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Mechanism for linear and nonlinear optical effects in $KBe_2BO_3F_2$ (KBBF) crystal

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Abstract

Electronic structure calculations of $KBe_2BO_3F_2$ crystal from first principles have been performed based on a plane-wave pseudopotential method for the first time. Its optical linear and second harmonic generation (SHG) coefficients are also calculated. The SHG coefficient measured early was much higher than that of our calculation, however, recent experiment confirms our calculated results. Moreover, a real-space atom-cutting method is adopted to analyze the respective contributions of the cation and anionic group to optical response. The results show that the contributions to the SHG coefficients from the $(BO_3)^{3-}$ and $(BeFO_3)^{5-}$ groups are dominant and comparable.

$KBe_2BO_3F_2$ (KBBF) crystal was first synthesized by Soviet scientists in 1968 [1,2], but a wrong space group was given. Later the crystal was successfully grown in our laboratory and its crystal structure was determined correctly [3]. The KBBF crystal has a relatively large Second Harmonic Generation (SHG) coefficient and a wide transparency range (155–3660 nm) [4]. Unfortunately, the crystals are very difficult to grow and easily decompose because of the strong layering tendency in their structures. After more than 10 years continuous efforts, its growth technique has been greatly improved that will impel wide applications of the KBBF crystal. For example, using a special prism coupling technique (PCT), fourth-harmonic generation of Ti:sapphire laser systems from 200 to 179.4 nm has been achieved [5]. Recently, sixth harmonic of Nd : YVO_4 laser (177.3 nm) has been also achieved by using an optical contact prism-coupled KBBF crystal [6]. These advances will greatly promote the developments of photolithography, laser micromaching as well as laser spectroscopy. Although the mechanism of producing SHG in the KBBF crystal can be understood by the anionic group theory (a quantum-chemistry local model) [7], a more comprehensive understanding can only be achieved by performing the ab initio energy band structure calculation, in which the

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influence of cations on the band structure and optical response can be directly evaluated.

CASTEP [8], a plane-wave pseudopotential total energy package, is used for solving the electronic and band structures as well as linear and nonlinear optical properties of the KBBF crystal. The theoretical basis of CASTEP is the density functional theory (DFT) [9] in the local density approximation (LDA) or gradient-corrected LDA developed by Perdew and Wang [10,11]. It is well known that the band gap calculated by the DFT is usually smaller than the experimental data due to the discontinuity of exchange–correlation energy. However, the energy band profiles of this theory are correct, especially for the valence bands. A scissors operator [12,13] is used to shift upward all the conduction bands in order to agree with measured values of the band gap for calculating the optical coefficients.

The geometric parameters of the KBBF crystal are as follows: (R32, $a = b = 4.427$ Å, $c = 18.744$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$) [4]. The basic structure of the KBBF crystal contains K^+ cation and $(BO_3)^{3-}$ and $(BeFO_3)^{5-}$ anionic groups, which is shown in Fig. 1.

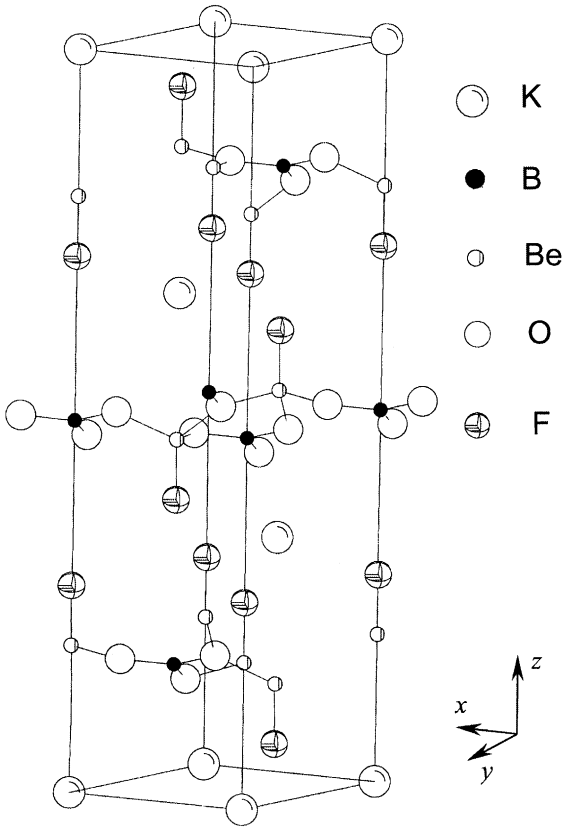

Fig. 1. The layer structure of KBBF.

