Plasmonic Enhancement or Energy Transfer? On the Luminescence of Gold-, Silver-, and Lanthanide-Doped Silicate Glasses and Its Potential for Light-Emitting Devices

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With the technique of synchrotron X-ray activation, molecule-like, non-plasmonic gold and silver particles in soda-lime silicate glasses can be generated. The luminescence energy transfer between these species and lanthanide(III) ions is studied. As a result, a significant lanthanide luminescence enhancement by a factor of up to 250 under non-resonant UV excitation is observed. The absence of a distinct gold and silver plasmon resonance absorption, respectively, the missing nanoparticle signals in previous SAXS and TEM experiments, the unaltered luminescence lifetime of the lanthanide ions compared to the non-enhanced case, and an excitation maximum at 300–350 nm (equivalent to the absorption range of small noble metal particles) indicate unambiguously that the observed enhancement is due to a classical energy transfer between small noble metal particles and lanthanide ions, and not to a plasmonic field enhancement effect. It is proposed that very small, molecule-like noble metal particles (such as dimers, trimers, and tetramers) first absorb the excitation light, undergo a singlet-triplet intersystem crossing, and finally transfer the energy to an excited multiplet state of adjacent lanthanide(III) ions. X-ray lithographic microstructuring and excitation with a commercial UV LED show the potential of the activated glass samples as bright light-emitting devices with tunable emission colors.

1. Introduction

The surface plasmon resonance of gold and silver nanoparticles is a remarkable phenomenon that already has fostered many new powerful analytical techniques and applications. The collective oscillation of the noble metal valence electrons resonantly excited by visible light, the surface plasmon resonance (SPR), causes a tremendous enhancement of the electromagnetic near-field in the immediate vicinity of the particles. Characteristic enhancement factors of the electric field E are in the range of 10^2.[1] This means that molecules adsorbed to these noble metal particles or that are at least not more than 10 nm apart from them feel up to a 100 times more intense field as opposed to the direct excitation in a plasmon-free environment. In this way, the Raman scattering of adjunct molecules as well as their luminescence can be enhanced enormously. These phenomena are commonly known as surface-enhanced Raman scattering (SERS)[1,2] and metal-enhanced fluorescence (MEF) or phosphorescence (MEP) (or generally metal-enhanced luminescence, MEL),[3,4] respectively.

However, MEL can be mistaken with a 'classical' luminescence energy transfer between the metal particle and the luminescent molecule. In a Förster resonance energy transfer (FRET) process, the donor chromophor absorbs the excitation light first and then transfers the energy by a non-radiative multipole coupling mechanism to the acceptor luminophor. For noble metal particles, the correct assignment of the different enhancement mechanisms becomes even more complicated, because the particles can also quench the luminescence of molecules by a non-radiative transfer of energy from the excited luminophor to the metal under excitation of plasmons that subsequently decay non-radiatively.[3,4] All these processes are a function of metal particle-luminophor distance, but are a function of particle size as well. Generally, gold and silver particles with diameters larger than 5 nm show a strong plasmon absorption, and therefore enhance the luminescence by a plasmonic near-field enhancement in a typical distance between 1 and 10 nm and/or quench the luminescence of atoms or molecules that are directly attached to them. In contrast, very small, sub-nanometer sized noble metal particles do not exhibit an SPR effect due to their low density of states.[1] Consequently, a plasmonic enhancement by these 'molecule-like' metal clusters is very unlikely. However, the fabrication of samples containing nearly monodisperse particles is especially for very small particles still not straightforward. And therefore, the differentiation between the different luminescence enhancement mechanisms has remained a challenge.

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Inorganic glasses have been proven as very suitable materials to stabilize gold and silver nanoparticles and to investigate their diverse optical properties.[5] One of the first attempts to study luminescene transfer processes in silver-containing boro-silicate glasses was made by Malta et al. in 1985.[6] As the luminophor to be studied the group chose europium(III) ions. Eu^{3+} in particular and lanthanide(III) ions (Ln^{3+}) in general are very promising components for the fabrication of a huge variety of multicolor light-emitting devices and laser materials.[7] In the last years, the investigation of the interaction between metal particles and lanthanides has triggered much attention due to the prospect of a tremendous enhancement of the lanthanides' photonic mode density (PMD).[8,9] An increased PMD would boost the excitation efficiency as well as the radiative decay rate and help to overcome the major drawback of usually very small absorption coefficients of lanthanide ions. Indeed, Malta et al. found a significant enhancement of the Eu^{3+} luminescence in the presence of silver nanoparticles.[6] This phenomenon was interpreted in terms of a silver plasmonic enhancement effect. The explanation is also used in very recent publications about the luminescence enhancement of Eu^{3+},[10] Pr^{3+},[11] or Er^{3+}[12] in silicate glasses containing silver. These interpretations are contrasted by experiments with glasses that contained Er^{3+} and silver, but no silver nanoparticles.[13,14] Here, the observed luminescence enhancement is explained by a classical energy transfer mechanism between pairs of silver ions and/or silver atoms and the lanthanide ions. This assumption is also supported by the observation of a luminescence enhancement of Er^{3+} in silicate glasses containing sub-nanometric, non-plasmonic gold clusters.[15]

Apparently, most of the aforementioned experiments suffer from the simultaneous appearance of ions, atoms, small particles and larger nanoparticles, which makes unambigous conclusions difficult if not impossible. Our group has just developed a technique to produce gold and silver particles in soda-lime silicate glasses by synchrotron X-ray activation.[5,16] In our approach, the nucleation can be separated from the growth of the particles enabling the design of glasses that contain only atoms or molecule-like metal species or only nanoparticles. Thus, we will show in this article that a co-doping of the glasses with lanthanide ions enables the differentiation between MEL and a classical energy transfer. As a result, we can exclude a lanthanide luminescence enhancement based on SPR excitation. Instead, the increased light emission observed under non-resonant excitation is due to a classical energy transfer process between molecule-like noble metal particles and lanthanide(III) ions.

