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Strong nuclear contribution to the optical Kerr effect in niobium oxide containing glassesArnaud Royon,^{1,4,*} Lionel Canioni,¹ Bruno Bousquet,¹ Vincent Rodriguez,² Michel Couzi,² Clara Rivero,^{3,4} Thierry Cardinal,³ Evelyne Fargin,³ Martin Richardson,⁴ and Kathleen Richardson⁵¹CPMOH-CNRS, University of Bordeaux I, 351 Cours de la Libération, 33405 Talence cedex, France²LPCM-CNRS, University of Bordeaux I, 351 Cours de la Libération, 33405 Talence cedex, France³ICMCB-CNRS, University of Bordeaux I, 87 Avenue du Docteur Schweitzer, 33608 Pessac cedex, France⁴College of Optics and Photonics/CREOL, UCF, 4000 Central Florida Boulevard, Orlando, Florida 32816, USA⁵School of Material Science and Engineering, Clemson University, 161 Sistine Hall, Clemson, South Carolina 29634, USA

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The electronic and nuclear contributions to nonlinear optical properties of niobium oxide-based glasses have been measured using third-harmonic generation and pump-probe techniques. The results have been found to be in agreement with Hellwarth's model for niobium oxide (Nb_2O_5) concentrations below 30 mol %. Above 30 mol % Nb_2O_5 , discrepancies with the theoretical model have been observed. It has been found that high niobium ion content induces a change of the local structure within the glass and favors the formation of three-dimensional blocks of corner-sharing NbO_6 octahedra. Since similarities with crystalline structures are present, we propose that some specific collective vibrational modes could be at the origin of the extra nuclear contributions to the optical Kerr effect.

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I. INTRODUCTION

Transparent optical glasses exhibiting nonlinearity in the visible and near-infrared (ir) range have been examined far from any resonance in order to avoid significant multiphoton absorption. These glasses are of interest and have been evaluated as possible candidates for optical switching. Among all vitreous systems, oxide glasses containing a large amount of heavy atoms (i.e., highly polarizable species) have attracted attention since they exhibit significant nonlinearity for use in the near-infrared telecommunication windows and appear to be promising candidates as Raman gain media.¹⁻⁴ Within the Born-Oppenheimer approximation, which indicates that optical pulses shorter than a few hundreds of picoseconds should be considered, the origin of the optical nonlinearity in glasses, far from any resonance, is attributed to electronic and nuclear contributions. The electronic response is related to the spontaneous nonlinear distortion of the electronic distribution around the nuclei while the nuclear response is due to a slower optical-field-induced change arising from the motions of the nuclei.⁵ It is known that these two contributions have distinctly different relaxation times, with the first (electronic) being less than 1 fs whereas the second process (nuclear) is on the order of several hundreds of femtoseconds to a few picoseconds. In 1975, Hellwarth *et al.*⁵ showed that the nuclear contribution to the nonlinear refractive index of some glasses is not negligible, being as high as up to 15–30 % of the total, depending on the glass composition.

Based upon the Born-Oppenheimer approximation, several measurements of the nuclear contribution in glasses have been performed in the femtosecond regime, either using time-resolved techniques⁶⁻⁸ or not.^{9,10} Smolorz *et al.*⁸ have, for instance, demonstrated that the relative nuclear contribution to the nonlinear refractive index increases upon addition of GeO_2 in a SiO_2 optical fiber. However, these results did not include the effect of the duration of the optical pulse,

despite previous work by Stolen and Tomlinson¹¹ and Santaran *et al.*¹⁰ which showed that the nuclear contribution is driven by the pulse duration. Hence, values of nuclear contributions are subject to change since they depend strongly on this important parameter.

Glasses containing niobium oxide (Nb_2O_5) have been widely studied and are currently reported to exhibit high nonlinearity in sodium borophosphate matrices containing a large amount of Nb_2O_5 .^{12,13} In particular, the increase of the third-order nonlinear optical response has been related to the atomic density of niobium in the glass. In addition, a nonlinear behavior of the nonlinear refractive index has been shown where a clear enhancement of the optical response occurs as the niobium ions are introduced in large quantities.^{12,13} The optical nonlinear response has been related to the specific three-dimensional (3D) corner-sharing arrangements of NbO_6 octahedra which enables the formation of a tungsten bronze-like local structure, at high niobium oxide concentration. Lipovskii *et al.*¹⁴ have observed similar behavior of the electro-optical Kerr effect, with the successive addition of Nb_2O_5 into silicate-based glasses. This work clearly illustrates a correlation between the increase of both the Raman spectral density and the Kerr response of the materials with an increase of NbO_6 tungsten bronze “crystal motifs” within the glass structure.

