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Ultrafast carrier dynamics in CdS-doped glasses

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Abstract

Luminescence dynamics of CdS-doped glasses were measured using up-conversion technique, and they were compared with transmission dynamics. An analysis of the decay curves of luminescence and transmission dynamics has been performed using a multi-exponential fit. Although slower decay component is large in transmission dynamics, it is negligibly small in luminescence dynamics. This difference is observed in all samples investigated, and this may be caused by the difference in relaxation paths of electrons and holes in CdS nanocrystals. Effect of induced absorption on transmission dynamics was examined.

Keywords: CdS; nanocrystal; photoluminescence; carrier dynamics

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1. Introduction

During last decade, great scientific effort has been made to investigate semiconductor nanocrystals. This effort was stimulated by fundamental questions of physics as well as by application prospective. The three-dimensional confinement of carrier wave-functions leads to the appearance of discrete energy levels, the position of which is given by the nanocrystal size (effect of quantum confinement). The physical properties of semiconductor nanocrystals are influenced strongly also by the presence of a great number of atoms located on the surface of nanocrystals, which give rise to a number of (intrinsic) surface states for charge carriers. Moreover, nanocrystals usually have a number of adatoms and/or vacancies preferably on the surface, which lead to additional (extrinsic) surface states. Semiconductor doped glasses are one of the most studied nanocrystalline systems. They have a large optical nonlinearity and a fast response time [1]. They have great potential in optoelectronic application, where carrier dynamics are of great importance. In this paper we report on ultrafast photoluminescence dynamics of a series of CdS-doped glasses, which were measured by up-conversion technique and compared with transmission dynamics.

2. Experiment

The samples investigated were commercial CdS-doped filter glasses: Asahi Y-44, Y-46, Y-48; Hoya Y-44, Y-46, Y-48; Corning 3-73, 3-72, 3-71; and Schott GG455 and GG475. Absorption edges of these glasses are approximately 430 nm for Y-44, 3-74; 450 nm for Y-46, 3-73, GG455; and 470 nm for Y-48, 3-71, and GG475. Different positions of the absorption edge are due to the different nanocrystal sizes (effect of quantum confinement). Thicknesses of samples for luminescence measurement were about 2.5 mm, and those for transmission measurement were about 0.2 mm. The concentration of CdS was about 0.4 wt%.

Luminescence and differential transmission were measured at 300 K. The excitation source was a frequency-doubled Ti:sapphire laser (Spectra Physics Tsunami 3960; wavelength = 410-440 nm, pulse duration = 80 fs, energy per pulse = 1 nJ, repetition rate = 82 MHz). Since the peak power density of laser light was intense (about 100 MW/cm^2), samples were photodarkend before measurement in both types of experiment. The luminescence dynamics were measured using standard up-conversion technique with time resolution of approximately 0.5 ps. In this

set-up, luminescence was overlapped spatially with the switching femtosecond pulse at fundamental laser wavelength in a non-linear BBO crystal to produce the light at the sum-frequency. This up-converted signal was detected by a photon-counting photomultiplier module (Hamamatsu). The luminescence dynamics were monitored by changing the time delay between the excitation of the sample and the switching laser pulse using an optical delay line.

Differential transmission was measured using standard single colour pump and probe technique with time resolution of 0.1 ps. In this set-up, the laser beam was divided into two parts: a pump beam and a probe beam. A combination of half-wave plate and of polarizers was used to set mutually orthogonal linear polarizations of both beams. Pump and probe beams were focused by a single lens on the surface of the sample under an angle of 5 degree. The pump beam was chopped at 1 kHz, a photodiode and a lock-in detection was used to measure the modulated part of the probe beam. The time delay between the pump and probe pulses was adjusted by an optical delay line.

3. Results and discussion

In our absorption experiments, we monitor the changes in the intensity of the transmitted probe beam caused by the pump. Due to a fairly large thickness of the samples we can use the often used approximation and associate the measured changes of the probe pulse energy with absorption. The changes of absorption can be understood as composed of two contributions, namely of bleaching (an increase in the transmission, *i.e.* a positive contribution to the signal) and of excited state absorption (a negative contribution to the signal, induced absorption). The bleaching signal is given by a difference of the electron and hole occupation numbers of states at given photon energy. The contribution of the excited state absorption is proportional to occupation numbers of excited carriers and absorption cross-section at given wavelength.

