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Citation: *J. Appl. Phys.* **110**, 023522 (2011); doi: 10.1063/1.3608172

View online: <http://dx.doi.org/10.1063/1.3608172>

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Structural origin of the nonlinear optical properties of lead niobium germanate film glasses

D. Munoz-Martin,¹ A. Ruiz de La Cruz,¹ J. M. Fernandez-Navarro,¹ C. Domingo,² J. Solis,¹ and J. Gonzalo^{1,a)}

¹Laser Processing Group, Instituto de Optica (CSIC), Serrano 121, 28006 Madrid, Spain

²Instituto de Estructura de la Materia (CSIC), Serrano 121, 28006 Madrid, Spain

(Received 22 November 2010; accepted 8 June 2011; published online 27 July 2011)

The structural origin of the nonlinear optical susceptibility ($/\chi^{(3)}/$) of lead-niobium-germanate film glasses with large Nb_2O_5 contents has been investigated. $/\chi^{(3)}/$ shows a strong enhancement with the Nb content in the films with $/\chi^{(3)}/$ values close to 2×10^{-11} esu at 800 nm for a Nb content as high as 0.71. Boling-Glass-Owyoung and Lines' semiempirical models predict accurately the values of $/\chi^{(3)}/$ for transparent bulk glasses but not for film glasses. This discrepancy is related to the remarkable structural differences between them. Raman spectroscopy suggests the formation of a three-dimensional (3D) structure of $[\text{NbO}_6]$ octahedra in the case of film glasses having large Nb contents, while X-ray photoelectron spectroscopy shows that a significant fraction of these units contain Nb^{4+} ions. The combination of a 3D structure of $[\text{NbO}_6]$ with the presence of Nb^{4+} polarons and their migration through electron intervalence transfer is proposed as the origin of the observed enhancement of $/\chi^{(3)}/$ in the film glasses. © 2011 American Institute of Physics. [doi:10.1063/1.3608172]

I. INTRODUCTION

The future development of all-optical communication networks requires materials with improved optical performance for the design and practical implementation of integrated photonic devices.^{1–3} Heavy metal, HM-, (Pb, Bi, Te) or transition metal, TM-, (Nb, Ti) oxide based glasses are promising candidates for the development of either passive or active devices due to their excellent optical properties. They present excellent transmission in the telecommunication windows, large refractive indices (typically above two) and finally, nonlinear refractive indices that are orders of magnitude larger than those of conventional silicate or borate glasses.^{3–6} The magnitude of the nonlinear response is related to the high hyperpolarizability of the HM and TM cations.^{3–7}

This characteristic is of extraordinary relevance for all-optical switching or power limiting among other applications. In this context, glasses containing Nb_2O_5 are of particular interest due to the close relationship between the nonlinear optical response and the Nb_2O_5 content in the glass.^{8–11} This behavior has been related to the formation of three dimensional arrangements of $[\text{NbO}_6]$ octahedra, which enhance the hyperpolarizability of the system. However, the bulk glass formation region may be limited to Nb_2O_5 contents below ≈ 50 mol% as it has been observed in the case of lead niobium germanate (NPG) glasses.¹² This limitation can be overcome by using film deposition techniques, such as sol-gel, sputtering or pulsed laser deposition (PLD),^{12–16} since the feasibility of synthesizing materials with very different properties than those corresponding to bulk glasses

has been demonstrated.^{12–14,17} In particular, PLD has been proven to be an excellent technique to produce complex oxide films, although the production of smooth films with the required optical quality is still challenging. PLD offers unprecedented possibilities to tailor the optical response of thin film glasses by using ablation targets having large contents of HM- or TM-oxides. These targets may indeed not necessarily be transparent glasses, as we have shown in the case of NPG thin film glasses with very large Nb fractions.¹² These film glasses were found to show good optical properties and a very intense nonlinear optical response ($/\chi^{(3)}/ \sim 10^{-11}$ esu), which is orders of magnitude higher than that of transparent NPG bulk glasses or other Nb_2O_5 -rich glasses.^{7–9,11,17} The singularity of these thin film NPG glasses was their significant fraction of Nb^{4+} with a single 4 *d*-electron. According Lines bond-orbital theory this may have a dramatic effect on their linear and nonlinear optical properties.^{2,5,15,18} However, the potential impact of the film glass structure on the nonlinear response has not been considered up to date.

In the present work we investigate the structural origin of the strong enhancement of $/\chi^{(3)}/$ observed in NPG film glasses with large Nb_2O_5 contents. For that purpose we compare their structure with that of parent bulk targets and perform a detailed comparison of the experimental results with the predictions of Boling-Glass-Owyoung^{2,19} and Lines'^{2,18} semiempirical models for the nonlinear optical response.

II. EXPERIMENTAL

Transparent lead-niobium-germanate (NPG) thin film glasses were produced by PLD using a KrF excimer laser ($\lambda = 248$ nm, $\tau = 12$ ns full width at half maximum). The laser was focused on the surface of bulk $\text{PbO} \cdot \text{Nb}_2\text{O}_5 \cdot \text{GeO}_2$ targets with increasing Nb_2O_5 contents that were prepared

^{a)}Author to whom correspondence should be addressed. Electronic mail: j.gonzalo@io.cfmac.csic.es.

TABLE I. (XPbO · YNb₂O₅ · ZGeO₂) Molar composition in mol% of bulk targets, [M]_B relative element content in % ([M]_B = 100 × N_M/N_{cat}, where N_M is the number of atoms of element M, with M = Pb, Nb, Ge or O and N_{cat} = N_{Pb} + N_{Nb} + N_{Ge}), and character of the bulk samples.

