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## Influence of the laser on the mechanical properties of GeSe<sub>9</sub> chalcogenide glasses

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### Abstract

Photoinduced changes in the mechanical properties of Ge-Se chalcogenide glasses produced by sub-band gap energy are studied by microindentation. The results show that the irradiation leads to an increase of the mechanical properties exactly module of Young and the hardness with a decrease of the viscosity in the case of the low intensities laser and a decrease of the mechanical properties with an increase of the viscosity in the case of the high intensities of irradiation.

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Keyword: GeSe<sub>9</sub> chalcogenide glasses, microindentation, energy sub-band gap photoinduced phenomenon, mechanical behavior.

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### 1. Introduction

Chalcogenide glasses are transparent materials in the infrared but on the other hand they exhibit different changes under light. Under irradiation, for energies near or below their energy of gap, the all of physical properties of chalcogenide glasses change. This changes pass the photodarkening (increased of absorption), to photobleaching, photoexpansion [1], photofluidité [2], the photocristallisation, the change in refractive index, the decrease in elastic moduli, the photorelaxation. These effects, coupling electronic modifications with structural modifications, are still very badly understood. However, they are already exploited for their applications in optoelectronique, for the manufacture of waveguides for example. La photoexpansion can be used for the shaping of micro-objects (microlenses), while the photofluidity is used for the he shaping of fibers [1,2]. The chalcogenide glasses show different properties of their similar crystalline. The structure and configuration of bonds of these disordered materials can be changed when exposed to a radiation source of energy near or below the bandgap energy. These energies cause important changes of physical properties (mechanical, optical,...) on glasses chalcogénures and even changes in the surface of this glasses. Photoinduced phenomena caused by Sub band gap energies are: photorelaxation, photocristalisation, photofluidity, photooxidation, photoexpansion. In the present work, we studied the effect of the laser on the surface of chalcogenide glasses GeSe<sub>9</sub> system. We could also characterize by micronindentation different changes in the mechanical behavior of these glasses before and after irradiation by the infrared laser.

### 2. Experimental methods

The selenium and germanium used for the Ge-Se glasses fabrication are of high purity. The glasses were obtained using melt-quenching method. The appropriate amount of arsenic (Ge) and selenium (Se) is introduced into a silica

ampoule, sealed under vacuum. After distillation to increase purity, the mixture is introduced in an oven to be heated at high temperature, typically between 750 °C and 950° C for 24 hours. It then undergoes specific cooling cycle. After quenching in water or ambient air, chalcogenide glasses of Ge-Se system are obtained. The composition studied is: GeSe<sub>90</sub>.

To study the mechanical behavior of chalcogenide glasses after irradiation we irradiated the sample chalcogenide glass with a continuous laser ( $\lambda = 800$ ) (Fig.2) The glasses are irradiated with Subband-gap energy, the output power of laser is 400 mW .

The mechanical characterization of samples is investigated with microindentation technique. The fisherscope H100XYP microindenteur is used, with a maximum load 1N. The principle of the indentation is to apply a load on the surface of the sample. The used indenter is the Vickers type with pyramid-shaped. Young's modulus and hardness are calculated from the load-displacement curve according to the model of Oliver and Pharr [12]. The mechanical properties were measured before and after ultraviolet irradiation.

### 3. Results and Discussion

#### 3.1. Low intensities of laser

The irradiation of the sample with low intensities of energy  $E = 1.54\text{eV}$  below the gap energy ( $E_g = 1.95\text{eV}$ ) leads to an increase in mechanical properties, Young's modulus (Fig. 1.a) and the hardness figure (fig.1.b) which is also accompanied by an increase in viscosity we can conclude by the decrease in the penetration depth (Fig. 2).

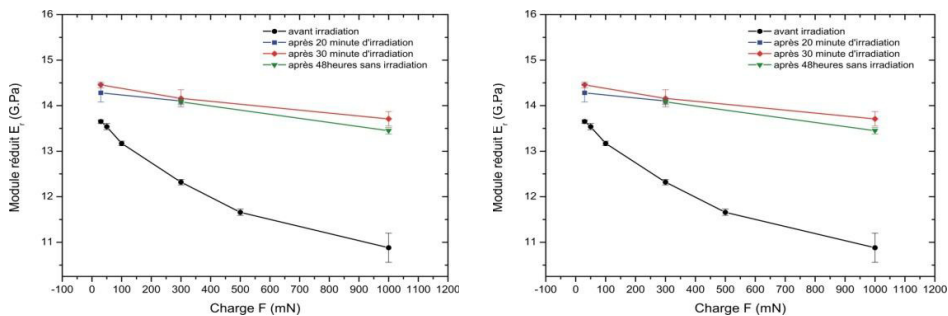


Fig.1. (a) Variation of the reduced modulus elasticity  $E_r$  as a function of the load, before and after irradiation.

(b) Variation of the hardness in function of the load, before and after irradiation.

This change in mechanical behavior that occurs in chalcogenide glasses under illumination by Subband-gap light with low intensity are accompanied by structural relaxation [6].

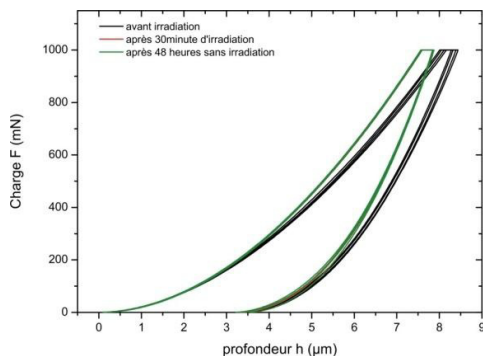


Fig.2. Response load / penetration depth with a maximum load (1000 mN) in the Ge10Se90 sample before and after laser irradiation.

