Fabrication and characterization of femtosecond laser induced microstructures in chalcohalide glasses

X. ZHENG[a,b*], H. TAO[a], C. LIN, X. ZHAO[a], G. GADRET[b], J.-C. JULES[b], F. SMEKTALA[b]
[a]*Key Laboratory of Silicate Materials Science and Engineering (Wuhan University of Technology), Ministry of Education, Luoshi Road 122, Hongshan District, Wuhan, Hubei 430070, P.R. China*
[b]*ICB Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 5209 CNRS-Université de Bourgogne, Av. A. Savary, 21078 Dijon, France*

We have discussed the structural changes induced in Ga-containing GeS_2 based chalcohalide bulk glasses (ChGs) by a 200fs, 780nm, and 76MHz femtosecond laser (fs-laser) irradiation. As a result, various microstructures include waveguide lines were created in $80GeS_2{\cdot}10Ga_2S_3{\cdot}10BaCl_2$ and $70GeS_2{\cdot}15Ga_2S_3{\cdot}15AgI$ glasses under various conditions of femtosecond laser irradiation. The refractive indices of the modified glasses have decreased compared with the as-prepared glasses. Using micro-Raman scattering, we demonstrate that the variation of refractive indices were directly linked to photoinduced structural changes in the glass network.

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1. Introduction

In the mid-90s of last century, several groups in Japan and USA [1-4] have discovered that tightly focused fs-laser pluses could be used to induce permanent structural changes in glasses, this phenomenon then attracts scientific interest due to its potential application for micromachining in transparent materials. Compared with continuous and long-pulsed (nano- and picosecond) laser, fs-laser have advantages of ultrashort laser pulse and ultrahigh light intensity, so the laser-materials interaction become highly nonlinear during the irradiation of fs-laser, and the modified part can differ from the unmodified material in a wide variety of properties including morphology, refractive index, optical nonlinearity, crystal structure, absorption coefficient etc. The structures that induced by this so-called fs-laser writing technique have much applications in the areas of integrated-optics devices, optical memory, telecommunications and bio-sensing and –imaging etc.

During the last decade, the glass category involved in the research of femtosecond laser-glass interaction have been extended from the beginning of silica glass to the present various glass system, including borate, phosphate, heavy metal oxide, and chalcogenide. Of these chalcogenide are especially attractive. It is well known that chalcogenide glasses have wide transparence in the mid-infrared, high nonlinearity, strong photosensitivity and several unique properties [5-6], so they are becoming more and more important for the fabrication of optoelectronic devices. In particular, Ga-containing GeS_2-based chalcogenide glasses are very promising due to their high rare-earth solubility, high halogens solubility (i.e. formation of ChGs), low toxicity, and wider transparency in the visible. So the research of fs-laser micromachining in such Ga-containing GeS_2-based ChGs has great potential application in the area of optoelectronics.

To date, most of the publications on fs-laser interaction with ChGs have been mainly focused on As-based ChGs [7-9], and reported the fabrication of waveguides, nanogratings and nanoholes after fs-laser irradiation. Spectral broadening in fs-laser written waveguides was also reported in Ga-La-S glass [10]. However, little attention have been devoted to the Ga-containing GeS_2 based ChGs yet, only recently N.D. Psaila et.al [11] have reported supercontinuum generation in an ultrafast laser inscribed Ge-Ga-S-CsI glass. So the study of microstructures induced in Ga-containing GeS_2 based ChGs by fs-laser irradiation will be highly significative, as the unique properties of these glasses could be tailored in a wide range by changing composition of the contained halides.

In this study, we have demonstrated the fabrication of various microstructures including waveguide lines in Ge-Ga-S-$BaCl_2$ and Ge-Ga-S-AgI ChGs, and investigated the structural changes by micro-Raman scattering. These works will allow improvements in efforts to predict the photoresponse of new material candidates suitable for waveguide writing.

