

Optical properties and ultrafast optical nonlinearity of Yb³⁺ doped sodium borate and bismuthate glasses

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In this paper, we report the optical and ultrafast nonlinear optical properties of Yb³⁺ doped sodium borate and bismuthate glasses. The glasses have been prepared through the melt quench technique. Optical absorption measurements show compositional dependent absorption spectrum of Yb³⁺, which is due to the higher crystal field induced by Bi³⁺ ions. Local structure of the glasses has been identified by using Fourier transform infrared and Raman studies. From open aperture *z*-scan measurements done by using 100 fs laser pulses, the ultrafast optical nonlinearity in these materials is calculated at the nonresonant excitation wavelength of 800 nm. The measured three-photon absorption originates from the glass host, with contributions from the nonbridging oxygens and the nonlinear electronic polarization of the Bi³⁺ ions. © 2008 American Institute of Physics. [DOI: 10.1063/1.2931029]

I. INTRODUCTION

The requirements of developing optical technologies continue to inspire the materials scientist to produce efficient laser and photonic materials. In this context, inorganic glasses, particularly borate glasses, are very interesting from a research and application point of view.¹⁻⁷ The presence of heavy metal oxides in the borate glassy system makes them resistant to atmospheric moisture and increases their linear and nonlinear refractive indices.^{8,9} The higher nonlinear index of these glasses also renders them suitable for optical switching applications. Heavy metal borate glasses doped with rare-earth ions are becoming important due to their host dependent absorption and emission properties.¹⁰⁻¹³ Depending on the dopant and the host, they find applications in optical amplifiers, fiber lasers, and solid state lasers. Among the various rare-earth ions, Yb³⁺ has a simple, single electronic absorption corresponding to the ²F_{5/2} → ²F_{7/2} transition, and it is very difficult to calculate its Judd–Ofelt parameters directly.¹⁴ The advantages of doping Yb in glasses are the following. First, the broad absorption of Yb³⁺ between 900 and 980 nm is compatible for pumping by several laser diodes and the Ti:sapphire laser. Second, Yb³⁺ does not show excited state absorption, cross-relaxation process, upconversion, or any other internal mechanism that can reduce the effective laser cross section. Third, the broad emission lying from 900 to 1150 nm makes Yb doped glasses suitable for the generation of ultrashort laser pulses. Apart from these, the Yb³⁺ doped glass also acts as a sensitizer for other rare-earth ions. Until recently, only a few research reports have appeared, which discuss the effect of host/composition on

the optical properties of Yb³⁺ in simple glass forming systems¹⁴ and crystals. Therefore, in this paper, we investigate the optical properties of Yb³⁺ doped in sodium borate and sodium bismuthate glasses. Sodium bismuthate is an unconventional glass because bismuth oxide is not a typical glass former as it is, but in the presence of other metal oxides, it will form glasses.

Nonlinear refractive index and nonlinear absorption coefficient are two components of the nonlinear optical susceptibility of materials. Heavy metal oxide glasses (glasses containing TeO₂, PbO, Ga₂O₃, and Bi₂O₃) are known to exhibit high linear and nonlinear refractive indices compared to other glassy materials because of the polarizabilities of the bonds between the constituents of the glass. The cubic optical susceptibility $\chi^{(3)}$ is related to the linear refractive index n_0 and nonlinear refractive index n_2 through the expression¹⁵ $\chi^{(3)} = (n_0 n_2 / 3\pi)$ (esu). Yousef *et al.*¹⁶ found that higher concentrations of Bi₂O₃ in glass increase its linear and nonlinear refractive indices. They attribute this increase to the higher polarizability of Bi³⁺ ions. In the present work, we have prepared Yb³⁺ doped sodium borate and bismuthate glasses, and in addition to their optical properties, the nonlinear absorption is also investigated under nonresonant excitation conditions.

