J. Sol. State Sci. Technol. Letts. Vol. 22 No. 1 & 2 (2021): 30-36
http://myjms.mohe.gov.my/index.php/jssstl

Lasing Capability Enhancement by Metallic Nanoparticles: A Short Review

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Abstract: The exploration of science and technology deal with the manipulation of the physical properties at the atomic scales has driven a new interest in coupling of metal nanoparticles in rare earth doped inorganic glasses. The coupling of nanoparticles into the rare earth doped glass brings significant enhancement in the luminescence intensity. This enhancement is expectedly due to the 'plasmonic wave' (referring to the coherent coupling of photons to free electron oscillations called plasmon) occurs at the interface between a conductor and a dielectric. Besides that, the efficient energy transfer between the excited rare earth ion and metal nanoparticles that act as a transmitter and receiver increased the radiative emission rate and reduced the non -radiative decay rates. This short review briefly discussed the phenomena of interaction of light with rare earth doped glasses embedded with metallic NPs and its significance influence on the performance of the lasing glass. On the other hands, the influence of magnetic nanoparticles in rare earth doped glass that possibly activate the luminescence quenching of lasing glass also will be elaborately discussed. Some significantly new findings are highlighted and facilely analyzed.

Keywords: Nanoparticles, plasmon, plasmonic wave, radiative emission, tellurite

The advances technological in lasing devices has created demands to develop a new high performance of lasing material. Compare to a natural and synthetic crystal, glasses can be tailored and obtained faster at reasonable prices along with its variety sizes and shape for laser applications purpose. A lot of effort has been devoted to study various glass material that fit to be used as a lasing medium. Tellurite (TeO_2) based glass is considered suitable for lasing action due to its unique properties. One of the main fundamentals that greatly affects the performance of lasers is the non- radiative relaxation since its effects the dynamic of the excited state population which consequently influenced by the lattice vibration of the host [1]. Tellurite exhibits low phonon energy which leads to the higher quantum energy efficiency compared to other glass host and able to improve their IR transmission up to 6 μm [2] . This characteristic is preferred to increase the stimulated emission cross-section of the lasing glass. Presently, RE ion doped with tellurite glass are prospective for high quality lasing action ultimately linked to the optical properties.

Numerous researches have been carried out on the ability of glass to incorporate with large doping of RE ions [3] It is reported that the doping level used when manufacturing novel optical glasses used in lasing glass are very critical to the performance of the envisaged devices. The concentration of RE ion play a major role in the performance of lasing glass [4]. The efficiency of devices such as lasers and amplifiers are reliant on upon the effects such as concentration quenching. The concentration quenching are more likely occurs at higher concentration of doping level. This is essentially a problem of cross-relaxation of the excited state energy levels induced by the proximity the dopant atoms to each other. This concentration quenching reduces the probability of achieving population inversion. Also, if the dopant concentration is too high crystallization within the glass matrix can occur which cause dramatically increasing optical losses within the material.

Being an essential parameter for a laser gain medium, the stimulated emission cross-section σ affects several laser parameters of an active medium such as the maximum achievable gain saturation power, laser threshold, etc. A larger value of stimulated emission cross-section σ is an essential and attractive feature for low threshold and high gain applications of lasers. It is reported that, highest values of stimulated emission cross-section, gain bandwidth, optical gain is suitable for low threshold and high gain laser applications. Z.A.Mahraz et al [5] have been reported the influence of concentration of Er^{3+} ion in boro tellurite media. From the studies, glass contain 0.5 mol % of Er^{3+} possess higher emission cross-section for green emission which is fit for lasing action. However, the reduction in the intensity of the green emission is observed when the Er^{3+} content reach 1.0 mol %. This can be correlated to energy transfer between two neighbouring Er^{3+}ions [6].

