Ultrafast dynamics in CdSSe-doped glasses

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There has been considerable interest in nonlinear optical properties of semiconductor-doped glasses, since they have large optical nonlinearity with a fast response time [1]. In recent years attention has been given to below band gap nonlinearities of semiconductor-doped glasses [2, 3]. Although the value of the optical nonlinearity is rather small, the response time can be very fast. In this letter, we report femtosecond dynamics in semiconductor-doped glasses below the band gap.

The samples investigated were commercial CdSSe-doped filter glasses: Asahi R-64, R-66; Hoya R-64, R-66, R-68; Schott RG645, RG665; and Corning 2–58 and 2–64. CdS-doped glass L-42 and undoped glass Y-0 were also investigated for comparison. Thickness of samples was approximately 2.5 mm. The concentration of CdSSe was approximately 0.4 wt % [4]. Sizes of CdSe nanocrystals were around 8 to 30 nm [4]. The degenerate four wave mixing (DFWM) experiments were performed with a Ti-sapphire laser and a regenerative amplifier (Spectra Physics Tsunami and Spitfire: wavelength = 780 nm, pulse duration = 130 fs, peak power density = 0.5–1 TW/cm^2, repletion rate = 1 kHz) using a box-car configuration at 300 K. The laser beam was divided into three parts: two pump beams and a probe beam. All beams were polarized in the same direction. Pump and probe beams were focused by a single lens on the surface of the sample. The peak power density of pump light was approximately 0.2 TW/cm^2, and that of probe light was 0.03 TW/cm^2. The time delay between the pump pulse and the probe pulse was adjusted by an optical delay line. Transient absorption in the infrared range was measured using pump and probe technique. Pump and probe pulses were delivered from optical parametric oscillators. The peak power density of pump light was 0.75 TW/cm^2. Wavelength of pump light was 482 nm, and that of probe light was 3 μm.

DFWM signal was observed in all glasses investigated. Fig. 1 shows dynamics of DFWM signal for Asahi Y-0, L-42 and R-64. There are two contributions to the DFWM signal. The fast contribution is observed in all glasses investigated. The profile of the fast contribution as a function of the time delay between pump and probe pulses follows closely that of the laser pulse. Note that the fast contribution is observed in glass without the semiconductor (Y-0). Since signal intensity of the fast contribution in the undoped glass is the same as those in the doped glasses, the fast contribution is attributable to the glass matrix. It is reported that the intensity of nearly degenerate frequency mixing signal in BK7 glass, which does not contain semiconductor, is comparable with those of CdSSe-doped glasses [3]. The nonlinearity of the glass is mainly due to electronic polarization of bound electrons.

The slow contribution is observed in glasses with longer cut-off wavelength: R-64, R-66 etc. Fig. 2 shows dynamics of DFWM signal for Asahi R-64 and Hoya R-68. The decay time of the slow contribution is approximately 4 ps for Asahi R-64 and 6 ps for Hoya R-68. Other samples also show similar decay times. The relative intensity of the slow contribution increases with decrease in band gap energy of semiconductor, E_g. The band gap energy corresponding to the absorption edge was derived from the measured cut-off wavelength. The value of E_g is 1.97 eV for R-64, 1.91 eV for R-66 and 1.85 eV for R-68. Two-photon absorption occurs when ratio of photon energy of laser light to band gap energy of semiconductor, $h\nu/E_g$, is larger than 1/2. When the value of $h\nu/E_g$ approaches to one, two-photon absorption is enhanced. It is reported that two-photon absorption coefficient at 790 nm ($h\nu = 1.57$ eV) is 0.022 cm/GW for RG630 ($E_g = 2.00$ eV) and 0.032 cm/GW for RG665 ($E_g = 1.89$ eV) [5]. Since the photon energy, $h\nu$, is 1.59 eV in the present experiments, the value of $h\nu/E_g$ is 0.86 for R-68. This value is close to one. Consequently, two-photon absorption is enhanced in R-68. Therefore, the slow contribution is considered to be attributable to photogenerated carries generated by two-photon absorption in semiconductor nanocrystals. The dynamics of this signal are indicative of carrier relaxation behavior. Relative intensity of slow contribution decreases with decrease in the value of $h\nu/E_g$ as shown in Fig. 3. The value of $h\nu/E_g$ is 0.86 for R-68, 0.83 for R-66 and 0.81 for R-64. Two-photon absorption may be very small in L-42, since the value of $h\nu/E_g$ is small (0.53). Consequently, the slow contribution is not observed in L-42 as shown in Fig. 1.

