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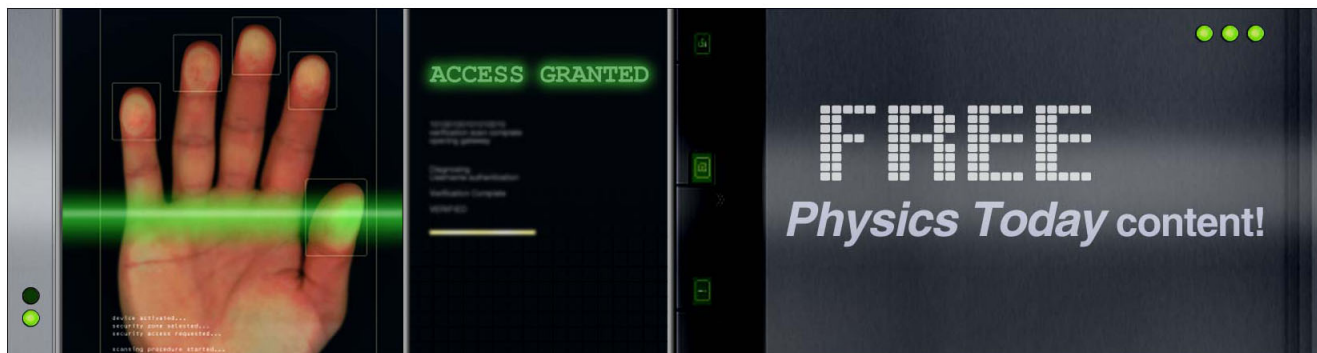
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## ADVERTISEMENT



## Near-infrared third-order nonlinearity of PbO–GeO<sub>2</sub> films containing Cu and Cu<sub>2</sub>O nanoparticles

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We report measurements of the nonlinear (NL) refractive index  $n_2$  of lead-germanium films (LGFs) containing Cu and Cu<sub>2</sub>O nanoparticles (NPs). The thermally managed eclipse Z-scan technique with 150 fs pulses from a laser operating at 800 nm was used. The NL refractive index measured,  $n_2 = 6.3 \times 10^{-12}$  cm<sup>2</sup>/W has electronic origin and the NL absorption coefficient  $\alpha_2$  is smaller than 660 cm/GW. The figure of merit  $n_2/\lambda\alpha_2$  is enhanced by more than two orders of magnitude in comparison with the result for the LGFs without the copper based NPs. © 2008 American Institute of Physics. [DOI: 10.1063/1.2908226]

Heavy metal oxide (HMO) glasses are of large interest for photonic applications because they present small absorption in the visible and in the near infrared, have small cutoff phonon energy, and present large nonlinear (NL) optical response. Accordingly, HMO glasses have been studied by many groups<sup>1–8</sup> that evaluated their performance for photonics. The samples' characteristics could be improved by changing their composition or by introducing metallic nanoparticles (NPs). One HMO glass of interest is based on the PbO–GeO<sub>2</sub> composition that is very stable and resistant to moisture.<sup>5,8</sup>

Recently, lead-germanium films (LGFs) were prepared from targets of PbO–GeO<sub>2</sub> glasses by the rf sputtering method. Giant nonlinearities of electronic origin were characterized for excitation at 1064 and 532 nm with 80 ps pulses. NL refractive indices  $n_2 \approx 10^{-12}$  cm<sup>2</sup>/W and NL absorption coefficients of  $10^2 < \alpha_2 < 10^3$  cm/GW were measured.<sup>9</sup> The NL parameters of the films were also characterized in the 150 fs regime by using a laser operating at 800 nm.<sup>10</sup> An ultrafast NL response of electronic origin was determined corresponding to  $n_2 \approx 2 \times 10^{-13}$  cm<sup>2</sup>/W and  $\alpha_2 \approx 3 \times 10^3$  cm/GW.

In this paper, we report experiments with LGFs containing copper (Cu) and copper-oxide (Cu<sub>2</sub>O) NPs. The changes introduced in the LGFs fabrication procedure and the contribution of the NPs originate an  $\approx 30$ -fold increase in the value of  $n_2$  and reduction in  $\alpha_2$  by about one order of magnitude. Therefore, the figure of merit  $n_2/\lambda\alpha_2$  was improved by more than two orders of magnitude with respect to the LGF without Cu based NPs.