2. Results and Discussion

The soda-lime silicate glass samples were produced by a melt-quenching technique and doped with different amounts of gold or silver as well as different lanthanide ions (Eu^{3+}, Tb^{3+}, Dy^{3+}, Sm^{3+}). As described previously, irradiation with synchrotron X-rays causes the formation of glass defect centers such as trapped and free electrons.[16] These electrons react with the noble metal ions to yield neutral silver and gold species, respectively, as could be proven by luminescence and electron paramagnetic

resonance (EPR) spectroscopy. Subsequent annealing induces the formation of plasmonic nanoparticles.

To understand the interactions between the noble metals and the lanthanides, we want first refer to our recently published results regarding glasses containing only gold and only silver, respectively.[16] After synchrotron irradiation gold-containing glasses exhibit a red luminescence peaking at 753 nm with 337 nm excitation, that could be assigned to gold dimers, Au_2, after comparison with optical spectra of gold species isolated in solid argon matrices at cryogenic temperatures.[17] Furthermore, the annealing of these glasses at 550 °C for 5 min induces a greenish luminescence with 337 nm excitation peaking at 525 and 555 nm. This broad luminescence band was explained by means of TD-DFT calculations by an energy transfer process between molecule-like gold species such as the gold dimer and glass defect centers such as non-bridging oxygen (NBO). In contrast, a further annealing at 550 °C decreases this luminescence and finally yields gold nanoparticles as evidenced by transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS).[16]

As for silver-doped samples, the irradiation with synchrotron X-rays causes the reduction of Ag^+ to Ag^0 as determined by EPR spectroscopy.[16] Annealing at 300 °C decreases the concentration of Ag_1, but triggers the appearance of an intense white luminescence with 337 nm excitation. The appropriate spectrum could be decomposed into bands that can be attributed to molecule-like silver species such as Ag_2, Ag_3, and Ag_4 and a band matching the green luminescence of gold-doped glasses described before. The luminescence band in the green part of the spectrum was – as also described before for gold-containing glasses - explained by an energy transfer between molecule-like silver particles and glass defect centers. Annealing of these samples at temperatures above 300 °C induces the growth of silver nanoparticles and a vanishing of the luminescence.

In the next paragraphs we will describe the new results of gold-containing soda-lime silicate glasses that were co-doped with Eu^{3+}. The samples were also irradiated with synchrotron X-rays and subsequently annealed at 550 °C. The aforementioned red luminescence of Au_2 after irradiation can also be detected in these glasses and is obviously not influenced by the lanthanide ions. Furthermore, a 5 min annealing at 550 °C induces the same green luminescence as already seen in the non-lanthanide containing samples. However, beside this band peaking at 525 and 555 nm the characteristic sharp Eu^{3+} emission lines at 586 and 609 nm can be observed with 337 nm excitation (Fig. 1a), a wavelength at which Eu^{3+} normally has only a very weak absorption cross section. Consequently, this excitation can be called a non-resonant excitation. The 586 and 609 nm emission peaks can be assigned to the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of europium(III) ions. A further annealing at 550 °C causes a decline and finally a disappearing of both the green and europium-specific luminescence, which points to a close relationship between these two emissions.

For comparison, we also produced glasses containing only Eu^{3+}, but no gold. A very weak peak at 609 nm with 337 nm excitation can be identified here as well (Fig. 1a). In an attempt to identify the influence of gold on the luminescence efficiency of Eu^{3+} and to calculate luminescence enhancement factors, we subtracted the normalized green luminescence band of an activated and 5 min at 550 °C annealed gold-containing glass from
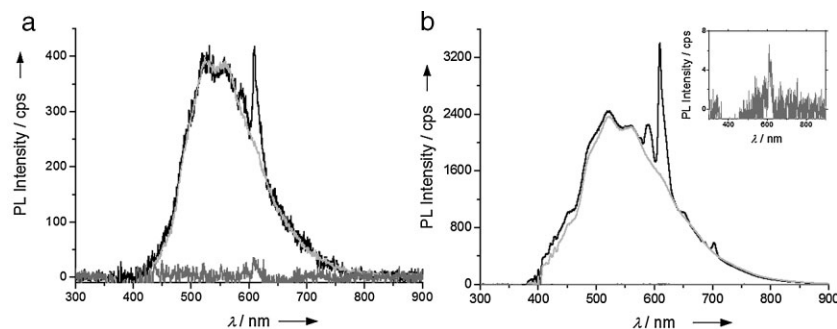
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Figure 1. a) PL spectra ($\lambda_{exc} = 337\,nm$) of a synchrotron activated (sy-activated) and subsequently for 5 min at 550 °C annealed soda-lime silicate glasses containing 0.005 mol% Au (light grey line, spectrum normalized), and both 0.005 mol% Au and 0.19 mol% Eu (black line: sy-activated +5 min 550 °C; dark grey line: non-activated and non-annealed). b) PL spectra ($\lambda_{exc} = 337\,nm$) of sy-activated and subsequently for 240 min at 300 °C annealed soda-lime silicate glasses containing 0.037 mol% Ag (light grey line, spectrum normalized), 0.19 mol% Eu (inset: dark grey line), and both 0.037 mol% Ag and 0.19 mol% Eu (black line).

