Optical and Photonic Glasses

Lecture 39:

Non-Linear Optical Glasses III – Metal Doped Nano-Glasses

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For New Functionality in Glass

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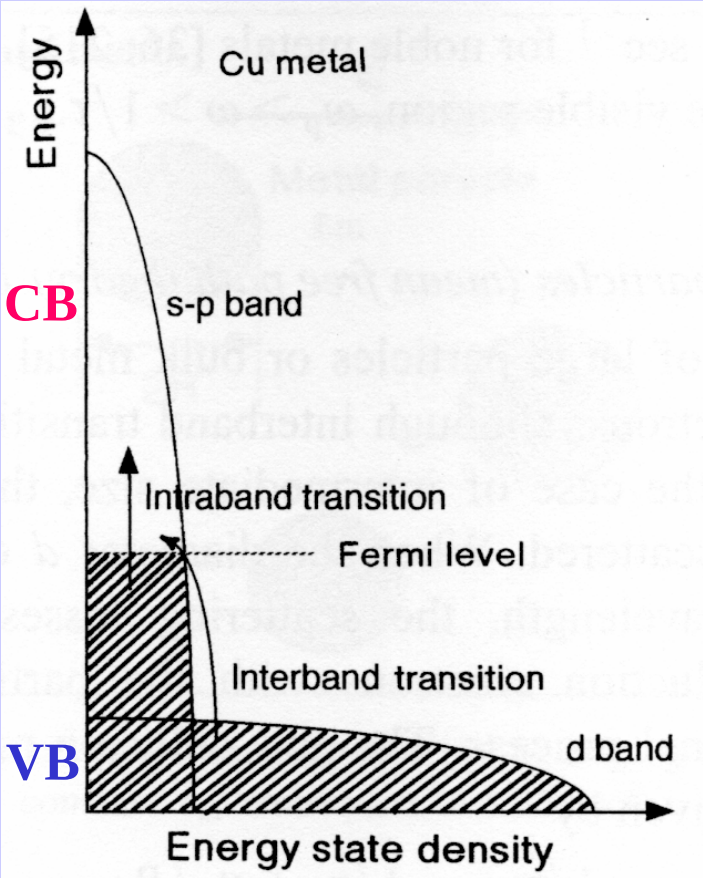
Metal-doped glasses

In noble metals like Cu, Ag and Au, the d-band overlaps the s-p CB, which makes possible *intraband* transitions in the CB and *interband* transitions between the d-bands and the CB.



Schematic expression of electron state density and band structure of Cu metal.

(Adapted from: *Glasses for photonics*, M. Yamane and Y. Asahara, Cambridge Univ. Press, 2000)

The dielectric constant of the metal particles is given by:

$$\varepsilon_m = \varepsilon_m' - i\,\varepsilon_m'' = 1 - \omega_p^2 / [\omega\,(\omega - i/\tau)]$$

where ω_p is the *plasma frequency* of the *bulk metal* ($\omega_p = (4\,\pi\,N\,e^2 / m^*)^{1/2}$ and m* is the effective mass of the $N \sim 10^{22}$ cm^{-3} conduction electrons per unit volume) and τ is the time between collisions among electrons. Therefore:

$$\varepsilon_m' = n^2 - k^2 = 1 - \omega_p^2\,\tau^2 / [1 + (\omega\tau)^2]$$

$$\varepsilon_m'' = 2\,n\,k = \omega_p^2\,\tau / \{\omega\,[1 + (\omega\tau)^2]\}$$

For a metal like Cu or Ag, the mean free path of the conduction electrons is ~ 50 nm and τ (= 50 nm / v_F) ~ 5 x 10^{-14} s. Thus, at visible or NIR frequencies ($\omega \sim 10^{15}$ s^{-1}) , one has $(\omega\tau)^2 >> 1$ and the simplified form of the equations:

$$\varepsilon_m' = 1 - \omega_p^2 / \omega^2$$

$$\varepsilon_m'' = \omega_p^2 / \omega^3\,\tau$$

For noble metals, $\omega_p \sim 10^{16}$ s^{-1}. Therefore, for Ag or Cu in the visible region, one has $\omega_p > \omega > 1/\tau$. (At ω_p, $\varepsilon_m = 0$; below ω_p, $\varepsilon_m < 0$ and n* is imaginary and % R ~ 1).

When the diameter (d = 2R) of spherical metal particles is << λ, scattering of the incident light beam is negligible. Also, collisions of the conduction electrons with the particle surfaces become important and the new collision relaxation time, τ_{eff}, is given by:

$$1 / \tau_{eff} = 1 / \tau_b + v_F / R$$

where τ_b is the bulk value and v_F is the Fermi velocity (= 1.4 x 10^6 m/s for Ag) and the mean free path is ($v_F \tau_b$) ~ 50 nm. If 2R << 50 nm, then the mean free path in the nanoparticle is ~ 2R and it is entirely limited by particle boundary scattering:

