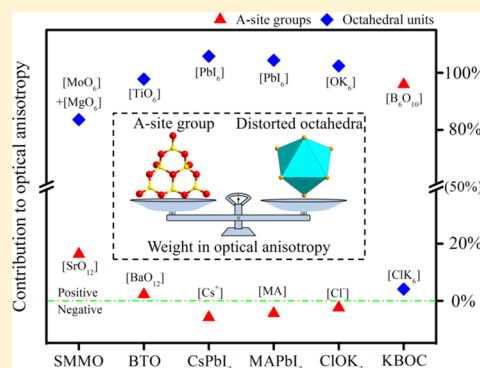


Transformation of Optical Anisotropy Origins in Perovskite-Related Materials: A First-Principles Study

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Supporting Information

ABSTRACT: Perovskite-related compounds are of vital significance in the optical element and laser industry and other fields. Exploring the contributions of microscopic units that form the perovskite framework is one efficient way to design new materials with targeted performance. In this work, we acquired the linear and nonlinear optical properties and analyzed the superior functional units in determining optical anisotropy and second harmonic generation (SHG) of typical perovskite-related compounds from inorganic to organic, namely, BaTiO₃, Sr₂MgMoO₆, CsPbI₃, CH₃NH₃PbI₃, ClOK₃, and B₆O₁₀ClK₃. The results indicate that distorted octahedral units are dominant in optical anisotropy for the vast majority of perovskite-related compounds. For instance, [TiO₆], [Mo₆], [PbI₆], and [OK₆] octahedral units are decisive birefringence origins to BaTiO₃, Sr₂MgMoO₆, CsPbI₃ and CH₃NH₃PbI₃, and ClOK₃, respectively, most of which contribute over 90%. When it comes to B₆O₁₀ClK₃, it is A-site [B₆O₁₀] groups but not [ClK₆] octahedral units that lead the optical anisotropy, as the A-site groups present stronger covalency than octahedral units. In addition, through SHG-density analysis, A-site [B₆O₁₀] groups are also dominant SHG origins, which means A-site ionic groups are possible linear and nonlinear optical origins in this case.



1. INTRODUCTION

In the field of linear and nonlinear optics, compounds are often sorted out by chemical composition or spatial structure because these two factors greatly influence optical properties. For instance, classified by chemical components, borates,^{1–7} phosphates,^{8–11} carbonates,^{12,13} and so on have attracted much attention and been explored systematically.^{14–19} In terms of spatial structure, materials with the frameworks akin to calcites, rutile, chalcopyrite, perovskite, and so forth are also outstanding optical categories that are worthy of attention. As is known to all, perovskite-related materials are superior not only in the solar cell but also in the optical element and other fields.^{20–23} For example, hybrid inorganic-organic solar cell (RNH₃)BX₃ (where R is C_nH_{2n+1}, X is the halogen I, Br, or Cl, and B is Pb or Sn) with power conversion efficiency of over 10%,^{24–26} optical anisotropy crystal BaTiS₃ with birefringence of 0.76,^{27–29} nonlinear optical (NLO) material BaTiO₃ (BTO) with second harmonic generation (SHG) coefficient of 2.13 pm/V.³⁰ As structural distortion is closely related to optical properties, perovskite-related materials, which are susceptible to distortions, have won a place in NLO materials for their large tendency to reveal a noncentrosymmetric structure and large SHG response.⁶ For conventional perovskites, the octahedral unit is considered to be the main contributor to the SHG effect, according to the anionic group theory which is based on structural chemistry.³¹ In perovskite-related materials,

compared with conventional perovskites, A-site of the latter is likely occupied by ionic groups. For instance, K₃B₆O₁₀Cl (KBOC),⁶ K₃B₆O₁₀Br,^{7,32} Na₃B₆O₁₀Br,³³ and Na₃B₆O₁₀Cl,³⁴ which were reported by the Pan group. With the A-site ions replaced by ionic groups, the octahedral unit is not the unique ionic group that may impact optical properties.

