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Sulfide–halide glasses with high nonlinear refractive index and low nonlinear absorption

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Determination of the composition with the best optical and physical properties in a sulfide–halide arsenic-free vitreous domain, GeS_2–Sb_2S_3–CsI, is described.

The characteristic temperatures: glass transition (T_g) and crystallization temperatures (T_x) are measured to determine the difference T_x–T_g. The nonlinear index and absorption, the linear index are measured on nine samples in the vitreous domain. With an experimental device, cartographies of each property are created. The model permits to find a composition with a good compromise for T_x–T_g, nonlinear index and nonlinear absorption. The model emphasizes the influence of each element on each property.

1. Introduction

Coherent broad-band light sources are of great interest for many applications and one of the most efficient ways to obtain these sources is by super continuum generation [1]. Infrared broad-band sources are particularly interesting for spectroscopic analysis [2,3]. Most super continuum sources cover the near infrared spectral region. Extension to the 3–5 μm atmospheric transmission would be of great interest for Lidar applications. These sources are still difficult to obtain because of the lack of transparent materials with high nonlinearity and low absorption.

Silica glass has extraordinary overall quality and can be manufactured into sophisticated micro structured optical fibers (MOF) to control the fiber dispersion and enhance the nonlinearity for light generation [4]. However, the intrinsic absorption of the chemical bond Si–O prevents any optical application beyond 2 μm. In order to go further into the infrared, it is indispensable to work with other glasses. Chalcogenide glasses are very interesting materials with a very broad transmission range which can extend from the visible up to 15 μm, and an optical nonlinearity 100–1000 higher than silica glass. Chalcogenide glasses show, for example, great potential for signal regeneration in telecommunication by using Kerr effect [5,6]. Guiding structures such as nano wires and fibers are used to increase the interaction length and intensity. The high nonlinearity allows reducing the switching power, leading to higher long-term stability of systems and lower energy consumption.

Associated with the high nonlinearity, chalcogenide glasses are also known to have relatively high linear and nonlinear absorptions [7]. As relatively high power is often necessary for super continuum generation and optical switching, a high absorption may even lead to the destruction of the material.

This study is motivated by the need of infrared transmitting materials with appropriate compromise between the nonlinear refractive index and nonlinear absorption. As we will demonstrate later in this paper, the intrinsic linear absorption in the transparent region is negligible.

The GeS_2–Sb_2S_3 glass forming system is selected as the base compositions for this study because of its good mechanical properties, wide infrared transmission and high nonlinearities [8]. Many studied systems until now contain arsenic which does not have a good reputation for practical applications. The original idea here is to introduce a halide, CsI, which is efficient to enlarge the band gap and consequently to decrease the linear and nonlinear absorption at the wavelength of Nd:YAG laser used for nonlinear property measurement. In fact, the electronegative halogen atoms, the iodine in this case, tend to decrease the energy level of the non-bonding lone electron pair σ_{nbl} of the Sb–S chemical bond by reducing the

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electronic delocalization. The electronic gap is determined by the difference between this level and the anti bonding level and a lowering of σ_{nbl} leads to an increase of the band gap. In this way, many compositions with very different nonlinear refractive indices and absorptions can be created and best compromise can be realized.

2. Experimental

High purity materials (99.999% for Ge Sb, S and 99.99% for CsI) are used for the glass preparation in silica tube under vacuum (10^{-5} mbar). The sealed silica tube is heated to 850 °C in a rocking furnace and maintained 10 h at this temperature to ensure a good reaction between the starting materials and a good homogenization of the melt. The glass is obtained by quenching the tube in water and by annealing the sample near its glass temperature, before cooling down to room temperature in order to release stresses induced by quenching. The glass is then cut into discs of about 1 mm thick, which are then polished to obtain two parallel faces. The glass transition and crystallization temperatures are determined with differential scanning calorimetry (DSC) with a heat rate of 10 °C min^{-1}.

The band gap of samples is determined with a UV–visible–NIR spectrometer (CARY500) on polished samples. The band gap wavelength is defined as the wavelength where the absorption is 10 cm^{-1}.

The linear indices were measured by a Metricon2010 prism coupler system. The measurements of high index materials require silicon prism, which is not transparent at 1.064 µm. Therefore, the indices were characterized at 1.3 µm.

