BaB₂O₄ (β -BBO) [7], LiB₃O₅ (LBO) [8] and KBe₂B₂O₆F₂ (KBBF) [9], are all discovered with the guidance of the anion group theory [10]. Anion group theory suggests that the primary contribution to static second-harmonic generation arises from the optical response of the anion group [11]. Recent *ab initio* calculations by Lei *et al.* reveal that orbitals from the top valence bands significantly impact SHG coefficients [12]. Hence, identifying NLO-active motifs with substantial SHG coefficients remains crucial in the search for NLO crystals.

However, the searching of NLO crystals in the deepultraviolet (DUV; wavelength $\lambda \leq 200$ nm or energy $\hbar\omega > 6.2 \text{ eV}$) and mid-infrared (MIR; wavelength 3 µm < $\lambda < 5$ µm or energy 0.25 eV < $\hbar\omega < 0.41 \text{ eV}$) frequencies faces limitations. Firstly, materials satisfying the criteria of NLO crystals working in DUV and MIR frequencies are rare due to the conflict requirement of a substantial bandgap/laser damage threshold and a large static SHG susceptibility [13,14]. Furthermore, due to the strict criteria, the traditional searching methods of NLO-active motifs based on chemical intuitions are inefficient. Even if an NLO-active motif is identified in one specific material, the transferability of the NLO-active motif among similar materials is not guaranteed.

As computational capacity rapidly increases, highthroughput calculations at the *ab initio* level have become an efficient method for predicting materials with desired NLO properties. Recently, high-throughput NLO screening has been applied to specific material types, such as borates [15] and chalcogenides [16], to screen out new NLO candidates, as many previously known NLO crystals are from these two material types. Moreover, material-type unbiased highthroughput calculations can lead to the discovery of diverse NLO-active motifs [17].

In this work, we performed material-type unbiased highthroughput first-principles calculations to study the electronic, linear, and nonlinear optical properties of more than 2000 materials from the Materials Project (MP) database [18]. Based on high-accuracy calculations of 229 materials, we screened out 5 NLO candidates working in the DUV

^{*}Contact author: mye@gscaep.ac.cn

[†]Contact author: yongxu@mail.tsinghua.edu.cn

frequencies and 40 NLO candidates working in the MIR frequencies. The majority of these candidates are covalent materials, oxides, and ionic crystals with mixed anions. Furthermore, through ab initio calculations we identified several novel NLO-active motifs in covalent materials, oxides and mixed anion crystals with substantial SHG contribution and good transferability. Additionally, we proposed an intuitive method to identify NLO-active motifs in ionic crystals, which serves as a coarse filter for discovering new NLOactive motifs. Finally, we presented a recommendation list for NLO candidates screened from 2389 materials calculated at medium accuracy based on a proposed NLO indicator. Our NLO crystal screening approach will significantly accelerate the experimental discovery of NLO crystals and our discovery of NLO-active motifs with good transferability will enrich our understandings of searching and designing NLO crystals.

II. METHODS

A. Electronic structure

We began with structures provided by the MP database and conducted first-principles calculations with the package OpenMX [19,20] to obtain band structures and the density functional theory (DFT) Hamiltonian. We adopted the exchange-correlation functional in the Perdew-Burke-Ernzerhof (PBE) [21] form and utilized norm-conserving pseudopotentials proposed by Morrison et al. [22]. The total energy is converged to within 3×10^{-8} hartree and the k-mesh density for self-consistent calculations exceeded 80³ Å³. In OpenMX, wavefunctions are spanned by a set of pseudo-atomic basis. We verified that our basis sets for highthroughput calculations yield similar band structures to those provided by the MP database. The pseudo-atomic basis for each element is listed in Table S6 within the Supplemental Material [23] (see also Refs. [24,25] therein). The cut-off energy for numerical integration is set to be 300 hartree.

B. Optical responses

Optical responses, including the linear susceptibility tensor $\chi^{(1)}$ and the second-order SHG susceptibility tensor $\chi^{(2)}$, are calculated using the HopTB package [26–28] based on the DFT Hamiltonian obtained from OpenMX. The number of bands we included in calculations is more than four times the number of valence bands. Our tests also show that the *k*-mesh density of 20³ Å³ is enough for the convergence of static SHG in most cases, while we also noticed that a denser *k* mesh is necessary for the convergence of frequency-dependent SHG. The relaxation energy $\hbar\epsilon$ in the optical process was set to be 0.1 eV.

It is worth mentioning that as we did not include spin-polarized materials and spin-orbit coupling in our calculations, spin-up and spin-down bands are doubly degenerate in the whole Brillouin zone and contribute equally to SHG susceptibility. As a result, we only labeled the spin-up bands and their band-resolved SHG in plots of band-resolved SHG, while the degenerate spin-down bands give exactly the same result. The influence of spin-orbit coupling on SHG is left for future investigation. Due to the limitation of our computational method, we did not include excitonic effects. Although excitons play important roles on the linear and SHG susceptibility around the bandgap energy, their influence on the linear and static SHG susceptibility evaluated at $\omega = 0$ eV is very weak. Therefore, computed results of static linear and SHG susceptibility based on the DFT method are still in good agreement with the values measured in experiments [29,30].

III. RESULT AND DISCUSSION

A. Criteria for nonlinear optical crystal

NLO crystals as frequency doubling crystals must satisfy the following criteria. First, a nonzero SHG response occurs only in materials lacking inversion symmetry. This symmetry can be broken either by the crystal structure or by the magnetic structure [31,32].

Second, the bandgap energy E_g of a NLO crystal should be at least twice the energy of the fundamental light [33,34]. Under this condition, the fundamental and second-harmonic light are away from resonant adsorption. As a result, heat generation is avoided and transmission is maximized.

