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Review

Recent advances in ultraviolet and deep-ultraviolet second-order nonlinear optical crystals

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ABSTRACT

Second-order nonlinear optical (NLO) crystals functioning in the ultraviolet (UV) and deep-ultraviolet (deep-UV) regions are critically important as frequency conversion materials for all-solid-state UV laser devices. In this review, we focus on recent studies of inorganic UV and deep-UV NLO crystals with wide UV transparency and SHG efficiency. Following an introduction describing crystal-design strategies for UV and deep-UV NLO materials, the manuscript is organized according to the type of inorganic anions (borates, carbonates, nitrates and phosphates). Special attention is given to the crystal structures, second-order NLO properties, and structure–property correlations. The concluding remarks highlight future prospects in the field, with emphasis on the superiority of the different types of UV and deep-UV NLO crystals and the importance of large-size crystal growth for practical application in electro-optic devices.

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1. Introduction

Coherent light generated by solid-state lasers is used in a wide variety of fields ranging from medical therapies to materials processing as well as information communication [1–3]. However,

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the wavelengths required for these applications cannot always be generated directly from a laser source, and so second-harmonic generation (SHG) from nonlinear optical (NLO) materials is an essential alternative means to afford the necessary wavelengths [4,5]. With this requirement in mind, the SHG-activity of a large number of inorganics, organics, organometallics, inorganic–organic hybrids, polymers and inorganic glasses have been investigated to date [6–10]. These second-order NLO-active materials are usually classified into four categories according to their working wavelength ranges in the spectrum: deep-ultraviolet (deep-UV, $\lambda < 200$ nm), ultraviolet (UV, $\lambda < 400$ nm), visible-near infrared (Vis-NIR), mid- and far-infrared (MFIR) materials. Amongst the materials under active current study, UV and deep-UV NLO crystals are attracting considerable attention for applications in, for example, semiconductor photolithography, laser micromachining, and scientific instrumentation [11–20,30]. The discovery and commercialization of second-order NLO inorganic crystals, such as β -BaB₂O₄ (β -BBO) [11,12], LiB₃O₅ (LBO) [13,14], CsLiB₆O₁₀ (CLBO) [15,16], CsB₃O₅ (CBO) [17,18], KBe₂BO₃F₂ (KBBF) [19,20] has progressed recently, but disadvantages have limited their practical use in optoelectronic devices. There remain great challenges to the development of new crystals that can directly generate UV or deep-UV coherent light by SHG, and the study of NLO crystals with high-performance SHG responses is therefore an important and high-profile topic in solid-state chemistry and laser technology [21,22].

From the perspective of crystal structure, promising second-order NLO crystals should crystallize in noncentrosymmetric (NCS) space groups. Several strategies towards the creation of novel NCS crystals that contain NCS chromophores have been developed [23], such as the use of anions in π -delocalized systems, transition-metal cations with d^0 electron configurations susceptible to second-order Jahn–Teller (SOJT) distortions, stereochemically-active lone-pair (SCALP) cations, and d^{10} transition-metal cations with polar displacements [24–28].

NLO-active crystals that can be used in the UV and deep-UV regions require a large transparency window (i.e., a wide bandgap), large SHG coefficients, moderate birefringence, chemical stability and facile growth of large single crystals [29,30]. The planar [BO₃]³⁻ and isoelectronic anions such as [NO₃]⁻ and [CO₃]²⁻, which possess moderate birefringence and large microscopic second-order hyperpolarizabilities β , are believed to be the most favorable anionic units for UV and deep-UV candidates [31,32]. Phosphates have attracted attention as potential UV and deep-UV NLO candidates in recent years due to their wide UV transparency and the ease with which one can grow bulk crystals [33]. As far as the metal cations are concerned, alkali and alkaline-earth cations with no d - d or f - f electronic transitions and rare-earth cations with fully-occupied d ($3d^{10}$) or half-occupied f ($4f^7$) electronic shells are commonly used in the pursuit of UV and deep-UV NLO crystals [34]. The introduction of halogens has been shown to influence crystal structure and cause a blue shift in the UV absorption spectra [35].

