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Femtosecond laser-induced damage characteristics of mid-infrared oxyfluorogallate glass

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HIGHLIGHTS

- A novel oxyfluorogallate glass with good mid-infrared property was provided.
- Femtosecond surface damage characteristics of oxyfluorogallate glass are investigated.
- Femtosecond nonlinear effect is studied to explain the damage mechanism.
- Surface damage thresholds show an evident reduction as pulses number increasing.
- No changes on the chemistry structure occur after femtosecond laser ablation.

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ABSTRACT

The femtosecond laser-induced damage characteristics of a novel oxyfluorogallate glass with good mid-infrared property are analyzed in detail and the surface-damage thresholds for single- and multi- pulses ablation are determined and an evident reduction trend is obtained. The nonlinear absorption coefficient measured through the femtosecond laser z-scan method is used to explain the damage mechanism according to the calculation of Keldysh parameter. The ablation characteristics of the oxyfluorogallate glass demonstrated a clear evidence of melting and the ablation rate decreased in the presence of the melting phenomenon. Based on subsequent X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy analyses, the chemistry of the mid-infrared oxyfluorogallate glass appeared to remain constant before and after femtosecond laser ablation. This work provides a reference to manufacture infrared optical devices and is useful in promoting the application of the mid-infrared glass material.

1. Introduction

In recent years, the usage of infrared windows and optics has received considerable attention by military and civilian applications such as infrared imaging, night vision, remote sensing, and free space optical communication [1,2]. The damage to infrared windows and optics induced by femtosecond laser pulses, which can restrict energy within the minimal range of both space and time, is meaningful for both fundamental physics and the applications of miniaturized and functional infrared devices. A series of infrared materials including sapphire, fused silica, calcium fluoride (CaF_2), ceramics (Al_2O_3 and AlN), borosilicate, and soda-lime glass have been studied for the damage characteristics of femtosecond, picosecond, and nanosecond lasers serving the microfabrication process [3–6]. The most significant discovery from these works was the deviation from the pulse duration dependence of the damage threshold. In the long-pulse regime, the thermal effect through the atomic lattice that scales with the pulse duration dominates the interaction process owing to the energy transfers from the electron subsystem to the lattice in this regime, which induces thermalization [7]. Whereas in the short-pulse regime, because it requires only several hundred femtoseconds to several picoseconds for electron distribution to attain thermal equilibrium [7,8], the thermal effect can be suppressed. The optical breakdown is primarily a non-thermal process despite the fact that it also generates heat and the nonlinear effect becomes important in this process [9]. Thus, the nonlinear and damage researches in the short-pulse regime are vital owing to the capacity to obtain a high-precision microstructure through the short-pulse laser micromachining of the materials.

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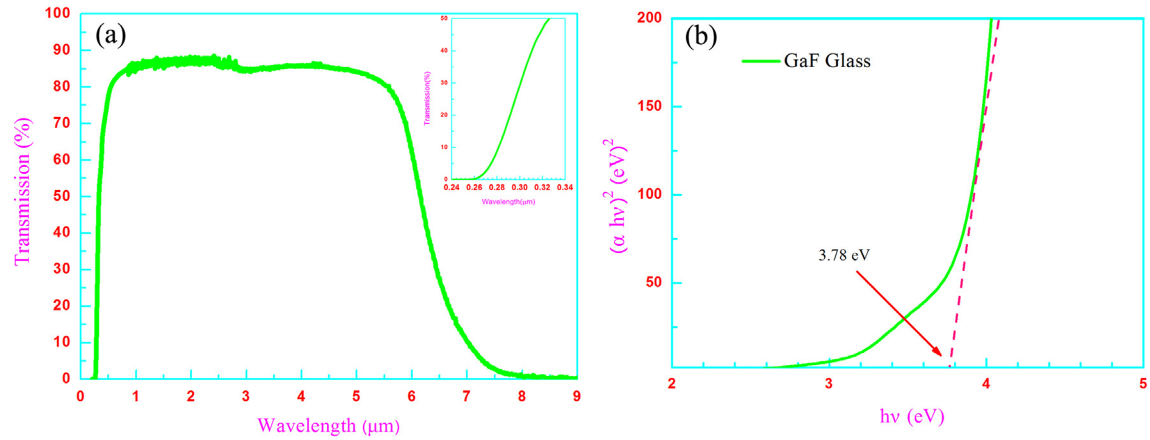

Fig. 1. Transmission performance (a) and bandgap (b) of mid-infrared oxyfluorogallate glass with the thickness 1 mm.