In the present work, a sodium borophosphate matrix, with varying Nb_2O_5 molar concentration in the glass system $(100-x)(95\text{NaPO}_3-5\text{Na}_2\text{B}_4\text{O}_7)-x\text{Nb}_2\text{O}_5$ has been investigated. Table I lists the optical properties of these glasses. Third-harmonic generation (THG) and Kerr effect susceptibility measurements have been performed with THG microscopy and pump-probe techniques, respectively. The first experiment gives direct access to the third-order electronic susceptibility whereas the second measurement directly probes both the electronic and nuclear contributions of the third-order Kerr effect susceptibility. From these measurements, the nuclear contribution to the Kerr effect has been

TABLE I. Cutoff wavelength, linear refractive indices at ω and 3ω , THG susceptibility, Kerr effect susceptibility (from Ref. 13), measured nuclear susceptibility, and calculated nuclear susceptibility for different Nb_2O_5 concentrations.

Borophosphate glass (mol % Nb_2O_5)	9.55	19.19	28.93	38.78
λ_c (nm)	308	322	337	351
$n(\omega)$ (± 0.02)	1.53	1.59	1.73	1.81
$n(3\omega)$ (± 0.02)	1.55	1.63	1.77	1.89
THG susceptibility $\sigma_{1111}^{(3)}$ ($\text{m}^2 \text{V}^{-2}$) ($\pm 30\%$)	6.78×10^{-22}	8.42×10^{-22}	11.63×10^{-22}	15.31×10^{-22}
Kerr effect susceptibility $\Lambda(u=0)$ ($\text{m}^2 \text{V}^{-2}$) ($\pm 10\%$)	8.68×10^{-22}	13.15×10^{-22}	17.67×10^{-22}	37.83×10^{-22}
Measured nuclear susceptibility $\Lambda(u=0) - \sigma_{1111}^{(3)}$ ($\text{m}^2 \text{V}^{-2}$) ($\pm 35\%$)	1.90×10^{-22}	4.73×10^{-22}	6.04×10^{-22}	22.52×10^{-22}
Calculated nuclear susceptibility $\frac{H(d_{1212}^{(3)}; u=0)}{G(u=0)}$ ($\text{m}^2 \text{V}^{-2}$) ($\pm 10\%$)	1.27×10^{-22}	3.20×10^{-22}	3.53×10^{-22}	5.20×10^{-22}

deduced. Additionally, Raman scattering experiments have been carried out to evaluate the nuclear contribution to the optical Kerr effect and compare it to that measured by THG. Effects of the modification of the local glass structure upon addition of niobium oxide are discussed in order to tentatively attribute the origin and behavior of the nuclear contribution to the nonlinear refractive index.

II. THEORY AND EXPERIMENTAL RESULTS

The general expression of the third-order nonlinear polarization assuming an entirely local response in the international unit system can be written as

$$\begin{aligned} \vec{P}_i^{(3)}(\vec{r}; t) = \epsilon_0 \int_{-\infty}^t \int_{-\infty}^t \int_{-\infty}^t R_{ijkl}^{(3)}(\vec{r}; t-t_1, t-t_2, t-t_3) \\ \times \vec{E}_j(\vec{r}; t_1) \vec{E}_k(\vec{r}; t_2) \vec{E}_l(\vec{r}; t_3) dt_1 dt_2 dt_3 \end{aligned} \quad (1)$$

where $R_{ijkl}^{(3)}$ is the total response function of the material.

Using the Born-Oppenheimer approximation, the third-order nonlinear polarization can be developed as a simple sum of an electronic polarization and a nuclear polarization:⁵

$$\begin{aligned} \vec{P}_i^{(3)}(\vec{r}; t) = \epsilon_0 \sigma_{ijkl}^{(3)} \vec{E}_j(\vec{r}; t) \vec{E}_k(\vec{r}; t) \vec{E}_l(\vec{r}; t) + \epsilon_0 \vec{E}_j(\vec{r}; t) \\ \times \int_{-\infty}^t d_{ijkl}^{(3)}(\vec{r}; t-\tau) \vec{E}_k(\vec{r}; \tau) \vec{E}_l(\vec{r}; \tau) d\tau \end{aligned} \quad (2)$$

where $\sigma_{ijkl}^{(3)}$ is the electronic coefficient and $d_{ijkl}^{(3)}$ the nuclear response function of the material.

