Ceramics International **23** (1997) 375–382

PII: S0272-8842(96)00012-0
0272-8842/97/$17.00 + 0.00

Non-linear Glass Materials

Yoshiyuki Asahara*

Materials Research Laboratory, Hoya Corporation, 3-3-1, Musashino, Akishima-shi 196, Tokyo, Japan

(Received 15 October 1995; accepted 28 November 1995)

Abstract: Two types of composite glass are of current interest as non-linear materials. One is glass doped with semiconductor microcrystallites. Their non-linearities mainly originate from quantum confinement and band filling effects and now are on the order of 10^{-6} esu as a result of the progress in new glass fabrication technologies. The non-linear time response is limited to 100 ps because of the existence of trap levels in the microcrystallites. Photo-annealing effects are now being intensely studied for a modification of the response time. The second type is glass doped with small metal particles. Their non-linearities originate from local field and hot electron effects in the metal particles. The non-linear response time is shorter than several ps. The non-linear susceptibilities are on the order of 10^{-12} esu, because of the very low volume fraction of the metal particles. The non-linear optical properties of these composite glasses are reviewed in this article. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

There is a great deal of interest in developing high-speed and low-power optical devices for future optical signal processing and optical communication systems. These devices make use of non-linear processes which generally occur in materials at high optical intensities.[1] The polarization (P) induced in a medium by an external optical electric field (E) is expressed by the power series:

$$P = \varepsilon_0 \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots\ldots), \qquad (1)$$

where ε_0 is the electric permittivity in vacuum and $\chi^{(1)}$, $\chi^{(2)}$ and $\chi^{(3)}$ are, respectively, the first-, second- and third-order susceptibilities. The first term in the expression expresses the linear optical properties, whereas the higher-order terms give rise to a large number of non-linear effects. In an isotropic medium such as glass, the non-linearity is mainly caused by the third-order term of eqn (1). Since the polarization and the refractive index are related to each other, third-order non-linearity is often expressed in terms of optically induced refractive index change and absorption change:

$$n = n_0 + \Delta n(I) = n_0 + n_2 I \qquad (2)$$

$$\alpha = \alpha_0 + \Delta\alpha(I) \quad \alpha_0 + \alpha_2 I \qquad (3)$$

where n_0 and α_0 are the linear refractive index and the absorption coefficient, respectively, and I is the light intensity. n_2 and α_2 are related to the third-order susceptibility by $n_2 = (3/4\varepsilon_0 n_0^2 c)\mathrm{Re}\chi^{(3)}$ and $\alpha_2 = (3\omega/2\varepsilon_0 n_0^2 c^2)\mathrm{Im}\chi^{(3)}$, respectively, where $\mathrm{Re}\chi^{(3)}$ and $\mathrm{Im}\chi^{(3)}$ represent the real part and the imaginary part of $\chi^{(3)}$. A large index change, for instance, may result in considerable non-linear phase changes.[1] The non-linear directional coupler and the optical bistability device can be made on the basis of such optically induced phase changes.

Recently, composite glass materials doped with nanometre-sized microcrystallites have become of current interest as non-linear materials because of their relatively large third-order non-linearities and fast response time. Two types of composite glass are presently of interest and intensely studied. One is glass doped with semiconductor microcrystallites and the other is glass doped with small

*Present address: 745-50 Ishihata, Mizuho-machi, Nishitama-gun, Tokyo, Japan.

metal particles. The present paper reviews the non-linear optical properties of these composite glasses.

2 GLASS DOPED WITH SEMICONDUCTOR MICROCRYSTALLITES

2.1 Non-linear susceptibilities

One of the most famous glasses doped with semiconductor microcrystallites is commercially available as sharp cut filter glass. The present interest in these glasses was initiated by Jain and Lind,[2] and research was first concentrated on these glasses. They reported that the third-order non-linear susceptibilities $\chi^{(3)}$ of these glasses were measured to be 10^{-9}–10^{-8} esu in a degenerate four wave mixing (DFWM) experiment. Yumoto *et al.*[3] observed optical bistability switching in a sharp cut filter glass with rise and fall times of 25 ps. The third-order non-linear susceptibility $\chi^{(3)}$ was estimated to be 1.3×10^{-9} esu from this experiment.

In the fabrication process of sharp cut filter glass, semiconductor materials (CdS and CdSe) are added to the batch materials in the form of CdO, CdS and elemental sulphur or selenium. The batch is typically melted within the range of 1300–1400 °C and then formed using conventional casting techniques. Upon subsequent heat treatment, the dopant forms microcrystallites of CdS_xSe_{1-x} with a typical diameter of $2R = 10$ nm inside the glass matrix.[4] Two quantum confinement regimes may be considered as origins of non-linear enhancement of semiconductor in these glasses, depending on the relative values of the sphere radius R and electron and hole Bohr radii ($a_{e,h} = \hbar^2\varepsilon/m_{e,h}\ e^2$),[5,6] where ε is the semiconductor dielectric constant and $m_{e,h}$ is the electron or hole effective mass.

