Effect of the Composition on the Nonlinear Optical Response of Au$_x$Ag$_{1-x}$ Nano-Alloys

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ABSTRACT: The synthesis of variable composition Au$_x$Ag$_{1-x}$ alloyed nanoparticles prepared by laser ablation in water is reported. The nanoalloys exhibited a single characteristic surface plasmon resonance peak, whose spectral position was lying between the surface plasmon resonance peaks of neat Ag and Au nanoparticles, at about 400 and 530 nm respectively, depending directly on the composition of the alloyed nanoparticles. The nonlinear optical response of the nanoalloys was studied in details under 532 nm (visible) 35 ps and 4 ns laser excitation and it was found to be significant and greatly influenced by the position of the plasmonic band relative to the laser excitation wavelength. In this respect, increase of the Au molar fraction resulted in shifting of the nanoalloy plasmon band toward the location of the plasmon band of neat Au nanoparticles, i.e., at about 530 nm, closer to the laser excitation wavelength, hence causing more efficient resonance enhancement of the nonlinear optical response. Moreover, the nanoalloys were found to exhibit strong saturable absorption behavior when excited by ps or ns pulses, in the latter case this behavior changing to reverse saturable absorption at high laser intensity. The origin, the magnitude and the sign of the observed optical nonlinearities of the alloyed nanoparticles are explained and discussed in terms of the hot-electron and the interband contributions taking place under laser excitation in such nanostructures. The possibility of controlling the magnitude and the sign of the nonlinear optical response of Au$_x$Ag$_{1-x}$ nanoalloys through their composition provides an attractive and efficient way to tailor the optical nonlinearities of noble metal nanoalloys, making them very useful for various emerging photonic, biophotonic, and optoelectronic applications.

1. INTRODUCTION

Noble metal nanoparticles (NPs) are among the most interesting and well-studied nanoparticles, basically due to their relatively easy preparation, physicochemical stability, and their attractive electrical and optical properties, which together with the characteristic surface plasmon resonance (SPR) they exhibit, constitute a combination of exciting characteristics. The spectral position of the SPR band of noble metal NPs, located in the visible region, can be easily tuned, in principle, through the modification of the NPs’ shape, size, their dielectric environment, the interactions occurring between them and also by appropriate surface-functionalization.$^1$ The plasmonic effects and their properties are of considerable interest for several state-of-the-art applications, as for example for the optical data storage and processing,$^2$ for making biosensors,$^8$ and plasmon-driven catalysts.$^9$ Several of these applications necessitate the fine-tuning of the spectral position of the NPs’ plasmonic band, which can be attained by modifying in a controllable way their morphological characteristics and/or compositional details as it happens for example through the preparation of alloyed, bimetallic or core–shell structures.$^{10}$ Among them, alloyed NPs are considered as the more versatile and flexible for the preparation of functional materials compared to the monometallic ones and other bimetals (as, e.g., some core–shell structures).$^{11,12}$ The most important reason is not only that they combine the advantages of their metallic counterparts, but also because they exhibit a single plasmonic band, instead of two, which depends only on the ratio of the mole fractions of the two components. In order to take advantage of the properties of alloyed NPs, the key factor is their preparation, which should facilitate the effective control of their composition. During the last few years, several methods have been developed for the synthesis of alloyed NPs, as for example pulsed electrodeposition,$^{13}$ chemical reduction method,$^{14}$ evaporation of metallic bulk solid solutions,$^{15}$ sol–gel,$^{16}$ molecular beam epitaxy,$^{17}$ biogenic synthesis,$^{18}$ microreaction,$^{19}$ digestive ripening,$^{20}$ and different laser ablation based approaches.$^{21}$ Among the various preparation techniques, laser ablation in liquids has been demonstrated as the most efficient and flexible and prevailed almost all other preparation techniques of NPs. Laser ablation in liquids is probably the most versatile method for fast production of nanoalloys with arbitrary composition In addition, by selecting the liquid environment to be, e.g., water, the use of hazardous chemicals

Received: December 12, 2014
Revised: March 6, 2015
can be avoided, the whole procedure becoming environmentally friendly (i.e., a green technique).\textsuperscript{22,23} Laser ablation in liquids allows for the control of the composition, thus being one of the most valuable methods to control the plasmonic properties.

Among the various alloyed NPs, the Au_{x}Ag_{1−x} ones have been prepared by various synthetic methods in the past toward their electronic,\textsuperscript{24} catalytic,\textsuperscript{25} biomedical,\textsuperscript{26} and optical properties.\textsuperscript{27−32} In particular, concerning their optical properties, some Au_{x}Ag_{1−x} alloyed nanostructures were shown to exhibit important three-photon luminescence upon irradiation with 1290 nm fs laser pulses showing their potential for tissue imaging,\textsuperscript{33} while their potential for SERS and optical trapping applications\textsuperscript{34} have been also searched. Moreover, some Au_{x}Ag_{y}@ZrO_{2} core−shell nanostructures were found to exhibit strong optical limiting behavior under visible nsec laser excitation.\textsuperscript{35} The various studies related to the potential applications of Au_{x}Ag_{y} alloyed NPs are not only limited to NPs with spherical geometry but they extend to nanoparticles having other geometries as well, such as nanorods, spheroids, triangles, pyramids etc., as they were found to exhibit very interesting and tunable plasmonic properties, attractive for several applications.\textsuperscript{36−38}

