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Energy transfer based emission analysis of Eu^{3+} doped Gd_2O_3-CaO-SiO_2-B_2O_3 glasses for laser and X-rays detection material applications

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ABSTRACT

The Eu^{3+}-doped CaO-Gd_2O_3-SiO_2-B_2O_3 glasses were prepared to study photoluminescence, lasing potential and scintillation properties. Glasses absorb photons in ultraviolet, visible light and near infrared regions and are assigned to the energy transitions of Gd^{3+} and Eu^{3+}. Ultraviolet with 275 nm can generate the strong red emission with 614 nm via energy transfer form Gd^{3+} to Eu^{3+}. X-ray scintillation study exhibits strong emission pattern due to Gd-Eu energy transfer. The optimum concentrations of Eu^{3+} ion in this glass is 0.30 mol% as it results maximum emission intensity. The fluorescence lifetime of the $^5D_0$ level decreases from 1.763 to 1.726 ms when concentration increased from 0.05 to 0.40 mol%. From Judd-Ofelt analysis, this glass exhibit high potential for using as laser medium for red laser device with high lasing power and energy extraction ratio. Moreover, this glass performs the integral scintillation efficiency as 13% compared with BGO.

1. Introduction

Rare-earth ion (RE^{3+}) doped glass has been potentially used as the photonic material in recent years. Since low synthesis cost, large-volume production, easy shaping, high optical homogeneity and the possibility of varying luminescence properties within broad limits [1,2]. Also glasses doped with RE^{3+} ions are promising choices to compensate single crystals and ceramics in photonic applications, especially scintillation material and laser medium. Among RE^{3+}, europium (Eu^{3+}) is anion in the class of lanthanide which have the electron configuration $[Xe]-4F^6$. The most intense emission of Eu^{3+} is placed at wavelength around 610 nm which is red color emitting and can be attributed to $^5D_0 \rightarrow {}^7F_2$ hypersensitive transition [3,4]. From this characteristic of Eu^{3+}, it has been doped in many kinds of host to research and develop for using as laser gain medium in red laser device [5,6] and scintillation material in x-ray imaging applications [7,8]. For glass former, silicaborate recombination is an interesting host material because of its thermal, mechanical and chemical resistance. Moreover, it has been used as fiber glass reinforcing organic matrix composites [9]. Adding calcium element can increase intensity of luminescence emission of glass [10]. While, Gd_2O_3 has been a popular oxide for photonic materials due to the efficient energy transfer from Gd^{3+} ions to luminescence activator, high thermal neutron capture cross-section and increase the light yield of emission [11,12]. Glass scintillator with a high Gd_2O_3 content are concentrated in various silicate, borosilicate, phosphate and germinate glasses with fast decay time and/or relative high light yield [13]. The Gd^{3+}-RE^{3+} energy transfer also can enhance the photo emission which improve laser ability. Therefore, it can be said that Eu^{3+}-doped calcium gadolinium silicoborate glass is very interesting for using in photonic application, such as scintillation material and laser medium.

This paper reports about the study of calcium gadolinium silicoborate glasses doped with Eu^{3+}. Physical, optical and luminescence properties were investigated as a function of Eu_2O_3 concentration. The scintillation and laser potential of glass were analyzed by X-ray induced optical luminescence and Judd-Ofelt theory, respectively.

2. Experiment

Eu^{3+} doped calcium gadolinium silicoborate (CaGdSiBEu) glasses with compositions of 10CaO-25Gd_2O_3-10SiO_2-(55-x)B_2O_3-xEu_2O_3 (where x is 0.05, 0.1, 0.2, 0.3 and 0.4 mol%) were prepared by melt

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quenching technique. The chemicals, CaO, Gd_2O_3, SiO_2, H_3BO_3 and Eu_2O_3 with high purity was totally weighted to 30 g and were mixed thoroughly in an alumina crucible and melted at 1400 °C for 3 h in an electric furnace. Generally, H_3BO_3 can be used instead of B_2O_3 in glass production because of cheaper and non-hygroscopic property. B_2O_3 can be produced from the chemical reaction $2H_3BO_3 \longrightarrow B_2O_3 + 3H_2O$. After melting, glassy liquid was quenched in preheated stainless-steel molds. Obtained glass were annealed at 550 °C for 3 h in order to remove thermal strains and then cut and polished for dimension of 1.0 × 1.5 × 0.3 cm^3. The densities of glasses were measured by applying the Archimedes principle, weighted samples in air and water via a 4-digit sensitive microbalance (AND, HR 200). The optical spectra were measured with a UV–VIS–NIR spectrophotometer (Shimadzu UV-3600) in the range of ultraviolet, visible and near-infrared region. The excitation, emission spectra and lifetime were collected by using a spectrofluorophotometer (Cary-Eclipse) with xenon lamp as a light source. The refractive indices (n), is measured by an Abbe refractometer which used light of 589 nm and 1-Bromonaphthalin as contact liquid. Absorption spectrum, emission spectrum and refractive indices were used to analyze lasing ability of glass via Judd-Ofelt (JO) theory [14–16] which contains spectroscopic interaction parameters such as oscillator strength (f), JO intensity parameter (Ω_λ, λ = 2, 4, 6), radiative transition possibility (A_R), stimulated emission cross-section (σ) and branching ratio (β_R). The emission spectra of glasses were used to study color of emission via CIE (Commission Internationale de l´Eclairage) 1931 chromaticity diagram. The X-ray induced optical luminescence spectra of glasses were measured by using a Cu target x-ray generator (Inel, XRG3D-E), whose was operated at 50 kV and 30 mA, and the spectrometer (QE65 Pro, Ocean Optics) with an optical fiber to detect the emission spectra.

