Ag NP enhanced photoluminescence study of Sm\(^{3+}\) ions in sol-gel silica glasses

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Abstract. Sm\(^{3+}\) ions singly doped and Ag NPs co-doped with Sm\(^{3+}\) ions for fixed concentrations of both Ag and Sm\(^{3+}\) ions in sol-gel silica glasses were fabricated and their spectroscopic behaviour studied. Phenomenological Judd-Ofelt (JO) theory has been utilized for the spectroscopic characterization of the studied samples. Significant enhancement in the Sm\(^{3+}\) ion emissions were observed with the addition of Ag NPs. The enhancement is attributed to the local surface plasmon resonance effect of the Ag NPs.

1. Introduction

Trivalent rare earth (RE) ions based materials have been studied extensively for last few decades due to their diverse applications in the field of lasers, sensors, telecommunications, fluorescent display devices etc [1,2]. The RE ions generally possess low absorption cross-section because of the parity forbidden f-f transitions which leads to low emission efficiency. Therefore, efforts have been going on for the enhancement in the absorption potential from the RE ions. Among them, incorporation of metal NPs in RE doped matrices is considered as one of the most versatile technique. The metal NPs possess many new features in their electronic and optical properties owing to a unique phenomenon known as surface plasmon resonance (SPR). SPR is a coherent excitation of all the free electrons within the conduction band of the metal NP that results in oscillation of the plasmon. When the wavelength of the incident radiation is larger than the size of the metal nanocrystal, an SPR is generated. Among the metal NPs, Ag NPs show highest efficiency SPR in the UV-Vis region of the electromagnetic spectrum [3]. The SPR absorption band of spherical Ag NPs is 420nm in silica glass [4].

Among the RE ions, samarium (Sm) is one of the important RE which shows sharp emissions in the visible spectral region (550-700nm). The larger energy gap between \(^4G_{5/2}\) excited level and its next sublevels permits the incorporation of Sm\(^{3+}\) ions in different glass hosts with larger phonon energy [5]. Glasses containing Sm\(^{3+}\) ions have gained much attention due to their potential applications in various optical devices such as for high density optical storage, visible solid state laser, colour display, temperature sensing devices etc. Owing to its optical efficiency, the spectroscopic properties of Sm\(^{3+}\) ions have been studied in different host matrices such as tellurite, phosphate, sodium borate, fluorophosphate, oxyfluoride, silicate [6] etc. Among different hosts, silica is considered to be an
excellent host for Sm$^{3+}$ ions as it possesses many advantages such as optical transparency, chemical durability, thermal stability etc.

The present work reports the effect of the incorporation of Ag NPs with Sm$^{3+}$ ions in sol-gel silica glasses. The dependence of the spectroscopic behavior of Sm$^{3+}$ ions with varying Ag concentration will be reported later in another work.

2. Experimental
Singly doped Sm$^{3+}$ and Ag co-doped Sm$^{3+}$ in silica matrix were fabricated by the sol-gel route. The starting precursors were C$_8$H$_{20}$O$_4$Si (Merck 98%) as organo metallic precursor, CH$_3$OH (Merck 99%), distilled H$_2$O as solvent, HNO$_3$ (Merck 70%) as catalyst and C$_2$H$_3$NO (DMF-Acros Organics, 99%) as reducing agent as well as drying control chemical additive. Sm(NO$_3$)$_3$.6H$_2$O (Sigma Aldrich, 99.999%) was used as source of Sm and AgNO$_3$ (Acros Organics, 99.85%) as source for Ag. (C$_6$H$_9$NO)$_x$ (PVP, k-30) (SRL, research grade) was used as capping and stabilizing agent for Ag. At first, stock solutions of AgNO$_3$ (sol 1) and PVP (sol 2) separately were prepared by dissolving in DMF and distilled H$_2$O respectively. The solutions were then mixed and kept for four hours for stabilization (sol 3). Other precursors CH$_3$OH, distilled H$_2$O and HNO$_3$ were prepared and mixed with 2.24wt% of Sm (NO$_3$)$_3$.6H$_2$O and magnetically stirred for 30 minutes. To this solution, C$_8$H$_{20}$O$_4$Si was added and further stirred for 60 minutes. The volumetric ratio of C$_8$H$_{20}$O$_4$Si, CH$_3$OH, distilled H$_2$O and HNO$_3$ used in the synthesis are 4: 5: 10: 1. The stirred solution was then mixed with the sol 3 and magnetically stirred till the gelation started. The gel was then poured into a plastic container and kept it for 21 days to dry and to form the xerogel. The resultant xerogels were annealed at 100 °C for an hour to obtain the resultant glass samples. The UV-Vis absorption spectra were recorded by using Shimadzu UV-2600 UV-Vis spectrophotometer, with halogen and deuterium lamp (50W) as excitation sources. Photoluminescence (PL) spectra were recorded by Horiba Jobin Yvon Fluromax-4P spectroflurometer with 150W CW xenon lamp as excitation source. All the measurements were done at room temperature.

