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Femtosecond Nonlinear Optical Properties of Heavy Metal Borate Glasses Studied Using Z–scan Technique

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Abstract. Inorganic glassy materials are most suitable for fabricating active as well as passive photonic devices. In view of this, the glasses with composition (mol %) $10La_2O_3$–$30HMO$–$60B_2O_3$ (HMO = PbO, Bi_2O_3) were fabricated by melt quenching method. The nonlinear optical (NLO) properties have been investigated through standard Z–scan method at 800 nm using 150 femtosecond (fs) laser pulses fired at a rate of 80 MHz. The NLO attributes obtained from our studies clearly demonstrate the studied glasses are useful for optical limiting applications in the protection of eyes and sensitive photonic devices from damage caused due to intense laser radiation.

INTRODUCTION

Recent developments in optical and laser technology have created a growing utilisation of lasers with enhanced power and of different spectral regions, which demands laser protection materials due to irreparable destruction that intense lasers may cause. To this end, optical limiting (OL) materials with enhanced third-order optical nonlinearities, strong damage thresholds, fast responsetime, excellent transmittance and broadband spectral protection which are beneficial for mode locking, frequency converters and protection of eyes and sensitive photonic devices from intense laser radiation [1].Several interesting materials (polymers, thin films, nanocomposites and crystals etc.) have been widely investigated to achieve good nonlinear optical (NLO) properties. Among wide range of interesting photonic materials, glasses have drawn special attention due to their ease of preparation in large scale in required shape and size, and also the glasses were investigated to tune the required property for a specific application owing to the good adjustability of compositions. In particular, the borate glasses are of most promising for NLO applications because of their low glass transition temperature, excellent mechanical strength and chemical durability [2,3]. It has been reported that, the glass host with heavy metal oxides (HMOs) viz., Bi_2O_3, PbO, Sb_2O_3, Nb_2O_5 and WO_3 increases the NLO parameters of the parent glass system due to their hyperpolarizabilities [4]. In this context, Bi_2O_3 and PbO are with drawn significant importance owing to their greater refractive indices and wide transmission window in the visible and near infrared (NIR) region, cost effective, stable and moisture resistant. The Z–scan technique is an ultra-sensitive technique to measure the NLO properties of materials using which both the nonlinear refraction index and absorption can be analysed at the same time. Keeping this in view, borate glasses were designed host with Bi_2O_3 and PbO by melt quench method. The present work reports on the NLO studies of heavy metal borate glasses studied through Z–scan technique at 800 nm.

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EXPERIMENTAL DETAILS

The glasses based on the chemical composition $10La_2O_3$–30HMO–$60B_2O_3$ (HMO=PbO, Bi_2O_3, all are in mol %) have been synthesised through melt quench technique. The glass samples are here after coded as LPB and LBB for the glasses which contain PbO and Bi_2O_3, respectively. High purity chemicals (AR grade) such as La_2O_3, PbO, Bi_2O_3 and H_3BO_3 (all the chemicals were purchased from SD Fine Chemicals Pvt. Ltd.) were weighed accurately and mixed well. Each glass composition of 15 g batch was filled in a porcelain crucible (J brand) and kept in a high temperature furnace for melting. The glass mixture was remained at 550 (±5) °C for 30 min for the decomposition of H_3BO_3, then the temperature was slowly tuned and remained at 1150 (±5)°C for 50 min for complete melting of batch. The crucibles were shaken frequently at interval of 15 min for a homogeneous and uniform mixing of all the glass constituents. The melt was then casted using brass moulds. The fabricated glasses are cut into proper shape and optically polished for further investigation. The thermal residual stresses occurred during quenching were removed by keeping the samples for annealing at 350 °C for 4h. Annealed and highly optically polished glass samples with a thickness of ~1 mm and diameter of ~10 mm were used for further characterization.

