



# Nonlinear optical properties of borate crystals

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## Abstract

We have studied the effect of different chemical bonding structures of boron atoms on the second-order nonlinear optical behavior of borate crystals from the chemical bond viewpoint. Several typical borate crystals, including  $\text{LiB}_3\text{O}_5$ ,  $\beta\text{-BaB}_2\text{O}_4$ ,  $\text{BiB}_3\text{O}_6$ ,  $\text{NdAl}_3(\text{BO}_3)_4$ ,  $\text{Ca}_4\text{LnO}(\text{BO}_3)_3$ ,  $\text{K}[\text{B}_5\text{O}_6(\text{OH})_4]\cdot 2\text{H}_2\text{O}$ ,  $\text{Eu}_2\text{B}_5\text{O}_9\text{Cl}$  and  $\text{Ca}_2\text{B}_5\text{O}_9\text{Br}$ , with different chemical bonding structures of boron atoms are investigated. The results show that the different chemical bonding structures of boron atoms have a strong effect on the second-order nonlinear optical behavior of borate crystals. Further, the calculated values show that forming B–O rings would decrease the NLO response of borate crystals and that  $[\text{BO}_3]^{3-}$  groups possess larger nonlinear optical contributions than  $[\text{BO}_4]^{5-}$  groups. © 2000 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

The increasing variety of applications of nonlinear optical (NLO) materials for second harmonic generation (SHG), sum or different frequency mixing, optical parametric oscillation or amplification have resulted in the development of numerous inorganic NLO crystals. Over the past 30 years, the search for new and better NLO materials has never ceased in the endeavor to develop new laser sources and extend applications. As a useful ultraviolet (UV) NLO material,  $\text{K}[\text{B}_5\text{O}_6(\text{OH})_4]\cdot 2\text{H}_2\text{O}$  ( $\text{KB}_5$ ) is the first NLO crystal discovered in the series of borates [1]. After that, various borate crystals, including  $\beta\text{-BaB}_2\text{O}_4$  (BBO) [2],  $\text{LiB}_3\text{O}_5$  (LBO) [3],  $\text{Sr}_2\text{B}_2\text{Be}_2\text{O}_7$  (SBBO) [4],  $\text{BiB}_3\text{O}_6$  (BiBO) [5] and the latest  $\text{Ca}_4\text{LnO}(\text{BO}_3)_3$  (CLnOB, where  $\text{Ln} = \text{Gd}, \text{La}, \text{Y}$ ) [6], have been studied as promising NLO crystals. Presently, the most efficient self-frequency doubling compound in still  $\text{YAl}_3(\text{BO}_3)_4:\text{Nd}$  [7]. The family of the various borate crystals thus plays a very important role in the field of nonlinear optics (for a recent review read e.g. Ref. [8]).

In borate crystals, the boron atom usually coordinates with either three or four oxygen atoms forming  $[\text{BO}_3]^{3-}$  or

$[\text{BO}_4]^{5-}$  groups. Accordingly, the electronic orbitals are hybridized to a planar  $sp^2$  or a three-dimensional  $sp^3$  structure. Further, the structural units can comprise several different typical  $\text{B}_x\text{O}_y$  groups through different combinations, such as the isolated  $\text{BO}_3$  group in  $\text{NdAl}_3(\text{BO}_3)_4$  (NAB) and CLnOB [9,10], a combination of  $\text{BO}_3$  and  $\text{BO}_4$  groups as in BiBO [11], the  $\text{B}_3\text{O}_6$  group in BBO [12], the  $\text{B}_3\text{O}_7$  group in LBO [12], the  $\text{B}_5\text{O}_{13}$  group with a single six-member B–O ring in  $\text{Ca}_2\text{B}_5\text{O}_9\text{Br}$  (CBOBr) [13], the  $\text{B}_5\text{O}_{10}$  group in  $\text{KB}_5$  [14], and the  $\text{B}_5\text{O}_{12}$  group in  $\text{Eu}_2\text{B}_5\text{O}_9\text{Cl}$  (EBOCl) [15] which have double connected six-member B–O rings. The structural situation for different  $\text{B}_x\text{O}_y$  groups is sketched in Fig. 1. These various structural possibilities for the boron atom are one of the reasons for the attractive versatility of borates in nonlinear optics. A comprehensive theoretical study of the structural influences thus can be the key for a profound understanding of this material group.

