

Review Article

Borate Crystals for Nonlinear Optical and Laser Applications: A Review

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The development of borate-based single crystals for laser and frequency conversion applications is reviewed. The basic idea behind nonlinear optics and the role of anionic groups in the borate crystals are summarized. The properties of borate crystals—BBO, LBO, CBO, KBBF, SBBO, CLBO, YCOB, GdCOB, GdYCOB, KAB and LCB—are discussed. The growth and characterization of several rare earth-based borate crystals are mainly focused. Several borate crystals are grown from the melt techniques and a few crystals are grown adopting the flux technique. Many rare earth-based borate crystals are extensively used in device applications as they exhibit the frequency conversion ability along with high laser-induced damage tolerance.

1. Introduction

1.1. Demand for UV and Visible Radiations. The development of lasers has played a key role in the past five decades for the development of mankind in various fields and to reach several technological advancements. The demand for laser beams in the ultraviolet and visible regions is growing enormously. The laser beams in the UV and visible regions find applications in several industries, medical surgeries, data storage, optical communication, and entertainment purposes. Advances in semiconductor photolithography, for example, are creating demand for 158 and 193 nm coherent light sources, while emerging micromachining and material-processing applications also need deep-UV laser radiation. In addition, research scientists would like a widely tunable coherent light source down to 200 nm for laser spectroscopy and photochemical synthesis.

Although excimer lasers can emit some isolated wavelengths of coherent light in the UV and deep-UV spectral region with a high average output power, compact and efficient solid-state lasers with nonlinear optical (NLO) crystals in this spectral region are still needed. Important solid-state benefits include narrow bandwidth, improved beam quality, tunability, and relative ease of handling. The performance of solid-state lasers in the UV and deep-UV spectral regions depends heavily on efficient NLO crystals, such as the borate

deep-UV crystals that are being developed over the last two decades.

1.2. Emphasis of the Present Review. The recent developments in NLO borate crystals for the generation of high power visible and ultraviolet laser radiations are reviewed. The basic principles behind nonlinear optical materials are also dealt with. The classification of borate crystals based on the “anionic group theory” is discussed. Few important aspects involved in the growth of borate crystals and their properties are also reviewed and presented. The borate based NLO crystals are classified into three categories.

- (i) CBO, LBO, and CLBO crystals
- (ii) KBBF, SBBO, and KAB crystals
- (iii) Rare-earth-based borate crystals

2. Nonlinear Optics and Borate Crystals

2.1. Basic Principles of Nonlinear Optics. The successful demonstration of lasers by Maiman and his coworkers in the year 1960 paved way for various scientific and technological advancements in the twentieth century [1]. A new field—nonlinear optics—came into being. Franken and his coworkers were the first to realize the nonlinear optical effect

when they observed light at twice the frequency of a ruby laser ($\lambda = 693.4$ nm) from a quartz crystal which was subjected to the ruby laser radiation. The practical observation of nonlinear optical phenomena would not have been observed if the lasers were not invented. This can be explained as follows. The field strengths of the conventional light sources used prior to the advent of lasers was of the order of 10^3 V/m. But the interatomic field strengths lie in the range between 10^7 and 10^{10} V/m. Hence, the conventional light sources are very less intense to affect the atomic fields to the extent of altering the optical parameters associated with it. The unique property of lasers, its coherence, helped in achieving radiations with the intensities of the order of 10^{10} V/m feasible. Hence, lasers serve as useful and essential tool in the field of nonlinear optics and other related interesting phenomena such as Kerr effect, Pockels effect, second- or higher-harmonic generations, and so on.