The optical properties of the Au_{x}Ag_{y} nanoalloys are determined to a large extent by the presence of a single plasmon band, lying between the positions of the plasmon bands of pure gold and pure silver, at about 400 and 530 nm, respectively. Its spectral position and intensity depends closely on the alloy’s composition.\textsuperscript{39−42} In fact, it is the presence of a single plasmon band that indicates the successful synthesis of the alloy and excludes the formation of core−shell like structure.\textsuperscript{40} Some efforts to explain and describe the plasmonic feature of nanoalloys have been based on the effective medium approximation, a method widely used for describing the optical properties of composite materials.\textsuperscript{43} According to this, the complex dielectric function of the composite can be expressed as a linear combination of the dielectric functions of the pure elements, similarly to the Maxwell−Garnet model.\textsuperscript{44} However, this method cannot reproduce efficiently the experimental absorption spectra of the Au_{x}Ag_{y} nanoalloys.\textsuperscript{45} On the other hand, employing the dielectric functions determined experimentally by Ripken\textsuperscript{46} studying alloys’ thin films, a very good agreement with the experiment is achieved, suggesting that the electronic band structure of the alloys is indeed different from that of pure Au or Ag.\textsuperscript{47} Recently, an analytical model for the prediction of the dielectric properties of such gold−silver nanoalloys was reported.\textsuperscript{48} This model, being a modification of the Drude−Lorentz model, was capable to describe successfully the dielectric function of variable composition thin alloy films as well as the UV−vis−NIR optical absorption spectra of alloyed nanoparticles.

Most of the investigations concerning the optical properties of Au_{x}Ag_{y} nanoalloys, are focused on the study of their (linear) optical and plasmonic properties,\textsuperscript{1,12,21,23,37−42,47} while the nonlinear optical response of these nanoalloys have been the object of a very limited number of studies. It is only very recently, to the best of our knowledge, that some studies investigating the nonlinear optical response of these nanoalloys have appeared in the literature.\textsuperscript{28,29,34,38,49−51} Even though, most of these studies were dealing with issues related to the optical limiting behavior of Au_{x}Ag_{y} alloyed NPs.\textsuperscript{28,29,34}

The influence of the composition of the Au_{x}Ag_{y} nanoalloys on the plasmon band characteristics has been also studied in the past. In particular, it has been shown that the spectral position of the plasmon band shifts to the longer wavelengths, toward the position of the Au nanoparticles plasmon resonance, with increasing the Au molar fraction, as a result of the strong effect of the composition on the plasmonic properties. On the other hand, it is known that the NLO response can be enhanced when the laser excitation takes place close to the plasmon resonance. In the case of Au_{x}Ag_{y} NPs, the NLO response follows such a behavior, being enhanced upon excitation taking place at the vicinity of the plasmon peak and decreasing moving away from it. Moreover, the sign of the nonlinearity depends on the relative position of the excitation wavelength regarding the plasmon peak. As a result, the third-order nonlinear susceptibility χ(3) can be of positive or negative sign depending if the incident laser excitation wavelength is to the higher or shorter wavelengths regarding the plasmon peak.\textsuperscript{52}

In that view, it was among the main motivations of the present work to demonstrate the possibility and the potential of using the spectral position of the plasmon band, in order to modify in a controlled way the nonlinear optical response of the Au_{x}Ag_{y} nanoalloys. Furthermore, in order to better understand the physical origins of the observed NLO properties and the complex interplay among the various underlying operating mechanisms, both 35 ps and 4 ns laser pulses, at 532 nm, have been employed for excitation. Moreover, the third-order nonlinear susceptibility χ(3) was determined as a function of the Au content of the nanoalloys (expressed by the gold-molar-fraction ratio, GMF). The results of the present study demonstrate the successful tuning of both the magnitude and the sign of the optical nonlinearities of alloyed NPs, by shifting the position of their plasmon band through modification of the gold-molar-fraction ratio (GMF). This finding can be useful for various photonic, biophotonic and optoelectronic applications making use of plasmonic nanoparticles.

2. EXPERIMENTAL SECTION

Preparation of the NPs. The details of the preparation of the gold−silver nanoalloys and the characterization methods employed have been reported elsewhere.\textsuperscript{53−58} Briefly, gold and silver NPs were prepared separately by laser ablation in solution, using the 40 fs pulses from a Ti:sapphire laser (Spitfire, Spectra-Physics) operating at 800 nm at a repetition rate of 1 kHz. Initially, the metallic targets immersed in 20 mL of an aqueous sodium citrate solution (2 μM) were irradiated to produce single Au and single Ag NPs of spherical shape. The pulse energy was 500 μJ and the diameter of the laser spot on the surface was about 350 μm. The target was constantly moving under the laser spot in order to scan the complete surface during ablation. The ablation was carried on for 15 min in each case. The targets were weighed before and after ablation to determine the metallic concentrations of the solutions. The resulting solutions were then diluted with 2 μM aqueous sodium citrate in order to adjust their metallic concentration to 300 μM. Then, the obtained Au and Ag colloids were mixed in varying volume ratios, with a total volume of 6 mL in glass vials; for example, to produce Au_{x}Ag_{y} alloyed NPs, 1.2 mL of the Au colloid was mixed with 4.8 mL of the Ag colloid. The resultant mixtures were further irradiated from the side by focusing the same laser source into the colloid with a 150 mm focal length plano-convex lens. This results in the generation of a white light supercontinuum into the NP solution.\textsuperscript{59} In this case, the pulse energy was 120 μJ and the laser treatment was carried on for 2
h, resulting in the formation of \( \text{Au}_{x}\text{Ag}_{1−x} \) nanoalloys. This procedure allowed the effective adjustment of the alloys’ composition, which can be expressed in terms of the gold molar fraction or GMF, \( x \), ranging from 0 (for pure Ag) to 1 (for pure Au). The solutions were prepared having similar metal concentration (i.e., of about 0.6 mM). In Figure 1 representative TEM images of some \( \text{Au}, \text{Ag} \) and \( \text{Au}_{0.5}\text{Ag}_{0.5} \) NPs are shown. From these measurements, the NPs were found to be almost spherical in size. In addition, the average diameters of the pure Au and the alloyed NPs were found to be about 15–20 nm, while those of pure Ag were about 30–40 nm. This difference in size is likely caused by the lower energy of the white light supercontinuum at the plasmon peak of silver compared to gold, resulting in less fragmentation and bigger particles.

