

EFFECT OF METALLIC NANOPARTICLES ON THE EMISSION OF ZINC TELLURITE GLASS

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ABSTRACT

The optical emission properties of a series of metallic nanoparticles doped zinc tellurite glasses are investigated using photoluminescence spectroscopy measurement. The melt quenching method was used to synthesize the metallic (Ag, Au, Fe₃O₄ and NiO) nanoparticles doped zinc tellurite glass. Series of Gold (Au) nanoparticles doped zinc tellurite glass at room temperature have been up conversion emission spectra under 779 nm. Excitation shows three peaks centered at 520, 550 and 660 nm corresponding to the transitions from ²H_{11/2}, ⁴S_{3/2} and ⁴F_{9/2} excited states to ⁴I_{15/2} ground state. The series of silver (Ag) nanoparticles and Er³⁺ ion doped zinc tellurite glass have been the up conversion luminescence spectra revealed three major emission peaks at 520, 550 and 650 nm originating from ²H_{11/2}, ⁴S_{3/2} and ⁴F_{9/2} levels, respectively. An efficient enhancement in visible region is observed for samples containing metallic nanoparticles (Ag and Au NPs). Meanwhile, The series tellurite glass embedded with magnetic (Fe₃O₄ and NiO) NPs are displayed tend to quenched as concentration of the Fe₃O₄ and NiO NPs is increased. The increasing NPs (Fe₃O₄ and NiO) concentration dependent luminescence quenching is attributed to the energy transfer from the rare earth ion to NPs.

Keywords: Glass; optical; emission; nanoparticles; metallic; magnetic;

INTRODUCTION

Recently, the study of the unique characteristic of emission in different glasses embedding metallic nano-sized structures has fascinated a large interest collective oscillation of free electrons of a metal interacting with electromagnetic field is called surface plasmon resonance (SPR) [1,2]. As a result, a very intense and localized electric field is generated around the metallic nanoparticles (NPs) [3]. The luminescence intensity of rare earth (RE) ions can be enhanced due to local field enhancement when RE ions lie in proximity of such nanostructures [4]. In addition, nanosized magnetic particles give more sensitive response to the charge of applied magnetic field and thus exhibit super-paramagnetic coexistence of single domain materials [5,6]. This reveals interesting optical and magnetic properties such as SPR absorption and super-paramagnetism [4].

The initiative of introducing the coupling of RE ions with metal nanoclusters is established as a precious strategy to enhanced the luminescence efficiency and absorption cross-section of RE ions [7]. The inclusion of metallic NPs in the glass matrix causes strong modification of the glassy network and consequently the local environment of RE ions [4]. The interplay between nanocomposite and NPs is capable in modifying the spectral features of nanocomposites to improve emission efficiency via charge transfer across the metal interface [8]. This efficiency decisively depends on the local environment of the emitting RE ions and the degree of crystallinity of the respective up-converted materials.

EXPERIMENTAL

The four series of the glasses with composition $70\text{TeO}_2\text{-}20\text{ZnO}\text{-}10\text{Na}_2\text{O}\text{-(x)Er}_2\text{O}_3\text{-(y)Au}$ (where $x = 0.0$ and 1.0 mol% and y 0.0 and 0.6 mol%) [4]; $30\text{B}_2\text{O}_3\text{-}10\text{ZnO}\text{-(59.5-x)TeO}_2\text{-}0.5\text{Er}_2\text{O}_3\text{-(x)AgCl}$ (where $x = 0.0, 0.1, 0.3, 0.5, 0.7, 1.0$ and 1.5 mol%) [9]; $(58-x)\text{P}_2\text{O}_5\text{-}40\text{ZnO}\text{-}1\text{Sm}_2\text{O}_3\text{-(x)NiO}$ (where $x = 0, 0.5, 1, 1.5$ and 2 mol%) [5] and $(89-x)\text{TeO}_2\text{-}10\text{MgO}\text{-}1\text{Er}_2\text{O}_3\text{-(x)Fe}_3\text{O}_4$ (where $x = 0.5, 1, 1.5$ and 2 mol%) are prepared by melt-quenching method. Stoichiometric amounts of reagent grade P_2O_5 (Fluka Chemical, 99.9%), ZnO (Sigma Aldrich, 99.9%), Er_2O_3 (Sigma Aldrich, 99.9%), Au NPs (Sigma Aldrich, 99.9%), AgCl NPs (Sigma Aldrich, 99.9%), NiO NPs (Sigma Aldrich, 99.9%), Fe_3O_4 NPs (natural Fe_3O_4 is acquired from the Indonesian coastal region). A well-mixed powder of about 20 g is placed in an alumina and platinum crucible and melted in an electric furnace (950°C) for 1 h at. Upon achieving the required viscosity, the melt is poured into a steel mold and annealed at 300°C for 3 h to release the stress. The glass samples are then cooled to room temperature and stored in a desiccator to prevent moisture attack. For optical emission measurements, all the samples are polished to a surface finish of $1\text{ }\mu\text{m}$ using diamond paste.

RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of the glass for TMEF1 sample. From Figure 1, it can clearly be seen that the glass sample is amorphous in nature. Figure 2 shows the luminescence spectra of the glass with Silver (Au) Nps in range of 500-800 nm under 476 nm excitation. Three bands are observed at 536, 550 and 632 nm and are attributed to transitions from $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$ and $^4\text{F}_{9/2}$ levels to ground state, respectively [4]. Emission bands are enhanced owing to the presence of silver NPs up to 1.0 mol%. However, further increase in the concentration of NPs diminishes the emission intensities in entire visible range. Although, the primary reason for enhancement (LFE) induced by SPR of the metal NPs. The energy transfer (ET) from the metal to RE ions is mainly proposed to be an inefficient factor for luminescence enhancements, since the lifetime of metal is extremely shorter than the excited states of RE ions [4]. On the other hand, the quench can be described by ET from Er^{3+} ions to Ag Nps and reabsorption by SPR of Ag Nps which is in resonance with the emissions from Er^{3+} ions [10].

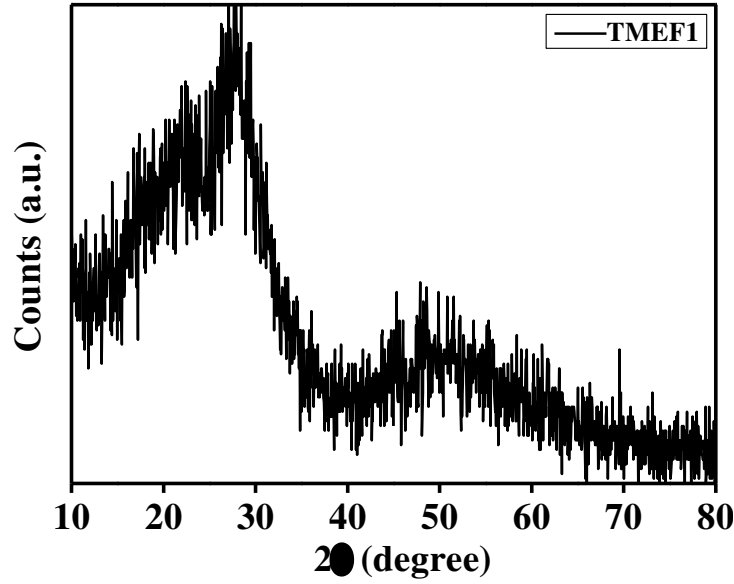


Figure 1: XRD pattern for the TMEF1 glass sample

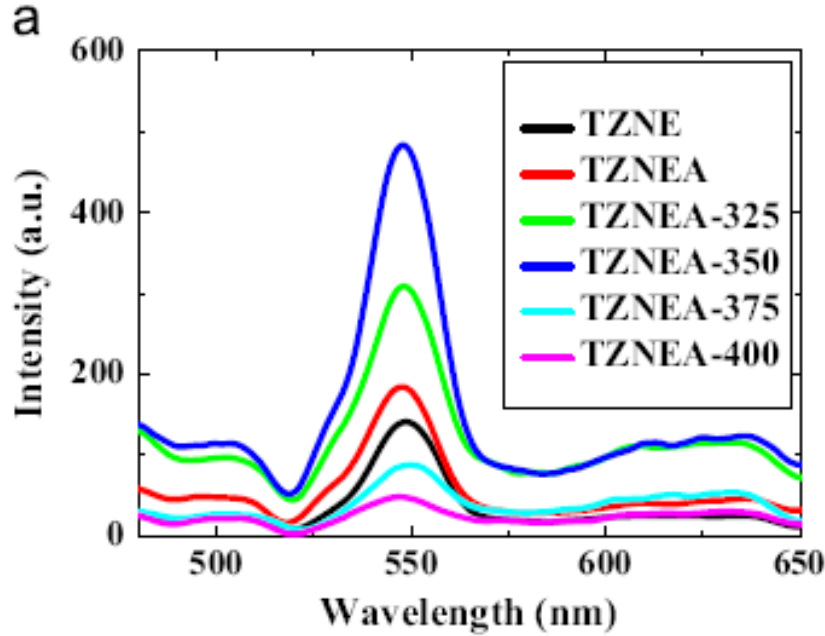


Figure 2: Luminescence spectra for all glass with gold nanoparticles [4]