In the weak confinement case, which corresponds to the conditions of radius R larger than Bohr radius, the Coulomb interaction is retained and the exciton is confined. In this case, discrete sub-bands of the exciton with lower energy levels are formed, and the space filling effect is the origin of non-linearity. The non-linear susceptibility $\chi^{(3)}$ can be given by the following equation:[7]

$$\chi^{(3)} = \left\{(2\sqrt{2}/\pi)^4|P_{cv}|^4\phi(0)^4pR^3\right\}/\left\{\hbar^3(\omega-\omega_x)^3\right\} \quad (4)$$

where P_{cv} is the dipole moment of transition, $\hbar\omega_x$ is the exciton energy, $\phi(0)$ is the wave function of the exciton at an origin, and R and p are the radius and volume fraction of semiconductor microcrystallites, respectively. Appropriate examples are provided by the glass doped with CuCl or CuBr microcrystallites.[8] Recently, the third-order non-linearity of 1×10^{-6} esu was measured for the glass doped with CuCl microcrystallites with a radius in the exciton confinement range.[9]

In the strong confinement case, microcrystallite radius is smaller than Bohr radius, and both electron and hole confinement were assumed to be dominant relative to the Coulomb interaction.[10] This results in a splitting of both the valence and conduction band into a series of sub-bands. This is appropriate for glasses doped with CdS or CdSe microcrystallites with a radius of 10 nm.[6] The band filling effect qualitatively explains the non-linearities of these glasses well. In this case, the non-linear susceptibility $\chi^{(3)}$ is given by the following equation:[7]

$$\chi^{(3)} = \left\{3p|P_{cv}|^4\right\}/\left\{4\pi R^3\hbar^3(\omega-\omega_1)^3\right\}, \quad (5)$$

where $\hbar\omega_1$ is the lowest energy of the electron. Hiraga *et al.*[11] have recently doped a large amount of CdSe microcrystallites into the zinc-phosphate glass matrix. As shown in Fig. 1, the third-order non-linear susceptibility $\chi^{(3)}$ on the order of 10^{-6} esu was obtained for these glasses.

The investigation for new fabrication technologies of non-linear glass materials has also proceeded at a rapid pace over the last few years. The precipitation process in porous glass, sol–gel process, and physical or chemical vapour deposition process have been applied successfully to the preparation of semiconductor-doped glasses with a significant quantum sized effect. Table 1 summarizes the non-linear characteristics of various glasses made by these new glass fabrication processes.[2–4,9,12–16]

2.2 Non-linear response time

The response time of the glass doped with semiconductor microcrystallites is usually limited to

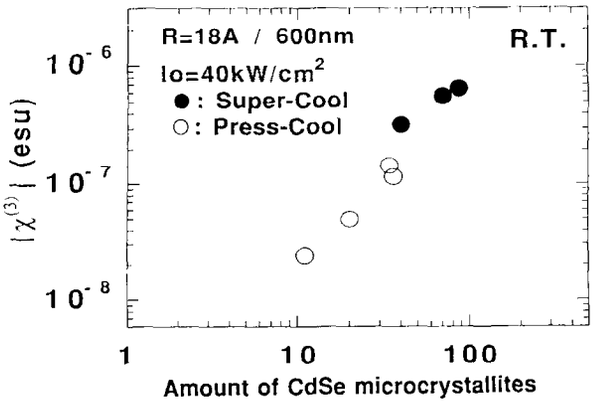

Fig. 1. The third-order non-linearity $\chi^{(3)}$ as a function of CdSe microcrystallite concentration.[11]

Table 1. Non-linear characteristics of semiconductor-doped glasses made by new fabrication processes

Dopant	Process	Non-linear susceptibility $\chi^{(3)}$ (esu)	Response time τ (s)	Refs
CdSSe	[MH]	1.3×10^{-9}	25×10^{-12}	3
CdSSe	[MH]	1.3×10^{-8}		2
CuCl	[MH]	1×10^{-6}		9
CdSe	[MH]	1×10^{-6}	100×10^{-12}	4
CdTe	[MH]	5×10^{-7}		12
CuBr	[MH]	10^{-7}		9
CdS	[PP]	2.5×10^{-11}		13
CdS	[SG]	10^{-6}		14
CdS	[SG]	3×10^{-10}		15
CuCl	[SG]	10^{-8}		16

[MH]: Melt-quench and heat treatment, [PP]: Porous process, [SG]: Sol–gel process.

100 ps because of the existence of trap levels with long lifetimes within the gap. These trap levels, which are most likely caused by surface or inner defects of the semiconductor microcrystallites, seem to affect the band-to-band recombination process. The existence of such trap levels is known by the fact that the glass shows very intensive photoluminescence spectra caused by trap levels in the near-infrared region. As shown in Fig. 2, the photoluminescence spectrum consists of two features:[17] a narrow band near the absorption edge and a broad band in the longer-wavelength region. The former is usually assigned to the direct recombination of the excited carriers to the valence band and the latter to the radiative recombination via the trap levels.

Several groups have attempted to modify such trap levels. Hata *et al.*[18] have found that when a CdSe-doped phosphate glass is treated with H_2O, the broad photoluminescence band disappears and the narrow photoluminescence band near the absorption edge increases, as shown in Fig. 3. This result indicates that, upon H_2O treatment, H_2O diffuses in the glass matrix as OH^- and neutralizes the trapping sites such as Se vacancy at the microcrystallite surface. The luminescence decay time is, however, on the order of 10 ns and is longer than that of the untreated sample.

