

SILVER NANOPARTICLES ASSISTED SPECTRAL FEATURES ENHANCEMENT OF SAMARIUM-ZINC-TELLURITE GLASS

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Abstract. Achieving the enhanced optical properties of rare earth doped inorganic glasses by embedding metallic nanoparticles (NPs) is ever-demanding in photonics. Optimized doping of NPs and subsequent thorough characterizations for improved absorption and emission are the key issues for lasing glasses. We inspect the influence of silver (Ag) NPs inclusion on the optical properties of Sm³⁺ doped zinc-sodium tellurite glasses having composition 65TeO₂-25ZnO-10Na₂O-(0.15 gram)Sm₂O₃-(y)AgCl, where y = 0, 0.03, 0.075, 0.12 and 0.18 gram (in excess). Glass samples are prepared using melt quenching technique and characterized via ultraviolet visible near infrared (UV-Vis-NIR) absorption and photoluminescence (PL) spectroscopy. The presence of NPs is verified from TEM images and the amorphous nature is confirmed from XRD pattern. The UV-Vis-NIR spectra revealing six absorption peaks centered at 472, 943, 1089, 1237, 1392, and 1491 nm are assigned to ⁶H_{5/2}→⁴I_{11/2}, ⁶F_{11/2}, ⁶F_{9/2}, ⁶F_{7/2}, ⁶F_{5/2}, ⁶F_{3/2} transitions, respectively. PL spectra exhibit two emission bands located at 599 nm (⁴G_{5/2}→⁶H_{7/2}) and 643 nm (⁶H_{9/2}). The observed enhancement in PL intensity is attributed to the highly localized electric field of Ag NPs positioned in the vicinity of Sm³⁺ ion. The mechanism of enhancement is identified, analyzed, and understood. The admirable features of our results are highly beneficial for solid-state laser and optical device fabrication.

Keywords: Tellurite glass, Nanoparticles, Optical properties, Surface plasmon.

1.0 INTRODUCTION

Nowadays, researchers are highly fascinated to enhance the performance of the optical devices such as laser and fiber amplifier. Doping of optimized concentration of rare earth ions (REIs) and nanoparticles (NPs) embedment is thought as an alternative route for such augmentation. In fact, combined effects of NPs and REIs in the luminescence enhancement and subsequent improvement of nonlinear optical properties are demonstrated [1]. Current studies verify that the enhancement of optical properties is due to the NPs surface plasmon (SP) mediated electromagnetic field confinement in the vicinity of RE ions and energy transfer (ET) from NPs to RE ions [2]. Lately, it is acknowledged that the presence of metallic NPs leads to the enhancement of luminescence because of surface plasmon effects [1, 3, 4]. However, luminescence quenching at higher NPs concentration is attributed to the energy transfer due to the interaction of RE ions and OH⁻ groups with NPs [5].

In this work, a series of Sm³⁺ ions doped zinc-sodium tellurite glasses containing different concentration of Ag NPs are prepared using melt-quenching method and characterized by spectroscopic means. The Ag NPs stimulated alteration in spectral properties is scrutinized. The absorption and luminescence enhancement due to the inclusion of Ag NPs in tellurite glass is analyzed, compared, and understood.

2.0 EXPERIMENTAL

Glasses with composition 65TeO₂-25ZnO-10Na₂O-(0.15)Sm₂O₃-(y)AgCl where y = 0, 0.03, 0.075, 0.12 and 0.18 gram are prepared by melt quenching technique. Analytical grade raw materials (all 99.99% purity) with an appropriate amount of TeO₂, ZnO, Na₂O, Sm₂O₃, and AgCl are weighted using the sensitive balance (Electronic Balance Precisa 205 SCS). The total weight of each batch glass is around 15 gram. The powders are thoroughly mixed together and are subjected to milling process at around 20 minute to get the homogeneity. A

platinum crucible containing the glass constituents is placed in an electrical furnace at 900 °C and heated for 20 minutes before the melt is poured in a brass mould. During the melting process, the molten mixture is stirred up in every 10 minutes interval to ensure the complete dissolution of constituents. Subsequently, the sample is transferred to an annealing furnace and kept for 3 hours at 300 °C to remove the residual thermal strain. Finally, the samples are rapidly cooled down to room temperature. All the glass samples are cut at 2 mm of thickness with flat surface using a glass cutter and polished using the sand paper and grinder-polisher to achieve scratches free sample with better transparency.