The origin of NLO processes is the response of a nonlinear dielectric medium to an oscillating electric field. For example, when a dielectric material is subjected to an electromagnetic (e.m) radiation, the propagation of the e.m wave through the material produces changes in the spatial and temporal distribution of electric charges due to the interaction between the e.m wave, electrons, and atoms. This perturbation creates electric dipoles whose manifestation is macroscopic polarization (P). When the applied electric field (E) is very small, the induced polarization can be expressed as,

$$P = \epsilon_0 \chi^{(1)} E, \quad (1)$$

where ϵ_0 is the permittivity of free space ($\epsilon_0 = 8.854 \times 10^{-12}$ C²s²/kg m³) and $\chi^{(1)}$ is the linear susceptibility term which is responsible for the optical properties such as absorption, index of refraction, dispersion, and birefringence of the medium. When the applied electric field is highly intense and comparable to the interatomic field, the induced polarization is given by,

$$P = \epsilon_0 (\chi^{(1)} E + \chi^{(2)} E \cdot E + \chi^{(3)} E \cdot E \cdot E + \dots), \quad (2)$$

where $\chi^{(2)}$, $\chi^{(3)}$ are the second- and the third-order nonlinear susceptibilities and their magnitude decreases as their order increases ($\chi^{(1)} : \chi^{(2)} : \chi^{(3)} = 1 : 10^{-8} : 10^{-16}$). The second order susceptibility term ($\chi^{(2)}$) gives rise to second-harmonic generation, frequency mixing and parametric generation and the third order susceptibility term ($\chi^{(3)}$) is responsible for the third harmonic generation, Stimulated Raman scattering, optical bistability, and phase conjugation.

For the purpose of reliable laser frequency conversion, NLO crystals with the following properties are desired: large NLO coefficient, moderate birefringence, small walk-off effect, large angular, spectral and temperature bandwidths, wide transparency in the wavelength of interest, high laser-induced damage threshold, ease of growth, low material cost, good chemical stability, and good mechanical stability.

Till 1975, extensive research on NLO crystals based on the P-O, I-O, and Nb-O bonds were carried out. The widely studied NLO crystals include KDP (KH₂PO₄), LN

(LiNbO₃), LiIO₃, and so forth as they fulfill the above listed requirements to a good extent. With the advent of potassium pentaborate, KB₅O₈ · 4H₂O, crystal in the year 1975, tremendous attention was directed to grow borate-based crystals for frequency conversion purposes.

2.2. Nonlinear Optical Borate Crystals. The large family of borate compounds is a suitable chemical playground now adopted by many materials scientists, because the extremely wide variability of borate crystal chemistry allows the creation of various different structure types [2]. Furthermore, among all the borate structures reported till date, 36% are noncentrosymmetric, while among the reported inorganic crystal structures there are in total only 15% of non-centrosymmetric structure [3].

Borate crystals are superior in UV applications to other commonly used NLO materials such as potassium dihydrogen phosphate (KDP) or lithium niobate (LN) because of their high transmittance at wavelengths down to 155 nm combined with higher damage threshold. A comparison of selected NLO materials is given in the Table 1. The first borate crystal described for UV light generation was potassium pentaborate (KB₅O₈ · 4H₂O) [4]. However, intense research work on borate crystals was initiated only after the development of β -BaB₂O₄ (BBO) and LiB₃O₅ (LBO). There are several borate crystals available today which cater the need of optical industry [5–10].

The optical properties of borate crystals can be related to their molecular structure. A few borate crystals are mentioned in the Table 1 as examples. These crystals are constructed from the three basic structure units: (B₃O₆)³⁻, (B₃O₇)⁵⁻, and (BO₃)³⁻ anionic groups. The (B₃O₆)³⁻, (B₃O₇)⁵⁻, and (BO₃)³⁻ anionic groups are shown in Figure 1. A model called the “anionic group theory” was designed by Chen and his coworkers and is used to understand the relation between composition, structure of borate materials, and the related NLO properties [11].

