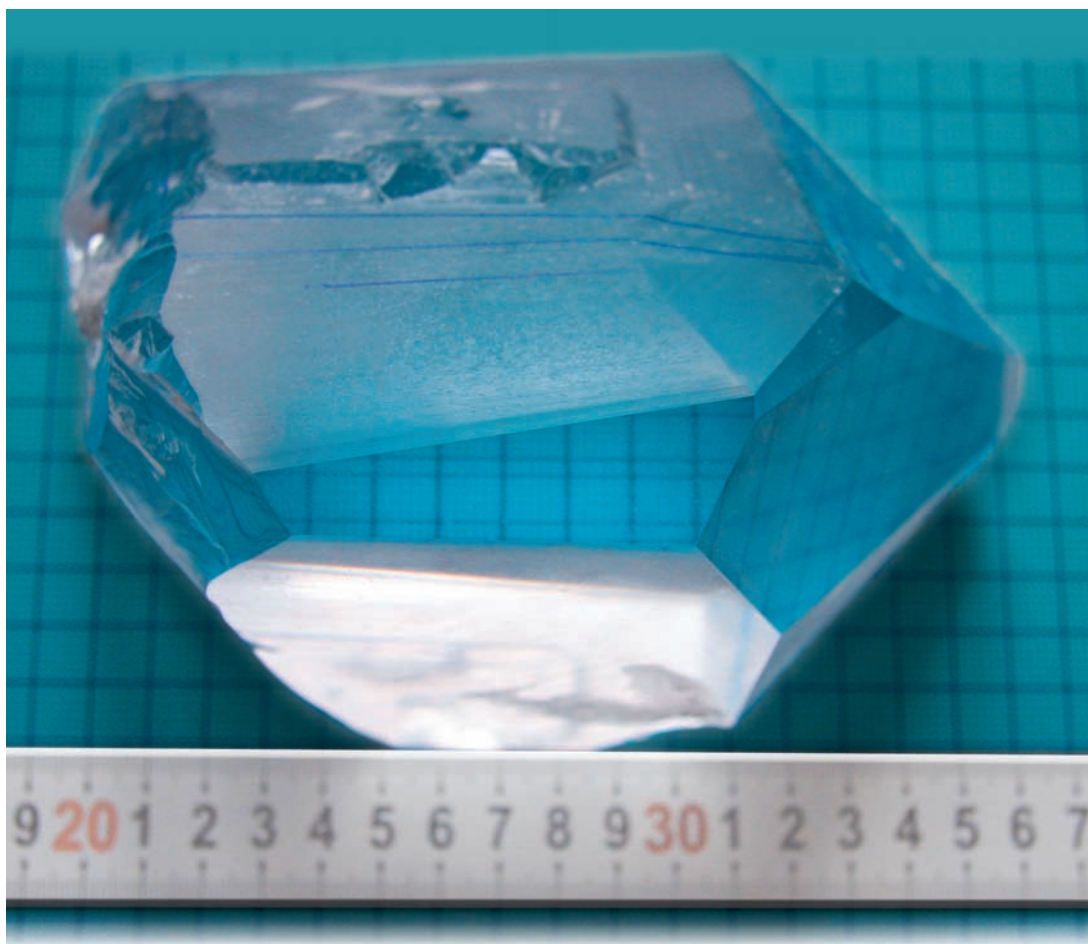


Chuangtian Chen, Takatomo Sasaki
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Nonlinear Optical Borate Crystals

Principles and Applications



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Z. Lin, Y. Mori, Z. Hu, J. Wang,
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Nonlinear Optical Borate Crystals

Principles and Applications



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Preface

At the beginning of 1960 when I was still a senior student at Beijing University, majoring in theoretical physics, I happened to hear of lasers. Though I became quite excited about this news, I little dreamed that all my life would tie to nonlinear optics and its materials.

In the summer of 1962, I graduated from the Physics Department of Beijing University. As it happened I was assigned to work in the Eastern Institute of Research on the Structure of Matter at the Chinese Academy of Sciences (now called the Fujian Institute of Research on the Structure of Matter at the Chinese Academy of Sciences), which is located in Fuzhou and at that time was a small, newly organized institute. It was founded in 1961, the same year that the nonlinear optical effect was discovered. What a coincidence! The institute was really very small at that time. Apart from several dozen university graduates, there were only one research professor and two assistant professors, and the equipment was very poor.

Fortunately, soon after I arrived at the institute, I was helped by Prof. Lu Jiayi, a famous expert in structure chemistry and at that time the Director of the institute. At his suggestion, I spent 3 years studying structure chemistry and quantum chemistry systematically and gained a good grasp of theoretical chemistry. The experience of this period later proved to be very helpful in my research into the relationship between structure and property in nonlinear optical (NLO) crystals.