As a prerequisite for optical materials, optical anisotropy is one of the most primary phenomena in optics, on which plenty of discoveries, inventions, and applications are based. Birefringent materials have attracted a great deal of academic and commercial interest, such as polarizer, wave plate, optical fiber isolator, phase-matching element, and so on.^{35–38} In these aspects, calcite,³⁹ rutile,⁴⁰ yttrium vanadate,⁴¹ KTiOPO₄ (KTP),⁴² and the like are widely applied for their superior combination properties. In general, optical anisotropy is closely connected with covalent bonding behavior in terms of orientation.^{43,44} Therefore, optical anisotropy is likely influenced by the covalent interaction of octahedral units as well as A-site ionic groups in perovskite-related compounds. There is no doubt that studying the bonding behavior and contributions of microscopic ionic groups is meaningful. Through rational analysis, contributory optical origins could

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be distinguished and adopted to explore or design functional materials on purpose.^{45–54}

In this work, to find the optical origins and explore superior functional units in determining optical anisotropy and SHG effect of the conventional perovskite and perovskite-related materials, BTO,⁵⁵ $\text{Sr}_2\text{MgMoO}_6$ (SMMO),⁵⁶ CsPbI_3 ,⁵⁷ $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃),⁵⁸ ClOK_3 ,⁵⁹ and KBOC⁶ were systemically studied by multiple analysis methods. Generally speaking, birefringence is the difference between the maximum and minimum refractive indices in principal axes (the maximum value), and it could be obtained from dielectric functions. With regard to the relationship between optical anisotropy and bonding electron distribution, the response electron distribution anisotropy (REDA) approximation provides a rational settlement for covalent systems, which concerns the bonding electron density, bond valence, bond angle, and so forth.^{47,60} Based on the REDA method, a larger REDA index reflects a larger contribution to the birefringence; therefore, the major contributor could be represented numerically. When it comes to compounds with weak covalence, the real-space atom-cutting (RSAC) method was adopted, which could analyze the properties of “changed crystal structure” by setting the band wave function as zero in the zones that belong to a specific ion or a cluster.⁶¹ The results of the latter are consistent with the ones from the density functional theory (DFT)⁶² and REDA. Through rational analysis of multi-aspect, we found that octahedral units are the major contributors to optical anisotropy for most perovskite-related compounds. For instance, $[\text{TiO}_6]$, $[\text{Mo}_6]$, $[\text{PbI}_6]$, and $[\text{OK}_6]$ octahedral units are decisive origins to birefringence in BTO, SMMO, CsPbI_3 and MAPbI₃, and ClOK_3 , respectively, most of which contribute more than 90%. However, in KBOC, A-site $[\text{B}_6\text{O}_{10}]$ groups acquire the leading role, as they present stronger covalent bonding behavior than octahedral units. A-site $[\text{B}_6\text{O}_{10}]$ groups are also main NLO origins by the SHG-density method.⁶³ In general, octahedral units are the decisive optical origins for most perovskite-related materials. Although, when A-site ions are replaced by ionic groups with strong bonding behaviors like $[\text{B}_6\text{O}_{10}]$, the origin of birefringence and SHG possibly transforms from the octahedral units to A-site groups.

