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Preparation and third-order optical nonlinearity of glass ceramics based on GeS_2–Ga_2S_3–CsCl pseudo-ternary system

Xiang Shen [a,*], Feifei Chen [a], Xin Lv [a], Shixun Dai [a], Xunsi Wang [a], Wei Zhang [a], Baoan Song [a], Tiefeng Xu [a], Qiuhua Nie [a], Chao Liu [b], Kai Xu [b], Jong Heo [b]

[a] College of Information Science and Engineering, Ningbo University, Ningbo 315211, China
[b] Center for Information Materials and Department of Materials Science and Engineering, Pohang University of Science and Technology, Pohang, Gyeongbuk 790-784, Republic of Korea

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ABSTRACT

Chalcohalide glass-ceramics based on GeS_2–Ga_2S_3–CsCl pseudo-ternary system were prepared by heat treatment method. X-ray diffraction and scanning electron microscope studies confirmed the formations of Ga_2S_3 and GeS_2 phase grains with sizes of 2–5 and 80 nm, respectively. Z-scan technology was employed to investigate the third-order nonlinear optical characteristics of both precursor glass and its glass ceramics at 800 nm. The results show that nonlinear refractive index n_2 as well as nonlinear absorption coefficient β increase after heat treatment, which is due to quantum effects, and the largest n_2 of the glass ceramics is 4.3×10^{-11} esu which is 4 times larger than that of the host.

1. Introduction

In recent years, materials with large third-order nonlinearity have been investigated extensively for their abilities to be utilized for ultrafast all-optical switching in optical communication network [1,2]. In particular, great attentions have been focused on chalcogenide glasses and thin films [3,4] because of their weak phonon energies, low probability of multiphonon relaxation, large third-order nonlinear susceptibility $\chi^{(3)}$ (about two or three orders of magnitude larger than that of silica glass) and fast response time [5,6]. However, compared to oxide glasses, chalcogenide glasses have relatively weak mechanical strength as well as high thermal expansion coefficient and low resistance to thermal shock. Consequently, it is difficult to optimize the design of infrared systems using these glasses. One promising way here is to prepare glasses-ceramics, i.e. glass materials with embedded crystallites possessing sizes lying below 10 μm [7].

In addition, the precipitation of nonlinear crystallites is also an attractive route to make chalcogenide glass a potential optical converter in the mid-IR region [8]. Because materials doped with nano-particles have been developed for their high optical nonlinearities that originated from resonance effect [9,10]. For example, large third-order optical nonlinearities had been reported in glasses embedded with CdTe [11], and Bi_2O_3 [12], ZnSe [13] nano-particles, which indicated that these quantum structures can be used for optoelectronic devices. However, according to previous reports, such composite materials were mostly limited in oxide-based systems, while chalcogenide glass-ceramic had rarely been studied for crystal growth which needs precisely controlled to obtain crystals with a size within submicrometers for keeping a good optical transparency.

In this paper, transparent glass-ceramics based on GeS_2–Ga_2S_3–CsCl system were synthesized by heat treatment method. Z-scan technique was employed to measure the third-order nonlinearities of both precursor glass and its glass ceramics at 800 nm. The dependence of crystalline processes on nonlinear refractive index γ and two-photon absorption coefficient β were investigated.

2. Experimental

Precursor glass in $75Ge_2S$–$10Ga_2S_3$–15CsCl (molar%) pseudo-ternary system were selected as host glass. Raw materials of germanium, antimony, sulfur and compound cesium chlorine were carefully weighed and sealed into quartz ampoules in vacuum, which were then inserted into a rocking furnace. The quartz ampoules were agitated and maintained at 900 °C for 12 h in the furnace in order to ensure homogeneity, and then quenched in water quickly to avoid crystallization. All samples were annealed at 30 °C below T_g for 3 h to minimize inner tension and cooled to room temperature. The samples were then cut and optically polished to mirror smoothness with a thickness of 1 mm for further testing. Glass ceramic samples were obtained by heat treating the annealed glass at 430 °C for different durations.

The absorption spectra of samples were recorded in the range of 350–2700 nm using Perkin–Elmer Lambda 950 UV–VIS-NIR spectrophotometer. Powder X-ray diffraction (XRD) technique at

* Corresponding author. Tel.: +86 57487600947; fax: +86 57487600946.
E-mail address: shenxiang_nbu@hotmail.com (X. Shen).

