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Luminescence properties of europium doped oxyfluorosilicate glasses for visible light devices

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ABSTRACT

Europium (Eu^{3+})-doped oxyfluorosiliacte (SALfSfEu: $SiO_2 + Al_2O_3 + LiF + SrF_2 + Eu_2O_3$) glasses have been fabricated by usual melt-quenching technique. These glasses were characterized through optical absorption, excitation, emission and decay curve analysis. The Judd-Ofelt (JO) parameters have been evaluated from the refractive index and luminescence spectrum of the 1.0 mol% Eu^{3+}-doped glass. The quantitative radiative properties including branching ratio, radiative lifetime and stimulated emission cross-sections of the fluorescent levels were predicted by using the JO parameters. Luminescence intensity increases as for as 0.5 mol% and then decreases with further increasing Eu^{3+} ion concentration. Photoluminescence quantum yield found to be as high as 74% for 0.05 mol% of Eu^{3+} ion concentration and decreased by increasing concentration. Luminescence intensity ratio is found to be 3.17 for 1.0 mol% Eu^{3+}-doped SALfSfEu1.0 glass which suggest that the occupation of high degree of symmetry by the Eu^{3+} ions. Fluorescent decay curves of the emitting level exhibit an exponential behaviour. Lifetime of $^5D_0 \rightarrow {}^7F_2$ transition was decreased slightly with increasing Eu^{3+} ion concentration, however, not significant for $^5D_1 \rightarrow {}^7F_1$ transition. Luminescence properties reveal that the red emission at 612 nm found to be suitable for developing the lasers and display devices in the visible region.

1. Introduction

Inorganic materials are playing a key role for the development of advanced photonic devices in modern science and technology. Over the past couple of decades, luminescence properties of lanthanide (Ln^{3+}) ions doped novel materials have been widely adopted for multiple photonic devices including lasers [1,2], optical amplifiers [3], spectral convertors [4], display devices [5–8], image production devices [9], white light emitting diodes [10], laser cooling [11,12], optical waveguides [13] and temperature sensors [14]. Much attention has been paid on Ln^{3+}-doped glasses due to their easy mass production, easy shaping, and flexibility in doping at relatively large amount of active ion concentration. Particularly, Eu^{3+}-doped glasses have great interest as their luminescence properties can be tailored by altering the active ion concentration [15], glass network modifiers [16], co-doping with metal nanoparticles [17], with the influence of high-energy radiation [18], through energy transfer [19], etc.

Eu^{3+} ion is of a special attention among the other Ln^{3+} ion from spectroscopic view point due to the following properties: (i) The multiplet splitting of the $^5D_0 \rightarrow {}^7F_J$ ($J = 0$–6) transitions in the emission spectra of Eu^{3+} ion depends strongly on the native environment nearby the Eu^{3+} ion and in particular the non-degeneracy of the ground ($^7F_0$) and the fluorescent ($^5D_0$) levels under any symmetry [20]; (ii) Ideally, Eu^{3+} ion is used to assess the inherent assembly of Ln^{3+} ions in any matrix because of its compact energy level scheme as well as a great sensitivity of its luminescence on the native environment [21]; (iii) A hole burning spectrum could be accomplished for the $^7F_0 \rightarrow {}^5D_0$ transition of Eu^{3+} ion that has a potential to use as an optical data storage devices at higher density [22]; (iv) The phonon side band (PSB) is always accompanying with the pure electronic band (PEB), $^7F_0 \rightarrow {}^5D_2$ transition that reveals the native assembly of Eu^{3+} ion position and modifies the non-radiative decay de-excitation processes; and (v) The integrated intensities of PSB and PEB were used to evaluate the electron-phonon coupling strength of a host [20].

