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Theoretical calculations and predictions of the nonlinear optical coefficients of borate crystals

TOPICAL REVIEW

Theoretical calculations and predictions of the nonlinear optical coefficients of borate crystals

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Abstract
Theoretical methods to calculate the optical response of crystals are reviewed. The second-harmonic generation coefficients of borate nonlinear optical crystals are calculated using the anionic group theory combined with the Gaussian'92 *ab initio* calculation method. Without adjusting the parameters, the calculated values are in good agreement with the experimental values. Meanwhile, a plane-wave pseudopotential total energy package is also used to calculate and discuss the theoretical background and accuracy of the theory. The results indicate that the anionic group theory can predict and calculate the nonlinear optical coefficients of borate crystals reliably, and the energy band calculations can reveal the relationship between nonlinear optical effects and microstructure.

1. Introduction

Nonlinear optical (NLO) crystals have played an important role in laser science and technology, and the search for new NLO crystals, particularly for the ultraviolet (UV) and infrared (IR) spectral regions, is still very active, even though intensive efforts in this field have been in progress for nearly forty years. Scientists working in this field realize the extreme importance, in the search for new NLO crystals, of a thorough elucidation of the structure–property relationship between NLO effects and microstructure.

Many attempts have already been made in this direction. Among them we may cite in particular the bond parameter methods, exemplified by the work during the 1960s to 1970s of Bloembergen [1], the anharmonic oscillator models of Kurtz and Robinson [2], and Garrett and Robinson [3], the bond parameter methods of Jeggo and Boyd [4], and Bergman and Crane [5], and the bond charge model of Levine [6]. In the above-mentioned works, Levine's model [7] is the most successful, and has been shown to be particularly useful in the elucidation of the

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structure–property relationship of the NLO effect in A-B type semiconductor crystals, in which the basic structural unit consists of sp^3-hybrid tetrahedrally coordinated atoms. However, this method has some limitations for other types of NLO crystals in which the basic structural unit does not belong to the category of simple bonds [8, 9].

Since the 1970s, several research groups have discovered that the second-order susceptibility of most NLO crystals arises from basic structural units with delocalized regions of valence electron orbitals belonging to more than two atoms, rather than from regions localized around two atoms connected by a simple σ-type bond. Davydov *et al* [10] proposed that the second-order susceptibilities of organic crystals originate from the molecules in their basic structural unit, and hence it is most likely that conjugated organic molecules with donor–acceptor radicals will exhibit large second-order susceptibilities. This idea was further developed by Chemla *et al* [11], Oudar and Chemla [12] and Oudar and Leperson [13]. With regard to inorganic NLO crystals, DiDomenico and Wemple [14] found that the second-order susceptibities of perovskite and tungsten–bronze type crystals are largely due to the distortion in the MO$_6$ oxygen-octahedra. Therefore, the latter is considered to be the basic structural unit for the production of second-order susceptibility in these crystals. However, because they only use a parametric method, based on the polarization potential tensor β_{ij}, it is impossible to ascertain the relationship between the electronic structure of the MO$_6$ oxygen-octahedra and the macroscopic second-order susceptibilities.

At the end of the 1960s, Chen initiated an extensive study to develop a general quantum-chemical NLO-active group theory of the structure–property relationship of NLO effects in some typical known inorganic NLO crystals. This work has led to the establishment of the so-called 'anionic group theory' [15] and an approximate method of calculation based on the second-order perturbation theory for the second-order susceptibilities of NLO crystals [16, 17]. On the basis of this theoretical model, Chen's group succeeded in a systematic elucidation of the structure–property relationship of the NLO effect for almost all the principal types of inorganic NLO crystals, namely the perovskite, tungsten–bronze, iodate, phosphate and nitrite crystals [17].

In the last two decades several first-principles calculations of the optical responses of NLO crystals have been performed. In the early years attention focused on the development of the calculation methods and the responses of certain semiconductor crystals. Later, with the consummation of the calculation method the band structures and optical responses were obtained for such complex crystals as β-BaB$_2$O$_4$ (BBO), LiB$_3$O$_5$ (LBO) and CsB$_3$O$_5$ (CBO).

In this review we concentrate on three theories and calculation methods for the optical response, and in particular focus on the calculations of the NLO coefficients of borate crystals: (1) the bond charge model, (2) the anionic group theory and (3) the first-principles calculation. The paper is organized in the following way. In section 2 we introduce the above three calculation methods and their applications. In section 3 the relation of the structure–optical properties of BBO crystal is discussed. In section 4 the results for the LBO family are given and discussed. In section 5 the calculations of various other borate crystals are given. In section 6 similar calculations and discussions are given for the ReCa$_4$O(BO$_3$)$_3$ family. Finally, some conclusions are made in section 7.

2. Three methods to calculate the optical response

2.1. The bond charge model

The bond charge and bond polarization model investigates the nonlinear susceptibility of materials from the view of the chemical bond and its polarizability [6–9]. The basic assumptions

of this model are: (1) the polarizabilities of individual bonds can be summed, and the material macrosusceptibility is equal to the sum of the microsusceptibilties of individual bonds in the crystal structure; (2) on the basis of the distribution of bond charges the susceptibility of an individual bond can be calculated with the parameter method. In the early years this model was established for calculating the linear susceptibility of materials. Later Robinson suggested that it could also be applied to nonlinear optical coefficients [18]. The NLO coefficients d can be written as

$$d_{mnp} = \sum_b G_{mnp}^b(qrs)\beta_{qrs}^b \qquad (1)$$

where b labels the bond, q, r and s are direction cosines, β is the NLO susceptibility of the bond, and the $G_m^b np(qrs)$ are the geometrical factors connecting the bond direction with the crystalline axes. Levine suggested calculating the microsusceptibility of the chemical bond with an oscillator model of the bond charge [7]. This model is the most successful and is particularly useful in the elucidation of the structure–property relationship of the NLO effect in A-B type semiconductor crystals. However, this model has some limitations for other types of NLO crystals in which the basic structural unit does not belong to the category of simple bonds [8, 9].