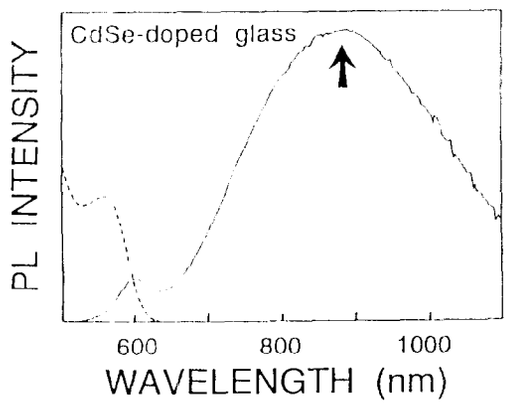

Fig. 2. Photoluminescence spectrum of CdSe-doped glass (R=3.0 nm) ($50ZnO\ 50P_2O_5$+4CdSe (mol%)).

Ohmi *et al.*[12] have recently developed glasses doped with a large amount of CdTe microcrystallites using the CdO–ZnO–P_2O_5 system. The photoluminescence spectrum consists of only one narrow peak near the band edge, as shown in Fig. 4, suggesting the absence of trap levels in this glass in contrast with the glass doped with CdSSe or CdSe microcrystallites. Figure 5 shows the photoluminescence decay curve of CdTe-doped glass compared with that of CdSe-doped glass. Although the slow decay element (μs) disappeared, as expected from the results in Fig. 4, the fast decay element (sub-ns) observed in the CdSe-doped glass also disappeared.

Another interesting effect for a modification of response time is the "Photo-Annealing (PA) Effect". This effect causes a permanent decrease in both $\chi^{(3)}$ and response time upon intense laser irradiation, and is sometimes accompanied by a permanent

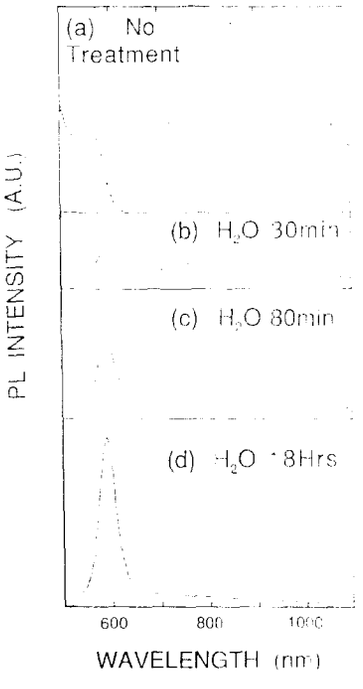

Fig. 3. Photoluminescence spectra of CdSe-doped glass before and after H_2O treatment.[18]

decrease in transmission. Figure 6 shows photoluminescence decay curves of CdSe-doped glass before and after 30 min. irradiation. The luminescence decay time decreases upon laser irradiation. Mitsunaga *et al.* found that the decay time of DFWM signal intensity of a sharp cut filter glass (HOYA R64) is on the order of 1 ns immediately after laser irradiation.[19] This component is, however, reduced dramatically with irradiation time and it becomes almost completely suppressed after 3 h of irradiation. The ultimate recombination time was estimated as 7 ps, which is 200 times shorter than in an unirradiated sample. An important advantage of this effect is that the decay time of the non-linear response decreases by one to two orders of magnitude, whereas $\chi^{(3)}$ decreases by one third.

The PA effect is not well understood and more experiments are needed to explain it. This effect was first explained as saturation or elimination of trap levels upon laser irradiation, based on the fact that luminescence via the trap disappeared after laser irradiation.[20] This interpretation is, however, inconsistent with the decay behaviours of CdTe-doped glasses or H_2O-treated glass upon laser irradiation. Furthermore, as shown in Fig. 7, photoluminescence decay is slow for these trap-free glasses and no changes in the decay behaviour have been observed upon laser irradiation.[21] Tomita *et al.*[22] recently attributed the PA effect to the creation of a new non-radiative decay route of the carriers from the trap levels upon laser irradiation. Malhotra *et al.*[23] also proposed a model in which some of the electrons in the trap levels are re-excited by a high-intensity beam to states created in the glass host matrix and relax non-radiatively.

As has been reported in several studies,[20 24] the energy level diagram proposed for CdSe- or CdSSe-doped glass is a three-level system including the valence band, the conduction band and the trap level, as shown in Fig. 8. Excited carriers in the conduction band will either relax directly down to the valence band at a relatively slow decay rate (ns) or will decay to the trap level non-radiatively at a fast decay rate (sub-ns) and then return to the valence band at a slow decay rate (μs). The PA effect has been explained by the creation of a different kind of trap opening an additional channel for non-radiative recombination of the excited carriers, or by the creation of a new non-radiative decay route of the carriers from the trap level.[21 23] The relatively slow decay rate of CdTe-doped glass is probably caused by the absence of fast non-radiative decay from the valence band to the trap level.[21] Upon laser irradiation, no change in the decay behaviour has been observed in the CdTe-doped glass, suggesting that the PA effect could well be interpreted as the creation of a new channel for non-radiative decay of carriers from the trap level.