2. Experimental

Using the conventional melt-quenching technique, the base homogeneous $80GeS_2{\cdot}10Ga_2S_3{\cdot}10BaCl_2$ and

$70GeS_2 \cdot 15Ga_2S_3 \cdot 15AgI$ (in mol%, labeled as GGB10 and GGA15 hereinafter, respectively) glasses were synthesized through high-purity raw materials (Ge, Ga, S, all of 5N, and $BaCl_2$, AgCl of 3N) in stoichiometry. Details of the synthesis were similar to the procedure in our previous paper [12]. The $10\times10\times1mm^3$ plate-like samples were prepared from the bulk glasses and polished to mirror smoothness on both sides.

A mode-locked titanium-sapphire laser (Coherent Mira 900-D) that generates a sequence of 200fs pulses and has a repetition rate of 76MHz was used as a laser-radiation source to create structural changes in the as-prepared glasses. The central wavelength of the Ti-sapphire laser radiation is 780nm. The average power of the laser beam at the sample location was controlled by a neutral-density filter that is inserted between the laser beam and the microscope objective. With the help of a high-precision translation stage (PI, M-415.DG), the samples were translated at speed of 100-1500μm/s either parallel or perpendicular to the direction of incident laser propagation. The laser beam was focused to a depth of approximately 100μm beneath the surface of the glasses by using different types of numerical aperture (NA) objectives. All the structures were fabricated with a fixed repetition rate and pulse width. The power of the laser radiation, sample translation speed and direction were varied in this case. After processing, the end faces of the samples were polished for the beneficial of subsequent characterization.

Optical transmission of the as-prepared glasses was recorded with a spectrophotometer (Shimadzu UV-1601) in the visible and near-IR region (Vis–NIR). A photomicroscope (Wild M450, Heerbrugg) was used to characterize the morphology of the fs-laser induced microstructures. The induced structural changes have been investigated by using micro-Raman spectroscopy, which is a valuable tool for revealing the photoinduced structural changes occurring in the glass matrix. Raman spectra were measured by using a Raman Spectrometer (Renishaw RM-1000) in back (180°) scattering configuration. Laser irradiation at the wavelength of 632.8nm (He-Ne laser line) was used for the excitation. The laser beam was focused into a spot with a diameter of 5μm. The resolution of the Raman spectra was $1cm^{-1}$. All the measurements were carried out at room temperature.

3. Results and discussion

Optical transmission spectra recorded for the as-prepared GGB10 and GGA15 glasses in the Vis-NIR region are shown in Fig.1. We could observe that both two glasses have high transmittance at wavelength of 780nm and 632.8nm, which correspond to wavelength of the used fs-laser and Raman characterization laser. So the influences of linear laser absorption on the laser-glass interaction could be irrespective.

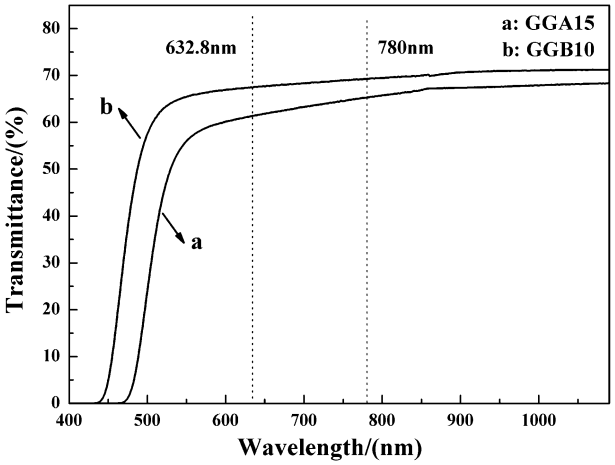

Fig.1. Optical transmission spectra of the as-prepared GGB10 and GGA15 glasses in the Vis-NIR region.