2.2. Anionic group theory

On the basis of an investigation of almost all principal types of NLO crystals known, such as perovskite, tungsten–bronze type, iodate, phosphate, molybdate and nitrite crystals, Chen discovered that in any crystal with large NLO effects, the basic structural unit is without exception built up from the anionic groups (or molecules for organic NLO crystals), which are capable of producing large microscopic second-order susceptibilities, such as the $(MO_6)^{n-}$ coordination octahedron in perovskite and tungsten–bronze type crystals, the $(IO_3)^-$ group in iodates, the $(PO_4)^{3-}$ and $(MoO_4)^{2-}$ group in, respectively, phosphates and molybdates, the $(NO_2)^-$ group in nitrites, and so on. On this basis, Chen proposed a theoretical model called the 'anionic group theory' for the NLO susceptibility of NLO crystals in 1976 [15]. This theory rests on the following two assumptions: (1) the overall SHG coefficient of the crystal is the geometrical superposition of the microscopic second-order susceptibility of the anionic groups, and has negligible contribution from the essentially spherical cations; (2) the microscopic second-order susceptibility of the basic anionic group can be calculated from the localized molecular orbitals of this group using quantum chemistry calculation methods. It can easily be shown that the two assumptions can be expressed by

$$\chi_{ijk}^{(2)} = \frac{F}{V} \sum_p N_p \cdot \sum_{i'j'k'} \alpha_{ii'}\alpha_{jj'}\alpha_{kk'}\chi^{(2)}i'j'k'(P) \qquad (2)$$

where $F = (n^2+2)/3$ (refractive index $n = n_x, n_y$ and n_z) is the local field factor [19], V is the volume of a unit cell, N_P is the number of pth groups in this unit cell, and $\alpha_{ii'}$, $\alpha_{jj'}$ and $\alpha_{kk'}$ are the direction cosines between the macroscopic coordinates of the crystal and the microscopic coordinates of the pth group. The $\chi_{i'j'k'}^{(2)}(P)$ is the microscopic second-order susceptibility of the pth group, which can be calculated with our subprogram based on the molecular orbital calculation results of the group. On the basis of second order perturbation theory, the formula for the microscopic SHG coefficients is

$$\chi_{ijk}^{2\omega} = \frac{-e^3}{4h^2} \cdot a_H^3 \cdot N \cdot S_{ijk}^{2\omega} \cdot \sum_{n,n'}{}' \{[\langle g|r_i|n\rangle\langle n|r_j|n'\rangle\langle n'|r_k|g\rangle$$
$$+ \langle g|r_i|n\rangle\langle n|r_k|n'\rangle\langle n'|r_j|g\rangle] \cdot L^{(ijk)}(\omega_{gn}; \omega_{gn'})$$
$$+ \langle g|r_j|n'\rangle\langle n'|r_i|n'\rangle\langle n|r_k|g\rangle L^{(00)}(\omega_{gn}; \omega_{gn'})\} \qquad (3)$$

where $\langle g|r_i|n\rangle = \langle \Psi_g | \sum r_i(p)\Psi_n \rangle$ is the matrix of the electron dipole moment between the ground and excited states, a_H is the Bohr radius, $S_{ijk}^{(2\omega)}$ is the conversion coefficient of the effective field given by [19]

$$S_{ijk}^{(2\omega)} = \left(\frac{n_e^2(2\omega)+2}{3}\right)\left(\frac{n_o^2(\omega)+2}{3}\right)\left(\frac{n_o^2(\omega)+2}{3}\right) \tag{4}$$

and $L^{(ijk)}$ and $L^{(00)}$ are energy factors expressed by

$$L^{(ijk)}(\omega_{gn};\omega_{gn'}) = \frac{1}{(\omega_{gn}-2\omega)(\omega_{gn'}-\omega)} + \frac{1}{(\omega_{gn}-2\omega)(\omega_{gn'}-\omega)},$$
$$L^{(00)}(\omega_{gn};\omega_{gn'}) = \frac{1}{(\omega_{gn}-\omega)(\omega_{gn'}+\omega)} + \frac{1}{(\omega_{gn'}-\omega)(\omega_{gn'}+\omega)}. \tag{5}$$

For $i = j = k$ the energy factor is

$$L^{(iii)}(\omega_{gn};\omega_{gn'}) = L^{(ijk)}(\omega_{gn};\omega_{gn'}) + L^{(ijk)}(\omega_{gn'};\omega_{gn}) + L^{(00)}(\omega_{gn};\omega_{gn'}) \tag{6}$$

where $\omega_{ng} = (E_n - E_g)/\hbar$ and E_n, E_g are the energies of the excited and ground states, respectively. Equation (1) is a widely accepted formula used for transforming the microscopic susceptibility of the pth group to a macroscopic coefficient. According to equations (2) to (6), we have written a subprogram for computation of the microscopic susceptibility using the results of the Gaussian'92 calculation.

During the 1980s, Chen's group turned its attention to the borate series and recognized that borate compounds have numerous structural types, since boron atoms have either three- or four-fold coordination. This complex structural nature of the borate compounds leads to a great variation in the selection of structures favourable for NLO effects, and the anionic group theory can be used to systematically elucidate which structural unit is most likely to exhibit large nonlinearities [20]. This theoretical analysis combined with systematic experimental studies led Chen's group to discover BBO (low temperature phase barium metaborate, β-BaB_2O_4), which has now become one of the most outstanding NLO crystals [21]. Meanwhile, scientists in Germany also discovered that powder BBO has a relatively large SHG effect [22].