II. EXPERIMENTAL

The glasses have been prepared by using high purity H₃BO₃, Bi₂O₃, Na₂CO₃, and Yb₂O₃, and the sample composition and codes are given in Table I. Appropriate quantities of ingredients are weighed and thoroughly mixed, and each composition is taken in an open silica crucible and kept in a muffle furnace for heat treatment. Initially, the samples are maintained at about 450–500 °C for 2 h for the decarbon-

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TABLE I. Glass composition (in wt %) and glass codes.

Glass code	Composition
FM1	19Na ₂ O–80B ₂ O ₃ –1Yb ₂ O ₃
FM2	19Na ₂ O–60B ₂ O ₃ –20Bi ₂ O ₃ –1Yb ₂ O ₃
FM3	19Na ₂ O–40B ₂ O ₃ –40Bi ₂ O ₃ –1Yb ₂ O ₃
FM4	19Na ₂ O–20B ₂ O ₃ –60Bi ₂ O ₃ –1Yb ₂ O ₃
FM5	19Na ₂ O–80Bi ₂ O ₃ –1Yb ₂ O ₃

ization of sodium carbonate and the decomposition of boric acid, and then, the temperature is raised and maintained at 1050 °C for 1–2 h. The crucibles are shaken frequently for a homogeneous mixing of all the constituents. The molten liquid is then poured between two brass plates which are pressed to each other. The prepared glasses are then cut into proper shape and polished for further studies.

In order to ascertain the glassy nature of the local structural units of the prepared glasses, we recorded the Fourier transform infrared (FTIR) transmission spectra in the region of 400–4000 cm⁻¹ by using a Shimadzu FTIR-8000 spectrometer employing the KBr pellet technique. The optical absorption spectra are recorded by using a PerkinElmer dual beam spectrophotometer. Raman spectral measurements were carried out with a JASCO NRS-2000 micro-Raman spectrophotometer. An Ar³⁺ ion laser (wavelength of 514.5 nm) was used as the excitation source, and spectra were recorded in the spectral range of 50–1650 cm⁻¹. The laser power was 40 mW.

We used an open aperture *z*-scan configuration to measure the nonlinear transmission. An ultrafast Ti:sapphire laser

(TSA-10, Spectra Physics) emitting at 800 nm was used for excitation. The output pulse width [full width at half maximum (FWHM)] of this chirped pulse amplifier laser is 100 fs. Samples are mounted on a motorized translation stage, and the data acquisition is automated by using a personal computer. The laser pulse repetition rate is 10 Hz. In the setup, two pyroelectric energy probes are used as detectors. One energy probe measures the transmitted energy, while the other measures a pickoff beam from the laser for normalizing input energy fluctuations. The pulse-to-pulse energy variation is typically within ±10% from the mean value.

III. RESULTS AND DISCUSSION

A. Optical properties

Figure 1 shows the optical absorption spectra of all the glasses. The broad absorption band at around 978 nm arises from the ²F_{5/2}→²F_{7/2} electronic transition in Yb³⁺ ions. However, from the deconvoluted figures, it is clear that there is a peak at around 909 nm in FM5, which is absent in FM1 glasses (containing only B₂O₃ as the network former). Addition of Bi₂O₃ in the glassy network will lead to the formation of [BiO₃] pyramidal and [BiO₆] octahedral units which will give Bi³⁺, resulting in the appearance of this new peak. The presence of Bi³⁺ will usually yield higher crystal field splitting/Stark splitting due to its higher polarizability. This splits the energy levels of ²F_{5/2} and ²F_{7/2}, giving well resolved peaks. However, the strong peak which is situated at 978 nm shows no change in the peak position. In Table II, we present the various crystal field absorption transitions. Ter-

