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Optical Properties of Sm^{3+} ions in Borate Glass

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Abstract: Samarium doped B_2O_3-Na_2O-Li_2O (BNaLi) glasses with concentration of 0.5 mol% were prepared by the conventional melting procedure. Optical absorption, excitation, luminescence spectra and lifetime have been measured at room temperature. Judd – Ofelt (JO) theory is used to study the spectral properties and to calculate the radiative transition probabilities. The predicted branching ratios (β_R), radiative lifetime (ι_R) and stimulated emission cross-sections ($\sigma(\lambda_p)$) of the $^4G_{5/2}$ excited level are reported.

Keywords: Borate glass, J-O theory.

1. Introduction

Glasses and crystals doped with various rare earth (RE) ions are important materials for making fluorescent display devices, optical detectors, laser, optical fibers, waveguides and fiber amplifiers [1-3]. Spectroscopic investigations of rare earth doped glasses and crystals provide valuable information that includes energy level structure, radiative properties, stimulated emission cross-sections, etc. These insights play a key role to improve the existing situation or to develop new optical devices like lasers, sensors, hole burning high-density memories, optical fibers and amplifiers. Compared to other glasses, borate glass has many advantages such as large transmission band, low melting temperature…. Samarium is one of the most popular rare earth elements, which is used extensively in optical devices. Spectroscopic studies of Sm^{3+} ions have been reported in different hosts such as water [4], crystals [5,6] and glasses [7,8,12,13]. The authors have investigated particularly the absorption, photoluminescence properties of Sm^{3+} ion in these hosts.

In the current work, we prepared Sm^{3+} doped borate glass and studied spectroscopic properties of Sm^{3+} ions in this glass. The Judd – Ofelt theory was used to determine intensity parameters Ω_λ (λ = 2,

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4, 6) by analyzing the absorption spectra of Sm^{3+} ions in borate glass. In addition, we calculated the radiative transition probabilities, branching ratios, radiative lifetimes of $^4G_{5/2}$ excited level, stimulated emission cross-section and briefly discussed the potential application of this material.

2. Experiment

BNaLi glass doped with 0.5 mol% of Sm^{3+} were prepared by conventional melt quenching technique. The molar composition of samarium doped BNaLi glasses investigated in this work is $69.5B_2O_3$+$15Na_2O$ + $15Li_2O$ + $0.5Sm_2O_3$. High purity chemicals of H_2BO_3, Na_2CO_3, Li_2CO_3 and Sm_2O_3 were used as starting materials. All the starting chemicals were weighed in the above mol% ratio, well mixed and heated for 60 min in a platinum crucible at 1050 ^oC in an electric furnace, then cooled quickly to 350 ^oC and annealed at this temperature for 5 h to eliminate mechanical remove thermal strains.

The optical absorption spectrum in the wavelength region from 300 nm to 2000 nm was performed using Jasco V670 spectrometer The excitation and photoluminescence (PL) spectra were recorded by Fluorolog - 3 spectrophotometer, model FL3 - 22, Horiba Jobin Yvon. All the measurements were performed at room temperature.

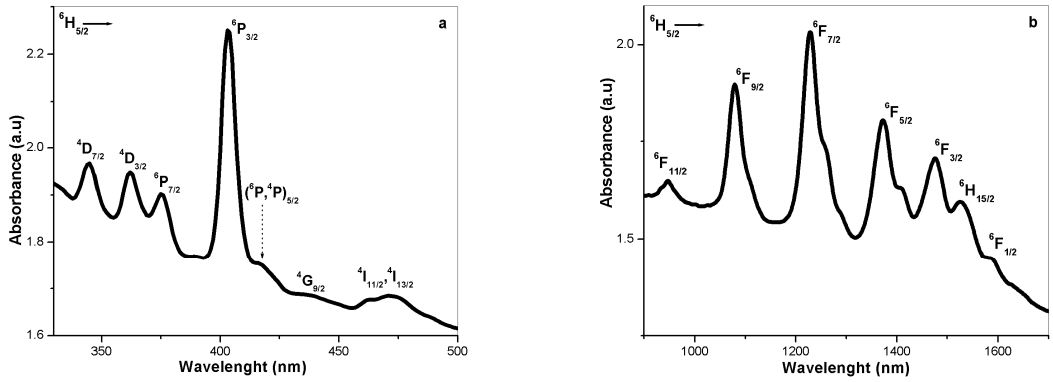

Fig. 1. The absorption spectra of BNaLi glass doped with 0.5 mol% of Sm^{3+} ions in range 300 -500 nm (a) and 900 -1700 nm (b).