Sample	XPbO·YNb ₂ O ₅ ·ZGeO ₂	[Pb] _B	[Nb] _B	[Ge] _B	[O] _B	Aspect Aspect
G45B	35-0-65	35	—	65	165	Transparent glass
G10B	25-15-60	22	26	52	191	Transparent glass
G1B	25-25-50	20	40	40	200	Transparent glass
G7B	35-35-30	26	52	22	200	Opal, partially crystallized
G40B	35-55-10	23	71	6	213	Opal, partially crystallized
G41B	65-35-0	48	52	—	178	Opal, partially crystallized

using standard melting methods as described elsewhere.¹² Targets with GeO₂ molar contents larger than 50% were transparent while the rest were partially crystallized opals. XRD analysis of the targets (not shown here) confirms that transparent targets are amorphous, while different lead-niobium oxide crystalline phases were identified in the opals. Table I summarizes the composition and character of the different bulk targets.

Film deposition from G10B, G1B, G7B and G40B bulk targets took place in a vacuum chamber first evacuated to a pressure of 5×10^{-4} Pa and then filled with an oxygen dynamic pressure of 5 Pa. Films with thicknesses in the range of 0.2–3.6 μm were deposited using a laser energy density of $\approx 2.5 \text{ J cm}^{-2}$ on substrates held at room temperature and placed at 3 cm from the target surface. Film glasses are expected to be amorphous since substrate temperatures $\approx 400^\circ\text{C}$ are required to induce crystallization in the case of lead germanate films deposited by PLD.²⁰ Sapphire, glass, and silicon substrates were used in order to match the characterization techniques employed.

The compositional and optical characterization of the deposited films have been presented in previous works. Compositional characterization included ion beam analysis techniques (Rutherford Backscattering Spectrometry and Nuclear Reaction Analysis) and X-ray photoelectron spectroscopy (XPS), which allowed us to determine the cation and oxygen relative content in the films¹² as well as their oxidation state.¹⁷ Spectroscopic ellipsometry and UV-visible absorption spectroscopy in the 0.3–1.7 μm wavelength range were used to determine the linear refractive index ($n + ik$) and the optical energy gap (E_g) of transparent glasses.¹² The modulus of the third order nonlinear optical susceptibility ($| \chi^{(3)} |$) was analyzed at $\lambda = 800 \text{ nm}$ by degenerate four wave mixing (DFWM) in the forward folded box configuration using a femtosecond Ti:Sapphire regenerative amplifier laser system (1kHz repetition rate, pulse duration of $\tau \sim 100 \text{ fs}$) as excitation source.¹⁷ Further details of the compositional and optical characterization techniques can be found elsewhere.^{12,17}

In the present work we have analyzed the bulk and film glass network structure by Raman spectroscopy. Raman spectra were recorded using a confocal Raman microscope equipped with a diode laser emitting at 785 nm. The output laser power was 30 mW and the beam was focused on the sample using a 50x objective. The elastic scattering was eliminated using a notch filter and the signal was detected by a cooled CCD camera. Acquisition time was 10 mins. The contribution of the substrate was carefully subtracted in the case of film glasses

III. RESULTS

Figure 1 summarizes the cation relative composition of bulk targets (B) and film glasses (F) calculated as $[M] = 100 \times N_M/N_{\text{cat}}$, where N_M is the number of atoms of element M, with M = Pb, Nb or Ge, and $N_{\text{cat}} = N_{\text{Pb}} + N_{\text{Nb}} + N_{\text{Ge}}$. Film glasses present cation relative contents similar to those of the targets except for the film having the largest [Ge]_F (G10F). In this case a moderate [Pb]_F enrichment/[Ge]_F deficiency was observed, while [Nb]_F $\approx$ [Nb]_B in all cases. On the contrary, film glasses were found to be oxygen deficient independently from the composition of the target.¹² This oxygen deficiency was related to the presence of Nb⁴⁺ ions in the film glasses. X-ray photoelectron spectroscopy analysis showed that the fraction of Nb⁴⁺ was found to be above 50% in all cases and to increase with [Nb]_F, while no evidence of Ge⁴⁺ or Pb²⁺ reduction was found.¹⁷ Table II summarizes the oxygen relative content in the films ($[O]_F = 100 \times N_O/N_{\text{cat}}$), the oxygen deficiency ($O_F \text{ def} = 100 \times [O]_F/[O]_B$) and the fraction of Nb⁴⁺ present in the films ($100 \times [\text{Nb}^{4+}]_F/[\text{Nb}]_F$) taken from previous works.^{12,17}

Figure 2 shows the reduced Raman spectra of the NPG bulk samples included in Table I. The presence of GeO₂ and Nb₂O₅ are known to lead to vibrational bands in the 400–900 cm^{-1} range,^{8–10,21–26} while bands associated to PbO appear at lower frequencies ($\leq 350 \text{ cm}^{-1}$) (Ref. 21 and 22). The presence of bands associated to Ge-O bending modes or Nb-O vibrations have been also reported to appear in that range,^{23,24,27,28} which makes difficult to resolve the Raman spectra in the region below 350 cm^{-1} . Thus, in order to distinguish between the vibrational modes of GeO₂ and Nb₂O₅

FIG. 1. (Color online) Cation relative composition in atoms % of NPG (Δ) bulk samples and ($\bullet$) film glasses.

TABLE II. ($[O]_F$) Oxygen relative content, (O_F def) Oxygen deficiency, ($[Nb]_F$) Niobium relative content, and ($\%Nb^{4+}$) fraction of Nb^{4+} ions in the film glasses. Values are taken from Refs. 12 and 17. All data are in %.

Sample	$[O]_F$	O_F def.	$[Nb]_F$	$\%Nb^{4+}$
G10F	168	12	24	55
G1F	180	10	39	70
G7F	172	14	54	68
G40F	172	19	71	—

two additional binary bulk samples containing PbO and GeO_2 (G45B) or Nb_2O_5 (G41B) have been synthesized and their Raman spectra analyzed.

