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Recent advances in self-frequency-doubling crystals

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Abstract

The self-frequency-doubling (SFD) crystal is a representative of multifunctional crystals. In recent years, SFD crystals and lasers have gained renewed attention based on the progress on SFD crystals and lasers and Nd:$RECa_4O(BO_3)_3$ (RE = Y or Gd) crystals, with SFD lasers becoming commercial products. Here, we review the advances of SFD crystals and lasers, including the basic selection rules, theoretical analysis and recent progress of some potential SFD crystals and lasers. The Nd:$RECa_4O(BO_3)_3$ crystals and lasers are highlighted, and their applications are also proposed and discussed, which may provide some inspiration for the further development of the SFD field and multifunctional materials.

Keywords: Multi-functional crystals; Self-frequency-doubling; Solid-state lasers

Contents

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1. Introduction

Since the first laser was demonstrated in 1960, laser techniques and materials have been developed for over fifty years [1]. To date, lasers have become important tools for revolutionizing the modern science research and techniques. Laser crystals are the fundamental materials. There are many practical laser crystals, among which Nd:YAG, Nd:YVO_4 and Ti:Al_2O_3 are three of the most widely-used crystals. Nd:YAG dominates in the high-power lasers, Nd:YVO_4 is used in low and moderate power applications, and Ti:Al_2O_3 is famous for its laser frequency tunability and ultrafast laser applications [2–10]. Currently, near infrared lasers are quite mature and commercially available. Based on the study of the history of laser development, it can be found that laser development is moving towards high power, ultrafast and extended wavelength, and many laser crystals have appeared, aiming at the requirement of the laser development by designing or optimizing the crystal lattices.

In general, one laser only operates at a certain specific wavelength. To obtain lasers of different wavelengths, nonlinear optics should be used [11]. Second-order nonlinear processes, including second-harmonic generation (SHG), sum-frequency generation (SFG), difference frequency generation (DFG), optical parametric oscillation (OPO) and optical parametric amplification (OPA), have become common approaches for expanding the available laser wavelengths in the visible and mid-infrared spectral ranges. Moreover, the uses of third-order harmonic, stimulated Raman scattering (SRS) and four-wave mixing are also promising techniques for the frequency conversion. However, in the visible range, the widely used technique is SHG. In 1961, frequency doubling was first observed by projection of an intense ruby laser through crystalline quartz, which marked the birth of the field of nonlinear optics [12]. Later, the nonlinear crystals KH_2PO_4 (KDP) and $LiNbO_3$ (LN) were found. In the 1980's, the nonlinear crystal was developed significantly. After development of the $KTiOPO_4$ (KTP) crystal [13,14], several non-linear crystals, including β-BaB_2O_4 (β-BBO), LiB_3O_5 (LBO) and KBe_2BO_3F (KBBF), were discovered by Chinese researchers [15–18]. The development of laser and nonlinear optical techniques is motivating the study of the effects of simultaneous lasing and SHG. In this regime, self-frequency-doubling (SFD) is the leader. In this work, we reviewed the development of SFD crystals and their SFD lasers. The potential applications were also highlighted.

2. Basic requirements of the self-frequency-doubling laser crystal

SFD crystals belong to multi-functional materials and possess both laser and frequency doubling properties. The crystals with structural high-symmetry, such as cubic YAG, are favorable laser applications because the high-symmetry structure determines the high isotropy in physical properties, including the thermal expansion, thermal conductivity, absorption and emission, resulting in simplicity in laser applications. However, the frequency-doubling crystals should be without inversion centers in the structure. Therefore, the mature frequency-doubling crystals are those with moderate and lower symmetrical structures. In addition, to achieve efficient frequency-doubled lasers, the momentum conservation, i.e., phase matching in optics, is necessary. We can conclude that the SFD performance is not a simple superposition of the laser and frequency-doubling, and the efficient SFD should result from efficient coupling and matching between the laser and frequency-doubling effects. Based on the analysis above, the basic requirements of an efficient SFD laser crystal are qualitatively summarized as follows [19]:

2.1. Excellent laser properties

Lasing is the basic property of SFD effects. The evaluation criterion for a promising laser crystal is also applicable to SFD crystals. Therefore, the lattice of the host crystals is suitable for doping with active ions, which determines that the mature nonlinear optical crystals, including KDP, KTP, LBO, BBO and KBBF, cannot be applied as SFD crystals, and the SFD crystal should have broadband absorption with large absorption peak suitable for the emission of diodes, large emission cross-sections, long fluorescence lifetime, high radiative quantum efficiency and low photon energy.

2.2. Excellent nonlinear optical properties with suitable birefringence

Nonlinear frequency conversion is another basis of the SFD effect. Therefore, the desirable nonlinear crystal should have a large effective nonlinear coefficient, a suitable birefringence for compensating the phase-mismatching, a large acceptance angle, wide-transmission spectra, etc. Note that phase-matching means that the polarized emission peak of the SFD crystal should agree with the phase-matching condition, for example, in the type I phase-matching condition, $o + o \rightarrow e$, where o is the ordinary light and e is the extraordinary light, the highest emission peak should be o light.

2.3. Excellent thermal properties

The favorable SFD crystals should have large thermal conductivities (enabling the efficient extraction of heat from the crystals), low anisotropy in thermal expansion (enabling simplicity in crystal growth), a large thermal damage threshold and low thermal focal effects (low thermal-optical coefficients minimize the effects of heat on the refractive indices, phase matching conditions and thermal induced loss).

2.4. Excellent physical and chemical stability

Excellent physical and chemical stability means that the crystals should be nonhygroscopic, have moderate hardness (simplifying cutting and processing), and have no phase-transition at the moderate high and room temperatures.