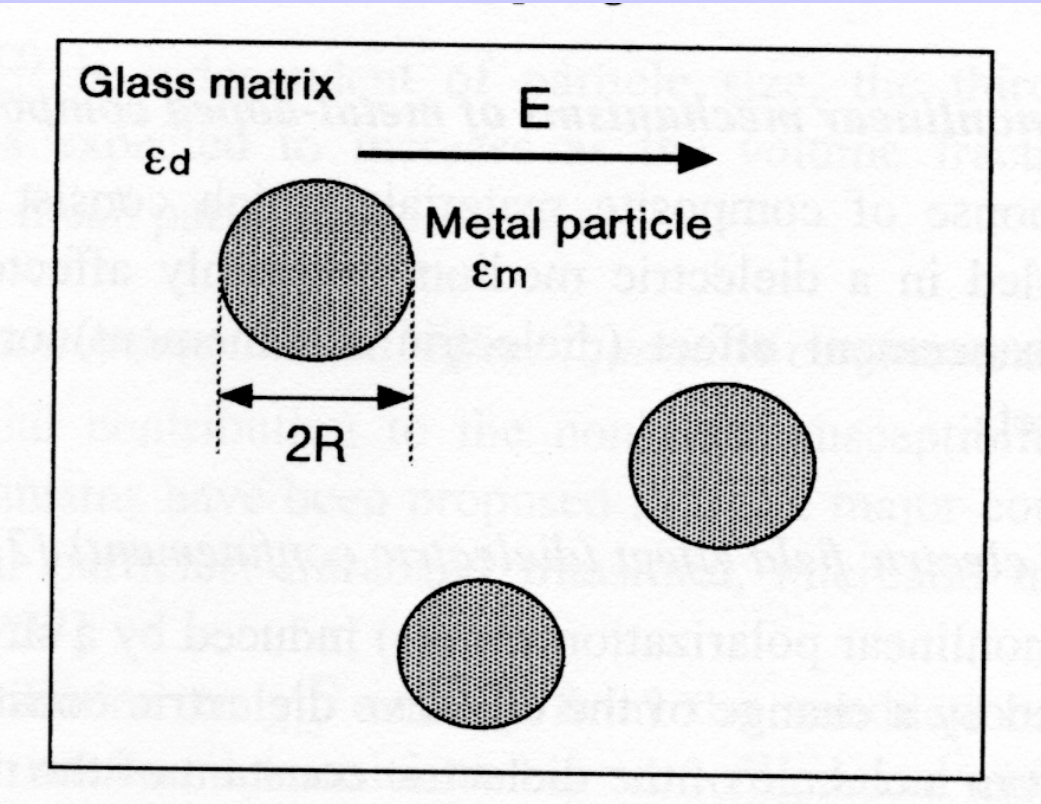
$$1 / \tau_{eff} = v_F / R$$

Glass / metal particle nanocomposites

Composites formed by spherical metal nanoparticles embedded in a dielectric glass with a real dielectric constant ε_d have rather interesting NLO properties. If 2R << λ and the volume fraction of spheres is p << 1, the effective dielectric constant of the composite will be:

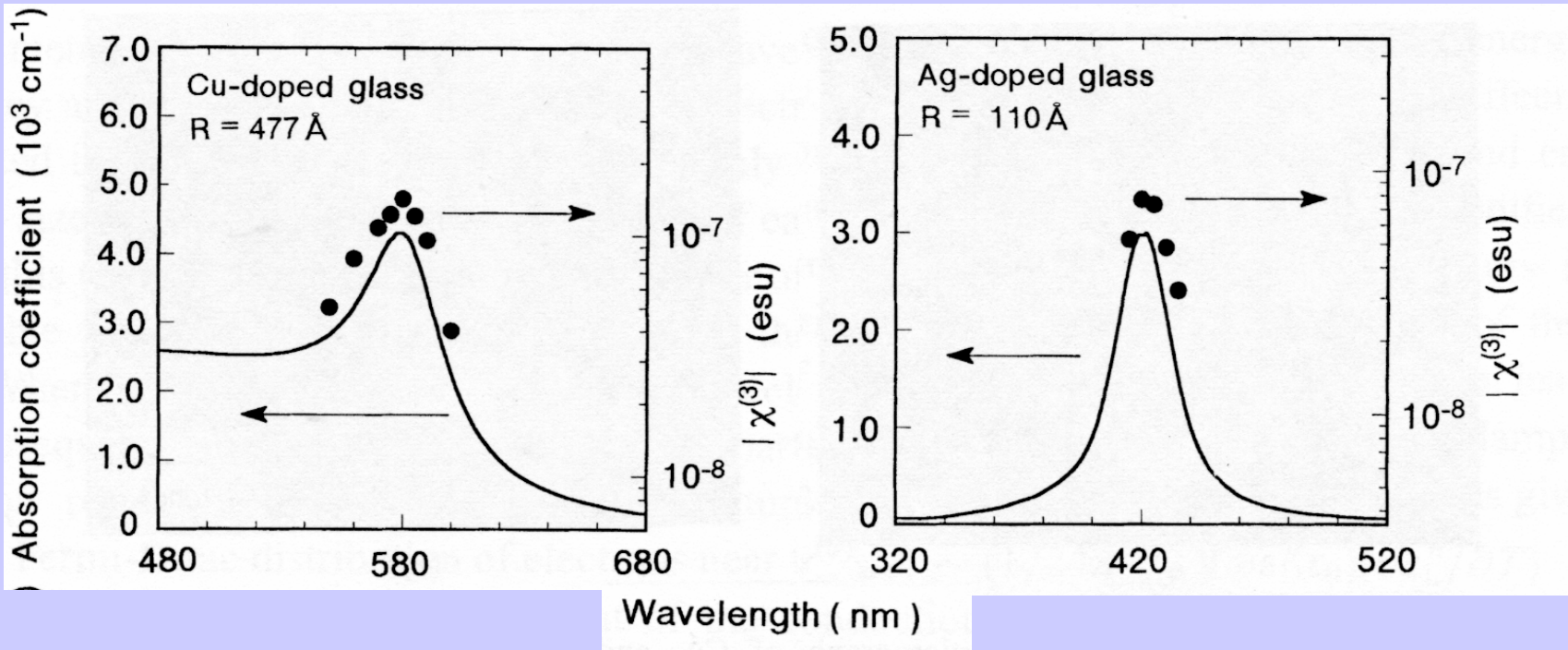
$$\varepsilon_{eff} = \varepsilon_d + 3\ p\ \varepsilon_d\ [(\varepsilon_m - \varepsilon_d) / (\varepsilon_m + 2\varepsilon_d)]$$

