Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Optical spectroscopy and emission properties of Ho^{3+}-doped gadolinium calcium silicoborate glasses for visible luminescent device applications

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ARTICLE INFO

Keywords:
Ho^{3+} glasses
Optical properties
Judd-Ofelt theory
Decay time
Resonant energy transfer

ABSTRACT

The Ho^{3+}-doped gadolinium calcium silicoborate glasses with the composition of $25Gd_2O_3 + 10CaO + 10SiO_2 + (55 - x)B_2O_3 + xHo_2O_3$, where x = 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 mol%, were synthesized by well-known melt quenching method. These glasses have been characterized through physical, structural, optical, visible emission and decay curve analysis. From the absorption spectrum, Judd-Ofelt intensity parameters for 1.0 mol% Ho_2O_3 doped glass have been carried out and were used to examine radiative properties for the important visible emitting levels of Ho^{3+} ions. The present Ho^{3+}:glasses show strong green emission at 545 nm and red emission at 655 nm under excitation at 452 nm. The radiative decay time and stimulated emission cross-section for the $(^5S_2, ^5F_4) \rightarrow {}^5I_8$ transition are found to be 280 μs and 0.63×10^{-20} cm^2, respectively. Decay curves for all the concentration of Ho^{3+} ions exhibit non-exponential nature for $(^5S_2, ^5F_4) \rightarrow {}^5I_8$ transition. The decrease in decay times is due to the resonant energy transfer among the excited Ho^{3+} ions. Hence, these results confirm that the present silicoborate glass system could be considered as a promising candidate for visible green laser applications.

1. Introduction

Rare-earth (RE) -doped glasses have attracted much attention for their potential applications such as visible lasers, optical fibers, amplifiers, waveguides, optical data storages, sensors, optical displays and optical devices due to their interesting optical and luminescence properties [1–4]. Therefore, the active research in the field of RE ion spectroscopy is to identify new hosts doped with trivalent RE ion and to characterize them for optical device applications. In this direction, search for novel hosts, silicoborate glasses can be a better host to enhance optical properties within silicate and borate glass systems. These silicoborate glasses are also found to be appropriate host for optically active ions due to relatively moderate melting point with high transparency, thermal stability, low non-linear refractive index and good RE ion solubility besides physical and chemical stability [5,6]. The main drawback of the silicoborate glasses has high phonon energy (~1400 cm^{-1}) [3] and may quench the radiative decay process. Therefore, the phonon energy can be reduced by adding heavy metal oxides to the borate glasses [4]. Moreover, borate glasses containing heavy metal oxides exhibit significant properties such as high refractive index, large polarizability, high optical basicity and small metallization criterion [4]. In general, the low phonon energy glass systems are highly acceptable for highly efficient lasers and fibers [7]. Hence, RE ions doped silicoborate glasses may be a best choice to develop novel materials for optical devices for efficient laser gain media applications in the visible, near infrared and mid infrared regions.

Among all the RE ions, trivalent holmium (Ho^{3+})-doped glasses are being considered as one of the most effective ions for spectral analysis due to intense emission channels both in visible and infra-red regions [8]. Therefore, optical properties of Ho^{3+}-doped systems have been investigated and reported luminescence properties both from down conversion as well as up-conversion that covers visible, near infrared and mid-infrared regions [8–14]. Rai [9] has reported optical properties of the Ho^{3+}-doped oxyfluoborate glasses. Srinivasa Rao et al. [10] analysed the Ho^{3+} ions in lead phosphate glasses for application in mid-infrared lasers at a wavelength of 2.0 μm. Mahamuda et al. [1] studied and reported the zinc alumino bismuth borate glasses doped with Ho^{3+} ions for the development of visible red, near infrared and mid infrared laser applications. Bhargavi et al. [11] examined the Ho^{3+}-doped lead silicate glasses with influence of Al^{3+} ions on self up-conversion for green emission applications. Venkateswarlu et al. [12] investigated lead tungsten tellurite glasses in Ho^{3+} ions for green

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http://dx.doi.org/10.1016/j.jnoncrysol.2017.08.018
Received 12 April 2017; Received in revised form 11 August 2017; Accepted 13 August 2017

luminescent applications at 546 nm in the visible region. Spectroscopic properties of Ho^{3+} and Al^{3+}-codoped silicate glasses for 2.0 μm laser materials have been investigated by Wang et al. [13], and heavily Ho^{3+}-doped lead silicate glass fiber was studied for single-frequency fiber laser applications by Liu et al. [14].

The aim of this work is to study the physical, structural, optical, excitation, emission and decay time measurements of Ho^{3+}-doped silicoborate glasses. By using the Judd-Ofelt (JO) theory [15,16], the three phenomenological JO intensity parameters (Ω_λ, λ = 2, 4 and 6) were evaluated from the absorption spectrum of 1.0 mol% Ho^{3+}-doped silicoborate glass. Based on the JO theory, large emission cross-sections for visible emission at 545 nm were derived. These optical and luminescence results of Ho^{3+}-doped silicoborate glasses reveal their promising application to develop efficient green laser and optical amplifiers at 545 nm in the visible region.

2. Experimental methods

Gadolinium calcium silicoborate glasses (GdCaSBHo) with the chemical composition of $25Gd_2O_3 + 10CaO + 10SiO_2 + (55 - x) B_2O_3 + xHo_2O_3$ (here after referred as GdCaSBHo0.5, GdCaSBHo1.0, GdCaSBHo1.5, GdCaSBHo2.0 and GdCaSBHo2.5, for x = 0.5, 1.0, 1.5, 2.0, and 2.5 mol%, respectively) were synthesized by well-known melt quenching method. The stochiometric compositions of the batch materials (~20 g) were taken in a platinum crucible and placed in an electric furnace at a melting temperature of 1400 °C for 90 min. The obtained glass melt was poured onto a preheated brass mold and subsequently annealed at 460 °C for 5 h to remove the thermal stress and strains. Afterwards, all the glass samples were cut and optically fine polished for spectral analysis.

