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Gold nanoparticles assisted structural and spectroscopic modification in Er^{3+}-doped zinc sodium tellurite glass

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ABSTRACT

Achieving enhanced spectroscopic properties of rare earth doped inorganic glasses by embedding metallic nanoparticles of controlled sizes is a challenging task. We report the gold (Au) NPs assisted modifications in structural and spectroscopic properties of melt-quench synthesized Er^{3+} doped zinc sodium tellurite glass. The growth of NPs is stimulated via time varying heat treatment at 300 °C. XRD patterns confirm the amorphous nature of glasses and TEM images manifest the growth of gold NPs with sizes between 6.1 and 10.7 nm. The heat treatment time dependent variations in physical properties are ascribed to the alteration in bonding of non-bridging oxygen ions. The UV–VIS–NIR spectra reveal six absorption peaks centered at 488, 523, 655, 800, 973 and 1533 nm corresponding to the transition from ground state of $^4I_{15/2}$ to $^4F_{7/2}$, $^2H_{11/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ excited states of Er^{3+} ions, respectively. Surface plasmon resonance (SPR) bands are observed in the range of 618–632 nm. Judd–Ofelt analyses demonstrate a significant increase of spectroscopic quality factors (0.86–1.05) and branching ratio (0.62–92.38%). The up-conversion emission spectra of Er^{3+} exhibit three prominent peaks of reasonable green (502 nm), a moderate green (546 nm) and a strong red (629 nm). An enhancement in the red band luminescence intensity by a factor of 8.19 and 8.54 times are achieved for 2 and 4 h of heat treatments, respectively. This enhancement is attributed to the SPR effects of gold NPs producing an intense local field in the proximity of Er^{3+} ions and subsequent energy transfer between RE ions and NPs. The FTIR spectra display the presence of vibrational modes for ZnO$_4$ bonds, Te–O bond in TeO$_3$ (tp) and TeO$_4$ (tbp) units and the hydroxyl groups. Excellent features of the results suggest that our method constitute a basis for tunable growth of gold NPs which is exceedingly useful for the optimization of optical and structural properties.

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1. Introduction

The never-ending quest of achieving highly efficient up-converted solid state lasers from rare earth doped inorganic glasses opened up a new avenue in glass plasmonics. Lately, the initiative to introduce the coupling between rare earth (RE) ions and metal nanostructures is proven as a precious strategy to enhance the luminescence efficiency and absorption cross-section of RE ions [1–6]. Meanwhile, the RE doped tellurite glasses emerged as promising materials in transmission windows, optical fibers, displays and solid state lasers, to cite a few [1,2]. Metallic nanoparticles (NPs) exhibit unique optical, electronic, magnetic, chemical and thermal properties due to their modified electronic density of states which originates from size and dielectric confinement

effects [3]. Portales et al. [7] established the role of silver (Ag) particles as sensitizer for erbium in silicate and phosphate glasses. They observed the enhancement in the luminescence intensity of Er^{3+} ions with the excitation wavelength in the same spectral range as that of plasmon absorption of silver particles. Besides, Maurizio et al. [8] studied the optical properties of Au–Ag sub-nanometer metal alloy clusters in silica and Er-doped silica thin films by multiple ion implantation followed by systematic annealing procedure. Interestingly, Au and Ag assisted significant enhancement in the luminescence intensity was evidenced.

The incorporation of metallic NPs in the glass matrix has generated great interest due to the potency to modify their structural and optical properties [1,4–6,9–11]. Glass is an excellent medium for growing NPs and their inimitable combination has given further impetus to lasing materials research [12]. Recently, the strong dependence of electronic structure properties of binary glasses on the size and shape of NPs are demonstrated [11,13]. Celebrated Judd–Ofelt (J–O) theory is often used to complement the

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experimental data on absorption and emission characteristics [14]. The J–O intensity parameters Ω_λ ($\lambda = 2, 4, 6$) provided in-depth understanding on the local structure, symmetry, co-ordination and bonding in the vicinity of RE ion [14,15].

It is established that the SPR mediated interactions of metallic NPs in the glass host are responsible for the improvements in optical properties [16]. However, the detail mechanism and the decisive factors of such modifications are far from being understood. It is believed that the emission and absorption features of the lasing glass may be modified by changing the structures and the neighboring states of doping ions [2]. The optical properties of pure gold in UV irradiated photosensitive glass under thermal treatment are reported by Kreibig [17]. The remarkable influence of monodisperse Au NPs on optical response of synchrotron light irradiated soda-lime silicate glasses are demonstrated [18]. Of late, the optical performances of tellurite glasses are manipulated by controlling the size of embedded NPs via thermal annealing. Despite few studies, the influences of metallic NPs on the structural and spectroscopic properties are not clearly documented.