The nonlinear properties are measured by using Z-scan method [9] inside a 4-f imaging system. The excitation is provided by a Nd:YAG laser delivering 17 ps single pulses at 1064 nm with a 1 Hz repetition rate to avoid thermal effect [10]. The focal length of the two lenses composing the 4-f system is $f_1 = f_2$ = 20 cm. The beam waist at the focal plane is ω_0 = 35 µm giving a Rayleigh range z_0 = 3.5 mm. This value is larger than 1 mm, the typical thickness of the samples. The peak intensity I_0 in the focal plane is kept in the range of 1–3 GW cm^{-2}, staying in the limit of both small nonlinear absorption and phase-shifts. The photoreceptor is a 1000 × 1018 pixels cooled (−30 °C) CCD camera with fixed linear gain. The camera pixels have 4095 gray levels and each pixel is 12 × 12 µm^2. To check that there is no permanent linear change during the scan (photo induced effect) that contributes to the measured nonlinear refractive index, three sequential Z-scan acquisitions, in linear, nonlinear and linear regimes were carried out illuminating the sample on the same impact position as in [10]. No photo induced effects were observed during the measurement (50 laser shots). The Z-scan setup was calibrated with CS_2 by considering $n_2 = 3.0 \times 10^{-18}$ m$^{2\ W-1}$ at 1064 nm in the picosecond regime [9].

3. Results

Considering the high number of possible compositions in the vast glass forming region of the GeS_2–Sb_2S_3–CsI pseudo ternary system, an advanced experimental design methodology is used. This methodology consists in performing a limited number of carefully selected experiments and the properties of all compositions in the experimental domain of interest can be predicted [8,11]. For this purpose, nine compositions have been selected and four additional glasses have been synthesized for validation of the prediction, as shown in Fig. 1. Table 1 shows the measured properties of the obtained glasses, except the composition F which does not lead to glass with our experimental conditions. The T_g values of the nine samples are included between 222 °C and 387 °C. The sample A has a high T_g compared to the other samples. This shows the importance of GeS_2 on the glass temperature.

For a glass, the difference between the glass transition temperature (T_g) and the crystallization temperature (T_x) is an important parameter for evaluating its stability against crystallization. A higher value is of course better and empirically we have found that a difference higher than 150 °C indicates a glass stable enough which can accept fiber drawing or hot pressing with a limited risk of crystallization. This is essential for keeping the high transparency of the materials after shaping.

In this ternary system, the band gap strongly depends on the composition. The band gap wavelength varies from 498 nm for the composition to 768 nm for 10(GeS_2)–90(Sb_2S_3). The concentration of CsI in the glass, and even more of Sb_2S_3, increase the gap and the refractive index from 2.1 to 2.8.

The results show that n varies from 2.1 for 90(GeS_2)–10(Sb_2S_3) to 2.8 for 10(GeS_2)–90(Sb_2S_3). For the glass composition C (material having the nearest band gap wavelength compared to the excitation one and for which theoretically α is the highest), the measured absorption coefficient was 10^{-2} cm^{-1}. So reasonably, the linear intrinsic absorption at 1064 nm for all the materials has been considered as negligible. The results indicate that this absorption is at least 400 times lower than the nonlinear absorption with the used incident power density of 1–3 GW cm^{-2}. The nonlinear indices are included in the range of 1.5×10^{-18} m^2 W^{-1} for 90(GeS_2)–10(Sb_2S_3) to 11×10^{-18} m^2 W^{-1} for 10(GeS_2)–90(Sb_2S_3). This is 100–500 times stronger than the nonlinear index of silica.

4. Discussion

Fig. 2 shows clearly that n_2 depends directly on the width of the band gap. A narrow band gap leads to a high n_2 and also to a high intrinsic absorption due to electronic transitions. A similar behavior has already been observed in [12] dealing with the glass forming system $x$$GeS_2$–(1−$x$) Sb_2S_3. The enhancement of the nonlinear refraction has been attributed to the increase of electronic lone pairs provided by antimony (Sb). Tanaka [13] pointed out that the optical gap is a decisive parameter determining optical nonlinearity in non-crystalline solids and nonlinear coefficients are enhanced for materials with small optical gap E_g. He formulated his conclusions by applying a theory developed for crystalline semiconductors by Sheik-Bahae [14,15] to amorphous materials considering indirect-gaps. Indeed, it was found in other works that for binary and ternary glasses, real and imaginary parts of the third order susceptibility (proportional to n_2 and β, respectively) increase monotonically with decreasing optical gap E_g and increasing linear refractive index n. This is also confirmed by our experimental results and by our previous work [16].

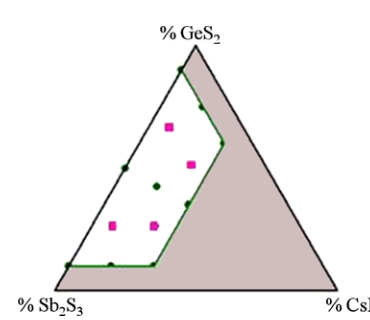

Fig. 1. The studied glass forming system with nine selected compositions (filled circles) in order to predict the properties of the glasses and the four compositions (squares) used to validate the theoretical predictions.