Solid State Science and Technology, Vol. 24, No 1 (2016) 163-170
ISSN 0128-7389 | *http://journal.masshp.net*

IMPROVED SPECTRAL FEATURES OF SILVER NANOPARTICLES SENSITIZED SAMARIUM DOPED ZINC-SODIUM-TELLURITTE GLASS

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ABSTRACT

Rare earth doped inorganic glasses with enhanced up-conversion emission and absorption properties are demanding for solid state lasers. Sensitizing the local environment of dopants/co-dopants via surface plasmon resonance (SPR) mediated effects of embedded metallic nanoparticles (NPs) is demonstrated to be prospective towards such endeavor. Silver (Ag) NPs being the creator of sharp SP is incorporated into the optimized glass composition to improve its spectral features. Glasses with chemical composition TeO_2-ZnO-Na_2O-Sm_2O_3-AgCl is prepared using melt-quenching method, where the concentration of AgCl (in excess) is varied and Sm^{3+} kept constant. Synthesized glasses are thoroughly characterized via UV-Vis-NIR absorption, photoluminescence and XRD measurements. The influence of varying Ag NPs contents on the spectral features of samarium (Sm^{3+}) doped zinc-sodium tellurite glasses is determined. XRD pattern confirmed the amorphous nature of as-prepared glasses. Ag NPs growth is primarily ascribed to the Ostwald ripening and coalescence processes. The absorption spectra revealed six peaks centered at 472, 943, 1089, 1237, 1392, and 1491 nm, which are allocated to $^6H_{5/2}\rightarrow{}^4I_{11/2}$, $^6F_{11/2}$, $^6F_{9/2}$, $^6F_{7/2}$, $^6F_{5/2,}$ $^6F_{3/2}$ transitions, respectively. Furthermore, the evaluation of refractive indices, polarizability, density, molar refraction, optical band gap and Urbach energy clearly exhibited the strong participation of Ag NPs in the glass network. PL spectra showed three emission bands located at 561, 599 and 643 nm, which are assigned to $^4G_{5/2}\rightarrow{}^6H_{5/2}$, $^6H_{7/2}$ and $^6H_{9/2}$ transitions, respectively. The observed enhancement in PL intensity is attributed to the highly localized electric field (SPR) of Ag NPs positioned in the vicinity of Sm^{3+} ion. The mechanism of enhancement is identified, analyzed and understood via partial energy level scheme of Sm^{3+} ion. The admirable features of this glass composition are highly beneficial for solid-state laser and optical device fabrication.

INTRODUCTION

Nowadays, researchers are highly fascinated to enhance the performance of the optical devices such as laser and fiber amplifier, where the up-conversion attribute is considered as a pre-requisite factor towards such accomplishments. Optimized concentration rare earth ions (REIs) doping and metal 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 subsequent 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 provided the NPs sizes and shapes are appropriately tuned [1, 3, 4]. The observed luminescence quenching at higher NPs concentration is attributed to the energy transfer due to the interaction of REIs and OH^- groups with bigger sized NPs, where NPs reabsorbs the strong local electromagnetic field instead of feeding the REIs [5]. Despite many efforts the mechanism of NPs SPR mediated enhancement and concentration dependent (higher) quenching of PL intensity remain unclear.

In this work, a series of Sm^{3+} 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 sensitized alteration in spectral properties is scrutinized. The mechanism behind absorption and luminescence enhancement of Sm^{3+} ions due to the inclusion of Ag NPs in tellurite glass is analyzed, compared, and understood.

EXPERIMENTAL

Glasses with composition $65TeO_2$-$25ZnO$-$10Na_2O$-$(0.15)Sm_2O_3$-$(y)AgCl$, where $y = 0$, 0.03, 0.075, 0.12 and 0.18 gram are prepared (Table 1) by melt quenching technique. An appropriate amount of analytical grade raw materials (all 99.99% purity, Sigma Aldrich) of TeO_2, ZnO, Na_2O, Sm_2O_3, and $AgCl$ are weighted using the electronic balance (Precisa 205 SCS). Around 15 gram of batch materials in the form of fine powder is thoroughly mixed together and subjected to milling process for 20 minutes to get the homogeneity. A platinum crucible containing these glass constituents is placed in an electrical furnace at 900 °C and heated for 20 minutes before the melt is poured in a brass mold. 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 to form the glass. All these 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 highly transparent samples devoid of scratches. During melting, first Ag^+ ions are formed from the dissociation of AgCl and then reduced to Ag^0 via redox reaction. Finally, through rapid cooling the favorable nucleation and growth kinetics allows the free Ag^0 atoms in the fluid phase get agglomerated together via Ostwald ripening and coalescence mechanism to form NPs.

