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Crystal growth and frequency conversion of $BaMgF_4$ single crystal by temperature gradient technique

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ABSTRACT

The $BaMgF_4$ single crystal was grown by the temperature gradient technique. Highly pure MgF_2 and BaF_2 powders were used as raw materials and CaF_2 single crystal was chosen as a seed to induce $BaMgF_4$ single crystal grow along $\langle 001 \rangle$ orientation. The short cut-off wavelength of $BaMgF_4$ single crystal was determined to be 130 nm which is consistent with the previously reported result. We realized second harmonic generation from 1064 nm to 532 nm laser, and 800 nm to 400 nm femtosecond laser in single domain $BaMgF_4$ by using birefringent phase matching. 355-nm-wavelength laser was produced by Sum-Frequency Generation from 1064-nm- and 532-nm-wavelength laser, which is the shortest coherent radiation obtained in the UV in the $BaMgF_4$ crystal.

1. Introduction

All solid-state lasers emitting in the UV/VUV are strongly requested for different applications: medicine, steppers for photolithography, etc. Currently used bulky excimer lasers, namely ArF (193 nm) and KrF (248 nm), have several disadvantages such as low beam quality, fast degradation and toxicity. On the other hand, quasi-phase matching (QPM) has received great attention in the frequency conversion field because it permits non-critical phase matching within the entire transparency range of nonlinear crystals and the use of the largest diagonal nonlinear coefficient. Therefore, the QPM technique is suitable in the generation of deep UV emission, where birefringent phase matching (BPM) becomes difficult due to the extremely small birefringence and low UV radiation resistance of nonlinear crystals [1]. Now new approach is to use fluoride crystals, which on the one hand, show high transparency and radiation resistance from UV/VUV to the IR and on the other hand, can be periodically poled (PP) for second harmonic generation (SHG) by the QPM technique [2]. Among these ferroelectric fluoride crystal, $BaMgF_4$ (BMF) is an attractive candidate because it is transparent in the deep UV, with a decreasing transparency towards the cut off wavelength at about 130 nm, where conventional ferroelectric oxide crystals such as $LiNbO_3$ and $LiTaO_3$ are opaque [3,4].

BMF compound is isomorphous, crystallizing in the orthorhombic system with $Cmc2_1$ (space group No. 36) structure, with unit cell parameters $a = 4.126$ Å, $b = 14.518$ Å, $c = 5.821$ Å and $Z = 4$ [5]. Japanese scientists have investigated its refractive indices in the entire transparent range as well as its domain properties and microdomain engineering [6–10]; they first reported on QPM using a PP ferroelectric BMF, emitting in the ultraviolet 396 nm laser light with a shortest period of 6.6 μm [4]. Up to now, large size BMF single crystals were primary grown from the melt using the Czochralski method [3,11]. However, scattering centers are always present in the BMF crystals grown by the Czochralski method, and they even lead to a milky appearance of the crystals [3,10–12]. It is well known that scattering centers decrease the transparency of the crystals, bring difficulties to the periodic poling process and restrict device performance significantly by causing optical loss, crystal damage, etc.

The temperature gradient technique (TGT) is a simple directional solidification technique, which has been adapted for the laser crystal growth, especially for CaF_2 single crystals, Yb:CaF_2 and Yb,Na:CaF_2 crystals [13,14]. Thus we make our effort to achieve the successful growth of BMF single crystals with TGT method, and the aim of this work is to search for new crystal growth technique for BMF as an alternative to Czochraiski method. Meanwhile, BMF is a nonlinear crystal which exhibits an extraordinary transparency range extended

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from the deep UV (∼125 nm) to the mid-infrared (∼13 μm) [15]. This constitutes an exceptional window for the observation of optical processes or transitions not possible in other systems, and offers a unique chance to fabricate optical devices operating in the UV and mid-IR, where other nonlinear materials cannot be used. Up to now, frequency conversion processes in both visible and UV spectral region have been recently reported based on the PP ferroelectric BMF [4]. In the present work, we will describe TGT growth and frequency generation experiment on in single domain BMF.

2. Experiment

The equipment of TGT for crystal growth of BMF single crystals is the same as that of CaF_2 single crystals described in the previous paper [13,14]. The raw materials were BaF_2 (99.99%), MgF_2 (99.99%) and PbF_2 (99%). In all cases, 0.5 wt% PbF_2 was used as oxygen scavenger. After being weighed in certain ratios, they were totally mixed, pressed into blocks, and loaded into the graphite crucible. The growth procedure started to run after the whole furnace was vacuumed to 10^{-3} Pa. The temperature was kept at 400 °C for 20 h to remove water in the raw materials and the furnace chamber. Then 1.1 atm highly pure Ar gas was filled into the furnace chamber before the procedure continued. After the raw materials were melted, the crystal growth was controlled by reducing the temperature at the rate of 2 °C/h. The crystal was then cooled to room temperature in an established procedure after the melting was completely crystallized.

