Femtosecond Z-scan measurement of third-order nonlinear refractive indices of $BaMgF_4$

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The $BaMgF_4$ single crystal is grown by Bridgman method. The third-order nonlinear refractive indices along three crystallographic axes are determined by Z-scan technique with femtosecond laser. The largest one that has a value of 2.35×10^{-18} m^2/W is along the c-axis and the corresponding third-order nonlinear susceptibility is 1.24×10^{-12} esu. This value is compared with $LiNbO_3$ through self-phase modulation effect. Furthermore, the mechanism and the possible applications of the relatively large third-order nonlinear refractive indices are also discussed at last. © *2011 American Institute of Physics*. [doi:10.1063/1.3587642]

In the past few years, how to fabricate an all solid-state laser (ASSL) working in the vacuum ultraviolet (VUV) region (<200 nm) has become a popular issue. The key part of ASSLs is the nonlinear medium used to produce the VUV coherent radiation by second-, third-, and fourth-harmonic generation. Unfortunately, conventional optical nonlinear crystals such as $LiNbO_3$, $KTiOPO_4$, and β-BaB_2O_4 cannot be applied due to the nontransparency in the VUV region. At the end of last century, $KBe_2BO_3F_2$ (KBBF) was found to be a good VUV nonlinear optical crystal[1–3] for its short cut-off wavelength at 155 nm.[4] However, due to the strong layer tendency along Z axis, the bulk crystal of KBBF is very difficult to grow.[4] This disadvantage greatly restricts KBBF to obtain shorter wavelength and higher conversion efficiency.

Recently, the ferroelectric fluoride $BaMgF_4$ crystal has been found widely transparent from 125 nm to 13 μm,[5] so that it is capable to be used in the VUV as well as midinfrared regions (MIRs). The ferroelectric properties[6,7] and the domain phenomena[8,9] have been deeply studied by researchers. Furthermore, the realization of the periodic domain reversal of the $BaMgF_4$ crystal[5,6,10] has also been demonstrated, indicating $BaMgF_4$ as the good candidate for the fabrication of VUV ASSLs by quasiphase-match (QPM) technique.[11] To characterize the $BaMgF_4$ crystal, linear refractive indices[5,10] and the second-order nonlinear coefficients[12] have been, respectively, measured for the QPM use. However, the third-order nonlinear property have not been determined for $BaMgF_4$ so far.

In this letter, the $BaMgF_4$ single crystal is grown by Bridgman method and cut into several wafers along different crystallographic axes. The third-order nonlinear refractive indices with the beam polarization along three principal axes are determined by femtosecond Z-scan technique. To verify the large value, the supercontinuum spectrum due to SPM effect is investigated in comparison with $LiNbO_3$.

The crystal growth was carried out by Bridgman method. The starting materials were prepared by mixing highly pure BaF_2 and MgF_2 powders (99.99%) according to the stoichiometric ratio, put in Pt crucible and sintered in the Muffle furnace under vacuum at 700 °C for 16 h. CaF_2 single crystal was chosen as a seed to induce $BaMgF_4$ crystal grow along ⟨001⟩ orientation in a self-made vacuum vertical Bridgman furnace. The furnace temperature was controlled in the range of 1000–1020 °C to melt the $BaMgF_4$ polycrystal. After growth, the crystal was cooled down to the room temperature at the rate of 30–80 °C/h. The temperature gradient was 50–80 °C/cm and the growth rate was 0.2–0.6 mm/h.

The third-order nonlinear refractive indices were measured by the standard Z-scan technique.[13–16] The schematic diagram of the experimental arrangement is shown in Fig. 1. The laser source we used was the mode-locked Ti:sapphire laser delivering 800-nm-wavelength, 150-fs-long, linear polarized pulses with 84 MHz repetition rate and about 9 kW peak powers. The beam waist spot size at the focal plane was about 17 μm. The sample was mounted on a translation stage driven by a computer controlled stepper motor to move along the Z axis around the focal point with the step length of 0.1 mm. A 5-mm-diameter aperture was placed on the Z axis in the far field and the second photodiode detector was put behind to record the transmission as a function of the sample position (closed aperture Z-scan). To measure the nonlinear refractive indices along three principal axes, the crystals were cut into two differently oriented (i.e., ⟨010⟩,

