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Enhanced nonlinear optical properties of oxygen deficient lead-niobium-germanate film glasses

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The third order nonlinear optical properties of oxygen deficient lead-niobium-germanate film glasses with heavy metal contents beyond that of the bulk glass formation region have been investigated. Values of the nonlinear third order optical susceptibility up to $|\chi^{(3)}| \approx 1.8 \times 10^{-11}$ esu have been measured by degenerate four wave mixing at 800 nm in films having large heavy metal fractions (0.93). The fast buildup and decay times (≈ 130 fs) of the nonlinear response confirm its nonresonant character. The partial reduction of Nb^{5+} to Nb^{4+} evidenced by x-ray photoelectron spectroscopy, which is associated with the oxygen deficiency, appears to be responsible for the strong enhancement of $|\chi^{(3)}|$. © 2007 American Institute of Physics.

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All-optical communication technologies require materials suitable for the design and fabrication of integrated photonic devices.¹ Heavy metal oxide (HMO) glasses having large Pb or Bi fractions exhibit properties that make them attractive for these applications. They are chemically stable, show a broad transparency range ($0.4 < \lambda < 8 \mu\text{m}$),² have low phonon energies ($\sim 800 \text{ cm}^{-1}$), present high linear refractive indices ($n_0 \geq 2$), and have large third order nonlinear optical susceptibilities ($\chi^{(3)}$) with respect to fused silica.²⁻⁵

The nonlinear optical properties of bulk HMO glasses have been extensively studied during the last years.⁵⁻¹¹ Experimental results demonstrate that the strength of the nonlinear response relates to the concentration of highly polarizable cations, such as empty *d*-band transition metals (Nb^{5+} , Ti^{4+}) or heavy metals having lone s^2 electron pairs (Pb^{2+} , Bi^{3+}).^{3,9} However, the glass formation region tends to be reduced in some cases such as Nb containing glasses, thus limiting the glass design possibilities. In a previous work, we showed that lead-niobium-germanate film glasses with large heavy metal fractions could be produced by pulsed laser deposition (PLD).^{11,12} Film glasses were oxygen deficient, and yet they were transparent with a n_0 and an optical energy gap E_g that depended on the heavy metal content. In this letter we report the nonlinear optical response of these film glasses in the femtosecond regime, compare it to that of transparent bulk glasses and discuss the origin of the strong enhancement observed.

Table I summarizes the composition and linear optical properties of the bulk glasses and the films produced from them by PLD taken from a previous work.¹² The compositional changes observed in the films with respect to the bulk glasses, namely, a slight increase of the heavy metal fraction and a significant oxygen deficiency, were found to have a clear effect on the optical properties of the films. Only bulk glasses having $[\text{Pb}] + [\text{Nb}] \leq 0.6$ were transparent, while all film glasses were transparent and with a value of the imagi-

nary part of the refractive index, $k < 10^{-4}$. The most significant difference between film and bulk glasses is the significant increase of E_g in the films with respect to bulk glasses. This is illustrated in Fig. 1 where the absorbance spectra measured for the G10B bulk glass and for two films deposited on sapphire having the smallest and the largest $[\text{Pb}] + [\text{Nb}]$ fractions are shown. The blueshift of the cutoff wavelength observed when comparing the film (G10F) to the corresponding bulk glass (G10B) is most likely a consequence of the oxygen deficiency of the films that leads to an increase of the fraction of bridging oxygen bonds. The oscillations observed in the film spectra are related to interference effects at the air/glass and the glass/substrate interfaces, whereas the high level of the base line is related to scattering and high surface reflection caused by the high n_0 of the films.

The third order nonlinear optical properties have been analyzed at $\lambda = 800$ nm by degenerate four wave mixing using the forward folded box configuration^{11,13} and a 1 kHz repetition rate femtosecond Ti:sapphire regenerative amplifier laser system as excitation source. The pulse compressor of the amplifier was adjusted to precompensate the dispersion of the optical elements located in front of the sample in order to produce the shortest possible pulse at the sample (~ 100 fs). The beam has been split in three parallel arms with equal power, allowing separate control of the delay and polarization. They are overlapped at the sample by means of a 75 mm focal length lens leading to a waist of $\approx 40 \mu\text{m}$. We have used copolarized pulses, and thus the evolution of the conjugated signal is a measure of the modulus of the diagonal component of the $\chi^{(3)}$ tensor ($|\chi_{xxxx}^{(3)}|$) that will be referred to from now on as $|\chi^{(3)}|$. The intensity of the conjugated beam follows the characteristic cubic dependence with the pump beam intensity. $|\chi^{(3)}|$ has finally been evaluated by using fused silica as reference material ($|\chi^{(3)}|_{\text{SiO}_2} = 1.5 \pm 0.5 \times 10^{-14}$ esu).¹³ In the case of film glasses, the contribution of the substrate to the measured conjugated signal was carefully subtracted.

