GOLD NANOPARTICLES ENHANCED OPTICAL PROPERTIES OF Sm^{3+} DOPED SODIUM-LITHIUM-TELLURITE GLASS

S. K. Ghoshal, Azmirawahida Zainuddin,
Ramli Arifin, and M. R. Sahar

Advanced Optical Materials Research Group, Department of Physics, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia.

Corresponding author: sibkrishna@utm.my

ABSTRACT

Enhancing the optical properties of rare earth (RE) doped tellurite glasses by embedding metallic nanoparticles (NPs) with controlled size and optimized concentration is ever-demanding in solid state lasing materials. The influences of gold (Au) NPs concentration on the optical and structural enhancements of sodium-lithium-tellurite glass are examined. Glasses with compositions $79TeO_2+10Li_2O+10Na_2O+1Sm_2O_3+yAuCl_3$ (where $0.03 \leq y \leq 0.15$ mol%) are prepared using melt-quenching technique and optical characterizations are made. Subsequent heat treatment (annealing) at 300°C for 3 hours is performed to control the growth of NPs. During melting, first Au^+ ions are formed and then reduced to Au^0 via redox reaction. Anneling above the glass transition temperature facilitates Au^0 to aggregate and form NPs. The annealing assisted NPs growth occurs via coarsening. XRD pattern confirms the amorphous nature of the prepared glasses. The TEM image reveals the growth of Au NPs with mean size ~18 nm. The enhancement in luminescence is attributed to the surface plasmon resonance effect and strong local field of NPs positioned in the proximity of Sm^{3+} ion. The presence of Au NPs alters the glass network structure and significantly modifies the physical, structural, and optical properties. The mechanism of enhancement is understood in terms of various mechanisms and compared. The excellent features of our results may nominate these glasses as a potential candidate for solid state laser, display, and amplifier.

Keywords: Gold Nanoparticles; Sm^{3+} ions; Absorption; Luminescence; Enhancement

INTRODUCTION

Definitely, RE doped tellurite glasses with embedded NPs are attractive due to their interesting properties such as high rare earth ions solubility, higher refractive indices than silicates and fluoride glasses, large amplification bandwidth, high infrared transmittance and good thermal and mechanical stability [1, 2]. They are promising for practical applications in photonics as optical amplifiers, optical recording, laser active media and infrared-to-visible converters. Different strategies are adopted to enhance the luminescence efficiency of these glasses decisive for solid state lasers. However, the concentration quenching and weak absorption cross-section of these glasses are

disadvantageous for devices. The ever-ending quest in this area is how to enhance the optical performance by increasing the emission and absorption cross-section. Despite extensive studies the understanding on the mechanism of improved optical properties is still lacking. The interest of the present study is driven by its frequency up-conversion properties that could lead to the development of new solid-state short-wavelength laser. The applications of RE doped glasses are limited by their miniature oscillator strength of the 4f-transitions of RE ions. Consequently, the emission intensity easily gets quenched due to the losses which are stimulated by the de-excitation of different energy levels. Modifications of the environment of RE ions by embedding metallic NPs in the glass host and exploiting their localized surface plasmon resonance (LSPR) effect is thought as an alternative route to overcome this shortcoming. It is demonstrated that the presence of NPs in the proximity of RE ion enhances their luminescence intensity [2]. Moreover, the influence of LSPR on the luminescence efficiency of RE strongly depend upon the separation between the RE and NP. Thus, the efficiency of the electric dipole coupling improves the optimal separation, where the enhanced local field can increase the oscillator strength [3]. In other words, the transition probabilities of the lanthanide ions can be altered substantially by incorporating metallic NPs inside the glass matrix [4].

To achieve efficiently enhanced luminescence the concentration ratio of metallic NPs and RE must be lower than one [5]. Otherwise, the higher probability of multi-poles (Er^{3+}:NPs) formation results undesirable effects. It is established that the energy transfer is a dipole-dipole mechanism between the metal nanocrystal (donor or sensitizer) and RE ions (acceptor). Concurrently, the increase in likelihood of energy transfer from RE to metallic NPs results considerable luminescence quenching. Hence, the concentration of RE must be greater than that of NP [5]. In these regard, controlled formation of metallic NPs inside the glass matrix is really the key issue from applied viewpoint.