the spectrum of a Eu^{3+} and gold co-doped sample in Figure 1a to obtain the "pure" Eu^{3+} transitions. Dividing the luminescence intensity at 609 nm in the obtained spectrum by the appropriate luminescence intensity of a glass containing only Eu^{3+} yields an enhancement factor of 5.0 caused by the presence of molecule-like gold particles.

Eu^{3+}- and silver-co-doped glasses exhibit a similar behavior. The luminescence spectrum in Figure 1b indicates that the Eu^{3+} emission can only be excited non-resonantly at 337 nm, if the sample was synchrotron irradiated and annealed at 300 °C. These conditions are the same prerequisites for the appearance of the white luminescence that was previously assigned to molecule-like silver species and glass defect centers. Annealing at 500 °C induces a decline of the Eu^{3+} as well as of the white luminescence. Apparently, the lanthanide-specific emission seems to be closely related to the silver- and glass-specific emission as already observed for gold-containing samples. The quantitative evaluation of the Eu^{3+} luminescence intensity (same calculation as described above for gold-doped glasses) gives an enhancement factor of 250(!) with 337 nm excitation as compared to samples containing only Eu^{3+}. The enormous difference of the enhancement factors in gold- (5.0) and silver-doped glasses (250) is most probably mainly caused by the different noble metal concentrations. The maximum amount of gold is limited by its dissolution in soda-lime silicate glasses. Thus, only a maximum concentration of about 50 ppm (measured by X-ray fluorescence (XRF) analysis) could be obtained without the formation of larger particles during the glass fabrication process. In contrast, the silver-doped glass contained 370 ppm. Thus, the number of particles contributing to the enhancement as well as the appropriate luminescence enhancement factor is much larger. Due to the higher achievable concentration and the accordingly stronger luminescence signals, we focused our experiments and in particular the quantitative

data evaluation mainly on silver-containing glasses. However, the silver-based interpretations should also be true for gold-containing samples since similar qualitative trends could also be determined for these glasses.

The relationship between the silver content, the white as well as the Eu^{3+} emission was thoroughly investigated by varying the silver concentration. PL spectra of synchrotron activated and 120 min at 300 °C annealed glasses containing 0.19 mol% europium, but different amounts of silver, are shown in Figure 2a.

As a result, both the white and the Eu^{3+}-specific luminescence increase with rising silver content. A plot of the luminescence intensity at 520 nm (caused by glass defects) versus the Eu^{3+} emission at 609 nm for different silver concentrations gives a distinct linear relation with a slope of 1.77 pointing to a linear correlation between these two luminescence centers (Fig. 2b).

So far, only the non-resonant lanthanide excitation at 337 nm has been reported. However, Eu^{3+} absorbs light very intensely ("resonantly") at 393 nm. The comparison of synchrotron activated and non-activated glasses containing only europium(III) shows no differences between the emission intensities with resonant 393 nm excitation. Hence, an influence of the synchrotron radiation on the resonantly excited Eu^{3+} emission in the absence of noble metals can be excluded. Furthermore, the resonant excitation efficiency was investigated in glasses doped with Au and Eu, and Ag and Eu, respectively. Neither the synchrotron activation, nor the thermal annealing influenced the emission intensity with resonant excitation at 393 nm. Consequently, the resonant excitation is not enhanced as opposed to the non-resonant excitation at 337 nm (a wavelength where Eu^{3+} normally shows only a very weak absorption).

In a further attempt, we wanted to figure out at which wavelengths the Eu^{3+} luminescence is enhanced most intensely. We therefore analyzed the excitation spectra of Au/Eu- and Ag/
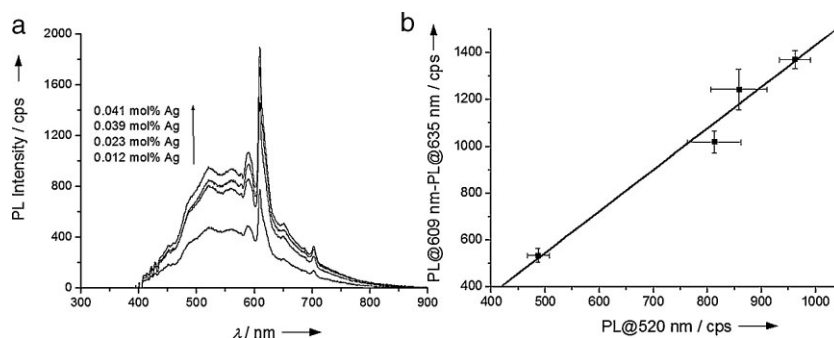

