Wide Tunable Angular Non-Critical Phase-Matching Wavelengths from 0.72 to 1.42 µm Based on RE\textsubscript{1}\textsubscript{x}RE\textsubscript{2}\textsubscript{1−x}COB Mixed Crystals

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Abstract: The angular non-critical phase-matching (A-NCPM) second-harmonic-generation (SHG) properties of RE\textsubscript{1}\textsubscript{x}RE\textsubscript{2}\textsubscript{1−x}COB (RE\textsubscript{1}, RE\textsubscript{2} = Y, Gd, La, Tm, Sm, and Nd) type mixed crystals including NCPM wavelength and conversion efficiency were detailedly investigated. Theoretical calculations manifest that the A-NCPM SHG scope of these crystals is 0.72–1.42 µm, and in experiments, the A-NCPM SHG waveband of 0.72–1.25 µm has been realized, by changing the ratio of the rare-earth elements RE\textsubscript{1} and RE\textsubscript{2} in RE\textsubscript{1}\textsubscript{x}RE\textsubscript{2}\textsubscript{1−x}COB crystals. Comparing to the temperature-dependent A-NCPM SHG of 0.95–1.34 µm in LiB\textsubscript{3}O\textsubscript{5} (LBO) crystal, the composition-dependent A-NCPM SHG of 0.72–0.95 µm in RE\textsubscript{1}\textsubscript{x}RE\textsubscript{2}\textsubscript{1−x}COB type crystals is unique and has special significance for the frequency conversion of Ti:Sapphire lasers. Relationships between the birefringence and radius of rare-earth ion RE\textsuperscript{3+} in RE\textsubscript{1}\textsubscript{x}RE\textsubscript{2}\textsubscript{1−x}COB mixed crystals were discussed. Aiming for the A-NCPM SHG of 0.72–1.42 µm, we supply a clear, completed, and optimized solution on how to select the compositions of RE\textsubscript{1}\textsubscript{x}RE\textsubscript{2}\textsubscript{1−x}COB mixed crystals. Under focusing light beam conditions, high efficient A-NCPM SHG for both OPO and Ti:sapphire lasers were realized experimentally by using long Y- and Z-cut RE\textsubscript{1}\textsubscript{x}RE\textsubscript{2}\textsubscript{1−x}COB crystal samples.

Keywords: RE\textsubscript{2}Ca\textsubscript{4}O(BO\textsubscript{3})\textsubscript{3}; non-critical phase-matching; second-harmonic-generation; nonlinear optical crystals; nonlinear optics

1. Introduction

Applications of visible laser beams have been growing rapidly in recent years, which can be used in the areas of entertainment, manufacturing, medicine, information technology, optical data storage, color display, and laser spectroscopy [1–3]. Currently, the availability of laser frequencies in visible spectral ranges are mainly via three ways. One is semiconductor lasers which directly produce visible lights [4,5], another is Pr\textsuperscript{3+}, Tb\textsuperscript{3+}, Sm\textsuperscript{3+} or Dy\textsuperscript{3+} ions doped laser crystals pumped by semiconductor lasers [6–8], the last one is frequency doubling of near-infrared lasers by nonlinear optical (NLO) crystals [9–11]. Using frequency doubling of lasers operating in the near-infrared ranges was the most efficient means to obtain visible lights, which usually contained two ways of phase-matching (PM) methods, i.e., critical phase-matching (CPM) and angular non-critical phase-matching (A-NCPM). Only the PM direction along the vertical to the optical axis of uniaxial crystals and principal axes...
of refractive indices of biaxial crystals is called A-NCPM, while in other cases, it is called CPM. Compared with CPM, the advantage of A-NCPM is it possesses no beam walk-off and a large angular acceptance angle, so that the fundamental and frequency-doubled beam profiles will be less separated and the NLO crystal sample can be made longer to improve conversion efficiency during the process of frequency doubling. Up to now, the A-NCPM is rare and precious, only LiB\(_3\)O\(_3\) (LBO) crystals have achieved broad waveband A-NCPM SHG of 0.95~1.34 \(\mu m\) by tuning the crystal temperature from \(-10^\circ C\) to \(270^\circ C\) [12]. In addition to the temperature-dependence, the component-dependence is a different way to obtain some specific A-NCPM laser wavelengths in suitable NLO crystals. For example, K(H\(_3\)PO\(_4\))\(_2\) (DKDP) crystals have realized the A-NCPM fourth-harmonic-generation (FHG) wavelengths of 1053 nm and 1064 nm at near room temperature [13]. In order to achieve component-dependence, the NLO crystals should be continuously doped uniform melts, and their refractive indices along with A-NCPM wavelengths could be controllable and tunable by changing the doped component parameters. Previous researches showed that the family of RE\(_2\)O\(_3\) \((\text{RECOB, RE} = \text{Y, Gd, La, Tm, Sm, and Nd})\) crystals were found to be melted congruently and could be grown into a large-size by the Czochralski (Cz) pulling method [14–17]. More meaningful, the substitutional solid solutions of RE\(_1\),RE\(_2\)-COB (RE\(_1\) = Y, RE\(_2\) = Gd, and La) crystals were found to have compositional uniformity along the growth direction [18–20]. Furuya et al. had found that the ratio of \(a/b\) and \(a/c\) for Gd\(_1\),Y\(_{1-x}\)-COB crystals were linear variation with the changing of chemical composition \(x\), and their A-NCPM third-harmonic-generation (THG) wavelengths were tunable to be around 1064 nm by keeping the variable \(x = 0.28\), in 1999 [21]. Afterward, the same results were also found in another three series of RE\(_1\),RE\(_2\)-COB mixed crystals, i.e., Lu\(_2\)Gd\(_1\)-COB, Sc\(_2\)Gd\(_1\)-COB, and La\(_2\),Y\(_{1-x}\)-COB [22–24]. In 2017, we discovered that RECOB (RE = Y, Gd, La, Tm, Sm, and Nd) crystals were found to possess a wide birefringence range of 0.0425~0.0279 [25], therefore, in theory, the A-NCPM SHG wavelengths might be changed dramatically for their mixed crystals RE\(_1\),RE\(_2\)-COB (RE\(_1\), RE\(_2\) = Y, Gd, La, Tm, Sm, and Nd), which showed the possibility of a widely tunable A-NCPM waveband.