**Nonlinear Optical Measurements.** The third-order nonlinear optical response of the prepared \( \text{Au}_{x}\text{Ag}_{1−x} \) alloyed NPs were investigated using the Z-scan technique, employing two different Nd:YAG laser systems; a 35 ps mode-locked Nd:YAG laser and a 4 ns Q-switched one, both operating at 532 nm at a repetition rate 1 to 10 Hz. Briefly, in the Z-scan, a sample moves along the propagation direction of a focused Gaussian laser beam (e.g., along the \( z \)-axis), therefore experiencing different intensity at each different \( z \)-position. Around the focal plane, the sample experiences the highest incident intensity, giving rise to nonlinear absorption and refraction, which on their turn modify the sample’s transmission characteristics. In order to determine the nonlinear absorption and refraction of a sample, the transmitted laser beam is divided into two parts, which are measured simultaneously for each position of the sample. So, one part of the transmitted laser beam is totally collected by a lens (i.e., the “open-aperture” Z-scan) and is measured by a photomultiplier tube (PMT), providing information about the nonlinear absorption (i.e., the nonlinear absorption coefficient \( \beta \)), while the other part of the laser beam, is also measured by a second PMT, after it has passed through a small aperture placed at the far field (i.e., the “closed-aperture” Z-scan), providing information about the nonlinear refraction of the sample. In the presence of weak nonlinear absorption, in order to remove its effect on the nonlinear refraction and determine the nonlinear refractive index parameter \( \gamma' \), the division of the “closed-aperture” Z-scan by the corresponding “open-aperture” one yields the so-called “divided” Z-scan, from which the nonlinear refractive index parameter \( \gamma' \) can be determined. The nonlinear absorption coefficient \( \beta \) is determined from the “open-aperture” Z-scan. The detailed procedure for the analysis of the Z-scan data can be found elsewhere.

In particular, the nonlinear absorption coefficient \( \beta \) is determined by fitting the “open-aperture” Z-scan with the following equation:

\[
T = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} \frac{\beta L_{\text{eff}}}{1 + z^2/z_0^2} \exp(-t^2) dt
\]

where \( L_{\text{eff}} = [1 - \exp(-\alpha_0 L)]/\alpha_0 \) is the effective sample thickness, \( \alpha_0 \) is the absorption coefficient at the excitation wavelength, \( L \) is the sample length, \( I_0 \) is the laser peak irradiance on the focal plane, \( z_0 \) is the Rayleigh length, and \( z \) is the position of the sample.

The nonlinear refractive index parameter \( \gamma' \) is determined from the following relation:

\[
\gamma' = \frac{\lambda \alpha_0}{1 - e^{-\alpha_0}} \frac{\Delta T_{p-v}}{0.812 \pi \alpha_0 (1 - S)^{0.25}}
\]

where \( \Delta T_{p-v} \) is the total variation of the normalized transmission, \( S = 1 - \exp(-2r_p^2/w_0^2) \) is the aperture linear transmittance with \( r_p \) and \( w_0 \) being the aperture and beam radii respectively and \( \alpha_0 \), \( L \), and \( I_0 \) as described before.

Finally, the real and imaginary parts of the third-order susceptibility \( \chi^{(3)} \) are obtained from the following relations:

\[
\text{Re} \, \chi^{(3)} \text{ (esu)} = \frac{10^{-6} \sin^2 \theta}{480 \pi} \gamma' \left( \text{cm}^2 \text{ W}^{-1} \right)
\]

\[
\text{Im} \, \chi^{(3)} \text{ (esu)} = \frac{10^{-7} \sin^2 \theta}{96 \pi} \beta \left( \text{cm} \text{ W}^{-1} \right)
\]

where \( c \) is the speed of light in cm/s, \( \omega \) is the excitation frequency in s\(^{-1} \), and \( n_0 \) is the linear refractive index.

**3. RESULTS**

**UV–Vis–NIR Optical Absorption Spectra.** The UV–vis–NIR optical absorption spectra of some water suspensions of different GMFs \( \text{Au}_{x}\text{Ag}_{1−x} \) nanoparticles are presented in Figure 2a. For completeness purposes, the absorption spectra of \( \text{Au}, \text{Ag} \) and \( \text{Au}_{0.5}\text{Ag}_{0.5} \) nanoparticles are clearly appearing at 415 and 520 nm respectively, in agreement with other literature...
reports, with the plasmon peak of the nanoalloys appearing in between, its exact position depending on the GMF value. As the GMF was increased, both broadening and red-shifting of the plasmonic peak have been observed, hence modifying significantly the absorption at 532 nm where laser excitation occurs. In fact, it is this change of absorption that gives rise to the enhancement of the NLO response as it will be discussed in more details in the next section. The existence of a single peak in the UV–vis–NIR spectra confirms the presence of alloyed NPs rather than bimetallic ones. With the increase of the GMF, the alloys’ dispersions were found changing their color gradually, from light yellow to light pink as it is shown in Figure 2b. The absorption spectra of the dispersions were measured regularly in order to ensure the stability of the dispersions and that they maintain the initial plasmonic characteristics.

**Z-Scan Measurements.** The “open-aperture” Z-scans of a Au$_{0.8}$Ag$_{0.2}$ and a Au$_{0.2}$Ag$_{0.8}$ NPs’ dispersions are presented in Figure 3a, both obtained using same intensity 35 ps laser pulses. As shown, the Z-scans of both samples exhibited a transmission maximum at the focal plane, revealing a saturable absorption (SA) behavior. In fact, all NPs’ dispersions studied here were found to exhibit SA behavior, corresponding to negative nonlinear absorption (i.e., $\beta$ or Im $\chi^{(3)} < 0$). Interestingly, the SA response of the different GMF NPs’ dispersions was observed stronger for higher GMF alloyed NPs (i.e., for NPs with more Au content). The SA behavior is an evidence of the almost resonant conditions of the excitation with the plasmonic band, while its increase with increasing GMF is due to the red-shift of the nanoalloys’ plasmonic band, causing increasing absorption at the laser excitation wavelength, as shown in Figure 2a.

