Structural characteristics and second order nonlinear optical properties of borate crystals

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Abstract: From the chemical bond viewpoint, the second order nonlinear optical (NLO) responses of some typical borate crystals with various crystal structures have been quantitatively studied. The correlations between structural characteristics and second order NLO properties of selected borate crystals are discussed. Calculations show that the isolated BO_3 infrastructure is advantageous for borate crystals with large NLO responses. On the contrary, borate crystals with the BO_4 or B_xO_y infrastructure forming various six-member B–O rings may be expected to be materials with smaller NLO responses.

OCIS codes: (160.4330) Nonlinear optical materials; (190.2620) Frequency conversion.

Introduction

Design of new second order nonlinear optical (NLO) materials requires a fundamental understanding of the structure and bonding features that promote efficient second harmonic generation (SHG) responses of corresponding materials. The necessary but not always sufficient crystallographic requirement for second order NLO effects is a noncentrosymmetric structure. Such a structure is favoured by certain infrastructural groups. So among all the borate structures reported until now 36% are noncentrosymmetric while among the reported inorganic crystal structures there are in total only 15% of noncentrosymmetric structure. Therefore, the probability that a new borate structure lacks a center of symmetry is more than twice as high than for non-borate structures [1]. In the past two decades, borate crystals thus have been attracting much attention due to their outstanding linear and nonlinear optical properties [2, 3]. As Becker [2] stated, the large family of borate compounds is a suitable chemical 'playground' now adopted by many materials scientists, because the extremely wide variability of borate crystal chemistry [1] allows the creation of very different structure types. Excellent NLO materials like $K[B_5O_6(OH)_4] \cdot 2\,H_2O$ (KB_5) [4], $Ba_3(B_3O_6)_2$ (i.e., β-BaB_2O_4, BBO) [5], LiB_3O_5 (LBO) [6], $Sr_2B_2Be_2O_7$ (SBBO) [7], $Ca_4LnO(BO_3)_3$ (CLnOB, where Ln = Gd, La, Y) [8], and BiB_3O_6 (BIBO)[9, 10] have been synthesized and investigated by different research groups. Presently, one of the most efficient self-frequency doubling compounds is still $YAl_3(BO_3)_4$:Nd [11]. As it can be expected that further borate crystals may become interesting for NLO applications, it is important to study the influence of different borate groups on the dielectric susceptibilities of the corresponding crystals. A better knowledge about the connection between crystal structure and NLO properties can guide the expensive search for new materials in this field.

Structure and property relationship is a classical and well-studied research area. Recently even commercial software (e.g., the Gaussian '92 program, the Castep 3.5 program) at the *ab initio* level is available which provides functions to predict the NLO-SHG effects of binary crystals. Yet it is still difficult or even impossible to use in calculating the nonlinear susceptibilities of complex solid state materials like borates[3, 12]. Therefore, inorganic crystals with complexer crystallographic structure have been theoretically treated with empirical approaches at different approximation

levels[3, 12–14]. The chemical bond method[14] indicates that properties of constituent chemical bonds determine both linear and second order nonlinear optical properties and related effects of an assigned crystal. It might not only form the basis but also provide an opportunity to improve the quality of the observed relationship between structure and property of solid state materials.
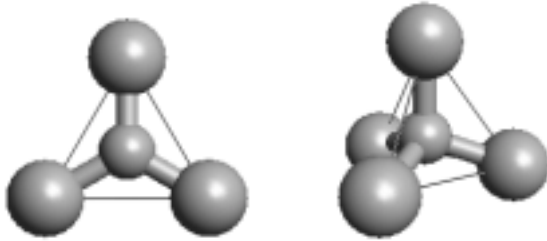

Figure 1: Schematic drawing of the planar $[BO_3]^{3-}$ group and the tetrahedral $[BO_4]^{5-}$ group which contain B atoms with sp^2 and sp^3 hybridization, respectively.

In borate crystals, the boron atom usually coordinates with either three or four oxygen atoms forming $[BO_3]^{3-}$ or $[BO_4]^{5-}$ groups. Accordingly, the electronic orbitals are hybridized to a planar sp^2 or a three dimensional sp^3 structure. The schematic structural drawing for these two groups is shown in Figure 1. Furthermore, several of these groups can be connected in different ways to typical B_xO_y infrastructures (as described in the second column in Table 1). These various structural possibilities for the boron atom are one of the reasons for the 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.

