The anionic group theory of the non-linear optical effect and its applications in the development of new high-quality NLO crystals in the borate series

Chuangtian Chen[ab]; Yicheng Wu[c]; Rukang Li[c]

[a] Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, People's Republic of China [b] Member of the Condensed Matter and Radiation Group, China Centre of Advanced Science and Technology (World Laboratory), Beijing, People's Republic of China [c] Department of Applied Chemistry, University of Science and Technology of China, Hefei, Anhui, People's Republic of China

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The anionic group theory of the non-linear optical effect and its applications in the development of new high-quality NLO crystals in the borate series

by CHUANGTIAN CHEN†

Fujian Institute of Research on the Structure of Matter,
Chinese Academy of Sciences, Fuzhou, Fujian,
People's Republic of China

YICHENG WU and RUKÁNG LI

Department of Applied Chemistry, University of Science and Technology
of China, Hefei, Anhui, People's Republic of China

Starting from a general quantum-mechanical perturbation theory on the non-linear optical (NLO) effect in crystals, this review gives a systematic presentation of the basic concepts and calculation methods of the 'anionic group theory for the NLO effect of crystals' and a brief discussion of the approximations involved. Calculations have been made for the second harmonic generation (SHG) coefficients of a few typical NLO crystals. Comparisions between these theoretical values and the experimental values made both on powdered crystals and on single crystals suffice to show the feasibility of the theoretical treatment and calculation methods. On this basis, borate ions of various structure types are classified and systematic calculations are carried out for the NLO susceptibilities of some typical borate crystals with good prospects of applications in opto-electronics.

Through these calculations, a series of structural criteria serving as useful guidelines for searching and developing new NLO crystals in borate series are presented. These structural criteria have good prospects of wider applications in searching and developing for other new types of NLO crystal materials. The criteria are as follows. (1) The planar six-membered ring $(B_3O_6)^{3-}$ and the planar trigonal $(BO_3)^{3-}$ group, each possessing a conjugated π-orbital system, are far more favourable for producing larger SHG coefficients than the non-planar tetrahedral $(BO_4)^{5-}$ group. Moreover, in the planar group, the larger the electronic population in the conjugated π-orbital system, the greater the SHG effects will be. As a result, the SHG effects will decrease in the order $\chi^{(2\omega)}_{(B_3O_6)} > \chi^{(2\omega)}_{(BO_3)} > \chi^{(2\omega)}_{(BO_4)}$. (2) The SHG coefficients can be adjusted to a certain extent by suitable arrangement of the three- and four-coordinated B atoms, such as $(BO_3)^{3-}$ and $(BO_4)^{5-}$, $(B_3O_6)^{3-}$ as opposed to $(B_3O_7)^{5-}$ and $(B_3O_8)^{7-}$.

On the basis of these structural criteria, we have been successful in developing some new high-quality NLO materials, including the LiB_3O_5 crystal as an excellent NLO material. Suggestions are put forward for searching for and developing other promising new NLO materials in the borate series. The recent development of two new-type NLO borate crystals, $\beta\text{-}BaB_2O_4$ and LiB_3O_5, is described.

1. Introduction

Non-linear optical (NLO) materials have played an important role in laser science and technology, and the search for new NLO materials, particularly for UV and far-IR applications, is still very active (Auston 1987), even though intensive efforts in this field

† Member of the Condensed Matter and Radiation Group, China Centre of Advanced Science and Technology (World Laboratory), Beijing, People's Republic of China.

have been in progress for about 20 years. Scientists working on laser materials realize the extreme importance, in the search of new NLO materials, of a thorough elucidation of the structure–property relationship between NLO effects and microstructure.

Many attempts have already been made in this direction. Among them we may cite in particular the bond parameter methods, exemplified by the work of Bloembergen (1965); the anharmonic oscillator models of Kurtz and Robinson (1967) and Garrett and Robinson (1966, 1968); the bond parameter methods of Jeggo and Boyd (1974) and Bergman and Crane (1974); and the bond charge model of Levine (1969, 1970) before the 1970s. Among these, Levine's (1969, 1970, 1973) model is the most successful, and has been shown to be particularly useful in the elucidation of the structure–property relationship of the NLO effect in A–B type semiconductor materials, the basic structural unit of which consists of sp^3-hybrid tetrahedrally coordinated atoms. However, this method has not been so successful for other types of NLO crystals in which the basic structural unit does not belong to the category of simple σ-type bonds. For example, if such a bond charge model should be extended to ferroelectric crystals consisting of oxygen octahedra with transition metal atoms as centres, some serious defects would at once become apparent (Fujii and Sakudo 1976, Levine 1976). Again, it would be difficult to understand how such a bond charge model could give rise to large NLO effects in crystals consisting of planar ions or molecules with conjugated π-orbital systems in their basic structural units.

Since the 1970s, several research groups have discovered that non-linear susceptibility arises from basic structural units with delocalized regions of valence electron orbitals belonging to more than two atoms, rather than regions localized around two atoms connected by a simple σ-type bond. Davydov *et al.* (1970) showed that non-linear susceptibilities of organic crystals arise from molecules in their basic structural units, and hence it is most likely that conjugated organic molecules with donor–acceptor radicals will exhibit large non-linear susceptibilities. This idea was further developed by Chemla *et al.* (1975), Ovdar and Chemla (1975) and Ovdar and Leperson (1975). Through a detailed analysis of the overall second-order susceptibilities of organic crystals and the microscopic second-order susceptibilities of the constituent molecules, they arrived at the following conclusions about the non-linear response in organic crystals. First, the bulk second-order susceptibility of an organic crystal can be considered as the geometric superposition of the microscopic second-order susceptibilities of its constituent molecules. Also, the π-conjugated orbital system of an acentric planar organic molecule with charge transfer between donor and acceptor substituent groups is mainly responsible for the presence of large second-order susceptibilities in such molecules. This novel idea enabled Chemla's group to develop a series of new organic NLO rystals exhibiting very large second-order susceptibilities, such as POM (Zyss *et al.* 1981), NPP (Zyss and Ovdar 1984) and MAP (Ovdar and Hierle 1977).

At much the same time, a new theoretical model called anionic group theory for NLO susceptibility in NLO crystals was proposed by Chen (1976). He pointed out that it is desirable to make a systematic exploration of the structure–property relationship of NLO effects in some typical known inorganic NLO crystals. On the basis of the proposed model and an approximate method of calculation based on the second-order perturbation theory for the SHG coefficients, Chen's group succeeded in making a systematic elucidation of the structure–property relationship of the NLO effect for almost all the principal types of inorganic NLO crystals, namely the perovskite and tungsten–bronze (Chen 1977), phosphate (Chen 1979), iodate (Chen and Chen 1980)

and nitrite crystals (Chen *et al.* 1980, 1981), and leading to the development of a new borate series of NLO crystals.

We now give a brief description of the 'anionic group theory' of the NLO effects in crystals, including its basic concepts and the methods of calculation adopted, with a discussion of the approximations involved, and then extend our treatment to the study of the NLO effect in borate anions of various known structure types.

2. The anionic group theory and the methods of approximate quantum-chemical MO adopted for the calculation of the NLO susceptibilities of crystals

Here we give only a brief description of this theory and the method of calculation used. For details the reader is referred to the literature (Chen 1979, 1985, Chen and Liu 1986).

It is well known that in linear optics, when an incident light beam with frequency ω impinges on a crystal (or another medium), the polarization P_i induced with the same frequency is given by the expression

$$P_i^{(\omega)} = \chi_0[\chi_{ij}E_j(\omega)], \tag{1}$$

where $\chi_0 = 4\pi\varepsilon_0$, ε_0 is the permittivity of free space, χ_{ij} is the linear polarizability of the crystal (a second-order tensor) and $E_j(\omega)$ is the amplitude of the optical electric field alternating with the same frequency. However, with an incident laser beam acting on the crystal, there may be additional induced non-linear polarizations with frequencies different from ω, given by new terms in the expression

$$P_i = \chi_0[\chi_{ij}^{(\omega)}E_j(\omega) + \chi_{ijk}^{(2\omega)}: E_j(\omega)E_k(\omega) + \chi_{ijkl}^{(3\omega)} \vdots E_j(\omega)E_k(\omega)E_l(\omega) + \ldots], \tag{2}$$

where $\chi_{ijk}^{(2\omega)}$, $\chi_{ijkl}^{(3\omega)}$, ... are the NLO coefficients.

Similarly, when two (or more) laser beams of different frequencies impinge at the same time on a crystal with acentric symmetry (or on the surface of a crystalline medium), new NLO effects with sum and difference frequencies will appear, as shown in the expression

$$P_i = \chi_0\{[\chi_{ij}^{(\omega_1)}E_j(\omega_1) + \chi_{ij}^{(\omega_1)}E_j(\omega_2)] + [\chi_{ijk}^{(2\omega_1)}: E_j(\omega_1)E_k(\omega_1)$$

$$+ \chi_{ijk}^{(2\omega_2)}: E_j(\omega_2)E_k(\omega_2) + 2\chi_{ijk}^{(\omega_1 \pm \omega_2)}: E_j(\omega_1)E_k(\omega_2)] + \ldots\}. \tag{3}$$

In modern laser technology, second-order NLO effects are widely used, such as SHG $\chi_{ijk}^{(2\omega)}$, sum or difference frequency generation [SFG $\chi_{ijk}^{(\omega_1 + \omega_2)}$ or DFG $\chi_{ijk}^{(\omega_1 - \omega_2)}$] and parametric amplification. In this review we confine ourselves to the discussion of only the SHG coefficients for most NLO crystals, since there is no significant difference between SHG and SFG, DFG, and so on, if the dispersions of the second-order susceptibilities are not considered.

Physical properties related to electron motion in crystals fall essentially into two categories. Some, such as the electrical properties of crystals, arise from long-range interactions in the lattice; here long-range forces from the electron–electron or the electron–core interactions play an important role. In these cases, the use of energy band theory is essential. On the other hand, in NLO effects, the process of electronic excitation by the incident radiation does not make any important contribution. They essentially arise from the process of scattering, where the action of the incident photons on the electrons in the crystal serves only as a kind of perturbation; in other words, the electrons are confined to their ground state. Hence the NLO effects should be classified into the second category where short-range forces play a decisive role. We therefore make the assumption that, in the NLO effects, the electron motion may be regarded as

confined to small regions. In other words, any NLO susceptibility (or second-order susceptibility) in crystals is a localized effect arising from the action of incident photons on the electrons in certain orbitals of atomic clusters.