Raman spectrum of G45B, which has the largest GeO_2 molar content (65 mol%) is characterized by two main bands: A very broad band at $350\text{--}550\text{ cm}^{-1}$ and a narrower band centered at 810 cm^{-1} . The low frequency band is related to a glass network composed of bridging Ge-O-Ge linkages,²¹ while the band at high wavenumbers is assigned to stretching vibrations of Ge-O bonds in $[GeO_4]$ tetrahedra, which constitute the basic structural units of GeO_2 -based

glasses.²² In fact, this band is a combination of the vibration modes of $[GeO_4]$ units with different number of non bridging oxygens (NBO). The frequency of the vibration mode decreases as the number of NBO surrounding Ge atoms increases, and thus, the addition of network modifiers that increases the number of NBO, shifts the peak of the band toward lower wavenumbers.²²

The “footprint” of Nb_2O_5 on the glass network can be deduced from the analysis of the Raman spectrum of sample G41B ($65PbO \cdot 35Nb_2O_5$) which presents bands narrower than G45B due to its partial crystallization. Several bands related to Nb_2O_5 can be identified: A broad band at $500\text{--}650\text{ cm}^{-1}$ (weak) and two peaks at 720 cm^{-1} (intense) and at 880 cm^{-1} (weak). The coordination of Nb^{5+} in oxide crystals is typically octahedral and rarely tetrahedral.²⁹ In the case of glasses most works assign the bands observed in Raman spectra to $[NbO_6]$ octahedra,^{8–10,24–26} although the existence of $[NbO_4]$ has been proposed in the case of niobium germanate glasses.^{28,30} Still, Nb-O bond lengths in $[NbO_6]$ (2.0 Å) and $[NbO_4]$ (1.9 Å) are so close that is extremely difficult to neatly assign Raman bands to modes associated to any of these units.^{25,31} We have assumed in the present work an octahedral coordination for the band assignment based on previously published works. The band at $500\text{--}650\text{ cm}^{-1}$ is related to a three-dimensional network formed by slightly distorted $[NbO_6]$ octahedra, whereas the peak at 880 cm^{-1} is assigned to vibrations of isolated $[NbO_6]$ octahedra with NBO.^{8–10,24–26} Finally, the sharp peak at 720 cm^{-1} is also associated to Nb-O vibrations in $[NbO_6]$ octahedra.³⁰

Raman spectra of ternary bulk samples present a combination of the vibrational modes observed in the binary samples. The position of the bands and their relative intensities depend on the exact composition of each sample. The spectrum of glass G10B, which has a similar GeO_2 molar content than G45B (60 and 65 mol%, respectively) presents a peak at high wavenumbers that is broader, and it is shifted toward lower frequencies (780 cm^{-1}) than in the case of G45B, whereas the intensity of the band at low frequencies (470 cm^{-1}) strongly decreases. These differences with respect to G45B can be understood by the addition of Nb_2O_5 . The decrease of the intensity of the 470 cm^{-1} band is associated with the cleavage of Ge-O-Ge linkages, which increases the number of NBO and shifts the high wavenumber peak toward lower frequencies.³⁰ Moreover, the addition of Nb_2O_5 leads to the appearance of two shoulders of the main band at 575 and 850 cm^{-1} , respectively. According to the band assignment made for G41B, we assign the first one to vibrations of slightly distorted $[NbO_6]$ octahedra without NBO, while the second is assigned to highly distorted $[NbO_6]$ octahedra having NBO.

As the GeO_2 molar content decreases (glass G1B), the position of the peak related to $[GeO_4]$ units continues broadening and shifting toward lower wavenumbers, which indicates an even larger fraction of NBO, while the shoulders at 575 cm^{-1} and 850 cm^{-1} , related to $[NbO_6]$ octahedra, become more intense due to the increase of the Nb_2O_5 content. The assignment of these shoulders is confirmed by the spectra of G7B and G40B. The spectrum of G7B is

FIG. 2. Raman spectra of NPG bulk samples. Spectra have been shifted vertically to ease comparison and they are ordered according to their GeO_2 molar content from G45B (65 mol%) to G41B (0 mol%).

TABLE III. Assignment of vibrational bands observed in the Raman spectra of bulk $\text{PbO-Nb}_2\text{O}_5\text{-GeO}_2$ samples. Bands appearing as shoulders of intense bands are indicated by (s).

Sample	Band (cm^{-1})	Assignment
G45B	325–400 (s)	Vibrational modes of Pb-O bonds
	430–550	Ge-O-Ge bridging linkages
	700–850	Stretching vibration of Ge-O bonds in $[\text{GeO}_4]$ tetrahedra
G10B	200–400 (s)	Vibrational modes of Pb-O bonds
	400–520	Ge-O-Ge bridging linkages
	550–625 (s)	Slightly distorted $[\text{NbO}_6]$ octahedra
	750–850	Stretching vibration of Ge-O bonds in $[\text{GeO}_4]$ tetrahedra
G1B	850–950 (s)	Highly distorted $[\text{NbO}_6]$ octahedra
	200–400 (s)	Vibrational modes of Pb-O bonds
	400–500	Ge-O-Ge bridging linkages
	550–650 (s)	Slightly distorted $[\text{NbO}_6]$ octahedra
	650–850	Stretching vibration of Ge-O bonds in $[\text{GeO}_4]$ tetrahedra
G7B	850–950 (s)	Highly distorted $[\text{NbO}_6]$ octahedra
	200–400	Vibrational modes of Pb-O bonds
	620–700	Slightly distorted $[\text{NbO}_6]$ octahedra
G40B	880–950	Highly distorted $[\text{NbO}_6]$ octahedra
	250–350	Vibrational modes of Pb-O bonds
	600–700	Slightly distorted $[\text{NbO}_6]$ octahedra
G41B	700–750 (s)	Nb-O vibrations in $[\text{NbO}_6]$ octahedra
	850–950	Highly distorted $[\text{NbO}_6]$ octahedra
	250–350	Vibrational modes of Pb-O bonds
	500–650	Slightly distorted $[\text{NbO}_6]$ octahedra
	690–750	Nb-O vibrations in $[\text{NbO}_6]$ octahedra
	840–920	Highly distorted $[\text{NbO}_6]$ octahedra

characterized by the presence of sharp peaks that are a consequence of the partial crystallization of the sample. The most intense peak that is observed at 670 cm^{-1} is assigned to vibrations of slightly distorted $[\text{NbO}_6]$ octahedra. Finally, the spectrum of G40B, which has a very low GeO_2 molar content (10 mol%), shows the same main peak, although in this case the peak is broader due to a shoulder at high wavenumbers ($700\text{--}750\text{ cm}^{-1}$), that we assign to Nb-O vibrations in $[\text{NbO}_6]$ as in the case of G41B. Table III summarizes the band assignment made, which is the basis to identify the vibrational bands observed in the film glasses.

