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Measurement of the third-order nonlinear susceptibility of Ag nanoparticles in glass in a wide spectral range

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Abstract. – We determined the third-order susceptibility $|\chi^{(3)}|$ of a thin composite film formed by silver nanoclusters embedded in soda-lime glass. Ag aggregation was promoted by irradiating an Ag-Na ion-exchanged glass with an N^+ beam. $|\chi^{(3)}|$ dispersion was measured by phase-mismatched degenerate four-wave mixing in the 380–470 nm spectral range, with 0.5 ps laser pulse duration. Close to the surface plasmon resonance of Ag metallic clusters, the $\chi^{(3)}$ amplitude exceeds by a factor of 10^4 the value of substrate glass. We also measured a phase of 83° and a dynamics characterized by ∼ 30, 3 and 0.9 ps decay times, ascribed to hot-electrons-lattice thermalization in the clusters, followed by thermal diffusion toward the matrix and relaxation of the whole system to the starting temperature.

Introduction. – Composite materials formed by nanometer-sized metal particles embedded in silicate glasses have drawn great interest owing to the large values of fast optical Kerr susceptibility, $\chi^{(3)}$, whose real part is related to the intensity-dependent refractive index n_2, defined by $n = n_0 + n_2 I$, where n and n_0 are the total and the linear refractive indices of the material, respectively, and I is the intensity of the light impinging on it [1]. Dielectric and quantum confinement effects come into play in the optical nonlinear response of the composite [2,3]. In particular, the quantum size effect is related to the nanoparticle dimensions,

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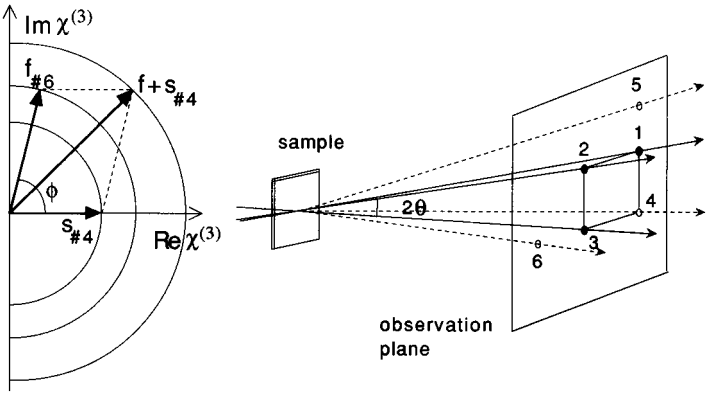

Fig. 1. – Left: diagram in the complex $\chi^{(3)}$ plane showing the quantities evaluated from measurements. Amplitudes of $\chi^{(3)}(f)$: central arc; $\chi^{(3)}(s)$: inner arc; $\chi^{(3)}(f,s)$: outer arc. Right: scheme of the beam geometry used in the DFWM experiment.

which are smaller than the mean free path of the metal conduction electron. Third-order nonlinearity is also related to the optical absorption of the composite. An optical absorption band is observed at the frequency where surface plasmon resonance (SPR) of the metallic particles takes place, following the relation $\varepsilon_{\mathrm{m}}(\omega) + 2\varepsilon_{\mathrm{d}}(\omega) = 0$, where $\varepsilon_{\mathrm{m}}(\omega)$ is the real part of the metal particle dielectric function and $\varepsilon_{\mathrm{d}}(\omega)$ is the dielectric function of the surrounding host. In the case of silver metal clusters in the nanometer range of size, SPR occurs around 400 nm [4].

A critical parameter for the evaluation of the nonlinear response is the laser pulse duration, since the fast electronic contributions can be overwhelmed by slower thermal effects when the pulse duration is relatively long [5]. Moreover, the nonlinear behaviour of the material across the SPR is of major importance —besides the technological implications— for the understanding of the actual electronic processes responsible for the observed nonlinearity. Uchida and co-workers presented [6] a study of the nonlinear response of a silver-cluster–doped glass around the SPR peak in the nanosecond time-scale. In this letter, we present for the first time a study of $\chi^{(3)}$ dispersion in the picosecond range around the SPR band peak for a composite glass containing silver particles.