Figure 2. a) PL spectra ($\lambda_{exc} = 337\,nm$) of sy-activated and subsequently for 240 min at 300 °C annealed soda-lime silicate glasses containing 0.19 mol % Eu and different amounts of Ag. b) Plot of the difference between the PL intensities at 609 and 635 nm versus the intensity at 520 nm of sy-activated and subsequently for 240 min at 300 °C annealed glasses containing 0.19 mol% Eu and 0.012, 0.023, 0.039 and 0.041 mol% silver, respectively. The line is the result of a linear regression yielding the equation $y = -338 + 1.77x$.
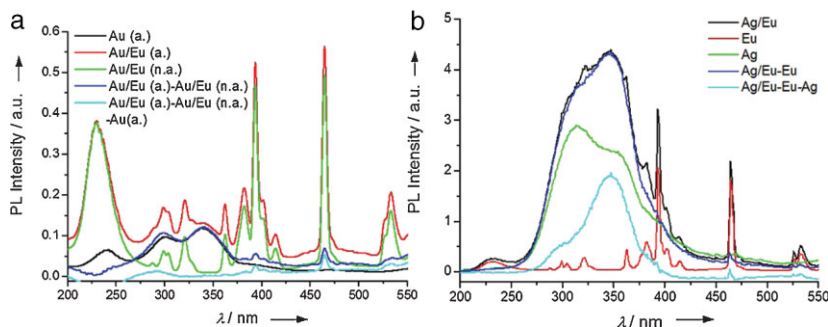
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Figure 3. a) Excitation spectra ($\lambda_{em} = 611\,nm$) of a sy-activated and for 5 min at 550 °C annealed sample containing both 0.005 mol% Au and 0.19 mol% Eu (red curve) and only 0.005 mol% Au (black) and of a non-activated and non-annealed Au/Eu-doped glass (green). Furthermore, the difference between the activated and non-activated Au/Eu-doped sample is shown (dark blue). Additionally, from the aforementioned difference spectrum the excitation spectrum of the activated and annealed Au-doped glass was subtracted (light blue). b) Excitation spectra ($\lambda_{em} = 611\,nm$) of a sy-activated and for 240 min at 300 °C annealed sample containing both 0.037 mol% Ag and 0.19 mol% Eu (black curve), only 0.037 mol% Ag (green) and only 0.19 mol% Eu (red). Furthermore, the difference between the sy-activated Ag/Eu-doped and the sy-activated Eu-doped sample is shown (dark blue). Additionally, from the aforementioned difference spectrum the excitation spectrum of the sy-activated and annealed Ag-doped glass was subtracted (light blue).

Eu-codoped glasses showing the largest enhancement effect. To identify the spectrum that causes only the excitation of the lanthanide ions, we subtracted the excitation spectrum of glasses containing only gold and silver, respectively, from the appropriate spectrum of glasses containing the noble metals and Eu^{3+} (Fig. 3). As a result, the Eu^{3+} emission can be non-resonantly excited most efficiently at 298 nm (Au, Fig. 3a) and 351 nm (Ag, Fig. 3b), respectively. It is also very interesting to compare the non-resonant with the resonant excitation efficiency. In the case of gold-doped glasses, the non-resonant gold-enhanced excitation at 298 nm is much smaller than the resonant one at 393 nm. However, the signals at 351 nm (non-resonant) for the silver-doped and at 393 nm (resonant) for the non-silver-containing samples have approximately the same intensity. Consequently, these two different excitation processes apparently have the same efficiency.

Appropriate experiments were also performed for silver-containing soda-lime silicate glasses co-doped with Sm^{3+}, Dy^{3+}, and Tb^{3+}, respectively. With 337 nm excitation enhancement factors of 5.0 (Sm), 2.6 (Dy), and 1.3 (Tb) could be determined. Figure 4 shows the PL spectra of silver-doped glasses co-doped with Sm^{3+}, Dy^{3+}, and Tb^{3+}, respectively, after annealing for 240 min at 300 °C with and without prior synchrotron irradiation.

The described investigations all show unambiguously that the lanthanide(III) luminescence is only enhanced in the presence of molecule-like noble metal particles. TEM as well as SAXS studies indicated, that these glasses contain no nanoparticles.[16] UV-vis spectroscopy data further proved, that neither gold- nor silver-containing glasses showing the most intense lanthanide luminescence exhibit a surface plasmon absorption (Fig. S2 and S3, Supporting Information). The absorption bands close to 300 nm in both gold- and silver-doped glasses are due to small "molecule-like" noble metal species according to literature data[17] and can be unambiguously distinguished from the