3. Judd-Ofelt theory

The Judd-Ofelt (JO) theory was shown to be useful to characterize radiative transitions for RE-doped solids, as well as aqueous solutions, and to estimate the intensities of the transitions for rare-earth ions [4-9]. This theory defines a set of three intensity parameters, Ω_λ ($\lambda = 2, 4, 6$), that are sensitive to the environment of the rare-earth ions.

According to the JO theory [10], the electric dipole oscillator strength of a transition from the ground state to an excited state is given by

$$f_{cal} = \frac{8\pi^2 mc\nu}{3h(2J+1)} \frac{\left(n^2+2\right)^2}{9n} \sum_{\lambda=2,4,6} \Omega_\lambda \left\langle \psi J \left\| U^{(\lambda)} \right\| \psi' J' \right\rangle^2 \quad (1)$$

where n is the refractive index of the material, J is the total angular momentum of the ground state, Ω_λ are the JO intensity parameters and $\left\| U^{(\lambda)} \right\|^2$ are the squared doubly reduced matrix elements of the unit tensor operator of the rank $\lambda = 2, 4, 6$ are calculated from intermediate coupling approximation for a transition $|\psi J\rangle \rightarrow |\psi' J'\rangle$. These reduced matrix elements do not nearly depend on host matrix as noticed from earlier studies [11].

The oscillator strengths, f_{exp}, of the absorption bands were determined experimentally using the following formula [10]

$$f_{exp} = 4.318 \times 10^{-9} \int \alpha(\nu) d\nu \quad (2)$$

where $\alpha(\nu)$ is molar extinction coefficient at energy ν (cm^{-1}). The $\alpha(\nu)$ values can be calculated from absorbance A by using Lambert – Beer's law, $A = \alpha(\nu)cd$, where c is concentration [dim: L^{-3}; units: $moll^{-1}$], d is the optical path length [dim: L; units: cm].

The oscillator strength of the various observed transitions are evaluated through Eq. (1) and Eq. (2). A least squares fitting approach is then used for Eq. (2) to determine Ω_λ parameters which give the best fit between experimental and calculate oscillator strength.

The JO parameters are used to predict the radiative properties of excited states of Ln^{3+} ion such as transition probabilities (A_R), radiative lifetime (ι_R), branching ratios (β_R), and stimulated emission cross-sections ($\sigma(\lambda_p)$). The details of this theory were shown in previous reports [6,9].

4. Results and discussion

4.1. Absorption spectra

Figures 1(a) and 1(b) show the absorption spectra of Sm^{3+} ions -doped borate glass in the UV-Vis and NIR regions, respectively. The absorption spectra contain 14 bands corresponding to transitions of Sm^{3+} ions from the ground state $^6H_{5/2}$ to the various excited states. The peaks in the spectra are inhomogeneously broadened due to the distribution of crystal field in the glass. The absorption band positions and its energy level assignments are reported in Table 1. From the absorption spectra, it is found that the NIR region contains most intense transitions of Sm^{3+} ions and in the UV-Vis region, various $^{2S+1}L_J$ energy levels are overlapped. The NIR region contains several intense transitions from the ground state $^6H_{5/2}$ to the various ^6F and ^6H terms of Sm^{3+} ions are spin-allowed transitions ($\Delta S = 0$). Moreover, the transitions to the ^6H terms are also allowed by the orbital angular momentum selection rule, $\Delta L = 0$. The transition from $^6H_{5/2}$ to the level $^6F_{1/2}$ and $^6F_{3/2}$ is hypersensitive in nature for Sm^{3+} ions which obeys the selection rule $|\Delta J| \leq 2$, $\Delta S = 0$ and $|\Delta L| \leq 2$ and any local structural change may sharply effect the position and intensity of this transition [10,12].

