Chemical-bond analysis of the nonlinear optical properties of the borate crystals LiB_3O_5, $CsLiB_6O_{10}$, and CsB_3O_5

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Abstract. The second-order nonlinear optical properties of practical borate crystals, LiB_3O_5, $CsLiB_6O_{10}$, and CsB_3O_5, which all contain the identical basic structural unit [the $(B_3O_7)^{5-}$ group], have been quantitatively studied from the chemical-bond viewpoint. Differences in the nonlinear optical properties among these three borate crystals arise from the contributions of the different cations, i.e., the different interaction between the cation and the $(B_3O_7)^{5-}$ anionic group. The chemical-bond method quantitatively expresses this important difference. At the same time, the current calculation also shows that the B_3O_7 group is a very important crystallographic frame in the crystalline borate solids; it offers different cations an excellent coordination environment.

The origin of the optical nonlinearities of nonlinear optical (NLO) materials is one of the most interesting subjects in the area of nonlinear optics; a comprehensive understanding has been intensively pursued by many research groups. Various theoretical methods starting from Miller's empirical rule up to the current first-principles calculations – at different approximation levels and from different starting points [1–6] – have been more or less successfully applied to this problem. However various controversies still exist, for example, with regard to the role of cations such as Li^+ and Cs^+ in the linear and nonlinear optical properties in borate crystals such as lithium borate and cesium borate [3–5, 7]. Therefore, further studies in this area are necessary.

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 of the boron atoms are hybridized forming sp^2 structures with trigonal symmetry or sp^3 structures exhibiting tetrahedral symmetry. Moreover, several of these two kinds of groups can be

connected in different ways to form typical B_xO_y infrastructures [8]. These various structural possibilities for the boron atom are one of the main reasons for the crystallographic versatility of borates. The basic $[BO_3]^{3-}$ and $[BO_4]^{5-}$ groups are noncentrosymmetric, the larger combined infrastructures and the crystals formed also often lack a center of symmetry. Such a noncentrosymmetric structure is one of the indispensable prerequisites for nonvanishing third-order property tensors governing most nonlinear optical and similar applications of materials (χ_{ijk} or d_{ijk} for second-order NLO tensors, r_{ijk} for Pockels tensors, etc.). Due to these special features of the borate groups, the probability of finding noncentrosymmetric crystal structures in the family of borate crystals is more than twice as high as in other crystal families [9]. In addition, borate crystals usually have the advantages of a low-absorption and high-transmission region extending from ultraviolet to infrared, as well as a high optical damage threshold and reasonable NLO coefficients, etc. [3, 10].

In the current work, we study the second-order NLO properties of three important borate crystals: LiB_3O_5 (LBO), $CsLiB_6O_{10}$ (CLBO), and CsB_3O_5 (CBO), starting from the chemical-bond viewpoint [6]. Structurally, these three crystals contain the same basic unit, the $(B_3O_7)^{5-}$ anionic group, the importance of which has been discussed, for example, by Chen et al. [3], and they only differ in their different cations. Published experimental data for the second-order NLO tensor coefficients of these three crystals have shown obvious differences [11–14]; therefore, finding a theoretical description for these differences will improve the understanding of the respective materials and finally facilitate the search for new types of NLO borate crystals.

1 Theoretical method

As shown in previous works (for an overview see [6]), the chemical-bond method regards certain macroscopic physical properties of a crystal as the combination of the contributions of all constituent chemical bonds. A multibond crystal $A_aB_b\ldots$ is split up into constituent bonds A–B with appropriately chosen partial charges which can be deduced from

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the detailed chemical-bonding structures of atoms A and B in the crystal. The distribution of the valence electrons of constituent atoms over the contributing bonds is defined by the so-called bond-valence equation which is formally derived from the bond graph of the compound [15].

To obtain the (isotropic) linear susceptibility of a crystal material, the contributions of all individual scalar linear bond susceptibilities have to be summed up. To obtain the nonlinear susceptibility, the individual tensorial nonlinear bond susceptibilities have to be summed up, now geometrically. The results thus obey automatically the symmetry rules for third-rank tensors and, moreover, the so-called Kleinman symmetry rule [16].

The macroscopic linear susceptibility of a crystal is given by the sum over all contributions and can be written as

$$\chi = \sum_\mu F^\mu \chi^\mu = \sum_\mu N_b^\mu \chi_b^\mu \,, \tag{1}$$

with

F^μ: fraction of bonds of type μ composing the crystal;
χ^μ: linear susceptibility contribution from μ type bonds;
N_b^μ: number of bonds of type μ per cm^3;
χ_b^μ: susceptibility of a single bond of type μ.

