# Realization of efficient red laser using europium doped new boro-telluro-dolomite glass hosts: Ag nanoparticles functionality

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**Abstract**. Achieving highly efficient visible red emission with high color purity from the rare earth ions doped glasses containing metallic nanoparticles is of scholastic significance in the quest of novel laser glass host. Stimulated by this demand, we synthesized some new class of silver nanoparticles (Ag – NPs) embedded europium ions ($Eu^{3+}$) doped boro – telluro – dolomite glasses (hereafter coded as BTDEA$x$, where $x$ = 0.0, 0.1, 0.3, 0.5, 0.8 and 1.0 mol%) by convectional melt quenching method. These glasses were optically characterized using UV – Vis – NIR absorption and photoluminescence (PL) spectroscopy's to ascertain their lasing candidacy. The absorption spectra of the $Eu^{3+}$ ion free sample (BTDA0.8) disclosed a single surface plasmon band characteristic of Ag – NPs at 464 nm. Meanwhile, the visible emission intensities (excited with 467 nm wavelength) of the glasses due to Ag – NPs inclusion were greatly intensified. Of all glasses, the sample prepared with 0.8 mol% of Ag NPs (BTDEAg0.8) revealed highest PL intensity enhancement. Furthermore, the attainment of high color purity (97.037 %) detected from the CIE diagram with chromaticity coordinates (0.63765, 0.36094) close to ideal red color phosphor (0.67, 0.33) indeed approved the suitability of the proposed glasses for solid state red laser construction.

## 1. Introduction

Synthetic rare earth doped calcium boro – tellurite (CBT) glasses owing to their remarkable properties such as low melting point, easy preparation, high rare earth solubility, good thermal stability, relatively low phonon energy and wide optical window transparency (350 – 2600 nm) have generated intense research interests over the past few decades [1-6]. These glasses offer significant applications in lasers, solid state lighting (SSL), display devices, sensors, telecommunications and optical amplifiers [7, 8]. Moreover, the high cost and hydroscopic property allied with the commercially chemical powder based glasses remains the key issue in achieving efficient luminescent glass host for the present and next generation technologies. To circumvent these shortcomings, in our recent studies we pioneered with

naturally stable and cost effective dolomite into boro – tellurite (BTD) glass host [9]. Indeed, this fusion produced better glass system with high optical filter prospective. Conversely, the luminescence performance of BTD glasses which disclosed the aptness of the glassy material for optical device fabrication to the best of our knowledge has not been reported.

Depending on the target applications, doping a glass host with rare earth (RE) ions can produce a new luminescent material to be exploited in devices [10]. However, low emission efficiency and the small absorption coefficient from RE doped glasses limit its practical applications [11]. The noted demerits can be defeated by introducing small amount of metallic nanoparticles into the host matrix to modify the emitting centers through surface plasmon resonance (SPR) [12, 13]. It has been established that the excitation of SPR in metallic nanoparticles induces significant enhancement in luminescence characteristics thereby yielding a wide range of technological usage [14]. Exclusively, the phenomenon of improving luminescence response in europium doped glasses by SPR of Ag nanoparticles has been described by many scholars [15-18].

Prompted by these benefits of Ag– NPs/$Eu^{3+}$ co – doped glasses, we prepared a novel series of $Eu^{3+}$ doped boro – telluro – dolomite glasses containing Ag nanoparticles to determine their lasing and visible light emission potency due to silver nanoparticles Ag – NPs inclusion. Additionally, the absorption and emission spectra were analyzed to verify their feasibility for solid state lasers and light emitting device applications. The functionality of Ag – NPs and its effects on $Eu^{3+}$ absorption and emission traits were emphasized.

## 2. Methodology

### *2.1. Glass synthesis*

The Ag nanoparticles embedded $Eu^{3+}$ doped boro – telluro – dolomite glasses with molar composition of $34B_2O_3 – 30TeO_2 – 20Dp – 15Dm – 1Eu_2O_3 – x$Ag NPs (Coded as BTDEA*x,* where $x$ = 0.0, 0.1, 0.3, 0.5, 0.8 and 1.0 mol%, Dp: Dolomite pebble and Dm: Dolomite marble) were synthesized by convectional melt quenching technique. High purity (99.99%) analytical grade chemicals such as tellurium dioxide ($TeO_2$), Boric acid ($H_3BO_3$), europium oxides ($Eu_2O_3$) and Ag– NPs purchased from sigma Aldrich together with dololomite $CaMg(CO_3)_2$ were used as raw materials for the glass preparation. About 15 g of the batch composition was thoroughly mixed in an alumina crucible and melted at 1200 ℃ for 1 h 30 min in an electrical furnace (Model, Nabertherm GmbH). Next, the melt was poured on a preheated stainless steel plate in a muffle furnace (Model, Nabertherm GmbH) and annealed at 500 ℃ for 3 h to release its thermal strains. Afterwards, as –prepared samples were polished for spectroscopic measurements