Table 1. Energy transitions (v), the experimental (f_{exp}) and calculated (f_{cal}) oscillator strengths for brate glass doped with 0.5 mol% of Sm^{3+} ions.

$^4H_{5/2} \rightarrow$	v_c (cm^{-1})	v_a (cm^{-1})	f_{exp} ($\times10^{-6}$)	f_{cal} ($\times10^{-6}$)
$^6H_{15/2}$	6,544	6,508	3.47	4.73
$^6F_{3/2}$	6,770	6,630	5.10	3.08
$^6F_{5/2}$	7,283	7,100	7.65	6.26
$^6F_{7/2}$	8,136	8,000	10.4	9.35
$^6F_{9/2}$	9,267	9,200	5.68	5.88
$^6F_{11/2}$	10,548	10,500	1.58	0.94
$^4I_{11/2}$,$^4I_{13/2}$	21,141	21,100	6.98	5.19
$^6P_{3/2}$, (^6P,$^4P)_{5/2}$	24,814	24,950	12.2	12.6
$^4P_{7/2}$	26,666	26,750	4.48	3.49
$^4D_{3/2}$	27,624	27,700	7.80	7.07
$^6D_{7/2}$	28,985	29,100	5.42	5.87
$\overline{\beta} = 1.0059; \delta = -0.57$			r.m.s = 1.33×10^{-6}	

4.2. Nephelauxetic effect- Bonding parameter

Nephelauxetic ratio and bonding parameter have been evaluated to find the nature of the Sm^{3+}-ligand bond in the glass. The nephelauxetic ratio (β) is calculated by $\beta = v_c/v_a$, v_c and v_a are energies of the corresponding transitions in the complex and in aqueous solution [10]. The bonding parameter (δ) is defined as $\delta = \left[\left(1-\overline{\beta}\right)/\overline{\beta}\right]\times100$, where $\overline{\beta} = \left(\sum\beta\right)/n$ and n is refers to the number of levels that are used to compute $\overline{\beta}$ values. With the borate glass doped with 0.5 mol% of Sm^{3+} ions, the values of $\overline{\beta}$ and δ bonding parameter are 1.0059, - 0.57, respectively. Thus, in this case the bonding of Sm^{3+} ions with the local host is ionic bonding.

4.3. Oscillator strengths, J – O parameters

The oscillator strength of an induced electric-dipole transition between J and J' states was calculated using Eqns. (1) and (2). The strong clear absorption bands have been analyzed by using JO theory and were least squared fitted to yield the best fit values for the JO parameters Ω_2, Ω_4 and Ω_6. The accuracy of the fit is estimated by the r.m.s deviation between the experimental (f_{exp}) and calculated (f_{cal}) oscillator strengths. For the borate glass doped with 0.5 mol% of Sm^{3+} ions, the best – fitted JO parameters are $\Omega_2 = 2.05\times10^{-20}$ cm^2, $\Omega_4 = 18.5\times10^{-20}$ cm^2 and $\Omega_6 = 10.5\times10^{-20}$ cm^2 with the r.m.s deviation of 1.33×10^{-6}. The JO parameter Ω_2 indicates the asymmetric nature of Sm^{3+} ion local environment and also the covalent nature of the Sm^{3+}-ligand bonds. The value of Ω_2 for BNaLi:Sm^{3+} glass exhibits strong ionic nature of the Sm^{3+}- ligand bonds and higher symmetric nature of the Sm^{3+} site in the host matrix compared to Sm^{3+}- doped lithium borate, lithium fluoroborate glasses and rare-earth borate glasses [12, 13] but lower symmetric compared to Sm^{3+}- doped K_2YF_5 crystal [6]. The Ω_4 and Ω_6 parameters are long range parameters that are related to the bulk properties of the glass such as basicity, rigidity and viscosity of the glass materials and these values for the BNaLi:Sm glass indicate

that the glass possesses more rigidity compared to Sm^{3+} - doped lithium borate, lithium fluoroborate glasses, rare-earth borate glasses and K_2YF_5 crystal.