In general, addition of Al_2O_3 to the glass network, Al^{3+} ions linked to tetrahedral and octahedral structural units. The magnitude of these units depends on the concentration of Al_2O_3 and other components in the glass matrix. Photoluminescence intensity of lanthanide ions enhanced significantly with increasing of Al_2O_3 content in the glass

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matrix. This increase leads to enhance the photoluminescence efficiency due to de-clustering of lanthanide ions by Al^{3+} ions in the glass matrix. In addition, the yellow to blue (Y/B) intensity ratio of Dy^{3+}-doped lead silicate glasses was decreased with increase in Al_2O_3 content [23]. Moreover, depolymerisation of the glass network and luminescence intensity of the $^4F_{3/2} \rightarrow {}^4I_{11/2,\ 13/2}$ transitions of Nd^{3+}-doped silicate glasses was increased with increase in Al_2O_3 content [24]. In addition, self-green upconversion of the $^5F_4 + {}^5S_2 \rightarrow {}^5I_8$ transition of Ho^{3+} ion was also enhanced significantly due to additional population of $^5F_2$ and $^5F_3$ levels with increasing Al^{3+} concentration [25]. Over all, addition of Al_2O_3 influences the upconversion properties, de-clustering effects, de-quenching of emission of lanthanide doped glasses. The addition of fluoride components such as LiF and SrF_2 to the glass matrix reduces the phonon energy of the glass matrix. In addition, the Ln ions can be incorporated selectively in the fluoride crystalline phase (glass-ceramics) at appropriate heat treatment temperature without losing the transparency of the glass [20,26].

Oxyfluoride glasses have greater advantage over fluoride and oxide glasses. The photoluminescence quantum yield (PLQY) of the Ln^{3+}-doped materials depends strongly on the maximum phonon energy of the host matrix. Moreover, it is favorable to achieve high value of PLQY in the case of fluoride glasses as they suppress the non-radiative relaxations. However, it is difficult to make use of them for practical applications due to their poor mechanical and chemical resistance. On the other hand, oxide glasses are the better choice because of their high chemical and mechanical strengths and the only drawback is higher in phonon energy. Oxyfluoride glasses containing transition metal fluorides have the superior advantages than the oxide and fluoride glasses as they exhibit the combine properties of oxide and fluoride materials such as low phonon energy, high chemical stability, low melting temperatures, tolerable mechanical strength, enhanced optical and luminescence properties [12,27–32].

This paper reports the optical and photoluminescence properties of Eu^{3+}-doped oxyfluorosilicate glasses at different Eu^{3+} ion concentration. Upon excitation at 393 nm, an intense red emission at 612 nm is obtained for Eu^{3+}-doped glasses by properly adjusting the Eu^{3+} ion concentration. A quantitative study has been carried out for evaluating the branching ratio (β_R), radiative transition probability (A_R) and radiative lifetime (τ_R) of Eu^{3+}-doped glasses by using the Judd-Ofelt (JO) theory [33,34]. The fluorescence intensity ratio among the $^5D_0 \rightarrow {}^7F_2$ and the $^5D_0 \rightarrow {}^7F_1$ transitions has been evaluated for estimating the native assembly about the Eu^{3+} ion. The results were compared to those of other reported Eu^{3+}: systems [15,31,35–41].

2. Experimental procedure

Oxyfluorosilicate glasses doped with Eu^{3+} ions were fabricated by usual melt-quenching technique. The molar composition of the as synthesized glasses and their labels along with the other reported glasses were collected in Table 1. An initial batch reagent weight of 30 g taken in a platinum-rhodium (Pt-Rh) crucible, that was placed in an electric furnace around 1450 °C for 2 h. Then the glass melt was casted on to a brass mold and subsequently annealed at 450 °C for 18 h. The samples were slowly cooled to room temperature to eliminate residual stress and strain. Samples were polished optically for optical characterization.

The densities of Eu^{3+}-doped glasses were calculated by using the Archimedes method with an immersion liquid (deionized water). The index of refraction was measured at 473, 532, 633, 1064 and 1552 nm by using the prism coupler set-up (Metricon, 2010/M). Absorption spectrophotometer (Cary 5000 spectrophotometer) was used to record the absorption spectrum in the wavelength range of 300–2400 nm. Photoluminescence emission and excitation spectra were attained by using Edinburgh FLS 980 spectrofluorometer (CW xenon lamp with a power of 450 W). Decay curves were acquired with the same instrument under pulsed xenon lamp excitation. The PLQY of the samples were obtained by using integrating sphere under the excitation of xenon lamp. The measurements were performed at ambient atmosphere.