Due to the planar hexagonal structure of the (B₃O₆)³⁻ anionic group, borate crystals constructed from this basic unit have greater $\chi^{(2)}$ compared to crystals composed of (B₃O₇)⁵⁻ and (BO₃)³⁻ anionic groups. Thus in terms of NLO coefficients, the (B₃O₆)³⁻ group is the most suitable as the basic structure unit of NLO borate crystals followed by (B₃O₇)⁵⁻ group and then (BO₃)³⁻ group. However, the UV absorption edge of the borate crystals constructed from the (B₃O₆)³⁻ group occurred at a longer wavelength (e.g., BBO) when compared to those constructed from (B₃O₇)⁵⁻ group (e.g., LBO, CBO, CLBO). Calculations showed that π -conjugated orbitals of planar (B₃O₆)³⁻ tend to shift the UV absorption edge toward the red. As one of the boron atoms in (B₃O₆)³⁻ changed from trigonal to tetrahedral coordination, thereby forming nonplanar (B₃O₇)⁵⁻ groups, the π -conjugated orbital system is weakened, as in the case of LBO and CBO and the UV absorption edge shifts to 160–170 nm. Both CBO and LBO are constructed from a continuous network of nonplanar (B₃O₇)⁵⁻ groups with interstitial cesium and lithium cations, respectively. Based on

TABLE 1: Selected properties of few borate crystals.

Crystals	Space group	Transparency range (nm)	Shortest SHG (nm)	Basic structure unit
β -BaB ₂ O ₄ (BBO)	R 3c	190–3300	205	B ₃ O ₆
LiB ₃ O ₅ (LBO)	Pnn 2 ₁	160–2600	277	B ₃ O ₇
CsB ₃ O ₅ (CBO)	P2 ₁ 2 ₁ 2 ₁	167–3400	273	B ₃ O ₇
KBe ₂ BO ₃ F ₂ (KBBF)	R 32	155–3660	185	BO ₃
Sr ₂ Be ₂ BO ₇ (SBBO)	P 6 ₃	155–3780	200	BO ₃
CsLiB ₆ O ₁₀ (CLBO)	142 d	180–2750	237	B ₃ O ₇

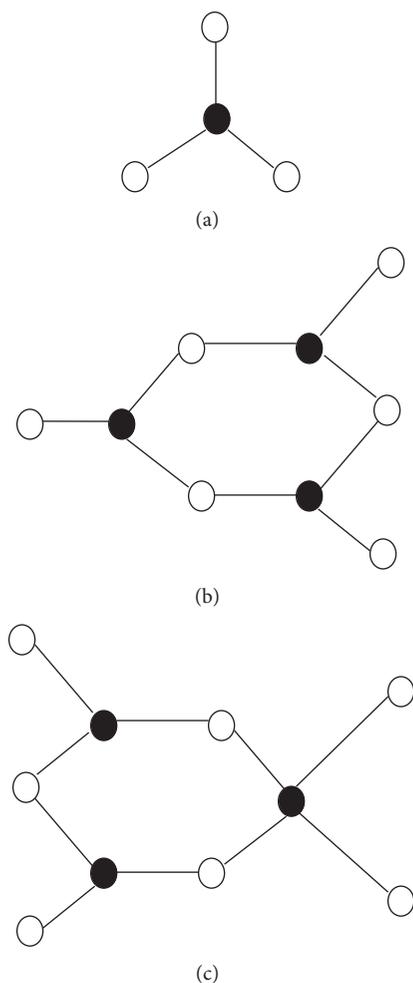


FIGURE 1: Basic structure units of (a) BO₃ (b) B₃O₆ (c) B₃O₇ borates (dark circles represent boron and bright circles represent oxygen atoms).

the absorption edge, therefore, (B₃O₇)⁵⁻ group is ideal as the basic structural unit of deep-UV NLO materials. Likewise, if the dangling bonds of the three terminated oxygen atoms of (BO₃)³⁻ groups are interlinked with cations, an absorption edge appearing at wavelengths as short as 155 nm is also feasible as in the cases with KBBF and SBBO.

