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Thermal correction Judd-Ofelt analyze of Eu^{3+} ion doped calcium gadolinium silicoborate oxyfluoride glass

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Abstract

The Calcium Gadolinium Silicoborate Oxyfluoride glass doped with 1.0 mol% of Eu^{3+} concentration. ($CaGdSiBF:Eu^{3+}$) was prepared by a melt quenching technique for study in the absorption and emission properties. Glass absorbed photon in ultraviolet, visible light and near infrared regions. The excitation with 275 nm of Gd^{3+} show the strongest red emission at 613 nm from $^5D_0 \rightarrow {}^7F_2$ transition. The Judd-Ofelt (J-O) intensity parameters are derived from the integrated area under absorption and emission, including the refractive index. The thermal correction was used to improve J-O analysis from an uncertainty of Eu^{3+} population on the ground state. The spectroscopic results were used to calculate the radiative parameter via J-O theory using a normal calculation method compared with a thermal-correction calculation method to analyze a potential in laser application. The color coordinates (x,y) under 275 nm excitation wavelength were (0.64, 0.36), that be plotted in the reddish orange region of CIE 1931 chromaticity diagram. $CaGdSiBF:Eu^{3+}$ glass performs the high lasing power and energy extraction ratio, which can be developed for using as a laser medium in red laser device.

1. Introduction

In present, optical devices are used extensively in several activity of human. New light source devices have been always studied and developed to get a good performance. A good light emitting is gained from quite material, it was found that glass doped with lanthanide ion is now very interesting for optical devices development including solid-state lasers, fiber amplifiers, infrared to visible light up-converters, field emission displays, etc. [1-4]. Borate compound can form glass by itself using low melting point, obtained glass shows good transparency and high chemical durability [5]. Silicate glass is the most refractory glass in commercial use. It has a high chemical resistance, low electrical conductivity, low thermal expansion and good UV transparency [5]. Oxyfluoride glasses are very attractive because of their various application in photonics devices [6]. Fluorides are known as excellent hosts for RE ions due to low phonon energy, small band gap, high density, substantial thermal and mechanical strength [7,8]. Gadolinium oxide (Gd_2O_3) has become a material of attention within the glass matrix because of highly efficient energy transfer from the Gd^{3+} ions to the incorporated activators, at an available cost [2]. The choice of silicoborate network is based on the fact that the addition of CaO into silicoborate glasses improves the intensity of optical absorption and luminescence emission in glass [2,9]. Among the RE^{3+} ions, Eu^{3+} is unique ion because of the strong emission in red–orange region [1,3,10]. The intra-4f shell transitions are relatively well shielded from the surrounding ligand field making Eu^{3+} narrow luminescence line positions nearly independent of the host material [6]. Since the ground $^7F_0$ state and the fluorescent $^5D_0$ state of Eu^{3+} ions are non-degenerate under any symmetry, information regarding the local environment around the Eu^{3+} ion strongly depends only on the splitting of the $^5D_0 \rightarrow {}^7F_{1,2}$ transitions in emission spectra [1,3]. It was performed for the $^7F_0 \rightarrow {}^5D_0$ transition of Eu^{3+} ion at room temperature which has potential use in high-density optical data storage [4,11].

In this work, we prepared the Eu^{3+} doped calcium gadolinium silicoborate oxyfluoride glass and then investigated its spectroscopic properties. The J-O

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analysis was used to determine this glass potential for using as laser gain medium.

2. Experimental

The Eu^{3+} doped calcium gadolinium silicoborate oxyfluoride (CaGdSiBFEu) glass with compositions of $10CaF\text{-}25GdF_3\text{-}10SiO_2\text{-}54B_2O_3\text{-}1Eu_2O_3$ was prepared by the melt quenching technique. The chemicals, CaF, GdF_3, SiO_2, H_3BO_3 and Eu_2O_3 with high purity was totally weighted to 10 g and was mixed thoroughly in an alumina crucible and melted at 1400 °C for 3 hours in an electric furnace. Glassy liquid was quenched in preheated stainless-steel molds. Obtained glass was annealed at 500°C for 3 hours in order to remove thermal strains and then cut and polished. The density of glass was measured by applying the Archimedes' principle, weighted sample in air and water via a 4-digit sensitive microbalance (AND, HR 200). The optical spectrum was measured with a UV-VIS-NIR spectrophotometer (Shimadzu UV-3600) in the range of ultraviolet, visible and near-infrared region. The excitation, emission spectrum and lifetime were collected by using a spectrofluorophotometer (Cary-Eclipse) with xenon lamp as a light source. The refractive index (n), is measured by an Abbe refractometer which used light of 589 nm and 1-Bromonaphthalin as contact liquid. The absorption spectrum, emission spectrum and refractive index were used to analyze lasing ability of glass via Judd-Ofelt (JO) theory [1] which contains spectroscopic interaction parameters such as oscillator strength (f), JO intensity parameter (Ω_λ, λ = 2, 4, 6), radiative transition probability (A_R), stimulated emission cross-section (σ) and branching ratio (β_R). Optical band gaps was calculated for indirect and direct transitions from the absorption spectrum of glass [12,13]. The chemical bonds inside the glass matrix was investigated by Fourier-transform infrared (FTIR) spectrometer. CIE 1931 chromaticity diagram (the diagram that defined quantitative links between physical pure color in the electromagnetic visible spectrum and physiological perceived color in human color vision) was used to determine color of the emitted light obtained from the emission spectrum.

