

Crystal growth, NCPM second harmonic generation, and infrared laser performance for SFD in $\text{Gd}_{1-x-y}\text{R}_x\text{Nd}_y\text{Ca}_4\text{O}(\text{BO}_3)_3$ (R = Sc or Lu) crystals

L. GHEORGHE^{*}, G. AKA^a

National Institute R&D for Laser, Plasma and Radiation Physics, Laboratory of Solid-State Quantum Electronics, P.O. Box MG 36, 077125, Bucharest-Magurele, Romania

^aEcole Nationale Supérieure de Chimie de Paris, LCMCP, CNRS-UMR 7574, 11 rue Pierre et Marie Curie, 75005 Paris, France

Nonlinear optical borate crystals of $\text{Gd}_{1-x-y}\text{R}_x\text{Nd}_y\text{Ca}_4\text{O}(\text{BO}_3)_3$ crystals with large size and good quality have been grown from the melt by the Czochralski pulling method. The chemical compositions of the grown crystals were determined and nonlinear optical properties of these new biaxial crystals are reported. According to our assumptions, the obtained results demonstrate that the grown crystals convert the near infrared radiation of ~ 936 nm into blue light (~ 468 nm) by type-I noncritical phase matching (NCPM) second harmonic generation (SHG) processes along Z axis. Preliminary investigations of self frequency doubling (SFD) processes in $\text{Gd}_{1-x-y}\text{R}_x\text{Nd}_y\text{Ca}_4\text{O}(\text{BO}_3)_3$ crystals have been carried out.

(Received November 17, 2010; accepted November 29, 2010)

Keywords: Crystal growth, Nonlinear optical materials, Noncritical phase matching, Second harmonic generation

1. Introduction

Extensive development of diode-pumped solid state lasers continuously triggers the search for new laser materials operating in the blue range which are of interest for various applications including high-density data storage, photo-therapy, medical diagnosis, etc. One way to obtain such coherent beams is by using frequency doubling of diode-pumped solid state lasers operating in the near infrared range.

Nonlinear optical (NLO) frequency conversion was demonstrated for the first time in 1961 by directing an incident laser beam generated from ruby ($\text{Cr}^{3+}:\text{Al}_2\text{O}_3$) propagated through a quartz ($\alpha\text{-SiO}_2$) crystal. Two light beams were observed. One beam was the original incident ruby laser with the wavelength of 694.3 nm and the other one was the newly produced ultraviolet light with the wavelength of 347.2 nm, which has two times the frequency of ruby laser [1]. In the following four decades, many NLO crystals were discovered. However, not all of them are good enough for practical applications. Some of the more important nonlinear oxide crystals that are used in current commercial applications include KTiOPO_4 (KTP) [2], KH_2PO_4 (KDP), $\beta\text{-BaB}_2\text{O}_4$ (BBO) [3], LiB_3O_5 (LBO) [4] and periodically poled LiNbO_3 (PPLN) [5], etc. All of them are used for frequency conversion with a compatible laser system. Despite of the wider usage, essentially all of these crystals melt incongruently with the exception of LiNbO_3 , so they all have to be grown by flux method, which makes them expensive, limited in size. Sometimes, even the crystal purity is questionable. The requirements to be an excellent NLO crystal include high

nonlinear coefficient, large birefringence for phase matching, high transparency for the wavelengths of interest, non-hygroscopic, high optical damage threshold, high thermal conductivity, and good mechanical properties. Finally, the feasibility to produce large crystals at low cost is also highly desirable. So, the invention of new NLO crystals is a very interesting and important task in material research.