2. CRYSTAL STRUCTURES

Crystallized in the $P4mm$ space group, BTO consists of $[\text{TiO}_6]$ octahedral units and A-site Ba^{2+} (Figure 1a). For the distorted $[\text{TiO}_6]$ octahedron (Figure S1a), observing in the c direction, four rotational symmetric Ti1–O2 bonds exhibit equal length, but two Ti1–O1 bonds along the c axis are in different extent—one is 1.8108 Å, whereas the other one is 2.2132 Å. In space group $P\bar{1}$, SMMO possesses a general chemical formula of $\text{A}_2\text{BB}'\text{X}_6$, which is known as a double perovskite. Sharing common corners, $[\text{MgO}_6]$ and $[\text{MoO}_6]$ octahedral units are linked as a three-dimensional framework with Sr^{2+} located in the A-site (Figure 1b). In Figure S1b, $\gamma\text{-CsPbI}_3$ is crystallized in a centrosymmetry space group $Pnam$, and Cs^+ is surrounded by slant $[\text{PbI}_6]$ octahedra. As shown in Figure 1c, MAPbI₃ is made up of $[\text{CH}_3\text{NH}_3]$ groups and the three-dimensional framework composed of $[\text{PbI}_6]$ octahedra. Especially, it could be seen as a substitution of Cs^+ by $[\text{CH}_3\text{NH}_3]$ in CsPbI_3 , as their octahedral frameworks are quite similar to each other.⁶⁴ In Figure S1c, ClOK_3 is made up of $[\text{OK}_6]$ octahedral units and A-site Cl^- . KBOC crystallizes in the trigonal crystal system with the space group of $R3m$ (Figure 1d). Comparing KBOC

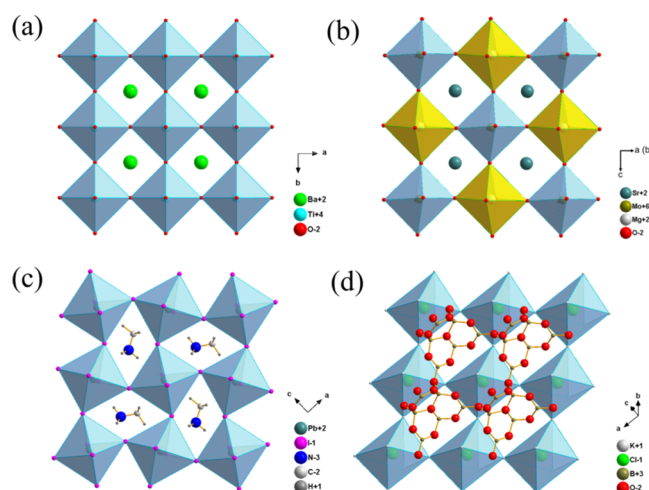


Figure 1. Crystal structures of BTO (a), SMMO (b), MAPbI₃ (c) and KBOC (d).

with conventional perovskite CaTiO_3 , A-site $[\text{B}_6\text{O}_{10}]$ ionic groups that consist of $[\text{BO}_3]$ and $[\text{BO}_4]$ units occupy the positions of atom Ca, whereas atom Cl takes up the positions of atom Ti, and the positions of atom K are similar to those of O. Therefore, analogous to conventional perovskite CaTiO_3 , KBOC could be represented as the formula of $(\text{B}_6\text{O}_{10})\text{ClK}_3$. Details of the crystal symmetry and unit cell dimensions for these compounds are listed in Table 1.

Table 1. Crystal Symmetry and Unit Cell Dimensions of Compounds Analyzed in This Work

compound	space group	symmetry	unit cell dimensions (Å)
BTO	$P4mm$ no. 99	NCS	4.0000(2), 4.0000(2), 4.0240(2)
SMMO	$P\bar{1}$ no. 2	CS	5.56906(4), 5.57039(4), 7.92407(5)
MAPbI ₃	$Pnma$ no. 62	CS	8.86574(30), 12.6293(4), 8.57689(31)
CsPbI_3	$Pnam$ no. 62	CS	8.8561(4), 8.5766(3), 12.4722(6)
ClOK_3	$Pbnm$ no. 62	CS	7.239(2), 7.239(2), 10.277(2)
$\text{B}_6\text{O}_{10}\text{ClK}_3$	$R3m$ no. 160	NCS	10.0624(14), 10.0624(14), 8.8361(18)