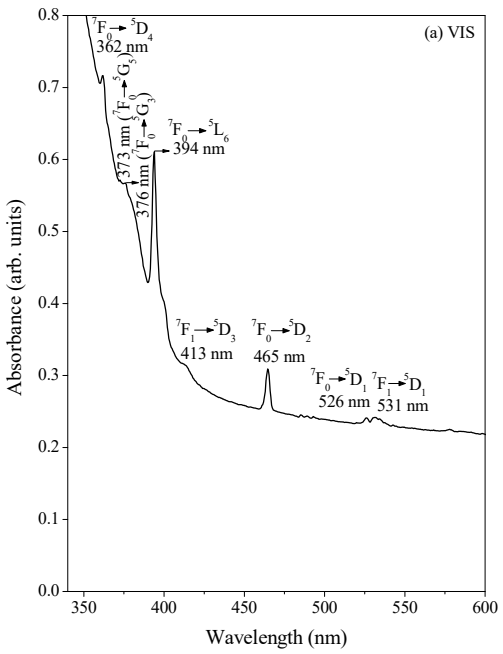

Figure 1. The absorption spectrum of the CaGdSiBFEu glass in VIS region.

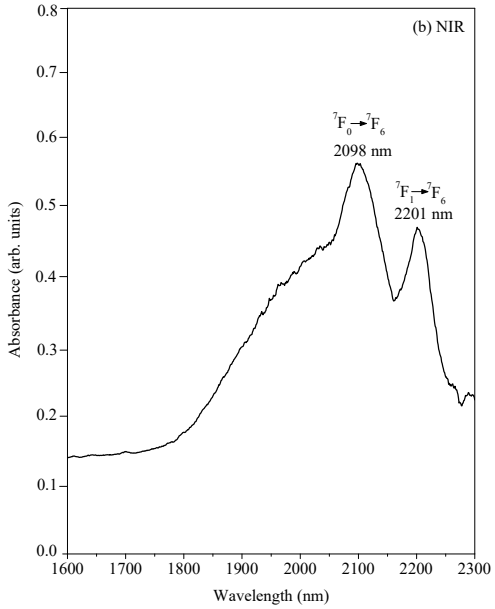

Figure 2. The absorption spectrum of the CaGdSiBFEu glass in NIR region.

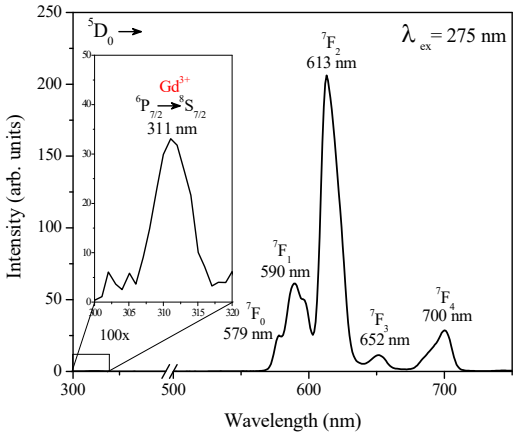

Figure 3. The emission spectrum of the CaGdSiBFEu glass.

