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Photoluminescence of atomic gold and silver particles in soda-lime silicate glasses

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Abstract

We report the chemistry and photophysics of atomic gold and silver particles in inorganic glasses. By synchrotron irradiation of gold-doped soda-lime silicate glasses we could create and identify unambiguously the gold dimer as a stable and bright luminescing particle embedded in the glassy matrix. The gold dimer spectra coincide perfectly with rare gas matrix spectra of Au₂. The glass matrix is, however, stable for years, and is hence perfectly suited for various applications. If the irradiated gold-doped sample is annealed at 550 °C a bright green luminescence can be recognized. Intense 337 nm excitation induces a decrease of the green luminescence and the reappearance of the 753 nm Au₂ emission, indicating a strong interrelationship between both luminescence centers. Time-dependent density functional theory (TD-DFT) calculations indicate that the green luminescence can be assigned to noble metal dimers bound to silanolate centers. These complexes are recognized as the first stages in the further cluster growth process, which has been investigated with small-angle x-ray scattering (SAXS). In silver-doped glasses, Ag⁰ atoms can be identified with electron paramagnetic resonance (EPR) spectroscopy after synchrotron activation. Annealing at 300 °C decreases the concentration of Ag₁, but induces an intense white light emission with 337 nm excitation. The white luminescence can be decomposed into bands that are attributed to small silver clusters such as Ag₂, Ag₃ and Ag₄, and an additional band matching the green emission of gold-doped glasses.

1. Introduction

Some 150 years after the Baker lecture of Michael Faraday at the Royal Society of London about the interaction of ‘very minute’ metal particles with light [1], small noble metal clusters are still revealing novel unexpected properties such as catalytic activity [2], intense photoluminescence [3], surface-enhanced Raman scattering (SERS) [4] or metal-enhanced fluorescence [5, 6]. The ‘minutest’ molecular particles consisting of only few atoms are most interesting, because they represent the missing link between atomic and nanoparticle or even bulk properties [7–9]. However, their direct experimental study is not always straightforward. Large amounts of small clusters tend to aggregate, and thus rapidly form larger particles, whereas low cluster concentrations are difficult to be analyzed. An alternative is the stabilization of metal clusters by organic ligands such as triphenyl phosphane [10], dendrimers [11], or thiolates [12, 13]. But the influence of the ligands on the optical properties of the metal–organic complex has to be considered, and it has been discussed controversially [13–15]. One way out of this dilemma was presented by the pioneering work of Ozin et al [16], Harbich et al [17] and Ertl et al [18], who isolated size-selected gold and silver clusters in solid rare gas matrices at cryogenic temperatures, and thus provided insights into their optical response. In contrast to the above-mentioned matrices, metal
oxide glasses can stabilize particles even at room temperature, which enables applications based on the surface plasmon resonance or the large third-order nonlinear susceptibilities of gold and silver [19–21]. If the stabilization of molecular metal particles in glassy matrices can be accomplished, their possible luminescence properties could open up new vistas in the field of photonic glasses. However, while gold and silver nanoparticles in glassy matrices have been studied intensively during recent years [21, 22], systematic investigations of subnanometer-sized particles are rare. Most often the noble metal colloids are generated by annealing, but the simultaneous nucleation, growth and ripening of the particles during the thermal treatment obviously inhibits the stabilization of small clusters with narrow size distributions.

Recently, we have presented a novel method to generate high concentrations of nearly monodisperse gold nanoparticles in soda-lime silicate glasses by irradiating samples with synchrotron light [23]. Irradiation with highly intense x-rays causes defect centers such as trapped holes and electrons in the glass network. X-ray generated electrons can combine to form neutral gold species. A subsequent annealing process (typically at 550 °C) induces the growth of larger gold particles. In this way, nucleation (by irradiation) and growth (by annealing) can be separated, allowing for a fine tuning of cluster size and number density by simply changing the annealing time or temperature. In this article, we report the generation of very small molecular gold and silver particles such as the luminescent gold dimer with the novel synchrotron activation procedure. The optical properties have been studied by photoluminescence (PL), UV–vis absorption, small-angle x-ray scattering (SAXS), electron paramagnetic resonance (EPR) spectroscopy, and time-dependent density functional theory (TD-DFT) calculations.