Glasses containing metallic nanostructures have already been developed through crystallization via controlled heat treatments. Glassy state being meta-stable tends to transform continuously towards the more stable state following the mechanisms of structural relaxation and crystallizations. The structural relaxation process is driven by the considerable amount of strain frozen-in during glass formation. Conversely, in the annealing process the material relaxes via atomic diffusion towards the internal equilibrium state of the liquid from which it was obtained [5]. The crystallization process which occurs via nucleation and growth depends critically on the kinetic and thermodynamic factors [4]. Interestingly, the growth and nucleation of NPs can be controlled through annealing above the glass transition temperature [6-8].

We report the Au NPs concentration dependent enhancement in absorption and emission charcteristics of sodium-lithium tellurite glass doped with Sm^{3+} ion. Glasses are prepared using the conventional melt-quenching method and characterized.

EXPERIMENTAL

Series of glasses are prepared by using melt quenching method. Various concentrations (mol%) of starting materials of $AuCl_3$ (sensitizer), TeO_2 (glass former) and Li_2O and Na_2O (modifier) as well as rare earth oxide Sm_2O_3 in the powder form of analytical grade purity are used . The glass compositions are $79TeO_2+10Li_2O+10Na_2O+1Sm_2O_3+yAuCl_3$ (where $0.00 \leq y \leq 0.15$ mol% in excess). Batch of 15 g powders are thoroughly mixed in a platinum crucible. The mixture then melted at 800 °C for 15 min in an electric furnace. The melt is then poured in a steel mould and annealed at 300°C for 3 hours to remove any thermal strain that cause embrittlement of glass. Finally, the samples are cut and polished for optical measurements. The amorphous nature of prepared samples is confirmed using the X-ray diffraction (XRD) analysis performed on Siemens Diffractometer D5000 using CuKα radiations (λ=1.54 Å) at 40 kV and 100 mA, with scanning angle 2θ ranges between 10-80° to identify the amorphous and crystalline nature of all samples. Optical absorption measurement in the wavelength region 400 -1800 nm is performed at room temperature using a Shimadzu 3101PC UV-VIS-NIR. The luminescence spectra between 550 and 750 nm are measured under 410 nm excitation wavelengths using Perkin-Elmer Luminescence Spectrometer (LS 55). Glass densities are determined by Archimedes method using toluene as an immersion liquid. Transmission electron miscroscopic measurement is performed using Phillips CM12 with Docu Version 3.2 image analysis is used to verify the presence of GNPs. Specimens for TEM are prepared by dispersing the powder sample in acetone using ultrasonic bath. The solution is then placed onto copper grid and allowed to dry before characterization. All the measurements are carried out at room tempearture.

RESULTS AND DISCUSSION

The typical XRD pattern of Sm^{3+}- doped sodium-lithium tellurite glass containing Au NPs is shown in Figure 1. The presence of a broad hump without any sharp crystallization peaks confirms the amorphous nature of the glass [3]. The calculated physical properties of all glass samples are listed in Table 1. The creation of more non-bridging oxygen (NBOs) due to the introduction of Au NPs into the glass matrix causes a decrease of glass density (ρ) [4]. The increase of molar volume (V_M) is attributed due to the growth of Au NPs which leads to the alteration of structural rearrangement of atoms and expand the glass network by creating more defects through the rupture of bridging oxygen bonds (BOs). Consequently, there is a change of geometrical configuration upon the Au NPs growth. This modification is ascribed to the increase in the inter-atomic spacing which weakens the stretching force constant of bond inside the glass network [5]. Besides, refractive index (n) shows an increase with the increase of Au NPs contents. This increase is interpreted in terms of the creation more NBOs which are found to be more polarizable than BOs because the refractive index is directly proportional to the polarizability [6].
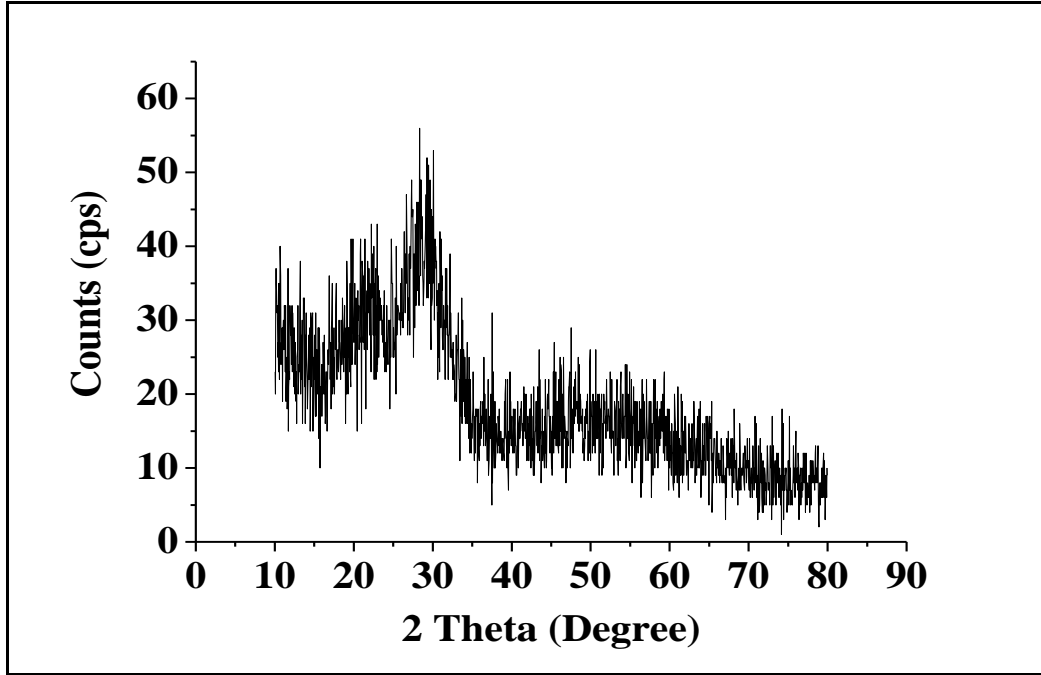
Figure 1: Typical XRD pattern of prepared glass sample

