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# Nonlinear optical borate crystals principals and applications pdf

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Edited by the inventor and user of this optical borat crystal, it is an easily accessible reading for semiconductors, applied and solid state physicists, materials scientists, solid state chemists, optoelectronic device manufacturers, and those working in the optical industry. Preface INTRODUCTION History of the Theoretical Understanding for Nonlinear Optical Crystals History of Development on Nonlinear Optical Borate CrystalsS FOR FREQUENCY CONVERSION B LBO Family LBO KBBF Family Of Borate Borate Crystals Other in Developing Applications Of Fast Proto-Typing Semiconductor Industry - Bia Hole Drilling - Anil - Tagging - Bio-Medical Application Inspection - Eye Surgery - Advanced Protein Processing Instruments Make This Clear and The independent review of the last four decades of research highlights in the field of heat nonlinear optical crystals (NLO), especially ultraviolet-based borate and deep ultraviolet NLO crystals, covers three main subjects: structure-property relationships in borate crystals, the structural and optical characteristics of various promising borate crystals, and their fruitful applications in various scientific and technological fields. Edited by the inventor and user of this optical borat crystal, it is an easily accessible reading for semiconductors, applied and solid state physicists, materials scientists, solid state chemists, optoelectronic device manufacturers, and those working in the optical industry. Development of borate-based single crystals for laser conversion applications and frequency reviewed. The basic idea behind nonlinear optics and the role of anionic groups in boratic crystals is summarized. The properties of borate crystals—BBO, LBO, CBO, KBBF, SBBO, CLBO, YCOB, GdCOB, GdYCOB, KAB and LCB—are discussed. Growth and characterization of some rare earth-based borat crystals Focused. Some borate crystals are planted from melting techniques and some planted crystals adopt flux techniques. Many rare Earth-based borat crystals are widely used in device applications as they demonstrate frequency conversion capabilities along with high laser-induced damage tolerance.1. Introduction1.1. Demand for UV and Visible Radiation Laser development has played a key role in the last five decades for the development of mankind in various fields and to achieve some technological advances. The demand for laser light in ultraviolet areas and looks to grow very large. Laser beams in UV and visible regions find applications in multiple industries, medical operations, data storage, optical communication, and entertainment purposes. Advances in semiconductor photolithography, for example, created demand for coherent light sources of 158 and 193 nm, while the application of micromachining and processing of emerging materials also required deep-UV laser radiation. In addition, the research scientists want a coherent light source that can be broadly tuned up to 200 nm for laser spectroscopy and photochemical synthesis. Although laser excimers can emit multiple coherent light isolated wavelengths in UV and deep-UV spectral areas with high average output power, a compact and efficient solid-state laser with nonlinear optical crystals (NLO) in this spectral region is still required. Important solid-state benefits include narrow bandwidth, improved beam quality, suitability, and relative ease of handling. Solid-state laser performance in UV and deep-UV spectral areas depends heavily on efficient NLO crystals, such as UV crystals in borate that are being developed over the past two decades.1.2. Emphasis Review Current Recent developments in NLO borate crystals for high power laser radiation generation are visible and ultraviolet reviewed. The basic principles behind nonlinear optical materials are also addressed. Classification of boratic crystals based on the theory of anionic group is discussed. Some important aspects involved in the growth of borate crystals and their properties are also reviewed and presented. Borate-based NLO crystals are classified into three categories. (i) CBO, LBO, and CLBO crystals (ii)KBBF, SBBO, and KAB(iii) rare earth-based boratic crystals2. Nonlinear