2. Experimental details

2.1. Glass production

Glasses composed of 70SiO2·20Na2O·10CaO (values in mol%) were doped with 0.005 mol% Au or 0.037 mol% Ag. Reagent grade and high purity grade SiO2 (99.99%), Na2CO3 (puriss. p.a.), CaCO3 (puriss. p.a.), CaO (puriss. p.a.), AuCl3·aq (puriss. p.a.) and AgNO3 (≥ 99.9% p.a.) 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 cooled down to room temperature. Samples of size 10 × 10 × 1 mm3 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).

2.2. Optical spectroscopy

UV–vis absorption spectra were recorded with the HR2000 (Ocean Optics) fiber spectrometer and the Stellar Net halogen/deuterium light source. For all spectra shown an analogically treated but non-activated glass sample was defined as reference and subtracted from the UV–vis spectra of activated glasses.

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 Nd:YAG laser MNL 103-PD (Laserotechnik Berlin; wavelength: 337.1 nm, pulse energy: 80 μJ, repetition rate: 20 Hz, pulse duration: 3.5 ns).

Excitation spectra and lifetime measurements in the microsecond range 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.

Nanosecond lifetimes were measured with time-correlated single-photon counting. Excitation was performed with the frequency-doubled fundamental of a femtosecond Ti:sapphire laser pumped by a diode solid-state laser. Additional information about the instrumental setup and data evaluation can be found in [24].

Photoluminescence quantum yields were determined at Friedrich-Schiller-Universität Jena with an adapted method as described in [25]. First, PL spectra were recorded with a fluorimeter by excitation at 355 nm of a 2 mm thick glass sample placed in an integrating sphere (perpendicular angle configuration, in the spectrometer plane). Second, scattered light at 355 nm with and without sample in the integrating sphere was detected. The quantum yield was calculated by dividing the integrated PL intensity between 365 and 700 nm by the difference of scattered quanta without and with the sample. All spectra were corrected for detector sensitivity and transmission of the integrating sphere.

2.3. Small-angle x-ray scattering

Small-angle x-ray scattering (SAXS) investigations were performed at BESSY at the 7T-WLS-HMI beam line. Scattering curves were measured at the energy of 11496 eV. SAXS data were interpreted by fitting the scattering curves with scattering of a model system of spherical particles with log-normal size distribution according to the equation

\[ I(q) = N \int \Delta \rho^2 f(R, R_0, \sigma) V^2(R) \Phi^2(q, R) dR + A + B q^2, \]

with \( q \) being the particle number density, \( \Delta \rho \) being the electron density difference between the particles and the glass matrix, \( V \) being the volume of a sphere with radius \( R \), \( \Phi(q, R) \) being the scattering form factor of a sphere, and \( q \) being the magnitude of the scattering vector [26]. The size distribution function is

\[ f(R, R_0, \sigma) = \frac{\exp \left\{ -[\ln(R) - \ln(R_0)]^2/(2\sigma^2) \right\}}{\sigma \sqrt{2\pi}}, \]

which was normalized to unity. The particle number density, \( N \), the particle radius at the distribution maximum, \( R_0 \), and the distribution variance, \( \sigma \), were fit parameters. The scattering contrast of pure Au particles and glass was used. The scattering of the glass matrix was approximated with the \( A + B q^2 \) term with, \( A \) and \( B \) as fit parameters [27].
Figure 1. UV–vis absorption spectrum (blue dashed curve) of a soda-lime silicate glass doped with 50 ppm gold after synchrotron irradiation. (a) PLE ($\lambda_{\text{em}} = 750$ nm) and (b) PL spectra ($\lambda_{\text{exc}} = 337$ nm) of irradiated gold-doped glasses (black curves) and gold dimers isolated in solid argon (red curves; reprinted with permission from [17]. Copyright 1993, American Institute of Physics). The peak marked with • is due to second-order diffraction of the excitation light. The peak at * is removed for clarity, because it was attributed to gold monomers. (c) Confocal fluorescence microscope image ($\lambda_{\text{exc}} = 366$ nm; image size: $1 \times 1$ mm$^2$) of an activated gold glass (red part (activated glass region) = luminescence light; blue part (non-activated) = scattered excitation light).