Third, to obtain large SHG conversion efficiency, NLO crystals should have large SHG susceptibility $\chi^{(2)}(2\omega; \omega, \omega)$ [33]. As the dispersion of SHG susceptibility much below the bandgap is weak according to the Kramers-Kronig relation, the SHG susceptibility in the zero-frequency limit, namely, the static SHG $\chi_0^{(2)}$, is commonly used to characterize the SHG response below the bandgap. The SHG coefficients can even be decoupled to each band, and the static SHG from the *n*th band for the pure interband term is

$$\chi_{e,n}^{\alpha\beta\gamma} = \frac{e^3}{6\hbar^2} P(\alpha\beta\gamma) \int \frac{d^3\mathbf{k}}{(2\pi)^3} \sum_{m,p} \operatorname{Re}\left\{r_{nm}^{\alpha}r_{mp}^{\beta}r_{pn}^{\gamma}\right\} \\ \times \frac{\omega_m f_{np} + \omega_p f_{mn} + \omega_n f_{pm}}{\omega_{mn}\omega_{pn}\omega_{mp}}, \tag{1}$$

and for the mixed term is

$$\chi_{i,n}^{\alpha\beta\gamma} = -\frac{e^3}{4\hbar^2} P(\alpha\beta\gamma) \int \frac{d^3\mathbf{k}}{(2\pi)^3} \sum_m \frac{f_{nm}}{\omega_{mn}^2} \operatorname{Im}\left\{r_{nm}^{\alpha} r_{mn;\gamma}^{\beta}\right\}, \quad (2)$$

where *n*, *m*, and *p* are band indices. Here α , β , and γ represent Cartesian directions and $P(\alpha\beta\gamma)$ denotes the full permutation of indices α , β , and γ . f_{nm} and ω_{nm} are the occupation difference and energy difference between bands *n* and *m*. $r_{nm}^{\alpha} = i\langle u_n | \partial_{k_{\alpha}} u_m \rangle$ is the interband Berry connection where $|u_m\rangle$ is the periodic part of the Bloch function. $r_{mn;\gamma}^{\beta} = \frac{\partial r_{mn}^{\beta}}{\partial k_{\gamma}} - i[\xi_{mm}^{\gamma} - \xi_{nn}^{\gamma}]r_{mn}^{\beta}$ is the general derivative, where ξ_{nn}^{γ} is the intraband Berry connection [35,36]. The total response is given by the sum of bands $\chi^{\alpha\beta\gamma} = \sum_n (\chi_{e,n}^{\alpha\beta\gamma} + \chi_{i,n}^{\alpha\beta\gamma})$.

Fourth, NLO crystals need to exhibit a sizable birefringence $\Delta n(\omega)$ to meet the phase matching condition [34]. The phase matching condition guarantees that the second-harmonic light generated by dipoles in materials interferes constructively so that the power of the SHG signal increases linearly with the thickness of the crystal. The birefringence is defined as $\Delta n(\omega) = \sqrt{\chi_{\text{max}}^{(1)}(\omega)} - \sqrt{\chi_{\text{min}}^{(1)}(\omega)}$, in which $\chi_{\text{max}}^{(1)}(\omega)$ and $\chi_{\text{min}}^{(1)}(\omega)$ are the maximum and the minimum

eigenvalues of the linear susceptibility $\chi^{(1)}(\omega)$. The linear susceptibility $\chi^{(1)}(\omega)$ is calculated by

$$\chi^{\alpha\beta}(\omega) = \frac{e^2}{\hbar} \int \frac{d^3 \mathbf{k}}{(2\pi)^3} \sum_{n,m} \frac{f_{nm} r^{\alpha}_{nm} r^{\beta}_{mn}}{\omega_{mn} - \omega - i\epsilon}, \qquad (3)$$

where $\hbar\epsilon$ is a small relaxation energy. Similar to the SHG susceptibility, the dispersion of $\Delta n(\omega)$ is also weak below the bandgap, and therefore the zero-frequency birefringence Δn_0 can serve as a good reference.

Aside from the four criteria, NLO materials should also exhibit a large laser damage threshold, which is positively correlated with the bandgap, to be stable under laser illumination and easy to grow into sizable crystals [37].

B. High-throughput workflow

Our high-throughput calculations are based on material structures in the MP database which contains computed information, e.g., band structure calculated at PBE level, of more than 140 000 known or predicted materials. To screen out potential NLO crystals, we placed the following filters to materials in the MP database. First, we selected materials without inversion symmetry based on their space group. As we only considered spin-unpolarized materials, we did not include magnetic materials where the inversion symmetry is breaking by their magnetic structures. Second, we selected materials with calculated bandgaps larger than 0.1 eV, to ensure the nonadsorption working frequency range. Third, we avoided elements with partially filled 3d orbitals, including V, Cr, Mn, Fe, Co, and Ni, due to the difficulty in determining the ground state of materials containing these elements. Fourth, we excluded materials reported with a nonzero magnetization in the database due to the difficulty in determining the magnetic ground state. Fifth, we also excluded elements from the lanthanide and actinium series due to the potential problem of DFT in treating localized f orbitals. Lastly, we only computed material with less than 20 atoms in a unit cell due to our limited computation resources. Other than these, we did not add any constraints on specific material types to guarantee an unbiased searching. After applying the above filters, 2389 materials from the MP database are selected for spin-unpolarized high-throughput calculations.

In our spin-unpolarized high-throughput workflow, we performed first-principles DFT calculations based on the local atomic basis. As calculations based on the plane-wave basis can scale with the number of atoms N as $O(N^3)$ while calculations based on the local basis scale as O(N), our method is more suitable for calculations of large systems [19]. Then the optical responses are calculated based on the DFT Hamiltonian under the nonorthogonal local atomic basis [27,28], which can achieve a very dense sampling in the Brillouin zone with high computation efficiency. Taking AgGaS₂ (eight atoms in the unit cell) as an example, our calculation based on the local basis takes 0.6 CPU core hour, while our calculation based on the plane-wave basis (using ABINIT [38]) takes 63 CPU core hour to get a similar convergence of static SHG value. Therefore, the above combined methods show sufficient accuracy and very high efficiency in the calculation of nonlinear optical properties.