The films were fabricated from glass targets prepared by melting 59 PbO–40 GeO<sub>2</sub>–1.0 Cu<sub>2</sub>O (in wt %) with purity of 99.999% in an alumina crucible at 1050 °C for 1 h. In the melting process, Cu<sub>2</sub>O dissociates according to  $\text{Cu}_2\text{O} \rightarrow 2\text{Cu} + \frac{1}{2}\text{O}_2$  because Cu<sub>2</sub>O is unstable at high temperatures. The glasses obtained were quenched in air, in a heated graphite mold, and annealed for 1 h at 420 °C. Afterwards, the

samples were cooled to room temperature inside the furnace. Targets with 3 cm diameter and 0.4 cm thickness, were obtained.

The films were deposited on silica substrates by using the rf sputtering method (14 MHz). Argon plasma was used at 5.5 mTorr; before the film deposition, the base pressure was 0.1 mTorr to minimize the presence of contaminants. The rf power was smaller than 50 W to prevent damage of the targets. The films were annealed in air, at 420 °C, to thermally reduce the Cu<sup>+</sup> ions, obtained in the melting process, to nucleate Cu<sup>0</sup> NPs. The large redox potential of Cu<sup>+</sup>/Cu<sup>0</sup> (0.52 V) favors this process. A mathematical model describing the formation of the Cu<sup>0</sup> NPs in HMO glasses is not available yet.<sup>11</sup> Films with thickness of 220 nm with high adherence to the substrates and high mechanical strength were obtained.

The NL experiments were made by using the thermally managed eclipse Z-scan (TM-EZ scan) technique.<sup>10,12,13</sup> This technique is a combination of eclipse Z-scan<sup>14</sup> with the thermally managed Z-scan<sup>15</sup> techniques. The large sensitivity of eclipse Z scan and the capability to distinguish between the electronic contribution to the sample's nonlinearity and cumulative effects are obtained by applying TM-EZ scan. A Ti-sapphire laser (800 nm, 150 fs, 76 MHz) was used. The laser beam was focused on the film by a lens of 10 cm focal length, and the incident intensity at the focal point was 2.7 GW/cm<sup>2</sup>. The detailed description of the setup and the data acquisition procedure are given in Ref. 10, 12, and 13.

Figure 1 shows an image for sample LGF-7 (LGF-17) annealed for 7 h (17 h) obtained with a 100 kV transmission electron microscope. Isolated NPs and aggregates with a variety of shapes and dimensions in the 1–15 nm range can be observed. The average diameter of the NPs is 2 nm and the width of the size distribution is  $\approx 1$  nm.

Figure 2 shows the absorbance spectra of the samples. A band centered at  $\approx 450$  nm is clearly seen and a very weak shoulder can be noticed at  $\approx 580$  nm. The feature at  $\approx 580$  nm is due to the surface plasmon resonance in the Cu NPs. The small amplitude is due to the small film's thickness, and the large bandwidth is due to the broad distribution

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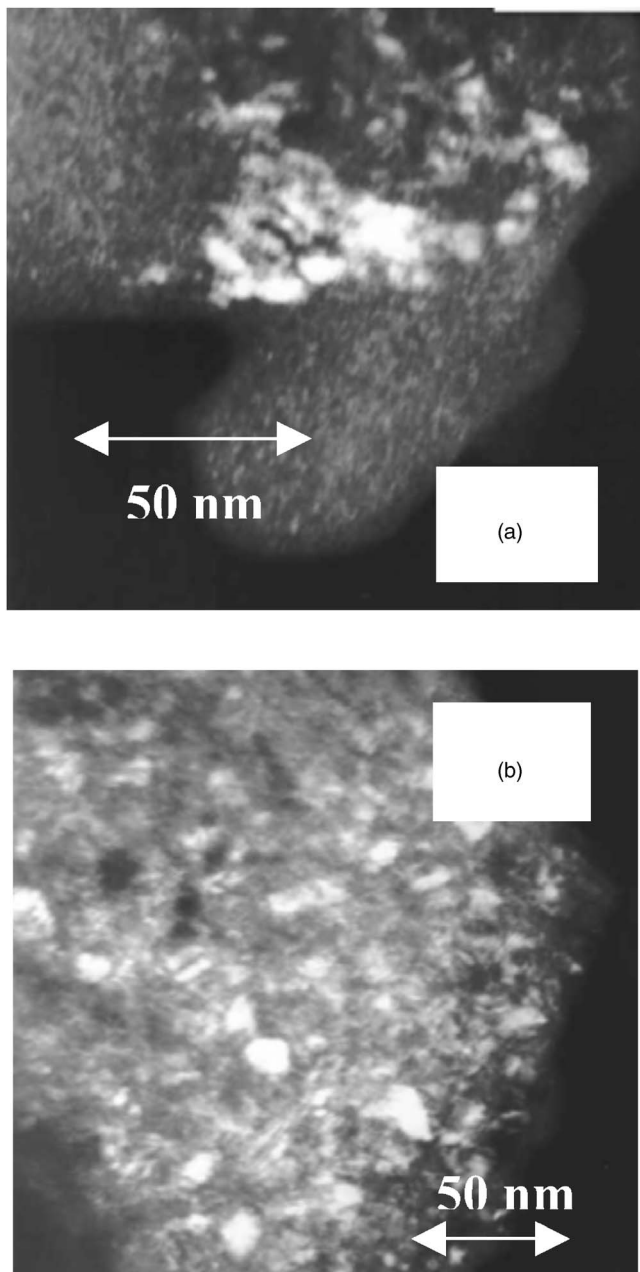