In 1965, I spent nearly a whole year investigating the literature, looking for a project that I would like to work on. With the approval of Prof. Lu, I took up my research on the relationship between the NLO effect in a crystal and its micro-structure. This was perhaps the most important step in my life as a scientist. It has affected all my life so far, and will probably do so in the years to come.

The year 1966 was a miserable year in the history of China, but from that very year I began to calculate the second harmonic generation (SHG) and the electric-optical (EO) coefficient of the BaTiO_3 crystal using quantum chemistry theory and its methods of approximation. At that time, there was no computer available in our institute and I had to use a calculator. It was extremely hard work, and it took a year and a half to finish my first paper on the calculation of SHG and EO coefficients of BaTiO_3 theoretically. For the first time, I put forward the “anionic group theory on the nonlinear optical effect of crystals.” Its basic concept is as follows: “The nonlinear optical effects of perovskite and tungsten-bronze type crystals depend upon

the distortion of the (MO_6) oxygen octahedron.” According to our knowledge, this is the first quantum chemical calculation of the SHG coefficient in the world; similar work was done abroad in 1985, for example, the calculation of the second-order susceptibilities β of nitroaniline, using the CNDO-type approximation.

Unfortunately, during the years of the “Cultural Revolution” all the academic periodicals in China were forbidden. Although I finished my first paper “A theoretical calculation of electro-optical and second optical harmonic coefficients of barium titanate crystal based on a deformed oxygen-octahedron model” in 1967, I was unable to publish it until 1974 when *Acta Physica Sinica* resumed publication. But even at that time it was unknown abroad. Then in 1986, I wrote an article titled “Recent advance in nonlinear optical and electro-optical materials,” in which the “anionic group theory” of the NLO effects in crystals was systematically described, for the journal *Annual Review of Materials Science*, and in the meantime 20 years had gone by!

I was deeply absorbed in my work. Years of research activities made me to clearly realize that the nonlinear optical effects of crystals are properties sensitive to microstructure. The macroproperty displayed by an NLO crystal is completely decided by its microstructure. Therefore, if systematic calculations of some known crystals with different structures were made, we would be able to set up some structure rules, which would make things easy for us in our search for new NLO crystals.

In 1968, the research work had to be stopped because of the reason known to everybody. Luckily, instead of being sent to work in the countryside as many scientists were forced to do during those years, I was assigned to grow KTN ($\text{KNb}_x\text{Ta}_{1-x}\text{O}_3$) and SBN ($\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$), and to test their optical properties. These two crystals were later given up because of their poor optical qualities. However, the experience gained in this period benefited me a great deal because it helped me understand that becoming a useful NLO crystal depends not only on NLO coefficient $\chi^{(2)}$ of the crystal but also on its linear optical properties, such as birefringence, absorption edge, optical homogeneity, and damage threshold, as well as the physical–chemical properties of the crystal. Unfortunately, some physicists always tend to pay attention to $\chi^{(2)}$ only and seem to ignore other important parameters when searching for new NLO materials.

Because of the accumulation of experience during the Cultural Revolution, we were able to organize a big research group to search for new NLO materials as soon as the Cultural Revolution ended. Before long we discovered that $(\text{B}_3\text{O}_6)^{3-}$ planar group in the borate compounds provides a very hopeful basic structural unit that could be produced with larger microscopic $\chi^{(2)}$. Through a series of experiments, including the systematic synthesis, the powder SHG test, the phase diagram investigations, the X-ray space structural determinations, as well as optical and electrical property measurements, we successfully established BBO (low-temperature modification, $\beta\text{-BaB}_2\text{O}_4$) as a high-quality UV-NLO borate crystal. On the basis of the achievements of the BBO crystal, we further performed a systematic classifications and calculations of microscope second-order susceptibilities for various known boron–oxygen groups using the anionic group theory of the NLO effects on

crystals. All these laid a sound basis for the discovery of so many borate NLO crystals, including LiB_3O_5 (LBO), CsB_3O_5 (CBO), $\text{LiCsB}_6\text{O}_{10}$ (CLBO), $\text{K}_2\text{Al}_2\text{B}_2\text{O}_7$ (KABO), $\text{KBe}_2\text{BO}_3\text{F}_2$ (KBBF), and so on.

Today, beyond my imagination, borate NLO crystals form the bulk of NLO crystals, and have so many applications in the different fields. As one of the main contributing researchers in this area for more than four decades, I am very proud of seeing these.