3. CALCULATION DETAILS

The electronic structures were obtained by ab initio calculations implemented in the CASTEP package.⁶⁵ The calculations of all crystals were done on experimental structures, and the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof functional⁶⁶ was employed for the exchange–correlation potential. The plane-wave basis set energy cutoff was 900 eV with Norm-conserving pseudopotential, and the Monkhorst–Pack⁶⁷ scheme was given by $6 \times 6 \times 6$, $6 \times 6 \times 4$, $6 \times 6 \times 4$, $6 \times 4 \times 6$, $6 \times 6 \times 4$, $6 \times 6 \times 6$ for BTO, SMMO, CsPbI_3 , MAPbI₃, ClOK_3 , and KBOC in the irreducible Brillouin zone. To ensure the convergence of optical properties, the empty bands were set as three times the number of valence bands in this work. Because of the strong relativistic effect of Pb, spin–orbit coupling (SOC) was previously reported for CsPbI_3 and MAPbI₃. However, the errors of GGA and SOC could counteract with

each other to some degree.²⁶ Therefore, the GGA provides more close results to experiment than GGA + SOC, and thus the GGA without SOC was adopted in this work. Adopting the parameters described above, calculation results of the birefringence for several known optical crystals such as calcite, rutile, YVO₄, and KTP are tabulated in Table 2. The results basically agree with experimental values, indicating the validity of the method used in this work.

Table 2. Calculated and Experimental Birefringence of Some Known Optical Materials under the Same Calculation Conditions in This Work

compound	space group	wavelength (nm)	Δn (cal.)	Δn (exp.)
CaCO ₃	$R\bar{3}c$	@533	0.161	0.174 ³⁹
TiO ₂	$P4_2/mnm$	@1500	0.231	0.249 ⁴⁰
YVO ₄	$I4_1/amd$	@1550	0.208	0.206 ⁴¹
KTP	$Pna2_1$	@1064	0.089	0.085 ⁴²

Under REDA approximation, the birefringence can be estimated by the anisotropic valence bond of anionic groups as

$$\Delta n = \frac{\mathcal{R} \sum_g [N_c Z_a \Delta \rho^b]_g}{2n_1 E_0} \quad (1)$$

Here, $\mathcal{R}$ is the correction coefficient, N_c is the coordination number of the nearest neighbor cations to the central anion, Z_a is the formal chemical valence of the anion, $\Delta \rho^b$ is the difference between the maximum and minimum bonding electron density of covalent bond in an anionic group on the optical principal axes of a crystal, E_0 is the optical band gap, n_1 is the minimum refractive index and usually has little change in a system. In this formula, $\zeta = \sum_g [N_c Z_a \Delta \rho^b / (n_1 E_0)]_g$ is called

the REDA index, which could be employed to characterize the optical anisotropy of materials.^{47,60} In the process of REDA calculation for BTO, SMMO, and KBOC, A-site ionic groups and octahedral units were analyzed separately. To further confirm the conclusions as well as to make a supplement for CsPbI₃ and MAPbI₃ which present weak covalence, the RSAC method was adopted. In detail, Cs⁺, [MA], Cl[−], and [KCl₆] were “cut” from CsPbI₃, MAPbI₃, ClO₃, and KBOC, respectively, to measure and compare the contributions of the A-site groups and octahedral units. The units were cut according to the ionic radius with corresponding charge (Table S1).

4. RESULTS AND DISCUSSION

4.1. Electronic Structures. Band structures and the partial density of states (PDOS) of the title compounds were calculated along the high symmetry lines. As shown in Figure 2a, BTO exhibits a 1.94 eV indirect optical band gap, which is smaller than the experimental value 3.27 eV due to the discontinuity of the derivative on exchange–correlation energy within DFT. An energy shift in the conduction bands or a so-called scissors operator was introduced to calculate optical properties in order to overcome such a difference,⁶⁸ and the value is 1.33 eV in this case. KBOC shows a direct band gap of 5.31 eV (Figure 2b). Compared with the experimental result of 6.89 eV, the scissors operator of 1.58 eV was adopted. Calculated and experimental band gaps of the other four compounds are listed in Table 3.