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TABLE I. Composition (in % molar) of $\text{XPbO}-\text{YNb}_2\text{O}_5-\text{ZGeO}_2$ bulk glasses, heavy metal fraction ($[\text{Pb}] + [\text{Nb}]$), oxygen content ($[\text{O}]$), linear refractive index (n_0 , at $\lambda=800$ nm), optical gap E_g (in eV), and binding energies of Nb $3d_{5/2}$ core electron level for Nb^{+5} and Nb^{+4} (in eV) determined within ± 0.1 eV and measured for the studied bulk (GXXB) and film (GXXF) glasses. The values in brackets for Nb $3d_{5/2}$ levels correspond to the % of Nb ions. Compositional and optical data were taken from Ref. 12.

Glass	X-Y-Z	$([\text{Pb}]+[\text{Nb}])$	$[\text{O}]$	n_0	E_g	Nb ⁺⁵ $3d_{5/2}$	Nb ⁺⁴ $3d_{5/2}$
G10B	25-15-60	0.48	1.91	1.97	2.97	206.9 (100)	...
G1B	25-25-50	0.60	2.00	2.05	2.75	206.9 (100)	...
G7B ^a	35-35-30	0.78	2.00	...	...	...	...
G40B ^a	35-55-10	0.94	2.13	...	...	...	...
G10F	G10B ^b	0.53	1.68	2.02	3.62	207.2 (45)	205.7 (55)
G1F	G1B ^b	0.62	1.80	2.07	3.52	207.0 (30)	206.1 (70)
G7F	G7B ^b	0.83	1.72	2.14	3.45	206.9 (32)	206.0 (68)
G40F	G40B ^b	0.93	1.72	2.24	3.40	206.8	206.0

^aNontransparent (opal) glass.

^bIn the case of film glasses, the corresponding bulk target is indicated.

Figure 2 shows that the $|\chi^{(3)}|_{\text{glass}}/|\chi^{(3)}|_{\text{SiO}_2}$ ratio increases as $[\text{Pb}]+[\text{Nb}]$ increases both for films and bulk glasses. The $|\chi^{(3)}|$ values of film glasses ($\sim 10^{-12}$ – 10^{-11} esu) are at least one order of magnitude higher than those of transparent bulk glasses having a similar heavy metal fraction ($\sim 10^{-13}$ esu), and up to three orders of magnitude higher than that of fused silica. The dependence of $|\chi^{(3)}|$ with $[\text{Pb}]+[\text{Nb}]$ is in good agreement both with semiempirical models for nonresonant optical nonlinearities^{3–5,7,8} and earlier results reported for glasses having large Pb or Nb fractions.^{5–11} The structural changes induced by large Pb or Nb fractions, such as Pb acting as network former with tetrahedral $[\text{PbO}_4]$ or octahedral configuration $[\text{PbO}_6]$ and Nb forming chains or even three-dimensional associations of $[\text{NbO}_6]$ octahedral groups through the formation of Nb–O–Nb bonds,^{6,9} were reported to increase the hyperpolarizability of both cations,^{7,10,14} and consequently led to an enhancement of $\chi^{(3)}$.

However, the fact that $|\chi^{(3)}|$ in film glasses is much higher than in the corresponding bulk glasses suggests additional factors contributing to $|\chi^{(3)}|$ in the films. The optical energy gap is $E_g \geq 3.4$ eV for film glasses, while the photon energy at 800 nm is $E_{\text{ph}} = 1.55$ eV. Thus the limit condition for two photon absorption (TPA) to occur, given by $2E_{\text{ph}} \geq E_g$,³ is not satisfied. An additional contribution to resonant nonlinearity would be the presence of TPA at defect bands in the UV-visible. In particular, the existence of a charge trans-

fer band related to electronic transfer ($\text{O}^{2-} + \text{Nb}^{5+} \rightarrow \text{O}^- + \text{Nb}^{4+}$) has been reported for Nb containing glasses.¹⁵ This band is not always observed^{6,10} and when observed, it is in the near UV (3.3–3.6 eV) and thus, it should not lead to significant TPA in the present case. In addition, the extremely fast (< 1 ps) buildup time of the nonlinear response observed in our case, as illustrated in the inset of Fig. 2, allows us to discard nonlinear absorptive contributions to $\chi^{(3)}$ as the origin of the enhanced nonlinear response of film glasses. At the wavelengths of interest for optical communications, such as $1.55 \mu\text{m}$, $|\chi^{(3)}|$ in the films is expected to be similar to those presented in Fig. 2, since the probability of two photon absorption is negligible at that wavelength [$2E_{\text{ph}}(1.55 \mu\text{m}) = 1.66 \text{ eV} \ll E_g$].

