Influence of silver nanoparticle on Raman and photoluminescence of heat treated Ag-Er codoped tungsten tellurite glasses

Sunil Patidar1, Ghizal F Ansari1 and S K Mahajan2*

1Physics Department, Madhyanchal Professional University, Bhopal (M.P.) 462044, India
2Departments of Applied Physics, Samrat Ashok Technological Institute, Vidisha (M.P.) 464001, India
*Corresponding author’s e-mail address: sachin_k_mahajan@rediffmail.com

Abstract. The glasses of composition TeO2-WO3-Li2O-Er2O3 with AgNO3 (TWLEOAG) were prepared by the high-temperature melting method. Surface Plasmon resonance (SPR) bands are observed in the range 520-535 nm and 640-650 nm of without erbium-doped glass by absorption spectrum. The TEM measurement reveals the presence of spherical AgNPs in this glass. The DSC has also been analyzed for the stability of transition temperature Tg and on set crystallization To of this glass system. The Raman spectrum revealed that TWLEOAG glasses were mainly formed by the [TeO4], {TeO3}, [WO4] and [WO6] units and [TeO4] units convert to [TeO3] units with the addition of WO3 and Li2O content into tellurite glasses system. In particular TWLEOAG05 glass samples, heat-treated different time interval system reveal the enhancement in Raman peaks intensity with small shift in due to Ag nanoparticle. Also photoluminescence enhancement of red upconversion compare to green emission of TWLEOAG05 for different annealing duration has been observed under 808 nm excitation. In this work optimum 0.5 mol% AgNP in TWE0AG glass would be useful for optical devices.

1. Introduction
In past decades tellurite based glasses with rare-earth ions have attracted much attention due to nonlinear properties, exhibit good infrared transmission and low phonon energy but could not improve the chemical and glass-forming ability of glass with addition of other oxide [1,2]. In most of tellurite glasses WO3, Bi2O3, PbO also are mixed to provide better stability, to improve the glass-forming ability and optical properties [3] for their promising applications in optical devices and photonics. Further Li2O or other alkali oxides are also mixed as a glass modifier, which changes its internal structure due to the formation of non-bridging oxygens [4]. When doping with rare-earth (RE) ions in such tellurite based glass host material may yield new material with modified in optical properties. It is also know that optical signal of RE ions will be enhance with codoping of other ions such as Yb3+ ions. Another way to embed nanoparticle (NPs) with rare-earth ions in glasses lead to enhance the optical emission. [5]. This enhancement may be progressed in the presence of the intense localized electromagnetic field in the interface of the surface of metallic Ag or Au nanoparticles (NPs) and dielectric medium. In such a situation, RE ions, photonic mode density would be enhanced tremendously by the interaction between the metal particle and rare-earth ions. Moreover, there is a limit of high concentration dopants beyond which tellurite glass displays luminescence quenching through energy transfer with Ag NPs in presence of alkali material. R.J. Amjad et al. [6] have reported the surface enhanced Raman and upconversion emission in Er3+-doped zinc-tellurite glasses contain silver NPs, and an enhancement by about four times in Raman signal and up to three times in
upconversion emissions of Er\(^{3+}\) ions was observed. M.R. Dousti et al. [7] have studied an efficient upconversion emission in Nd\(^{3+}\)-Ag doped tellurite glasses for enhanced upconversion emissions of Nd\(^{3+}\) under the excitation of 800 nm. Thus in addition of silver compound in telluride based glasses are investigated for new results due to low toxicity, low signal attenuation, absorption and impurities of optical glasses for biomedical and Fiber communications applications. The present work we have examined the influence of heat-treated samples of metallic NPs and erbium-doped tungsten tellurite glasses for the Raman and photoluminescence measurement. This study wills helpful Raman signal amplification for optical devices.

