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In this paper, we present results on UV pulsed laser-induced birefringence in La_2O_3-B_2O_3-GeO_2 (LBG) glasses. Samples are irradiated at a wavelength of 355 nm delivered by an Nd-YAG laser operating in the nanosecond regime. After irradiation, glasses are analyzed by Micro Raman spectroscopy and Small Angle X-ray Scattering (SAXS). Raman spectra show figures characteristic of a light polarization rotation effect in agreement with an anisotropic distribution of the scattering intensity observed by SAXS measurements. These results are interpreted as the interaction of the glass with the electromagnetic field of the UV beam (UV poling).

Keywords: pulsed laser, glass, UV poling, birefringence, Raman spectroscopy, SAXS

1. Introduction

Since the beginning of the eighties, photosensitivity of glasses has created a great interest for the development of integrated optoelectronic devices allowing high-speed signal processing in telecommunications. This domain is still actually subjected to many studies of research because photo written optical components in waveguides can be obtained in very compact forms and at low costs. Moreover, a few years ago, it was demonstrated that permanent refractive index variations could be induced by laser irradiations. Pulsed lasers with ultrashort pulses duration are particularly adapted for waveguide inscriptions because highly localized refractive index variations can be obtained at the focal point [1]. Laser-induced defects can be responsible for photosensitivity but volume changes such as densification are considered to have the main contribution [2, 3]. Glass properties modifications proceed via photolytic or thermal pathways which are the two principal schemes of laser-light interaction [1].

In this paper, we investigate photo-induced modifications by pulsed laser irradiations of La_2O_3- B_2O_3-GeO_2 (LBG) glasses. Results are analysed in terms of birefringence in agreement with the non linear optical behaviour of the irradiated glasses. Anisotropy induced by thermal poling was previously obtained on these glasses [4]. The LBG system of the same stoichiometric composition as the stillwellite-like $LaBGeO_5$ crystal is chosen because

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second harmonic generation (SHG) $\chi^{(2)}$ signals can be obtained from this crystal characterized by a non centrosymmetric structure [5]. SHG was recently measured in surface crystallized stillwellite-type glasses with the same composition as that of our samples [6].

2. Experimental

2.1 Glasses elaboration

LBG glasses are prepared from commercial reagent-grade powders of La_2O_3, H_3BO_3 and GeO_2 mixed in a platinum crucible using a conventional melt-quenching method. The melt conditions are 1300-1320°C for 40 minutes. The melt is then quenched at room temperature. Investigated glasses are characterized by the nominal composition 25 La_2O_3, 25 B_2O_3, 50 GeO_2.

All glasses are transparent and without any crystalline inclusions. The glass transition T_g and the crystallisation T_p temperatures, determined by differential thermal analysis (DTA), are 685°C and 931°C respectively. Previous results have shown that the LBG glass crystallized in a stillwellite-type structure [7].

2.2 Samples preparation

Glass samples are cut in slices of 1 mm thick; they are mechanically polished on both sides for optical measurements and treatments. They are then cleaned in acetone. For SAXS measurements, glasses are thinned by polishing until a thickness of about 200 µm is attained to limit X-rays absorption for an optimized transmitted signal.

Before poling, glasses are annealed for 2 hours below T_g to remove internal stress. It is checked that no birefringence induced by defects and/or by the polishing process remains into the samples using a polarizing microscope in a crossed polarized configuration.

2.3 Irradiation by UV laser

The irradiation is performed by heating the glass plate to 400°C in a temperature-regulated cell (Linkam TMS 92) while injecting the focused laser beam into the sample via a microscope setup equipped with a UV objective (X15) as shown in Fig.1. The third harmonic (355 nm) of a linearly polarized Q-switched YAG laser (repetition rate = 10 Hz, pulse duration =10 ns) is used for the irradiation. The diameter of the focused beam is estimated to be around 10 µm and the laser irradiance on the sample equal to a few tens of $kW.cm^{-2}$. The laser intensity and the temperature are adjusted in order to obtain marked birefringence phenomena without cracks. After different times of irradiation at high temperature, the heater is switched off and the glass plate is cooled down to room temperature. The laser irradiation is stopped only after the cooling down of the sample to room temperature. **(Insert Fig. 1 about here)**

