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Compositional dependence of the nonlinear refractive index of new germanium-based chalcogenide glasses

L. Petit [a,*], N. Carlie [a], H. Chen [a], S. Gaylord [a], J. Massera [a], G. Boudebs [b], J. Hu [c], A. Agarwal [c], L. Kimerling [c], K. Richardson [a]

[a] School of Materials Science and Engineering, Clemson University, Clemson, SC 29634, USA
[b] Laboratoire des Proprietes Optiques des Materiaux et Applications, UMR CNRS 6163, Universite d'Angers, 2 Boulevard Lavoisier, 49045 Angers Cedex 01, France
[c] Microphotonics Center, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

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ABSTRACT

In this paper, we report results of n_2 measurements of new chalcogenide glasses in the Ge–Sb–S–Se system using a modified Z-Scan technique. Measurements were made with picosecond pulses emitted by a 10 Hz Q-switched mode-locked Nd-YAG laser at 1064 nm under conditions suitable to characterize ultrafast nonlinearities. The nonlinear index increases up to 500 times the n_2 of fused silica with an increase in the Ge/Se ratio and a decrease with an increase of the Ge/Sb ratio. We confirmed, using Raman spectroscopy, that the nonlinear refractive index depends on the number of Ge–S(Se) and Sb–S(Se) bonds in the glass network. Sulfide glasses were shown to have a nonlinear FOM near or <1, at 1064 nm.

1. Introduction

Chalcogenide glasses (ChGs) have received increased interest due to their high linear and nonlinear indices of refraction and good transmittance into the infrared region. These materials are seen as potential candidates for infrared optics, photonic devices, reversible optical recording media, all-optical switching, and inorganic photoresists [1]. The nonlinear properties of glasses in the As–Se–S system have been largely studied [2]. The introduction of selenium to the As–S system increases n_2 up to 400 times the n_2 of fused silica [3] while still maintaining low nonlinear absorption (β) and a figure of merit [4] <1. High Se content within the As–S/Se binary and ternary systems has been shown to further increase $n_2/n_{2(SiO_2)}$ but at the expense of a marked increase in linear and nonlinear absorption [5]. The nonlinear properties of chalcogenide glasses in the systems: Ge–S(Se), Ge–As–S(Se), As–S–Se, and Ge–As–S–Se, have been also extensively investigated [6–9]. Recently, the effects of halogen or halide addition on glass-forming ability, structural organization or band-gap energy have also been studied in As–S, Ge–S, Sb–S and Ge–Ga–S based chalcogenide glasses [2,10–13]. It was found that the introduction of halogen generally decreases the band-gap wavelength towards the blue region of the visible spectrum due to the electronegativity of the halogen atoms reducing the electron delocalization in the glass network, and consequently, decreasing the nonlinear refractive index of chalcogenide glasses [10].

Despite the extensive work in this area in the past decade, the origin of the nonlinearity of glass in general and chalcogenide glasses in particular, is still largely unclear. Cardinal et al. [3] showed that the large n_2 for glasses in the As–S–Se systems with small As/(S+Se) molar ratios was correlated with the presence of covalent, homopolar Se–Se bonds in the glass structure as identified by Raman spectroscopy; in the equimolar chalcogen contributions, n_2 could not be attributed to any red shift in the absorption edge or to a resonant effect, unlike that seen in high chalcogen content in binary As_2Se_3 materials [6]. Subsequent to this, Harbold et al. [14] showed that n_2 is not solely dependent on the lone pair electron concentration associated with the chalcogen and group V species, but also on resonant enhancement of the optical band gap, as defined by a normalized photon energy which takes into account incident energy of the wavelength of use and the material's band-gap energy [14]. Recently, Sanghera et al. related the nonlinear index to the normalized photon energy and provided a predictive capability for the nonlinear index, over a large wavelength range, if the band gap of the glass is known [15].

Recent studies in our group have further compared the relationship of glass composition and structure, refractive index (linear and nonlinear) to other high intensity effects such as Raman Gain. Our results in heavy metal oxide glasses [16–18] as well as in diverse chalcogenide glass systems [19] illustrates the ability to tailor material structure and optical response (linear and nonlinear), along with laser damage resistance (critical for use of

* Corresponding author.
E-mail address: lpetit@clemson.edu (L. Petit).

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chalcogenides in high intensity applications) through selective choice of glass constituents. In a recent study of the glasses with the composition $Ge_{23}Sb_7S_{70-x}Se_x$, [20], we further showed using X-ray photoelectron spectroscopy (XPS) in conjunction with n_2 measurements that an increase of Ge–Se bond from 2×10^{21} to $8\times10^{21}/cm^3$ leads to an increase of the n_2 from 2×10^{-18} to 10×10^{-18} m^2/W indicating that n_2 depends on the number of heteropolar and homopolar bonds forming the glass network. To confirm this hypothesis, new glasses in the same Ge–Sb–S(Se) systems have been prepared with varying Ge/chalcogen [S,Se] and Ge/Sb ratios to evaluate the specific impact of constituents and their structural role, on resulting nonlinear material response.

In this paper, we report the physical, thermal and optical properties of the new glasses and present corresponding evaluation of their structure via Raman spectroscopy, thus correlating structural changes to physical property evolution with constituents. The nonlinear refractive index and absorption of the new glasses are presented and we interpret the variation in behavior to chemical composition and structure of the glass network.