Sample preparation. – Several methods have been investigated for the fabrication of metal-nanocluster–doped glasses, namely, ion implantation [7,8], sol-gel routes [9], sputtering or other co-deposition techniques [10,11], or combined methodologies such as ion exchange followed by either low-mass ion irradiation [12,13] or annealing in hydrogen atmosphere [14]. Colloidal glasses were obtained in this experiment by a methodology exploiting the combination of ion exchange and ion irradiation techniques. Standard soda-lime glass slides were first ion-exchanged in a molten salt bath of 20% mol $AgNO_3$ in $NaNO_3$ for 60 s at 350 °C, so obtaining planar optical waveguides with silver diffusion up to a few microns of depth, and silver concentration values of a few 10^{21} atoms/cm^3 at the surface. The samples were subsequently irradiated with a 100 keV N^+ beam at the fluence of $4 \times 10^{16}\,N^+/cm^2$, in order to promote the silver migration and aggregation due to electronic energy deposition mechanisms [15]. In this way, we obtained glasses containing silver clusters of a few nanometers of radius, as reported elsewhere [16]. The samples were analysed by cross-sectional transmission electron microscopy with a Philips CM30 TEM, operated at 300 kV, and by optical absorption spectroscopy with a Cary 5 UV-VIS-NIR double-beam spectrophotometer.

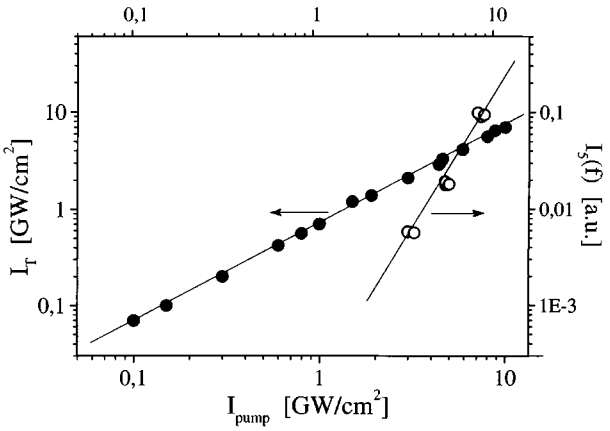

Fig. 2. – Right: example of the cubic dependence of I_5 on the incident pump intensity at 400 nm. The linear fit has slope 3.15 ± 0.2. Left: transmitted intensity of the glass substrate at 400 nm.

$\chi^{(3)}$ *measurements and discussion.* – The experiment has been performed at the Optical Nonlinear Processes laboratory in Como, using a feedback-controlled mode-locked and chirped-pulse amplified Nd:glass laser system, Twinkle, pumping a BBO traveling-wave parametric amplifier TOPAS (both from Light Conversion, Vilnius, Lithuania). After frequency doubling, the system provides, at 3 Hz repetition rate, pulses of 50 μJ, 0.5 ps of duration, tunable in the 320–527 nm range. We accomplished the $\chi^{(3)}$ measurements following the elegant and simple method recently proposed by Strohkendl *et al.* [17], which evaluates both amplitude and phase of the $\chi^{(3)}$ in a single setup and discriminates between the contributions of the active film and of the substrate. The basic idea is presented in fig. 1. The measured quantities, *i.e.* the $\chi^{(3)}$ amplitudes, correspond to the radii of the nanocluster-doped layer (f), substrate (s) and layer+substrate ($f + s$) circumferences in the complex plane. By assuming a real positive contribution to $\chi^{(3)}$ of the substrate and a definite sign of the layer $\mathrm{Im}(\chi^{(3)})$, the phase ϕ is determined by simple geometrical considerations.

