On the Anionic Group Approximation to the Borate Nonlinear Optical Materials

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Abstract: In this mini-review type of article, a brief summary of the anionic group approximation as it relates to the borate nonlinear optical (NLO) crystals, an idea firstly proposed by Professor Chen, is presented. The basic idea, calculation method, tabulated coefficients of various common borate, as well as nitrate or carbonate groups, in their ideal geometries will be presented. New practices reveal that those parameters can still give very accurate predicted NLO coefficients for recently found NLO crystals without any adjustment of parameters.

Keywords: nonlinear optical; borates; structure-property relations; semi-classical calculation

1. Introduction

Just one year after the first laser was demonstrated, the nonlinear optical (NLO) effect was observed in the SiO_2 crystal [1]. The next decade saw the first burst era of new NLO crystals with the findings of some now well-known NLO materials, e.g., KDP, $AgGaS_2$, $ZnGeP_2$, $LiNbO_3$, $LiIO_3$, urea, etc. [2–5]. Through nonlinear optical processes, such as second harmonic generation (SHG), sum frequency generation (SFG) or optical parametric chirped pulse amplification (OPCPA), NLO materials can expand the laser wavelength to a much greater range from UV to far-IR and even the THz range, help to reduce the laser peak width to a femto-second or even an atto-second time frame, and can increase the laser peak power to the petawatt level. At the same time, great efforts were also devoted to the understanding of the structure-property relations of those new materials, though the microscopic basic mechanism at the quantum mechanics level [6] of the NLO property was known just one year after the NLO effect was found,

$$\beta_{ijk}^{2\omega} = \frac{e^3}{2\hbar^2} \sum_{n,n'} \left\{ \begin{array}{l} \langle g|r_i|n\rangle\langle n|r_j|n'\rangle\langle n'|r_k|g\rangle \frac{1}{\left(\omega_{ng}+2\omega\right)\left(\omega_{n'g}+\omega\right)} + \\ \langle g|r_j|n'\rangle\langle n'|r_k|n\rangle\langle n|r_i|g\rangle \frac{1}{\left(\omega_{ng}-2\omega\right)\left(\omega_{n'g}-\omega\right)} + \\ \langle g|r_k|n\rangle\langle n|r_i|n'\rangle\langle n'|r_j|g\rangle \frac{1}{\left(\omega_{ng}-\omega\right)\left(\omega_{n'g}+\omega\right)} \end{array} \right\} \tag{1}$$

where $\beta_{ijk}^{2\omega}$ is the SHG coefficient, which is a special case of the second-order susceptibilities when the incident beams involved are at the same frequency ($\omega = \omega_1 = \omega_2$). All the other symbols in the above equation take their usual meanings. Due to the lack of high-performance computers, semi-classical approximations to the materials had to be made. The three most successful ones were: the double-level or single oscillator model, the bond-parameter model and the charge transfer model [7–9]. The single

oscillator model simplifies the energy levels in a crystal to just two levels and if the optical wavelength is far from resonance, then Equation (1) reduces to:

$$\beta_{ijk}^{2\omega} = \frac{e^3}{2\hbar^2} \{ \langle g|r_i|n\rangle \langle n|r_j|n\rangle \langle n|r_k|g\rangle \omega_{ng}^{-2} + \ldots \} \tag{2}$$

