Three-photon absorption and nonlinear refraction of $BaMgF_4$ in the ultraviolet region

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The nonlinear refraction and nonlinear absorption phenomena are investigated in $BaMgF_4$ single crystal using the *Z*-scan technique in the ultraviolet region with a pulsed laser at 400 nm with 1 ps pulse duration. The remarkable nonlinear absorption behavior is identified to be three-photon absorption under the experimental conditions. In addition, both nonlinear refraction and nonlinear absorption have relatively large values and possess small anisotropy along three different crystallographic axes. The large values of nonlinear refractive index are demonstrated through the self-phase modulation effect.

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1. Introduction

There is a great need for ultraviolet (UV) lasers, especially in the vacuum ultraviolet (VUV) range, (UV: 200–400 nm, VUV: 100–200 nm), owing to its promising applications in laser spectroscopy, photoemission spectroscopy, micromachining, photochemical synthesis, and many other fields. Compared with conventional excimer lasers, UV/VUV all-solid-state lasers through cascaded frequency conversion using UV/VUV nonlinear optical (NLO) crystals present great advantages for their simplicity, stability, narrow spectral bandwidth, better beam quality, and continuous tunability in the UV and VUV spectral regions. Thus, looking for a kind of suitable and high-performance crystal becomes the most exciting task in nonlinear optics.

In the past few years, the borate-based NLO crystals, such as BBO [1], LBO [2], and CLBO [3] have been used for UV laser generation through the birefringent phase matching technique. However, because of the nontransparency in the VUV region and short-wavelength limit inherent to the birefringent phase matching, these crystals cannot be applied to the VUV light generation. Although there have been some reports about the achievements in producing VUV coherent light based on KBBF [4–7], it is still desirable to search other NLO crystals for the development of VUV all-solid-state lasers because the KBBF crystal is very difficult to grow owing to its strong layering tendency [4]. Recently, the ferroelectric crystal of $BaMgF_4$ has become a promising candidate for VUV frequency conversion since it has a shorter cutoff wavelength (125 nm) [8] and can be used for quasi-phase-matching (QPM) interactions [9], which eliminate short-wavelength limit in the case of birefringent phase matching. As we know, the parameters of nonlinear refraction (NLR) and nonlinear absorption (NLA) are essential for UV/VUV light generation. Recently, our group has reported some nonlinear optical properties of $BaMgF_4$, for example, the measurements of its third-order nonlinear refractive indices [10] and second-order nonlinear coefficients [11]. However, in [10], only an 800 nm laser source is used to measure the NLR index and no NLA is observed. For future applications, we should know the optical nonlinearity (NLR and NLA) behaviors of $BaMgF_4$ in the UV region. There are several experimental methods for

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measurement of NLR index and NLA coefficient in material, such as degenerate four-wave mixing [12], nonlinear interferometry [13], ellipse rotation [14], and Z-scan method [15–18]. Among these methods, a relatively simple one is the Z-scan technique shown by Sheikh-Bahae [15] *et al.* It is based on the principles of spatial beam distortion. By this method, we can easily determine the sign and magnitude of the NLR index and NLA coefficient with high sensitivity.

In this work, in order to investigate the nonlinear behaviors of $BaMgF_4$ in the UV region, the Z-scan method with a subpicosecond laser at 400 nm is implemented to measure the NLR index and NLA coefficient of $BaMgF_4$ single crystal. We believe that this work will contribute to further understanding of the nonlinear properties of UV nonlinear optical crystal $BaMgF_4$.

2. Experiment Setup

The $BaMgF_4$ crystals were grown by the Bridgman method at the Institute of Ceramics, Shanghai, China. The samples used in the experiment were cut into several plates with the size of 15 mm* 15 mm*1 mm along three different crystallographic axes (x-cut, y-cut, and z-cut, respectively).

A mode-locked Ti:sapphire laser delivering 800 nm wavelength with a pulse width of 100 fs and a repetition rate of 1 kHz was used for the experiment. To avoid optical damage and continuum generation in the crystal, the pulse duration was stretched to approximate 1 ps (FWHM). By second-harmonic generation through BBO crystal, we got laser pulses with $\lambda = 400$ nm, $E = 0.5\ \mu$J, $f = 1$ kHz, and the pulse duration was estimated to 1 ps.