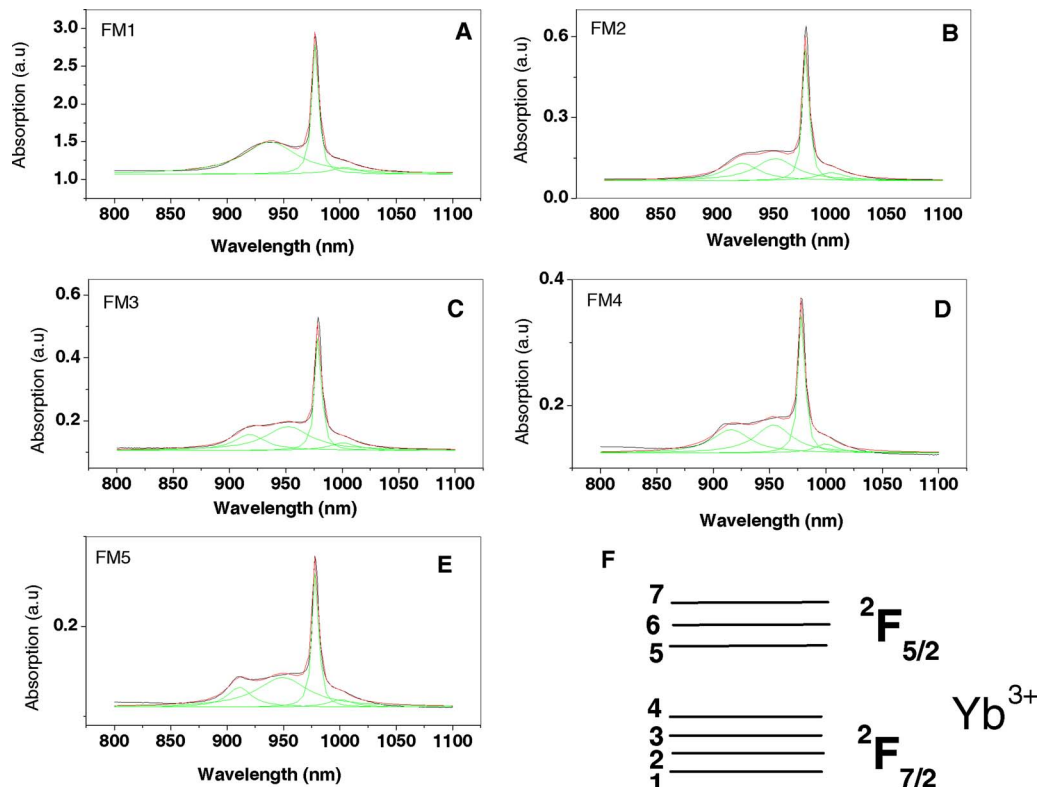


FIG. 1. (Color online) Optical absorption spectra of FM glasses (see Table I). Deconvolution shows the crystal field splitting of various transitions (see Table II). (a)–(e) show the deconvoluted absorption spectra. (f) shows crystal field splitting of the Yb³⁺ ions.

TABLE II. Various optical absorption transitions of ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ due to crystal field splitting [see Fig. 1(f)].

Spectrum No.	Glass	Crystal field splitting transitions of ${}^2F_{7/2(1,2,3,4)} \rightarrow {}^2F_{5/2(5,6,7)}$ (wavelengths are in nm)			
		1 \rightarrow 7	1 \rightarrow 6	1 \rightarrow 5	2 \rightarrow 5
1	FM1	910	...	978	1005
2	FM2	921	953	978	1000
3	FM3	917	952	978	1001
4	FM4	911	950	978	1001
5	FM5	910	949	978	1003

ane *et al.*¹⁷ found a similar kind of splitting in oxyboropate crystal fibers, and their absorption spectrum shows a clear separation of peaks, but in our case, these peaks are merged because the present system is glassy in nature. Figure 2 shows the optical absorption spectra of prepared glasses in the lower wavelength region, ranging from 200 to 800 nm. The broad absorption band in the 375–330 nm region is attributed to $6s^2 \rightarrow 6s6p$ transitions of Bi^{3+} ions,¹⁸ which merges with glass absorption, extending up to 200 nm.