In addition, the basic requirements for the crystals only determine the available series for SFD, but the efficient output of SFD lasers requires good coupling between the lasing and nonlinear optical properties. To achieve the optimized SFD lasers, the lasing efficiency should be equal to that of SHG, i.e., the generated laser in the SFD crystal can be converted to the frequency-doubled output. To satisfy this criterion, the designing of the SFD devices should be optimized, including the doping concentration of the active ions in the crystal, crystal length, thermal engineering for the efficient transported heat during the SFD process, etc. SFDs require more than SHG and lasing, which hinders the development of SFDs.

3. Theoretical analysis of the self-frequency-doubling laser process

To achieve experimental realization of high-efficiency SFD lasers, the relationship between the concentration of active ions and the crystal length of the SFD laser crystal is key. The conservation of energy is the universal principle in all the light-matter interaction processes. Considering this principle, the pump power is the source of energy, the output power and generated heat are the results, and the laser oscillation is the intermediate process, if the coating is ideally perfect and no fundamental laser is transmitted from the SFD crystal of linear polarization emission. In the following, we focus on the Nd^{3+} ions doped SFD laser materials because the SFD process of Nd^{3+} doped laser crystal is more complicated and universal than that of Yb^{3+} doped materials due to the absorption of Nd^{3+} ions at approximately 532 nm [19]. In fact, the absorption at 532 nm can be assumed as the pump source for the generation of fundamental lasers; however, the quantum efficiency γ_{SFD} is 50%.

In the assumption shown above, the pump power (P_{abs}) absorbed by the SFD laser crystal consisted of four terms:

$$P_{abs} = P_{SFD} + P_F + P_Q + P_{re} \tag{1}$$

where P_{SFD} is the output power of the SFD laser, P_F is the power contributed to the fluorescence emission, P_Q is the power due to the quantum defect during the lasing process, P_{re} is the quantum defect generated by the reabsorption at the SFD laser, which can be assumed as the re-pumping source.

In the lasing process, the fluorescence emission part is negligible. In an end-pumped Nd^{3+} SFD laser, the absorbed pump power is determined by the incident pump power P_{in} and absorption efficiency of the crystal. The absorption efficiency can be calculated as follows:

$$\eta_{abs} = 1 - \exp(-\alpha_0 L) \tag{2}$$

where α_0 is the absorption coefficient, and L is the thickness of the crystal. The efficiency for the generated heat during laser oscillation can be shown as

$$\eta_Q = \eta_q \eta_{abs} = \eta_q[1 - \exp(-\alpha_0 L)] \tag{3}$$

where η_q is the quantum defect. In addition to the terms described above, there is also intrinsic loss γ and absorption with the absorption coefficient of γ_{abs} at the SFD laser. Therefore, the conversion efficiency η of SFD laser can be expressed as

$$\eta = \frac{P_{out}}{P_{in}} = \left(1 - \eta_Q\right)\eta_{abs}(1 - \gamma - \gamma_{abs} - \gamma_{SFD}) \tag{4}$$

Because the absorption coefficient is proportional to the doping concentration c, the relationship among the conversion efficiency, doping concentration and SFD crystal length can be estimated.

Based on the developed model for analyzing the relationship among the conversion efficiency, doping concentration and SFD crystal length, the optimized parameters of Nd:GdCOB were calculated. During the calculation, the pump wavelength was chosen to be 811 nm, and the fundamental wavelength is 1060 nm, with the SFD wavelength of 530 nm. The absorption coefficients in the optimized phase-matching direction at 811 nm and 530 nm were experimentally determined to be 17.96 cm^{-1} and 17.4 cm^{-1}, respectively. The intrinsic loss γ and the absorption coefficient γ_{abs} at the fundamental wavelength are estimated to be 2% and 0.25%, respectively. The results are shown in Fig. 1. From this figure, we can find that the maximum conversion efficiency is 36.8% and the optimized crystal length is dependent on the doping concentration. However, the doping concentration determines the optical damage threshold, which indicates that the doping concentration should not be higher than 10 at.%. Therefore, the optimized doping concentration should be 5 at.% − 8 at.%, with the optimized length of approximately 1 cm. Moreover, we also find that the absorption of the SFD laser is significant for the conversion efficiency, and the SFD laser at 545 nm can be absorbed by the SFD crystal to achieve a conversion efficiency of 75%.

4. Development of SFD crystal and lasers

Since the first demonstration in 1969 [20], SFD lasers and materials are still under development; however, the watt-level SFD output are only obtained from the Yb^{3+} doped

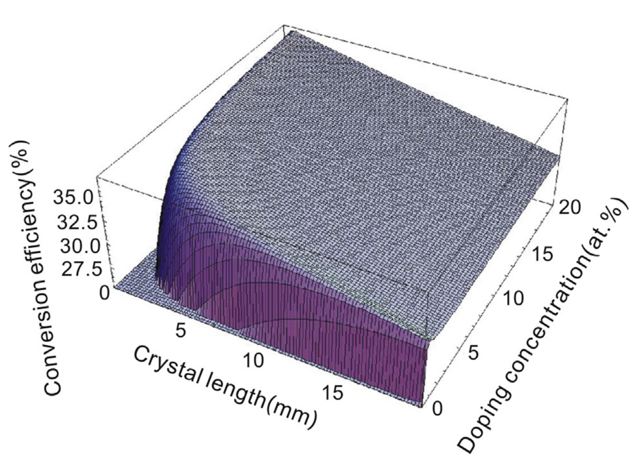

Fig. 1. Relationship among the conversion efficiency, crystal length and doping concentration.