Therefore, what we need to do is to define the region of the localized motion of these electrons in order to make reasonable estimates of the bulk second-order susceptibility of the cyrstal. Previously (Garrett and Robinson 1966, 1968, Jeggo and Boyd 1974, Bergman and Crane 1974, Levine 1969, 1970) the NLO effect was analysed in some typical known NLO materials with the structure types such as perovskite and tungsten–bronze, iodate, phosphate, molybdate and nitrite as the geometrical superposition of each bond's NLO susceptibilities, such as Nb–O, P–O, I–O and N–O bonds but, as pointed out by Chen (1976, 1977, 1979, 1985) the major NLO-active units are anionic groups in inorganic crystals, such as the $(MO_6)^{n-}$ coordination octahedron in perovskite and tungsten–bronze type materials; the $(IO_3)^-$ group in iodates; the $(PO_4)^{3-}$ group in phosphates; the $(NO_2)^-$ group in nitrites rather than the bonds, except for sp^3-hybrid semiconductor materials. On this basis we were able to propose a theoretical model called the 'anionic group theory' for NLO susceptibility, with the following two assumptions as the basic premises: (i) the overall SHG coefficient of the crystal is the geometrical superposition of the microscopic second-order susceptibility tensors of the relevant ionic groups, and has nothing to do with the essentially spherical cations; (ii) the microscopic second-order susceptibility of the basic anionic group can be calculated from the localized molecular orbitals of this group using quantum chemistry calculation methods. It can easily be shown that $\chi_{ijk}^{(2\omega)}$ is given by the expression

$$\chi_{ijk}^{(2\omega)} = \frac{N}{V} \sum_p \sum_{i'j'k'} \alpha_{ii'} \alpha_{jj'} \alpha_{kk'} \chi_{i'j'k'}^{(2\omega)}(p), \qquad (4)$$

where V is the volume of a unit cell, N is the number of basic structural groups in this unit cell, $\alpha_{ii'}$, $\alpha_{jj'}$, $\alpha_{kk'}$ are the direction cosines between the microscopic coordinates of the crystal and the microscopic coordinates of the pth group and $\chi_{i'j'k'}^{(2\omega)}(p)$ is the microscopic second-order susceptibility of this pth group.

To understand the implication of the above two assumptions, let us turn to the question of what approximations there are in these assumptions from the viewpoint of the electronic structure of crystals. An ionic crystal must consist of a series of structural units, anionic groups and cations stacked up in a regular manner. Thus the Hamiltonian of the whole system can be written as

$$\hat{H} = \sum_p \hat{H}_p + \sum_i \hat{H}_i + \frac{1}{2} \sum_{p',p} \hat{H}_{p'p} + \frac{1}{2} \sum_{i',i} \hat{H}_{i'i} + \sum_{p,i} \hat{H}_{pi}, \qquad (5)$$

where $\hat{H}_p$, $\hat{H}_i$ are the total Hamiltonians of the pth anionic group and the ith cation respectively, and $\hat{H}_{p'p}$ and $\hat{H}_{i'i}$ are the interaction Hamiltonians between different anionic groups and different cations. Hence the first approximation made in our theory implies that the interaction Hamiltonians $\hat{H}_{p'p}$, $\hat{H}_{i'i}$ and $\hat{H}_{pi}$ may be replaced by average potentials of the types V_p, V_i and V_{pi}:

$$\left. \begin{array}{l} \dfrac{1}{2} \sum_{p',p} \hat{H}_{p'p} = \sum_p \left(\dfrac{1}{2} {\sum_{p'}}' \hat{H}_{p'p} \right) = \sum_p V_p; \\[3mm] \dfrac{1}{2} \sum_{i'i} \hat{H}_{i'i} = \sum_i \left(\dfrac{1}{2} {\sum_{i'}}' \hat{H}_{i'i} \right) = \sum_i V_i; \quad \sum_p \left(\sum_i \hat{H}_{pi} \right) = \sum_p V_{pi}. \end{array} \right\} \qquad (6)$$

The whole Hamiltonian for the crystal is then given by the following approximate expression:

$$\hat{H} = \sum_p (\hat{H}_p + V_p + V_{pi}) + \sum_i (\hat{H}_i + V_i + V_{ip}).$$ (7)

On using the Hartree approximation, the wavefunctions of the whole system are given by

$$\psi = \prod_p \psi_p \prod_i \psi_i$$ (8)

so that the Schrödinger equation of the system is

$$\left.\begin{array}{c} (\hat{H}_p + V_p + V_{pi})\psi_p = E_p\psi_p, \\ (\hat{H}_i + V_i + V_{ip})\psi_i = E_i\psi_i. \end{array}\right\}$$ (9)

The second approximation made in our theory comes from the fact that all cations in the NLO crystals are essentially spherical, implying the conservation of parity for all the eigenstates of the cation. As the second-order susceptibility of the system is a third-rank tensor, contributions from these essentially spherical cations can only be vanishingly small, although their contributions to the linear susceptibility cannot be ignored. Now, let us denote by $\hat{P}$ the total polarization operator:

$$\hat{P} = \sum_p \hat{P}_p + \sum_i \hat{P}_i.$$ (10)

Here, $\hat{P}_p$ and $\hat{P}_i$ are used to denote the total polarization operators for the pth anionic group and the ith cation respectively. The average value of the polarization operator of the whole system is thus given by

$$\langle\psi|\hat{P}|\psi\rangle = \sum_p \langle\psi_p|\hat{P}|\psi_p\rangle + \sum_i \langle\psi_i|\hat{P}_i|\psi_i\rangle.$$ (11)

Since we confine ourselves to the calculation of the second-order susceptibility of the system, the second summation in the right-hand expression may be neglected.

Let us denote by $|\psi_0(p)\rangle$ the antisymmetric ground-state vector and by $|\psi_n(p)\rangle$ the antisymmetric excited-state vectors of the pth anionic group, which can in principle be determined from the first equation (9). It can be deduced from the second-order perturbation theory of quantum chemistry that the microscopic second-order susceptibility $\chi_{ijk}^{(2\omega)}(p)$ is given by

$$\chi_{ijk}^{(2\omega)}(p) = \frac{-e^3}{4\hbar^2} a_0^3 S_{ijk}^{(2\omega)} \sum_{n,n'}{}' \left\{\left[\langle\psi_0(p)| \sum_{l=1}^m \gamma_i^{(p)}(l)|\psi_n(p)\rangle \right.\right.$$

$$\times \langle\psi_n(p)| \sum_{l=1}^m \gamma_j^{(p)}(l)|\psi_{n'}(p)\rangle \langle\psi_{n'}(p)| \sum_{l=1}^m \gamma_k^{(p)}(l)|\psi_0(p)\rangle$$

$$+ \langle\psi_0(p)| \sum_{l=1}^m \gamma_i^{(p)}(l)|\psi_n(p)\rangle \langle\psi_n(p)| \sum_{l=1}^m \gamma_k^{(p)}(l)|\psi_{n'}(l)\rangle$$

$$\left.\left.\times \langle\psi_{n'}(p)| \sum_{l=1}^m \gamma_j^{(p)}(l)|\psi_0(p)\rangle \right]L^{(ijk)}(\omega_{g\to n}; \omega_{g\to n'}) + \ldots\right\}$$ (12)

where a_0 is the Bohr radius of the hydrogen atom, $S_{ijk}^{(2\omega)}$ is the conversion factor between the external optical field and the internal optical field acting on the anionic group;

$$\left\langle \psi_0(p) \left| \sum_{l=1}^{m} \gamma_i^{(p)}(l) \right| \psi_n(p) \right\rangle$$

is the electronic dipole transition matrix element of the pth anionic group, m is the number of electrons in the anionic group, $r=x$, $r=y$, $r=z$, and $L^{(ijk)}(\omega_{g\to n}; \omega_{g\to n'})$ is the energy factor that can be expressed as

$$L^{(ijk)}(\omega_{g\to n}; \omega_{g\to n'}) = \frac{1}{(\omega_{g\to n} - 2\omega)(\omega_{g\to n'} - \omega)} + \frac{1}{(\omega_{g\to n} + 2\omega)(\omega_{g\to n'} + \omega)}. \tag{13}$$

Here $\omega_{g\to n} = (E_n - E_g)/\hbar$ and E_g, E_n are the energies of the ground-state vector $|\psi_0(p)\rangle$ and the excited-state vector $|\psi_n(p)\rangle$ respectively.

The next step is to determine the localized molecular orbital of the anionic group. Of course, there are many methods available for the calculation of the molecular orbitals in our theory; the CNDO approximation (Pople and Deveridge 1970) seems to serve our purpose adequately. With the CNDO approximation, we have found it convenient to use the point charge model to calculate the average potentials V_p and V_{pi} in the equation (6). It can be easily shown that

$$V_{pi} = \sum_i \frac{(g_i e)}{|\hat{R}_i - \hat{r}|}, \tag{14}$$

where $(g_i e)$ is the effective charge on the ith cation, $\hat{R}_i$ is the radius vector from the origin of the anionic group to this cation; $\hat{r}$ is the vector of each electron in the anionic group, and $\sum$ represents the sum over all the cations in the crystal. On the basis of our adopted method of calculation, a complete computer programme consisting of three main parts can easily be written for such a calculation. The three parts are as follows: (*a*) the CNDO part for calculation of the localized electron orbitals in the anionic group; (*b*) the transition matrix element calculation part; and (*c*) the second-order susceptibility part for the calculation of the microscopic susceptibility of the anionic group followed by the calculation of the macroscopic SHG coefficients of the crystal.

Generally, the CNDO/2 approximation is used for the calculation of the electronic state for non-planar groups and the CNDO/S approximation is used for planar groups. In these calculations, the standard CNDO parameters are used without adjustment; however, in the case of polar crystals, with a certain degree of spontaneous polarization, some adjustments are generally necessary. Here an odd-ordered crystal field is added to the Hamiltonian of the anionic group as a correction term, which may be obtained from equation (14) with the symmetry of the lattice taken into consideration.

It is obvious that our 'anionic group theory' can be generalized into an 'NLO-active group theory', thus permitting a straightforward extension to the consideration of discrete uncharged groups (such as urea or substituted benzene) and even cationic groups as basic NLO-active structural units.

3. Examples of theoretical calculations for typical NLO crystals of various structure types

The anionic group theory proposed in 1967–68 was at first only an assumption. Through systematic theoretical investigations during the 1970s, convincing evidence accumulated to show that the theory leads to a fairly simple elucidation of the objective

truth behind the NLO effects. Moreover, it can be used to explain the structure–property relationship in most known NLO crystals of various structure types and to work out guidelines for searching for and developing new NLO materials. Here we cite a few early examples.

(*a*) Of the perovskite and tungsten–bronze type of crystals, three NLO crystals LiNbO$_3$, KNbO$_3$ and BNN (Ba$_2$Na(NbO$_3$)$_5$) are well known. In these NLO crystals, the common basic structural unit is the (NbO$_6$) coordination octahedra but deformed in different ways. For instance, the (NbO$_6$) octahedron in LiNbO$_3$ is deformed along a threefold body diagonal direction of the cubic unit cell. In KNbO$_3$, it is deformed along a twofold axis. In BNN, on the other hand, it is deformed mainly along a four-fold axis (see figure 1). According to our anionic group theory, the magnitude of the SHG coefficients in these three crystals should depend on the localized molecular orbitals of these deformed octahedra, and thus on the modes of deformation in particular, with only negligible contributions from the cations. We have calculated in detail on the basis of our theory, without introducing any adjustable parameters, the SHG coefficients of these three crystals by making use of the Wigner–Eckart theorem in group representations (Chen 1977). The results are shown in table 1. The fact that the SHG coefficients of these three crystals differ substantially from one another both in relative signs and in absolute magnitudes is another straightforward vindication that their differences depend essentially on the deformation modes of the (NbO$_6$) octahedra (Chen 1977).