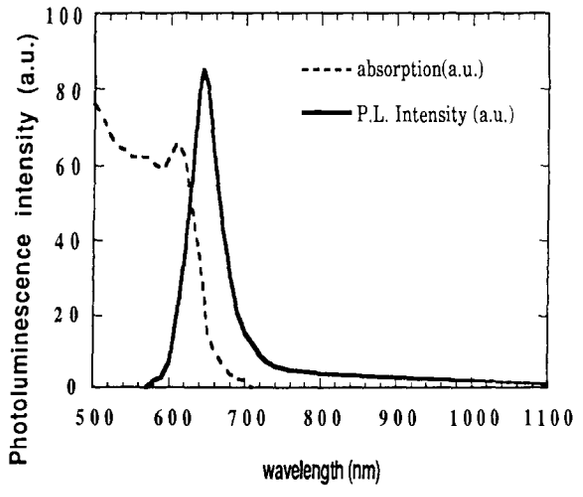

Fig. 4. Photoluminescence spectrum of CdTe-doped glass ($20CdO–30ZnO–50P_2O_5 + 10CdTe$).[12]

3 GLASS DOPED WITH SMALL METAL PARTICLES

3.1 Non-linear susceptibilities

Composite glass doped with small metal particles (10 nm diameter) is also a very attractive optical non-linear material for optical switching and computing because of its ultrafast non-linear response.[25]

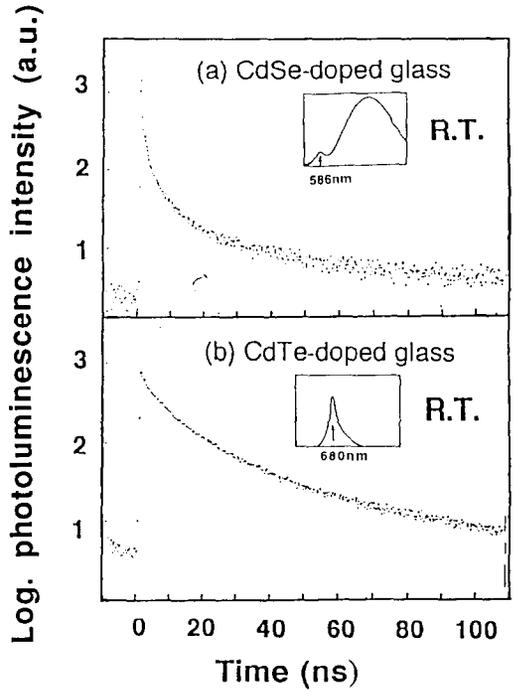

Fig. 5. Photoluminescence decay curves of CdSe- and CdTe-doped glasses.[12]

Most of the available literature on the silver and gold colloids report that the non-linear response is shorter than the laser pulse duration of several ps,[25-28] which appears to be sufficient for use as non-linear materials.

The large third-order susceptibility $\chi^{(3)}$ of these glasses is attributed to local field enhancement near the surface plasmon resonance of the metal particles by Hache and co-workers.[26,27] The local electric field E_i inside the particles, which usually differs from the applied field E_0, is given by the well-known formula:[29]

$$E_i = 3\varepsilon_d(\omega)E_0/\{\varepsilon_m(\omega) + 2\varepsilon_d(\omega)\} = f_i(\omega)E_0. \quad (6)$$

where $\varepsilon_m = \varepsilon'_m + i\varepsilon''_m$ is the dielectric constant of the metal particles, ε_d is the dielectric constant of the matrix material and $f_i(\omega)$ is defined as the local field factor. The non-linear susceptibility $\chi^{(3)}$ of such a composite can be written as:

$$\chi^{(3)} = p|f_i(\omega)|^2 f_i^2(\omega)\chi_m^{(3)}, \quad (7)$$

where p is the volume fraction of metal particles in the composite materials and $\chi_m^{(3)}$ is the optical non-linear susceptibility of a metal particle itself.

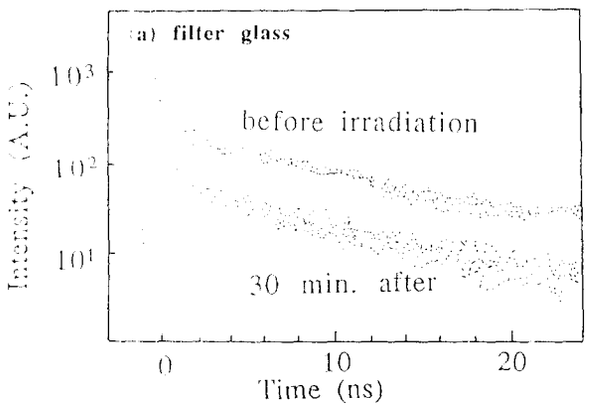

Fig. 6. Photluminescence decay curves of CdSe-doped glass before and after 30 min. irradiation.[21]