We prepared new kinds of Er^{3+}-doped zinc-sodium tellurite glasses containing Au NPs by using melt-quenching technique. The growth of NPs (sizes and shapes) in the glass matrix is tuned via controlled thermal annealing time. The optical absorption and upconversion (UC) fluorescence are measured. Heat treatment (HT) dependent physical and structural parameters influenced by the growth of Au NPs are calculated. The intensity parameters are determined using J–O theory. Theoretical and experimental oscillator strengths are compared. The data on structural and spectroscopic properties are analyzed and interpreted using different mechanisms. The achieved Au NPs size dependent strong and moderate UC luminescence in red and green bands suggest that these glasses can be nominated for solid state lasers and amplifiers.

2. Experimental

2.1. Samples preparation

Glass samples having composition $70TeO_2$–$20ZnO$–$10Na_2O$–$(x)Er_2O_3$–$(y)Au$ (with $x = 0.0$ and 0.5 mol%; $y = 0.0$ and 0.15 mol% in excess) are synthesized using the conventional melt quenching method. The specific weight of powdered materials of TeO_2, ZnO, Na_2O, Er_2O_3 and Au (analytical grade purity) are mixed thoroughly. A platinum crucible containing these mixtures of glass constituents is placed in a furnace and heated at 900 °C for 25 min. The melt is then casted in a brass mold before transferred to the annealing furnace at 295 °C with holding time 3 h which removes the residual thermal strain and improves the mechanical strength of the glass. The samples are then cooled down to room temperature and subsequently subjected to heat treatment (annealing) at 300 °C for the duration of 1, 2, 4 and 8 h allowing the growth and nucleation of gold NPs. The nominal compositions of glasses without and with erbium at fixed concentration of Au NPs (0.15 mol%) together with their codes under various time of heat treatments are listed in Table 1.

2.2. Characterization

The amorphous nature of glasses are examined via a Bruker D8 Advance X-ray diffractometer which uses Cu Kα radiations ($\lambda = 1.54$ Å) at 40 kV and 100 mA with 2θ ranges from 10° to 80°. The room temperature absorption spectra is recorded in the range of 400–1650 nm by using Shimadzu UV-3101PC scanning spectrophotometer (Kyoto, Japan). Transmission Electron Microscope (TEM) from Philips CM12 operating at 200 kV is employed to image the existence of NPs of distinct sizes. The emission measurement is

Table 1
The compositions (mol%) of glass series with codes and the time durations of heat treatment (HT) performed at 300 °C.

Glass	TeO_2	ZnO	Na_2O	Er_2O_3	Au	HT (h)
TZNEA	70	20	10	0.5	0.15	0
TZNEA-1H	70	20	10	0.5	0.15	1
TZNEA-2H	70	20	10	0.5	0.15	2
TZNEA-4H	70	20	10	0.5	0.15	4
TZNEA-8H	70	20	10	0.5	0.15	8
TZN	70	20	10	0	0	0
TZNA	70	20	10	0	0.15	0
TZNA-1H	70	20	10	0	0.15	1
TZNA-4H	70	20	10	0	0.15	4

performed by Perkin Elmer LS-55 photoluminescence (PL) spectrometer (UK). Fourier transform infrared (FTIR) transmission measurements in the range of 450–4000 cm^{-1} are carried out by a Perkin Elmer FTIR 1660 spectrometer using KBr pellets.

The density (ρ) of the glass is determined by Archimedes method (Analytical balance of specific density-PrecisaXT220A) using the expression,

$$\rho = \frac{W_a}{W_a - W_b} \rho_x \tag{1}$$

where W_α is weight of the glass sample in air and W_b is the weight of the sample when immersed in toluene of density $\rho_x = 0.8669$ - g cm^{-3}. Toluene is used as immersion liquid due to their superior chemical stability against hygroscopic attack to the glass and relatively low toxicity [19]. The molar volume (V_m) is obtained from the equation,

$$V_m = \frac{M}{\rho} \tag{2}$$

where M is the molecular weight of the sample.

The refractive index (n) of glasses are calculated following,

$$\frac{n^2 - 1}{n^2 + 2} = 1 - \sqrt{\frac{E_{opt}}{20}} \tag{3}$$

where E_{opt} is the optical band gap of the glass obtained from the UV–Vis absorption data. The molar refractivity (R_M) yields,

$$R_M = \frac{n^2 - 1}{n^2 + 2}(V_m) \tag{4}$$

where V_m is the molar volume. The polarizability (α_e) of glasses is estimated using the equation,

$$\frac{n^2 - 1}{n^2 + 2}(V_m) = \frac{4}{3}\pi N_0 \alpha_e \tag{5}$$

where N_0 is the Avogadro's number.

3. Results and discussion

3.1. Physical properties

Understanding of physical properties is prerequisite in deciding the optical performance of lasing glass materials [20,21]. The achieved physical properties of our glass samples as summarized in Table 2. All the samples without and with heat treatment are found to be transparent while orange in color. The observed decrease in density from 5.206 to 5.187 g cm^{-3} caused by heat treatment is ascribed to the modification of glass network structure [22] via the rupture of tellurium–oxygen links [23]. The error associated to the measurement of the density is ±0.007. The increase in molar volume from 26.202 to 26.298 cm^3 mol^{-1} is related to the increase in the free volume and the elongation in