FIG. 1. High-throughput screening workflow. First, filters based on symmetry, energy gap, number of atoms, magnetic properties, and element types are placed. Then DFT calculations are performed to extract the band structure and DFT Hamiltonian. After that, the DFT Hamiltonians are used to calculate the optical responses of 229 materials with scissors correction and 2389 materials without scissors correction. Finally, based on the NLO criteria and NLO indicator, the target candidates are screened out and a PBE level suggest list is given.

Our DFT calculations adapt the PBE-form exchangecorrelation functional which usually underestimates the energy gap and results in the overestimation of $\chi^{(1)}$ and $\chi^{(2)}$. On the contrary, the bandgap value obtained from the hybrid functional is closer to the experimental value at the expense of a higher computation demand. Therefore, we applied the scissors correction [39] to optical responses (both SHG and birefringence) according to their Heyd-Scuseria-Ernzerhof (HSE) [40] hybrid functional bandgap value reported in the MaterialsGo [41] database. Due to the limited overlap between the MP database and the MaterialsGo database, 229 materials with a HSE bandgap larger than 3.0 eV adopted the scissors correction. All calculations including the electronic structure and optical responses are performed using an automatic workflow, which is illustrated in Fig. 1.

C. Validation

To validate our calculation methods and results, we compared our calculated bandgap, birefringence, and static SHG with experimental measured values for ten most wellstudied NLO crystals, including $AgGaS_2$ [42], $AgGaSe_2$ [42], $ZnGeP_2$ [43], BiB_3O_6 [44], $CsLiB_6O_{10}$ [45], CsB_3O_5 [46], KBBF [47], LBO [8], $Li_2B_4O_7$ [48] and SrB_4O_7 [49]. As shown in Figs. 2(a) and 2(c), calculations based on PBE approximation (red circles) generally underestimate the energy gap by 1–2 eV and greatly overestimate the static SHG by two to three times. In contrast, the energy gap obtained from HSE calculations and the static SHG modified by scissors correction according to the HSE bandgap (blue squares) give better agreements with experimental values. A more detailed comparison of experimentally measured and our calculated frequency-dependent linear and SHG susceptibility and the



FIG. 2. Comparison of our calculation results with experimental values of ten well-studied NLO crystals. The diagonal line is a guide to the eye. The closer the data dots to the diagonal line, the better agreement between experimental and calculated values of energy gap E_g , birefringence $\Delta n(\omega)$, and static SHG $\chi_0^{(2)}$. (a) The HSE energy gap (blue squares) obtained from the MaterialsGo database [41] and our calculated PBE energy gap (red circles) versus the experimental energy gap. (b) The calculated birefringence comparing with experimental values at certain wavelengths. We presented results both at the long-wavelength limit $\omega = 0$ (green triangles) and at experimentally measured wavelength $\omega \neq 0$ (red circles and blue squares). For AgGaS₂, AgGaSe₂, and ZnGeP₂ [42], Δn are extracted at 5300 nm, and for the other seven materials, Δn are extracted at 1024 nm. Furthermore, blue squares and red circles indicate the birefringence with and without the scissors correction. (c) The calculated static SHG comparing with experimental values. max $|\chi^{(2)}|$ is the largest absolute value among all allowed independent SHG tensor components. Blue squares and red circles indicate the largest absolute value of the allowed independent SHG tensor max $|\chi^{(2)}|$ with and without the scissors correction.

influence of scissors correction are included in Figs. S1–S4 of the Supplemental Material [23].

For the birefringence, we not only showed results with and without applying scissors operation (red circles versus the blue squares), but also demonstrated the influence of different probing frequencies to the birefringence (green triangles versus blue squares) in Fig. 2(b). Indeed, the influence of an enlarging bandgap through the scissors operation is equivalent to probing the linear susceptibility at a lower frequency, as both lead to the increase of denominator in the linear susceptibility tensor by a constant, according to Eq. (3). While increasing the denominator leads to the decrease of the linear susceptibility tensor, the influence on the birefringence is more subtle, as Δn is related to the difference in square root of eigenvalues of the linear susceptibility tensor. In the high-throughput workflow, we calculated the birefringence at the static limit with HSE bandgap correction (green triangles), and as Fig. 2(b) indicated, our calculated Δn_0 is generally smaller than Δn at finite frequency (blue squares) below bandgap and therefore, our calculations have the tendency to underestimate the birefringence compared to experimental values. As the birefringence of NLO crystals has a lower bound in our screening, our calculated birefringence results are overqualified for the criterion of NLO crystals.

D. Screening for candidates working in the DUV frequencies

The criteria for DUV materials are max $|\chi^{(2)}| > 0.78 \text{ pm V}^{-1}$, $E_g > 6.3 \text{ eV}$, and $\Delta n > 0.08$ [50], where max $|\chi^{(2)}|$ is the maximum absolute value of the SHG tensor components. Five materials are screened out, which are KCN (mp-20134) [51,52], urea (mp-23778) [53–56], PNF₂

(mp-560008) [57,58], BH₆CN₃F₄ (mp-862539) [59] and PNO (mp-36066) [60]. Their energy gap and nonlinear optical properties are listed in Table S1 within the Supplemental Material [23]. Different from the previous designed DUV NLO crystals which are based on KBBF [61,62], these five materials show very diverse structures. Notably, these five materials all share the common features that they are beryllium-free and their band-edge orbitals all form covalent bonds. Among them, KCN, urea, and PNF₂ are known NLO crystals verified both by theory and experiments, which again validates our calculations. The NLO properties of BH₆CN₃F₄ have not been investigated in theory or in experiments before. However, as BH₆CN₃F₄ has been successfully synthesized [59], the predicted NLO properties can be easily verified.