The NLO absorption and refraction properties were evaluated through the open aperture (OA) and closed aperture (CA) Z–scan modes, respectively. The NLO measurements performed at 800 nm using 150 femtosecond (fs) laser pulses produced from Ti:sapphire laser at a frequency of 80 MHz. Due to the high repetition rate of the input pulses the NLO coefficients measured will have significant contribution from thermal effects.

RESULTS AND DISCUSSION

The NLO transmission is dependent with the laser radiation intensity hence position-based intensity setup is essential to investigate the nonlinearities in the glasses. The Z-scan technique is the one which offers such facility by focusing the laser beam using a convex lens. The nonlinear absorption of present glass samples was evaluated in OA Z-scan mode. In OA Z–scan mode, the output nonlinear light transmission through the glass sample was recorded with respect to input intensity. A different output laser light intensity at the sample was obtained by moving the sample through the focal region of the laser beam. A convex lens a focal length of 10 cm was used to focus the laser radiation, which gives the beam with spot radius of 2 mm at focal point. The direction of propagation of focused laser beam was taken as the Z–axis. The glass sample experienced maximum pump intensity at the focal point and in either direction from the focus, the pump intensity was decreases. At each position (i.e. *Z)* the sample experiences different laser intensity and the position-dependent transmittance was collected manually using a detector placed after the sample. The position v/s transmittance curve thus obtained is known as the Z–scan curve. The same procedure is fallowed to measure the non–linear refraction by allowing only 40 % laser light to reach the detector. OA and CA Z–scan plots of LPB glass are shown in figure 1 (a) and (b) respectively. From Fig. 1, it can be seen that, OA Z–scan signature depicted a dip at focal point which represent reverse saturable absorption (RSA) kind nonlinearity whilst CA Z–scan plots demonstrated a characteristic feature of positive non–linear refraction. Further, OA and CA Z–scan plots of LBB glass sample are shown in Fig. 2(a) and (b) respectively. Both OA and CA Z–scan signatures of LBB glass also demonstrated same features of that of LPB glass.

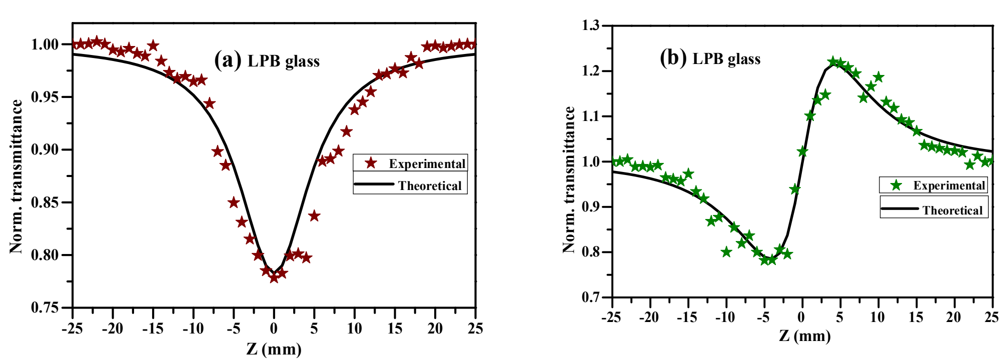

FIGURE 1. Z–profiles of LPB glass, (a) OA Z–scan plot, (b) CA Z–scan signature. In above figures the solid star symbols represent experimental data and solid lines represent the theoretical fits.