The composition and origin of calculated bands could be obtained by analyzing the PDOS. In Figure 2a, the main states that determine the gap and electronic transitions are in the range of −5 to 10 eV near the Fermi surface for BTO. The top of the valence bands is greatly composed of O-p orbitals,

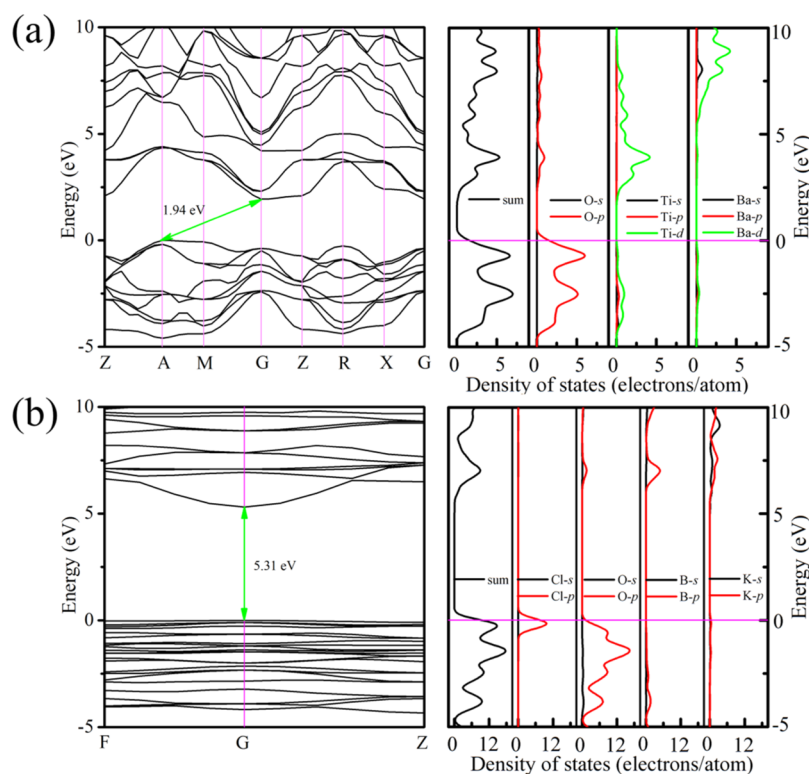


Figure 2. Band structures and PDOS of BTO (a) and KBOC (b).

Table 3. Calculated and Experimental Band Gaps, SHG Coefficients (d_{ij}), and Birefringence (Δn) with the Corresponding Wavelength of the Title Compounds

compound	band gap (eV) (cal./exp.)	d_{ij} (pm/V) (cal./exp.)	Δn (cal./exp.)	wavelength (nm)
BTO	1.94/3.27 ⁶⁹	2.09/2.13 ³⁰	0.059/0.051 ⁷⁰	@633
SMMO	1.90/3.16 ^a		0.016/—	@1064
CsPbI ₃	2.08/2.13 ^a		0.275/—	@1064
MAPbI ₃	2.07/2.13 ^a		0.292/—	@1064
CIOK ₃	0.91/2.35 ^a		0.042/—	@1064
KBOC	5.31/6.89 ⁶	1.02/1.56 ⁶	0.046/0.046 ⁷¹	@1064

^aObtained by PWmat code⁷² HSE06.

whereas the bottom of the conduction bands is mainly derived from Ti-d orbitals and marginally from O-p orbitals. For KBOC (Figure 2b), the top of the valence bands is greatly composed of Cl-p and O-p orbitals, and the bottom of the conduction bands is mainly derived from B-p orbitals. As is well-known, electron transition near the Fermi surface determines material optical properties. Therefore, it is likely that [TiO₆] octahedron is the decisive optical origin for BTO, whereas the B–O group makes more contributions than [KCl₆] octahedral units to optical properties in KBOC. Band structures and PDOS of the other four compounds are presented in Figure S2. Similar to the analysis above, [MoO₆], [PbI₆], and [OK₆] octahedral units are likely dominant in optical properties for SMMO, CsPbI₃, MAPbI₃, and ClOK₃ crystals.