Microstructures with some complex geometry have been fabricated in the interior of the glasses with various scanning parameter after fs-laser irradiation. Two types of structures were created in this study: with displacement of the sample perpendicular and parallel to the direction of laser propagation (perpendicular and parallel recording geometry, respectively).

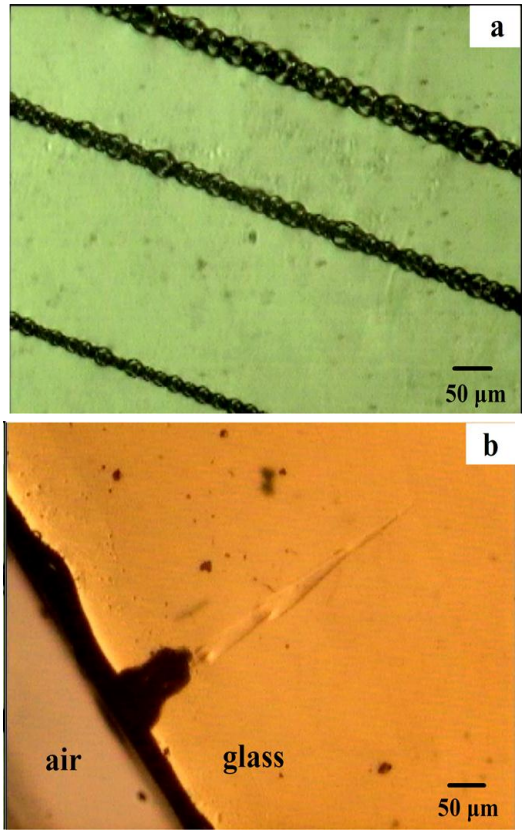

Fig.2. Optical micrographs of the perpendicular recording geometry in GGB10 glass (a) and the parallel recording geometry in GGA15 glass (b).

Optical micrograph of the perpendicular recording geometry that induced in GGB10 glass is shown in Fig.2a. The sample was irradiated by using a 10×0.25NA objective, with a fixed minimum laser-scan speed of 100μm/s, three lines contained successive spherical elements could be observed in Fig.2a. The average width of these lines varied from 20μm to 50μm along with the average laser power varied from 200mW to 400mW. We could see a dark point located in the center of each spherical element, which probably due to discontinuous scattering centers with a size of several hundred nanometers. The scattering centers may result from laser induced composition and density variation such as bubble formation in the laser irradiation region [13]. And the outer structure of the spherical element could result from high temperature elevation [14].

Optical micrograph of the parallel recording geometry that induced in GGA15 glasses is shown in Fig.2b. The sample was irradiated by using a 20×0.4NA objective, with a fixed minimum laser-scan speed of 100μm/s and an average laser power of 250mW. A short line with a spiry shape could be observed in Fig.2b, and a dark hole located between the short line and the glass surface. When the laser focus point moved close to the surface between glass and air, the glass around the focus point could be easily melt and even volatilized into the air, so a dark hole formed after laser irradiation. It should be noted that perpendicular recording allows for arbitrary structure length and arbitrarily sharp turns in the plane perpendicular to the laser beam, and creates an elliptical profile. However, for parallel recording, the structure length is physically limited to the working distance of the microscope objective, and creates a circular profile, which could be seen in the latter insert photographs of Fig.4 and 5.

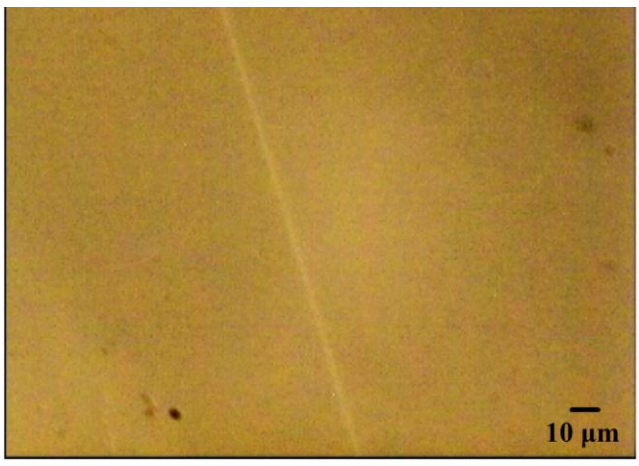

Fig.3. Optical micrograph of the perpendicular recording waveguide line in GGA15 glass.