Summary of calculation methods

Chemical bond is one of the most popular concepts that have been widely accepted by scientists in various fields of condensed matter chemistry and physics. Chemical bond and related chemical bond terms are also one of the explicit languages that have been preferred to express the interaction of two atoms or ions (e.g., A and B), which are located at the distance about the sum of both atomic or ionic sizes (i.e., $r_A + r_B$, where r_A and r_B can be regarded as their covalent radii or ionic radii, respectively). The dielectric theory of solids proposed by Phillips and van Vechten (also called as PV theory) [15, 16], the bond-charge model found by Levine [17, 13], as well as the bond-valence model perfected by Brown [18], show that chemical bonding behaviors and related bond parameters of a crystal are the important indices that allow us to properly express complicated interactions among all constituent atoms or ions. Chemical bond is thus an effective starting point to understand the complex relationship among the composition, crystallographic structure, chemical and physical properties of condensed matters. Therefore, to study properties of constituent chemical bonds in a crystal is one of the most fundamental methods for us to understand its various properties, which also would be potentially applicable to the prediction of properties of new crystals and the designing of new types of functional crystal materials.

The PV theory can successfully deal with chemical bond properties of binary crystals, e.g., A^NB^{8-N} type crystals [15, 16], Levine improved this theory and made it applicable for multibond crystals [17, 13]. Levine's bond charge model can successfully deal with ABX_2 type semiconductors, but is not applicable to all multibond crystals. As shown in the previous publication[14], the chemical bond method regards a complex crystal as the combination of all constituent chemical bonds. That is to say, a multi-bond crystal can be theoretically decomposed into various single

bonds corresponding to all constituent atoms or ions, according to their detailed chemical bonding structures. Any kind of chemical bond like $A - B$ in the multi-bond crystal $A_a B_b D_d G_g \ldots$ can be expressed as

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

where $A, B, D, G, \ldots$ represent different elements or different sites of an element in the crystal formula, and $a, b, d, g, \ldots$ represent the quantities of the corresponding element, $N(B-A)$ represents the number of B ions in the coordination group of the A ion, and N_{CA} represents 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 multi-bond crystal is ascribed to contributions from all contained chemical bonds, which is also what Levines model shows us. During the decomposition of a multi-bond crystal into its constituent single chemical bonds, the charge-neutrality principle in any crystal formula should be obeyed, and each atom shares its valence as equally as possible among the bonds that it forms [18]. Therefore, the following two network equations (the same meaning as what Brown proposed [18]) should be always kept:

$$\sum_B s_{AB} = V_A \tag{2}$$

and

$$\sum_{loop} s_{AB} = 0 \tag{3}$$

where each atom A in the corresponding lattice is assigned a formal charge equal to its atomic valence or oxidation state (V_A) and each bond between atoms A and B is assigned a bond valence (s_{AB}). The sum of the bond valences around any loop (having regard to the direction of the bonds) is zero.

The above idea makes PV theory and Levine's model successfully applicable to any kind of multi-bond crystals. As shown in the previous publication [14], the chemical bond method regards certain macroscopic physical properties of a crystal as the combination of the contributions of all constituent chemical bonds. Therefore, the linear and nonlinear optical properties of any crystal – even with complex structure – can be calculated using the appropriate geometric sum of the respective properties of its constituent chemical bonds.

In a multi-bond crystal, its linear optical property χ can be ascribed to contributions χ^μ from the various types of bonds

$$\chi = \sum_\mu F^\mu \chi^\mu = \sum_\mu N_b^\mu \chi_b^\mu \tag{4}$$

where F^μ is the fraction of bonds of type μ composing the actual crystal. N_b^μ is the number of chemical bonds of type μ per cm^3. χ_b^μ is the susceptibility of a single bond of type μ.

$$\chi^\mu = (4\pi)^{-1} \left(\hbar \Omega_p^\mu / E_g^\mu \right)^2 \tag{5}$$

where Ω_p^μ is the plasma frequency, E_g^μ is the average energy gap between the bonding and the antibonding states, $(E_g^\mu)^2 = (E_h^\mu)^2 + (C^\mu)^2$ [17, 13, 14]. Furthermore, the fractions of ionic and covalent characteristics of the individual bonds, f_i^μ and f_c^μ, are defined by

$$f_i^\mu = (C^\mu)^2 / (E_g^\mu)^2, \qquad f_c^\mu = (E_h^\mu)^2 / (E_g^\mu)^2 . \tag{6}$$

