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Origin of the Large Nonlinear Optical Coefficients in Bismuth Borate BiB_3O_6

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Introduction. For nonlinear optical applications, the family of borate crystals is of exceptional importance (for a recent review read e.g. Ref. [1]). Especially the monoclinic bismuth borate BiB_3O_6 shows up remarkably large nonlinear optical coefficients [2]; yet up to now there is no appropriate theoretical model for their origin. From the chemical bond viewpoint, we try to find an explanation for these large values.

Theory. To describe the nonlinear optical properties of a complex crystal, it may be regarded as a combination of all constituent chemical bonds, i.e., the macroscopic tensor elements of the nonlinear susceptibility can be expressed as an appropriate sum over the contributions of single bonds [3,4]

$$d_{ijk} = \sum_{\mu} \frac{G^{\mu}_{ijk}}{d^{\mu} q^{\mu}} \left\{ N^{\mu}_{\mathrm{b}}(0.5)\, \frac{(Z^{\mu}_{\mathrm{A}})^{*} + n(Z^{\mu}_{\mathrm{B}})^{*}}{(Z^{\mu}_{\mathrm{A}})^{*} - n(Z^{\mu}_{\mathrm{B}})^{*}}\, f^{\mu}_{i} (\chi^{\mu}_{\mathrm{b}})^{2} + \frac{N^{\mu}_{\mathrm{b}} s(2s-1)(r^{\mu}_{0})^{2}}{(r^{\mu}_{0} - r^{\mu}_{\mathrm{c}})^{2}}\, f^{\mu}_{\mathrm{c}} (\chi^{\mu}_{\mathrm{b}})^{2}\, \varrho^{\mu} \right\}, \qquad (1)$$

where ϱ^{μ} is the difference in the atomic sizes, r^{μ}_{c} is the core radius, q^{μ} is the bond charge of the μ-th bond, and G^{μ}_{ijk} 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 [3,4].

Results. From the complete crystal structure [5], the chemical bonding situations of all constituent atoms or ions in BiB_3O_6 can be derived. On the basis of this structural information the decomposition formula of BiB_3O_6 can be written as

$$\begin{aligned} BiB_3O_6 = {} & (1/3)\,BiO(12)_2 + (1/3)\,BiO(2)_2 + (1/3)\,BiO(2')_2 \\ & + (1/2)\,B(1)O(11)_2 + (1/2)\,B(1)O(12)_{4/3} \\ & + (2/3)\,B(2)O(11)_{3/2} + (2/3)\,B(2)O(12) + (2/3)\,B(2)O(2)\,. \end{aligned} \qquad (2)$$

Using the detailed structural data, the contributions of all constituent bonds (Eq. (2)) of BiB_3O_6 have been calculated. The results are summarized in Tables 1 and 2.

As can be concluded from the results in Table 2, the main contributions to the nonlinear susceptibility arise from B–O bonds in the BO_3^{3-} groups, i.e. B2 ions.

It should be emphasized that two of the four tensor elements (d_{112} and d_{233}) agree very well with the experimental values [2] whereas the agreement of the two other ones is only poor. This may be due to the fact that a lone-pair electron at the Bi atom [2] cannot be accounted for in the calculation. Furthermore, the triangular structure of the BO_3^{3-} groups is slightly distorted which probably leads to a deviation from symmetric linear bonds that are assumed in the calculation.

Table 1
Chemical bond parameters of all constituent chemical bonds of BiB_3O_6

	d^{μ} (Å)	E^{μ}_{h}	C^{μ}	f^{μ}_{c}	χ^{μ}	χ^{μ}_{b}	q^{μ}/e
Bi–O12	2.3901	4.5788	8.2088	0.2373	2.2900	1.2682	0.7320
Bi–O2	2.6324	3.6038	6.6312	0.2280	2.6761	1.4820	0.6632
Bi–O2′	2.0865	6.4131	10.9811	0.2543	1.8659	1.0333	0.8308
B1–O11	1.4364	16.1877	29.3323	0.2335	1.3466	0.7457	1.9487
B1–O12	1.4875	14.8434	10.6369	0.6607	2.0704	1.1465	0.9968
B2–O11	1.3386	19.2812	18.4794	0.5212	2.7842	1.5418	1.6020
B2–O12	1.4105	16.9349	10.8326	0.7096	4.2952	2.3786	1.4974
B2–O2	1.3650	18.3696	11.5706	0.7159	4.0584	2.2475	1.5393

Table 2

Geometry factors and second order nonlinear optical properties of all constituent chemical bonds of BiB_3O_6 at 1.0795 μm. The resulting macroscopic tensor elements d_{ijk} are given in the last line. All d_{ijk} in 10^{-9} esu

	G^{μ}_{112}	d^{μ}_{112}	G^{μ}_{123}	d^{μ}_{123}	G^{μ}_{222}	d^{μ}_{222}	G^{μ}_{233}	d^{μ}_{233}
Bi–O12	−0.0614	0.1610	0.1007	−0.2640	−0.0139	0.0364	−0.1650	0.4326
Bi–O2	0.2971	−0.9145	−0.1006	0.3097	0.0597	−0.1837	0.0341	−0.1049
Bi–O2′	−0.2577	0.5705	−0.1586	0.3511	−0.3482	0.7709	−0.0976	0.2161
B1–O11	−0.3581	−0.2109	0.0978	0.0576	−0.1991	−0.1173	−0.0267	−0.0157
B1–O12	0.0295	−0.1387	0.1023	−0.4814	0.2062	−0.9702	0.3551	−1.6708
B2–O11	−0.0300	0.0866	.0278	−0.0804	−0.0002	0.0051	−0.0258	0.0745
B2–O12	−0.3823	6.4059	−0.0214	0.3577	−0.2218	3.7160	−0.0119	0.1998
B2–O2	0.0003	−0.0053	−0.0115	0.1766	0.1652	−2.5325	0.3833	−5.8750
d_{ijk} (sum)		5.95		0.43		0.72		−6.74

Conclusion. All chemical bond parameters and their contributions to the nonlinear optical susceptibility of BiB_3O_6 have been computed from its reported crystal structure. The detailed calculation shows that the main contributions to the large tensor coefficients arise from the bonds in the BO_3^{3-} groups. Yet further remarkable contributions may be due to the lone-pair electron at the bismuth atom.

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