Such an approximation was applied to the crystals with diamond-type and zinc blend–type structures and satisfactory SHG coefficients for both value and parity were obtained [7]. However, this model actually neglects all the contributions of the triple energy level systems; in some materials such approximation is not allowed, hence wrong results were found using this model. The more successful model is the bond-charge model developed by Levine and others [8]; this model proposed that the polarizabilities of both the first (related to refractive indices) and second order (related to electro-optical and SHG coefficients) can be divided into the contributions of individual chemical bonds. By definition of series of bond parameters, this model could obtain SHG coefficients with 20% accuracy for most of the NLO crystals found at the time, including AB_2, ABC_2, ABC_4 and $LiNbO_3$, $LiTaO_3$, $Ba_2NaNb_5O_{15}$. Nevertheless, this model still failed to account for the NLO coefficients of crystals with strongly anisotropic bonds, e.g., $NaNO_2$, urea, $LiCHO_2 \cdot H_2O$, and needed more parameters for crystals containing distorted MO_6 octahedral anionic groups. The third successful model was the charge transfer model proposed by Davidov et al. [10] and developed by Oudar and Chemla [11]. This model treats the organic NLO compounds with a long π-conjugated system; when an electron transitions in a molecule accompanied by large changes of the dipole moment, large second-order susceptibility will be observed. In addition, it was found that molecules with donor and acceptor functional groups just fulfil such conditions and organic crystals with large NLO coefficients were found, e.g., MNA, POM and NPP [12]. This model still plays a role in the recent findings of organic crystals of DAST, DMTS, etc., which are suitable for the generation of THz radiations.

Taking into consideration the successes and failures of the bond-charge model, Prof. Chen in the mid-1970s proposed that the anionic groups rather than the individual chemical bonds should be considered as the basic structural units for the generation of the nonlinear optical effects [13–15]. Calculations on the crystals with distorted octahedral MO_6 units showed that such a model gave a perfect fit to the experimental results [16,17].

2. Results

When I first entered this field as a postgraduate student in 1982, Prof. Chen directed me towards applying the quantum chemical calculation method to the borate system specifically to understand the exact mechanism of the nonlinearity of the newly found, now-famous BBO (β-BaB_2O_4) [18]. Borrowing a FORTRAN code of the CNDO (Complete Neglecting of Differential Overlap) program [19] from a neighbouring quantum chemistry group at the Fujian Institute on the Structure of Matter, I started to modify the original code of the CNDO and to program new subroutines applicable to calculate the second-order susceptibility based on Equation (1). After about half a year of frustrating and difficult work on checking the original and newly programmed FORTRAN codes sentence by sentence, the correct results showed up at the end of 1983 and the first ever paper on the calculation of the NLO properties of the borate crystal (β-BBO) was published in 1985 [20]. The calculation showed that the large nonlinearity of the β-BBO crystal comes solely from the anionic $[B_3O_6]^{3-}$ group, whereas the contribution from the cation Ba^{2+} can be completely neglected. The macroscopic NLO coefficients can be obtained by the geometric superposition of the second-order susceptibilities of the $[B_3O_6]^{3-}$ groups in the crystal unit cell with the following equation:

$$d_{IJK}^{2\omega} = \frac{S_{IJK}}{V} \sum_{ijk,g} T_{Ii} T_{Jj} T_{Kk} \beta_{ijk}^{2\omega}(g) \tag{3}$$

where V is the unit cell volume, T_{Ii}, T_{Jj}, T_{Kk} are the direction cosines of the local Cartesian axes of individual anionic group to the crystal axes, and S_{IJK} is the local field correction factor which can be obtained from refractive indices as: $S_{IJK} = \frac{n_I^2+2}{3} \cdot \frac{n_J^2+2}{3} \cdot \frac{n_K^2+2}{3}$.

After the success of the calculation of the BBO crystal, Wu Yicheng, another student (Doctoral) of Prof. Chen, who then worked on the synthesis and growth of yet another famous LiB_3O_5 (LBO) crystal, joined in. After calculations of various commonly found anionic groups in the borate crystals, we published a series of papers on the application of anionic group approximation to the development of NLO borate crystals [21–23]. Afterwards, we extended the calculation to real materials: The SHG coefficients of LiB_3O_5 and CsB_3O_5 (CBO) were calculated before the measured values could be obtained [24]. The calculation actually helped the orientation settings for the measurements and the determination of the relative signs of the measured coefficients of LBO [24]. The measurements on CBO came four years later, after the publication of the calculated results, when a large-enough crystal was obtained finally [25]. However, it should be noted that the above calculations all took the geometries of the individual borate groups in real crystals and were not idealized and so cannot be directly shifted from one crystal to another. The results on idealized anionic groups were never formally published [26], but are given now in Table 1.

