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Surface enhanced Raman scattering and up-conversion emission by silver nanoparticles in erbium–zinc–tellurite glass

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ABSTRACT

Enhancing the up-conversion luminescence and Raman intensity in rare-earth doped glasses is an important issue for nanophotonics. Erbium-doped zinc tellurite glass with and without silver nanoparticles (NPs) were prepared using melt quenching method. The effect of NPs concentration and annealing time on the Raman and photoluminescence (PL) response were investigated. The presence of silver NPs with Gaussian size distribution having average size ~12 nm were confirmed by transmission electron microscopy. The Raman spectra consist of six peaks that show red shift. The up-conversion emission exhibits three major visible lines corresponding to the transitions from $^2H_{11/2}$, $^4S_{3/2}$ and $^4F_{9/2}$ excited states to $^4I_{15/2}$ ground state of Er^{3+} ion. An eight times enhancement in the Raman and five times in photoluminescence (PL) intensities were attributed to the large electric field originated from the face-centered cubic silver NPs. Quenching of PL emission in the visible range for longer annealing time interval was observed and attributed to dissolution of the growth of NPs in the host glass. The prominent absorption plasmon bands of silver were also evidenced that confirms the non-spherical shape of nanoparticles.

1. Introduction

Raman spectroscopy is a powerful technique to study the vibrational modes of molecules through inelastic scattering of a monochromatic excitation source in the routine range of 200–4000 cm^{-1}. Molecular vibrations are either infrared (IR) and/or Raman active. Therefore, Raman technique is mainly used to complement the IR measurements. The efforts to improve the detection ability by Raman spectroscopy have yielded the Surface-Enhanced Raman Spectroscopy (SERS) [1] technique, where the enhancement factor up to 10^{10}~10^{11} times may be exploited to detect a single molecule [2–5]. The enhancement is due to the intense localized electromagnetic field in the interface of the surface of metallic nanoparticles (NP) and dielectric medium. Furthermore, the topological change of NPs in dielectrics promotes the local electric field further by lightening rod effects (LRE) at surface of non-spherical NPs (elliptical, cube, pyramid shapes and so on) which can enhance the intensity of scattered Raman signal up to 10^{14} times [3]. This phenomenon is typically discussed in the field of plasmonics [6].

Surface plasmon resonance (SPR) is the basic concept of plasmonics which describes the interaction of the light with metallic surface. Oscillations of electronic cloud of metallic NPs when excited by the light with wavelength larger than the size of particles result in strong field around these nanostructures. Firstly, the excitation light is enhanced by the large localized electric field between two NPs and the Raman modes of probing molecule will be enhanced by a factor of η^2, where η is the enhancement factor. Moreover, the emitted Raman signals experience further enhancement by same SPR effect. Therefore, output Raman signal is enhanced by a factor of η^4 [7]. The maximum enhancement happens near the plasmon frequency (ω_P) [8]. Even if, the plasmon resonance may not be efficient in special cases, LRE aims to confine the large electric field in the sharp edges of metal surface or at curved surfaces.

The dielectric hosts with high nonlinearity provide better confinement of localized field. Therefore, SPR has been known, recently, a remarkable phenomenon to enhance the fluorescence emissions from rare earth (RE) doped heavy metal glasses. In 1985, Malta [9] reported the enhancement of emissions in Eu^{3+}-doped silicate glass due to introduction of silver particles. Very few studies have been made on such enhancements of RE-doped materials in the past. It is only in the last decade that numerous efforts have been made in order to increase the luminescence intensity of Er^{3+} [10], Sm^{3+}[11], Pr^{3+}, Tm^{3+}, Eu^{3+} and Nd^{3+} [12 and references within] doped glasses by noble metallic NPs (Au and Ag). Moreover, the reactivation of Raman signals has been studied in an Ag NPs-deposited thin films prepared by silicate glass as the

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substrate and observed enhancements of Raman scattering have been attributed to the surface plasmon excitation of silver particles [13]. Upender et al. [14] showed that the enhancements of Raman signals by Ag nanoclusters deposited on glass substrate is higher than that of p-type Si(100) substrate. However, to the best of our knowledge, the study of the mechanism of SERS by SPR of Ag NPs embedded in the bulk tellurite is not available and is far from being understood.

Among the known hosts to embed the REs, tellurite glass shows superiority due to the large linear and nonlinear refractive indices, high solubility of RE ions, good chemical, mechanical and thermal stability, large density and low cut-off phonon energy [15,16]. Optical and structural properties of Er^{3+}-doped zinc tellurite glasses have been investigated widely [16–18]. However, there is no report on the influence of the silver NPs on PL and Raman signals of this glass. The aim of the present report is to synthesize the Er^{3+}-doped zinc tellurite glasses containing silver NPs and to investigate their spectroscopic characteristics by PL and Raman spectroscopy. The effect of the concentration of NPs and annealing time on the optical behavior are discussed and analyzed.

2. Experimental procedure

The glasses with composition $(80-x)TeO_2$–20ZnO–$1Er_2O_3$–xAgCl ($x=0$, 0.5, 1.0, 2.0) were prepared by melt quenching method. Here and after, they will be referred as E1AxHt, where x and t represent the concentration of AgCl and annealing time respectively above the glass transition temperature (T_g). The well-mixed powder was melted in porcelain crucible at 800 °C for 15 min and then poured between two preheated stainless steel plates at 300 °C and kept inside the furnace for 3 h before cooling gradually down to the room temperature. The samples with $x=0.5$ and 1 mol% AgCl were prepared in two different molds, where the second sample of each composition was annealed at 350 °C. The measured glass transition temperature of zinc tellurite glass is about T_g~320 °C [18].