Because of the near resonant excitation conditions encountered in these experiments and in order to avoid any unwanted saturation effects, measurements were performed at laser intensities low enough to avoid any saturation of the NLO response but capable to ensure a good signal-to-noise ratio. Separate Z-scan measurements of the deionized water and some deionized water–sodium citrate solutions performed under identical experimental conditions with those used for the NPs, revealed that sodium citrate exhibited negligible NLO response, while the deionized water had significant NLO response. This last has been taken into account for the determination of the optical nonlinearities of the alloyed NPs. The values of the nonlinear parameters of water have been determined and are included in Table 1 for completeness purposes and for comparison with other published values.

![Figure 2](image1.png)

**Figure 2.** (a) UV–vis–NIR optical absorption spectra of some water dispersions of Au$_x$Ag$_{1-x}$ nanoalloys with different GMF. All dispersions had the same concentration of metal (i.e., 0.6 mM). The inset presents the variation of the position of the plasmonic peak with GMF. (b) Photograph of the samples placed in 1 mm quartz cells.

![Figure 3](image2.png)

**Figure 3.** “Open-aperture” (a) and “divided” (b) Z-scans of nanoalloys, obtained under 35 ps, 532 nm laser excitation, and intensity of 53 GW/cm$^2$ (corresponding to 9.5 $\mu$J or 0.93 J/cm$^2$).
presence of a prefocal transmission minimum followed by a postfocal transmission maximum (i.e., a valley-peak configuration) indicating positive sign nonlinear refraction. In fact, all NPs’ dispersions were found to exhibit significant positive sign nonlinear refraction. However, as can be seen from the “divided” Z-scans of Figure 3b, the magnitude of the ΔT_{p,v} of the NPs’ dispersions was smaller than that of the solvent, both measured under the same conditions, suggesting that the solute (i.e., the NPs) and the solvent (i.e., the deionized water) exhibit opposite sign refractive nonlinearity. Therefore, since the water exhibits positive nonlinear refraction, in agreement with literature,62 it becomes obvious that the nanoalloys exhibit negative nonlinear refraction, corresponding to self-defocusing behavior (i.e., γ’ or Re χ(3) < 0). In all cases, the ΔT_{p,v} parameter was found to scale linearly with the laser intensity, as expected for third-order optical nonlinearities.

It is important to mention at this point, that in the case of pure Au and Au_{0.8}Ag_{0.2} NPs, negligible nonlinear refraction was observed. This observation is attributed to the opposite sign nonlinear refraction between the solvent and the NPs, which can result to the cancellation of the nonlinear refraction of the dispersion under some concentration conditions. This allows an approximate evaluation of the nonlinear refraction of pure Au and Au_{0.8}Ag_{0.2} NPs’, as it has also suggested previously in another study concerning the NLO response of some 20 nm diameter, spherical Au NPs under 532 nm, 50 ps laser excitation.63

Table 1. Nonlinear Optical Parameters of Au, Ag, and Au_{x}Ag_{(1−x)} Nano-Alloys under 532 nm, 35 ps Laser Excitation

<table>
<thead>
<tr>
<th>sample</th>
<th>β (10^{-13} m/W)</th>
<th>γ’ (10^{-20} m^2/W)</th>
<th>Im χ(3) (10^{-15} esu)</th>
<th>Re χ(3) (10^{-15} esu)</th>
<th>χ(3) (10^{-15} esu)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>−49.6 ± 8.0</td>
<td>−(10.7 ± 1.0)</td>
<td>−(22.8 ± 4.0)</td>
<td>−(12.0 ± 1)</td>
<td>25.8 ± 4.0</td>
<td>this work</td>
</tr>
<tr>
<td>Au_{0.2}Ag_{0.8}</td>
<td>−(30.0 ± 6.0)</td>
<td>−(10.7 ± 1.0)</td>
<td>−(13.8 ± 3.0)</td>
<td>−(12.0 ± 1)</td>
<td>18.3 ± 3.0</td>
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</tr>
<tr>
<td>Au_{0.4}Ag_{0.6}</td>
<td>−(6.1 ± 0.9)</td>
<td>−(6.4 ± 1.0)</td>
<td>−(2.8 ± 0.4)</td>
<td>−(7.2 ± 1)</td>
<td>7.7 ± 1.1</td>
<td></td>
</tr>
<tr>
<td>Au_{0.6}Ag_{0.4}</td>
<td>−(2.8 ± 0.4)</td>
<td>−(6.1 ± 1.0)</td>
<td>−(1.3 ± 0.2)</td>
<td>−(6.8 ± 1)</td>
<td>6.3 ± 1.0</td>
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</tr>
<tr>
<td>Au_{0.8}Ag_{0.2}</td>
<td>−(2.2 ± 0.6)</td>
<td>−(3.3 ± 1.0)</td>
<td>−(1.0 ± 0.3)</td>
<td>−(3.7 ± 1)</td>
<td>4.2 ± 1.0</td>
<td></td>
</tr>
<tr>
<td>Au_{1.0}Ag_{0.0}</td>
<td>−(0.9 ± 0.2)</td>
<td>−(2.8 ± 1.0)</td>
<td>−(0.4 ± 0.1)</td>
<td>−(3.2 ± 1)</td>
<td>3.2 ± 1.0</td>
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</tr>
<tr>
<td>Au</td>
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<td>−(1.1 ± 0.3)</td>
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<td>−(1.2 ± 0.4)</td>
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<td>H_{2}O</td>
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<tr>
<td>PI-b-PAA/Au</td>
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<td>0.4−1.4</td>
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<td></td>
<td></td>
<td>65</td>
</tr>
<tr>
<td>Au</td>
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<td>−</td>
<td></td>
<td></td>
<td></td>
<td>66</td>
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<tr>
<td>Ag</td>
<td>−(14.0 ± 7.0)</td>
<td>−</td>
<td></td>
<td></td>
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<td>66</td>
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</table>