In sequence to surmount the quenching effects in RE doped glass, the incorporation of metal NPs has been proposed to encounter the proposed effects. Uniquely, the optical and absorption properties of metallic NPs are differs drastically from the behaviour of bulk metals [7]. In most cases NPs such as Ag NPs and Au NPs play major contribution in the enhancement of RE ions in which these noble materials give significant effect in quantum efficiency and larger cross section area [8]. Theoretically, the enhancement in photoluminescence intensity due to the increment in electric local field surrounding the RE ion close to metallic NPs and the energy transfer from metallic NPs to the RE ions. However, if the lighting source is too close to the metal, its excited state may be quenched by energy transfer to the metal and this causes the excitation to decay non–radiatively. This phenomenon of enhancing or quenching is due to the distance between the RE ions and NPs [9]. The interaction between light sources and metallic NPs is governed by a Surface Plasmons Resonance (SPR). SPR is a phenomenon where the free conduction electron in the metallic NPs are driven into excitation of the coherent oscillation due to strong coupling with physical origin of light [10]. Excitation of SPR causes the creation of local electric field close to the surface of NPs. The strong local electric field enhances the induced radiative inter-band transitions in the metallic NPs leading to a huge enhancement of PL intensity [8]. The collective oscillation of electron at the interface of metallic NPs are generated through the electromagnetic phenomenon arise when the incident light wave interact with electron [11]. The electric field displace the electron in order to create the uncompensated charges at the surface of metallic NPs. When the particle size is much smaller than wavelength of light which is in the range of 400 nm to 700 nm, creates a dipole due to the accumulation of the electrons at one end and the reduction of electron at the other end. This dipole produces restoring force for the electron cloud. At a certain frequency of the incident light, there is a resonance at which there is a maximum absorption of energy from the incident light wave and a peak is observed in the absorption spectra. known as SPR peak [12].The local electric field is governed by how much the concentration of metallic NPs can be grown up. The concentration of metal NPs increases up to certain concentration then saturated. The electric field is contributing to the luminescence process which can be noticed from the enhancement intensity in the emission peak. The enhancement intensity is due to the increase of photon emitted that results in efficiently light emitting. Conversely, the quenching in luminescence intensity is due to the energy transfer from rare earth ions to metal NPs [13]. The quenching in luminescence intensity also attributed to the accumulation of metal NPs [14].

The SPR wavelength can be notice from UV-Visible spectroscopy. The spherical metals NPs usually consist of a single plasmon peak correspond to transverse oscillation. Meanwhile for non- spherical metal NPs, they possess two plasmons peaks due to transverse and longitudinal oscillation [15]. Figure 1 illustrate the surface plasmon resonance peak at 540 nm and 570 nm.

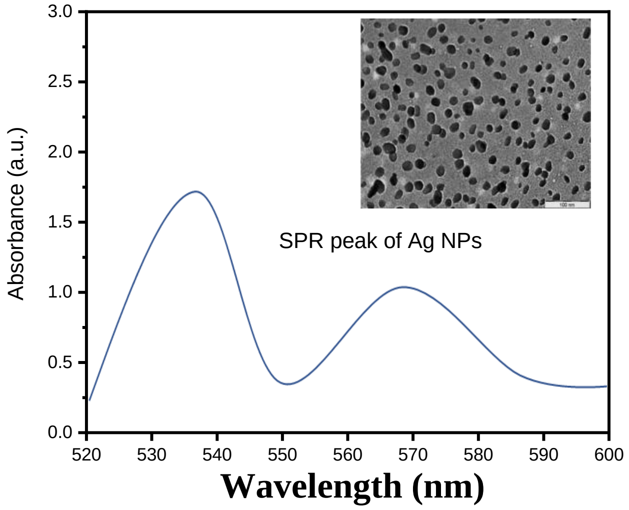

Figure 1**:** SPR Band of glass containing two plasmon peak correspond to transverse and longitudinal pea and inset shows the dispersion of spherical and non- spherical Ag NPs in Er^{3+} doped tellurite glass.

The role of Ag NPs in enhancing luminescence emission of Er $^{3+}$ doped tellurite glass can be observed in visible up-conversion emission spectra of Ag NPs embedded Er^{3+}under an excitation of 980 nm in Figure 2. One intense green and one intense red emission centered around 545 nm and 657 nm which associated with the transition $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$.From the figure, it is observed that the intensity is enhanced up to 0.6 mol % at least 2 times for both transitions compared to the samples transition compared to the glass sample without Ag NPs. This enhancement is attributed by two main reason. Firstly, is due to the local field effect of Ag NPs in the surrounding of Er^{3+} ion. This is due to the difference in the permittivity of the metal and the surrounding glass matrix which allow the SPR to produce surface waves that moves along the metal dielectric surfaces. This causes the electromagnetic energy will be concentrated and produce intense electric field. Next, is due to the energy transfer between the Ag NPs to Er^{3+} ion. However, the quenching effect can be observed in sample more than 0.6 mol % where the emission intensity is decreased which is due to the energy transfer from Er^{3+} to Ag NPs.

