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Supporting Information

The partition principles for atom scale structure and its physical property: application to the nonlinear optical crystal material $KBe_2BO_3F_2$

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S1. Computational Details

S1.1. First-principle calculations

The structural and electronic properties KBBF were calculated within the framework of density functional theory (DFT) [1, 2] by using the Vienna *ab-initio* simulation package (VASP) [3-5] with the projector augmented wave (PAW) method [6]. The generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE)-type exchange-correlation potentials [7] was used throughout this work. The employed PAW-PBE pseudopotentials [8] of B, O, F, and K treat 2*s*2*p*, 2*s*2*p*, 2*s*2*p,* and 3*s*3*p*4*s* as the valence states, respectively. The plane wave cutoff energy for the expansion of wave functions was set at 650 eV and the tetrahedron method with Blöchl corrections was used for integrations in the *k* spaces with the *k*-meshes (17×17×17). The quasi-Newton algorithm as implemented in the VASP code was used in all structural relaxations. In this work, both the cell volume and the atomic positions were all allowed to relax to minimize the internal forces. Excellent convergence of the energy differences (0.01 meV) and stress tensors (0.1 meV/Å) were achieved.

The nonlinear optical properties were calculated by employing the "sum over states (SOS)" methods using the results obtained from the VASP optical module.[9,‡] The SOS formalism for second-order susceptibility was derived by Aversa and Sipe [10] and later modified by Rashkeev *et al.* [11, 12] and Sharma *et al*.[13, 14] As the DFT electronic structure calculations underestimate bandgaps, the scissor operation[15] was used to correct this deficiency.

The TB-LMTO calculation[16] was performed by choosing 2s, 2p, as basis for O, F, Be, B and 4s for K, respectively. The *k*-mesh for self-consistent calculations is set as 12x12x12.

S1.2 Partial response functional (PRF) method

The PRF method we used in this work was developed in our previous work[9]. This method is based on the SOS formalism first developed by Aversa and Sipe [10] and later modified by Rashkeev *et al.* [11, 12] and Sharma *et al*.[13, 14] Our PRF method uses Rashkeev *et al.*'s formulation; however, the summation orders over the band indexes for both the interband and intraband contributions are changed to first perform that for the intermediate states. This operation leaves us integrands depending only on the valence band and conduction band indexes for either interband or intraband contributions in calculating the SHG coefficients. The integrands obtained can thus be used to describe virtual excitations mediated by the intermediate states between the valence bands and conduction bands. The contribution of a certain occupied energy region between E_B and valence band maximum (VBM), $\zeta_V(E_B)$, to each SHG coefficient $\chi_{ijk}^{(2)}$ is determined by considering those virtual excitations from all occupied states between E_B and VBM to all the unoccupied states of the conduction bands

(CBs), and the contribution, $\delta\zeta_V(E_B)$, of specific occupied states of energy E_B to each $\chi_{ijk}^{(2)}$ by the excitations from that energy to all unoccupied states of the CBs.

$$\delta\zeta_V(E_B) = -\frac{d\zeta_V(E_B)}{dE_B} \tag{1}$$

Similarly, the contribution, $\zeta_C(E_B)$, of a certain unoccupied region between conduction band minimum (CBM) and E_B to each $\chi_{ijk}^{(2)}$ is determined by those virtual excitations from all occupied states of the VBs only to all unoccupied states between CBM and E_B, and the contribution, $\delta\zeta_C(E_B)$, of specific unoccupied states of energy E_B to each $\chi_{ijk}^{(2)}$ by the virtual excitations from all occupied states of the VBs only to that energy.

$$\delta\zeta_C(E_B) = \frac{d\zeta_C(E_B)}{dE_B} \tag{2}$$

S1.3 Atom response theory (ART) analysis

To evaluate the individual atom contributions to the SHG components, d_{ij}, it is computationally more convenient to express the corresponding PRFs in terms of the band index I_B, $\zeta(I_B)$,[9] where the band index I_B runs from 1 to N_{tot} (i.e., the total number of band orbitals) with increasing energy, E_B, from E_{min} to E_{max}. Here, $\zeta_V(I_B)$ and $\zeta_C(I_B)$ are denoted as ${}^{VB}\zeta_j$ and ${}^{CB}\zeta_j$, respectively, with I_B replaced by a subscript *j*.