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room temperature using CuK radiation was used to find out the amorphous and crystalline nature of annealed and heat-treated samples. For observation under scanning electroic microscope, polished discs were coated with a very thin platinum film. And some small cracks were created using a cutter. Observed inside these cracks and gives images with higher resolution.

The third-order optical nonlinearity of the glass and glass ceramic samples were measured by Z-scan technique using a 76 MHz repetition rate mode-locked Ti: Sapphire laser (Coherent Mira 900-D) with 200 fs pulse width. The schematic diagram of the experimental setup was depicted in Ref. [14]. The laser radiation was split into two beams. One was detected by detector 1 (D1) to monitor the fluctuation of the laser energy, the other was focused on the sample by a lens with 150 cm focal length. As the sample moved along a motor track near the focal point, the transmitted light changing with excitation intensity was recorded by detector 2 (D2). D1 and D2 were connected to a Dual-Channel Power Meter, from which the relative transmittance can be gained directly. Z-scan of each sample was performed in the case of open-aperture and closed-aperture. Measurements were performed at the wavelength of 800 nm.

3. Results and discussion

3.1. Thermal and structural characterization

DTA curve of $75GeS_2$–$10Ga_2S_3$–15CsCl bulk glasses at a heating rate of 10 °C/min is shown in Fig. 1. The transition temperatures T_g and crystallization beginning temperature T_x are 400 and 510 °C, respectively. Based on the DTA results and previous studies [15–17], the temperature of 430 °C (T_g+30 °C) was chosen for crystallization process. The host glasses were heat treated at this temperature for different durations ranged from 5 to 20 h.

X-ray diffraction patterns of the crystallized glasses are presented in Fig. 2. After 5 h of heat treatment at 430 °C, the diffraction spectra of the samples show the formation of crystals from the glass matrix. The main diffraction peaks (2θ) located at 32° and 54° can be attributed to Ga_2S_3 phases (JCPDF No. 26–693). By using Debye–Scherrer formula, the average sizes of Ga_2S_3 grains in 5, 10 and 15 h treated samples were estimated to be 2.3, 2.6, 5.2 nm, respectively.

Notice that Ge_2S_3 crystallites (JCPDF No. 45–891) are only precipitated on the surface of the longest treated (15 h) sample. The average grain size of the Ge_2S_3 crystals was estimated to be 86 nm by Debye–Scherrer formula. In order to directly evaluate the size and distribution of the crystalline particles, the samples were measured by SEM at room temperature. The image of SEM in Fig. 3(b) shows that

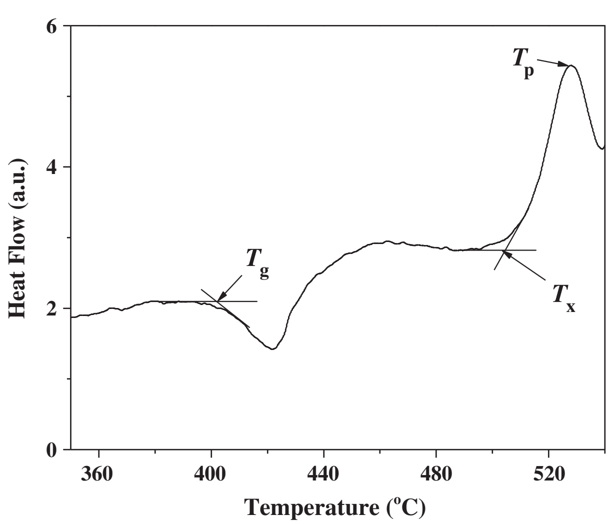

Fig. 1. Differential thermal analysis (DTA) curve of host glass.