A moderate photolytic radiation (355 nm or 3,5 eV) is chosen for irradiation in order to avoid strong structural modifications in the glass by direct UV bond breaking [8]; this can be especially critical for the Ge-O bond present in LBG glasses : in fact, a bond energy value of 3.7 eV can be given as a good estimation from literature data on germanosilicate glasses [9]. It can be noticed that the laser wavelength is higher than the band edge wavelength located near 260 nm (Fig.2). In this case, the absorption is low at the incident wavelength and is due to the glass matrix principally if there is no strong dopant absorption [1]. In fact, the attenuation length of the wave calculated at 355 nm is in the order of the millimetre range. Consequently, the penetration depth of the radiation is limited by the focused point of the laser beam into the glass so that points of birefringence are localized at 150 -200 µm below the surface. **(Insert Fig. 2 about here)**

2.4 Light scattering analyses

Light scattering analyses are performed by sending the analysing beam perpendicularly to the S_2 surface of the glass containing the poling electric field.

2.4.1 Micro Raman spectroscopy

Raman spectra are recorded by means of a RM 100 Renishaw monochromator in a backscattering configuration using a microscope equipped with an X50 objective. The excitation source is a 514.5 nm line of an Ar laser. The laser power is equal to 50 mW. The signal detection is carried out by a cooled CCD camera.
A half wave plate is used to rotate the polarization of the incident laser beam (V vertical or H horizontal). Spectra are recorded in the VV or VH crossed configuration by keeping a constant direction for the scattered beam (V). The sample can be rotated around the axis defined by the laser beam direction: micro Raman analyses are performed at 45° of H and V axes, inside the glass. In order to focus the laser beam in birefringent regions, irradiated samples are observed in transmitted light through crossed polarizers.

2.4.2 SAXS measurements

SAXS experiments are carried out at the European Synchrotron Radiation Facility (ESRF) at Grenoble on the D2AM beam line. SAXS profiles are recorded by means of the two-dimensional detector of the line. The X-rays energy is equal to 12 keV in order to avoid the K fluorescence of germanium in LBG samples. The beam is focused on a 0.3 mm diameter spot.

3. Results

Birefringence observations on the UV irradiated samples are shown in Fig. 3. The direction of the electric field of the laser beam irradiating the glass sample is given Fig. 3a: the field is orientated along the S_2 face of the glass where birefringence effects due to the poling process can be detected. In fact, the observation of the irradiated S_2 face through crossed polarization in a microscope exhibited birefringence zones whose intensities are maximal when the electric field direction makes an angle of 45° between the polarizer (P) and analyser (A) directions (Fig. 3b). More precisely, when the sample is rotated at 360° with respect to the zero position, four positions of extinction at 0°, 90°, 180° and 360° and four positions of maximal intensity at 45°, 135°, 225° and 315° are found respectively. No degradation of the birefringence is observed after several months at room temperature. **(Insert Fig. 3a and 3b about here)**
Micro Raman measurements are performed on the laser-induced birefringence domains. For an accurate localization of these regions, glasses are observed with polarized light before probing them with the laser beam. Spectra displayed in Fig. 4 are recorded in the VH configuration at 45°. Two clear differences are observables between spectra obtained from these birefringent domains and those relative to the unmodified regions of the glass: an evolution of the intensity ratio of peaks located near 300 and 800 cm^{-1} respectively and the

growth of a new peak close to 550 cm^{-1} for spectra recorded in the birefringence area. In fact, spectra performed in birefringent regions are very similar to that obtained by probing non irradiated points in the VV configuration (inset of Fig. 4). **(Insert Fig. 4 about here)**
As shown in Fig.5 representing the 2D SAXS profile of a UV poled LBG glass, anisotropic scattering is obtained when X-rays are focused on the S_2 face: the ellipsoidal shape of the scattering figure indicates that X-rays are not scattered in the same way in the whole cone of the angle opening; in fact, they are scattered in the two mutual perpendicular directions, parallel and perpendicular to the direction of the electric field of the laser beam [10].
(Insert Fig. 5 about here)