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I also would like to thank Dr. Zheshuai Lin, Dr. Guochun Zhang, Dr. Xiaoyang Wang, Dr. Guilin Wang, Dr. Lijuan Liu, and my Ph.D students Wenjiao Yao, Lei Bai, and Ran He who spent a lot of time and energy in the preparation of this book.

This book is edited by Prof. Sasaki of Osaka University of Japan and me. Prof. Sasaki has been my good friend for many years. His group has made significant contributions to the development of the borate NLO crystals. Especially, they discovered the CLBO crystal and have grown the single crystal with high quality and large size, which provide its many important applications in the UV spectral

region. I express my gratitude to him and his group for their outstanding contributions to this book.

I thank and beg pardon of all whose names are omitted here either for space or memory limitations. A final thank you is due to the people at Wiley-VCH, and most of all to Anja Tschörtner, for waiting patiently for the completion of this work.

Chuangtian Chen

1

Introduction

Nonlinear optical (NLO) crystals are a key material for the development of laser science and technology because there is almost only this kind of materials that have functions to change frequency of laser beam and modulate it in amplitude and phase. It may be said that lasers could not be used so widely in modern science and technology as they have been today, without NLO crystals. Development of NLO crystals with better linear optical (LO) and NLO properties, wider spectral transmission, and phase-matching range in particular is obviously essential for further widening the application field of lasers, particularly in the deep-UV, far IR, and even THz spectral regions. That is why many scientists working in the field today are still putting in great effort to search for new NLO crystals, even more than four decades after the invention of the laser.

In this chapter, we will first review the history of the theoretical understanding of NLO crystals and place emphasis on the anionic group theory that we suggested during 1968–1976. And then, the history of the discovery of the borate series NLO crystals will be introduced in Section 1.2. In the end, we will review the general crystal growth method for borate crystals in particular.

1.1

History of the Theoretical Understanding of Nonlinear Optical Crystals

The development of the theoretical understanding of NLO crystals can be divided basically into three periods. The first period was from 1961, which is the year Franken, *et al.* [1] discovered optical second harmonic generation (SHG) in quartz crystal, to mid-1960s. In this stage, the NLO response of matter was recognized only in theory to depend upon the susceptibilities $\chi^{(n)}$ and the applied optical electric fields, as illustrated by

$$P = \chi^{(1)} \cdot E + \chi^{(2)} : EE + \chi^{(3)} : EEE + \dots \quad (1.1)$$

The ratio of successive terms in the polarization P can be described approximately by

$$P^{(n+1)}/P^{(n)} \approx (E/E_{\text{at}}) \quad (1.2)$$

Here E is the applied electric field and E_{at} is the atomic field strength with the absolute value $E_{\text{at}} \sim 3 \times 10^8 \text{ V/cm}$ [2] in general. It is well known that two facts have been implied in (1.2).

- i) NLO effects on matter can be observed only with a sufficiently powerful source. For example, despite the laser source with a power density of up to 10^9 W/cm^2 , the electric field strength is about 10^6 V/cm , which is quite small in comparison with E_{at} .
- ii) The generation of new frequencies, not available with the existing laser sources, is easily done via the lowest order NLO response of matter, that is, the second term in (1.1), with a high-enough peak intensity of the laser. Therefore, it is obvious that new frequencies or, in other words, NLO effects, cannot be generated if the structure of a crystal or other matter is centric. It was this important conclusion that enabled scientists to search for NLO materials successfully among the numerous known piezoelectric, ferroelectric, and electrooptical crystals. KDP-type NLO materials were thus found on the basis of this idea.

In this period, there was an important development, the semiexperimental understanding of the structure–property relation of NLO crystals now known as *Miller's rule*. In 1964, Miller [3] proposed that the $\chi^{(2)}$ coefficient in (1.1) can be expressed as

$$\chi_{ijk}^{(2)} = \chi_{ii}^{(1)} \chi_{jj}^{(1)} \chi_{kk}^{(1)} \Delta_{ijk}^{(2)} \quad (1.3)$$

Here, $\chi^{(1)}$ is the linear susceptibility, and $\Delta_{ijk}^{(2)}$ is now known as the *Miller coefficient*. It is a remarkable constant for NLO materials, in spite of the fact that $\chi^{(2)}$ varies over four orders of magnitude, as *Miller* noted in his paper. This was a very important step toward a quantitative estimate of the SHG coefficients for crystals with acentric space structures and, what is more, it led to the search for NLO materials in crystals with high refrangibility. On the basis of this idea, perovskite and tungsten-bronze materials, such as LiNbO_3 [4] and KNbO_3 [5], were found in succession. At the same time, it accelerated progress in understanding the physical origin in this direction.

To sum up, the theoretical understanding of the NLO effect in a crystal was still preliminary, that is to say, scientists only knew the Miller rule and had a general knowledge of the second-order susceptibility of the crystals in this period. As a result, the “try and test” method for searching new NLO materials was used.

