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Characterization of the third-order optical nonlinearity spectrum of barium borate glasses

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A B S T R A C T

Borate glasses have proven to be an important material for applications ranging from radiation dosimetry to nonlinear optics. In particular, B_2O_3-BaO based glasses are attractive to frequency generation since their barium metaborate phase (β-BaB_2O_4 or β-BBO) may be crystallized under proper heat treatment. Despite the vast literature covering their linear and second-order optical nonlinear properties, their third-order nonlinearities remain overlooked. This paper thus reports a study on the nonlinear refraction (n_2) of BBO and BBS-DyEu glasses through femtosecond Z-scan technique. The results were modeled using the BGO approach, which showed that oxygen ions are playing a role in the nonlinear optical properties of the glasses studied here. In addition, the barium borate glasses containing rare-earths ions were found to exhibit larger nonlinearities, which is in agreement with previous studies.

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1. Introduction

The study of nonlinear optical properties of materials has been pushed by the need of developing novel technologies in optics and photonics, such as all-optical switching [1], optical limiting [2], and amplifiers [3]. Different types of solid-state materials, from polymers to crystals [4–7], have been developed and investigated as feasible candidates for such purposes [8–10]. In this direction, glasses have received considerable attention because of their excellent optical properties and flexibility to be produced with different compositions and shapes, aside from their mechanical stability, ease of handling and fast production process, which make them useful for several purposes [11]. Moreover, glasses can exhibit significant optical nonlinearities depending on the chemical nature of their constituents that can be easily manipulated in order to meet specific needs for a given application.

Among oxide glasses, the borate ones are known for their thermal stability, low melting point, and good solubility of rare-earth (RE) ions. Because borate glasses in its pure form are hygroscopic, their physical and optical properties are usually improved by the addition of modifiers, such as alkaline and earth alkaline ions. There are several applications of borate glasses containing alkaline and earth alkaline ions such as, for example, vacuum ultraviolet optics, radiation dosimetry, solar energy conversion, optoelectronic and nonlinear optics [12–14]. Particularly, the glass system based on B_2O_3-BaO has attracted interest for nonlinear optics [15], because when subjected to a proper heat-treatment, the barium metaborate (β-BaB_2O_4 β-BBO) phase is crystallized, configuring an important material for frequency-doubling devices [15]. In addition, such borate glasses are stable hosts for the development of optical devices doped with rare-earth ions. For instance, the system B_2O_3-BaO-SiO_2 doped with dysprosium (Dy^{3+}) and europium (Eu^{3+}) ions has been studied for white light generation [16–19]. Other applications of borate glasses doped with RE include the development of new light sources, display devices, UV sensors and tunable visible lasers [20,21].

Because B_2O_3-BaO based glasses, including the RE doped ones, are important materials for new frequency generation, investigations have been mostly focused on their linear and second-order optical nonlinearities, though the third-order ones have been overlooked. Motivated by the importance of barium borate based glasses as a nonlinear optical material, this paper reports a study on the nonlinear refraction spectra of such glasses using ultra-short laser pulses to evaluate their usage in optical Kerr gate devices, thus expanding their application in nonlinear optics. We have not only evaluated the nonlinear index of refraction of the borate

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glasses in a wide wavelength range (460–1500 nm), but also the influence of the rare-earth ions Dy^{3+} and Eu^{3+} on the nonlinearity. The experimental results, obtained through femtosecond Z-scan technique, were modeled using the BGO approach, which indicated that the optical nonlinearity may also be related to the oxygen ions present in the glass matrix.