Transmission dynamics reflect relaxation, trapping and recombination of carriers. In particular, the decay of bleaching is given by the rate at which the energy states of photoexcited carriers are depleted (by carrier relaxation and/or trapping). This rate usually depends on the carrier excess energy. Due to the bandwidth of pulses used in the femtosecond experiments and due to a large hole-electron mass ratio (about seven times), the bleaching dynamics are dominated by the electron contribution [2]. A large excess energy of photo-excited carriers leads

to a faster carrier relaxation and more efficient trapping. The excited state absorption in semiconductor nanocrystals is not strongly spectrally selective and that is why its dynamics reflects rather the whole number of photoexcited carriers and is not influenced by fast relaxation processes. The quality of the nanocrystal surface affects inherently the trapping rate and excited state absorption which is mainly due to the surface states.

The decay of photoluminescence (proportional to the product of electron and hole populations) reflects rather the hole dynamics [3].

3.1 Comparison of transmission dynamics with luminescence dynamics

Here we concentrate mainly on three filters with nominal absorption edge at about 450 nm fabricated by different producers. Dynamics of differential transmission are shown in Fig. 1 for three samples, namely Corning 3-72 (upper curves), Asahi Y-46 (middle curves), and Hoya Y-46 (lower curves). Differential transmission is defined as follows: $\Delta T/T = (T^*-T)/T$, where T and T^* are transmissions in the absence and in the presence of the pump, respectively. The measured curves are shown with the fitted curves obtained in the framework of a model that includes a two exponential decay, $a_1\exp(-t/\tau_1)+a_2\exp(-t/\tau_2)$, and excitation by femtosecond pulse. The fast decay time constants (τ_1 = 880 fs for Corning 3-72, 580 fs for Asahi Y-46, and 320 fs for Hoya Y-46) are of the order of the fast decay times observed in luminescence measurements shown in Fig. 2. A direct comparison is difficult, since decay times depend on wavelength as shown in Table 1. Transmission measurements (both pump and probe at 410 nm) and luminescence measurements (excitation 410 nm, luminescence dynamics monitored at 470 nm) are done at different wavelengths. However, the slower picosecond decay (τ_2 = 60 ps for Corning 3-72, 6 ps for Asahi Y-46, and 2.6 ps for Hoya Y-46) is well pronounced in the transmission dynamics. The slower picosecond decay is not apparent in luminescence dynamics except in the sample Asahi Y-46 (but the relative weight of the picosecond component in luminescence dynamics, a_2/a_1, is about 0.06 while about 0.6 in transmission dynamics). The luminescence dynamics are fitted by monoexponential (two-exponential in case of Asahi Y-46) decay. The luminescence decay times are of about 1 ps (τ_1 = 0.74 ps for Corning 3-72, 1.26 ps for Asahi Y-46, and 1.41 ps for Hoya Y-46). Table 2 shows decay times for all samples investigated. Since induced absorption is overlapped with absorption bleaching in some samples [4], it is difficult to evaluate decay time

in Asahi Y-48 and Corning 3-71. The induced absorption is discussed in more detail in the next subsection.

We attribute the fast (subpicosecond) component observed in both transmission and luminescence dynamics to the hole trapping. The values we obtained are in accord with those observed by Klimov *et al*. [2,3]. The slower picosecond component is attributed to the electron trapping and relaxation. Our results obtained on samples of different producers show that the time constants depend on glass matrix composition and/or on technology of colour glass production. The electron and hole trapping processes are influenced in different ways in accord with different origin of the trapping states for electrons (Cd dangling bonds) and holes (S dangling bonds) [5]. The role of material type is pronounced in case of electrons whereas there are only small changes in the hole trapping rates. Klimov *et al*. [3] suggested that the hole traps are intrinsic nanocrystal states or intrinsically interface states. We observed that an ESR (electron spin resonance) signal associated with hole traps almost disappeared after annealing in a hydrogen atmosphere [6]. This indicates that hole traps are passivated by hydrogenation.

3.2 Effect of induced absorption on transmission dynamics

We observed absorption bleaching in almost all samples investigated, and photoinduced absorption in Corning 3-71, 3-72, Asahi Y-48, Y-46 and Hoya Y-48 and Y-46. Figs. 3 and 4 show transmission dynamics of Corning 3-71. Fig. 5 shows samples in which induced absorption is observed. Induced absorption is observed in Corning 3-71, when wavelength of laser light is 383 nm, 410 nm and 439 nm. On the other hand, induced absorption is not observed in Hoya Y-48 and the other samples, when wavelength of laser light is 439 nm. Induced absorption is observed in Corning 3-72 and Asahi Y-48, when wavelength of laser light is 410 nm. Induced absorption is not observed in GG475 in all wavelengths investigated. Absorption edges of Y-48 and GG475 are almost the same as that of 3-71, and glass compositions of Y-48 and GG475 are different from that of 3-71. These results suggest that the magnitude of induced absorption depends on glass composition. This is in accord with the conjecture that excited state absorption is due to the surface states as surface states are affected by glass composition.