Room temperature optical absorption measurement in the wavelength range of 400-1800 nm is performed using UV-VIS-NIR (Schimadzu UV-3101PC) double beam spectrophotometer. Emission spectra are recorded using a Perkin Elmer LS-55 Photoluminescence spectrometer, which is equipped with a pulsed Xenon lamp (as excitation source) in the wavelength range of 300-1300 nm. The emitted light is dispersed by Monk-Gillieson monochromator and detected with standard photomultiplier tube.

RESULTS AND DISCUSSION

Figure 1 shows the Ag NPs concentration dependent UV-VIS-NIR absorption spectra of as synthesized Sm_2O_3 doped glasses. It revealed six absorption bands centered at 472, 943, 1089, 1237, 1392 and 1491 nm, which are originated from the Sm^{3+} ions ground state ($^4G_{5/2}$) to excited states ($^4I_{11/2}$, $^6F_{11/2}$, $^6F_{9/2}$, $^6F_{7/2}$, $^6F_{5/2}$ and $^6F_{3/2}$) transitions, respectively [6, 7]. The absorption bands are classified into two energy groups, where the lower one contained the transition up to 10,700 cm^{-1} (~935 nm) and the higher one in the range of 17,600 - 32,000 cm^{-1} (~570 - 313 nm) [8]. Most of the absorption bands are found to originate from the electric dipole contribution ($\Delta J \leq 6$) except few transitions that emerges from magnetic dipole contribution ($\Delta J = 0, \pm 1$). For instance, $^6H_{5/2} \rightarrow {}^4G_{5/2}$ is assigned to the magnetic dipole transition [6]. The presence of NPs in the glass is 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 compare to their free counterpart remained unchanged even in the presence of Ag NPs in the host matrix. The UV absorption edge is further used to calculate the optical band gap and Urbach energy via Tauc plot.

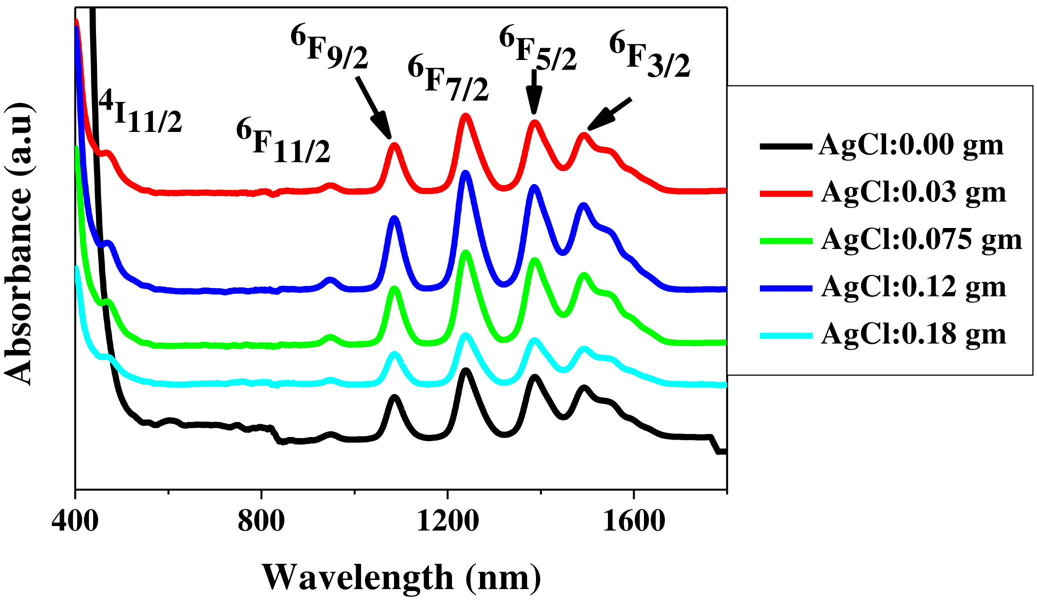

Figure 1: Room temperature absorption spectra of prepared glasses with varying AgCl concentration

Table 1: AgCl concentration dependent optical band gap (Direct: E_{dir} and Indirect: E_{indir}) and Urbach energy (E_u) of synthesized glasses

Glass code	AgCl (gm)	E_{dir} (eV)	E_{indir} (eV)	E_{tail} (eV)
S1	0	2.596	2.951	0.191
S2	0.03	2.959	3.368	0.224
S3	0.075	3.229	3.476	0.189
S4	0.12	3.110	3.368	0.168
S5	0.18	2.724	3.175	0.334

Generally, both direct and indirect band gap as well as Urbach energy is observed to increase with the increase of Ag NPs contents. This enhancement in band gap energy band gap is attributed to the alteration of glass electronic band structure due to the insertion of Ag NPs. Addition of Ag NPs ruptured many bridging oxygen bonds and generated non-bridging oxygen. These non-bridging oxygen atoms in turn altered the density and polarizability of the glass. The other possibility is the metallization of the glasses in the presence of Ag NPs, which broadened the valance band or multivalence band structure [11]. This is achieved by introducing defect states in the band gap that acted as electron donor or acceptor states [4]. It is demonstrated that the embedment of Ag NPs in the glass matrix indeed widened the band gap by altering the optical and electronic properties of the amorphous sample.