(*b*) As can be seen from our theoretical calculations (Chen 1979, 1985, Chen and Liu 1986), the SHG coefficients in perovskite and tungsten–bronze type crystals are closely dependent on the magnitude of the odd-ordered crystal field V_s induced by the spontaneous polarization P_s in crystals. On taking the point charge model as a first approximation, the odd-ordered crystal field V_s would be given by

$$V_s = \frac{2ge}{R_0^3}(2\,\Delta z),\qquad(15)$$

where ge is the effective charge on the oxygen atom and z is the z coordinate of the electron along the deformation axis. It is further borne out by our calculations that when the displacement Δz of the central metal ion relative to its oxygen ligands is small (roughly less than 0·06 Å; cf. figure 1) and $V_s \ll E(\mathrm{p}) - E(\mathrm{s})$, where here $E(p)$ and $E(s)$ denote the energies of the outermost p and s orbitals respectively in the central metal
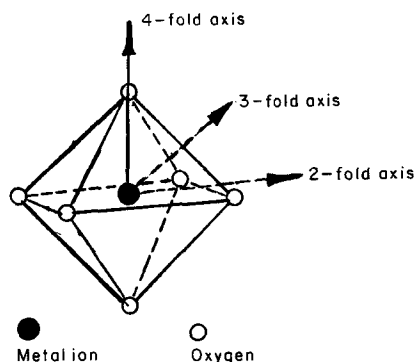

Figure 1. The (MO$_6$)$^{n-}$ coordination octahedron and its three different deformation modes.

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Table 1. SHG coefficients of LiNbO$_3$, KNbO$_3$ and BNN crystals (units: 10^{-9} e.s.u.; $\lambda = 1.064$ μm).

Crystal		$\chi^{(2\omega)}_{333}$	$\chi^{(2\omega)}_{311}$	$\chi^{(2\omega)}_{322}$	$\chi^{(2\omega)}_{113}$	$\chi^{(2\omega)}_{233}$	$\chi^{(2\omega)}_{111}$
LiNbO$_3$	Exptl.	$-(72 \cdot 0 \pm 18 \cdot 0)$	$-(12 \pm 1)$				$5 \cdot 74 \pm 2 \cdot 26$
	Calcd.	$-77 \cdot 5$	$-15 \cdot 26$				$7 \cdot 096$
KNbO$_3$	Exptl.	$-(53 \cdot 0 \pm 2 \cdot 8)$	$30 \cdot 68 \pm 2 \cdot 8$	$-(34 \cdot 87 \pm 2 \cdot 8)$	$32 \cdot 09 \pm 5 \cdot 6$	$-(33 \cdot 47 \pm 5 \cdot 6)$	
	Calcd.	$-57 \cdot 85$	$28 \cdot 15$	$-35 \cdot 9$	$33 \cdot 2$	$-28 \cdot 0$	
BNN	Exptl.	$-(47 \cdot 6 \pm 3 \cdot 47)$	$-(34 \cdot 65 \pm 1 \cdot 74)$	$-(34 \cdot 65 \pm 3 \cdot 47)$	$-(34 \cdot 65 \pm 3 \cdot 47)$	$-(32 \cdot 95 \pm 1 \cdot 74)$	
	Calcd.	$-46 \cdot 98$	$-47 \cdot 24$	$-47 \cdot 24$	$-35 \cdot 85$	$-35 \cdot 85$	

ion, the SHG coefficients are directly proportional to Δz and P_s for BNN under C_{4v} symmetry, as given by the equations

$$\left.\begin{array}{l}\chi^{(2\omega)}_{333}=\alpha_{333}\,\Delta z=\alpha'_{333}P_s;\\[2mm]\chi^{(2\omega)}_{311}=\alpha_{311}\,\Delta z=\alpha'_{311}P_s.\end{array}\right\} \tag{16}$$

However, if Δz increases continuously and V_s comes close to the energy of $E(p)-E(s)$, this proportionality will cease to hold and a kind of saturation effect shows up. This has been found to be true experimentally. Let us consider the following finding:

(i) Fujii and Sakudo's (1976) measurement of the SHG coefficients of $SrTiO_3$ and $KTaO_3$ crystals induced by an external electrostatic field. It is well known that at room temperature both these crystals and their (MO_6) octahedra possess inversion symmetry. Hence neither of them will exhibit any SHG effect. However, when an external electric field is applied along a certain symmetry axis, say the z direction in the crystal, there will appear a displacement Δz of the central metal ion relative to its oxygen ligands and at the same time an induced polarization P_s. According to our anionic group theory, the crystal will now exhibit an overall SHG coefficient reflecting the existence of a new C_{4v} symmetry. Fujii and Sakudo (1976) showed clearly that the electric field-induced SHG coefficients in these $SrTiO_3$ and $KTaO_3$ crystals are indeed directly proportional to P_s. Their experimental results are shown in figure 2.

(ii) In the light of the anionic group theory, the electric field-induced SHG coefficients of the $SrTiO_3$ crystal must essentially be similar to those of $BaTiO_3$ with C_{4v} symmetry, except that in $BaTiO_3$ $z=0.15$ Å whereas in $SrTiO_3$ Δz is about 0.01 Å. Hence it will be appropriate to apply all the equations and parameters used for $BaTiO_3$ to the calculation of the SHG coefficients for $SrTiO_3$. It is worth noting that for the $BaTiO_3$ crystal $\Delta z \gg 0.06$ Å, and hence there will no longer be any proportionality between the SHG coefficients and P_s. Therefore, we have to solve the secular equation
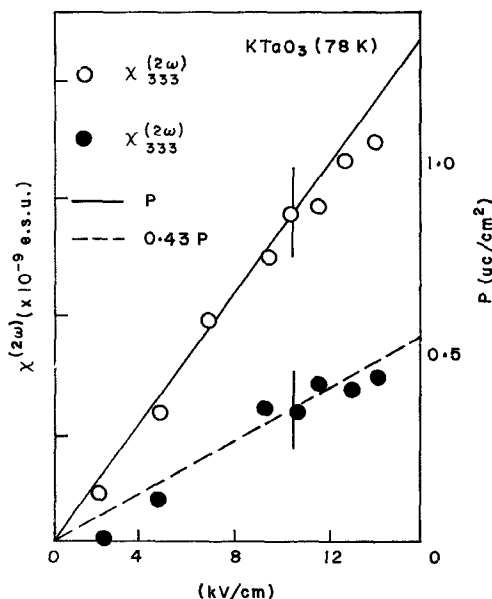

Figure 2.   The electric field-induced SHG coefficients of the $KTaO_3$ crystal.

Table 2. SHG coefficients of $BaTiO_3$ crystal with T_i coordination octahedra in C_{4v} symmetry (units: 10^{-9} e.s.u.; $\lambda = 1 \cdot 064 \, \mu m$).

	$\chi^{(2\omega)}_{333}$	$\chi^{(2\omega)}_{311}$
Experimental	$-(18 \cdot 6 \pm 2 \cdot 789)$	$-(42 \cdot 49 \pm 4 \cdot 71)$
Calculated	$-24 \cdot 467$	$-42 \cdot 608$

instead of using the first-order perturbation theory to determine the mixing of the outermost ns and np orbitals of the central metal ion induced by the odd-ordered crystal field V_s. The calculated and experimental values are shown in table 2. The agreement is fairly satisfactory.

Our calculation also reveals that although it is the same (TiO_6) basic structural unit in $SrTiO_3$ and $BaTiO_3$ crystals that contribute to the SHG effect, the ratio $\chi^{(2\omega)}_{333}/\chi^{(2\omega)}_{311}$ is different, being 0·75 in the former but 0·40 in the latter. Levine (1976) attributed this difference to certain differences in the nature of the Ti–O bonds in these two crystals. This does not seem to be a reasonable explanation. However, it is understandable from our theory, because as under C_{4v} symmetry Δz is larger than the critical value 0·06 Å, $BaTiO_3$ will give rise to some saturation effect.

(c) With iodates, the SHG coefficients have been determined for the four crystals α-$LiIO_3$, α-HIO_3, $K_2H(IO_3)_2Cl$ and $Ca(IO_3)_2.6H_2O$. X-ray structural analysis reveals that these four crystals all consist of the IO_3 group as the basic structural unit (although they are oriented differently). Again, the overall SHG coefficients arise from geometrical superposition of the microscopic SHG coefficients of the $(IO_3)^-$ groups, and the contribution from the cations is almost negligible. Hence it is simple to calculate the overall SHG coefficients of these iodate crystals with acentric symmetry. The results of our calculation are shown in table 3.

It is beyond doubt that our calculated values are in better agreement with experiment than are values calculated by the I–O bond parameter method. Take $K_2H(IO_3)_3Cl$ crystal for instance: the calculated value of $\chi^{(2\omega)}_{322}$ by the bond parameter method is eight times larger than the experimental value, whereas $\chi^{(2\omega)}_{311}$ is three times smaller. This implies at once that the assumption of the $(IO_3)^-$ group as the localized basic structural unit in the calculation of microscopic SHG coefficients is much more feasible than the simple I–O bond.

(d) In a similar manner, the SHG coefficients of several crystals of the KDP structure type, such as KDP, D–KDP and CsH_2PO_4, can also be calculated by equation (4), so long as the microscopic SHG coefficients of the $(PO_4)^{3-}$ group can be found. From the experimental SHG coefficients d_{36} of the KDP crystal, it is straightforward to calculate the microscopic SHG coefficient $\chi^{(2\omega)}_{312}$ of the $(PO_4)^{3-}$ group and from these all the macroscopic SHG coefficients of these phosphate crystals. The average deviation from the experimental values is only 17%.

Jeggo (1969) has shown that the following equation may be used for the calculation of the electro-optic coefficient of the KDP-type crystals:

$$\chi^{(\omega)}_{ijk} = \chi^{(0)}_{ii} \chi^{(\omega)}_{jj} \chi^{(\omega)}_{kk} N K_n \alpha^{(\omega)}_{ijk}, \tag{17}$$

where $\chi^{(0)}_{ii}$, $\chi^{(\omega)}_{jj}$ and $\chi^{(\omega)}_{kk}$ denote the linear polarizability, N is the number of $(PO_4)^{3-}$ groups per unit volume and K_n is the orientation factor of the $(PO_4)^{3-}$ groups.

Table 3. SHG coefficients of some iodate crystals (units: 10^{-9} e.s.u.; $\lambda = 1 \cdot 064 \, \mu m$).