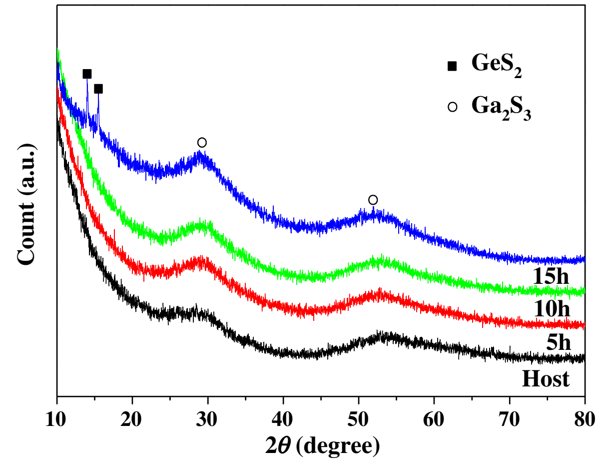

Fig. 2. X-ray diffraction pattern of samples heat-treated at 430 °C for different time.

the more probable value of the grain size is 80–100 nm, which is in agreement with the XRD results.

3.2. Absorption spectra

The naked eye observation of the different samples indicates a continuous evolution in the transparency of the glass-ceramic

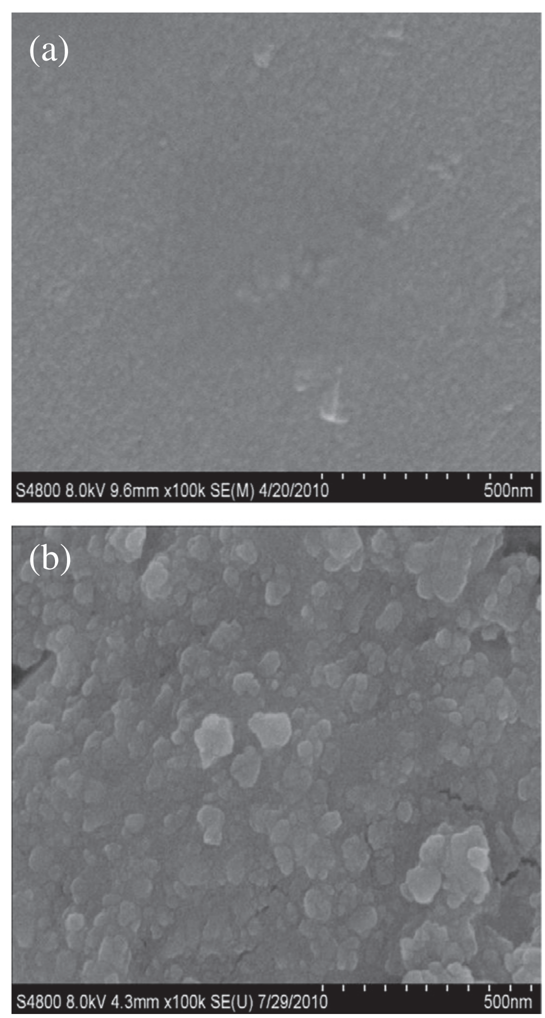

Fig. 3. SEM of the glasses after treated at 430 °C for different durations, (a) 10 h and (b) 15 h.

samples which become more and more opaque with the treating times. As indicated in Fig. 4 (a), the spectra of Vis-NIR transmission for the base and crystallized glasses, it can be clearly seen that the cut-off edge of short wavelength is red-shifted as a function of annealing time, which is due to the formation of sub-micron crystallites in the matrix which increase the scattering loss at the visible wavelengths [18]. The cutting-off wavelengths for host, 5 h and 10 h treated samples are 524, 525 and 558 nm corresponding to band gap energy of 2.37, 2.36 and 2.22 eV, respectively.

Notably, the presence of sub-micron size particles does not have significant influence on the mid-infrared transmission. The glass and glass-ceramic have the same transmission beyond 5 μm as the Fig. 4 (b) shows.

3.3. Nonlinear optical properties

The nonlinear refraction index n_2 and nonlinear absorption coefficient β of the samples were determined using a single beam Z-scan technique at the wavelength λ of 800 nm. The laser pulses are 200 fs wide, thus the optical nonlinear contribution from nuclear component can be neglected. Therefore, the third-order nonlinear responses of the glasses are only induced by the electronic effects.