IV. FTIR SPECTROSCOPY

Since B_2O_3 is a good glass former, the addition of alkali and other metal ions to it will lead to the formation of several borate groups. To identify the local structure of the glasses, the FTIR spectra of all the glasses have been taken, which are shown in Fig. 3. The vibrational modes belonging to the borate groups are divided into three main IR spectral regions. The first region between 1200 and 1600 cm^{-1} is due to the asymmetric stretching relaxation of the B–O bond of trigonal BO_3 units. The second region starts at 800 cm^{-1} and ends at 1200 cm^{-1} , which is assigned to the B–O bond stretching of BO_4 units. The final region lies at around 700 cm^{-1} , and it is due to the B–O–B linkages in the borate network. In the present glassy system, all glasses except FM5 contain B_2O_3 as a glass former, while in the FM5 system, Bi_2O_3 functions as the glass former. In the IR spectral region, the vibrational modes of the bismuthate network have three fundamental vibrational bands which are observed at 820, 618, and 543 cm^{-1} , respectively. With the strong polarizing cations, Bi^{3+} can reduce their oxygen-coordination number (6) from the $[\text{BiO}_6]$ octahedral units and form a glass network into $[\text{BiO}_3]$ pyramidal units which belong to the C_{3v} point group.

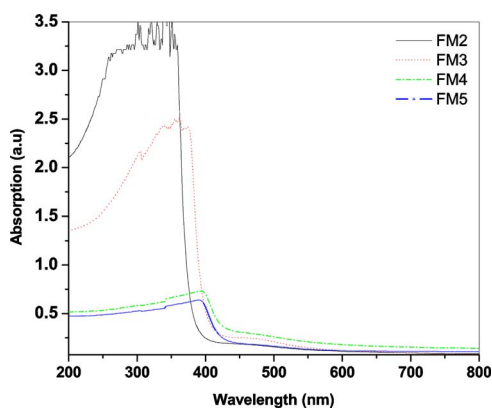


FIG. 2. (Color online) Optical absorption spectra of FM glasses in the range of 200–800 nm.

From the IR spectra, it is observed that there are several peaks which are either sharp, broad, or medium in bandwidth. The broad bands result from the highly degenerate vibrational states, thermal broadening of the lattice dispersion, and mechanical scattering of the powdered samples. Both FM1 and FM2 glasses show a broad band between 1023 and 920 cm^{-1} . This is assigned to the vibrations of some boron atoms attached to nonbridging oxygen atoms in the form of BO_4 units. The peak at 1100 cm^{-1} arises from the stretching vibrations of B–O bonds. The vibrational peaks which are above 1400 cm^{-1} are attributed to vibrations of B–O rings attached to bigger groups. Interestingly, in FM3, FM4, and FM5 glasses, several vibrational modes are missing. However, all three glasses show similar kind of spectra. The weak band at 460 cm^{-1} is assigned to Bi–O symmetric stretching of $[\text{BiO}_3]$ pyramidal unit, and the strong band at 671 cm^{-1} is assigned to bending vibrations of B–O–B in $[\text{BO}_3]$ triangle units.¹⁹ FM3 and FM4 show the band at 1330 cm^{-1} because of CO_3^{2-} dissolved in the glasses, which arise from the Na_2CO_3 used as a starting material. The vibration frequencies agree well with the values given in literature.^{20–23}

V. RAMAN SPECTROSCOPY

Local and short range structural units can be easily identified by Raman spectroscopy. Figure 4 shows the Raman spectral profiles of the prepared glasses. Among these, FM1 has a profile that is completely different from those of the other glasses. This is because FM1 contains only borate

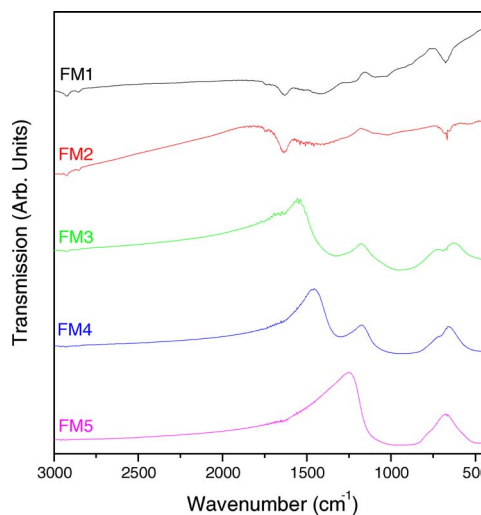


FIG. 3. (Color online) FTIR spectra of FM glasses (see Table I).