A. THG microscopy measurements

Assuming an electric field of the form $\vec{E}(\vec{r}; t) = \vec{A}(\vec{r}; t) \cos(\vec{k}_\omega \cdot \vec{r} - \omega t)$, the third-order nonlinear polarization associated to the THG process is given by

$$\vec{P}_{i-3\omega}^{(3)}(\vec{r}; t) = \frac{1}{4} \epsilon_0 \sigma_{ijkl}^{(3)} \vec{A}_j(\vec{r}; t) \vec{A}_k(\vec{r}; t) \vec{A}_l(\vec{r}; t) \cos(3\vec{k}_\omega \cdot \vec{r} - 3\omega t). \quad (3)$$

The electronic susceptibility can be independently measured with a THG microscopy setup¹⁵ since only the electronic polarization is able to quickly respond to a high-frequency all-optical field excitation.¹⁶ THG experiments have been carried out using 130 fs pulses with a 3 nJ pulse energy at a 80 MHz repetition rate from an optical parametric oscillator at 1500 nm, focused with a 0.7 numerical aperture microscope objective, on 300- μm -thick samples. The measurements have been calibrated with respect to a fused silica sample with a similar thickness. The THG signal has been measured for the beam waist at the vicinity of the first interface (i.e., air/glass interface) to obtain the best point of focus; moreover, it should be noted that the third harmonic is not absorbed because the absorption coefficient is low at 500 nm. Indeed, no absorption could be measured using a standard spectrophotometer with 1-mm-thick samples. The absorption cutoff values are given in Table I. Fresnel transmission and refractive index dispersion corrections have been performed. Since no significant two-photon absorption occurs at this wavelength, the imaginary part of the electronic susceptibility has been neglected and the calculated modulus of the susceptibility was set equal to the real part. Finally, the electronic susceptibility is given by

$$\begin{aligned} \sigma_{1111}^{(3)} = \sqrt{\frac{T_{3\omega, \text{SiO}_2} T_{\omega, \text{SiO}_2}^3}{T_{3\omega} T_{\omega}^3}} \\ \times \sqrt{\frac{I_{3\omega}}{I_{3\omega, \text{SiO}_2}}} \sqrt{\frac{n_{3\omega} n_{\omega}^3}{n_{3\omega, \text{SiO}_2} n_{\omega, \text{SiO}_2}^3}} \left| \frac{J_{3\omega, \text{SiO}_2}}{J_{3\omega}} \right| \sigma_{1111, \text{SiO}_2}^{(3)} \end{aligned} \quad (4)$$

where T_ω , n_ω , $T_{3\omega}$, and $n_{3\omega}$ are the Fresnel transmission co-

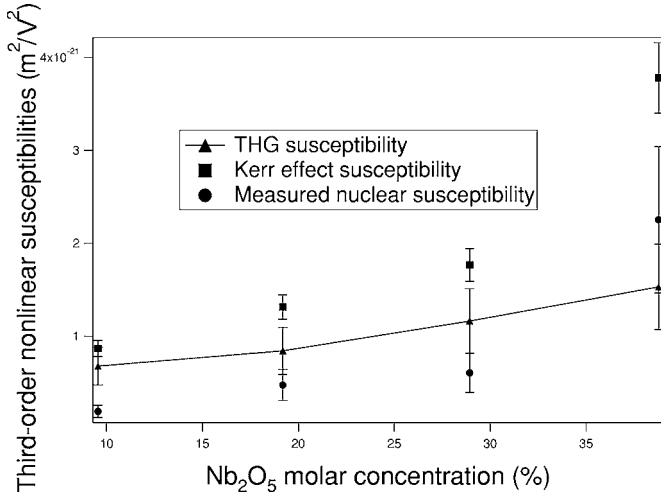


FIG. 1. THG susceptibility ($\sigma_{1111}^{(3)}$), Kerr effect susceptibility [$\Lambda(u=0)$], and measured nuclear susceptibility [$\Lambda(u=0) - \sigma_{1111}^{(3)}$] versus Nb₂O₅ molar concentration.

efficients and the refractive indices at ω and 3ω , respectively, $I_{3\omega}$ the detected third-harmonic irradiance,

$$J_{3\omega} = \int_0^L \frac{\exp(i\Delta k u)}{(1 + 2iu/b)^2} du$$

the third-harmonic interaction length, $\Delta k = 3k_\omega - k_{3\omega}$ the phase mismatch, $b = 2\pi w_0^2/\lambda$ the confocal parameter, w_0 the beam waist, and L the sample thickness. The SiO₂ subscript refers to fused silica and no subscript alludes to the investigated glass under study. The obtained values of $\sigma_{1111}^{(3)}$ for all samples are summarized in Table I and depicted in Fig. 1.