The emission spectra of Er^{3+} doped zinc-sodium tellurite glass samples containing gold NPs, heat treated at 325, 350, 375 and 400 °C as shown in Figure 3 comprised of three prominent bands arise from $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$ and $^4\text{F}_{9/2}$ to $^4\text{I}_{15/2}$ transitions, respectively [9]. A comparison among spectra without and with NPs clearly reveal that transitions with wavelength near the surface plasmon band are considerably red shifted. The overall modifications in the spectral line shape are related to the alteration of the local

symmetries of Er^{3+} ions which [9] originate from the shape and size variations of Au NPs in the glass matrix. The intensities associated with all three transitions for the glass samples TZNEA, TZNEA-325 and TZNEA-350 are significantly enhanced as shown in Figure 3. the observed fluorescence enhancement can be interpreted using the following interaction mechanism (a) excitation light with Er^{3+} ions, (b) excitation light with gold NPs and (c) Er^{3+} ions gold NPs [11].

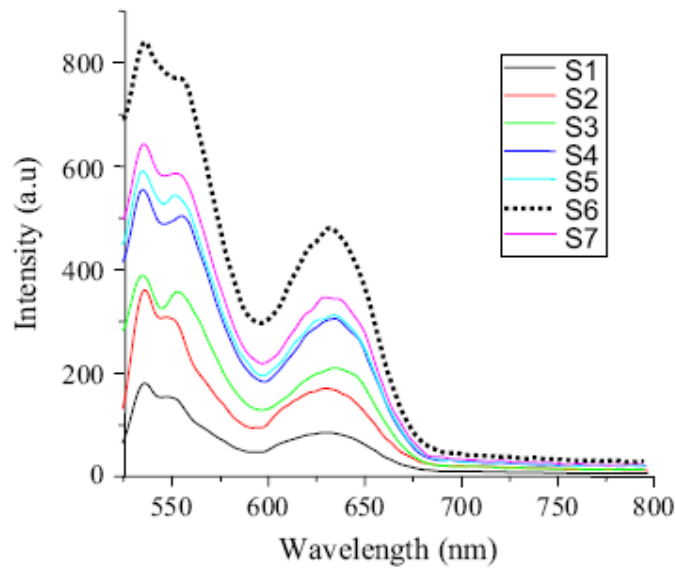


Figure 3: Luminescence spectra for all glass with silver nanoparticles [9]

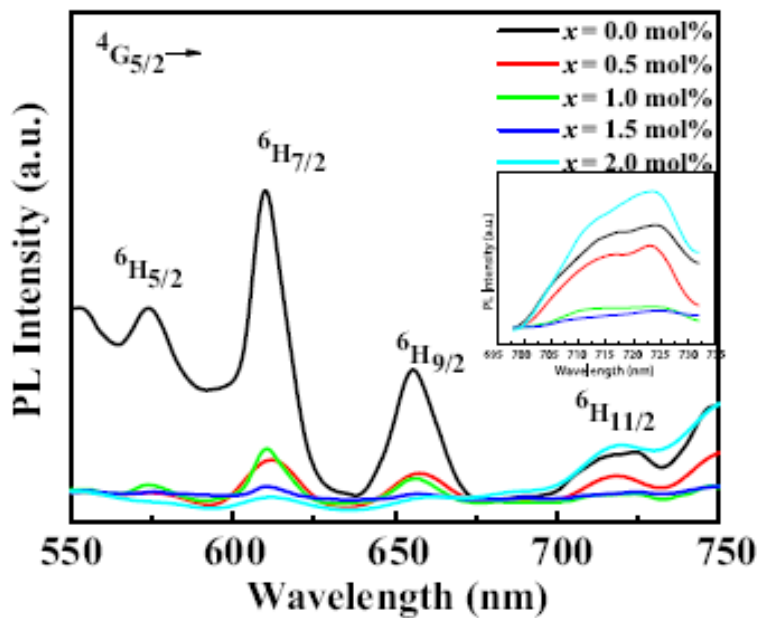


Figure 4: Luminescence spectra for all glass with nickel nanoparticles [5]