4. Discussion

The intensity variation of light with a $\pi/2$ periodicity and the coincidence of light maxima with the electric field direction at 45° respect to the polarizers are an evidence for localized birefringence into the LBG sample (Fig. 3b). This observation is in a good agreement with microRaman measurements (Fig.4): spectra recorded in the VH configuration evolve towards the VV spectra (inset of Fig.4) when domains of birefringence are probed whereas no evolution of spectra is observed during analysis of non irradiated points. Similar results were obtained previously in thermally poled LBG glasses where orientation of hyperpolarisable moieties in the bulk sample could be responsible for birefringence effects [4].
Moreover, anisotropy is clearly demonstrated by SAXS measurements performed in laser irradiated area with this marked ellipsoidal shape of diffusion visible on Fig.5. For non poled glasses, a circular shape of scattering characteristic of isotropy is observed. One can notice that this anisotropy is stronger than that observed in thermally poled LBG samples of the same composition [10].
The origin of this laser-induced anisotropy in LBG glasses can now be discussed. No external electric field is applied during irradiation: the electric field only of the laser wave is sufficient to induce birefringence effects in the glasses and the process is comparable to UV poling. The field value is estimated to be around a few $kV.cm^{-1}$ which is very similar to field values applied during thermal poling processes [11]. Moreover, the role of temperature seems to be critical to induce birefringence: heating of the samples during irradiation increases the glass network mobility. Several mechanisms have been proposed in literature to explain the photosensitivity of different kinds of glasses. Pre-existing defects in glasses can largely contribute to refractive index variations by a photoinduced change of absorption after UV laser irradiation according to the Kramers-Krönig relationship (color centre model) [12]. This mechanism is well-known for germanosilicates glasses characterized by a defect centre at 240 nm. In our case, samples are excited by laser at the onset of the glass matrix absorption and no characteristic absorption band can be clearly evidenced at 355 nm (excitation wavelength) as shown in the inset of Fig. 1. Densification is a possible mechanism too explaining the photosensitivity of glasses. Laser-induced volume compaction or expansion can occur depending on the glass composition and structure [1]. Moreover, if chemical bonds or glass microstructure are modified under laser light irradiation, the refractive index variation will not only depends on volume modifications but also it will be strongly influenced by changes of the electronic polarisability [13]. In addition, other effects induced by laser such as stresses and changes in glass composition can also contribute to refractive index variations [1]. Until now, our results do not permit to conclude about the mechanism implied in laser-induced birefringence in LBG glasses. However, the parallel behaviour of thermal poling and UV poling leads to consider the electromagnetic field of the laser as the driven force for the birefringent effects.

5. Conclusion

A permanent change in refractive index is observed after UV nanosecond laser irradiations of LBG glasses. The interaction between the electric field of the laser wave and the glass can be interpreted as a UV poling process. This local modification could lead to directly written waveguides. New experiments are in progress and will be discussed in a next paper.

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Figures captions

Figure 1: Experimental setup used for pulsed laser irradiation of glasses. 1: pulsed laser source; 2: microscope; 3: heating cell; M_1, M_2: highly reflective mirrors at 355 nm; S: glass sample; O: objective

Figure 2: Absorption curve of LBG glasses. The arrow indicates the position of the 355 nm wavelength used for samples irradiation.

Figure 3: Localized laser-induced birefringence in LBG glasses observed with a polarizing microscope: (a) Electric field direction of the laser wave along the S_2 face of the glass, (b) Irradiated S_2 face observed through crossed polarization showing maximal intensities for the electric field direction at 45° between the polarizer (P) and analyser (A) directions. The picture covers a 2 mm x 1.5 mm area. Domains of birefringence are spreading on a length scale of about 10 µm.

Figure 4: Raman spectra performed at 45° of H and V axes, inside the glass. Spectra of the birefringent points evolve towards the VV spectra depicted in the inset.

Figure 5: Two-dimensional SAXS profile of a UV irradiated LBG glass showing the ellipsoidal shape of the figure of scattering.