2. Experimental

The glass compositions studied are (mol%) $60B_2O_3$-40BaO (designated here as BBO) and ($42.5B_2O_3$-42.5BaO-$15SiO_2$):0,1Dy-0.05Eu (BBS-DyEu). The samples were prepared by the melt-quenching technique in a platinum crucible using an electrically heated furnace and high purity row materials (>99.99%) [22]. Polished flat samples with ~1 mm of thickness, free of inclusions or cords were used for the optical measurements. The nonlinear refractive index (n_2) and the two-photon absorption (β) spectra were analyzed using closed and opened aperture Z-scan technique, respectively [23,24]. An optical parametric amplifier (OPA) was used as the excitation light source, which provided pulses of 120-fs from 460 to 1500 nm. The OPA is pumped by a Ti:Sapphire laser amplified system (*CPA 2001*, *Clark MXR*®) at 775 nm with 150-fs pulses at 1 kHz repetition rate. A Gaussian profile for the laser beam used in the Z-scan measurements was achieved by a spatial filter placed before the Z-scan experimental setup. Fused silica has been used as reference material, whose nonlinear refractive index was found to be approximately 2.1×10^{-20} m^2/W from visible to infrared, which is in accordance with the literature [25]. A Pulfrich refractometer (*Carl Zeiss Jena Pulfrich Refractometer PR2*®) was employed to measure the linear refractive indices using Hg and He lamps as spectral sources.

3. Results

The linear absorption spectra of BBO (a) and BBS – DyEu (b) are shown in Fig. 1. While BBO sample is transparent for wavelengths longer than 400 nm, the spectrum of BBS-DyEu presents narrow absorption peaks that are characteristic of Dy^{+3} and Eu^{+3}. For Dy^{+3}, eight absorption bands, related to electronic transitions from the ground state ($^6H_{15/2}$) to excited states, can be identified; at 349 nm ($^6H_{15/2}$ - $^6P_{7/2}/^4M_{15/2}$), 386 nm ($^6H_{15/2} \rightarrow {}^4F_{7/2}/^4I_{13/2}/^4M_{19/2,21/2}/^4K_{17/2}$), 424 nm ($^6H_{15/2} \rightarrow {}^4G_{11/2}$), 453 nm ($^6H_{15/2} \rightarrow {}^4I_{15/2}$), 747 nm ($^6H_{15/2} \rightarrow {}^6F_{1/2}/^6F_{3/2}$), 797 nm ($^6H_{15/2} \rightarrow {}^6F_{5/2}$), 890 nm ($^6H_{15/2} \rightarrow {}^6H_{5/2}/^6F_{7/2}$) and 1080 nm ($^6H_{15/2} \rightarrow {}^6H_{7/2}/^6F_{9/2}$). For Eu^{3+}, one absorption band from ground state ($^7F_0$), can be identified at 393 nm ($^7F_0$ - $^5L_7$). The absorption band at 364 nm is an overlap of the bands of the ions Dy^{+3} ($^6H_{15/2} \rightarrow {}^4I_{11/2}$) and Eu^{+3} ($^7F_0 \rightarrow {}^5D_4$) [18].

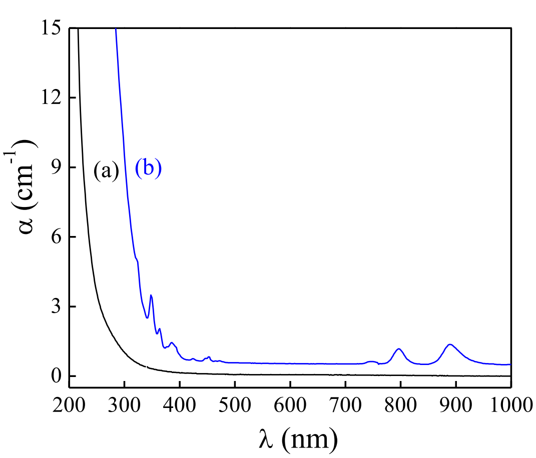

Fig. 1. Linear absorption spectrum of BBO (a) and BBS – DyEu (b). The absorption spectrum of BBS-DyEu sample was vertically shifted for better visualization of the Dy^{+3} and Eu^{+3} absorption peaks.