The experimental results, reported in Fig. 1, have been normalized to the value given by Hellwarth in 1977 for fused silica¹⁶ ($\sigma_{1111}^{(3)} = 2.65 \times 10^{-22} \text{ m}^2 \text{ V}^{-2} \pm 30\%$ at 694 nm). More recent measurements including electronic and nuclear effects have been performed over a broad wavelength range and experience a weak dispersion in the visible range.¹⁷ Moreover, Hellwarth *et al.*⁵ and Stolen and Tomlinson¹¹ have shown that the nuclear contribution in fused silica does not exceed 20%. Hence, at 500 nm, all the compiled values are between 2×10^{-22} and $3 \times 10^{-22} \text{ m}^2 \text{ V}^{-2}$, neglecting the nuclear contribution. The reference value is in this range, to within uncertainties of the measurement (30%).

B. Pump-probe measurements

The third-order nonlinear polarization associated with the optical Kerr effect is given by

$$\begin{aligned} \vec{P}_{i-\omega}^{(3)}(\vec{r}; t) = & \frac{3}{4} \epsilon_0 \sigma_{ijkl}^{(3)} \vec{A}_j(\vec{r}; t) \vec{A}_k(\vec{r}; t) \vec{A}_l^*(\vec{r}; t) \\ & + \frac{1}{2} \epsilon_0 \vec{A}_j(\vec{r}; t) \int_{-\infty}^t d_{ijkl}^{(3)}(\vec{r}; t - \tau) \vec{A}_k(\vec{r}; \tau) \vec{A}_l^*(\vec{r}; \tau) d\tau. \end{aligned} \quad (5)$$

Third-order optical susceptibility measurements have been carried out on these glasses from an induced refractive

index change experiment at 800 nm for a 100 fs pulse duration.¹³ Such experiments based on the optical Kerr effect are sensitive both to electronic and nuclear contributions. The equation describing the probe intensity variations is given by Santran *et al.*¹⁰

$$I_S \propto I_S^0 \left(1 - \frac{k_0^2}{4\sqrt{2}} \frac{P_m T}{c \epsilon_0} F(w_0; k_0; L) \Lambda(u) G(u) \sin(2\omega_0 u) \right) \quad (6)$$

where I_S^0 is the incident probe irradiance, $k_0 = \omega/c$ the wave vector in the vacuum, P_m the average power, T the repetition rate of the laser, $F(w_0; k_0; L)$ a numerical factor depending on the spatial properties of the laser beam, and u the variable delay between the pump and the probe pulses.

Λ is the global Kerr effect susceptibility including both electronic and nuclear phenomena and it is given by

$$\Lambda(u) = \sigma_{1111}^{(3)} + \frac{H(d_{1212}^{(3)}; u)}{G(u)} \quad (7)$$

where $G(u)$ and $H(d_{1212}^{(3)}; u)$ are two functions that will be explicitly described later.

The values of Λ for all samples, measured in Ref. 13, are gathered in Table I and reported in Fig. 1. Since Nb₂O₅ concentrations of the glasses studied in this previous paper¹³ were slightly different from ours, extrapolated values of the Kerr effect susceptibility have been considered using a linear regression method.

C. Experimental nuclear contribution to the pump-probe signal

Knowing the values of Λ and $\sigma_{1111}^{(3)}$, one can deduce the nuclear susceptibility from Eq. (7) and thus the nuclear contribution to the Kerr effect susceptibility. These two quantities are shown in Table I.

Nevertheless, one has to consider that THG and pump-probe experiments have been carried out at different wavelengths (i.e., 1500 and 800 nm). In the transparency region of these glasses, in the visible and near-ir range, the THG susceptibility follows a normal dispersion, and decreases with increasing wavelength, meaning that the susceptibility value is smaller at 800 nm than at 500 nm. A possible resonance effect might occur as the third harmonic (at 500 nm) which is close to the electronic gap wavelength of these glasses, leading to an over-estimation based on this measurement. This effect implies that the measured nuclear contribution might be slightly larger than shown in Table I.