Figure 1

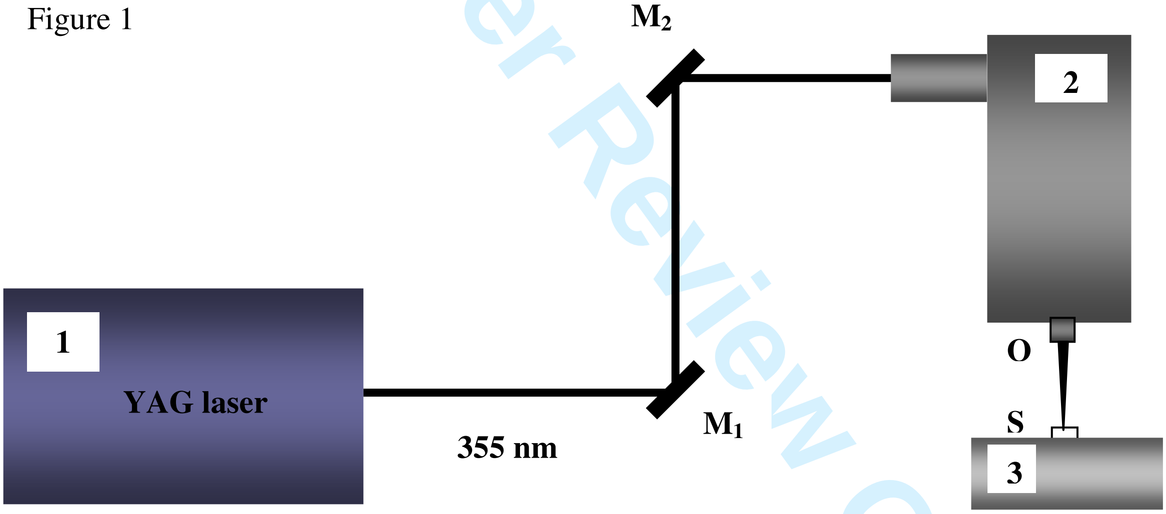

Figure 2

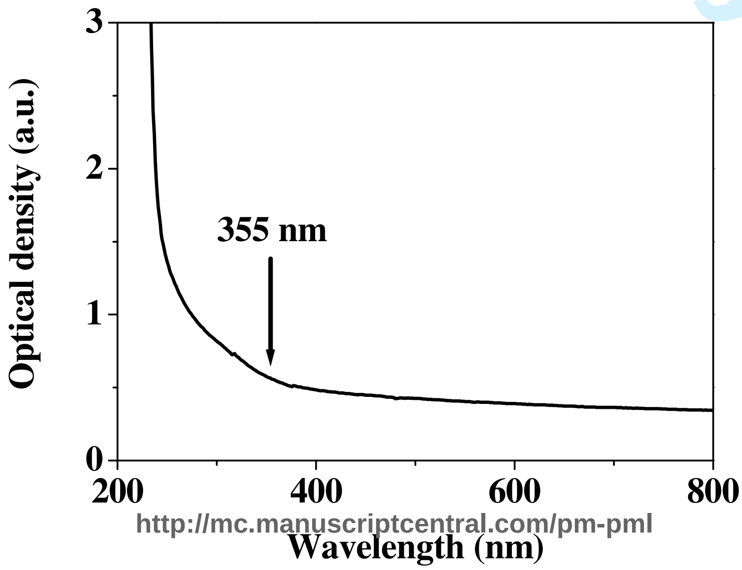

Figure 3a