PL spectroscopy technique gives the characteristic of luminescence spectra of the samarium ions of the prepared glasses obtained in the region of 550 - 750 nm excited under 401 nm wavelength in Figure 4. Five samples are studied by varying concentration of Ni NPs up to 2.0 mol% [5]. The luminescence spectra consist of four emission transitions $^4G_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$ and $^6H_{11/2}$ to $^6H_{5/2}$ transitions. The fluorescence intensities are quenching for transition of $^4G_{5/2}$ to $^6H_{5/2}$, $^6H_{7/2}$ and $^6H_{9/2}$. It is reported that the quenching is due to the energy transfer from the excited samarium ions to the nickel ions NPs [4].

The luminescence spectra (Figure 5) recorded in the range of 420 - 600 nm upon 375 nm excitation exhibits two pronounced peaks centered at 420, 460, 490 and 546 nm originate from the transitions of $^4F_{3/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$. Interestingly, the quenching in luminescence intensity with the increase of Fe_3O_4 NPs concentration is ascribed to the energy transfer from the erbium ion to NPs. Consequently, more inhomogenous distribution of Er^{3+} sites leads to higher inhomogenous broadening of the emission spectra. The change of Fe^{2+} ions in the glasses play an important role because the valence band are dominated by electrons of Fe atom [6]. Moreover, an energy transfer from excited states of Er^{3+} ions to the surface of Fe_3O_4 NPs could result an unfavorable quenching. Hence, the concentration of Er^{3+} ions in glass must be higher than that of metallic NPs to achieve the maximum luminescence intensity [11].

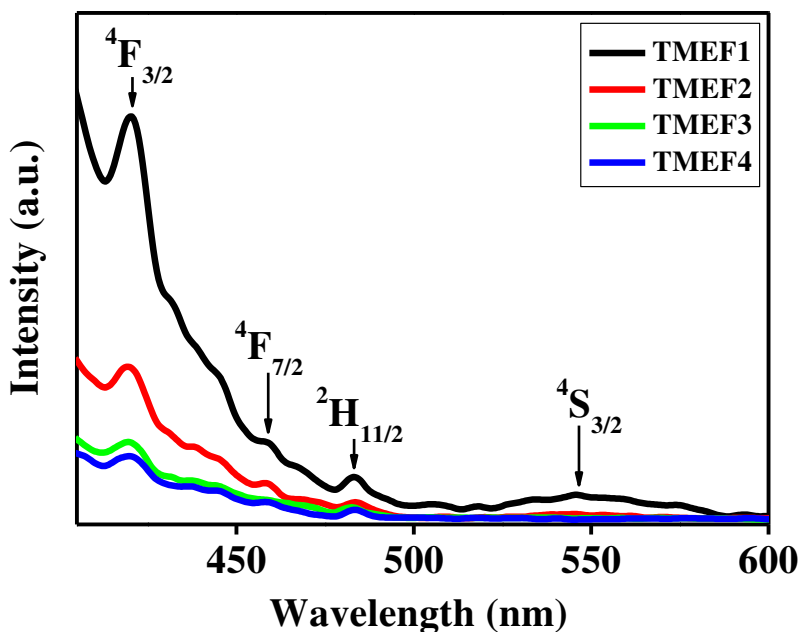


Figure 5: Luminescence spectra for all glass with ferrite oxide nanoparticles

CONCLUSIONS

Rare earth (RE) doped tellurite glass embedded with different metallic nanoparticles concentration are prepared by melt-quenching technique. We establish that the metallic nanoparticles (Au and AgCl) in Er^{3+} doped tellurite glass triggers the improved results

in significant enhancement of Er^{3+} luminescence. The up-conversion are explained using the optical interaction of excitation high with Er^{3+} ion, excitation light with gold NPs and Er^{3+} ion with gold NPs. For AgCl NPs, maximum enhancement in visible fluorescence is obtained for 1 mol% of AgCl. The photoluminescence spectra are strongly influenced by the variation of magnetic materials NPs (Fe_3O_4 and NiO) concentration. The observed luminescence quenching beyond magnetic nanoparticles is attributed to the energy transfer from rare earth ion to NPs. The results suggest that metallic nanoparticles (Au and AgCl) and magnetic nanoparticles (Fe_3O_4 and NiO) glass could be a favorable host for the development of optoelectronics and magneto-optic devices, respectively.

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