III. RAMAN NUCLEAR CONTRIBUTION

It is possible to determine the nuclear susceptibility for our samples by computing the ratio $H(d_{1212}^{(3)}; u=0)/G(u=0)$, from the Raman spectra of the glasses.

The function $G(u)$ is a temporal term, delay dependent, which represents the electronic contribution to the signal, and it is defined as

$$G(u) = \frac{\int_{-\infty}^{+\infty} s(t)s(t-u)dt}{\left(\int_{-\infty}^{+\infty} s(t)dt\right)^2} \quad (8)$$

where s is the temporal shape of the pump or probe pulse. At zero delay, this function is equal to the ratio between the

$$H(d_{1212}^{(3)};u) = \frac{\int_{-\infty}^{+\infty} \left(s(t)s(t-u) \int_0^{+\infty} d_{1212}^{(3)}(t-t_1)s(t_1)s(t_1-u)dt_1 \right) dt}{\left(\int_{-\infty}^{+\infty} s^2(t)dt\right)^2}. \quad (9)$$

This function includes the correlation of a classical convolution of the nuclear response function of the material with the temporal shape $s(t)$ of the laser pulse.

The nuclear response functions $a(t)$ and $b(t)$, defined as $d_{ijkl}^{(3)}(t) = a(t)\delta_{ij}\delta_{kl} + \frac{1}{2}b(t)(\delta_{il}\delta_{jk} + \delta_{ik}\delta_{jl})$ where δ is the Kronecker delta, can be computed from differential Raman scattering cross section, corrected by the Bose-Einstein population factor⁵

$$\text{Im}\{A(\omega_V)\} = \frac{160\pi^3\epsilon_0c^4}{\hbar\omega_L(\omega_L - \omega_V)^3} \left(\frac{1}{2} \frac{\partial^2\sigma_{\parallel}}{\partial\Omega\partial\omega_S} - \frac{\partial^2\sigma_{\perp}}{\partial\Omega\partial\omega_S} \right) \times \left[1 - \exp\left(-\frac{\hbar\omega_V}{k_B T}\right) \right], \quad (10)$$

$$\text{Im}\{B(\omega_V)\} = \frac{160\pi^3\epsilon_0c^4}{\hbar\omega_L(\omega_L - \omega_V)^3} \frac{\partial^2\sigma_{\perp}}{\partial\Omega\partial\omega_S} \left[1 - \exp\left(-\frac{\hbar\omega_V}{k_B T}\right) \right], \quad (11)$$

where $A(\omega)$ and $B(\omega)$ are the Fourier transforms of the nuclear response functions $a(t)$ and $b(t)$, respectively, $\partial^2\sigma_i/\partial\Omega\partial\omega_S$ represents the differential Raman scattering cross sections when the incident and scattered polarizations are either parallel ($i=\parallel$) or perpendicular ($i=\perp$), ω_L is the laser angular frequency, ω_V is the vibrational angular frequency, and $\omega_S = \omega_L - \omega_V$ is the Stokes angular frequency. Because the functions a and b are real and causal, one can easily compute them¹⁸ and obtain the functions $G(u)$ and $H(d_{1212}^{(3)};u)$, assuming a Gaussian temporal shape of the laser pulse. The functions $G(u)$ and $H(d_{1212}^{(3)};u)$ are plotted in Fig. 2 and the ratio $H(d_{1212}^{(3)};u=0)/G(u=0)$ is shown in Table I for each glass.

The polarized (VV) and depolarized (VH) Raman experiments have been carried out from 90° spontaneous Raman scattering measurements at 514.5 nm using an experimental system allowing low-frequency measurement. Raman spectra have also been measured with longer excitation wave-

lengths at 632.8, 752, and 1064 nm using a notch filter which does not allow measurement below 145 cm⁻¹. To be able to compare the Raman nuclear contributions with that obtained from THG and pump-probe experiments, the dispersion of the differential Raman scattering cross section must be taken into account. A similar evolution to that reported by Rivero *et al.*¹⁹ for glasses having an absorption edge around 350 nm, have been observed showing that no significant dispersion in the 750–1064 nm range could be measured. Moreover, no distortion of the spectra for different excitation wavelength has been observed. To obtain the Raman spectra of the studied glasses, the measured data at 514.5 nm have been rescaled to the spectra obtained at 1064 nm and compared to the reported value of silica⁵ [$\partial^2\sigma_{\parallel}/\partial\Omega\partial\omega_S = 2.25 \times 10^{-10}$ cm⁻¹ sr⁻¹ cm \pm 10% for the 440 cm⁻¹ line at 514.5 nm, where $\sigma_S = \omega_S/(2\pi c)$] after reflection, refraction, and wavelength corrections²⁰ by using a fused silica reference sample. The absolute polarized (VV) and depolarized (VH) Raman spectra are shown in Figs. 3 and 4, respectively.

