Development of new NLO borate crystals

Y MORI* and T SASAKI

Department of Electrical Engineering, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

Abstract. Recently new borate crystals, $\text{CsLiB}_6\text{O}_{10}$ (CLBO), $\text{YCa}_4\text{O}(\text{BO}_3)_3$ (YCOB) and $\text{Gd}_x\text{Y}_{1-x}\text{Ca}_4\text{O}(\text{BO}_3)_3$ ($\text{Gd}_x\text{Y}_{1-x}\text{COB}$) have been developed by the present authors. Here, the growth and nonlinear optical properties of CLBO, YCOB and $\text{Gd}_x\text{Y}_{1-x}\text{COB}$ crystals are reviewed and their properties are discussed in relation to those of other nonlinear optical crystals, such as $\beta\text{-BaB}_2\text{O}_4$ (BBO), and LiB_3O_5 (LBO).

Keywords. Nonlinear optical material; frequency conversion; ultraviolet generation; solid-state lasers; CLBO; noncritically phase-matching; YCOB; GdYCOB .

1. Introduction

Many researchers have devoted their efforts to the development of ultraviolet (UV) lasers for industrial and medical applications. The frequency conversion technique of solid state laser radiation in nonlinear optical (NLO) crystals is an effective method for obtaining UV radiation with high beam quality and stability. Borate series, such as $\beta\text{-BaB}_2\text{O}_4$ (BBO); LiB_3O_5 (LBO) and CsB_3O_5 (CBO) have been searched as UV NLO crystals (Chen *et al* 1984, 1989; Wu *et al* 1993). Recently other new borate crystals, $\text{CsLiB}_6\text{O}_{10}$ (CLBO), $\text{YCa}_4\text{O}(\text{BO}_3)_3$ (YCOB) and $\text{Gd}_x\text{Y}_{1-x}\text{Ca}_4\text{O}(\text{BO}_3)_3$, ($\text{Gd}_x\text{Y}_{1-x}\text{COB}$) have been discovered and developed by the present authors (Mori *et al* 1995a; Iwai *et al* 1997; Yoshimura *et al* 1998). CLBO crystals can generate the fourth and fifth harmonic of a Nd : YAG laser radiation due to their relatively large birefringence. YCOB is phase-matchable for the third harmonic generation of a Nd : YAG laser. We also confirmed that $\text{Gd}_{0.28}\text{Y}_{0.72}\text{COB}$ makes possible the generation of the $(\theta, \phi) = (90^\circ, 90^\circ)$ phase-matched third harmonic of 1064 nm light. Here, the growth, NLO and frequency conversion properties of CLBO, YCOB and $\text{Gd}_x\text{Y}_{1-x}\text{COB}$ crystals are reviewed and their properties are discussed in relation to those of other nonlinear optical crystals, such as BBO and LBO.

2. Borate crystals

2.1 CLBO crystals

CLBO has a tetragonal structure with a space group of $I4_2d$ (#122) and cell dimensions of $a = 10.494(1)$ and $c = 8.939(2)$ for $Z = 4$ (Sasaki *et al* 1995). The structure comprises isolated Cs cations and network of chains

formed from B_3O_7 groups and Li cations. It consists of a six-membered ring, where two of the boron atoms are three-fold coordinated and the third boron atom in the ring is four-fold coordinated by oxygen atoms. The borate network of CLBO surrounds eight-coordinate Cs atoms and four-coordinate Li atoms.

