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Flux growth and 266nm generation of $GdAl_3(BO_3)_4$ crystal

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Abstract：The study focused on optimization of growing conditions of $GdAl_3(BO_3)_4$(GAB). Using Al_2O_3-B_2O_3-Li_2O-NaF as fluxes, inclusion-free GAB crystal with sizes up to 18×18×35 mm^3 had been successfully grown by the top-seeded solution growth technique. Preparation process of starting materials, flux selection and optimization of growing parameters were discussed in the paper. The laser radiation at 266 nm was firstly generated by the type Ⅰ phase-matching GAB crystal.

Introduction

The ultraviolet (UV) region lasers emitting at 266nm can be used in many fields, such as microelectronics and micromachining etc.[1] Such UV laser input can be obtained by frequency conversion of solid-state IR laser by using nonlinear optical (NLO) crystals. At present, $CsLiB_6O_{10}$ (CLBO), β-BaB_2O_2 (BBO), $KBr_2BO_3F_2$(KBBF) and $YAl_3(BO_3)_4$ (YAB) among NLO crystals can realize the fourth-harmonic generation (FoHG) of an all-solid-state Nd:YAG laser.[2-5] However, there are its own disadvantages of every borate for practical application. CLBO crystals have a moderate NLO coefficient but high hygroscopicity, and BBO crystals have a high NLO coefficient but unfavorable properties such as large walk-off angle, small angular bandwidth and photorefractive damage.[6] KBBF and YAB have excellent properties for UV region application, but they are difficult to be grown: layer structure for the former one, and twin crystal for the latter one.[3, 7] So it still is great of interest in searching a potential NLO crystal which is able to realize FoHG.

As an excellent UV nonlinear crystal, it must have a moderate NLO coefficient, low absorption coefficient in input wavelength region and a cut-off edge shorter than 266 nm. Gadolinium aluminum borate crystals $GdAl_3(BO_3)_4$ (GAB) may be a possible candidate. GAB crystal, which was discovered in the 1960s, belongs to the carbonate huntite structure in the space group R32, and the crystal has good physicochemical properties, such as high hardness, nonhygroscopicity and high chemical stability.[8] Additionally, since high NLO coefficient (3.5 times larger than that of KDP), high transmittance and the easily doped characterize which the octahedral sites can be easily substituted by other lanthanide ions, GAB crystals doped with Nd^{3+}, Yb^{3+}, which can be used as self-frequency doubling crystals, have attracted many attentions.[9-11] The growth of GAB or doped GAB crystals had been studied in $K_2Mo_3O_{10}$ - B_2O_3 flux system, and the results indicated the crystals were easily grown.[12, 13] But few reports had focused on the application as a NLO material to realize the FoHG, because the cut-off edge of GAB crystal at UV region was located at 310 nm.[13, 14] From the conclusion in the growth of YAB crystal, the long cut-off edge come from flux system, and it had been confirmed by the fact that the cut-off edge of YAB crystals grown from flux system without molybdate was shorter than 190nm.[15-17] To overcome the drawback of GAB, we developed a new flux system: Al_2O_3-B_2O_3-Li_2O-NaF.[18] The cut-off edge of GAB crystal grown from the new flux was shifted to 175 nm, and the size reached to 18×16×15 mm^3. The phase matched angle was calculated from Sellmeier equation, and the result indicated the GAB crystal may realize the FoHG of an Nd: YAG laser. But the size of as-grown crystal limited the device fabrication for the laser experiment, so 266 nm emitting had not yet been obtained.

So in this paper, we had optimised the flux system and growth parameters to obtain the large crystal. Then a GAB crystal by TSSG with the size of 18×18×35 mm^3 had been successfully obtained from the Al_2O_3-B_2O_3–Li_2O-NaF flux system. And the details of the growth were also discussed. Furthermore, as-grown GAB crystal was characterized by powder X-ray diffraction, the powder SHG coefficient and transparency spectrum measurement in the range of 180–3000 nm. The generation of 266 nm radiation based on the second harmonic of 532 nm using the prism cut from as-grown GAB crystal was firstly reported.