Figure 4. “Open-aperture” (a−c) and “divided” (d) Z-scans of some Au_{x}Ag_{(1−x)} dispersions, obtained under 4 ns, 532 nm laser excitation.
The values of the nonlinear optical parameters (i.e., nonlinear refractive parameter \( \gamma' \), nonlinear absorption coefficient \( \beta \)) and the corresponding real (Re \( \chi^{(3)} \)) and imaginary (Im \( \chi^{(3)} \)) parts of the third-order susceptibility \( \chi^{(3)} \) together with the magnitude of \( \chi^{(3)} \) of the Au\(_{x}\)Ag\(_{1-x}\) alloyed NPs determined under 35 ps, 532 nm laser excitation are summarized in Table 1. As can be seen, the values of the nonlinear optical parameters were following the increase of Ag content; in particular, the nonlinear susceptibility \( \chi^{(3)} \) was found to exhibit an almost 20-fold enhancement comparing the value determined for pure Ag (where GMF = 0) to pure Au (where GMF = 1) NPs. The observed trend in the NLO response of the nanoalloys is a direct result of the regularly increasing (linear) absorption of the nanoalloys’ at 532 nm, as GMF increased and the subsequent more resonant excitation conditions attained. For comparison purposes of the present results with other previously reported results, the nonlinear optical parameters of Au and Ag NPs reported in the literature and measured under similar excitation conditions are also given in this table.

Then, the NLO response of the alloyed NPs under 4 ns, 532 nm laser excitation conditions has been studied. In Figure 4, the representative “open-aperture” and “divided” Z-scans of some Au\(_{x}\)Ag\(_{1-x}\) dispersions are shown. For the range of laser intensities used, the solvent did not exhibit any measurable response, the observed response being due exclusively to the NPs. The Au and Ag NPs were found to exhibit saturable absorption (SA) behavior (i.e., \( \beta < 0 \)), the corresponding “open-aperture” Z-scans displaying the characteristic transmission maximum (see, e.g., Figure 4a for Au NPs). However, the SA behavior of the NPs was found to switch to reverse saturable absorption (RSA) behavior (i.e., \( \beta > 0 \)) above a certain laser intensity. In fact, the laser intensity necessary for this switching of behavior was found to depend on the GMF. So, while the switching of the NLO response, from SA to RSA, of a Au\(_{0.2}\)Ag\(_{0.8}\) sample was determined to occur at an intensity of 220 MW/cm\(^2\) (Figure 4b), in the case of the Au\(_{0.2}\)Ag\(_{0.4}\) sample only 83 MW/cm\(^2\) were needed (Figure 4c). In general, it was established that the higher the GMF, the lower the laser intensity, required for switching the SA response to RSA.

In order to better describe the switching of the NLO response from SA to RSA, the following intensity dependent absorption coefficient \( \alpha(I) \) is used: \(^{67-70}\)

\[
\alpha(I) = \frac{\alpha_g}{1 + (I/I_s)} + \beta_{RSA} I
\]

where \( \beta_{RSA} \) is the nonlinear absorption coefficient, \( I \) is the laser intensity and \( I_s \) is the saturation intensity, the first term corresponding to the saturation of the absorption and the second one to the reverse saturable absorption.

Then, the equation describing the propagation of radiation, assuming a thin sample, can be expressed as follows:

\[
\frac{dI}{dz'} = -\alpha(I)I
\]

where \( z' \) is the propagation distance in the sample. The numerical integration of this last equation in space and time, using the appropriate boundary conditions, can provide the variation of the transmission of the sample. By fitting the “open-aperture” Z-scans (see, e.g., the solid lines in Figure 4c), the nonlinear absorption coefficients \( \beta_{RSA} \) and the saturation intensities \( I_s \) can be determined. The variation of the saturation intensity \( I_s \) as a function of the GMF is depicted in Figure 5a.

As shown, the saturation intensity \( I_s \) decreases as the GMF increases. Moreover, the Au NPs were found to exhibit higher saturation intensity than the alloyed NPs and the Ag NPs, a rather surprising finding, which however has been reported previously as well.\(^{50}\) The nonlinear absorption coefficient \( \beta_{RSA} \) was found to vary with GMF as well, ranging between 2.4 \( \times \) \( 10^{-11} \) m/W for the Au\(_{0.2}\)Ag\(_{0.8}\) NPs and 9.2 \( \times \) \( 10^{-11} \) m/W for the Au\(_{0.8}\)Ag\(_{0.2}\) NPs. Moreover, the \( \beta_{RSA} \) value for a given GMF was observed to increase at higher laser intensities, most probably reflecting the increasing contribution of higher order NLO effects occurring at high enough laser intensity. In order to avoid this complication, the NLO parameters, \( \beta \) and Im \( \chi^{(3)} \), were determined from measurements performed at low enough laser intensities where only saturable absorption was observed (see also Table 2).

All alloyed NPs investigated in the present work were found to exhibit negative NLO refraction, corresponding to self-defocusing behavior, as it is indicated by the presence of the peak-valley configuration of the “divided” Z-scans (see e.g., Figure 4d). The variation of the \( \Delta T_{pe} \) values of the Z-scans with the laser energy is presented in Figure 6, while the slopes of the solid lines correspond to the nonlinear refractive index parameter \( \gamma' \). From the increasing slopes of the solid lines it becomes evident that the nonlinear refractive index parameter \( \gamma' \) increases importantly with the GMF. The NLO parameters of the Au\(_{x}\)Ag\(_{1-x}\) alloyed NPs of Au and Ag NPs, all determined under 4 ns, 532 nm laser excitation together with
The saturation intensities have been determined by using eq 5. The nonlinear absorption coefficient $\beta$ corresponds to the saturable absorption and has been determined from eq 1.