Room temperature optical absorption measurement is performed using UV-VIS-NIR (Schimadzu UV-3101PC) double beam spectrophotometer in the range of 400–1800 nm. A Perkin Elmer LS-55 photoluminescence spectrometer with a pulsed Xenon lamp ($300 < \lambda < 1300$ nm) as excitation source is used to record the emission spectra. The emitted light is dispersed by Monk-Gillieson monochromator and detected with standard photomultiplier tube.

3.0 RESULTS AND DISCUSSION

Figure 1 shows the room temperature UV-VIS-NIR absorption spectra of Sm_2O_3 doped glasses in range of 400–1600 nm at different concentration of Ag NPs. It comprises of six absorption bands centered at 472, 943, 1089, 1237, 1392 and 1491 nm originate from the ground state of $^4\text{G}_{5/2}$ to $^4\text{I}_{11/2}$, $^6\text{F}_{11/2}$, $^6\text{F}_{9/2}$, $^6\text{F}_{7/2}$, $^6\text{F}_{5/2}$ and $^6\text{F}_{3/2}$, excited states of Sm^{3+} ions, respectively as reported [6, 7]. The absorption bands can be classified into two groups. The low energy group contains the transition up to $10,700 \text{ cm}^{-1}$ (~935 nm) and the high energy group forms the transition in the range of $17,600 - 32,000 \text{ cm}^{-1}$ (~570 - 313 nm) [8]. The absorption band assignments are accomplished based on the energy level positions. Most of the absorption bands originate from the electric dipole contribution ($\Delta J \leq 6$) whereas few transitions emerge from electric and magnetic dipole contribution ($\Delta J = 0, \pm 1$). For instance, $^6\text{H}_{5/2} \rightarrow ^4\text{G}_{5/2}$ is assigned to the magnetic dipole transition [6]. The presence of NPs in the glass maybe responsible for the disappearance of some of the absorption transition of Sm^{3+} ion at higher energy range [10]. Furthermore, the peak positions of all transition of Sm^{3+} ion remain unchanged in the presence of AgCl NPs in the host matrix.

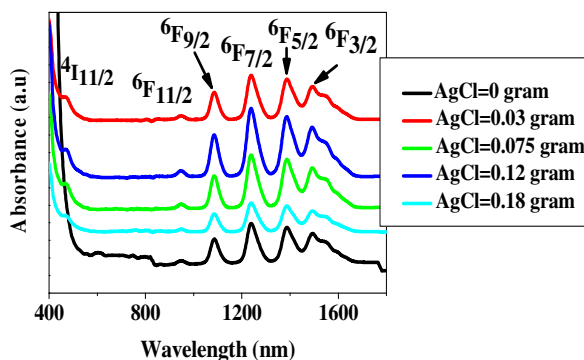


Figure 1: Room temperature absorption spectra of prepared glasses with varying concentration of AgCl.

Figure 2 displays the room temperature PL spectra for samples in the absence and presence of Ag NPs at different concentration. The spectra exhibit two significant emission bands centered at 599 (orange) and 643 nm (red) corresponding to ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ and ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$ transitions, respectively. The orange peak is observed to be stronger than the red one.

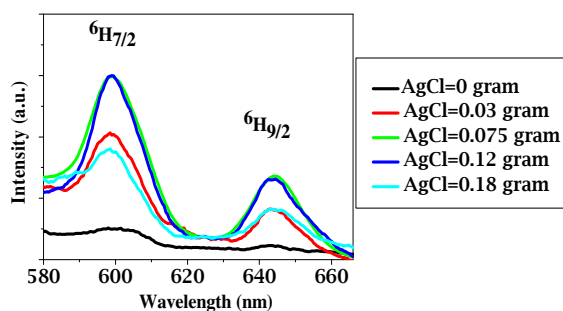


Figure 2: The emission spectra of glass with varying concentration of AgCl.

Figure 3 summarizes the PL peak intensity as a function of AgCl NPs concentration of for both the transitions. Glass with 0.075 gram AgCl exhibits the highest intensity in the entire spectra range from ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ (orange band) and ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$ (red band). The achieved highest enhancement in luminescence intensity for glass containing 0.075 gram of AgCl NPs is attributed to the surface plasmon resonance mediated effects [9]. The transition ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ containing

both electric and magnetic dipole contribution obey the selection rule $\Delta J = 0, \pm 1$ [8]. Besides the transition ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$ results from pure electric dipole interaction.