FIG. 1. Transmission electron microscope images: (a) LGF-7 and (b) LGF-17 samples.

of NPs sizes and large carriers' relaxation rate. The band at  $\approx 450$  nm, attributed to  $\text{Cu}_2\text{O}$  particles, is in agreement with Refs. 16–18.

Figure 3 shows typical profiles obtained with the TM-EZ scan technique. A peak (valley) before (after) the focus point ( $z=0$ ) indicates a self-focusing nonlinearity. The behavior of the peak and valley transmittance as a function of time  $t$  is also shown in Fig. 3. The absence of a crossing between the curves corresponding to the prefocal and postfocal positions indicates that the influence of cumulative effects is small. The solid lines were obtained by following the procedure in Ref. 12. The value of  $\Delta T_{pv}$  for  $t=0$  allows the calculation of  $n_2$  by using Eq. (2) of Ref. 14 with  $S=0.98$ . The values obtained for  $n_2$  were  $(6.3 \pm 0.7) \times 10^{-12} \text{ cm}^2/\text{W}$  (LGF-7) and  $(7.0 \pm 0.7) \times 10^{-12} \text{ cm}^2/\text{W}$  (LGF-17). The experimental setup was calibrated by using liquid  $\text{CS}_2$  with  $n_2=2.3 \times 10^{-15} \text{ cm}^2/\text{W}$ .<sup>19</sup> The value of  $\alpha_2$  is determined by measur-

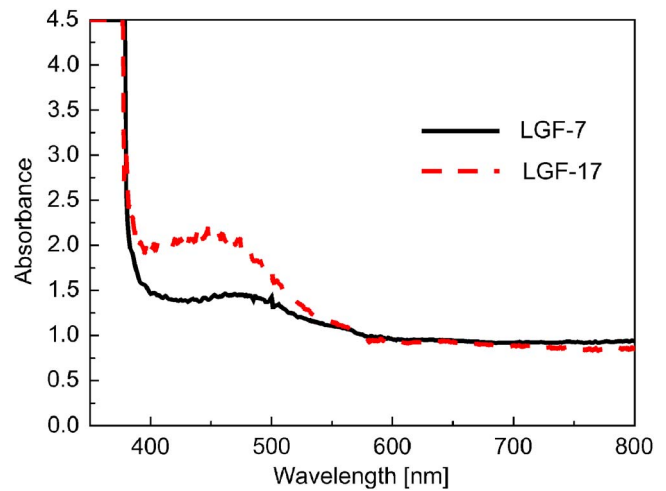


FIG. 2. (Color online) Absorbance spectra of the LGF-7 and LGF-17 samples.

ing  $\Delta T_{pv}$  for the detector with open aperture. However, in the present experiment, the samples' NL absorption was smaller than the minimum value that our setup allows to measure, i.e.,  $660 \text{ cm}^2/\text{GW}$ , because of the small samples' thickness. We note that in experiments with bulk samples,<sup>13</sup> the mini-