### *2.2. Samples characterizations*

The absorption spectra of glasses were recorded in the wavelength range 380 – 2300 nm using a Perkin-Elmer lambda 950 UV-VIS-NIR spectrophotometer that operated with a spectral resolution of 1.0 nm. The luminescence spectra of as-prepared samples in the wavelength range of 400 – 750 nm were measured using Perkin-Elmer LS55 spectrophotometer with a spectral resolution of 1.0 nm.

## 3. Results and Discussion

### *3.1. Absorption spectra and SPR band*

Figure 1a displays the UV– Vis – NIR absorption spectra of the glasses. Obviously, surface plasmon resonance (SPR) band of silver was not observed in these spectra due to the dominance of $Eu^{3+}$ absorption and spectral overlap. In this view, one sample free of $Eu^{3+}$ that contained 0.8 mol% of Ag – NPs (BTDA0.8) was prepared in order to monitor the SPR band. The broad SPR band of Ag – NPs in the BTDA0.8 glass (figure 2) was probed at 464 nm which is in accordance with the previous findings on other Ag/$Eu^{3+}$ co – doped glasses [19, 20].

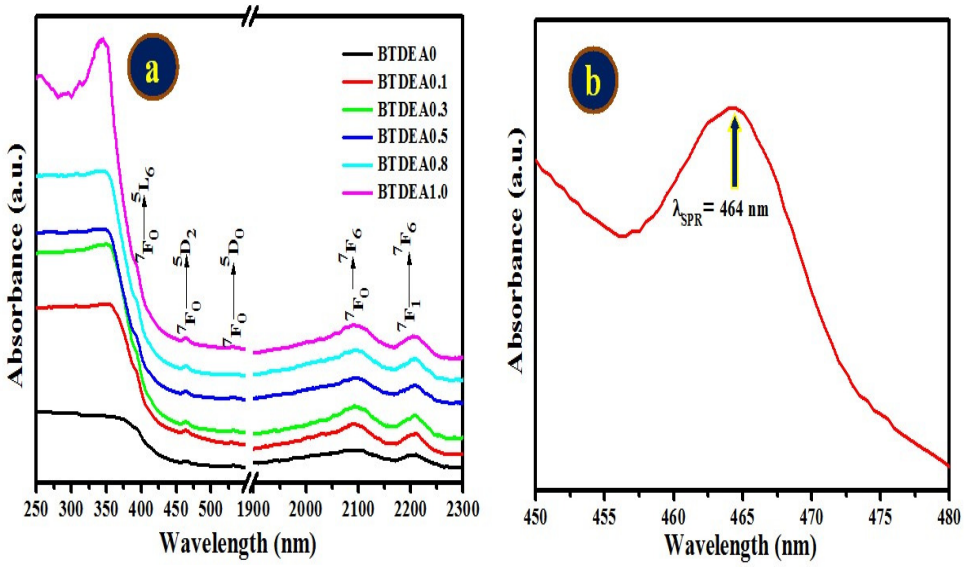


**Figure 1.** (a) Absoprtion spectra of Ag – NPs embedded $Eu^{3+}$ doped BTD glasses and (b) SPR band at 464 nm for $Eu^{3+}$ free BTD glass (BTDA0.8 sample).