After discovering BBO, Li and Chen correctly calculated the SHG coefficients of BBO using the anionic group theory combined with the complete neglect of differential overlap (CNDO) approximation [23]. The results revealed that the SHG coefficients of BBO are determined by the $(B_3O_6)^{3-}$ group, and the contribution of cation Ba^{2+} to the macroscopic SHG coefficients is negligible. On the basis of this method, Chen's group further calculated the SHG coefficients of various borate crystals from the mid-1980s to the beginning of the 1990s, and discovered a series of new borate and berritoborate NLO crystals, such as LiB_3O_5 (LBO) [24], CsB_3O_5 (CBO) [25], $KBe_2BO_3F_2$ (KBBF) [26, 27], $Sr_2Be_2B_2O_7$ (SBBO) [28], $Ba_2Be_2B_2O_7$ (TBO) [29], $BaAl_2B_2O_7$ (BABO) [30] and $K_2Al_2B_2O_7$ (KABO) [31]. Meanwhile, several other groups also discovered other borate series NLO crystals, typical representatives being $CsLiB_6O_{10}$ (CLBO) [32, 33], $ReCa_4O(BO_3)_3$ (Re=Y, Gd) [34–36], $BaCaBO_3F$ [37] and LiB_4O_7 [38]. The SHG coefficients of these newly discovered borate NLO crystals have also been correctly calculated with the anionic group theory. We will discuss these calculations in sections 5 and 6. Recently, Backer [39] has given a review on borate NLO materials which discusses the further developments of recent years.

However, due to limited computation methods and facilities, in the 1980s Chen's group only used the CNDO-type approximation to calculate the molecular orbitals of anionic groups, so there may be some doubts about their calculated results. To investigate the reliability of the anionic group theory in determining the SHG coefficients of borate NLO crystals we used a more precise method to calculate the SHG coefficients by means of the anionic group formulae again, namely, an *ab initio* method with the Gaussian'92 package [40].

On the other hand, the contribution of cations to the overall SHG coefficients is totally neglected in the anionic group theory. However, it is obvious that there are, to a certain degree, interactions between the anionic groups and cations in the lattice. Recently, some authors have even supposed that the cations may account for a major contribution to the SHG coefficients of borate NLO crystals [41]. In order to answer these questions, we need to use the first-principles energy band calculation method to analyse the action of cations on the effect of SHG coefficients, at least for the borate series NLO crystals.

2.3. First-principles calculations

The first-principles calculation, due to its predictive power and systematic way, has become a more favourable approach to study the NLO properties of materials, especially the SHG properties. Early in 1963, Butcher and McLean [42] presented the formalism to calculate SHG coefficients based on band structure. However, due to the difficulty in dealing with the explicit divergence in the static limit of their formula, the calculation was not practical until recently when some groups [43–47] greatly improved the evaluation methods. After Aspnes [43] gave a formalism free of divergence in cubic crystals, Ghahramani et al [44] took another important step to present a general approach to avoid the divergence by a new sum rule and calculated $\chi^{(2)}$ of $(Si)_n/(Ge)_n$. Afterwards, Sipe and Ghahramani [45] improved the methodology by systematic separation of interband and intraband motion. Aversa and Sipe [46] used the length gauge instead of velocity gauge in their formulation to give expressions free from the unphysical divergence. Rashkeev et al [47] later rearranged this formalism to make the symmetries more apparent, and calculated $\chi^{(2)}$ for the zinc-blende GaAs, GaP and wurtzite GaN, AlN. Very recently, Duan et al [48–50] presented an evaluation technique to reduce the number of k points needed for convergence of the formula given by Ghahramani et al. They calculated the first and second optical responses of BBO, LBO and CBO crystals and pointed out the dominant source of the optical nonlinearities of these crystals. In 1999, we briefly reviewed the above-mentioned progress [51], and gave an improved formula based on [47]. We slightly rearranged the terms to eliminate those denominators that may cause divergence, and made use of Duan's method to improve efficiency in reducing the number of k points necessary for convergence. At the same time, we suggested a real-space atom-cutting method to analyse the respective contributions of various transitions among ions and ion groups to optical response. The calculated energy gaps of some NLO borate crystals on the first-principles level are listed in table 1 in which we also give a note about the calculated optical properties.

We used CASTEP [55], a plane-wave psuedopotential total energy package, to develop a new way to calculate the SHG coefficients using band wave functions. The static limit of the SHG coefficients plays the most important role in the application of SHG crystals, so we

Table 1. Energy gaps of LBO, CBO, CLBO and BBO crystals from energy band calculations (eV).

	Exp.	OLCAO[54]	LCAO[53]	LAPW[48−50]	CASTEP[51, 52]
LBO	7.78	7.37	6.9	6.95	4.825
CBO	7.28			5.86	4.463
CLBO	6.87				4.321
BBO	6.55	5.60	4.9	4.88	4.80
Note[a]		$\varepsilon(0)$	Optical conductivity	$\chi^{(2)}$, n	$n_x, n_y, n_z, \chi^{(2)}$

[a] Note shows the calculated optical properties: ε is the dielectric constant, n the refractive index and $\chi^{(2)}$ the SHG coefficients.

adopted the formula originally proposed by Rashkeev *et al* [47] and further improved by us [51]

$$\chi^{\alpha\beta\gamma} = \chi^{\alpha\beta\gamma}(\text{VE}) + \chi^{\alpha\beta\gamma}(\text{VH}) + \chi^{\alpha\beta\gamma}(\text{two bands}) \tag{7}$$

where $\chi^{\alpha\beta\gamma}(\text{VE})$ and $\chi^{\alpha\beta\gamma}(\text{VH})$ denote the contributions from virtual-electron processes and virtual-hole processes, respectively, where $\chi^{\alpha\beta\gamma}(\text{two bands})$ devote the contribution to $\chi^{(2)}$ from two band processes. The formule for calculating $\chi^{\alpha\beta\gamma}(\text{VE})$, $\chi^{\alpha\beta\gamma}(\text{VH})$ and $\chi^{\alpha\beta\gamma}(\text{two bands})$ are given in reference [51].