The second stage in the theoretical understanding of NLO crystals was from the mid-1960s to the beginning of the 1980s. It was an important period in the development of a theoretical understanding of NLO crystal.

Because of an increasingly large number of NLO crystals studied, and numerous experimental data and theoretical calculations accumulated in the previous stage, scientists began to study the relationship between the macroscopic properties of NLO

crystals and their microscopic structures. This was because they realized that the more they knew about the physical origin of NLO phenomenon in crystals, the faster they would succeed in their search for new NLO materials.

In the early stage of the development (from 1965 to 1969), some simple localized bond parameter methods were utilized to elucidate the structure–property relationship. Representatives of this period are the following: the anharmonic oscillator models put forward by Bloembergen [6], Kurtz and Robinson [7], and Garret and Robinson [8]; the bond parameter model of Jeggo and Boyd [9] and Bergman and Crane [10]; and the bond charge model of Phillips and Vechten [11] and Levine [12, 13]. All of them have proved to be particularly useful in elucidating the structure–property relationship for the NLO effect, of which the basic structure unit is made of simple σ -type bonds, such as the sp^3 -hybrid tetrahedral coordinated compound.

Since the 1970s, several research groups have discovered that the second-order susceptibilities arise from the basic structure units of the crystals with delocalized valence electron orbitals belonging to more than two atoms, rather than those with localized valence electron orbitals around two atoms connected by a simple σ -type bond. The charge transfer model of conjugated organic molecules with donor–acceptor radicals and the anionic group theory of NLO effect on crystals are the two major representatives of this kind of work. The former was first suggested by Davydov *et al.* in 1970 [14] and was farther developed by Chemla *et al.* [15–17]. The latter, an anionic group theory of NLO effects in crystals, was suggested by Chen in 1968–1970 and published in 1976–1979 [18–21]. In addition, DiDomenico and Wemple proposed the deformed energy band model of BO_6 oxygen-octahedra [22, 23], which is basically consistent with the anionic group model. But this model dealt only with perovskite and tungsten-bronze-type crystals and used a simple parameter method. All of the above studies in theory revealed the origin of NLO effects at the microscopic level and, therefore, enabled scientists to construct certain structure criteria to make the search for new NLO crystals more efficient.

On the other hand, because of advances in various NLO applications and devices, scientists in this field came to understand that only a larger $\chi^{(2)}$ coefficient of NLO crystal is far from being sufficient. More comprehensive criteria, such as proper birefringence, absorption cutoff, damage threshold, optical homogeneity, and so on, are necessary in the evaluation of NLO crystals.

Yet another major advance of this period should be mentioned here, namely, the work done by Kurtz and Perry at the Bell Laboratories in 1968 [5]. They developed a powder SHG test technique that permits rapid evaluation of the order of $\chi^{(2)}$ coefficients and the determination of whether or not the crystals can be phase matched in powder samples without the growth of single crystals. Then, in 1978, Tang and coworkers [24] improved this technique by using a dye laser source to decide not only the effective SHG coefficient but also the phase-matchable region of materials in powder.

Furthermore, the SHG powder test technique is not only quick to determine the order of NLO effect in crystals but also quick to check on the correctness of various theoretical modes suggested in this period.

The third stage of the development started in the mid-1990s and continues to the present.

At the beginning of the anionic group theory in the 1980s, we only used the CNDO-type approximation to calculate the molecular orbitals of the anionic groups due to limited computation methods and facilities available, so there may be some doubt about the calculated results. To investigate the reliability of the anionic group theory in determining the SHG coefficients of the NLO crystals, borate NLO crystals in particular, we began to use a more precise method to calculate the SHG coefficients by means of the anionic group theoretical formulae with an *ab initio* molecular orbital calculation method, that is, the Gaussian '92 package [25]. The results were very encouraging. Now, we have set up a computer program with the Gaussian '92 package and can easily calculate the SHG coefficients for almost all major NLO crystals.

