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Luminescence Enhancement in Eu(III)-Doped Tellurite Glass Embedded Silver Nanoparticles

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Abstract

Introduction of the metallic nanoparticles (NPs) in the bulk glass received a large interest due to their versatile applications. The effect of silver NPs on optical properties of the Eu^{3+}-doped zinc tellurite glasses is presented for the first time. Glass samples are prepared by melt-quenching technique. The surface plasmon absorption bands of silver NPs are recorded in the visible region. The enhancements in the order of 2.2-2.4 times are observed in the luminescence of the Eu^{3+} ions by introduction of silver NPs up to 1 mol% and are attributed to contribution of the NPs with average size of about 8 nm. In addition, energy transfer from surface of the metal to the rare earth ion is discussed as the second channel for the enhancement. This report highlights the excellent performance of tellurite glasses for applications such as LEDs, color displays and nanophotonics.

1. Introduction

Recently, a lot of research on nanotechnology and nanophotonics are turned to synthesize the novel materials with remarkable optical and electrical properties [1-3]. The density of the electronic states and dielectric confinement in nanostructured materials and materials containing noble metallic nanoparticles (NP) nominate them as promising hosts with exceptional optical, electronic, thermal, magnetic and chemical properties [4]. The preparation of the NPs and investigations on their optical properties has been emerged into a new area of science and technology, called “Plasmonics” [5].

The glass nanocomposites containing metallic NPs are among the motivating materials due to their high potency for the applications in various branches of science and technology, e.g. photo-chemical materials, multi-dimensional and colorful industrial objects, non-linear nanophotonic fabrics, memory devices, and optical switches [6-8]. Therefore, some properties of the glasses such as

wide transparency window, simple methodology for preparation, and high mechanical strength are added to those noble significances of metal-NPs in order to synthesize the new composites in which the metallic NPs are protected from air oxidation and other environmental effects.

The scheme of the incorporation of the metallic NPs inside the hosts containing rare earth (RE) ions was introduced in order to alert the optical properties of glasses and glass-ceramic nano-composites. Besides, different proposals were also established to improve the optical properties of the RE ions by modifying the crystal field. Introduction of semiconducting dopant, quench-reducing shell or second RE ion with high dose are among the proposed methods to overcome the optical deficiencies in RE-doped glasses [9].

The interaction of light with metallic surfaces having sizes smaller than the wavelength of incident light results in confinement of a large electric field around the NPs. Localized surface plasomon resonance (LSPR) field is induced by the oscillations of free electrons in the conduction band of the metal. Such oscillations are generated through the polarization of NPs by electromagnetic field of incident light and a restoring coulomb force from positive charges (nuclei). The LSPR field inside the dielectric host is more effective in presence of the non-spherical NPs (e.g. elliptical NPs and nanorods) since a large electric field could be stimulated at the interface of the dielectric host and sharp edges of the NP.

Recently, the introduction of noble (gold and silver) metallic NPs in the glasses containing RE ions captured a large interest. Malta et al. [10] reported on the large enhancement of the Eu^{3+} luminescence intensity in the borosilicate glass by small silver particle. Som and Karmakar prepared core-shell (silver-gold) NPs embedded antimony nanocomposites [11]. Large enhancement in the intensity of the Nd^{3+} ion in their glassy system is attributed to the effect of LSPR on the fluorescence of RE ions. Almeida et al. [12] also reported on the enhancement of the Eu^{3+} ion luminescence intensity in the presence of gold NPs in tellurite glass. Dousti et al. [13] and Amjad et al. [14] investigated the effect of silver NPs on the upconversion emission of the Er^{3+}-doped zinc-tellurite and magnesium-tellurite, respectively. Furthermore, enhances in the upconversion emission (from 980 to 810 nm) are reported in Er^{3+}-doped tellurite glass by Rivera et al. [15] and they concluded that the manipulation of gold NPs results in reduction of the lifetime of $^4I_{13/2}$ excited state. However, to the best of our knowledge, there is no report on the effect of silver NPs on the optical properties of the Eu^{3+}-doped zinc-tellurite glasses. Moreover, different mechanisms for interaction of the light with RE ions in vicinity of the metallic NPs are not clearly understood. The aim of the current study is to investigate the effect of silver NPs on the optical properties of Eu^{3+}-doped zinc tellurite glasses.