An analysis of the decay curves of transmission dynamics in CdS-nanocrystalline films was performed using a multi-exponential fit. Since induced absorption is overlapped with

absorption bleaching, the effect of induced absorption should be under consideration in a quantitative analysis of the decay curves of absorption bleaching. Induced absorption reduces the magnitude of the nonlinear absorption. However, the dynamics of induced absorption is different from that of absorption bleaching, and the fast component is not observed in induced absorption. Consequently, the fast component of absorption bleaching remains. This leads to the fast response time by adjusting wavelength of laser light and sample. For example, Corning 3-71 shows the fast response time, when wavelength of laser light is 439 nm as shown in Fig. 4. On the other hand, response time in Hoya Y-48 (Fig. 6) is slower than that in Corning 3-71. In this way transmission dynamics can be tailored by tuning the light wavelength and by changing glass composition.

4. Conclusion

Luminescence dynamics of CdS-doped glasses were measured, and they were compared with transmission dynamics. An analysis of the decay curves of luminescence and transmission dynamics has been performed using a multi-exponential fit. The fast decay time constants of differential transmission are of the order of the fast decay times observed in luminescence measurements (about 1 ps). Although slower decay component is large in transmission dynamics, it is negligibly small in luminescence dynamics. This difference is observed in all samples investigated, and this may be caused by the difference in relaxation paths of electrons and holes in CdS nanocrystals. We attribute the fast component to the hole trapping and the slow component to the electron trapping and relaxation. Since induced absorption is overlapped with absorption bleaching, the effect of induced absorption should be under consideration in a quantitative analysis of the decay curves of transmission dynamics in some cases.

Acknowledgements

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Table 1 Decay times of luminescence and differential transmission in Asahi Y-46. Excitation wavelength is 410 nm in luminescence measurement. τ_1 and τ_2 are decay time constants, and a_1 and a_2 are amplitudes of fast and slow components, respectively.

Luminescence				Transmission			
Wavelength (nm)	τ_1 (ps)	τ_2 (ps)	a_2/a_1	Wavelength (nm)	τ_1 (ps)	τ_2 (ps)	a_2/a_1
449	0.95	27	0.02	410	0.58	6	0.6
465	1.26	12	0.06	425	1.00	20	1.7
481	1.46	15	0.08	440	1.25	33	3.1

Table 2 Decay times of luminescence and differential transmission in all samples investigated. Excitation wavelength is 410 nm in luminescence measurement, and transmission measurements are done at 410 nm. τ_1 and τ_2 are decay time constants, and a_1 and a_2 are amplitudes of fast and slow components, respectively. Decay times are not evaluated in Asahi Y-48 and Corning 3-71, since effect of induced absorption is large. $\Delta T/T(0)$ is differential transmission at t = 0 fs.

	Luminescence				Transmission			
Sample	Wavelength (nm)	τ_1 (ps)	τ_2 (ps)	a_2/a_1	τ_1 (ps)	τ_2 (ps)	a_2/a_1	$\Delta T/T(0)$
Y-48(A)	482	1.27	17	0.07				-0.005
Y-46(A)	465	1.26	12	0.06	058	6	0.6	0.018
Y-44(A)	449	1.13	18	0.03	0.96	15	1.0	0.0025
Y-48(H)	478	0.80	-	-	0.35	10	0.2	0.005
Y-46(H)	474	1.41	-	-	0.32	2.6	0.7	0.005
Y-44(H)	449	1.49	-	-	1.04	20	1.6	0.040
3-71	476	1.13	-	-				-0.007
3-72	451	0.74	-	-	0.88	60	1.3	0.030
3-73	449	0.93	-	-	1.30	49	2.1	0.018
GG475	471	1.03	-	-	0.36	27	0.5	0.010
GG455	450	0.67	-	-	0.15	2.5	0.4	0.0006

Figure captions

Fig. 1 Dynamics of differential transmission measured by single colour pump and probe technique at 410 nm. Dynamics of three samples with nearly the same absorption edge (nanocrystal mean size) are shown, namely Corning 3-72 (upper curves), Asahi Y-46 (middle curves), and Hoya Y-46 (lower curves). The smooth curves are two exponential fits as described in the text. Values of differential transmission at t = 0 fs, $\Delta T/T(0)$, are normalized. The absolute values of $\Delta T/T(0)$ are 0.030 for Corning 3-72, 0.018 for Asahi Y-46 and 0.005 for Hoya Y-46.