In this work, the A-NCPM SHG properties for RE\(_1\),RE\(_2\)-COB (RE\(_1\), RE\(_2\) = Y, Gd, La, Tm, Sm, and Nd) crystals with different RE ratios are comprehensively reported. The relationship between the A-NCPM SHG wavelength and the rare earth radius of RE\(_1\),RE\(_2\)-COB (RE\(_1\), RE\(_2\) = Y, Gd, La, Tm, Sm, and Nd) mixed crystals is analyzed. This paper supplies a complete A-NCPM solving scheme for the frequency doubling of 0.72~1.42 \(\mu m\) lasers based on the pure RECOB (RE = Y, Gd, La, Tm, Sm, and Nd) and their derivative mixed crystals, which can generate 0.36~0.71 \(\mu m\) visible lasers with high efficiency. Under focusing light beam conditions, efficient NCPM SHG for both OPO and Ti:sapphire lasers were realized experimentally.

2. A-NCPM SHG Wavelengths

For RECOB crystals, A-NCPM is the PM direction along the principal axes of refractive indices, i.e., optical principal axes, which are famous for large angular acceptance and absence of beam walk-off. Therefore, long crystal samples could be used to obtain the high SHG conversion efficiency in this PM style. RECOB type crystals possess three different optical principal axes i.e., \(X\), \(Y\), and \(Z\), and each axis has two A-NCPM SHG wavelengths (type-I and type-II). The effective NLO coefficients \(d_{\text{eff}}\) for type-I along the \(X\)-axis and type-II along the \(Z\)-axis were found to be zero. Although the \(d_{\text{eff}}\) of type-II A-NCPM for the \(X\)-axis was found to be the largest value (1.67 pm/V) among all of the A-NCPM styles for RECOB crystals, the theoretical calculations based on refractive-index equations showed that the type-II A-NCPM SHG wavelength for the \(X\)-axis was greater than 3 \(\mu m\), which had no practical application significance [17]. According to the previous reports, there were three practical A-NCPM SHG styles (type-I along the \(Y\)-axis, type-I along the \(Z\)-axis, and type-II along the \(Y\)-axis) for pure RECOB (RE: Y, Gd, La, Tm, Sm, and Nd) crystals, which were determined and listed in Table 1.
Table 1. Angular non-critical phase-matching second-harmonic-generation (A-NCPM SHG) wavelengths of pure RECOB crystals.

| Crystals | Optical Principal Axis | Type-I A-NCPM Wavelength (nm) | Type-II A-NCPM Wavelength (nm) | References |
|----------|------------------------|-------------------------------|-------------------------------|------------|
| SmCOB    | Y                      | 900                           | 1390 *                        | [25]       |
|          | Z                      | 1116                          | Inexistence                   |            |
| NdCOB    | Y                      | 927                           | 1578 *                        | [25]       |
|          | Z                      | 1205                          | Inexistence                   |            |
| LaCOB    | Y                      | 808                           | 1178                          | [18]       |
| TmCOB    | Y                      | 716                           | 1011                          | [26]       |
|          | Z                      | 815                           | Inexistence                   |            |
| YCOB     | Y                      | 725                           | 1032                          | [27,28]    |
|          | Z                      | 826                           | Inexistence                   |            |
| GdCOB    | Y                      | 831                           | 1255                          | [27,28]    |
|          | Z                      | 973                           | Inexistence                   |            |

* The values are calculated based on the Sellmeier equations of SmCOB and NdCOB crystals [25].

For multiple component RE₁ₓRE₂₁−ₓCOB (RE₁, RE₂ = Y, Gd, La, Tm, Sm, and Nd) type mixed crystals, the A-NCPM SHG wavelengths are tuned continuously with the changing of chemical composition x. For NdₓY₁−ₓCOB crystals, the type-I A-NCPM SHG wavelengths along Y and Z axes were found to be tuned in the ranges of 723–927 nm and 827–1205 nm, respectively, and the tuning range of type-II A-NCPM SHG wavelengths along the Y-axis was 1023–1578 nm, which could be deduced from Table 1. The tuning waveband of 0.723–1.578 μm has been covered absolutely by such developed NdₓY₁−ₓCOB mixed crystals. In the meantime, such A-NCPM SHG waveband is much broader than the theoretical values of GdₓY₁−ₓCOB crystals (724–826 nm, 1032–1255 nm, and 833–960 nm), which can be also deduced from Table 1. The A-NCPM SHG wavelengths for other mixed RE₁ₓRE₂₁−ₓCOB (GdₓY₁−ₓCOB, GdₓLu₁−ₓCOB, GdₓSc₁−ₓCOB, LaₓGd₁−ₓCOB, NdₓGd₁−ₓCOB, and TmₓGd₁−ₓCOB) crystals are listed in Table 2. In the experiments, the Y- and Z-cut NdₓGd₁−ₓCOB (x = 0.08) and TmₓGd₁−ₓCOB (x = 0.02) crystal samples were processed for measuring A-NCPM SHG wavelengths. The tunable laser source was an OPO (Opolette HE 355 II, 410–2400 nm, 5 ns, 20 Hz, OPOTEK Inc., Carlsbad, California, USA), and its output laser was linearly polarized with the output power varied in the range of 0–12 mW. For GdₓLu₁−ₓCOB and GdₓSc₁−ₓCOB crystals, only the type-I A-NCPM SHG wavelengths along Y and Z axes were reported [22,24], the type-II A-NCPM wavelengths along the Y-axis was calculated by us based on their Sellmeier equations, as is shown in Table 2.