2. Experimental procedures

Tellurite glasses having compositions (80-*x*) TeO_2-20ZnO-*y*$EuCl_3$-*x*AgCl (where *y*=0, 1, *x*=0, 0.5 and 1 mol%) were prepared by conventional melt-quenching technique. Twenty grams of the starting powder materials with high purity were weighted carefully and mixed thoroughly. Then, the mixtures were melted at 900^{o}C in a raising heart electric furnace for 20 minutes. During this process, the molten was stirred regularly to avoid the formation of bubbles and to achieve the homogenous glass. Next, the molten was poured between two stainless steel moulds in the

secondary furnace pre-heated at 300°C and kept for 3 hours in order to reduce the mechanical strains and thermal stress. Finally, the samples were allowed to cool down to ambient temperature. The glass samples in the dimensions of 20×20×2 mm were grained and polished carefully to obtain suitable transparency for optical measurements.

The crystallographic structure of the samples was investigated by a Burker D8 Advanced X-ray diffractometer (XRD) using Cu Kα (λ=1.53 Å). The photoluminescence emission spectra were recorded using a Perkin-Elmer LS55 luminescence spectrophotometer in the 500-900 nm region under 460 nm excitation wavelength originated from an internal Xenon flash lamp. The slit widths of the excitation and emission beams were kept fixed for all the samples. The experiments were performed at room temperature. The presence of the NPs in the tellurite host glass was confirmed using the transmission electron microscope (TEM) technique. The JEOL 2100 TEM working at 200 kV was utilized to capture the silver NPs and to study the size, shape and distribution of the metallic NPs.

3. Results and discussion

Fig. 1 illustrates the schematic step by step preparation of the Ag NP:Eu^{3+}-co-doped zinc tellurite glass. The yellow color is the intrinsic characteristic of the Eu^{3+}-doped zinc tellurite glass. The glass compositions and their corresponding labels are listed in Table 1. Since there is no absorption peak due to the presence of silver NPs observed at glasses B and C, the sample D is synthesized with same methodology in order to track the peak of the surface plasmon resonance (SPR) of silver NPs which was previously reported in our latest paper [16]. The SPR bands of the glass D are centered at around 560 and 594 nm.

The frequency and the intensity of the SPR band strongly depend on the type of NPs, size, geometry, distribution, inter-particle distance, density and shape of the NPs. By and large, the decreases in the size of NPs or refractive index of the host emerge as a blue-shift in the SPR band frequency [17]. The presence of the non-spherical NPs shifts the SPR band of the metallic NPs to the smaller frequencies [18].

Table 1. Glass compositions (mol%) and their labels.

Glass	TeO_2	ZnO	$EuCl_3$	AgCl
A	79	20	1	0
B	78.5	20	1	0.5
C	78	20	1	1
D	79	20	0	1

Fig.2 shows the XRD pattern of the glass A. The absence of any sharp peak and presence of a broad hallo in the 20-40 degrees region confirm the amorphous nature of the tellurite glass sample. The XRD pattern of the other glasses are also possess same shape and there is no peak observed due to silver NPs likely due to the small concentration of metallic NPs.

The ionic phase of the silver (Ag^+) is reduced to its neutral form (Ag^0 atom) in the glass during the melting process as discussed earlier [19], while the growth and the aggregation of silver NPs takes place throughout the annealing time interval. The aggregations of the NPs in this study do not occur effectively due to the annealing process in which the temperature is near to the glass transition temperature (~ 330°C [16]). However, the probability of such aggregations increases by further introduction of the metallic NPs content since the NP-NP distances are reduced.

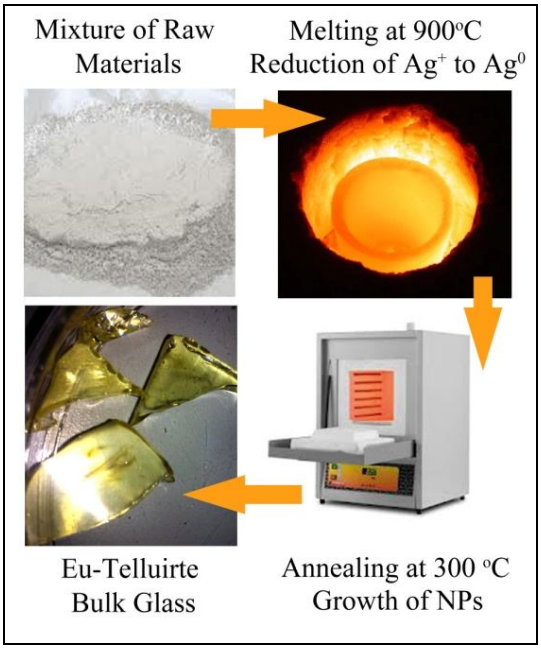

Fig. 1. Schematic steps of the glass preparation by the melt-quenching technique.