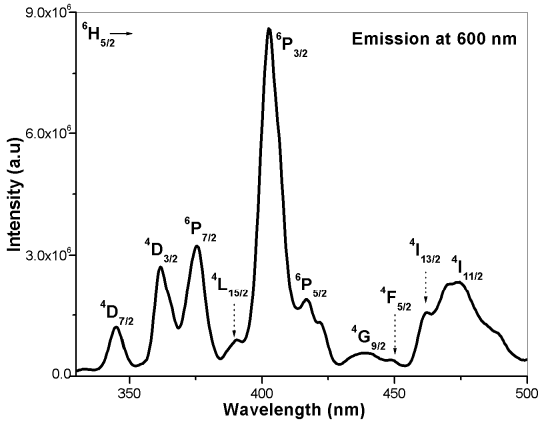

Fig. 2. The excitation spectrum of BNaLi:Sm^{3+} glass.

4.4. Excitation spectra

Excitation spectra of BNaLi:Sm^{3+} glass at the emission wavelength 600 nm is depicted as figure 2. The excitation spectra consists of 10 peaks corresponding to the transitions from the ground state $^6H_{5/2}$ to the various excited states $^4D_{7/2}$, $^4D_{3/2}$, $^6P_{7/2}$, $^4L_{15/2}$, $^6P_{3/2}$, $^6P_{5/2}$, $^4G_{9/2}$, $^4F_{5/2}$, $^4I_{13/2}$, $^4I_{11/2}$ at the wavelengths of 344, 361, 375, 389, 401, 416, 438, 450, 462 and 473 nm, respectively. The optical absorption spectrum of BNaLi:Sm^{3+} glass in the UV-Vis region (figure 1(a)) is compared with this excitation spectrum and it is confirmed that these transitions of Sm^{3+} ions are similar.

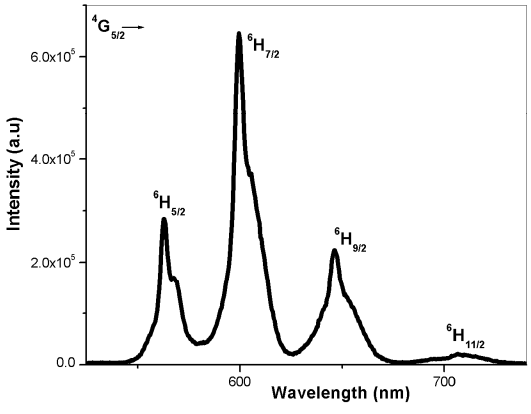

Fig. 3. The emission spectra of BNaLi:Sm^{3+} glass.

4.5. Fluorescence properties

Figure 3 displays the emission spectra of BNaLi:Sm^{3+} glass. It exhibitst four emission bands at 561, 600, 645 and 707 nm which are assigned to $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$ and $^6H_{11/2}$ transitions, respectively. The highest intensity obtained at wavelength of 600 nm corresponding to $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition. From the absorption, excitation and emission spectra of BNaLi:Sm^{3+} glasses, the energy level diagram of Sm^{3+} in borate glass was defined and shown in Fig 4.

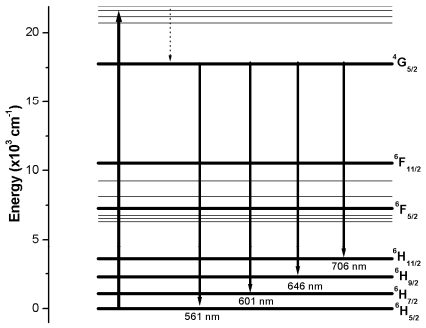

Fig. 4. The energy level diagram of Sm^{3+} ions in borate glass.

The JO intensity parameters, the energy level diagram and refractive index are used to calculate the radiative properties of the 0.5 mol% Sm^{3+} - doped BNaLi glass. The radiative transition rates (A_R), radiative lifetime (τ_R), stimulated emission cross-section $\sigma(\lambda_p)$, branching ratios (β_R) and measured branching ratios (β_{mes}) were determined for the transitions from the $^4G_{5/2}$ excited level to lower levels. The results are displayed in Table 2.