Suppose that a specific atom τ has L atomic orbitals with a coefficient ${}^{VB}C_{L\tau}^{\vec{k}j}$ in the valence band *j* at a wave vector $\vec{k}$. The total contribution ${}^{VB}A_\tau$ of an atom τ makes to the SHG coefficient from all the VB bands *j* is written as

$${}^{VB}A_\tau = \frac{\Omega}{(2\pi)^3} \int d\vec{k} \cdot \sum_{L,j} {}^{VB}\zeta_j \left| {}^{VB}C_{L\tau}^{\vec{k}j} \right|^2 \tag{3}$$

where Ω is the unit cell volume, ${}^{VB}\zeta_j$ is the corresponding PRFs in terms of the band index j. Similarly, the total contribution ${}^{CB}A_\tau$ of an atom τ makes to the SHG coefficient from all the CB bands *j* is written as

$${}^{CB}A_\tau = \frac{\Omega}{(2\pi)^3} \int d\vec{k} \cdot \sum_{L,j} {}^{CB}\zeta_j \left| {}^{CB}C_{L\tau}^{\vec{k}j} \right|^2 \tag{4}$$

in which we assumed that the atom has L atomic orbitals with the coefficient ${}^{CB}C_{L\tau}^{\vec{k}j}$ in the conduction band *j* at a wave vector $\vec{k}$. To calculate the actual contribution of each constituent atom in a unit cell to the total SHG response, one needs to consider the signs of ${}^{VB}\zeta_j$ and ${}^{CB}\zeta_j$.

The total contribution, A_τ, each individual atom makes to the SHG response from both the VBs and the CBs (i.e., from all the bands) is given by

$$A_\tau = \frac{\left({}^{VB}A_\tau + {}^{CB}A_\tau\right)}{2} \tag{5}$$

where the factor of 1/2 is applied to remove the double counting of each excitation.

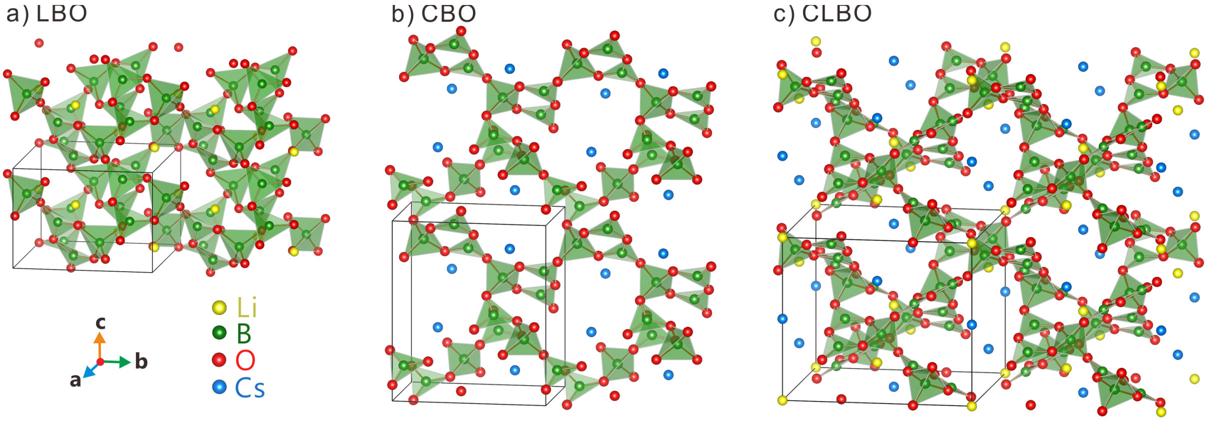

Figure S1 Crystal structures of LBO, CBO, and CLBO.

References

‡ The software that allows one to carry out the ART analysis can be obtained upon request until it is publicly released.

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