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Negative and positive nonlinear absorption in CdS-doped glasses

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Since Jain and Lind [1] first reported that semiconductor-doped glasses have a large optical nonlinearity and a fast response time, the optical properties of these materials have been investigated extensively [2, 3]. Both negative nonlinear absorption (absorption saturation) and positive nonlinear absorption (induced absorption) have been observed in CdS-, CdSSe- and CdS-doped glasses. Absorption saturation is attributable to a state filling effect [4]. On the other hand, the induced absorption is attributable to a biexciton effect [5], a dc electric-field-induced shift of the optical transition caused by charge seperation [6], a red shift of an absorption edge caused by band gap renormalization [7] and dangling-bond surface states [8]. Here, we report a pump-probe experiment on the absorption band edge of CdS-doped glasses to investigate the origin of the induced absorption in these glasses.

The samples investigated were commercial CdS-doped filter glasses: Toshiba L-42, Y-43, Y-44, Y-46, Y-48, Corning 3-74, 3-73 and 3-71. Thickness of samples were 2.5 mm (L-42), 1 mm (3-74), 0.6 mm (Y-43 and 3-73), 0.4 mm (Y-44), 0.3 mm (Y-46) and 0.2 mm (Y-48 and 3-71). The concentration of CdS is about 0.4 wt%.

Transient absorption was measured using the following apparatus at 300 K. The pump and probe light was a frequency-doubled Ti:sapphire laser (Spectra Physics Tsunami 3960; wavelength = 380–440 nm, pulse duration = 80 fs, energy per pulse = 1 nJ, repetition rate = 82 MHz). 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°. 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. The peak power density of pump light is about 100 MW/cm^2. We investigated photodarkend samples, which were exposed to pump light for a long time (about 1 h).

Fig.1

The optical transmission spectra of the samples studied are shown in Fig. 1. All the samples are doped by CdS, and different positions of the absorption edge are due to the different nanocrystal sizes (effect of quantum confinement). We observed negative

differential absorbance due to absorption saturation in almost all samples investigated, and positive differential absorbance due to photoinduced absorption in Corning 3-71 and Toshiba L-42. The sign of differential absorbance depends on wavelength of laser light in Toshiba Y-46 and Y-48. Fig. 2

Fig. 2 shows the transient absorption of Toshiba Y-48. Absorption saturation is observed when wavelength of laser light is 440 nm (a). On the other hand, induced absorption is observed when wavelength of laser light is 396 nm (b). Fig.3

Fig. 3 shows summary of results. Absorption saturation is observed when photon energy of laser light is almost the same as band gap energy of semiconductors [4]. The lower conduction sublevels were occupied by photogenerated electrons (state filling effect). Decay rate of transient absorption (rate of absorption recovery) increases with increase in photon energy of laser light. This is due to the relaxation of carriers. When we use laser light with higher photon energy, we observe the state filling effect in higher sublevels. Photogenerated carriers in the higher sublevels relax rapidly to the lower sublevels. The induced absorption is observed in some samples. Decay rate of the induced absorption is slower than that of absorption saturation as shown in Fig. 2.

The induced absorption has already been reported in semiconductor-doped glasses. Klimov *et al.* [5] observed the induced absorption in CdSe-doped glass, and the absorption was explained by a biexciton effect. The induced absorption was observed in longer wavelength region. Klimov and McBranch *et al.* [6] observed the induced absorption in CdS-doped glass, and the absorption was explained by a dc electric-field-induced shift of the optical transition caused by charge seperation. The induced absorption was observed in longer wavelength region. Baltramiejunas *et al.* [7] observed the induced absorption in CdS-doped glass, and the absorption was explained by a red shift of an absorption edge caused by band gap renormalization. The induced absorption was observed in shorter wavelength region. Zhang and Izutsu [8] observed the induced absorption in CdSSe-doped glass, and the absorption was explained by dangling-bond surface states. The induced absorption was observed over a wide spectral range.