Fig. 2 Dynamics of photoluminescence measured by up-conversion technique (excitation wavelength 410 nm, photoluminescence monitored at about 460 nm). Dynamics of two samples with nearly the same absorption edge (nanocrystal mean size) are shown, namely Corning 3-72 (lower curves) and Asahi Y-46 (upper curves). The smooth curves are monoexponential fit for Corning 3-72 and two-exponential fit for Asahi Y-46. Intensities at t = 0 fs are normalized.

Fig. 3 Dynamics of differential transmission in Corning 3-71 measured at 410 nm.

Fig. 4 Dynamics of differential transmission in Corning 3-71 measured at 439 nm.

Fig. 5 Samples in which induced absorption is observed.

Fig. 6 Dynamics of differential transmission in Hoya Y-48 measured at 439 nm.

Fig. 1.

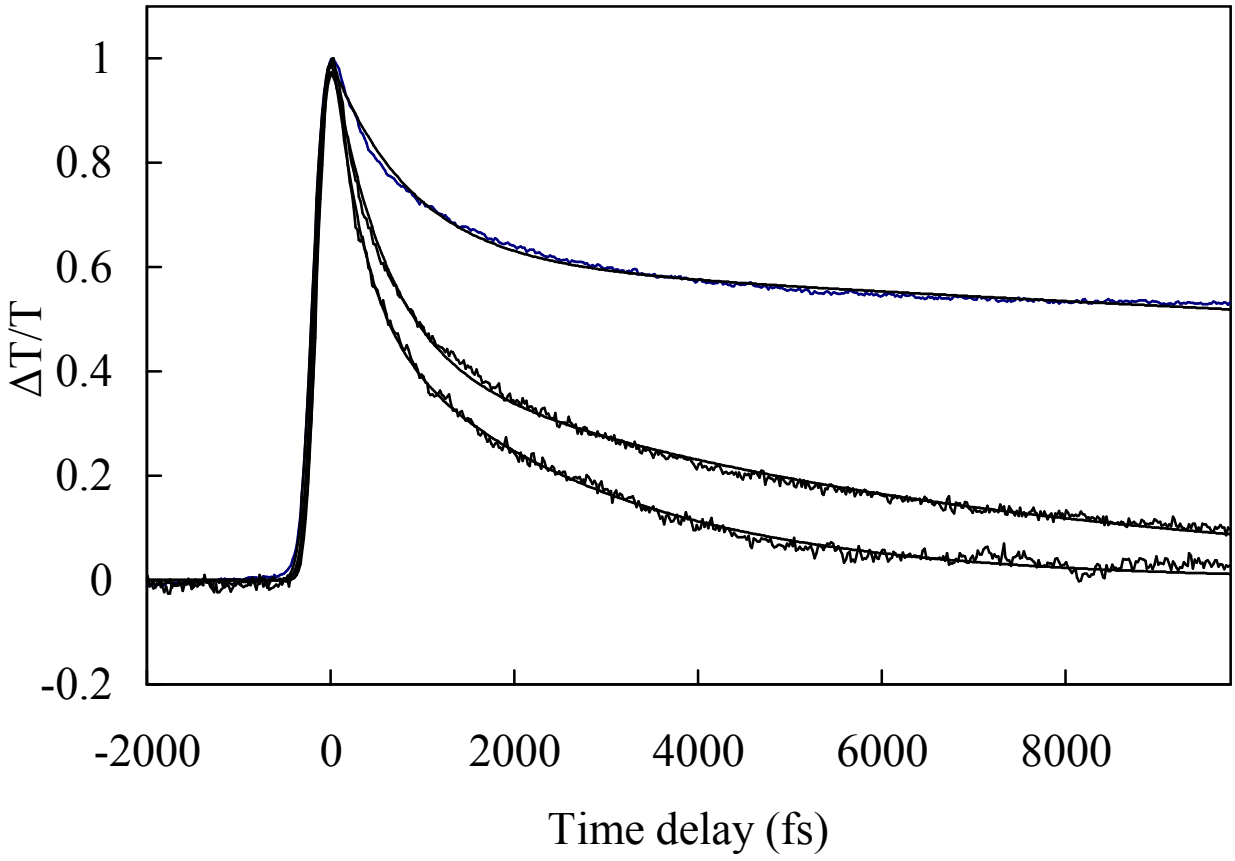


Fig. 2.

