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# ENHANCED OPTICAL PROPERTIES OF $TeO_2$-PbO-$PbCl_2$-$Er_2O_3$-$AuCl_3$ GLASS

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Rare earths (RE) doped inorganic glasses are attractive due to their excellent optical performance. Light energy up-conversion of such glass is the key issue. Nanoparticles (NPs) dispersed up-converted (UC) glasses seem to be the ideal candidates in terms of both efficiency and large area coverage provided the absorption cross-section be enhanced. The glasses containing gold NPs doped with optimum concentration of RE ions are of particular interest to us. We report the influence of embedded gold NPs on the luminescence and absorbance characteristics of erbium ($Er^{3+}$) ions doped tellurite glass prepared by melt-quenching method. The absorption and emission spectra displays several prominent peaks corresponding to the transitions from the ground state to the excited states of $Er^{3+}$ ion. The observed efficient enhancement of up-conversion emissions and absorbance in the entire visible region is attributed to strong localized electric field in vicinity of NPs. Improvements of radiative emissions suggests that the proposed glasses are potential for the development of solid state lasers, color displays and nanophotonic devices.

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*Keywords:* Gold nanoparticles, Rare earth, Tellurite glass, Luminescence, Absorption

## 1. Introduction

Tellurium oxide ($TeO_2$) based glasses are attractive due to their high efficiency towards the development of optical devices [1-3]. Besides, the understanding of the microscopic mechanism related to optical enhancement is fundamentally interesting for both academic and the industry [4]. The large third-order nonlinear optical susceptibility of tellurite glass containing RE elements are promising for diverse applications [5]. The interaction of light with such glasses containing metallic NPs received tremendous attention due to their relevance in optoelectronics, photonics and optical telecommunications [6] Furthermore, RE doped tellurite glasses are excellent host matrix for the formation, growth and diffusion of NPs into the network [7-10]. The transitions intensities of RE ions strongly depend on the environment and greatly influenced by metal NPs that significantly enhance the RE fluorescence [11]. The incorporation of metallic NPs in glass matrix has generated renewed interest due to the considerable improvements of structural and optical properties [12-13].

We prepare a series of $Er^{3+}$ doped lead-tellurite glass without and with gold NPs is using the conventional melt-quenching method and perform optical characterization. The UV-Vis absorption and UC luminescence show significant improvement in the presence of Au NPs. The mechanism for the influence of the gold NPs in enhancing the red and green emissions of $Er^{3+}$ ions are analyzed, compared and understood.

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## 2. Experimental

A series of $Er_2O_3$ doped $TeO_2$-PbO-$PbCl_2$ glasses without and with 0.1 mol% $AuCl_3$ NPs are synthesized. TEM analyses are carried out using Philips CM12 operating at accelerating voltage. The room temperature optical absorption measurement is performed in the wavelength range of 200-1000 nm using UV-Vis-NIR spectrophotometer and the luminescence spectra is obtained using Nanosecond Luminescence Spectroscopy System, Ekspla Model NT340/1 tunable Nd:YAG laser system and scanned in the wave-number range of 200–900 $cm^{-1}$. Xenon lamp ($300 < \lambda < 1300$ nm) is used as a pumping source.

## 3. Results and discussion

The TEM image of the glass with 0.1 mol% $AuCl_3$ is shown in Fig. 1(a). A homogenous distribution of gold NPs inside the glass matrix with estimated average diameter ~6.09 nm is displayed. Fig. 1(b) shows the appearance of Gaussian NPs size distribution ascribed to diffusion limited growth [14]. The occurrence of broad size distribution is due to non-homogenous distribution of $Au^+$ ions into the glass grown at different times. The shapes of the NPs exert prominent effects in the optical absorption spectra of metal NPs compared to the size and surrounding (matrix) effect [15]. The fusion of Au NPs within glass matrix restricted the electromagnetic energy or optical excitation in a nanoscale volume and the local field enhancements mediated strong optical interactions within this volume [16].

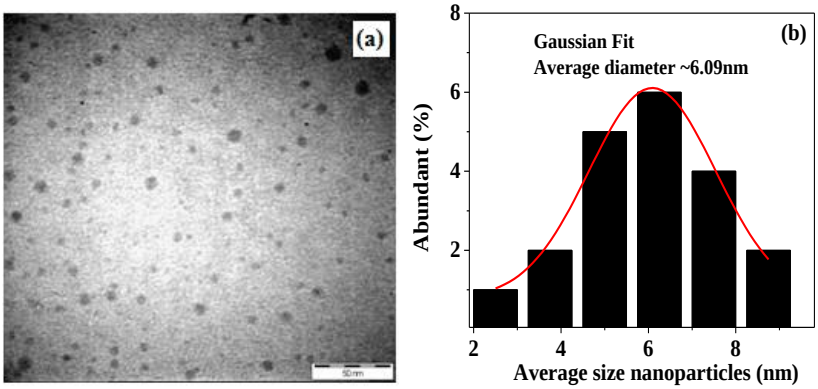


*Fig. 1(a): TEM image of the glass with 0.1 mol% $AuCl_3$.*
*(b) Histogram of Au NPs size from figure (a).*