Figure 3 compares Raman spectra of film glasses and the corresponding bulk samples in the $300\text{--}900\text{ cm}^{-1}$ range. All film spectra present broad bands without sharp peaks, which evidences their amorphous character. As it is clearly deduced from the figure, the structural differences between bulk targets and film glasses increase as the GeO_2 molar content decreases, since the dominant feature in the film spectra is in all cases a broad and intense band at $700\text{--}900\text{ cm}^{-1}$. Films G10F and G1F that were deposited from bulk glasses with a large GeO_2 molar content ($\geq 50\text{ mol}\%$), show similar spectra than the corresponding bulk glasses, although their main band is shifted toward higher wavenumbers and an intense shoulder in the $800\text{--}900\text{ cm}^{-1}$ region appears. As discussed in the case of bulk samples (Fig. 2), the main contribution to this band is the vibration of Ge-O bonds in $[\text{GeO}_4]$ tetrahedra, while the band shift and the shoulder

FIG. 3. (Color online) Raman spectra of (blue line) film glasses and (black line) corresponding bulk samples. Spectra have been shifted vertically to ease comparison, and they are ordered according to their GeO_2 molar content from G10F (60 mol%) to G40F (10 mol%).

are likely due to the presence of Nb in octahedral coordination.²⁹

The important role that Nb plays in the film glass network is confirmed by the spectra of films G7F and G40F. These samples have very low GeO_2 molar contents and thus, the main band at 800 cm^{-1} can be only assigned to vibrations of $[\text{NbO}_6]$. This band has been previously observed in glasses with large Nb_2O_5 molar contents ($> 20\text{ mol}\%$),^{8–10,27} and assigned to Nb-O vibrations in $[\text{NbO}_6]$ chains. The band shows shoulders at low ($600\text{--}750\text{ cm}^{-1}$) and high ($> 800\text{ cm}^{-1}$) frequencies, which are assigned to slightly and highly distorted $[\text{NbO}_6]$, respectively. Finally, the shoulder at $600\text{--}750\text{ cm}^{-1}$ increases significantly for the film having the largest [Nb] (G40F).

Despite the oxygen deficiency and the structural differences, the deposited films were transparent in all the compositional range as opposite to what it is observed in the case of bulk targets. Figure 4 shows the dispersion of n obtained from a Cauchy fitting of the ellipsometric parameters for one of the transparent bulk glasses (G10F) and the film glasses

FIG. 4. (Color online) Dispersion of the real part of the refractive index (n) of G10B bulk glass and films having the smallest (G10F) and largest (G40F) $[\text{Nb}]_F$. The inset shows $(n^2 - 1)^{-1}$ vs E^2 (Wemple's plot) for these glasses.

with the lowest (G10F) and the highest (G40F) Nb contents ($[\text{Nb}]_F$). A strong decrease of n is observed for wavelengths up to 700 nm whereas the decrease is much slower at longer wavelengths. The values of n at 550, 800 and 1480 nm determined for transparent bulk glasses and films are summarized in Table IV. The inset in Fig. 4 shows that the dispersion of n is well described by the single oscillator Wemple's model:^{15,32,33}

$$\frac{1}{(n^2 - 1)} = \frac{E_0}{E_d} - \frac{E^2}{E_0 E_d}, \quad (1)$$

where E is the photon energy, E_d is the dispersion energy that is a measure of the electronic oscillator strength and E_0 is the average oscillator energy that is considered to be a good estimation of the Sellmeier gap (E_S). The values of E_d and $E_0 \approx E_S$ determined for the different glasses are included in Table IV. The curvature deviation observed for G10B at high photon energies in the inset of Fig. 4 is attributed to the proximity of the bandedge.³² The imaginary part (k) of the refractive index is below our experimental resolution limit ($< 10^{-4}$) for wavelengths longer than 450 nm in all cases except for G1F for which $k < 10^{-4}$ for $\lambda > 650$ nm (Ref. 12). The experimental absorbance spectra measured for G10B, G10F and G40F are shown in Fig. 5, while the energy gaps (E_g) calculated for transparent bulk and film glasses are

included in the inset. The high level of the absorbance baseline is related to the high refractive index ($n > 1.9$) whereas the oscillations observed in the film spectra are related to interference effects at the interfaces.¹⁷ The most significant difference observed is the increase of E_g in the films with respect to the transparent bulk glasses: $\Delta E_g \approx 0.6$ – 0.7 eV when comparing a film and the corresponding bulk glass. This behavior was attributed to an increase of the fraction of bridging oxygen bonds in the film glass network caused by the oxygen deficiency.¹⁷ Moreover, E_g slightly decreases when increasing the Nb content, although in this case we cannot rule out the contribution of $[\text{Pb}]$ to this behavior even if the $[\text{Pb}]_F$ range is much smaller than the $[\text{Nb}]_F$ range in the films (0.23–0.29 versus 0.24–0.71). Finally, nonlinear optical susceptibilities determined at $\lambda = 800$ nm for transparent bulk ($/\chi^{(3)}/_B$) and film ($/\chi^{(3)}/_F$) glasses are summarized in Table IV. $/\chi^{(3)}/_B \sim 10^{-13}$ esu, while $/\chi^{(3)}/_F$ is one order of magnitude larger than that of the corresponding transparent bulk glass in the case of G10 and G1. $/\chi^{(3)}/_F$ increases as $[\text{Nb}]_F$ increases to reach values as large as $/\chi^{(3)}/_F \approx 2.5 \times 10^{-11}$ esu in the case of films deposited from non transparent bulk targets with very large $[\text{Nb}]$ (G40B). The build-up time of the nonlinear response was found to be extremely fast (~ 130 fs) in the case of the transparent bulk glasses.¹⁷ However, the very low level of the DFWM conjugated signal due to the very short interaction length made it impossible to measure it accurately in the case of films.