2.4. Electron paramagnetic resonance

EPR spectra were recorded at the X-band spectrometer ERS 300 (ZWG/Magnettech Berlin/Adlershof, Germany) equipped with a fused quartz Dewar for measurements at liquid nitrogen temperature. The g-factors were calculated with respect to a Cr$^{3+}$/MgO reference ($g = 1.9796$).

2.5. TD-DFT calculations

To understand the optical spectra, cluster model DFT calculations were performed. A Si$_5$O$_9$H$_7$ cluster was constructed to model the SiO$_2$ surface; it has the cage structure of edingtonite, and is composed by three 4-member SiO rings. The cluster’s geometrical structure, with and without adsorbates, was fully optimized. The hybrid Becke3 functional for exchange [28] and the Lee–Yang–Parr functional for correlation [29] was employed (B3LYP) as implemented in the Gaussian03 code [30]. We used the 6-311+G* basis set on O, Si, and Na and the 6-31G basis on H; the Au atoms were treated with a 19-electron effective core potential (ECP) [31] and a Lanl2dz basis set. The optical transitions were determined using the time-dependent DFT approach, TD-DFT, as implemented in Gaussian03.

3. Results and discussion

3.1. Atomic gold and silver species after synchrotron activation

As mentioned in the introductory remarks, the synchrotron activation process induces point defects such as E’ centers (holes trapped in oxygen vacancies, $\equiv$Si$^-$), nonbridging oxygen hole centers (NBOHCs, $\equiv$Si–O–) and trapped electrons (TEs) in soda-lime silicate glasses (the notation ‘≡’ represents three bonds with oxygen atoms in the glassy matrix). The point defects can be identified by a brownish coloring of the irradiated glass. The absorption peaks at 315, 420, and 605 nm in the UV–vis spectrum of an activated gold-containing sample (figure 1) are assigned to trapped electrons and the NBOHC hole centers HC1 and HC2, respectively [32–34]. According to the literature, E’ centers absorb at wavelengths $< 300$ nm and could not be detected with our spectroscopical setup [33, 34]. Moreover, paramagnetic centers that were generated by synchrotron irradiation have been studied with EPR. In the EPR spectrum of an activated gold-containing sample (figure 1) are assigned to trapped electrons and the NBOHHC hole centers HC1 and HC2, respectively [32–34]. According to the literature, E’ centers absorb at wavelengths $< 300$ nm and could not be detected with our spectroscopical setup [33, 34].

Furthermore, a signal at $g = 1.950$ can be identified, and it is associated with trapped electrons [34]. These signals coincide with the defect absorption after the activation process (figure 1), and can also be found in the EPR spectra of irradiated silver-doped and undoped soda-lime silicate glasses.
Beside these observations, in activated samples doped with 0.037 mol% silver, signals of Ag\(^0\) atoms for both isotopes \(^{107}\text{Ag}\) and \(^{109}\text{Ag}\) with typically large hyperfine splittings can be identified (figure 2(b)). The hyperfine splitting of both isotopes is due to the electron–nucleus coupling of silver \((I = 1/2)\) \([34, 36, 37]\). After annealing for 10 min at 300 °C, the signals attributed to defect centers such as NBOHCs and TEs decrease. The Ag\(^0\) doublets vanish nearly completely (figure 2(b), inset). Instead, an intense doublet with an anisotropic g-factor \((g_\parallel = 2.27, g_\perp = 2.04)\), characteristic for Ag\(^{2+}\) \([37–39]\), can be identified in the EPR spectrum. This signal can already be observed before annealing, but overlaps with the NBOHC and Ag\(^0\) signals. After further annealing at 300 °C, the Ag\(^{2+}\) bands decrease.

