

NANO-SILVER ENHANCED UPCONVERSION EMISSION IN Nd³⁺: Ag-ZINC-TELLURITE GLASS

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In this paper, enhanced infrared (IR) to visible upconversion (UC) emission in Nd³⁺ doped zinc-tellurite glass embedded with silver nano-particles is reported. Nucleation and growth of nano-particles are controlled with heat treatment above the glass transition temperature. Under an excitation of 797 nm which is in resonance with Nd³⁺ transition ⁴I_{9/2}-⁴F_{5/2}, three prominent upconverted bands, centered at 535, 600 and 668 nm, are observed in the visible region attributed to the ⁴G_{7/2}→⁴I_{9/2}, ⁴G_{7/2}→⁴I_{11/2} (⁴G_{5/2}+²G_{7/2}→⁴I_{9/2}) and ⁴G_{7/2}→⁴I_{13/2} (⁴G_{5/2}→⁴I_{11/2}) transitions, respectively. Furthermore, all the bands are enhanced significantly in the presence of silver nano-particles. The transition centered at 535 nm is much more enhanced (~8 times) which is attributed to the local field effect of silver nano-particles as well as an energy transfer from silver species to Nd³⁺ ions (Ag→Nd³⁺).

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1. Introduction

Photon upconversion (UC) is an anti-Stokes type emission process in which two or more photons are sequentially absorbed leading to emission of shorter wavelength light than the wavelength excited [1,2]. This phenomenon may occur in organic material such as polycyclic aromatic hydrocarbons and in inorganic materials like ions of elements of d and f block elements.

With the development of nanomaterials, it was revealed that these have a very vast potential for being used in different technologies due to their photon upconversion properties and such materials are known as Upconverting Nanoparticles (UCNPs).

Changing the glass matrix environment can alter the optical properties of rare-earth (RE) ions [3, 4]. Luminescence efficiency of RE ions can be enhanced by coupling of these ions with metallic nanoparticles (NPs). Metallic NPs display fascinating optical phenomenon termed as surface plasmon resonance (SPR), known as collective oscillations of electrons in an electromagnetic field [4-6]. Due to SPR induced local field enhancement (LFE), free space spectroscopic properties of RE ions lying within the vicinity of these nanostructures is modified and weak optical transitions are largely enhanced known as metal enhanced fluorescence (MEF) phenomenon [7, 8]. MEF has applications in newly rising technology of nano-photonics [9].

Neodymium (Nd) is a soft silvery rare earth metal that is found in the Earth's crust which is very prone to aerial oxidation; its small sample (a centimeter-sized) gets oxidize completely within a year [10]. Neodymium has a wide range of industrial applications and is being used as cryocoolers due to its large specific heat capacity, as plant growth regulators, in glass dyes and magnets. Due to its characteristics, it may also be used in high power appliances [11] such as electric motors, generators, hybrid cars etc. A small amount of Nd ions along with certain materials may also be used in lasers as gain media for infrared radiations. Neodymium doped laser sources have shown technological interest since their exploitation in industry, defense, high-resolution spectroscopy etc. [12-14]. These applications stimulated the advancement of high gain,

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low threshold host media for doping Nd^{3+} ions [12-14]. The most favorable properties for the development of host media for Nd^{3+} ions are low phonon energy and minimum content of OH^- groups in order to minimize the multiphonon relaxation due to excitation losses. Physico-chemical properties of Nd compounds make them suitable for numerous applications such as advanced NP based high-tech materials, surface catalytic systems, protective coating materials and photonics [15,16].

Usually, phosphate and silicate glasses are used as host materials for Nd^{3+} doped laser glasses [17, 18], while tellurite glasses are getting large attention for optoelectronics applications [19]. These glasses are suitable especially because of their low phonon energies, high refractive index, good chemical durability and stability and wide transmission window (0.4-6 μm) that makes them potentially appropriate for photonic applications such as laser, non-linear optical devices, optical fiber amplifier, etc [20-24]. Usage of TeO_2 alone makes the glass preparation difficult and to overcome this problem, certain modifiers such as zinc oxide and other alkali elements are added in glass for their transparency and homogeneity [20].

Effect of gold NPs on upconversion (UC) emissions of Nd^{3+} in antimony glass was studied by Som et al in which, TEM images reveal that dichroic behaviors are observed due to elliptical Au^0 NPs of 12–21 nm size [25], while in another study, influence of silver NPs on the upconversion emission of Nd^{3+} in lead germanate glass [26] is discussed.

In continuation of our work on doped tellurite glasses [27-31], Nd^{3+} -doped zinc-tellurite glass is prepared through melt-quenching process both with and without silver NPs followed by investigation of the effect of silver (treated by heating the samples) on different transitions of Nd^{3+} .