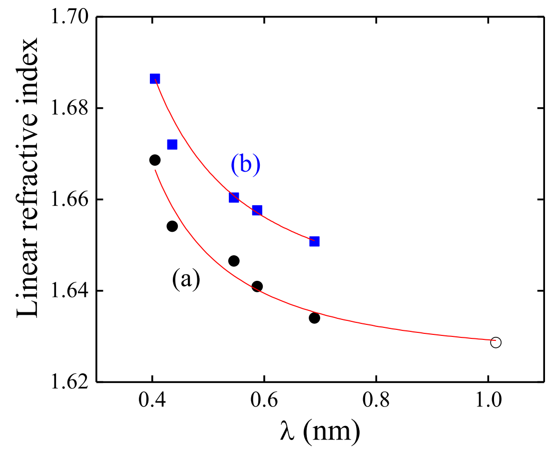

Fig. 2. Linear refractive index of (a) BBO and (b) BBS-DyEu glasses. The solid line represents the fitting with Sellmeier equation (Eq. (1)), whose coefficients are shown in Table 1. The open symbol in spectrum (a) corresponds to n_0 at 1.014 μm obtained from Ref. [28] for the same glass composition and was added to improve the fitting.

The linear refractive index is an important optical parameter for the development of optical devices, as well as for understanding the nonlinear index of refraction of materials. In Fig. 2, we present the dispersion curve for the samples BBO (a) and BBS–DyEu (b), along with the fitting obtained using the two-pole Sellmeier dispersion equation, given in Eq. (1) [26].

$$n^2 = \sqrt{A + \frac{B\lambda^2}{\lambda^2 - C} + \frac{D\lambda^2}{\lambda^2 - E}} \tag{1}$$

where λ is the wavelength in micrometers, and A, B, C, D and E are the dispersion parameters of the material absorption [27]. The Sellmeier coefficients obtained through the fitting are listed in Table 1, for both samples.

The insets in Fig. 3 show typical closed-aperture (refractive) Z-scan signatures for BBO (a) and BBS–DyEu (b) samples, at 800 and 750 nm, respectively. From Z-scan curves, similar to the ones displayed in the insets of Fig. 3, obtained at various wavelengths, we are able to obtain the dispersion of n_2 (nonlinear refraction spectrum). The spectra of n_2 obtained for both samples are shown in Fig. 3, and exhibit a nearly constant behavior as a function of the wavelength, considering the experimental error. For comparison purposes, we determined the mean values of n_2 for BBO and BBS – DyEu as 3.43 and 5.27×10^{-20} m^2/W, respectively. Such values are 1.63 and 2.51, respectively, higher than the ones reported for fused silica [25]. No nonlinear absorption signal was observed in open-aperture Z-scan measurements, indicating that two-photon absorption in absent in the analyzed wavelength range.

In order to further understand the optical nonlinearities of the studied glasses, we modeled the experimental n_2 spectra using the

Table 1
Sellmeier coefficients for the BBO and BBS–DyEu glasses obtained from the fitting shown in Fig. 2.

Samples glass	A	B	C	D	E
BBO	2,37621	0,26279	0,05645	0,01126	50
BBS - DyEu	2,15076	0,52816	0,03901	0,07	90

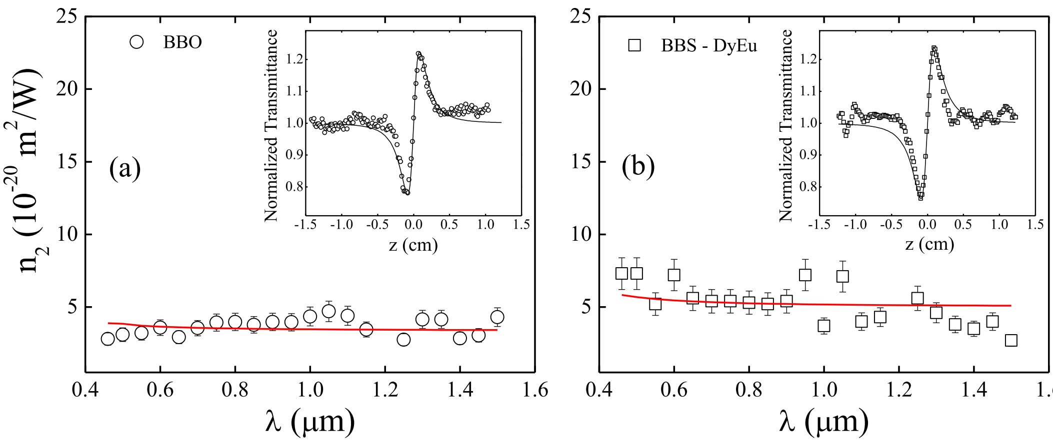

Fig. 3. Spectra of the nonlinear refractive index (n_2) of BBO (a) and BBS – DyEu (b). The solid lines along the symbols represent the fit obtained with the BGO model, with parameters given in the text. The insets show closed-aperture Z-scan measurements for BBO sample at 800 nm and BBS - DyEu at 750 nm, while the line is the fitting from which n_2 is extracted.