The calculated band structures of the KBBF crystal in the unit cell are plotted along the symmetry lines in Fig. 2. Obviously, the energy band can be divided into three regions. The lower region is located below −15 eV, and mainly consists of 2s orbitals of oxygen atoms. The middle region is the valence band (VB) from about −10 to 0 eV. This region can be separated into two pieces, of which the lower ones are very flat. The upper one is the conduction band (CB) with a total width of about 7 eV, in which a band of large dispersion spanning about 3 eV appears at the bottom of its conduction bands on the G point. The calculated band gap is 5.259 eV, while the corresponding experimental data is 7.982 eV. On the other hand, we have tried to use other kinds of pseudopotentials to calculate the bands and found that the change of the results is not apparent.

Fig. 3 gives the total density of states (DOS) and partial DOS (PDOS) projected on the constitutional atoms of the KBBF crystal. In addition, the orbital-resolved PDOS were calculated, but they did not be shown in here due to the limitation of the length of Letter. Several characteristics can be seen from Fig. 3: (1) The bands lower than −15 eV mostly consist of 2s orbitals of oxygen atoms of both $(BO_3)^{3-}$ and $(BeFO_3)^{5-}$. In fact, the 2s orbitals of the oxygen atoms are strongly localized at −17 eV. (2) The valence bands are mainly composed of 2p orbitals of oxygen atoms. In addition, a peak of the p orbitals of the cation K^+ occurs at about −10 eV. Moreover, the PDOS plot reveals the reason why the gap between the valence and conduction bands of KBBF is wider than that of BBO (β-BaB_2O_4) and LBO (LiB_3O_5). A mixture of the 2p orbitals of fluorine and oxygen atoms decreases the energy of the valence band which result in a short cut-off wavelength to be approached at 155 nm. At the very top of the VB (from 0 to −3 eV), there is no obvious hybridization between the orbitals of B and O atoms. (3) The bottoms of conduction bands are mainly

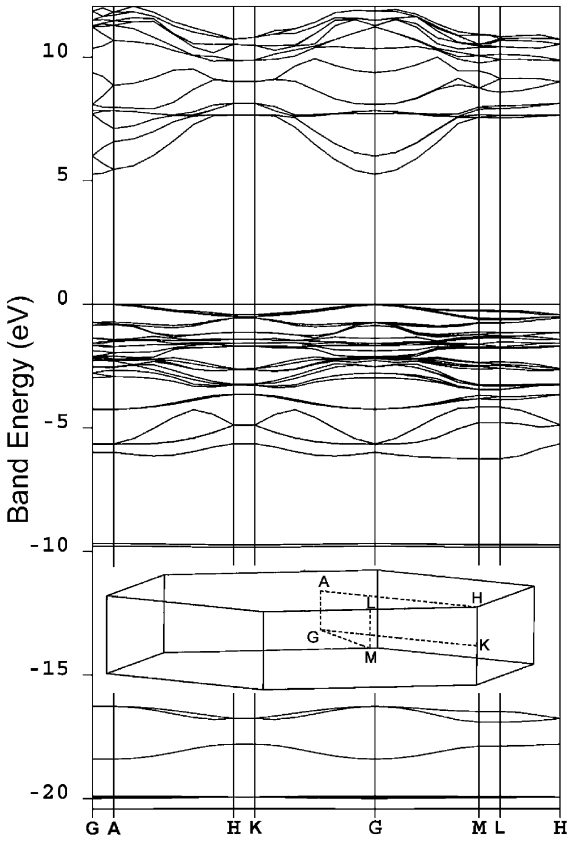

Fig. 2. Band structures of KBBF.

composed of valence orbitals of O and B atoms, while the 2p orbitals of Be are contribute the upper conduction bands in some degree.

It is well known that the refractive indices are obtained theoretically from the dielectric constants. The real part of the dielectric function can be obtained from its imaginary part using the Kramer–Kroning transformation. The imaginary part can be calculated with the matrix elements that describe the electronic transitions between the ground and excited states in the crystals considered [14]. The calculated and experimental values of refractive indices for KBBF crystal at 1064 nm wavelengths are listed in Table 1.