The schematic diagram of our experimental arrangement is shown in Fig. 1. The 400 nm radiation of the laser was directed into the sample. A beam splitter divided the laser beam into two parts. The reflected beam detected by D1 was taken as the reference light and the transmitted beam was focused into the sample. The beam waist radius ω_0 at the focus was 21 μm and the Rayleigh length $z_0(\pi\omega_0^2/\lambda) = 3.46$ mm, which was longer than the thickness of the $BaMgF_4$ samples. The linear transmittance $S(S = 1 - \exp(-2r_a^2/\omega_a^2))$, which was defined as the ratio of the pulse energy passing the small aperture to the total energy, was calculated to be 0.1. The on-axis transmitted beam energy through a closed-aperture (CA) or an open-aperture (OA) was measured by detector D2. The radiation energy registered by D2 was normalized with respect to the radiation energy registered by D1 to avoid the influence of nonstability of the laser parameters. A lock-in amplifier was used for signal averaging and its output was given to a computer. The output data was collected at every 0.1 mm by translating the plate through the focal point using a computer controlled stepper motor. The distance between the detector and the focal of the lens was about 160 mm, much larger than the Rayleigh length of laser.

Before dealing with the $BaMgF_4$ samples, the Z-scan experiment on BaF_2 with the thickness of 1 mm was first done for testing and calibration. Through measurement and calculation, the NLR index and NLA coefficient of BaF_2 was 3.13×10^{-20} m^2/W (1.1×10^{-13} esu), 1.4×10^{-27} m^3/W^2, respectively. The value of NLR was in good agreement with $(9.7 \pm 1.9) \times 10^{-14}$ esu reported previously [19] to make sure that the experiment system was

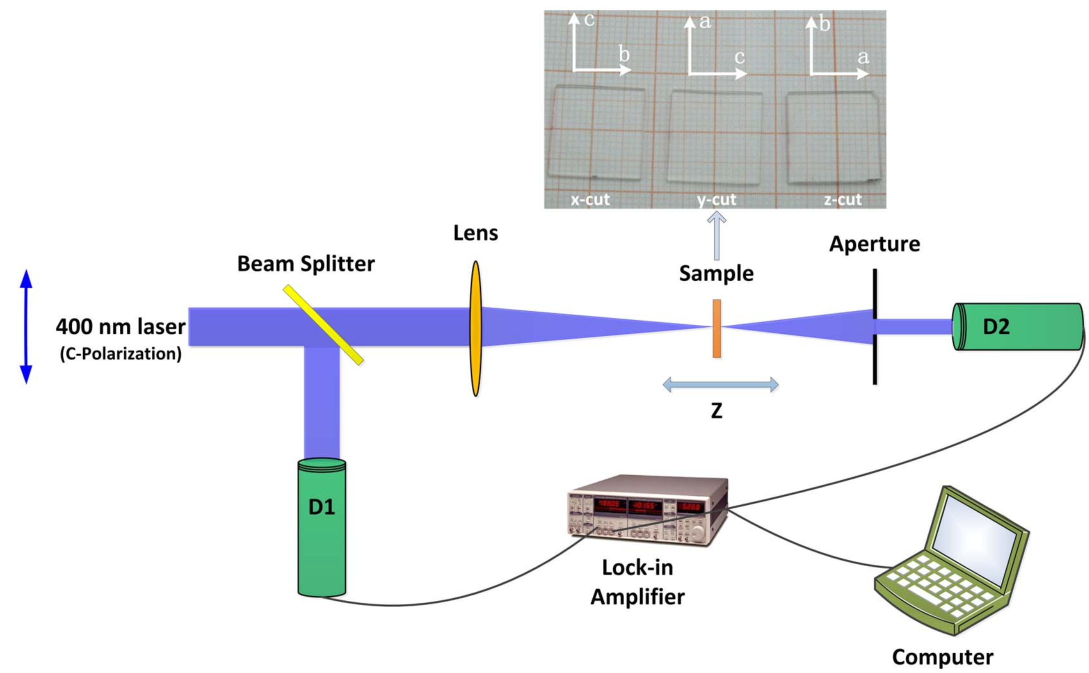

Fig. 1. (Color online) Experimental schematic diagram for single-beam z-scan technique. The inset shows the photos of the $BaMgF_4$ crystal samples with different crystallographic axes (x-cut, y-cut and z-cut, respectively).

working normally. After that, the OA and CA Z-scan measurements of $BaMgF_4$ were performed.

