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Spectroscopic properties and upconversion studies of Er^{3+}-doped SiO_2-Al_2O_3-Na_2CO_3-SrF_2-CaF_2 oxyfluoride glasses for optical amplifier applications

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ABSTRACT

Er^{3+} doped SiO_2-Al_2O_3-Na_2CO_3-SrF_2-CaF_2 oxyfluoride glasses have been prepared by melt quenching method and were investigated by optical absorption spectra. Judd-Ofelt intensity parameters were calculated and used to predict radiative properties of 1.0 mol% of Er^{3+} ions doped glass. The visible photoluminescence and lifetime spectra were recorded under the 379 nm excitation source. In the near infrared region the emission spectra and their decays corresponding to $^4I_{13/2} \rightarrow {}^4I_{15/2}$ laser transition of Er^{3+} ions, were recorded by excitation source of laser diode at wavelength of 980 nm. The lifetime of $^4I_{13/2}$ level has been decreased (6.38–1.95 ms) with increasing of Er^{3+} ion concentration from 0.1 to 2.0 mol%. The upconversion studies were investigated as a function of Er^{3+} ions concentration in oxyfluoride glasses. The mechanism involved in the energy transfer process corresponding to an increase in the green and red emission upconversion intensities with increasing of Er^{3+} ions concentration were discussed. The spectroscopic characteristics of 1 mol% of Er^{3+}doped oxyfluorosilicate glasses were compared with other host materials. The stimulated emission cross-section and gain bandwidth have been calculated and found to be 9.8×10^{-21} cm^2 and 0.52×10^{-25} cm^3 for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ (1.535 μm) transition and is most useful for optical amplifier applications.

1. Introduction

In the recent decades an extensive research work has been carried out on glasses and glass ceramics with rare-earth (RE) ions for their use in telecommunication system elements such as up-converters, fibers, optical amplifiers, solid state lasers and 3D displays. Particularly, Er^{3+} doped materials are more attractive due to the infrared spectral emission at 1.55 μm ($^4I_{13/2} \rightarrow {}^4I_{15/2}$) transitions. Especially the Er^{3+} doped glasses are attractive for numerous applications such as microchip lasers [1], erbium-doped fiber amplifier (EDFAs) in wavelength division multiplexing (WDM) systems [2,3], eye safe laser systems [3], waveguide amplifiers [4] and lidar transmitters [5]. In addition to the excellent infrared amplifying and lasing properties, Er^{3+} ions have rich energy level structures. The erbium ion has very attractive for infrared to visible upconversion applications such as high density optical storage, color displays, temperature sensors, optoelectronics and medical diagnosis [6–9].

Upconversion process is strongly influenced by the characteristics (maximum phonon energy) of the host. As usual, the glasses with lower phonon energy with worse chemical and mechanical stabilities are not suitable for upconversion studies. Oxide glasses have better chemical and mechanical stabilities but higher phonon energy [10,11]. Tanabe et al. [12,13] discussed the effect of Al_2O_3 on SiO_2-Al_2O_3-NaO_2 glass and reported that addition of Al_2O_3 in the glasses exhibits high chemical durability, low thermal expansion coefficient and more thermally and electrically resistant. In addition to that, the authors are modified the present glass system by adding SrF_2 and CaF_2 to reduce the non radiative channels and to enhance the fluorescence and upconversion studies in the present host.

Silicate based oxyfluoride glasses have been investigated for several years due to their potential applications optical amplifiers and fiber lasers. Over the last decade, Qiao et al. [14] reported Er^{3+} doped CaF_2 glass ceramics and Feng et al. [15] studied optical properties of Er^{3+} doped SiO_2-Al_2O_3-Na_2CO_3-ZnF_2. Recently, Kesavulu et al. [16] discussed upconversion properties of Er doped SrF_2 nano-crystals in SiO_2-Al_2O_3-LiF-SrF_2 glass ceramics and Feng et al. [17] described the

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effect of ZnF_2 on upconversion studies of SiO_2-BaF_2-ZnF_2 glasses. And also, several articles were evidenced in literature, on erbium ions doped silicate based glasses exploring the various applications, nevertheless, very few report on silicate based oxyfluoride glasses for enhancing fluorescence studies to develop the optical fiber amplifiers [18–20]. From the literature review, it has been outlined that the silicate based oxyfluoride glasses have many applications in optical technology due to their unique spectroscopic behavior and with their excellent thermal and chemical stability, high mechanical strength, as well as low phonon energy environment for luminescence ions.