The pseudo binary $(\text{Cs}_2\text{O} + 3\text{B}_2\text{O}_3) - (\text{Li}_2\text{O} + 3\text{B}_2\text{O}_3)$ and $(\text{Cs}_2\text{O} + \text{Li}_2\text{O}) - (2\text{B}_2\text{O}_3)$ phase diagrams were investigated in the ternary $\text{Cs}_2\text{O} - \text{Li}_2\text{O} - 3\text{B}_2\text{O}_3$ system using differential temperature analysis and X-ray diffractometer as shown in figures 1a and b (Mori *et al* 1995b). Figure 1 shows stoichiometric congruent point at 848°C , meaning that it is easy to grow CLBO crystal compared to BBO and LBO. Phase diagrams show that CLBO crystals can be grown from fluxes that are either poor or rich in B_2O_3 . This is an advantage for flux growth of CLBO compared with that of LBO, which grows only from a flux rich in B_2O_3 . This is because crystal growth from a flux rich in B_2O_3 is often difficult due to the high viscosity. Therefore, the flux poor in B_2O_3 was used to grow large crystals. The starting charges were prepared from a mixture of Cs_2CO_3 , Li_2CO_3 , and B_2O_3 with ratio of 1 : 1 : 5.5 (73.3% B_2O_3). The measured saturation temperature was 845°C . The growth temperature was varied from 845°C to 843.5°C with a temperature decrease of $\sim 0.1^\circ\text{C}/\text{day}$. The growing crystal was rotated at a rate of 15 rpm with inverting the rotation direction every 3 min. Figure 2 shows a CLBO crystal with dimensions of $14 \times 11 \times 11 \text{ cm}^3$ grown under this condition for three weeks (Mori *et al* 1995a). This crystal exhibited well distinguishable facets.

The transmission range of CLBO crystal was from 180 nm to 2750 nm. The absorption edge of CLBO at 180 nm is shorter than the reported value of BBO (189 nm) but longer than those reported for LBO (160 nm). The refractive indices were determined by the method of minimum deviation. The Sellmeier equations predict

*Author for correspondence

the limits of types I and II PM wavelengths to be 472 and 640 nm, respectively. The Sellmeier equations also predict the fifth-harmonic generation (5HG) of Nd:YAG laser radiation in CLBO crystal by mixing the first and fourth harmonics radiations (Mori *et al* 1995c). Table 1 shows values of angular, spectral and temperature bandwidths and walk-off angle for various frequency conversion process in the CLBO and BBO for 266 nm and 213 nm generations. Despite the smaller nonlinear coefficient, CLBO possesses smaller walk-off angle, and larger angular and spectral bandwidths compared to BBO. The temperature acceptance of CLBO is larger than that of BBO. As shown in table 1, CLBO exhibits better NLO properties compared to BBO and this is supported by the following experimental results as well.

High average power all solid state UV laser was obtained at a pulse rate of 100 Hz and 1000 Hz by CLBO. In case of 100 Hz pulse rate, 9.7 W of 266 nm and 4.0 W of 213 nm were detected. The conversion efficiency from 1064 nm to 213 nm was 11.8% (Yap *et al* 1996). In case of 1000 Hz pulse rate, 2.5 W of 266 nm and 1.0 W of 213 nm were obtained from fundamental of 8.8 W, which correspond to an efficiency of

11.4% from 1064 nm to 213 nm (Stamm *et al* 1997). Moderate birefringence made CLBO possess a smaller walk-off angle so as to achieve better spatial overlapping of the mixing beams compared to BBO. Thus, higher conversion efficiency and better beam pattern of harmonics generation can be achieved. Its relatively large angular, spectral and temperature acceptance bandwidths at 532 nm have favoured CLBO for stable 266 nm generation of high power Nd:YAG laser. All these properties and its shorter absorption edge down to 180 nm eventually lead to a high conversion efficiency and stable 213 nm generation.

3. YCOB and Gd_xY_{1-x} COB crystals

Khamaganova *et al* (1991) grew a new borate crystal of $Ca_8Sm_2O_2(BO_3)_6$ from a PbO flux. Norrestam *et al* (1992) succeeded in synthesizing a borate series of $Ca_4RO(BO_3)_3$, where $R^{3+} = La, Nd, Sm, Gd, Er$ and Y . Following these developments, Aka *et al* (1996a, b) reported the crystal growth and nonlinear optical properties of $GdCa_4O(BO_3)_3$ (GdCOB) as a new NLO crystal. This crystal is an excellent candidate for practical NLO devices, because it is nonhygroscopic and chemically stable with good mechanical properties, allowing easy polishing. Although they have mentioned an isomorph $Ca_4O(BO_3)_3$ (YCOB) briefly, its detailed characteristics have not been shown yet.