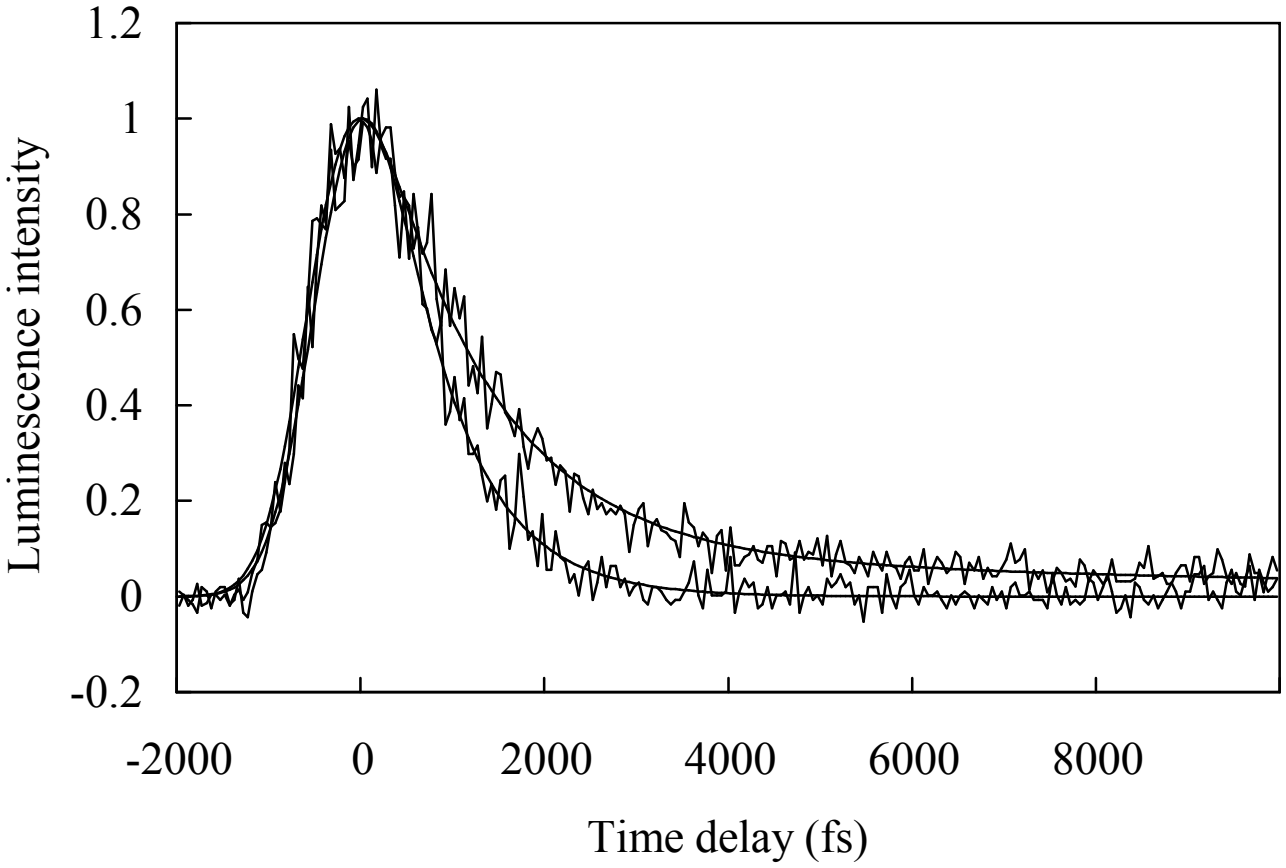

1.2
1
0.8
0.6
0.4
0.2
0
-0.2
Luminescence intensity
-2000
0
2000
4000
6000
8000
Time delay (fs)

Fig. 3.