Experimental

Crystal growth

Firstly, the appropriate composition of the growth system was decided. GAB, Al_2O_3, H_3BO_3, Li_2CO_3, and NaF with different molar ratios were as the raw materials. The raw materials

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were grounded to mix uniformity in an aluminum oxide mortar. Then they were molten in a ϕ70×60 mm^3 platinum crucible at 1250 °C and hold at this temperature until the solution became transparent. Afterwards the melt was allowed to cool at a rate of 1-2 °C per hour to process the spontaneous nucleation. When enough small single crystals presented in the solution, the crucible was cooled with 20-30 °C per hour down to room temperature. Then the crucible was boiled in hot nitric acid solution to obtain small GAB crystals. The range of the molar ratio of the starting material was determined with three factors: the temperature where spontaneous nucleation present, the amount of the nucleation and the size of the crystals. From the spontaneous nucleation experiments, we can conclude that the appropriate molar ratio of GAB: Al_2O_3: H_3BO_3: Li_2CO_3: NaF for GAB crystal growth was in the range of 1:(2-4):(15-25):(2-5):(0.5-3).

For GAB crystal growth, the TSSG method was used. The starting materials were prepared by solid state reaction of G_2O_3, Al_2O_3, H_3BO_3, $LiCO_3$, and NaF powders of 4N with appropriate molar ratios. The reaction was as follows:

$G_2O_3+3Al_2O_3+8H_3BO_3=2GAl_3(BO_3)_4+12H_2O$.

After mixing homogeneously in an agate mortar, the starting materials were molten quickly in a ϕ80×65 mm^3 platinum crucible in a preheated muffle furnace at 1250 °C, until there was about 60 percent charge in the crucible for crystal growth. Then the crucible was placed in an electric resistive furnace, as shown in Fig. 2, which was controlled by a programmable Eurotherm (model 818) temperature controller. After the temperature was raised to 1160 °C, the melt was stirred by a platinum stirrer for 48 h. The saturation temperature was determined exactly by the repeated seeding method with an attempted seed crystal. After that a [0 0 1] seed crystal with 1.5×1.5 mm^2 transverse section was slowly introduced into the melt at a temperature of 5–10 °C above the saturation temperature. Then the temperature was lowered to the saturation point in an hour. The growth rate was controlled to be very slow at the beginning with the cooling rate in the range of 0.1–0.3 °C/day. During its growth, the seed crystal was rotated at 10–20 rpm with the rotation direction inverted every 2 min. After the growth completed, the crystal was slowly drawn out of the melt and the furnace was cooled to room temperature at a rate of 15–20 °C/h. A GAB crystal with the dimensions of 18×18×35 mm^3 was obtained, as shown in Fig. 3. The GAB crystal was prismatic with the c-axis along the seed direction.

Characterization

The viscosity of growth solution was measured by a DV-II +(American Brookfield Co.) viscosity meter. The measured temperature range was from 1080 °C to 950 °C.

For the measurement of the temperature gradient in the growth crucible, platinum-rhodium thermocouple and a mixture of ice and water were used. The temperature gradient was measured from 10 mm above the melt to 30 mm underneath the melt.

The UV transmittance spectrum was recorded at room temperature by using Lambda 900 UV/VIS/NIR (Perkin–Elmer) spectrophotometer, and a 1 mm thick slab of GAB crystal grown in the Al_2O_3-B_2O_3–Li_2O-NaF flux polished on both sides were used with a wavelength range of 0-220 nm.

For FoHG, a crystal prism with dimension of 3×3×5 mm^3 was cut from as-grown GAB crystal, which yields type-I phase matching with θ=62.5 ° and ψ=0 ° for frequency doubling 532 nm radiation of a Nd laser.[19] An uncoated GAB device was used. The experimental laser source was PL2143 Series Laser System (Ekspla Co.) with pulse width of 25 ps, repetition rate of 10 Hz, and beam diameter of 1 mm at 532 nm. The average power of the input and output was measured by an Ophir 3A-SH power meter (Ophir Optronics Ltd.). The diameter of the output beam was focused to 1.5 mm.