The as-grown BMF single crystal was cut to disk-shaped samples along various orientations of the crystals using a diamond wheel. The UV transmission spectrum of the $BaMgF_4$ single crystal was measured by UV spectrophotometer (Cary 500) under vacuum condition. We realized SHG from 1064 nm to 532 nm laser in single domain BMF with BPM by Q-switched Nd:YAG pump lasers and 800 nm to 400 nm femtosecond laser by a commercial femtosecond Ti:sapphire laser system. Sum-Frequency Generation (SFG) on BMF single crystal was carried by mixing 1064 nm and 532 nm lasers produced by a Q-switched Nd:YAG pump lasers.

3. Results and discussion

3.1. TGT growth of BMF single crystal

A distinguishing feature of the TGT, as compared with Czochralski method and Bridgman method, is that the solid–liquid interface is absolutely submerged beneath the melt surface and is surrounded by the high-temperature melt. The effect of hot spots, temperature variations and mechanical perturbations can be damped out by the surrounding molten mass before they reach the solid–liquid interface. Crystal growth is carried out under stable temperature gradients; the temperature field in high-temperature melt is opposite to the gravitation field orientation. Therefore, melt convection will not happen under this condition. TGT crystal growth is, therefore, simple directional solidification under stable temperature gradients with a submerged solid–liquid interface, and there are no moving parts [16]. The characteristic of temperature field and solid and liquid interface in TGT method make the growth of high-quality and relatively large-sized crystal possible.

In order to achieve fluoride crystals with high transparency in VUV region, PbF_2, ZnF_2 additive and CF_4 gas were applied as scavengers for removing oxygen-related contaminants attributed to the reaction of water molecules with fluoride. Ko et al. found that PbF_2 additive produce more CO_2 in the range from 600 to 1000 °C [17], which is suitable for BMF crystal growth (the melting point of BMF is 920 °C). Therefore, 0.5 wt% PbF_2 was used as oxygen scavenger in this work.

BMF crystals were grown in the TGT furnace, a typical as-grown BMF boule obtained using TGT method is shown in Fig. 1. The upper edge of the boule is slightly cracked and the typical dimensions are diameter 75 mm with the height 50 mm. In the TGT growth of BMF single crystals, a ⟨1 1 1⟩ orientation CaF_2 single crystal was used as a seed. Several samples were cut directly from the cross-section of the BMF boule perpendicular to the growth direction. X-ray Laue analysis showed all of the samples display ⟨0 0 1⟩ orientation of the BMF crystal. It is clearly shown growth direction corresponds with the *c*-axis, which is agreement with Czochralski growth of BMF crystal.

BMF crystal was cut several wafers along different crystallographic axes. The second-order and third-order nonlinear refractive indices along three crystallographic axes and other nonlinear optical properties were measured on these samples [18–20]. The transmission spectra in the UV/VUV wavelength region of ⟨0 0 1⟩ orientation BMF sample was measured by UV spectrophotometer (Cary 500). Considering the strong absorption of air to the light with wavelength lower than 180 nm, the experiment was carried out under vacuum condition. The transmission spectrum of BMF single crystal is shown in Fig. 2. Meanwhile, we measured the transmission spectrum of BMF single crystal from visible to mid-IR, there is no absorption peak in the wavelength range of 300–2000 nm. In the case of BMF single crystal; there is a monotonous decrease in transparency towards the absorption edge, which lies at about 130 nm. These results are in accordance with previous observations [3,21], which indicated a decay in transparency origin from the scattering centers. The amount of scattering centers can be effectively lowered by optimizing growth parameters in Czochralski growth of BMF crystal [3]. Thus, the growth processing of BMF single crystal TGT growth need to optimize in order to obtain high-quality and relatively large-sized crystal in the future.

3.2. Frequency conversion of BMF single crystal

Fluoride compound has been shown to be transparent from UV to the mid-infrared. In the search for more transparent materials, BMF has been the focus of attention for its pyroelectric and nonlinear optical properties. The linear and nonlinear optical properties of some fluoride crystals are shown as Table 1 [22]. Recently, the use of this BMF ferroelectric crystal as a host matrix for optically active ions appears as a very interesting subject [23,24]. Thus the investigations on the frequency conversion of BMF single crystal become essential. Up to now, there are some reports on the frequency conversion of BMF single crystal. Recently, Villora

Fig. 1. $BaMgF_4$ crystal grown by temperature gradient technique.