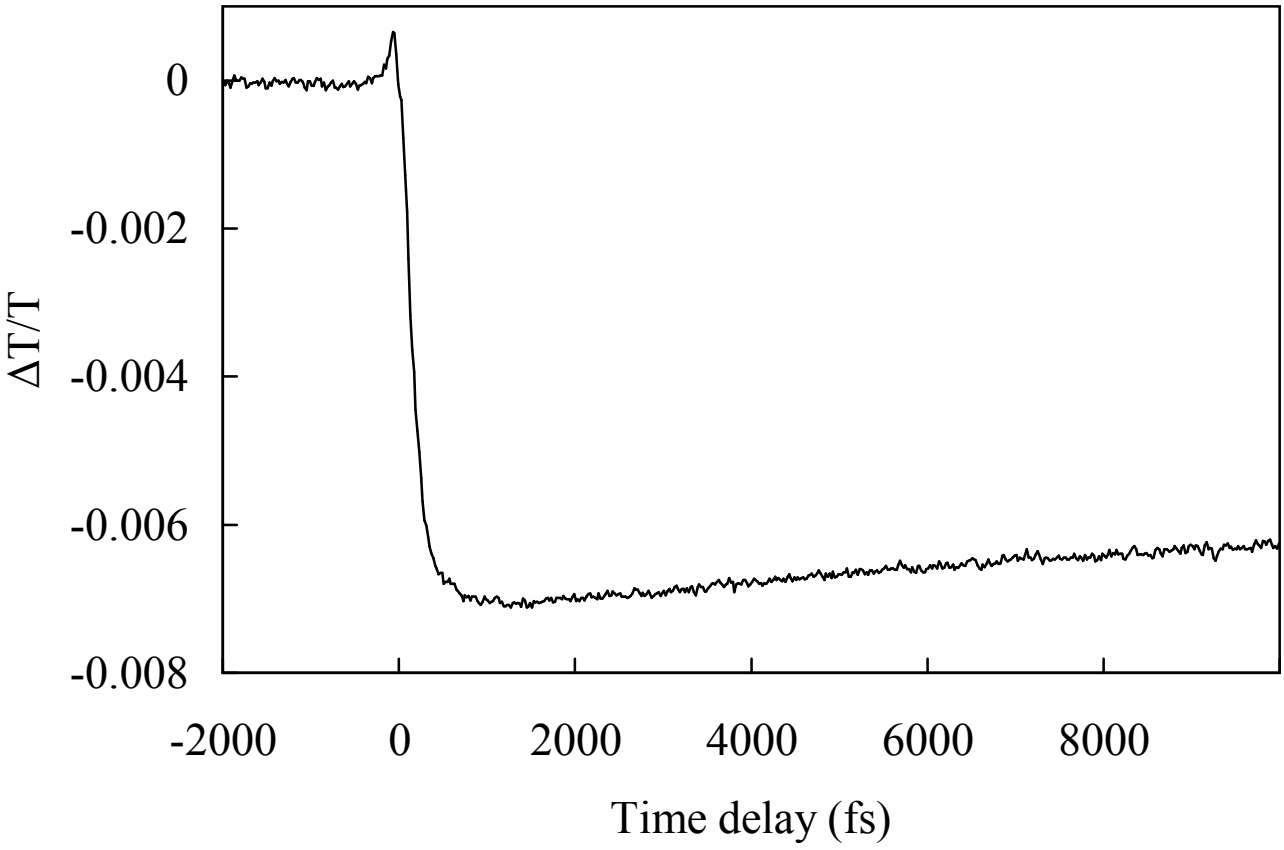

0
-0.002
-0.004
-0.006
-0.008
ΔT/T
-2000
0
2000
4000
6000
8000
Time delay (fs)

Fig. 4.

