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Reduction of non-radiative decay rates in boro-tellurite glass via silver nanoparticles assisted surface plasmon impingement: Judd Ofelt analysis

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ABSTRACT

We report an enhancement in the absorption and emission cross-section of erbium ions (Er^{3+}) inside zinc-boro-tellurite glass due to the impingement of silver (Ag) nanoparticles (NPs) into the host matrix. The impacts of varying Ag NPs concentration on the spectroscopic, structural, and thermal properties of such glass samples are evaluated. Synthesized glass samples are characterized using imaging and spectroscopic tools. XRD spectra confirmed the amorphous nature of glass samples and EDX spectra detected appropriate elements present in the glass including Ag. TEM micrographs revealed the distribution of Ag NPs with average size ~8.4 nm. FTIR spectra exhibited the fundamental stretching vibrations modes of glass network. Two surface plasmon resonance (SPR) peaks of Ag are divulged at 550 and 580 nm. Bonding parameters displayed the ionic nature of the Er−O metal-ligand linkages. Judd-Ofelt analysis is performed to calculate the radiative transition probability, stimulated emission cross-section, radiative lifetime and branching ratio for the excited levels of Er^{3+} ions in the prepared glass system. Intensity parameters and quality factors are calculated. Silver NPs impingement is found to augment the luminescence intensity by a factor as much as 3.32 times than the glass without NPs. The decay curves for the $^4S_{3/2}$ level of Er^{3+} ion are recorded under 476 nm excitations, where the emission at 550 nm is registered. The lifetime is elongated from 6.36 μs to 9.07 μs with increasing silver NPs concentration from 0.0 to 0.9 mol%. Present glass compositions are established to be promising for the development of photonic devices.

1. Introduction

Rare earth (RE) ions with their special unfilled *4f* shells are emerged as promising dopants in various glass hosts for the fabrication of optical fibers and solid state lasers [1]. It is worth to mention that in RE ions the electric-dipole intra *4f* transitions are forbidden due to the matching parity of all levels. Nevertheless, when RE ions are incorporated in solid matrix, the *4f* states are slightly perturbed due to the existence of surrounding atoms (random potential) with two important consequences that remains unexplained. First, the host material (environment) can introduce odd-parity character in the *4f* wave functions, making radiative transitions weakly allowed. Second, the host material causes Stark-splitting (from the perturbation of the glass ligand field) of the different energy levels thereby broaden the optical transitions. The efficiency of the RE ion emission transitions depends upon several processes including the light absorption of the local field, energy transfer from the ligand environment to the RE ions, multiphonon relaxation associated with the phonon energy of the host matrices and energy back transfer through non-radiative cross-relaxation [2]. Despite much research on RE doped and NPs embedded glass systems an all-inclusive clarification of these mechanisms is far from being completed.

A popular approach in determining the transition probabilities between *4f* states and radiative lifetime is based on the so-called Judd-Ofelt (J-O) theory [3,4]. Generally, J-O theory is used to calculate (under certain legitimate approximations) transition probabilities from the absorption data of various *f-f* transitions. In this theory, the strength of an *f-f* transition is often expressed as the sum of the products of three phenomenological intensity parameters (Ω_t with $t = 2, 4, 6$) and the squared matrix elements $U(t)$ between the initial state (J) and the final state (J'). Once these phenomenological parameters are calculated, it is possible to derive the strength of any absorption or emission transition, the stimulated emission cross-section, the fluorescence branching ratio between two levels, and the radiative lifetime of an excited level. These radiative parameters are further used to determine the spectroscopic parameters of the host materials and the structural properties of RE-ion sites in the host. Therefore, a basic understanding of the glass composition dependent J-O parameters of RE-ions is very useful for designing the optical materials with the desired properties. In most multi-component glass system is the very difficult to predict the local structures and the site selectivity of RE ions inside the host matrix. Nevertheless,

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the J-O analysis emerged as a powerful tool for the systematic analysis of the structure dependent spectroscopic properties of RE doped glass system useful for specific purposes.