The *absorption coefficient* of the *composite* ($\alpha = 2\ \omega\ k / c$) has a *maximum* at the "surface plasma resonance" frequency, ω_s: ε_{eff}" maximum <=> $\varepsilon_m'(\omega_s)+2\varepsilon_d = 0$. This corresponds to collective electronic excitations at the metal/glass interface.



Schematic diagram of a composite material consisting of a metal particles of radius R with complex dielectric constant ε_m embedded in a dielectric matrix with a real dielectric constant ε_d.

(Adapted from: *Glasses for photonics*, M. Yamane and Y. Asahara, Cambridge Univ. Press, 2000)



Absorption spectra and wavelength dependence of $\chi^{(3)}$ for Cu- and Ag-doped glasses. [Reprinted from K. Uchida, S. Kaneko, S. Omi, C. Hata, H. Tanji, Y. Asahara, *et al. J. Opt. Soc. Am.* **B11** (1994) 1236, copyright (1994) with permission from the Optical Society of America.]

(Adapted from: *Glasses for photonics*, M. Yamane and Y. Asahara, Cambridge Univ. Press, 2000)

The absorption spectra have a Lorentzian shape, whose FWHM coincides with the damping constant $\gamma = 1/\tau_{eff} = v_F / R$. Therefore:

$$R = v_F / \text{FWHM}$$

The optical response of such metal particle/glass composites is determined either by an *enhancement of the electric field* near the metal particles (*dielectric confinement*), or also by *quantum confinement*.

Dielectric confinement

The local field enhancement inside the nanoparticles, relative to the external field (E), $f_{loc} = (E_{loc} / E)$, is maximum at the frequency ω_s, for which $(\varepsilon_m' + 2\,\varepsilon_d) = 0$:

$$f_{loc} = 3\,\varepsilon_d / (\varepsilon_m + 2\,\varepsilon_d) = 3\,\varepsilon_d / \varepsilon_m''(\omega_s) = 3\,\varepsilon_d /(\omega_p^2/\omega_s^3\,\tau_{eff}) = 6\,\varepsilon_d\,\omega_s^3\,R / (\omega_p^2\,v_F)$$

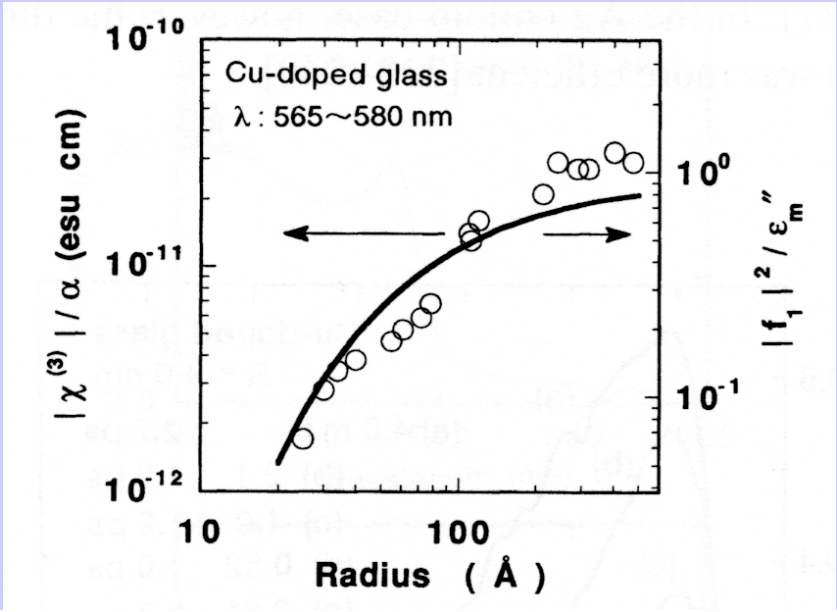
Also it is possible to show that $\chi^{(3)}$ of the composite is related to that of the metal particles:

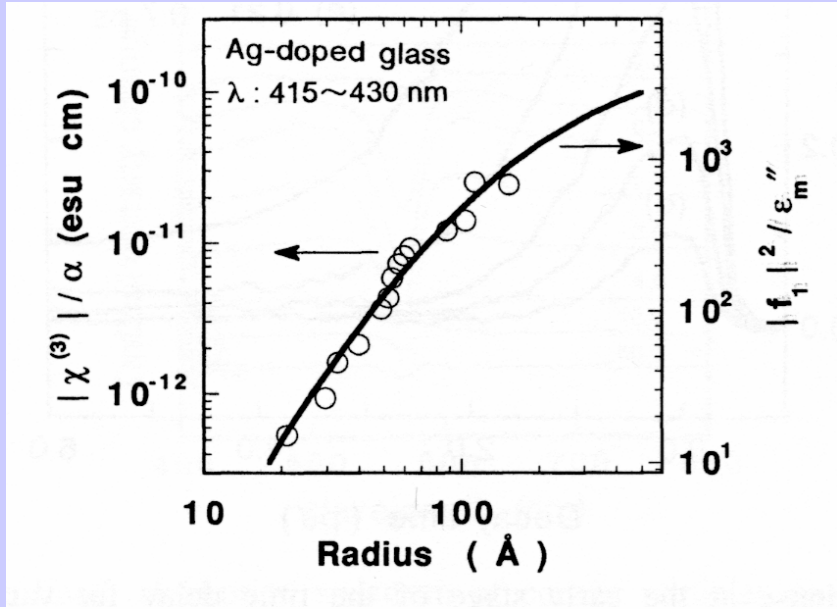
$$\chi^{(3)} = 3\,p\,f_{loc}^4\,\chi_m^{(3)}$$

So, if one assumes $\chi_m^{(3)}$ independent of particle size, then the 3rd order susceptibility, $\chi^{(3)}$ will increase as the volume fraction of metal particles and their size increases.

A *figure of merit* often used for evaluation of a NLO material involves a large $\chi^{(3)}$ and a low absorption coefficient, α, for the composite:

$$F = \chi^{(3)} / \alpha$$





$\chi^{(3)}/\alpha$ and f_i^2/ε_m'' as a function of particle size. [Reprinted from K. Uchida, S. Kaneko, S. Omi, C. Hata, H. Tanji, Y. Asahara, *et al. J. Opt. Soc. Am.* **B11** (1994) 1236, copyright (1994) with permission from the Optical Society of America.]

Note: the values of $f_{loc}^2 / \varepsilon_m$" were calculated based on the mean free path theory.

(Adapted from: *Glasses for photonics*, M. Yamane and Y. Asahara, Cambridge Univ. Press, 2000)

Quantum confinement

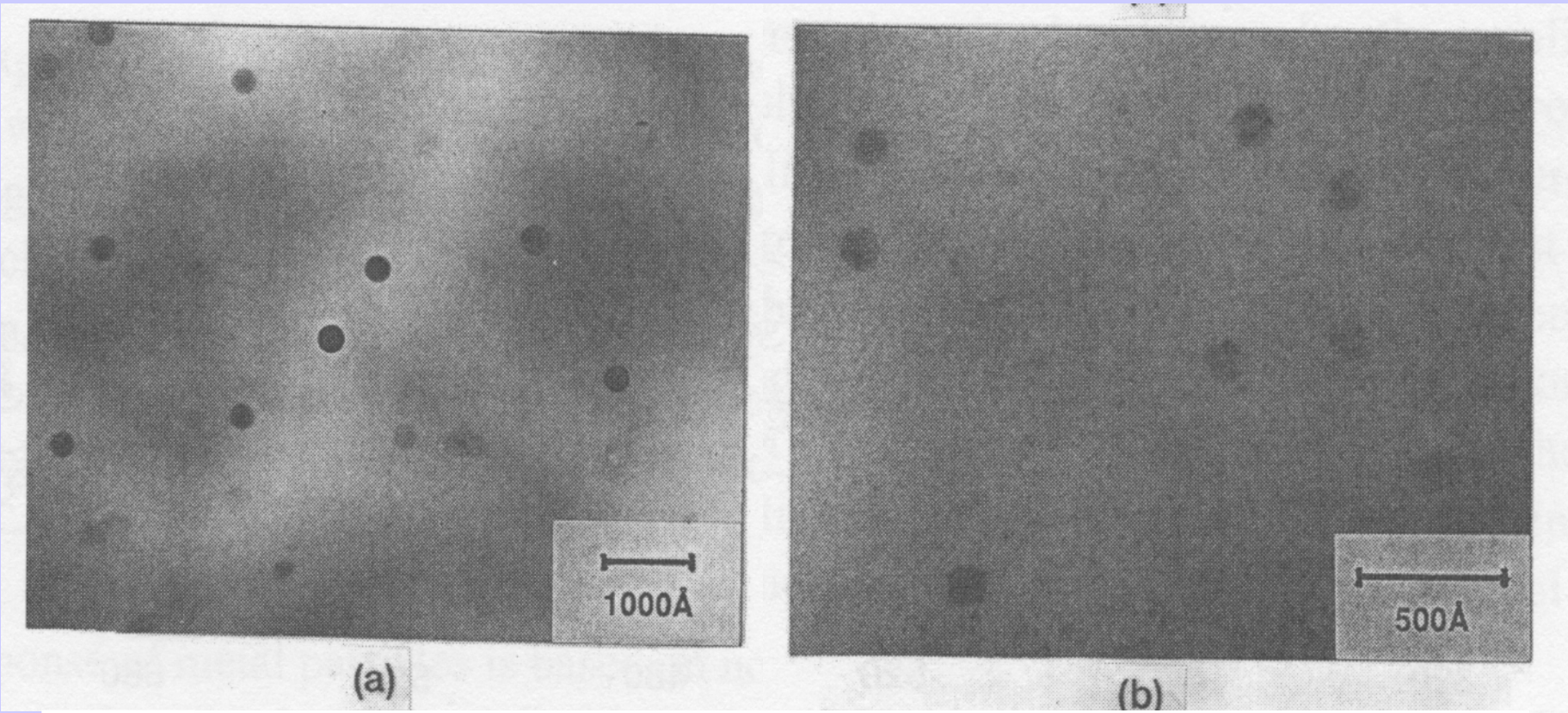
The main contribution to quantum confinement comes from intraband transitions between filled and empty states in the CB, with the CB split into discrete levels due to the small size of the metal particles, or interband transitions between the d and s-p (CB) bands.