### 4. DISCUSSION

The NLO response of Au and Ag NPs is usually described in terms of contributions being related with the interband transitions (between the $d$-band and the conduction $s$–$p$ band), the intraband transitions (within the $s$–$p$ band), the hot electrons’ contributions and the contribution of free carriers.\(^72,73\) Briefly, the interband transitions are taking place when the photon energy exceeds the energy gap, which is 1.7 and 4 eV for Au and Ag, respectively.\(^72,73\) The interband transitions are responsible for saturable absorption, corresponding to a negative sign contribution to $\text{Im} \chi^{(3)}$, in the same way as it occurs in a two-level system when it is strongly pumped. Since interband transitions are one-photon processes, they are expected to be more intense in the case of Au excitation under 532 nm radiation. On the other hand, in the case of off-resonant excitation (e.g., at 1064 nm) the nonlinear absorption of Au and Ag is significantly less influenced by this mechanism, instead, it can be affected by two- and/or three-photon absorption processes.\(^50\) Concerning the intraband transitions, their contribution to the $\text{Im} \chi^{(3)}$ is of negative sign as well, giving rise therefore to SA-like NLO response. Nevertheless their contribution is much weaker than that of the interband transitions.\(^72\)

Moreover, when the excitation occurs closer to the plasmonic band, a part of the incident photons is absorbed by the $d$-electrons which can be further promoted to the $s$–$p$ conduction band near the Fermi level, while the remaining photons are absorbed by the $s$–$p$ electrons. Many of these free electrons are very energetic, and their temperature can rise to several hundred degrees. These “hot electrons” have different Fermi–Dirac distribution and they are not in equilibrium with the lattice. The modified distribution of the hot electrons below and above the Fermi level modifies the absorption coefficient,\(^72\) leading to a positive sign contribution to the $\text{Im} \chi^{(3)}$, a phenomenon usually called “plasmon band bleach”.\(^74\) However, within few picoseconds, the hot electrons will relax, through electron–phonon coupling, the heat they release being dissipated to the lattice and the surrounding environment via phonon–phonon interactions. These slow processes can induce thermal effects which can contribute to the NLO response as well, if the pulse duration is long enough (e.g., longer than 50 ps).\(^49\) Finally, other mechanisms can occur at even higher intensities also contributing to $\text{Im} \chi^{(3)}$ for example multiphoton absorption and photo-ejection of electrons.

The saturation intensity $I_s$ determined for each GMF sample are summarized in Table 2.

As can be seen from the Tables 1 and 2, the NLO parameters determined in the present study are in reasonable agreement with other results obtained under similar excitation conditions. Some differences existing between the present results and those of some other studies could be attributed to the differences in size, size distributions, morphology, and the dielectric environment of the NPs. The variation of the magnitude of the third-order susceptibility $\chi^{(3)}$ as a function of the GMF is presented in Figure 5b for both excitation conditions. In both cases, the important enhancement of $\chi^{(3)}$ of the nanoalloys is evident, confirming the effect of the spectral position of the plasmonic band regarding the laser excitation wavelength and the NLO response.

### Table 2. Nonlinear Optical Parameters of Au, Ag, and Au$_{0.4}$Ag$_{0.6}$ Nano-Alloys under 532 nm, 4 ns Laser Excitation

<table>
<thead>
<tr>
<th>Sample</th>
<th>$I_s$ (10$^{11}$ W/m$^2$)</th>
<th>$\beta$ (10$^{-15}$ m/W)</th>
<th>$\gamma$ (10$^{-19}$ m$^2$/W)</th>
<th>$\text{Im} \chi^{(3)}$ (10$^{-13}$ esu)</th>
<th>$\text{Re} \chi^{(3)}$ (10$^{-13}$ esu)</th>
<th>$\chi^{(3)}$ (10$^{-15}$ esu)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>23.0 ± 1.3</td>
<td>(17.6 ± 2.2)</td>
<td>(30.1 ± 5.8)</td>
<td>(8.3 ± 1.0)</td>
<td>(33.7 ± 6.4)</td>
<td>35.0 ± 6.0</td>
<td>this work</td>
</tr>
<tr>
<td>Au$<em>{0.6}$Ag$</em>{0.4}$</td>
<td>6.0 ± 0.5</td>
<td>(6.8 ± 1.2)</td>
<td>(26.4 ± 2.6)</td>
<td>(3.2 ± 0.6)</td>
<td>(29.7 ± 3.0)</td>
<td>30.0 ± 3.0</td>
<td></td>
</tr>
<tr>
<td>Au$<em>{0.4}$Ag$</em>{0.6}$</td>
<td>6.1 ± 1.2</td>
<td>(6.9 ± 1.8)</td>
<td>(23.1 ± 3.5)</td>
<td>(3.3 ± 0.8)</td>
<td>(26.0 ± 3.0)</td>
<td>26.0 ± 4.0</td>
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<tr>
<td>Au$<em>{0.8}$Ag$</em>{0.2}$</td>
<td>9.6 ± 1.9</td>
<td>(3.4 ± 1.2)</td>
<td>(13.7 ± 0.7)</td>
<td>(1.6 ± 0.5)</td>
<td>(16.0 ± 6.0)</td>
<td>16.0 ± 6.0</td>
<td></td>
</tr>
<tr>
<td>Au$<em>{0.2}$Ag$</em>{0.8}$</td>
<td>14.0 ± 2.8</td>
<td>(2.9 ± 0.2)</td>
<td>(12.4 ± 1.6)</td>
<td>(1.4 ± 0.1)</td>
<td>(14.0 ± 1.8)</td>
<td>14.1 ± 1.8</td>
<td></td>
</tr>
<tr>
<td>Au-PVA</td>
<td>16.0 ± 3.4</td>
<td>(2.2 ± 0.3)</td>
<td>(8.4 ± 1.0)</td>
<td>(1.04 ± 0.10)</td>
<td>(9.5 ± 1.0)</td>
<td>9.6 ± 1.0</td>
<td></td>
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<tr>
<td>Ag</td>
<td>17.0 ± 1.2</td>
<td>(2.0 ± 0.9)</td>
<td>(2.6 ± 0.8)</td>
<td>(0.9 ± 0.4)</td>
<td>(2.9 ± 0.9)</td>
<td>3.0 ± 0.9</td>
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</tr>
<tr>
<td>Au-PVA</td>
<td>50.0 × 10$^{-2}$</td>
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<td></td>
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<td></td>
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<tr>
<td>Ag-PVA</td>
<td>11.0 × 10$^{-2}$</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au$<em>{0.4}$Ag$</em>{0.6}$-PVA</td>
<td>8.0 × 10$^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Au</td>
<td>−27.0</td>
<td>−37.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Ag</td>
<td>−25.7</td>
<td>−22.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Au–Ag</td>
<td>−26.5</td>
<td>81.3</td>
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<td></td>
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</tbody>
</table>