$YAl_3(BO_3)_4$ (Yb:YAB) and Nd^{3+} doped $GdCa_4O(BO_3)_3$ (Nd:GdCOB) crystals [21−23]. In the past few decades, the representative SFD crystals and lasers are the following:

4.1. Active-ion doped $LiNbO_3$ series crystals

$LiNbO_3$ and $LiTaO_3$ are famous frequency-doubling crystals and belong to the 3 m point group. The nonlinear coefficients are $d_{22} = 2.46 \pm 0.23$ pm/V, $d_{31} = -4.64 \pm 0.66$ pm/V, $d_{33} = -41.7 \pm 7.8$ pm/V in stoichiometric crystals (mole ratio Li/Nb = 1) and $d_{22} = 2.10 \pm 0.21$ pm/V, $d_{31} = -4.35 \pm 0.44$ pm/V, $d_{33} = -27.2 \pm 2.7$ pm/V in congruent crystals (mole ratio Li/Nb = 0.946). The transmission spectra range is from 0.4 to 5.5 μm, and its largest thermal conductivity is 4.6 W/(mK). There are also ferroelectric domains in the crystal that can be periodically poled under a high-electric field to generate reciprocal vectors compensating the phase-mismatching. Based on the periodic poling technique, the maximum effective nonlinear coefficient can be employed, and different nonlinear processes could be realized, including simultaneous frequency-doubling of different fundamental wavelengths, sum-frequency, and third-harmonic generation [24−26].

$LiNbO_3$ can become a laser material when doped with active ions. Tm:$LiNbO_3$ is the first SFD crystal at the SFD wavelength of 926.6 nm and a fundamental wavelength of 1853.2 nm [20]. Subsequently, SFD was reported with a Nd:$LiNbO_3$ crystal pumped by a xenon lamp [27]. Unfortunately, the photorefractive damage caused by either the pump or emitted radiation and relatively low conversion efficiency during the SFD process blocked the practical applications of $LiNbO_3$ crystals. To reduce the photorefractive damage in $LiNbO_3$, the oxides including Sc_2O_3, MgO, and ZnO [28−30], were co-doped with Nd^{3+} ions. Fig. 2 shows the grown Nd:MgO:$LiNbO_3$ crystal by the Czochralski method. In the end of the 1980s, MgO:$LiNbO_3$ was developed and found that it has an improved damage threshold, which aroused the fervor for the investigation of SFD with MgO:$LiNbO_3$ as the host for SFD. In 1986, the continuous-wave SFD green laser was realized with Nd^{3+} doped MgO:$LiNbO_3$ crystal, as the SFD crystal and the output power of more than 1 mW was achieved [31]. In 1999, the SFD green laser at 530 nm was achieved by using a Yb:MgO:$LiNbO_3$ as the SFD crystal and a Ti:sapphire laser as the pump source, and the maximum output power was 60 mW under the pump power of 800 mW [30]. Moreover, the periodically poling technique can increase the conversion efficiency and realize different nonlinear optical processes. With periodically polled Nd:MgO:$LiNbO_3$ crystals, the frequency-doubled blue, green and red lasers were demonstrated; in addition, the self-pumped optical parametric oscillator and quasi-phase-matched self-sum-frequency-mixing of 1084.4 and 1373.6 nm, corresponding to the laser channels of $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{13/2}$, respectively, were also reported with a wavelength of 606 nm and output power of 15.6 mW [32,33]. Recently, with an optimized periodically poled Nd:MgO:$LiNbO_3$ crystal, the SFD green laser was reported with a maximum output power of 80 mW and a laser-diode as the pump source [34]. Nd^{3+} and Yb^{3+} doped $LiTaO_3$ crystals were also investigated, aiming at SFD applications [35,36].

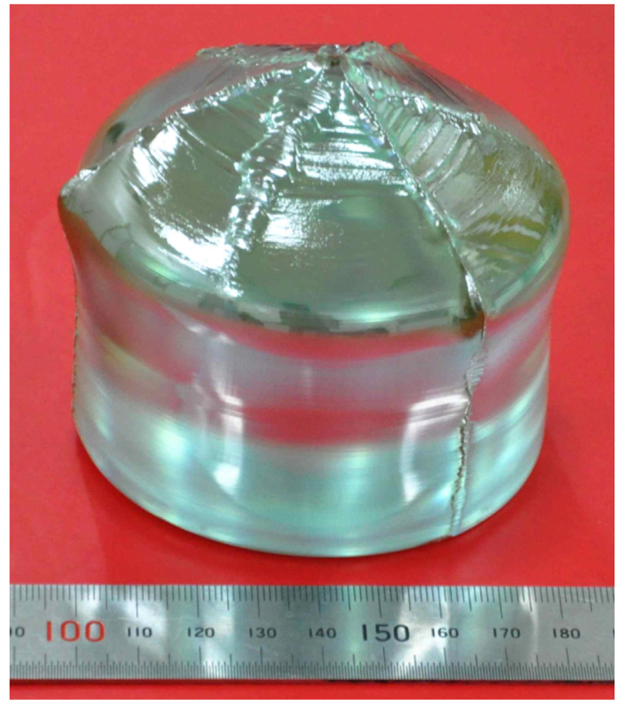

Fig. 2. As-grown Nd:MgO:$LiNbO_3$ crystal boule provided by Prof. Hong Liu's group of Shandong University.

Above all, the active ions doped $LiNbO_3$ series crystals were identified as SFD crystals, and the maximum SFD output power has been demonstrated to reach tens of milliwatts. The periodically poling techniques broaden the potentials and improve the SFD output power. However, perhaps constrained by the crystal quality when doping with active ions and the intrinsic photorefractive damage, there is still a way to achieve practical applications of SFD of active ions doped $LiNbO_3$.