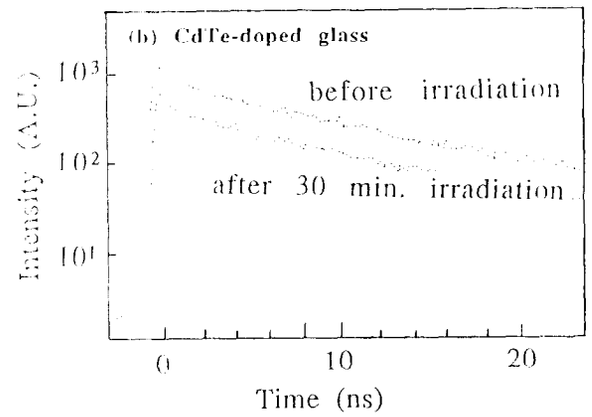

Fig. 7. Photoluminescence decay curves of CdTe-doped glass before and after 30 min. irradiation.[21]

Since the local field factor $f_i(\omega)$ enters into the expression for $\chi^{(3)}$ to the fourth power, a large enhancement is expected in the non-linear susceptibility near the plasmon resonance frequency ω_s for which:

$$\varepsilon'_m(\omega_s) + 2\varepsilon_d = 0. \quad (8)$$

Another essential contribution to the non-linear susceptibility is $\chi_m^{(3)}$. There are three mechanisms that can contribute to the non-linearity: intraband transition, interband transition and the hot electron effect.[25-27] Based on the fact that there is no substantial size dependence of $\chi_m^{(3)}$, the non-linear response of metal particles is thought to be caused by nonequilibrium electron heating (hot electron).[28] The pump pulse energizes the conduction electrons, resulting in high electronic temperature while the lattice remains cool. This electron heating leads to Fermi smearing, which affects the transition probability of the d-band electrons to the conduction band energies near the Fermi level, leading to changes in the reflectivity at the surface of the metal. The hot electron gas cools to the metal lattice through electron–phonon scattering in 2–3 ps. The value of $\chi_m^{(3)}$ measured by Ricard *et al.*[25] is 1.5×10^{-9} esu for gold particles and 2.4×10^{-9} esu for silver particles. Despite these encouraging results, the value of $\chi^{(3)}$ for the composite glasses are on the order of 10^{-12} esu, because of the very small volume fraction p on the order of 10^{-6}.

Recently the investigation of new fabrication technologies offers high non-linear susceptibilities of composite glasses doped with metal particles. Table 2 summarizes the non-linear characteristics of various composite glasses made by these new glass fabrication processes.[25,27,30-45] Uchida *et al.* have also recently developed glasses containing a higher amount of thermally developed copper and silver metal particles.[38] Glass was prepared by melting and heat-treatment processes. A transmission electron micrograph of a Cu-doped glass after treatment is shown in Fig. 9. Most of the metal particles

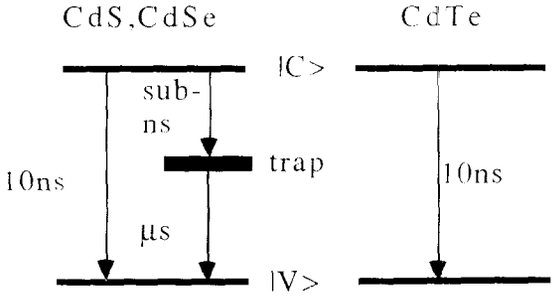

Fig. 8. Energy level diagrams of glasses doped with semiconductor microcrystallites.[21]

Table 2. Non-linear characteristics of metal-doped glasses made by new fabrication processes

Metal	Process	Non-linear susceptibility $\chi^{(3)}$ (esu)	Response time τ (ps)	Non-linear susceptibility of metal $\chi_m^{(3)}$(esu)	Refs
Au	[MH]		28	1.5×10^{-8}	25
	[MH]	5.5×10^{-11}	5	5×10^{-8}	27
	[SPT]	1.3×10^{-7}			30
	[IMP]	1.2×10^{-7}		8×10^{-8}	31
	[SG]	7.7×10^{-9}		6×10^{-8}	32
	[SPT]	3.5×10^{-8}		3×10^{-8}	33
	[IMP]	2.5×10^{-11}		7×10^{-8}	33
	[IMP]	1.7×10^{-10}	35		34
	[SPT]	$\sim10^{-7}$			35
	[SG]	2.5×10^{-8}			36
	[SPT]			$5\text{–}20\times10^{-8}$	37
Ag	[MH]			2.4×10^{-9}	25
	[MH]	9×10^{-8}		$2\text{–}4\times10^{-9}$	38
Cu	[MH]	1.3×10^{-7}	1	$1\text{–}2\times10^{-6}$	38,39
	[SPT]	4×10^{-9}			40
	[IMP]	8.4×10^{-10}		$4\text{–}50\times10^{-9}$	41
	[IMP]	$\sim10^{-8}$	5		42,43
a-P	[IMP]	5×10^{-11}			44
Sn	[IMP]	3×10^{-6}			45

[MH]: Melt-quench and heat treatment, [SPT]: Sputterint, [IMP]: Ion implantation, [SG]: Sol–gel process.

appear as dark spheres of roughly 100 Å diameter. Figure 10 represents the dependence of $\chi^{(3)}$ on the pumping wavelength together with the absorption spectrum. The value of $\chi^{(3)}$ exhibits a peak at almost the same wavelength as the plasmon resonance wavelength. The maximum value of $\chi^{(3)}$ is on the order of 10^{-7} esu, which is surprisingly large compared with values in metal-doped materials reported in other publications. The numerical estimation of $\chi_m^{(3)}$ for copper particles was $2\text{–}4\times10^{-6}$ esu and roughly independent of particle size. This value is larger than those of the other noble metals, which may be because of the differences in the hot electron contribution and interband contribution to the plasmon resonance.