We observed the induced absorption when photon energy of laser light was higher than the band gap energy of semiconductor except for Toshiba L-42. We consider that the in-

duced absorption occurs in wide wavelength region. When photon energy of laser light is almost the same as band gap energy of semiconductors, absorption saturation dominates, and the induced absorption is not observed. Effect of absorption saturation becomes weak, when photon energy of laser light is lager than band gap energy of semiconductors. Thus, we observe the induced absorption in this case. The induced absorption is observed in Toshiba L-42, however, it is not observed in Corning 3-74. We measured transient absorption in Hoya L-42 and Schott GG420, and we did not observe the induced absorption. This result suggests that the induced absorption depends on glass composition. Thus, the induced absorption may be caused by dangling-bond surface states, and it is considered to be due to transition from the surface states to the upper states. Since Toshiba L-42 may contain high density of the surface states, we observe the induced absorption.

Absorption saturation is observed, when photon energy of laser light is lager than band gap energy of semiconductors in Toshiba Y-48 (380 nm). The induced absorption may depend on wavelength, since the absorption depends on energetic position of localized states. Thus, the induced absorption may be smaller than absorption saturation at 380 nm. The energetic position of surface states in Corning 3-71 is different from that in Toshiba Y-48. Thus, the induced absorption is observed at 380 nm in Corning 3-71. Absorption saturation was observed in the spectral range of the absorption band edge in Corning 3-71 and Toshiba Y-48 (around 460 nm), when we used a femtosecond white light continuum for probe light and 390 nm light for pump light (pulse duration = 130 fs, peak power density = 100 GW/cm^2). Fig. 4 shows differential absorption spectra of 3-71. The induced absorption is not observed, since signal intensity is weak. Similar spectra were also observed in Y-48. The transient characteristics of absorption saturation are similar to those obtained by single color experiment shown in Fig. 2 (a). Fig.4

In a previous paper [9], we reported that a two-step excitation process plays an important role for photodarkening. Electrons in the valence sublevels of semiconductor nanocrystals are excited to the conduction sublevels (first step), some of which relax into traps at the glass-semiconductor interface. Before the electrons recombine, laser light reexcites some of these trapped electrons to higher-energy surface states (second step), from which they migrate into the glass. These electrons eventually relax to deep levels in

the glass. The induced absorption is considered to be related to the second step.

In summary, we measured transient absorption in CdS-doped glasses. Negative nonlinear absorption (absorption saturation) and positive nonlinear absorption (induced absorption) were observed. The sign of nonlinear absorption depends on wavelength of laser light and manufacturers of glasses. The induced absorption is considered to be related to the surface states.

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References

1) R. K. JAIN and R. C. LIND, *J. Opt. Soc. Am.* **73** (1983) 647.

2) V. S. WILLIAMS, G. R. OLBRIGHT, B. D. FLUEGEL, S. W.KOCH and N. PEYGHAMBARIAN, *J. Modern Opt.* **35** (1988) 1979 and references therein.

3) G. P. BANFI, V. DEGIORGIO and D. RICARD, *Adv. Phys.* **47** (1998) 447 and references therein.

4) M. C. NUSS, W. ZINTH and W. KAISER, *Appl. Phys. Lett.* **49** (1986) 1717.

5) V. KLIMOV, S. HUNSCHE and H. KURZ, *Phys. Rev.* B **50** (1994) 8110.

6) V. I. KLIMOV and D. W. MCBRANCH, *Phys. Rev.* B **55** (1997) 13173.

7) R. BALTRAMIEJUNAS, S. PAKALNIS and G. TAMULAITIS, *J. Crystal Growth* **117** (1992) 622.

8) X. ZHANG and M. IZUTSU, *Jpn. J. Appl. Phys.* **37** (1998) 6025.

9) T. MIYOSHI, K. NITTA, H. OHKUNI, K. SHIRAISHI and N. MATSUO, *Jpn. J. Appl. Phys.* **37** (1998) 4330.

Figure captions

Fig. 1. Optical transmission spectra of CdS-doped glasses at 300 K. The spectral shapes of 3-73, 3-74 and L-42 are similar to that of Y-43.

Fig. 2. Transient absorption of CdS-doped glass, Toshiba Y-48.

Fig. 3. Sign of transient absorption in CdS-doped glasses as a function of wavelength of laser light. Open circles represent negative nonlinear absorption and solid triangles represent positive nonlinear absorption.

Fig. 4. Differential absorption spectra of 3-71 at different delay times for the pump wavelength at 390 nm.