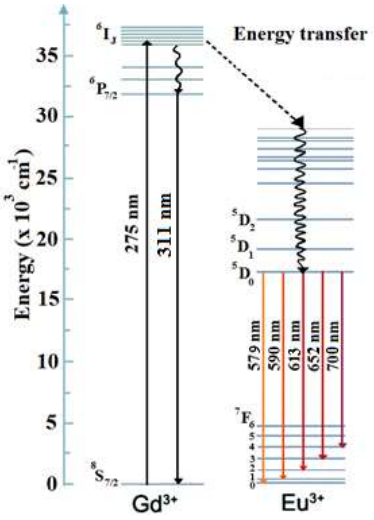

Figure 4. Energy level diagram of Gd^{3+} and Eu^{3+} ions in glass.

3. Results and discussion

The absorption spectrum of CaGdSiBFEu glass was recorded from visible light (VIS) to near infrared (NIR) region and shown in figure 1 and 2. The absorption spectrum contains ten absorption bands, 362, 373, 376, 394, 413, 465, 526, 531, 2098 and 2201 nm, which correspond to energy transitions of Eu^{3+} from ground state ($^7F_0$ or $^7F_1$) to excited states of $^7F_0 \rightarrow {}^5D_4$, $^7F_0 \rightarrow {}^5G_5$, $^7F_0 \rightarrow {}^5G_3$, $^7F_0 \rightarrow {}^5L_6$, $^7F_0 \rightarrow {}^5D_3$, $^7F_0 \rightarrow {}^5D_2$, $^7F_0 \rightarrow {}^5D_1$, $^7F_1 \rightarrow {}^5D_1$, $^7F_0 \rightarrow {}^7F_6$ and $^7F_1 \rightarrow {}^7F_6$, respectively [1,3]. The emission spectrum of the CaGdSiBFEu glass under 275 nm of Gd^{3+} excitation was recorded and shown in figure 3. It was found five emission bands at 579, 590, 613, 652 and 700 nm representing the energy transitions of the Eu^{3+} such as $^5D_0 \rightarrow {}^4F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$, respectively [1,3]. The strongest band belongs to 613 nm wavelength ($^5D_0 \rightarrow {}^7F_2$). For inset picture in figure 3, it shows the enlargement of Gd^{3+} emission band at 311 nm. All process of luminescence such as Gd^{3+} excitation and emission, Gd^{3+}-Eu^{3+} energy transfer, non-radiative relaxation and Eu^{3+} emission are shown in figure 4.

The J–O analysis to study potential of glass for laser medium applications. In the case of Eu^{3+} ion, the absorption transitions starting not only from $^7F_0$ state but also from $^7F_1$ state can be observed and some of these transitions often overlap which makes J–O analysis [1,3] to be complicate at room temperature. Since, ^7F_J (J = 0, 1 and 2) levels are populated thermally at room temperature, the fractional thermal populations of the $^7F_0$, $^7F_1$ and $^7F_2$ levels are calculated to be 59%, 38% and 3%, respectively. Therefore, the population of $^7F_1$ level cannot be neglected at room temperature. The absorption spectrum and refractive index were used to analyse the lasing ability of glass via the J–O theory with and without correction from fractional thermal populations. As the absorption originates from the ground $^7F_0$ as well as thermally populated $^7F_1$ states, the oscillator strengths are corrected for thermalization effect at room temperature by dividing the respective population of $^7F_{0,1}$ levels [1,3]. The experimental (f_{exp}) and calculated (f_{cal}) oscillator strengths of observed absorption levels and J-O parameters (Ω_λ) with and without thermal correction are presented in table 1. The f_{exp} and f_{cal} are close together representing the good fitting result. The oscillator strengths values of $^7F_0 \rightarrow {}^5L_6$ (394 nm) and $^7F_0 \rightarrow {}^7F_6$ (2098 nm) transition is higher more than others in VIS and NIR region, respectively which corresponds to the peak absorbance in spectrum. The J-O parameters obtained from without thermal correction are Ω_2 = 10.41×10^{-20} cm^2, Ω_4 = 10.05×10^{-20} cm^2 and Ω_6 = 1.99×10^{-20} cm^2, while values obtained with thermal correction are Ω_2 = 25.66×10^{-20} cm^2, Ω_4 = 20.34×10^{-20} cm^2 and Ω_6 = 4.70×10^{-20}. The Ω_2 parameter often used to determine the level of asymmetric environment around Ln^{3+} and covalency between Ln^{3+} and neighbour particle [3,10]. The Ω_4 and Ω_6 show the viscosity and rigidity level of glass host [1,3,10]. The JO parameters of glass show the trend of $\Omega_2 > \Omega_4 > \Omega_6$. From overall value of f_{exp}, f_{cal} and Ω_λ, the thermal correction enhances these values to be higher than