The non-radiative decay is being essentially a competing process to the fluorescence a low non-radiative decay rate can lead to increased luminescence efficiency for many important RE transitions (when coupled with good environmental properties). Experimentally, the non-radiative decay rate (W_{NR}) is obtained from combination of the measured fluorescence lifetime by luminescence decay measurement and the radiative lifetime which can be estimated from a J-O analysis of RE doped glass absorption spectrum [5]. Since the luminescence quantum efficiency and emission transitions band widths of the doped RE ions strongly depends on the structural changes of the host matrices, appropriate selection of a suitable host material is very much essential in order to obtain better luminescence efficiency needed for the design and development of an optical devices [6].

Among various optical glasses available, tellurite (TeO_2) glasses are the most important glassy systems owing to their peculiarities such as high refractive index (~2.0) and large transparency window in the visible–infrared region (up to 5 μm) nominated them as good candidates for photonic and optoelectronic functions. It has been reported that, these glasses are good candidates for hosting rare-earth (RE) ions because of their low phonon-energy (~700 cm^{-1}) environment, good chemical durability and optical properties [7–9]. Nevertheless, TeO_2 under normal conditions does not have the ability to form glass easily without a modifier like alkali, alkaline earth and transition metal oxide or other glass modifiers [10]. For example, addition of boron trioxide (B_2O_3), which is known as a good glass former, has some improving effects on thermal and chemical stability of the tellurite glasses. Boro-tellurite glasses have also been proven as an excellent choice for laser active medium due to their intricate structure of both boron and tellurium exhibiting the two types of coordination with the surrounding oxygen. Moreover, addition of ZnO modifier oxides into the TeO_2-B_2O_3 will completely change the host structure, borate network changes from BO_3 to BO_4 and the tellurite network from trigonal bipyramid [TeO_4] to trigonal pyramid [TeO_3]. This will lead to improve the glass forming ability (GFA), and lowers the crystallization rates. In addition to that, it reduces the hygroscopic nature, improves the glass quality and enhances the IR transmission. Further, the boro-tellurite glasses upon addition of ZnO as network modifiers (NWM) could strengthen (or) enhance certain electrical, thermal and optical properties [11]. Due to these favorable properties, a considerable number of publications have been published on boro-tellurite glasses by different researchers.

Among the RE ions, erbium (Er^{3+}) ions show luminescence in the visible and near-infrared spectral regions which known to be applicable in solid state laser and broadband communications respectively. Although, the increment the concentration of REs in the glasses is found to intensify the up-and/or down-conversion luminescence but often it cause strong quenching at higher doping. At higher concentration the local environment of RE and optical properties of glassy host are influenced due to clustering of REs which is disadvantageous for applications. Aggregation and clustering of RE ions increase the interaction between RE ions which results in the quenched luminescence [12,13]. To surmount this effect an alternative route is thought to overcome this shortcoming, where metallic nanoparticles are embedded into the glass matrix. The presence of noble metal NPs in glass network induce the formation of electric dipoles activated by radiative transitions of RE ions forming localized SPR through energy transfer [14]. The influence of SPR on the luminescence efficiency of RE strongly depend upon the separation between the RE and NP. Thus, the efficiency of the electric dipole coupling improves the optimal separation where the enhanced local field can increase the oscillator strength.

Consequently, the aim of this research is to embed Ag NPs in Er^{3+}-doped zinc-boro-tellurite glass matrix and to determine the SPR mediated influence on spectroscopic, structural, and thermal properties. The spectroscopic data is complemented through J-O intensity parameters calculation. Furthermore, non-radiative decay rate for $^4S_{3/2}$ transition in the synthesized glass systems are measured.

Table 1
Glass codes and the nominal composition (in mol%) of glass system.