Although the anionic group theory is very useful to understand the relationship between the SHG coefficients and the microscopic structure in NLO crystals, the theory is, of course, only an approximation method because the contribution of cation to the overall SHG coefficients in NLO crystals is totally neglected in the theory. So, we still need to use a first-principles energy band calculation method to analyze the effect of cations on the SHG coefficients, at least for the borate-series NLO crystals. On the other hand, we also need the first-principles energy band calculation method to evaluate other important optical parameters of NLO crystals, that is, band gap and refractive indexes, birefractive indexes in particular. Therefore, at the beginning of the new century with rapid increase in computational capability, we adopted CASTEP, a plane wave pseudopotential total energy package [26, 27], to develop a new method to calculate the SHG coefficients, band gap, and refractive indexes, and at the same time, to analyze the contribution of cation and anionic groups separately to the SHG coefficient in NLO crystals. As a result, we were the first in the world to present a model called the real-space atom-cutting method [28], which allows us to calculate separately the contributions of cation and anionic groups to the SHG coefficients and refractive indexes in NLO crystals. These *ab initio* calculations have strongly proved the anionic group theory to be a reasonable model to understand the relationship between the SHG coefficients and the microstructure of the major NLO crystals, borate series NLO crystals in particular, that is, the anionic groups in inorganic NLO crystals (or molecules in organic NLO crystals) make a major contribution to both the SHG coefficients and the birefractive indexes, and the contribution of cations to the SHG coefficients and birefractive indexes is only 15–20% for nearly all major NLO crystals.

From the beginning of the 1990s, on the basis of the theoretical model, we have set up a molecular design system to search for new NLO crystals. This molecular design system helps our group to discover a new borate series deep-UV NLO crystals KBBF family.

1.2

History of Development of NLO Borate Crystals

In the 1970s, the main experimental method to search for new NLO crystals was to use SHG powder test technique among the ferroelectric materials. The typical

representatives discovered as new NLO crystals were KDP(KH_2PO_4) family, including $\text{KD}^*\text{P}(\text{KD}_2\text{PO}_4)$, $\text{KDA}(\text{KH}_2\text{AsO}_4)$, and $\text{ADP}(\text{NH}_4\text{H}_2\text{PO}_4)$ [29–31], and the perovskite and tungsten-bronze-type crystals, including the famous $\text{LiNbO}_3(\text{LN})$ [4], $\text{KNbO}_3(\text{KN})$ [5, 32], and $\text{Ba}_2\text{Na}(\text{NbO}_3)_5(\text{BNN})$ [33, 34] crystals. Before long in 1976, Bierlein *et al.* at Dupont company discovered another new series of NLO crystals of $\text{KTP}(\text{KTiOPO}_4)$ [35] and its isomorphs (RbTiOAsO_4 , KTiOAsO_4 , and RbTiOPO_4) [36], which are still widely used in laser industry today, with the same SHG powder test technique. Dr. J. Bierlein has made a big contribution to the development of NLO crystals; Dr. J. Bierlein was one of my best friends, but sadly passed away 15 years ago. It was a great loss to all of us.

Thus, when our group was involved in this field in the end of 1970s, nearly all ferroelectric materials discovered at that time have been tested by the SHG powder technique. Therefore, we must look for new NLO crystals in the numerous acentric compounds. Obviously, it is very difficult and time consuming to use only the SHG powder test technique. The situation becomes too difficult when we search particularly for the applications of the ultraviolet (UV) and deep-UV spectral ranges because there is no experimental method available to determine the absorption edge and birefringence of compounds in the powder stage. Fortunately, from the very beginning, it was instructive for us to realize that an understanding of the relationship between the NLO effects and the microstructure of crystals can be extremely helpful to make the search routine easy. Furthermore, it made us capable of predicting the more favorable structures for large NLO effects, on the molecular and atomic levels, at the powder test stage.

In the period 1974–1986, we suggested a theoretical model for NLO effects of crystals, called anionic group theory, and an approximate method of calculation of the effects based on the second-order perturbation theory of NLO susceptibilities of crystals as mentioned above. On the basis of this model, we systematically elucidated the structure–property relationship for almost all principal types of inorganic NLO crystals, namely, perovskite and tungsten-bronze, phosphate, iodate, and nitrite, and, later, borate crystals. The successes of the theoretical investigations combined with the systematic experimental efforts, including chemical syntheses, SHG powder test, and X-ray space structural determination, significantly helped us to select the suitable candidates in the acentric compounds. It was proved that this procedure, now we call it molecular design system, is greatly time saving and increases the efficiency of the search for new NLO crystals.

In 1979, the interest of my group was focused on the research for new NLO crystals in the UV-spectral region. Two reasons made us to change our focus: the one was that both KTP and CN crystals were too powerful for frequency conversion in the visible spectral region, the second reason was that, in the UV spectral region there were only two “weak” NLO crystals at that time, that is, urea ($(\text{NH}_2)_2\text{CO}$) [5, 37, 38] and KB5 ($\text{KB}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$) [39]. Urea is an organic crystal and has many disadvantages, for example, its cutoff wavelength reaches only 200 nm and this crystal is very sensitive to moisture in practical applications. Concerning KB5 crystal, although its absorption edge is at 165 nm and the phase-matching range of the crystal is down to 200 nm, the application of the crystal in the UV region is

severely limited by its very small effective SHG coefficient d_{eff} —only about $0.1 \times d_{36}$ (KDP). Nevertheless, the identification of KB5 as a UV-NLO crystal gave us a green light to work for the development of UV-NLO crystals in the borate series because there are many different structural types in the borate series that can be selected as candidates for searching new NLO crystals. So, it was surprising that during the 1970s there was no major breakthrough on borate NLO crystals until our group was involved in this area. This void was mainly due to the fact that no other appropriate theoretical models, which could be used to evaluate the linear and nonlinear optical properties for inorganic materials, were fully developed at that time.

