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Investigation of third-order optical nonlinearities of copper doped germanium-gallium-sulfur chalcogenide glasses

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ABSTRACT

A series of copper doped germanium-gallium-sulfur (GGS-Cu) chalcogenide glasses were synthesized by melt-quenching method. Raman spectra showed that the introduction of Cu could alter the main structure of GGS network, leading to modification of thermal, mechanical and optical properties of the GGS glasses, even at very low doping level. Femtosecond *Z*-scan measurements were employed to study the third-order optical nonlinearities (TONL) of the GGS-Cu glasses at wavelength of 1550 nm. Significant improvement of TONL performance due to the Cu doping was observed, and its possible mechanism was studied.

1. Introduction

The development of all-optical communication network requires photonic devices with small size, low energy consumption as well as fast processing speed. High optical nonlinear fibers have been considered as a key component for the fabrication of such devices due to their small modefield radius that would keep the propagation light power density at very high level [1]. In various fiber materials, chalcogenide glasses (ChGs) that refer to a category of glass constructed by chalcogen elements (S, Se, and Te) have attracted considerable attentions for their large third-order nonlinear susceptibility ($\chi^{(3)}$, at least two orders of magnitude larger than that of silica glasses) and fast nonlinear response time ($<$ 200 fs) [2,3], as well as their very wide transmission range (0.4–25 μm), thus they have great potentials in realization of key devices in all-optical communication network as well as integrated photonic systems that based on infrared technologies [4,5].

In various kinds of ChGs, most of them are As-based glasses, however, As is a highly toxic element, therefore some new glass compositions without As have draw people's attention [6,7]. In particular, sulfide glasses based on germanium-gallium-sulfur (Ge-Ga-S, GGS) ternary system have been intensively studied for its visible transparency, high chemical stability, as well as its flexibility of glass property modification by means of changing chemical composition and post treatments [8–10], which made GGS ChGs a promising candidate for optics device fabrication. However, as compared to other category of ChGs (i.e. Se- and Te-based), sulfide glasses are known to manifest relatively small third-order optical nonlinearities (TONL), thus then many attempts had been made to engineer TONL properties of GGS ChGs for higher $\chi^{(3)}$ value [11–13]. It have been reported that introduction of noble metal, such as Ag and Au could modify optical properties of the GGS ChGs and improve their TONL performance [13,14]. Copper as a common noble metal is known to have the capacity to inhibit the appearance of photoinduced phenomena in ChGs [15], and its enhancement to TONL properties of ChGs had also been reported [16]. However, few studies were conducted on Cu doped GGS ChGs, and its influence on optical properties as well as inner structural order of GGS ChGs remains unclear. On the other hand, little is known about the TONL properties of GGS-based at telecom wavelength of 1550 nm.

In this paper, we introduced copper to GGS (GGS-Cu) ChGs by melt-quenching method. Different from Ag and Au doping as reported in previous studies [13,14], the variation of GGS glass network induced by Cu doping is firstly observed in present study by Raman spectra. TONL properties of the GGS-Cu glasses are studied by femtosecond *Z*-scan technique at the wavelength of 1550 nm, and the significant enhancement of TONL properties by the introduction of Cu is observed and the possible mechanism is discussed.

2. Experimental

GGS glass with the molar composition of 10Ga-25Ge-65S (referred

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to as GGS-Cu0) and the same type of glasses doped with 0.1, 0.2, and 0.3 wt% copper (referred to as GGS-Cu01, GGS-Cu02, and GGS-Cu03) were prepared from high-purity polycrystalline germanium (5 N), gallium (5 N), sulfur (5 N), and copper powder (4 N). Raw materials were carefully weighed (10 g) and sealed in evacuated (10^{-4} Pa) silica glass ampoules. The materials were then melted at 950 °C in a rocking furnace for 24 h and then quenched in water quickly to avoid crystallization. The resultant glasses were annealed at the temperature that 20 °C below T_g for 4 h to minimize inner stress and cool down to room temperature. Finally, the glasses were cut into discs and optically polished.

The transition temperatures (T_g) and crystallization temperature (T_x) of the glasses were measured by differential scanning calorimetry (DCS, TA-Q series). Vickers micro-indenter (Everone MH-3, Everone Enterprises Ltd., Shanghai, China) is used to obtain the Vickers-hardness of the glasses with a charge of 100 g for 5 s. Absorption spectra of the samples were measured in the range of 400–2000 nm using Perkin-Elmer Lamda 950 UV-VIS-NIR spectrophotometer. For the measurement of optical band gap (E_{opg}), the glasses were polished to thickness of 0.1 mm which is available for determination of E_{opg} proposed by Davis and Mott [17]. Raman spectra were obtained through back scattering (180°) configuration with a Renishaw inVia laser confocal Raman spectrometer. The excitation wavelength is at 488 nm, and the frequency resolution is $\pm 1\ \mathrm{cm}^{-1}$.

TONL properties of the GGS-Cu glasses at wavelength of 1550 nm were measured by single beam Z-scan technique using a Mendocino fiber laser (CALMAR LASER FPL style) with 51 fs pulse width and 50 MHz repetition rate. The incident laser power is set at 82 mW, corresponding to laser density I_0 of 1.0 GW/cm^2 at lens focus.