4.2. Active ions doped YAB crystals

In the Nd^{3+} doped SFD crystal, there is a strong absorption peak at approximately 532 nm, which brings the difficulty for the efficient green SFD laser converted from 1.06 μm. YAB is not only a well-known nonlinear material but also a good host material of solid laser crystal. It is a negative uniaxial crystal with an $R32$ space group and 32 (D_3) point group symmetry [37,38]. The lattice parameters of YAB crystal are $a = b = 9.295$ Å, $c = 7.243$ Å, $\alpha = \gamma = 90°$ and $\beta = 120°$ [39]. YAB melts incongruently at 1280 °C and decomposes into YBO_3 and $AlBO_3$. Therefore, YAB cannot be crystallized from stoichiometric melts. The crystal exhibits unique properties of high damage threshold, acceptable phase matching range and good NLO coefficients. By the phase matching method, the effective NLO coefficient d_{eff} of YAB was determined to be 1.11 pm/V. YAB also has good mechanical and chemical stability, which are beneficial for manufacturing.

Thus, because of the advantages mentioned above, many researchers focused on the YAB and rare-earth doped YAB crystals for their nonlinear and laser properties. In 1981, $Nd_{0.2}Y_{0.8}Al_3(BO_3)_4$(Nd:YAB) crystal was developed and identified as a SFD crystal by the experimental realization of a 660 nm SFD laser pumped by a flash lamp [40]. In 1986, B. S. Lu et al. achieved the self-doubling effect from 1.06 μm to 532 nm by adjusting the proportion of Nd^{3+}/Y^{3+} in the Nd:YAB crystal [41]. With the development of laser-diodes, the first all solid-state SFD Nd:YAB green laser was reported in 1990. To date, the maximum SFD Nd:YAB green laser is 225 mW under the pump power of 1.6 W with a laser diode as the pump source, and the maximum output power of 450 mW was realized under the pump power of 2.2 W with a Ti:sapphire as the pump source [42]. Besides the absorption of Nd^{3+} ions at the green wavelength band, the $NdAl_3(BO_3)_4$ (NAB) and $YAl_3(BO_3)_4$ (YAB) belong to the monoclinic and trigonal groups, respectively [39,43], and they coexist in Nd:YAB independently. The NAB monoclinic has no nonlinear optical properties, due to its inversion center in structure. The coexistence of NAB and YAB generated the layered distribution of different materials with different groups, which determines the great difficulty of acquiring high-quality Nd:YAB crystals. Associated with the absorption of Nd^{3+} ions, it is very difficult for Nd:YAB crystal to be applied in the efficient SFD green lasers. Similar to Nd:YAB, the Nd:$GdAl_3(BO_3)_4$ (Nd:GAB) crystal is also an important laser crystal that belongs to the Nd:$RAl_3(BO_3)_4$ (R = Y, Gd, Nd, La, Lu, Tb, Dy, Er, Yb) borate family. In 2001, a green SFD laser of 119.5 μJ/pulse with a 4.3% yield was obtained [44,45]. The inhomogeneity problem also exists in the Nd:GAB crystal; thus, high-quality crystal was very difficult to obtained. In addition, the effective nonlinear coefficients of GAB are also slightly smaller than those of YAB. Thus, a high efficiency SFD green laser is also very difficult to obtain using a Nd:GAB crystal.

Fortunately, $YbAl_3(BO_3)_4$ (YbAB) has the same symmetry in its structure, and Yb^{3+} is a promising active ion and has no absorption at approximately 532 nm [46,47]. It was proposed that the Yb:YAB should be a potential SFD crystal. With the top seeded high temperature solution growth method (TSSG), the Yb:YAB crystal was grown, as shown in Fig. 3. The refractive indices of Yb:YAB crystal were measured using the V-prism method. According to the measured refractive indices, it was calculated that its type I and II phase matching angle are $\theta_{PM}(I) = 34°12'$ and $\theta_{PM}(II) = 49°43'$, respectively, and for the generation of green lasers with the corresponding maximum effective nonlinear coefficient, they are $\chi_{eff}(I) = 0.822d_{11}$ and $\chi_{eff}(II) = 0.418d_{11}$, respectively. In 2001, the maximum output power of 1.1 W was realized in the SFD Yb:YAB green laser under the pump power of 11 W with the wavelength of 977 nm [21]. Under this pump power, the maximum output power of a fundamental laser is 4.3 W, with a slope efficiency of 48%. Due to the wide emission spectra of Yb^{3+} ions, the tunability of SFD Yb:YAB laser is in the range of 510−545 nm.

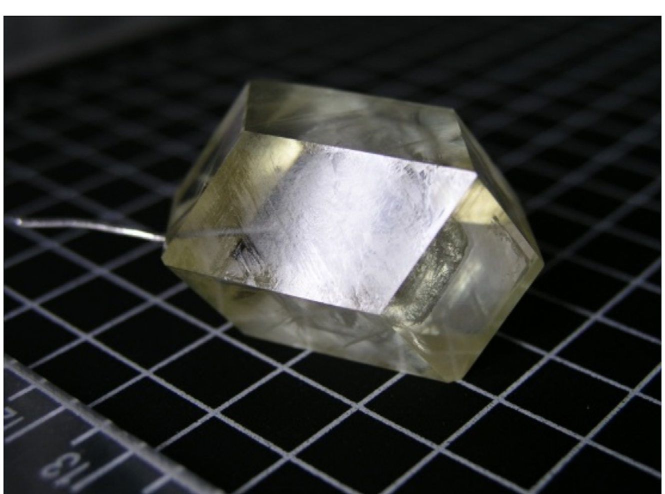

Fig. 3. As-grown Yb:YAB crystal boules.