In previous work (Iwai *et al* 1997; Yoshimura *et al* 1998), we found that the substitution of a smaller radius cation such as Y^{3+} (0.900 Å) (Shannon 1976) for Gd^{3+} (0.938 Å) on the trivalent rare earth site leads to larger optical birefringence. As a result, the wavelength limit of type I second harmonic generation (SHG) can be shortened to 720 nm. In addition, YCOB is phase-matchable for the third harmonic generation (THG) of

Figure 1. The pseudo binary $(Cs_2O + 3B_2O_3)-(Li_2O + 3B_2O_3)$ and $(Cs_2O + Li_2O)-(2B_2O_3)$ phase diagrams investigated in the ternary $Cs_2O-Li_2O-B_2O_3$ system.

Figure 2. Photograph of large CLBO crystal with dimensions of $14 \times 11 \times 11 \text{ cm}^3$.

Table 1. NLO properties of CLBO and BBO for 266 nm and 213 nm generations.

Wavelength (nm)	Crystal	PM angle (deg.)	d_{eff} (pm/V)	Angular bandwidth (mrad cm)	Spectral bandwidth (nm cm)	Temperature bandwidth (°C cm)	Walk-off angle (deg)
532 + 532 = 266	CLBO	62	0.85	0.49	0.13	8.3	1.83
	BBO	48	1.32	0.17	0.07	4.5	4.80
1064 + 266 = 213	CLBO	67	0.88	0.42	0.16	4.6	1.69
	BBO	51	1.26	0.11	0.08	3.1	5.34

a Nd:YAG laser by type I mixing between 1064 and 532 nm, whereas GdCOB is not. Here, we present the crystal growth and NLO properties of $\text{YCa}_4\text{O}(\text{BO}_3)_3$ (YCOB) compared with those of GdCOB. Furthermore, we confirmed that a substitutional solid solution of $\text{Gd}_x\text{Y}_{1-x}\text{Ca}_4\text{O}(\text{BO}_3)_3$ ($\text{Gd}_x\text{Y}_{1-x}\text{COB}$) has compositional uniformity along the growth direction. We also report the THG phase-matching properties of $\text{Gd}_x\text{Y}_{1-x}\text{Ca}_4\text{O}(\text{BO}_3)_3$ ($\text{Gd}_x\text{Y}_{1-x}\text{COB}$) crystal in various compositions to achieve a noncritically phase matching (NCPM) condition at room temperature. For frequency conversion applications, the NCPM condition is advantageous due to its large angular acceptance and the elimination of walk-off between fundamental and harmonic lights.

Single crystals of YCOB and $\text{Gd}_x\text{Y}_{1-x}\text{COB}$, up to 1 cm in diameter by 5 cm in length, were grown by the conventional Czochralski technique. YCOB was grown in an Ar atmosphere at 1510°C, which is about 30°C higher than the temperature used for growing GdCOB; the increase of Gd concentration in $\text{Gd}_x\text{Y}_{1-x}\text{COB}$ lowers the growth temperature. The typical pull and rotation were 3 mm/h and 20 rpm, respectively. Although numerous cracks tended to form during the cooling process, the (010) oriented seed prevented the cracks. Figure 3 shows the typical $\text{Gd}_x\text{Y}_{1-x}\text{COB}$ crystal.

We examined the compositional uniformity along the growth direction of $\text{Gd}_x\text{Y}_{1-x}\text{COB}$ crystals, sampling at the positions of 5, 20 and 35 mm from the seed crystal, by means of inductively coupled plasma (ICP) atomic emission spectroscopy. Two samples of $\text{Gd}_x\text{Y}_{1-x}\text{COB}$ ($x=0.13, 0.48$) single crystals were used. It was found that the crystals showed a high uniformity of composition with 13 and 48% of Gd, respectively, along the growth direction as shown in figure 4. We also measured the ratios of lattice constants ($a/c, a/b$) in $\text{Gd}_x\text{Y}_{1-x}\text{COB}$ ($x=0, 0.48, 1$) crystals by means of a four-circle X-ray diffractometer as shown in figure 5. The ratios of lattice constants a/c and a/b in $\text{Gd}_x\text{Y}_{1-x}\text{COB}$ linearly change as the compositional parameter x increases. This result implies that $\text{Gd}_x\text{Y}_{1-x}\text{COB}$ is a substitutional solid solution and that it is possible to vary the refractive indices continuously.