To analyse the contribution of an ion (or cluster) to the nth order susceptibility $\chi^{(n)}$, we present a model called the real-space atom-cutting method. In the calculation we divide the real space into individual zones, each of which contains an ion. For simplicity, we define the zones to be spheres centred on a specific ion. When we set the band wave function to zero in the zones that belong to a specific ion (which we refer to as 'cutting'), the contribution of the ion is assumed to be cut away. Therefore, the contribution of an ion is extracted when we cut other ions from the total wave functions. For example, if the contribution of ion A to the nth order susceptibility is denoted as $\chi(n)(\text{A})$, we can obtain it by cutting all ions except A from the original wave functions, i.e.,

$$\chi_A^{(n)} = \chi_{\text{All ions except } A \text{ are cut}}^{(n)} \tag{8}$$

where the expression for $\chi_A^{(n)}$ and computation details are given in [51]. The definition of the boundary of two nearest ions is given by the points at which the charge density in real space reaches a local minimum. By this strategy, the cutting radius of two nearest ions can be determined.

3. Structural origin of the NLO effect for BBO crystal

The structural unit of BBO crystal is composed of two parts: the $(B_3O_6)^{3-}$ group and the Ba^{2+} cation. The point group of BBO is C_{3v} [56] and, therefore, according to the IEEE/ANSI standard for the definition of the SHG coefficients of an NLO crystal [57], BBO has mainly three independent non-vanishing SHG coefficients: d_{22}, d_{31} and d_{33} ($d_{15} \approx d_{31}$ from Kleinman symmetry [58]). According to the anionic group theory, $(B_3O_6)^{3-}$ group is the basic structural unit which produces NLO effects in BBO. In other words, the macroscopic SHG coefficient of BBO is the geometrical superposition of the microscopic second-order susceptibility tensor of the $(B_3O_6)^{3-}$ group; the cations have been neglected in the first-order approximation. On the basis of this theory, Li and Chen calculated the SHG coefficients of BBO crystal using the CNDO/S quantum chemistry approximate method, and obtained satisfactory results [23]. However, the CNDO/S method partly relies on the parameters. Thus, we re-calculated the SHG coefficients of BBO crystal based on a first-principles method that consists of two steps: first we use the Gaussian'92 *ab initio* method to calculate the localized orbitals of the $(B_3O_6)^{3-}$ group, then we determine the microscopic SHG coefficients with the self-consistent field orbitals obtained. Furthermore, the macroscopic SHG coefficients of the crystal are calculated by expression (1). Table 2 lists the results obtained by the two different methods. These calculations clearly support the conclusion that the SHG coefficients of BBO crystal indeed come mainly from the contribution of $(B_3O_6)^{3-}$ groups. However, the contribution of coplanar $(B_3O_6)^{3-}$ groups to the d_{31} and d_{33} vanishes when the crystal lattice fields produced by Ba^{2+} cations and the other $(B_3O_6)^{3-}$ groups are not considered. This means that d_{31} is the same as d_{33} and equal to zero, if the effects of the odd-order lattice fields Vs, which are produced by $(B_3O_6)^{3-}$ groups and cations, are not included in the calculation. If an odd-order lattice field Vs is added to the Hamiltonian of the $(B_3O_6)^{3-}$ groups, the theoretical values of the d_{31} and d_{33} for BBO crystal would appear. Obviously, the odd-order lattice field Vs is produced

by the non-symmetrical distribution of Ba^{2+} cations and the other $(B_3O_6)^{3-}$ groups along the z-axis. However, the size of the d_{31} and d_{33} coefficients is only 6% ~ 7% of that of the d_{22} coefficients in BBO crystal. This means that the contribution of the Ba^{2+} cation to the SHG coefficients can be completely neglected under the first-order approximation.

To investigate the limitation and degree of approximation of the above-mentioned calculation results based on the anionic group theory, we have performed energy band calculations with the CASTEP package [55] and 'cutting' analysis for BBO crystal [51]. Table 3 lists the contributions of the $(B_3O_6)^{3-}$ group and Ba^{2+} to the refractive indices of BBO. Obviously, the contributions from the cation Ba^{2+} are about 10%, but only 1% in the case of the birefringence. Table 4 lists the contributions of the $(B_3O_6)^{3-}$ group and Ba^{2+} to the SHG coefficients. The contribution of cations is only 15%–20%. The error is at the same level in calculations of SHG coefficients based on the anionic group theory, thus we are convinced that the anionic group theory is suitable for dealing with the relationship between the microscopic structure and the SHG coefficients of various borate crystals.

Obviously, the anionic group theory method is based on an approximate localized orbital model since it considers neither the contribution of cations nor that of the interaction between groups to the SHG coefficients. However, we believe that the theory is accurate enough for analysing the SHG effects of the borate NLO crystals and has a firm theoretical basis. The reasons are: (1) the results of energy band calculations of BBO, LBO, CBO and CLBO by our group using the CASTEP method [51, 52] indicate that the charge density of cations and the

Table 2. SHG coefficients of BBO (pm/V; $\lambda = 1.064$ μm).

d_{ij}	Experiment	Calculated	
		CNDO	Gaussian'92
d_{22}	$\pm 1.60(1 \pm 0.05)^a$	2.2(CNDO/S)	2.03^c
	$\pm 2.20(1 \pm 0.05)^b$	1.2(CNDO/2)	1.73^d
d_{31}	$\leqslant -(0.07 \pm 0.03)d_{22}^a$	−0.03	
d_{33}	$\approx 0^*$	−0.0039	

[a] Reference [21].
[b] Reference [63].
[c] Average boron–oxygen bond length in the $(B_3O_6)^{3-}$ group used.
[d] Real boron–oxygen bond length in the $(B_3O_6)^{3-}$ group used.