distinct wavelengths and shapes of the well-known surface plasmon resonance absorption of gold (peaking at 540 nm) and silver (410 nm) nanoparticles[1] (which are only observed after longer annealing times or annealing at higher temperatures). Additionally, the Ln^{3+} emission is most enhanced with about 300 and 350 nm excitation for gold- and silver-containing samples, respectively. These wavelengths do not match at all with the SPR absorption of gold and silver nanoparticles peaking at about 540 and 410 nm, respectively. Consequently, a plasmonic enhancement of the lanthanide emission can be definitely ruled out. We also investigated the influence of gold and silver on the lanthanide luminescence lifetime. A plasmonic enhancement would boost the PMD of the lanthanide ions, thus increasing the radiative decay rate, as mentioned before. As a result, the lifetime of the emission is proposed to decrease significantly.[8,9] Soda-lime silicate glasses containing only Eu^{3+} ions exhibit a luminescence lifetime of 2.34 ms with excitation at 393 nm and measuring the Eu^{3+}-specific emission at 611 nm (Fig. S4a, Supporting Information). Eu^{3+}-containing samples co-doped with gold and silver, respectively, show at 611 nm a bi-exponential (Au, Fig. S4b, Supporting Information) and tri-exponential decay (Ag, Fig. S4c, Supporting Information), respectively, with 337 nm excitation. The shorter decay times in the microsecond range can be assigned to glass defect centers and noble metal species that give rise to the broad luminescence band observed for both glasses. The lifetimes in the millisecond range at 2.58 (Au) and 2.34 ms (Ag) are very close to the values of the "pure" Eu^{3+} sample (2.34 ms). Hence, nearly no change of the lifetime and consequently no altering of the radiative decay rate is observed for the enhanced lanthanide luminescence in gold- and silver-containing glasses excluding an enhancement of the europium PMD. For FRET processes, the luminescene decay rate is
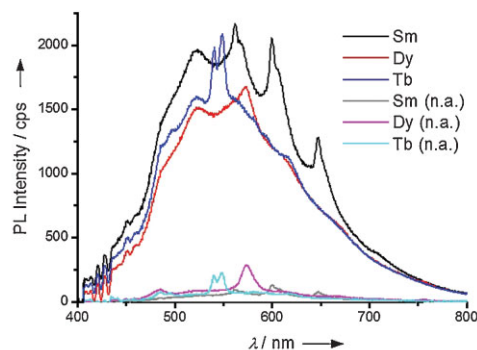

Figure 4. PL spectra ($\lambda_{exc} = 337\,nm$) of sy-activated and 240 min at 300 °C annealed 0.037 mol% Ag containing glasses co-doped with 0.19 mol% Sm (black curve), Dy (red), and Tb (blue), respectively, and of non-activated and non-annealed (n.a.) 0.037 mol% Ag containing samples co-doped with 0.19 mol% Sm (grey), Dy (magenta), and Tb (light blue).

determined by the lifetime of the donor chromophor or the acceptor, whichever excited state lives longer. As for this case, the accepting Eu^{3+} acceptor obviously defines the lifetime.

Since a plasmonic enhancement effect can be excluded, a possible classical energy transfer process has to be taken into account. The linear relationship between the glass-intrinsic luminescence band and the Eu^{3+} emission after varying the silver concentrations shown in Figure 2b strongly supports the involvement of an energy transfer process between molecule-like silver species and both glass-defect centers and Eu^{3+} ions. Luminescence spectroscopical experiments indicated, that synchrotron X-ray activated glasses containing gold and silver, respectively, exhibit distinct luminescence peaks that could be assigned to very small particles such as Au_2, Ag_2, Ag_3, and Ag_4.[16] The analysis of the excitation spectra showed that the lanthanide emission is enhanced most efficiently in the range between 300 and 400 nm. This is also the range in which these molecule-like gold and silver species are absorbing. The results indicate that these species act as donor chromophors in the same way organic sensitizers do. Thus, we propose an energy transfer process between these small noble metal species and the lanthanide ions in soda-lime silicate glasses as an explanation for the lanthanide luminescence enhancement with non-resonant excitation.

In general, the number of emitted quanta (or the light output) depends on the ability of the luminophor to occupy efficiently an electronically excited state (described by the absorption coefficient), as well as the ability to prevent its non-radiative decay (described by the quantum yield). Even though lanthanides usually exhibit large luminescence quantum yields, the molar absorption coefficients of the parity-forbidden 4f–4f lanthanide transitions are very small. This major drawback can be overcome by the usage of so called sensitizers (or "antennae"). Very often organic ligands that can complex lanthanide ions such as bipyridine, terpyridine or chinoline, etc. are applied for this purpose.[7] In addition, certain lanthanide ions, transition metals, and well selected hosts are widely used as sensitizers also.[18–20] Our results indicate that molecule-like noble metal particles can act as sensitizers, too. These molecules can be excited by irradiation with the appropriate wavelengths, transfer the energy to the lanthanide ions, and therefore trigger the occupation of their excited states that finally decay radiatively by the emission of light. The quantum yield Q_{sens}^{Ln} of this indirect (or non-resonant) excitation can be expressed by Equation 1, where Q^{Ln} denotes the quantum yield of the lanthanide ion with direct (resonant) excitation and η_{sens} the energy transfer efficiency between the sensitizer and the lanthanide ion.

$$Q_{sens}^{Ln} = \eta_{sens} Q^{Ln} \tag{1}$$

For the discussion of the energy transfer process the multiplicity of the excited state plays an important role. Most of the here discussed lanthanide electronic transitions causing the emission of light (e.g., $Eu(^5D_0 \rightarrow {}^7F_J)$) are characterized by a change in total electron spin ($\Delta S \neq 0$). Following IUPAC rules the result of a spin-forbidden transition process is referred to as phosphorescence.[21] For aromatic sensitizers the simplified energy transfer model sensitizer $(S_1) \rightarrow$ sensitizer $(T_1) \rightarrow Ln^*$ is often dicussed, where S_1 describes the excited singlet and T_1 the

energetically lowest triplet state of the sensitizer. Both from the sensitizer's excited singlet and triplet state energy can be transfered to the lanthanide ion. However, due to the usually short lifetime of the S_1 state, this transfer is very inefficient and can be disregarded. Thus, Equation 1 can be substituted by Equation 2, where η_{isc} describes the intersystem crossing efficiency between the sensitizer's S_1 and T_1 state and η_{et} the efficiency of the energy transfer between the sensitizer and the lanthanide ion.