Table 2. The A-NCPM SHG wavelengths of mixed RE₁ₓRE₂₁−ₓCOB crystals.

| Crystal       | Optical Principal Axis | Type-I A-NCPM SHG Wavelength (nm) | Type-II A-NCPM SHG Wavelength (nm) | Reference |
|---------------|------------------------|-----------------------------------|-----------------------------------|-----------|
| Sm₀.₄₄Y₀.₅₆COB | Y                      | 794                               | 1165                              | [29]      |
|               | Z                      | 940                               | Inexistence                       |           |
| Sm₀.₅₅Y₀.₄₅COB | Y                      | 817                               | 1203                              | [29]      |
|               | Z                      | 977                               | Inexistence                       |           |
| La₀.₉₀Gd₀.₀₁COB | Y                      | 840                               | 1262                              | [18]      |
|               | Z                      | 987                               | Inexistence                       |           |
Table 2. Cont.

| Crystal                   | Optical Principal Axis | Type-I A-NCPM SHG Wavelength (nm) | Type-II A-NCPM SHG Wavelength (nm) | Reference   |
|---------------------------|------------------------|-----------------------------------|------------------------------------|-------------|
| La$_{0.123}$Gd$_{0.877}$COB | Y                      | 849                               | 1265                               | [18]        |
|                           | Z                      | 996                               | Inexistence                        |             |
| Gd$_x$Y$_{1-x}$COB (0 < x < 1) | Y                      | 724–826                           | 1032–1255                          | [27,28]     |
|                           | Z                      | 833–960                           | Inexistence                        |             |
| Gd$_{0.871}$Lu$_{0.129}$COB | Y                      | 792.5                             | 1160 *                             |             |
|                           | Z                      | 922.4                             | Inexistence                        | This work and [24] |
| Gd$_{0.953}$Lu$_{0.070}$COB | Y                      | 806.3                             | 1190 *                             |             |
|                           | Z                      | 938.9                             | Inexistence                        | This work and [24] |
| Gd$_{0.963}$Sc$_{0.037}$COB | Y                      | 801.3                             | 1171 *                             |             |
|                           | Z                      | 932.0                             | Inexistence                        | This work and [24] |
| Nd$_{0.085}$Gd$_{0.92}$COB | Y                      | 837                               | 1260                               | This work   |
|                           | Z                      | 982                               | Inexistence                        |             |
| Tm$_{0.02}$Gd$_{0.98}$COB  | Y                      | 827                               | 1238                               | This work   |
|                           | Z                      | 968                               | Inexistence                        |             |

* The values are calculated from the Sellmeier equations of Gd$_x$Lu$_{1-x}$COB and Gd$_x$Sc$_{1-x}$COB crystals [24].

3. Influence of RE$^{3+}$ in RE$_1$RE$_{2-xxxx}$COB Crystals

The different RE$^{3+}$ ions in RE$_1$RE$_{1-xxxx}$COB type mixed crystals will lead to the difference in transmission and birefringence properties. As shown in Tables 1 and 2, the type-I A-NCPM SHG wavelength along the Y-axis is the shortest among the three available NCPM styles, which is also called the short limit SHG wavelength. The variation of birefringence (at 800 nm) and short limit SHG wavelength (type-I A-NCPM SHG along the Y-axis) with rare-earth radius for pure RECOB and RE$_1$RE$_{2-xxxx}$COB mixed crystals were presented in Figure 1. The ionic radius for La$^{3+}$, Nd$^{3+}$, Sm$^{3+}$, Gd$^{3+}$, Y$^{3+}$, Tm$^{3+}$ and Ca$^{2+}$ positive ions in pure RECOB crystals are 1.032 Å, 0.983 Å, 0.958 Å, 0.938 Å, 0.890 Å, 0.880 Å, and 0.995 Å, respectively. For RE$_1$RE$_{2-xxxx}$COB mixed crystals, the comprehensive ionic radius of RE$^{3+}$ can be interpreted as $x_{RE1}^{3+} + (1 - x)_{RE2}^{3+}$. Take La$_{0.09}$Gd$_{0.91}$COB crystal for example, the comprehensive ionic radius of RE$^{3+}$ can be interpreted as $0.09r_{La^{3+}} + 0.91r_{Gd^{3+}}$, i.e., 0.946 Å. Thus, the comprehensive ionic radius of RE$^{3+}$ ions for Gd$_{0.871}$Lu$_{0.129}$COB, Gd$_{0.96}$Sc$_{0.04}$COB, and Gd$_{0.933}$Lu$_{0.07}$COB ($r_{Sc^{3+}} = 0.750$ Å, $r_{Lu^{3+}} = 0.861$ Å, $r_{Gd^{3+}} = 0.938$ Å) crystals in Figure 1 are represented as 0.928 Å, 0.936 Å, and 0.933 Å, respectively.