Non-linear properties of metal-doped glasses

The large value of $\chi^{(3)}$ of these glasses arises mostly from the local electric field enhancement near the surface of the metal particles in the vicinity of ω_s, due to their surface plasma resonance.

In the following figure, most noble metal particles appear as spheres ~ 10 nm in diameter. Their absorption spectra and $\chi^{(3)}$ values are shown next.

TEM micrographs of glasses doped with metal particles: (a) Cu and (b) Ag.



Transmission electron micrograph of Cu- and Ag-doped $BaO-P_2O_5$ glass. (a) $50P_2O_5-50BaO-6SnO-6Cu_2O$, (b) $50P_2O_5-50BaO-4SnO-4Ag_2O$. [Reprinted from K. Uchida, S. Kaneko, S. Omi, C. Hata, H. Tanji, Y. Asahara, *et al. J. Opt. Soc. Am.* **B11** (1994) 1236, copyright (1994) with permission from the Optical Society of America.]

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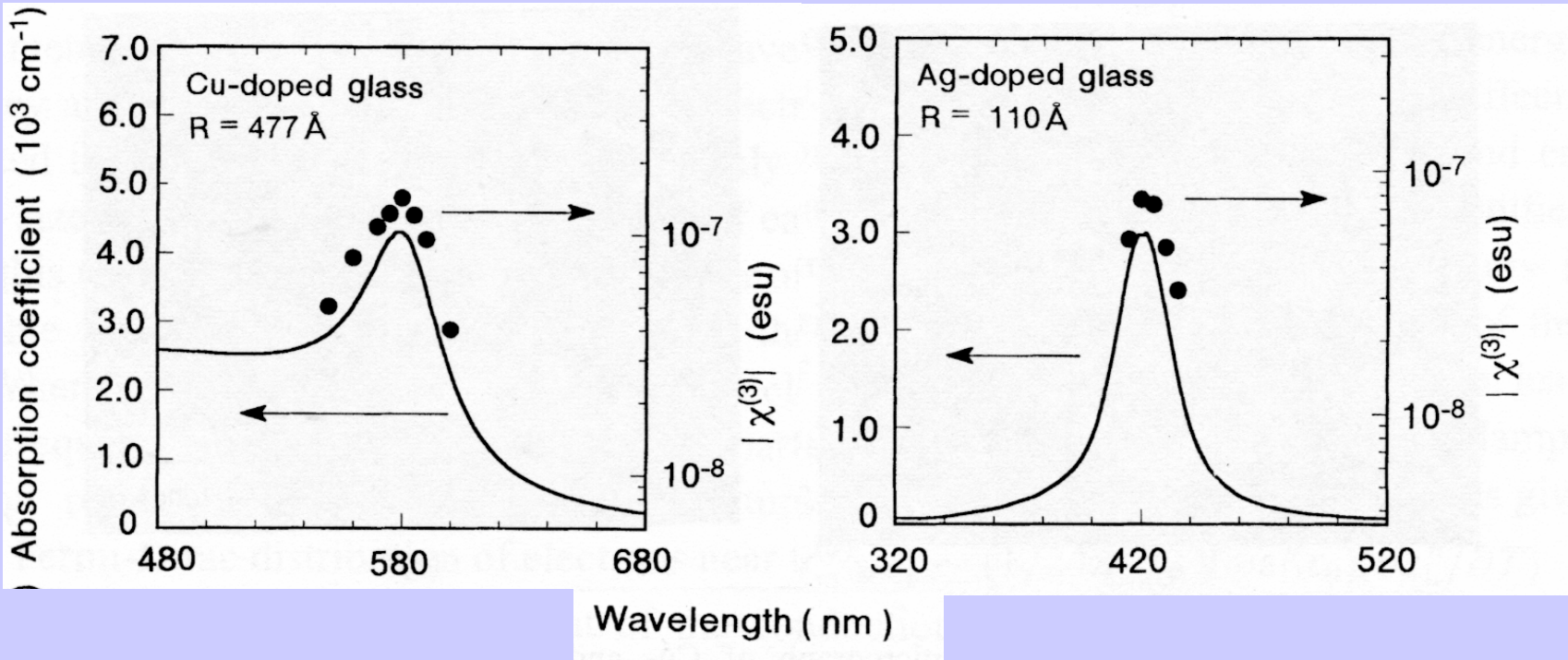
The values of $\chi^{(3)}$ (filled circles) exhibit a peak (~ 10^{-7} esu) at almost the same wavelength as the surface plasma absorption. Calculating f_{loc} from the values of the dielectric constants and p from the measured absorption coefficient, the value of $\chi_m^{(3)}$ can be obtained from the $\chi(3)$ data: ~ 2-4 x 10^{-9} esu for Ag and ~ 10^{-6} for Cu. In this latter case, the shoulder is due to interband transitions from the d-band to the CB.



Absorption spectra and wavelength dependence of $\chi^{(3)}$ for Cu- and Ag-doped glasses. [Reprinted from K. Uchida, S. Kaneko, S. Omi, C. Hata, H. Tanji, Y. Asahara, *et al. J. Opt. Soc. Am.* **B11** (1994) 1236, copyright (1994) with permission from the Optical Society of America.]