The origin of the strong enhancement of $|\chi^{(3)}|$ must instead be related to the oxygen deficiency observed in film glasses ($\approx 10\%$ – 15% , Table I), since it must increase the fraction of bridging oxygen bonds to maintain the glass structure, and this has to occur along with the partial reduction of the cations present in the glass. The oxidation state of cations and the composition of glasses have been determined by x-ray photoelectron spectroscopy (XPS) using a Mg $K\alpha$ x-ray source (1253.6 eV). The background pressure during the analysis was below 2×10^{-9} mbar. The binding energy scale was calibrated versus the Au $4f_{7/2}$ level (Au metal) at 83.8 eV and depth profiling was achieved by Ar^+ sputtering (1.7 kV, sputtering rate of $\sim 1 \text{ nm min}^{-1}$). The composition

FIG. 1. (Color online) Absorbance measured for a (dash-dotted) G10B bulk glass and for the films having the (dashed) smallest and the (solid) largest $[\text{Pb}]+[\text{Nb}]$ fractions (G10F and G40F, respectively). The vertical line corresponds to twice the photon energy at 800 nm ($2E_{\text{ph}} = 3.11$ eV).

FIG. 2. Dependence of $(\blacksquare, \square)$ the $|\chi^{(3)}|_{\text{glass}}/|\chi^{(3)}|_{\text{SiO}_2}$ ratio with the heavy metal $[\text{Pb}]+[\text{Nb}]$ content for $(\blacksquare)$ film and $(\square)$ transparent bulk glasses. The dashed line is a guide for the eyes. The inset shows the time evolution of the nonlinear response for a 25PbO–15Nb₂O₅–60GeO₂ bulk glass.

FIG. 3. (Color online) Nb 3d core-level spectra of G10B (bulk), G10F, and G7F, (films) glasses. The dashed and solid lines correspond to Nb⁵⁺ and Nb⁴⁺ bands, respectively.

determined by XPS was in all cases within 5% the one reported earlier¹² and shown in Table I.

The Nb 3d core-level spectrum is shown in Fig. 3 for the G10B bulk glass. The peaks at 206.9 and 209.6 eV correspond to the Nb⁵⁺ 3d_{5/2} and 3d_{3/2} levels, respectively. The spectra obtained for films glasses show broader peaks, as illustrated by the spectra of G10F and G7F film glasses. The spectrum of G10F shows only a broad peak, that is compatible with the presence of additional bands associated with the presence of Nb⁴⁺ peaking at 205.7 (3d_{5/2}) and 208.5 eV (3d_{3/2}).¹⁶ The spectrum for G7F films presents two peaks, that are broader and shifted to lower energies than in the case of the G10B bulk glass indicating that the Nb⁴⁺ bands are the most intense. The measured binding energies of Nb 3d_{5/2} levels for bulk and film glasses are shown in Table I. Nb⁴⁺ bands are observed in all films, the only difference being the relative intensity of the Nb⁵⁺ and Nb⁴⁺ contributions. The fraction of Nb⁴⁺ is above 50% in all cases, and it increases with the heavy metal fraction. A possible reduction of Pb or Ge has been discarded by analyzing the most intense Pb 4f_{7/2} and Ge 2p_{3/2} levels. Only Pb²⁺ and Ge⁴⁺ were found both in bulk or film glasses, with binding energies of 137.5±0.2 and 1219.3±0.1 eV, respectively. Nb⁴⁺ presents the same octahedral coordination than Nb⁵⁺. This similar coordination together with the necessary increase of the fraction of bridging bonds should favor the formation of Nb–O–Nb bonds.^{6,9} From the optical point of view, the presence of a single elec-

tron in the 4d shell would enhance the polarizability of the ion,¹⁴ and this should contribute to the increase of $|\chi^{(3)}|$. It must be noted here though that Nb⁴⁺ should lead to a reduced transmission in the visible range.^{3,16} However, this is not the case, as shown in Fig. 1.

In summary, oxygen deficient transparent PbO–Nb₂O₅–GeO₂ film glasses with heavy metal contents beyond that of the bulk glass formation region show values of the third order optical susceptibility as high as $|\chi^{(3)}| \approx 1.8 \times 10^{-11}$ esu, that is 10³ times higher than that of fused silica. The fast buildup and decay times of the nonlinear response supports the nonresonant character of the nonlinear response. The presence of Nb⁴⁺ combined with the formation of Nb–O–Nb bonds with a large hyperpolarizability is proposed as mechanisms responsible for the enhancement of $|\chi^{(3)}|$. The fast nonlinear response times ($\tau < 1$ ps) and large figure of merit^{4,5} ($|\chi^{(3)}|/\tau^{-1}\alpha^{-1} > 3 \times 10^{-2}$ cm³/W s) of PbO–Nb₂O₅–GeO₂ film glasses make them candidates for optical beam processing applications.

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