In this work, we systematically investigate the NLO responses of different borate crystals, using the chemical bond method, which has been successfully applied to calculations of  $d_{ij}$  tensors of complex crystals with various crystal structures [9,10,12,14]. The main principle of this method is that linear and nonlinear optical properties of a multi-bond crystal are ascribed to the microscopic contributions of its constituent chemical bonds. Therefore, one can calculate and predict linear and nonlinear optical properties of any crystals with various structures on the basis of their constituent chemical bonds. The calculated results are

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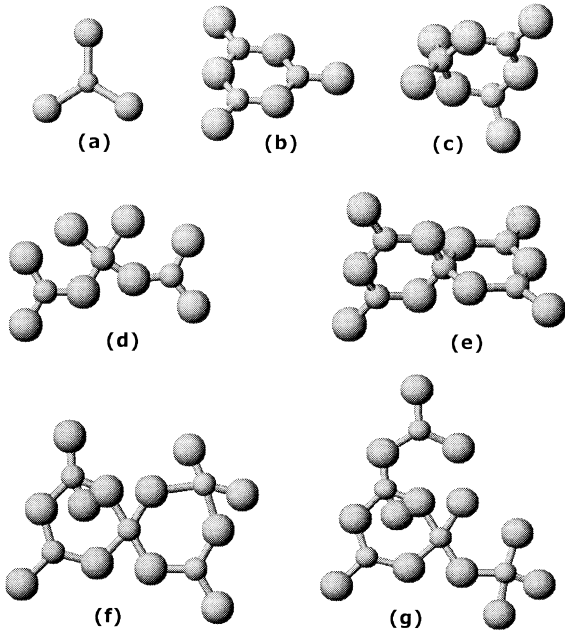


Fig. 1. Geometric structure and chemical bonding situation of each  $B_nO_m$  group in the crystal structure frame (small spheres: boron, large spheres: oxygen): (a) the isolated  $BO_3$  groups in NAB and  $CLnOB$ ; (b) the  $B_3O_6$  group in BBO; (c) the  $B_3O_7$  group in LBO; (d) the  $B_3O_8$  group in BiBO; (e) the  $B_5O_{10}$  group in  $KB_5$ ; (f) the  $B_5O_{12}$  group in EBOCl; and (g) the  $B_5O_{13}$  group in CBOBr.

compared to the experimental values as well as to the results gained by the anionic group theory [16] in order to get an estimate for the possibilities and limits of theoretical predictions in this field.

## 2. Theoretical methods

As shown in previous publications [9,10,12,14], the chemical bond method, which is based on the bond charge model of Levine [17] and the dielectric theory of Phillips [18] and van Vechten [19], regards a complex crystal as the combination of all constituent chemical bonds. A multi-bond crystal thus can be theoretically decomposed into single bonds, according to the detailed chemical bonding structures of all constituent atoms. Any kind of chemical bond like A–B in the multi-bond crystal  $A_aB_bD_dG_g, \dots$  can be expressed as:

$$\frac{N(B-A)a}{N_{CA}} AB \frac{N(A-B)bN_{CA}}{N(B-A)aN_{CB}} \quad (1)$$

where A, B, D, G, ... represent different elements or different sites of an element in the crystal formula, and  $a, b, d, g, \dots$  the quantities of the corresponding element,  $N(B-A)$  the number of B ions in the coordination group of the A ion, and  $N_{CA}$  the total number of ions that can be considered as the

bonded ions in the first coordination sphere of ion A. On the basis of this idea, the physical property of an assigned crystal is ascribed to contributions from all contained chemical bonds. Therefore, the linear and nonlinear optical properties of an assigned crystal can be calculated by analyzing the linear and nonlinear optical properties of its constituent chemical bonds.