Figure 1 exhibits the dependencies of the ionic radius of RE$^{3+}$ on the birefringence, which can be defined that the lesser the difference of ionic radius between the RE$^{3+}$ and Ca$^{2+}$ ions, the smaller birefringence for RECOB crystals. The theoretical derivation had demonstrated that the A-NCPM SHG wavelengths were in inverse proportion to the birefringence at the fundamental laser, that is to say, the smaller crystal birefringence would generate the longer A-NCPM SHG wavelength, which had been proved in our previous work [25]. The intrinsic factor is the difference in radius between the RE$^{3+}$ and Ca$^{2+}$ ions in RECOB crystals, rather than the simple radius of RE$^{3+}$ ions. From Figure 1, it can be seen that the radius difference between Gd$^{3+}$ and Nd$^{3+}$ (Ca$^{2+}$) is almost equal to the value between La$^{3+}$ and Nd$^{3+}$ (Ca$^{2+}$), so the birefringence and A-NCPM SHG wavelengths of GdCOB and LaCOB crystals are quite close. The small content doping of La$^{3+}$ into NdCOB is a feasible approach to decrease the crystal birefringence, and further increase the A-NCPM SHG wavelengths. The theoretical criterion for designing new RECOB type crystals is the lesser the difference of ionic radius between the RE$^{3+}$ and Ca$^{2+}$ ions, the smaller birefringence, and then it brings about the redshift of A-NCPM SHG wavelength.
weaker than those of TmCOB, SmCOB, and NdCOB crystals, respectively. The existence of absorption peaks in visible and near-infrared regions for Tm\(_{x}\)Gd\(_{1-x}\)COB, Sm\(_{x}\)Y\(_{1-x}\)COB, NdCOB, and Nd\(_{x}\)Gd\(_{1-x}\)COB are obviously weaker than those of TmCOB, SmCOB, and NdCOB crystals, respectively. The existence of absorption peaks in visible and near-infrared regions for Tm\(_{x}\)Gd\(_{1-x}\)COB, Sm\(_{x}\)Y\(_{1-x}\)COB, NdCOB, and Nd\(_{x}\)Gd\(_{1-x}\)COB mixed crystals will restrict their A-NCPM SHG applications more or less, and the relevant discussions will be given in part 4 of this paper when the practical A-NCPM SHG wavelength is concerned.

Figure 1. Variation of birefringence and short limit of SHG wavelength with the rare-earth ion radius in RECOB crystals.

At room temperature of 25 °C, the optical transmission spectra of RECOB (RE: Tm, Tm\(_{0.02}\)Gd\(_{0.98}\), Sm, Sm\(_{0.44}\)Y\(_{0.56}\), Nd, and Nd\(_{0.08}\)Gd\(_{0.92}\)) crystals were measured by a NIR-UV-VIS spectrophotometer (U-4001, Hitachi, Tokyo, Japan). All of the experimental samples were cut along the Y-axis direction with a thickness of 2~3 mm, and the end faces were mechanically polished and uncoated. The measuring scope was 190~1600 nm with a scanning step of 1 nm. The transmission spectra of several representative RECOB type crystals were presented in Figure 2, including TmCOB, Tm\(_{0.02}\)Gd\(_{0.98}\)COB, SmCOB, Sm\(_{0.44}\)Y\(_{0.56}\)COB, NdCOB, and Nd\(_{0.08}\)Gd\(_{0.92}\)COB. Table 3 listed the absorption wavebands for different RECOB crystals. For illustration, the wavelengths of the absorption peak were marked in brackets. Comparing Figure 2a,c,e with Figure 2b,d,f, it can be seen that the location of the absorption peaks in Figure 2a,c,e are almost the same as in Figure 2b,d,f, respectively. However, the peak intensities and absorption waveband width of Tm\(_{0.02}\)Gd\(_{0.98}\)COB, Sm\(_{0.44}\)Y\(_{0.56}\)COB, and Nd\(_{0.08}\)Gd\(_{0.92}\)COB are obviously weaker than those of TmCOB, SmCOB, and NdCOB crystals, respectively. The existence of absorption peaks in visible and near-infrared regions for Tm\(_{x}\)Gd\(_{1-x}\)COB, Sm\(_{x}\)Y\(_{1-x}\)COB, and Nd\(_{x}\)Gd\(_{1-x}\)COB mixed crystals will restrict their A-NCPM SHG applications more or less, and the relevant discussions will be given in part 4 of this paper when the practical A-NCPM SHG wavelength is concerned.

Table 3. Absorption properties of RECOB (RE: Tm, Tm\(_{0.02}\)Gd\(_{0.98}\), Sm, Sm\(_{0.44}\)Y\(_{0.56}\), Nd, Nd\(_{0.08}\)Gd\(_{0.92}\), Y, Gd, and La) crystals.

| RECOB      | Tm       | Tm\(_{0.02}\)Gd\(_{0.98}\) | Sm       | Sm\(_{0.44}\)Y\(_{0.56}\) | Nd       | Nd\(_{0.08}\)Gd\(_{0.92}\) | Y, Gd, La |
|------------|----------|-----------------------------|----------|-----------------------------|----------|-----------------------------|-----------|
| Absorption waveband (Absorption peak) /nm | 336~374 (356) | 355~357 (356) | 355~371 (362) | 356~368 (362) | 344~372 (360) | 347~368 (354) |          |
|            | 442~489 (470) | 475~477 (476) | 395~427 (405) | 397~425 (405) | 493~550 (533) | 496~549 (534) |          |
|            | 614~730 (686) | 685~689 (687) | 1018~1133 (1070) | 1023~1126 (1075) | 551~623 (587) | 553~622 (587) |          |
|            | 730~839 (792) | 798~801 (799) | 1248~1271 (1224) | 1250~1240 (1221) | 713~762 (738) | 715~758 (741) |          |
|            | 1022~1297 (1208) | 1203~1212 (1207) | 1379~1423 (1394) | 1380~1417 (1394) | 775~832 (811) | 777~830 (810) |          |
|            | -         | -                           | 1424~1494 (1466) | 1426~1488 (1462) | -         | -                           |          |

No absorption peak at 350~2200 nm [15,17,30]
Figure 2. Transmission spectra of RECOB (RE: Tm, Tm\textsubscript{0.02}Gd\textsubscript{0.98}, Sm, Sm\textsubscript{0.44}Y\textsubscript{0.56}, Nd, and Nd\textsubscript{0.08}Gd\textsubscript{0.92}) crystals: (a) Transmission spectrum of TmCOB crystals; (b) Transmission spectrum of Tm\textsubscript{0.02}Gd\textsubscript{0.98}COB crystals; (c) Transmission spectrum of SmCOB crystals; (d) Transmission spectrum of Sm\textsubscript{0.44}Y\textsubscript{0.56}COB crystals; (e) Transmission spectrum of NdCOB crystals; (f) Transmission spectrum of Nd\textsubscript{0.08}Gd\textsubscript{0.92}COB crystals.