Fig. 1

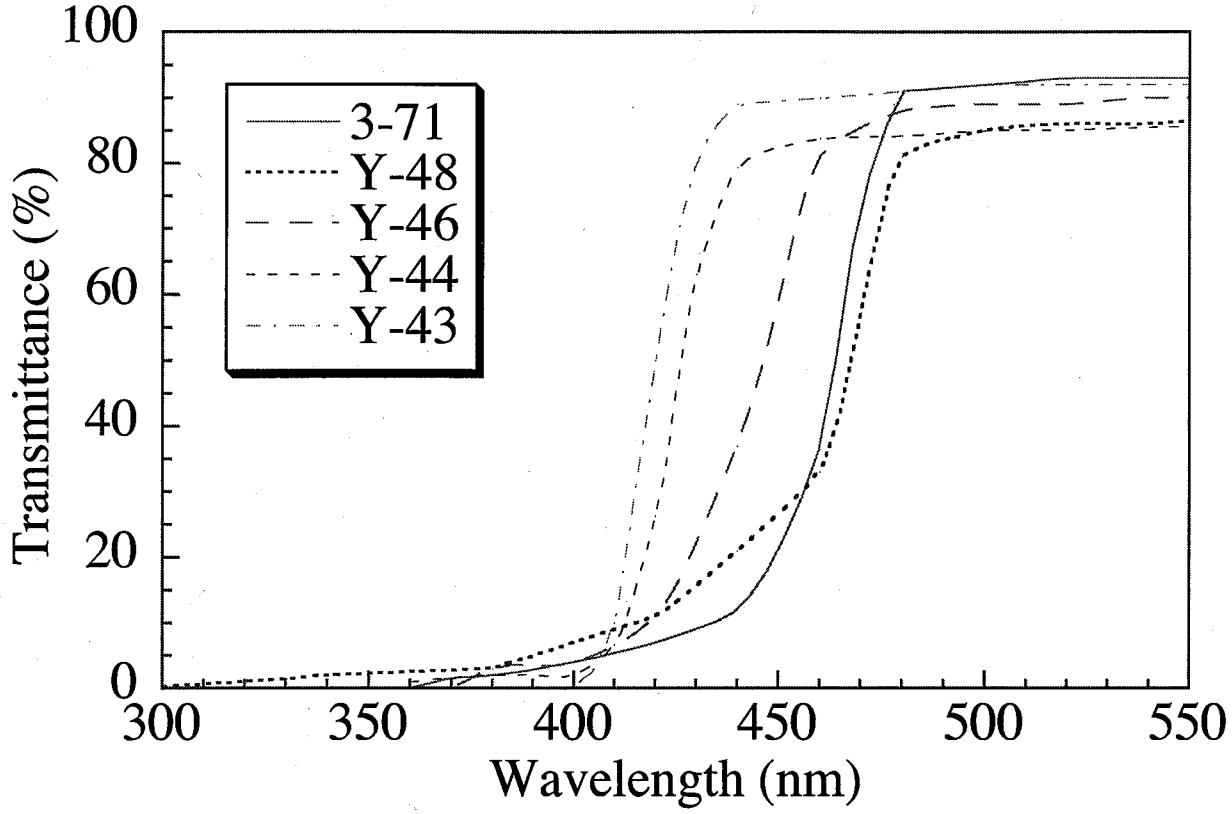

100
80
60
40
20
0
Transmittance (%)
300
350
400
450
500
550
Wavelength (nm)
3-71
Y-48
Y-46
Y-44
Y-43

Fig. 2(a)