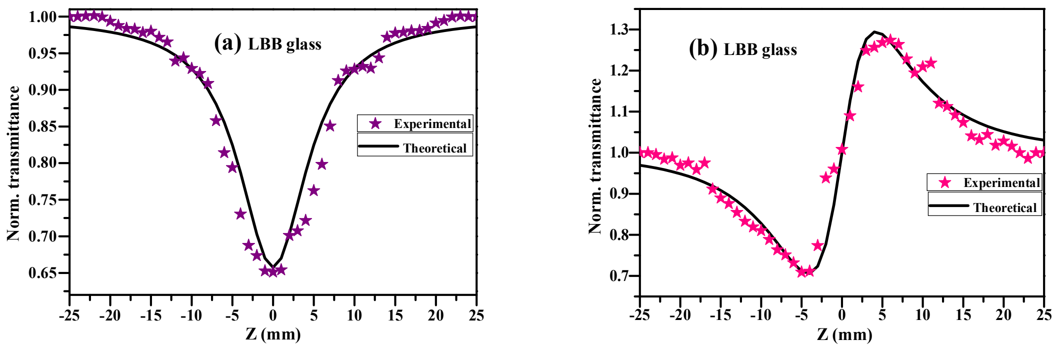

FIGURE 2. Z–profiles of LBB glass, (a) OA Z–scan signature, (b) CA Z–scan profile. In above figures the solid star symbols represent the experimentally measured data and solid lines represent the theoretical fits.

The obtained Z–scan results were analysed to evaluate the values of non–linear absorption and refraction coefficients. The OA experimentally measured Z–scan data points were fitted with the fallowing equation [5],

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

In above equation, I_{00} is the laser irradiance intensity, sample position is Z, Z_0 be the Rayleigh Range, λ is the excitation spectral wavelength and L_{eff} is effective path length in the sample having a length L. The measured CA Z-scan data were fitted the with below equation [5],

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

Where, $\Delta\Phi_0$be the phase difference of the laser radiation attributed to nonlinear refraction and is estimated by fitting the experimental data. The nonlinear refractive index (n_2) was obtained using,

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

Experimentally measured OA Z–scan data of LPB and LBB glasses were well fitted with equation (1), which means that the nonlinear absorption observed in both LPB and LBB glasses is attributed to two photon absorption (2PA). The manually collected CA Z–scan data of both glasses were neatly fitted with equation (2) and this nonlinear refraction attributed to self–focusing effect. The 2PA coefficient (α_2) value of LPB and LBB glasses is found to be 8.51 cm/GW and 9.22 cm/GW, respectively. The α_2 value of the present glasses is greater than recently reported 10RO–35Bi_2O_3 - 55B_2O_3 (where R =CaO, SrO) [6] heavy metal borate glasses and are smaller than 45Bi_2O_3-30ZnO-25B_2O_3glasses [2]. The calculated value of n_2 of LPB and LBB glasses is found to be 0.89 × 10^{-15} cm^2/W and 1.06 ×10^{-15} cm^2/W respectively, these values are small compared to the n_2 values of 40Bi_2O_3-30ZnO-25B_2O_3 and 45Bi_2O_3-30ZnO-25B_2O_3 glasses [2]. It has been reported, when PbO is incorporated to borate network which enters to the borate glass network in the form of Pb^{2+} ions, hence the observed optical nonlinearity in LPB glass is attributed to the Pb^{2+} ions [7]. Whereas, in LBB glass the observed optical nonlinearity is probably due to the presence of Bi^{3+} ions [4]. In the present investigation it is also observed that, the values of α_2 and n_2 are greater for LBB glass compared that of LPB glass. The optical nonlinearity was recorded by exciting the samples at 150 fs laser pulses and, therefore, we can expect the nonlinearity to have an ultrafast component [4]. On the application point of view, the RSA and positive nonlinear refraction are the characteristic features of optical limiters, hence the studied glasses are potential candidates for ultrafast optical limiting applications. The nonlinear investigations of same glasses in wide spectral range with fs pulses is under progress.

CONCLUSIONS

Heavy metal borate glasses with the nominal composition $10La_2O_3$–30HMO–$60B_2O_3$ have been prepared through conventional melt quench method. The NLO attributes were evaluated through OA and CA Z–scan modes respectively. In both glasses, OA Z–scan plots demonstrated a RSA due to 2PA and CA Z–scan profiles signifies positive nonlinear refraction due to self–focusing. The NLO properties observed in LPB and LBB glasses are due to presence of Pb^{2+} and Bi^{3+} ions respectively. The NLO results of studied glasses demonstrate, the investigated glasses are advantageous for designing the optical limiters under fs regime.

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