Table 2. Predict the radiative transition rates, branching ratios and radiative lifetime of $^4G_{5/2}$ level

Transition $^4G_{5/2} \rightarrow$	E (cm^{-1})	A_R	β_R (%)	β_{mes} (%)	$\sigma(\lambda_P)$ (10^{-22} cm^2)	τ_R (μs)
$^6F_{11/2}$	6,851	0.87	0.01	-	-	1110
$^6F_{9/2}$	8,350	2.54	0.28	-	-	
$^6F_{172}$	9,637	11.52	1.29	-	-	
$^6F_{5/2}$	10,493	21.55	2.39	-	-	
$^6F_{3/2}$	11,016	2.11	0.23	-	-	
$^6H_{15/2}$	11,091	1.09	0.12	-	-	
$^6F_{1/2}$	11,203	1.11	0.12	-	-	
$^6H_{13/2}$	12,578	17.21	1.91	-	-	
$^6H_{11/2}$	14,025	127.24	14.21	4.82	0.74	
$^6H_{9/2}$	15,480	239.35	23.60	20.57	1.07	
$^6H_{7/2}$	16,667	449.45	**53.30**	**55.97**	**26.21**	
$^6H_{5/2}$	17,762	25.33	2.81	18.64	1.18	

The luminescence branching ratio is a critical parameter to the laser designer, because it characterizes the possibility of attaining stimulated emission from any specific transition. The predicted branching ratio of $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition gets a maximum value of 53.3 % where as the measured ratio is 55.97 %. Thus there is a good agreement between experimental and calculated branching ratios.

The stimulated emission cross-section ($\sigma(\lambda_p)$) signifies the rate of energy extracted from the lasing material and it provides interesting information about the potential laser performance of a material. The values of $\sigma(\lambda_P)$ for $^4G_{5/2}$ emission transition are in order of $^4G_{5/2} \rightarrow {}^6H_{7/2} > {}^6H_{9/2} > {}^6H_{5/2} > {}^6H_{11/2}$. It is found that $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition exhibits maximum $\sigma(\lambda_P)$ (26.4×10^{-22} cm^2).

The measured and calculated lifetime of $^4G_{5/2}$ level is 1020 μs and 1110 μs, respectively. The discrepancy between the measured and calculated lifetime may be due to the additional non-radiative transitions and energy transfer through cross-relaxation. The luminescence quantum efficiency of the fluorescent level is defined as the ratio of the measured lifetime to the calculated lifetime by JO theory, $\eta = \tau_{mes}/\tau_R$ [10]. For the BNaLi doped with 0.5 mol% of Sm^{3+} ions, the luminescence quantum efficiency is 91.2 %.

Due to the high values obtained for branching ratios, stimulated emission cross-section and luminescence quantum efficiency for $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition of BNaLi:Sm^{3+} glass, it is concluded that the present glass system investigated is adequate for making visible laser and optical fiber amplifiers.

5. Conclusion

The physical and optical properties of Sm^{3+}- doped BNaLi glasses have been investigated. Negative value for the bonding parameter (δ) and the small value of JO parameter (Ω_2) have substantiated the ionic nature of Sm^{3+} - ligand bond in the Sm^{3+}- doped BNaLi glass. Judd-Ofelt intensity analysis for 0.5 mol% Sm^{3+}- doped BNaLi glass has been carried out. In BNaLi:Sm^{3+} glass, the value of Ω_2 is lager then that in K_2YF_5:Sm^{3+} crystal but it is less than that in lithium borate, lithium fluoroborate glasses and rare-earth borate glasses. This is shown that the Sm^{3+} - ligand bonds in BNaLi:Sm^{3+} glass has higher symmetric than that in lithium borate and lithium fluoroborate glasses but lower symmetric than that in K_2YF_5 crystal. The radiative properties for the BNaLi:Sm^{3+} glass were forecast through JO theory. The present glass system investigated is suitable for developing visible laser and optical fiber amplifiers due to its high values of branching ratios and stimulated emission cross-sections.

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