According to Phillips [17] and Van Vechten [18] the linear susceptibility χ^μ contributed by the bonds of type μ in a crystal can be defined as

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

where Ω_p^μ is the plasma frequency and E_g^μ is the average energy gap between the bonding and antibonding states of the bond. E_g^μ can be separated into homopolar and heteropolar (i.e., covalent and ionic) contributions E_h^μ and C^μ

$$(E_g^\mu)^2 = (E_h^\mu)^2 + (C^\mu)^2 \,, \tag{3}$$
$$E_h^\mu = K_1/(d^\mu)^{2.48} \,, \tag{4}$$
$$C^\mu = K_2 b^\mu \exp(-k_s^\mu r_0^\mu)\left[(Z_A^\mu)^* - n(Z_B^\mu)^*\right]/r_0^\mu \,, \tag{5}$$

where K_1 and K_2 are constants consisting only of fundamental physical constants such as $\hbar$, e, etc., and adapted to the units of measure used in the concrete calculation (for lengths in Å and energies in eV, the numerical values are $K_1 = 39.74$ and $K_2 = 14.4$ [19]). $d^\mu = 2r_0^\mu$ is the bond length of the μ-type bond A–B; $\exp(-k_s^\mu r_0^\mu)$ is the Thomas–Fermi screening factor. $(Z_A^\mu)^*$ and $(Z_B^\mu)^*$ are the effective numbers of valence electrons of the two atoms in the bond, n is the ratio of the numbers of the two elements B and A in the bond-valence equation [7, 20]. Because the true screening behaviour in a solid is more complex than this simple Thomas–Fermi description, a correction factor b^μ is introduced [18]. This factor is also used to correct for d-electron influences not accounted for in the effective Z^*. These d-electron effects on the bond susceptibilities were at first considered by Levine [19] but are still in controversial discussion [21, 22]. According to Levine's conclusion [2], the different factors b^μ can be written as $b^\mu = \beta(\bar{N}_c^\mu)^2$, with one global parameter, β – global for all of the different bonds in the compound – and where $\bar{N}_c^\mu$ is the average coordination number of the ions A and B in the bond μ. If the linear susceptibility, i.e., the refractive index, of a crystal is known, this parameter β can

be adjusted to describe the linear susceptibility exactly. Thus in general also the results for the nonlinear susceptibility are improved.

The description of the second-order nonlinear susceptibility can be derived in a similar way; this was basically done by Levine [2]; extensions for complex crystals were developed by Xue and Zhang [6]. The final result for the second-order nonlinear optical tensor coefficients d_{ij} can be written as the appropriate geometric sum over the contributions of all constituent bonds:

$$d_{ij} = \sum_\mu \frac{G_{ij}^\mu N_b^\mu (\chi_b^\mu)^2}{d^\mu q^\mu}\left\{ \frac{f_i^\mu\left[(Z_A^\mu)^* + n(Z_B^\mu)^*\right]}{2\left[(Z_A^\mu)^* - n(Z_B^\mu)^*\right]} + \frac{s(2s-1)(r_0^\mu)^2 f_c^\mu \varrho^\mu}{(r_0^\mu - r_c^\mu)^2} \right\} \,. \tag{6}$$

The first part denotes the ionic fraction, the second part the covalent fraction of the nonlinear optical coefficient. The meaning of the constants on the right-hand side of (6) includes:

G_{ij}^μ: geometrical contribution of chemical bonds of type μ;
N_b^μ: number of bonds of type μ per cm^3;
χ_b^μ: susceptibility of a single bond of type μ;
$(Z_A^\mu)^*$, $(Z_B^\mu)^*$: effective number of valence electrons of A and B ions, respectively;
n: ratio of numbers of two elements B and A in the bond valence equation [7, 20];
f_i^μ, f_c^μ: fractions of ionic and covalent characteristics of the individual bonds [see (3)],
      $f_i^\mu = (C^\mu)^2/(E_g^\mu)^2$ and $f_c^\mu = (E_h^\mu)^2/(E_g^\mu)^2$;
d^μ: bond length of the μ type bonds in Å;
q^μ: bond charge of the μth bond [7];
s: exponent in the bond force constant (2.48);
$r_c^\mu = 0.35 r_0^\mu$: core radius, where $r_0^\mu = d^\mu/2$;
$\varrho = (r_A^\mu - r_B^\mu)/(r_A^\mu + r_B^\mu)$: difference in the atomic sizes, r_A^μ and r_B^μ are the covalent radii of atoms A and B.