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

$$
d_{ij} = \sum_\mu \left\{ \frac{G_{ij}^\mu N_b^\mu (0.5) \left\{ [(Z_A^\mu)^* + n(Z_B^\mu)^*] / [(Z_A^\mu)^* - n(Z_B^\mu)^*] \right\} f_i^\mu (\chi_b^\mu)^2}{d^\mu q^\mu} \right.
$$
$$
\left. + \frac{G_{ij}^\mu N_b^\mu s(2s - 1) [r_0^\mu / (r_0^\mu - r_c^\mu)]^2 f_c^\mu (\chi_b^\mu)^2 \rho^\mu}{d^\mu q^\mu} \right\} , \tag{7}
$$

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

Results and discussion

Starting from the chemical bonding structures of all constituent atoms, we have quantitatively calculated all independent second order NLO tensor coefficients d_{ij} for several borate crystals containing different B_xO_y infrastructures (as described in the second column of Table 1). The calculated results – shown in Table 1 – agree satisfactorily with available experimental data [19–24].

The detailed quantitative calculations for these borate crystals[25] show that the isolated BO_3 infrastructures possess highly localized valence electrons and are advantageous for synthesizing borate crystals with large NLO responses. In contrast to this, borate crystals with BO_4 or B_xO_y infrastructures forming various six-member B–O rings contain constituent boron atoms with less localized valence electrons. Furthermore, the formation of B–O rings in borate crystals generally decreases their NLO response. From the chemical bond viewpoint, we therefore expect constituent B–O bonds to possess as many localized valence electrons as possible while searching for new SHG borate crystals, so that large NLO-SHG responses can be finally expected.

In the design of new borate crystals $[BO_3]^{3-}$ groups should be preferred compared with $[BO_4]^{5-}$ groups. The formation of B–O rings should be avoided, yet corner connections between the groups forming an open structure do not decrease the NLO susceptibility, as the case of BiB_3O_6 shows. Of course it should be avoided that a total or partial cancellation of the contributions due to symmetry effects plays any role, highly asymmetric structures always are a *conditio sine qua non*.

Table 1: Structural characteristics and calculated second order NLO tensor coefficients d_{ij} (10^{-9} esu) of some selected borate crystals

Borate crystal	Structural characteristics	Tensor coefficients d_{ij}
$NdAl_3(BO_3)_4$	isolated planar $[BO_3]^{3-}$ groups [19]	d_{11} (−5.81)
$Ca_4GdO(BO_3)_3$	isolated planar $[BO_3]^{3-}$ groups [20]	d_{11} (−10.46); d_{12} (−1.03); d_{13} (−0.37); d_{31} (−2.15); d_{32} (−0.73); d_{33} (−0.22)
BiB_3O_6	open $[B_3O_6]^{3-}$ groups with corner-sharing $[BO_3]^{3-}$ planar groups (two) and $[BO_4]^{5-}$ tetrahedral group (one) [9, 21]	d_{21} (5.95); d_{15} (0.43); d_{22} (0.72); d_{23} (−6.74)
$Ba_3(B_3O_6)_2$	nearly planar $[B_3O_6]^{3-}$ groups with three corner-sharing $[BO_3]^{3-}$ planar groups forming a single six-member B–O ring [22, 23]	d_{11} (−0.07); d_{22} (4.45); d_{31} (−0.12); d_{32} (−0.12); d_{33} (−0.12)
LiB_3O_5	$[B_3O_7]^{3-}$ groups with corner-sharing $[BO_3]^{3-}$ planar groups (two) and $[BO_4]^{5-}$ tetrahedral group (one) forming a single six-member B–O ring [22]	d_{31} (−2.22); d_{32} (2.06); d_{33} (−0.43)
$K[B_5O_6(OH)_4] \cdot 2H_2O$	$[B_5O_{10}]^{5-}$ groups with corner-sharing $[BO_3]^{3-}$ planar groups (four) and $[BO_4]^{5-}$ tetrahedral group (one) forming double connected six-member B–O rings [24]	d_{31} (−0.12); d_{32} (0.02); d_{33} (−1.03)
$Ca_2B_5O_9Cl$	$[B_5O_{12}]^{9-}$ groups with corner-sharing $[BO_3]^{3-}$ planar groups (two) and $[BO_4]^{5-}$ tetrahedral group (three) forming double connected six-member B–O rings [26]	d_{31} (0.96); d_{32} (0.74); d_{33} (−0.03)
$Eu_2B_5O_9Br$	$[B_5O_{13}]^{11-}$ groups with corner-sharing $[BO_3]^{3-}$ planar groups (two) and $[BO_4]^{5-}$ tetrahedral group (three) forming a single six-member B–O ring [27]	d_{31} (0.05); d_{32} (0.04); d_{33} (−0.38)

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