3. Results and discussion

3.1. Thermal analysis

Thermal analysis of the host glass has been carried out and found to be similar to our previous work [42]. From the thermal analysis (DTA), the glass transition temperature (T_g) and crystallization temperature (T_x) found to be 532 °C and 655 °C, respectively. From these two T_g and T_x values, the glass thermal stability ($\Delta T = T_x - T_g$) is calculated and it was found to be 123 °C. The larger value of ΔT (> 100 °C) of the present glass could be considered as a good thermal stability and it can be used for laser action.

3.2. Linear index of refraction

Linear index of refraction of Eu^{3+}-doped glass was measured at five different wavelengths, as shown in Fig. 1 and presented in Table 2. The value of index of refraction lies in the range of 1.5601–1.5937. It is well known that the index of refraction decreases with increase in the spectral wavelengths of 473, 532, 633, 1064 and 1552 nm. The variation of indices of Eu^{3+}-doped glasses at 473 nm is shown in the inset of Fig. 1. Abbe number (υ) can be evaluated from the values of index of refraction by using the following formula

$$\upsilon = \frac{n_e - 1}{n_f - n_c} \tag{1}$$

where υ is the Abbe number, n_e, n_f and n_c are the indices of refraction at three wavelengths, 532, 473 and 633 nm, respectively. The 'υ' values of the Eu^{3+}-doped glasses are also presented in Table 2. The value of 'υ' explains the material dispersion of the glass and it lies in the range of 50–100 which indicates that these glasses can be considered as optically active materials [43,44]. The value of 1/υ denotes the dispersive power of the glass. As can be seen from Table 2, Abbe number is found to be as low as 55 for SALfSfEu2.0 glass and as high as 66 for SALfSfEu0.01 glass. It is observed that the index of refraction decreases slightly for Eu^{3+}-doped glasses at low Eu^{3+} ion concentration, i.e. up to 0.1 mol%, thereafter, it increases significantly with further increasing Eu^{3+} ion concentration (till 3.0 mol%). The later one is due to increase in density and modification of network of glasses with increasing Eu^{3+} ion concentration as it contributes linear polarizability.

3.3. Absorption spectra

Optical absorption spectrum of Eu^{3+} ions in SALfSfEu1.0 glass in the range of 340–2400 nm is shown in Fig. 2(a) and (b). It consists of several absorption bands which are originated from both the ground state ($^7F_0$) and first excited state ($^7F_1$) of Eu^{3+} ions. These bands were centered at 362 nm ($^5D_4$), 366 nm ($^5L_8$), 376 nm ($^5G_3$), 382 nm ($^5G_2$), 393 nm ($^5L_6$), 464 nm ($^5D_2$), 526 nm ($^5D_1$) and 2083 nm ($^7F_6$) originating from the $^7F_0$ ground state, whereas the bands originated from $^7F_1$ level (thermally populated even at room temperature) are centered at 401 nm ($^5L_6$), 414 nm ($^5D_3$), 532 nm ($^5D_1$) and 2207 nm ($^7F_6$). It is observed that the $^7F_0 \rightarrow {}^5L_6$ transition found to be more predominant compared to all the other transitions.

3.4. Excitation spectrum

The absorption peaks disappear perhaps in the UV or deep UV region due to the host absorption, which can be resolved and assigned from the excitation spectrum. The excitation spectrum of Eu^{3+} ions in the SALfSfEu1.0 is obtained in the range of 310–590 nm by observing the emission at 612 nm ($^5D_0 \rightarrow {}^7F_2$) and is shown in Fig. 3. There are eleven excitation peaks including $^7F_0 \rightarrow {}^5H_4$ (320 nm), $^7F_0 \rightarrow {}^5D_4$