Table 3. Contribution of Ba^{2+} and $(B_3O_6)^{3-}$ group to the linear refractive indices of BBO by CASTEP

	Total	Ba^{2+} cut out ($r = 1.35$ Å)	Contribution of Ba^{2+}
n_o	1.6851	1.5280	9.3%
n_e	1.5695	1.4114	10%
$\Delta n = |n_o - n_e|$	0.1156	0.1166	0.86%

Table 4. Contribution of Ba^{2+} and $(B_3O_6)^{3-}$ group to SHG coefficients of BBO by CASTEP (pm/V).

	Total	Ba^{2+} cut out ($r = 1.20$ Å)	$(B_3O_6)^{3-}$ ($r(B) = 0.8$ Å, $r(O) = 1.2$ Å)
d_{22}	−2.76	−1.50	−0.36
d_{31}	−0.107	−0.059	−0.039
d_{33}	−0.0077	0.045	−0.030

B–O groups can be separated, while the B_3O_6 group in BBO and the B_3O_7 group in the LBO family should be treated as a whole. (2) The dipole transition from the cation to B–O group is the off-site transition. Its value is about one order smaller than the dipole transition of the intra-atomic transitions within B–O groups or cations [51]. The result is shown in figure 1, where VB represents valence band and CB represents the conduction band. This conclusion allows us to calculate the optical coefficients, such as linear and second-order susceptibility, of cations or anionic groups separately. (3) The Madelung potential should be considered in the crystal lattices; it arises from electrovalent cations and anionic groups and shifts the bands of cations upward and the bands of anionic groups downward. However, it is difficult to theoretically predict this potential for different lattices. Thus, if the cations were included in the localized model, an arbitrary parameter of the Madelung potential has to be introduced during the localized molecular orbital calculation. Obviously, this is not what we want. On the other hand, addition of the cations to the anionic group, which forms a cluster, will produce a problem known as the electric charge balance. Thus, we believe that it is reasonable to choose the anionic group as the basic structure unit to study the relationship between the microscopic structure and the SHG effects of borate NLO crystals.
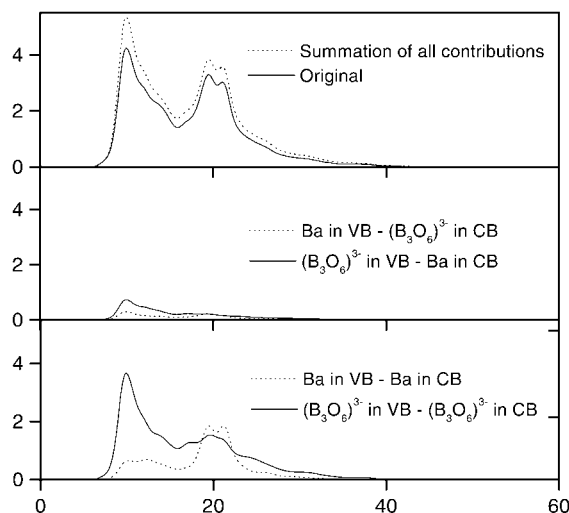

Figure 1. Imaginary part of the dielectric function

4. Calculation of SHG coefficients for the LBO family

On the basis of the anionic group theory, Chen's group and co-workers systematically studied the relationship between the microscopic NLO coefficients and the structure of various boron–oxygen groups using a CNDO-type approximation from the end of the 1970s to the beginning of the 1980s [23]. To confirm the reliability of the results, we calculate the microscopic susceptibilities of various boron–oxygen groups by means of the Gaussian'92 *ab initio* method again. Some results are listed in table 5. These calculations support two obvious conclusions as follows. (1) The coplanar $(BO_3)^{3-}$ or $(B_3O_6)^{3-}$ group which has conjugated π orbitals should have relatively large microscopic SHG coefficients, but its z component is small. (2) The $(B_3O_7)^{5-}$ group should be formed if one boron of the $(B_3O_6)^{3-}$ group is changed from trigonal to tetrahedral coordination. The $(B_3O_7)^{5-}$ group gives rise to a relatively large z component of

Table 5. Calculated values of the microscopic susceptibility of some typical boron–oxygen groups (10^{-31} esu; $\lambda = 1.064\ \mu$m).

Group	Microscopic susceptibility	CNDO	Gaussian'92
$(BO_3)^{3-}$	$\chi_{111}^{(2)}$	0.64	0.4715
	$\chi_{122}^{(2)}$	−0.64	−0.4715
$(B_3O_6)^{3-}$	$\chi_{111}^{(2)}$	1.591	1.5597
	$\chi_{122}^{(2)}$	−1.591	−1.5520
$(B_3O_7)^{5-}$	$\chi_{111}^{(2)}$	−2.9308	−1.8593
	$\chi_{122}^{(2)}$	0.8212	0.7618
	$\chi_{133}^{(2)}$	−0.6288	−0.4142
$(BO_4)^{5-}$	$\chi_{123}^{(2)}$	−0.1578	−0.1404
	$\chi_{113}^{(2)}$	0.0335	0.0055
	$\chi_{223}^{(2)}$	−0.0329	−0.0139

Table 6. SHG coefficients of LBO family (pm V^{-1}; $\lambda = 1.064\ \mu$m).

Crystal	d_{ij}	Experiment[a]		Calculated	
		C T Chen et al[b]	Velsko et al[c]	CNDO/2	Gaussian'92
LBO	d_{31}	±0.97	±0.71 ± 0.05	−0.94	−0.94
	d_{32}	±1.05	±0.83 ± 0.06	1.04	1.00
	d_{33}	±0.053	0 ± 0.1	0.21	0.20
CBO	d_{14}	±0.75	±1.04[e]	−0.65	−0.68
CLBO	d_{36}	±0.95[d]		−0.58	−0.57

[a]d_{36}(KDP) = 0.39 pm V^{-1} adopted as criterion.
[b]Reference [24]
[c]Reference [64].
[d]Reference [32].
[e]Reference [25].

the SHG coefficients while the *x* and *y* components are nearly unchanged. From the quantum chemistry calculation it is known that this structure is beneficial for a wider transparent range on the UV side [59]. Therefore, it is advantageous to choose $(B_3O_7)^{5-}$ groups instead of the $(B_3O_6)^{3-}$ as the basic structure in the search for new borate NLO crystals for UV and DUV applications. Based on this model, LBO crystal was discovered in 1988 [24], and Wu's group and Keszler's group respectively discovered NLO effects in CBO [25] and CLBO [32], in which the basic structural unit is also the $(B_3O_7)^{5-}$ group.