ones without thermal correction. Obtained Ω_2, Ω_4 and Ω_6 are used to evaluated the radiative parameters from the emission spectra consisting of radiative transition possibility (A_R), stimulated emission cross-section (σ) and branching ratio (β_R) for with and without thermal correction as shown in table 2. The $^5D_0 \rightarrow {}^7F_2$ transitions (613 nm emission) performs the highest value of A_R, σ and β_R. The highest A_R represents the highest transition probability of Eu^{3+} from $^5D_0$ to $^7F_2$, corresponding with the intensity in spectrum. The largest σ show that $^5D_0 \rightarrow {}^7F_2$ transition use the lowest threshold energy for the laser generation and release the highest laser gain application [3,10,14], compared with other transitions in this glass. The highest β value with higher than 0.50 performs the highest lasing power produced form $^5D_0 \rightarrow {}^7F_2$ transition. The β_R values are compared with β_{exp} evaluated form the integrated intensity of each emission peak [3]. The difference of β_R and β_{exp} value for some transitions comes from the mathematical deviation of Judd-Ofelt analysis. From overall value of radiative parameters, the thermal correction enhances these values to be higher than ones without thermal correction. J-O analysis indicates that CaGdSiBFEu glass performs a good potential for using as laser medium with 613 nm emission under $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+}.

Table 1. Transition, wavenumber (υ, cm^{-1}), experimental (f_{exp}) and calculated (f_{cal}) oscillator strengths ($\times 10^{-6}$), and the Judd-Ofelt parameters Ω_λ (λ= 2, 4 and 6) ($\times 10^{-20}$ cm^2) without and with thermal correction of the 1.0 mol% Eu^{3+} ion doped glass.

Transition	υ	Oscillator strengths			
		Without thermal Correction		With thermal correction	
		f_{exp}	f_{cal}	f_{exp}	f_{cal}
$^7F_0 \rightarrow {}^5D_4$	27624	0.611	0.499	1.018	1.010
$^7F_0 \rightarrow {}^5G_5$	26810	0.211	0.000	0.352	0.000
$^7F_0 \rightarrow {}^5G_3$	26596	0.041	0.000	0.068	0.000
$^7F_0 \rightarrow {}^5L_6$	25381	2.367	1.277	3.945	3.019
$^7F_1 \rightarrow {}^5D_3$	24213	0.201	0.214	0.503	0.457
$^7F_0 \rightarrow {}^5D_2$	21505	0.268	0.293	0.447	0.721
$^7F_0 \rightarrow {}^5D_1$	19011	0.042	0.000	0.070	0.000
$^7F_1 \rightarrow {}^5D_1$	18832	0.281	0.278	0.703	0.684
$^7F_0 \rightarrow {}^7F_6$	4766	2.789	2.243	4.648	5.304
$^7F_1 \rightarrow {}^7F_6$	4543	1.785	1.854	4.463	4.385
rms		± 0.410		±0.401	
Ω_2		10.41		25.66	
Ω_4		10.05		20.34	
Ω_6		1.99		4.70	

Table 2. Emission band positions (λ_p, nm), radiative transition probabilities (A_R, s^{-1}), peak stimulated emission cross-sections ($\sigma(\lambda_p)$, $x10^{-22}cm^2$), and experimental and calculated branching ratios (β_R) for $^5D_0 \rightarrow {}^7F_J$ (J = 1, 2, 3 and 4) transitions without and with thermal correction of the 1.0 mol% Eu^{3+} ion doped glass.

$^5D_0 \rightarrow$	λ_p	Without thermal Correction				With thermal correction			
		A_R	$\sigma(\lambda_p)$	β_R		A_R	$\sigma(\lambda_p)$	β_R	
				β_{R_Exp}	β_{R_Cal}			β_{R_Exp}	β_{R_Cal}
$^7F_0$	579	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.03
$^7F_1$	590	64.30	2.38	0.21	0.09	64.30	2.38	0.19	0.21
$^7F_2$	613	438.40	19.63	0.62	0.61	1080.40	48.37	0.68	0.62
$^7F_3$	652	0.00	0.00	0.03	0.00	0.00	0.00	0.04	0.00
$^7F_4$	701	211.90	14.98	0.09	0.30	428.80	30.31	0.09	0.27

The indirect and direct band gap energy of glass are evaluated in figure 5 as 2.795 and 3.242 eV, respectively. Figure 6 shows the FTIR spectrum of the CaGdSiBFEu glass. The strong infrared absorption band at 1165 cm^{-1} originates from the vibration of BO_3 and BO_4 with tri-, tetra-, pentborate and diborate unit structure, along with the asymmetric stretching of Si-O-Si bonds [15,16]. The CIE 1931 chromaticity diagram was used to analyze color of emission, which indicate the chromaticity visible to the human eye. The emission spectrum with 275 excitation wavelength of the CaGdSiBFEu glass was selected to monitor the color of emitted light. The CIE color coordinate (x, y) shows at (0.64, 0.36), which were plotted at the edge of reddish orange region in color diagram as shown in figure 7.