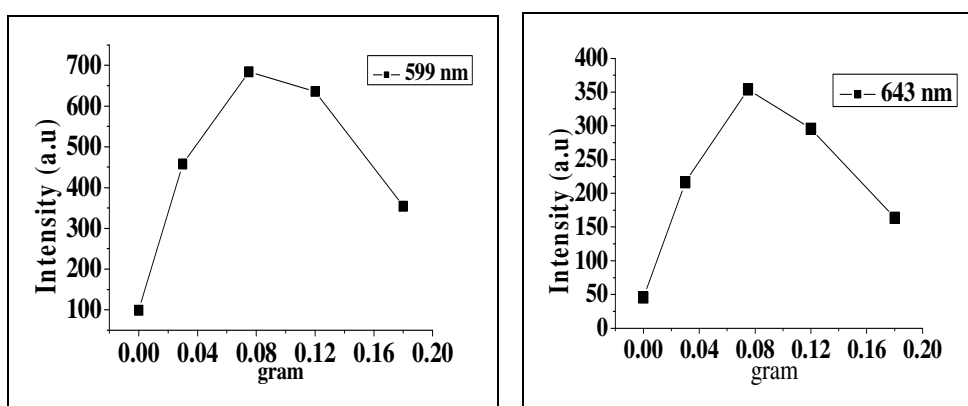


Figure 3: AgCl NPs concentration dependent PL peak intensity for red (643 nm) and orange (599 nm) transitions. (correct Mistake in x axis)

The SPR mediated intensified electromagnetic field around Sm^{3+} ions results an enhancement in Sm^{3+} ions luminescence. The giant and highly localized electric field around the Ag NPs is ascribed to increase greatly the transition yield of Sm^{3+} ions that positioned in the close proximity of Ag NPs. However, the sudden decrease in the luminescence intensity at high concentration of AgCl (0.12 gram and beyond) is due to the energy transfer from Sm^{3+} ions to Ag NPs surface.

The mechanisms involved in the spectroscopic modification of Ag NPs embedded zinc-sodium tellurite glasses are interpreted using the partial energy level diagram of Sm^{3+} ion as illustrated in Figure 4. When the Sm^{3+} ions are excited to the energy levels above ${}^4G_{5/2}$, there is a fast non-radiative relaxation to this level and the emission takes place from ${}^4G_{5/2}$ energy level to its lower levels. The closely spaced higher energy levels cause fast non-radiative (NR) decay from ${}^6P_{3/2}$ excited state to ${}^4G_{5/2}$ metastable state. The radiative decay through intense reddish-orange emission occurs from all the samples due to the large energy gap of $\sim 7000 \text{ cm}^{-1}$ between ${}^4G_{5/2}$ state and its next lower state ${}^6F_{11/2}$ [8]. In addition, the main reason for emission quenching is due to energy transfer process via the cross-relaxation (CR) between the pairs of trivalent samarium ions.

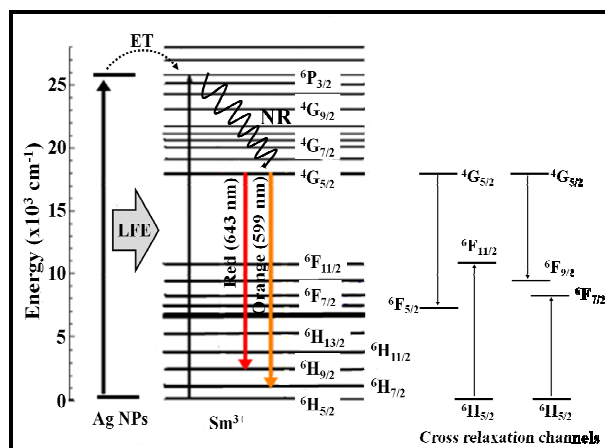


Figure 4: Partial energy level diagram of Sm^{3+} ions in AgCl embedded tellurite glass system.

4.0 CONCLUSIONS

A series of samarium doped tellurite glasses with different concentration of AgCl are synthesized to determine their absorption and photoluminescence characteristics in the presence of Ag NPs. The UV-VIS-NIR absorption spectra reveal six absorption bands with considerable intensity enhancements. The observed peaks transition of Sm^{3+} ions which is located approximately in the same wavelength of Ag NPs verifies the effect of Ag SP. The glass network structure do not alter much due to the incorporation of Ag NPs. PL spectra of glasses without and with Ag NPs at different concentration display two prominent emission bands for red and orange color. It is demonstrated that the glass with 0.075 gm AgCl acquires the highest intensity in the entire spectral range. The spectral features are notably modified due to the inclusion of Ag NPs. The achieved highest enhancement in luminescence intensity for glass containing 0.5 mol% AgCl is attributed to the SPR mediated interaction with the Sm^{3+} ions. The present glass composition is suitable for the fabrication of various photonic devices including solid state lasers.

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Lots of typo mistakes in the references!! Correct all!!

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