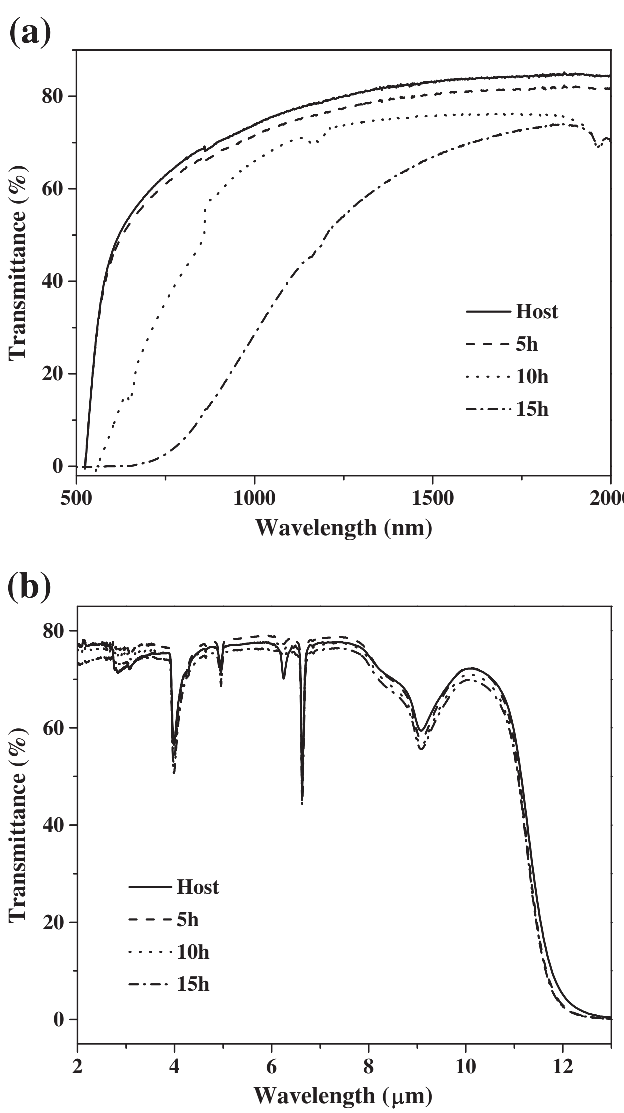

Fig. 4. (a) Visible and near infrared, (b) Mid-infrared transmission of the glasses after treated at 430 °C for different durations.

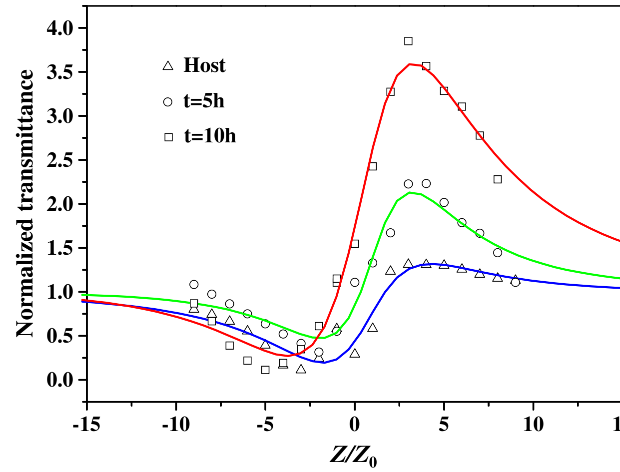

Fig. 5. Closed aperture Z-scan curves of the host glass and glass ceramic samples.

Fig. 5 shows the normalized transmittance versus the sample position Z were measured by closed-aperture Z-scan technique. Some information can be acquired directly from the experimental curves: First, all curves exhibit a typical valley-peak shape which indicates the sign of n_2 of the samples is positive; second, the volumes of both peak and valley increase, which implies the increase of nonlinear refraction after heat treatment. In Fig. 6, it can be seen the open aperture Z-scan curves exhibits a reverse saturated type absorption (valley in the centre) which is indicative of two-photo absorption (TPA) since the photon energy of measuring wavelength (800 nm: 1.55 eV) is between band gap and half band gap of the samples.