Figure 3. Typical $\text{Gd}_x\text{Y}_{1-x}\text{COB}$ ($x=0.24$) single crystal grown by the Czochralski method.

The ranges of transparency for YCOB and $\text{Gd}_{0.48}\text{Y}_{0.52}\text{COB}$ were determined in samples of 2 and 5 mm thickness. The transmission ranges of these samples are from 250 nm to 2500 nm. The absorption edges are 210 nm. For Gd-contained crystals, six sharp absorption lines due to Gd^{3+} ions were observed in the range 240–320 nm, whereas no absorption was observed in YCOB.

$\text{Gd}_x\text{Y}_{1-x}\text{COB}$ is a biaxial crystal and belongs to the monoclinic system with C_m space symmetry. The dielectric axes (XYZ) are labelled by the refractive index associated with them, $n_x < n_y < n_z$. The Y axis is parallel to the crystallographic b axis. The magnitude of birefringence $n_z - n_x$ relates to the phase-matching conditions for frequency conversion. The three principal refractive indices of GdCOB and YCOB were measured at wavelengths between 270 and 1200 nm by the method of minimum deviation (Iwai *et al* 1997; Yoshimura *et al* 1998). The shortest type I SHG wavelength calculated from the Sellmeier equations is 720 nm. This is shorter than that for GdCOB (840 nm), because birefringence of YCOB is greater than that of GdCOB. For instance, the magnitudes of birefringence $n_z - n_x$ at 1064 nm for YCOB and GdCOB are 0.041 and 0.033, respectively. In addition to SHG of a Nd:YAG laser, THG can be

realized in YCOB by type I mixing between 1064 and 532 nm, whereas in GdCOB it cannot.

YCOB and $\text{Gd}_x\text{Y}_{1-x}\text{COB}$ crystals, typically 9 mm long in various compositions, were cut at the Y axis or phase-matching direction for THG. The faces were polished and uncoated. The measurements for phase-matching properties were performed by using a Q-switched Nd:YAG laser (Spectra-Physics GCR190) which is operated at a repetition rate of 10 Hz. The type I phase-matching angles for THG ($1064 + 532 \rightarrow 355$ nm) in YCOB were experimentally determined to be $(\theta, \phi) = (90^\circ, 73.2^\circ)$ and $(58.7^\circ, 90^\circ)$ in the XY and YZ planes, respectively. In general, as the birefringence of biaxial crystal decreases, the phase-matching angles in the XY and YZ planes change toward $(\theta, \phi) = (90^\circ, 90^\circ)$. Partial substitution of Gd for Y in YCOB crystals makes the birefringence small, therefore we expect to achieve NCPM THG along the Y axis by adjusting the Gd-concentration.

Figure 4. Uniformity of crystal composition of (a) $\text{Gd}_{0.48}\text{Y}_{0.52}\text{COB}$ and (b) $\text{Gd}_{0.13}\text{Y}_{0.87}\text{COB}$ along the growth direction.

Figure 5. The ratios of lattice constants ($a/c, a/b$) in $\text{Gd}_x\text{Y}_{1-x}\text{COB}$ ($x=0, 0.48, 1$) crystals.

We examined the phase-matching angles on the principal planes (XY, YZ) for various $\text{Gd}_x\text{Y}_{1-x}\text{COB}$ compounds. The experiments were carried out at room temperature. Figure 6 represents the phase-matching angles for THG as a function of the compositional parameter x in $\text{Gd}_x\text{Y}_{1-x}\text{COB}$ crystals. For curve **a**, the wave vector $\mathbf{k}$ is in the XY plane and the phase-matching angle is ϕ from the X axis. Similarly, for curve **b** the phase-matching angle is θ from the Z axis in the YZ plane. The phase-matching angles gradually changed to 90° due to an increase of x in $\text{Gd}_x\text{Y}_{1-x}\text{COB}$. At $x=0.24$ the phase-matching angle reaches $(\theta, \phi) = (90^\circ, 90^\circ)$, which is type I noncritical phase-matching at room temperature. For $x > 0.28$, the third harmonic lights were also generated at $(\theta, \phi) = (90^\circ, 90^\circ)$, although the intensity gradually declined due to an increase of x . $\text{Gd}_{0.29}\text{Y}_{0.71}\text{COB}$ crystal generated detectable third harmonic lights, this means that the compositional parameter x is not critical for NCPM THG.