We used the same experimental setup as in [17], with the three co-polarized forward pump beams intersecting on the sample with the same angle 2θ, as illustrated also in fig. 1. It is easily verified that among the diffracted beams, number 4 exhibits zero **k**-vector mismatch, $|\Delta\mathbf{K}| = |\mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3 - \mathbf{k}_4| = 0$, where $\mathbf{k}_i$, $i = 1, 2, 3$, are the wave vectors of the three pump beams and $\mathbf{k}_4$ the one of the signal. The diffracted beam 5, on the other hand, completely equivalent to beam 6 in the co-polarized configuration, exhibits a wave vector mismatch $|\Delta\mathbf{k}| = |\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3 - \mathbf{k}_5| \cong 8\pi^2/n\lambda_0$, n being the index of refraction of the glass host (1.5 in all cases) and λ_0 the vacuum wavelength of the laser light. In our experiment, θ was set at 2°, so, at 400 nm of wavelength, Δk resulted to be 510 cm^{-1}. From the theory [18] the intensities of the generated beams are

$$I_{4,5} \propto |\chi^{(3)}|^2 \cdot z^2 \cdot (I_{\mathrm{pump}})^3 \cdot F\,, \tag{1}$$

where the modulation factor of the signal intensity is $F = (\sin(x)/x)^2$, with $x = |\Delta\mathbf{k}|z/2$ and z the sample thickness (1 μm for the doped layer and 1 *mm* for the substrate). Supposing $|\chi^{(3)}(s)| < 10^{-3}|\chi^{(3)}(f)|$, an assumption consistent with our measurements, one gets that $I_i(s)/I_i(f) \cong F(s)/F(f) = 1$ for $i = 4$ (or for all beams in collinear FWM) and $\sim 2 \times 10^{-4}$ for $i = 5$. This guarantees that beam 5 is due only to contributions from the film, whereas in

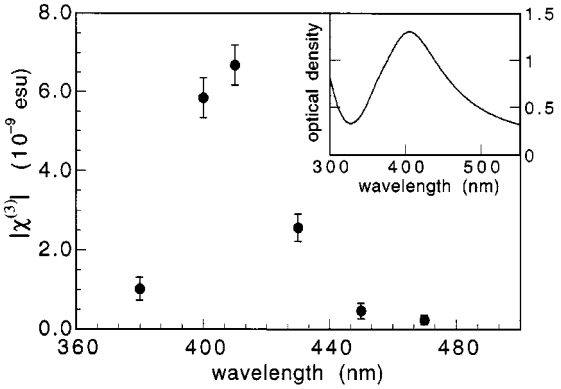

Fig. 3. – $|\chi^{(3)}|$ dispersion for a layer of Ag nanoclusters embedded on a glass substrate. Optical absorption of the sample is reported on the inset.

beam 4 both layer and substrate contributions, which interfere with each other, are present. Therefore, the layer, substrate and layer+substrate contributions to $|\chi^{(3)}|$ can be evaluated from $I_5(f)$, $I_4(s)$ and $I_4(f,s)$ measurements, respectively. Note that, with co-polarized pumps, the sole $\chi^{(3)}_{\mathrm{xxxx}}$ element of the tensor is obtained.

The measurements were made with pump intensity, I_{pump}, in the 1–10 GW/cm^2 range and with 60 μm FWHM beam diameters. The intensity values were set taking into account the sensitivity of the CCD camera used for detection and the onset of sample modification. In fig. 2 we report an example of the dependence of $I_5(f)$ on I_{pump}, which confirms the cubic nature of the nonlinearity. In the same figure, we also plot the transmittance of the pump intensity through the substrate. The linear behaviour indicates that nonlinear absorption of the substrate is negligible at these intensities.

Figure 3 shows the measured dispersion of the amplitude of $\chi^{(3)}(f)$ from 380 nm to 470 nm.