According to the principle of anionic group theory, we gradually recognized that borate compounds afforded us many advantages in our search for new UV-NLO crystals. First, most borate crystals are transparent far into the UV and even deep-UV regions because of the large difference in the electronegativities of the B–O bond. Second, the borate compounds have hundreds of different structure type. These abundant structural types, anionic group types in particular, gave us more chances to select suitable compounds for new NLO crystals. Third, the intrinsic damage threshold of most borate crystals is very high on account of the wide band gap in the electronic structure and the strong inertness of ion–electron transport in these compact lattices, even under very intense laser power density.

In 1979, it came to be known that the small d_{eff} of KB5 comes from its basic structural unit $[\text{B}_5\text{O}_6(\text{OH})_4]^-$ group. According to our evaluation for the second-order susceptibilities of $[\text{B}_5\text{O}_6(\text{OH})_4]^-$, the group is unfavorable to produce larger microscopic $\chi^{(2)}$ (see Section 2.2.6). However, there are other boron–oxygen groups that may exhibit larger microscopic second-order susceptibilities. For example, it was also known in 1979, by our group, that the planar $(\text{B}_3\text{O}_6)^{3-}$ anionic group has π -conjugate orbital and could produce a larger microscopic $\chi^{(2)}$, analogous to the organic molecular with π -conjugate orbital. On the basis of the theoretical analysis and the extensive experimental efforts, including the SHG powder tests, the phase diagram investigations, the crystal structure determination, and optical and electric property measurements, our group eventually successfully established BBO [40] (barium metaborate, low-temperature modification, $\beta\text{-BaB}_2\text{O}_4$) as an excellent UV-NLO borate crystal.

After the discovery of BBO, our group promoted two projects: first, much broader theoretical activities were carried out to elucidate the structure–property relations from only SHG coefficients to linear optical properties (see Chapter 2) because some linear optical properties of the crystals, such as the absorption edge, birefringence, and the damage threshold of the crystal, remain important for sophisticated technical applications in optical electronic devices. Second, we systematically classified all borate series compounds according to the anionic group theory and calculated the second-order susceptibilities of most borate–oxygen groups with the theoretical method [41] (see Chapter 2).

We understood that although BBO is an excellent UV-NLO crystal, the capability of the crystal to produce deep-UV harmonic generation below 200 nm was limited by its absorption edge ($\lambda_{\text{cutoff}} = 185 \text{ nm}$).

So the next step in our search for new NLO crystals in the deep-UV spectral region turned to the $(\text{B}_3\text{O}_7)^{5-}$ group since it can produce not only relatively large second-order susceptibility but also has a wide energy gap (see Chapter 2). These ideas led us to the discovery of another new NLO crystal LiB_3O_5 (LBO) crystal [42].

Following the same idea and nearly the same experimental procedure, several other groups also found two other members of LBO family, CsB_3O_5 (CBO) [43] and $\text{CsLiB}_6\text{O}_{10}$ (CLBO) [44, 45], with the same basic structural unit $-(\text{B}_3\text{O}_7)^{5-}$ group.

From the beginning of the 1990s, we have further understood that although BBO and LBO crystals are very excellent for frequency conversion of laser beam from infrared (IR) wavelength to visible and UV wavelengths, but both $(\text{B}_3\text{O}_6)^{3-}$ and $(\text{B}_3\text{O}_7)^{5-}$ groups were not suitable to our search for new borate NLO crystals in the deep-UV spectral region because theoretical calculations show that π -orbital of the $(\text{B}_3\text{O}_6)^{3-}$ group limits the band gap of BBO crystal, and although $(\text{B}_3\text{O}_7)^{5-}$ group has a wider energy gap (see Chapter 2) to deep-UV spectral region, the spatial arrangement of the endless helices of $(\text{B}_3\text{O}_7)_{n \rightarrow \infty}$ chains in the lattice of LBO family along the Z-axis is unfavorable for producing a large birefringence. Therefore, all members of the LBO family have a small birefringence ($\Delta n \approx 0.045\text{--}0.055$), which is too small to produce second harmonic generation below 200 nm.