$^a$The saturation intensities have been determined by using eq 5. $^b$The nonlinear absorption coefficient $\beta$ corresponds to the saturable absorption and has been determined from eq 1.

Figure 6. Variation of the $\Delta T_{\text{p}}$ parameter versus the incident laser energy for different GMF values $x$ of the nanoalloys dispersions under 4 ns, 532 nm laser excitation.

XXX, XXX, XXX
Laser-induced fragmentation of metallic NPs is a well-documented topic and several experimental and theoretical studies have appeared in the literature during the last few years.\textsuperscript{25–36} So, the use of femtosecond, picosecond, or nanosecond laser pulses can induce fragmentation of NPs under some conditions. Photofragmentation is a cumulative process, growing with the number of laser pulses, and depending on the (initial) size of the NPs, their surface roughness, the metal absorption cross section at the laser excitation wavelength, the dielectric environment (e.g., solvent, capping agents, surface functionalization, etc.), and the experimental parameters related with the laser radiation (i.e., intensity, fluence, focusing conditions, etc.). Briefly, there are two basic mechanisms leading to NPs’ photofragmentation, the Coulombic explosion and the photothermal evaporation. The former presumes electron ejection to generate multiply ionized NPs that undergo fission through charge repulsion. This mechanism becomes dominant under femtosecond laser excitation. According to the latter mechanism, the absorption of photons increases the surface temperature, resulting in melting of the NP surface with several consequences (i.e., fragmentation, shape change, etc.). Photothermal evaporation dominates under nanosecond laser excitation. In the case of ps laser excitation, both Coulombic explosion and photothermal evaporation mechanisms can occur, their relative contribution depending on the details of the excitation conditions. During the present ps measurements, fluence and peak intensity up to 0.9 J/cm\(^2\) and 5 × 10\(^4\) MW/cm\(^2\) respectively were used, while in the ns case, up to 2.0 J/cm\(^2\) and 2.5 × 10\(^5\) MW/cm\(^2\), respectively. However, it should be noted that these fluence and intensity values correspond to the highest values employed, and they were used only for the pure Ag and the Au\(_{0.2}\)Ag\(_{0.8}\) samples, which were exhibiting the lower absorption cross sections. All the other samples were measured at significantly lower values as can be seen in Figure 6.

As it has been discussed elsewhere, photofragmentation might occur during the ps irradiation of NPs, as a result of Coulombic explosion, following two- or multiphoton absorption and subsequent electron ejection. However, in this case nonlinear absorption should be manifested in the “open-aperture” Z-scans exhibiting a transmission valley, denoting a reverse saturable absorption (RSA) behavior. Nevertheless, this was not the case, since in all the ps experiments, of all samples studied, saturable absorption has been clearly observed. In addition, as it has been discussed by Kamat et al.,\textsuperscript{76} investigating the dynamics of the electron photoejection and the subsequent fragmentation of some Ag nanoclusters, under 18 ps, 532 nm laser excitation, it takes about 1.5 ns for the formation of a transient intermediate, while 14.2 ns are needed for the completion of fragmentation. Therefore, it can be assumed that under 35 ps laser excitation, the NPs’ fragmentation is completed after the laser pulse end and its effect will be weak or not significant on the NLO measurements.

In support to this conclusion are the following experimental evidence. Measurements performed at different repetition rates (i.e., 1–10 Hz), using different averaging conditions (i.e., averaging 3–100 laser shots per measuring point) and moving the sample continuously, in order to irradiate always fresh and nonirradiated sample volume, no detectable changes of the Z-scan recordings were observed, suggesting that no significant variation (e.g., arising from fragmentation) of the NPs characteristics has occurred. Of course the beam waist volume is quite small, but the total number of laser shots that a sample was experiencing was quite large, making probably possible the observation of any change of the Z-scan. This experimental evidence suggests that probably fragmentation was limited under these experimental conditions. Unfortunately, in the case of ns excitation, fragmentation resulting from photothermal evaporation cannot be ruled out and might take place. However, again, no measurable changes of the Z-scan recordings have been observed by performing the above-described experimental procedures.