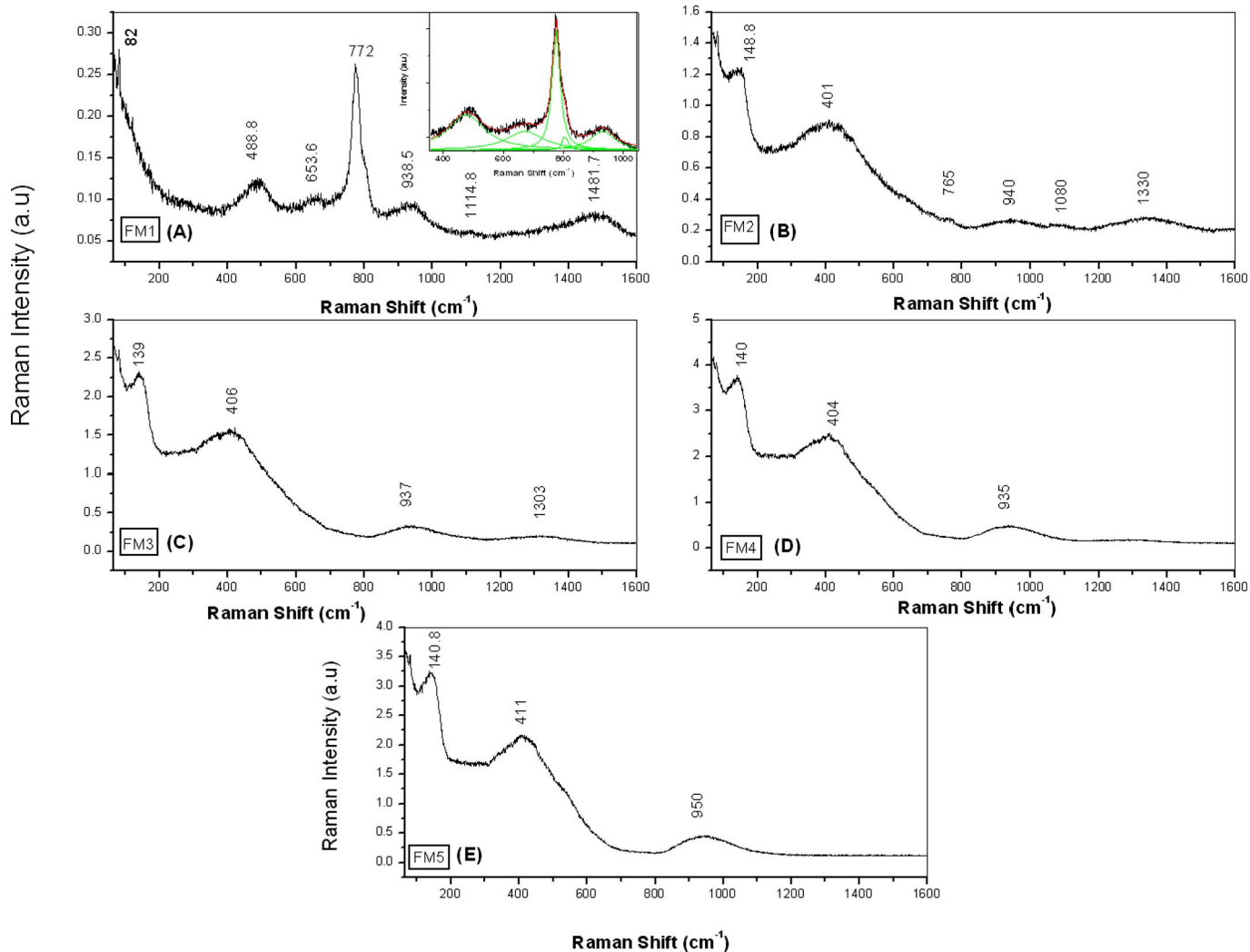


FIG. 4. (Color online) Raman spectra of the glasses.