Table 1: Refractive indices (n), densities (ρ, g mol^{-3}), molar volumes (V_M, cm^3 mol^{-1}), molar refractions (R_M, cm^3), polarizibilities (α_e, x 10^{-24} cm^3), indirect band gap (E_{ind}, eV), direct band gap (E_{dir}, ev) and Urbach energy (E_{urb}, eV) of all samples

Au	n	ρ	V_M	R_M	α_e	E_{ind}	E_{dir}	E_{urb}
0.00	2.584	5.040	27.531	18.012	7.140	1.7280	3.3030	0.4940
0.03	2.550	6.141	22.610	14.632	5.801	2.3900	2.8541	0.2519
0.06	2.542	6.030	23.041	14.872	5.896	2.4912	2.8710	0.2531
0.09	2.532	5.566	24.978	16.069	6.370	2.5149	2.8339	0.2374
0.12	2.541	4.875	28.538	18.414	7.300	2.5431	2.8416	0.2508
0.15	2.865	4.341	32.069	22.644	8.977	2.5172	2.8423	0.2588

Figure 2 illustrates optical absorption spectra of all samples. The UV-VIS spectra exhibit eight prominent absorption bands corresponding to the transition from $^6H_{5/2}$ ground state to $^4I_{3/2}$, $^6F_{11/2}$, $^6F_{9/2}$, $^6F_{7/2}$, $^6F_{5/2}$, $^6F_{3/2}$, and $^6F_{1/2}$ excited state of Sm^{3+} ion. The UV-Vis spectra are further used to obtain the transition energies. Mott and Davis relation of electronic transition is exploited [7]. Direct and indirect optical band gap energies are found to vary from 2.8339 - 2.8710 eV (direct, E_{dir}) and 2.3900 - 2.5431 eV (indirect, E_{ind}), respectively together with the increase in Urbach energy (E_{urb}) as summarized in Table 1. The increase in Urbach energy is attributed to the more compactness of the glass due to the generation of non-bridging oxygens and the tendency of weak bond converted to defects.
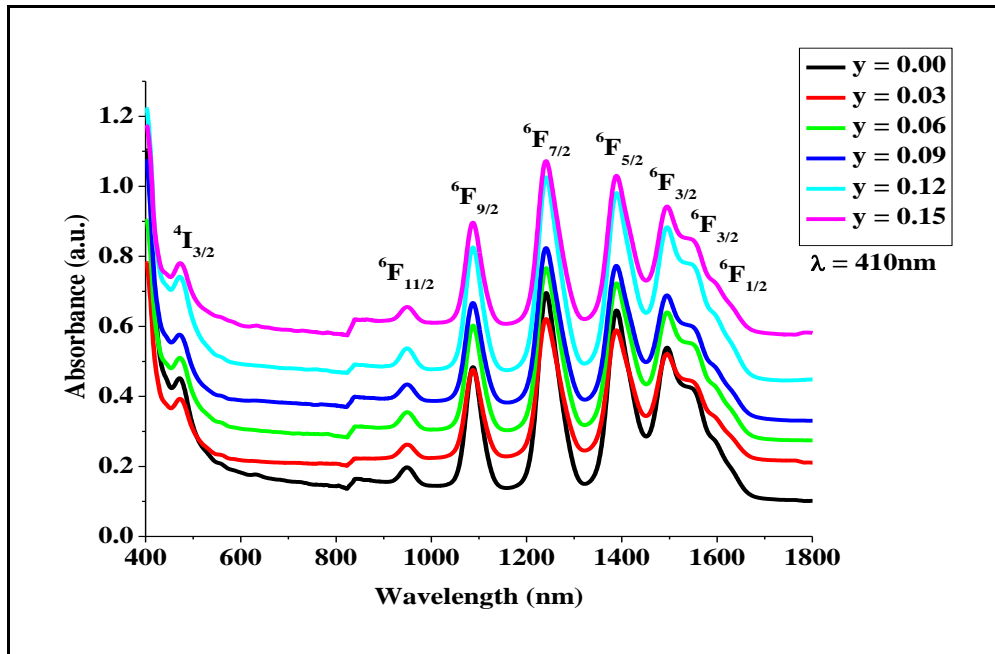
Figure 2: Room temperature UV-Vis absorption spectra of glass samples