In a multi-bond crystal, its linear optical property  $\chi$  can be ascribed to contributions  $\chi^\mu$  from the various types of bonds

$$\chi = \sum_{\mu} F^{\mu} \chi^{\mu} = \sum_{\mu} N_b^{\mu} \chi_b^{\mu} \quad (2)$$

where  $F^{\mu}$  is the fraction of bonds of type  $\mu$  composing the actual crystals,  $N_b^{\mu}$  the number of chemical bonds of type  $\mu$  per  $\text{cm}^3$ ,  $\chi_b^{\mu}$  the susceptibility of a single bond of type  $\mu$ .

The susceptibility  $\chi^{\mu}$  of any bond of type  $\mu$  is expressed as:

$$\chi^{\mu} = (4\pi)^{-1} (\hbar \Omega_p^{\mu} / E_g^{\mu})^2 \quad (3)$$

where  $\Omega_p^{\mu}$  is the plasma frequency,  $E_g^{\mu}$  the average energy gap between the bonding and the antibonding states,  $(E_g^{\mu})^2 = (E_h^{\mu})^2 + (C^{\mu})^2$ . Further, the fractions of ionic and covalent characteristics of the individuals bonds,  $f_i^{\mu}$  and  $f_c^{\mu}$ , are defined by

$$f_i^{\mu} = (C^{\mu})^2 / (E_g^{\mu})^2, \quad f_c^{\mu} = (E_h^{\mu})^2 / (E_g^{\mu})^2. \quad (4)$$

Chemical bond nonlinearities are evaluated on the basis of linear results by means of a geometrical addition of nonlinear contributions  $d_{ij}^{\mu}$  of all bonds  $\mu$ . The corresponding macroscopic property is the NLO tensor coefficient  $d_{ij}$  that can be expressed as:

$$d_{ij} = \sum_{\mu} d_{ij}^{\mu} = \sum_{\mu} F^{\mu} [d_{ij}^{\mu}(C) + d_{ij}^{\mu}(E_h)] \quad (5)$$

$$F^{\mu} d_{ij}^{\mu}(C) = \frac{G_{ij}^{\mu} N_b^{\mu} (0.5) \{ [(Z_A^{\mu})^* + n(Z_B^{\mu})^*] / [(Z_A^{\mu})^* - n(Z_B^{\mu})^*] \} f_i^{\mu} (\chi_b^{\mu})^2}{d^{\mu} q^{\mu}} \quad (6)$$

$$F^{\mu} d_{ij}^{\mu}(E_h) = \frac{G_{ij}^{\mu} N_b^{\mu} s(2s-1) [r_0^{\mu} / (r_0^{\mu} - r_c^{\mu})]^2 f_c^{\mu} (\chi_b^{\mu})^2 \rho^{\mu}}{d^{\mu} q^{\mu}} \quad (7)$$

where  $\rho^{\mu}$  is the difference in the atomic sizes,  $r_c^{\mu}$  the core radius,  $q^{\mu}$  the bond charge of the  $\mu$ th bond, and  $G_{ij}^{\mu}$  the geometrical contribution of chemical bonds of type  $\mu$ . All of the above parameters can be deduced from the detailed chemical bonding structures of all constituent atoms, as described in previous publications [9,10,12,14].

It should be pointed out that the chemical bond method applied in the present work is fundamentally different from the anionic group theory proposed by Chen [2–4]. The anionic group theory of the NLO susceptibility is based on the assumption that the overall SHG coefficient of a crystal

Table 1

Comparison of the experimental and calculated (Chen et al. and this work) NLO tensor coefficients of BBO, LBO, KB<sub>5</sub> and BiBO crystals; units are pm/V