4.3. Active ions doped rare-earth calcium oxyborate (RECOB) crystals

4.3.1. Summary of the RECOB crystals

Since 1990, a new member of the rare-earth calcium oxyborate (RECOB) crystals with the chemical composition of $RECa_4O(BO_3)_3$ (RE = Y, La, Gd, and Sm) has attracted a great deal of research interest [48−54]. The RECOB single crystals exhibit the monoclinic crystal structure with the *C*m space group. The discovery of rare-earth calcium oxyborate family compounds brought new hope for SFD materials. Among these crystals, the YCOB and GdCOB both possess the high effective nonlinear coefficients and can realize phase matching in the near-infrared range. When doping with the laser-active ions, such as Nd^{3+}, Er^{3+}, and Yb^{3+}, the RECOB crystals became SFD laser crystals with both the laser and nonlinear functions. Among these rare earth doped RECOB crystals, Nd:GdCOB, Yb:GdCOB, Nd:YCOB, and Yb:YCOB are some of the most intensively studied laser host materials [22,23,53−57].

GdCOB and YCOB crystals belong to the monoclinic system with the *C*m space group and the m point group. The structure of GdCOB and YCOB is shown in Fig. 4. In these crystals, the Ca^{2+} ions have two positions, as shown in Fig. 3 b and c, which induce structural disorder. These crystals have similar unit cell parameters: for GdCOB, the unit cell parameters are $a = 0.8106$ (2), $b = 1.6028$ (3), $c = 0.3557$ (1) nm, and $\beta = 101.25°$ [51]; for YCOB, the unit cell parameters are $a = 0.8046$, $b = 1.5959$, $c = 0.3517$ nm, and $\beta = 101.19°$ [49]. The GdCOB crystal has a wide transparency range from 0.2 to 3.7 μm. There are three sharp absorption peaks in the UV region, centered at approximately 0.25, 0.28 and 0.31 μm. In the IR region, three absorption bands were observed, centered at 2.72, 2.90 and 3.25 μm.

The YCOB crystal, also has a wide transparency range from 0.202 to 3.700 μm. There are no obvious absorption peaks in the UV region compared with the GdCOB crystal. In the IR region, three absorption band are observed, centered at 2.70, 2.90 and 3.25 μm.

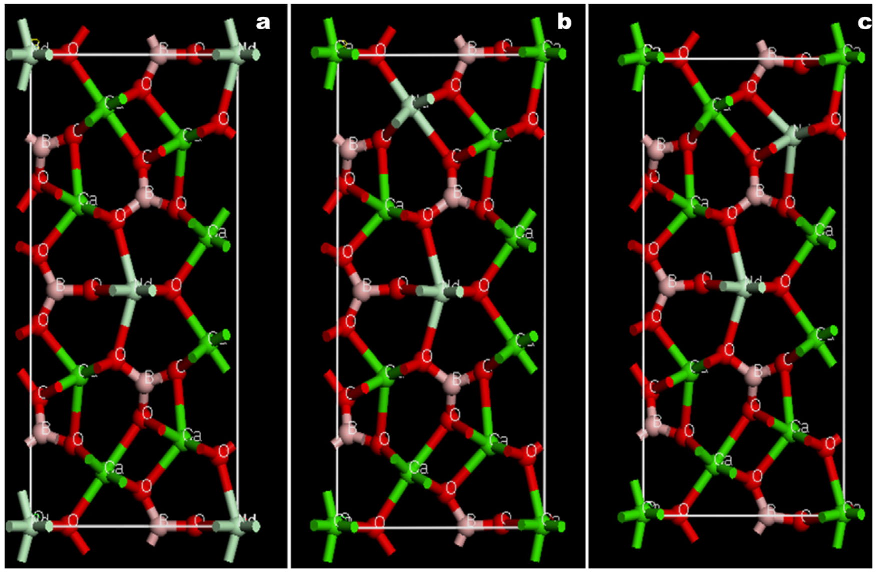

Fig. 4. Structure of GdCOB and YCOB. a. The ordered structure. b. Ca^{2+} ions in the 1 positions. c. Ca^{2+} ions in the 2 positions.

Regarding nonlinearity, there are six independent nonlinear coefficients obtained by considering the Kleimann symmetry condition. The reduced matrix nonlinear coefficients are described as follows:

$$[d_{in}] = \begin{bmatrix} d_{11} & d_{12} & d_{13} & 0 & d_{31} & 0 \\ 0 & 0 & 0 & d_{32} & 0 & d_{12} \\ d_{31} & d_{32} & d_{33} & 0 & d_{13} & 0 \end{bmatrix}$$

The second-order nonlinear optical coefficients of GdCOB are $d_{11} = 0$, $d_{12} = 0.27$, $d_{13} = -0.85$, $d_{31} = 0.20$, $d_{32} = 2.23$, and $d_{33} = -1.87$ pm/V. The second-order nonlinear optical coefficients of YCOB are $d_{11} = 0$, $d_{12} = 0.24$, $d_{13} = -0.73$, $d_{31} = 0.41$, $d_{32} = 2.00$, and $d_{33} = -1.60$ pm/V [52]. Both GdCOB and YCOB crystals have moderate hardness, with the Mohs hardness of 6.5 and excellent physical and chemical stability.