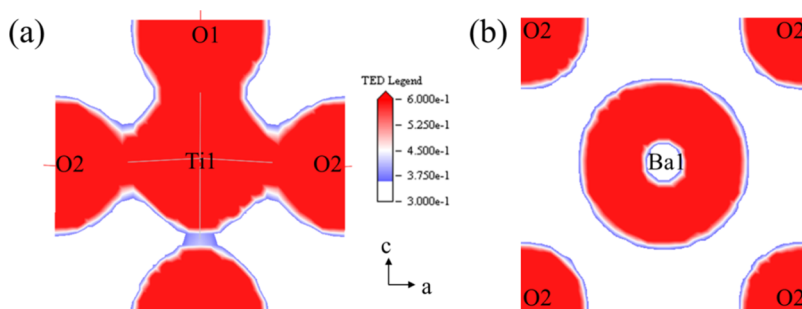
4.2. Linear and NLO Properties. Described by birefringence (Δn), optical anisotropy could be obtained in the form of dispersion refractive indices. Calculated and experimental birefringence are shown in Table 3. BTO exhibits moderate optical anisotropy of 0.059 at 633 nm, and the birefringence of KBOC is 0.046 at 1064 nm. Comparatively, SMMO shows a smaller birefringence of 0.016. With similar [PbI₆] octahedral frameworks, CsPbI₃ and MAPbI₃ exhibit the large optical anisotropy of 0.275 and 0.292 at 1064 nm. In addition, theoretical calculations of SHG coefficients were also performed, and the results are listed in Table 3 as well. Crystallized in centrosymmetry space groups, SMMO, CsPbI₃, and MAPbI₃ conduct no SHG response. For BTO and KBOC, the SHG coefficients are $d_{15} = 2.13$ pm/V and $d_{22} = 1.56$ pm/V, respectively, which are much larger than that of potassium dihydrogen phosphate ($d_{36} = 0.39$ pm/V) and enough for ultraviolet (UV)/ deep UV (DUV) light frequency conversion.

4.3. Origins of Optical Properties. The total electron density (TED) clearly reflects the redistribution of electrons by the form of density maps. In order to make the electron

distribution distinguishable and comparable, a uniform density criterion was adopted for BTO and KBOC (Figure 3). In BTO, observing from the *b* axis, the electron density around Ti1 overlaps with O2 along the Ti1–O2 direction (Figure 3a). At the same time, more conspicuous electron density overlaps show up between Ti1 and O1, which are closely associated with distorted [TiO₆] octahedra described in the crystal structure paragraph. It is worth noting that, in Figure 3b, the spherical appearances of electron density are uniform and isolated around Ba1 atoms. Therefore, the Ti–O bond tends to present more stronger covalency than the Ba–O bond. Taking the relationship between optical properties and covalent behavior into consideration, this phenomenon illustrates that the contributions of [TiO₆] octahedra are likely to exceed that of Ba–O units.

When it comes to KBOC shown in Figure 4a, under the same density criterion with BTO, there is no overlap between Cl[−] and K⁺. Meanwhile, the electron density of [B₆O₁₀], which consists of [BO₄] (Figure 4a,b) and [BO₃] (Figure 4c) units, shows great overlap along B–O bonds, and no barrier appears within the group. In other words, the [B₆O₁₀] groups exhibit more powerful covalency than the [ClK₆] octahedral units, tending to lead the optical anisotropy in KBOC. TED maps with a lower density criterion (Figure S3a) of the other four compounds are shown in Figure S3. For SMMO, there are strong overlaps along the Mo–O bonds, whereas Mg–O shows weak overlaps comparatively which are slightly stronger than the Sr–O bonds. Compared with SMMO, there are few overlaps in CsPbI₃, MAPbI₃, and ClOK₃ along the Pb–I and O–K bonds, whereas no overlaps are present among the A-site groups. In general, octahedral units exhibit stronger bonding behavior than A-site groups in most title compounds, tending to lead the optical anisotropy and NLO properties.