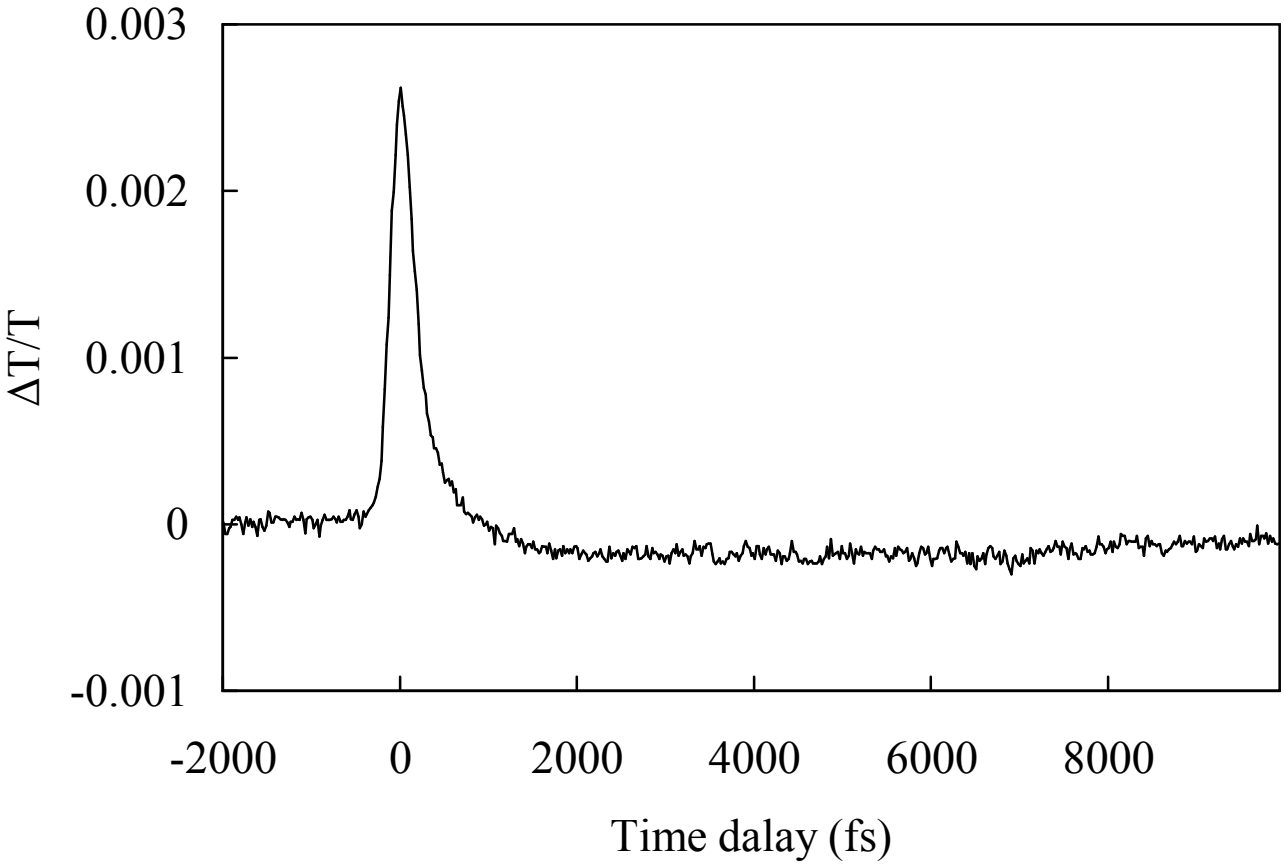

0.003
0.002
0.001
0
-0.001
ΔT/T
-2000
0
2000
4000
6000
8000
Time dalay (fs)

Fig. 5.