Crystal		$\chi_{333}^{(2\omega)}$	$\chi_{311}^{(2\omega)}$	$\chi_{322}^{(2\omega)}$	$\chi_{123}^{(2\omega)}$
α-LiIO$_3$	Exptl.	$-(12 \cdot 4 \pm 2 \cdot 5)$	$-(11 \cdot 9 \pm 2 \cdot 38)$	$-(11 \cdot 9 \pm 2 \cdot 38)$	
		$-(14 \cdot 01 \pm 3 \cdot 34)$	$-(13 \cdot 37 \pm 0 \cdot 70)$	$-(13 \cdot 37 \pm 0 \cdot 70)$	
	Calcd.	$-12 \cdot 4$	$-11 \cdot 96$	$-11 \cdot 9$	
α-HIO$_3$	Exptl.				$-(11 \cdot 53 \pm 2 \cdot 94)$
	Calcd.				$9 \cdot 987$
K$_2$H(IO$_3$)$_2$.Cl	Exptl.	$-(12 \cdot 43 \pm 0 \cdot 565)$	$-(2 \cdot 49 \pm 0 \cdot 542)$	$-(0 \cdot 136 \pm 0 \cdot 113)$	
	Calcd.	$-10 \cdot 497$	$-3 \cdot 5944$	$-0 \cdot 105$	
Ca(IO$_3$)$_2$.6H$_2$O	Exptl.	$-(5 \cdot 65 \pm 1 \cdot 47)$	$+(1 \cdot 75 \pm 0 \cdot 44)$	$-(0 \cdot 226 \pm 0 \cdot 057)$	
	Calcd.	$-6 \cdot 3097$	$1 \cdot 243$	$-0 \cdot 120$	

Table 4. SHG coefficients of NaNO$_2$ crystal (units: 10^{-9} e.s.u.; $\lambda = 1 \cdot 064 \, \mu m$).

	Calculated		Experimental
	Total	Contribution from π-orbitals	
$\chi_{222}^{(2\omega)}$	$-0 \cdot 3094$	$-0 \cdot 1700$	$\mp(0 \cdot 276 \pm 0 \cdot 024)$
$\chi_{211}^{(2\omega)}$	$0 \cdot 1981$	$0 \cdot 0000$	$\pm(0 \cdot 216 \pm 0 \cdot 024)$
$\chi_{233}^{(2\omega)}$	$-9 \cdot 486$	$-9 \cdot 1407$	$\mp(5 \cdot 52 \pm 0 \cdot 07)$

Jeggo (1969) pointed out that for the phosphate crystals, the value of $\chi_{ijk}^{(\omega)}$ may differ by a factor as large as 26, although the values of $\alpha_{ijk}^{(\omega)}$ deviate from one another by a factor of no more than two. This provides further strong support for our anionic group theory, which applies equally well to the phosphate crystals.

(e) The calculation of the SHG coefficients for the inorganic nitrite crystals such as NaNO$_2$ is another excellent example to test the feasibility of our anionic group theory. The SHG coefficients of the NaNO$_2$ crystal have been measured by Inoue (1970). Our interest in the SHG behaviour of this crystal is focused on the following features: (i) the electronic structure of the 'planar' anionic group (NO$_2$)$^-$ in the crystal is characterized by two simple σ-type N–O bonds sharing one common N atom plus one conjugated π-orbital system over the planar three-atom ONO group; (ii) this crystal exhibits large anisotropy in its SHG coefficients which cannot be accounted for by any bond charge model. We have attempted to make a careful calculation of the overall SHG coefficients on the basis of our theory by means of equations (4) and (12) (Chen *et al.* 1980, 1981) and the results are shown in table 4. It is obvious that the calculation has elucidated the nature of this interesting feature of large anisotropy in the SHG coefficients, which arises mainly from the conjugated π-orbital system of the (NO$_2$)$^-$ group. It is this π-conjugated orbital system that makes a large contribution to the coefficient $\chi_{223}^{(2\omega)}$ but none to the other SHG coefficients $\chi_{222}^{(2\omega)}$ and $\chi_{211}^{(2\omega)}$ because of its symmetry restriction. Our calculation has also demonstrated that, in general, the contribution to the SHG coefficient $\chi_{ijk}^{(2\omega)}$ from the conjugated π-orbital will be larger than that from the σ-type orbitals by more than one order of magnitude under the same symmetry conditions. We are led to the conclusion that a planar group with a conjugated π-orbital system over it (or at least an essential part of the group) is favourable to the appearance of a large SHG effect.

However, it must be pointed out that our calculation has also shown the limitation of our model on careful comparison of the calculated and experimental values of the

SHG coefficients. The deviation is small for $\chi_{222}^{(2\omega)}$ and $\chi_{211}^{(2\omega)}$, whereas the calculated value of $\chi_{233}^{(2\omega)}$ is twice as large as the experimental value. This apparent discrepancy can be resolved by the following argument.

Energy band theory leads to a whole series of diffuse electronic orbitals, diffuse over the entire lattice continuum, whereas the anionic group theory gives localized electronic orbitals of the anionic groups, tending to confine themselves very much to regions in the close vicinity of these groups. The true situation must lie somewhere in between. Therefore, either we choose a better approximation method other than the CNDO-type approximation for the determination of these localized molecular orbitals so as to make them less confined, or we take into consideration interactions between the neighbouring anionic groups and also anionic group–cation interactions. We shall discuss this problem later.

4. The basic structural units in borate crystals and their NLO susceptibilities

We now proceed to apply our anionic group theory to a systematic investigation of the NLO effect in borate crystals, in which the large difference in the electronegativities of the boron and the oxygen atom on the B–O bond will favour transmission of UV radiation of shorter wavelengths and help us in the search for and development of new UV NLO materials for use in the intermediate and far UV spectral regions.

First, the bulk second-order susceptibility of a non-centrosymmetric crystal is additive, it is practically the 'geometric sum' of the microscopic second-order susceptibilities of the constituent basic structural units, which are anionic atom clusters like anionic groups or monoatomic cations (which usually make negligible contributions to the overall SHG effect). Therefore, if the NLO crystals are to exhibit large optical non-linearities, their basic structural units must be capable of exhibiting large microscopic second-order susceptibilities. On the basis of the series of theoretical calculations made for typical NLO crystals of various structure types, we have been able to propose the following structural criteria for prospective good-quality NLO basic structural units and crystals in general, applicable also to our discussion of new NLO crystals of the borate series.

(i) *Large deformation of* (MO_6) *coordination octahedra or other* (MX_n) *anionic groups.* The larger the deformation, the larger the microscopic second-order susceptibility will be. An outstanding example which may be cited to support this idea is the recently developed KTP ($KTiOPO_4$) NLO crystal (Zumsteg, Bierlein and Gier 1976), which has been found to exhibit the largest non-linear susceptibility among the NLO crystals with basic anionic structural unit of the TiO_6 type. In this crystal, the TiO_6 octahedron is made to undergo extremely large deformations by linking each of the six oxygen ligands with PO_4 tetrahedra or TiO_6 octahedra (Ishida and Yajiman 1987) so as further to deform the TiO_6 octahedron such that the difference between the longest and shortest Ti–O bonds is increased to $0·395$ Å (the largest ever found in the deformed MO_6 octahedra), thus enhancing the SHG effect of this new perovskite-type NLO crystal and making it the best known SHG crystal (Chen and Chen 1979).

(ii) *The NLO effect of a lone electron pair.* Our calculations made on the $(IO_3)^-$ and $(SbF_5)^{2-}$ groups, each of which contains a lone electron pair, have demonstrated the existence of large microscopic second-order susceptibilities, augmented by one order of magnitude compared with groups without any lone electron pair such as $(PO_4)^{3-}$ (cf. figure 3) (Chen *et al.* 1979).
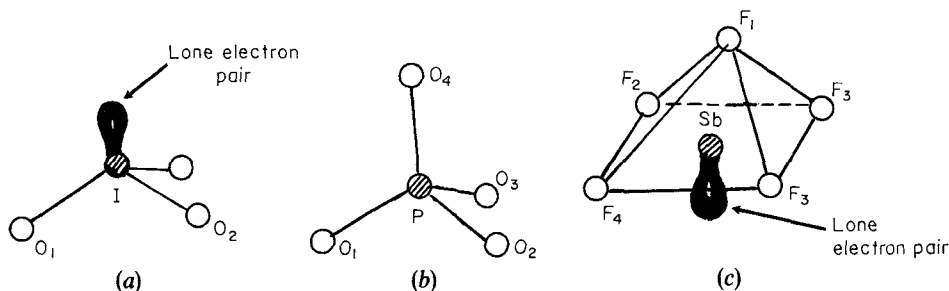
Figure 3. The molecular configurations of (*a*) $(IO_3)^-$, (*b*) $(PO_4)^{3-}$ and (*c*) $(SbF_5)^{2-}$ anionic groups.

(iii) *The NLO effect of a planar structure carrying a conjugated π-orbital system.* As pointed out by Chemla's group (Chemla *et al.* 1975, Ovdar and Chemla 1975, Ovdar and Leperson 1975), and other research workers in this field (Morrell and Albrecht 1979, Lalama and Garito 1979), aromatic molecules with large delocalized charge-transfer electronic systems may exhibit microscopic SHG effects two or even three orders of magnitude larger than σ-type molecules of the same size. Our calculations (Chen *et al.* 1980, 1981) have also shown that under non-centrosymmetric conditions, an ionic group containing a conjugated π-orbital system makes contributions to the SHG effect larger than simple σ-bond orbitals by an order of magnitude for inorganic groups. Thus large SHG effects can also be produced in inorganic crystals by planar ionic groups containing a conjugated π-orbital system possessing a non-centrosymmetric electron cloud distribution.

Secondly, in addition to the requirement of large microscopic SHG effects in the basic structural units, these groups must be spatially oriented in the crystal in such a manner that these microscopic SHG effects will reinforce each other. Moreover, it is important to have as many contributing structural units as possible per unit volume of the crystal. In other words, the crystal space should be packed as closely as possible by these groups.

Let us discuss the situation of the NLO effects in crystals of the borate series. It is well known that there are numerous structure types in borate series, including the trigonal $(BO_3)^{3-}$, the tetrahedral $(BO_4)^{5-}$ and the planar six-membered-ring $(B_3O_6)^{3-}$ anionic groups. There are, therefore, good prospects of finding suitable anionic borate structural units capable of exhibiting large (or even unusually large) second-order and other higher order NLO susceptibilities and to provide new candidates for further tests of the feasibility of our theory. The extension of our investigation into the NLO effects of borate crystals has great practical significance in two respects. On the one hand, most borate crystals are transparent far into the intermediate UV region and occasionally even further, which is one of the most interesting spectral regions at which laser material scientists are looking for new NLO applications. The damage threshold of most borate crystals is very high on account of the existence of wide band gaps and difficulty of ion and electron transport in these compact lattices, even under very intense irradiation of laser beams. Again, most borate crystals can be grown from high-temperature melts by top seeding methods, resulting generally in good yields of high optical quality crystals for making NLO devices.
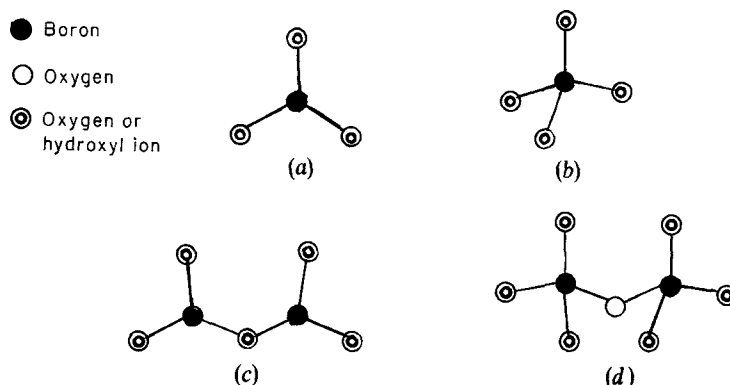
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● Boron
○ Oxygen
◎ Oxygen or hydroxyl ion

Figure 4.   The molecular configurations of (a) $(BO_3)^{3-}$, (b) $(BO_4)^{5-}$, (c) $(B_2O_5)^{4-}$ and (d) $(B_2O_7)^{8-}$ anionic groups.