Near the plasmon resonance frequency ω_s, the local field factor becomes:[27,37,46]

$$f_i(\omega_s) = 3\varepsilon_d/\varepsilon_m'' = 3n_d^2/\varepsilon_m'', \tag{9}$$

where n_d is the refractive index of the matrix material. By using the expression for absorption coefficient:[27]

$$\alpha = p(\omega_s)|f_i|^2\varepsilon_m'', \tag{10}$$

the materials figure of merit, $\chi^{(3)}/\alpha$, can now be written as:[46]

$$\chi^{(3)}/\alpha \sim n_d^5\varepsilon_m''^{-3}\chi_m^{(3)}. \tag{11}$$

In contrast, the size dependence of ε_m'' is given by:[47]

$$\varepsilon_m''(R) = \varepsilon_{mb}'' + A(\omega)/R, \tag{12}$$

where ε_{mb}'' is the imaginary part of dielectric constant of bulk metal and R is the particle radius.

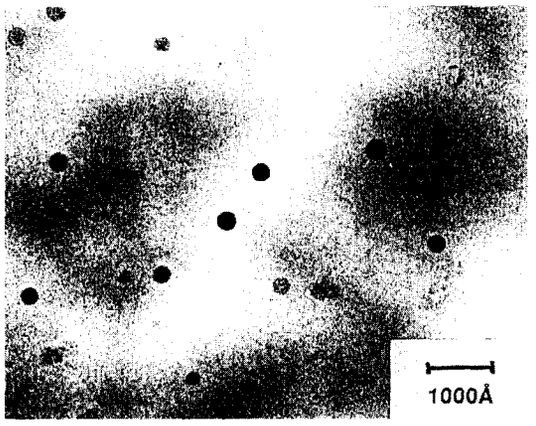

Fig. 9. TEM image of $50P_2O_5$–50BaO–6SnO glass doped with $6Cu_2O$.[38]

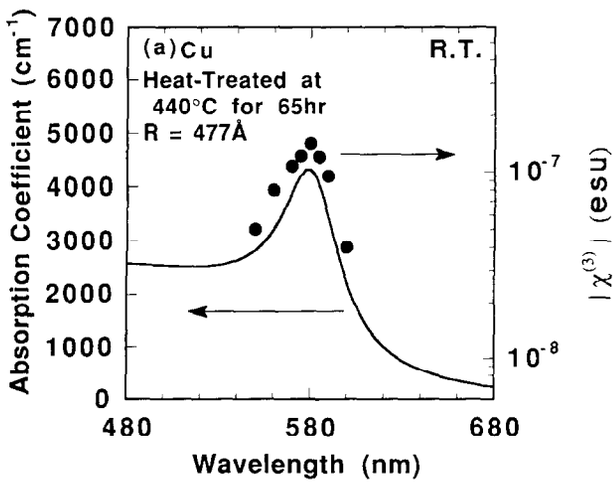

Fig. 10. The dependence of $\chi^{(3)}$ on the pumping wavelength: $50P_2O_5$–50BaO–6SnO glasses doped with $6Cu_2O$.[38]

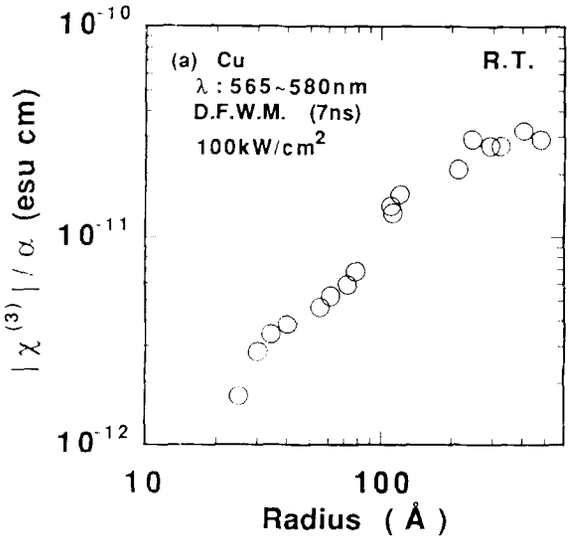

Fig. 11. Figure of merit, $\chi^{(3)}/\alpha$, as a function of particle size.