$$Q_{sens}^{Ln} = \eta_{isc} \eta_{et} Q^{Ln} \tag{2}$$

This means in the case of the investigated noble metal-doped glasses that an intersystem crossing between the excited singlet state and the triplet state of the noble metal particles is needed. In a recent publication[16] we assigned the 753 nm emission observed with 337 nm excitation in gold-doped glasses after synchrotron irradiation to gold dimers due to the nearly perfect match of the optical properties (in contrast, e.g., gold atoms in solid argon exhibit a strong luminescence band at 454 nm, a weaker band at 815 nm, and absorption maxima between 225 and 255 nm[17]). Furthermore, the identified gold dimer luminescence was assigned to the triplet-singlet transition $X^1\Sigma_g^+ \rightarrow a^3\Sigma_u^+$ due to the large Stokes shift of the luminescence and the long lifetime of 26 μs after comparison with R2PI (resonant 2-photon ionization) studies of Au_2 in the gas phase[22] and theoretical DFT studies,[23] thus showing the high probability of intersystem crossing processes for such gold species. Similar intersystem crossing processes are possible for small silver particles as well due to generally strong spin-orbital coupling in heavy nuclei.[24] After the noble metal cluster-centered intersystem crossing, the energy is transferred from the excited triplet state to the excited 4f lanthanide state.

The evaluation of the excitation spectra of an Ag/Eu-co-doped glass indicated, that the Eu^{3+} emission can be excited non-resonantly at 351 nm as efficient as resonantly at 393 or 465 nm. If every Eu^{3+} ion is sensitized by a silver particle, η_{sens} in Equation 1 would be close to 1. However, the glass contains only 0.037 mol% silver, but 0.19 mol% europium, which means that in an ideal case only every fifth lanthanide ion is sensitized by a silver atom. This ratio is most likely even larger due to the random distribution of the silver atoms in the glass (according to the FRET theory, the sensitizers can be maximal 10 nm apart of the acceptors for a successful energy transfer) and the contribution to the transfer process of particles consisting of at least two atoms. Consequently, η_{sens} should be even larger than 1 for a single Ag_n/Eu^{3+} unit. Therefore, Eu^{3+} can be excited more efficiently by indirect excitation via a silver particle as opposed to the direct excitation, a phenomena that can be explained by means of a more likely intersystem crossing if centered at the silver nuclei as opposed to an intersystem crossing that is centered at the lanthanide ion.

For the sensitizer $T_1 \rightarrow Ln^*$ transition, generally two mechanisms can be discussed, a non-radiative transfer by electron exchange between excitation and emission center (Dexter mechanism), and a non-radiative transfer by electric multipole interaction (Förster mechanism). The electron exchange transfer demands an excellent overlap between the involved orbitals. This
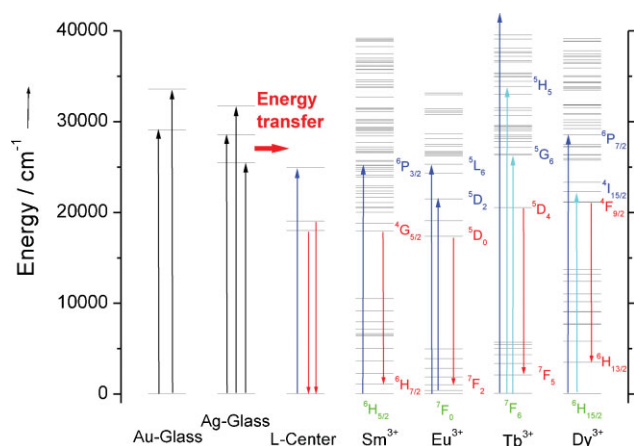
Figure 5. Schematic of energy levels of the investigated Ln^{3+} ions and comparison with the excitation maxima of Au-doped (sy-activated +5 min 550 °C) and Ag-doped (sy-activated +240 min 300 °C) glasses and with proposed emission and excitation transitions of the L-center (glass defect center). Blue arrows represent most intense absorption transitions (dark blue: very intense, light blue: less intense) and red arrows reflect most intense emission transitions in soda-lime silicate glasses at ambient temperature.

mechanim is proposed for some lanthanide-doped phosphors such as YVO_4:Eu.[19] The multipole interaction mechanism requires a coupling of multipole moments (e.g., dipole–dipole, dipole–quadrupole coupling) between the T_1 state of the sensitizer and the excited 4f state of the lanthanide and is proportional to the energy overlap of the sensitizer's emission with the acceptor's absorption, to the reciprocal radiative decay time of the sensitizer, and to the reciprocal of a certain power of the sensitizer-acceptor distance.[6,7] This mechanism is most likely if organic ligands are used as sensitizers, but it is generally very difficult to distinguish between the two processes, especially in inorganic matrices.