We interpret this in terms of an oxidation and a reduction of Ag\(^+\) during the irradiation process caused by trapping hole centers and electrons, respectively, via reactions such as

\[
\text{Ag}^+ + h^+ (\text{e.g. } \equiv\text{Si}–\text{O}–) \rightarrow \text{Ag}^{2+} (\equiv\text{Si}–\text{O}–^-) \tag{1} \\
\text{Ag}^{2+} + e^- \rightarrow \text{Ag}^0. \tag{2}
\]

In activated gold-doped glasses no additional EPR signals characteristic for paramagnetic gold species (such as Au\(^0\)) were found. Nevertheless, a reduction of gold during irradiation is very likely, too. In a recent study we could show with Au L\(_{III}\)-edge XANES spectroscopy that gold has mainly the oxidation state 0 after synchrotron activation \([23]\). Since Wagner \textit{et al} have found with Mössbauer spectroscopy that gold is in the oxidation state +I in melt-quenched glasses, independent of the precursors used (Au\(^+\) or Au\(^{3+}\) salts) \([40]\), we propose a reduction of Au\(^+\) to neutral gold species by electron trapping during synchrotron irradiation, similar to the mechanism observed for silver.

While undoped samples show no photoluminescence with excitation at 337 nm, a red luminescence peaking at 753 nm is observed for glasses containing 50 ppm gold, which can be seen with the naked eye (figure 1). To the best of our knowledge, this light emission has never been detected before in glasses. In the PL excitation (PLE) spectrum three maxima at 330, 360, and 375 nm can be recognized. The latter peak is due to second-order diffraction at the grating monochromator caused by the detection of the emission at 750 nm. The luminescence time dependence shows a monoexponential behavior with a lifetime of 30 μs. To identify the origin of the red PL, we carefully analyzed the optical properties of plausible luminescence centers such as point defects \([33, 41]\), gold atoms bound to point defects \([42, 43]\), gold clusters, dimers and atoms \([16, 17, 44, 7, 45, 46]\). Gold dimers isolated in solid argon by Harbich \textit{et al} \([17, 44]\) exhibit a PL at 757 nm. Remarkably, a nearly perfect overlap between the PL spectrum of the activated gold glass and the gold dimers was found with a PL shift of only 4 nm (figure 1). Additionally, a very good agreement between the excitation bands was obtained. The PLE peak at 360 nm in glasses matches excellently with the maximum at 360 nm of Au\(_2\) in solid Ar. The band at 330 nm with highest intensity is comparable to the 305 nm peak of the gold dimer. The wavelength shift of 25 nm can be explained by the strong absorption of point defects (especially E’ centers, TEs, and NBOHCs) and the glass matrix at \(\lambda \leq 300\) nm, which most probably significantly decreases the PL excitation in this range, leading to a red shift of the PLE maximum. These results are also in agreement with early investigations of gold dimers in argon by Klotzbücher and Ozin, who found absorptions at 365 and 317 nm \([16]\), and are comparable to the optical transition at 389 nm of Au\(_2\) in the gas phase \([7]\). The generation of diamagnetic dimers would also support the absence of gold-specific signals in the EPR spectra. Conclusively, we attribute the 753 nm emission to gold dimers formed during synchrotron irradiation, most probably by the combination of x-ray generated electrons and gold cations and a subsequent aggregation at room temperature. The relatively long lifetime of 30 μs and the large Stokes shift of approximately 1.8 eV point to a phosphorescence process. Wang \textit{et al} calculated the optical transitions of Au\(_2\) with TD-DFT \([46]\). As a result, they found a vertical excitation energy of 1.875 eV (661 nm) for the singlet–triplet transition \(X^1\Sigma^+_g \rightarrow a^3\Sigma^+_u^+\), which is in good agreement with our experimental results. Furthermore, Bissha and Morse investigated the optical properties of gold dimers in the gas phase with resonant two-photon ionization \([47]\). They determined for the 0–0 transition \(X^1\Sigma^+_g \rightarrow a^3\Sigma^+_u^+\) an excitation energy of 16630 cm\(^{-1}\) (601 nm). Interestingly, for the excited state \(a^3\Sigma^+_u^+\) a lifetime of 40 μs has been measured. This value is in very good agreement with the lifetime of 30 μs of the gold-doped glass luminescence, and thus points as well to the involvement of a triplet state.