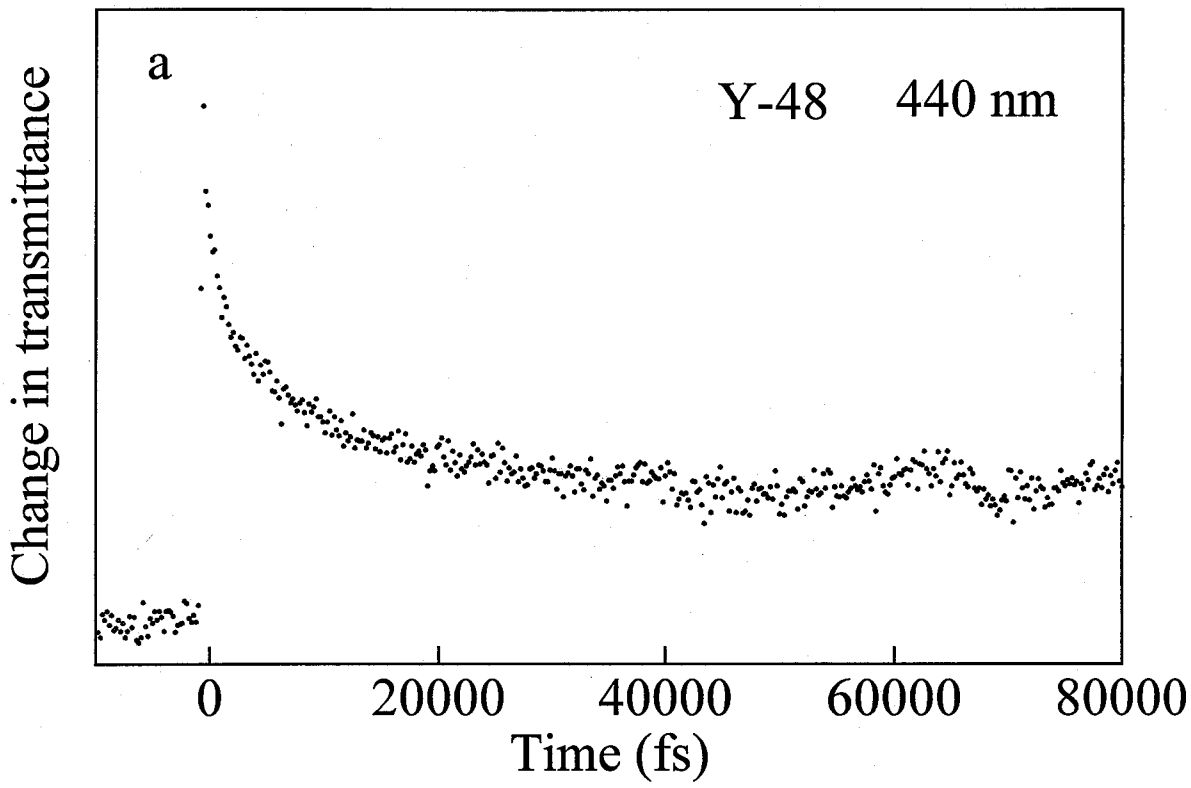

a
Y-48 440 nm
Change in transmittance
0
20000
40000
60000
80000
Time (fs)

Fig. 2(b)