3. NLO Borate Crystals

3.1. CBO, LBO, and CLBO Crystals. There is a tremendous amount of work on CsB₃O₅ (CBO) and LiB₃O₅ (LBO) crystals by flux techniques for the fourth- and the fifth-harmonic generations of Nd : YAG lasers. Another derivative of LBO is CsB₃O₅ (CBO). CBO compound melts congruently at 842°C. Crystals with dimensions of 20 mm in diameter and 30 mm in length were grown with the pulling rate of 8 mm/day. In general, a good NLO crystal that can generate deep-UV light effectively is required to have a birefringence between that of BBO ($\Delta n = 0.12$ at $\lambda = 1064$ nm) and LBO ($\Delta n = 0.04$ at $\lambda = 1064$ nm). This property allows the expansion of the phase matching range for SHG at a reasonably low walk-off effect and significantly large phase-matching bandwidths. The earlier mentioned CLBO crystal has $\Delta n = 0.052$ at $\lambda = 1064$ nm and hence, it is widely used for deep-UV light conversion. Thus several NLO crystals like CLBO that possess a birefringence between BBO and CLBO are desired.

CsLiB₅O₁₀ (CLBO) crystals, which are the structural derivatives of LBO crystals, are grown in larger dimensions from their melts. Very large CLBO single crystals with the dimensions of 140 × 110 × 110 mm³ with good optical quality were grown and reported [12].

3.2. KBBF, SBBO, and KAB Crystals. Isostructural borate crystals of SrB₄O₇ and PbB₄O₇, both of which belong to the orthorhombic crystal system are grown from their melts. Large single crystals of PbB₄O₇ were grown by the Czochralski technique from a melt with a slight excess of PbO to lower the viscosity of the melt at 774°C. Seed crystals with the [100] or [001] orientations were preferred for single crystal growth. Growth runs, with a cooling rate of 0.7°C/day and a pulling rate of 4 mm/day have yielded single crystals with 20 × 28 × 55 mm³ dimensions. In the similar manner, single crystals of SrB₄O₇ were grown from its stoichiometric melt at 994°C. Single crystals with 25 mm diameter and 20 mm length were grown using pulling rates of 2 mm/day with the crystal rotation of 20 rpm.

Intense research on the incongruently melting borate crystals is also in progress. Due to the fact that a few incongruently melting borate materials are transparent down to vacuum-UV region, single crystal growth of these materials is undertaken. The family MBe₂BO₃F₂, with M = Na, K, is an example of a structure type with isolated [BO₃] triangles, crystallizing in the noncentrosymmetric space group R32. The potassium compound KBe₂BO₃F₂ (KBBF) was first

TABLE 2: Comparison between RECOB crystals.

Properties	YCOB	GdCOB	LCOB
Unit cell parameters	$a = 8.04 \text{ \AA}$	$a = 8.09 \text{ \AA}$	$a = 8.16 \text{ \AA}$
	$b = 15.95 \text{ \AA}$	$b = 16.01 \text{ \AA}$	$b = 16.08 \text{ \AA}$
	$c = 3.51 \text{ \AA}$	$c = 3.55 \text{ \AA}$	$c = 3.63 \text{ \AA}$
Bond angle	$\alpha = \gamma = 90^\circ$	$\alpha = \gamma = 90^\circ$	$\alpha = \gamma = 90^\circ$
	$\beta = 101.19^\circ$	$\beta = 101.27^\circ$	$\beta = 101.3^\circ$
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C_m	C_m	C_m
Hygroscopicity	Nonhygroscopic	Nonhygroscopic	Nonhygroscopic
Transparency range	220–3600 nm	320–2700 nm	Above 210 nm
Melting point	1510°C	1480°C	1410°C

synthesized in the year 1968. These crystals were grown from flux melts with KBF_4 and BeO . The plate-like crystals with the dimensions of $10 \times 10 \times 0.3 \text{ mm}^3$ were reported.