Fig. 1 GAB crystal grown by TSSG method in Al_2O_3-B_2O_3–Li_2O-NaF flux

Results and discussion

GAB crystal growth

As mentioned above, the new flux system should be found to grow GAB crystals to overcome the drawback that the impurities of Mo exist in crystals grown from the $K_2Mo_3O_{10}$–B_2O_3 systems. Since YAB crystal with UV cut-off edge located shorter than 170 nm was successfully grown from the flux system of B_2O_3–Li_2O or Al_2O_3-B_2O_3-Li_2O, and the cut-off edge of as-grown YAB crystal was shifted to 170 nm, we developed the new flux system of Al_2O_3-B_2O_3–Li_2O-NaF based on the previous work.

After the appropriate molar ratio of flux system had been determined, a large GAB single crystal was successfully grown from the new flux. In the process of GAB crystal growth, we found characterizes of the melt, such as viscosity and saturation temperature, would varied with the different molar ratio of H_3BO_3 and Li_2CO_3, which had been seen from YAB crystal growth.[19] The phenomenon could be very helpful to quickly find appropriate ratio of B_2O_3 and Li_2O in the flux system. Moreover, a proper addition of Al_2O_3 could expand the crystalline region of alumina borate salt, though more excessive would lead to restriction of crystalline region.[20] So the addition of Al_2O_3 could improve the crystalline quality and extend the cooling range of temperature. However, the additions of B_2O_3 and Al_2O_3 could cause the high viscosity in the melt. Since the low viscosity of the melt would be good for heat and mass transfer, and help to obtain good quality crystal

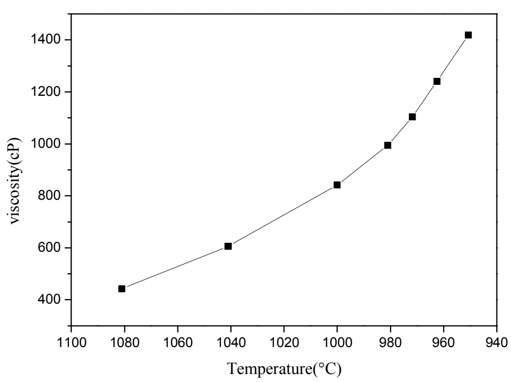

Fig. 2 Viscosity of the system with appropriate molar ratio

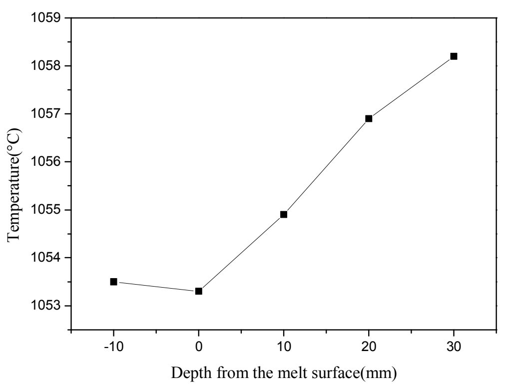

Fig. 3 The temperature gradient of the melt

in the growth region, the viscosity of melt should be improved. Hence, some simple fluorides, such as LiF, NaF or BaF_2, were tried as additives to decrease the viscosity of the flux system. Based on the results of spontaneous nucleation, proper excessive of NaF would reduce the viscosity of melt without reducing crystalline quality. So Al_2O_3, B_2O_3, Li_2O, NaF with appropriate molar ratio could be used as flux system.

The viscosity of the solution is shown in Fig. 2. When the temperature is lower than 1060 °C, the viscosity is higher than 500 cp. So we could determine that the viscosity of the melt is much higher. The reason for this phenomenon is the high mass of H_3BO_3 in the raw material. However, the high H_3BO_3 content make the melt a low saturation temperature, which would reduce the volatility of the system flux.

In the previous growth, the seed crystal was 3×3 mm^2, but there were many conclusions under the seed crystal because of strong growth habit. To reduce the conclusions and improve the quality of the crystal, we take 1.5×1.5 mm^2 crystal oriented at c axis as the seed. In the growth, the small seed crystal was stable and the conclusions were absence in the crystal, which could be seen in the Fig. 1.

The temperature gradient of the melt was shown in Fig. 3. As shown in the figure, the temperature gradient along the vertical direction in the melt was positive, and there was about 4.6 °C from 0 mm to 30 mm underneath the melt. Since the viscosity of the melt is high, large temperature gradient is benefit for the mass and heat transfer, and then for the crystal growth.