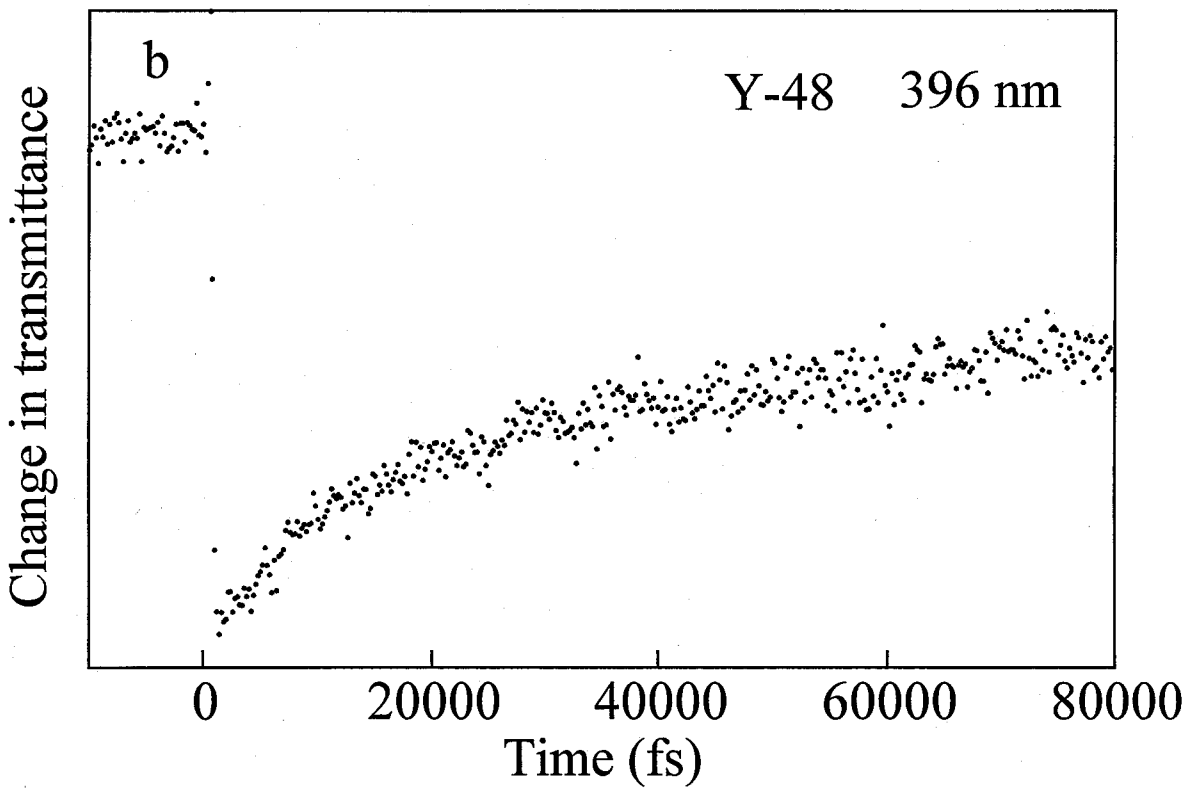

b
Y-48 396 nm
Change in transmittance
0
20000
40000
60000
80000
Time (fs)