Glass codes	Glass composition (mol%)				
	TeO_2	B_2O_3	ZnO	Er_2O_3	AgCl
TBZEA0.0	59.5	30.0	10.0	0.5	0.0
TBZEA0.5	59.0	30.0	10.0	0.5	0.5
TBZEA0.7	58.8	30.0	10.0	0.5	0.7
TBZEA0.9	58.6	30.0	10.0	0.5	0.9
TBZEA1.1	58.4	30.0	10.0	0.5	1.1

2. Experimental

The raw materials to prepare TeO_2-B_2O_3-ZnO-Er_2O_3-AgCl glass samples are obtained in the powder form. Analytical grade chemicals of TeO_2 (Sigma-Aldrich ≥ 99%), B_2O_3 (Sigma-Aldrich 99.999%), ZnO (Sigma-Aldrich 99.99%), Er_2O_3 (Sigma-Aldrich ≥ 99.99%) and AgCl (HmbG 99%) are used in this work. The glass samples have nominal composition of (59.5-x)TeO_2-30B_2O_3-10ZnO-0.5Er_2O_3-xAgCl where x = 0.0, 0.5, 0.7, 0.9 and 1.1 mol% are prepared using melt-quenching technique. The composition of all prepared glass samples are listed in Table 1. The raw materials with required proportion are weighted using a very sensitive weighing machine (Electronic Balance Precisa 205A SCS). The total weight of each batch of glass is 11.0 g and calculated in mol percent (mol%).

The selected composition is placed in a porcelain crucible and then melted by raising the temperature of the electrical furnace (Model: Carbolite Aston Lane, Hope Sheffield S30 2RR, England) to 950 °C for 20 min for homogenous melting. In order to obtain transparent viscous melt, the batches are stirred frequently. The quenching process started by pouring the melt between two preheated stainless steel moulds in an alternate furnace as fast as possible to avoid solidification due to humidity. Then the glass samples are kept at 300 °C for about 3 h for annealing process to reduce the thermal and mechanical strains. After three hours, the furnace is switched off and the samples are allowed to cool down gradually to room temperature (25 °C). The prepared glass samples are cut at 2.8 ± 0.1 mm of thickness with flat surface using a diamond cutter. Finally, the samples are polished for structural and optical measurements.

The amorphous nature of glasses are examined via a Bruker D8 Advance X-ray diffractometer (XRD) which uses CuK_α radiations (λ = 1.54 Å) at 40 kV and 100 mA with 2θ ranges from 10° to 80° with step size 0.02° and resolution of 0.01°. Transmission electron microscopy (TEM) (Philips CM12) with an acceleration voltage of 200 kV is used to investigate the presence of silver NPs inside the glass host. The elemental analysis of prepared glasses is made using energy dispersive spectrometry (EDX) (SwiftED300 EDX). The Fourier transform infrared (FTIR) of the glass samples in this study are carried out in the range of 400–4000 cm^{-1} using a Perkin Elmer FT-IR 1660 spectrometer using KBr pellets. The resolution of the measurement is ± 4 cm^{-1}. Differential thermal analyzer (DTA) (Model: Pyris Diamond TG-DTA, Japan) is used to analyze the thermal parameters of the samples under a heating rate of 10 °C/min. The experiment is performed under N_2 atmosphere with a rate flow of about 200 mL/min.

Shimadzu ultraviolet visible near infrared (UV–Vis–IR) spectrophotometer (Model: UV-1301PC) is used to record the absorption spectra of the glass samples with a resolution of 1.0 nm. The absorption spectrum is measured in spectral range of 200–2000 nm by using Tungsten Halogen lamp (HL) as a radiation source. Both sides of the glass samples are polished to avoid any unfavorable surface scattering during optical measurements. Perkin-Elmer photoluminescence (PL) spectra (Model: LS 55) (in which a pulsed Xenon lamp operates as a source of excitation) is used