According to the dispersion equation, the effective nonlinear coefficients on the spatial distribution can be calculated. We found that the largest effective nonlinear coefficients of GdCOB or YCOB are not in the principle planes but rather at a special angle. Their largest effective nonlinear coefficients were both approximately $\theta = 113°$ in the second quadrant. The corresponding phase matching angles of GdCOB and YCOB are (113.2°, 47.4°) and (113°, 36.5°), respectively [52]. Thus, the crystal sample cut along the special angle should have the optimal nonlinear property. When doped with the active ions, the nonlinear property is little changed. For the SFD Nd:GdCOB laser crystal, to a large extent, its output characteristics are determined by the effective nonlinear coefficient. We can thus conclude that the optimal direction of the self-frequency-doubling is the optimal direction of the frequency doubling.

When doped with the Nd^{3+} or Yb^{3+} laser-active ions, their basic properties of the crystals, including the hardness, stability and nonlinear optical properties, are almost unchanged, and the crystals can be grown by the Czochralski method. Fig. 5 is the photograph of the as-grown Nd:GdCOB (7.5 at.%) crystal boule along the *b* direction. In the viewpoint of crystal chemistry, the ionic radii of Nd^{3+} and Yb^{3+} are similar to Gd^{3+} and Y^{3+}, respectively. Therefore, the doping of Nd^{3+} ions in GdCOB and Yb in YCOB crystals would not change the lattice obviously, and high-quality crystals can be achieved. Moreover, observed from the emission spectra of the Nd:GdCOB, we can find that there is an emission peak at approximately 1.09 μm, which can

Fig. 5. The as-grown Nd:GdCOB (7.5 at.%) crystal boule.

depress the output of 1.06 μm by augmenting the temperature. By the SFD process, a green laser at 545 nm can be achieved that escapes the absorption of Nd^{3+} ions at approximately 532 nm.

4.3.2. Laser operation of Nd:GdCOB crystal

The application of self-doubling crystals in the laser technique is an important feature as it is significant for estimating the application value. The stimulated emission cross section of Nd:GdCOB along the three principle axes at 1060 nm are $\sigma_x = 1.3 \times 10^{-20}$ cm^2, $\sigma_y = 1.4 \times 10^{-20}$ cm^2, and $\sigma_z = 2.8 \times 10^{-20}$ cm^2 [52]. Based on the symmetry of the crystal, the cross sections of the fast and slow light versus phase angles can be determined. We can also find that among the full range of phase angles, cross sections of the slow light are greater than that of the fast light. Due to the dispersion of the crystal, the large emission cross section of slow light is beneficial to the phase matching of the self-doubling process. Meanwhile, in accordance with the comparison of emission cross sections, it can be clearly seen that the laser along the z polarized direction has the best laser characteristics.

The laser characteristics at 1060 nm of three principal axes have been reported by Mougel et al. in the year 1997 [53]. The results showed that the crystals along the Y axis possessed a lower threshold and higher efficiency. In the year of 2000, Lucas-Leclin et al. reported the microchip laser output characteristics of Nd:GdCOB [54]. It was found that a dual-wavelength laser output of 1060 and 1091 nm was obtained when pumped by the high power. In addition, the power of laser at 1060 nm reduces and that at 1091 nm increases with the pump power increased. According to their analysis, the $^4F_{3/2}$ state of Nd^{3+} ions undergoes the Stark energy level splitting effect, with the upper level corresponding to the start of transition of 1091 nm and the lower level corresponding to the start of transition of 1060 nm. With increasing pump power, the temperature of the crystal increases. On the basis of Boltzmann Statistics, the number of electrons of lower level reduced with the increasing of the upper level, and the gain of 1060 nm decreased with the increase in the level of 1091 nm, leading to the increasing output of 1091 nm and the reducing output of 1060 nm. They also measured the temperature spot that equally split the output power of 1091 and 1060 nm, which was 55 °C.

Before we started to study the Nd:GdCOB crystal, its SFD property was the main research topic of the crystal. The output power of the fundamental frequency laser of the crystal was only in the milliwatt range. Thus, much work is required to further the exploration for the higher output power.

Through theoretical computation and analysis, the optimal doping concentration of Nd^{3+} was determined to be approximately 10 at.%, and the sample length was determined to be approximately 10 mm. We obtained an efficient SFD yellowish green laser at 545 nm by using the Nd:GdCOB crystal [23]. The experimental configuration is exhibited in Fig. 6. The pump source was a fiber-coupled laser-diode with a central wavelength approximately 808 nm. The core size (ω) of the fiber is 100 μm in radius, with a numerical aperture of 0.22. The pump light was focused into the Nd:GdCOB crystal

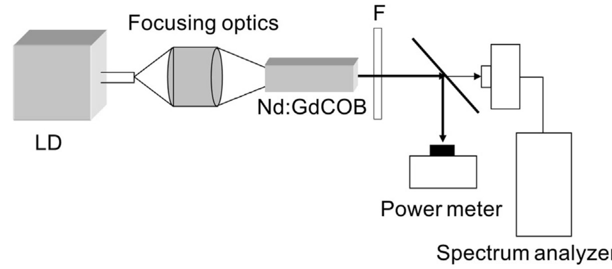

Fig. 6. Experimental configuration of the Nd:GdCOB SFD lasers.

by an imaging unit with a beam compression ratio of 1:1. To cool Nd:GdCOB under high pump power levels, the SFD crystal was wrapped with indium foil and mounted in a water-cooled copper block. To accurately measure the output power of the green lasers, a mirror (F) was all-reflection coated at 1060–1091 nm and high-transmission (HT) coated at 530–545 nm (transmission of 78%). In this experiment, the Nd:GdCOB was cut along the type I phase-matching direction (113°, 49°) out of its principal planes, with a fundamental wavelength of 1091 nm and lengths of 8 mm. The Nd concentration was determined to be 8 at.% to compensate for its small emission cross-section. The sample faces were polished and the front antireflection (AR) coated at 808 nm and high-reflection ($R > 99{:}8\%$) coated at both 1060–1091 nm and 532–545 nm. To maximize the absorption, the end face was high-reflection (HR) coated at both 808 nm and 1060–1091 nm and HT coated at 530–545 nm.