To investigate the influence of the ions on the optical response, a real-space atom-cutting method has been used. The atom-cutting method means that if the contribution of ion A to the nth-order polarizability is denoted as $\chi^{(n)}(A)$, we can obtain it

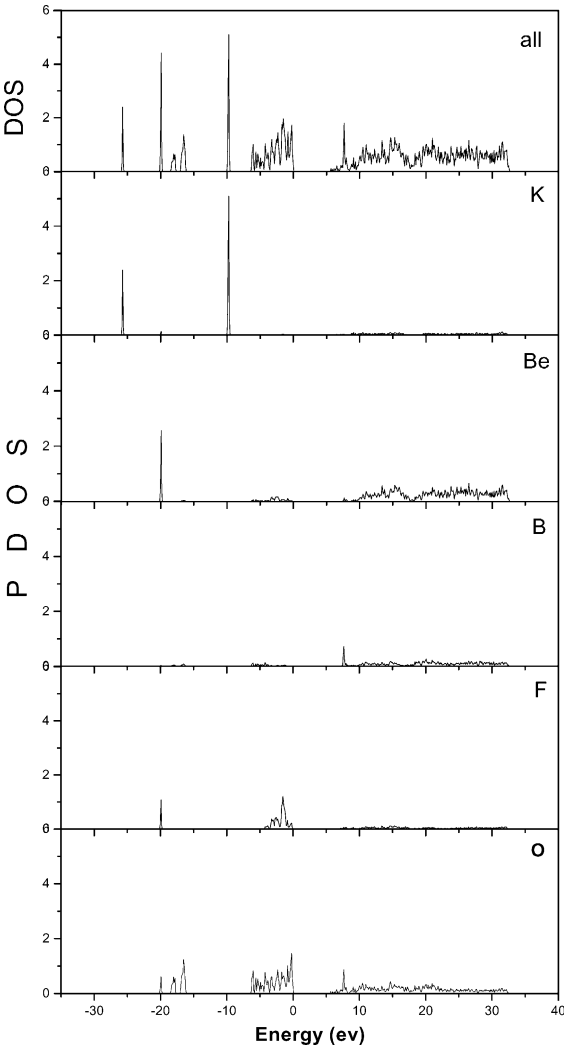

Fig. 3. Total DOS and partial DOS of KBBF.

Table 1
Calculated and experimental values of refractive indices and SHG coefficients of KBBF at 1.064 μm

	Experimental values[a]	Calculated values
n_o	1.477	1.4759
n_e	1.400	1.4150
Δn	0.077	0.061
d_{14} (pm/V)	±0.76, ±0.49[b]	−0.351[c]

[a] Ref. [3].
[b] Ref. [17].
[c] The value is calculated in static limited.

by cutting all ions except A from the original wave functions $\chi^{(n)}(A) = \chi^{(n)}$ (all ions except A are cut). In our previous paper [15] it was found that the charge density around cation (M) is spherical. Thus we first choose the cutting radius of K to be 1.40 Å. Following the rule of keeping the cutting spheres of M and O in contact and not overlapped, the cutting radius of O is set to be 1.10 Å. Finally, the covalent radius 0.88 Å of B is chosen as its cutting radius and the cutting radius of Be is set as 0.66 Å. The cutting-analysis results are given in Table 2.

Our conclusions from the above calculations are the following: (i) The calculated refractive indices (see Table 1) are in good agreement with the experimental values (the relative error is less than 3–5%). The theoretical birefringence Δn is also in good agreement with the experimental value. The agreement proves the validity of our investigation on KBBF crystal with the pseudopotential method. The results should be very helpful for the designing of NLO crystals. (ii) Table 2 shows that the contributions of K^+ cation to the refractive indices are comparable to those of $(BO_3)^{3-}$ and $(BeFO_3)^{5-}$ anionic groups, but their contributions to the anisotropy of refractive indices can be neglected. Moreover, we can easily find that the contribution of the $(BeFO_3)^{5-}$ group to birefringence is much smaller than that of $(BO_3)^{3-}$. It is because the $(BO_3)^{3-}$ group of coplanar configuration responses an incident optical light more anisotropy than that of the $(BeFO_3)^{5-}$ group which has tetrahedral configuration. The results are consistent with those obtained by the anionic group theory [7].

