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Optical and nonlinear optical properties of copper nanocomposite glasses annealed near the glass softening temperature

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Abstract

Copper nanocomposite glasses have been prepared by the ion-exchange method, and annealed at different temperatures up to and above the glass softening temperature. The absorption spectra, fluorescence spectra, and nonlinear optical transmission of the samples at 532 nm for nanosecond laser pulses, have been investigated. The optical and nonlinear optical properties of the glasses are found to be distinctly different below and above the glass softening temperature. For instance, thermal annealing up to the glass softening temperature makes the samples behave like saturable absorbers, while annealing at higher temperatures makes them behave like optical limiters. Such flexibility in controlling the optical nonlinearity in these materials makes them potential candidates for photonic applications.

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Keywords: Metal nanocomposite; Nonlinear absorption; Optical limiting; Saturable absorption; Surface plasmon resonance

1. Introduction

Metal nanocluster composite glasses (MNCGs) are potential candidates for photonic nanodevice fabrication. For instance, their large and fast optical nonlinearity can find applications in optical switching devices. Nanocomposite glasses can be prepared through the sol–gel [1], melt-quench [2], ion implantation [3,4] and ion-exchange [5] methods. Among these, ion-exchange is one of the oldest and most successful techniques. Noble metal clusters (copper, silver and gold) have gained a lot of attention because of their optical nonlinearities, which are substantial due to the surface plasmon resonances (SPR) lying in the visible region. The dispersive third order nonlinear susceptibility $\chi_m^{(3)}$ of metal nanoclusters will be very strong when excited near the SPR, due to the local field enhancement effect. The use of MNCGs as ultrafast optical switches is known before [6], and there are previous reports on their near and off-resonant nonlinear optical properties at various cluster sizes [3,7]. Thermal annealing is a common route used for changing the particle size.

In the present work, we have prepared copper nanocomposite glasses by the ion-exchange method, which are annealed at different temperatures up to and above the glass softening temperature (600 °C). The absorption and fluorescence spectra of the samples have been measured. The nonlinear optical transmission of nanosecond laser pulses through the samples also has been measured at the

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wavelength of 532 nm. The nonlinearity is found to originate mostly from the Kerr nonlinearity and free carrier absorption occurring in the samples. In general, the samples are found to behave as saturable absorbers below the glass softening temperature, and optical limiters above the glass softening temperature. Thus the glass softening temperature turns out to be a critical control parameter for optical nonlinearity in these materials. This observation may be generally true for glass hosts embedded with nonlinear media, in which case it is important information for fabricating photonic devices with controlled and predesigned optical nonlinearities.

2. Experimental

In our experiment, metal ions are incorporated into sodalime glass through the thermal ion-exchange method. Commercial soda lime glasses are initially cleaned using an ultrasonic cleaner. The glass slides are then immersed in a molten salt bath containing $CuSO_4$ and Na_2SO_4 in the 1:3 wt. ratio. The ion-exchange process is allowed to take place at 500–560 °C for a period of 1 min. The copper ions in the molten salt bath penetrate and occupy the sites left by the Na^+ ions which are the glass modifiers in the host matrix. The prepared glass slides are air annealed at 500, 550, 600 and 650 °C (Cu-500, Cu-550, Cu-600 and Cu-650, respectively) for 5 h and then furnace cooled. Transmission electron micrographs (TEM) of the as-prepared glass, obtained using a Teenai F30 machine, are shown in Fig. 1. The pictures reveal that the as-prepared Cu nanoclusters are about 3–4 nm in diameter.

Optical absorption spectra were recorded using a dual beam Perkin Elmer spectrophotometer. Steady state fluorescence spectra were recorded using a Perkin Elmer spectrofluorometer, with a xenon arc lamp source and a photomultiplier detection system. Samples were excited at 340 nm and the fluorescence spectra were recorded from 550 to 660 nm.

To measure the optical nonlinearity, open aperture z-scan measurements were done at 532 nm using 7 ns laser pulses from a frequency-doubled Nd:YAG laser (Quanta Ray-Spectra Physics). In the z-scan the laser beam is focused using a lens, and the sample is translated along the beam axis (z-axis) through the focal region over a distance several times that of the diffraction length. At each position z the sample sees a different laser intensity, and the position dependent (ie, intensity-dependent) transmission is measured using an energy meter placed after the sample. Laser pulses are fired at a repetition rate of 1 Hz, and the data acquisition is automated. The low repetition rate is chosen for avoiding heating-up of the samples during measurement. The pulse energy reaching the sample is approximately 60 μJ.

3. Results and discussion

The optical absorption spectra of the Cu nanocomposite glasses are shown in Fig. 2. All spectra show the surface plasmon resonance (SPR) around 560 nm. Under the dipole approximation, Mie theory gives the extinction cross-section of spherical nanoparticles as [8]

$$\sigma_{\mathrm{ext}}(\omega) = 9p\frac{\omega}{c}\varepsilon_d^{3/2}\frac{\varepsilon_{m(R)}(\omega)}{[\varepsilon_{m(I)}(\omega)+2\varepsilon_d]^2+\varepsilon_{m(R)}^2(\omega)} \tag{1}$$

where p is the volume fraction, and ω is the applied optical frequency. The SPR maximum occurs at $\varepsilon_m(l)(\omega) + 2\varepsilon_d = 0$ where $\varepsilon_m(\omega) = \varepsilon_{m(R)}(\omega) + i\varepsilon_{m(I)}(\omega)$ is the frequency dependent, complex dielectric constant of the metallic particle, and ε_d is the dielectric constant of the host matrix which is assumed to be real and nondispersive. The SPR is superposed over the interband absorption that gains strength in the short-wavelength region in the measured spectral range. The net absorption increases with annealing temperature up to the glass softening temperature, after which it is found to decrease. In fact the absorption of

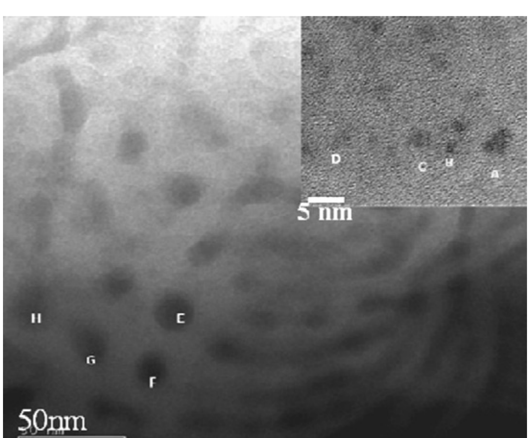

Fig. 1. TEM micrographs of as-prepared Cu nanocomposite glass (labels A–H represent the Cu nanoparticles).

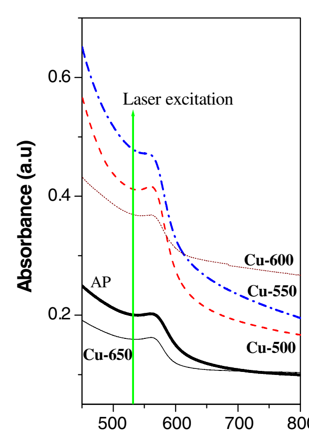

Fig. 2. Optical absorption spectra of annealed Cu nanocomposite glasses. Annealing was done at various temperatures for 5 h. Glass softening temperature is 600 °C. AP means as-prepared glass.