*3.2. Luminescence spectra*

Figure 2 illustrates the three dimensions (3D) luminescence emission spectra of the BTDEA$x$ glasses (excited with 467 nm wavelength). The top inset pie chart shows the emission intensities enhancement at $^5D_0 \rightarrow 7F_2$ transition due to Ag-NPs incorporation in the glass network. Five distinct bands at 578 nm (yellow), 590 nm (orange), 611 nm (red), 652 nm (deep – red) and 701 nm (deep – red) were registered attributed to $^5D_0 \rightarrow {}^7F_J$ transitions (where J = 0, 1, 2, 3, and 4). The emission intensity of the prominent peak at 611 nm ($^5D_0 \rightarrow {}^7F_2$) was increased up to 0.8 mol% of Ag-NPs content (see the inset pie chart) and subsequently quenched beyond. On this note, BTDEA0.8 glass sample was chosen to assess the asymmetric (R:O) ratio, luminescence enhancement factor and the CIE chromaticity color purity (CP). Moreover, the energy transfer process which plays a major role in luminescence enhancement is schematically demonstrated in figure 3. Upon 467 nm laser excitation, Ag – NPs are excited from the ground state to the excited state and since the excited state of the Ag – NPs and $^5L_6$ level of $Eu^{3+}$ are in close vicinity, the energy transfer from Ag – NPs to $Eu^{3+}$ ion can easily take place. The excited Ag – NPs relaxes non-radiatively from the excited state to the ground state thereby transferring the excitation energy to the neighbouring $Eu^{3+}$ ion (i.e. $^7F_0$ are elevated to $^5L_6$ level). Afterwards, $Eu^{3+}$ ions in the populated $^5L_6$ level experienced multi-phonon relaxation to luminescent $^5D_0$ level and relax radiatively to $^7F_J$ level, resulting in visible light emission of $Eu^{3+}$ ions.