Experimental results show that borate crystals are a very vast and useful family for NLO crystal research [6]. In recent years, many kinds of new borate NLO crystals have been developed, such as $\text{CsLiB}_6\text{O}_{10}$ (CLBO), BiB_3O_6 (BiBO), $\text{K}_2\text{Al}_2\text{B}_2\text{O}_7$ (KABO), $\text{KBe}_2\text{BO}_3\text{F}_2$ (KBBF), $\text{RECa}_4\text{O}(\text{BO}_3)_3$ - RECOB (RE = Gd, Y, La) [6-12]. Among them, the monoclinic gadolinium calcium oxoborate (GdCOB) can be grown with large dimensions and high optical quality by the Czochralski method, and is an efficient NLO crystal to be used as frequency converter in solid state laser systems [11, 13]. Moreover, Nd^{3+} doped GdCOB has shown good properties both as a laser crystal and as a self frequency doubling (SFD) crystal, combining the active laser medium and the nonlinear frequency conversion medium into a single crystal. Mougel [14] have achieved 114 mW of green light from a laser diode pumped Nd: GdCOB laser. Previously, it was found that the substitution of the trivalent Gd^{3+} cations with smaller radius cations lead to larger optical birefringence [10]. Our previous researches showed that in GdCOB crystal, the Gd^{3+} cations can be partially substituted by smaller radius ions Sc^{3+} or Lu^{3+} in order to tune the chemical composition of the crystal [15]. It was demonstrated that by changing the compositional parameter x of $\text{Gd}_{1-x}\text{R}_x\text{Ca}_4\text{O}(\text{BO}_3)_3$ (R =

Lu, Sc) crystals, their optical birefringence can be controlled in order to achieve second harmonic generation (SHG) in noncritical phase matching (NCPM) conditions of specific near infrared laser emission wavelengths shorter than phase matching cutoff wavelength of GdCOB crystal (824 nm along Y axis and 963 nm along Z axis at room temperature [11]).

For biaxial crystals like GdCOB family compounds, NCPM is the phase matching along one principal axis of the crystal, and for frequency conversion applications, NCPM is advantageous because of its large angular acceptance and because it eliminates spatial walk-off between fundamental and harmonic radiations which leads to the highest efficiency.

Since NCPM is determined by the optical birefringence and is accomplished to a unique wavelength for each NLO process, the objective of this study is to investigate the laser emission around 1060 nm of Nd^{3+} doped $\text{Gd}_{1-x}\text{R}_x\text{Ca}_4\text{O}(\text{BO}_3)_3$ ($\text{Gd}_{1-x-y}\text{R}_x\text{Nd}_y\text{Ca}_4\text{O}(\text{BO}_3)_3$ - $\text{Gd}_{1-x-y}\text{R}_x\text{Nd}_y\text{COB}$) crystals and to evaluate the potential of new nonlinear $\text{Gd}_{1-x-y}\text{R}_x\text{Nd}_y\text{COB}$ crystals as frequency converters for the self laser emissions around 936 nm, in order to obtain blue (~ 468 nm) laser radiation by type-I NCPM SFD processes at room temperature.

In this aim, crystal growth, NCPM frequency conversion properties and laser emission characteristics of $\text{Gd}_{1-x-y}\text{R}_x\text{Nd}_y\text{Ca}_4\text{O}(\text{BO}_3)_3$ crystals are reported in this work.

2. Experimental

$\text{Gd}_{1-x-y}\text{R}_x\text{Nd}_y\text{COB}$ compounds were prepared by classical solid state reaction. Chemicals of Gd_2O_3 , Nd_2O_3 , CaCO_3 , B_2O_3 , Lu_2O_3 , and Sc_2O_3 of 99.99% purity were used as starting materials. The oxide mixtures, weighing in stoichiometric ratio, were ground, mixed and pressed into tablets, then heated at 900°C for 18h to decompose CaCO_3 completely. They were then ground, mixed and pressed again, and then heated at 1350°C for 24h. Two single crystals of $\text{Gd}_{0.835}\text{Lu}_{0.095}\text{Nd}_{0.07}\text{COB}$ and $\text{Gd}_{0.73}\text{Sc}_{0.20}\text{Nd}_{0.07}\text{COB}$ (starting compositions), were grown using the conventional radio frequency (RF) heating Czochralski method from iridium crucibles under nitrogen atmosphere.

Chemical compositions of the grown crystals were determined by microprobe analysis by the central service of the microanalysis of "Centre National de la Recherche Scientifique (CNRS)" from Vernaison, France. For experimental determination of the doubled frequencies along the Y and Z crystallophysic axes, an optical parametric oscillator (OPO) pumped at 355 nm (triple harmonic of a 10 Hz, 7 ns, Q-switched YAG: Nd laser) was used as pump source.