All of the above constants have to be deduced from a structural analysis based on the crystallographic structure and taking into account the detailed chemical-bonding situation of all constituent atoms [6]. It should be emphasized that besides the parameter β, introduced for the linear susceptibility, no further adjustable parameters are included.

2 Results and discussion

The three crystals discussed here – LBO, CLBO and CBO – are structurally closely related due to their similar atomic arrangement. Starting from LBO, for example, a complete substitution of Li by Cs yields CBO, a partial substitution (50%) yields CLBO. LBO belongs to the orthorhombic space group $Pna2_1$ with unit cell dimensions $a = 8.4473$, $b = 7.3788$, and $c = 5.1395$ [23]; CLBO crystallizes in the tetragonal space group $I\bar{4}2d$ with unit cell dimensions $a = 10.494$, $c = 8.939$ [24]; CBO is in the orthorhombic space group $P2_12_12_1$ with unit cell dimensions $a = 6.213$, $b = 8.521$, and $c = 9.170$ [25]. Each of these three crystals has 36 atoms, i.e., four formula units LiB_3O_5 or CsB_3O_5 or two formula units $CsLiB_6O_{10}$, respectively, in one unit cell. The detailed structural properties of LBO have already been discussed in a previous publication [7]; therefore we will mainly concentrate

Table 1. Chemical-bond parameters of constituent chemical bonds of CLBO

Chemical bond	$d^\mu(\text{Å})$	f_c^μ	χ^μ	G_{36}^μ	$d_{36}^\mu(\frac{pm}{V})$
Cs–O2	3.1455	0.3408	2.2855	−0.0906	1.0154
Li–O3	1.9617	0.4369	0.8634	−0.1351	0.1634
B1–O2	1.4671	0.1904	0.6776	−0.1566	−0.0186
B1–O3	1.4683	0.1903	0.6782	−0.1428	−0.0170
B2–O1	1.3892	0.1781	0.7881	−0.1576	−0.0227
B2–O2	1.3522	0.3443	1.5507	−0.1698	−0.0264
B2–O3	1.3637	0.3424	1.5682	−0.0024	−0.0004

Table 2. Chemical-bond parameters of constituent chemical bonds of CBO

Chemical bond	$d^\mu(\text{Å})$	f_c^μ	χ^μ	G_{36}^μ	$d_{36}^\mu(\frac{pm}{V})$
Cs–O1	3.2725	0.2348	2.6424	−0.0552	0.2405
Cs–O2	3.2030	0.2364	2.5450	−0.1452	0.5925
Cs–O4	3.0303	0.2409	2.3148	−0.0141	0.0490
Cs–O5	3.1866	0.2367	2.5224	−0.1309	0.5261
B1–O1	1.3346	0.2323	1.5519	−0.1675	−0.0514
B1–O3	1.3614	0.0863	0.6988	0.0151	0.0010
B1–O5	1.3998	0.2974	1.6228	−0.1766	−0.0445
B2–O2	1.3660	0.2287	1.5999	−0.1689	−0.0562
B2–O4	1.3479	0.2307	1.5721	0.0101	0.0032
B2–O5	1.3955	0.2255	1.6458	−0.1463	−0.0523
B3–O1	1.4858	0.1168	0.6467	−0.1815	−0.0133
B3–O2	1.4635	0.1181	0.6351	−0.1647	−0.0117
B3–O3	1.4578	0.0491	0.2223	−0.1577	−0.0013
B3–O4	1.4837	0.1169	0.6456	−0.1760	−0.0128

Fig. 1. Li and Cs cations around the $(B_3O_7)^{5-}$ anionic group in CLBO. Atomic positions are labeled according to the bond designations in Table 1

here on the other two compounds. Their structural arrangement is shown in Figs. 1 and 2. One of the four symmetry-equivalent basic $(B_3O_7)^{5-}$ anionic groups in the unit cell – together with representative cations – is sketched in Fig. 1 for CLBO and in Fig. 2 for CBO. As in LBO, two $(BO_3)^{3-}$ planar groups and one $(BO_4)^{5-}$ tetrahedral group form a slightly distorted six-member B–O ring, sharing corner oxygen ions. The additional bonds, different for each compound, are introduced by the different cations.

