

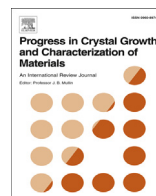


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# Progress in Crystal Growth and Characterization of Materials

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## Review

# Recent advances in rare earth-based borate single crystals: Potential materials for nonlinear optical and laser applications



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## A B S T R A C T

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Nonlinear optical materials  
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Optical transmission  
Second harmonic generation  
Laser damage threshold

Due to an increase in the requirement for ultraviolet and visible laser sources nonlinear optical crystals are gaining importance. Borate-based nonlinear optical crystals such as lithium borate  $\text{LiB}_3\text{O}_5$  (LBO),  $\text{CsLiB}_5\text{O}_{10}$  (CLBO),  $\text{SrBe}_2\text{B}_2\text{O}_7$  (SBBO),  $\text{KBe}_2\text{BO}_3\text{F}_2$  (KBBF) and  $\text{K}_2\text{Al}_2\text{B}_2\text{O}_7$  (KAB) have excellent transmission ranges extending from the ultraviolet into the infrared region. But their hygroscopic nature retards their use in real-time applications. Rare earth-based borate crystals such as rare earth calcium oxy borate  $\text{RECa}_4\text{O}(\text{BO}_3)_3$  (RECOB) and rare earth calcium borate  $\text{RE}_2\text{CaB}_{10}\text{O}_{19}$  (RECB) have excellent nonlinear optical behaviour and also allow the substitution of 'laser-active' ions to create 'laser crystals'. Further they are non-hygroscopic which favours them in practical applications. A review on RECOB and RECB crystals is presented along with a discussion on our attempts to grow yttrium calcium oxy borate  $\text{YCa}_4\text{O}(\text{BO}_3)_3$  (YCOB), lanthanum calcium oxy borate  $\text{LaCa}_4\text{O}(\text{BO}_3)_3$  (LCOB), yttrium calcium borate  $\text{Y}_2\text{CaB}_{10}\text{O}_{19}$  (YCB) and lanthanum calcium borate  $\text{La}_2\text{CaB}_{10}\text{O}_{19}$  (LCB) crystals. These crystals possess excellent transmission properties combined with nonlinear optical behaviour. They also exhibit high laser damage threshold (LDT) values.

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## 1. Introduction

Soon after the demonstration of the first laser in 1961, Franken and his co-workers observed the second harmonic generation (SHG) of a ruby laser beam when passed through a quartz crystal [1]. Since then, intense work began in developing new materials for nonlinear optical (NLO) applications. The advantage of NLO materials in expanding the frequency range provided by the conventional laser sources was identified to be a major advantage. Nowadays, NLO materials find a variety of applications in surgery, signal processing, data communications and entertainment purposes [2].

The application of NLO crystals is required in all frequency ranges, but their demand in producing laser beams in the ultraviolet (UV) and visible regions is growing enormously. Lasers in the UV and visible regions find applications in several industries including micro-precision machining, performing atomic and molecular spectroscopy-based characterization, data storage devices, cosmetic dentistry, and so on. In addition, scientists also require a widely tunable coherent light source down to 200 nm for laser spectroscopy and photochemical synthesis. Green lasers are used in projection displays, printing, interferometers, bioinstrumentation, medical scanning, and for pumping solid-state lasers (eg. titanium-sapphire lasers), and etc [3]. In materials processing, green lasers when compared with near-infrared lasers can bring benefits through their much higher absorption coefficient e.g. in copper, gold. Green lasers are efficiently being produced by the second harmonic generation of Nd:YAG laser using NLO crystals.

Various modes for generating UV and visible lasers are being exploited. Excimer lasers can emit wavelengths of coherent light in the UV and deep-UV spectral region with a high average output power. But the use of excimer lasers involves corrosive gases and is bulkier in dimension. In addition, it requires complicated maintenance procedures. But compact and efficient solid-state lasers with NLO crystals in this spectral region are still needed [4]. The important benefits of solid-state lasers 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 to a great extent on efficient NLO crystals with better optical properties. NLO crystals with tailored structures to achieve the desired wavelengths of interest are gaining importance over the past three decades. Among the category of NLO crystals, several families exist [5], and in this review the advantages of the borate family is considered.

### 1.1. Emphasis of the present review

The latest advances in NLO borate crystals for the generation of high power visible and ultraviolet laser radiations are reviewed. In addition to their frequency conversion applications, rare earth-based borate crystals are also finding preferred use as laser crystals, since they provide suitable sites for 'laser-active' ion doping [6]. Leonyuk et al. have made pioneering attempts to grow rare earth-based borate crystals [7,8]. Crystals with the general chemical formula  $RAI_3(BO_3)_4$  (RAB) were synthesized and grown using the flux technique by their group. Laser emission from  $Nd_xGd_{(1-x)}Al_3(BO_3)_4$  crystal was successfully demonstrated by them [8]. Later research on the RAB family of crystals gained momentum and today several publications are available on such crystals [9,10]. In the present review, the growth and the properties of rare earth-based borate crystals are mainly focussed. Few important aspects involved in the growth of these crystals and their properties are also reviewed and presented. The rare earth borate-based NLO crystals are classified into two categories, in the present review.

- i.  $RECa_4O(BO_3)_3$  (RECOB, RE-Rare earth) crystals
- ii.  $RE_2CaB_{10}O_{19}$  (RECB, RE-Rare earth) crystals

Our recent results involving the growth and systematic analysis of yttrium calcium oxy borate  $YCa_4O(BO_3)_3$  (YCOB), lanthanum calcium oxy borate  $LaCa_4O(BO_3)_3$  (LCOB), lanthanum calcium borate  $La_2CaB_{10}O_{19}$  (LCB) and yttrium calcium borate  $Y_2CaB_{10}O_{19}$  (YCB) are also presented.

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