A Cary 5 spectrophotometer from Varian Associates was used to record the optical absorption spectra of the grown crystals at room temperature. The spectra were recorded with different polarizations of incident light. The emission spectra were obtained with a continuous waved (cw) Ti: sapphire laser (Coherent 890) pumped with an

argon ion laser (Coherent Innova 90). The spectra were analyzed with an ARC Spectrapro-750 monochromator and detected with a cooled InGaAs photodiode. We used a Glan-Thomson calcite polarizer before the entrance slit of the spectrometer to select the polarization of the digitally recorded spectra. Laser performances of $\text{Gd}_{0.835}\text{Lu}_{0.095}\text{Nd}_{0.07}\text{COB}$ and $\text{Gd}_{0.73}\text{Sc}_{0.20}\text{Nd}_{0.07}\text{COB}$ crystals samples of different lengths were investigated using a plane-concave laser resonator end pumped with a cw Ti: sapphire laser.

3. Crystal growth

Based on our previous results [15, 16], the calculation regarding the relationship between the compositional parameters x and y and the NCPM wavelengths along Z axis, revealed that is possible to obtain room temperature type-I NCPM SHG of the 936nm wavelength using GdCOB crystals doped with small amounts of Sc or Lu ions and co-doped with Nd^{3+} ions ($\text{Gd}_{1-x-y}\text{R}_x\text{Nd}_y\text{COB}$ type crystals). In this order, two single crystals of $\text{Gd}_{0.835}\text{Lu}_{0.095}\text{Nd}_{0.07}\text{COB}$ and $\text{Gd}_{0.73}\text{Sc}_{0.20}\text{Nd}_{0.07}\text{COB}$ (for starting melts) were grown by the Czochralski pulling method. The diameters of the crystals were controlled by a computer through the feedback of weight measurement. The typical pulling rate was 0.6 - 0.8 mm/h, and the rotation rate was 30–45 rpm. In all growth processes $\langle 010 \rangle$ oriented single crystal samples of pure GdCOB were used as seeds. As much as 20% of the melt was converted into a single crystal in approximately one week. The growth temperatures were about $1480 \pm 10^\circ\text{C}$. The crystals were cooled to room temperature at a rate of $30^\circ\text{C}/\text{h}$. The grown crystals have good optical quality and are highly transparent, nonhygroscopic, and chemically stable. The crystals also have good mechanical properties, which make them easier for cutting and polishing. Figure 1 shows the as-grown crystals. Typically, they have 25 mm in diameter and 120 mm in length.

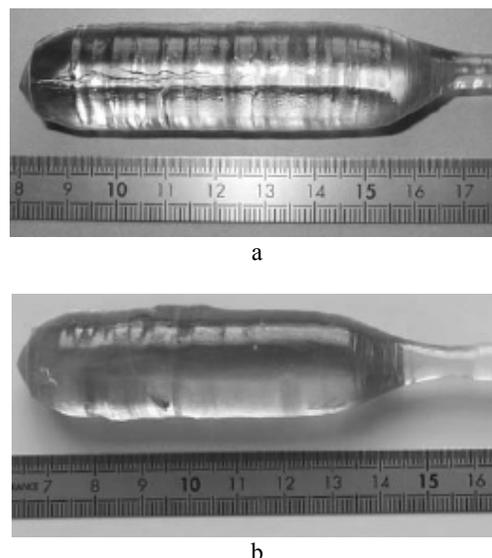


Fig. 1. $\text{Gd}_{1-x-y}\text{R}_x\text{Nd}_y\text{Ca}_4\text{O}(\text{BO}_3)_3$ as-grown crystals: (a) $\text{Gd}_{0.84}\text{Lu}_{0.11}\text{Nd}_{0.05}\text{Ca}_4\text{O}(\text{BO}_3)_3$, (b) $\text{Gd}_{0.92}\text{Sc}_{0.02}\text{Nd}_{0.06}\text{Ca}_4\text{O}(\text{BO}_3)_3$.

We have examined the compositional uniformity along the growth direction by means of inductively coupled plasma (ICP) atomic emission spectroscopy, on the samples exerted from the beginning, middle, and end of each grown crystal. It was found that the crystals had a high uniformity of composition because they were pulled from a large amount of the melt charge. The chemical compositions of grown crystals were also determined and they were found to be $\text{Gd}_{0.84}\text{Lu}_{0.11}\text{Nd}_{0.05}\text{COB}$ and $\text{Gd}_{0.92}\text{Sc}_{0.02}\text{Nd}_{0.06}\text{COB}$, respectively.