In order to solve these problems, our group turned attention to the trigonal borate $(\text{BO}_3)^{3-}$ group and found that the group could be the most suitable structural unit among all borate groups to search for new borate NLO crystals in the deep-UV spectral region. On the basis of this idea, soon we found that the $\text{KBe}_2\text{BO}_3\text{F}_2$ (KBBF) [46] space structure is one of the rare compounds that is suitable of all borate compounds to search for new deep-UV NLO crystals. Now the KBBF family, including RBBF ($\text{RbBe}_2\text{BO}_3\text{F}_2$) [47] and CBBF ($\text{CsBe}_2\text{BO}_3\text{F}_2$) (Huang, H. W., Chen C.T., et al (2011) Ultraviolet nonlinear optical crystal: $\text{CsBe}_2\text{BO}_3\text{F}_2$. J. Opt. Soc. Am. B28, 2186–2196.), has been proved excellent NLO crystals for frequency conversion into the deep-UV spectral range.

As it followed, there was another climax to the search for new NLO crystals based on the $(\text{BO}_3)^{3-}$ unit group. Many new borate NLO crystals were discovered by different groups, such as $\text{K}_2\text{Al}_2\text{B}_2\text{O}_7$ (KABO) [48], $\text{GdCa}_4\text{O}(\text{BO}_3)_3$ (GdCOB) [49], $\text{YCa}_4\text{O}(\text{BO}_3)_3$ (YCOB) [50], and $\text{BaAlBO}_3\text{F}_2$ (BABF) [51], and more work is now being carried out.

1.3

History of Crystals for Frequency Conversion

In this section we deal with only second harmonic and sum-frequency generation.

1.3.1

Frequency Conversion Efficiency of Second Harmonic Generation

When the input fundamental power $I^{(\omega)}$ does not decrease by frequency conversion, that is, in the nondepleted regime, the second harmonic power $I^{(2\omega)}$ in plane wave

approximation is expressed as follows:

$$I^{(2\omega)} = 8 \left(\frac{\mu_0}{\varepsilon_0} \right)^{3/2} \frac{\omega^2 d^2 L^2 (I^{(\omega)})^2}{n^{(2\omega)} (n^{(\omega)})^2 A} \left(\frac{\sin x}{x} \right)^2 \quad (1.4)$$

$$x = \Delta k \cdot L/2, \quad \Delta k = 2k^{(\omega)} - k^{(2\omega)} \quad (1.5)$$

where L is the crystal length, A is beam cross section, d is the second-order nonlinear coefficient, and $k^{(\omega)}$ and $k^{(2\omega)}$ are the wave numbers of the fundamental and the second harmonics, respectively.

When $\Delta k = 0$ hence $x = 0$ in Equation 1.4, $I^{(2\omega)} \propto L^2$ and the output power increases with the square of the crystal length L , so the second harmonics can be obtained efficiently. This condition is called the phase matching. When $\Delta k \neq 0$, the SHG power becomes zero at every coherent length $l_c = \pi/\Delta k$.

1.3.2

Methods to Obtain Higher Efficiency for Frequency Conversion

In order to obtain the higher efficiency for frequency conversion, the increase of the input power ($I^{(\omega)}$) and the adoption of the longer crystal (L) with the bigger SHG coefficient (d) is necessary, as clearly shown in Equation 1.4.

At the same time, the phase matching condition, $x = (\Delta k =) 0$, must be satisfied, which can be fulfilled in two ways:

- a) Birefringence method
- b) Quasi-phase matching (QPM) method

In addition, the increase in the input fundamental power $I^{(\omega)}$ can be achieved by (c) beam confinement in optical waveguide and (d) beam enhancement by resonator.

1.3.3

Desirable Conditions for Frequency Conversion Crystals

The desirable conditions of crystals for practical use are as follows:

- 1) Large effective nonlinear coefficient d
- 2) Larger angle, temperature, and wavelength acceptance
- 3) Wide spectral range of transparency
- 4) High laser damage threshold
- 5) Easy to grow large and optically good crystals
- 6) Chemically stable, especially antideliquescent
- 7) Mechanically hard and easy to polish
- 8) Large thermal conductivity

1.3.4

History of Crystals and Techniques for Frequency Conversion

Since the invention of laser in 1960, various crystals were developed. Despite that so many crystals were invented or developed, at present the research on the crystals that can be used for practical devices is still going on.

From 1960 to 1980, nonlinear optical crystals that have the molecular bonding such as P–O, I–O, and Nb–O were developed, including KDP(KH_2PO_4) family, LiIO_3 , LN(LiNbO_3), LT(LiTaO_3), KN(KNbO_3), banana ($\text{Ba}_2\text{NaNb}_5\text{O}_{15}$), and so on.