The efficiency of the energy transfer process depends on many complex parameters such as the energy gap between the lowest chromophor triplet and the excited Ln^{3+} states, as well as on competitive non-radiative deactivation processes. A closer look at the enhancement factors for the various investigated lanthanides bears remarkable differences. As for silver-doped glasses, factors of 250 (Eu^{3+}), 5.0 (Sm^{3+}) 2.6 (Dy^{3+}), and 1.3 (Tb^{3+}) were determined. Figure 5 shows the energy levels of the appropriate lanthanide(III) ions contributing to the most intense absorption and emission lines. For comparison, the absorption maxima of the synchrotron activated gold- and silver-doped glasses and the transitions of the glass-intrinsic defect center (L-center) causing the green luminescence are depicted as well.

Apparently, the excited states contributing to the luminescence are all in an energy range below the excited state energies of the donors. Hence, these states can be in principal populated by a noble metal → Ln^* energy transfer process. Furthermore, it is obvious that for the glass-defect center as well as for Eu^{3+} and Sm^{3+} absorption levels at about $25\,000\,cm^{-1}$ and emission levels in the range of $17\,000$–$19\,000\,cm^{-1}$ exist. These are also the emission centers exhibiting the largest luminescence enhancement factors. Consequently, these excitation and emission wavenumbers should be the 'ideal' ranges for a most efficient energy transfer process. The much higher enhancement factor of Eu^{3+} as compared to Sm^{3+} can be explained by the fact that Eu^{3+} has nearly no density of states at $29\,000\,cm^{-1}$, which is the energy range of the donor excitation. Therefore, the emission intensity difference between non-resonant excitation and resonant excitation becomes largest for Eu^{3+}. All the other investigated lanthanide ions can absorb in this range and are therefore strictly spoken not merely excited non-resonantly. The very low Tb^{3+} enhancement factor of 1.3 is most likely due to the missing density of states in the energy range between $20\,000$ and $25\,000\,cm^{-1}$. Dy^{3+} absorbs most intensely at $42\,700\,cm^{-1}$ and offers only a weak transition at the for the energy transfer process interesting wavenumber of $28\,500\,cm^{-1}$, which might explain the moderate enhancement factor of 2.6.

As already descrived above, the lanthanide photoluminescence has a great technical potential. E.g., the 1540 nm emission of Er^{3+} is an ideal optical communication wavelength. Hence, Ln-doped components are very promising materials for the fabrication of waveguides,[25] fiber lasers,[26,27] luminescent liquid crystals,[28] or light-emitting diodes (LEDs).[29,30] Additionally, the visible
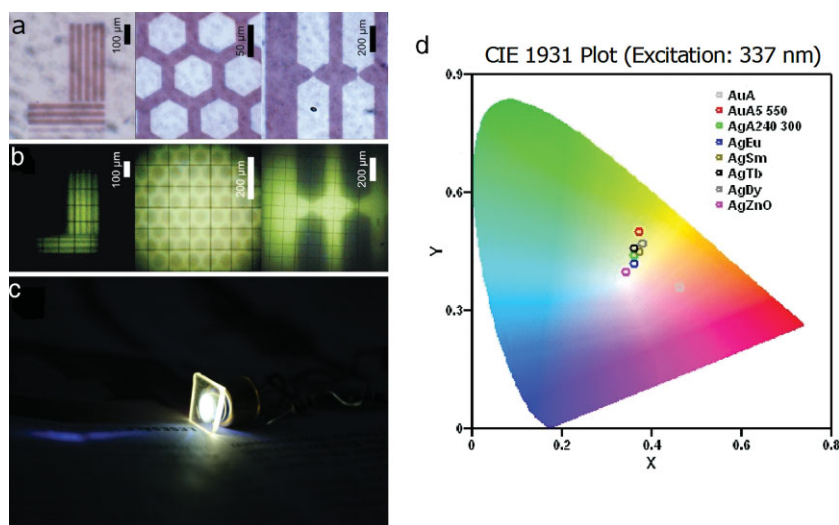

Figure 6. a) Light micrograph of lithographically sy-activated Au-doped glasses after 45 min annealing at 550 °C. b) Confocal luminescence microscope images ($\lambda_{exc} = 366\,nm$) of the same structures shown in a, but annealed for 5 min at 550 °C. c) Digital photograph of a sy-activated and 240 min at 300 °C annealed Ag-doped glass excited with a 305 nm AlInGaN LED. d) CIE 1931 color plot of different sy-activated glasses with 337 nm excitation. Code: Au, Ag, Eu, Sm, Tb, Dy = Soda-lime silicate glasses doped with the appropriate ions. All Ag-doped glasses were annealed for 240 min 300 °C. AuA = sy-activated, AuA5 550 sy-activated +5 min at 550 °C. AgZnO = 0.02 mol% Ag-doped SiO_2 (68.0 mol%)-Na_2O(15.1)-ZnO(5.1)-Al_2O_3 (3.9)-NaF(7.2) glass, sy-activated + 240 min 300 °C.

lanthanide emission is already used in fluorescent lamps.[31] The reported synchrotron activation of inorganic glasses and the generation of novel noble metal/Ln^{3+} energy transfer pairs could also play an important role for the implementation and improvement of the manifold optical applications. Another advantage of our technology is the optical nature of the activation process enabling a spatially resolved writing of luminescent structures by means of synchrotron lithography as shown in Figure 6a. Furthermore, a similar spatially resolved activation process is possible by means of titanium:sapphire fs-laser irradiation of the noble-metal-doped glasses, thus proving the versatility of our approach.