Table 1. The second-order NLO susceptibilities of some simple anionic groups * (in unit: 10^{-31} esu, conversion factor: 1 esu $= 4\pi/3 \times 10^{-4}$ m/V).

$\beta_{ijk}^{2\omega}$	NO_2^-	NO_3^-	CO_3^{2-}	BO_3^{3-}	$B_3O_6^{3-}$	BO_4^{5-}
111	−0.0481	0.7852	0.5911	0.6353	1.8029	-
122	−0.6288	−0.7852	−0.5911	−0.6353	−1.8029	-
133	0.0082	-	-	-	-	-
123	-	-	-	-	-	0.1621

* Idealized bond lengths: 1.24 Å (NO_2), 1.22 Å (NO_3), 1.283 Å (CO_3), 1.38 Å (BO_3), 1.48 Å (BO_4).

With the above tabulated values we calculated the SHG coefficients of crystals with reported structures containing some isolated anionic groups. The calculated results showed good agreement with experimental results whenever available (Table 2).

Table 2. Calculated SHG coefficients of selected crystals with isolated anionic groups (in unit: 10^{-9} esu, conversion factor: 1 esu $= 4\pi/3 \times 10^{-4}$ m/V).

Crystals	Calculated	Experimental
$CaMg_3(CO_3)_4$	$d_{11}^{2\omega} = 2.24$	-
$YAl_3(BO_3)_4$	$d_{11}^{2\omega} = 3.30$	3.82
$LiCdBO_3$	$d_{11}^{2\omega} = 4.96$	3.0 *
$Na_2Ca_2(CO_3)_3$	$d_{31}^{2\omega} = 2.24, d_{32}^{2\omega} = 0.21,$ $d_{33}^{2\omega} = -1.31$	-
LiK_2BO_3	$d_{21}^{2\omega} = -0.28, d_{22}^{2\omega} = -0.73$ $d_{23}^{2\omega} = 0.92, d_{14}^{2\omega} = -0.66$	-
$LiNaCO_3$	$d_{11}^{2\omega} = 2.50$	3.0 *
β-BaB_2O_4	$d_{11}^{2\omega} = 3.78$	3.82
$KBe_2BO_3F_2$	$d_{11}^{2\omega} = 1.87$	1.17
$Be_2BO_3OH \cdot H_2O$	$d_{11}^{2\omega} = 2.21$	-

* From powder SHG tests of the Kurtz-Perry method.

One of the fascinating and practically important characteristics of the borate crystals is that within their structures, the borate groups of BO_3 and BO_4 can condense into larger structural units or into one- to three-dimensional skeletal structures [27]. When calculating the NLO properties of those structures, there can be different choices of the sizes for the basic structural units to obtain the microscopic SHG coefficients. For example, when calculating BBO, LBO, CBO, CLBO ($CsLiB_6O_{10}$) [28], the basic units for the structures were chosen as B_3O_6, B_3O_7, respectively. We further made the calculations of those crystals by decomposing their structural units into the smallest possible ones of BO_3 and BO_4. Apart from a sign change in the smallest SHG coefficient of LBO, the final results (Table 3) showed the same level of agreement to the experimental ones [29].

Table 3. Calculated SHG coefficients of crystals' large anionic groups or skeleton borate networks (in unit: 10^{-9} esu, conversion factor: 1 esu = $4\pi/3 \times 10^{-4}$ m/V).

Crystals	Calculated	Experimental	Calculated with BO_3 and BO_4
$\beta\text{-}BaB_2O_4$	$d_{11}^{2\omega} = 3.78$	$d_{11}^{2\omega} = 3.82$	$d_{11}^{2\omega} = 4.00$
LiB_3O_5	$d_{31}^{2\omega} = -2.24$ $d_{32}^{2\omega} = 2.69$ $d_{33}^{2\omega} = 0.61$	$d_{31}^{2\omega} = -2.34,$ $d_{32}^{2\omega} = 2.50$ $d_{33}^{2\omega} = 0.14$	$d_{31}^{2\omega} = -2.77,$ $d_{32}^{2\omega} = 2.87$ $d_{33}^{2\omega} = -0.11$
$C_SB_3O_5$	$d_{14}^{2\omega} = 2.08$	$d_{14}^{2\omega} = 2.79$	$d_{14}^{2\omega} = 2.30$
$LiCsB_5O_{10}$	$d_{36}^{2\omega} = 1.48$	$d_{36}^{2\omega} = 1.77$	$d_{36}^{2\omega} = 2.15$