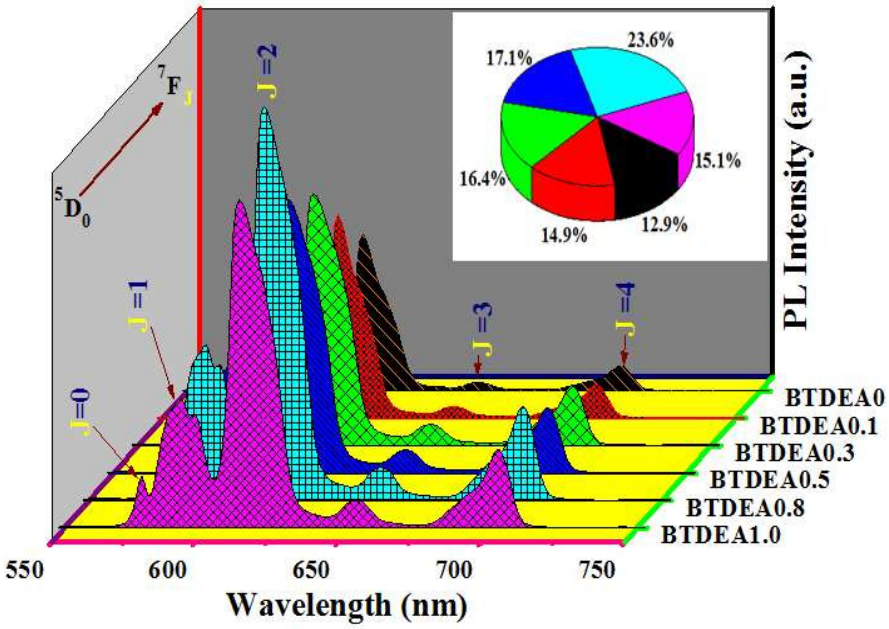


**Figure 2.** 3D emission spectra of the studied BTDEA$x$ glasses.

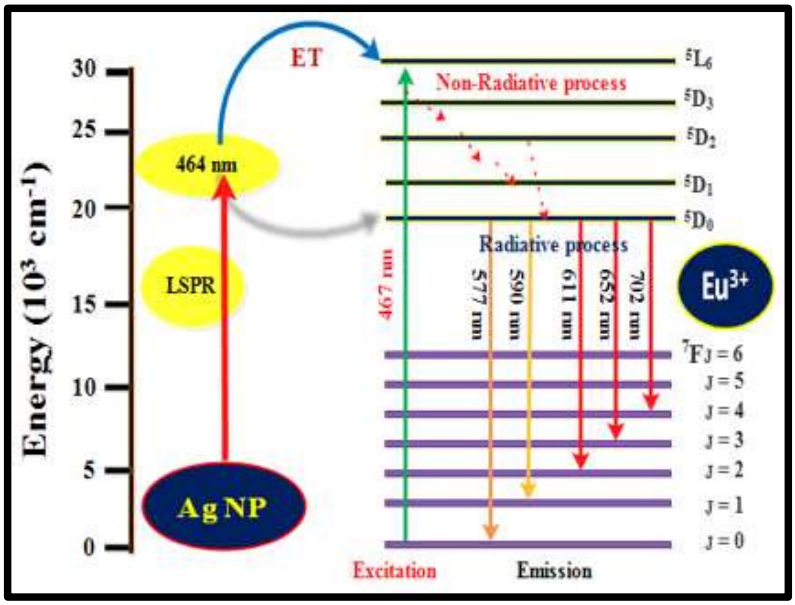


**Figure 3.** Energy level diagram of Ag – NP in $Eu^{3+}$ doped BTD glass and the possible energy transfer process.

*3.3. Asymmetric ratio (R:O) and enhancement factor ($I_{\lambda-pe}$ ) analysis*

Asymmetric ratio (R:O) is defined as the ratio of integral intensity of the electric dipole (ED) transition ($^5D_0 \rightarrow {}^7F_2$) to the magnetic dipole transition ($^5D_0 \rightarrow {}^7F_1$). It gives information about the symmetry of the ligand field and covalency of the metal ligand bond. The R:O ratio is given by [21]:

$$R:O = \frac{\int I_{0\rightarrow 2}(\lambda)d\lambda}{\int I_{0\rightarrow 1}(\lambda)d\lambda} \quad (1)$$

The estimated R:O value (3.563 ) of BTDEA0.8 glass sample presented in table 1 signified that the $Eu^{3+}$ ions are located in the higher asymmetric environment due to the aggregation of Ag–NPs in the glass network. To further, asses the influence of Ag – NPs inclusion, the luminescence enhancement factor ( $I_{\lambda-pea}$ ) was deduced by using the following relation [22]:

$$I_{\lambda-p} = \frac{AREA_{\lambda-peak-wit\ \ Ag-}}{AREA_{\lambda-peak-withou\ \ Ag-NP}} \quad (2)$$

The maximum enhancement factor (2.170) achieved in the present glass was attributed to large localized field in the proximity of $Eu^{3+}$ ions which is assisted by surface plasmon resonance. The acquired R:O and $I_{\lambda-peak}$ of the as – prepared (BTDEA0.8) glass are presented in table 1 and compared with other existing Ag – NPs and $Eu^{3+}$ co-doped glasses.

**Table 1.** The asymmetric ratio (R:O) and the luminescence enhancement factor at $^5D_0 \rightarrow {}^7F_2$ transition of the Ag/ $Eu^{3+}$ co-doped glasses along with existing literature on other glasses conatining Ag – NPs and $Eu^{3+}$ ions.

| Glass code | R:O | $I_{\lambda-peak}$ | Reference |
|---|---|---|---|
| BTDEA0.8 | 3.563 | 2.170 | Present work |
| $44.5P_2O_5 – 44.55Na_2O – 10ZnO – 1Eu_2O_3$ | 2.42 | – | [16] |
| $45SiO_2 – 19PbF – 20K_2O – 5Na_2O – 10LiF – 1\ Eu_2O_3$ | 2.44 | – | [23] |
| $10Li_2O – 10PbO – 7Al_2O_3 – 70B_2O_3 – 3Eu_2O_3$ | 2.02 | – | [24] |
| $44.5P_2O_5 – 44.55Na_2O – 10ZnO – 1Eu_2O_3 – 0.5AgNO_3$ | 2.53 | – | [16] |
| $54.9B_2O_3 – 9P_2O_5 – 15BaO – 15ZnO– 5Al_2O_3 – 1Eu_2O_3 – 0.1AgNO_3$ | 2.49 | 1.26 | [13] |
| $54.75B_2O_3 – 9P_2O_5 – 15BaO – 15ZnO– 5Al_2O_3 – 1Eu_2O_3 – 0.25AgNO_3$ | 2.17 | 1.81 | [13] |
| $54.5B_2O_3 – 9P_2O_5 – 15BaO – 15ZnO– 5Al_2O_3 – 1Eu_2O_3 – 0.5AgNO_3$ | 2.21 | 2.29 | [13] |

*3.4. CIE 1931 chromaticity analysis*

In order to ascertain the foremost emission color of the as – prepared glasses, emission spectra data were analysed by CIE 1931chromaticity diagram and well presented in figure 4 (inset shows the digital photograph of BTDEA0.8 glass sample under 467 laser excitation). The chromaticity color coordinates (x.y), correlated color temperature (CCT) and color purity (CP), respectively were analyzed by using interactive CIE software and the fundamental formulae described in [25, 26]. Evident from fig. 4 and table 2 revealed that the color coordinates of the BTDEA0.8 glass lies in the reddish color region (marked in star and filled with yellow color) with coordinates (0.63765, 0.36094) which is very close to standard values for red emitting phosphor ($x = 0.67, y = 0.33$) and the commercial red phosphor $Y_2O_2S:Eu^{3+}$ ($x = 0.622, y = 0.351$). Besides, the attainment of CCT value of 2188K with high color purity of 97.037% further declared the candidateship of this glass for solid state red lasers device fabrication.