2. Experimental Method

The glass samples were prepared with high purity (99.9\%) chemical powders according to compositions in mol% of 70TeO\(_2\)-15Li\(_2\)O-14WO\(_3\)-1Er\(_2\)O\(_3\)-xAgNO\(_3\) (x = 0, 0.5, 1.0 in mol %). About 4-6 gm batches of starting materials were melted at 950\(^\circ\)C-1050\(^\circ\)C in alumina crucible about 30-45 min. The melts were cast to form glasses by pouring it on stainless steel plate heated at 150\(^\circ\)C. These glass samples with and without Ag were annealed at 300\(^\circ\)C for 3h. All samples again submitted for heat treatment at 350\(^\circ\)C continuously for long duration to thermally reduce Ag\(^{+}\) ions into Ag\(^{0}\) which is needed to nucleate metallic nanoparticles and two were selected with Ag (x=0.5) for 18h and 30h for optical measurement. For the SPR absorption band of the glass was recorded by UV/VIS/NIR spectrometer (GBC Scientific equipment) in the range 400-900nm. Differential scanning calorimeter (DSC) was conducted with a Perkin-Elmer DSC 4000 instrument, at a heating rate 10\(^\circ\)C min\(^{-1}\), between 150\(^\circ\)C and 450\(^\circ\)C. The Transmission Electron Microscope (TEM) operating at 200kV was employed to confirm the presence of the silver NPs. The Raman spectrum of the glass sample was measured in the range 200-1100 cm\(^{-1}\) by W1 Tech Alpha 300R confocal Raman microscope with Ar\(^{3+}\) ions laser wavelength 514.5nm at power 15mW was used. The photoluminescence upconversion of glasses was obtained in range from 400nm to 700 nm by using a model Ava Spec 2048 Avantes, Fibre Optics Spectrometer excited by CW 808nm diode laser.

3. Result and discussions

Figure 1 shows absorption spectra in room temperature of without Er\(^{3+}\) ions doped TWLOAG (with Ag 0.5 mol%) glass heated 18 hrs sample and different wavelength of the absorption bands of this sample clearly indicates the presence of silver. Thus surface plasmon bands (SPR) of the silver denoted the presence metallic AgNPs may be in form of spherical and non-spherical [8]. It is noted that of SPR band then SPR band will move to longer wavelength as if refractive index of the glass material is higher, [9]. Also altering heat treating duration and AgNPs concentration of glasses modifies the optical properties.
The pattern of DSC curve of TWLOAG glasses (annealed for 3hrs) heating at rate 10 °K/min of as shown in figure 2. This sample curve suggest glass transition temperature $T_g = 330°C$ and $T_x$ glass exothermic peak at $380°C$. Thus small value $\Delta T$ fast nucleation and crystallization for AgNPs growing and therefore crystallization may starts at $370°C$. Hence, the glasses are heat-treated at $350°C$ were the viscosity of the sample is enough to move, grow and aggregate for effective optical properties. In this glass Li$_2$O is taken between 5 to 10 mol% results in a decrease of $T_g$ [10,11] that lead to the cleavage of the networks formed by TeO$_4$ trigonal bipyramid units and the increase of non-bridging oxygen (NBO) atoms. Figure 3 showed the TEM image of the TWLEOAG 18h glass sample with spherical and non-spherical silver NPs are gathered. The size of NPs varies between 35nm-40nm, with average value 38nm.

![Figure 3. TEM image of Ag NPs in TWLEOAG (0.5) 18h glass.](image)

Raman spectra of TWLEOAG (Ag 0.5mol%) samples for 18hrs and 30hrs heat-treated glasses gives the main Raman peaks are centered at 281, 367, 761 and 930 cm$^{-1}$ belongs to the linkages in the bulk matrix as shown Figure 4. Due to the limitation of Raman measurement for all glass samples at low-frequency Boson band region (< 200 cm$^{-1}$) may not be observed. However this band peaks are nearly same for different glasses and does not normally depend on chemical compositions [12] but it may affirm the presence of glass structure. Raman peaks above the wave number 200 cm$^{-1}$, increase

![Figure 4. Raman spectra of 18h and 30h heat-treated TWLEOAG glasses](image)
broad shoulder at 340 cm\(^{-1}\) is occurs on account of symmetric and flexible vibration of Te-O-Te chain. Further band peak at 780 cm\(^{-1}\) is attributed to anti symmetric vibration of Te-O bond in TeO\(_3\) trigonal pyramid (tp) units due to stretching vibrations of TeO\(_3\) and/or TeO\(_4\) [13]. This non-bridge between oxygen and tellurium can be broken easily by rare-earth cations for weak binding energy. This band agrees well with the reported spectrum of the nearly same composition tellurite tungsten glass in ref. paper [14, 15]. The highest peak at about 930 cm\(^{-1}\) is observed corresponds to the stretching vibrations of W=O and W-O- bonds associated with WO\(_3\) and WO\(_6\) groups [16]. Compare to other oxide glass such as silicate, phosphate and borate glass [17], maximum phonon energy of this tellurite glass (930 cm\(^{-1}\)) is smaller.