In order to confirm the assumption described above, we measured intensities of fast and slow contributions to the DFWM signal as a function of laser intensity for Hoya R-68. If carriers are generated by two-photon absorption, I^5 dependence should be observed, where I is the laser intensity (power density of laser light). I^5 dependence is typical for a fifth-order nonlinearity attributed to electron-hole pairs generated by two-photon

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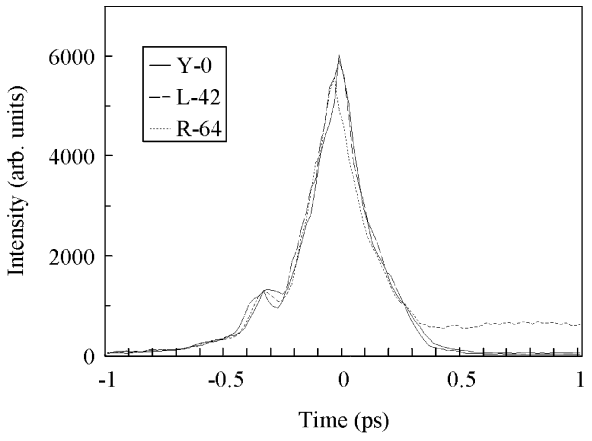

Figure 1 Dynamics of DFWM signal for Asahi Y-0, L-42 and R-64. Peak power density of laser light is 0.5 TW/cm^2.

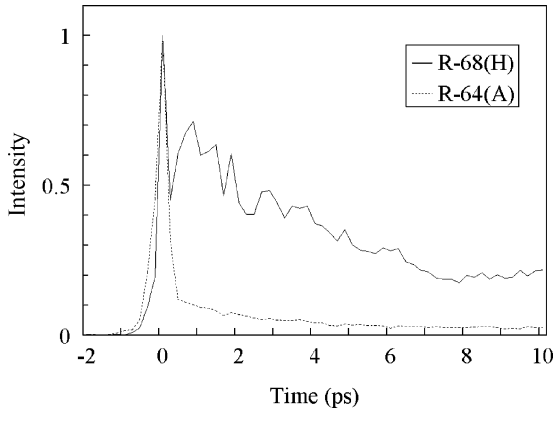

Figure 2 Dynamics of DFWM signal for Asahi R-64 and Hoya R-68. Peak power density of laser light is 0.5 TW/cm^2. Signal intensities at $t = 0$ ps are normalized.

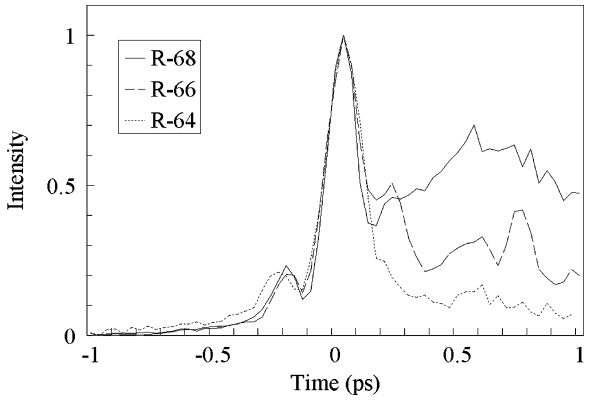

Figure 3 Dynamics of DFWM signal for Hoya R-64, R-66 and R-68. Peak power density of laser light is 0.5 TW/cm^2. Signal intensities at $t = 0$ ps are normalized.

absorption. Fig. 4 shows the results. Other samples also show similar results. The fast contribution shows I^3 dependence. This behavior is typical for a third-order nonlinearity. The slow contribution shows nearly I^4 dependence. This behavior is apparently typical for a forth-order nonlinearity. However, isotropic media, such as semiconductor-doped glasses, have only odd order nonlinearities. We consider that photodarkening [6] reduces the slope of the curve for the slow contribution, since we measured the intensity dependence of the