groups but other glasses contain Bi_2O_3 groups also. In FM1 glass, the shoulder at 805 cm^{-1} is attributed to localized breathing motions of the oxygen atoms inside the boroxol ring [Fig. 3(a)]. The 775 cm^{-1} band is attributed to planar six-membered rings with one BO_4 tetrahedron, i.e., pentaborate, tetraborate, and triborate. In B_2O_3 glasses, occurrence of bands at around 930 , 770 , 650 , and 500 cm^{-1} is an indication of the presence of pentaborate groups in the borate glasses.²⁴ The inset of Fig. 3(a), the deconvoluted Raman spectrum, shows the presence of these peaks very clearly. In addition to that, individual peaks also are assigned to several borate groups. The band at 490 cm^{-1} is due to contributions from a variety of borate groups, including six-membered rings with one or two BO_4 tetrahedral and diborate groups. In all of the glasses (except FM5 glass), the presence of the broad weak band at around 940 cm^{-1} is due to vibrations of pentaborate, tetraborate, and connected diborate groups.²¹ The very weak broad band at 1115 cm^{-1} is due to interconnected diborate groups. The band at 1490 cm^{-1} is assigned to the stretching of nonbridging B–O bonds attached to large borate segments. In particular, even though FM2 and FM3 glasses contain almost equal concentrations of Bi_2O_3 and B_2O_3 , their IR and Raman profiles are completely different

from that of the FM1 glass. In FM2 glasses, the sharp band at 772 cm^{-1} is missing, showing that the formation of planar six-membered rings with one BO_4 tetrahedron is controlled by the addition of Bi_2O_3 .

In bismuth borate glasses, Bi_2O_3 appears as deformed $[\text{BiO}_6]$ groups, combinations of $[\text{BiO}_6]$ and $[\text{BiO}_3]$ groups, or only as $[\text{BiO}_3]$ groups. The Raman spectrum of heavy metal oxides such as Bi_2O_3 may be classified into four main regions,²² which are the low wave number Raman modes (less than 100 cm^{-1}), heavy metal ion vibrations in the range of 70 – 160 cm^{-1} , bridged anion modes in the intermediate 300 – 600 cm^{-1} region, and nonbridging anion modes at higher wave numbers.

Considering Bi_2O_3 containing FM glasses, the band at 140 cm^{-1} is due to the presence of Bi^{3+} cations as $[\text{BiO}_6]$ octahedral and $[\text{BiO}_3]$ units.^{25,26} We conclude that the broad band centered at 401 cm^{-1} probably originates from Bi–O–Bi vibrations of the distorted $[\text{BiO}_6]$ units. The very weak shoulder at around 635 cm^{-1} present in FM2 and FM3 is due to Bi–O–stretching vibrations of $[\text{BiO}_6]$ octahedral units as well as *meta*-borate vibrations, but this shoulder disappears in FM4 and FM5 glasses, and the shoulder that appears at around 535 cm^{-1} is attributed to Bi–O–Bi stretching vibra-

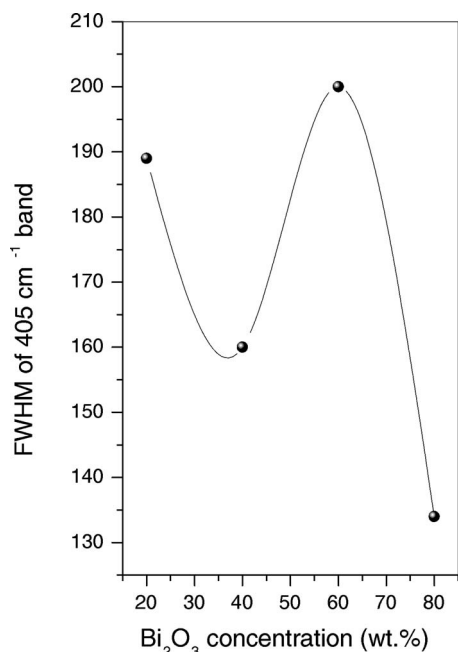


FIG. 5. Variation of FWHM of the 405 cm^{-1} band with the concentration of Bi_2O_3 .