Starting from the chemical-bonding structures of all constituent atoms in each crystal, we have quantitatively calculated the chemical-bond parameters of all constituent chemical bonds, and further all independent second-order NLO tensor coefficients d_{ij} of these three crystals possessing different cations and the same $(B_3O_7)^{5-}$ anionic group. For the calculations we used the structural data measured by Ihara et al. for LBO [23], by Krogh-Moe for CLBO [24] and by Sasaki et al. for CBO [25]. The calculated results for CLBO and CBO are summarized in Tables 1 and 2; detailed results for LBO have been published in a previous study [7].

As already discussed for LBO [7], the calculations show that the $(B_3O_7)^{5-}$ structural unit is of great importance for the NLO properties of all three compounds. This is in good agreement with the conclusions on NLO borates with $(B_3O_7)^{5-}$ groups derived using the so-called anionic group theory [3]. In all three crystals, the central structural unit $(B_3O_7)^{5-}$ is of nearly identical size. Yet there are expressed differences in the bond covalency values and the bond susceptibilities for this anionic group between the three crystals. This indicates that not only the influence of the anionic groups but also that of the cations, i.e., the contributions of all constituent bonds, have to be considered thoroughly. Different ions at the cation sites seem to affect the NLO properties of the LBO family crystals quite strongly.

Two main effects can be clearly stated from the data calculated: (a) cations with lower electronegativity values (Cs: 0.7, Li: 1.0) reduce the bond covalency values in the anionic group when replacing Li; (b) Cs–O bonds introduce higher bond susceptibilities than Li–O bonds.

These effects, especially the second one, finally lead to an increase in the NLO susceptibility such that

$$d^{\text{LBO}} < d^{\text{CLBO}} < d^{\text{CBO}}. \qquad (7)$$

Our results for the NLO susceptibilities are summarized in Table 3 together with experimental data and data calculated by other schemes. The comparison shows that the chemical-

Fig. 2. Cs cations around the $(B_3O_7)^{5-}$ anionic group in CBO. Atomic positions are labeled according to the bond designations in Table 2

Table 3. Second-order NLO tensor coefficients d_{ij} (in $\frac{pm}{V}$) of LBO, CLBO and CBO. Comparison of experimental results with different calculation schemes. LDA: local density approximation. CNDO: complete neglect of differential overlap

		Experiment	Band calculations [5]		Anionic group theory [3]		Present Calculation
			Plain LDA	Scissors	CNDO/2	Gaussian'92	
LBO	d_{31}	$-(1.05\pm0.13)$ [a] $-(0.83\pm0.06)$ [b]	-2.22	-1.70	-1.14	-0.92	-0.92
	d_{32}	0.98 ± 0.09 [a] 0.71 ± 0.05 [b]	1.77	1.37	0.94	0.81	0.80
	d_{33}	$-(0.06\pm0.004)$ [a] 0 ± 0.1 [b]	-0.11	-0.10	-0.21	-0.34	-0.23
CLBO	d_{36}	0.95 [c]			-0.58	-0.58	1.09
CBO	d_{36}	$1.04(1\pm0.2)$ [d]	-1.93	-1.22	-0.65	-0.71	1.17

[a] [11]
[b] [12]
[c] [14]
[d] [3, 13]

bond scheme is quite reliable for calculating linear and nonlinear optical properties.

3 Conclusion

The second-order nonlinear optical susceptibilities of three similar borate materials – lithium borate, cesium lithium borate, and cesium borate – have been quantitatively studied from the chemical-bond viewpoint of crystal materials. The results show that as well as the anionic group $(B_3O_7)^{5-}$, which is identical for all three compounds, the different cations involved influence the susceptibility in a characteristic way. Heavier cations decrease the covalency values for the bonds in the anionic group and increase the susceptibility of the cation–oxygen bond. Especially the latter leads to an increase in the resulting macroscopic susceptibility induced by the heavier cation.

The present work shows that heavier cations strengthen the interaction between the cation and the $(B_3O_7)^{5-}$ anionic group. From the chemical-bond viewpoint, the crystals can be considered to consist of two parts, the fundamental structural frame of anionic groups, nearly identical for all three compounds, and the individual cations, which, in addition, impose characteristic modifications on the linear and nonlinear optical properties of the crystals.

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