2. Experimental

Glasses in the Ge–Sb–S and Ge–Sb–Se systems are prepared from high purity elements (Ge Aldrich 99.999%, Sb Alpha 99.9%, S and Se Cerac 99.999%). Starting materials are weighed and batched into quartz ampoules inside a nitrogen-purged glove box and sealed under vacuum using an oxygen gas torch. Prior to sealing and melting, the ampoule and batch are pre-heated at 100 °C for 4 h to remove surface moisture from the quartz ampoule and the batch raw materials. After sealing, the ampoule is heated for 24 h between 900 and 975 °C, depending on the glass composition. Once homogenized, the melt-containing ampoule is air–quenched to room temperature. To avoid fracture of the tube and glass ingot, the ampoules are subsequently returned to the furnace for annealing for 15 h at 40 °C below the glass transition temperature, T_g. The same procedure is used for selenium-substituted compositions. The glass samples are then cut, optically polished and visually inspected for defects that reduce optical quality needed for the Z-scan measurements.

The glass transition temperature (T_g) is determined by differential scanning calorimetry (DSC) at a heating rate of 10 °C/min from 50 to 450 °C using a commercial DSC apparatus (TA Instrument Inc.). The measurements are carried out in a hermetically sealed aluminum pan.

The density of the resulting bulk glass materials is measured by Archimedes' principle using diethylphthalate at room temperature. The measurement accuracy is better than 0.3%.

Spectroscopic ellipsometry is used to examine the refractive index of the glasses using a J.A. Woollam model M-44 spectroscopic ellipsometer which incorporates a variable angle stage allowing adjustment of the incident angle. The instrument operates on a rotating polarizer principle, in which the polarization of incoming light is varied, and reflected intensity is recorded with a grating coupled CCD over a wavelength range of 600–1100 nm. Multiple measurements and subsequent curve fitting allowed a calculation of index variation with wavelength with a final error of approximately ±0.05. This technique allowed relative comparison of bulk glass refractive indices as a function of composition.

Absorption spectra of the investigated glasses are obtained at room temperature using a dual beam UV–Vis–NIR Perkin Elmer Lambda 900 spectrophotometer from 300 to 1500 nm.

The Raman spectra are recorded at room temperature, in backscattering geometry, using a Kaiser Hololab 5000R Raman spectrometer with Raman microprobe attachment (typical resolution of 2–3 cm^{-1}). The system consists of a holographic notch filter for Rayleigh rejection, a microscope equipped with 10×, 50× and 100× objectives (the latter allowing a spatial resolution of $<2\,\mu m$), and a CCD detector. A 785 nm semiconductor laser (Invictus 785, Kaiser Optical Systems Inc.) was used for excitation with incident power of around 2 mW. The use of a 785 nm source with a low power and short data collection time was deemed essential to our study to avoid photostructural changes which the laser beam may induce in the samples.

The nonlinear refractive index of the glasses is measured using the Z-scan method [21]. Excitation is provided by a Nd:YAG laser delivering linearly polarized 15 ps single pulses at $\lambda=1064$ nm with 10 Hz repetition rate. Other experimental parameters in the classical Z-scan method include: f (focal length of the focusing lens) = 20 cm; d (distance from the beam waist plane to the camera) = 26 cm. The beam waist at the focal plane is $\omega_0=30\,\mu m$ giving a Rayleigh range $z_0=\pi\omega_0^2/\lambda\approx2.6$ mm. This value is larger than the sample thickness (typically 1 mm). The photodetector is a 1000×10^{-18} pixels cooled camera (Hamamatsu C4880) with fixed linear gain. The camera pixels have 4095 gray levels and each pixel is $12\times12\,\mu m^2$. Two sets of acquisitions (in the linear and the nonlinear regime) are carried out for the measurement to correct for inhomogenities and surface imperfections in the sample. Open and closed Z-scan normalized transmittances are numerically processed from the acquired images by integrating over all the pixels in the first case and over a circular numerical filter (with radius equal to 1 mm) in the second case.

3. Results and discussion

Recently, we showed that with a progressive replacement of S by Se in the Ge–Sb–S glass network, the non-resonant n_2 increases from 50 up to 350 times the value for fused silica [20]. Contrary to results seen in other As-based chalcogenide glass systems [5], these results were not seen to be simply related to the formation of homopolar Se–Se bonds and the associated increase in lone pair electron (LPE) concentration. Using XPS, we postulated that the increase of nonlinear refractive index in Ge–Sb–sulfo-selenide glasses may be attributed to the increase of Ge–Se and Sb–Se bonds in the glass network [20]. To validate more precisely this proposed interpretation observed for the glasses previously measured, we have expanded our study to systematically vary the types and number of Ge-chalcogen and Ge/Sb bonds in the glass network. With such analysis, the role of bond type, the chalcogen content and thus the LPE concentration on the resulting nonlinear optical material properties could be confirmed.

Table 1 summarizes the composition of the investigated glasses including the glass transition temperature (T_g), density, molar volume, the number of the lone pair electron (LPE), the normalized photon energy ($h\nu/E_{gap}$) and the glass' linear and nonlinear refractive index at 1064 nm. The lone pair electron concentration has been estimated assuming one electronic lone pair per Sb ion, two per S and Se ion, and no pairs per Ge ion. The number of ions has been calculated using the density and the molar weight of the glasses. The large bars seen for the reported index (n) and n_2 data are related to within-sample measurement variation due to poor surface quality of the glass samples. While care has been taken during polishing, Se-containing glasses are softer than Se-free compositions and thus are especially susceptible to scratching. Note that the n_2 measured in this study are in agreement with those reported by [22,23]. In agreement with [24,25], we see that the nonlinearity is determined completely by E_g. Both n_2 and β are strongly dependent upon E_g as $n_2\propto1/E_g^4$ and $\beta\propto1/E_g^3$.