In this direction, the authors are motivated to study the absorption, emission, decay properties and upconversion studies of Er^{3+} doped SiO_2-Al_2O_3-Na_2CO_3-SrF_2-CaF_2 oxyfluoride glasses are presented. The Judd-Ofelt (JO) theory [21,22] has been used to determine the radiative properties for the important luminescent levels of Er^{3+} ions. The emission cross-section of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition has also been calculated from the absorption and emission spectra. The obtained results are discussed with respect to the Er^{3+} ions concentration and also compared with other reported glasses.

2. Experimental techniques

The oxyfluorosilicate glasses (SANSCEr) having a nominal composition of (45-x)SiO_2-5Al_2O_3-17Na_2CO_3-18SrF_2-15CaF_2- x Er_2O_3 (where x = 0.1, 0.5, 1.0 and 2.0 mol%) were prepared and referred as SANSCEr01, SANSCEr05, SANSCEr10 and SANSCEr20, respectively. The glasses were prepared by mixing of corresponding high purity (99.9%) oxides and fluorides in an agate mortar. The mixed powder was melted in alumina crucible using an electrical furnace at 1400 °C, with duration of 2.30–3.00 h. The glass melts were poured on preheated brass plate at 480 °C (near glass transition temperature, T_g). The samples were annealed for 15 h at constant temperature to release thermal stress/strain and allowed to cool to room temperature. The optical measurements were performed out on polished glass slab of about 1–2 mm thickness. The refractive indices (n = 1.58) have been acquired by using an Abbe's refractometer. The optical absorption spectrum was recorded using a JASCO V-770 spectrophotometer in the range from UV to NIR region. The visible emission spectra were measured with Photo multiplier tube (PMT) detector under xenon lamp (379 nm). The NIR spectra in the range 1400–1700 nm were recorded by using an excitation source of laser diode at wavelength of 980 nm. The emitted signal was focused onto a PC-controlled FLS-980 series of fluorescence spectrophotometer and detected by InGaAs detector (Thorlabs DET10C). Fluorescence lifetime was measured using a pulsed 980 laser diode. A digital phosphor oscilloscope (Tektronics/TDS 3012 C) was used to record the decay curves. All spectroscopic measurements were accomplished at room temperature.

3. Results and discussion

3.1. Judd-Ofelt analysis

The absorption spectra of SANSCEr10 glass in the visible and NIR region were shown in Fig. 1. All the absorption bands and their barycenter's are found to be almost identical except with some differences in the band intensities. The absorption bands are originated from the ground state $^4I_{15/2}$ to the excited states $^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$, $^4F_{7/2}$, $^4F_{5/2}$, $^4F_{3/2}$, $^2G_{9/2}$, $^4G_{11/2}$, $^4G_{9/2}$ and $^2G_{7/2}$ respectively. According to previous reports [21–24], experimental (f_{exp}) and calculated (f_{cal}) oscillator strengths and JO intensity parameters (Ω_λ, λ = 2, 4 and 6), radiative transition probabilities (A_R) fluorescence branching ratios (β) and radiative lifetimes (τ_{rad}) were calculated. The absorption band transitions and energies, f_{exp} and f_{cal} values are shown in Table 1. The root mean square (rms) deviations of f_{exp} and f_{cal} expressing the accuracy of fit are also presented Table 1. The rms deviation of the present glass has been obtained as 0.29 × 10^{-6} and it is very small and suggests a good agreement between f_{exp} and f_{cal} values.