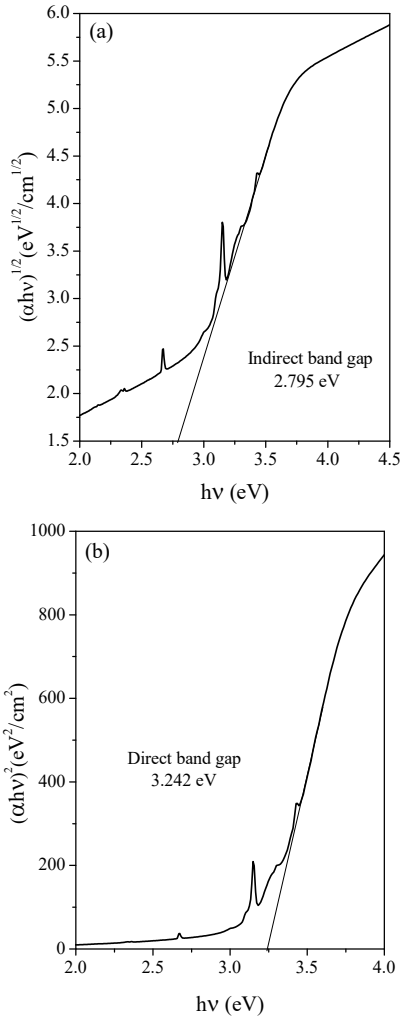

Figure 5. (a) Indirect band gap and (b) direct band gap of the CaGdSiBFEu glass.

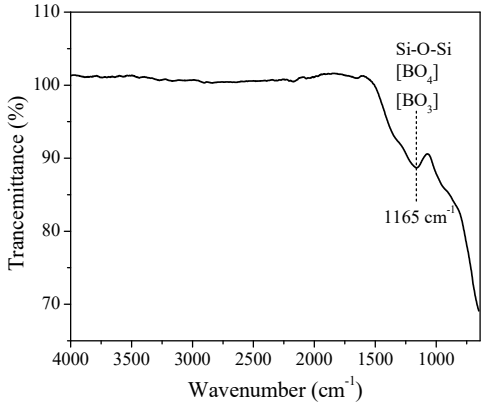

Figure 6. FTIR spectrum of the CaGdSiBFEu glass.

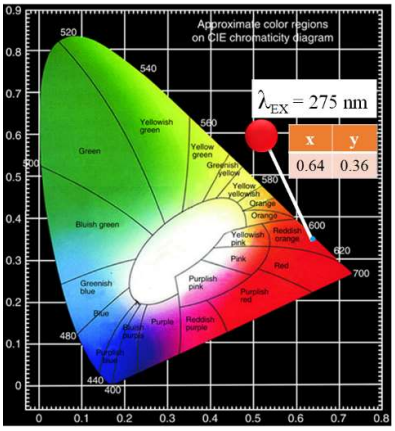

Figure 7. The CIE 1931 chromaticity diagram of the CaGdSiBFEu glass.

4. Conclusions

The Eu^{3+} ion doped calcium gadolinium silicoborate oxyfluoride glass was prepared by melt-quenching technique. The results of glass absorbed photon in ultraviolet, visible light and near infrared regions. This glass shows the strongest emission with 613 nm ($^5D_0 \rightarrow {}^7F_2$) when it was excited by 275 nm wavelength. The detailed and systematic analysis of optical intensities has been performed from absorption and emission spectrum using J–O theory. The thermal correction method can improve the J-O and radiative parameters in J-O analysis process. The σ (λ_p) and β_R values for the $^5D_0 \rightarrow {}^7F_2$ transition revealed that CaGdSiBFEu glass could be used for the development of laser device with 613 nm emission. The indirect and direct band gap energy of glass are 2.795 and 3.242 eV, respectively. The color coordinates (x,y) of glass is located at the point (0.64, 0.36) in reddish orange region of CIE 1931 chromaticity diagram.

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