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Response time

Most of the available data for Ag and Au colloids in glasses show NLO responses on a several ps time scale.

Fabrication techniques

Several methods have been used in order to prepare glasses containing metal nano-particles, including melt-quenching, sol-gel processing, sputtering and ion implantation.

The following table lists the main NLO properties of metal-doped glasses prepared by different techniques.

Nonlinear characteristics of metal-doped glasses made by new fabrication processes

Dopant	Matrix	Diam. (nm)	Process	Measurement (λ, nm)	α (cm^{-1})(λ, nm)	$\lvert\chi^{(3)}\rvert$ (esu)	τ (ps)	$\chi_m^{(3)}$ (esu)	Ref.
Au	glass	2.8 ~ 30	MQH	DFWM	(~530)	~5.5 (10^{-11})	5	~8.2 (10^{-8})	224
		10	MQH	DFWM (532)			28	1.5 (10^{-8})	223
	SiO_2	5.5	SPT	DFWM (532)		1.3 (10^{-7})			246
	SiO_2	5.8	IP	DFWM (532)		1.2 (10^{-7})		8 (10^{-8})	247
	SiO_2	~3	IP	DFWM (532)		10^{-7} ~ 10^{-8}		2.5 (10^{-8})	252
	SiO_2	5.8	SPT	DFWM (532)		3.5 (10^{-8})		3 (10^{-8})	249
	SiO_2	8.8	MQH	DFWM (532)		2.5 (10^{-11})		7 (10^{-8})	249
	SiO_2	1.4 ~ 6	SG	DFWM (532)	3 (10^3) (450)	~7.7 (10^{-9})		10^{-7}	229
	SiO_2	5 ~ 30	IP	DFWM (532)		1.7 (10^{-10})			248
	SiO_2		SG	TBSD	~5.5 (10^5) (450)	~6.3 (10^{-8})		~2 (10^{-6})	230
	Water	5 ~ 30		DFWM (532)			29	2 ~ 5 (10^{-8})	233
	SiO_2		SPT	DFWM (532)				5 ~ 20 (10^{-8})	242
	SiO_2	10	SG	TBSD (540)	2.6 (10^3)	2.3 (10^{-8})		1.1 (10^{-6})	231
	SiO_2	3 ~ 80	SPT	DFWM (532)		2.5 (10^{-6})			259
	SiO_2	3 ~ 33.7	SPT	DFWM (530)		2.0 (10^{-7})		3.0 (10^{-7})	243
	SiO_2		SPT	DFWM (532)		~4 (10^{-6})		~4.2 (10^{-8})	260
Ag		7		DFWM (400)				2.4 (10^{-9})	223
	glass	4 ~ 30	MQH	TBSD (532)	~3.5 (10^3) (532)	~7.6 (10^{-8})		2 ~ 4 (10^{-9})	228
	glass		IE, IP	ZS (591)		$n_2'' = (10^{-10})(cm^2/W)$			258
	SiO_2	2 ~ 5	SPT	TBSD (400)	5.7 (10^4) (400)	1.6 (10^{-8})			256
	glass		MQH	TBSD			0.75	–	264
Cu	glass	5 ~ 100	MQH	TBSD (532)	~4.7 (10^3) (532)	1.2 (10^{-7})		1 ~ 2.5 (10^{-6})	228
	glass	8	MQH	PP		3.5 (10^{-9})	0.7	1.4 (10^{-6})	236
	SiO_2	2 ~ 28	IP	ZS (532)		$n_2'' = \sim 2.3\ (10^{-7})(cm^2/W)$			235
							<5		
	SiO_2		IP	ZS (570 ~ 600)	~(10^4)	~ (10^{-8})			250
						$2.0 < n_2'' < 4.2\ (10^{-10})\ (cm^2/W)$			
	SiO_2	5.2 ~ 12.6	IP	DFWM (532)		~8.4 (10^{-10})		~46.8 (10^{-9})	226
	SiO_2	12 ~ 28	SPT	DFWM (532)		4 (10^{-9})			251
	SiO_2	5.2 ~ 12.6	IP	ZS (570)		$n_2'' = \sim 6\ (10^{-10})\ (cm^2/W)$			259
	SiO_2	~10	IP	ZS (770)	1.2 (10^4)	$n_2'' = 5\ (10^{-11})\ (cm^2/W)$			262
Au–Cu	SiO_2	~30	IP	ZS (570)	4.6 ~ 5.9 (10^4)	$n_2'' = \sim 1.6\ (10^{-9})(cm^2/W)$			254
Ag–Cu	SiO_2	1 ~ 10	SG	DFWM (532)		~1.06 (10^{-7})			261
P	SiO_2	3 ~ 5	IP	TBSD (390)		1.2 (10^{-6})			253
Sn	SiO_2	4 ~ 20	IP	TBSD		3 (10^{-6})			255
Ni	SiO_2	~10	IP	ZS (770)	1.4 (10^4)	$n_2'' = 1.7\ (10^{-10})\ (cm^2/W)$			262
Cu–Ni	SiO_2	~10	IP	ZS (770)	4.0 (10^4)	$n_2'' = 6.8\ (10^{-10})\ (cm^2/W)$			262
Co	SiO_2		IP	ZS (770)		$n_2'' = 1.8\ (10^{-10})\ (cm^2/W)$			263

MQH, melt-quench and heat-treatment; SPT, spattering; IP, ion implantation; IE, ion exchange; SG, sol-gel process; PP, Porous process.
DFWM, degenerate four-wave mixing; TBSD, two beam self diffraction; ZS, z-scan technique; PP, pump-probe.