The mechanism of up conversion process of Er^{3+} can be understood by the partial energy level diagram as shown in Figure 3**.** There are three mechanism involved such as ground state absorption (GSA), excited state absorption and energy transfer. The Er^{3+} ion is excited at 980 nm from the ground state to the higher energy state at $^4I_{11/2}$ level. Then, the ions are promoted to $^4F_{7/2}$ level before decay non radiatively to the $^4S_{3/2}$ that gives pronounced green emission at 554 nm and $^4I_{11/2}$ level that gives red emission at $^4I_{11/2}$ due to the combined effect of the ESA and energy transfer mechanism.

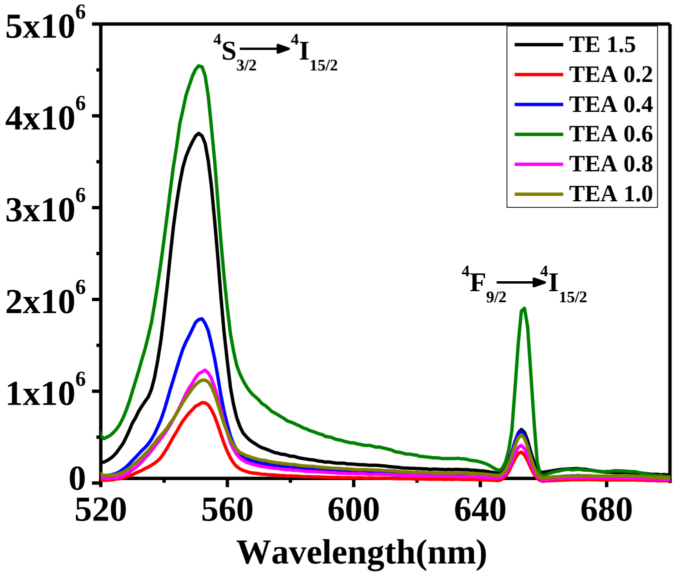

Figure 2**:** Emission spectra of Er^{3+} doped Tellurite glass embedded with Ag NPs

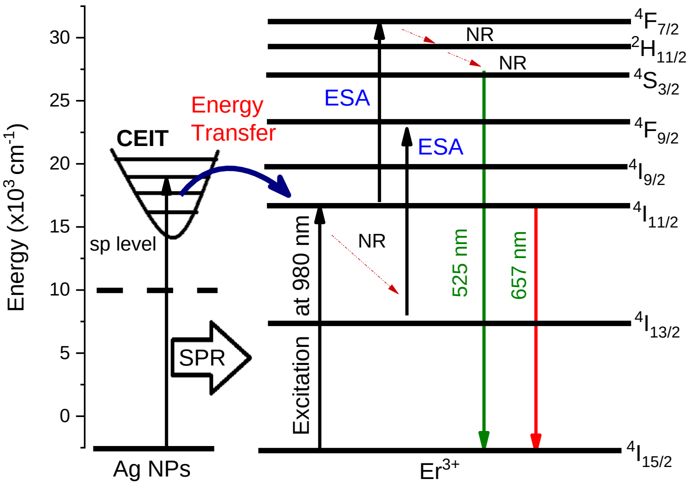

Figure 3**:** Schematic energy level diagram of Er^{3+} ion doped tellurite glass embedded with Ag NPs

Recently, the impact of magnetic nanoparticles such as Ni^{2+}, Fe^{2+} and Co^{2+} (transition metal) NPs on the structural, physical and magneto-optic properties of REIs doped binary glasses is examined. Literatures hinted that these types of glasses are greatly potential for the advancement of magneto-optic devices including isolators, switches [16]. However magnetic nanoparticles such as Fe_3O_4 NPs tends to suppress luminescence intensity, A more likely explanation is the enhanced cross-relaxation process, reduced absorption capability. Figure 4 depicts the emission intensity of Er^{3+} doped with Fe_3O_4 NPs. Glass contain 0.2 mol% of Fe_3O_4 NPs enhance the emission intensity of $^4S_{3/2}\rightarrow{}^4F_{3/2}$ due to the efficient energy transfer from Fe_3O_4 NPs to $Er^{3+\cdot}$ On the other hand, the emission intensity of $^4S_{3/2}\rightarrow{}^4F_{7/2}$ and $^4S_{3/2}\rightarrow{}^2H_{3/2}$ observed to drop with increase of Fe_3O_4 NPs. This luminescence quenching is observed due to high rate of intersystem crossing, ISC. ISC is favoured in paramagnetic species causes energy loss when some electrons pass from the singlet states S_1 and triplet states T_1 or conversely a triplet transitions to a singlet [17]. The probability of this process likely to occur when the vibrational levels of the two excited states overlap or known as spin orbital coupling [18]. This spin orbit coupling will take a longer lifetime that finally contribute deactivation of luminescence performance [19] .