Additionally, PNO is also a promising candidate formed by covalent bonds which has been predicted in theory recently [60] and needs more experimental confirmations. According to our calculations, PNO (mp-36066) has $E_g =$ 6.39 eV, $\Delta n_0 = 0.167$, and the largest SHG component $\chi^{(2)}_{223} = 7.041 \text{ pm V}^{-1}$ as shown in Fig. 3(b), which are also consistent with the recent theoretical predictions [60]. Its structure is composed of a three-dimensional network of tetrahedrons connected through N and O corners, with P at the center of each tetrahedron as shown in Fig. 3(a). This structure is fairly stable with a tiny positive energy above hull (0.003 eV/atom). The band-resolved SHG for the $\chi^{(2)}_{223}$ component in Fig. 3(d) shows that band edges (denoted by the red circles) along with their neighboring bands make the most contribution of $\chi^{(2)}$ in PNO. Orbital projected band structure shows that the band edge of the conduction band is composed of 3p orbitals of P atoms and the valence bands near the bandgap are formed by 2p orbitals of N and O atoms,



FIG. 3. Atomic structure, band structure, and SHG of PNO. (a) Atomic structure of PNO. (b) Allowed independent SHG tensors and their values of PNO. (c) Element projected band structure of PNO. (d) Band-resolved SHG of PNO. The *x* axis represents the band index for spin-up bands, and the *y* axis is the $\chi^{(2)}$ value of each band. The two red circles highlight the band-edge position.

as shown in Fig. 3(c) (each band is doubly degenerate in Fig. 3). Usually, to get converged SHG results, the number of conduction bands (N_c) needs to be twice or even three times larger than the number of valence bands (N_v). However, our test shows that in PNO, if we only include $N_v = 16$ valence bands and $N_c = 4$ conduction bands, it is sufficient to give 84.8% of the converged SHG response. These again confirm the dominant contribution of band edges to SHG.

Materials formed by PNO tetrahedrons can adapt many different structures with slightly different tetrahedron connections. Interestingly, we found materials formed by cornersharing PNO tetrahedrons all have large bandgaps. For the most stable PNO (mp-753671) in Table S4 within the Supplemental Material [23], its HSE bandgap is $E_g^{\text{HSE}} = 6.29 \text{ eV}$ which is just below our searching criterion. Its SHG susceptibility and birefringence scissored according to this bandgap is $\max |\chi^{(2)}| = 7.36 \text{ pm V}^{-1}$ and $\Delta n_0 = 0.11$ which satisfy the criteria for NLO crystals in DUV frequency. Therefore, stable and metastable PNOs are all DUV candidate materials (consistent with Ref. [60]), and the tetrahedron formed by PNO is an important NLO-active motif to achieve a large static SHG.

E. Screening for candidates working in the MIR frequencies

Based on the elementary requirements for NLO materials working in the MIR frequencies $(\max|\chi^{(2)}| > 7.8 \text{ pm V}^{-1}, E_g > 3.0 \text{ eV}, \text{ and } \Delta n > 0.04)$ [37], we screened out 40 candidates out of 229 materials, and among them there are 8 candidates satisfying a more strict criteria with $\max|\chi^{(2)}| >$ 15.6 pm V⁻¹, and $E_g > 3.5 \text{ eV}$. The 8 most promising candidates are labeled MIR-preferred and the remaining 32 candidates are labeled MIR-elementary, as shown in Fig. 4. Among the eight MIR-preferred materials, three of them have



FIG. 4. Distribution of E_g and max $|\chi^{(2)}|$ for screened NLO materials working in the MIR frequencies calculated at HSE level. Red circles stand for MIR-preferred materials and blue circles stand for MIR-elementary materials. The green dashed line shows the difference between MIR-preferred and MIR-elementary. The DUV candidate PNF₂ also is a MIR-preferred candidate, which is beyond the scale of this plot.

been previously studied as NLO materials, which are CIN (mp-30068) [52], LiNbO₃ (mp-3731) [63] and PNF₂ (mp-560008) [58]. And five are newly found, which are BrF_3 (mp-23297), CaGeN₂ (mp-7801), LiBiB₂O₅ (mp-755256), Zr₃N₂O₃ (mp-755132), and Ti₃TeO₈ (mp-774922). Detailed information of these NLO candidates including material ID in the MP database, chemical formula, and SHG coefficients are listed in Tables S2 and S3 within the Supplemental Material [23]. Among the 40 candidates, 8 materials are mainly formed by covalent bonds. For the remaining 32 candidates formed by ionic bonds, classified based on their anion types, there are 18 oxides, 2 nitrides, 2 chalcogenides, and 1 fluoride. There are also 9 candidates with more than one type of anion, e.g., NbO₂F (mp-752467) and Cs₂RbZrOF₅ (mp-42022). Classified based on dimensionality, while most of the discovered NLO candidates form three-dimensional network structures, we also found molecular crystals CIN and BrO₂F, stacked one-dimensional chain structures, i.e., PNF₂, SeO₂, and SbOF, and a stacked two-dimensional layered structure BrF₃. By analyzing the SHG contribution and orbital character of each band, we can figure out promising NLO-active motifs that dominate the NLO response. Here we introduce the structures of a few NLO candidates with representative motifs in oxides and ionic crystals with mixed anions.