4. NCPM wavelengths

NCPM SHG experiments on $\text{Gd}_{0.84}\text{Lu}_{0.11}\text{Nd}_{0.05}\text{COB}$ and $\text{Gd}_{0.92}\text{Sc}_{0.02}\text{Nd}_{0.06}\text{COB}$ crystals were performed at room temperature. All crystals samples were cut in Z-direction (which was the direction for NCPM) and their faces were polished and uncoated. By using an OPO tunable from 420 to 2000 nm as laser source, the NCPM wavelengths were determined by tuning the OPO wavelength around 936 nm to find the wavelength yielding the maximum harmonic conversion efficiency (maximum blue output power). The input light was linearly polarized and it was irradiated along Z axis of the crystals samples. According to our assumptions, the obtained results demonstrate that $\text{Gd}_{0.84}\text{Lu}_{0.11}\text{Nd}_{0.05}\text{COB}$ and $\text{Gd}_{0.92}\text{Sc}_{0.02}\text{Nd}_{0.06}\text{COB}$ crystals convert the near infrared radiation of $936 \pm 0,6$ nm into blue light (~ 468 nm) through type-I NCPM along Z axis at room temperature (Table 1).

Table 1. Phase matching wavelengths in type-I NCPM along Z axis of grown crystals.

Crystal	λ_{NCPM} (nm)
$\text{Gd}_{0.84}\text{Lu}_{0.11}\text{Nd}_{0.05}\text{COB}$	936.6
$\text{Gd}_{0.92}\text{Sc}_{0.02}\text{Nd}_{0.06}\text{COB}$	935.8

5. Spectroscopic and laser characteristics

Samples with dimensions of $7 \times 7 \times 13$ mm³ (along crystallophysic axes) were cut from the as-grown $\text{Gd}_{0.84}\text{Lu}_{0.11}\text{Nd}_{0.05}\text{COB}$ and $\text{Gd}_{0.92}\text{Sc}_{0.02}\text{Nd}_{0.06}\text{COB}$ crystals and polished along Z axis. For each sample the absorption and emission spectra were measured at room temperature with light propagation along Z axis for both X and Y polarizations. For both crystals the maximum absorption cross section were obtained for Y polarization at 812 nm with values of $\sigma_{\text{abs}} = 2.04 \times 10^{-20}$ cm² for $\text{Gd}_{0.84}\text{Lu}_{0.11}\text{Nd}_{0.05}\text{COB}$ crystal and $\sigma_{\text{abs}} = 1.60 \times 10^{-20}$ cm² in the case of $\text{Gd}_{0.92}\text{Sc}_{0.02}\text{Nd}_{0.06}\text{COB}$ crystal. Consequently, for Y-polarized incident light, the maximum emission cross section for both crystals was obtained for X-polarized emissions at 1061 nm with values of $\sigma_{\text{em}} = 2.57 \times 10^{-20}$ cm² for $\text{Gd}_{0.84}\text{Lu}_{0.11}\text{Nd}_{0.05}\text{COB}$ crystal and $\sigma_{\text{em}} = 2.85 \times 10^{-20}$ cm² for $\text{Gd}_{0.92}\text{Sc}_{0.02}\text{Nd}_{0.06}\text{COB}$ crystal. The gain cross sections (σ_g), which leads to an

estimation of the probable operating laser wavelengths, were calculated according to the following relation:

$$\sigma_g(\lambda) = \beta\sigma_{\text{em}}(\lambda) - (1-\beta)\sigma_{\text{abs}}(\lambda)$$

where β is the transition branching ratio. The polarized gain cross section spectra of $\text{Gd}_{0.84}\text{Lu}_{0.11}\text{Nd}_{0.05}\text{COB}$ (Fig. 2a) and $\text{Gd}_{0.92}\text{Sc}_{0.02}\text{Nd}_{0.06}\text{COB}$ (Fig. 2b) crystals at room temperature show that we can achieve laser emissions at 936 nm and implicitly at 468 nm by SFD processes of laser emissions at 936 nm.

