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Influence of Eu^{3+} ions on Nonlinear Optical Properties of Alklai Borate Glasses at Near-Infrared Wavelengths

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Abstract. Optical glasses with enhanced third order nonlinear attributes are promsing materials for photonic applications, particularly for optical limiting and switching devices. With the aim of obtaining enhanced nonlinear optical (NLO) properties, Eu^{3+} doped borate glasses have been prepared through method of melt quench. NLO properties of fabricated glasses were investigated using Z–scan techinique as a function of Eu_2O_3 concentration at near-infrared (NIR) wavelength (800 nm) by utilising 150 femtosecond (fs) laser pulses generated at a repetetion rate of 80 MHz from sapphire laser. The investigated glasses demonstrated a reverse saturable absorption (RSA) type of behaviour in open aperture (OA) configuration and positive nonlinear refraction in closed aperture (CA) configuration. The retrieved NLO coefficients evidently demonstrate the studied glasses are competing materials for photonic applications under fs regime.

INTRODUCTION

The investigation of applied photonic materials with strong odd-order non–linear optical (NLO) properties has provided significant advancements in the field of photonics and non–linear optics. Particularly, inorganic oxide glasses are of great important due to their better performance than other materials. Generally, glasses are highly transparent over wide spectral regions with several interstinng properties such as compatibility for wide variation in composition, highlaser damage threshold to irradiation [1] and the properties of glasses can be tailored in order to meet the needs of a specific application for required uses, and also the prepration of glasses in desired shape and size in bulk scale is easy and cost effective compared to other avilable materials. To develop the glassy materials with improved third order nonlinearities, the diverse glasses (tellurite, germanate, silicate and phosphate etc.) have been widely investigated. In view of this, borate glasses are of intense subject of interest in recent past because of their good sloubility of the compositions, excellent mechanical strength, high chemical durability, thermal stability along with its interesting optical and NLO properties [2]. Further, the intense investigations on borate glasses for nonlinear optical applications are due to their excellent physical, chemical and mechanical properties. To the best of our knowledge, no report in literature studied the effect of Eu_2O_3concentration on NLO properties of brate glasses. The interst is also due to the fact that when RE is doped to the glass host generates the non–bridging oxygens (NBOs) [3], which are very fundamental for improving the third order nonlinear susceptibility values (χ^3) [4]. Nonetheless, the incorporation of alkali oxide to the glass matrix enhanced the NLO properties of glasses [5]. In addition, the pure borate glass is hygroscopic in nature, the incorporation of alklai (particularly Na_2O) reduces the hygroscopic property of the borate glasses and also improves the RE solubility leading to the possibility of using a high concentration of dopants [6]which is very essential for the generation of NBOs in glasses. Also the presence of Na_2O in the glass supports the suitability for the preperation of photonic wave guide devices via ion exchange method [6]. In our previous report, we have observed that, borate glasses host with small amount of Sb_2O_3 (2 mol %) resulted in small two photon absoprtion (2PA) [7]. Hence in the present investgation it is raised to 5 mol %. Furthermore, most of the commercially avilable lasers are operating in the region of near infrared region (NIR), therefore it is crucila to study the NLO properties in this region to deveolop the materials for practical applications.

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In view of above all, the glasses with nominal composition (mol %) $25Na_2O–5Sb_2O_3–(70-x)B_2O_3-xEu_2O_3$ (x=0, 0.5, 1, 1.5 and 2.0 mol %) were prepared throgh melt quench method and their NLO properties were studied at 800 nm using Z–scan technique by utilisign 150 femtosecond (fs) laser pulses.