The output power versus increase of incident pump power is presented in Fig. 7. It can be found that the sample with a length of 3 × 3 × 8 mm^3 shows the best performance. The threshold (P_{th}) was measured to be 2.16 W, and highest output power was 3.01 W under the pump power of 14.56 W, with the optical conversion efficiency of 20.7%. To the best of our knowledge, this report is the highest output power and efficiency in the SFD laser field. With an optical spectrum analyzer, the spectrum was found to be centered at 545 nm in all the operations, as shown in Fig. 8. This figure shows that

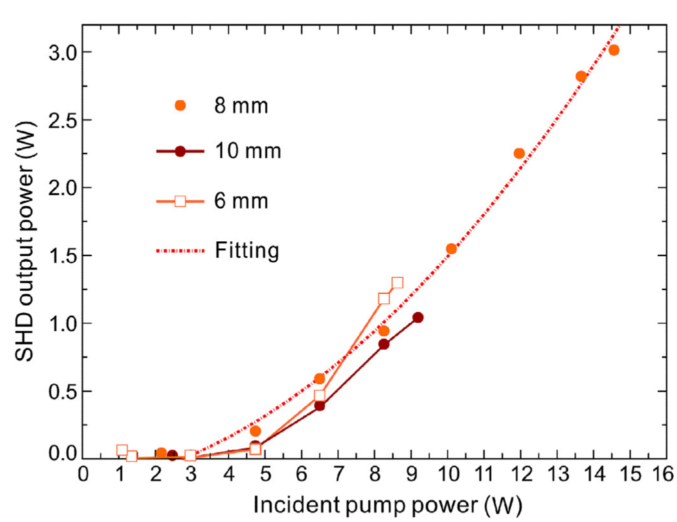

Fig. 7. Output powers versus incident pump power of the Nd:GdCOB lasers at approximately 545 nm with the crystal lengths of 8 mm, 10 mm and 6 mm.

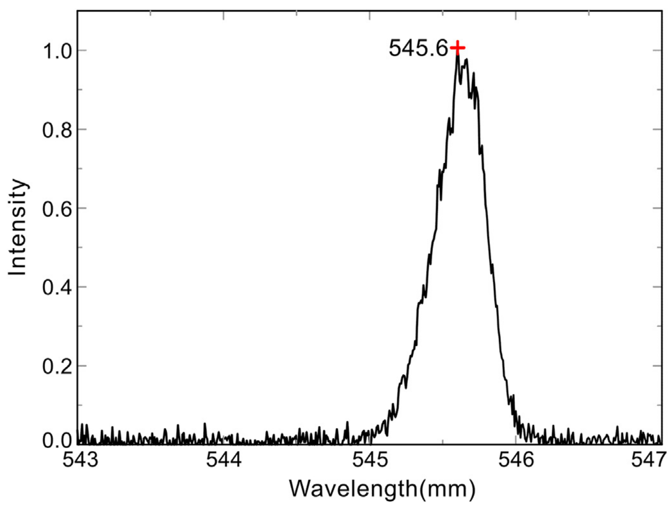

Fig. 8. Spectra of the Nd:GdCOB SFD lasers at the peak of 545 nm.

the spectrum is wide, and the laser is multimode. With the model of continuous-wave end-pumped lasers, the final temperature in the crystal was calculated to be 36 °C.

4.3.3. Applications of Nd:GdCOB crystal

1) Nd:GdCOB green laser pointer

Currently, the module of Nd:YVO_4 and $KTiOPO_4$(KTP) is the most commonly used for designing the green laser pointer. The Nd:YVO_4 crystal possesses a high absorption coefficient, large absorption and emission cross-sections and polarization emission, and the KTP crystal has the advantages of a large nonlinear coefficient. The green laser pointer designed by combining the two crystals thus has the high optical conversion efficiency, and its output power could reach 10−200 mW. Although the module of Nd:YVO_4 and KTP has been used very commonly, it still has some disadvantages, including the complex and long-time growth process of KTP and difficulty in obtaining the eye-safe power ($\leq$1 mW). Nd:GdCOB crystal can be grown with the commercial Czochralski method, and large crystals with high quality can be achieved in a short time. Moreover, the Nd:GdCOB crystal has a smaller emission cross-section than that of Nd:YVO_4 and a smaller nonlinear coefficient than that of KTP, which indicates that the absorbed pumped power range between the threshold and a relatively low power (such as ~ 1 mW) is large. Thus, it is easy to obtain a 1-mW eye-safe green laser pointer.

2) Potential application in laser displays

Currently, the laser display technology based on the three primary lasers (RGB) could realize over a 90% coverage of the color space. The main way to obtain the green laser is by using the KTP, PPLN, or LBO frequency doubling crystals. However, the SFD laser system possesses the advantages of simple structure, good stability, and low cost, which deserves further research because of their potential application in the laser displays field. In the laser displays field, the green laser of wavelengths smaller than 532 nm combined with the red and blue laser could realize the largest coverage of the color space. For the SFD Nd:GdCOB laser crystal, there are several emission peaks located at 1040, 1046, 1060, 1064 and 1090 nm. At room temperature, the emission cross-section at 1060 nm is the largest one. Through the SFD effect of the Nd:GdCOB crystal, we can easily obtain the laser output at 530 nm. Thus, we believe that the Nd:GdCOB crystal has potential for application in laser displays.