Table 5.   Microscopic second-order susceptibilities of $(BO_3)^{3-}$, $(B_2O_5)^{4-}$, $(BO_4)^{5-}$ and $(B_2O_7)^{9-}$ anionic groups (units: 10^{-31} e.s.u.; $\lambda = 1.064\,\mu m$; CNDO/2 approximation used in calculation).

$(BO_3)^{3-}$	$(B_2O_5)^{4-}$	$[B_2O_4(OH)]^{3-}$	$(BO_4)^{5-}$	$[B(OH)_4]^-$	$(B_2O_7)^{8-}$	$[B_2O(OH)_6]^{2-}$
0·641	0·3308	0·5383	−0·1578	−0·2068	0·1240	0·2278
−0·641	−1·0238	−1·9184	0·0335	−0·1598	−0·03885	−0·0160
	0·0956	0·4398	−0·0329	−0·06251	−0·05267	−0·09836
	1·0441	−0·8571				
	0·1476	0·0251				
	−0·1391	−0·2114				

Nowadays, there are hundreds of different structure types of basic structural units (anionic groups) in known borate crystals. However, as far as our anionic group theory is concerned, only the following types of basic structure units are of practical interest.

(a)   *The trigonal anionic group* $(BO_3)^{3-}$ (Δ_1) [*figure 4(a)*]. The molecular symmetry of this anionic group is D_{3h}. Its 3-fold axis passes through the central B atom, which is trigonally coordinated by the three O atoms. The B–O bond length is 1·39 Å. The NLO crystals $RAl_3\,(BO_3)$ (Leonyuk and Flimonov 1974, Lutz 1983) (where R is a rare earth such as Y or Nd) and α-$LiCdBO_3$ (De et al. 1985) contain this basic structural unit (cf. table 5).

(b)   *The tetrahedral anionic group* $(BO_4)^{5-}$ (T_1) [*figure 4(b)*]. There are two kinds of basic structural units for this tetrahedral configuration: one is $(BO_4)^{5-}$ and the other is $[B(OH)_4]^-$ (or $[BO_2(OH_2)_2]^-$), which exists in the form of a hydrated metaborate. The ideal molecular symmetry is T_d. The average B–O bond length is 1·47 Å. The crystals $MgAlBO_4$ and $Ca[B(OH)_4]_2$ (Mellor 1980, Wells 1975) contain these anionic groups. Although no measurement of their NLO effects has been reported, it can be seen from table 5 that they cannot be large.

(c)   *A ditrigonal anionic group* $(B_2O_5)^{4-}$ (Δ_2) [*figure 4(c)*]. This anionic group may be visualized as two trigonal $(BO_3)^{3-}$ structural units joined by sharing one common O atom. A variation of this structure type is $[B_2O_3(OH)_2]^{2-}$ or $(B_2O_4OH_2)^{2-}$. The crystals $Mg_2B_2O_5$, $MgB_2O_4.2H_2O$ and $MnB_2O_4.H_2O$, contain these anionic groups. None of these crystals has been shown to exhibit any significant SHG effect (cf. table 5).
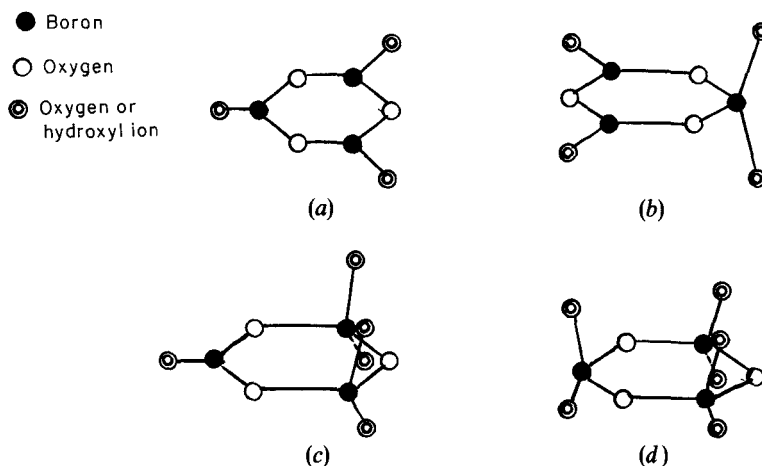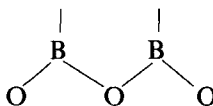
Figure 5. The molecular configurations of (a) $(B_3O_6)^{3-}$, (b) $(B_3O_7)^{5-}$, (c) $(B_3O_8)^{7-}$ and (d) $(B_3O_9)^{9-}$ groups.

(d) *A ditetrahedral anionic group* $(B_2O_7)^{8-}$ (T_2) [*figure 4(d)*]. This anionic group may be visualized as two tetrahedral $(BO_4)^{5-}$ structural units joined by sharing one common O atom. A variation of this structure type is $[B_2O(OH)_6]^{2-}$ (or $[B_2O_4(OH_2)_3]^{2-}$). The average B–O bond length is $1·47$ Å. The crystal $MgB_2O_4.3H_2O$ contains this anionic group. It has not been known to exhibit any appreciable SHG effect (cf. table 5).

(e) *The planar six-membered-ring anionic group* $(B_3O_6)^{3-}$ (Δ_3) [*figure 5(a)*]. This benzene-like anionic group consists of three coplanar (BO_3) groups joined by three common O atoms to form a planar six-membered ring. Its molecular symmetry is D_{3h}. In this ring, the average bond length is $1·38$ Å and the average bond angle is $120°$. The crystals BaB_2O_4 (or $Ba_3(B_3O_6)_2$) (Levin and McMurdie 1949, Hubner 1969, Mighell *et al.* 1966) and $M_3(B_3O_6)$ ($M = Na$, K) (Mellor 1980) contain such an anionic group. Of these crystals the β-BaB_2O_4 (BBO) crystal (low-temperature modification of BaB_2O_4) is a good SHG crystal with very large NLO susceptibility (cf. table 10).

(f) *A non-planar six-ring anionic group* $(B_3O_7)^{5-}$ $(\Delta_2 T_1)$ [*figure 5(b)*]. This anionic group may be visualized as derived from the planar six-membered-ring benzene-like $(B_3O_6)^{3-}$ structure by replacing one of the three trigonal (BO_3) groups by one tetrahedral (BO_4) group so as to deform the ring planarity to a rather slight extent. A variation of this structure type is $[B_3O_3(OH)_4]^{-}$ (or $[B_3O_5(OH_2)_2]$). The crystals $Ca[B_3O_3(OH)_4]_2.nH_2O$ ($n=0$, 2, 8) and $Sr[B_3O_3(OH)_4].2H_2O$ contain this anionic group. No such crystal with discrete $(B_3O_7)^{5-}$ anionic group has been shown to exhibit any SHG effect (cf. table 6).

(g) *Another non-planar six-membered-ring anionic group* $(B_3O_8)^{7-}$ (Δ_1, T_2) [*figure 5(c)*]. When two of the trigonal $(BO_3)^{3-}$ groups are replaced by two tetrahedral $(BO_4)^{5-}$ groups so that the ring planarity is deformed to a larger extent, the less planar anionic group (B_3O_8) is obtained. There is one possible variation of this structure type $[B_3O_3(OH)_5]^{2-}$. The crystal $Ca[B_3O_3(OH)_5].H_2O$ contains an anionic group of this structure group. No SHG effect has been reported for such crystals (cf. table 6).

Table 6. Microscopic second-order susceptibilities of $(B_3O_6)^{3-}$, $(B_3O_7)^{5-}$, $(B_3O_8)^{7-}$ and $(B_3O_9)^{9-}$ groups (units: 10^{-31} e.s.u.; $\lambda = 1 \cdot 064\ \mu m$).

$(B_3O_6)^{3-}$		$(B_3O_7)^{5-}$	$[B_3O_3(OH)_4]^-$	$(B_3O_8)^{7-}$	$[B_3O_3(OH)_5]^{2-}$	$(B_3O_9)^{9-}$	$[B_3O_3(OH)_6]^{3-}$
CNDO/S	CNDO/2	CNDO/2	CNDO/2	CNDO/2	CNDO/2	CNDO/2	CNDO/2
2·9323	1·5921	−2·9308	−2·8204	0·2906	0·2877	−0·2785	−0·3677
−2·9323	−1·5921	0·8212	0·6933	1·2628	0·2955	0·2785	0·3671
0·0000	0·0000	−0·6288	−0·4556	0·4671	1·1621		
					0·3785		
					0·2154		

(h) *Another non-planar* (*chair form*) *six-membered-ring anionic group* $(B_3O_9)^{9-}$ (T_3) [*figure 6* (a)]. When all the three trigonal $(BO_3)^{3-}$ groups are replaced by three tetrahedral (BO_4) groups, a chair-form T_3 anionic group $(B_3O_9)^{9-}$ is obtained. A possible variation of this structure type is $[B_3O_3(OH)_6]^{3-}$ (or $[B_3O_6(OH_2)_3]^{3-}$), another hydrated metaborate. No crystals containing anionic groups of this structure type have been reported.

(i) *A Siamese-twinned double six-membered-ring anionic group* $(B_5O_{10})^{5-}$ $(\Delta_4 T_1)$ [*figure 6* (a)]. This anionic group may be visualized as formed from two nonplanar six-membered-ring quintanions $(B_3O_7)^{5-}$ joined by sharing the tetrahedrally coordinated B atom, with the two six-membered-ring 'planes' almost perpendicular to each other (for structural data see Zachariasen and Plettinger (1963)). A variation of this structure type is $[B_5O_6(OH)_4]^-$ (or $[B_5O_8(OH)_2]^{3-}$). The well known NLO crystal KB5 (KB$_5$O$_8$.4H$_2$O) (Dewey *et al.* 1975, Dewey 1976) contains such an anionic group (cf. table 7).