Improvement of the NLO properties by increasing the number of NLO active $[\text{BO}_3]$ groups per unit volume of the crystal structure was attempted by creating $\text{Sr}_2\text{Be}_2\text{B}_2\text{O}_7$ (SBBO). These crystals exhibit the hexagonal crystal system and were grown by the TSSG technique. These crystals are grown by slow cooling with the cooling rate of $1\text{--}2^\circ\text{C}/\text{day}$. Crystals with the dimensions of $7 \times 7 \times 3 \text{ mm}^3$ with good optical quality are obtained and reported. SBBO ($\Delta n = 0.062$ at $\lambda = 589 \text{ nm}$) and KBBF crystals ($\Delta n = 0.072$ at $\lambda = 589 \text{ nm}$) are attractive candidates in this aspect. However, because of the weak binding between the layered structural units, KBBF is difficult to grow and is mechanically fragile [13]. The SBBO has strong covalent bonds between beryllium atoms and oxygen atoms in adjacent layers. This makes SBBO mechanically stronger and relatively easy to grow compared to KBBF. However, beryllium is toxic, which makes crystal growth inconvenient. Thus, it is important that the Be atoms in SBBO be replaced by a nontoxic element. Sasaki and his coworkers had attempted to replace the $(\text{BeO}_4)^{6-}$ with $(\text{AlO}_4)^{5-}$ and had replaced Sr^{2+} with M^+ ($\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+$ and Cs^+) according to the concept of ionic compensation ($\text{Al}^{3+} + \text{K}^+ \rightarrow \text{Be}^{2+} + \text{Sr}^{2+}$). In this way, potassium aluminum borate crystal with the chemical formula $\text{K}_2\text{Al}_2\text{B}_2\text{O}_7$ (KAB) was discovered. KAB has the spatial arrangement similar to that of SBBO.

The structure of the KAB crystal is trigonal with the P321 space group. The lattice parameters of the crystal are $a = b = 8.5657 \text{ \AA}$, $c = 8.463 \text{ \AA}$, $V = 537.7 \text{ \AA}^3$, and $Z = 3$ [14]. The KAB crystals are grown from flux technique. Different fluxes such as B_2O_3 , K_2CO_3 , and $\text{K}_2\text{CO}_3\text{--B}_2\text{O}_3$, alkali halides such as KF and NaF were used for the growth of KAB crystals and are reported. The KAB crystal is transparent from 180–3600 nm. The thermal property of the KAB crystal is also studied. The linear thermal expansion coefficient of the KAB crystal along the x , y , and z directions are very lesser. The specific heat values of KAB crystal at 47.6°C and 294.6°C are $1.0084 \text{ J/g}^\circ\text{C}$ and $1.39 \text{ J/g}^\circ\text{C}$ [15].

3.3. Rare-Earth-Based Borate Crystals. Borate crystals are not only employed for frequency conversion applications but also as self-frequency doubling (SFD) active laser sources in the recent years. Rare-earth-based borate crystals are employed both for NLO and SFD applications.

3.4. Huntite Family Crystals. The families of borate crystals with the general chemical formula, $\text{RAl}_3(\text{BO}_3)_4$ with $\text{R} = \text{Y}$, Nd , Sm , Eu , Tb , Dy , Er , and $\text{RX}_3(\text{BO}_3)_4$ with $\text{R} = \text{Gd}$, Sm , $\text{X} = \text{Cr}$, Al are termed as “huntite” family crystals. The emissions of sharp bright lines from these crystals were observed. These crystals are chemically stable, nonhygroscopic, and have high hardness. These crystals melt incongruently and are grown from flux methods only. All these crystals are trigonal with the space group R32. The widely studied huntite-type borate crystal is $\text{YAl}_3(\text{BO}_3)_4$ (YAB) [16]. These crystals are doped with Er , Nd , and Yb ions for making them as SFD crystals. It is commonly grown by top seeded solution growth (TSSG) method.

YAB is a noncentrosymmetric crystal and as early as in 1974, it was reported as a very effective second-harmonic generating material. Furthermore, owing to its good chemical stability and the possibility of substituting Y^{3+} ions with other lanthanide ions, namely Nd^{3+} , Yb^{3+} , and Er^{3+} , it is a good material for laser applications. The nonlinear optical properties of this material along with lasing properties led to the fabrication of numerous systems generating red, green, and blue lights due to self-frequency doubling effect [17]. They also possess relatively large two-photon absorption. These compounds are promising candidate as second- and third-order optical materials [18]. At the same time they are good matrices for different rare-earth ions [19, 20]. Reports are also available on the Nd^{3+} -, Tb^{3+} -, Yb^{3+} -, and Er^{3+} -doped YAB crystals [21–23].