In principle, the reduction of the silver NPs are more facile than that gold as they are reduced respectively in one and three steps,

$$Ag^{+} + 1e^{-} \rightarrow Ag^{0}$$
$$Au^{3+} + 3e^{-} \rightarrow Au^{0}$$

On the other hand, the reduction potential of the silver (E^{0}=0.7996) in room temperature and at equilibrium with air is smaller than that gold (E^{0}= 1.498) [20], which facilitates and speed-ups the reduction of the silver with respect to its counterpart. Thus, in a core-shell system, the gold NPs are usually defined as the protective shells for silver atoms [11]. On the other hand, enhancement of the luminescence by Ag NPs is more studied due to its better performance and lower losses than Au NPs [17].

Fig.3 shows the TEM image of the sample C. Some of the silver NPs are demonstrated by small arrows. The average size of the NPs is estimated to be ~ 8 nm. Beside the preparation of silver NPs during the melting and annealing periods, presence of silver in other forms (e.g. atoms, ions, neutral dimmers and multimers) is still probable [21,22].

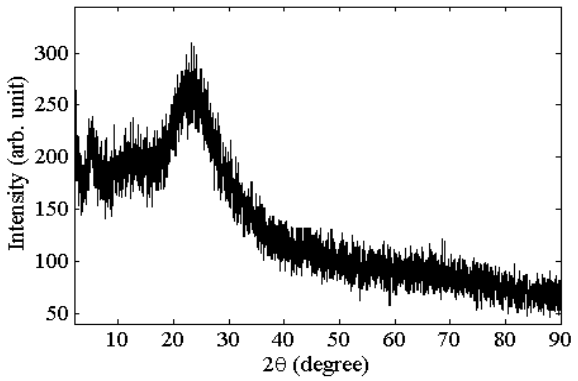

Fig. 2. XRD pattern of the glass A.

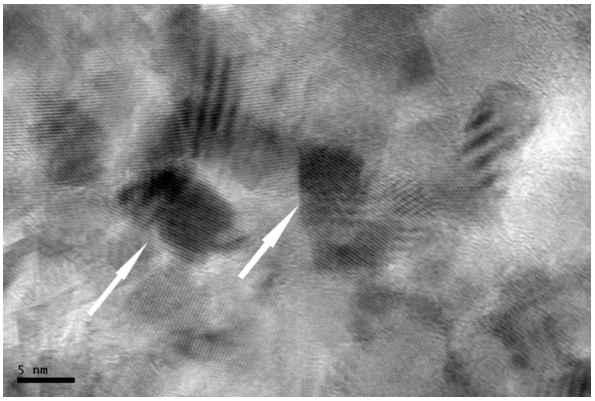

Fig. 3. TEM image of sample C. Few NPs are pointed by arrows. The scale bar is 5 nm.

Eu^{3+}-doped tellurite glass presents five emission peaks at visible region. Fig.4(a) presents the luminescence spectra of proposed glasses under 460 nm excitation wavelength. The emissions centered at 585, 595, 611, 647 and 696 are attributed to the transitions from $^{5}D_{0}$ excited state to $^{7}F_{0}$, $^{7}F_{1}$, $^{7}F_{2}$, $^{7}F_{3}$, and $^{7}F_{4}$ lower-lying levels. Large enhancement of the luminescence of Eu^{3+} ions is observed and associated to the effect of the SPR of silver NPs on the electric field around the NPs. Therefore, excitation and emission rates increase which lead to a decrease in the lifetime. As the result, an avalanche of emitting photons

participating in different emissions depopulates the $^5D_0$ excited state. The exploitation of the enhancement factor of different emissions against the concentration of the silver NPs is illustrated in Fig. 4(b). The enhancement factor for the sample B (0.5 mol% silver NPs) decreases from 1.7 to 1.4 as the emission wavelength shifts towards red region. Similar trend is observed in the spectrum of glass C. Therefore, we can conclude that the proximity of the emission and the SPR frequencies drastically affects the enhancements factor, and the influence of the SPR band on the emissions lying far from resonance is weak. Such enhancements in frequency resonance conditions may also be attributed to the energy transfer from surface of the small metallic NPs to RE ions through a phonon-assisted process.

The interactions of the light with Eu^{3+}-doped tellurite glass containing silver NPs can be explained by three different approaches;

1) Interaction of light with Eu3+ ion, when the 406 nm excitation photons excite the ions from 7F0 ground state to 5D2 excited state. Phonon-assisted non-radiative decays from 5D2 level to its lower-lying levels (5D1 and 5D0) results in the population of 5D0 level, as illustrated in Fig.5.

2) Interaction of light with NPs. As discussed earlier, the large localized electric field known as localized surface plasmon resonance (LSPR) field enhances the excitation and the emission rates. As a result, the emission intensity of the emitting ions in vicinity of the metallic NPs increases. On the other hand, in certain concentration of the NPs, the emitters are highly affected by the strong local field at “hot-spots” [4]. Moreover, the presence of the non-spherical metallic NPs may contribute to additional enhancements.