EXPERIMENTAL DETAILS

Alkali borate glasses based on the molar composition $25Na_2O–5Sb_2O_3–(70-x)B_2O_3-xEu_2O_3$ (x=0, 0.5, 1, 1.5 and 2.0 mol %) were designed by conventional melt quench technique, here onwards the glasses samples are named as NBEu0, NBEu0.5, NBEu1, NBEu1.5 and NBEu2 based on the concentration of Eu_2O_3 present in the glass composition. The AR grade SD fine chemical such as Na_2CO_3, Sb_2O_3, H_3BO_3 and Eu_2O_3 are grinded well for homogeneous mixing. The crucible containing glass ingredients were kept in furnace for thermal treatment. The crucibles were remained for 10 min at 500 °C for completer decarbonisation present in Na_2CO_3, the temperature was slowly increased to 1100 °C and was remained for 50 min with frequent shaking of glass melt at an interval of 15 min. The homogeneous glass melt was then casted in to circular shapes using brass moulds. The prepared samples were annealed at 300 °C to reduce thermal stress occured while quenching. Highly polished samples were used for further charecterization.NLO measurements were performed through standard Z–scan techniques. Nonlinear absorption and refraction measurements were performed in the open aperture (OA) and closed aperture (CA) Z–scan configurations, respectively. The NLO coefficients were evaluted from Z–scan plots have an error of ±15 % in CA and ±10 % in OA, these are errors are owing to errors in laser intensity fluctuations, errors in estimation of spot size at focus and experimental data fitting errors.

RESULTS AND DISCUSSION

The Z–scan data were collected in OA and CA Z–scan modes to analyse the nonlinear absorption and refraction respectively. The aperture is placed near to the detector and kept open in OA, the output laser transmitted signal was fully allowed to reach the detector which being placed after the sample. While the intensity of the transmitted beam was controlled in CA mode by varying the aperture size (S). Therefore, OA corrosponding to normalized transmittance where S = 1 whereas the S value lies in between 0.1 < S < 0.5 for CA. Inset of figure 1 represent the typical Z–scan signature of NBEu2 glass sample. The valley at Z=0 (focal point) demonstrate the reverse saturable absorption (RSA) kind of nonlinearity in the Eu^{3+} doped alkali borate glasses. Whereas, the inset of Fig. 2 represent the typical CA Z–scan plot of NBEu2 glass, the valley–peak kind of signature is saying the observed nonlinear refraction in Eu^{3+} doped alkali borate glasses is positive. The solid symbols in both inset of Fig. 1 and 2 are indicating experimentally collected Z–scan data, whilst the solid lines are representing the theoretical fits to the measured Z–scan data points.

OA Z–scan data were well fitted with two photon absorption (TPA) equation mentioned below [8],

$$T_{OA}(TPA) = \frac{1}{1+\alpha_2 L_{eff}\left[I_{00}\Big/\left(1+\left(Z/Z_0\right)^2\right)\right]} \tag{1}$$

Where, peak intensity of laser beam is represented by I_{00}, Z is being the sample position, the Rayleigh Range is Z_0, λ is the wavelength at which NLO measurements were performed and L_{eff} be the effective path length in the sample whose length is L.

CA Z–scan data were fitted the with below equation [8]

$$T_{CA} = 1 + \frac{4\Delta\phi_0\left(Z/Z_0\right)}{\left[\left(1+\left(Z/Z_0\right)^2\right)\left(9+\left(Z/Z_0\right)^2\right)\right]} \tag{2}$$

Here, the phase difference of the laser beam is $\Delta\Phi_0$. The experimental data is fitting with equation (2) to obtained $\Delta\Phi_0$. The nonlinear refractive index (n_2) was calculated using,

$$n_2 = \frac{\left|\Delta\phi_0\right|\lambda}{2\pi I_{00} L_{eff}} \tag{3}$$

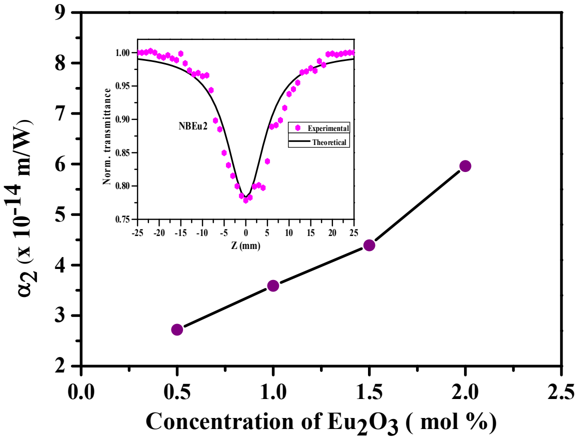

FIGURE 1. Variation of TPA coefficient as a function of Eu_2O_3, inset depicting typical OA Z–scan plot for NBEu2 sample in which solid symbols are representing experimental data and solid line is theoretically fitted data.