4. Selecting RE\textsubscript{1}RE\textsubscript{2}\textsubscript{1-x}COB Crystals

For mixed RE\textsubscript{1}RE\textsubscript{2}\textsubscript{1-x}COB crystals, the A-NCPM SHG wavelengths are continuously adjustable by varying the component x. As shown in Figure 2, the crystals containing Tm\textsuperscript{3+}, Sm\textsuperscript{3+} and Nd\textsuperscript{3+} rare-earth ions have some strong absorption peaks in their transmission wavebands, so the A-NCPM SHG wavebands demonstrated in Tables 1 and 2 will not be practical. In this part, we will give a discussion on how to select mixed RE\textsubscript{1}RE\textsubscript{2}\textsubscript{1-x}COB crystals to effectively realize the A-NCPM SHG in different wavebands, which may be a good reference for practical applications. For the sake of simplicity, we only consider the mixed RE\textsubscript{1}RE\textsubscript{2}\textsubscript{1-x}COB crystals with two different RE\textsuperscript{3+} ions. For SHG of near-infrared laser, people hope that the NLO crystal is colorless and no absorption peak exists in fundamental and SHG wavebands. So from the viewpoint of the transmission characteristics, the mixed crystals of Gd\textsubscript{x}Y\textsubscript{1-x}COB, La\textsubscript{x}Gd\textsubscript{1-x}COB, and La\textsubscript{x}Y\textsubscript{1-x}COB are more favorable. Previous works had confirmed that LaCOB was much easier to crack than YCOB and GdCOB crystals [31]. The main reason is that the large La\textsuperscript{3+} ionic radius can result in increasing the bond length, attenuating the electronegativity of RE, lowering the melting temperature, and enlarging the lattice stress, all of which will elevate the risk of the crystal cracking. It indicates that if the comprehensive RE\textsuperscript{3+} ionic radius of La\textsubscript{x}Gd\textsubscript{1-x}COB or La\textsubscript{x}Y\textsubscript{1-x}COB crystals is close to the radius of Ca\textsuperscript{2+}, for obtaining the
smaller birefringence and the longer A-NCPM SHG wavelengths than those of SmCOB and NdCOB, the component x of La$^{3+}$ should be 0.5 or larger, which will lead to severe crystal cleavage, and greatly increase the difficulty of crystal growth. So considering the crystal integrity and optical quality, the La$^{3+}$ should not be added with large quantities, and the Gd$_x$La$_{1-x}$COB and La$_x$Y$_{1-x}$COB are not ideal mixed crystals for A-NCPM SHG in a wide waveband scope. For the remaining colorless mixed crystal, Gd$_x$Y$_{1-x}$COB, the A-NCPM SHG wavelength scopes are 725–831 (type-I on Y-axis), 1032–1255 nm (type-II on Y-axis), and 826–973 nm (type-I on Z-axis), as seen in Tables 1 and 2.

To explore the wider A-NCPM SHG waveband, we need to consider another type of mixed RECOB crystal. The RE$^{3+}$ ions of such a crystal is composed by one of the colorless particles Y$^{3+}$, Gd$^{3+}$, La$^{3+}$, and one of the colorful particles Tm$^{3+}$, Sm$^{3+}$, Nd$^{3+}$ (here we do not consider the mixing of two types of colorful particles, because the transmission spectrum will be quite chaotic, and the usability for A-NCPM SHG is very poor). Considering the limitation to crystal quality of La$^{3+}$ ions, we only suggest the other two colorless particles, Y$^{3+}$ and Gd$^{3+}$, corresponding with six series mixed crystals can be formed, including Tm$_x$Y$_{1-x}$COB, Tm$_x$Gd$_{1-x}$COB, Sm$_x$Y$_{1-x}$COB, Sm$_x$Gd$_{1-x}$COB, Nd$_x$Y$_{1-x}$COB, and Nd$_x$Gd$_{1-x}$COB. Based on Figure 1, the possible tuning wavebands of these crystals are determined and listed in Table 4, along with the data of Gd$_x$Y$_{1-x}$COB. Combing with Table 1, we can delete the absorption wavebands in the fundamental and SHG spectral scopes, and obtain the practical tuning wavebands, as shown in Figure 3 and Table 4. Below we will discuss these wavebands according to the NCPM styles.