Considering the present excitation conditions (i.e., 532 nm or 2.33 eV), the interband transitions should be more favorable for Au NPs while the intraband ones should be more efficient for Ag NPs. In any case, both types of transitions result to SA behavior and are in full agreement with the present results. The NLO behavior of Au NPs observed in the present study has been also reported previously.\textsuperscript{63,64} However, some studies have reported switching from SA to RSA\textsuperscript{69,74} and only RSA have been reported.\textsuperscript{54} The wealth of all these different NLO behaviors can be explained by considering the complex interplay of several factors, such as the size, the dielectric environment,\textsuperscript{83} the presence of capping agents and/or stabilizers,\textsuperscript{84–86} the colloidal state and the laser intensity. As a matter of fact, all these parameters can influence the electron dynamics and consequently the NLO response. The size of the NPs and the dielectric properties of the host material/environment are important parameters for the determination of the characteristics of the SPR band (i.e., its spectral position and width) according to the Mie theory, affecting the mean free path of the electrons and the dephasing of the plasmon resonance, hence the electron’s dynamics. The presence of capping agents or surface functionalization can drastically modify the electron dynamics because in this case, excited electrons can be trapped on the surface of the nanoparticles, experiencing different de-excitation path. As a result, the NLO response can be affected by resonance enhancement, de-excitation lifetimes, free-carrier absorption etc. Most of these issues have been discussed elsewhere as, e.g., by Hartland,\textsuperscript{87} by Hubenthal,\textsuperscript{88} by Gómez et al.,\textsuperscript{89} etc. Similar observations have been reported previously, in studies concerning the NLO response of some Au nanoislands and some continuous Au thin films.\textsuperscript{89,90} In both cases, the NLO response was found to depend strongly on the morphological characteristics and the implying electron dynamics.

Concerning the NLO refractive response of the alloyed NPs under ns excitation, all NPs were found to exhibit negative sign NLO refraction, i.e., Re $\chi^{(3)} < 0$, in agreement with other works,\textsuperscript{52} where the dispersion curves of Re $\chi^{(3)}$ and Im $\chi^{(3)}$ of some Ag nanocrystal–glass composites around the surface–plasmon resonance energy was studied. So, it was shown that when the excitation occurs at the low-energy side of the plasmonic peak the sign of Re $\chi^{(3)}$ is negative. In fact, as can be seen from Figure 2a, this condition holds for all the NPs’ dispersions studied, suggesting negative NLO refraction in agreement with the present experimental results. On the other hand, when the excitation occurs at the high-energy side of the plasmonic peak the Re $\chi^{(3)}$ is positive, a result which has been also confirmed\textsuperscript{82,89} Moreover, the Im $\chi^{(3)}$ is negative from both
sides of the plasmonic peak and is positive far from the plasmonic peak.

Regarding the NLO properties of the AuAg_{1-x} NPs under ps excitation, the findings of the present work are in good agreement with, e.g., the findings of ref 49, where some 3 nm diameter monolayer-protected Au, Ag, and Au–Ag alloy nanoclusters in toluene were studied under identical excitation conditions. So, negative sign NLO refraction and SA at low intensities switching to RSA at higher intensities were reported for all NPs in ref 49 in excellent agreement with the results of the present work. It is interesting to notice that no switching from SA to RSA was observed for intensities as high as 300 GW/cm² in the present work. This important difference could be attributed to the capping agents of the NPs used in ref 49.

In the literature, there are several investigations concerning the NLO response of Au–Ag nanomaterials. Most of these studies have been performed using nanosecond laser excitation. Among these studies, Karthikeyan et al.30 have studied the NLO properties of some Au–Ag nanocomposite polymer films, using Z-scan under 7 ns 1064 and 532 nm excitations. In agreement with the present work, under 532 nm excitation, the Au–Ag films were found exhibiting switching from SA to RSA which was not observed for the Au-polymer films, while all films were found to exhibit a clear RSA behavior under 1064 nm excitation. Moreover, Jafarkhani et al.31 having studied some necklace-shaped Au, Ag, and Au_{0.8}Ag_{0.2} nanoalloy water dispersions under 10 ns, 532 nm excitation have found that pure Au and Ag exhibited SA for all laser intensities, while the Au–Ag NPs exhibited RSA. It is worth to mention that the structure of the NPs, if they are alloyed or core–shell nanostructures, can affect strongly their NLO response. As a matter of fact, in a previous report32 on the NLO properties of Au NPs and Au/Ag core–shell, the Au NPs exhibited switching from SA to RSA, while the Au/Ag core–shell ones exhibited only RSA.

As demonstrated in the present work, the AuAg_{1-x} alloyed NPs possess important NLO properties which can be tailored in a controllable way by varying the composition and shifting the spectral position of their plasmonic band. In general, the possibility to tune the NLO properties by means of the composition is an interesting and simple strategy, however, it has been barely investigated so far. In fact, a similar viewpoint investigation, appeared recently concerning however some other nanoalloys, namely some ternary CdSe_{x}S_{1−x} alloyed quantum dots, which are variable band gap semiconducting systems.92 Similarly, it has been shown the tunability of their linear and NLO properties by modifying the Au/Ag mass ratio of some Au/Ag bilayer films studied by pump–probe femtosecond laser excitation.93

5. Conclusions

In summary, in this work a systematic study of the influence of the composition of some AuAg_{1−x} alloyed nanoparticles on their third-order NLO response has been performed. The NLO properties of the NPs have been investigated by means of the Z-scan technique employing visible, 4 ns, and 35 ps laser excitation. The ease of tunability of the plasmonic band of these nanoalloys through the GMF makes this simple approach particularly attractive for various applications in photonics and opto-electronics, since it allows the modulation of their optical nonlinearities. So, the third-order susceptibility \( \chi^{(3)} \) of the alloyed NPs was found to be significantly enhanced with increasing the GMF. In addition, the nanoalloys were found to exhibit strong self-defocusing behavior and saturable absorption under both nanosecond and picosecond laser excitation, while in the former case they exhibited a switching behavior from SA to RSA increasing the excitation intensity. The saturation intensity \( I_{s} \) needed to observe this switching was found to depend on the GMF. Finally, the physical origins of the NLO response of the AuAg_{1−x} nanoalloys was discussed and explained in terms of the basic process which occurs during the interaction of intense laser light with nanosized particles. The present findings are in very good agreement with other literature reports.

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### Notes

The authors declare no competing financial interest.

## Acknowledgments

This work was supported by the European Union (European Social Fund—ESF) and Greek national funds through the Operational Program “Education and Lifelong Learning” of the National Strategic Reference Framework (NSRF)—Research Funding Program: THALIS (ISEPUMA) and HERAKLEITUS II: Investing in knowledge society through the European Social Fund.

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