3. Discussion

After the success of the anionic group approximation for the calculation of real or potential NLO materials as shown in last section, one may draw the following conclusion from the results:

1. The anionic groups with π-conjugated electron systems, such as NO_2, NO_3, CO_3, BO_3, have the same level of enhanced (four times) second-order susceptibility over those (BO_4) without the π-conjugated systems.
2. The second-order susceptibilities of the condensed structural units show directional additive properties over smaller fragments, e.g., $B_3O_6 \approx 3BO_3$ and $B_3O_7 \approx BO_4 + 2BO_3$, etc.
3. Therefore, the contributions for all the borate skeletons can be calculated by decomposition to the smallest units of BO_3 and BO_4.

It is also worth noting that the same level of approximation has also been applied to predict birefringence [30] and to understand the absorption cut-off at the UV side [31], both of which are also critical parameters for a NLO material.

With the above tabulated second-order NLO susceptibilities for the simple ideal anionic groups (Table 1), it should not be difficult to apply them to the recently found or proposed NLO borate or carbonate crystals [32]. For example, recently we succeeded in growing a new NLO crystal with a chemical formula of $K_3B_6O_{10}Br$ (Figure 1) [33] into a sufficient size, which was first reported by Al-Ama et al. [34], and it contains a borate network skeleton with an exceptionally large anionic group, B_6O_{13}, composed of three BO_3 and three BO_4 groups (Figure 2). The SHG coefficients of this crystal were carefully measured by the Maker Fringe method [33] and a series of mixed crystals with compositions of $K_3B_6O_{10}Br_{1-x}Cl_x$ were also grown [35]. Ab initio calculations on the mixed crystals were obtained previously and can therefore be compared with the calculation purely based on the BO_3 and BO_4 groups, as shown in Table 4. It is shown that absolute values of the greater $d_{22}^{2\omega}$ of the present calculation agree with the experimental and ab initio results satisfactorily, while the smaller $d_{33}^{2\omega}$ changes sign with the ab initio results. It will be interesting to measure the relative sign of $d_{22}^{2\omega}$ and $d_{33}^{2\omega}$ in the future to see which one reproduces the actual case. It is also interesting to note that the present calculation correctly reflects (with all the calculated coefficients in opposite signs) that the

crystals with compositions of x = 0.21, 0.57 and 0.75 are actually inversion twins (Figure 1b) of the mother compounds $K_3B_6O_{10}Br$ [35] and $K_3B_6O_{10}Cl$ [36].
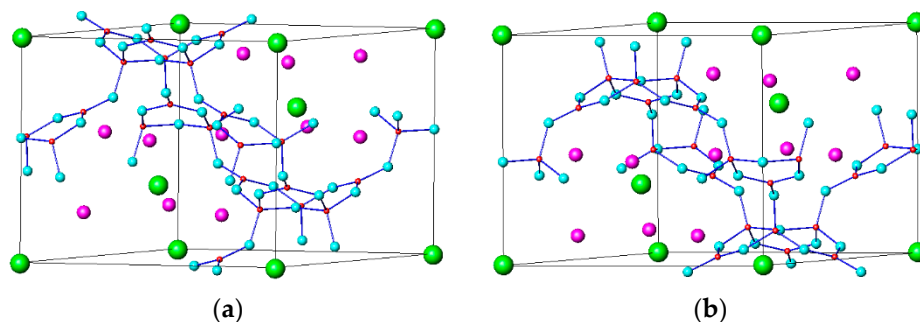

(**a**)   (**b**)

Figure 1. The crystal structure of $K_3B_6O_{10}Br$ (**a**) and its inversion twin (**b**).
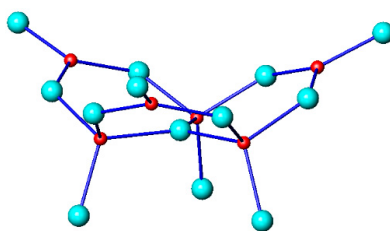

Figure 2. The B_6O_{13} groups in the $K_3B_6O_{10}Br$ structure condensed by $3BO_3$ and $3BO_4$ groups.