Optics and Borate Crystals2.1. Basic Principles of Nonlinear Optics A successful laser demonstration by Maiman and his co-workers in 1960 paved the way for various scientific and technological advances in the twentieth century. A new field—nonlinear optics—becomes. Franken and his co-workers were the first to realize the nonlinear optical effects when they observed light at twice the frequency of ruby lasers ( = 693.4 nm) of quartz crystals targeted by ruby laser radiation. Practical observations of nonlinear optical phenomena will not if the laser is not found. This can be explained as follows. The field strength of conventional light sources used before the advent of lasers is the sequence of 103 V/m. But the strength of the interatomic field lies in the range between 107 and 1010 V/m. Therefore, conventional light sources are very less intense at affecting atomic fields as far as changing the optical parameters associated with them. The unique nature of the laser, its coherence, helps in achieving radiation with a sequence intensity of 1010 V/m feasible. Therefore, lasers serve as useful and important tools in the field of nonlinear optics and other interesting related phenomena such as the Kerr effect, Pockels effect, second generation or higher harmonics, and so on. The origin of the NLO process is the response of nonlinear diaelectric media to oscillating electric fields. For example, when dielectric materials experience electromagnetic radiation (e.m), the tethering of e.m. waves through materials results in changes in the spatial and temporal distribution of electrical charges due to the interaction between e.m. waves, electrons, and atoms. This perturbation creates a polished electricity whose manifestation is macroscopic polarization (P). When the field of applied electricity (E) is very small, induced polarization can be expressed as, where is an empty space permit ( = 8,854 × 10−12 C2s2/kg m3) and is a term of linear vulnerability responsible for optical properties such as absorption, resuscation index, dispersion, and media birefringence. When the applied electric field is very intense and comparable to the interatomic field, the induced polarization is given by, where, is the nonlinear vulnerability of the second and third order and the amount decreases when their order increases ( : = 1 : = 1 : 10−8 : 10−16). The term second order vulnerability () gives rise to the second harmonic generation, the mixing of frequency and parametric generation and the third sequence vulnerability term () responsible for the third harmonic generation, the scattered Stimulated Raman, optical bistability, and phase conjugation. For the purpose of converting reliable laser frequencies, NLO crystals with the following properties are desirable: large NLO coefficients, moderate birefringence, small walk-off effects, angular bandwidth, spectral and large temperatures, wide transparency in wavelengths of interest, high laser-induced damage thresholds, ease of growth, low material costs, good chemical stability, and good mechanical stability. Until 1975, extensive research on NLO crystals based on P–O, I–O, and Nb–O bonds was conducted. Widely studied NLO crystals include KDP (KH2PO4), LN (LiNbO3), LiIO3, and so on when they meet the requirements listed above to a good degree. With the advent of potassium pentaborate, KB5O8 4H2O, crystals in 1975, tremendous attention was directed to growing borate-based crystals for frequency purpose.2.2. Nonlinear Optical Borate Crystals Large family of borate compounds is a suitable chemical playground now adopted by many materials scientists, since the very wide variability of borate crystal chemistry allows the creation of different types of structures[2]. In addition, among all the borate structures reported to date, 36% are noncentrosymmetric, while among the reported inorganic crystal structures there are only 15% non-centrosimtic structures[3]. Borate crystals are superior in UV applications with other commonly used NLO materials such as potassium in hydrogen phosphate (KDP) or lithium niobate (LN) due to their high transmission at wavelengths of up to 155 nm combined with higher damage thresholds. A comparison of the selected NLO material is given in Table 1. The first boratic crystal described for UV light generation