Figure 2 displays the Ag NPs concentration dependent room temperature PL spectra of glass samples under 406 nm wavelength excitations. The spectra exhibited 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.

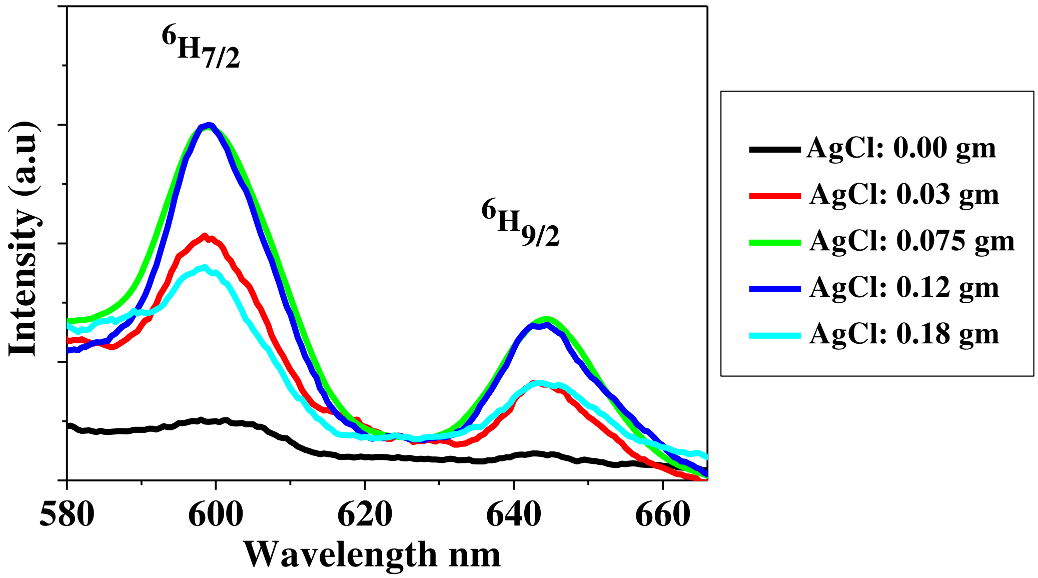

Figure 2: The emission spectra of glass with varying concentration of AgCl

Figure 3 illustrates the PL peak intensity as a function of Ag NPs concentration of for both the transitions. Glass with 0.075 gm AgCl exhibited the intensity enhancement in the entire spectral range. This enhancement in luminescence intensity is attributed to the Ag NPs SPR mediated effects [9]. Furthermore, the transition $^4G_{5/2} \rightarrow {}^6H_{7/2}$ containing both electric and magnetic dipole contribution obeyed the selection rule $\Delta J = 0, \pm 1$ [8]. The transition $^4G_{5/2} \rightarrow {}^6H_{9/2}$ resulted from the pure electric dipole interaction.