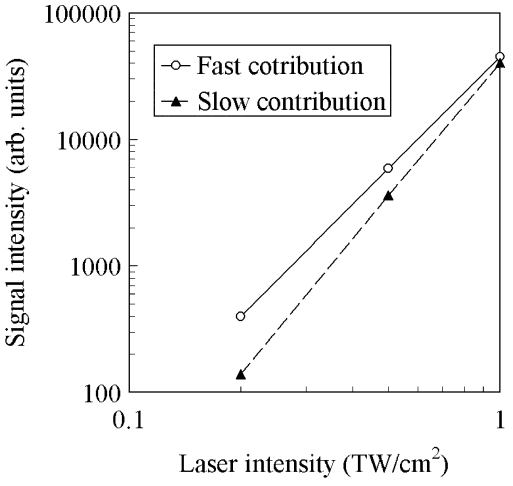

Figure 4 Intensities of fast and slow contributions to the DFWM signal as a function of laser intensity for Hoya R-68.

DFWM signal with increasing laser intensity, and the measured samples were not darkened prior to the measurement. Photodarkening is considered to be due to photoinduced defect centres which act as nonradiative recombination centres [7, 8]. Consequently, the intensity and response time of nonlinear signal decreases by light irradiation. The intensity of the slow contribution decreases after irradiation of laser light for a long time. When peak power density of laser light is 1 TW/cm^2 and irradiation time is 10 min, the intensity after irradiation is about 60% of initial intensity for Hoya R-68. Other samples also show similar results.

Since surface states of semiconductor nanocrystals are located below the conduction band of semiconductor, filling of the surface states by one-photon absorption may occur, and it may cause nonlinearity. However, it should show I^3 dependence. This disagrees with the I^4 dependence shown in Fig. 4. Therefore, two-photon absorption is considered to be dominant in the present experiments.

In order to compare the decay times of photogenerated carriers with those evaluated from another experimental method, we measured transient absorption in the infrared range. In this experiment, carriers are generated by inter-band transition from valence band to conduction band of semiconductor nanocrystals. Photogenerated carriers cause absorption in the infrared range by intra-band transition from the lowest state in the conduction band to higher states in the conduction band (or valence band). Therefore, the intensity of absorption is related to the population of photogenerated carriers, and the dynamics of absorption signal are indicative of carrier relaxation behavior [9]. Fig. 5 shows the transient absorption of Hoya R-68. The decay time is approximately 1 ps. This value should be almost the same as that of slow contribution of the DFWM signal. However, the decay time of the former is shorter than that of the latter. The difference in the decay times between the transient absorption and the DFWM is considered to be due to photodarkening and Auger effect [10]. Since photon energy of pump light (2.57 eV) is higher than band gap energy of semiconductor (1.85 eV) in R-68, high density of carriers are generated

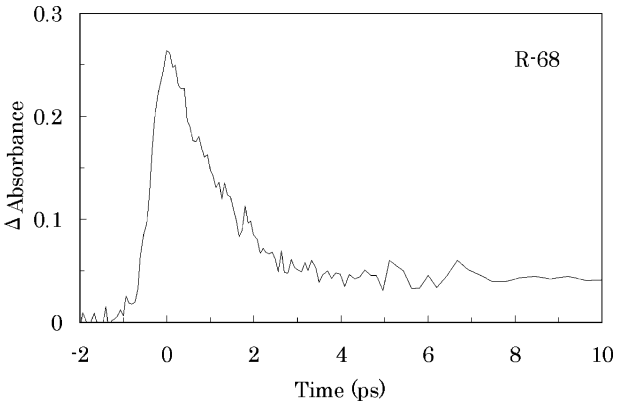

Figure 5 Transient absorption of Hoya R-68 in the infrared range. Peak power density of pump light is 0.75 TW/cm^2. Wavelength of pump light is 482 nm and that of probe light is 3 □m.

by one-photon absorption for the transient absorption experiment. Consequently, electron-electron interaction leading to Auger recombination may be efficient and may cause a substantial shortening of the response time. Photodarkening also causes shortening of the response time [6].

In summary, femtosecond dynamics in semiconductor-doped glasses were investigated by DFWM experiments. Two contributions were separately observed in DFWM signal. The fast contribution is attributable to glass matrix. The slow contribution is attributable to photogenerated carriers in semiconductor nanocrystals. The decay time of the slow contribution is approximately 5 ps. On the other hand, the decay time of transient absorption in the infrared range is about 1 ps. Difference in the decay times is attributable to photodarkening and Auger effect.

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