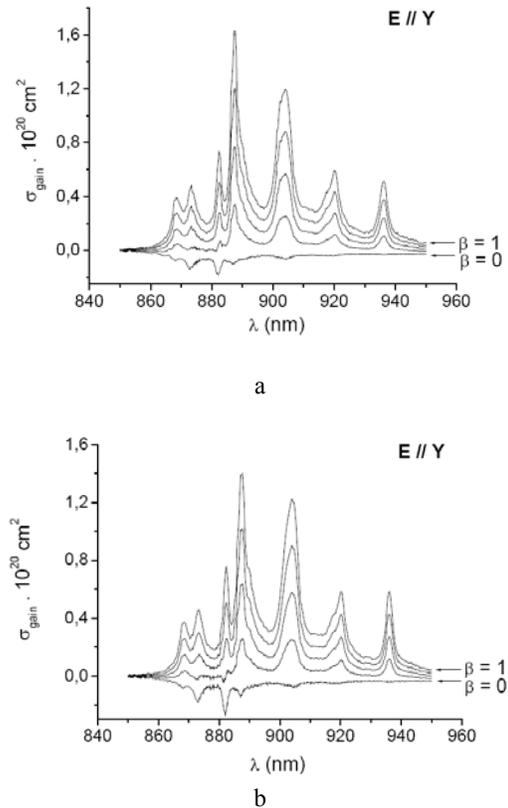


Fig. 2. Gain cross section spectra of: (a) $\text{Gd}_{0.84}\text{Lu}_{0.11}\text{Nd}_{0.05}\text{COB}$, (b) $\text{Gd}_{0.92}\text{Sc}_{0.02}\text{Nd}_{0.06}\text{COB}$ crystals ($\beta = 0, 0.25, 0.5, 0.75, 1$).

The first laser experiments on $\text{Gd}_{0.84}\text{Lu}_{0.11}\text{Nd}_{0.05}\text{COB}$ and $\text{Gd}_{0.92}\text{Sc}_{0.02}\text{Nd}_{0.06}\text{COB}$ crystals were performed in order to investigate the influence of crystal length on the laser emissions at 1061 nm, for a given Nd^{3+} concentration (2.08×10^{20} ions cm⁻³ in the case of $\text{Gd}_{0.84}\text{Lu}_{0.11}\text{Nd}_{0.05}\text{COB}$ crystal and 2.74×10^{20} ions cm⁻³ for the $\text{Gd}_{0.92}\text{Sc}_{0.02}\text{Nd}_{0.06}\text{COB}$ crystal). The direction of propagation was Z axis and the pump beam was Y polarized. The laser cavity consisted of a planar input mirror (HR@1061 nm, HT@812 nm) and a concave output mirror (R = 100 mm, TOC = 2%@1064 nm). The 812 nm pump wavelength of a cw Ti: sapphire laser was focused into the crystals by an 80 mm focal length lens. The crystals samples of different lengths along Z axis (2.8 mm, 4.8 mm and 6.3 mm for $\text{Gd}_{0.84}\text{Lu}_{0.11}\text{Nd}_{0.05}\text{COB}$

respectively 3.7 mm and 6.8 mm for $\text{Gd}_{0.92}\text{Sc}_{0.02}\text{Nd}_{0.06}\text{COB}$ crystal) were AR coated at 936 nm and 468 nm. The best slopes efficiency obtained were 40.1% for $\text{Gd}_{0.84}\text{Lu}_{0.11}\text{Nd}_{0.05}\text{COB}$ crystal with $L = 4.8$ mm, and 32% for $\text{Gd}_{0.92}\text{Sc}_{0.02}\text{Nd}_{0.06}\text{COB}$ crystal with $L = 3.7$ mm. In all experiments the laser emission was Y-axis polarized against an X-axis polarization like in the case of Nd:GdCOB crystal. This is a very important result because it offer the possibility to obtain a more efficiently SFD of 1061 nm laser radiation in Nd^{3+} doped and R^{3+} co-doped GdCOB crystals, this time in the ZX plan where the effective nonlinear coefficient is approximately three times bigger than in the plan XY [17]. The laser experiments regarding the achievement of blue laser emission by SFD of 936 nm laser radiation of $\text{Gd}_{1-x-y}\text{R}_x\text{Nd}_y\text{COB}$ grown crystals are now in progress.