tions. The broad band which is present only in FM2 at 1345 cm^{-1} and which is shifted toward 1303 cm^{-1} in FM3 and FM4 glasses is attributed to BO_2O triangles linked to BO_4 units. Interestingly, this particular band is absent in FM1 and FM5 glasses. It clearly implies that a moderate concentration of Bi_2O_3 will yield the above specified borate group.

In Raman spectroscopy on glasses, the measure of the disorder in the amorphous structure is represented by the half width of Raman bands.^{25,27} Figure 5 shows the variation of half widths of 405 cm^{-1} bands with the concentration of Bi_2O_3 . It is clear that the FWHM is reducing with the increase in Bi_2O_3 concentration, implying that the disorder degree of $[\text{BiO}_6]$ is reducing. Optical absorption spectroscopy results also support the above result; i.e., with the increase in Bi_2O_3 concentration/decrease in disorder degree of Bi^{3+} ions, the new transition ${}^2F_{7/2(1)} \rightarrow {}^2F_{5/2(6)}$ transition starts appearing (see Table I).

VI. NONLINEAR OPTICAL PROPERTIES

In glasses containing heavy metal ions such as Pb^{2+} and Bi^{3+} , the filled electronic shells of the ions effectively screen the outer electrons from the nucleus, thus permitting large charge displacements to occur under the influence of an applied electric field (optical field). These large displacements cause anharmonic effects resulting in large cubic hyperpolarizabilities.²⁸ In addition, the ions give rise to the highly distorted coordination polyhedral, and they contain nonbonding lone electron pairs, further contributing to the nonlinearity. Structural studies show that these glasses have Bi–O–Bi, Bi–O–B, and Bi–O–Na local structures. These local structures will generate a large number of nonbridging oxygens (as O_2^- ions), which will enhance the molar refraction of the glasses. Increasing the ionic radius of nearby cations is found to enhance the molar refraction of oxide glasses

further, because the ion refraction of the cation itself increases and the asymmetry of the electric field around the O_2^- ion becomes large.²⁹ The electronic third order susceptibilities of these type of glasses will be in the order of 10^{-13} esu,³⁰ making them suitable candidates for all-photonic devices.⁹ From our previous studies on sodium borobismuthate and lead borate glasses, we found that there is no appreciable change in the nonlinear absorption coefficient between resonant and nonresonant excitations, when excited by 100 fs laser pulses.³¹ In the present work, we investigate the absorptive nonlinearity of the glasses by performing open aperture z -scan measurements at 800 nm using ultrashort laser pulses of 100 fs pulse duration.

By studying the temporal dynamics in glasses containing Bi_2O_3 , Sugimoto *et al.*²⁹ found that these glasses show electronic response times faster than 200 fs. Similarly, Yu *et al.*³² have measured the optical nonlinearity of lead bismuth gallium glasses through the optical Kerr gate method and found that the temporal response is faster than 350 fs. These results show that the obtained nonlinearity originates mostly from electronic polarization.³³ z -scan experiments are single beam experiments, where the pumping and probing of the medium are done by the same laser pulse. Therefore, the observation of an optical nonlinearity when excited by 100 fs laser pulses indicates that the nonlinearity has an ultrafast component, with an onset time of less than 100 fs. It may be noted that excitation and measurement with the same ultrashort pulse will prevent nonlinear thermal effects in the sample from being measured. Moreover, nonlinear effects arising from excited state populations will also not be measured. Thus, the measured nonlinearity will originate primarily from the nonlinear electronic polarization.