3. Results and Discussions

3.1. Absorption and JO analysis

![Absorption spectra for SiO$_2$ glasses at room temperature. Inset shows the SPR band of Ag NPs peaked at ~ 470nm & 570nm.](image)
Figure 1 shows the UV-Vis absorption spectra for as prepared glass samples at room temperature. All the observed absorption bands were assigned and shown in table 1 [2]. The spectra show an increase in absorption intensity of Sm$^{3+}$ ions in presence of Ag NPs clearly indicating the influence of the NPs on the absorption of Sm$^{3+}$ ions, owing to the SPR by Ag NPs. The SPR band observed for Ag NPs is shown in the inset of the figure 2 [7]. The absorption spectra were analyzed with the help of JO theory [8]. The experimental oscillator strengths for the observed electric dipole transitions are evaluated from the relation,

$$f_{\text{exp}} = 4.319 \times 10^{-6} \int \epsilon(\nu) \, d\nu \quad (1)$$

where, $\epsilon(\nu)$ is molar extinction co-efficient at wave number $\nu$ (cm$^{-1}$) obtained from Beer-Lambert law.

The experimentally measured oscillator strengths are co-related with its corresponding theoretical expression for oscillator strengths of the electric dipole transitions between the initial and final states to obtain the JO parameters $T_t$ ($t=2,4$ and $6$) with the help of the following expression,

$$f_{\text{cal}} = \sum_{t=2,4,6} T_t \nu \left( \left( \Psi J \Psi U(t) \Psi J \right) \right)^2 \quad (2)$$

where, $T_t$ represents a tensor operator of rank $t$ calculated in mean field approximation. The values for $U(t)$ were considered from Carnell et. al. [9] for these calculations. Moreover, the effect of refractive index $n$ of the silica host is incorporated in the JO parameters through the expression,

$$\Omega_t = \frac{3h}{8\pi^2 mc} \frac{9n}{(n^2+2)^2} (2J+1) T_t \quad (3)$$

Here, $h$ is Planck’s constant, $c$ is velocity of light, $(2J+1)$ is the multiplicity of the lower state and $m$ is the mass of electron.

Table 1. Judd Ofelt parameters for Ag-Sm$^{3+}$ doped SiO$_2$ glass and comparison with other glasses.

| Transitions       | Wavelength (nm) | $f_{\text{cal}} \times 10^6$ | $f_{\text{exp}} \times 10^6$ |
|-------------------|-----------------|-----------------------------|-----------------------------|
| $^6H_{5/2} \rightarrow ^4D_{3/2}$ | 362             | 0.835                       | 0.835                       |
| $^6P_{5/2}$       | 375             | 6.129                       | 5.913                       |
| $^6P_{3/2}$       | 403             | 10.621                      | 10.722                      |
| $^6P_{3/2}$       | 418             | 1.599                       | 0.997                       |
| $^4I_{17/2}$      | 464             | 1.641                       | 1.102                       |
| $^4I_{13/2}$      | 479             | 1.926                       | 3.014                       |