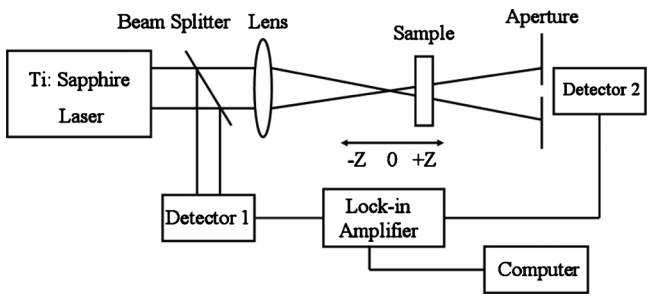

FIG. 1. Schematic diagram of the Z-scan experimental setup using femtosecond laser as light source.

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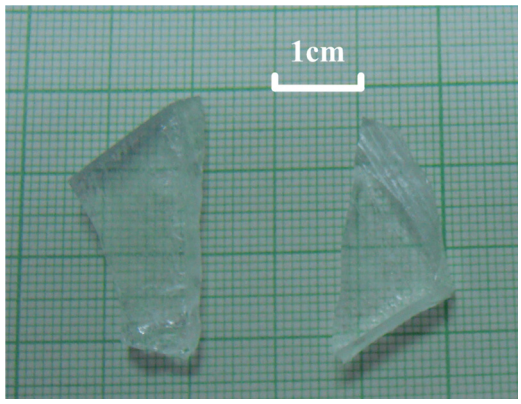

FIG. 2. (Color online) Some parts of $BaMgF_4$ crystal grown at a rate of 0.2–0.6 mm/h with CaF_2 as seed. The growth direction is along c-axis.

⟨001⟩) square plates with a precision better than 30′. The size of the plates was $15\times15\times1$ mm^3.

To measure the supercontinuum spectra, the 50-fs pulses centered at 800 nm with 1 kHz repetition rate were focused in both $BaMgF_4$ and $LiNbO_3$ wafers with the thickness of 1 mm. The peak intensity at the focus reached 1×10^{18} W/m^2. The transmission spectra were measured by spectrometer HR4000.

Some parts of the as-grown $BaMgF_4$ crystal are shown in Fig. 2. The crystal was grown along c-axis at a growth rate of 0.2–0.6 mm/h. Due to the extremely different thermal expansion coefficients between a-, b-, and c-axes,[17] the crystal was easy to crack during the cooling process.

Before dealing with the $BaMgF_4$ samples, the Z-scan experiment on CS_2 with the thickness of 1 mm was first done for testing and calibration. Through measurement and calculation, the third-order nonlinear refractive index of CS_2 was equal to 2.99×10^{-18} m^2/W, namely, 1.16×10^{-11} esu, which was in good agreement with $(1.3\pm0.3)\times10^{-11}$ esu reported previously.[18] So it might be sure that the experiment setup was working normally. After that, the open-aperture (OA) Z-scan measurements of $BaMgF_4$ were performed, whereas no obvious nonlinear absorption peak or valley was recorded at this irradiance, indicating relatively short nonlinear absorption in $BaMgF_4$.

The Z-scan measurements of $BaMgF_4$ at incident irradiance of 4.3 GW/cm^2 are presented in Fig. 3, which exhibit the normalized transmission in closed-aperture (CA) Z-scan scheme as a function of sample position. The prefocal valley and the postfocal peak suggest the positive sign of the third-order nonlinear refractive index, indicating a self-focusing effect. Neglecting the nonlinear absorption, n_2 is capable to be extracted by fitting the CA Z-scan traces using the well-established formulae[13]

$$T_{\mathrm{CA}} = 1 - \frac{4x}{(x^2+9)(x^2+1)}\Delta\Phi_0 \quad \text{with} \quad \Delta\Phi_0 = kn_2I_0L_{eff}, \tag{1}$$

where T_{CA} is the normalized transmittance for CA, $x=z/z_0$, $z_0=\pi w_0^2/\lambda$, $\Delta\Phi_0$ is the on-axis nonlinear shift at the focus, k is the wavelength number, I_0 is the irradiance at the focus, L_{eff} is the sample's effective length. Owing to the little nonlinear absorption, the third-order nonlinear susceptibility only has its real part as shown below[19]