### 3.2. Photoluminescence, UV–vis absorption and SAXS studies of the cluster growth process

At the beginning of this article we pointed out that the annealing at 550 °C of a synchrotron-activated gold-doped glass causes the formation of gold nanoparticles. We then were interested in the question, whether we are able to identify the very early stages of the cluster growth process. That is why we investigated the optical properties of the activated glass samples during annealing at 550 °C. As a result, gold-containing samples annealed for a very short time (typically 1–20 min) emit exceedingly bright green light with two maxima at 525 and 555 nm in the PL spectrum, which is not observed in as-treated pure soda-lime silicate glasses (figure 3). In the PLE spectrum three peaks at 240, 300 and 340 nm can be identified. These luminescent samples are transparent in the visible range and show only a slight absorption at wavelengths smaller than 350 nm. A PL quantum yield of 3% was determined and a radiative lifetime of 30 μs was measured.

Interestingly, an increasing annealing time is accompanied by a decreasing PL. After 30 min at 550 °C the luminescence has nearly completely vanished (figures 4(a) and (b)). Meanwhile, the absorbance increases, and after approximately 30 min the surface plasmon resonance of gold at 540 nm can be observed, which is a first indication for the proceeding cluster growth process and the appearance of nanoparticles. For a detailed analysis of the annealing time dependence of the particle size distribution, small-angle x-ray scattering (SAXS) measurements were performed. As can be seen in figures 4(c)–(e), the gold cluster radius increases with annealing time from
different. The luminescence spectrum of an activated silver-doped glass after annealing at the higher temperature of 500°C very strongly supports our first assumption that the PL of the silver sample and the green gold glass emission are similar. While the overall luminescence intensity decreases, the intensity at $\lambda > 600$ nm vanishes, thus leading to a perfect overlap of the long-wavelength tail of the spectra of both gold- and silver-containing samples (figure 5(c)). The matching of the PL curves strongly points to the same origin of this luminescence. The PLE spectrum of the silver sample annealed at 300°C exhibits peaks at 305, 350 and 400 nm (figure 5(b)), whereas the excitation at 305 nm leads to an increased emission at approximately 600–800 nm, and the excitation at 400 nm amplifies the 450 nm PL. The luminescence time dependence analysis (biexponential fit of the deconvoluted decay curves) supports the division of the PL spectrum into three parts. (1) The range between 400 and 500 nm ($\lambda_{\text{exc}} = 355$ nm) with lifetimes of 2.79 ns (87.5%) and 0.46 ns. (2) The part between 500 and 600 nm ($\lambda_{\text{exc}} = 337$ nm) with lifetimes of 166 $\mu$s (53.3%) and 56 $\mu$s (similar to the green PL of the gold sample with $\tau = 30$ $\mu$s). (3) The long-wavelength tail at $\lambda > 600$ nm ($\lambda_{\text{exc}} = 305$ nm) with lifetimes of 451 $\mu$s (80.5%) and 114 $\mu$s.

The luminescent silver samples only absorb at wavelengths shorter than 400 nm (figure 5(a)), and neither the surface plasmon resonance absorption nor an SAXS signal of silver nanoparticles can be observed. This clearly indicates that silver clusters in the highly luminescent samples, if they exist, are in the subnanometer size range, too.