IV. DISCUSSION

The intense nonlinear optical response of glasses containing large fractions of heavy metals or transition metals has been undoubtedly related to their large hyperpolarizability associated to either the lone pair e^- or the empty d -band orbitals, respectively.^{3,5,6,33} In particular, the nonlinear response of Nb-containing glasses has previously been observed to increase with the molar fraction of Nb_2O_5 .^{8–10,25,33,34} This is the trend observed in the present work in the case of transparent bulk glasses. However, when comparing film and bulk glasses with similar Nb contents (G10, G1), an increase of $/\chi^{(3)}/$ close to one order of magnitude is observed, which has not been previously reported. In order to elucidate the origin of this behavior, we have

TABLE IV. (Th) Thickness; $[\text{Nb}]$ Niobium relative content; (n_i) linear refractive index at $\lambda = 550$ nm, 800 nm and 1480 nm; (E_d) dispersion energy; (E_S) Sellmeier energy gap; (l_B) characteristic bond length; $/\chi^{(3)}/_{\text{exp}}$ experimental third order optical susceptibility; $(n_{2\text{exp}})$ nonlinear refractive index calculated from $/\chi^{(3)}/_{\text{exp}}$ by assuming a pure refractive nonlinearity (Ref. 37) and theoretical predictions from $(n_{2\text{BGO}})$ BGO or $(n_{2\text{Lines}})$ Lines' models.

Sample	Th (μm)	$[\text{Nb}]$ (%)	n_{550}	n_{800}	n_{1480}	E_d (eV)	E_S (eV)	l_B ($\text{\AA}$)	$/\chi^{(3)}/_{\text{exp}}$	$n_{2\text{exp}}$	$n_{2\text{BGO}}$	$n_{2\text{Lines}}$
									($\times 10^{-12}$ esu)	($\times 10^{-12}$ esu)	($\times 10^{-12}$ esu)	($\times 10^{-12}$ esu)
G10B	800	26	2.01	1.97	1.95	20.4	7.0	1.96	0.2 ± 0.1	0.9 ± 0.1	0.9 ± 0.4	2.0
G1B	1400	40	2.12	2.06	2.03	20.7	6.6	1.98	0.3 ± 0.1	1.2 ± 0.2	2.0 ± 1.0	4.2
G10F	3.6	24	2.05	2.00	1.97	18.3	6.4	1.96	2.1 ± 0.6	10 ± 3	1.6 ± 0.8	3.8^b
G1F	1.5	39	2.12	2.07	2.03	20.6	6.7	1.94	—	—	1.8 ± 0.9	3.8^b
G7F	2.9	54	2.24	2.17	2.14	22.4	6.4	1.95	12 ± 2.0	53 ± 9	2.2 ± 1.1	4.5^b
G40F	1.5	71	2.32	2.24	2.20	23.3	6.2	1.96	18 ± 2.0	76 ± 8	3.0 ± 1.5	7.5^b

^a $l_B = (\sum x_i l_{Bi}^3)^{1/3}$, where x_i is the molar fraction of component i (with $\sum x_i = 1$) and l_{Bi} is the corresponding metal-oxygen bond length (Ref. 40)

^b Lines model is only applicable to materials with empty d -orbitals. The calculation of $n_{2\text{Lines}}$ in this case only aims at estimating the value of n_2 in absence of Nb^{4+} .

FIG. 5. (Color online) Absorbance measured for (dash-dotted) G10B, (dashed) G10F, and (solid) G40F glasses. The inset shows the optical energy gap determined for (Δ) transparent bulk and ($\bullet$) film glasses as a function of their [Nb] content. The dashed line is a guide for the eyes.

evaluated $\chi^{(3)}$ of transparent bulk and film glasses in the frame of Boling, Glass & Owyong (BGO)^{2,19,35} and Lines,^{2,18} semiempirical models, as they are known to predict the value of $\chi^{(3)}$ within at least the order of magnitude in the case of TM-oxide glasses.⁴ Then we have analyzed the structural differences between bulk and film glasses and their impact on $|\chi^{(3)}|$, to finally propose a mechanism responsible for the observed enhancement of $|\chi^{(3)}|$ in the film glasses.

A. Evaluation of the nonlinear response in the frame of BGO and Lines' models

From the optical point of view, film glasses present values of n and E_g that are significantly larger than those measured for bulk glasses (Figs. 4 and 5). The impact of these parameters on $|\chi^{(3)}|$ (Ref. 3, 5, and 15), can be evaluated using the BGO model, which considers a single polarizable constituent that dominates the optical response of the material, and a single frequency of resonance (ω_0) that determines the optical dispersion. Even considering that this might not be the case of NPG glasses, as both Pb and Nb are expected to contribute to the nonlinear response of the glass, Wemple's plot shown in Fig. 4 evidences that the dispersion of n is well described by a single oscillator model. Based on easily accessible physical parameters, the BGO model allows a estimation of n_2 that is correct within less than one order of magnitude in the case of multicomponent glasses.⁴ In the low frequency limit ($\omega \ll \omega_0$) the BGO model leads to an expression of n_2 given by:^{2,19,35}

$$n_{2BGO}(esu) = \frac{(n^2 + 2)^2 (n^2 - 1)^2 (gs)}{48\pi n \hbar \omega_0 (Ns)}, \quad (2)$$

where N is the density of nonlinear oscillators, s is the effective oscillator strength, and g is a dimensionless parameter related to the anharmonic coefficient. The refractive index n can be expressed as:^{2,19,35}