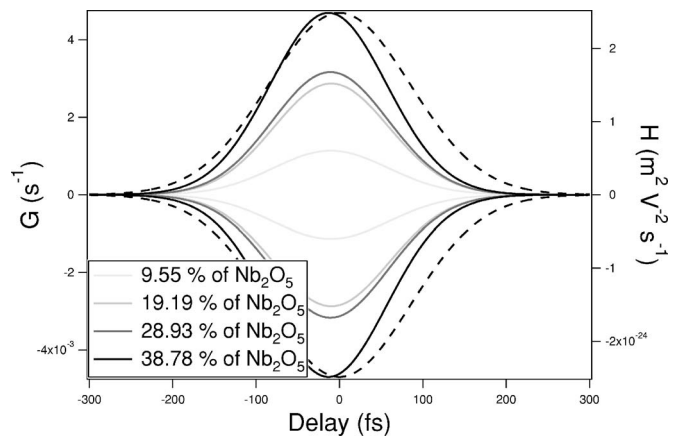


FIG. 2. Functions $G(u)$ (dashed curve) and $H(d_{1212}^{(3)};u)$ (full curves) versus time delay between the pump and the probe pulses for a 100 fs pulse at 800 nm for different Nb₂O₅ concentrations.

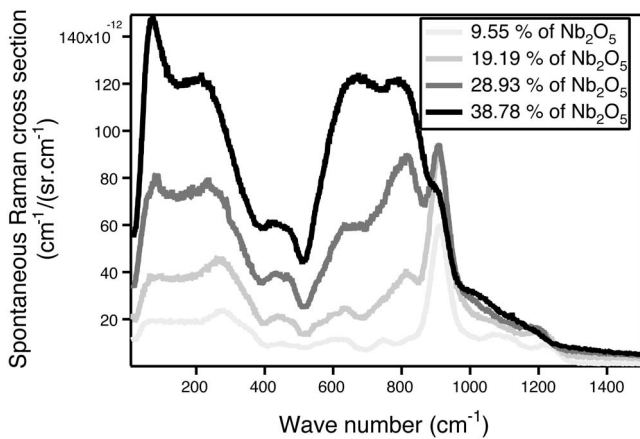


FIG. 3. Absolute polarized (VV) Raman spectra of the borophosphate matrix glasses with different Nb_2O_5 concentrations at 1064 nm.

For a 100 fs optical pulse at 800 nm (i.e., 140 cm^{-1} bandwidth), it appears that the mode at 230 cm^{-1} contributes mostly to the nuclear susceptibility (about 75% of the total nuclear susceptibility) whereas the modes above 500 cm^{-1} have a negligible influence. To participate in the nuclear nonlinearity, the vibrational modes must present both a low wave number and a large bandwidth, i.e., a low oscillation frequency and a high damping in the time domain, so that the convolution of the nuclear response function with the optical pulse is maximal.

IV. COMPARISON BETWEEN THE MEASURED AND CALCULATED NUCLEAR CONTRIBUTIONS AND DISCUSSION

Calculation and experimental results are in agreement to within uncertainties of the measurements as long as the Nb_2O_5 concentration is less than 28.93 mol %. For the 38.78 mol % Nb_2O_5 concentration, a significant nuclear fraction to the nonlinear refractive index has been measured ($\sim 60\%$). The results ($\sim 22\text{--}36\%$) obtained for low niobium