So in the new Al_2O_3-B_2O_3-Li_2O-NaF flux system a GAB crystal with the size of 18×18×35 mm^3 was grown. The crystal was mainly transparency, but there were a few inclusions on the bottom of as-grown crystal.

In this work, GAB growth region in the flux system was over 40 °C. However, the region may be extended, because the melt was also transparent at the end of the growth, only the size of crucible limited the crystal growth.

Optical properties

The transparency spectrum of as-grown GAB crystal measured under air atmosphere is displayed in Fig. 4. The spectrum showed the transmittance of GAB at the wavelength range of 185-3000 nm, and the inner was the transmittance of GAB crystal at wavelength range of 185 nm to 500 nm. The transmittance was about 80% at visible region, and no special absorption band existed. As shown in the inner, the cut-off edge of GAB crystal is shorter than 266 nm, which make GAB crystal grown from Al_2O_3-B_2O_3-Li_2O-NaF flux a promising material for FoHG of Nd: YAG. However, there are some absorption bands at the wavelength range of 200 nm to 300 nm, which were also observed in the KABO crystal and assigned to $O2p^5$-$Fe3d^6$ transitions.[21] In the literature, this phenomenon contributed to the impurity of Fe^{3+}, which may come from the impurity of the starting material or the contamination of growth furnace. The absorption band would be weakened or disappear when the content of Fe^{3+} impurity is small to a certain extent.

To verify the nonlinear optical property in UV region, the efficiency of 266 nm radiation on the 532 nm input peak power density was measured. When the input peak power density was 1.5 Gw/cm^2 (3.75 mJ of single pulse energy with 25 ps and 10 Hz), the output peak power density only was 0.021 Gw/cm2 at 266 nm (0.0525 mJ of single pulse energy with 25 ps and 10 Hz). The conversion efficiency from 532 nm to 266 nm radiation of GAB crystal remained almost unchanged when the 532 nm input peak power density

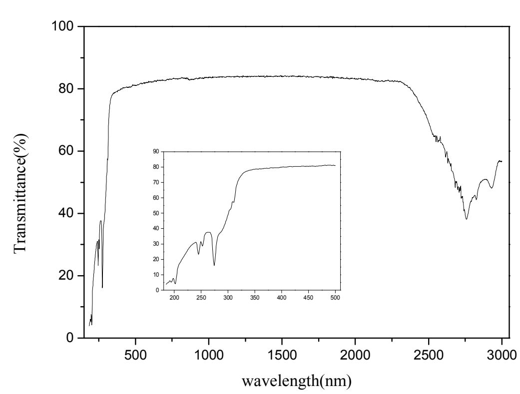

Fig. 4 The transmittance spectrum of GAB crystal at wavelength range of 180-3000 nm

increased. It was much lower than that of the other crystal used as NLO crystals to realize FoHG.[5, 22, 23] The reason for the low conversion efficiency may be the absorption at 266nm, the quality of as-grown GAB crystal and the size of GAB sample. To make GAB crystal a NOL crystal in UV region, the absorption of GAB crystals in the range of 200–300 nm should be reduced, and large size crystal with high quality should be grown. It had been reported YAB crystal grown from the Al_2O_3-Li_2O-B_2O_3 flux by top-seeded solution growth in a non-oxygen atmosphere was free of UV absorption.[24] So we could grow GAB crystal with no UV absorption in non-oxygen atmosphere and the work is in progress.

Conclusions

To overcome the shortcomings of the flux systems with molybdate, GAB crystals were grown from the Al_2O_3-B_2O_3–Li_2O-NaF flux system. The suitable molar ratio of the Al_2O_3-B_2O_3–Li_2O-NaF flux was determined by spontaneous nucleation. The result suggested that the range of molar ratio within GAB: Al_2O_3: H_3BO_3: Li_2CO_3: NaF =1:(2-4):(15-25):(2-5):(0.5-3) was suitable for GAB crystal growth. An 18×18×35 mm^3 GAB crystal was obtained from the new flux system. The cut-off edge of the as-grown GAB crystal was shorter than266 nm. In addition, there were some absorption bands from 200 to 320 nm, which may be caused by the Fe^{3+} impurity. The laser radiation at 266 nm was obtained and the conversion efficiency from 532 to 266 nm was only 1.4 %. This work will promote the application of YAB crystal for the FoHG of Nd:YAG lasers.