3. Results and discussion

Characteristic temperatures of the GGS-Cu glasses measured by DSC are shown in Table 1. It can be seen both glass translation temperature (T_g) and crystallization temperature (T_x) of the GGS-Cu glasses decreases with increase of Cu doping level. However, the glass stability parameter ΔT ($\Delta T = T_x - T_g$) increase gradually with increasing content of Cu, and all the Cu doped GGS glasses have $\Delta T > 100$ °C, which indicated that the introduction of Cu could promote the thermostability of the ChGs. Meanwhile, measurement of Vickers-hardness of the GGS-Cu glasses shows that hardness of the GGS glass exhibits a significantly increase after the introduction of Cu. As compared to that of the host glass, sample with highest Cu content have increased the H_v value by ~50%, indicating that introduction of Cu could improve the mechanical strength of GGS glass due to the highest coordination number (4 and 6) and relatively small covalent radius ($r_{Cu} = 1.17$ Å, $r_{Ge} = 1.22$ Å, $r_{Ga} = 1.26$ Å) of copper in the GGS-Cu system.

The remarkable improvement of thermal and mechanical properties of the GGS glass can be attributed to the introduction of copper that broke the chemical ordering of the precursor GGS glass, and similar behavior in silver doped Ge-Ga-S and As-S glasses had been reported by other researchers [13,18]. For present GGS-Cu glasses, chemical composition of the host GGS glass (10Ga-25Ge-65S in molar percentage) is in stoichiometry, thus further introduction of 'cations' to the glass matrix that consists of covalent bonds would induce network demixing or nanoscale phase separation effect [9,19], leading to remarkable change of various properties of the GGS glass, including optical and nonlinear properties as shown below.

Table 1
Thermal parameters (T_g, T_x and ΔT), Vickers-hardness (H_v) and optical band gap (E_{opg}) of the GGS-Cu glasses.

Sample no.	T_g (± 1 °C)	T_x (± 1 °C)	ΔT (± 2 °C)	H_v (± 1%)	E_{opg} (± 0.01 eV)
GGS-Cu0	446	535	89	207.4	2.64
GGS-Cu01	428	533	105	245.2	2.62
GGS-Cu02	410	524	114	257.3	2.60
GGS-Cu03	395	519	124	308.9	2.46

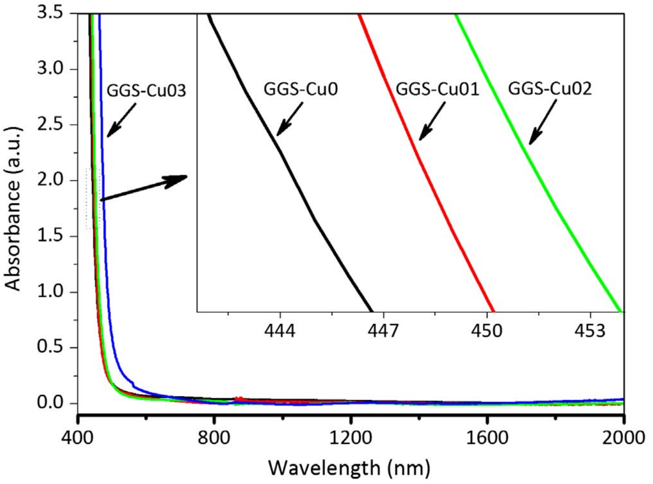

Fig. 1. Absorption spectra of the GGS-Cu glasses; inset is the enlarged spectra to show the variation of absorption cut-off with addition of Cu.

Absorption spectra of the samples with range from 400 to 2000 nm are showed in Fig. 1. It can be seen that short wavelength absorption edge of the GGS-Cu glasses red-shifted with increase of Cu content. By using the well-known Tauc's theory [20], variation of the absorption edge with addition of Cu can be numerically represented by optical band gap (E_{opg}) using the following equation:

$$\alpha h\nu = B(h\nu - E_{opg})^m, \tag{1}$$

where hν is the incident photon energy, α is linear absorption coefficient, B is a constant which is related to electron transition probability, the exponent m is a parameter which relies on the type of electron transition. Here m equals to 2 representing the indirect allowed electron transition for amorphous materials. By linear fitting the edge of Tauc plotting as seen in Fig. 2, E_{opg} were determined and shown in Table 1. Red-shifting of absorption cut-off resulted in decrease of E_{opg}, in other words, the energy gap between conduction and valence band of the ChGs decreased with addition of Cu. Inset of Fig. 2 shows that the dependence of E_{opg} on Cu content is nonlinear, indicating that the structural change of GGS network caused by Cu doping is different at different Cu content, which was confirmed by the Raman spectra in following section.

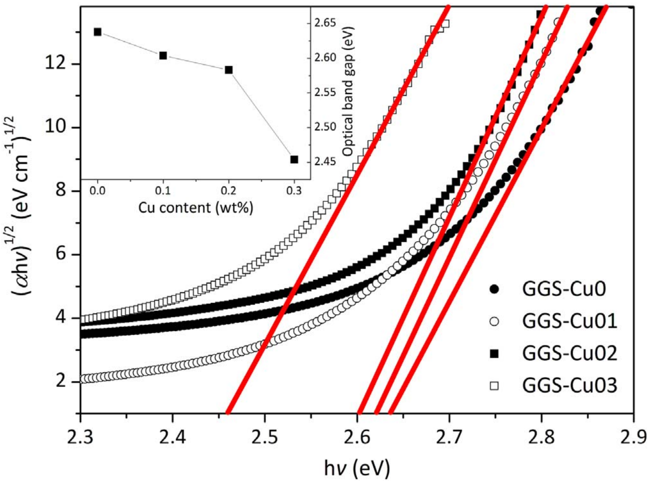

Fig. 2. Tauc plotting of indirect allowed band gap of the GGS-Cu glasses; inset shows the dependence of E_{opg} value on Cu content.