(Adapted from: *Glasses for photonics*, M. Yamane and Y. Asahara, Cambridge Univ. Press, 2000)

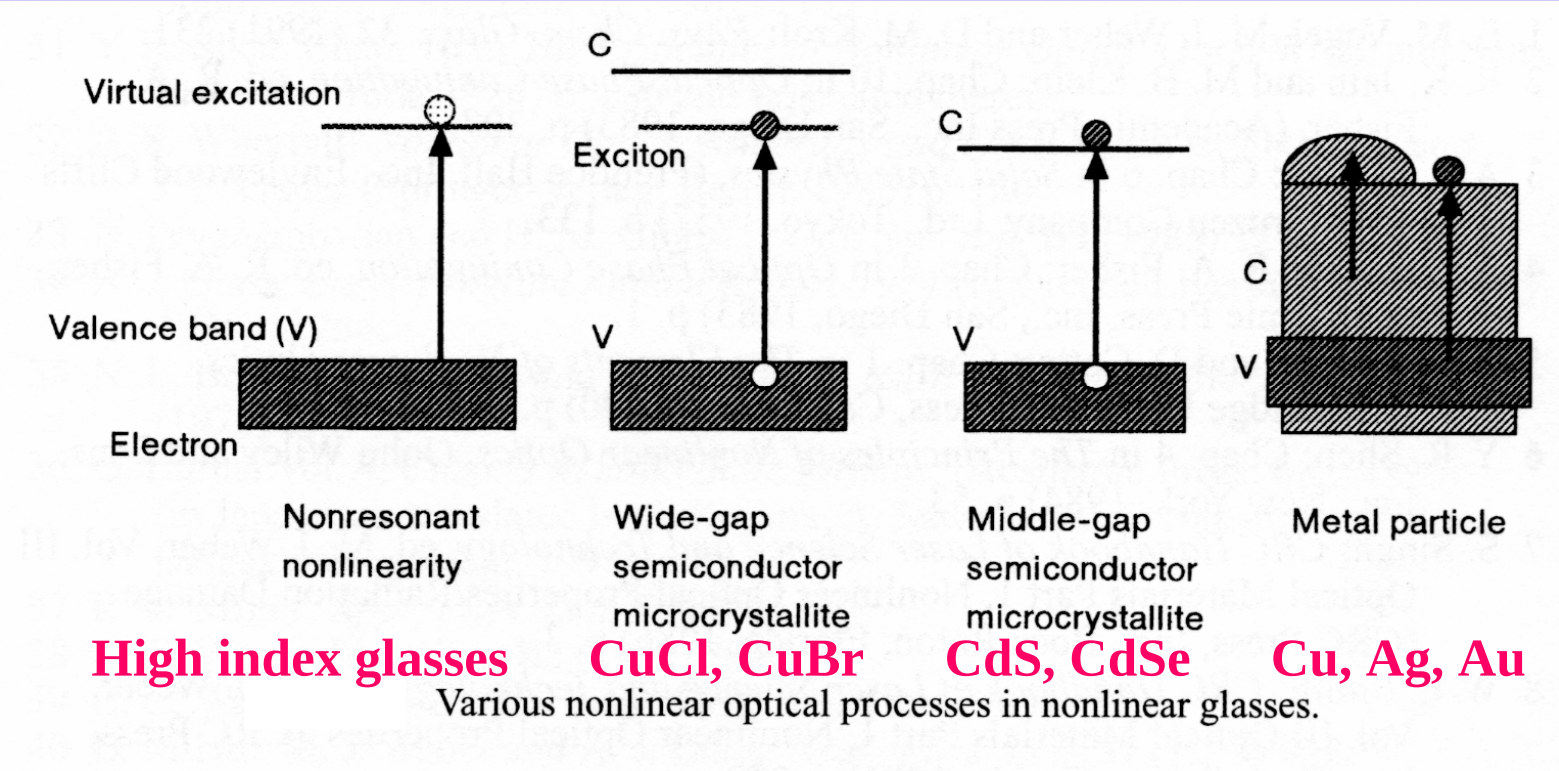
Main NLO processes and mechanisms in glasses

Classification and main nonlinear mechanisms of representative nonlinear glass materials

Dopant	Carrier	Mechanism of optical nonlinearity	
		Dopant	Glass materials – Size effect
Nonresonant • High index glasses • Chalcogenide glasses	Insulator • Bound electron	• Unharmonic terms of electronic polarization	
Resonant • CuCl and CuBr-doped glasses	Wide-gap semiconductor (Bound exciton)	• Biexciton • Phase space filling • Plasma screening • Exchange effect	Weak quantum confinement • Enhancement of space filling • Super-radiation • Giant oscillation
• CdSSe, CdSe and CdTe-doped glasses • Color filter glasses	Middle-gap semiconductor (Electron and hole)	• Band filling effect (Blocking effect) • Auger recombination • Free electron absorption • Trapping effect • Thermal effect	Strong quantum confinement • Enhancement of state filling • Auger recombination • Free electron absorption • Trapping effect • Photodarkening effect
• Ag, Cu, and Au-doped glasses	Conductor (Free electron)	• Hot electron (Fermi smearing) • Saturation of interband and intraband absorption	Dielectric confinement • Local field effect • Hot electron scattering (Fermi smearing) Quantum confinement • Enhancement of saturation of intra- and inter-band absorption

(Adapted from: *Glasses for photonics*, M. Yamane and Y. Asahara, Cambridge Univ. Press, 2000)

Schematic representation of the different NLO processes in glasses



Various nonlinear optical processes in nonlinear glasses.