3. Result and Discussion

First, the OA Z-scan technique is used to measure NLA coefficient β_n. The measurement results at irradiance of $3.61 \times 10^{14}\ \mathrm{W/m^2}$ are presented in Fig. 2(a), which exhibit a large minimum transmittance (valley) in the focus. This result confirms the occurrence of multiphoton absorption (two or three photon absorption) in $BaMgF_4$ at this irradiance of 400 nm.

The expressions of 2PA and 3PA conditions are shown as follows [20]:

$$T_{\mathrm{OA(2PA)}}(z) = \frac{1}{\pi^{1/2} q_0} \int_{-\infty}^{\infty} \ln[1 + q_0 \exp(-x^2)] \mathrm{d}x, \qquad (1)$$

$$T_{\mathrm{OA(3PA)}}(z) = \frac{1}{\pi^{1/2} p_0} \int_{-\infty}^{\infty} \ln\{[1 + p_0^2 \exp(-2x^2)]^{1/2} + p_0 \exp(-x^2)\} \mathrm{d}x, \qquad (2)$$

where $T_{\mathrm{OA}(n\mathrm{PA})}$ is the normalized OA transmittance; n is the number of photons involved in the nonlinear absorption process; $q_0 = \beta_2 I_0 L_{\mathrm{eff}}$; $p_0 = (2\beta_3 I_0^2 L'_{\mathrm{eff}})^{1/2}$; $I_0 = I_{00}/(1 + z^2/z_0^2)$ is the excitation intensity at position z; $I_{00}(3.61 \times 10^{14}\ \mathrm{W/m^2})$ is the laser peak intensity at the focal point; z is the sample position; z_0 is the Rayleigh length; β_2 is the 2PA coefficient; β_3 is the 3PA coefficient; $L_{\mathrm{eff}} = [1 - \exp(-\alpha_0 L)]/\alpha_0$ and $L'_{\mathrm{eff}} = [1 - \exp(-2\alpha_0 L)]/2\alpha_0$ are the effective length of the sample for 2PA and 3PA processes, respectively; α_0 is the linear absorption coefficient and L is the sample thickness. Figures 2(b)–2(d) respectively show the fitting plots of the OA data to 2PA and 3PA processes for three crystallographic axes. As an example for nonlinear absorption in $BaMgF_4$, the solid line in Fig. 2(b) is fitted by using Eq. (1) with $\beta_3 = 4.2 \times 10^{-27}\ \mathrm{m^3/W^2}$, which agrees well with the experiment data, and the dashed line is fitted by Eq. (2) with $\beta_2 = 1.20 \times 10^{-12}\ \mathrm{m/W}$. Comparison between the two fittings strongly indicates that 3PA processes dominate the nonlinear absorption in $BaMgF_4$ at 400 nm. This result can also be explained by bandgap cutoff of $BaMgF_4$. The bandgap energy of our experimental $BaMgF_4$ samples estimated from the absorption cutoff wavelength (135 nm) is about 9.2 eV, while the photon energy of 400 nm is 3.1 eV. Consequently, the electrons from valence band to conduction band only need to absorb three photons simultaneously, which rules out the possibility of 2PA process.