Luminescence measurement renders the signature materials capability to absorb and reemit energy [17]. Fig. 2 shows the luminescence spectra of the glass without and with 0.1 mol% Au. Under 779 nm excitation, three emission bands corresponding to $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$, and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions of erbium are observed. The luminescence peak of $Er^{3+}$ in red region is evidenced in the absorption spectra as shown in the inset of Fig. 2 with magnification. The obtained emission peaks of $Er^{3+}$ doped tellurite glass system cofirms the presence of erbium trivalent state that results large luminescene efficiency.

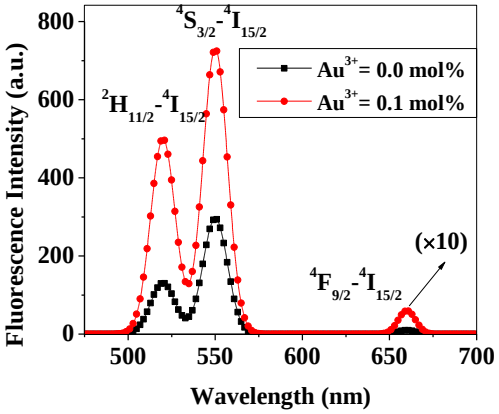


*Fig. 2: Photoluminescence spectra of $Er^{3+}$ doped tellurite glass with Au NPs.*

A change in the emission profile with the introduction of Au NPs is clearly noticeable. Furthermore, the glass containing Au NPs possess higher intensities for all emission bands. The enhancement in the green intensity associated with $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions is described to the increase of local field due NPs present in the vicinity of RE [7]. The red emission also shows enhancement due to the introduction of Au NPs. Other possible mechanism may be the energy transfer from gold that remain in the form of ions, atoms, charged or neutral dimmers and multimmers [7]. Undoubtedly, the incorporation of Au NPs in the glass host cause significant modifications of the network structure and consequently the local environment of RE ions. The enhancement of photoluminescence originates from the field change on local structure. The localized surface plasmons are generated from collective excitation of the conductive electron due to the interaction of NPs with irradiated light beam (oscillating electric field) are the source of strong local field. Other possible mechanism of enhancement may be the energy transfer from gold that remain in the form of ions, atoms, charged or neutral dimers and multimers [18]. The emergence of enhanced local field is related to the difference between the relative permittivity of the surrounding host matrix and the Au NPs [4].

The absorption spectra exhibit six absorption bands in the visible regions centered at 490, 526, 652, 800, 982 and 1520 nm corresponding to the transition from ground state to the $^4F_{7/2}$, $^2H_{11/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^2H_{11/2}$ and $^4I_{13/2}$ excited states, respectively. The increase in absorption in the visible range due to the presence of Au NPs is attributed to the drastic reduction in transmission caused by metallic structures. This observation is in agreement with other findings [19, 20].

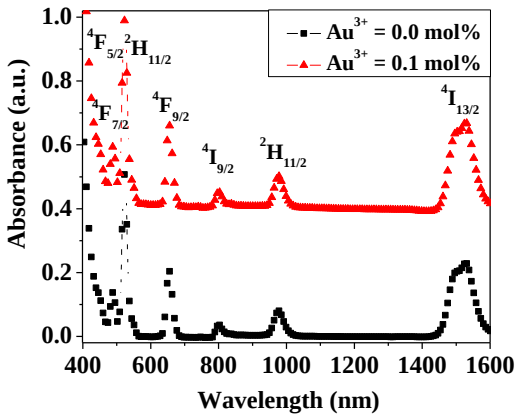


*Fig 3: Absorption spectra of glasses with different 0.1 mol % $AuCl_3$.*

## 4. Conclusions

$Er_2O_3$ doped glasses of the form $TeO_2$-PbO-$PbCl_2$ embedded with and without $AuCl_3$ NPs are successfully prepared using conventional melt quenching technique. TEM micrograph confirms the existence of NPs and with homogenous distribution inside the glass matrix having average diameter ~6.09 nm. The luminescence spectra consists of emission peaks for $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions (green) and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition (red) display significant enhancement due to the introduction of Au NPs. The absorption spectra comprised of six bands with different relative intensities reveal increased absorption in the presence of NPs. Our systematic characterization and analyses of improved optical properties may contribute towards the development of tellurite glass based up-converted solid state lasers.

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