From this expression, a large figure of merit is expected by increasing particle radius or by increasing refractive index of the matrix material. The materials figure of merit, $\chi^{(3)}/\alpha$, is roughly independent of absorption coefficient α, but increases with increasing particle radius and reaches 2×10^{-11} for $R = 500$ Å, as shown in Fig. 11.[38] The enlargement of $\chi^{(3)}/\alpha$ owing to the enlargement of refractive index of the matrix material was observed for Au-doped $SrTiO_3$ and $BaTiO_3$ thin films[37] and for Cu-doped glasses with high refractive indices.[46]

3.2 Non-linear response time

Tokizaki *et al.*[39] showed that the plasmon resonance peak was broadened upon intense pump pulse irradiation. Time response of optical density change at the plasmon resonance peak is negative with a time constant of 1 ps, followed by change with a longer delay time. The slower component is ~150 ps and depends weakly on the metal particle radius. The fast component is most likely the result of the relaxation dynamics of hot electrons from the non-equilibrium heating state through the electron–phonon interaction. The slower component can be explained by diffusion of heat from metal particles to the glass matrix.[39]

4 SUMMARY

Non-linear optical properties of composite glass materials doped with nanometre-sized microcrystallites are reviewed. The non-linearities of the glass doped with semiconductor microcrystallites mainly originate from quantum confinement and band filling effects and are now on the order of 10^{-6} esu as a result of progress in new glass fabrication technologies. Photo-annealing effects are now intensely studied for a modification of the response time. The non-linear susceptibilities of the glases doped with small metal particles originate from the local field effect and non-equilibrium electron heating effect, and are on the order of 10^{-7} esu. The non-linear response is shorter than 1 ps.

A part of the work reported in this review was performed under the management of the Japan High Polymer Center as a part of the R and D of Nonlinear Photonics Materials supported by NEDO (New Energy Industrial Technology Development Organization).

REFERENCES

1. STEGEMAN, G. I. & STOLEN, R. H., *J. Opt. Soc. Am.*, **B6** (1989) 652.
2. JAIN, R. K. & LIND, R. C., *J. Opt. Soc. Am.*, **73** (1983) 647.
3. YUMOTO, J., FUKUSHIMA, S. & KUBODERA, K., *Opt. Lett.*, **12** (1987) 832.
4. VOGEL, W., *Chemistry of Glass* (translated by N. Kreidle). The American Ceramic Society Inc., Columbus, OH, 1985, p. 163.
5. EFROS, Al. L. & EFROS, A. L., *Sov. Semicond.*, **16** (1982) 772.
6. ROUSSIGNOL, P., RICARD, D. & FLYTZANIS, C., *SPIE* **1127** (1982) 109.
7. HANAMURA, E., *Oyo Butsuri*, **59** (1990) 352.
8. EKIMOV, A. I., EFLOS, Al. L. & ONUSHCHENKO, A. A., *Solid State Commun.*, **56** (1985) 921.
9. SUKIMOTO, N., MANABE, T., ITO, S., TOKIZAKI, T., KATAOKA, T. & NAKAMURA, A., *Topical Meeting on Non-linear Optical Materials, Phenonmena and Devices*, Hawaii, 16–20 July 1990, ThP13.
10. EKIMOV, A. I. & ONUSHCHENKO, A. A., *JETP Lett.*, **40** (1989) 1136.
11. HIRAGA, H., HATA, C., UCHIDA, K., OHMI, S., ASAHARA, Y., IKUSHIMA, A. J., TOKIZAKI, T. & NAKAMURA, A., *The 2nd Meeting on Glass for Optoelectronics*, Tokyo, 18 January 1991, p. 6.
12. OHMI, S., HIRAGA, H., UCHIDA, K., HATA, C., ASAHARA, Y., IKUSHIMA, A. J., TOKIZAKI, T. & NAKAMURA, A., *Proc. Int. Conf. on Sci. and Technol. of New Glass*, 1991, p. 181.
13. TANAHASHI, I., MANABE, Y., TSUJIMURA, A., MITSUYU, T., TOKIZAKI, T. & NAKAMURA, A., *The 32nd Glass and Photonics Materials Meeting*, Ohsaka, 25–26 November 1991, p. 63.
14. TAKADA, T., YANO, T., YASUMORI, A., YAMANE, M. & MACKENZIE, J. D., *The 32nd Glass and Photonics Materials Meeting*, Ohsaka, 25–26 November 1991, p. 67.
15. NOGAMI, M. & NAKAMURA, A., *The 32nd Glass and Photonics Materials Meeting*, Ohsaka, 25–26 November 1991, p. 75.
16. NOGAMI, M., OZAKI, K., NAGASAKA, K. & NAKAMURA, A., *The 37th Spring Meeting of Japan Applied Physics*, 31a-N-1, 1990.
17. SHINOJIMA, H., YUMOTO, J., UESUGI, N., OHMI, S. & ASAHARA, Y., *Appl. Phys. Lett.*, **55** (1989) 1519.
18. HATA, C., HIRAGA, H., OHMI, S., UCHIDA, K.,