Under identical conditions, the nature of the NLR index is examined using the CA Z-scan technique. Figure 3(a) presents the CA experimental results

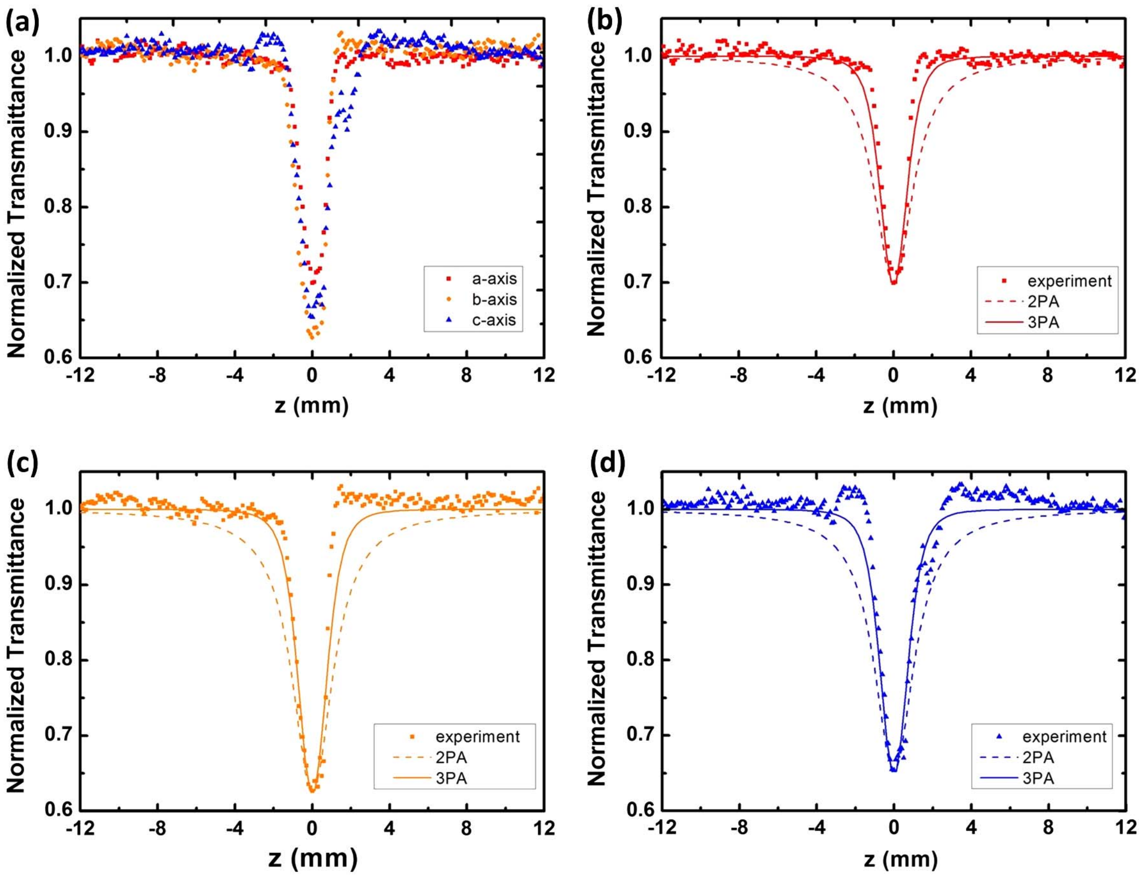

Fig. 2. (Color online) (a) Normalized open aperture (OA) Z-scan curses and the theoretical fits (lines) for OA data by 3PA (solid line) and 2PA (dashed line) along (b) a axis, (c) b axis, and (d) c axis.