was potassium pentaboration (KB5O8 4H2O) [4]. However, intense research work on borate crystals began only after the development of β-BaB2O4 (BBO) and LiB3O5 (LBO). There are several borate crystals available today that meet the needs of the optical industry [5–10]. CrystalsSpace groupTransparency range (nm)Shortest SHG (nm)Basic structure unitβ-BaB2O4 (BBO)R 3c190–3300205B3O6LiB3O5 (LBO)Pnn 21160–2600277B3O7CsB3O5 (CBO)P212121167–3400273B3O7KBe2BO3F2 (KBBF)R 32155–3660185BO3Sr2Be2BO7 (SBBO)P 63155–3780200BO3CsLiB6O10 (CLBO)142 d180–2750237B3O7 The optical properties of borate crystals can be related to their molecular structure. Some borate crystals are mentioned in Table 1 as examples. These crystals are constructed from three basic structural units: (B3O6)3−, (B3O7)5−, and (BO3)3− anionic groups. Anionic groups (B3O6)3−, (B3O7)5−, and (BO3)3− are displayed in Figure 1. The so-called anionic group theory was designed by Chen and his co-workers and used to understand the relationship between composition, structure of borate materials, and related NLO properties. (a) (b) (c) (a) (b) (c) Due to the planar hexagonal structure of the anionic group (B3O6)3−, the boric crystals built from this base unit are larger than the crystals consisting of (B3O7)5− and (BO3)3− anionic groups. Thus in the case of the NLO coefficient, the group (B3O6)3− is the most suitable as a unit of the base structure of the NLO borate crystal followed by (B3O7)5− group and then (BO3)3− group. However, uv absorption edges of borate crystals built from groups (B3O6)3− occur at longer wavelengths (e.g., BBO) when compared to those built from (B3O7)5− groups (e.g., LBO, CBO, CLBO). Calculations show that π conjugated planar (B3O6)3− π tend to shift the edges of UV absorption towards red. As one of the boron atoms in (B3O6)3− changes from trigonal to tetrahedral coordination, thus forming a nonplanar group (B3O7)5−, the π-conjugation orbital system weakens, as in the case of LBO and CBO and edges UV shifts to 160–170 nm. Both CBO and LBO LBO of nonplanar sustainable tissue (B3O7)5− groups with intersitial cesium and lithium cathec, respectively. Based on the advantages of absorption, therefore, (B3O7)5− the group is ideal as a basic structural unit of deep-UV NLO material. Likewise, if the dangling bonds of the three oxygen atoms are stopped from the (BO3)3− group associated with the cation, the absorption edge appears at wavelengths as short as 155 nm is also feasible as in cases with KBBF and SBBO.3. NLO Borate Crystals3.1. CBO, LBO, and CLBO CrystalsThere are a large number of jobs on csb3o5 crystals (CBO) and LiB3O5 (LBO) with flux techniques for the fourth and fifth generation harmonic Nd: YAG lasers. Another derivative of LBO is CsB3O5 (CBO). The CBO compound melts simultaneously at 842 °C. Crystals with dimensions diameter of 20 mm and length of 30 mm are planted at a tensile rate of 8 mm/day. In general, good NLO crystals that can produce deep-UV rays are effectively required to have birefringence between BBO (Δn = 0.12 at ττ = 1064 nm) and LBO (Δn = 0.04 at τ = 1064 nm). This property enables the expansion of the phase matching range for SHG with a fairly low walk-off effect and very large phase matching bandwidth. The previously mentioned CLBO crystal has Δn = 0.052 at ττ = 1064 nm and hence, is widely used for deep-UV light conversion. Thus some NLO crystals such as CLBO that have birefringence between BBO and CLBO are desirable. CsLiB5O10 crystals (CLBO), which are structural derivatives of LBO crystals, are planted in dimensions larger than their melt. A very large CLBO single crystal with dimensions of 140 × 110 × 110 mm3 with good optical quality grows and is reported [12].3.2. KBBF, SBBO, and KAB Crystals Isostructural Crystals SrB4O7 and PbB4O7, both of which are included in the orthorhombic crystal system are planted from their melting. Large single crystal PbB4O7 is planted by czochralski technique of melting with little excess PbO to lower melt viscosity at 774°C. Seed crystals with or orientation are preferred for single crystal growth. Growth is running, with a cooling rate of 0.7°C/day and a tensile rate of 4 mm/day has produced a single crystal with 20 × 28 × 55 mm3 dimensions. In the same way, a single crystal SrB4O7 is planted from stoichiometric melt at 