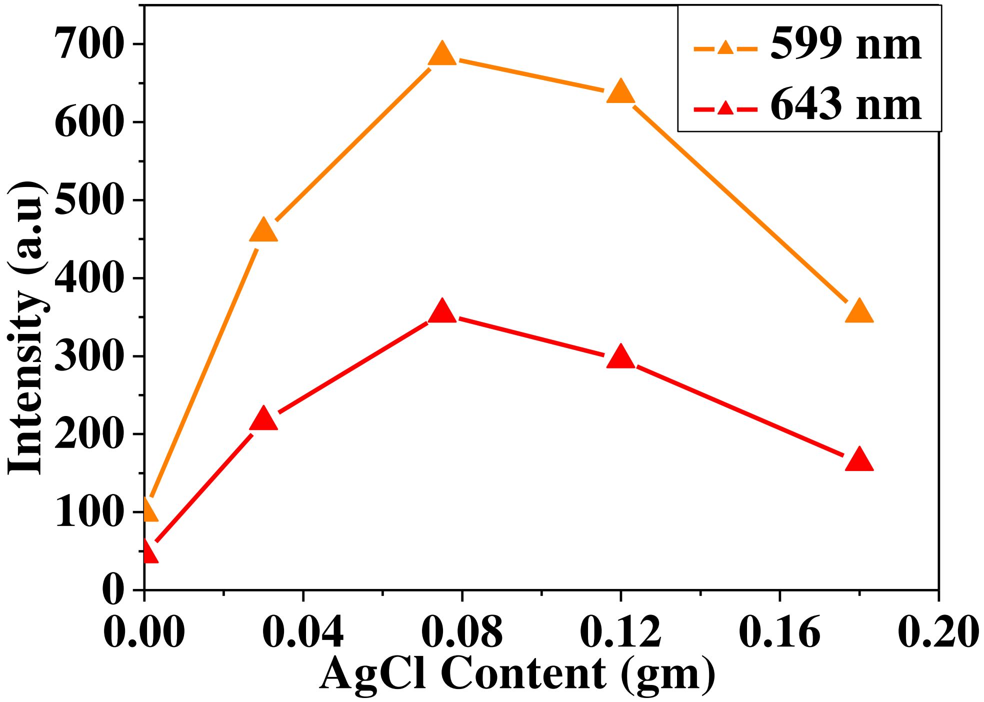

Figure 3: AgCl NPs concentration dependent PL peak intensity for red (643 nm) and orange (599 nm) transitions

The SPR mediated intensified electromagnetic field around Sm^{3+} ions resulted an enhancement in Sm^{3+} ions luminescence. This 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 higher concentration of AgCl (0.12 gram and beyond) is due to the transfer of energy 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 ~7000 cm^{-1} between $^4G_{5/2}$ state and its next lower state $^6H_{9/2}$ [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.

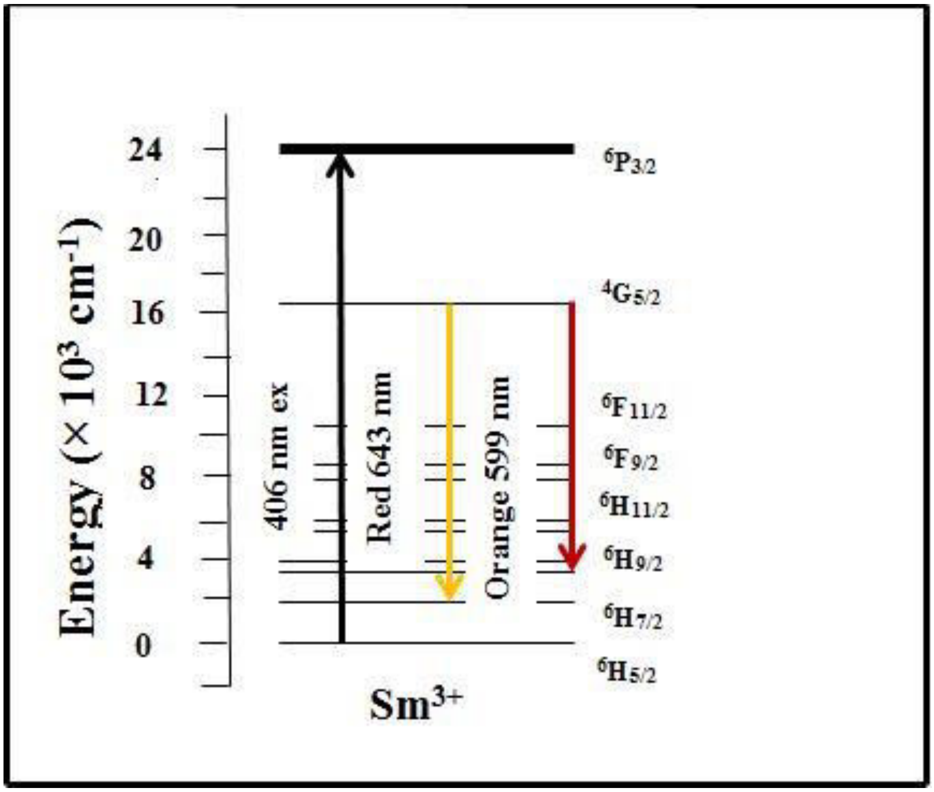

Figure 4: Partial energy level diagram of Sm^{3+} ions in AgCl embedded tellurite glass system

CONCLUSIONS

A series of Sm^{3+} ions doped tellurite glasses containing concentration of Ag NPs are synthesized. The spectral features of prepared glasses in terms of their absorption and photoluminescence are determined. Absorption spectra revealed 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 and associated intensity enhancement verified the role of Ag NPs sensitization. The optical band gap and Urbach energy is greatly affected due to the sensitization of Ag NPs. PL spectra of glasses without and with Ag NPs at different concentration displayed two prominent emission bands (red and orange color). It is demonstrated that the glass with 0.075 gm AgCl acquired 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 0.075 gram AgCl is attributed to the Ag NPs 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.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support from UTM and Malaysian Ministry of Education through Vot.05H36 (GUP) and 4F424 (FRGS).

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