ASAHARA, Y., IKUSHIMA, A. J., TOKIZAKI, T. & NAKAMURA, A., *Technical Digest of Optical Society of America, 1991 Annual Meeting*, San Jose, California, 3–8 November 1991, MSS-4.
19. MITSUNAGA, M., SHINOJIMA, H. & KUBODERA, K., *J. Opt. Soc Am.*, **B5** (1988) 1448.
20. ROUSSIGNOL, P., RICARD, D., LUKASIK, J. & FLYTZANIS, C., *J. Opt. Soc. Am.*, **B4** (1987) 5.
21. HIRAGA, H., HATA, C., UCHIDA, K., OHMI, S., ASAHARA, Y., IKUSHIMA, A. J., TOKIZAKI, T. & NAKAMURA, A., *XVI Int. Congress on Glass Vol. 3*, ed. D. E. de Ceramica y Vidrio, 1992, p. 421.
22. TOMITA, M. & MATSUOKA, M., *J. Opt. Soc. Am.*, **B7** (1990) 1198.
23. MALHOTRA, J., HAGAN, D. J. & POTTER, B. G., *J. Opt. Soc. Am.*, **B8** (1991) 1531.
24. OKAMOTO, H., MATSUOKA, J., NASU, H., KAMIYA, K. & TANAKA, H., *J. Appl. Phys.*, **75** (1994) 2251.
25. RICARD, D., ROUSSIGNOL, P. & FLYTZANIS, C., *Opt. Lett.*, **10** (1985) 511.
26. HACHE, F., RICARD, D. & FLYTZANIS, C., *J. Opt Soc. Am.*, **B3** (1986) 1647.
27. HACHE, F., RICARD, D., FLYTZANIS, C. & KREIBIG, U., *Appl. Phys.*, **A47** (1988) 347.
28. BLOEMER, M. J., HAUS, J. W. & ASHLEY, P. R., *J. Opt. Soc. Am.*, **B7** (1990) 790.
29. SHMITT-RING, S., MILLER, D. A. B. & CHEMLA, D. S., *Phys. Rev.*, **B35** (1987) 8113.
30. WAKABAYASHI, H., YAMANAKA, H., KADONO, K., SAKAGUCHI, T. & MIYA, M., *Proc. Int. Conf. on Sci. and Technol. of New Glass*, 1991, p. 412.
31. FUKUMI, K., CHAYAHARA, A., KADONO, K., SAKAGUCHI, T., HORINO, Y. & MIYA, M., *Jpn J. Appl. Phys.*, **30** (1991) L742.
32. MATSUOKA, J., MIZUTANI, R., KANEKO, S., NASU, H., KAMIYA, K., KADONO, K., SAKAGUCHI, T. & MIYA, M., *J. Ceram. Soc. Jpn*, **101** (1993) 53.
33. KADONO, K., SAKAGUCHI, T., WAKABAYASHI, H., FUKUMI, T., YAMANAKA, H., MIYA, M. & TANAKA, H., *Mater. Res. Soc. Symp. Proc.*, **283** (1993) 903.
34. MAGRUDER, R. H. III, YANG, LI, HAGLUND, R. F. JR, WHITE, C. W., YANG, LINA, DORSINVILLE, R. & ALFANO, R. R., *Appl. Phys. Lett.*, **62** (1993) 1730.
35. TANAHASHI, I., YOSHIDA, M., MANABE, Y., TOHDA, T., SASAKI, S., TOKIZAKI, T. & NAKAMURA, A., *Proc. 35th Meet. on Glass and Photonics Mater.*, 1994, p. 53.
36. KINERI, T., MATANO, E. & TSUCHIYA, T., SPIE 2288, *Sol–Gel Optics III*, 1994, p. 145.
37. KINERI, T., MORI, M., KADONO, K., SAKAGUCHI, T., MIYA, M., WAKABAYASHI, H. & TSUCHIYA, T., *J. Ceram. Soc. Jpn*, **103** (1995) 117.
38. UCHIDA, K., KANEKO, S., OHMI, S., HATA, C., TANJI, H., ASAHARA, Y., IKUSHIMA, A. J., TOKIZAKI, T. & NAKAMURA, A., *J. Opt. Soc. Am.*, **B11** (1994) 1236.
39. TOKIZAKI, T., NAKAMURA, A., KANEKO, S., UCHIDA, K., OHMI, S., TANJI, H. & ASAHARA, Y., *Appl. Phys. Lett.* **65** (1994) 941.
40. ARAI, T., KADONO, K., YAMANAKA, H., SAKAGUCHI, T., MIYA, M. & WAKABAYASHI, H., *J. Ceram. Soc Jpn*, **101** (1993) 105.
41. YANG, LI, BECKER, K., SMITH, F. M., MAGRUDER, R. H. III, HAGLUND, R. F. JR, YANG, LINA, DORSINVILLE, R., ALFANO, R. R. & ZUHR, R. A., *J. Opt. Soc. Am.*, **B11** (1994) 457.
42. MAGRUDER, R. H. III, HAGLUND, R. F. JR, YANG, L., WITTIG, J. E., BECKER, K. & ZUHR, R. A., *Mater. Res. Soc. Symp. Proc.*, **244** (1992) 369.
43. HAGLUND, R. F. JR, YANG, L. MAGRUDER, R. H. III, WITTIG, J. E., BECKER, K. & ZUHR, R. A., *Opt. Lett.*, **18** (1993) 373.
44. HOSONO, H., ABE, Y., LEE, Y. L., TOKIZAKI, T. & NAKAMURA, A., *Appl. Phys. Lett.*, **61** (1992) 2747.
45. TAKEDA, Y., HIOKI, T., MOTOHIRO, T. & NODA, S., *Appl. Phys. Lett.*, **63** (1993) 3420.
46. UCHIDA, K., KANEKO, S., OHMI, S., HATA, C., TANJI, H., ASAHARA, Y., TOKIZAKI, T. & NAKAMURA, A., *Annual Meeting Optical Society of America*, Dallas, 2–7 October 1994, TuI4.
47. KREIBIG, U. & FRAGSTEIN, C. V., *Z. Physik.*, **224** (1969) 307.