3. Judd-Ofelt theory

3.1. Oscillator strengths and Judd-Ofelt parameters

The experimental oscillator strengths (f_{exp}) were calculated from absorption spectrum by using the following formula [14–16]

$$f_{exp} = \frac{2.303mc^2}{N\pi e^2}\int \varepsilon(\nu)d\nu = 4.318\times10^{-9}\int \varepsilon(\nu)d\nu \tag{1}$$

where m and e are the mass and charge of an electron, c is the velocity of light, N is the Avagadro's number, $\varepsilon(\nu)$ is the molar extinction coefficient at wavenumber ν (cm^{-1}) of each absorption band which can be obtained from the Beer-Lamber's law.

$$\varepsilon(\nu) = \frac{1}{Cl}\log\frac{I_0}{I} \tag{2}$$

where C is the concentration of the Ln^{3+} ions (mol/l), l is the light path length of medium (cm) and $\log (I_0/I)$ is the absorbance. The calculated oscillator strengths can be obtained as shown below:

$$f_{total} = \frac{8\pi^2mc\nu}{3he^2(2L+1)}\frac{(n^2+2)^2}{9n}S_{ed}+\frac{8\pi^2mc\nu}{3he^2(2L+1)}nS_{md} \tag{3}$$

where h is Planck's constant, L is orbital angular momentum, n is refractive index, υ is wavenumber, The electric (S_{ed}) and magnetic (S_{md}) dipole line strengths

S_{ed} and S_{md} that appear in Eq. (3), can be calculated from the formula (4) and (5), respectively,

$$S_{ed} = e^2\sum_{\lambda=2,4,6}\Omega_\lambda(\Psi J\|U^\lambda\|\Psi' J')^2 \tag{4}$$

$$S_{md} = \frac{e^2h^2}{16\pi^2m^2c^2}(\Psi J\|L+2S\|\Psi' J')^2 \tag{5}$$

where Ω_λ(λ = 2, 4, 6) is the J-O intensity parameter [15,16], $\|U^\lambda\|$ is reduced matrix elements, J and J' are the total angular momentum of initial Ψ state and final Ψ' state of transition, respectively. For calculation of oscillator strength with thermal correction, the method and expression were followed with literatures [17,18].

3.2. Radiative properties

The Ω_λ and n are used to evaluate the radiative transition probability (A_R) from relation (6).

$$A_R(\Psi J,\Psi' J') = \frac{64\pi^2\upsilon^2}{3h(2J+1)}\frac{n(n^2+2)^2}{9}S_{ed}+\frac{64\pi^4\upsilon^3}{3h(2J+1)}n^3S_{md} \tag{6}$$

The total radiative transition probability (A_T) from excited state Ψ to lower Ψ' state is sum of $A_R(\Psi J,\Psi' J')$ value as Eq. (7), while radiative lifetime (τ_R) of excited state relates with A_T as Eq. (8).

$$A_T(\Psi J) = \sum A_R(\Psi J,\Psi' J') \tag{7}$$

$$\tau_R(\Psi J) = \frac{1}{A_T(\Psi J)} \tag{8}$$

The calculated branching ratio (β_R) of each emission corresponding to transition $\Psi \to \Psi'$ is given by

$$\beta_R(\Psi J,\Psi' J') = \frac{A_R(\Psi J,\Psi' J')}{A_T(\Psi J)} \tag{9}$$

The experiment branching ratio (β_{exp}) can be calculate from area ratio of each emission peak and total peaks. Area of emission peak and A_R value also were used to evaluate the stimulated emission cross-section (σ_p) by relation (10)

$$\sigma_p(\lambda_p),(\Psi J,\Psi' J') = \frac{\lambda_p^4}{8\pi n^2\Delta\lambda_{eff}}A_R(\Psi J,\Psi' J') \tag{10}$$

where λ_p is the emission peak wavelength and $\Delta\lambda_{eff}$ is its effective line width found by portioning the area of the emission bands by average height.

4. Results and discussion

Fig. 1 shows the appearance of Eu^{3+} doped CaO-Gd_2O_3-SiO_2-B_2O_3 (CaGdSiBEu) glasses with colorless and high transparency body. Both features of glass are independent with Eu^{3+} concentration.

4.1. Density

The densities of the CaGdSiBEu glasses are collected in Table 1. As seen from Table 1, the densities increase with increasing of Eu^{3+} concentration. This variation is a result from replacement of B_2O_3 via Eu_2O_3 in glass composition. Higher density of Eu_2O_3 (7.40 g/cm^3) than B_2O_3 (2.460 g/cm^3) makes total density of glass rise with increasing of Eu_2O_3 in glass.

4.2. Optical properties

The absorption spectra of CaGdSiBEu glasses were recorded from visible light (VIS) to near infrared (NIR) region and shown in Fig. 2. The absorption spectra contains four absorption bands, 392, 465, 531, 2098 and 2200 nm, which correspond to energy transitions of Eu^{3+} from ground state ($^7F_0$ or $^7F_1$) to excited states of $^7F_0 \to {}^5L_6$,

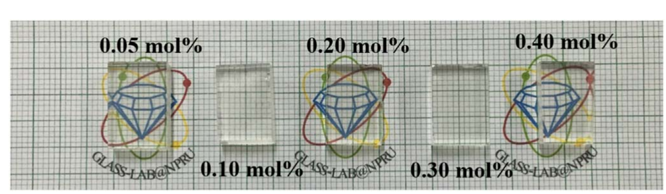

Fig. 1. The CaGdSiBEu glasses.

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