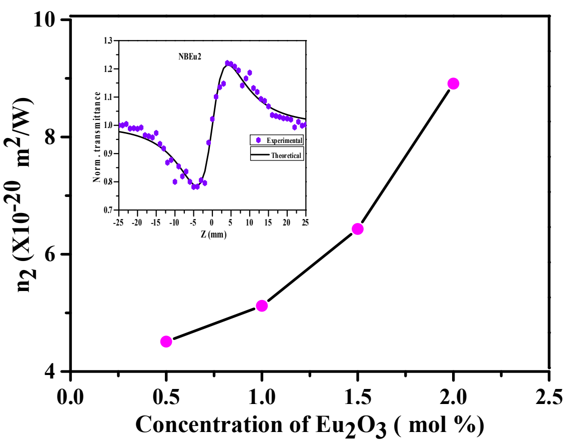

FIGURE 2. Variation of nonlinear refractive index (n_2) as a function of Eu_2O_3, inset depicting typical CA Z–scan signature for NBEu2 glass sample in which solid symbols are indicating experimental data and solid line is theoretically fitted data.

The variation of TPA coefficient (α_2) as a function of Eu_2O_3 content is shown in Fig.1, from which it is clear that the α_2 showed a monotonous increase with respect Eu_2O_3concentration and is maximum for 2 mol %. The n_2 values are also showed an increase trend with variation inEu_2O_3 content in the glasses as shown in Fig. 2. In the present investigation the glass which host with 2 mol % of Eu_2O_3 posses a maximum value of α_2 and n_2. The value of obtained α_2 of NBEu2 glass sample is greater than Sm^{3+} doped borate glasses [9] and smaller than xBi_2O_3-30ZnO-(70-x)B_2O_3 (where x=30, 35, 40, and 45 mol %) glasses [10]. Further, the n_2 values of present glasses are greater than that of Sm^{3+} doped borate glasses [9] and lesser than those n_2 values of 50B2O3–(50-x)PbF_2–PbO (x=25, 35 and 50 mol %) glasses [4]. It is well known that, when RE ions are incorporated to the glass matrix, the optical band gap energies are found decrease with respect to RE concentration. This decrease in optical band gap energy might be due to the formation of NBOs when RE^{3+} added to the glass host [9]. Thus, produced NBOs are fundmental to enhance the nonlinearities in the glasses [4]. Therefore, the enhancement in α_2 and n_2 values as a function of Eu_2O_3 content in the glasses is due to the formation of NBOs produced due to the polarizability of Eu^{3+} ions. To the application end, the glasses possessing large nonlinear absorption coefficient and nonlinear refractive index are suitable materials for designing optical limiters. The figure of merit (F) can be used to know optical characteristics i.e. The condition $F < 1$ is satisfied, then the glass material could be used for all-optical switching devices if not the materials are suitable for optical limiting devices. Hence, F was determined using [11],

$$F = \frac{2\alpha_2 \lambda}{n_2} \quad (4)$$

The F for all the glass samples was measured and found to be >1 (except NBEu0 glass) suggesting that these glasses are suitable for optical limiting applications at in the NIR wavelengths and under fs excitaiton.

CONCLUSIONS

A series of Eu^{3+} doped sodium borate glasses have been fabricated by melt quench technique. The NLO properties have been investigated at a wavelength of 800 nm by Z–scan technique using 150 fs laser pulses fired at a repetition rate of 80 MHz. The OA Z–scan datademonstrated RSA type of nonlinearity attributed to 2PA whilst CA Z–scan signatures showed positive nonlinear refraction accredited to self–focusing effect. The improvement in nonlinear coefficient is due the creation of NBOs produceed due to the incorporation of Eu^{3+} to the glass matrix.The value of F is evaluated and is >1 for all the glass samples (except NBEu0). Hence, the studied alkali borate glasses are suitable in ultrafast optical limiting applications for the protection of sensitive devices (including human eyes) from high energy laser radiation and operating at NIR wavelengths.

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