We have observed the Raman intensity enhancement of embedding silver NPs in TWLEOAG glasses heated in different duration. For selected sample TWLEOAG(0.5) 18 hrs give maximum fivefold enhancement compare to TWLEO (without AgNPs) glass due to local electromagnetic field which is surface-enhanced Raman scattering effect [18]. However this sample gives 20% more enhance Raman peaks intensity as compare to TWLEOAG(0.5) 30 hrs sample. In our measurement TWLEOAG(0.5) glass sample Raman broad peaks centered at 210 cm\(^{-1}\) is shifted to 213 cm\(^{-1}\) and these are assigned to W-O stretching and O-W-O linkage bending vibration [16] and thereby numbers of NBO sites are proportionately increased. But band intensity around 352–355 cm\(^{-1}\) and 450–452 cm\(^{-1}\) showed the characteristics of the corner-linked octahedral in WO\(_3\) as in ref. [19] for niobium oxide. Hence with the addition of Ag NPs in glass indicating the conversion of the TeO\(_2\) (tpb) units into TeO\(_3\) (tp) units lead to intensity of all Raman bands are first increased and decreased, and then maximum intense [20]. Thus in our Raman measurement, selected only 0.5 mol% Ag NPs doped glass samples with different heat treated duration results can be compare to ref. [21] reported Raman Intensity for 1 mol% AgNPs tellurite-based glass.

![Figure 5. Emission spectra of TWLEOAG samples for the different heating duration under 808nm excitation.](image)

The red and green photoluminescence upconversion are observed under 808 nm laser excitation of silver doped TWLEOAG glasses annealed for 18 h and 30 h and without silver doped glass for their comparison as shown in figure 5. On increasing the annealing duration of 0.5 mol% AgNPs doped TWLEOAG glass emits green at 550 nm transition \(^4S_\text{V} \rightarrow ^4I_{15/2}\) intensity increase due to transverse SPR and on the other hand TWLEOAG(0.5) 18h glass emits enhance red upconversion \(^4F_\text{V} \rightarrow ^4I_{15/2}\) intensity due to longitudinal SPR as reported in ref [22]. However the maximum red upconversion enhancement (2 fold) is measured, which is due to local field enhancement or and energy transfer (ET) from Ag NPs to Er\(^{3+}\) ions but for broad red band emission ET process is more probable. Also more likely scattering or re-absorbance of excitation light lower the green emission at 550 nm intensity.
which is around plasmon band. Thus tune ability of green to red intensity enhancement can be maintained with increases annealing duration TWLEOAG glasses.

Figure 6 shows energy transfer from AgNPs to Er$^{3+}$ ions, during ground state absorption 808nm photon the first excited at to the $^5F_{2}$ level of the Er$^{3+}$ ion and then quickly decays non-radiatively to the $^5H_{11/2}$ and $^5S_{3/2}$ levels [23-24] from which the upconversion transition of green emission takes place. After then fraction of Er$^{3+}$ ions in the $^5S_{3/2}$ states would decay non-radiatively into the slightly lower $^5H_{11/2}$ energy level where the red upconversion transition originates. One additional path for the red emission comes from the energy transfer upconversion of Er$^{3+}$ ion from $^1I_{15/2}$ level which is populated by non-radiative decay from the $^1I_{11/2}$ level. There are other processes that compete with upconversion processes such as radiative and non-radiative decays from AgNPs ions to $^4I_{11/2}$ level of Er$^{3+}$ ions, and cross-relaxation of Er$^{3+}$ ion pairs. But cross-relaxation of Er$^{3+}$ ions is a major quenching mechanism at high Er$^{3+}$ concentrations [25,26]. Main result of this work sample heat treated by 18hrs presents enhancement in red upconversion photoluminescence as well as Raman signal. Furthermore, in presence of AgNP with RE ions doped TWLEOAG glasses show intensity variation in Raman and upconversion emission intensity denote no evidence of the formation of clusters.

Figure 6. Energy-level diagram of AgNPs and Er$^{3+}$ ions TWLOAG glass

4. Conclusions
The influence of silver nanoparticles on the Raman structure and photoluminescence of heat treated Ag-Er$^{3+}$ codoped tellurite glasses were investigated. Absorption and TEM measurement confirm the Ag nanoparticles exist in the glass matrix. However, not much large temperature difference of DSC curves indicating that favourable for Ag NPs nucleation growth and crystallization. The Raman spectra indicate TeO$_4$, TeO$_3$, TeO$_3+$1, WO$_4$, WO$_6$ structural units are small shifted and five-fold enhancement of the TWLEOAG(0.5)18hrs glass comparatively to without Ag doped glass has been observed. Also relative red upconversion intensity at 650nm due to SPR band enhances as compare to green upconversion intensity at 808nm excitation. In our work better result of TWLEOAG(0.5) 18hrs (0.5% mol Ag) glass for Raman spectra and upconversion emission reveals the strong influence of Ag NPs on the different heat-treated glass will provide a potential application for optical devices.

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