We measured the phase-matching properties for THG in 9.3 mm long $\text{Gd}_{0.28}\text{Y}_{0.72}\text{COB}$ and 9.6 mm long YCOB crystals. The effective nonlinear coefficients d_{eff} were calculated from the third harmonic energy and the refractive indices by comparison with those of LBO. A type I LBO (XY) with a length of 7.5 mm ($d_{\text{eff}} = 0.68$ pm/V) was used as a reference (Roberts 1992; Kato 1994). The ambiguity in the refractive indices of $\text{Gd}_{0.28}\text{Y}_{0.72}\text{COB}$ gives no significant error in the value of d_{eff} . Therefore, the refractive indices were interpolated between the indices of GdCOB and YCOB. It was found that the d_{eff} of $\text{Gd}_{0.28}\text{Y}_{0.72}\text{COB}$ is 0.55 pm/V, which is slightly larger than that for YCOB (XY) at 0.52 pm/V.

Figure 6. Phase-matching angles for THG in $\text{Gd}_x\text{Y}_{1-x}\text{COB}$ in the XY and YZ planes of $\text{Gd}_x\text{Y}_{1-x}\text{COB}$ as a function of the compositional parameter x . For curve **a** the wave vector $\mathbf{k}$ is in the XY plane and the phase-matching angle is ϕ from the X axis. Similarly, for curve **b** the phase-matching angle is θ from the Z axis in the YZ plane.

Table 2. Phase-matching properties for type I THG (1064 + 532 → 355 nm) of $\text{Gd}_x\text{Y}_{1-x}\text{COB}$.

	d_{eff} (pm/V)	External angular acceptance bandwidth (mrad cm)		Temperature bandwidth (°C cm)	Walk-off angle (mrad)
		$\Delta\theta$ 1	$\Delta\phi$ 1		
YCOB (XY)	0.52	—	3.2	9.7	8.5
YCOB (YZ)	0.43	5.6	—	8.5	4.7
GdYCOB	0.55	114 mrad cm ^{1/2}	65.6 mrad cm ^{1/2}	6.6	0

The d_{eff} of monoclinic crystals with Cm space symmetry are given by

$$d_{\text{eff}} \text{ (type I, XY)} = d_{13} \sin \phi,$$

$$d_{\text{eff}} \text{ (type I, YZ)} = d_{12} \sin^2 \theta + d_{13} \cos^2 \theta.$$

Hence the difference in d_{eff} between YCOB ($\phi = 73.2^\circ$; XY) and $\text{Gd}_{0.24}\text{Y}_{0.76}\text{COB}$ seems to be caused by the term of $\sin \phi$.

The acceptance angles $\Delta\theta$ and $\Delta\phi$ of $\text{Gd}_{0.24}\text{Y}_{0.76}\text{COB}$ were measured by rotating the crystal about the X axis in the Y - Z plane (θ direction) and about the Z axis in the X - Y plane (ϕ direction). The FWHM acceptance angles (external) were found to be 33 and 9.7 mrad for the rotation of the θ and ϕ directions, respectively. These values correspond to angular acceptance bandwidths of $\Delta\theta^{1/2} = 34$ and $\Delta\phi^{1/2} = 9.3$ mrad (cm)^{1/2}. The temperature tuning curve for THG in $\text{Gd}_{0.24}\text{Y}_{0.76}\text{COB}$ was also measured. The FWHM value phase-matched at 28°C is 10.4°C, corresponding to the temperature bandwidth ΔT of 9.7°C cm. Table 2 shows the phase-matching properties for THG of $\text{Gd}_x\text{Y}_{1-x}\text{COB}$. The walk-off angles of YCOB are calculated values. The walk-off angle of $\text{Gd}_{0.28}\text{Y}_{0.72}\text{COB}$ is an estimated value. We have improved the angular properties for THG by the substitution of Gd for Y in YCOB. These results suggest that $\text{Gd}_{0.28}\text{Y}_{0.72}\text{COB}$ is suitable for THG and that a longer crystal can be utilized for higher frequency conversion efficiency.