The densities of the title glasses were determined by Archimedes's method using distilled water as an immersion liquid within an error of ± 0.001 g/cm^3. Refractive indices were measured using an Abbe refractometer at sodium wavelength (589.3 nm) with 1-bromonapthalene ($C_{10}H_7Br$) as a contact liquid within an error of ± 0.0001. To confirm amorphous nature of glasses, Philips XPERT-MED X-ray diffractometer (XRD) equipped with conventional Cu Kα radiation within 2θ range (10-80°) with the scan rate of 0.020°/s and step size of 0.03° at 40 kV and 30 mA has been used. Raman spectrum was recorded at room temperature in the Raman shift range of 100–2800 cm^{-1} with a QE Pro-Raman spectrometer by exciting at 785 nm with a spectral resolution of ± 4 cm^{-1}. Absorption spectrum was measured on a Perkin Elmer Spectrophotometer (Lambda-950) in the wavelength range of 300–2200 nm with a spectral resolution of ± 1 nm. The excitation, emission and decay curve measurements were carried out with a Jobin Yvon (HORIBA) fluorolog-3 spectrometer using xenon flash lamp as radiation source by exciting the samples with 452 nm. The fluorescence quantum yield of the samples was measured by using on integrating sphere which connected to the fluorescence spectrometer (Oriel, Model 70451). The integrating sphere was mounted on the side of the fluorescence spectrometer sample chamber, opposite to the excitation source. All the measurements were carried out at room temperature.

3. Results and discussions

3.1. X-ray diffraction

In order to prove amorphous nature of the obtained samples, the structural analysis was done by using X-ray diffraction. Fig. 1 shows the typical X-ray diffraction patterns for the studied un-doped and 1.0 mol % Ho^{3+}-doped silicoborate glasses. The X-ray diffraction pattern does not indicate any sharp crystalline features and clearly reveal the amorphous nature of the present studied glasses. X-ray diffraction patterns found to be agreed to that of similar host glasses reported [6].

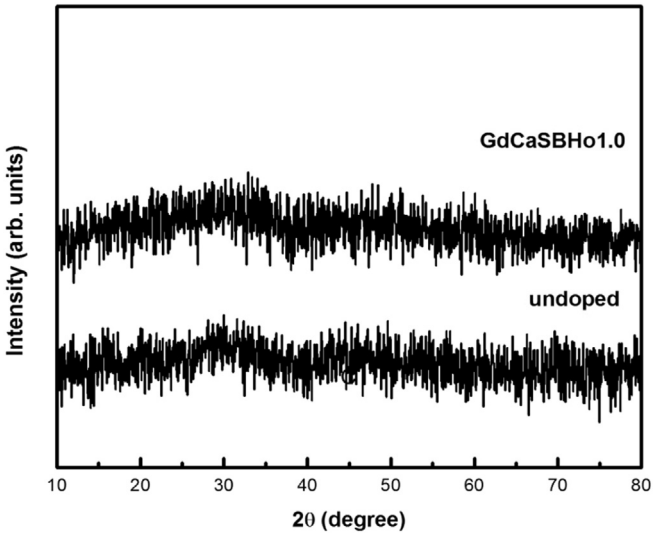

Fig. 1. XRD pattern spectra of un-doped and GdCaSBHo1.0 glasses.

3.2. Physical properties

The important physical parameters for GdCaSBHo glasses have been calculated by using predicted formulae [17], the two important physical parameters of density (d) and refractive index (n) and several other parameters such as Ho^{3+} ion concentration (N), average molecular weight (M_{Av}), molar volume (V_m), polaron radius (r_P), inter-nuclear distance (r_i) and field strength (F) in the present glass network has been estimated following the equations and were depicted in Table 1.

The density (ρ) was obtained from the relation

$$\rho = \frac{a}{(a-b)} \times \rho_x \tag{1}$$

where a is the weight of the glass sample in air, b is the weight of the glass sample when immersed in distilled water density (ρ_x) of 1 g/cm^3. The average molecular weight (M_{Av}) was estimated from the following relation,

$$M_{AV} = \sum_i X_i M_i \tag{2}$$

where X_i is the molar fraction of the each molecule in the glass composition (mol%) and M_i is the molecular weight of the ith component of each molecule in the glass composition (g/mol). The molar volume (V_m) was calculated from the below equation,

$$V_m = \sum_i \frac{x_i M_i}{\rho} \tag{3}$$

The Ho^{3+}-ion concentration is obtained from [17]

$$N\left(\frac{ions}{cm^3}\right) = (\text{mol\%of RE}) \times \frac{N_A \times \rho}{M_{AV}} \tag{4}$$

where N_A is the Avogadro's number. The three other related physical parameters have also been determined as

$$r_p = \frac{1}{2}\left(\frac{\pi}{6N}\right)^{\frac{1}{3}} \tag{5}$$

$$r_i = N^{-\frac{1}{3}} \tag{6}$$

$$F = \frac{Z}{r_p^2} \tag{7}$$

where N and Z are the Ho^{3+} ion concentration and atomic mass of holmium, respectively [17].

Density is used to calculate the degree of structure compactness, modifications of the geometrical configurations of the glass network,