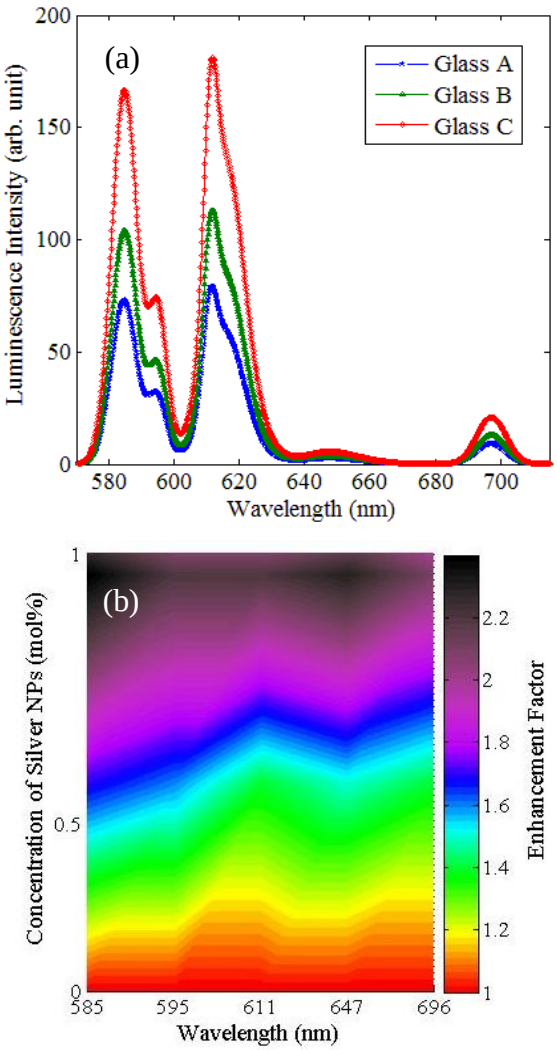

Fig. 4. (a) Photoluminescence spectrum of the Eu^{3+}-doped tellurite glass with (B,C) and without (D) silver NPs. (b) Enhancement factor as a function of emission wavelength and concentration of the silver NPs.

3) Interactions between metallic NPs and the Eu3+ ion. As shown above, the proximity of the SPR band and emission wavelength may also leads to further enhancements by an energy transfer from the surface of the NPs to the Eu3+ ions. However, in higher concentration of NPs an unfavourable back-energy transfer from ion to NP (re-absorption by metal) may cause the quenching of the luminescence intensity.

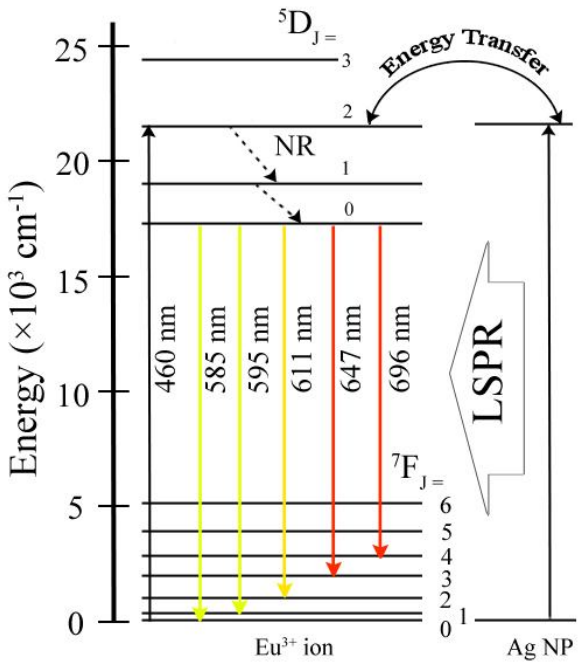

Fig. 5. Schematic partial energy level diagram of the Eu^{3+} ion in vicinity of a silver NP doped tellurite glass.

4. Conclusion

Tellurite glasses are promising materials due to their great optical, structural and thermal characteristics. Eu^{3+}-doped tellurite glass shows potential emission lines in visible range of spectrum, suitable for the versatile applications in photonics and optical devices. The effect of silver NPs on the luminescence of such optical materials is studied in this manuscript. Addition of silver NPs in the form of AgCl in Eu^{3+}-doped zinc tellurite glass modifies its optical properties and the luminescence intensity of the rare earth dopant enhances up to 2.4 times. The enhancement is attributed to the presence of silver NPs with average size of 8 nm and SPR bands centered at 560 and 594 nm, either by modifying the local field or energy transfer from surface of metal to the Eu^{3+} ion.

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