(j) *Another Siamese-twinned double six-membered-ring anionic group* $(B_4O_9)^{6-}$ $(\Delta_2 T_2)$ [*figure 6* (b)]. This anionic group may be visualized as formed from two planar six-membered-ring trianions $(B_3O_6)^{3-}$ joined by sharing a common

'half-ring' segment, thus leading to the formation of a butterfly-shaped $(B_4O_9)^{6-}$ hexanionic group and the destruction of coplanarity each of the
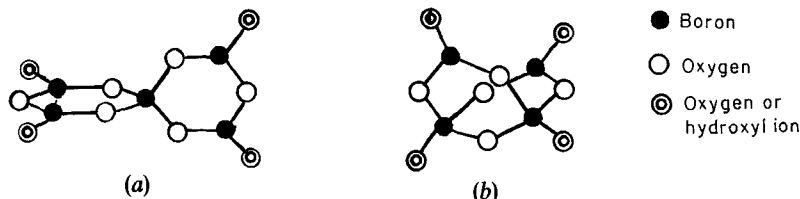

Figure 6. (a) The molecular configuration of the Siamese-twinned double six-membered-ring $[B_5O_6(OH)_4]^-$ anionic group $(\Delta_4 T_1)$. (b) The molecular configuration of another Siamese-twinned double six-membered-ring $[B_4O_5(OH)_4]^{2-}$ anionic group $(\Delta_2 T_2)$.

Table 7. Microscopic second-order susceptibilities of $(B_5O_{10})^{5-}$, $[B_5O_6(OH)_4]^-$, $(B_4O_9)^{6-}$ and $[B_4O_5(OH)_4]^{2-}$ anionic groups (units: 10^{-31} e.s.u.; $\lambda = 1.064\,\mu m$; CNDO/2 approximation used in calculation).

$(B_5O_{10})^{5-}$	$[B_5O_6(OH)_4]^-$	$(B_4O_9)^{6-}$	$[B_4O_5(OH)_4]^{2-}$
−1·335	−1·1402	0·05540	−1·3038
0·01732	0·0542	−0·0215	0·2016
−0·04583	−0·6178	−0·3682	−0·6649
−0·06141	−0·6311	−0·5633	−0·7088
		0·6918	−0·0682
		0·6918	0·1333
		0·8215	−0·9444
		−0·3176	−0·3464
		−0·2074	−0·2864
		−0·6555	−0·6160

other two 'half-ring' segments with this common B_2O_3 'half-ring' segment. A variation of this structure type is $[B_4O_5(OH)_4]^{2-}$ (or $[B_4O_7(OH_2)_2]^{2-}$). The crystals $M_2[B_4O_5(OH)_4].nH_2O$ ($M = Na$ ($n = 3, 8$) or K ($n = 2$)) contain this anionic group. The Na salt trihydrate and the K salt dihydrate may exhibit some SHG effect, although no detailed investigation has been reported (cf. table 7).

In addition to the basic structure types mentioned above, there are other structure types in crystals of this borate series. However, some of them are unstable at room temperature, and others are not worth discussing. On the other hand, there are a few borate polymers with acentric monomeric structural units capable of exhibiting appreciable SHG effects. These prospective NLO borate polymers will be discussed elsewhere.

Using the computer programme (Li and Chen 1985), it is simple to calculate systematically the microscopic second-order susceptibilities of all the structural units shown in figures 4–6 and then proceed to formulate a few structural guidelines useful in organizing the systematic search for and development of new UV NLO crystals of the borate series. Before doing so it may be worth mentioning the following points.

(a) The calculation discussed by Wu and Chen (1986) has demonstrated that the presence of hydrogen bonds in the aforementioned anionic group may have an appreciable effect on the microscopic second-order susceptibility. Two separate cases have been discussed. In one the H atomic orbitals are directly attached so as to form the σ-bond orbitals of B–O–H; in the other, the H atomic orbitals are not included at all, corresponding to the H-bond orbitals of B–O $\cdots$ H.

(b) No calculation discussed in this review includes the effect of the crystal field on the microscopic susceptibilities, because when the constituent entities are stacked up together in the course of crystal growth, we are not able to predict the space structure of the resulting crystal and therefore the magnitude of the resulting crystal field.

Tables 5, 6 and 7 list the results calculated for the second-order susceptibilities of seven anionic groups $(BO_3)^{3-}$, $(B_2O_5)^{4-}$, $[B_2O_4(OH)]^{3-}$, $(BO_4)^{5-}$, $[B(OH)_4]^-$, $[B_2O_7]^{8-}$ and $[B_2O(OH)_6]^{2-}$, those of another seven anionic groups, $(B_3O_6)^{3-}$, $(B_3O_7)^{5-}$, $[B_3O_3(OH)_4]^-$, $(B_3O_8)^{7-}$, $[B_3O_3(OH)_5]^{2-}$, $(B_3O_9)^{9-}$ and $[B_3O_3(OH)_6]^{3-}$, and those of four larger anionic groups, $(B_5O_{10})^{5-}$, $[B_5O_6(OH)_4]^-$, $(B_4O_9)^{6-}$ and $[B_4O_5(OH)_4]^{2-}$. It must be noted that, for those anionic groups with OH groups in their structural formulae, the H atomic orbitals have been included in the calculations.

Through these calculations, we have been able to summarize some structural regularities as a useful guide in the search for and development of new UV NLO crystals of the borate series.

First, the planar six-membered-ring $(B_3O_6)^{3-}$ and the trigonal $(BO_3)^{3-}$ anionic groups containing conjugated π-orbital systems are more favourable to the appearance of large second-order susceptibilities than the non-planar tetrahedral $(BO_4)^{5-}$ anionic groups with no conjugated π-orbital systems.

The results of our calculated show that the second-order susceptibilities of $(BO_3)^{3-}$ and $(B_3O_6)^{3-}$ are in general one order of magnitude larger than those of $(BO_4)^{5-}$ and $[B(OH)_4]^-$. Moreover, in the planar anionic groups, the larger the electron population of the conjugated π-orbital system, the larger the second-order susceptibilities will be.

As an example, the electron population of the conjugated π-orbital system is 6·00 for $(BO_3)^{3-}$ but 6·8592 for $(B_3O_6)^{3-}$. Hence it is obvious that the second-order susceptibility of $(B_3O_6)^{3-}$ will be larger than that of $(BO_3)^{3-}$. This has been found to be true from measurements of the SHG coefficients of β-BaB_2O_4 vs $LiCdBO_3$ and $YAl_3(BO_3)_4$ made in our Institute.

To investigate the effect of electron population in the planar or essentially planar conjugated anionic group on the second-order susceptibility, we made calculations on the other three six-membered-ring anionic groups, $B_3F_3N_3F_3$, $B_3H_3N_3H_3$, $B_3F_3N_3H_3$ and $B_3H_3N_3F_3$. The results are given in table 8, together with electron population data taken from Midwinter and Warner (1965). It is apparent that under the condition of similar molecular symmetry, the electron population in $B_3F_3N_3F_3$ is larger than that of $B_3H_3N_3H_3$, so the second-order susceptibility of $B_3F_3N_3F_3$ is also larger than that of $B_3H_3N_3H_3$. Similarly, the electron populations of all four six-membered-ring anionic groups are larger than that of the $(BO_3)^{3-}$ anionic group, so their second-order susceptibilities will be larger than that of $(BO_3)^{3-}$.

Secondly, let us look further into the relationship between the second-order susceptibilities and the coordination modes of the B atoms in the groups.

On account of the symmetry requirement of the second-order susceptibility in the D_{3h} point group, for the planar six-membered-ring $(B_3O_6)^{3-}$ group (and also for the $(BO_3)^{3-}$ group with the same point group symmetry) there will be only two non-vanishing second-order susceptibilities, $\chi_{111}^{(2\omega)} = -\chi_{122}^{(2\omega)}$, when the normal to the plane is taken to be the z direction. In general, for a planar structure with a symmetry plane, all the z components (if the normal to this is the z axis) of the 27 components of the second-order susceptibility tensor must be zero (Pressley 1971). Since the planar groups are usually oriented parallel to the (001) lattice net or at most slightly tilted to it, the z components of the macroscopic SHG coefficients of the crystal will usually be very small or even vanish altogether. Therefore, the effective SHG coefficient (d_{eff}) (Midwinter and Warner 1965) will be reduced to zero on account of the $\cos \theta_{pm}$ factor when the phase-matching angle θ_{pm} changes from a small angle to 90°. This will be unfavourable to harmonic generation in the UV range, because for this range a large phase-matching angle θ_{pm} is generally required in practice. It is intuitively obvious that the simplest way to increase the z coordinate of some atoms in the anionic group is to change one or more B atoms from trigonal to tetrahedral coordination. For β-BaB_2O_4 there are only two non-vanishing components $\chi_{111}^{(2\omega)}$ and $\chi_{122}^{(2\omega)}$ of the microscopic

Table 8. Microscopic second-order susceptibilities of planar six-membered-ring molecules $B_3N_3H_6$, $B_3F_3N_3F_3$, $B_3H_3N_3F_3$ and $B_3F_3N_3H_3$ (units: 10^{-31} e.s.u.).

Molecule	Electron population†	Second-order susceptibility (CNDO/S approximation used in calculation)
$B_3H_3N_3H_3$	6·0000	2·3410
		−2·3410
$B_3F_3N_3F_3$	6·6858	2·7917
		−2·7917
$B_3H_3N_3F_3$	6·0768	2·4829
		−2·4829
$B_3F_3N_3H_3$	6·5928	3·163
		−3·163

† Haworth and Scherr (1975).

second-order susceptibility tensor of the planar six-membered-ring $(B_3O_6)^{3-}$ anionic group. Hence the z components of the macroscopic SHG coefficients can be very small, in fact only one twentieth of the microscopic $\chi_{111}^{(2\omega)}$; however, when one of the B atoms is changed to tetrahedral coordination, thus forming a $(B_3O_7)^{5-}$ or $[B_3O_3 (OH)_4]^-$ group, the macroscopic coefficient of this slightly non-planar anionic group will become larger numerically, whereas the $\chi_{111}^{(2\omega)}$ and $\chi_{122}^{(2\omega)}$ coefficients will remain almost unchanged in magnitude (Chen *et al.* 1985a, b) (see figure 5(b) and table 6). This is obvious when we take into consideration the fact that there are still seven p_π orbitals perpendicular to the 'plane' of the $(B_3O_7)^{5-}$ six-membered-ring, and these p_π orbitals will remain conjugated to a considerable extent so as to make sufficiently large contributions to the $\chi_{111}^{(2\omega)}$ and $\chi_{122}^{(2\omega)}$ coefficients without too much reduction in their magnitude from the corresponding values for the $(B_3O_6)^{3-}$ anionic group. By the same reasoning, it might be inferred that if a second B atom were to be changed into tetrahedral coordination, the situation would be further improved. This is, however, not at all sure, as the conjugated π-orbital system would be weakened to such an extent that the reduction in the magnitudes of the $\chi_{111}^{(2\omega)}$ and $\chi_{122}^{(2\omega)}$ coefficients could no longer be compensated for by the gain in the z components on account of the change in coordination. This is borne out by the results of the calculations shown in table 6.

Another point which may be raised in this connection is the effect of configurational symmetry of similar anionic groups in the borate series on the microscopic second-order susceptibility.