3) Other potential applications

Based on the compactness, stability, high efficiency, etc., the Nd:GdCOB SFD laser with a single frequency may also be easily achieved, which can be applied for the pump source of Raman spectrometers. In theory, the Nd:GdCOB is a type of crystal for lasers and SHG which indicated that some laser and SHG applications in their own fields may also be possible, and other potential applications, including self-mode-locking based on the laser and cascading SHG processes, should be achieved in the near future.

4.4. Other potential SFD crystals

4.4.1. Active ion (Yb^{3+} or Nd^{3+}) doped $La_2CaB_{10}O_{19}$ (LCB) crystal

LCB crystal [58−61] is biaxial and belongs to the *C*2 monoclinic space group. In the crystal, the principal axis of refractive index (X, Y and Z) does not correspond to the crystallographic axis (*a*, *b* and *c*) and b//Y, (a, Z) = 46.03°, and (c,X) = 47.5°. The transmission range is from 0.185 μm to 3.0 μm. The nonlinear coefficients are d_{21} = 0.433 pm/V, d_{22} = 0.484 pm/V, d_{23} = 0.437 pm/V and d_{14} = 0.64 pm/V. The effective nonlinear coefficient for type I phase matching at 1064 nm → 532 nm is 1.05 pm/V. In this crystal, Nd^{3+} ions or Yb^{3+} ions can occupy La^{3+} and Ca^{2+} positions, which can split the emission spectra [62], for example, the Nd^{3+} ions doped LCB, the ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition corresponds to the wavelength spectra peaked at 1051 nm and 1069 nm [63], and the ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$ transition corresponds to the wavelength spectra peaked at 1343 nm and 1322 nm [64]. To date, SFD green and red lasers have been obtained, with the maximum output power of 100 mW at the wavelength of 525 nm in Nd:LCB crystal [65].

4.4.2. Neodymium doped ferroelectric crystals

Ferroelectric crystals are also frequency-doubled materials. In the SFD field, Nd^{3+} ions doped $LaBGeO_5$ and $Sr_xBa_{1-x}(NbO_3)_2$ (SBN) series ferroelectric crystals have been the focus of much attention [32,66,67]. In recent years, $Ca_xBa_{1-x}(NbO_3)_2$ (CBN) series ferroelectric SFD crystals were also developed, and the SFD laser was demonstrated [68]. However, the diffraction loss generated by the ferroelectric domains are serious in Nd:SBN and Nd:CBN crystals, which may constrain the efficient generation of SFD lasers. As an example, $LaBGeO_5$ crystal and SFD lasers are combined as follows:

$LaBGeO_5$ is a nonlinear positive uniaxial crystal and belongs to the point group of 3. Due to the component of rare earth La^{3+} ions, the Nd^{3+} ions are easily incorporated. This crystal has ferroelectric domains and a transmission range from 0.19 to

4.5 μm. The effective nonlinear coefficients are $d_{11} = 0.46 \pm 0.07$ pm/V, $d_{22} = 0.23 \pm 0.074$ pm/V, $d_{31} = 0.41 \pm 0.06$ pm/V, and $d_{33} = 0.35 \pm 0.05$ pm/V at the fundamental wavelength of 1064 nm. The fluorescence lifetime is approximately 280 μs at room temperature [69]. In 1990, Kaminskii et al. reported the laser properties of the Nd:LaBGeO$_5$ crystal [70]. In 1998, the SFD green Nd:LaBGeO$_5$ crystal laser was realized at 524 nm with an output power less than 100 μW [66]. In 1999, the SFD red Nd:LaBGeO$_5$ crystal laser was reported with an output power of approximately 0.8 mW at the wavelength of 657 nm [71]. In Nd:LaBGeO$_5$ crystal, the SFD green laser can be absorbed by the crystal, which also induced large loss and instability [66], and the SFD red laser was from the $^4F_{3/2} \rightarrow {}^4I_{13/2}$ transition, which generates two emission peaks at 1314 and 1386 nm but with different polarizations [71].

4.4.3. Recent developed SFD crystals

Aiming at the applications of visible SFD lasers, there are also some novel SFD crystals developed recently, including Nd:Ca$_3$TaGa$_3$Si$_2$O$_{14}$ (Nd:CTGS) [72], Nd:Ca$_5$(BO$_3$)$_3$F [73], Nd:BaCaBO$_3$F [74], and whitlockite-type vanadates crystals [75]. In those crystals, the maximum SFD output power of approximately 18.8 mW at the wavelength of 533 nm was achieved in the Nd:CTGS crystal [72]. The potential applications of novel SFD crystals are still under study, and the efficient coupling between the frequency-doubling and laser properties requires further study. Thus, we believe that how to achieve the high efficient and multi-wavelength lasers will be the ultimate goal and direction for SFD crystals. In addition, easy preparation and low cost are also necessary for SFD crystals.

5. Conclusions

In conclusion, the recent advances in the SFD laser crystal and lasers were reviewed, including the theoretical analysis, experimental development and potential applications. Some important SFD crystals were summarized and compared with each other, and the SFD Nd:GdCOB crystal was highlighted because the highest SFD output power (3 W and 27% efficiency) was achieved in these crystals, and the SFD Nd:GdCOB lasers have been used in commercial products in recent years. The potential applications include eye-safe green lasers and laser displays. We believe that SFD crystals and lasers will play important roles in the visible laser regimes due to their compactness and stability; however, SFD is a complex process, and the progress of SFD lasers requires the comprehensive development of crystalline science, crystalline physics, crystal lasers and nonlinear optics.

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We reviewed the advances of self-frequency-doubling (SFD) crystals and lasers, including the basic selection rules, theoretical analysis and recent progress of some potential SFD crystals and lasers.

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