| Crystals     | Axis | Possible Waveband (nm) | Absorption Waveband (nm) | Practical Waveband (nm) | Possible Waveband (nm) | Absorption Waveband (nm) | Practical Waveband (nm) |
|--------------|------|------------------------|--------------------------|-------------------------|------------------------|--------------------------|-------------------------|
| Gd$_x$Y$_{1-x}$COB | Y    | 725–831                | -                        | 725–831                 | 1032–1255              | -                        | 1032–1255               |
|              | Z    | 826–973                | -                        | 826–973                 | Inexistence            |                          |                         |
| Tm$_x$Y$_{1-x}$COB | Y    | 716–725                | 358–363                  | 1011–1032               | 1022–1032              | 1011–1022                |                         |
|              | Z    | 815–826                | 815–826                  | Inexistence             |                        |                         |                         |
| Tm$_x$Gd$_{1-x}$COB | Y    | 716–826                | 730–826                  | 358–374                 | 1011–1255              | 1022–1255               | 1011–1255               |
|              | Z    | 815–960                | 815–839                  | 442–480                 | Inexistence            |                          |                         |
| Sm$_x$Y$_{1-x}$COB | Y    | 725–900                | 395–427                  | 742–790                 | 1032–1390              | 1032–1133               | 1248–1271               | 1379–1390              |
|              | Z    | 826–1116               | 1018–1116                | 413–427                 | 854–1018               | Inexistence             |                         |
| Sm$_x$Gd$_{1-x}$COB | Y    | 831–900                | 415.5–427                | 854–900                 | 1255–1390              | 1255–1271               | 1379–1390              | 1271–1379              |
|              | Z    | 973–1116               | 1018–1116                | 973–1018                | Inexistence            |                         |                         |
| Nd$_x$Y$_{1-x}$COB | Y    | 725–927                | 725–762                  | 775–832                 | 1032–1578              | 516–623                 | 713–789                 | 1246–1426              |
|              | Z    | 826–1205               | 826–832                  | 493–602.5               | 832–986                | Inexistence             |                         |
| Nd$_x$Gd$_{1-x}$COB | Y    | 831–927                | -                        | 831–927                 | 1255–1578              | 713–789                 | 1255–1426              |
|              | Z    | 973–1205               | 493–602.5                | 973–986                 | Inexistence            |                         |                         |

*a* in the fundamental and SHG spectral scopes. *b* 1390 nm is the calculated value from Sellmeier equations [25], which has not been observed in the experiment. *c* 1578 nm is the calculated value from Sellmeier equations [25], which has not been observed in the experiment.
Figure 3. A-NCPM SHG wavebands of various RE1-RE2-x-COB crystals.

(1) Type-I A-NCPM SHG wavelengths along the Y-axis. The 742–790 nm for SmxY1-x-COB, 762–775 nm for Nd1-xY1-COB are in the scope of 725–831 nm for GdxY1-x-COB, which has no new expansion. Comparing with the 854–900 nm for SmxY1-x-COB and SmxGd1-x-COB, the 832(831)–927 nm for Nd1-xY1-COB, Nd1-xGd1-x-COB is broader. As for Nd3+xY1 COB and Nd3+xGd1-x COB, the wavelength variation depending on the component x is more sensitive in Nd3+xY1 COB, while the close ion radius of Nd3+ and Gd3+ makes the growth of Nd3+xGd1-x COB relatively easier.

(2) Type-II A-NCPM SHG wavelengths along the Y-axis. For TmxY1-x-COB and TmxGd1-x-COB, the giant absorption waveband from 1022 nm to 1297 nm of Tm3+ ions covers most parts of the possible wavebands. The remaining practical waveband is 1011–1022 nm. Considering TmCOB still possesses high transmittance of 83.9% at 1032 nm, the available type-II A-NCPM SHG wavelength can extend to 1032 nm or even longer for TmxY1-x-COB or TmxGd1-x-COB crystals, which connect with the 1032–1255 nm waveband of Gd1-xY1-COB. Between TmxY1-x-COB and TmxGd1-x-COB, the wavelength variation depending on the component x is more sensitive in TmxGd1-x-COB, while the similar ion radius of Tm3+ and Y3+ is helpful to obtain the large size TmxY1-x-COB with high optical quality. The 1133–1248 nm for SmxY1-x-COB are in the scope of 1032–1255 nm for GdxY1-x-COB, which has no new expansion. Comparing to the 1271–1379 nm for SmxY1-x-COB and SmxGd1-x-COB, the 1246(1255)–1426 nm for Nd3+xY1-COB (1246–1426 nm) and Nd3+xGd1-x-COB (1255–1426 nm) is broader. For SmxY1-x-COB crystal, since the practical waveband of 1246–1426 nm is in the middle of the possible waveband of 1032–1578 nm, it will be difficult to determine the component x, at the same time the large ion radius discrepancy of Sm3+ and Y3+ will increase the crystal growth difficulty when a middle component (e.g., 0.4 ≤ x ≤ 0.6) is needed. Relatively, by gradually increasing the component x from zero, the adjusting of the A-NCPM SHG wavelength of SmxGd1-x-COB from 1255 nm towards infrared direction is easier, and the close ion radius of Sm3+ and Gd3+ will be helpful for crystal growth.

(3) Type-I A-NCPM SHG wavelengths along the Z-axis. The 839–884 nm for TmxGd1-x-COB is in the scope of 826–973 nm for Gd3+xY1-x-COB, which has no new expansion. As to the 854–1018 nm for SmxY1-x-COB and 832–986 nm for Nd1-xY1-COB, the former will be a better choice because their difference in the short wavelength range (832–854 nm) can be replaced by the A-NCPM scope of Gd3+xY1-x-COB (826–973 nm), while in the long wavelength range, the value of SmxY1-x-COB (1018 nm) is more than 30 nm longer than that of Nd1-xY1-COB (986 nm). On the other hand, the 973–1018 nm for SmxGd1-x-COB is much broader than the 973–986 nm for Nd3+xGd1-x-COB. For SmxY1-x-COB (854–1018 nm) and SmxGd1-x-COB (973–1018 nm), they exhibit the same expansion (973–1018 nm) for the A-NCPM scope of Gd3+xY1-x-COB. As mentioned above, because 973–1018 nm is in the middle of the
infrared direction is easier, and the close ion radius of Sm 3+ and Gd 3+ will be helpful for crystal growth.