LEDs have just begun to replace the traditional halogen light bulbs or toxic mercury-containing energy-saving lamps in everyday applications. This success story became mainly possible due to the development of InGaN-based LEDs with an emission maximum in the blue.[32] Its invention has stimulated much research to find suitable luminescent materials that can be excited in this spectral range and emit visible light to fabricate blue LED-pumped lighting devices. White LEDs can be produced by mixing green, red and blue or blue and yellow light-emitting materials. However, there are still much efforts needed to find the right materials to manufacture a white light source which combines the tremendous advantages of the LED technology such as long lifetimes, low power consumption, fast response times, huge flexibility in forms and sizes, etc. with the 'warm' color temperature of conventional halogen light bulbs. A very promising approach to tackle this challenge is based on lanthanide-containing compounds. In a recently published article Eu^{2+}-doped nitride and oxo-nitride phosphors are used to convert the light of a blue-emitting diode to white light.[30] As a proof of principle, we produced synchrotron activated silver-doped glasses and excited these samples by a commercial UV AlInGaN LED. In this way, we could build a white light-emitting device (Fig. 6c). By co-doping the glasses with various lanthanide ions and/or by substituting CaO in the soda-lime silicate glasses by the blue emitting ZnO, the photoluminescence spectrum can be altered. Thus, it is possible to tune the emission color as shown by the CIE color diagram in Figure 6d. Consequently, the presented technology might pave the way to a new class of lighting devices.

3. Conclusions

Within this work, we implemented the technique of synchrotron X-ray activation to generate molecule-like, non-plasmonic gold and silver particles in soda-lime silicate glasses and studied the luminescence energy transfer between these species and lanthanide(III) ions. As a result, a significant lanthanide luminescence enhancement by a factor of up to 250 under non-resonant UV excitation was observed. The absence of a distinct gold and silver plasmon resonance absorption, respectively, the missing nanoparticle signals in previous SAXS and TEM experiments, the unaltered luminescence lifetime of the lanthanide ions compared to the non-enhanced case, and an excitation maximum at 300–350 nm, which is far away from the plasmon resonance absorption of both gold and silver, but is equivalent to the absorption range of small noble metal particles,

all indicate unambiguously that the observed enhancement is due to a classical energy transfer between noble metal particles and lanthanides rather than due to a plasmonic field enhancement effect. We propose that very small, molecule-like noble metal particles such as dimers, trimers and tetramers first absorb the excitation light, undergo a singlet-triplet intersystem crossing, and finally transfer the energy to an excited multiplet state of adjacent lanthanide(III) ions.

Furthermore, we could show that co-doping of synchrotron activated gold- and silver-containing glasses with different lanthanides, X-ray lithographic microstructuring and the excitation of these samples with commercial UV LEDs enables the fabrication of functionalized glass samples with tunable emission spectra opening up new vistas for the development of multi-colored light-emitting devices.

4. Experimental

Glasses composed of $70SiO_2 \cdot 20Na_2O \cdot 10CaO$ (values in mol%) were doped with 0.005 mol% Au or 0.037 mol% Ag and co-doped with 0.19 mol% Eu, Tb, Dy, and Sm, respectively. Reagent grade and high purity grade SiO_2 (99.99%, Umicore), Na_2CO_3 (puriss. p.a., Fluka), $CaCO_3$ (puriss. p.a., Riedel-de Haën), $AuCl_3$ (aq) (puriss. p.a., Fluka), $AgNO_3$ ($\geq$99.9% p.a., Carl Roth), $Eu(NO_3)_3 \cdot 5H_2O$ (puriss.$>$98.5%, Sigma–Aldrich), $Sm(NO_3)_3 \cdot 6H_2O$ (99.9%, Sigma–Aldrich), $Dy(NO_3)_3 \cdot 5H_2O$ (99.9%, Sigma–Aldrich), and $Tb(NO_3)_3 \cdot 5H_2O$ (99.9%, Sigma–Aldrich) were used as starting materials. For comparison undoped glasses were prepared, too. Approximately 35 g batches were mixed and melted at 1450 °C for 120 min in an electric furnace. The glass melt was then slowly cooled down to room temperature. Samples of sizes $10 \times 10 \times 1$ mm^3 were cut and polished.

Selected samples were subsequently irradiated with white synchrotron light (dose: 40 J cm^{-2}; energy range: 3–15 keV) at the Berlin electron storage ring facility BESSY with the dipole X-ray scanner DEX02 (Jenoptik) of Anwenderzentrum für Mikrotechnik (AZM) under clean room conditions. X-ray lithography was carried out with a gold test mask with different micrometer structures. More details on the synchrotron activation technology are given in the Supporting Information.

Subsequent thermal treatments of the activated glasses were realised by putting the glasses into a platinum crucible and annealing it in a muffle furnace.

PL spectra were recorded at room temperature with the spectrometer HR2000 (Ocean Optics) equipped with a KV370 long pass filter (Schott) to suppress the excitation light. Excitation was carried out with the pulsed N_2-laser MNL 103-PD (Lasertechnik Berlin; wavelength: 337.1 nm, pulse energy: 80 μJ, repetition rate: 20 Hz, pulse duration: 3.5 ns).

Excitation spectra and lifetime measurements were made with an Aminco Bowman Series 2 Luminescence Spectrometer equipped with a continuous and pulsed xenon lamp, respectively, and a KV370 long pass filter (Schott). All spectra were measured at room temperature and corrected for detector sensitivity.

Acknowledgements

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