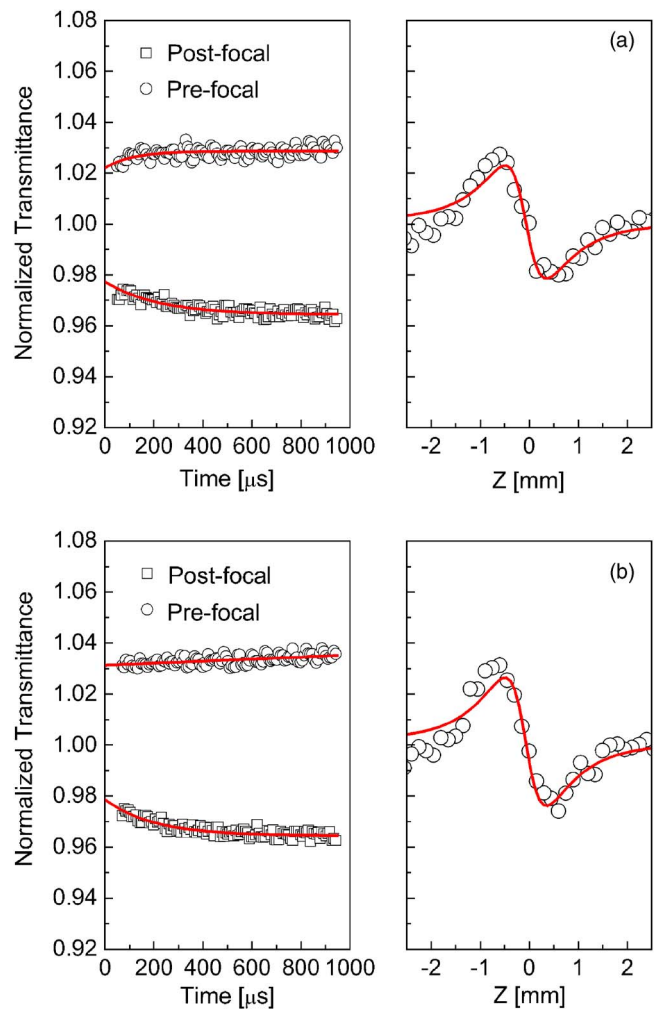


FIG. 3. (Color online) TM-EZ scan profiles and time evolution of the peak and the valley transmittance in the prefocal and postfocal positions: (a) LGF-7 and (b) LGF-17 samples.

TABLE I. Third-order NL parameters of the studied films and results from other references for comparison of the materials' performance.

Material	$\lambda$ (nm)	Pulse duration	$n_2$ (cm <sup>2</sup> /W)	$\alpha_2$ (cm/GW)	$n_2/\lambda\alpha_2$	Ref.
PGO film	1064	15 ps	$6 \times 10^{-12}$	200	$2.8 \times 10^{-1}$	9
PGO film	532	15 ps	$6 \times 10^{-12}$	1200	$9.4 \times 10^{-2}$	9
PGO film	800	150 fs	$(2 \pm 1) \times 10^{-13}$	$(3 \pm 1) \times 10^{-3}$	$8.3 \times 10^{-4}$	10
PGO film with Cu and Cu <sub>2</sub> O nanoparticles	800	150 fs	$6.3 \times 10^{-12}$	<660	$>1.2 \times 10^{-1}$	This work
Bi <sub>2</sub> Nd <sub>2</sub> Ti <sub>3</sub> O <sub>12</sub>	532	35 ps	$7 \times 10^{-10}$	$3.1 \times 10^4$	$4 \times 10^{-1}$	20
Bi <sub>3.25</sub> La <sub>0.75</sub> Ti <sub>3</sub> O <sub>12</sub>	532	35 ps	$3.1 \times 10^{-10}$	$3 \times 10^4$	$1.9 \times 10^{-1}$	21

imum value of  $\alpha_2$  that could be measured by using the same setup was 0.01 cm/GW.

The present results may be compared with the published data shown in Table I. We notice that the figure of merit  $n_2/\lambda\alpha_2$  presented here is better than it was obtained for LGFs without metallic NPs.<sup>10</sup> The results are also good when compared to the data obtained at 532 nm.<sup>9</sup> We notice also that LGFs with NPs are competitive with Bi<sub>2</sub>Nd<sub>2</sub>Ti<sub>3</sub>O<sub>12</sub> and Bi<sub>3.25</sub>La<sub>0.75</sub>Ti<sub>3</sub>O<sub>12</sub> films.<sup>20,21</sup> However, we emphasize that  $\alpha_2$  may be much smaller than 660 cm/GW because of the limited sensitivity of the experimental setup. For instance, if we calculate the figure of merit using the value of  $\alpha_2$  determined for bulk samples,  $\leq 0.1$  cm/GW,<sup>4</sup> it will reach values that indicate a large potential of LGFs for all-optical switching.

In summary, the NL behavior of LGFs containing Cu and Cu<sub>2</sub>O NPs was characterized at 800 nm. The use of the TM-EZ scan technique allowed the determination of the NL refractive index which is attributed to electronic effects. Enhancement of two orders of magnitude in the figure of merit  $n_2/\lambda\alpha_2$  was obtained in comparison with films without copper based NPs.

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