KBrO₃ (mp-22958) is a NLO candidate belonging to oxides, and its atomic configuration is shown in Fig. 5(a). Br and three O ions form the four corners of a tetrahedron, while K ions are far away from both Br and O ions with the shortest distance between K and the nine nearest neighboring O ions to be 3.13 Å. The structure has *R3m* symmetry with three independent static SHG components χ^{112} , χ^{113} , and χ^{333} as listed in Fig. 5(b). As shown in Fig. 5(d), the main SHG contribution of the largest tensor component χ^{112} comes from bands near band edges, and the projected band structure in Fig. 5(c) reveals that those are the 3*p* orbitals of Br in the



FIG. 5. Atomic structure, band structure, and SHG components of KBrO₃. (a) Atomic structure of KBrO₃. (b) Static SHG value for all allowed tensor components. (c) Element projected band structure. (d) Band-resolved SHG for the χ^{112} component. Red circles highlight the contribution from band edges.

conduction band and the 2p orbitals of O in the valence band. On the contrary, the empty 3s orbitals of K ions are far away from the conduction band edge and do not contribute much to the SHG. Therefore, the [BrO₃] tetrahedron is a typical NLO-active motif that contributes most of the SHG. Similar oxide motifs discovered among our NLO candidates are the [IO₃] tetrahedron in CsIO₃ and the [NO₃] triangle in RbNO₃.

The NLO candidate Cs₂RbZrOF₅ (mp-42022) has two types of anions, F⁻ and O²⁻, and belongs to fluozirconate. Cs₂RbZrOF₅ has the space group *I*4mm and is formed by face-sharing polyhedra as shown in Fig. 6(a). Rb and Zr are in distorted octahedra formed by five F ions and one O ion, while each Cs is surrounded by ten F ions and two O ions with the shortest distance between Cs and F to be 3.39 Å and Cs and O to be 3.42 Å. There are only two independent tensor components χ^{113} and χ^{333} for static SHG, as shown in Fig. 6(b). A detailed band-resolved SHG analysis and element projected band structure in Figs. 6(d) and 6(c) reveal that the major contributions of χ^{333} are from Zr and O 2*p* orbitals near band edges while the s orbitals of Cs and Rb are too high in the conduction and the 2p orbitals of F are a few electron volts away from the valence band edge. While F has a minor contribution to SHG, the existence of F increases structural anisotropy and therefore can contribute to birefringence [61]. As a result, the structural motif that contributes the most to SHG is the [ZrF₅O] octahedron. In addition to the combination of anions O^{2-} and F^- , there are also several candidates formed by the combination of anions O^{2-} and N^{3-} , such as Ge_2N_2O (mp-4187). In short, the combination of anions can create more structural flexibility, eliminate dangling bonds to ensure a large bandgap, and even create a more asymmetric structural motif to ensure large birefringence.

Analysis based on first-principles calculations as shown above is the most rigorous method to identify NLO-active



FIG. 6. Atomic structure, band structure, and SHG components of Cs₂RbZrOF₅. (a) Atomic structure of Cs₂RbZrOF₅. (b) Static SHG value for all allowed tensor components. (c) Element projected band structure. (d) Band-resolved SHG for the χ^{333} component. Red circles highlight the contribution from band edges.

motifs and NLO crystals. However, in ionic crystals, analysis based on Pauli electronegativity and crystal structures can also give us a rough estimation of the NLO-active motifs and NLO crystals. Firstly, we can use the table of electronegativity to figure out the element character at the conduction band edge which is usually the cation with the smallest electronegativity. and at the valence band edge which is usually the anion with the largest electronegativity [64]. Taking KRb₂ZrOF₅ as an example, we deduced that the band edges are composed by orbitals of Zr and O. Then, by scrutinizing the crystal structure, we can identify the NLO-active motifs made from the band-edge elements, and regard it as the NLO-active motifs. For KRb₂ZrOF₅, Zr and O form the ZrOF₅ octahedron and hence [ZrF₅O] is the NLO-active motif. Finally, if this specific motif has been reported in a known NLO material, we can speculate that this newly investigated material has the potential to be a NLO material. For KRb₂ZrOF₅, as the NLO crystal Cs₂RbZrOF₅ also possesses the same NLOactive motif [ZrF₅O], KRb₂ZrOF₅ is very likely to be a NLO crystal and indeed our first-principles results also confirm this speculation.

F. High-throughput data analysis

Up to now, we have applied the scissors operation to 229 materials according to E_g^{HSE} (see Table S4 within the Supplemental Material [23]) and screened out 5 DUV and 40 MIR NLO crystals. However, we still have 2160 materials with bandgap, SHG, and the birefringence calculated at PBE level without applying the scissors operator. Figure 7(a) shows the bandgap and the maximum tensor component of SHG susceptibility max $|\chi_{PBE}^{(2)}|$ calculated at PBE level for most materials in our high-throughput calculations. Among them, red points represent the screened-out NLO crystals, blue points represent the materials with HSE bandgap but failed to meet the criteria



FIG. 7. PBE bandgap vs $\chi_{PBE}^{(2)}$ of materials in our high-throughput calculations. Red circles represent the 45 selected NLO candidates (including DUV, MIR-preferred, and MIR-elementary). Blue circles represent the 229 materials with HSE bandgap but fail to meet the criteria of NLO crystals. All the green circles are materials without HSE bandgap corrections. (a) The linear plot and (b) the log-log plot of PBE bandgap vs $\chi_{PBE}^{(2)}$ of materials in our high-throughput calculations. The dashed lines $F = 200, 2000, 20\,000$ are shown as a reference.

of NLO crystals, and green points are materials without HSE bandgap data. It is clear that there are many green points close to red points. That is to say, at PBE level, those materials (green points) are as good as the selected NLO crystals (red points). Therefore, there are still many potential NLO crystals that are largely unexplored due to the absence of HSE bandgap data.