6. Conclusions

Two nonlinear crystals of $\text{Gd}_{0.84}\text{Lu}_{0.11}\text{Nd}_{0.05}\text{COB}$ and $\text{Gd}_{0.92}\text{Sc}_{0.02}\text{Nd}_{0.06}\text{COB}$ with large size and good optical quality have been grown by Czochralski method and their NCPM properties were studied. According to our assumptions, we have demonstrated that the grown crystals convert the near infrared radiation of $936 \pm 0,6$ nm into blue light (~ 468 nm) by type-I NCPM SHG processes along Z axis. Y-axis polarized laser emission at 1061 nm of Nd:GdCOB crystals co-doped with Sc^{3+} and/or Lu^{3+} ions ($\text{Gd}_{1-x-y}\text{R}_x\text{Nd}_y\text{COB}$) has been obtained for the first time. Preliminary investigations concerning the SFD processes of 936 nm laser radiation of the grown crystals have been carried out and laser experiments are in progress.

Acknowledgements

This work was supported by the "Ideas" Romanian Research Programme of the National Plan II (NP II) under Project ID_248, Contract No. 491/2009.

References

- [1] K. C. Zhang, X. M. Wang, *Materials Science of Nonlinear Optical Crystals*, Beijing, 1 (1996).
- [2] Z. Y. Ou, S. F. Pereira, E. S. Polzik, H. J. Kimble, *Opt. Lett.* **17**, 640 (1992).
- [3] L. K. Cheng, W. R. Bosenberg, C. L. Tang, *Prog. Cryst. Growth Charact. Mater.* **20**, 9 (1990).
- [4] T. Izawa, R. Uchimura, S. Mtsui, T. Arichi, T. Yakuoh, *OSA Technical Digest of Conference on Lasers and Electro-Optics* **6**, 322 (1998).
- [5] G. D. Miller, R. G. Batchko, W. M. Tulloch, D. R. Weise, M. M. Fjer, R. L. Byer, *Opt. Lett.* **22**, 1834 (1997).
- [6] T. Sasaki, Y. Mori, M. Yoshimura, Y. K. Yap, T. Kamimura, *Mat. Sci. Eng.* **30**, 1 (2000).
- [7] P. Becker, J. Liebertz, L. Bothty, *J. Cryst. Growth* **203**, 149 (1999).
- [8] C. Zhang, J. Wang, X. Hu, H. Jiang, Y. Liu, C. Chen, *J. Cryst. Growth* **235**, 1 (2002).
- [9] J. Lu, G. Wang, Z. Xu, C. Chen, J. Wang, C. Zhang, Y. Liu, *Opt. Comm.* **200**, 415 (2001).
- [10] M. Iwai, T. Kobayshi, H. Furuya, Y. Mori, T. Sasaki, *Jpn. J. Appl. Phys.* **36**, L276 (1997).
- [11] G. Aka, A. Kahn-Harari, F. Mougél, D. Vivien, F. Salin, P. Coquelin, P. Colin, D. Pelence, J. P. Damelet, *J. Opt. Soc. Am. B* **14**, 2238 (1997).
- [12] H. J. Zhang, H. D. Jiang, J. Y. Wang, X. B. Hu, G. W. Yu, W. T. Yu, L. Gao, J. A. Liu, S. J. Zhang, M. H. Jiang, *Appl. Phys. A* **78**, 889 (2004).
- [13] G. Aka, A. Kahn-Harari, D. Vivien, J. M. Benitez, F. Salin, J. Godard, *Eur. J. Solid State Inorg. Chem.* **33**, 727 (1996).
- [14] F. Mougél, G. Aka, A. Kahn-Harari, H. Hubert, J. Benitez, D. Vivien, *Opt. Mater.* **8**, 161 (1997).
- [15] L. Gheorghe, P. Loiseau, G. Aka, V. Lupei, *J. Cryst. Growth* **294**, 442 (2006).
- [16] L. Gheorghe, V. Lupei, P. Loiseau, G. Aka, T. Taira, *J. Opt. Soc. Am. B* **23**, 1630 (2006).
- [17] M. V. Pack, D. J. Armstrong, A. V. Smith, G. Aka, B. Ferrand, D. Pelenc, *J. Opt. Soc. Am. B* **22**, 417 (2005).

*Corresponding author: lucian.gheorghe@inflpr.ro