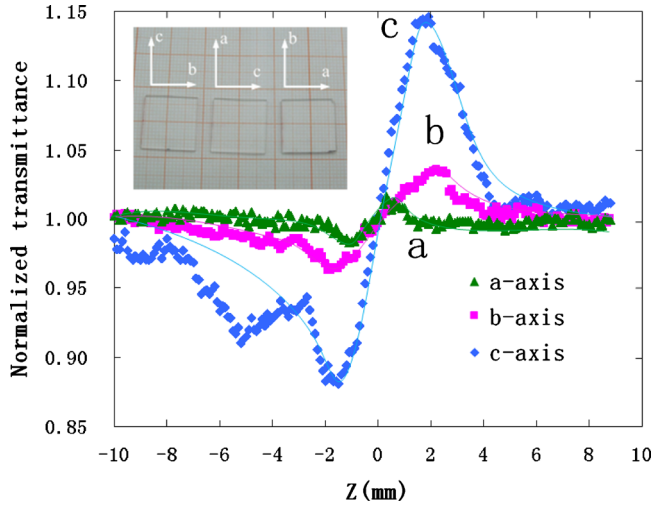

FIG. 3. (Color online) Z-scan traces and fittings of the $BaMgF_4$ crystal along a-, b-, and c-axes, respectively. The irradiance at the focus is 4.3 GW/cm^2.

$$\chi^{(3)}\ (\mathrm{esu}) = \frac{cn_0^2}{120\pi^2}n_2\ (\mathrm{m^2/W}), \tag{2}$$

where c is the velocity of light in vacuum. Substituting the experiment data into the above equations, the third-order nonlinear refractive indices of three principal axes (i.e., $n_{2,a}$, $n_{2,b}$, and $n_{2,c}$) and the corresponding third-order nonlinear susceptibilities (i.e., χ_{1111}, χ_{2222}, and χ_{3333}) are all derived and presented in Table I.

Since the linear refraction of $BaMgF_4$ is about 1.47 at 800 nm (Ref. 5) and the Rayleigh range n_0z_0 equals to 1.7 mm, the samples with 1 mm thickness satisfy the thin-sample condition $L<n_0z_0$ (Ref. 13) in our Z-scan experiment. It is known that the $\chi^{(2)}:\chi^{(2)}$ cascading effect may obviously affect the value of n_2 in the near-phase-matched SHG process.[20] However, in our Z-scan experiment, this effect can be neglected since the system is faraway from the phase-matching point when 800 nm laser beam is polarized along any of three crystallographic axes in the $BaMgF_4$ crystal.[5] The experimental error is about 15%, which mainly comes from the determination of the beam waist and the calibration of the laser power. Why the nonlinear absorption cannot be observed in the experiment is because of the large band gap of $BaMgF_4$ up to 9.5 eV, which is six times larger than the photon energy at 800 nm (1.55 eV). Thus, only more than six photons absorption may occur in the medium, the possibility of which is very small. Consequently, the mechanism of the Z-scan traces can be regarded as the bound electronic Kerr nonlinearity. As it can be seen, the three susceptibilities are significantly different from each other, conforming to the orthorhombic crystal system with space group $Cmc2_1$ (Ref. 21) for $BaMgF_4$ which has the indepen-

TABLE I. Third-order nonlinear refractive indices and corresponding third-order susceptibilities of the $BaMgF_4$ crystal.