The static limit of the SHG coefficients plays the most important role in the application of SHG crystals, so we adopt the formula presented by Rashkeev et al. [16] and improved by us [15]

Table 2
Comparison of refractive indices and SHG coefficients, birefringence of KBBF at the static limit derived from cut-M ($M = K^+$) and anion-cut functions with origin values

	BO_3^{3-}	$BeFO_3^{5-}$	K^+	Sum	Original
n_o	1.3397	1.4083	1.1214		1.476
n_e	1.2500	1.3574	1.1151		1.415
Δn	0.089	0.051	0.006		0.061
d_{11} (pm/V)	0.312	0.268	0.017	0.597	0.351

$$\chi^{\alpha\beta\gamma} = \chi^{\alpha\beta\gamma}(\mathrm{VE}) + \chi^{\alpha\beta\gamma}(\mathrm{VH}) + \chi^{\alpha\beta\gamma}(\mathrm{twobands}),$$

where $\chi^{\alpha\beta\gamma}(\mathrm{VE})$ and $\chi^{\alpha\beta\gamma}(\mathrm{VH})$ give the contributions to $\chi_i^{(2)}$ from virtual-electron processes and virtual-hole processes, respectively; $\chi^{\alpha\beta\gamma}(\mathrm{twobands})$ is the contribution to $\chi_i^{(2)}$ from the two-band processes. The formula for calculating $\chi^{\alpha\beta\gamma}(\mathrm{VE})$, $\chi^{\alpha\beta\gamma}(\mathrm{VH})$ and $\chi^{\alpha\beta\gamma}(\mathrm{twobands})$ are given in [15].

Using the above formalism, the SHG coefficients of KBBF crystal have been calculated from the band wave functions. The theoretical and experimental SHG values are also listed in Table 1. In order to calculate the respective contributions of cations and the anionic group to the SHG coefficients of crystals, we also adopt the real-space atom-cutting method in which the same atom-cutting radii mentioned above are used. The decomposition results are also given in Table 2. These calculated results lead to the following conclusions:

(i) Our plane-wave pseudopotential approach is suitable for studying the SHG coefficients of KBBF crystal. We can see that the agreement of calculated and experimental values of the SHG coefficients is very good. For the crystal early experimental measurements gave an SHG coefficient $d_{11} = 0.76$ pm/V [3] which is much larger than our present theoretical value $d_{11} = 0.351$ pm/V. To decide what is right and what is wrong, recently our laboratory performed a new experiment to measure the SHG coefficients of KBBF, and obtained a reliable value $d_{11} = 0.49$ pm/V. The new measured data and detailed description of the experiment is submitted elsewhere [17]. In addition, in our previous paper about the mechanism of the linear and nonlinear optical properties of the LBO family [18] we also came across a similar problem. In that paper our theoretical SHG value of CLBO ($CsLiB_6O_{10}$) was $d_{36} = -0.546$ pm/V, but at that time there was only an experimental value $d_{36} = \pm 0.959$ pm/V [19]. Obviously, the discrepancy between theory and experiment was quite large, so we suggested that the SHG coefficients should be re-measured. Last year Shoji et al. [20] published a new measure value $d_{\mathrm{eff}}(\approx 1/2 \cdot (d_{36} + d_{14})) = 0.67$ pm/V at 1.064 μm, which confirms our former theoretical calculation and prediction.

(ii) From Table 2 we can see that the contributions of K^+ to the SHG coefficients is only about 3%, and the contribution of $(BO_3)^{3-}$ and $(BeFO_3)^{5-}$ anionic groups are dominant and comparable. Moreover, the sum of the contributions from individual anionic groups in the crystal is larger than the original calculated value of the whole crystal. This is because in the atom-cutting analysis some atoms (the oxygen atoms) shared by two groups are repeatedly calculated. This also explains why the SHG coefficient calculated to be 0.64 pm/V by the anionic group theory [7], is nearly the same as the result of the sum of contributions from individual anionic groups in this work.

In summary we conclude that the plane-wave pseudopotential approach is suitable to calculate and predict the linear and nonlinear optical properties for the borate series NLO crystals. The analysis of a real-space atom-cutting method shows that the contributions of K^+ cation to birefringence and SHG coefficients are very small and can be neglected, and the contributions of $(BO_3)^{3-}$ and $(BeFO_3)^{5-}$ anionic groups to them are dominant and comparable. Moreover, the sum of the contributions from individual anionic groups in the crystal is larger than the original calculated value of the whole crystal due to the repeated calculation of the wavefunctions of some shared oxygen atoms.

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