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Notes and references

1. S. Ilas, P. Loiseau, G. Aka and T. Taira, *Optics express*, 2014, **22**, 30325-30332.
2. Y. Mori, I. Kuroda, S. Nakajima, T. Sasaki and S. Nakai, *Applied Physics Letters*, 1995, **67**, 1818.
3. L. Wang, N. Zhai, L. Liu, X. Wang, G. Wang, Y. Zhu and C. Chen, *Optics express*, 2014, **22**, 27086-27093.
4. L. Qiang, Y. Xingpeng, G. Mali, L. Hua, Z. Ge and Y. Ning, *Optics letters*, 2011, **36**, 2653-2655.
5. R. Bhandari, T. Taira, A. Miyamoto, Y. Furukawa and T. Tago, *Opt. Mater. Express*, 2012, **2**, 907-913.
6. Q. Liu and X. P. Yan, *Laser Physics Letters*, 2009, **6**, 203-206.
7. S. Zhao, J. Wang, D. Sun, X. Hu and H. Liu, *Journal of Applied Crystallography*, 2001, **34**, 661-662.
8. G. H. Jia, C. Y. Tu, J. F. Li, Z. J. Zhu, Z. Y. You, Y. Wang and B. C. Wu, *Journal of Applied Physics*, 2004, **96**, 6262.
9. J. Liao, Y. Lin, Y. Chen, Z. Luo and Y. Huang, *Journal of Crystal Growth*, 2004, **269**, 484-488.
10. G.-F. Wang, Z. Lin, Z. Hu, T. P. J. Han, H. G. Gallagher and J.-P. R. Wells, *Journal of Crystal Growth*, 2001, **233**, 755-760.
11. A. Brenier, C. Tu, Z. Zhu, J. Li and B. Wu, *Journal of Applied Physics*, 2005, **97**, 013503.
12. G. Wang, H. G. Gallagher, T. P. J. Han and B. Henderson, *Journal of Crystal Growth*, 1996, **163**, 272-278.
13. F. G. Yang, Z. J. Zhu, Z. Y. You, Y. Wang, J. F. Li, C. L. Sun, J. F. Cao, Y. X. Ji, Y. Q. Wang and C. Y. Tu, *Laser Physics*, 2011, **21**, 750-754.
14. C. Sun, Y. Wang, C. Tu and D. Xue, *CrystEngComm*, 2015, **17**, 3208-3213.
15. H. Liu, X. Chen, L. X. Huang, X. Xu, G. Zhang and N. Ye, *Materials Research Innovations*, 2011, **15**, 140-144.
16. H. Liu, J. Li, S. H. Fang, J. Y. Wang and N. Ye, *Materials Research Innovations*, 2011, **15**, 102-106.
17. D. Rytz, A. Gross, S. Vernay and V. Wesemann, YAl3(BO3)4: a novel NLO crystal for frequency conversion to UV wavelengths, 2008.
18. Y. Yue, Y. Zhu, Y. Zhao, H. Tu and Z. Hu, *Crystal Growth & Design*, 2015.
19. X. Yu, Y. Yue, J. Yao and Z.-g. Hu, *Journal of Crystal Growth*, 2010, **312**, 3029-3033.
20. S. Fang, H. Liu and N. Ye, *Crystal Growth & Design*, 2011, **11**, 5048-5052.
21. L. Liu, C. Liu, X. Wang, Z. G. Hu, R. K. Li and C. T. Chen, *Solid State Sciences*, 2009, **11**, 841-844.
22. G. Wang, A. Geng, Y. Bo, H. Li, Z. Sun, Y. Bi, D. Cui, Z. Xu, X. Yuan, X. Wang, G. Shen and D. Shen, *Optics Communications*, 2006, **259**, 820-822.
23. T. Sasaki, Y. Mori and M. Yoshimura, *Optical Materials*, 2003, **23**, 343-351.
24. J. Yu, L. Liu, N. Zhai, X. Zhang, G. Wang, X. Wang and C. Chen, *Journal of Crystal Growth*, 2012, **341**, 61-65.