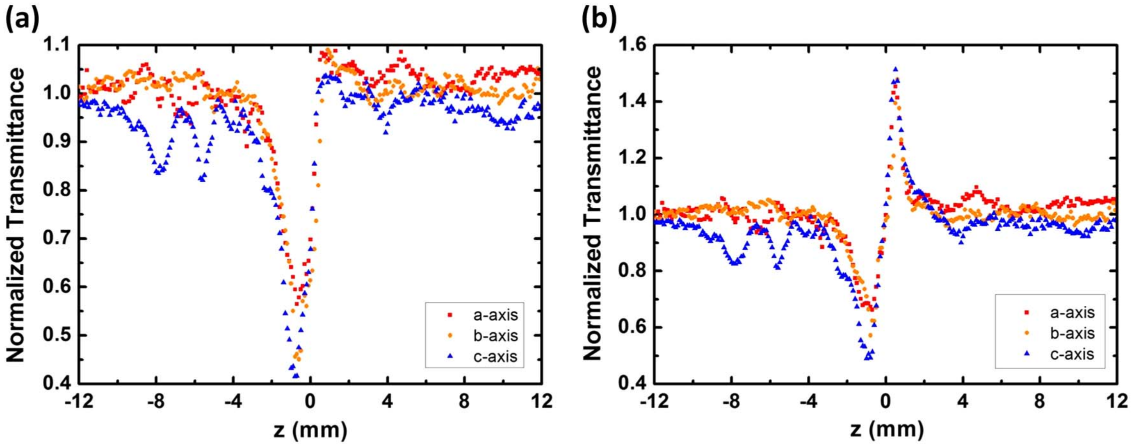

Fig. 3. (Color online) (a) Normalized closed aperture (CA) and (b) CA/OA transmittance data in $BaMgF_4$ crystal along three different crystallographic axes.

of three crystallographic axes of $BaMgF_4$, which exhibit a pronounced asymmetry. This indicates that nonlinear absorption that suppresses the valley and enhances the peak plays a significant role in the nonlinear process of the $BaMgF_4$ crystal. The valley–peak configuration of the CA curve suggests the positive sign of the third-order nonlinear refractive index, exhibiting a self-focusing effect.

In order to get the magnitude of n_2, we must remove the influence of nonlinear absorption. Therefore, a simple and approximate method is used that the CA data is divided by the corresponding OA data. The divided result is shown in Fig. 3(b), which shows a symmetrical valley–peak configuration.

The NLR index n_2 is calculated using the following equations [15]:

$$\Delta\Phi_0 = kn_2 I_{00} L_{\mathrm{eff}}, \quad (3)$$

$$\Delta T_{P-V} = 0.406(1 - S)^{0.25} |\Delta\Phi_0|, \quad (4)$$

where $\Delta\Phi_0$ is the nonlinear phase shift, $k = 2\pi/\lambda$ is the wave vector, λ is the laser wavelength. $\Delta T_{P-V} = T_P - T_V$ is the difference between the transmittance at the peak and valley, $S = 1 - \exp(-2r^2/\omega_0^2)$ is the linear transmittance of the aperture. The calculated values of n_2, β_3 are shown in Table 1.

The transmittances for *x*-cut, *y*-cut, and *z*-cut $BaMgF_4$ plates were measured with linear polarization beam at $\lambda = 400$ nm. For each crystal cut, several series of measurements were made for ensuring the credibility of our experiment. For each crystallographic axis, the nonlinear optical values, which can be got from two different cuts are in good accordance within $\pm 2\%$ accuracy. Nevertheless, the overall experimental uncertainty is approximately $\pm 20\%$. The main uncertainties are from the determination of the irradiance distribution used in the experiment (i.e., beam waist, pulse width, and energy calibration). In our experiment, thermal effects can be neglected because of the low repetition rate of 1 kHz. As we know, second-harmonic generation (SHG) is concomitant with nonlinear absorption. The effect of SHG on the nonlinear absorption transmittance change can be neglected in our experiment because the birefringent phase matching cutoff wavelength is 573 nm [8] for $BaMgF_4$. Accordingly, SHG can't contribute to the optical Kerr-like effect through the cascaded second-order nonlinear effects, either.

Table 1. Measured Results of Nonlinear Optical Parameters of the $BaMgF_4$ Crystal

Crystallographic Axis	(β_3(10^{-27} m^3/W^2)	n_2(10^{-19} m^2/W)
a	4.2	3.52
b	6.1	4.04
c	5.3	4.57

As it can be seen, both the nonlinear refraction and nonlinear absorption contribute to the large third-order nonlinearities of $BaMgF_4$ crystal. Compared with the previous report [10], the values of third-order nonlinear refraction of the three axes are slightly different from each other. With a decrease of anisotropy in linear refraction [8], the nonlinear behavior presents reduced anisotropy along the three axes. Besides, the NLR index of $BaMgF_4$ is 1 order of magnitude larger than the values of those conventional nonlinear optical crystals, such as BBO ($n_2 = 0.4 \times 10^{-19}$ m^2/W) and LBO ($n_2 = 0.26 \times 10^{-19}$ m^2/W) [21]. In order to clarify it, the large n_2 of $BaMgF_4$ is further studied by supercontinuum spectra generation, which is shown in Fig. 4.