Through the series of second-order susceptibility calculations (Chen *et al.* 1979, Chen 1979, 1985, Chen and Liu 1986) for the borate anionic groups, we were led to the idea that the lower the symmetry of the anionic group, the larger the microscopic second-order susceptibility will be. From table 5, it can be seen that the microscopic second-order susceptibility of the $(B_2O_5)^{4-}$ anionic group is almost one order of magnitude larger than that of the $(B_2O_7)^{8-}$ anionic group. This arises from the fact that the symmetry of the $(B_2O_5)^{4-}$ anionic group formed from trigonal $(BO_3)^{3-}$ groups sharing one oxygen atom is lower than that of the $(B_2O_7)^{8-}$ anionic group formed from two tetrahedral $(BO_4)^{5-}$ groups also sharing one oxygen atom, because the $(BO_3)^{3-}$ group is planar and, therefore, lower in symmetry relative to the $(BO_4)^{5-}$ group, which is close to a sphere as far as symmetry is concerned. This explans why the second-order susceptibility of the $(BO_3)^{3-}$ is one order of magnitude larger than that of the $(BO_4)^{5-}$ group. Such an idea is further supported by the calculated microscopic second-order susceptibilities for the series $(BO_3)^{3-}$, $[BO_2(OH)]^{2-}$, $[BO(OH)_2]^-$, $B(OH)_3$, as shown in table 9. It is obvious from the series of molecular configurations shown in figure 7 that the symmetry increases from $[BO_2(OH)]^{2-}$, followed by $[BO(OH)_2]^-$, and then $(BO_3)^{3-}$, up to $B(OH)_3$. The magnitudes of the microscopic second-order susceptibilities of these groups shown in table 9 follow just this sequence. It can therefore be inferred that if we were able to obtain crystals or polymer films consisting

Table 9. Microscopic second-order susceptibilities of $(BO_3)^{3-}$, $[BO_2(OH)]^{2-}$, $[BO(OH)_2]^-$ and $B(OH)_3$ anionic groups or molecules (units: 10^{-31} e.s.u.; $\lambda = 1.064\,\mu m$; CNDO/S approximation used in calculation).

	$(BO_3)^{3-}$	$[BO_2(OH)]^{2-}$	$[BO(OH)_2]^-$	$[B(OH)_3]$
$\chi_{111}^{(2\omega)}$	0·641	−0·8014	0·0142	0·5854
$\chi_{122}^{(2\omega)}$	−0·641	−1·2109	−0·8421	−0·5854
$\chi_{222}^{(2\omega)}$	0·000	0·2744	−1·1918	−0·1306

O Oxygen

● Boron

o Hydrogen

(BO₃)³⁻
(a)

[BO₂(OH)]²⁻
(b)

[BO(OH)₂]⁻
(c)

B(OH)₃
(d)
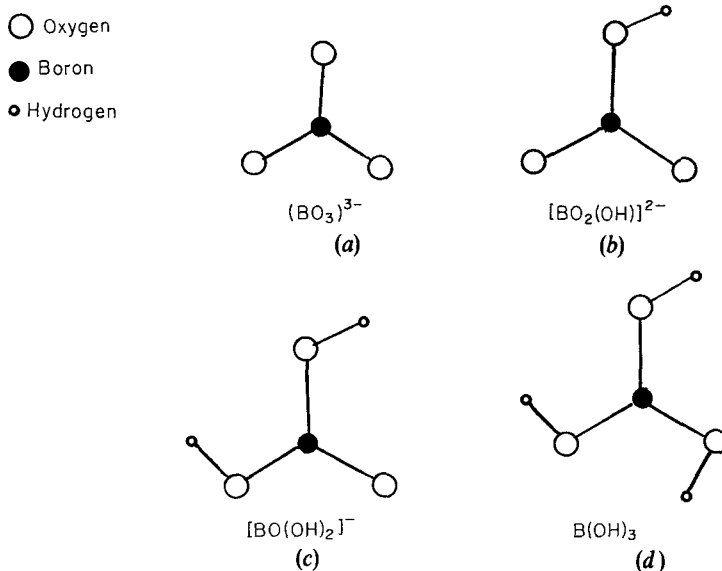
Figure 7. The molecular configurations of $(BO_3)^{3-}$, $[BO_2(OH)]^{2-}$ and $[BO(OH)_2]^-$ anionic groups and the $B(OH)_3$ molecule.

of $(BO_2)_{n \to \infty}$ chains as their basic structural unit, so stacked that their spatial arrangement is favourable to reinforcing rather than annihilating superposition of their SHG coefficients, these crystals or polymer films would be expected to exhibit very large SHG effects, much larger than those of the borate crystals $YAl_3(BO_3)_4$ and $LiCdBO_3$, the basic structural unit of which is only the discrete planar trigonal $(BO_3)^{3-}$ group.

5. Measurements and calculations of the SHG coefficients for two of the recently developed UV NLO crystals of the borate series

We have given a systematic discussion on the second-order susceptibilities of several basic structural units of the borate series, thus leading us to the formulation of some structural guidelines useful in the search for and development of certain borate crystals as new UV NLO materials. Through a series of time-consuming but rewarding efforts in our Institute during the past few years, we have succeeded in the development of two high-quality UV NLO borate crystals, BBO (barium metaborate, low-temperature modification, β-BaB_2O_4) and LBO (lithium triborate, LiB_3O_5) and thus confirmed the validity of our theoretical considerations.

5.1. *BBO [the low-temperature modification of BaB_2O_4 or $Ba_3(B_3O_6)_2$]*

On the basis of our theoretical analysis, we were able to point out as early as in 1979 (Chen *et al.* 1980, 1985 c) that the planar $(B_3O_6)^{3-}$ anionic group possessing a six-membered-ring conjugated π-orbital system can be an ideal structural unit capable of exhibiting large NLO effects, provided that the borate crystal is not centrosymmetric. This possibility is particularly attractive in view of the fact that the B–O bond is ideal for the transmission of UV light because of the large difference in the electronegativities of the B and O atoms. After a series of strenuous efforts lasting for several years, including the synthesis of the metaborate with $(B_3O_6)^{3-}$ as the basic structural unit, some powder SHG tests, phase equilibrium studies, crystal growth (Jiang *et al.* 1986),

crystal structure determinations (Lu *et al.* 1982) and a series of measurements of various physical properties, Chen's group was able to establish BBO as a high-quality NLO material capable of exhibiting efficient harmonic generation up to the fifth and also very high damage threshold. We are now able to grow large transparent BBO crystals of good optical quality up to 120×80 mm by the high-temperature melt top-seeding method. This metaborate crystal exists in two phases, α and β (Levin and McMurdie 1949) with a transition temperature of $925 \pm 5°C$ (Hubner 1969). The α-phase is centrosymmetric in its crystal structure and this exhibits no NLO effect. On the other hand, the β-phase crystallizes in a non-centrosymmetric space group and is found to be ideal for UV NLO applications.

As reported by Lu *et al.* (1982), its space group was once found to be R3, yet very close to R3c, with cell dimensions $a = 12.532$ Å and $c = 12.717$ Å. Liebertz and Stahr (1983) reported its space group as R3c with almost the same unit cell dimensions. Frölich (1984) re-examined the BBO structure and confirmed it to be a trigonal structure belonging to R3c. The main difference between R3c and R3 of the BBO crystal structure, insofar as its NLO effect is concerned, lies in whether the SHG coefficient d_{22} (if the *a* axis is taken to be the *x* axis) should vanish or not. According to our measurements made with the Maker fringe method, the d_{22} coefficient is very small, certainly smaller than $(1/20)d_{11}$, and we are therefore more inclined to consider R3c to be the correct space group.

There are three non-vanishing SHG coefficients, d_{33}, d_{31} and d_{11}, for R3c. By means of the Maker fringe technique (Jerphagnon and Kurtz 1970) and the phase-matching method (Bjorkholm 1968), Chen *et al.* (1985c) determined these SHG coefficients with the results shown in table 10. The very large anisotropy of the SHG effect is just as expected, with $d_{33}/d_{11} < 0.001$. Li and Chen (1985) made detailed calculations of the SHG coefficients for this BBO crystal and their results are also given in table 10. It is obvious that the agreement between the experimental and the calculated values is satisfactory. Moreover, it confirms our prediction that the planar $(B_3O_6)^{3-}$ with the six-membered-ring conjugated π-orbital system is mainly responsible for the large d_{11} coefficient, whereas the very small d_{31} and d_{33} coefficients arise mainly from the small deformation of the π-orbital system due to the presence of an odd-ordered crystal field along the threefold axis, following the spontaneous polarization produced by the arrangement of the Ba cations around the $(B_3O_6)^{3-}$ anionic groups. Figure 8 shows the relationship between the second-order susceptibilities of the $(B_3O_6)^{3-}$ anionic group and the odd-ordered crystal field acting on the group (Li and Chen 1985).

Table 10. SHG coefficients of β-BaB$_2$O$_4$ crystal (units: 10^{-9} e.s.u. for the SHG coefficient; $\lambda = 1.079\,\mu$m for the fundamental wavelength).

Anionic group	d_{ij}†	Calculated	Experimental	Relative value of $I^{(2\omega)}$ for the powder SHG effect test ‡
$(B_3O_6)^{3-}$	d_{11}	3·78	$-(4.60 \pm 0.30)$	$d_{\text{eff}} \approx 5\text{–}6\,d_{\text{eff}}$ (KDP)
	d_{31}	-0.038	$> -(0.07 \pm 0.03)d_{11}$	
	d_{32}	-0.038	$= d_{31}$	
	d_{33}	-0.0038	≈ 0	

† $d_{11} = \chi_{111}^{(2\omega)}$, $d_{31} = \chi_{311}^{(2\omega)}$, etc.; data quoted from *Standards on Piezoelectric Crystals, Proc. IRE*, 1949, **37**, 1378.
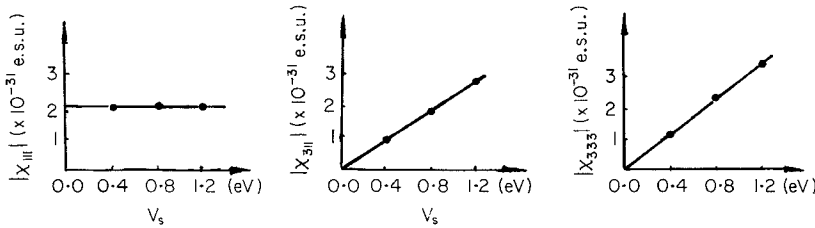‡ Standard sample: KDP powder.

Figure 8. Relationship between the second-order susceptibilities of the $(B_3O_6)^{3-}$ anionic group and the odd-ordered crystal field acting on the group.

Table 11. SHG coefficients of $LiCdBO_3$ and $YAl_3(BO_3)_4$ crystals ($\lambda = 1.079\,\mu$m for the fundamental wavelength).