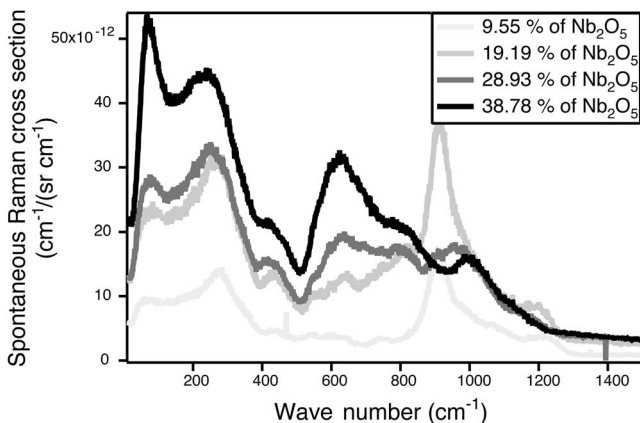


FIG. 4. Absolute depolarized (VH) Raman spectra of the borophosphate matrix glasses with different Nb_2O_5 concentrations at 1064 nm.

oxide content are in accordance with data previously reported for silicate based materials by Hellwarth *et al.*⁵ The evolution of the nonlinearity for low niobium oxide content is driven by the electronic contribution. The results obtained validate the model proposed for summation of Nb-O bond electronic contribution to the nonlinearity previously proposed.¹³ For high Nb^{5+} ion concentration, the measured nuclear fraction to the nonlinear refractive index is the highest reported to date in inorganic glasses. Moreover, discrepancies between calculated and measured nuclear contributions deduced from THG and Kerr effect measurements seem to indicate that the present Raman measurements do not entirely take into account the true nuclear contribution.

The evolution of the glass structure with increasing Nb_2O_5 concentration in borophosphate glasses has been investigated.^{12,13} The introduction of Nb_2O_5 in small quantities gives rise to the formation of hyperpolarizable “isolated” distorted NbO_6 octahedra with a characteristic Raman signature around 900 cm^{-1} . As the Nb_2O_5 concentration increases, corner-sharing NbO_6 octahedra are formed and, progressively, a one-dimensional Nb-O-Nb framework corresponding to chains of octahedral can be distinguished with a Raman band around 830 cm^{-1} . For high Nb_2O_5 concentration, a two-dimensional and finally three-dimensional (3D) framework is created. This local structure has a strong similarity with crystalline structures such as $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$, NaNb_3O_8 , or NaNbO_3 involving NbO_6 octahedra sharing a common corner.

The formation of the 3D octahedral structure within the glass is correlated to the Raman band around $250\text{--}300 \text{ cm}^{-1}$ in the low-frequency domain increasing in intensity and a new sharp vibration at 70 cm^{-1} . These vibrations are strongly related to the vibration around 650 cm^{-1} . Recently, Malakho *et al.*²¹ have shown that in this glass system, the first crystallization phase observed is NaNb_3O_8 , which can be compared to NaNbO_3 or $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ crystalline structures. In these crystalline phases (KNbO_3 , NaNbO_3 , or $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$), vibrations around 650, 250–300, and 50–70 cm^{-1} are also present.^{22–24} Numerous articles have mentioned correlations between the intensity of the low phonon bands and the phase transition observed in niobate crystals leading to ferroelectricity.^{22,23} In glasses, such effects cannot occur due to their disordered structure but nevertheless, the presence of similar vibrations to those observed in the crystalline phases, and particularly the band around 250 cm^{-1} , could be related to collective motion of 3D associated NbO_6 octahedra. Significant nuclear contribution to the nonlinear refractive index appears for Nb_2O_5 molar concentration above 28.93%, which corresponds to the existence of the NbO_6 tungsten bronze structure and to the largest intensities of the vibrations around 650, 250–300, and 50–70 cm^{-1} . The calculation of the nuclear contribution thus indicates, according to Eqs. (10) and (11) (for a pulse of 100 fs), that the major contribution to the nonlinear refractive index is associated to the vibration located around $250\text{--}300 \text{ cm}^{-1}$. Clear assignment of NbO_6 collective motion in the glass leading to such vibration would be of importance to understand how local structure can significantly affect the nonlinear response.

V. CONCLUSION

The electronic and nuclear contributions to the optical Kerr effect of niobium oxide containing glasses have been measured with THG microscopy and pump-probe experiments. For a 38.78 mol % niobium oxide (Nb_2O_5) concentration, the nuclear contribution to the optical Kerr effect has been found to be about 60%, which is the highest value reported to date in inorganic materials.

Additionally, the nuclear contribution to the optical Kerr effect of these glasses has been calculated from Raman scattering experiments and it has been compared to the measurements. Results are in good agreement to within uncertainties of the measurements as long as the niobium oxide concen-

tration is below 28.93 mol %. Above this value, the theoretical model no longer agrees with the measurements. Collective vibrational modes of 3D associated NbO_6 octahedra in these glasses have been proposed as an explanation for this discrepancy.