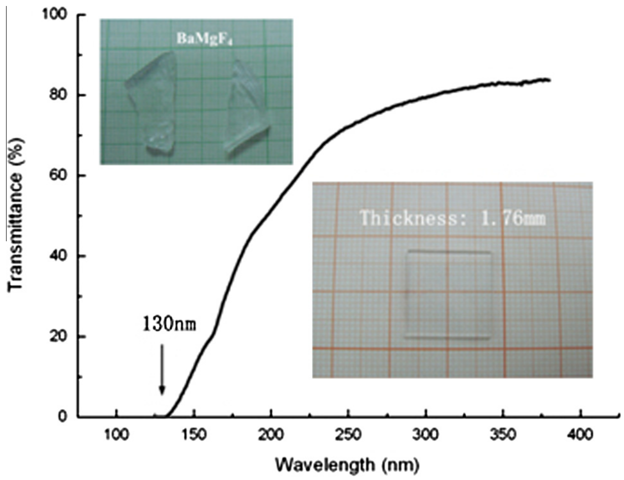

Fig. 2. The transmission spectrum of $BaMgF_4$ single crystal.

Table 1
Calculated and experimental values of linear and nonlinear optical coefficients for some fluoride crystals (values in parentheses are experimental ones).

Crystal	Na_2SbF_5	$BaMgF_4$	$BaZnF_4$
Space group	$P2_12_12_1$	$Cmc2_1$	$Cmc2_1$
Energy gap (eV)	4.3(5.0)	6.7(9.28)	4.66(7.27)
Energy scissors (eV)	0.7	3.0	2.6
n_x	1.566(1.499)	1.462(1.467)	1.428(1.514)
n_y	1.573(1.467)	1.470(1.439)	1.441(1.490)
n_z	1.510(1.462)	1.463(1.458)	1.432(1.507)
$\Delta n(n_{max}-n_{min})$	0.063(0.041)	0.008(0.028)	0.013(0.024)
d_{ij} (pm/v)	d_{123} −0.154(0.121)	d_{31} 0.0286(0.0259) d_{32} 0.0022(0.0481) d_{33} 0.0828(0.0185)	d_{31} 0.019(0.009) d_{32} 0.033(0.012) d_{33} 0.029(0.041)

et al. visualized 396 nm SHG femtosecond pulse by means of PP ferroelectric BMF [4]. In this work, we realized SHG from 1064 nm to 532 nm laser, and 800 nm to 400 nm femtosecond laser in single domain BMF by using BPM. In the frequency conversion experiment, the sample shape, angle and phase matching conditions play principal role for the laser pulse [25]. As to BMF crystal, all these nonlinear optical parameters need systemically investigated in future. In this work, we made some frequency conversion experiments by means of ⟨001⟩ orientation BMF sample.

In these experimental investigations, we used 1 mm ⟨001⟩ orientation BMF sample in thickness. A Q-switched Nb:YAG laser was used to output 1064 nm lasers as the pump lasers with pulse duration of 38 ps, repetition frequency of 10 Hz and the average power of 10–180 mW. The two-dimension angle maker was used to change the angle of the incident light. The pulse energy was measured by means of pyroelectric detectors PD300-UV-193. We measured several SHG output energies with different angles of BPM. The highest conversion efficiency is achieved to be 1.4% with pump power of 60 mW. In addition, we measured the change of conversion efficiency versus input power. From Fig. 3, we can obtain that the conversion efficiency of SHG of BMF shows a rising trend with the increase of the input power, the conversion efficiency is 2.0% while the pump power is 180 mW.

In the 800 nm to 400 nm femtosecond laser experiment, the laser system is a commercial femtosecond Ti:sapphire laser system (USA Newport Company, Spitfire). The Ti:sapphire oscillator producing 50 fs pulse at 800 nm with average power of 200 mW, 1 kHz repetition frequency, The pulse energies were measured by means of pyroelectric detectors PD300-UV-193. The spectrum of

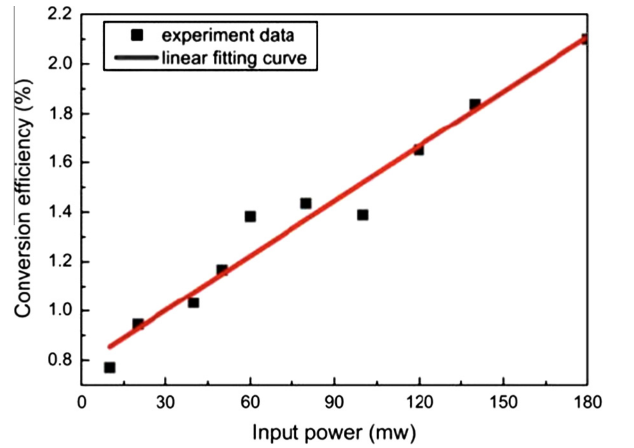

Fig. 3. Conversion efficiency of generation of harmonic with the wavelength of 532 nm in $BaMgF_4$ crystal.