(Adapted from: *Glasses for photonics*, M. Yamane and Y. Asahara, Cambridge Univ. Press, 2000)

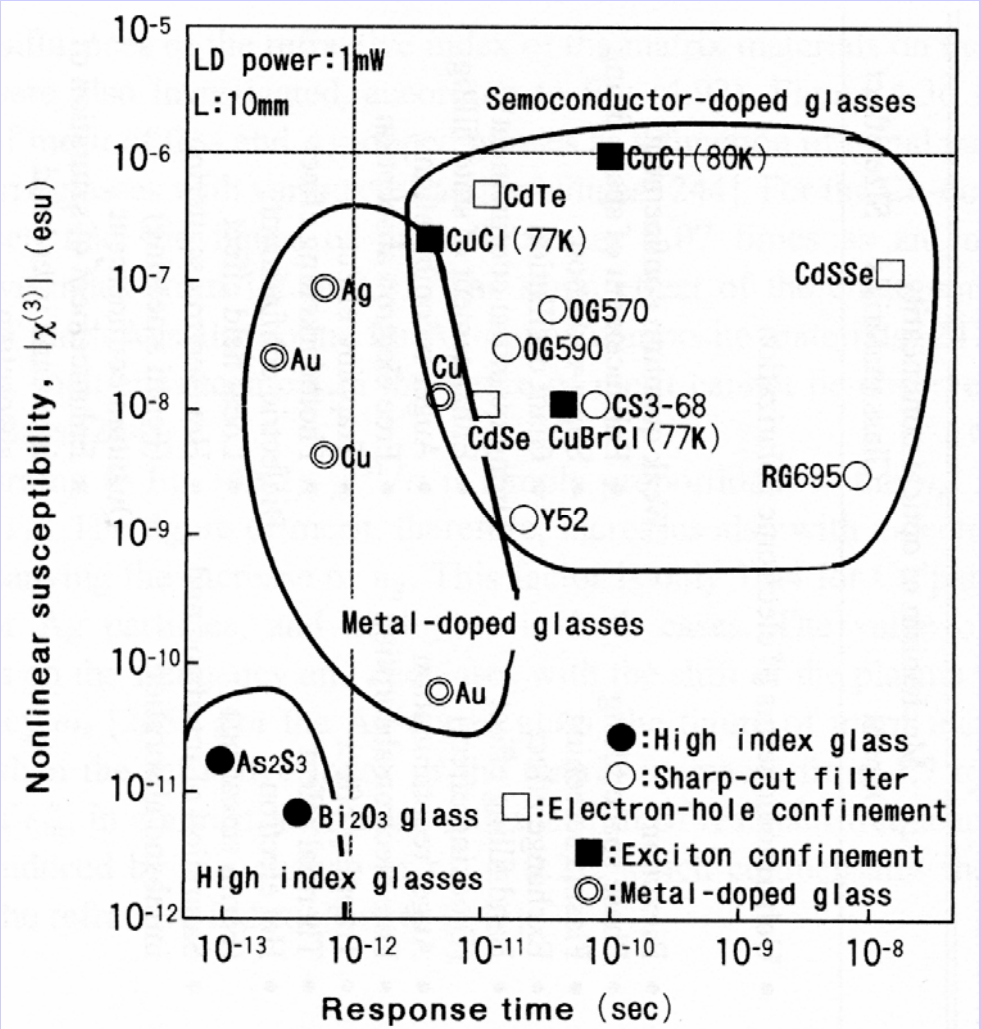
The intrinsic (**non- resonant**) glass nonlinearities are excited in the transparent region, well below the bandgap. The advantages are negligible linear optical losses in the wavelength range of interest and extremely fast response times.

The other nonlinearities are **resonant**, therefore involving electronic transfers from one energy level to another. The resultant optically induced absorption changes yield optically induced (non-linear) refractive index changes (through the K-K transformations), corresponding to significant third order NLO effects. Glasses doped with SC or metal nanoparticles exhibit such effects.

Band-filling effects mainly produce the NLO absorption changes (β being a function of Im $\chi^{(3)}$) which lead to the optical nonlinearities in SC-doped glasses and the quantum size (confinement) effect leads to a further enhancement of these nonlinearities. A major advantage of these glasses are the large NLO effects even under a small applied optical field, but the response times have limited speeds. In the presence of SC nanoparticles, the exciton states result in much higher nonlinearities than for bulk SC.

In metal nanoparticle-doped glasses, the nonlinearities are mainly attributed to local electric field enhancement near the surface plasma resonance of the particles. These glasses exhibit large optical nonlinearities, as well as fast response times near ω_s.

$\chi^{(3)}$ vs. response time diagram for typical NLO glasses



The nonlinear susceptibilities versus nonlinear response time. (Data from Table 4.4, 4.5, 4.6 and 4.7. The broken lines (response time: 10^{-12} sec, $|\chi^{(3)}|$: 10^{-6} esu) indicate the conditions required for obtaining 2π phase shift when pulse selector is made using 1 mW-LD and 10 mm optical path [265].)

(Adapted from: *Glasses for photonics,* M. Yamane and Y. Asahara, Cambridge Univ. Press, 2000)