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*Email address: a.royon@cpmoh.u-bordeaux1.fr

- ¹A. E. Miller, K. Nassau, K. B. Lyons, and M. E. Lines, *J. Non-Cryst. Solids* **99**, 289 (1988).
- ²R. Stegeman, L. Jankovic, H. Kim, C. Rivero, G. Stegeman, K. Richardson, P. Delfyett, Y. Guo, A. Schulte, and T. Cardinal, *Opt. Lett.* **28**, 1126 (2003).
- ³C. Rivero, K. Richardson, R. Stegeman, G. Stegeman, T. Cardinal, E. Fargin, M. Couzi, and V. Rodriguez, *J. Non-Cryst. Solids* **345&346**, 396 (2004).
- ⁴C. Rivero, K. Richardson, R. Stegeman, G. Stegeman, T. Cardinal, E. Fargin, and M. Couzi, *Proceedings of the Seventh European Society of Glass Science and Technology Conference*, Athens, Greece, 2004 [*Glass Technol.* **46**, 80 (2005)].
- ⁵R. W. Hellwarth, J. Cherlow, and T.-T. Yang, *Phys. Rev. B* **11**, 964 (1975).
- ⁶I. Kang, S. Smolorz, T. Krauss, F. Wise, B. G. Aitken, and N. F. Borrelli, *Phys. Rev. B* **54**, R12641 (1996).
- ⁷S. Montant, A. Le Calvez, E. Freysz, A. Ducasse, and M. Couzi, *J. Opt. Soc. Am. B* **15**, 2802 (1998).
- ⁸S. Smolorz, F. Wise, and N. F. Borrelli, *Opt. Lett.* **24**, 1103 (1999).
- ⁹Z. Pan, S. H. Morgan, and B. H. Long, *J. Non-Cryst. Solids* **185**, 127 (1995).
- ¹⁰S. Santran, L. Canioni, L. Sarger, T. Cardinal, and E. Fargin, *J. Opt. Soc. Am. B* **21**, 2180 (2004).
- ¹¹R. H. Stolen and W. J. Tomlinson, *J. Opt. Soc. Am. B* **9**, 565 (1992).
- ¹²T. Cardinal, E. Fargin, G. Le Flem, M. Couzi, L. Canioni, P. Segonds, L. Sarger, A. Ducasse, and F. Adamietz, *Eur. J. Solid State Inorg. Chem.* **33**, 597 (1996).
- ¹³T. Cardinal, E. Fargin, G. Le Flem, and S. Leboiteux, *J. Non-Cryst. Solids* **222**, 228 (1997).
- ¹⁴A. A. Lipovskii, D. K. Tagantsev, A. A. Vetrov, and O. V. Yanush, *Opt. Mater.* **21**, 749 (2003).
- ¹⁵R. Barille, L. Canioni, L. Sarger, and G. Rivoire, *Phys. Rev. E* **66**, 067602 (2002).
- ¹⁶R. W. Hellwarth, *Prog. Quantum Electron.* **5**, 1 (1977).
- ¹⁷D. Milam, *Appl. Opt.* **37**, 546 (1998).
- ¹⁸R. H. Stolen, J. P. Gordon, W. J. Tomlinson, and H. A. Haus, *J. Opt. Soc. Am. B* **6**, 1159 (1989).
- ¹⁹C. Rivero, R. Stegeman, M. Couzi, D. Talaga, T. Cardinal, K. Richardson, and G. Stegeman, *Opt. Express* **13**, 4759 (2005).
- ²⁰F. L. Galeener, J. C. Mikkelsen, Jr., R. H. Geils, and W. J. Mosby, *Appl. Phys. Lett.* **32**, 34 (1978).
- ²¹A. Malakho, M. Dussauze, E. Fargin, B. Lazoryak, V. Rodriguez, and F. Adamietz, *J. Solid State Chem.* **178**, 1888 (2005).
- ²²A. Boudou and J. Sapriel, *Phys. Rev. B* **21**, 61 (1980).
- ²³Z. X. Shen, Z. P. Hu, T. C. Chong, C. Y. Beh, S. H. Tang, and M. H. Kuok, *Phys. Rev. B* **52**, 3976 (1995).
- ²⁴E. Bouziane, M. D. Fontana, and M. Ayadi, *J. Phys.: Condens. Matter* **15**, 1387 (2003).