BGO model [29], which describes the interaction of electromagnetic radiation with matter through a classical nonlinear oscillator. In this model, the second hyperpolarizability is assumed to be proportional to the linear polarizability squared and the incident light field frequency is considered to be far from any resonance ($\omega << \omega_0$), in such a way that the nonlinear refractive index is written in SI units (m^2/W) as [29],

$$n_{2(BGO)} = \frac{5(n_0^2+2)^2(n_0^2-1)^2(gs)}{6n_0^2 c\hbar\omega_0(Ns)} \quad (2)$$

where c is the speed light in (m/s), g is an anharmonicity parameter, s is the effective oscillator strength, N is the density of nonlinear oscillators, $\hbar$ is the Planck's constant and n_0 is the linear refractive index of light at the wavelength λ. The product Ns as well as the resonance frequency ω_0 are obtained from Eq. (3).

$$\frac{4\pi}{3}\frac{(n_0^2+2)}{2(n_0^2-1)} = \frac{m(\omega_0^2-\omega^2)}{e^2(Ns)} \quad (3)$$

where e and m are the electron charge and mass, respectively. The product Ns and ω_0 in Eq. (3) can be obtained from the linear index of refraction n_0 (Fig. 2), for each sample. The dispersion of n_0 in the BGO model is included by using the Sellmeier equation (Eq. (1)), with the parameters given in Table 1.

By using the BGO model, the mean nonlinear refractive index of BBO and BBS-DyEu was calculated as 3.4×10^{-20} m^2/W and 5.2×10^{-20} m^2/W, being in good agreement with the mean values of n_2 measured experimentally. The parameter g, obtained through the fitting, was found to be 0.4312 and 0.6228 for BBO and BBS-DyEu, respectively. The effective oscillator strength, estimated from the ratio between the density of nonlinear oscillators (Ns) and the density of oxygen ions in the samples, matched the typical value obtained for oxide glasses ($s \cong 3$), which suggests that oxygen is playing a role in the nonlinearities of the glasses analyzed herein [29].

Studies on the nonlinear refractive index on the BaO-ZnO-B_2O_3 system doped with Sm^{3+} [30] demonstrated an increase of n_2 from 0.77 up to 1.22×10^{-20} m^2/W when the dopant concentration varies from 0.5 mol% to 2.0 mol%. Eevon et al. [1] also observed an increase of the n_2 value from about 6.3×10^{-19} m^2/W to 9.4×10^{-19} m^2/W when the concentrations of the rare-earth ion Gd^{3+} is increased from 1 mol% to 5 mol% in a zinc borotellurite glass. Such observation is in agreement with our results, which revealed larger nonlinear refractive index values for the glass containing RE ions, thus confirming the influence of the polarizability of Dy^{3+} and Eu^{3+} ions on the nonlinear optical properties of the BBS-DyEu glass.

4. Conclusion

The nonlinear refractive index of two barium borate based glasses were characterized by the Z-scan technique and modeled using the BGO empirical method. Both glasses exhibited a nearly constant nonlinear refractive index for the 460–1500 nm spectral window, within the experimental error. This behavior was confirmed by the BGO model, which also showed that the oxygen ions present in the glass matrix play a role in its third-order nonlinearities. Furthermore, the n_2 value of BBS-DyEu glass was found to be larger than that of the BBO, indicating that polarizability of the rare-earth ions contributed to the nonlinear increase. This study represents an advance towards the understanding of the nonlinear properties of borate glasses, mainly the ones related to the third-order susceptibility, thereby meeting the needs for the development of new optical devices based on optical Kerr effect.

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