According to the expression of static SHG in Eqs. (1) and (2) and the model analysis in Refs. [14,65], the scaling of static SHG susceptibility with respect to bandgap follows

$$\left|\chi^{(2)}_{\alpha\alpha\alpha}\right| = \frac{F}{E_g^4},\tag{4}$$

where α is the Cartesian direction. F is determined by material specific properties, such as the lattice structure, the measurement direction, the hopping strength, etc. The PBE results of all 2389 materials are reported in Table S5 within the Supplemental Material [23] in the descending order of F, and the log-log plots of most results are also shown in Fig. 7(b) with the curve $F = 200, 2000, 20000 \text{ (eV)}^4 \text{ pm V}^{-1}$ as reference. According to Table S5 within the Supplemental Material [23], we find materials with the same NLO-active motif have a similar F value [e.g., RbLiMoO₄ and CsLiMoO₄, KRb_2ZrOF_5 and $Cs_2RbZrOF_5$, $Ca(ClO_3)_2$, $Ba(ClO_3)_2$, and $Sr(BrO_3)_2$], implying the universality for F as a NLO-active motif indicator. Furthermore, we discovered that most of the materials in the database satisfy F < 20000, which suggests the existence of an upper boundary for F [14]. Moreover, our screened NLO crystals are all in the range of $F \in$ [200, 20000] (eV)⁴ pm V⁻¹ and therefore, we suggest that materials with PBE results falling in the range of $F \ge 200$ are worth detailed scrutiny at HSE level.

We noticed a similar independent work published recently [17]. As they also performed unbiased high-throughput calculations based on the MP database, we want to emphasize the difference in data sets between Ref. [17] and our current work. The major differences are in the filter and screening criteria. They only considered materials with a bandgap provided by MP between 2 and 4 eV, while we included materials with a bandgap larger than 0.1 eV. Therefore, materials with a seriously underestimated PBE bandgap but a suitable HSE bandgap are only included in our data set. In addition, the maximum number of atoms we considered is 20 while they considered 30. Along with other preliminary filter criteria, they filtered out 601 materials, while we filtered out 2389 materials to perform the calculations. As for the screening criteria, they did not apply the constraint on the birefringence when screening for NLO crystals, while we included this constraint. Additionally, they used the thermal conductivity as a signal of laser damage threshold while we constrained the bandgap value to ensure a large laser damage threshold. With all these differences in filters and screening criteria, we found more oxides, covalent, and mixed-anion materials as NLO crystals and we labeled the NLO crystals discovered in Ref. [17] in Table S5 within the Supplemental Material [23].

IV. CONCLUSION

The discovery of new types of DUV and MIR nonlinear optical materials are important for fundamental understanding of light-matter interaction and optical device applications. The traditional searching strategy based on specific NLOactive motifs is limited by efficiency and localized searching space. In this study, we performed unbiased first-principles high-throughput screening from materials database and calculated the linear and nonlinear optical responses by linearly scaled DFT method and optical response methods based on nonorthogonal localized orbitals. We screened out 5 DUV candidate materials, 8 MIR-preferred materials and 32 MIR-elementary materials, a majority of which are covalent materials, oxides, and ionic crystals with mixed anions. Furthermore, we identified several NLO-active motifs in covalent materials, oxides and mixed anion crystals with substantial SHG contribution and good transferability, and even presented an intuitive argument to deduce NLO-active motifs without performing calculations. Moreover, we proposed an universal NLO-active motif indicator F based on the scaling law of bandgap and static SHG, according to which we presented a list of recommended materials calculated at PBE level that are worth further high-accuracy calculations or experiments at high priority. Our NLO crystal screening from database will greatly accelerate the experimental discovery of NLO crystals. Our discovery of NLO-active motifs with good transferability will enrich the understandings in searching and designing NLO crystals.

- [1] D. F. Eaton, Nonlinear optical materials, Science **253**, 281 (1991).
- [2] P. A. Franken, A. E. Hill, C. W. Peters, and G. Weinreich, Generation of optical harmonics, Phys. Rev. Lett. 7, 118 (1961).
- [3] M. Sheik-Bahae, A. Said, T.-H. Wei, D. Hagan, and E. Van Stryland, Sensitive measurement of optical nonlinearities using a single beam, IEEE J. Quantum Electron. 26, 760 (1990).
- [4] Y. Shen, *Principles of Nonlinear Optics* (Wiley-Interscience, New York, NY, 2008).
- [5] C. Chen, Y. Wang, B. Wu, K. Wu, W. Zeng, and L. Yu, Design and synthesis of an ultraviolet-transparent nonlinear optical crystal Sr₂Be₂B₂O₇, Nature (London) **373**, 322 (1995).
- [6] M. Fiebig, V. V. Pavlov, and R. V. Pisarev, Second-harmonic generation as a tool for studying electronic and magnetic structures of crystals: Review, J. Opt. Soc. Am. B 22, 96 (2005).
- [7] C. Chen, Y. Wu, and R. Li, The development of new NLO crystals in the borate series, J. Cryst. Growth 99, 790 (1990).
- [8] C. Chen, Y. Wu, A. Jiang, B. Wu, G. You, R. Li, and S. Lin, New nonlinear-optical crystal: LiB₃O₅, J. Opt. Soc. Am. B 6, 616 (1989).
- [9] C. Chen, Z. Xu, D. Deng, J. Zhang, G. K. L. Wong, B. Wu, N. Ye, and D. Tang, The vacuum ultraviolet phase-matching characteristics of nonlinear optical KBe₂BO₃F₂ crystal, Appl. Phys. Lett. **68**, 2930 (1996).
- [10] C. Chen, An ionic grouping theory of the electro-optical and nonlinear optical effects of crystals (I)—A theoretical calculation of electro-optical and second optical harmonic coefficients of barium titanate crystals based on a deformed oxygenoctahedra, Acta Phys. Sin. 25, 146 (1976).
- [11] C. Chen, T. Sasaki, R. Li, Y. Wu, Z. Lin, Y. Mori, Z. Hu, J. Wang, S. Uda, M. Yoshimura, and Y. Kaneda, *Nonlinear Optical Borate Crystals* (Wiley, New York, 2012).
- [12] B.-H. Lei, S. Pan, Z. Yang, C. Cao, and D. J. Singh, Second harmonic generation susceptibilities from symmetry adapted Wannier functions, Phys. Rev. Lett. **125**, 187402 (2020).
- [13] Y. Sun, Z. Yang, D. Hou, and S. Pan, Theoretical investigation on the balance between large band gap and strong SHG response in BMO_4 (M = P and As) crystals, RSC Adv. 7, 2804 (2017).
- [14] A. Taghizadeh, K. S. Thygesen, and T. G. Pedersen, Twodimensional materials with giant optical nonlinearities near the theoretical upper limit, ACS Nano 15, 7155 (2021).
- [15] B. Zhang, X. Zhang, J. Yu, Y. Wang, K. Wu, and M.-H. Lee, First-principles high-throughput screening pipeline for