To realize shorter A-NCPM SHG wavelengths than 0.725 µm, Lu 3+, Yb 3+, and Sc 3+ with the smaller rare-earth ions can be tried to be doped into YCOB crystal. Although some researchers have found that the pure LuCOB, YbCOB, and ScCOB are non-congruent, a small amount doping of Lu3+, Yb3+ or Sc3 into YCOB is still possible, to increase the birefringence and decrease the A-NCPM SHG wavelength.

Based on the above discussions, we can obtain the following enlightenments and conclusions:

To realize shorter A-NCPM SHG wavelengths than 0.725 µm, Lu 3+, Yb 3+, and Sc 3+ with the smaller rare-earth ions can be tried to be doped into YCOB crystal. Although some researchers have found that the pure LuCOB, YbCOB, and ScCOB are non-congruent, a small amount doping of Lu3+, Yb3+ or Sc3 into YCOB is still possible, to increase the birefringence and decrease the A-NCPM SHG wavelength.

Synthetically considering the factors of waveband width, the difficulty of component determination, and the convenience of crystal growth, we select an optimized A-NCPM SHG scheme from the numerous practical plans in Table 4 or Figure 3 and exhibit it in Figure 4. With four types of crystals including GdxY1−xCOB, SmxGd1−xCOB, TmxGd1−xCOB, and Nd4Gd1−xCOB, the whole waveband from 0.72 to 1.42 µm is covered (As mentioned above, the short broken band at 1022~1032 nm for type-II A-NCPM SHG along the Y-axis can be mended by TmxGd1−xCOB, which has a small absorption in this scope). Comparing to the previous results of GdxY1−xCOB, the present investigation in Figure 4 has three primary advantages: (1) The fundamental wavelength for the type-I A-NCPM SHG on the Y-axis (the optimum A-NCPM style of RE1xRE21−xCOB crystals which possess the largest d_{eff}) is extended from 831 nm to 927 nm. (2) The broken band at 973~1032 nm is mended. (3) The longest fundamental wavelength is extended from 1255 nm to 1426 nm.

Figure 4. An optimized crystal selecting scheme to completely cover the waveband of 0.72~1.42 µm.

5. High-Efficiency A-NCPM SHG Experiments

5.1. For OPO Laser

The A-NCPM SHG experiments were carried out on an OPO laser (Opolette HE 355 II, 410~2400 nm, OPOTEK Inc., Carlsbad, CA, USA). In order to increase the intensity of the fundamental laser, the beam was focused by a long focal length lens. In the output of the 700~900 nm waveband, the maximum incident average power was 5~7 mW, with a repetition rate of 20 Hz, and a pulse width of 5 ns or so. The SHG signal was separated from the remaining fundamental laser with a filter and then measured by a power meter. For taking advantages of A-NCPM, the RECOB crystal samples were
prepared as long as possible, including Y-cut YCOB (4 × 4 × 30.2 mm³), Gd₀.₂Y₀.₈COB (4 × 4 × 20 mm³), 
LaCOB (4 × 4 × 24.8 mm³), La₀.₀₉Gd₀.₉₁COB (4 × 4 × 26.7 mm³), Nd₀.₀₈Gd₀.₉₂COB (4 × 4 × 16 mm³), 
and Z-cut YCOB (4 × 4 × 23.5 mm³). During the SHG experiments, the OPO laser was adjusted to the 
A-NCPM SHG fundamental wavelength of each crystal sample. The change of the SHG conversion 
efficiency with the fundamental power was shown in Figure 5. It could be seen that although the 
experimental conditions were not ideal, including inferior beam spatial quality, small pulse energy 
(~0.3 mJ), low power density (6~7 MW/cm²), and large beam divergence after focusing via a long-focus 
 lens, the single-pass SHG conversion efficiencies were still elevated to 20~35% by using long crystal 
samples, taking advantage of A-NCPM for RECOb crystals, i.e., large deff, absence of beam walk-off, 
and large angular acceptance. The short limit wavelength of our OPO laser was 410 nm, and it could 
be extended to 362 nm by using the A-NCPM SHG of GdₓY₁₋ₓCOB crystals. These experiments prove 
that RE₁ₓRE₂₁₋ₓCOB crystals are highly efficient A-NCPM SHG materials for OPO lasers.

Figure 5. Type-I A-NCPM SHG conversion efficiency of RE₁ₓRE₂₁₋ₓCOB crystals for the OPO laser.