2. Experimental procedure

Samples under study were prepared with 74.5 TeO_2 -25 ZnO -0.5 Nd_2O_3 composition with zero and 0.3 mol % silver chloride as doping material employing conventional melt-quench process. All the powdered ingredients were mixed together and the resultant mixture was kept in a furnace set at 950 $^\circ\text{C}$. Melted contents were then poured in a steel mold which was retained at 250 $^\circ\text{C}$ for 3 hours for reduction of mechanical stress. First annealing temperature was set at 250 $^\circ\text{C}$ [below the glass transition temperature ($T_g \sim 320^\circ\text{C}$)] [29] in order to avoid any theoretical possibility of growth of silver NPs.

Glass A was prepared using Nd^{3+} alone without Ag^+ , while glasses B, C & D were prepared incorporating Nd^{3+} and Ag^+ particles. Glasses B, C & D were given heat treatment (HT) for period of 4, 12 and 24 hours respectively. In order to maintain the viscosity of the glass suitable for growth of silver NPs, diffusion and aggregation, temperature was maintained higher than T_g [32].

One sample labeled as glass E was prepared by doping Ag alone (without using Nd) for the location of surface plasmon resonance (SPR) peak. Composition of all the glass samples prepared is listed in Table 1.

Table 1. Labels, glass compositions (mol %) and heat-treatments durations (Hours) of the studied glass

Glass	TeO_2	ZnO	Nd_2O_3	AgCl	HT < T_g	HT > T_g
A	74.5	25	0.5	0	3	0
B	74.2	25	0.5	0.3	3	4
C	74.2	25	0.5	0.3	3	12
D	74.2	25	0.5	0.3	3	24
E	74.0	25	0	0.5	3	4

Nucleation of silver NPs was studied with the help of Transmission Electron Microscope “Phillips CM12” and image analysis was carried out with Docu Version 3.2. Powdered samples were dispersed in acetone using ultrasonic bath and these dispersed solutions were allowed to dry

after their placement on copper grid. Visible and near infra-red region (190-2000nm) absorption spectra were taken on Shimadzu UV-3101PC scanning spectrophotometer, while emission spectra were recorded on a Flouorolog (Horiba, US). Tungston lamp was used as light excitation source using a standard photomultiplier tube for detection of resultant signals.

3. Results and discussion

Transmission electron microscope (TEM) image of the sample for glass C displaying spherical and non-spherical nanoparticles is shown in Fig. 1(a), while Fig. 1(b) demonstrate the histogram for distribution of size of NPs with average diameter ~ 20 nm.

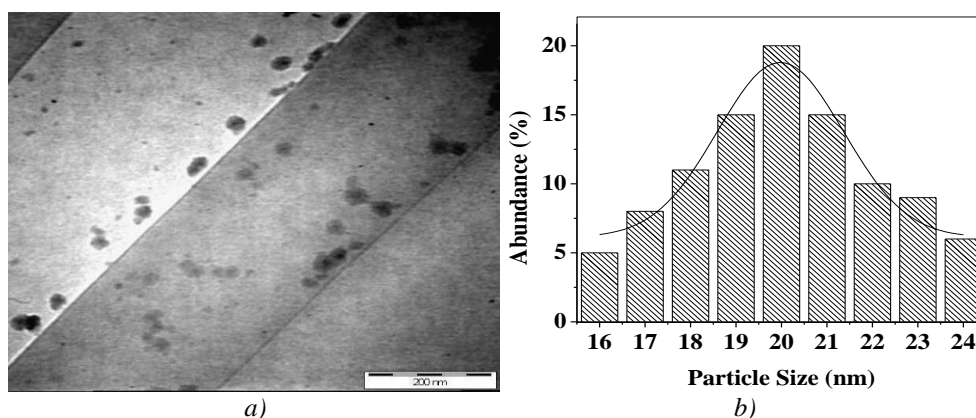


Fig. 1. (a) Homogenous distribution of silver NPs as seen in TEM image for glass C (b) Size distribution histogram of the metallic NPs.