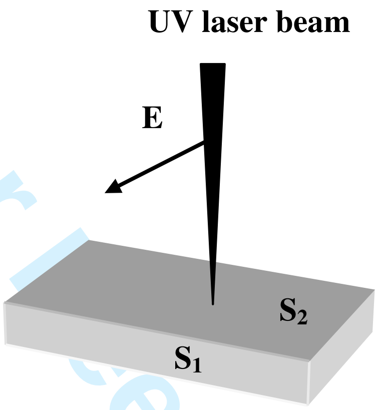

Figure 3b

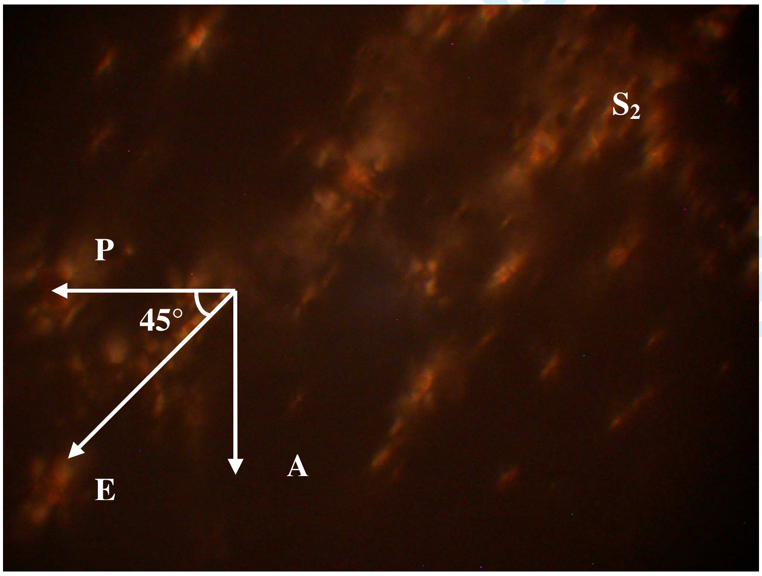

Figure 4

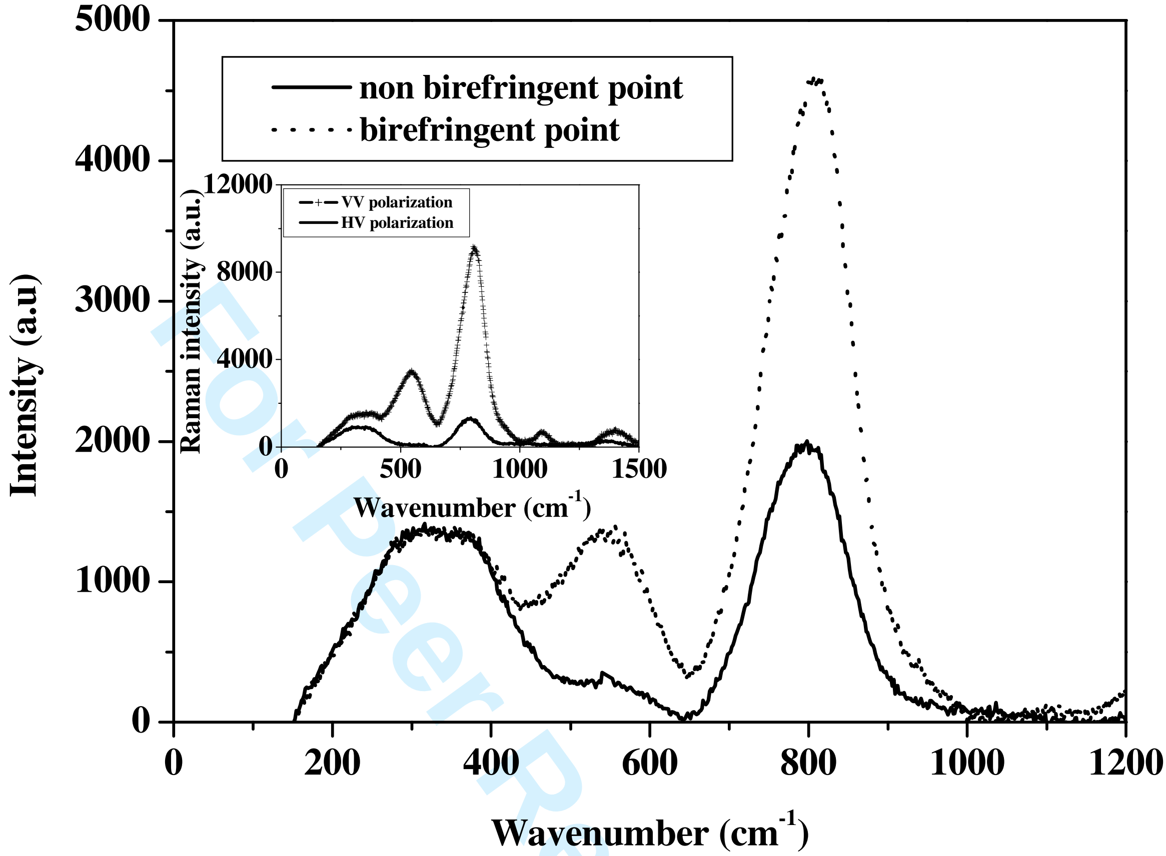

Figure 5