As the laser repetition rate reaches at MHz level, the time interval between successive laser pulses is much shorter than the time scale for diffusion of heat out of the focal volume, successive laser pulses deposit energy faster than it can diffuse away. So at the laser focal point, energy accumulates to intensity high enough for multiphoton ionization to occur, which created plasma in the glass around the laser focal point. Then the energy from the hot plasma transfer to the lattice, resulting in the modified regions in glasses.

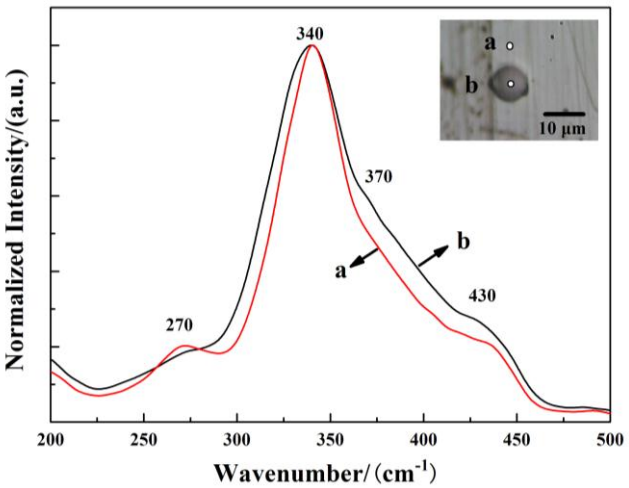

Fig.4. Micro-Raman spectra of GGB10 glass before (a) and after (b) laser irradiation.

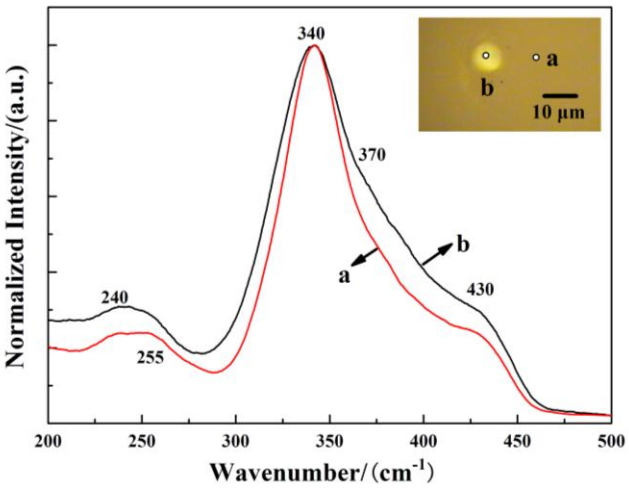

Fig.5. Micro-Raman spectra of GGA15 glass before (a) and after (b) laser irradiation.

Different variables control the fs-laser modification process: the speed and direction with the sample is moved, the number of the laser scans, the laser repetition rate, the laser fluence and the laser wavelength. In our experiments, we fixed the laser repetition rate and laser wavelength. On the base of large number of laser irradiation experiments in both two composition glasses with different variables, we could obtained some well waveguide lines inside the glasses. As shown in Fig.3, a waveguide line with a homogeneous width of around 2μm has been obtained in

GGA15 glasses after laser irradiation, by using a 40×0.65NA objective, with a laser-scan speed of 100μm/s and an average laser power of 400mW.