Table 4. Calculated SHG coefficients of crystals $K_3B_6O_{10}Br_{1-x}Cl_x$ (in unit pm/V).

Crystals (x)	Calculated (ab initio)	Experimental	Calculated with BO_3 and BO_4
0	$d_{22}^{2\omega} = -1.247$ $d_{31}^{2\omega} = 0.067$ $d_{33}^{2\omega} = 0.381$	$\lvert d_{22}^{2\omega}\rvert = 1.23$ $\lvert d_{33}^{2\omega}\rvert = 0.43$	$d_{22}^{2\omega} = -1.174$ $d_{31}^{2\omega} = 0.059$ $d_{33}^{2\omega} = -0.219$
0.21	$d_{22}^{2\omega} = -1.119$ $d_{31}^{2\omega} = 0.041$ $d_{33}^{2\omega} = 0.358$		$d_{22}^{2\omega} = 1.190$ $d_{31}^{2\omega} = -0.062$ $d_{33}^{2\omega} = 0.222$
0.35	$d_{22}^{2\omega} = -1.113$ $d_{31}^{2\omega} = 0.036$ $d_{33}^{2\omega} = 0.358$		$d_{22}^{2\omega} = -1.179$ $d_{31}^{2\omega} = 0.059$ $d_{33}^{2\omega} = -0.218$
0.47	$d_{22}^{2\omega} = -1.110$ $d_{31}^{2\omega} = 0.035$ $d_{33}^{2\omega} = 0.357$		$d_{22}^{2\omega} = -1.181$ $d_{31}^{2\omega} = 0.060$ $d_{33}^{2\omega} = -0.221$
0.57	$d_{22}^{2\omega} = -1.103$ $d_{31}^{2\omega} = 0.031$ $d_{33}^{2\omega} = 0.360$		$d_{22}^{2\omega} = 1.193$ $d_{31}^{2\omega} = -0.063$ $d_{33}^{2\omega} = 0.229$
0.75	$d_{22}^{2\omega} = -1.095$ $d_{31}^{2\omega} = 0.026$ $d_{33}^{2\omega} = 0.363$		$d_{22}^{2\omega} = 1.196$ $d_{31}^{2\omega} = -0.064$ $d_{33}^{2\omega} = 0.233$
1.0	$d_{22}^{2\omega} = -1.078$ $d_{31}^{2\omega} = 0.024$ $d_{33}^{2\omega} = 0.364$		$d_{22}^{2\omega} = -1.182$ $d_{31}^{2\omega} = 0.060$ $d_{33}^{2\omega} = -0.226$

4. Materials and Methods

We firstly applied the CNDO program to obtain the ground $|g\rangle$ and excited states $|n\rangle$ of the anionic groups in ideal geometries as listed in the footnotes of Table 1. Then the microscopic second

order susceptibilities $\beta_{ijk}^{2\omega}$ (Table 1) of the idealized anionic groups were obtained by Equation (1). The macroscopic NLO coefficients of certain crystals can be obtained by the geometric superposition of the second order susceptibilities of the anionic groups in unit cell with Equation (3), and the refractive indices of the crystal were assumed to a mean value of 1.65 whenever they were unknown.

5. Conclusions

Anionic group approximation has been shown to give good agreements and even success in predicting new nonlinear optical crystals in borate compounds. Similar results can be expected with the present tabulation of the calculated second-order susceptibilities for the carbonate and nitrate groups that have been drawing attention in recent years.

Conflicts of Interest: The author declares no conflict of interest.

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