As already done for gold-doped samples, the PL bands were compared with PL data of silver clusters embedded in solid Ar matrices. The 400–450 nm band could be related to the 458 nm emission of $\text{Ag}_2$ clusters ($\lambda_{\text{exc}} = 405$ nm) and/or to the emission at 479 nm of silver dimers ($\lambda_{\text{exc}} = 384$ nm). Although the silver monomer has a very broad emission peaking at 450 nm [17, 49], we would exclude $\text{Ag}_0$ (as well as $\text{Ag}^{2+}$) as a luminescence center. Otherwise, this would contradict the observation that the $\text{Ag}^{2+}$ EPR signals decrease during annealing at 300°C (figure 2), whereas the PL intensity increases. Moreover, these findings indicate the agglomeration of silver atoms forming small clusters during annealing at 300°C. The emission at 600–800 nm may be assigned to $\text{Ag}_3$, which emits at 608 nm in an argon matrix after excitation at 387 nm [17, 49]. Several authors attribute luminescence bands of silver-containing glasses to cationic silver clusters such as $\text{Ag}_2^+$ or $\text{Ag}_3^{2+}$ [50–52], but we could not detect paramagnetic species such as $\text{Ag}_2^+$ with EPR spectroscopy.

### 3.3. Interaction of gold and silver with the glassy matrix: the very early stages of cluster growth

We shall now explain the origin of the PL observed for both silver- and gold-containing glasses. This coincidence could be explained best by considering an intrinsic glass emission or impurities. To exclude the influence of impurities, glasses were made of highest purity grade chemicals. As a result, the luminescence behavior did not change. Additionally, x-ray fluorescence analysis was performed, but no luminescent impurities such as Mn, Zr, Cu, Fe, etc with concentrations...
in the ppm range could be detected. Consequently, these results indicate an alternative origin of the green PL. Because of the coincidence of cluster growth and decreasing PL during annealing at 550 °C (figure 4) and since the excitation spectrum and the lifetime of the green emission are very similar to those of the red emission (τ = 30 μs for both), a contribution of gold particles (especially Au$_2$) to the luminescence seems plausible. An important remarkable experimental hint for this thesis is given by the PL bleaching behavior of gold-doped glasses during excitation at 337 nm with a pulsed N$_2$-laser. While the green PL rapidly decreases during excitation, a red emission peaking at approximately 750 nm, previously attributed to gold dimers, appears and increases (figure 6). The intersection (isosbestic point) at 723 nm is an unambiguous indication for a photoreaction with Au$_2$ as product and the green luminescent species as precursor.

For the interpretation of the green luminescence observed in both gold- and silver-containing glasses, the contribution of a glass-intrinsic luminescence center is most probable. Interestingly, undoped soda-lime silicate glasses show a weak but broad PL between 400 and 700 nm with excitation at 240 nm (figure 7, inset). In the literature this PL is assigned to L-centers, described by a sodium cation bound to a silanolate center, $\equiv$Si–O–Na [33, 53]. One possible explanation for the observed green emission and the intimate relation to the red Au$_2$ luminescence could be that the gold dimer acts as an absorption center and transfers energy to the L-center, which gives rise to the observed green light emission. In a classical singlet–singlet Förster resonance energy transfer (FRET) process the luminescent species can be excited resonantly, i.e. at the absorption wavelength of
The L-center. However, neither in the PLE, nor in the UV–vis spectrum of doped or undoped glasses was a significant absorption between the excitation wavelength of 337 nm and the emission wavelength of 555 nm found. The gold dimers as possible energy donors do not luminesce in this range either, a second prerequisite for FRET. However, it could be shown experimentally and theoretically that gold atoms and dimers can stably bind to silica dangling bonds (E’ centers, \( \equiv Si \cdot \)), NBO hole centers (\( \equiv Si-O \cdot \)), and silanolates (\( \equiv Si-O^- \)) [42, 43]. In the latter case the species could be formed by simply replacing the sodium ion in L-centers by gold atoms or dimers.