Crystal	NLO tensor	Experimental data	Calculated values	
			Chen et al.	This work
BBO	$d_{22}$	$\pm (1.93 \pm 0.13)^a, 2.10^b$	1.58 <sup>a</sup>	1.86
	$d_{31}$	$\mp (0.03 \pm 0.01)^a$	-0.016 <sup>a</sup>	-0.05
	$d_{32}$	$= d_{31}^a$	-0.016 <sup>a</sup>	-0.05
LBO	$d_{31}$	$-(1.05 \pm 0.13)^c, -(0.83 \pm 0.06)^d$	-0.92 <sup>c</sup>	-0.93
	$d_{32}$	$0.98 \pm 0.09^c, 0.71 \pm 0.05^d$	0.80 <sup>c</sup>	0.86
	$d_{33}$	$-(0.06 \pm 0.004)^c, 0 \pm 0.1^d$	-0.23 <sup>c</sup>	-0.18
KB <sub>5</sub>	$d_{31}$	0.046 <sup>e</sup> , 0.047 <sup>f</sup>	0.109 <sup>g</sup>	-0.049
	$d_{32}$	0.003 <sup>e</sup>	0.003 <sup>g</sup>	0.008
	$d_{33}$	-	0.137 <sup>g</sup>	-0.431
BiBO	$d_{21}$	2.3 <sup>h</sup> ; 2.8 <sup>h</sup>		2.49
	$d_{14}$	2.3 <sup>h</sup> ; 2.4 <sup>h</sup>		0.18
	$d_{22}$	2.53 <sup>h</sup>		0.30
	$d_{23}$	-0.9 <sup>h</sup> ; -1.3 <sup>h</sup>		-2.82

<sup>a</sup> Taken from Refs. [2,20].

<sup>b</sup> Taken from Ref. [21].

<sup>c</sup> Taken from Ref. [22].

<sup>d</sup> Taken from Ref. [23].

<sup>e</sup> Taken from Ref. [24] (absolute value only given).

<sup>f</sup> The value was obtained by Cleveland Crystal, Inc. under US Patent no. 3934154. Its value is 0.12  $d_{36}$  (KDP) (absolute value).

<sup>g</sup> Taken from Ref. [25].

<sup>h</sup> Taken from Ref. [5].

is a geometrical addition of the microscopic second-order susceptibility tensors of the anionic groups (i.e.  $[\text{BO}_3]^{3-}$ ,  $[\text{BO}_4]^{5-}$  or their combination units) and that any influence of the cations can be widely neglected.

### 3. Results and discussion

Starting from the detailed structural characteristics of  $[\text{BO}_3]^{3-}$  and  $[\text{BO}_4]^{5-}$  infrastructures (i.e. the isolated  $\text{BO}_x$  groups and  $\text{B}_x\text{O}_y$  groups with various B–O rings, as shown in Fig. 1), the second-order NLO behavior of some representative borate crystals containing only  $[\text{BO}_3]^{3-}$  groups or both  $[\text{BO}_3]^{3-}$  and  $[\text{BO}_4]^{5-}$  groups is quantitatively studied. In the calculation, all constituent chemical bonds of each borate crystal are considered. To get an impression of the reliability of the calculation, available experimental data (BBO, LBO, KB<sub>5</sub> and BiBO) are compared with Chen's

and our calculated results in Table 1. For BBO, LBO and KB<sub>5</sub> both types of calculations agree reasonably well with experimental data, although quite different theoretical methods are used. This shows that both the anionic group theory and the chemical bond method are well applicable in dealing with optical nonlinearities of borate crystals. Both methods thus can serve as powerful tools for the pre-investigation of the NLO behavior of borate crystals.

Special care yet has to be taken in the case of BiBO: no reasonable results could be achieved with the anionic group theory [5]; using the chemical bond method, on the contrary, two of the four NLO tensor coefficients are massively underestimated [26]. The problems might originate from the special role of bismuth. The influence of the cation on the NLO properties is fully neglected by the anionic group theory, the chemical bond method only considers the bonds. The influence of a lone-pair electron at the Bi atom