Normalized Raman spectra of GGB10 and GGA15 glass, both in prior and after laser irradiation are shown in Fig.4 and 5. The insert photographs are the cross-section of the glasses with a parallel recording, and a visible circle modified glass part could be observed. It should be noted that both two insert photographs were taken by the CCD equipped in Raman Spectrometer, the graph insert in the Fig. 4 was taken by a visible reflected light, and the graph insert in Fig. 5 is taken by a visible transmitted light.

In the fig. 4 and 5, we can see that the Raman spectra of both two composition glasses prior laser irradiation are dominated by a broad band between 300 and 450cm^{-1}, which is composed of several overlapping bands. Three bands (340, 370, 430cm^{-1}) have been reported typically on the Raman spectrum of *g*-GeS_2 glass [15]. In this glass, the basic structure units are [GeS_4] tetrahedra, which are connected through the bridging sulfur atoms to form a three-dimensional network. The strongest peak at 340cm^{-1} is assigned to the υ_1(A1) symmetrical stretching vibration of [GeS_4] tetrahedra. The shoulder at 370cm^{-1} is considered a companion band (A^c), which is due to the symmetric stretching vibrations of the four outer sulfurs of the two edge-shared [GeS_4] tetrahedra. The band at 430cm^{-1} is ascribed to the vibrational mode of the two inner sulfurs of the two edge-shared [GeS_4] tetrahedra [16]. For GGB10 glass, a small prominence centered at about 270cm^{-1} is observed, it is assigned to the vibration of Ga-Ga homopolar bond in [S_3Ga-GaS_3] ethane-like units [17]. For GGA15 Glass, a broad prominence centered at around 250cm^{-1} is observed, it is formed by the overlap of two bonds that centered at 255cm^{-1} and 240cm^{-1}, which attributed to the vibration of Ge-Ge homopolar bond in [S_3Ge-GeS_3] ethane-like units [18] and the vibration of [$S_{(4-x)}GeI_x$] mixed tetrahedra units [19], respectively.

Based on the previous studies [12], in GeS_2-Ga_2S_3 based glasses, the formation of metal homopolar bonds (Ge-Ge or Ga-Ga) was due to the sulfur stoichiometric deficiency. After some halides introduce into these glasses, [$S_3Ge(Ga)$-$Ge(Ga)S_3$] units will be gradually substituted by [$S_{(4-x)}Ge(Ga)X_x$] (X=Cl, Br, I) mixed tetrahedra units to compensates for sulfur deficiency and for the need of homopolar metal bonds. When the atomic ratio of halogen to Ga is larger than one, complete substitution occurs, which results in vanishing of the bands at 255cm^{-1} and 270cm^{-1}. So for GGA15 glass, as the atomic ratio of I to Ga is 1/2, incomplete substitution of [S_3Ge-GeS_3] units by two [$S_{(4-x)}GeI_x$] units will results in the broad band at around 250cm^{-1} which is overlap of two bands at 255cm^{-1} and 240cm^{-1} . However, for GGB10 glass, although the atomic ratio of Cl to Ga is 1, the band at 270cm^{-1} still exist, this indicates that chloride ions do not participate in the building of the glass forming units [$S_{(4-x)}GaCl_x$] in this case. Because of the strong ion field strength, Ba^{2+} ions are supposed to homogeneously disperse in the glassy network as Cl^- ions for their nearest neighbor in the form of ($BaCl_n$) clusters, so this will confine Cl^- ions to participate in the substitution of [S_3Ga-GaS_3] units by two [$S_{(4-x)}GaCl_x$] units, which results in the exist of band at 270cm^{-1}.