Further, in the family of borate crystals with huntite structure, research on crystals such as $\text{NdAl}_3(\text{BO}_3)_4$ (NAB), $\text{ErAl}_3(\text{BO}_3)_4$ (ErAB), or $\text{YbAl}_3(\text{BO}_3)_4$ (YbAB) is carried out in the present years [24]. The melting points of these materials are below 1300°C . These crystals are grown by flux techniques and are mainly employed in SFD purposes.

3.5. Rare-Earth Calcium Oxy Borate (RECOB) Crystals. The first member of the rare-earth calcium oxy borate (RECOB) crystals with the chemical composition of $\text{RECa}_4\text{O}(\text{BO}_3)_3$ (RE = Sm) was synthesized by Khamaganova and his coworkers in the year 1991 [25]. Later intense work on the growth and characterization of this family of crystals with various rare-earth elements such as La, Nd, Gd, Er, and Y were carried out and reported. The RECOB family of crystals appears to be attractive candidates for NLO applications as they possess the noncentrosymmetric structure which is an essential parameter for any NLO material. Widely studied RECOB crystals include YCOB, GdCOB, and LCOB crystals. The RECOB crystals with the rare-earth ions with electronic configurations $4f^n$, $n \neq 0, 7, 14$ give rise to electronic transitions in the visible region that would interfere with the expected NLO properties.

The RECOB crystals melt congruently and were conventionally grown by the Czochralski and Bridgman techniques of crystal growth. The melting temperatures of the RECOB crystals increase with a decrease in the ionic radii of the rare-earth ion present in it [26]. Accordingly, the melting points of LCOB, GdCOB, and YCOB single crystals are 1410, 1480, and 1510°C, respectively [27].

The RECOB single crystals exhibit the monoclinic crystal structure with the C_m space group. They are biaxial crystals. These crystals offer the advantage in providing suitable sites for doping them with “laser-active” ions, since the widely used “laser-active” ions such as neodymium, erbium, and ytterbium have similar ionic radii and occur in the trivalent state as that of the rare-earth ion present in the RECOB crystals [28, 29]. The flux growth of yttrium calcium oxy borate (YCOB) single crystals by flux technique was also carried out by our group earlier and reported [30]. The growth and characterization of pure and Nd^{3+} present lanthanum calcium oxy borate (LCOB) were performed and reported [31]. A comparison between YCOB, LCOB, and GdCOB crystals are summarized in Table 2.

3.6. Rare Earth Calcium Borate (RCB) Crystals. Another emerging borate-based crystal family is rare-earth calcium borate (RCB) crystals, with the general chemical formula $\text{R}_2\text{CaB}_{10}\text{O}_{19}$ (R represents rare-earth element). In this series of crystals, only crystal growth of pure and doped lanthanum calcium borate (LCB) are performed and reported in literature. There are no reports available on any other materials in the RCB family of crystals. The LCB crystal is reported to be insensitive to moisture, has high hardness (6.5 mhos), and is transparent from 180 nm to 3300 nm. Moreover, the laser damage threshold (LDT) value of the LCB crystal is also very high (11.5 GW/cm² for 1064 nm, 8 ns radiation) [32]. Various reports on “laser-active-” ion-doped LCB crystals are also available in literature [33].

4. Conclusion

Growth and material characteristics of several borate-based single crystals were discussed. Borate crystals are grown from melt and flux techniques. Anionic group theory plays an

essential theory for selecting borate materials for nonlinear optical applications. Several borate-based crystals act as desirable host materials for fabricating lasers. Borate crystals offer themselves as suitable candidates for both nonlinear optical and laser applications.

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