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

where m is the electron mass and e its charge in Gaussian units. This expression allows the evaluation of Ns and ω_0

from the values of n at two frequencies that can be determined from the dispersion relation for n shown in Fig. 4. The factor gs has been found to be 3 in the case of materials with small nonlinear optical coefficients, while gs values in the range 1–2 provide a better agreement with experimental results in glasses presenting large nonlinear refractive indices.^{4,19,36} In the present case we have considered the values of n at 550 nm and 1480 nm and a value of $gs = 1.5 \pm 0.5$ to evaluate first Ns and ω_0 and then n_{2BGO} at 800 nm. The theoretical values are included in Table IV where they are compared to the experimental results by assuming for them a pure refractive nonlinearity ($|\chi^{(3)}|_{\text{exp}} \propto \text{Re}[\chi^{(3)}]$) through the relationship: $n_{2\text{exp}}(esu) = (3\pi/n) |\chi^{(3)}|_{\text{exp}}(esu)$ (Ref. 37). Boling, Glass & Owyong model leads to n_{2BGO} values in the range of $\sim 10^{-12}$ esu for transparent bulk glasses, while the values calculated for film glasses are slightly higher but still of the same order of magnitude. If we compare the theoretical and the experimental values (Table IV) we observe that the model allows an accurate estimation in the case of bulk glasses but not for the films. The use of $gs = 3$ would increase n_{2BGO} by a factor of two, yet the calculated value for film glasses would be one order of magnitude smaller than the experimental value, which suggest additional contributions to the nonlinear response.

Alternatively, Lines' bond-orbital theory^{2,18} models the optical response in terms of the perturbations induced by the applied electric fields on the local bonding orbitals. In the case of transparent TM-oxides, Lines' model allows considering the contribution of the empty “ d ” orbitals to n_2 for materials with a single constituent oxide. In this case, Lines derived a semiquantitative expression to estimate n_2 :^{2,18,33}

$$n_{2\text{Lines}}(esu) = \frac{25l_B^2(n^2 - 1)f_L^3 E_S^2}{n(E_S^2 - E^2)^4} \times 10^{-13}, \quad (4)$$

where $f_L = (n^2 + 2)/3$ is Lorentz local-field correction factor, E_S (in eV) is the Sellmeier gap determined from Eq. (1), and l_B (in Å) is the bond length. In the case of TM-oxides, the contribution of empty d -orbitals to the nonlinear response is negligible for $l_B > 2.3$ Å, whereas it increases when decreasing l_B to become dominant for $l_B < 2.0$ Å.^{15,18} Although Lines' model has been extended to multicomponent glasses,⁹ it is difficult to evaluate n_2 in these cases due to the inherent complexity in the assignation of a single characteristic l_B for a multicomponent glass.^{38,39} In the case of NPG transparent bulk glasses we have estimated l_B using the approximation proposed by Nassau:^{39,40}

$l_B = (\sum x_i l_{Bi}^3)^{1/3}$, where x_i is the molar fraction of component i (with $\sum x_i = 1$) and l_{Bi} is the corresponding bond length (2.24 Å (Pb-O), 2.0 Å (Nb-O), and 1.8 Å (Ge-O)).^{18,39,40} The calculated l_B as well as the values of $n_{2\text{Lines}}$ at 800 nm determined from Eq. (4) are included in Table IV. As in the case of the BGO model, Lines' model predicts well n_2 for transparent bulk glasses. In addition, we have estimated which would be the values for the film glasses should they had no Nb^{4+} . As it is seen in Table IV, these values are still one order of magnitude below the experimental ones.

The comparison of the experimental results with the values calculated using either BGO or Lines' models suggests the existence of additional factors contributing to the nonlinear response in the case of the film glasses. The structural analysis performed demonstrates the existence of two clear differences between bulk and film glasses that should be in the origin of the observed increase of $\chi^{(3)}/F$: First, film glasses possess a very large $[\text{Nb}]_F$ and second, they contain a large fraction of Nb^{4+} with a single d -electron. In the following we analyze their impact on the nonlinear optical response.

B. Effect of $[\text{Nb}]_F$ on the glass structure and $\chi^{(3)}/F$

In the case of niobio-(boro)phosphate glasses,^{8–10,24,25} the observed significant increase of the nonlinear response has been related to the formation of first two-dimensional (2D) and then three-dimensional (3D) associations of Nb-oxygenated sites by clustering of $[\text{NbO}_6]$ octahedra as $[\text{Nb}]$ increases.^{7,9,10,26} Taking this into account along with the structural analysis made by Raman spectroscopy, it is possible to depict the evolution of the film glass structure as $[\text{Nb}]_F$ increases. At low $[\text{Nb}]_F$ (G10F, G1F), Nb acts as a glass modifier, as evidenced by the presence of isolated $[\text{NbO}_6]$ with vibration bands at $>800\text{ cm}^{-1}$. As $[\text{Nb}]_F$ increases, the isolated octahedra link to form chains, which leads to the appearance of a vibration band at $\approx 800\text{ cm}^{-1}$. Finally, at very high $[\text{Nb}]_F$ (G40F), $[\text{NbO}_6]$ octahedra form a 3D-structure with $[\text{NbO}_6]$ linked through the corners that are responsible for the characteristic vibration band at $\approx 650\text{ cm}^{-1}$. Nb acts then as glass former and Nb-O-Nb bridges are present in the glass.