generation of harmonic with the wavelength of 400 nm in $BaMgF_4$ crystal is shown in Fig. 4. The power value of SHG pulse is 45 μW, the conversion efficiency is only 0.0225%, which can be attributable to both the narrow phase matching of femtosecond pulse and thin $BaMgF_4$ crystal sample.

According to previous reports, the frequency conversion experiments of light in $BaMgF_4$ crystal were all achieved by SHG by means of PP ferroelectric BMF. In order to obtain short femtosecond pulse in $BaMgF_4$ crystal, the method of Sum-Frequency Generation (SFG) was used to obtain 355 nm laser in this work.

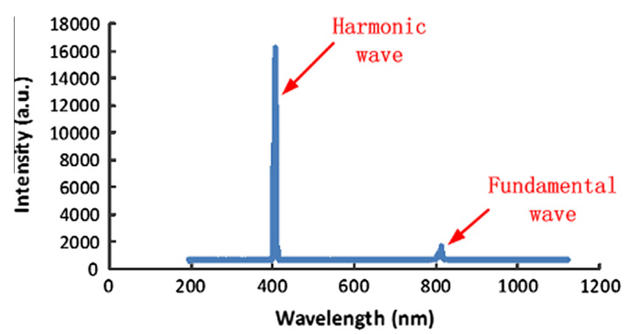

Fig. 4. Spectrum of generation of harmonic with the wavelength of 400 nm in $BaMgF_4$ crystal.

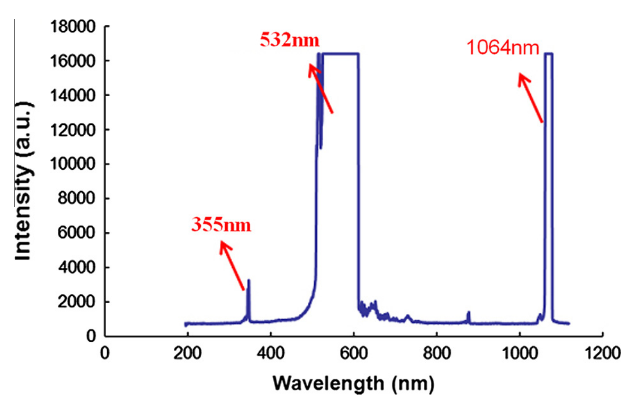

Fig. 5. Spectrum of sum frequency generation of 355 nm-wavelength laser from 1064 nm- and 532 nm-wavelength laser.

The optical pumping was done by using Q-switched Nd:YAG laser (USA Continuum Company, Surelite), both 1064 nm and 532 nm lasers as the pump lasers were output simultaneously through adjusting Nd:YAG laser. Further parameters of the pump lasers were: pulsewidth 10 ns, repetition frequency 10 Hz, the average power of 400 mW (1064 nm) and 89 mW (532 nm), respectively. Several 1064 nm and 532 nm holophotes were utilized to make the two pump lasers collinear before they were illuminated onto the $BaMgF_4$ crystal. After passing the filter system, 355 nm wavelength signal was extracted from the beam and detected by the spectrometer (HR4000). The shortest coherent radiation is obtained in the UV at 355 nm in the $BaMgF_4$ crystal by means of SFG method. The spectrum of SFG of 355 nm-wavelength is shown in Fig. 5. The low power value and conversion efficiency is mainly ascribed to no phase matching in the process of SFG.

4. Conclusions

The temperature gradient technique was successfully used to prepare BaMgF4 single crystal. $BaMgF_4$ as-grown crystal with 75 mm in diameter and 50 mm in height was grown along ⟨001⟩ orientation by means of a CaF_2 single crystal as a seed. The short cut-off wavelength of $BaMgF_4$ single crystal was determined to be 130 nm which is consistent with the previously reported result. The frequency conversion of BMF single crystal were carried by using birefringent phase matching method and Sum-Frequency Generation method, the shortest coherent radiation was obtained in the UV at 355 nm in the $BaMgF_4$ crystal. However this result is obtained by means of ⟨001⟩ orientation BMF sample, the optimal frequency conversion conditions, the relation between nonlinear properties and intrinsic anionic defects are the interesting subjects for the BMF crystals in the future.

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