It is well known that the nonlinear refraction and the TPA always present together in a single closed-aperture measurement [19]. For the far-field condition, the closed-aperture transmittance change data can be fitted by

$$T(x) = 1 + \frac{4x}{(x^2+9)(x^2+1)}\Delta\phi - \frac{2\left(x^2+3\right)}{(x^2+9)(x^2+1)}\Delta\psi \tag{1}$$

$$x = \frac{z}{z_0} = \frac{2z}{k\omega_0^2} \tag{2}$$

Where $\Delta\phi = k\gamma I_0 L_{eff}$, $\Delta\psi = \beta I_0 L_{eff}/2$, $k = 2\pi/\lambda$, L_{eff} is the sample effective length defined as $L_{eff} = [1-\exp(-\alpha L)]/\alpha$ with L the sample length; λ is the wavelength; α is the linear absorption coefficient.

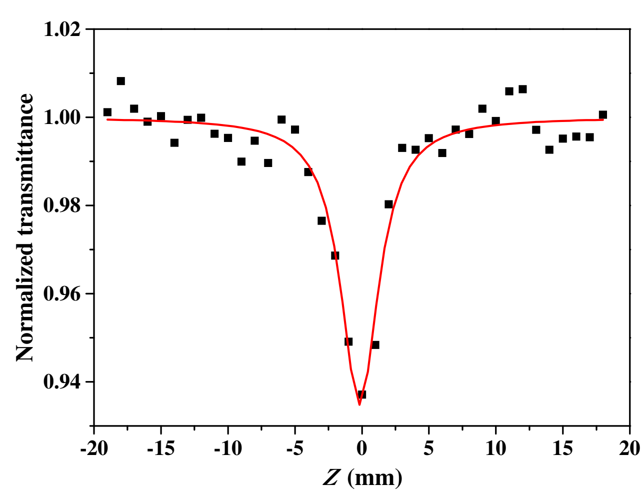

Fig. 6. Open aperture Z-scan curves of the 10 h treated glass ceramic.

Table 1
Nonlinear refractive indexes (n_2), nonlinear absorption coefficients (β) and third-order nonlinear susceptibilities ($\chi^{(3)}$) of the samples investigated and references.

Samples	n_2 (10^{-11} esu) ± 30%	β (cm/GW) ± 30%	$\chi^{(3)}$ (10^{-13} esu) ± 40%
Host	1.33	25.62	0.71
GGSC-5 h	2.46	27.46	2.58
GGSC-10 h	4.34	38.78	3.69
$90GeS_2$–$5Ga_2S_3$–5CdS[20]	–	–	1.3
$90GeS_2$–$5Ga_2S_3$–$5PbI_2$[21]	–	–	2.07

According to Eq. (1), both nonlinear refractive index $n_2 = cn_0\gamma/40\pi$ (n_0 is refractive index of the host of 2.03) and TPA coefficient β can be extracted from the fitting closed Z-scan measurement. The calculated results listed in Table 1. According to the date, it can be seen that with the increase of heat treatment time, nonlinear refractive index n_2 is markedly increased. It should be noted that maximum n_2 value is 4.34×10^{-11} esu, which is about 4 times larger than that of host glass.

During the laser excitation, the optical nonlinear behaviors may be due to two effects: first, the partial increase of the non-centrosymmetric charge density distribution due to the optically-induced alignment of the principal chemical bonds. Second, the increase of the effective third-order non-linear susceptibility is due to quantum effects: the zero-dimensional Ga_2S_3 nano-particles whose diameter is much smaller than the wavelength of the incident laser (800 nm) is limited to GeS_2–Ga_2S_3–CsCl glass matrix where the conduction and valence bands were decomposed into a series of discrete energy levels. At the same time, the quantum states of electrons has changed, which enhanced the interaction and intraband transition between the embedded crystallites and the surrounding glass matrix. Therefore, under the influence of the electric field, both nonlinear refraction and nonlinear absorption of the samples after crystallization were significantly enhanced.

4. Conclusion

In summary, we have prepared and glass-ceramics based on $75GeS_2$–$10Ga_2S_3$–15CsCl (in molar%) glass by heat treatment method. Third-order optical nonlinearities of the both glass and glass-ceramic containing nanocrystals were investigated by Z-scan experiment with femto-second laser pulses at $\lambda = 800$ nm. We have discovered that the exploitation of the heat-treatment procedure is able to modify the nonlinear refractive index n_2 and two-photon absorption coefficient β of this material. The maximum $n_2 = 4.34\times10^{-11}$ esu in the transparent glass-ceramics is much larger than that of the as-quenched glass. These properties make this material promising candidate for future optical devices.

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