BBO and LBO were discovered in the 1980s [11–14]. These two crystals exhibit excellent NLO performance in both the visible and the UV regions. Nevertheless, the relatively narrow energy bandgap ($E_g = 6.5$ eV, $\lambda = 190$ nm) in BBO and the small birefringence value ($\Delta n = 0.04@400$ nm) in LBO restrict their applications in the deep-UV region. KBe₂BO₃F₂ (KBBF) [19,20,36] and thereafter RbBe₂BO₃F₂ (RBBF) [36,37] and CsBe₂BO₃F₂ (CBBF) [36,38] were developed through molecular engineering design. The KBBF family possesses almost the same absorption edge (150 nm), moderately large SHG coefficients, and large birefringence. The shortest SHG phase-matching wavelength in KBBF is 161 nm, while in RBBF and CBBF it red-shifts to 170 nm and 201 nm, respectively. However, the KBBF family of crystals exhibits a serious layering tendency during single-crystal growth due to their weak interlayer

bonding, while the need for highly toxic beryllium oxide powders in the synthesis and crystal growth remains a major obstacle to their broader technological application. Further study directed to next-generation NLO crystals with good UV (and especially deep-UV) NLO performance is urgently needed.

This review highlights recent progress in the construction of second-order NLO inorganic crystals that are active in the UV and deep-UV regions, with a particular focus on their crystal structures, SHG properties, and structure–property relationships. Well-known NLO-active crystals such as β -BaB₂O₄ (BBO) [11,12], LiB₃O₅ (LBO) [13,14], CsLiB₆O₁₀ (CLBO) [15,16], CsB₃O₅ (CBO) [17,18], Sr₂Be₂B₂O₇ (SBBO) [39], and KBe₂BO₃F₂ (KBBF) [34] have been extensively studied and commercialized, so they are not the focus of this review [40]. For the convenience of discussion, NLO crystals functioning in the UV and deep-UV regions are classified into four categories according to the anions: (1) metal borates, (2) metal carbonates, (3) metal nitrates, and (4) metal phosphates. We conclude the review by identifying the current critical challenges that impede the progress of the different types of UV and deep-UV NLO-active crystals into practical applications.

2. Metal borates

Combinations of [BO₃] planar triangles and [BO₄] tetrahedra give rise to a diverse array of borate structures. These compounds possess several interesting features. The large difference in electronegativity of the boron and oxygen atoms favors transmission of short-wavelength light, while the conjugated π -orbitals and highly anisotropic electron distribution in the [BO₃] groups is beneficial for the generation of large microscopic second-order susceptibilities and birefringence [41,42]. It has also been noted that elimination of dangling bonds at the oxygens in the B–O groups can effectively increase the energy bandgap and blue-shift the absorption edge of borate crystals [43]. SHG-active metal borates can be classified into four categories based on their chemical composition: (1) metal borates without additional anions; (2) metal borates containing halides; (3) metal hydrated borates; (4) metal borates with mixed anions.

2.1. Metal borates without additional anions

Metal borates that do not possess additional anions are listed in Table 1. NaBe₃O₆ (**1**) (space group $Pna2_1$), β -KBe₂B₃O₇ (**2**) ($Pmn2_1$), γ -KBe₂B₃O₇ (**3**) ($P2_1$), and RbBe₂B₃O₇ (**4**) ($Pmn2_1$) were obtained from high-temperature solution syntheses using alkaline borates as the flux [44]. The solid-state structure of **1** contains nearly coplanar fused six-membered rings [Be₂B₃O₁₁] connected by [BeO₄] units. **2** and **4** are isostructural and, similar to **3**, contain [Be₂B₃O₁₁]_∞ layers that are linked by B–O groups (Fig. 1). The strong connections in these compounds provided by the covalent bonds between the layers may reduce the tendency for growth by layering that has hindered the applications of KBBF crystals. The absorption edges are below 200 nm for all four compounds. The phase-matchable SHG responses of **1–4** are about 1.6, 0.75, 0.68 and $0.79 \times$ KDP, respectively; the small SHG responses likely stem from the significant distances between the adjacent [Be₂B₃O₁₁]_∞ layers in **2–4** which reduce the density of [BO₃] groups.

To reduce the interlayer spacing in beryllium borates and thereby increase the density of SHG-active [BO₃] groups, Na₂CsBe₆B₅O₁₅ (**5**) (C2) [45], Na₂Be₄B₄O₁₁ (**6**) (P1) [46], and LiNa₅Be₁₂B₁₂O₃₃ (**7**) (Pc) [46] were grown by spontaneous crystallization from a molten flux based on Na₂O–Cs₂O–B₂O₃, Na₂O–BeO–B₂O₃ and Li₂O–Na₂O–BeO–B₂O₃, respectively. Their structures also feature [Be₂B₃O₁₁]_∞ layers that are bridged by

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