Although we have discarded the presence of $[\text{NbO}_4]$ tetrahedra in the film glasses, it is important to emphasize that even in that case, the structure of film glasses having large $[\text{Nb}]_F$ would be dominated by a 3D association of $[\text{NbO}_6]$ octahedra based in a Nb-O-Nb glass network as above described. Following the work of Kolovkoba *et al.* on niobium germanate glasses,³⁰ the main difference on the evolution of the glass structure with $[\text{Nb}]$ with the image above depicted would rely on the fact that at low $[\text{Nb}]_F$, $[\text{NbO}_4]$ would substitute a fraction of network former $[\text{GeO}_4]$ tetrahedra. The formation of a Ge-O-Nb mixed network would lead then to a band in the $450\text{--}500\text{ cm}^{-1}$ range, whereas the presence of $[\text{NbO}_4]$ tetrahedra would be evidenced by a band at $\approx 810\text{ cm}^{-1}$ that would shift to higher wavenumbers when increasing $[\text{Nb}]_F$. A further increase of $[\text{Nb}]_F$ would lead to the emergence of $[\text{NbO}_6]$ octahedra evidenced by a band in the Raman spectra at $700\text{--}750\text{ cm}^{-1}$. Finally, the excess of $[\text{NbO}_6]$ would lead to the formation of a 3D-structure of $[\text{NbO}_6]$ evidenced by a band at $\approx 600\text{ cm}^{-1}$ at large $[\text{Nb}]_F$. All these bands ($450\text{--}500\text{ cm}^{-1}$, $\approx 600\text{ cm}^{-1}$, $700\text{--}750\text{ cm}^{-1}$, $\approx 810\text{ cm}^{-1}$) are observed in the Raman spectra of the NPG film glasses, and thus from the Raman spectra alone is extremely difficult to completely discard the presence of $[\text{NbO}_4]$.^{28,30,31} EXAFS or NMR complementary experiments would be required to determine unambiguously the presence of $[\text{NbO}_4]$. However, it must be noted that this does not affect the structure of film glasses having very large

$[\text{Nb}]_F$ (like G7F, G40F) as it is dominated, in any case, by a 3D-structure of $[\text{NbO}_6]$ octahedra.

These 3D-structures have been proposed to increase the delocalization of $(\text{Nb-O})_6$ electronic clouds toward Nb atoms to form Nb-O bonds. This gives rise to a large hyperpolarizability of the octahedra, and therefore to an increase of the nonlinear response of Nb-rich glasses.^{7,9,10} Moreover, the collective motion of these $[\text{NbO}_6]$ based structures has been proposed to lead to a strong nuclear contribution to the nonlinear response ($\approx 60\%$ of the total) in glasses with very large Nb_2O_5 contents ($\sim 40\text{ mol } \%$).¹¹ The typical values of $\chi^{(3)}$ determined for Nb-rich glasses in which the formation of 3D Nb-based structures has been observed, are all in the range $1\text{--}5 \times 10^{-13}\text{ esu}$,^{8,9,11} which are similar to those reported in the present work for G10B and G1B glasses, and allow us to conclude that the above discussed structural factors lead to $\chi^{(3)} \sim 10^{-13}\text{ esu}$. However, these values are still well below those measured for film glasses. Therefore this effect alone is not enough to explain the origin of the large $\chi^{(3)}/F$, and suggests that the large fraction of Nb^{4+} in the films must have a role on the nonlinear optical response.

C. Effect of Nb^{4+} on $\chi^{(3)}/F$

Nb^{4+} ions possess a highly delocalized single $4d$ -electron,⁴¹ which could increase significantly the hyperpolarizability of the 3D Nb-based structures,³⁴ but at the same time this single electron may be responsible of significant resonant absorption in the visible range due to electronic transitions,^{5,42} as it has been evidenced in Ti^{3+} containing glasses,^{34,43} or in the case of iron oxides with partially filled d -bands.⁴⁴ In this latter case, the role of the overlapping of p - d orbitals and thus, of the bond length (l_B), on the intense nonlinear response ($\chi^{(3)} \sim 10^{-11}\text{--}10^{-10}\text{ esu}$) was evidenced. A similar effect of l_B in $\chi^{(3)}$ can be deduced from the results obtained in the present work. According to Wemple's single oscillator approximation,^{15,32,33} E_d is proportional to $(l_B)^2$, which leads to the modified Line's equation given by,^{33,38}

$$\chi^{(3)}(\text{esu}) = A(n^2 + 2)^3(n^2 - 1) \frac{E_d}{E_0^2}, \quad (5)$$

where E_d and $E_0 \approx E_S$ have the meaning defined in Eq. (1) and A is a phenomenological constant. The fact that $\chi^{(3)}/F$ holds the modified Lines' equation as shown in Fig. 6, suggests that E_0 must be as small as possible in order to have large $\chi^{(3)}/F$ values and moreover, it evidences the effect of l_B on $\chi^{(3)}$. To see this clearly we must recall that $E_d \sim (l_B)^2$ and $E_S (\text{eV}) \approx 15(l_B(\text{\AA}) - 1.6)$ in the case of TM-oxides.^{15,18} Using these approximations we reach that:

$$\chi^{(3)}(\text{esu}) \propto (n^2 + 2)^3(n^2 - 1) \left(1 - \frac{1.6}{l_B}\right)^{-1}. \quad (6)$$

According to this expression, $\chi^{(3)}/F$ should increase as n increases and l_B decreases. We observe experimentally that $\chi^{(3)}/F$ increases by one order of magnitude when n increases from 2.02 (G10 F) to 2.24 (G40 F) (Table IV). According to Eq. (6), such an increase of n would increase $\chi^{(3)}/F$ by a factor ≈ 2 . This suggests that the dominant contribution to

FIG. 6. (Color online) Dependence of $\chi^{(3)}$ versus $(n^2 + 1)^3(n^2 - 1)E_d/E_o^2$ (modified Lines' equation) for (■) film and (□) transparent bulk glasses. (○) Values calculated using Lines' model for transparent bulk glasses. The dashed line is a linear fit of the experimental data.