Crystallographic axes	Subscripts of $\chi^{(3)}$ tensor	$n_{2,\alpha}$ (10^{-19} m^2/W)	$\chi^{(3)}_{ijkl}$ (10^{-13} esu)
a	1111	2.90 ± 0.45	1.58 ± 0.24
b	2222	6.38 ± 0.96	3.46 ± 0.52
c	3333	23.5 ± 3.5	12.4 ± 1.9

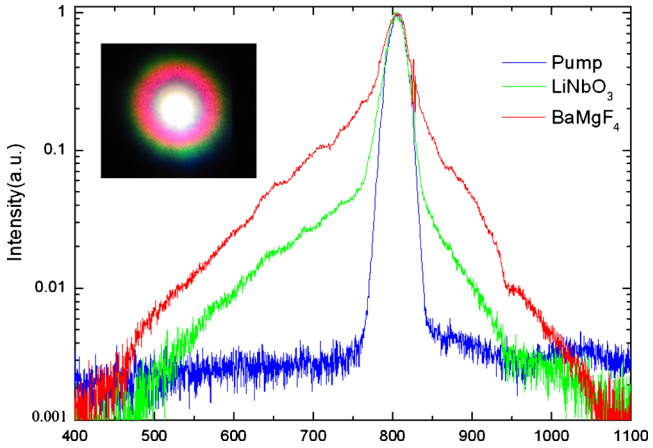

FIG. 4. (Color online) Supercontinuum spectra of $BaMgF_4$ and $LiNbO_3$. The propagation distance in the crystal is 1 mm and the irradiance is 1×10^{18} W/m^2. The inset shows profile of the beam through $BaMgF_4$ in the far field.

dent nonvanishing tensor elements $\chi_{1111}\neq\chi_{2222}\neq\chi_{3333}$. The strong anisotropy of the susceptibilities may result from the crystal cell with the slab structure and the c-axis orientated dipoles.[22] Furthermore, the largest third-order nonlinear refractive index is along c-axis, possessing a value of 2.35 $\times10^{-18}$ m^2/W which is almost as large as that of CS_2 (3.35×10^{-18} m^2/W) (Ref. 18) and one order of magnitude larger than that of $LiNbO_3$ along a- and b- axes (1.13×10^{-19} m^2/W).[23]

To further show the large n_2 of $BaMgF_4$, the supercontinuum spectra of $BaMgF_4$ and $LiNbO_3$ are obtained and shown in Fig. 4. The two samples are all 1 mm thick and the beam polarizations are all along the c-axis. The frequency deviation resulting from the SPM effect can be described in the form[24]

$$\delta\omega(\tau) = -\frac{4\pi n_2 kz}{c}\times\frac{\partial I(\tau)}{\partial\tau}, \tag{3}$$

where $\delta\omega(\tau)$ is the frequency deviation varying with the pulse duration τ, z is the propagation distance of the pump beam in the medium, and $I(\tau)$ is the instantaneous intensity. It can be seen that the frequency deviation is proportional to n_2 when other conditions are identical. That means larger n_2 will lead to wider supercontinuum spectrum. As it is illustrated in Fig. 4, the spectrum of $BaMgF_4$ is obviously wider than that of $LiNbO_3$, and it conversely demonstrates that $BaMgF_4$ has larger n_2.

In application, such a large value of n_2 indicates that when we focus the Gaussian beam into the $BaMgF_4$ crystal in SHG process, the self-focusing effect cannot be neglected because the profile of the Gaussian beam changes significantly and the ideal QPM condition turns correspondingly.[25] Thus, to obtain the higher conversion efficiency, the beam waist should be adjusted according to the third-order nonlinearities. What is more, many significant phenomena and effects such as SRS, FWM, and SPM associated with third-order nonlinearities may be observed in $BaMgF_4$. These effects may play an important role in fabricating the ASSL in the VUV region and applications in the MIR region. In addition, such a good property may allow $BaMgF_4$, as a ferroelectric crystal, to be a good candidate of all-optical switching and storage for all-optical processing[26,27] which require the large third-order refraction as well as short linear and nonlinear absorptions. The other nonlinear susceptibilities is able to be determined by the recently proposed scheme,[28] which takes into account the polarization influence in the Z-scan measurement. Although some thin-film material[29] may have larger n_2, the investigation of $BaMgF_4$ is still very interesting because the bulk material has more spatial freedom.

In summary, we have investigated the third-order nonlinearities of $BaMgF_4$ by Z-scan technique with femtosecond laser. The SPM effect of $BaMgF_4$ is compared with that of $LiNbO_3$. The possible applications in VUV ASSLs and all-optical processing are envisaged due to the relatively large third-order refraction.

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