Figure 3 displays the room temperature luminescence spectra of all glass samples under 410 nm laser excitations. It reveals four prominent emission peaks centered at 573, 613, 658 and 718 nm corresponding to the transitions from the state $^4G_{5/2}$ to $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$, and $^6H_{11/2}$ excited states, respectively. An enhancement in emission peaks is evidenced for 0.06 and 0.09 mol% of $AuCl_3$. This enhancement is attributed to the SPR effect and strong local field of NPs positioned in the proximity of Sm^{3+} ion. However, at higher concentration of $AuCl_3$ quenching effect is observed due to energy transfer from Sm^{3+} ion to NPs [8, 9].
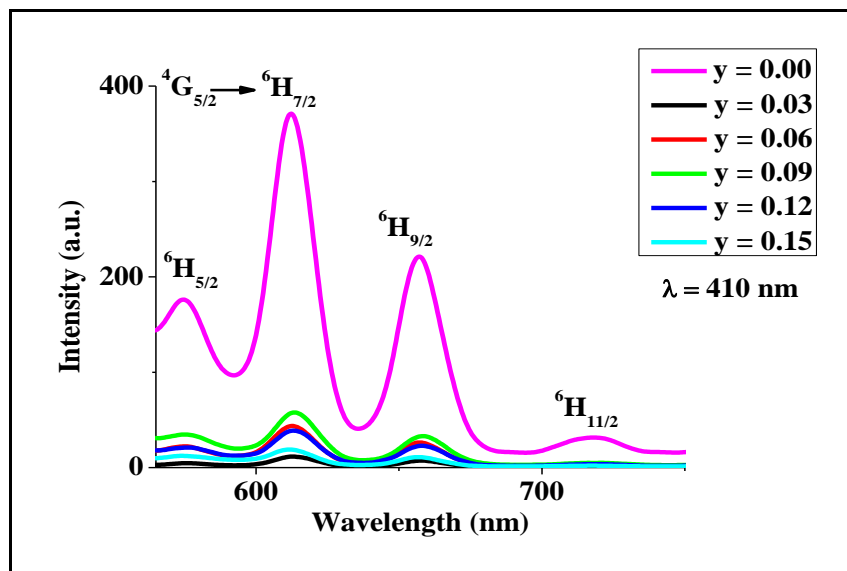