For a profound understanding of the optical spectra, cluster model DFT calculations were performed. A \( Si_5O_9H_7 \) cluster was constructed to model the defect sites of soda–lime silicate glasses such as the species mentioned above; it has the cage structure of edingtonite, and is composed by three 4-member SiO rings. The cluster’s geometrical structure, with and without adsorbates, was fully optimized. The optical transitions were determined using the time-dependent DFT approach, TD-DFT. First, the L-center was simulated by a sodium ion bound to silanolate, \( \equiv Si-O^-Na^+ \). TD-DFT calculation of the optical transitions gave values at 202 nm (oscillator strength 0.0073), 206 nm (0.0064), 268 nm (0.0184) and 281 nm (0.0066), which are very close to the predicted lowest-lying transition at 380 nm has pure gold dimer \( \equiv Si-O^-Na^+ \) complex a (red bars) and of the \( \equiv Si-O^-Au_2^+ \) complex b (black bars). Color coding of complexes a and b: blue spheres, H; red spheres, Si; yellow spheres, O; purple sphere, Na; golden spheres, Au. Distances are in angstroms. For comparison, the PLE spectrum of gold dimers in solid argon is shown (blue dashed curve; reprinted with permission from [17]). Copyright 1993, American Institute of Physics. The peak at * is removed for clarity because it was attributed to gold atoms). Inset: PL spectrum \( (\lambda_{exc} = 240 \text{ nm}) \) of a non-activated undoped soda-lime silicate glass. The peak marked with • is due to second-order diffraction of the excitation light.

Figure 6. PL spectra of an activated gold-doped glass after 5 min at 550°C and after 0 s (a), 20 s (b), 80 s (c) and 180 s (d) of N2-laser excitation at 337 nm (pulse energy 80 \( \mu J \), repetition rate 20 Hz, pulse width 3.5 ns). (e) PL spectrum of the same glass before annealing at 550°C \( (\lambda_{exc} = 337 \text{ nm}) \).

Figure 7. PLE spectra of a non-activated undoped soda-lime silicate glass (red curve, \( \lambda_{exc} = 580 \text{ nm} \)), of an activated gold-doped glass after 5 min at 550°C (black curve, \( \lambda_{exc} = 525 \text{ nm} \)) and calculated optical transitions of the \( \equiv Si-O^-Na^+ \) complex a (red bars) and of the \( \equiv Si-O^-Au_2^+ \) complex b (black bars). Color coding of complexes a and b: blue spheres, H; red spheres, Si; yellow spheres, O; purple sphere, Na; golden spheres, Au. Distances are in angstroms. For comparison, the PLE spectrum of gold dimers in solid argon is shown (blue dashed curve; reprinted with permission from [17]). Copyright 1993, American Institute of Physics. The peak at * is removed for clarity because it was attributed to gold atoms). Inset: PL spectrum \( (\lambda_{exc} = 240 \text{ nm}) \) of a non-activated undoped soda-lime silicate glass. The peak marked with • is due to second-order diffraction of the excitation light.

one order of magnitude when compared to \( \equiv Si-O^-Na^+ \), a result corroborated by the dramatic intensity difference between the bright green luminescence only observed in gold-containing glasses and the weak L-center emission of undoped samples. The calculated transitions at 320 and 380 nm match very well with the experimental PLE maxima at 300 and 340 nm (figure 7). It is remarkable that the predicted lowest-lying transition at 380 nm has pure gold dimer character, \( \sigma (6s-6s) \rightarrow \sigma^* (6s-6s) \), which would perfectly explain the similarities between the PLE spectra of the green (attributed to \( \equiv Si-O^-Au_2^+ \)) and red luminescence (\( Au_2 \)). Another supporting fact for this interpretation is given by the luminescence behavior on changing the glass composition. Therefore, the \( Na_2O \) concentration was decreased from 20 to 15 mol%. As a result, the luminescence intensity dropped to only one third of the former value. \( Na_2O \) is a network modifier, i.e. it breaks silicon–oxygen bonds and forms silanolate groups, \( \equiv Si-O^\cdot \). Consequently, with decreasing \( Na_2O \) content the concentration of the luminescent \( \equiv Si-O^-Au_2^+ \) species should also decrease, which supports the experimental
results. With this knowledge the appearance of the 753 nm PL during N\textsubscript{2}-laser excitation (figure 6) can be interpreted in terms of a fragmentation of the [≡Si–O–Au\textsubscript{2}]\textsuperscript{−} complex into Au\textsubscript{2}, emitting at 753 nm, and [≡Si–O\textsuperscript{−}].