5.2. For Ti:Sapphire Laser

Besides the OPO, the Ti:sapphire laser is another important, popularly used, 
and wavelength-tunable solid laser source. Its frequency doubling laser can reach the blue-violet 
spectral region. In this experiment, six RECOb crystals were prepared, including Y-cut GdCOB 
(4 × 4 × 30.6 mm³), La₀.₀₉Gd₀.₉₁COB (4 × 4 × 26.7 mm³), La₀.₁₃Gd₀.₈₇COB (4 × 4 × 18.5 mm³), LaCOB 
(4 × 4 × 24.8 mm³), Nd₀.₀₈Gd₀.₉₂COB (4 × 4 × 16 mm³), and Z-cut YCOB (4 × 4 × 23.5 mm³). The 
fundamental laser source was a mode-locked Ti:sapphire laser (Verdi-v10+Mira900, Coherent Inc., Santa Clara, CA, United States). It supplied a tuned wavelength range of 740~900 nm laser 
pulses with 120 fs and 76 MHz repetition rate. The fundamental laser was had a long-focus lens to 
increase the power density. The maximal fundamental power available for the SHG crystals was 
about 1.1 W. During the SHG experiments, the Ti:sapphire laser was adjusted to the A-NCPM SHG 
fundamental wavelength of each crystal sample. Figure 6 presented the variation of the SHG conversion 
efficiencies as a function of fundamental power for different crystal samples, which were measured at 
room temperature. The maximum SHG output power was 497 mW obtained from a Y-cut GdCOB 
crystal sample under the fundamental power of 1052 mW, which was corresponding to a conversion 
efficiency of 47.2%. It was superior to those of the Y-cut La₀.₀₉Gd₀.₉₁COB (45.3%), LaCOB (45.1%), 
La₀.₁₃Gd₀.₈₇COB (40.2%), and Nd₀.₀₈Gd₀.₉₂COB (37.4%) crystals, owing to the longer crystal length 
(30.8 mm). Under the same fundamental power of 1020 mW, the SHG conversion efficiency of the Z-cut
YCOB crystal ($4 \times 4 \times 23.5 \text{ mm}^3$) was 33.4%. It was obviously lower than that of La$_{0.13}$Gd$_{0.87}$COB crystal (40.2%) with a length of 19 mm, which could be attributed to the small $d_{\text{eff}}$ for the Z-axis ($-0.22 \text{ pm/V}$). In Figure 6, the maximum fundamental power the SHG conversion efficiency was not saturated and still increased. It is a great pity that the SHG output power and conversion efficiency cannot be obtained was used in the experiments to better the results, limited by the output power of the Ti:sapphire laser. Nevertheless, the present experiments have fully illustrated that the A-NCPM of RECOB type crystals are highly efficient SHG styles for the Ti:sapphire laser to generate blue-violet coherent lights.

![Figure 6. Type-I A-NCPM SHG conversion efficiency of RE$_1$RE$_{21-x}$COB crystals for the Ti:sapphire laser.](image)

Over the past two decades, many NLO crystals such as KH$_2$PO$_4$ (KDP), LBO, BaB$_2$O$_4$ (BBO), and BiB$_2$O$_6$ (BIBO) were attempted to be used for frequency doubling of Ti:sapphire lasers to get blue-violet coherent lights. With different lengths of KDP, LBO, BBO, and BIBO crystal samples (0.5~40 mm), most of the single-pass frequency doubling efficiencies of femtosecond pulses (790~810 nm, 100~150 fs) generated by Ti:sapphire lasers were reported to be in the ranges of 30~50%, which were considered to be affected by many complex factors such as group-velocity mismatch, spectral acceptance, third-order nonlinearity, thickness of NLO crystal, intensity of the fundamental laser, and the laser damage threshold [32–34]. In order to decrease group-velocity mismatch and increase spectral acceptance for ultrafast laser pulses, short NLO crystal samples are selected, nevertheless, a higher incident light intensity is needed to maintain high conversion efficiency, which will be limited by the laser damage threshold and produce more third-order nonlinear phenomena. Comparing with the CPM of KDP, LBO, BBO, and BIBO crystals for frequency doubling of Ti:sapphire lasers, the A-NCPM of RECOB were found to possess large angular acceptance ($60^\circ$~$80^\circ$, Y-axis, type-I) and no beam walk-off ($0^\circ$, mrad-cm), which would be beneficial for using the long crystal sample to improve conversion efficiency [25]. Then, the spectral acceptance at about 0.7~0.9 μm for RECOB is measured in the order of 4.3~8.7 nm·cm$^{-1}$, which is several times larger than those of KDP (1.6 nm·cm$^{-1}$) and BBO (0.74 nm·cm$^{-1}$) crystals [25,32]. In addition, the largest thermo-optic coefficients of GdCOB ($dn_Y/dT = 2.1 \times 10^{-6} \text{ °C}^{-1}$) and YCOB ($dn_Z/dT = 5.0 \times 10^{-6} \text{ °C}^{-1}$) are much smaller than those of KDP ($dn_Y/dT = -33.1 \times 10^{-6} \text{ °C}^{-1}$), LBO ($dn_Y/dT = -13.0 \times 10^{-6} \text{ °C}^{-1}$), BBO
we theoretically determine that they can realize the A-NCPM SHG of 0.72~1.42 µm. At the same time, this work provides a good reference for future A-NCPM researches of other frequency conversion styles and other NLO crystals.

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6. Conclusions

By investigating RE1_xRE2_{1-x}COB (RE1, RE2 = Y, Gd, La, Tm, Sm, and Nd) mixed crystals, we theoretically determine that they can realize the A-NCPM SHG of 0.72~1.42 µm fundamental lights. Based on the A-NCPM SHG experimental results, there is an important rule that the lesser the difference of ionic radius between RE1_xRE2_{1-x} (xRE1^{3+} + (1-x)RE2^{3+}) and Ca^{2+} (rCa^{2+}), the smaller birefringence, and then it leads to the redshift of the A-NCPM SHG wavelength. Under focusing light beam conditions, efficient NCPM SHG for both OPO and Ti:sapphire lasers were realized experimentally. The present researches illustrate that RE1_xRE2_{1-x}COB (RE1, RE2 = Y, Gd, La, Tm, Sm, and Nd) crystals are practical A-NCPM SHG materials for various near-infrared wavelengths. Comparing with bulk NLO crystal LBO, the main advantages of RE1_xRE2_{1-x}COB type crystals are large size, rapid Czochralski growth, and further extending work wavelength (720~950 nm) towards a visible direction. So RE1_xRE2_{1-x}COB (RE1, RE2 = Y, Gd, La, Tm, Sm, and Nd) mixed crystals are irreplaceable NLO materials for large aperture beam, high energy, near-infrared A-NCPM applications. At the same time, this work provides a good reference for future A-NCPM researches of other frequency conversion styles and other NLO crystals.

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