As shown in the Fig. 4 and 5, after laser irradiation, the Raman spectra of both two composition glasses have some common variations: the main peak at 340cm^{-1} shifted slightly to a lower wavenumber associated with an broaden of its bandwidth, while the intensity of the whole spectra of recorded wavenumber have been enhanced a lot. At the same time, for GGB10 glass, the intensity of prominence centered at 270cm^{-1} decreased sharply, and for GGA15 glass, the broad prominence centered at around 250cm^{-1} shifted slightly to a lower wavenumber. In the case of GGB10 glass, as a result of fs-laser interaction with glass, Cl^- ions became more activity and less confined by the Ba^{2+} ions nearby, so more Cl^- ions will participate in the substitution of [S_3Ga-GaS_3] units by two [$S_{(4-x)}GaCl_x$] units, which results in a sharply decrease of the intensity of prominence centered at 270cm^{-1}. It is well known that [$Ge(Ga)S_4$] tetrahedra and [$S_{(4-x)}Ge(Ga)X_x$] complex units have an edge-sharing tendency, so in the case of GGA15 glasses, after laser irradiation, some [$S_{(4-x)}GeI_x$] units have formed [$S_{(6-x)}Ge_2I_x$] edge-sharing units, the formation of these complex units compensates for some sulfur deficiency and for the need of Ge-Ge bonds, which results in a moderate shift of prominence centered at around 250cm^{-1} to a lower wavenumber. Because of the overweight of Cl and I atoms compared to S atom, the vibration of [$S_{(6-x)}Ge(Ga)_2X_x$] edge-sharing units should located at wavenumber lower than 340cm^{-1}, which results a slight shifted of main peak at 340cm^{-1} to a lower wavenumber in both two composition glasses after laser irradiation. So after fs-laser interaction within these two glasses, some structural changes have been induced by the formation of some complex mixed units containing halogens, which decreases the rigidity and creates a more open structure of the glass. Thus, the enhanced intensity of the whole spectra of recorded wavenumber in these two composition glasses is accounted for by a greater randomness of glass structure.

According to the review of Laeticia Petit [20], the laser irradiation breaks bonds with creation of new ones in network organized in layers such as the As-based glass network leading to an increase of refractive index. However, in well organized 3-D networks, such as the Ge-based glass network, the laser irradiation only modifies the bonding between the units that forming the network leading to a decrease of refractive index. This is consistent with the GGB10 and GGA15 glasses studied here. From the photographs insert in Fig. 4 and 5, we could see that the modified glass part have a higher transmittance and lower reflectance compared to the as-prepared glass part, which indicates that the refractive index of modified glass part should lower than the as-prepared glass part, this is also the result of the relax and randomness of glass network that induced by fs-laser irradiation.

Although some structural changes have been observed according to the Raman characterization, still no crystal

structures have been induced after laser irradiation. Some researches [21-22] have reported that by irradiation of glasses with fs-laser, some functional crystals such as optical nonlinear crystals could be induced in oxide glasses. As some optical nonlinear crystals have been induced in Ga-containing GeS_2 based ChGs by heat-treatment [23-24], it should be expectantly that these crystals could also be induced by fs-laser irradiation. This is a very interesting phenomenon as we could induce crystals at arbitrary sites within the bulk glasses by using an fs-laser. The investigation of inducing optical nonlinear crystals within the bulk ChGs by optimizing the experiment parameters, and also further characterizations of the refractive index changes in waveguide lines are underway.

4. Conclusions

In summary, this work include a series of experiments on the induction of structural changes under the action of femtosecond laser irradiation in bulk sample of $70GeS_2{\cdot}15Ga_2S_3{\cdot}15AgI$ and $80GeS_2{\cdot}10Ga_2S_3{\cdot}10BaCl_2$ glasses. The influence of the recording geometry on the morphology of the structures was also investigated. And well waveguide lines with a homogeneous width of around 2μm could be created inside both two composition glasses. The structural changes inside glasses after laser irradiation have been investigated by micro-Raman scattering. It was found that some complex mixed units containing halogens have been formed as a result of laser-glass interaction, and these units make the glass network more relax and finally decreased the refractive index. These results will be valuable for next generation optoelectronic applications and use of these materials in fibers or planar structures.

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*Corresponding authors: zhengxl0615@hotmail.com