The crystals with P–O and I–O bonding, such as KDP(KH_2PO_4) family and LiIO_3 , do not possess very large nonlinear coefficients d (0.3–4 pm/V) but are easy to grow in a large scale over a few centimeters. They are deliquescent and do not have large thermal conductivity. Therefore, they were used only for tools in laboratory experiments and not used for industrial application after other crystals with more desirable properties appeared. Only the KDP with huge size ($>100 \times 50 \times 50 \text{ cm}^3$) has been used for third harmonic generator in the laser system for fusion experiment.

The crystals with Nb–O bonding have large nonlinear coefficients d beyond several pm/V s. At present, LiNbO_3 and LiTaO_3 are used widely, but KNbO_3 and $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ are very difficult to grow in the size for practical applications and cannot be utilized extensively in industry even if they have the larger d coefficients.

1) Green blue light generation.

From the 1960s to the early 1980s, the phase matching method using birefringence of crystal (method (a) in Section 1.3.2) was exclusively used for frequency conversion.

In the late 1980s, green or blue lasers were demanded for future information process, especially next-generation optical disk. In those days, infrared laser diodes had already been used for writing to and reading from compact discs. To increase the amount of the information stored in the same physical size, compact green or blue lasers were required as the light source. However, the oscillation of green or blue semiconductor lasers had not been successful at the time.

Therefore, the investigation of compact green or blue lasers using the frequency conversion method became active. Unfortunately, the frequency conversion efficiency was very low at that time because the fundamental power $I^{(\omega)}$ is small. To overcome this problem, the methods (c) and (d) mentioned in Section 1.3.2 were used, that is,

- c) to increase the frequency conversion efficiency by confining the input power to optical waveguide and holding the power density high;
- d) to increase the frequency conversion efficiency by enhancing the input power density using resonator.

QPM method ((b) in Section 1.3.2) was first proposed by Bloembergen in the 1960s. This method does not use the birefringence of the crystal; instead, it uses multiple plates each with the thickness of coherence length, stacked together with

inverting the direction of optical axis of the ferroelectric crystal such as LN or LT. The total length of the device is typically a few micrometers, in which several hundreds plates are attached together to satisfy QPM. Nevertheless, the optical loss was too large because of multiple reflections of surfaces/interfaces among these plates and could not be used as a real device in these early days. In the 1990s, the domain inversion technique by electric field poling was invented and QPM was successfully demonstrated in a monolithic structure. Optical waveguide was one of the techniques to enhance the power of green to blue light. Periodically poled QPM devices of LN and LT are called PPLN and PPLT. Now, green CW laser source of W level with PPLN devices has been developed for laser display and projector systems.

There are two methods to use a resonator to enhance the conversion efficiency. One is called the intracavity method. Both a laser material and a nonlinear optical crystal are placed in the same cavity. Compact and highly efficient green lasers with the combination of Nd:YAG and KTP (KTiOPO₄) or Nd:YVO₄ and KTP in an oscillator cavity have been demonstrated. Self-doubling method with one crystal for laser oscillation and simultaneous frequency doubling such as Nd:YAB (yttrium aluminum borate) was also investigated.

The other method is called the external cavity. In this case, the frequency doubling crystal is placed in the cavity separate from the laser oscillator. This is mainly for enhancing the fundamental laser intensity by resonance and for obtaining high frequency conversion. Continuous wave 1 W of 266 nm generation from BBO by the external resonator method is now being used for information process.

From the 1980s to the 1990s, the investigation of organic optical nonlinear materials for frequency doubling in low and high molecular compounds, poled polymers doped with low molecule with large nonlinear susceptibility, such as Langmuir–Blodgett films and liquid crystals, became active with the same purposes as mentioned above. The organic materials with one or two order of magnitude larger nonlinear optical coefficient than that of inorganic materials could be designed. However, almost all such materials have large optical absorption in green or blue regions and are too weak to withstand cutting and polishing for the fabrication of practical devices; so, they are difficult to be used. The important criteria for selecting the applicable materials are not only the large nonlinearity but also the good transparency and mechanical hardness.

In the 1990s, the GaN semiconductor laser appeared. Blue lasers at wavelength 400 nm could be obtained easily and adopted for information processing. In the beginning of the 2000s, the investigations on green or blue laser by frequency doubling for information process rapidly diminished. Only the green laser with an output power of W level by frequency doubling survived for the large screen display because the green light of W level is still difficult to produce from semiconductor lasers.

2) Ultraviolet (UV) and deep UV (DUV) light generation.

In China, the development of crystals with B–O bonding for UV and deep UV harmonic generation is still active. Since Professor Chuangtian Chen presented a