UV-VIS-NIR absorption spectra in 500-900 nm range of Nd^{3+} doped zinc-tellurite glasses are shown in Fig. 2a. Seven bands are identified as a resultant of excitations from $^4\text{I}_{9/2}$ ground state to $^4\text{F}_{3/2}$, $^4\text{F}_{5/2} + ^2\text{H}_{9/2}$, $^4\text{F}_{7/2} + ^4\text{S}_{3/2}$, $^4\text{F}_{9/2}$, $^2\text{F}_{11/2}$, $^4\text{G}_{5/2} + ^2\text{G}_{7/2}$ and $^2\text{K}_{13/2} + ^4\text{G}_{7/2} + ^4\text{G}_{9/2}$ excited states. Plasmon band related to silver NPs was not appeared in the samples prepared with silver chloride and neodymium oxide probably either due to the smaller or zero amounts of silver chloride or and/ or due to overlapping of the bands of two dopants. Therefore, one sample was prepared with slightly higher concentration of AgCl , but without Nd_2O_3 and it was observed that no plasmon band appeared at 484 nm. (Fig.2 (b)).

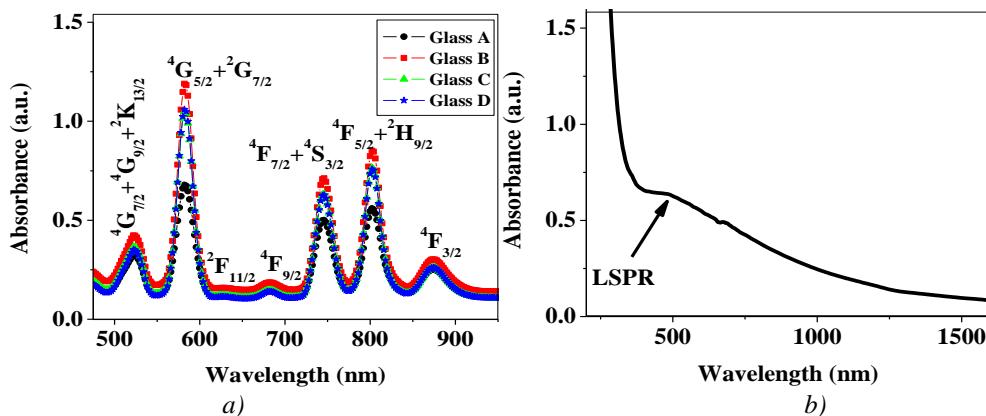
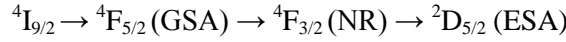


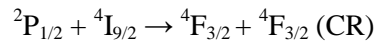
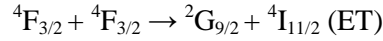
Fig. 2. (a) UV-Vis-NIR absorption spectra of zinc-tellurite glasses. (b) plasmon band for glass sample without Nd^{3+} ions.

Upconversion of luminescence spectra of glass samples doped with Nd^{3+} under 797 nm laser excitation is shown in figure 3a where three prominent bands at 535, 600 and 668 nm. These three bands are attributed to the ${}^4\text{G}_{7/2} \rightarrow {}^4\text{I}_{9/2}$, ${}^4\text{G}_{7/2} \rightarrow {}^4\text{I}_{11/2}$ (${}^4\text{G}_{5/2} + {}^2\text{G}_{7/2} \rightarrow {}^4\text{I}_{9/2}$) and ${}^4\text{G}_{7/2} \rightarrow {}^4\text{I}_{13/2}$ (${}^4\text{G}_{5/2} \rightarrow {}^4\text{I}_{11/2}$) transitions respectively.

Under lying mechanism of these transitions perhaps involves excitation of one Nd^{3+} ion by 797 nm laser excitation from their ground state to ${}^4\text{F}_{5/2}$ level known as ground state absorption (GSA) process followed by its non-radiative decay to ${}^4\text{F}_{3/2}$ with relatively longer life time. By absorbing a second IR photon (excitation at 7097 nm) Nd^{3+} ion from ${}^4\text{F}_{3/2}$ level is excited to ${}^2\text{D}_{5/2}$ level and the process being called as excited state absorption (ESA)



The population of the ${}^4\text{G}_{7/2}$ energy level can be enhanced by the non-radiative decay from ${}^2\text{D}_{5/2}$ energy state to ${}^4\text{G}_{7/2}$ energy state. Relaxation of ${}^2\text{P}_{1/2}$ and ${}^4\text{G}_{7/2}$ excited states to their lower-lying state result in different emissions bands, as shown in Fig. 5. The up-conversion efficiency can be improved through Energy transfer (ET) and cross-relaxation (CR) mechanism by populating the higher states as follows, (See also Fig.4)



It is interesting to note that heat treatment up to 12 hours significantly enhances intensity of all the bands, however bands are quenched with increased heat treatment duration (~ 24 Hours) (for enhancement factor; see Fig. 3b).