994°C. Single crystals with a diameter of 25 mm and a length of 20 mm are planted using a tensile rate of 2 mm/day with a crystal rotation of 20 rpm. Intense research on incongruently melted borate crystals is also underway. Due to the fact that some borate materials that melt in harmony are transparent to the vacuum-UV region, the growth of a single crystal of these materials is carried out. The MBe2BO3F2 family, with M=Na, K, is an example of a structure type with an isolated [BO3] triangle, crystallized in the R32 noncentrosymmetric space group. Compounds KBe2BO3F2 (KBBF) was first synthesized in 1968. This is It growing from melting flux with KBF4 and BeO. Plate-like crystals with dimensions of 10 × 10 × 0.3 mm3 are reported. An increase in the NLO property by increasing the number of active NLO groups [BO3] per volume of crystal structure units is attempted by creating Sr2Be2B2O7 (SBBO). These crystals show a hexagonal crystal system and are planted by the TSSG technique. These crystals are planted with slow cooling at a cooling rate of 1-2°C/day. Crystals with dimensions of 7 × 7 × 3 mm3 with good optical quality are obtained and reported. SBBO crystals (Δn = 0.062 at ττ = 589 nm) and KBBF crystals (Δn = 0.072 at ττ = 589 nm) are interesting candidates in this aspect. However, due to weak binding between layered structural units, KBBF is difficult to grow and mechanically fragile. SBBO has a strong covalent bond between beryllium atoms and oxygen atoms in adjacent layers. This makes SBBO mechanically stronger and relatively easy to grow than KBBF. However, beryllium is toxic, which makes the growth of crystals uncomfortable. Thus, it is important that atom be in SBBO is replaced by nontoxic elements. Sasaki and her co-workers have attempted to replace (BeO4)6− with (AlO4)5− and have replaced Sr2+ with M+ (M+ = Li+, Na+, K+, Rb+ and Cs+) in accordance with the ionic compensation concept (Al3+ + K + → Be2+ + Sr2+). In this way, potassium aluminum boric crystals with the chemical formula K2Al2B2O7 (KAB) were found. KAB has a similar layout to SBBO. Trigonal KAB crystal structure with P321 space group. The crystal lattice parameters are =b=8.5657 Å, c=8.463 Å, V=537.7 Å3, and Z=3[14]. KAB crystals are grown from flux techniques. Different fluxes such as B2O3, K2CO3, and K2CO3–B2O3, alkaline halides such as KF and NaF are used for kab crystal growth and are reported. Transparent KAB crystals from 180–3600 nm. The thermal properties of KAB crystals were also studied. The linear thermal expansion coefficient of KAB crystals along the x, y, and z directions is greatly lacking. Kab crystal specific heat values at 47.6 °C and 294.6°C are 1.0084 J/g °C and 1.39 J/g °C [15].3.3. Rare-Earth-based Borate CrystalsBorate crystals have not only been used for frequency conversion applications but also as a source of self-contained frequency multiplier (SFD) active lasers in recent years. Rare earth-based borat crystals are used for both NLO and SFD.3.4 applications. Huntite Family Crystal Family borate crystals with common chemical formulas, RAl3(BO3)4 with R=Y, Nd, Sm, Eu, Tb, Dy, Er, and RX3(BO3)4 with R=Gd, Sm, X=Cr, Al are referred to as huntite family crystals. The emission of sharp bright lines from these crystals is observed. These crystals are chemically stable, nonhygroscopic, and have high hardness. These crystals melt in harmony and are planted from flux methods only. All these crystals are trigonal with the R32 space group. Tje studying huntite-type borate crystals is YAl3(BO3)4 (YAB) [16]. These crystals are processed with Er, Nd, and Yb ions to make them as SFD crystals. This is generally planted with the top seeded solution growth (TSSG) method. YAB is a noncentrosymmetric crystal and as of early 1974, it was reported to be a highly effective harmonic second generating material. In addition, due to its good chemical stability and possible replacement of Y3+ ions with other lanthanide ions, namely Nd3+, Yb3+, and Er3+, it is a good material for laser applications. The nonlinear optical properties of this material along with the lash properties led to the fabrication of many systems resulting in red, green, and blue lights due to the effect of self-frequency multiplication[ 17]. They also have a relatively large absorption of two photons. This compound