$\chi^{(3)}/F$ is associated to l_B and implies that the effective l_B must decrease as $[\text{Nb}]_F$ increases from 0.24 to 0.71. The Nb-O bondlength in the case of octahedra containing Nb^{4+} ($l_B \approx 1.8$ Å) (Ref. 45) is shorter than in the case of Nb^{5+} ($l_B \approx 2.0$ Å) (Ref. 15). Thus, the effective l_B of film glasses should be smaller than that of transparent bulk glasses (G10B and G1B), and it should decrease even further when increasing $[\text{Nb}]_F$ which agrees with the observed increase of Nb^{4+} in the films. This behavior should lead to an increase of the contribution of d -orbitals to the nonlinear response, thus leading to the enhancement of $\chi^{(3)}$ observed in Fig. 6. This reasoning confirms the influence of Nb^{4+} on the enhancement of the nonlinear optical response of film glasses, although the ultimate responsible process is not clear.

D. Resonant character of the Nb^{4+} induced enhancement of $\chi^{(3)}/F$

Lines' theory,^{5,18} and the enhancement of the nonlinear response observed in glasses containing ions with non empty d -orbitals (Ti^{3+} , Fe ions)^{43,44} support the resonant character of the enhancement of $\chi^{(3)}/F$ in the case of NPG film glasses. It must be noted, however, that while optical absorption bands related to d - d electronic transitions peaking at $E \approx 2.8 \pm 0.2$ eV have been observed in glasses⁴³ or LiNbO_3 (Ref. 46) containing Ti^{3+} impurities no absorption related to d - d transitions was observed in the optical range in the case of LiNbO_3 containing Nb^{4+} impurities,⁴⁶ although they are predicted in the case of NbO_2 (Ref. 47). There are other possible electronic processes associated to Nb^{4+} that may lead to optical absorption bands in the visible or near infrared range. In the case of glasses²⁷ or crystalline materials such as LiNbO_3 (Ref. 46, 48, and 49), HLaNb_2O_7 (Ref. 50), or SBN (Ref. 51), the presence of Nb^{4+} gives rise to bands peaking at 2.5 ± 0.1 eV (Ref. 27, 48, and 49), 1.6 ± 0.1 eV (Ref. 46), 1.1 eV (Ref. 50) and 0.7 eV (Ref. 51) that have been attributed to "small" polarons (2.5, 1.6 and 0.7 eV) or charge transfer of electrons ($\text{Nb}^{4+} + \text{Nb}^{5+} \rightleftharpoons \text{Nb}^{5+} + \text{Nb}^{4+}$) (1.1 eV). The latter process can be regarded as the migration of a Nb^{4+} polaron⁴⁹ and thus, the absorption band at 1.1 eV may appear simultaneously to the bands associated to Nb^{4+} polarons.

All these bands are broad, and show bandwidths in the range from 1 to 1.8 eV (Ref. 46, 48, and 50). Thus, either the presence of small Nb^{4+} polarons or their migration inside the glass could lead to absorption at the excitation wavelength of 800 nm (1.55 eV), which would lead to a resonant contribution to the nonlinear response of the film glasses. However, no absorption bands associated to the presence of Nb^{4+} ions were identified in any of the film glasses as it is illustrated in Fig. 5. This fact can be related to the combination of the reduced value of the above mentioned absorption bands (≤ 50 cm⁻¹),^{27,43,48,49} and the reduced thickness of the films considered for the determination of $\chi^{(3)}/F$ (≤ 3.6 μm, Table IV), which leads to absorbance values < 0.02 that are below our experimental resolution. Therefore, we propose that nonlinear absorptive contributions associated to the presence of Nb^{4+} are responsible for the enhancement of $\chi^{(3)}/F$ in the film glasses. On the contrary, in the case of transparent bulk glasses (G10B and G1B) having no Nb^{4+} , the observed fast buildup time of the nonlinear response confirms its non resonant and pure refractive character.

V. CONCLUSIONS

Lead niobium germanate film and transparent bulk glasses present clear structural differences that lead to large $\chi^{(3)}/F$ values in the case of film glasses with $[\text{Nb}]_F > 50\%$, such as G7F or G40F. In these cases the glass structure is dominated by a bi- or three-dimensional network based on corner sharing $[\text{NbO}_6]$ octahedra that is characterized by the presence of Nb-O-Nb bridges, which increases the hyperpolarizability of the octahedra and it allows the formation of transparent glasses at these large Nb concentrations. The very large $\chi^{(3)}/F$ ($\approx 2 \times 10^{-11}$ esu at 800 nm) measured in the case of G40F ($[\text{Nb}]_F = 0.71$) results from the combination these 2D or 3D Nb-based networks with the presence of a significant fraction of Nb^{4+} in the films. On the one hand, the shorter Nb-O average bondlength increases the contribution of d -orbitals to the nonlinear response leading to an increase of refractive contribution ($\text{Re}[\chi^{(3)}]/F$) to $\chi^{(3)}/F$, while on the other hand, the presence of highly delocalized Nb^{4+} d -electrons may increase even further the hyperpolarizability of the Nb-based glass network, while at the same time, this glass network may favor the migration of Nb^{4+} d -electrons through intervalence charge transfer when the films glass is excited at 800 nm, which would increase even further $\chi^{(3)}/F$ through a nonlinear absorptive contribution ($\text{Im}[\chi^{(3)}]/F$).

ACKNOWLEDGMENTS

The authors acknowledge the financial support of Spanish Ministry of Science and Innovation (Grants Nos. TEC2008-01183 and MAT2009-14282-C02-01). D. M. and A.R. acknowledge a CSIC-JAE predoctoral grant and an I3P-CSIC postdoctoral contract respectively. The authors acknowledge J.L.G. Fierro (I. de Catálisis y Petroleoquímica, CSIC), and J. Garcia-Lopez (Centro Nacional de Aceleradores) for the XPS and compositional analysis, respectively.

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