In the mid-infrared spectral region from 2 to 5 μm, oxyfluoride glasses are particularly promising materials owing to their low intrinsic loss (1 dB/km at 2.5 μm) and suitable matrix materials doped with rare earth ions for mid-infrared optics application [10,11]. To date, researches including optical waveguides [12,13] and the high-laser induced damage threshold [14] have been reported for oxyfluoride glass. However, fewer investigations of femtosecond-induced damage have been reported for mid-infrared oxyfluorogallate glass [15], which has a high refractive index (1.7), high density (4.4), acceptable chemical and mechanical stability, low OH^- content (< 2–5 ppm), wide infrared transmission range, acceptable thermal properties, the ability to prepare large-sized samples (up to 500 mm), and low cost compared with other infrared materials. Owing to these characteristics, it is useful for optical applications and has been an attractive alternative material for infrared devices. Moreover, as a kind of heavy metal-ion glass, oxyfluorogallate glass possesses a large nonlinearity. Hence, it is important and interesting to study the nonlinear optical property and damage characteristics of oxyfluorogallate glass in the short-pulse regime.

In this work, we firstly investigate the infrared transmission properties and bandgap of mid-infrared oxyfluorogallate glass material, then the damage threshold values for the femtosecond laser single- and multi- pulses are studied. The nonlinear optical property is also measured and analyzed based on the bandgap and laser wavelength to explain the ablation mechanism according to the Keldysh parameter using the femtosecond z-scan technique. Moreover, the damage characteristics including incubation effect and ablation rate for single- and multi-pulses ablation of mid-infrared oxyfluorogallate glass during femtosecond laser ablation are researched to provide a reference for microstructure fabrication. Finally, the possibility of changes occurring in the chemistry components before and after femtosecond laser ablation is determined by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy.

2. Experiments

Glass samples with molar composition of $10BaF_2$–60CaO–$30Ga_2O_3$, called FGa glass, were prepared by conventional melting and quenching methods at 1400 °C for 30 min in a covered platinum crucible under a nitrogen atmosphere. After sufficient melting, the glass melt was cast by pouring into a preheated platinum mold and annealed in a furnace near the glass transition temperature. The annealed samples were fabricated to the size of 10 mm × 10 mm × 1 mm and polished for optical property measurements. The optical absorption and transmission spectra of the samples were collected from 0.2 to 2.5 μm using a Perkin-Elmer Lambda 750 UV/VIS/NIR spectrophotometer and Fourier transform infrared spectroscopy (FT-IR, Nicolet 6700 Spectrometer, Thermo Nicolet, USA) over a range of 2.5–10 μm. The band gap energy was obtained from the cutoff range of the ultraviolet spectrum.

The ablation of these samples were performed in normal atmospheric conditions using a high repetition rate and one-box ultrafast amplifier with direct diode pumped technology developed by Spectra-Physics. The laser wavelength λ used in the experiment was 520 nm, the pulse duration was 350 fs, the adjustability of the repetition rate was from single shot to 1 MHz, and the maximum single pulse energy was up to 40 μJ. The objective was from Olympus with a multiple of 10× and an N.A. of 0.3. The focal length of the objective is about 10 mm. The width and depth of the ablation craters were measured using a field emission-scanning electron microscopy (FE-SEM, ZEISS, Germany) and an atomic force microscope (AFM), respectively. To examine the changes in the chemical composition of the ablated samples, the unablated and ablated samples were analyzed using X-ray photoelectron spectroscopy (XPS) measurement (Microlab 310F) and Raman spectroscopy measurement (LabRAM HR Evolution, Horiba). All of the measurements were conducted at room temperature.

3. Results and discussion

3.1. Infrared-visible spectral and bandgap of FGa glass

To determine the suitability for potential applications in mid-wavelength infrared windows, the UV/VIS/IR transmission spectra and the bandgap energy of the FGa glass samples with the thickness 1 mm were measured. The results are displayed in Fig. 1. The infrared cutoff wavelength of FGa glass was approximately 6 μm. The FGa glass demonstrated acceptable infrared transmittance of 85% and visible transmittance of 87%. The transmission loss was primarily attributed to the Fresnel reflections and the scattering as well as the absorption can approximately be ignored. An OH^- absorption peak (2.7 μm) was not observed in all the FGa glass samples, which indicated that the glass samples had acceptable water removal abilities. Owing to the isoelectronic properties and similar ionic sizes of the F^- and OH^- ions, the F^- ions could efficiently replace the OH^- ions during glass melting [16]. The ultraviolet cutoff wavelength of FGa glass was approximately 280 nm as indicated in the inset of Fig. 1(a). The absorption edge of the FGa is attributed to the band gap (E_g), which can be calculated by the Urbach plot expressed as an $(\alpha h\nu)^2 \sim h\nu$ diagram, using the following formulas [17]:

$$\begin{cases} \alpha = \frac{1}{d}\ln\frac{1}{T} \\ \alpha h\upsilon = B(h\upsilon - E_g)^{1/2} \end{cases} \tag{1}$$

where α is the optical absorption coefficient, d is the sample thickness, T is the transmittance, $h\upsilon$ is the photon energy, and B is a constant. The E_g value is obtained from the crossing point of the x axial and the tangent