promises candidates as optical materials in the second and third place. At the same time they are a good matrix for different rare ions [19, 20]. Reports are also available on YAB Nd3+-, Tb3+-, Yb3+-, and Er3+-doped crystals [21–23]. Furthermore, in the borate crystal family with huntite structure, crystal research such as NdAl3 (BO3)4 (NAB), ErAl3(BO3)4 (ErAB), or YbAl3(BO3)4 (YbAB) was conducted in the current years[ 24]. The melting point of these ingredients is below 1300 °C. These crystals are grown by flux techniques and are mainly used in the purpose of SFD.3.5. Calcium Crystal Calcium Oxy Borate (RECOB) Rare-EarthCrysKrik The first member of a rare calcium oxy borate (RECOB) crystal with the chemical composition RECa4O(BO3)3 (RE = Sm) synthesized by Khamaganova and his co-workers in 1991[ 25]. Then intense work on the growth and characterization of this crystal family with various rare earth elements such as L.A., Nd, Gd, Er, and Y was done and reported. The RECOB crystal family seems to be an attractive candidate for NLO applications because they have a noncentrosymmetric structure which is an important parameter for any NLO material. Widely studied RECOB crystals include YCOB, GdCOB, and LCOB crystals. RECOB crystals with rare-earth ions with an electronic configuration of 4, give rise to electronic transitions in visible regions that would interfere with the expected nature of NLO. RECOB crystals melt simultaneously and are conventionally grown by czochralski and bridgman crystal growth techniques. Recob crystal melting temperatures increased with a decrease in the radii of rare Earth ions in them. Thus, the single crystal melting points of LCOB, GdCOB, and YCOB are 1410, 1480, and 1510 °C, respectively. Recob's single crystal shows the monoclinical crystal structure with the space group. They are breeding crystals. These crystals offer an advantage in providing a suitable site for doping them with laser-active ions, as widely used laser-active ions such as neodymium, erbium, and ytterbium have similar ionic radii and occur trivalent states such as rare earth ions found in RECOB crystals [28, 29]. The growth of single crystalline flux yttrium calcium oxy borate (YCOB) with flux technique was also carried out by our previous group and reported [30]. Pure growth and characterization and Nd3+ now lanthanum calcium oxy borate (LCOB) performed and reported [31]. Comparison between YCOB, LCOB, and GdCOB crystals summarized in Table 2.PropertiesYCOBGdCOBLCOBUnit cell parameters Å Å Å Å Å Å Å Å ÅBond angle Crystal systemMonoclinicMonoclinicMonoclinicMonoclinicSpace group Hygroscopicity Nonhygroscop NonhygroscopicNonhygroscopicTransparency range 220–3600 nm320–2700 nmAbove 210 nmMelting point1510°C1480°C1410°C3.6. Rare Earth Calcium Borate (RCB) CrystalsAnother appears the borate-based crystal family is a rare-earth calcium boratic crystal (RCB), with the common chemical formula R2CaB10O19 (R representing rare-earth elements). In this series of crystals, only pure and doped growth of lanthanum calcium borate (LCB) crystals is performed and reported in literature. There are no reports available on other materials in the RCB crystal family. LCB crystals are reported to be insensitive to moisture, have high hardness (6.5 mhos), and are transparent from 180 nm to 3300 nm. In addition, the laser damage threshold (LDT) value of LCB crystals is also very high (11.5 GW/cm2 for radiation of 1064 nm, 8 ns) [32]. Various reports of laser-active ion-doped LCB crystals are also available in the literature[33].4. Growth conclusions and material characteristics of multiple single borate-based crystals are discussed. Boratic crystals are grown from melting and flux techniques. Anionic group theory plays an important theory for selecting borate materials for nonlinear optical applications. Some borate-based crystals act as the desired host material for making lasers. Borate crystals offer themselves as suitable candidates for nonlinear optical and laser applications. The Author's Recognition thanks the Science and Engineering Research Board (SERB), Department of Science and Technology (DST), Government of India, for providing the Major Research Project to work on a single borate-based crystal. Hak © 2013 R. Arun Kumar. 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