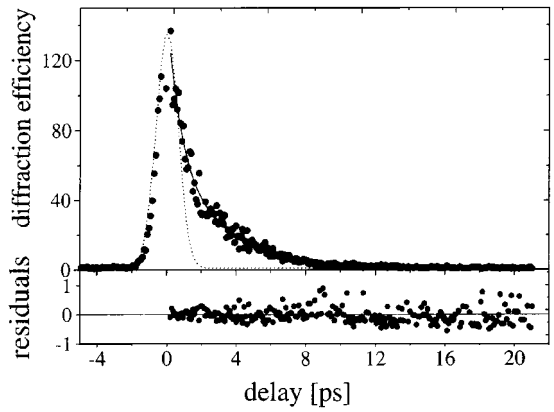

Fig. 4. – Temporal response of the FWM signal (No. 4) measured by delaying one of the pump beams (No. 3). Dashed curve: $\chi^{(3)}$ autocorrelation of the laser pulse, obtained with the sole substrate. Full line: fit with three exponential decay curves, of 0.9, 3 and 30 ps. The normalized residuals are shown to underline the quality of the fit.

Within the grid of the measured wavelengths, the maximum coincides with the SPR peak. This same behaviour near the SPR has already been observed, in the case of copper clusters, by Haglund and co-workers [19]. The values in the figure were obtained according to

$$|\chi^{(3)}(f)| = |\chi^{(3)}(c)|\frac{l_c}{l_f}\sqrt{\frac{\eta_5(f)}{\eta_4(c)}}, \tag{2}$$

where c refers to sapphire used as a calibrator, $\eta_i = (I_i/I_{\text{pump}})^3$ are diffraction efficiences and l_i are the corresponding thicknesses. The reported values take into account the linear absorptions on both pump and diffracted beams. $|\chi^{(3)}(c)|$ was obtained assuming a value for the sapphire $n_2 = 1.6 \times 10^{-13}$ esu, as measured by DeSalvo *et al.* [20] at 355 nm.

Finally, assuming $\text{Im}(\chi^{(3)}) = 0$ for the substrate (see fig. 2), the absolute value of the phase of $\chi^{(3)}$ results to be $|\phi| = 83°$ at 400 nm, as obtained from [18]

$$\eta_4(f,s) = \eta_5(f) + \eta_4(s) + 2\sqrt{\eta_5(f)\eta_4(s)}\cos\phi\,. \tag{3}$$

Close to resonance and with co-polarized beams, we observed a mostly imaginary $\chi^{(3)}$, with $\text{Im}(\chi^{(3)}) > 0$. This is consistent with a major contribution from hot electrons [1] to $\chi^{(3)}$. This is in good agreement with our result, allowing to choose the positive sign of the measured phase.

The experimental setup is also well suited for studying the dynamical response of the nonlinearity, by simply delaying one input beam (in our case beam number 3 of fig. 1b) with respect to the others. The results are illustrated in fig. 4 for phase-matched conditions at 400 nm, using $I_{\text{pump}} = 5$ GW/cm^2. The diffracted signal exhibits a peak whose rise-time, 0.35 ps, strictly follows the $\chi^{(3)}$ autocorrelation trace of the pump pulse. The relaxation dynamics instead is characterized by three different decay processes, with time constants of 0.9, 3 and ~ 30 ps. The determination of the longest time constant is affected by the limited time scan.

The observed dynamics resembles that measured recently by Stella *et al.* [21] on a similar system (tin nanoclusters with diameters 2 to 3 times smaller than ours). They measured 1, 10 and > 100 ps decay times. According to their interpretation, one could attribute the first two decay times to a) hot electron thermalization with the cluster lattice and b) thermal diffusion toward the glass matrix, driven by sharp thermal gradients, characteristic of nanostructures. Finally, on an even longer time scale, the nanocluster-matrix system relaxes to its initial temperature.

Conclusions. – The $|\chi^{(3)}|$ dispersion is for the first time measured for the case of silver colloidal glasses around the SPR resonance. The measurements have been performed in a wide spectral interval, giving for $|\chi^{(3)}|$ peak values four orders of magnitude greater than those of glasses. As expected for close-to-resonance conditions, a measurement of the phase has indicated a prevalence of the imaginary part. Time-resolved measurements show a decay of nonlinear signals in the ps regime. Work is in progress to extend the measurements in the IR range down to 1.6 μm, of great importance for practical application.

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