Although the SHG coefficients of LBO, CBO and CLBO have already been calculated by the CNDO approximation, we use the Gaussian'92 *ab initio* method to determine them once more. The calculated and experimental values are listed in table 6. The results of both methods show no difference from the measured values, which implies the reliability of both methods. However, the d_{36} coefficient of CLBO calculated by either method is somewhat smaller than the value measured by Sasaki's group [32]. To investigate the inconsistency of the theoretical value with the measured value, we determine the SHG coefficients of the three crystals by means of the CASTEP package, and find that the theoretical d_{36} value of CLBO is even smaller. The results are also listed in table 7. Therefore, we suggest that the measured value of Sasaki's group is not sufficiently accurate. We will measure the d_{36} coefficient of CLBO in a later study. Moreover, we have calculated the contribution of cation and anion groups to the SHG coefficients of these three crystals on the basis of the CASTEP package and

Table 7. Contributions of Li^+, Cs^+ and $(B_3O_7)^{5-}$ group to SHG coefficients of LBO family by CASTEP (pm V^{-1}).

Crystal	Contributions			
LBO		d_{31}	d_{32}	d_{33}
	Li^+	−0.008	0.002	−0.001
	$(B_3O_7)^{5-}$	−0.496	0.571	−0.006
	Sum	−0.504	0.573	−0.007
	Original[a]	−0.505	0.582	0.014
	Experiment[b]	∓0.67	±0.85	±0.04
CBO		d_{14}		
	Cs^+	−0.098		
	$(B_3O_7)^{5-}$	−0.342		
	Sum	−0.440		
	Original	−0.577		
	Experiment	±1.04[c], ±0.75[d]		
CLBO		d_{36}		
	Li^+	−0.006		
	Cs^+	−0.138		
	$(B_3O_7)^{5-}$	−0.222		
	Sum	−0.366		
	Original	−0.546		
	Experiment[e]	±0.95		

[a] Original means the SHG coefficients without cutting.
[b] Reference [65].
[c] Reference [26].
[d] Reference [66].
[e] Reference [32].

real-space atom-cutting methods [51]. The computational details are given in references [51] and [52], and table 7 shows the results. One can easily see from the table that the contribution of the Li^+ cation to the SHG coefficients of LBO is nothing, while that of the Cs^+ cation to the coefficients of CBO and CLBO is about 15%. Therefore, we are convinced that the SHG coefficients of the LBO family can be determined based on the anionic group theory.

5. Calculation of SHG coefficients of various other borate crystals

The KBBF crystal has relatively large SHG coefficients ($d_{14} = 0.76$ pm V^{-1}) and a wide transparency range (155–3660 nm) [26, 27]. Unfortunately, the crystals are very difficult to grow and easily decompose due to the strong layering tendency in their structures. Thus it is necessary to find other new ultraviolet (UV) NLO crystals which can achieve SHG phase-matching below 200 nm. In order to attain this target we used a molecular engineering approach to search for new UV NLO crystals in borate-based compounds. As a result, SBBO, BABO and KABO were discovered during the 1990s. Recently, electronic structure calculations of KBBF, BABO, KABO and BPO_4(BPO) nonlinear optical crystals from first-principles were carried out based on a plane-wave pseudopotential method with the CASTEP package [55]. On the basis of the band structure and wave functions the linear and nonlinear optical coefficients were obtained for the four NLO crystals. A real-space atom-cutting method was also adopted to give the respective contributions of cations and anionic groups to the optical response. Table 8 gives the calculated and experimental SHG coefficients of the four crystals.

The calculated refractive indices, birefringence (table 9) and SHG coefficients are in good

Table 8. SHG coefficients of miscellaneous borate crystals by CASTEP (pm V^{-1}; $\lambda = 1.064\,\mu$m).

Crystal	d_{ij}	Experiment	Calculated
KBBF	d_{11}	0.76	−0.35
BABO	d_{11}	0.75	0.745
KABO	d_{11}	0.48	−0.317
BPO	d_{15}	0.585^a	−0.358

[a] Reference [66]

Table 9. Refractive indices and birefringence of KBBF, BABO, KABO and BPO crystals, as calculated by CASTEP and experimental values.

Crystal	Wavelength	Calculated			Experiment		
	(μm)	n_o	n_e	Δn	n_o	n_e	Δn
KBBF	1.064	1.4759	1.4150	0.061	1.477	1.400	0.077
BABO	1.064	1.5757	1.5257	0.050	1.570	1.517	0.053
KABO	1.064	1.5590	1.5071	0.052	1.560	1.492	0.068
BPO	1.064	1.6046	1.600	0.0046	1.600	1.595	0.005

agreement with experimental values for these crystals. The results of the atom-cutting method reveal that the contributions from K^+ and Ba^{2+} to the refractive indices are comparable with those from the anion groups BO_3^{3-} and AO_4^{5-}, but their contributions to the anisotropy of the refractive index can be neglected. The contributions to the SHG coefficients from the $(BO_3)^{3-}$ and AlO_4^{5-} go beyond 95% for KABO, but as the radius of the cation M^+ increases their contributions to the SHG coefficients become slightly more important. As a result, for BABO crystal the contribution to the SHG coefficients from Ba^{2+} goes beyond 12%. This conclusion is the same as that for BBO and the LBO family.