4. Conclusions

The NLO crystals, CLBO, YCOB and $\text{Gd}_x\text{Y}_{1-x}\text{COB}$ have been reviewed. CLBO showed the ease in growth and excellent NLO properties for 4 and 5 harmonics generations. YCOB and $\text{Gd}_x\text{Y}_{1-x}\text{COB}$ crystals also showed the ease in growth without cracks and bubbles by the Czochralski method. $\text{Gd}_x\text{Y}_{1-x}\text{COB}$ crystals had an uniformity of crystal composition along with growth direction so these crystals confirmed a substitutional solid solution of $\text{Gd}_x\text{Y}_{1-x}\text{COB}$. We have succeeded to generate noncritical phase matched THG of Nd:YAG laser (1064 nm) light in $\text{Gd}_{0.28}\text{Y}_{0.72}\text{COB}$.

Acknowledgements

This work was supported by the 'Research for the Future' Program of the Japan Society for the Promotion of Science (No. 97R-16101). The authors would like to thank Y Okada, Kogaku Giken Co. Ltd. for polishing the crystals.

References

- Aka G *et al* 1996a in *OSA TOPS on advanced solid state lasers* (eds) S A Payne and C R Pollock (Washington DC: Optical Society of America) Vol. 1
- Aka G, Kahn-Harari A, Vivien D, Salin F, Godard J and Benitez J M 1996 *Eur. J. Solid State Inorg. Chem.* **33** 727
- Chen C, Wu B, Jiang A and You G 1984 *Sci. Sin.* **B7** 579
- Chen C, Wu Y, Jiang A, Wu B, You G, Li R and Lin S 1989 *J. Opt. Soc. Am.* **B6** 616
- Iwai M, Kobayashi T, Furuya H, Mori Y and Sasaki T 1997 *Jpn J. Appl. Phys.* **36** 276
- Kato K 1994 *IEEE J. Quantum Electron.* **30** 2950
- Khamaganova T N, Trunov V K and Dzhurinskii B F 1991 *Russian J. Inorg. Chem.* **36** 484
- Mori Y, Kuroda I, Nakajima S, Sasaki T and Nakai S 1995a *Appl. Phys. Lett.* **67** 1818
- Mori Y, Kuroda I, Nakajima S, Sasaki T and Nakai S 1995b *J. Cryst. Growth* **156** 307
- Mori Y, Kuroda I, Nakajima S, Sasaki T and Nakai S 1995c *Jpn J. Appl. Phys.* **34** L296
- Norrestam R, Nygren M and Bovin J-O 1992 *Chem. Mater.* **4** 737
- Roberts D A 1992 *IEEE J. Quantum Electron.* **28** 2057
- Sasaki T, Mori Y, Kuroda I, Nakajima S, Yamaguchi K and Nakai S 1995 *Acta Crystallogr.* **C51** 2222
- Shannon R D 1976 *Acta Crystallogr.* **A32** 751
- Stamm U, Zschocke W, Schroder T, Deutsch N and Basting D 1997 Technical Digest of CLEO '97, 11, CFE7
- Wu Y, Sasaki T, Nakai S, Yokotani A, Tang H and Chen C 1993 *Appl. Phys. Lett.* **62** 2614
- Yap Y K, Inagaki M, Nakajima S, Mori Y and Sasaki T 1996 *Opt. Lett.* **21** 1348
- Yoshimura M, Furuya H, Kobayashi T, Murase K, Yamada I, Mori Y and Sasaki T 1998 *SPIE proc. of third int. conf. on solid state lasers for application to inertial confinement fusion* (in print)