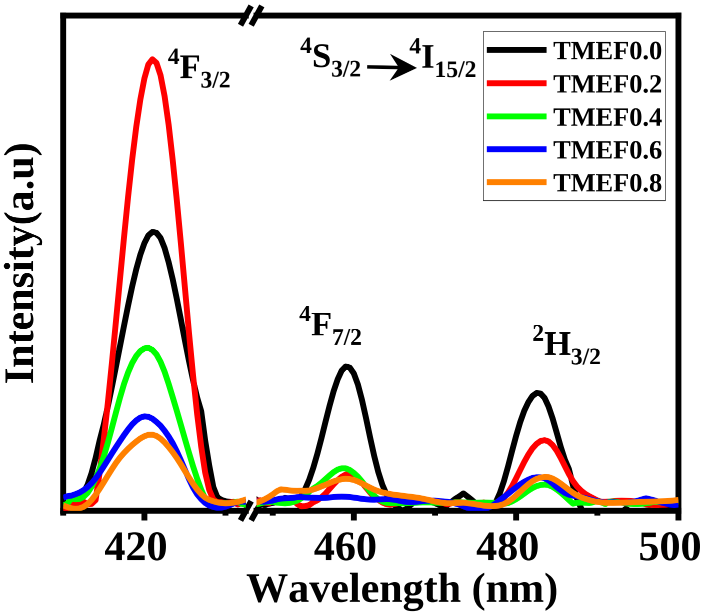

Figure 4: Emission spectra of Er^{3+} doped Tellurite glass embedded Fe NPs

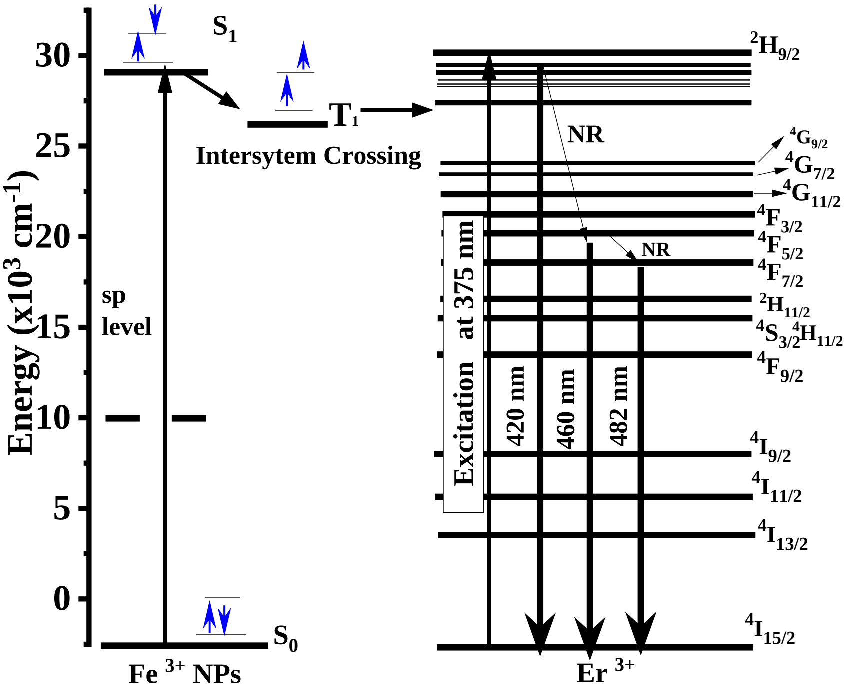

Figure 5: Energy level diagram of Er^{3+}doped Fe_3O_4 nanoparticles

In conclusion, this short review demonstrates the intuitive of embedding nanoparticles is proven to enhance the lasing capability in terms of emission intensity of RE doped glass. Glass doped with RE containing noble NPs shows enhance emission intensity with the aid of SPR and efficient energy transfer. Glass containing magnetic NPs activate fluorescence quencher due to the spin orbit coupling.

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