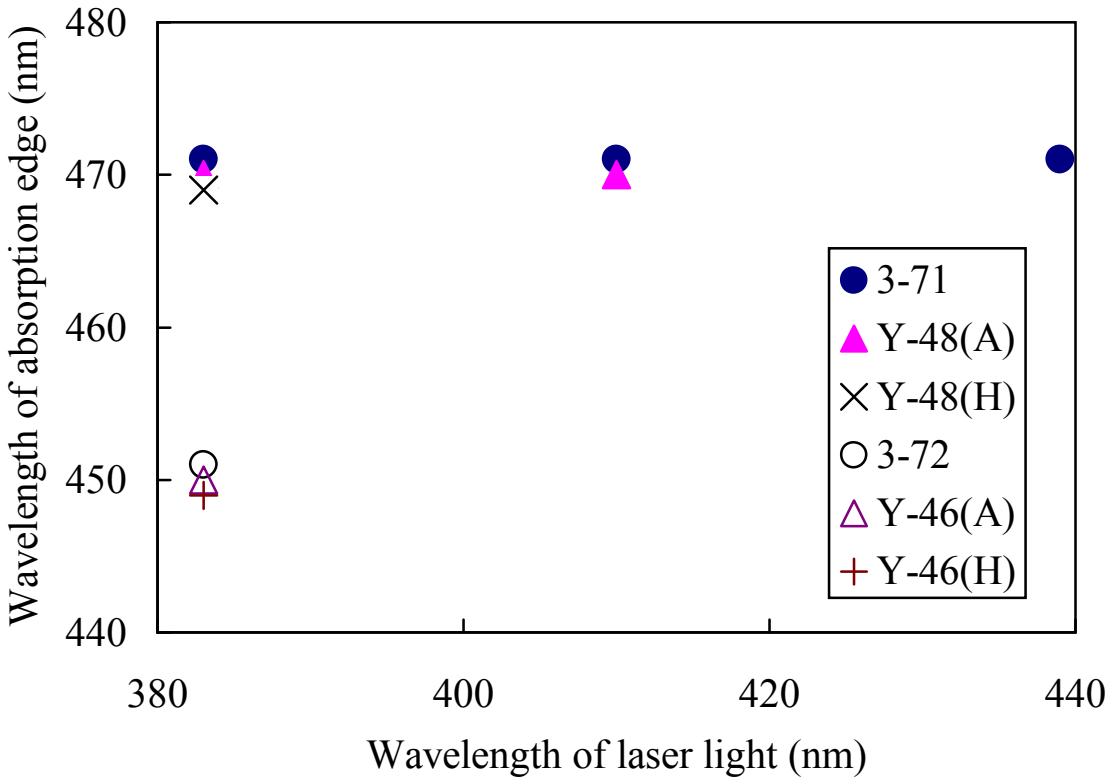
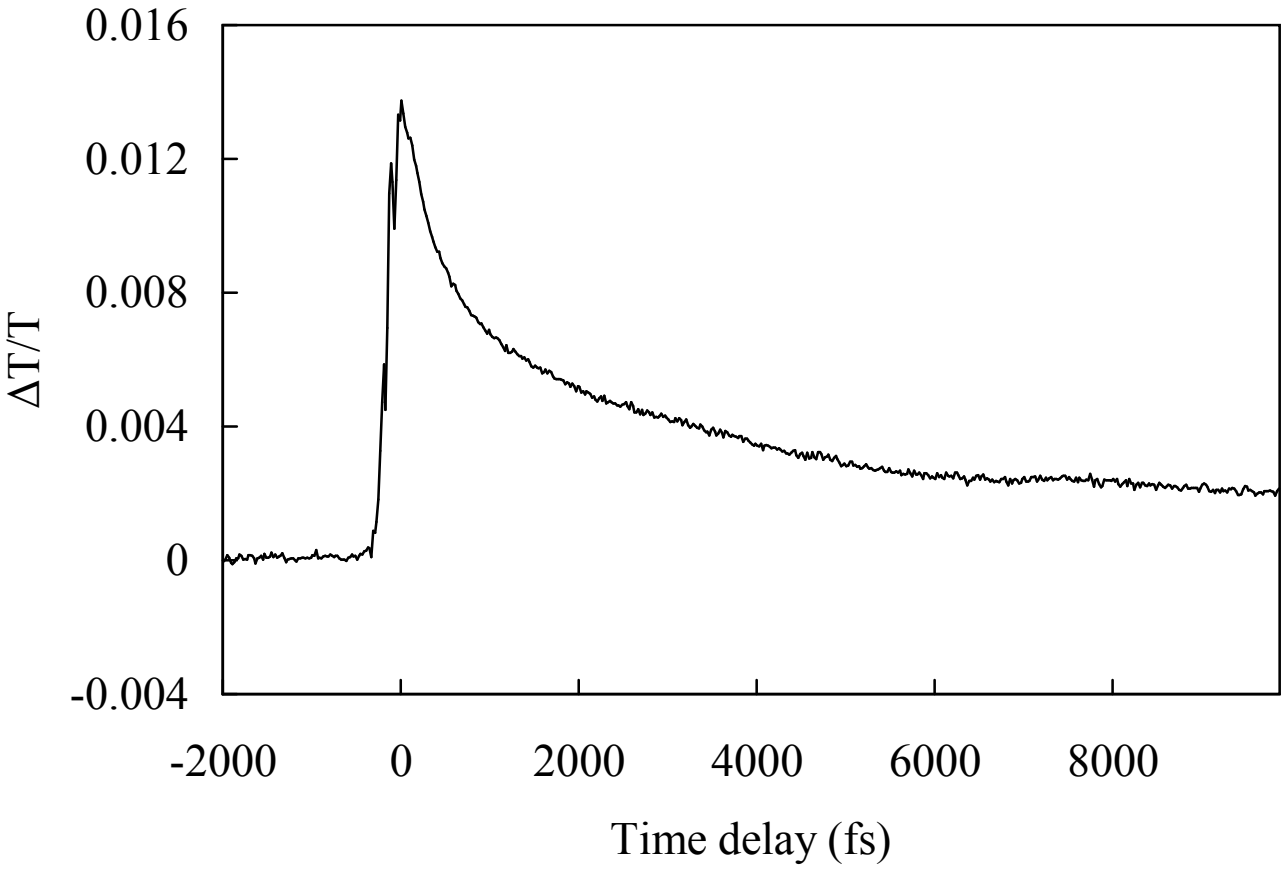

480
470
460
450
440
380
400
420
440
Wavelength of absorption edge (nm)
Wavelength of laser light (nm)
3-71
Y-48(A)
Y-48(H)
3-72
Y-46(A)
Y-46(H)

Fig. 6.


0.016
0.012
0.008
0.004
0
-0.004
ΔT/T
-2000
0
2000
4000
6000
8000
Time delay (fs)