### 3.2. High intensities of laser

In this second experiment, we worked with the same laser; we just changed the irradiation time (10 minutes) and the distance between the laser and the sample (2cm). In this time we observe a change in the surface after irradiation, we observe the formation of a crater with 1.7 mm of diameter (Fig. 3) in the area where the laser beam was focused.

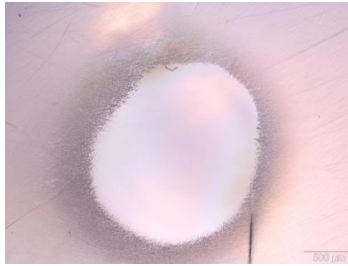


Fig. 3. Optical microscope image of the exposed region.

We observe a region that extends; it is a manifestation of giant photoexpansion. This expansion occurs as a result to expansive forces and the fluidity of an illuminated volume. We note here that the surface of the irradiated area is much smoother than that of the non-irradiated region. Depending on the intensity of the laser used and the irradiation time, we observe a photofluidity or photoexpansion of irradiated area (Fig. 4). The two phenomena represent a change in volume in this area.

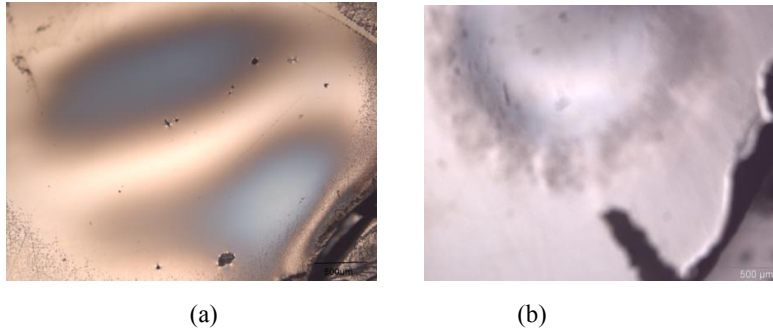


Fig.4. Influence of the laser on the glass surface, (a) photofluidity, (b) photoexpansion.

However photoexpansion the phenomenon is probably the easiest to understand because it simply results in a change in the density of atomic packing and it disappears only through structural relaxation. The photoexpansion disappears after annealing [3]. Then a laser exposure led to an increase in penetration depth up to 4.5 micro for a load of 300 mN (Fig.5). We can assume that the exposed region becomes more viscous. It should be emphasized that such a deformation is produced by the effect of light and not temperature.

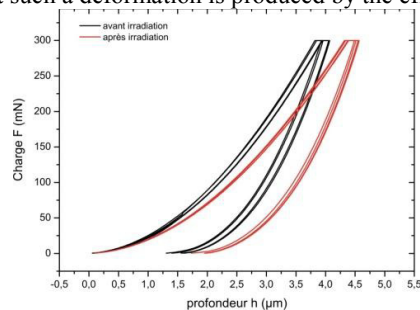


Fig.5. Response load / penetration depth with a maximum load (1000 mN) in the Ge<sub>10</sub>Se<sub>90</sub> sample before and after laser irradiation.

We conclude that in the context of photoinduced phenomena, the mechanical properties are sensitive to different parameters: intensity of the irradiation source, wavelength, glass dimensions or distance between the sample and the irradiation source (the laser). In the case of high intensity a decrease in the Young's modulus (fig. 6.a) and hardness (Fig.6.b) occurs.

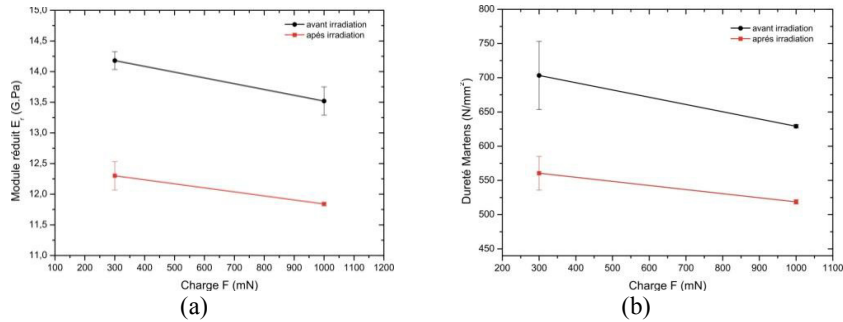


Fig.6. (a)Variation of the modulus of elasticity  $E_r$  reduced as a function of the load, before and after irradiation  
(b)Variation of the hardness as a function of the load, before and after irradiation.

A model recently discovered by Tanaka and Hisakuni could explain the photoinduced fluidity in chalcogenide glasses based on which the atomic motions and the connections between the different atoms that also cause a variety of reversible and irreversible photostructural changes of chalcogenide glasses. They mounted the photofluidity it is not caused by the heating of the material but by the photoelectronic excitations caused by photons of energy less than or equal to the bandgap [4].

#### 4. Conclusion

We studied the effect of light on the sub-bandgap chalcogenide glasses GeSe<sub>9</sub>, by using microindentation technique. After irradiation by the infrared laser two types of structural changes are observed. For low intensities the relaxation of the glassy system occurred along with increased of mechanical properties (Young's modulus, hardness) while for high intensities of the laser the photoexpansion or photofluidité occur with decrease of mechanical properties. Concerning applications, photoinduced fluidity can be used for manipulating microscopic forms of chalcogenide glasses, for example, a modified form of As<sub>2</sub>S<sub>3</sub> fiber was already demonstrated [5]. On the other hand, the giant photoexpansion was used to produce optical components such as microlenses [6,7].

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