Especially, REDA and RSAC methods were adopted for further optical anisotropy analysis. By REDA approximation, the $\Delta\rho$ of the A-site ionic groups and octahedral units on the optical principal axes were analyzed, respectively. As shown in Figure 5, for SMMO, where the quantity ratio of [MgO₆] and [MoO₆] octahedra is 1:1, Mg–O bonds exhibit weak covalency which is close to that of Sr–O bonds (Figure S3a). As a result, A-site [SrO₁₂] units make about 20% contributions to birefringence. In BTO, $\Delta\rho$ of the [TiO₆] and the [BaO₁₂] units are 0.002585 and 0.000058, respectively, which indicates that the [TiO₆] units make about 97.8% of the source of birefringence. However, when it comes to KBOC, $\Delta\rho$ of the [ClK₆] units and the [B₆O₁₀] groups are 0.000482 and 0.011414, respectively, making about 4.1 and 95.9% contributions to optical anisotropy. To further verify the consequence from REDA and make a supplement for

**Figure 3.** TED of [TiO₆] unit (a) and [BaO₁₂] group (b) in BTO along the *b* axis.

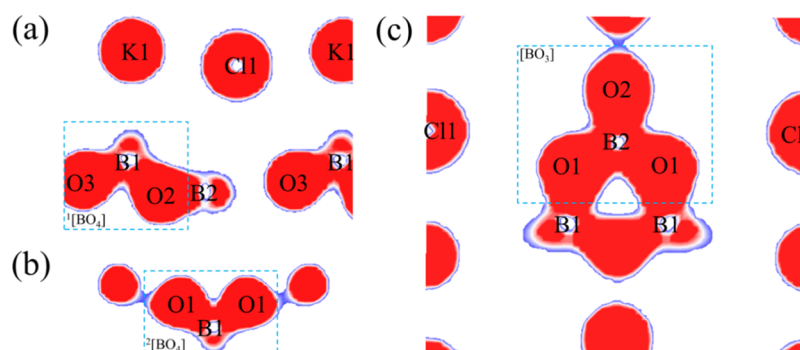


Figure 4. TED of $[\text{ClK}_6]$ unit (a) and $[\text{B}_6\text{O}_{10}]$ group, which consist of $[\text{BO}_4]$ [a combination of $^1[\text{BO}_4]$ (a) and $^2[\text{BO}_4]$ (b)] and $[\text{BO}_3]$ (c), and the direction is shown in Figure S4.

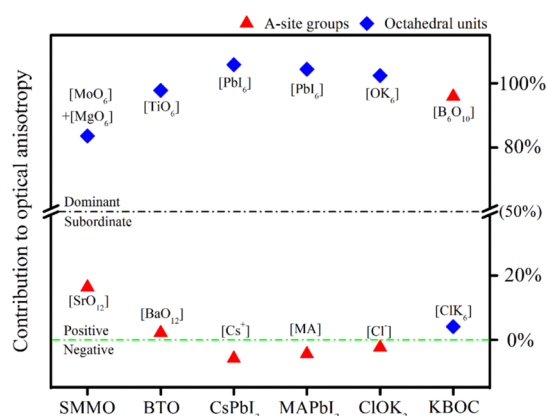


Figure 5. Group contributions of title compounds to optical anisotropy by REDA and RSAC.

compounds with weak covalency, the RSAC method was introduced. In CsPbI_3 , the $[\text{PbI}_6]$ framework presents a birefringence of 0.291, which is larger than the value 0.275 of the entirety. Therefore, $[\text{PbI}_6]$ octahedra contribute 105.8%, whereas Cs^+ contribute about -5.8% . In MAPbI_3 , without $[\text{MA}]$ units, the left $[\text{PbI}_6]$ octahedra exhibit a birefringence of about 0.305. Compared with the result of 0.292, about 104.5% of influence is exerted by $[\text{PbI}_6]$ octahedra. For ClOK_3 , $[\text{OK}_6]$ units contribute 102.4%, and Cl^- take about -2.4% . However, in KBOC, the left $[\text{B}_6\text{O}_{10}]$ units make about 97.8% contributions (the ratio of 0.045–0.046), and it is in good accordance with the result of 95.9% from REDA. Details of the REDA and RSAC results of title compounds are listed in Table S2.