Anionic group	Crystal	Calculated SHG coefficient† (units: 10^{-9} e.s.u.)		Relative value of $I^{(2\omega)}$ from powder SHG effect test‡
$(BO_3)^{3-}$	LiCd(BO)	d_{11}	2·7039 to 1·74	
		$d_{eff} \approx 3.0 d_{eff}(KDP)$§		
		d_{16}	4·2144 to 2·715	
		d_{12}	−2·7039 to −1·742	
		d_{22}	−4·2144 to −2·715	
	$YAl_3(BO_3)_4$	d_{11}	3·40 to 2·20	$d_{eff} \approx 2.5 d_{eff}(KDP)$
		d_{12}	−3·41 to −2·20	

† The range of the calculated SHG coefficients is determined by the range of the strengths of the odd-ordered crystalline field in the crystal.
‡ Standard sample: KDP powder.
§ $d_{eff}(KDP) \approx 0.66 d_{36}(KDP) = 0.72 \times 10^{-9}$ e.s.u. ($d_{36}(KDP)$ is taken to be 1.1×10^{-9} e.s.u.).

For readers interested in applications of the BBO crystal, details can be found in several papers (Kato 1986, Miyazaki *et al.* 1986, Chen *et al.* 1987, Ishida and Yajima 1987, Vanherzeele and Chen 1988, Fan *et al.* 1989).

5.2. *LiCdBO and YAl₃ (BO₃)₄ crystals*

We have shown in the previous section that the $(BO_3)^{3-}$ anionic group is also favourable for the production of large second-order susceptibilities, although the NLO effect will be expected to be smaller than that of $(B_3O_6)^{3-}$. Powdered samples and tiny crystals of $LiCdBO_3$ and $YAl_3(BO_3)_4$, with the $(BO_3)^{3-}$ anionic group as their structural unit, have been synthesized and grown in our Institute. Powder SHG tests have been carried out on these samples. In the light of our anionic group model, with the help of the crystal structures determined by Lutz (1983) and Leonyuk and Flimonov (1974), it is simple to calculate their macroscopic SHG coefficients. Although powder tests can only give rough relative values for the SHG coefficients, the data in table 11 show satisfactory agreement between theoretical and experimental results, leading to the following sequence of SHG coefficients (d_{eff}) for β-BaB_2O_4, $LiCdBO_3$, and $YAl_3(BO_3)_4$: β-$BaB_2O_4 > LiCdBO_3 \approx YAl_3(BO_3)_4$.

5.3. *LBO (LiB₃O₅)*

In section 4, it was shown that when one of the three trigonally coordinated B atoms in the planar $(B_3O_6)^{3-}$ anionic group is changed to tetrahedral coordination, thus forming a B_3O_7 group, the z components of the SHG coefficients, such as $\chi_{133}^{(2\omega)}$ (which

Table 12. SHG coefficients of LiB_3O_5 crystal (units: 10^{-9} e.s.u., $\lambda = 1.079\,\mu m$)†.

	d_{33}	d_{31}	d_{32}	d_{15}	d_{24}
Calculated	0·61	-2.24	2·69	$=d_{31}$	$=d_{32}$
Experimental	$\pm 0.15(1\pm 0.1)$	$\mp 2.75(1\pm 0.12)$	$\pm 2.97(1\pm 0.01)$	$\approx d_{31}$	$\approx d_{32}$

† $d_{36}^{(KDP)} = 1.1 \times 10^{-9}$ e.s.u.

plays an important role in the NLO effect of the UV spectral range for 90° non-critical phase matching) will become larger, whereas $\chi_{111}^{(2\omega)}$ or $\chi_{122}^{(2\omega)}$ more or less retain their magnitudes as in $(B_3O_6)^{3-}$ (cf. table 6). This important result has been confirmed by our recent work on LBO, another new UV NLO crystal of the borate series developed in our Institute.

This LiB_3O_5 crystal crystallizes in the space group $Pna2_1$ (Konig and Hoppe 1978, Tham *et al.* 1980). It is built up of a continuous network of endless $(B_3O_5)_{n\to\infty}$ spiral chains (running parallel to the z axis) formed from B_3O_7 anionic groups with each of the four exo-ring O atoms shared between the B_3O_7 groups in the same chain or neighbouring chains, and Li cations located in the interstices. There are five non-vanishing SHG coefficients, d_{33}, d_{31}, d_{32}, d_{15} and d_{24}, for the point group C_{2v}. Again with the help of the Maker fringe and phase-matching methods, we have been able to measure all these SHG coefficients, with the results listed in table 12. The macroscopic SHG coefficients of the LiB_3O_5 crystal have also been calculated on the basis of the anionic group model without any adjustable parameters by using the structural data reported by Konig and Hoppe (1978). The results are shown in table 12. The agreement between the calculated and the experimental results is satisfactory. The successful development of this new UV NLO crystal LBO adds convincing support to our conclusion that the anionic group model is indeed a good working model for the search and development of new NLO materials in borate crystals and in crystals of other structure types.

As pointed out by Chen *et al.* (1989), the fact that one of the three trigonal B atoms in the $(B_3O_6)^{3-}$ anionic group has been changed to tetrahedral coordination to form the $(B_3O_7)^{5-}$ group is bound to weaken the conjugated π-orbital system to an appreciable extent and tends to shift the absorption edge to a shorter wavelength in the UV region, in fact down to 160 nm†, around 30 nm shorter than that of BBO, which is useful for applications as a UV NLO material. Moreover, we have also found that this new NLO crystal offers the following useful advantages (Chen *et al.* 1989): (i) It possesses a much higher damage threshold‡, close to 25 GW cm^{-2} for a 1·064 μm, 0·1 ns laser pulse, the highest of all the NLO crystals; (ii) it has a very large acceptance angle, for both θ and ϕ, namely 27 mrad cm for $\theta \neq 90°$ and 57 mrad cm for $\theta = 90°$; and (iii) it can be characterized as inclusion free, and is thus antideliquescent and optically highly homogeneous with good mechanical properties for cutting and polishing. All these suffice to demonstrate its great potential in applications for harmonic generation of high power density laser systems.

† The absorption edge of LiB_3O_5 crystal was determined by Dr R. H. Frence, Central Research and Development Department, E. I. Du Pont de Nemours and Co. (1986).
‡ The damage threshold of LiB_3O_5 was determined by Professor D. Y. Fan, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai, P.R. China (1987).

Table 13. SHG coefficients of KB5 crystal (units: 10^{-9} e.s.u. for SHG coefficient; $\lambda = 1.064\,\mu m$ for fundamental wavelength).

Anionic group	d	Calculated	Experimental (1)‡	Experimental (2)†
$[B_5O_6(OH)_4]^-$	d_{31}	2·61	1·09	$(-)2.53$
	d_{32}	0·07	0·08	1·04
	d_{33}	3·26		2·88

† The second set of experimental measurements was made by the Institute of Crystalline Materials, Shangdong University (personal communication).

‡ Dewey (1976)

5.4. *KB5 ($KB_5O_8.4H_2O$ or $K[B_5O_6(OH)_4].2H_2O$)*

The macroscopic SHG coefficients of KB5 crystal have been calculated on the basis of our anionic group model (Wu and Chen 1986), with the $[B_5O_6(OH)_4]^-$ anionic group as the primary active group responsible for the production of SHG effects (cf. figure 6(a)). The calculated SHG coefficients of this KB5 crystal are shown in table 13 together with the experimental data. It has been pointed out (Wu and Chen 1986) that the largest component of the microscopic second-order susceptibility of B_5O_{10} group is $\chi_{123}^{(2\omega)}$, which, unfortunately, does not contribute to the macroscopic SHG coefficients of KB5 as the point group of this crystal is C_{2v}, and thus the macroscopic SHG coefficient d_{14} $(= 2\chi_{123}^{(2\omega)})$ vanishes identically. This accounts primarily for the fact that the macroscopic SHG coefficients of KB5 amount only to one tenth that of KDP. In case there exists a crystal consisting of the same basic structural unit $[B_5O_6(OH)_4]^-$ but crystallizing in point group either C_2 or D_2, the component $\chi_{123}^{(2\omega)}$ of the microscopic second-order susceptibility will make its contribution to the overall SHG effect of the crystal and exhibit as large an overall effect as half of that of KDP. This is left for further consideration.

6. Summary

The boron atom is capable of two different modes of coordination, namely trigonal and tetrahedral. It is therefore possible for borates to exist in a wide variety of structure types, and therefore to possess great potential for applications. We have shown that theoretical calculations and considerations on the basis of our anionic group model can be very helpful in this connection. From measurements of the SHG coefficients of the crystals BBO, LBO and KB5 and also powder SHG tests made on these three together with $YAl_3(BO_3)_4$ and $LiCdBO_3$, it is seen that the sequence of the SHG effects of these NLO crystals is in line with the macroscopic SHG effects calculated or estimated from the microscopic second-order susceptibilities of the anionic groups $(B_3O_6)^{3-}$, $(B_3O_7)^{5-}$, $(BO_3)^{3-}$ and $(BO_4)^{5-}$ and $(B_5O_{10})^{5-}$, considered as their respective basic structural units or primary active groups. We are led to the conclusion that the microscopic SHG effect can be arranged in the decreasing sequence $\chi_{(B_3O_6)}^{(2\omega)} \approx \chi_{(B_3O_7)}^{(2\omega)} > \chi_{(BO_3)}^{(2\omega)} > \chi_{(B_5O_{10})}^{(2\omega)}$, which may serve as a useful structural guideline in organizing a systematic search and development of new UV NLO crystals of the borate series.

There is a possibility of adjusting to some extent the magnitude of the microscopic second-order susceptibility of borate anionic groups through suitable arrangement of the coordination modes of the B atoms and occasionally the type of stacking of these basic structural units. One good example is the $(B_3O_6)^{3-}$ anionic group. Table 6 shows that the $\chi_{111}^{(2\omega)}$ and $\chi_{122}^{(2\omega)}$ components of this anionic group rank among the largest $\chi_{ijk}^{(2\omega)}$

known so far. However, all the z components of this second-order susceptibility tensor vanish. This is why BBO possesses a very small d_{31} coefficient, and hence d_{eff} will be reduced when the wavelength of SHG is shifted towards the UV region, obviously limiting its usefulness in the 201–196 nm range. For the same reason, BBO cannot be used effectively for 90° non-critical phase-matching, because when the phase-matching angle θ_{pm} is changed towards 90°, d_{eff} will be continuously reduced to zero. To overcome this drawback, we have succeeded in making use of the unusual $(B_3O_7)^{5-}$ anionic group, and are developing LBO as a new UV NLO crystal. It is worth pointing out that LBO and BBO are more or less complementary to each other.

The $(BO_2)_{n \to \infty}$ chain is capable of exhibiting large NLO effects. Hence, if some polymer can be synthesized with $(BO_2)_{n \to \infty}$ as its basic structural unit or primary active group, there is a possibility of developing a borate UV NLO film or waveguide for use in the visible to UV range. In view of the recent development of integrated optics in opto-electronics, such a film or waveguide will be useful in various NLO applications in the UV range. There is a good prospect that such a film or waveguide will be developed before long.

Acknowledgments

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