ACKNOWLEDGMENTS

This work was supported by the Basic Science Center Project of NSFC (Grant No. 52388201), the National Science Fund for Distinguished Young Scholars (Grant No. 12025405), the Ministry of Science and Technology of China (Grant No. 2023YFA1406400), the National Natural Science Foundation of China (Grant No. 12334003), the Beijing Advanced Innovation Center for Future Chip (ICFC), the Beijing Advanced Innovation Center for Materials Genome Engineering, and the NSAF center project of NSFC No. U2330401. The calculations were done on Hefei Advanced Computing Center.

nonlinear optical materials: Application to borates, Chem. Mater. **32**, 6772 (2020).

- [16] Q. Wu, L. Kang, and Z. Lin, A machine learning study on high thermal conductivity assisted to discover chalcogenides with balanced infrared nonlinear optical performance, Adv. Mater. 36, 2309675 (2024).
- [17] D. Chu, Y. Huang, C. Xie, E. Tikhonov, I. Kruglov, G. Li, S. Pan, and Z. Yang, Unbiased screening of novel infrared nonlinear optical materials with high thermal conductivity: Long-neglected nitrides and popular chalcogenides, Angew. Chem., Int. Ed. **62**, e202300581 (2023).
- [18] A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, and K. A. Persson, Commentary: The Materials Project: A materials genome approach to accelerating materials innovation, APL Mater. 1, 011002 (2013).
- [19] T. Ozaki, Variationally optimized atomic orbitals for large-scale electronic structures, Phys. Rev. B 67, 155108 (2003).
- [20] T. Ozaki and H. Kino, Numerical atomic basis orbitals from H to Kr, Phys. Rev. B 69, 195113 (2004).
- [21] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77, 3865 (1996).
- [22] I. Morrison, D. M. Bylander, and L. Kleinman, Nonlocal Hermitian norm-conserving Vanderbilt pseudopotential, Phys. Rev. B 47, 6728 (1993).
- [23] See Supplemental Material at http://link.aps.org/supplemental/ 10.1103/PhysRevMaterials.8.085202 for frequency-dependent optical response; effect of scissors correction; formula, Materials Project ID, band gap, birefringence, and SHG coefficients data; OpenMX basis. It also contains Refs. [24,25].
- [24] R. K. Chang, J. Ducuing, and N. Bloembergen, Dispersion of the optical nonlinearity in semiconductors, Phys. Rev. Lett. 15, 415 (1965).
- [25] D. E. Aspnes and A. A. Studna, Dielectric functions and optical parameters of Si, Ge, GaP, GaAs, GaSb, InP, InAs, and InSb from 1.5 to 6.0 eV, Phys. Rev. B 27, 985 (1983).
- [26] https://github.com/HopTB
- [27] C. Wang, X. Liu, L. Kang, B.-L. Gu, Y. Xu, and W. Duan, Firstprinciples calculation of nonlinear optical responses by Wannier interpolation, Phys. Rev. B 96, 115147 (2017).
- [28] C. Wang, S. Zhao, X. Guo, X. Ren, B.-L. Gu, Y. Xu, and W. Duan, First-principles calculation of optical responses based

on nonorthogonal localized orbitals, New J. Phys. 21, 093001 (2019).

- [29] M. Lee, Y. Youn, K. Yim, and S. Han, High-throughput *ab initio* calculations on dielectric constant and band gap of non-oxide dielectrics, Sci. Rep. 8, 14794 (2018).
- [30] Z. Lin, X. Jiang, L. Kang, P. Gong, S. Luo, and M.-H. Lee, First-principles materials applications and design of nonlinear optical crystals, J. Phys. D: Appl. Phys. 47, 253001 (2014).
- [31] R.-C. Xiao, D.-F. Shao, W. Gan, H.-W. Wang, H. Han, Z. G. Sheng, C. Zhang, H. Jiang, and H. Li, Classification of second harmonic generation effect in magnetically ordered materials, npj Quantum Mater. 8, 62 (2023).
- [32] J. Wang, K. Jin, J. Gu, Q. Wan, H. Yao, and G. Yang, Direct evidence of correlation between the second harmonic generation anisotropy patterns and the polarization orientation of perovskite ferroelectric, Sci. Rep. 7, 9051 (2017).
- [33] L. Kang, D. M. Ramo, Z. Lin, P. D. Bristowe, J. Qin, and C. Chen, First principles selection and design of mid-IR nonlinear optical halide crystals, J. Mater. Chem. C 1, 7363 (2013).
- [34] L. Kang, M. Zhou, J. Yao, Z. Lin, Y. Wu, and C. Chen, Metal thiophosphates with good mid-infrared nonlinear optical performances: A first-principles prediction and analysis, J. Am. Chem. Soc. 137, 13049 (2015).
- [35] J. E. Sipe and A. I. Shkrebtii, Second-order optical response in semiconductors, Phys. Rev. B 61, 5337 (2000).
- [36] H. Chen, M. Ye, N. Zou, B.-L. Gu, Y. Xu, and W. Duan, Basic formulation and first-principles implementation of nonlinear magneto-optical effects, Phys. Rev. B 105, 075123 (2022).
- [37] L. Kang, F. Liang, X. Jiang, Z. Lin, and C. Chen, Firstprinciples design and simulations promote the development of nonlinear optical crystals, Acc. Chem. Res. 53, 209 (2020).
- [38] X. Gonze *et al.*, The ABINIT project: Impact, environment and recent developments, Comput. Phys. Commun. 248, 107042 (2020).
- [39] F. Nastos, B. Olejnik, K. Schwarz, and J. E. Sipe, Scissors implementation within length-gauge formulations of the frequency-dependent nonlinear optical response of semiconductors, Phys. Rev. B 72, 045223 (2005).
- [40] J. Heyd, G. E. Scuseria, and M. Ernzerhof, Hybrid functionals based on a screened Coulomb potential, J. Chem. Phys. 118, 8207 (2003).
- [41] http://www.pkusam.com
- [42] G. C. Catella and D. Burlage, Crystal growth and optical properties of AgGaS₂ and AgGaSe₂, MRS Bull. 23, 28 (1998).
- [43] M. C. Ohmer and R. Pandey, Emergence of chalcopyrites as nonlinear optical materials, MRS Bull. 23, 16 (1998).
- [44] R. Fröhlich, L. Bohatý, and J. Liebertz, Die kristallstruktur von wismutborat, BiB₃O₆, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. 40, 343 (1984).
- [45] T. Sasaki, Y. Mori, and M. Yoshimura, Progress in the growth of a $CsLiB_6O_{10}$ crystal and its application to ultraviolet light generation, Opt. Mater. (Amsterdam, Neth.) **23**, 343 (2003).
- [46] Y. Wu, T. Sasaki, S. Nakai, A. Yokotani, H. Tang, and C. Chen, CsB₃O₅: A new nonlinear optical crystal, Appl. Phys. Lett. 62, 2614 (1993).
- [47] C. Chen, Y. Wang, Y. Xia, B. Wu, D. Tang, K. Wu, W. Zeng, L. Yu, and L. Mei, New development of nonlinear optical crystals for the ultraviolet region with molecular engineering approach, J. Appl. Phys. 77, 2268 (1995).