The SHG-density method, which could visualize the SHG response from electronic states, was adopted to analyze the contributions of various ionic groups. As shown in Figure 6a, the SHG density of occupied and unoccupied states indicates that there is almost no contribution to the SHG response from the Ba–O units. In contrast, $[\text{TiO}_6]$ octahedra exhibit a strong SHG response. When it comes to KBOC, the contributions of $[\text{ClK}_6]$ octahedra are appreciable and not negligible. As shown in Figure 6b, comparatively speaking, the A-site B–O units provide more powerful contributions than those from the distorted $[\text{ClK}_6]$ octahedra, as the unoccupied state of O^{2-} is more distinct than that of Cl^- .

5. CONCLUSIONS

In conclusion, we have successfully acquired the optical properties and explored the contributions of microscopic groups to optical anisotropy and NLO response on crystal structure and bond character in conventional perovskite and perovskite-related materials. For BTO, SMMO, CsPbI_3 , MAPbI_3 , and ClOK_3 crystals, $[\text{TiO}_6]$, $[\text{MoO}_6]$, $[\text{PbI}_6]$, and $[\text{OK}_6]$ octahedral units are the major origins to birefringence, most of which make over 90% contributions. But in KBOC, the A-site $[\text{B}_6\text{O}_{10}]$ groups contribute over an order of magnitude more than the $[\text{ClK}_6]$ octahedron. Moreover, by the SHG-density analysis, the $[\text{B}_6\text{O}_{10}]$ group is also the dominant NLO origin in KBOC. In general, octahedral units are the major contributors to both linear and NLO properties in most perovskite-related compounds. However, in KBOC, where the A-site ionic groups present stronger bonding behavior than octahedral units, the A-site ionic group still possibly performs as the main optical origin. We believe this

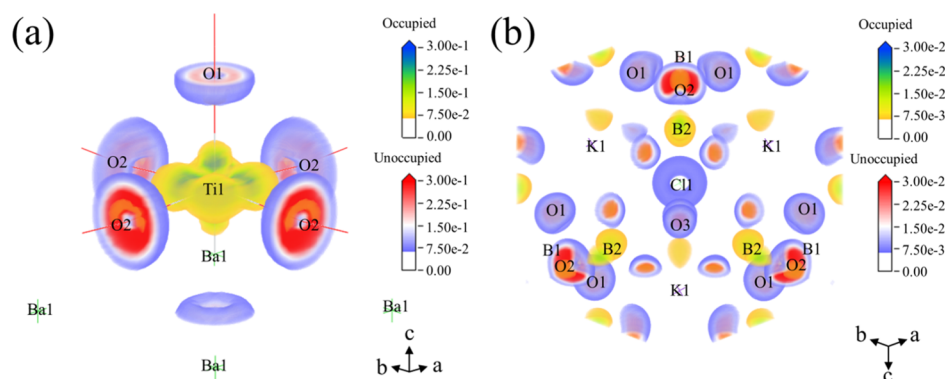


Figure 6. SHG density of occupied and unoccupied states in BTO and KBOC.

work will be helpful to gain more awareness about perovskite-related compounds in microscopic structure, electron distribution, as well as optical properties, or provide inspiration to explore materials with targeted performance.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.9b08478>.

Distorted $[\text{TiO}_6]$ octahedral units in BTO and structures of CsPbI_3 and CLOK_3 ; band structures and PDOS of SMMO , CsPbI_3 , MAPbI_3 , and CLOK_3 ; TED of SMMO , CsPbI_3 , MAPbI_3 and CLOK_3 ; TED planes of $[\text{BO}_3]$, $^1[\text{BO}_4]$, and $^2[\text{BO}_4]$ in KBOC lattice; cut ionic radius for MAPbI_3 , CLOK_3 , and KBOC in RSAC method; and REDA contribution ($\Delta\rho$) of measured units and RSAC results (Δn) of left units after atom-cutting. (PDF)

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Notes

The authors declare no competing financial interest.

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