6. Determination of the SHG coefficients of GdCOB and YCOB

GdCOB and YCOB are newly developed NLO crystals [34–36] which have aroused wide interest because they can be pulled directly from melts which are nearly congruent. Thus, it is relatively easy to grow large and high quality crystals. However, the symmetry of both crystals is very low, belonging to C_m [61]. According to the IEEE/ANSI standard definition for NLO coefficient [57], the d_{ij} of YCOB crystal can be written in the following form:

$$d_{ij} = \begin{bmatrix} d_{11} & d_{12} & d_{13} & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & d_{35} & 0 \end{bmatrix} \quad (m \perp Y). \tag{9}$$

By Kleinman symmetry [58], $d_{31} = d_{15}$, $d_{32} = d_{24}$, $d_{13} = d_{35}$ and $d_{26} = d_{12}$, so a total of six independent d_{ij} coefficients, $d_{11}, d_{12}, d_{13}, d_{31}, d_{32}$ and d_{33} should be measured. However, it is very difficult to measure them with the Maker fringes and the phase-matching methods, since the d_{32} and d_{12} are mixed, and no previous experimental data exist. To overcome this difficulty, we first calculate all six d_{ij} coefficients of YCOB and GdCOB, then prove the reliability of the theoretical values using the Maker fringes method.

On the basis of the anionic group theory, the macroscopic SHG coefficients of GdCOB and YCOB are determined by the microscopic SHG coefficients of the $(BO_3)^{3-}$ group with equation (1), and the microscopic SHG coefficients are calculated by the Gaussian'92 *ab initio* method. The results are shown in table 10. The Maker fringes method was then used to

Table 10. SHG coefficients of GdCOB and YCOB (pm V^{-1}).

Crystal	d_{ij}	Experiment (Maker fringes)	Gaussian'92[a]
GdCOB[b]	d_{33}	± 0.5761	-0.903
	d_{11}	≈ 0.0	0.050
	d_{12}	≈ 0.0	0.128
	d_{13}	$\ll d_{33}$	-0.183
	d_{31}	≈ 0.0	0.127
	d_{32}	± 0.6846	0.741
YCOB^{rmb}	d_{33}	± 0.93	-1.018
	d_{11}	≈ 0.0	-0.104
	d_{12}	≈ 0.0	-0.015
	d_{13}	$\ll d_{33}$	-0.253
	d_{31}	$\ll d_{33}$	0.120
	d_{32}	± 1.36	0.757

[a] According to optical axes in [34].
[b] $Ca_4GdO(BO_3)_3$; $Ca_4YO(BO_3)_3$.

Table 11. Relationship between the effective SHG coefficients and phase-matching angles (θ, ϕ) of YCBO (d_{eff}(KTP, $\theta = 90°$, $\varphi = 23.6°$) = 2.45 pm V^{-1}a[a]; = 3.2 pm V^{-1}[b]).

Sampler number	Phase-matching angle (θ, φ)	Crystal length (mm)	d_{eff}(pm V^{-1}) Experiment (a)	Experiment (b)	Calculated[e]
1	32°, 0°	2	0.528	0.689	0.55
2	33°, 9°	2	0.518	0.699	0.515
3	64.50°, 35.50°	2	0.707	0.923	0.72
4	66.8°, 35.4°	2	0.66	0.861	65.9°, 36.5°
5	113.20°, 35.40° [c]	2	0.707	0.923	0.91
6	115.5°, 35.5° [d]	2	0.754	0.985	113.7°, 36.5°

[a] Reference [67].
[b] Reference [63].
[c] Equivalent to 66.8°, 144.6°.
[d] Equivalent to 64.5°, 144.5°.
[e] d_{32}, d_{33} used in calculation were obtained from Maker fringes.

determine two of the six d_{ij} coefficients which are not mixed with the other d_{ij} coefficients and so can be measured independently. The two coefficients are d_{33} and d_{11}, and their values are also listed in table 10. On the other hand, according to the theoretical evaluation, d_{12} is much smaller than d_{32}. If the Maker fringes of d_{32} can be exactly measured, then d_{12} is certainly very small because the Maker fringes of d_{32} and d_{12} are always mixed with each other. Figures 2(a) and 2(b) give the recorded Maker fringes curves of d_{33} and d_{32} for YCOB, respectively. Although the Maker fringes of d_{32} are mixed with those of d_{12}, we can obtain standard Maker fringes for d_{32}, which means that d_{12} is very small. Moreover, from the amplitudes of the Maker fringes and the coherence lengths of d_{13} and d_{31} compared with those of d_{33}, we can deduce that d_{13} and d_{31} are much smaller than d_{33}. The results prove the fact that the theoretical values are in good agreement with the experimental values, except that the calculated ratio of d_{32} and d_{33} is slightly different from its experimental value. Therefore, the theoretical SHG coefficients of YCOB are reliable.