The measured ($f_{\text{exp}}$) and calculated ($f_{\text{cal}}$) oscillator strengths, JO parameters ($\Omega_2$, $\Omega_4$, $\Omega_6$), spectroscopic quality factor $\Omega_4/\Omega_6$ for the studies glasses are calculated and are shown in table 1. The values of $f_{\text{exp}}$
and $f_{cal}$ are in good agreement with rms deviation of $0.5616 \times 10^{-6}$. The larger differences observed between the calculated and the experimental values of oscillator strengths in the transitions $^6P_{5/2}$ and $^4I_{13/2}$ are because of 4f-5d mixing which may contribute to intensities with odd values of $t$ in $[U(t)]$ matrix elements which are neglected in the J.O. model [11]. The values of the JO parameters in the zinc bismuth borate and tellufluoroborate glasses are also shown in table 1 for comparison. Comparatively higher value of $\Omega_2$ parameter in the studied glasses indicates higher asymmetry and stronger covalent environment around Sm$^{3+}$ ions in Ag-Sm$^{3+}$ co doped SiO$_2$ glass. This result is significant since the emission probabilities for RE ions are expected to increase with increase in the covalency [12]. A modification in the spectroscopic quality factor $\Omega_2/\Omega_3$ is also observed with the addition of Ag NPs.

3.2. Photoluminescence analysis

Figure 2 shows the room temperature PL spectra for the studied glasses under 401nm excitation wavelength. Three PL bands of Sm$^{3+}$ ions centered at ~ 560nm, 593nm and 640nm originating from the transitions $^4G_{5/2} \rightarrow ^6H_{5/2}$, $^4G_{5/2} \rightarrow ^6H_{9/2}$ and $^4G_{5/2} \rightarrow ^6H_{11/2}$ were observed [2]. An enhancement in the PL peak intensity by 3.2 times and yield by 5.57 times is observed with the introduction of Ag NPs. This enhancement in PL intensity as well as yield is attributed to the local field enhancement induced by the SPR effect of Ag NPs. In the process, the electric field around the Sm$^{3+}$ ions, lying in the proximity of Ag NPs is enhanced which in turn increase the excitation rates of the Sm$^{3+}$ ions. Consequently, the PL intensity and yield from the Sm$^{3+}$ ions in the studied silica glass is enhanced. Moreover, energy transfer between the Ag NPs and Sm$^{3+}$ ions also plays an active role in the PL enhancement. Figure 3 shows the schematic energy level diagram for Ag-Sm$^{3+}$ co-doped SiO$_2$ glass. The 4f electrons of Sm$^{3+}$ ions at the ground $^5H_{5/2}$ state are first excited to the $^6P_{3/2}$ level under 403nm excitation. From this level, the excited ions decay non-radiatively and populate the lower excited $^4G_{5/2}$ level which further de-excites radiatively to $^4H_{5/2}$, $^4H_{9/2}$ and $^6H_{9/2}$ levels resulting in the observed PL emissions.
4. Conclusion

In the present work, the influence of Ag NPs on Sm$^{3+}$ ion emissions in SiO$_2$ glasses were studied by analyzing their absorption and PL behavior. Modifications in the glass network as well as in the PL intensities were observed with the addition of Ag NPs. An enhancement in the PL intensity by 3.2 times and yield by 5.57 times is observed in presence of Ag NPs which is explained in terms of localized SPR around the Ag NPs.

### Table 2. PL intensities and Yield (integrated intensities) for the samples.

| Peak positions (nm) | $\text{Sm}^{3+}: \text{SiO}_2$ Intensity ($\times 10^7$) | $\text{Ag-Sm}^{3+}: \text{SiO}_2$ Intensity ($\times 10^7$) |
|---------------------|-------------------------------------------------|-------------------------------------------------|
| 559                 | 0.507                                           | 1.127                                           |
| 594                 | 0.575                                           | 1.404                                           |
| 640                 | 0.510                                           | 1.649                                           |

| Integrated Intensity /Yield ($\times 10^7$) | 559 | 10.231 | 22.832 |
|--------------------------------------------|----|--------|--------|
|                                            | 594| 14.825 | 38.910 |
|                                            | 640| 11.279 | 62.903 |
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