In our z -scan experiment, femtosecond pulses of approximately 7.5 microjoules energy were focused by using a lens, and the sample was translated along the beam axis through the focal region over a distance longer than the confocal distance. For an exciting Gaussian beam of wavelength λ , the beam radius at position z is given by $\omega(z) = \omega(0)[1 + (z/z_0)^2]^{1/2}$, where $\omega(0)$ is the focal spot radius and z_0 is the Rayleigh range given by $\pi \omega(0)^2/\lambda$. Therefore, knowing the energy of the laser pulse, the input laser fluence, and intensity can be calculated for each z value. Results obtained from the open aperture z scan are redrawn in Fig. 6, where we have plotted the normalized transmission of the sample as a function of the input laser intensity. The nonlinear transmission data fit well for a three-photon type absorption nonlinearity. The transmission equation for a three-photon nonlinearity is given by¹⁵

$$T = [(1 - R)^2 \exp(-\alpha_0 l) / p_0 \sqrt{\pi}] \times \int_{-\infty}^{\infty} \ln[\sqrt{1 + p_0^2 \exp(-2t^2)} + p_0 \exp(-t^2)] dt, \quad (1)$$

where R is the surface reflectivity. p_0 is given by $[2\gamma(1 - R)^2 I_0^2 L]^{1/2}$, where γ is the three-photon absorption coefficient. L is given by $[1 - \exp(2 - \alpha_0 l)] / 2\alpha_0$, where l is the sample length. α_0 is the linear absorption coefficient and I_0 is the on-axis peak intensity. The calculated three-photon coefficients are given in Table III. The values are found to in-

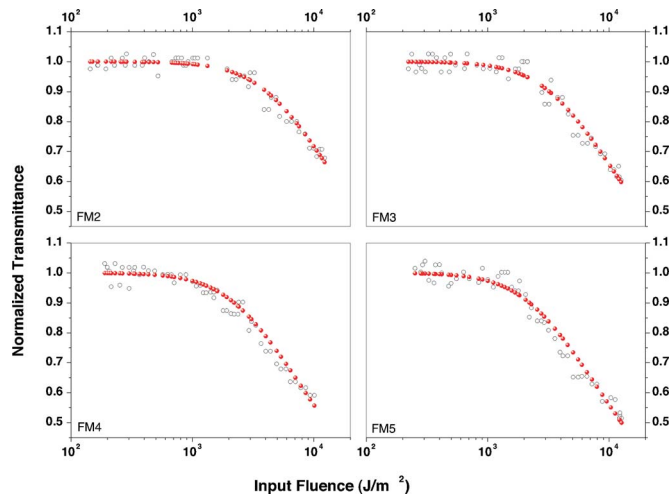


FIG. 6. (Color online) Nonlinear light transmission plots of the FM glasses, derived from the z -scan curves. Samples are nonresonantly excited by 100 fs laser pulses at 800 nm.

crease with the Bi_2O_3 concentration, clearly indicating the high polarizability of Bi^{3+} ions.

VII. CONCLUSION

In summary, we prepared Yb^{3+} doped sodium borate and bismuthate glasses through the melt quenching technique. Optical absorption spectroscopy shows that due to crystal field splitting, there is a new transition ${}^2F_{7/2(1)} \rightarrow {}^2F_{5/2(6)}$ appearing in bismuth containing glasses. FTIR and Raman spectral studies employed to identify the local structure confirm that the glass contains several borate groups and $[\text{BiO}_6]$ units. In addition, Raman spectroscopy also shows that the new peak (located at $\sim 405 \text{ cm}^{-1}$) arises from the decrease in the degree of disorder of $[\text{BiO}_6]$ units. The increase in three-photon absorption coefficient with Bi_2O_3 concentration observed from z -scan studies can be attributed to the highly

TABLE III. Three-photon absorption coefficients of the prepared glasses at 800 nm, measured using the open aperture z -scan method.

Spectrum No.	Glass	Three photon absorption coefficient (m^3/W^2)
1	FM2	5×10^{-31}
2	FM3	8×10^{-31}
3	FM4	17×10^{-31}
4	FM5	17×10^{-31}

polarizable nature of Bi^{3+} ions. The glass host and the non-bridging oxygens also contribute substantially to the nonlinearity.

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