Figure 3(a) presents a three-dimensional space relationship between the effective SHG coefficient d_{eff} and the phase-matching angle (θ, Φ) of YCOB crystal for type I phase matching with the fundamental wave at 1064 nm in the range of $0° < \theta < 90°$ and $0° < \Phi < 180°$. The
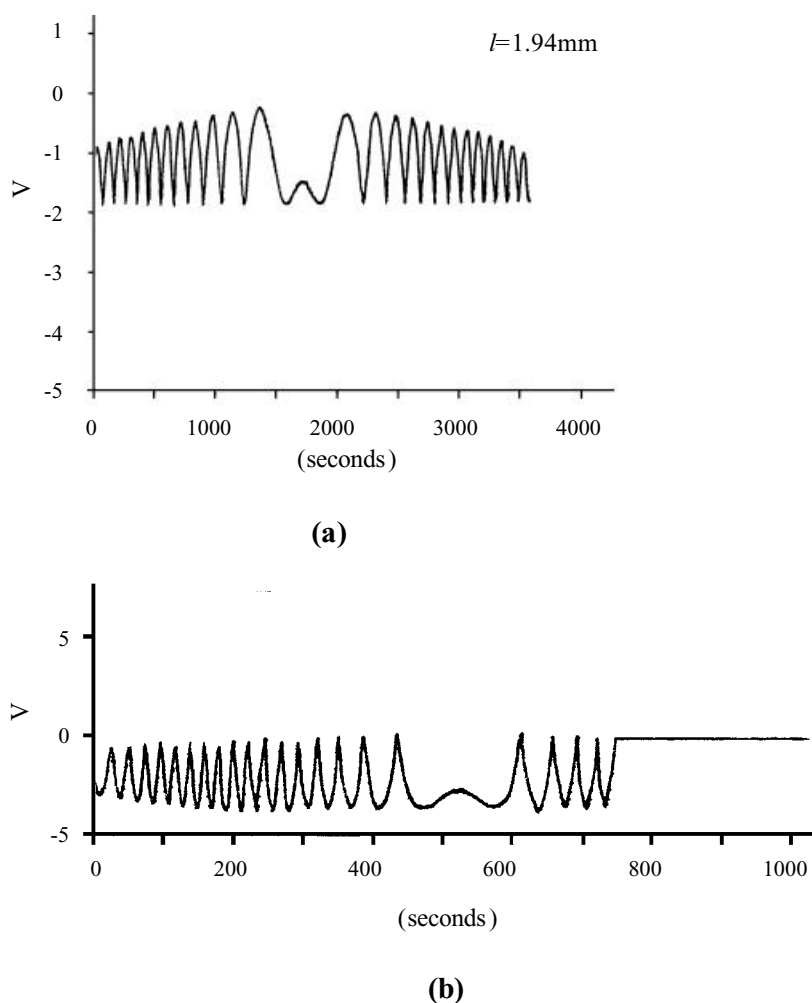
(a)

(b)

Figure 2. (a) Maker fringes of d_{33} of YCOB; (b) the Maker fringes of d_{22} of YCOB.

experimental values of d_{33} and d_{32} and the theoretical values of d_{11}, d_{12}, d_{13} and d_{31} are adopted in the calculation. Furthermore, figure 3(b) shows the curves calculated with the all-theoretical values of the d_{ij} coefficients, also in the range of $0° < \theta < 90°$ and $0° < \Phi < 180°$. From figure 3 we see that the agreement between these two curves is quite good. These two curves reveal the important fact that the maximum d_{eff} is found not in the x–z principal plane [11] but at the positions $\theta = 65.9°, \phi = 36.5°$ and $\theta = 113.7°, \phi = 36.5°$.

Recently, Jiang and Shao's group in Shangdong University performed some experiments to prove our conclusion [62]. Their measurements explicitly show that the largest SHG coefficient is indeed not found in the principal plane, but at the positions $\theta = 65.9°, \phi = 36.5°$ and $\theta = 66.3°, \phi = 143.5°$, which is in very good agreement with our calculated results (see table 11). The successful determination of the SHG coefficients of GdCOB and YCOB prove that the anionic group theory is reliable for predicting and calculating the SHG coefficients of borate crystals.
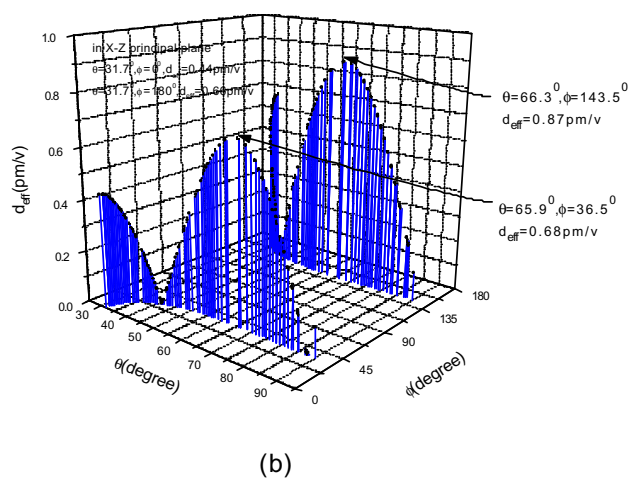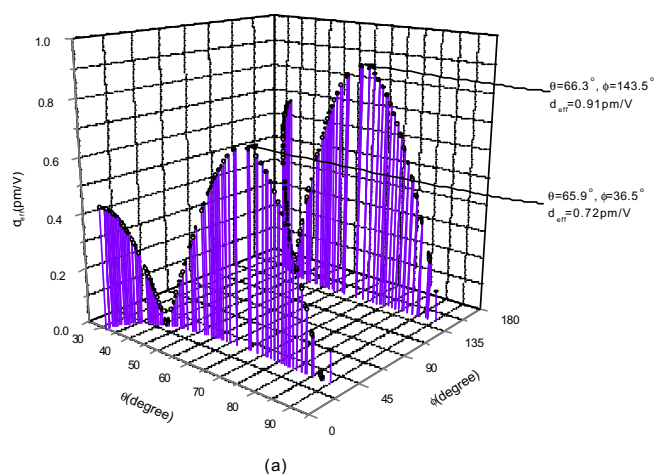
(a)

(b)

Figure 3. Three-dimensional space relationship between d_{eff} coefficient and the phase-matching angle. (a) Curves calculated with the experimental values of d_{33} and d_{32} and theoretical values of d_{11}, d_{12}, d_{13} and d_{31}; (b) curves calculated with all-theoretical values of the d_{ij} coefficients.

7. Conclusion

On the basis of the anionic group theory of NLO crystals, we have systematically calculated the SHG coefficients of borate crystals by using the Gaussian'92 *ab initio* method. Our results indicate that this method can predict and calculate the SHG coefficients of borate crystals with an accuracy of 80%–85%. The calculations based on energy band theory for the nonlinear optical coefficients of certain other borate crystals clearly reveal the relationship between the NLO effects and the microstructures.

Acknowledgments

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