SPR frequency of sample with 0.5 and 1 mol% AgCl was measured by synthesizing two new samples to avoid the overlap of strong absorption peaks of Er^{3+} ions with SPR bands in the spectrum. The crystallographic nature of the glass was examined using a Bruker D8 Advanced diffractometer (by a Cu Kα radiation, $\lambda=1.54$ Å working at 40 kV and 100 mA). The Shimadzu (UV-3101PC) spectrophotometer was used to obtain the absorption in UV–vis region with a resolution of 0.5 nm. The Raman spectrum was taken using a confocal Horbia Jobin Yvon (Model HR800 UV) in the range of 200–2000 cm^{-1}. The argon ion laser operating at 514.55 nm was used as the excitation source with 5 mW power. The up-conversion spectrum of Er^{3+} ions was recorded using a Perkin-Elmer (LS 55) PL spectrometer, under 786 nm excitation originated from a Xenon flash lamp. Transmission electron microscopy was carried out by a 200 kV TEM (JEOL 2100).

3. Results and discussion

The X-ray diffraction (XRD) pattern of the based erbium-doped zinc tellurite glass sample is presented in Fig. 1. The presence of no sharp crystallization peak and a broad hump between $2\theta=20°$ and 30° confirms the amorphous nature of the prepared glass. The refractive index of the glasses varies between 2.360 and 2.364, for sample without Ag NPs (E1A0H0) and the sample containing 1 mol% of AgCl (E1A1H0) as given earlier [18]. Fig. 2a shows the plasmon peaks of silver NPs in the zinc tellurite glasses in the absence of Er^{3+} ions. The glasses containing 0.5 mol% AgCl (E1A05H8) shows three prominent plasmon peaks at 562,598 and 628 nm, while the sample containing 1 mol% AgCl (E0A10H8) reveals two peaks at 550 and 578 nm, after 8 h of annealing at 350 °C. Occurrence of different plasmon peaks of the silver NPs can be attributed to the presence of non-spherical metallic NPs which oscillate in two different frequencies corresponding to their longer and shorter oscillation axis [19]. Fig. 2b shows the TEM image of E1A0.5H8 that confirms the average size of ~12 nm. The presence of NPs with non-spherical shapes is clearly evidenced. The relative abundance of the NPs size in the sample E1A0.5H8 (Fig. 2c) shows the Gaussian size distribution. Moreover, Fig. 2d presents the high resolution transmission electron microscopy (HR-TEM) of the sample E1A10H8. The silver lattice fringe corresponding to (311) plane is observed with spacing about 0.125 nm (JCPDS card no. 04-0783).

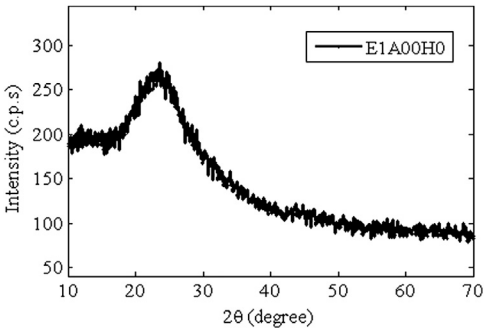

Fig. 1. XRD pattern of the sample E1A00H0 confirming the amorphous nature of the based glass.

Silver NPs are formed from AgCl throughout the melting procedure and grown during the annealing. Moreover, the heat-treatment above the glass transition temperature allows the metallic NPs to aggregate and grow, where the viscosity of the glass is enough for NPs to travel along the glass. The choice of intermediate time interval for heat-treatment and suitable annealing temperature also lead to avoid any crystallization in glass resulting in the formation of glass-ceramics. The reduction of the silver NPs can be discussed by the reduction potentials (E°) of redox system elements, as [20,21]

$$Ag^+/Ag^0 = 0.7996\ V, \quad (1)$$

$$Er^{3+}/Er^0 = -2.331\ V, \quad (2)$$

$$Er^{3+}/Er^{2+} = -3.0\ V, \quad (3)$$

$$Te^{6+}/Te^{4+} = 1.02\ V, \quad (4)$$

Following reduction processes are likely to ensue

$$Te^{4+} + 2Er^{3+} \rightarrow Te^{6+} + 2Er^{2+} \quad \Delta E^o = -7.02, \quad (5)$$

$$3Te^{4+} + 2Er^{3+} \rightarrow 3Te^{6+} + 2Er^0 \quad \Delta E^o = -7.722, \quad (6)$$

$$Te^{4+} + 2Ag^+ \rightarrow Te^{6+} + 2Ag^0 \quad \Delta E^o = +0.5792, \quad (7)$$

where ΔE° is the total potential of reduction process. The only feasible reaction (with $\Delta E^\circ > 0$) is equation (7) which guarantees the presence of Ag NPs in the system in addition to the UV–vis absorption results and TEM images.

Fig. 3a presents the Raman spectra of studied samples. The peaks centered at 280, 366 and 603 cm^{-1} belongs to the linkages in the bulk matrix that show maximum enhancements of 8.62, 8.29 and 8.18 times respectively. The enhancements may be attributed to the SPR contribution which enlarges the local electric field. The increased concentration of silver NPs intensified the Raman signal, while the grown NPs (in samples with HT, such as