Fig. 3

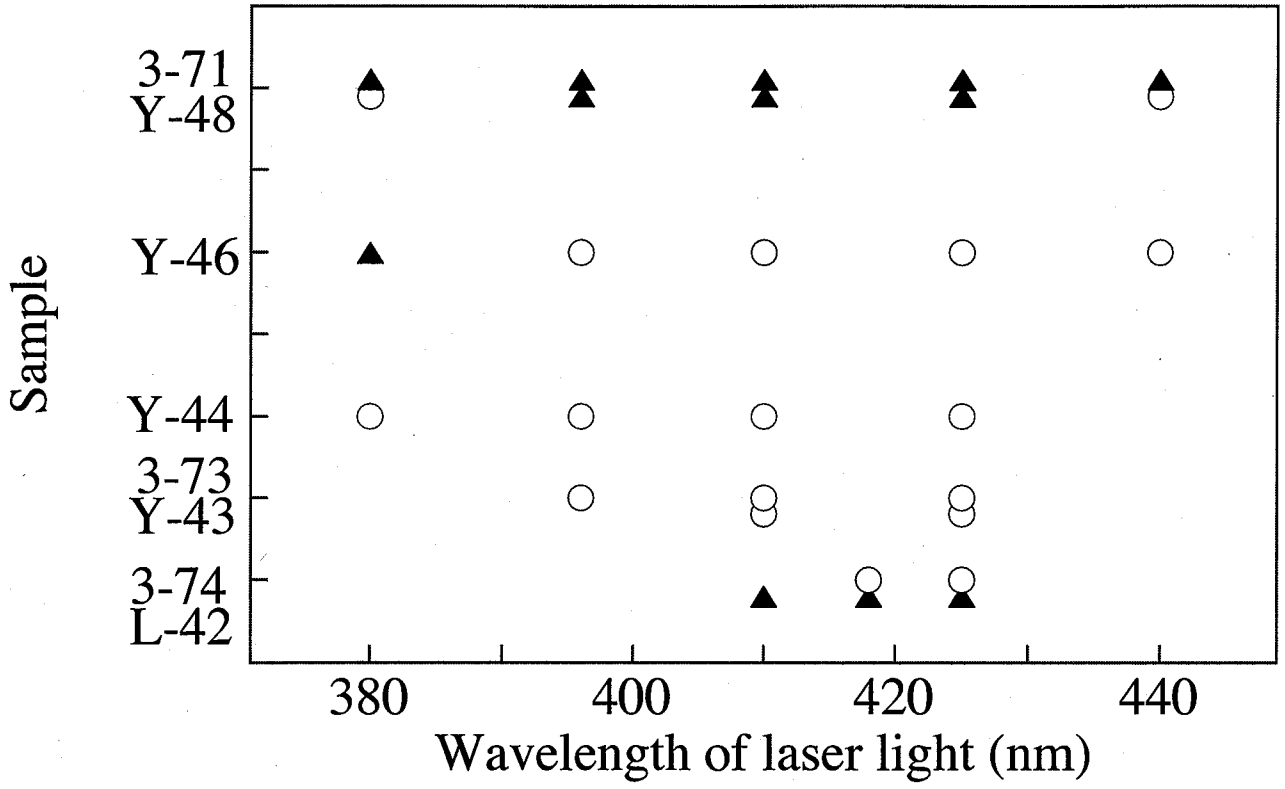
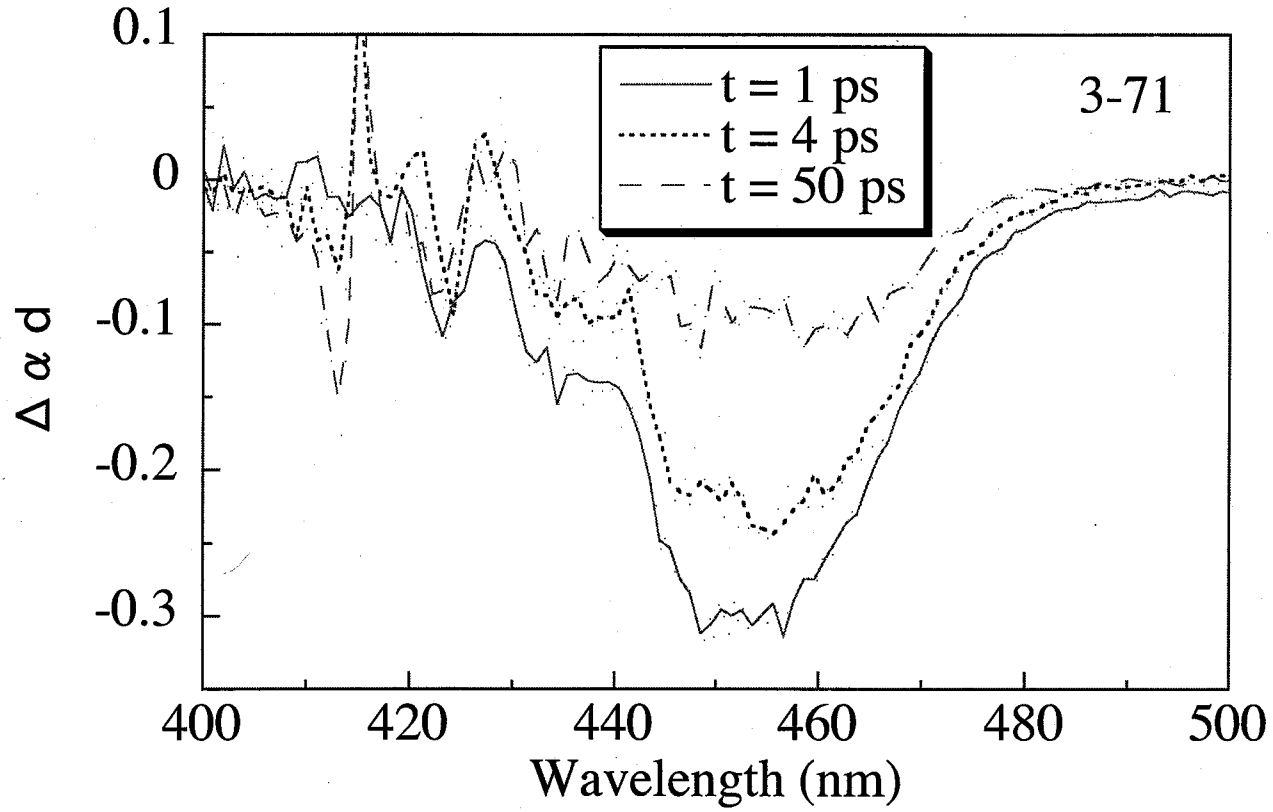

Sample
3-71
Y-48
Y-46
Y-44
3-73
Y-43
3-74
L-42
380
400
420
440
Wavelength of laser light (nm)

Fig. 4


0.1
0
-0.1
-0.2
-0.3
Δ α d
400
420
440
460
480
500
Wavelength (nm)
t = 1 ps
t = 4 ps
t = 50 ps
3-71