- [48] T. Kwon, J. Ju, J. Cha, J. Kim, and S. Yun, Characteristics of critically phase-matched second-harmonic generation of a $Li_2B_4O_7$ crystal grown by the Czochralski method, Mater. Lett. **20**, 211 (1994).
- [49] A. I. Zaitsev, A. S. Aleksandrovskii, A. V. Zamkov, and A. M. Sysoev, Nonlinear optical, piezoelectric, and acoustic properties of SrB₄O₇, Inorg. Mater. 42, 1360 (2006).
- [50] P. S. Halasyamani and J. M. Rondinelli, The must-have and nice-to-have experimental and computational requirements for functional frequency doubling deep-UV crystals, Nat. Commun. 9, 2972 (2018).
- [51] D. L. Decker, R. A. Beyerlein, G. Roult, and T. G. Worlton, Neutron diffraction study of KCN III and KCN IV at high pressure, Phys. Rev. B 10, 3584 (1974).
- [52] L. Kang, F. Liang, Z. Lin, F. Liu, and B. Huang, Cyano-based materials with giant optical anisotropy and second harmonicgeneration effect, Inorg. Chem. 57, 15001 (2018).
- [53] D. Bäuerle, K. Betzler, H. Hesse, S. Kapphan, and P. Loose, Phase-matched second harmonic generation in urea, Phys. Status Solidi A 42, K119 (1977).
- [54] K. Betzler, H. Hesse, and P. Loose, Optical second harmonic generation in organic crystals: Urea and ammonium-malate, J. Mol. Struct. 47, 393 (1978).
- [55] J. A. Morrell, A. C. Albrecht, K. H. Levin, and C. L. Tang, The electro-optic coefficients of urea, J. Chem. Phys. 71, 5063 (1979).
- [56] J.-M. Halbout, S. Blit, W. Donaldson, and C. Tang, Efficient phase-matched second-harmonic generation and sumfrequency mixing in urea, IEEE J. Quantum Electron. 15, 1176 (1979).
- [57] H. R. Allcock, R. L. Kugel, and E. G. Stroh, Phosphonitrilic compounds. XIII. Structure and properties of poly(difluorophosphazene), Inorg. Chem. 11, 1120 (1972).
- [58] L. Kang, X. Zhang, F. Liang, Z. Lin, and B. Huang, Poly(difluorophosphazene) as the first deep-ultraviolet nonlinear optical polymer: A first-principles prediction, Angew. Chem., Int. Ed. 58, 10250 (2019).
- [59] A. Kozak, M. Grottel, A. E. Koziol, and Z. Pajak, An X-ray and NMR cross-relaxation study of structure and ion motions in C(NH₂)₃BF₄, J. Phys. C: Solid State Phys. **20**, 5433 (1987).
- [60] C. Xie, A. Tudi, and A. R. Oganov, PNO: A promising deep-UV nonlinear optical material with the largest second harmonic generation effect, Chem. Commun. 58, 12491 (2022).
- [61] B. Zhang, G. Shi, Z. Yang, F. Zhang, and S. Pan, Fluorooxoborates: Beryllium-free deep-ultraviolet nonlinear optical materials without layered growth, Angew. Chem., Int. Ed. 56, 3916 (2017).
- [62] Z. Zhang, Y. Wang, B. Zhang, Z. Yang, and S. Pan, Polar fluorooxoborate, NaB₄O₆F: A promising material for ionic conduction and nonlinear optics, Angew. Chem., Int. Ed. 57, 6577 (2018).
- [63] G. D. Boyd, R. C. Miller, K. Nassau, W. L. Bond, and A. Savage, LiNbO₃: An efficient phase matchable nonlinear optical material, Appl. Phys. Lett. 5, 234 (1964).
- [64] F. N. Hooge, Relation between electronegativity and energy bandgap, Z. Phys. Chem. 24, 275 (1960).
- [65] L. Z. Tan and A. M. Rappe, Upper limit on shift current generation in extended systems, Phys. Rev. B 100, 085102 (2019).