Figure 3: Au NPs concentration dependent PL spectra for all glass samples

From Figure 4, it can be concluded that the transition $^4G_{5/2}$ to $^6H_{7/2}$ recorded the maximum fluorescence intensity. This result is confirmed by the maximum values of transition probability and branching ratio [10, 11]. The corresponding values of branching ratio can be used to characterize the laser power for laser active transition [12]. Furthermore this shows that the $^4G_{5/2}$ to $^6H_{7/2}$ transition has high potential in realizing optical amplification. Thus, the transition of $^4G_{5/2}$ to $^6H_{7/2}$ is essential for laser emission [13].
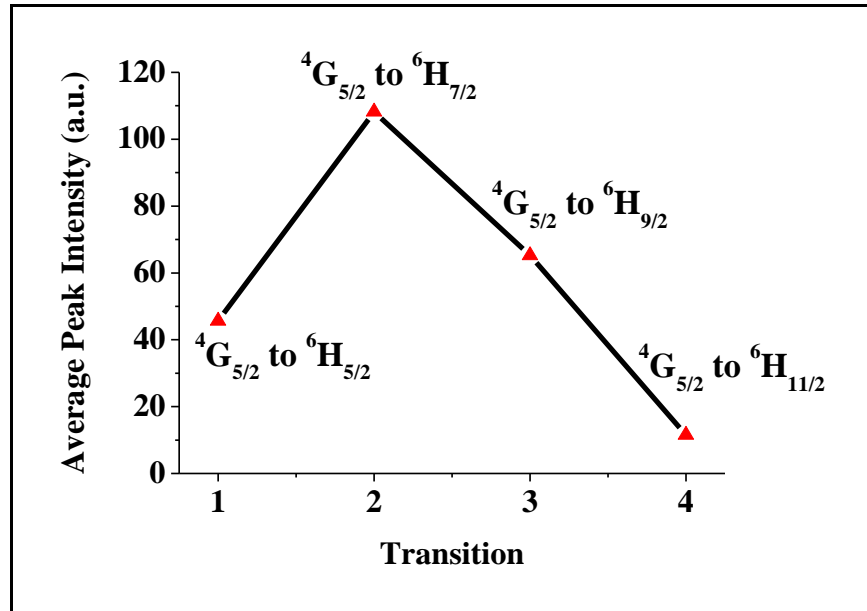

Figure 4: Average peak intensity for different transition

CONCLUSION

A series of tellurite glasses of the form with varying concentration of Au NPs are prepared using melt quenching method. XRD pattern confirmed their amorphous nature. Photoluminescence shows significant enhancement for samples with 0.06 and 0.09 mol% of $AuCl_3$. However, samples with higher concentration of $AuCl_3$, shows quenching. The optical absorption spectra shows eight bands for different transitions. The absorption spectra is used to extract Urbach energy. The optical and structural parameters are strongly correlated with increasing $AuCl_3$ concentration. Our results suggest that Sm^{3+} doped tellurite with Au NPs glass may be nominated for fabricating lasers and photonic devices operating in the visible region.

ACKNOWLEDGEMENTS

REFERENCES

[1]. J.S. Wang, E.M. Vogel, E. Snitzer, *Opt. Mater. 3, 187* 5050-505 (1994)

[2]. T. Kosuge, Y. Benino, V. Dimitrov, R. Sato, T. Komatsu, *J. NonCryst. Solids,* **242** 154-164 (1998)

[3]. N.A Zarifah,. M.K. Hashim, M. Azmi, W.M. Daud, *Chalcogenide Letters,* **51** 565-571 (2010)

[4]. M.K. Halimah, W.M. Daud, H.A.A. Sidek, A.W. Zaidan, A.S. Zainal, *Mater. Sci. Pol.* **28** 173 (2010)

[5]. HA.A. Sidek, S. Rosmawati Z.A Talib,. M.K. Halimah, W.W. and Daud, *Am J.Appl. Sci.* **6** 1489 (2009)

[6]. R .El-Mallawany, M.D. Abdalla, I.A. Ahmed, *Chemistry and Physics,* **109** 291–296 (2008)

[7]. M. A. Chaudhry and M. Altaf, *Materials Letters* 34 (1998) 213-216

[8]. A.Awang, S.K. Ghoshal, M.R. Sahar, R. Arifin, F. Nawaz, *Journal of Luminescence* **149** 138-143

[9]. V. A. G. Rivera, D. Y, M. Manzani, L. A. O. Nunes, and E. M.Jr, Study of Er^{3+} fluorescence on tellurite glasses containing Ag nanoparticles. J. Phys: Conferences Series 274, (2011).

[10]. K. Annapurna, R. N. Dwivedi, A. Kumar, A. K. Chaudhuri, and S. Buddhudu, *Spectrochimica Acta Part A* **56** 103-109 (1999)

[11]. A. M. Babu, B.C. Jamaliah, J. S. Kumar, T. Sasikala, and L. R. Moorthy, *J. Alloys Comp.* **509** 457-462 (2011)

[12]. B. C. Jamalaiah, M. V. V Kumar,. and K. R. Gopal, *Optical Materials,* 33 1643-1647 (2011)

[13]. T. Suhasini, J. S. Kumar, T. Sasikala, K. Jang, H. S. Lee, M. Jayasimhadri, J. H. Jeong, S. S. Yi and L. R. Moorthy, *Optical Materials,* **31** 1167–1172 (2009)