Metal enhanced fluorescence of RE ions inside the glass matrix was first studied by Malta [33] who proposed that attenuation in Eu^{3+} luminescence in glass and glass ceramics may occur due to energy transfer between silver NPs and Eu^{3+} ions or due to enhanced local field around Eu^{3+} ions. Hayakawa et al. [34] also proposed local electric field to be the main reason for the enhancement in the RE emissions, however, lately LFE is not nominated for the quenching the RE emissions.

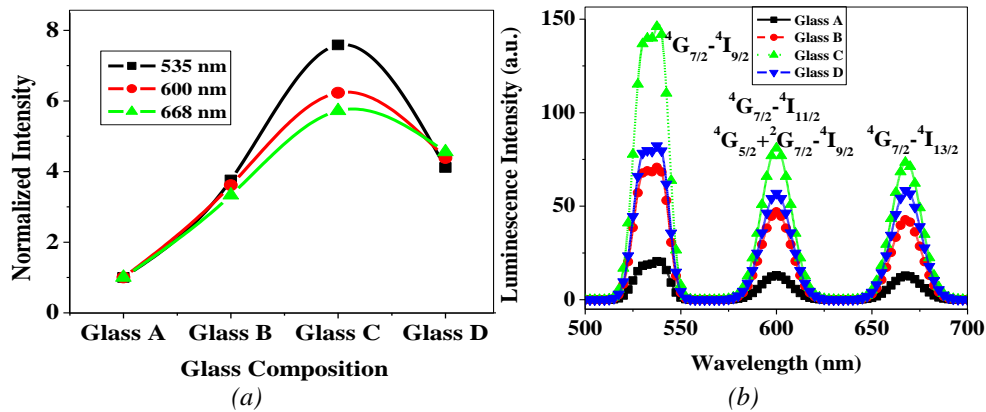


Fig. 3. (a) Luminescence spectra for Nd^{3+} -doped glass samples (b) Heat treatment effects on intensity of fluorescence bands due to Nd^{3+} .

The principal reason for increased luminescence may be ascribed to the local field enhancement (LFE) generated by SPR of silver NPs [32-34].

Due to the oscillation of electrons, surface plasmon polaritons (plasmon waves) moving along surface of metallic NPs, confine light in the sub-wavelength structures as dielectric function of metal is different from that of the surrounding host [36]. Local electric field is amplified with respect to incident field due to light confinement and metallic screening termed as "Lightning Rod

Effect” [36-39], which is most probable to be occurred in the presence of non-spherical metallic particles having some sharp edges. This enhanced local electric field due to metallic NPs increases the excitation rate of RE ions lying within the vicinity of these nanostructures.

Influence of added excitation field is shown in Fig. 4. Furthermore, enhancement in RE luminescence depends upon cluster formation; NPs concentration is increased due to enhanced annealing time as more NPs nucleate and grow together and coalesces known as Ostwald’s ripening. It is expected that electric fields of these NPs superimpose and give “hot spots” resulting in stronger surface enhanced fluorescence [36, 40, 41]. NPs with anisotropic shapes (elliptical, hexagonal etc) are expected to induce larger electric fields as compared to that produced by spherical NPs [41, 42].

Energy transfer from Ag^0 NPs to Nd^{3+} ions could be the other possibility for the enhancement in the luminescence [34], although it was rejected by Malta et. al. [33] as life time of metal plasmon is much shorter than the excited state of rare earth ion.

A quench was observed with increasing heat treatment time up to 24 hours, which may be considered due to energy transfer from Nd^{3+} ions to Ag^+ NPs ($\text{Nd}^{3+} \rightarrow \text{Ag}^0$) [43] and probability of this energy transfer depends on concentration of both the species, ion-metal distance and nanoparticle size.

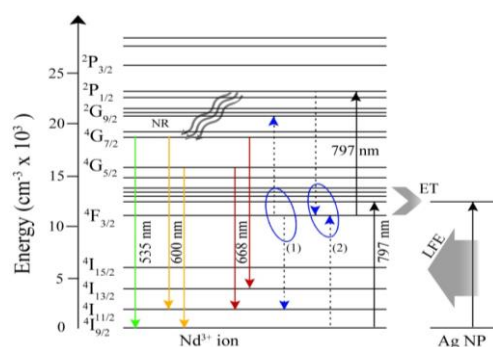


Fig.4. Partial energy level diagram of Nd^{3+} ion in zinc-tellurite glass indicating emissions at 535, 600 and 668 nm.

4. Conclusion

In summary, it has been demonstrated with the present results that luminescence efficiency of rare-earth ion inside the glassy matrix can be controlled and enhanced by the local electric field of silver nanoparticles. These glasses may be commercially exploited in optical memory devices, lasers and optical displays due to their significantly enhanced fluorescence. In our view, this process has the potential to be scaled-up to larger quantities for bulk composites due to its simplicity.

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