While the excitation transitions obviously have gold dimer character, the radiative transitions causing the luminescence may have NO\textsuperscript{−} (or L-center) character, because of the PL spectra similarities between gold and silver samples (figure 5(c)). The long lifetimes in the microsecond range, large Stokes shifts between and different curve shapes of PLE and PL spectra strongly support the contribution of a radiative transition different from the excitation, i.e. most probably a triplet–singlet decay. This is corroborated by the L-center emission, where slow decay components due to singlet–triplet transitions have been observed [33, 53]. Due to relativistic effects and the strong spin–orbit coupling [45], gold dimers bound to silanolate could sensibilize an efficient intersystem crossing between singlet and triplet states. Alternatively, triplet–triplet energy transfer between gold dimer and glass matrix triplet states could explain the observed strong green luminescence. As for silver-doped samples, atomic silver particles could sensibilize the glass luminescence in a similar way.

4. Conclusions

In conclusion, we have been able to show that the novel synchrotron activation procedure enables the formation and investigation of atomic noble metal particles in soda-lime silicate glasses. After synchrotron x-ray activation, Au-containing glasses exhibit a red luminescence under UV light excitation. The red 753 nm light emission is assigned to gold dimers, because of the nearly perfect match with PL and PLE spectra of Au\textsubscript{2} isolated in solid argon. After annealing of the sample for 5 min at 550 °C, a bright green luminescence with maxima at 525 nm and 555 nm can be detected. The bleaching of the green PL and the simultaneous reappearance of the Au\textsubscript{2} emission during intense 337 nm excitation of gold-doped glasses indicates a strong interrelationship between both luminescence centers. TD-DFT calculations indicate that the green light emission can be assigned to gold dimers bound to silanolate centers.

In the case of silver-doped glasses, Ag\textsuperscript{0} atoms can be identified with EPR spectroscopy after synchrotron irradiation. Additionally, these glasses exhibit a white light emission under 337 nm excitation. After annealing at 300 °C the Ag\textsubscript{1} concentration decreases, but the white PL increases. The corresponding luminescence spectrum can be decomposed into three sub-bands. The PL bands at 400–450 and 600–800 nm are attributed to small silver clusters such as Ag\textsubscript{2}, Ag\textsubscript{3}, and Ag\textsubscript{4}, which are obviously generated by the agglomeration of silver atoms during annealing. Remarkably, a nearly perfect overlap between the band peaking at 525 and 560 nm and the green gold luminescence is obtained, which points to a similar luminescent silanolate species as in the case of gold.

The generation and stabilization of small noble metal particles at room temperature is not only important for basic research, but can also be promising for the development of devices such as (single-) photon emitters in miniaturized optical circuits. Synchrotron x-rays for crack-free nanostructuring of glasses have several advantages compared to UV–visible radiation such as short x-ray wavelengths, high brilliance and intensity, coherence, low beam divergence and the exclusion of a thermal influence due to infrared radiation.

The investigated glass samples have been stored for more than one year at room temperature without deterioration of the luminescence properties. Advanced experiments indicated, furthermore, that the red, green and white emissions can be activated by intense titanium:sapphire femtosecond laser irradiation and subsequent annealing of noble metal-doped glasses, too. The different activation methods and the control of the emission colors point to a great potential of silver- and gold-doped glasses for the realization of various devices such as glass (fiber) lasers, optical memory or novel (white) light sources.

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Note added in proof. Recently, we became aware of a comprehensive work by Expius de Lamaestra et al [54], which showed that the activation of silver-doped soda-lime silicate glasses with gamma or MeV ion radiation induces a similar nucleation and growth process of silver clusters as in the case of synchrotron activation.

References

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