The phenomenological JO parameters (Ω_λ, λ = 2, 4 and 6) have been evaluated for SANSCEr10 glass and compared with the reported values and are presented in Table 2. In general, the position and oscillator strengths of absorption transitions are sensitive to the local environment of RE ion sites within the glass network. Therefore, the parameter provides the information of the nature of bond between RE ions to the surrounding ligands. Among these, Ω_2 is most sensitive to local structure and it explains the covalency of the glass system. For SANSCEr10 glass Ω_2 value is 7.04 × 10^{-20} cm^2, indicates the existence of a high degree of covalency in the present glass system and is compared with other reported silicate based glasses [10,11,13–17,25–28] in Table 2. The spectroscopic quality factor (χ) found to be 1.23 for SANSCEr10 glass. The quality factor is very important predictor for stimulated emission in a laser active medium [29].

From the calculated JO intensity parameters, the radiative transition probabilities (A_R), branching ratios (β_R) and radiative lifetime (τ_R) for the excitation levels $^4F_{7/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$ have been evaluated and presented in Table 3. These transitions possess a high fluorescence branching ratio and higher radiative lifetimes, which indicates that they are most possible laser transitions. Among all the laser transitions the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ (1535 nm) has highest branching ratio (100%) and radiative lifetime (5.18 ms). These results suggest that the glass samples might be potential optical material for optical communications.

3.2. Fluorescence studies

3.2.1. NIR emission and Lifetime analysis

The room temperature fluorescence emission spectra for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} doped SANSCEr glasses upon 980 nm laser excitation are shown in Fig. 2. The emission intensity increases with increasing Er^{3+} ion concentration from 0.1 to 1.0 mol% and then decreases for 2.0 mol% due to concentration quenching. The NIR emission transition mechanism was detailed in partial energy level diagram as shown in inset of Fig. 2. When the $^4I_{11/2}$ level is directly excited by diode laser operating at 980 nm, the excited energy stored in the $^4I_{11/2}$ level relaxes to the $^4I_{13/2}$ fluorescent level. The fluorescent level radiates energy to ground state i.e., $^4I_{13/2} \rightarrow {}^4I_{15/2}$ is observed at 1535 nm. For the highest emission intensity observed at 1535 nm ($^4I_{13/2} \rightarrow {}^4I_{15/2}$), the radiative transition properties were bandwidth (53 nm), the transition probability (193 s^{-1}), stimulated emission cross-section (9.8 × 10^{-21} cm^2), gain band width parameter (0.52 × 10^{-25} cm^3), experimental lifetime (3.83 ms), radiative lifetime (5.18 ms), quantum efficiency $\eta = \tau_{exp}/\tau_{rad}$ (74%) and gain per unit lengths (37.57 × 10^{-24} cm^2 s) calculated for SANSCEr10 glass and compared with other reported systems in Table 4. [4,16,30–33]. Among these the present glass SANSCEr10 laser transition ($^4I_{13/2} \rightarrow {}^4I_{15/2}$) has found low FWHM (53 nm) with compare to the [16,30–33] and higher than [4]. The emission cross-section 9.8 × 10^{-21} cm^2 is higher than [4] and comparable with other reported systems [16,30–33]. The radiative lifetime for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of 1.0 mol% of Er^{3+} ions is found 5.18 ms which is lower than SANZ10 (7.16 ms) [15], SBZ10 (7.91 ms) [17] and BYL (7.87 ms) [33] glasses and higher than SALSFEr10 (3.99 ms) [16], TZNEr10 (2.92 ms) [30] and PKAlCaFEr10 (4.47 ms) [31] glasses. Hence, the present oxyfluoride silicate glasses can be considered as an active medium to achieve good lasing action.

The decay time measurement of the ($^4I_{13/2} \rightarrow {}^4I_{15/2}$) transition has been measured as a function of Er^{3+} ions concentration. Fig. 3 represents the decay times for 1535 nm emission for the SANSCEr glasses. All the decay curves are well fitted to the single exponential decay, the experimental lifetime (τ_{exp}) for the SANSCEr01, SANSCEr05, SANSCEr10 and SANSCEr20 have been found to be 6.38, 4.53, 3.83 and 1.95 ms, respectively. This clearly indicates that the quenching of