Table 2

The calculated largest NLO tensor coefficients  $d_{ij}$  (pm/V) of some selected borate crystals (This is the largest  $d_{ij}$  tensor among all  $d_{ij}$  tensors of the corresponding crystals. These calculated tensors are:  $d_{11}$ (CGdOB),  $d_{23}$ (BiBO),  $d_{11}$ (NAB),  $d_{22}$ (BBO),  $d_{31}$ (LBO),  $d_{33}$ (KB<sub>5</sub>),  $d_{31}$ (EBOCl) and  $d_{33}$ (CBOBr), respectively)

	CGdOB	BiBO	NAB	BBO	LBO	KB <sub>5</sub>	EBOCl	CBOBr
$d_{ij}^{\max}$	-4.38	-2.82	-2.43	1.86	-0.93	-0.43	0.40	-0.16

[5], which obviously plays an important role in BiBO, cannot be accounted for in the calculation.

For a concise comparison of the different borate infrastructures, the calculated values of the respective largest NLO tensor coefficients  $d_{ij}$  of all selected borates are listed in Table 2. For the calculation the chemical bond method was used as it was successful in the calculation of linear and nonlinear optical susceptibilities also in various other crystals without separable anionic groups as e.g. potassium niobate [27].

In the theoretical treatment, much attention was paid to characteristics of all kinds of constituent B–O bonds in different  $B_xO_y$  infrastructures of these borate crystals since this type of infrastructure is very particular in the borate crystal structures.

The calculations show that the localization degree of the valence electrons of the constituent boron atoms as well as the geometrical factor of the B–O bonds in the  $[BO_3]^{3-}$  and  $[BO_4]^{5-}$  groups are the two important factors that determine the NLO contributions of the  $[BO_3]^{3-}$  and  $[BO_4]^{5-}$  groups. The localized degree, which describes how valence electrons are distributed in the area of the B–O bonds, in quantitatively determined by the fraction of covalency of the B–O bonds,  $f_c^{B-O}$ . The geometrical factor is the influence of the chemical bonding direction on the respective coefficient of the susceptibility tensor. It is derived from direction cosines in the unit cell, which is used to obtain the geometrical addition of nonlinear contributions of all chemical bonds.

In general, the planar  $[BO_3]^{3-}$  groups possess strongly localized valence electrons, and often have quite large geometrical factors at least along one spatial direction. Compared with the  $[BO_3]^{3-}$  groups, the three-dimensionally extended  $[BO_4]^{5-}$  groups do not exhibit such good properties; they have less localized valence electrons and often smaller geometrical factors. The calculations also show that the six-member B–O ring leads to a delocalization of valence electrons of the boron atoms, a common feature in any ring system.

The above considerations are reflected by the results summarized in Table 2. Borate crystals containing isolated  $BO_3$  groups exhibit large NLO coefficients due to the highly localized valence electrons. In contrast, crystals with  $BO_4$  groups or  $B_xO_y$  groups with various B–O rings, i.e. boron atoms with less localized valence electrons, show up considerably smaller NLO responses. Therefore, in order to achieve large nonlinear optical susceptibilities, it would be advantageous to concentrate on crystals containing  $[BO_3]^{3-}$  infrastructures in highly asymmetric unit cells. Low susceptibilities are to be expected from crystals with B–O ring infrastructures. Yet—as BiBO shows—special care has to be taken on the incorporation of distinct cations. Their influence is not or only partially accounted for in the usual calculations.

#### 4. Conclusion

The effect of different chemical bonding structures of

boron atoms on the second-order nonlinear optical behavior of borate crystals has been analyzed from the chemical bond viewpoint. Typical borate crystals containing different  $B_xO_y$  infrastructures were selected for the calculations. From the bonding characteristics of their constituent boron atoms, useful information was obtained for these borate crystals, this information is important for the search for new types of NLO crystals. In the material design of new borate crystals, one should concentrate on crystals containing a large amount of (isolated)  $BO_3^{3-}$  infrastructures and avoid crystals where the typical six-member B–O rings are formed from  $BO_3^{3-}$  and  $BO_4^{5-}$  groups. The influence of special cations (like Bi in BiBO) on the dielectric response—especially the nonlinear—is, at present, not adequately described by the two theoretical approaches discussed and should be studied in more detail.

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