The 1 ps pulses centered at 400 nm with 1 kHz repetition rate were focused in $BaMgF_4$ and $LiNbO_3$ with the same thickness of 1 mm and the same peak intensity at the focus reached 8×10^{17} W/m^2. The transmission spectra were recorded by using a UV-VIS-IR scanning spectrometer (HR 4000).

The polarization of the input light is adjusted to be along the *c*-axis. One explanation of supercontinuum spectrum generation is on the basis of a simple model [22], where the maximum relative broadening $\Delta\omega/\omega_0$ is proportional to the pulse intensity in the medium with instantaneous Kerr nonlinearity. The

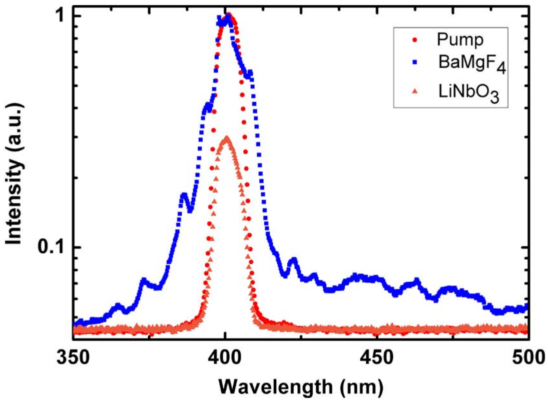

Fig. 4. (Color online) Supercontinuum spectra of $BaMgF_4$ and $LiNbO_3$. The irradiance is approximately $8 \times 10^{17}\ \mathrm{W/m^2}$ and the beam profile is recorded in the far field.

frequency deviation can be described in the following form:

$$\delta\omega(\tau) = -kzn_2 \times \frac{\partial I(\tau)}{\partial \tau}, \quad (5)$$

where $I(\tau)$ is the instantaneous intensity varying with the pulse duration, τ, z is the propagation distance of the pump beam in the medium, and k is the wavenumber. It shows that the frequency deviation $\delta\omega(\tau)$ is proportional to n_2 when other conditions are the same. That is to say, the larger NLR n_2 will lead to wider supercontinuum spectrum. As it is illustrated in Fig. 4, the spectrum of $BaMgF_4$ is obviously broadened, while $LiNbO_3$ has not any change in the aspect of spectrum width. This fully demonstrates that $BaMgF_4$ has large third-order nonlinearities in the ultraviolet region, whereas it is unable to achieve for other NLO crystals.

For such a large value of NLR in the ultraviolet region, $BaMgF_4$ crystal may have more applications. Many interesting phenomena and effects, such as third-harmonic generation, self-phase modulation, and stimulated Raman scattering associated with third-order nonlinearities, may be observed in $BaMgF_4$ in the UV region. Moreover, such a good property may allow $BaMgF_4$ to be applied for all-optical processing. Of course, the large magnitudes of the NLR index and NLA coefficient also indicate that when $BaMgF_4$ crystal is used in the frequency conversion process as well as QPM process, the third-order nonlinearities cannot be neglected. This means the laser beam waist should be adjusted to third-order nonlinearities for obtaining higher conversion efficiency. Further study of nonlinear properties of $BaMgF_4$ in the deep UV region may be conducted in the future.

4. Conclusion

In summary, the nonlinear refractive index and nonlinear absorption coefficient of $BaMgF_4$ single crystal have been investigated by the Z-scan technique using 1 ps laser pulse at 400 nm. The relatively large values of the NLR index and NLA coefficient have been got and both of them possess slight anisotropy. The 3PA process is identified to be the mechanism responsible for the nonlinear absorption. Furthermore, the supercontinuum spectrum generation proves the large value of n_2.

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