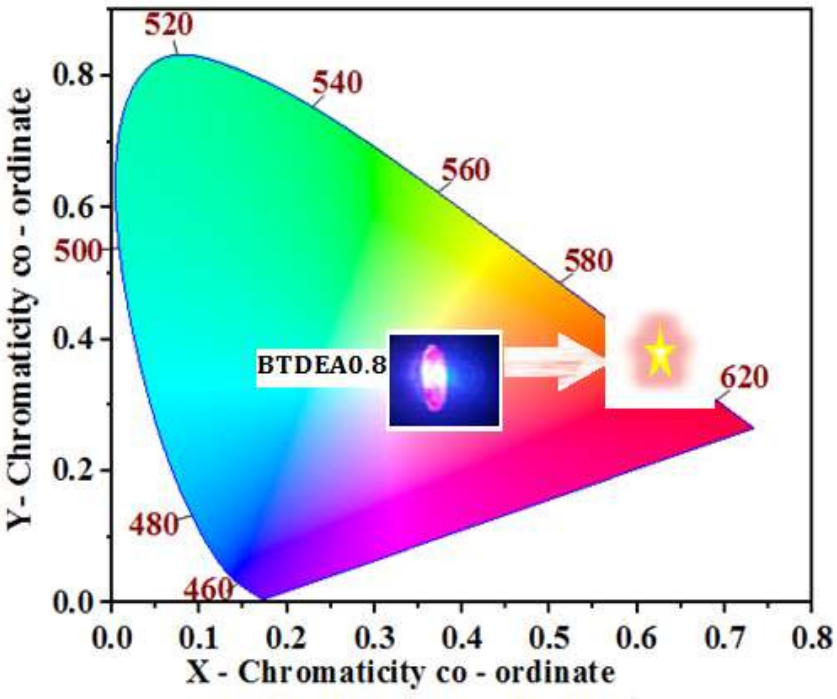


**Figure 4.** CIE 1931 chromaticity diagram of BTDEA0.8 glass.

**Table 2:** CIE chromaticity coordinates (x,y), the excitation wavelength , correlated color temperature (CCT) and color purity (CP) of BTDEA0.8 glass with existing literature on other Ag – NPs and $Eu^{3+}$ co – doped glasses

| Glass code | $\lambda_{exc}$ (nm) | Chromaticity co-ordinates | | CCT (K) | CP (%) |
|---|---|---|---|---|---|
| | | x | y | | |
| BTDEA0.8 | 467 | 0.63765 | 0.36094 | 2188 | 97.037 |
| TNZ:Ag/Eu [18] | 457 | 0.62 | 0.37 | – | – |
| BPEu0.75A [13] | 457 | 0.646 | 0.354 | – | – |
| TNW15 [22] | 393 | 0.646 | 0.353 | – | 91.33% |
| 1Eu24Li75Te [27] | 395 | 0.56 | 0.32 | – | – |

## 4. Conclusion

For the first time we have examined the possibility of achieving a new class of efficient red laser glass host by admixing naturally abundant (low-cost) dolomite mineral with commercially available boro – tellurite matrix. In this melt – quench synthesized transparent $Eu^{3+}$ doped boro – telluro – dolomite glass host, the luminescence intensity was greatly enhanced by Ag – NPs inclusion in the glass network. Indeed, the noted improvement was attributed to the local electric field around $Eu^{3+}$ site produced by the surface Plasmon resonance (SPR) of Ag –NPs appeared in the close proximity of $Eu^{3+}$. Furthermore, the optimum concentration of Ag –NPs occurred at 0.8 mol%. This BTDEA0.8 glass exhibited excellent red emission upon excitation with blue light (467 nm) with a very high color purity (97.037%), indicating the potency of the proposed glass for red laser and color display devices.

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