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Radiative emission probabilities of Dy^{3+}-doped alkali borate and fluoroborate glasses

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Abstract

Optical absorption and photoluminescence properties of Dy^{3+}-doped alkali borate: $59\ H_3BO_3 + 30\ Li_2CO_3 + 10\ Al_2O_3 + 1\ Dy_2O_3$ (Glass-A) and alkali fluoroborate: $59\ H_3BO_3 + 30\ LiF + 10\ Al_2O_3 + 1\ Dy_2O_3$ (Glass-B) glasses have been investigated. From the measured absorption spectra, the oscillator strengths are determined from the area under the absorption bands. Judd-Ofelt analysis was applied and the intensity parameters ($\times 10^{-20}$ cm^2) $\Omega_2 = 4.620$, $\Omega_4 = 2.706$, $\Omega_6 = 2.087$ and $\Omega_2 = 5.306$, $\Omega_4 = 2.027$, $\Omega_6 = 1.511$ for glasses A and B, respectively were evaluated with a reasonable agreement between the measured and calculated *f*-values. These parameters were used for the calculation of radiative transition rates (A_R), branching ratios (β_R), radiative lifetimes (τ_R) and integrated absorption cross-sections (Σ) for the $^4F_{9/2}$, $^6H_{5/2}$, $^6H_{9/2}$, $^6F_{11/2}$, $^6H_{11/2}$ and $^6H_{13/2}$ electronic excited states and are compared with those of other glasses reported in the literature. From the radiative spectroscopic parameters, it is predicted that these Dy^{3+}-doped glasses A and B are found to be more attractive for blue–green solid-state laser devices.

Keywords: Oscillator strengths; Intensity parameters; Radiative emission probabilities

1. Introduction

Rare-earth-doped glasses are of particular interest for optical communications such as glass lasers, optical fiber amplifiers, memory devices and flat-panel displays [1]. Glass hosts activated with RE^{3+} ions have much wider absorption and emission bands and therefore provide better opportunities for Q-switching and tuning. Glasses offer as a medium for the production of optical devices that are both small and efficient. Electronic transitions between several pairs of energy levels of Dy^{3+} ion which are capable of emitting mid-infrared fluorescence around 2.9 and 4.4 μm due to the $^6H_{13/2} \rightarrow {}^6H_{15/2}$ and $^6H_{11/2} \rightarrow {}^6H_{13/2}$ transitions, respectively, were reported in literature [2–4]. Radiative transition rates for several excited states were evaluated [5–9] from the absorption spectra of Dy^{3+} ions in different glasses using the Judd-Ofelt theory [10,11]. Re-absorption of fluorescence emission centered at 810 nm from the Tm^{3+}: $^3H_4 \rightarrow {}^3H_6$ transition, by Dy^{3+}: $^6H_{15/2} \rightarrow {}^6F_{7/2}$ transition in tellurite glasses was demonstrated and some numerical estimations for optical fiber amplifications were delivered [12]. The temperature dependence of mid-infrared emissions and multiphonon relaxation rates in Dy^{3+}-doped chalcohalide glasses was investigated to understand the interactions between the rare-earth ions and phonon vibrations [13]. Spectroscopic properties such as the intensity parameters, transition probabilities, branching ratios and radiative lifetimes from the absorption spectra of Dy^{3+} ions in fluoroindate glasses were determined and compared with those of other glasses reported in the literature [14]. The visible luminescence quenching of silicate glasses doped with various concentrations of dysprosium was experimentally observed and explained by Nagli et al. [15].

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The host glasses play a very important role in determining the strength of the crystal field as well as the intensities of the spectral lines both in the absorption and emission spectra. In the present work, we present a systematic spectroscopic study of Dy^{3+} ions in alkali borate (Glass-A) and fluoroborate (Glass-B) glasses, since these glasses are non-hygroscopic, possess good optical properties and have important applications in laser engineering. Optical absorption spectra were used to identify the energy level positions of the absorption bands as well as to determine the transition intensities. The knowledge of these energy level positions and intensities helps in understanding the optical response of Dy^{3+} ion in these glasses and will be useful to estimate/predict the lanthanide–ligand, ion–ion and ion–host interaction mechanisms. The JO theory has been applied to predict the radiative probabilities, branching ratios, radiative lifetimes and integrated absorption cross-sections for various excited luminescent levels. An attempt was also made to assess the potential of dysprosium-doped glasses A and B as laser active materials operating in the blue–green region.

2. Experimental procedure

Ten gram batches of dysprosium-doped alkali borate: 59 $H_3BO_3 + 30\,Li_2CO_3 + 10\,Al_2O_3 + 1\,Dy_2O_3$ (Glass-A) and alkali fluoroborate: 59 $H_3BO_3 + 30\,LiF + 10\,Al_2O_3 + 1\,Dy_2O_3$ (Glass-B) were melted in an electric furnace at 950 °C for about 30 min and then quenched with subsequent annealing at 450 °C for 3 h. The method for the preparation of these glasses has been described in our previous reports [7,8]. Mechanically polished glass samples of thickness nearly 0.3 and 1.0–2.0 cm in diameter were used for spectroscopic measurements. Room temperature optical absorption spectra in the wavelength region 340–1850 nm were recorded using double beam Varian Cary 5E UV–VIS–NIR spectrophotometer to obtain the absorbance data from which the oscillator strength of the absorption bands could be measured experimentally. An undoped glass with the same thickness was used as a reference in order to reduce the influence of the intrinsic absorption of the host glass. The refractive indices (n) 1.570 and 1.549 for glasses A and B, respectively were measured with an Abbe refractometer using sodium lamp. Emission spectra in the region 400–650 nm were obtained using Hitachi F-3010 fluorescence spectrophotometer by exciting the samples at 350 nm.

3. Results and discussion

Absorption spectra of Dy^{3+} in glasses A and B in the wavelength regions 340–500 and 700–1850 nm are shown in Figs. 1 and 2, respectively. Each spectra exhibit similar characteristic features with a slight change in the intensities of various absorption bands. The observed 12 absorption bands, which originate from the $^6H_{15/2}$ ground state were assigned to different transitions between the energy levels of $4f^9$ electronic configuration of Dy^{3+} ions by comparing the peak positions with those reported previously [6]. At high energies (Fig. 1) the absorptions of different electronic levels overlap and the assignments to particular transitions cannot be made easily due to the dense energy-level scheme of Dy^{3+} ions. The energy gap between the sextet and quartet states is ~7800 cm^{-1} (Table 1). No absorption band corresponding to the transition $^6H_{15/2} \rightarrow {}^6F_{1/2}$ around ~730 nm is observed conforming the selection rule that allows only transitions with $\Delta J \leq 6$ for electronic dipole transitions. The oscillator strength 'f' of the absorption bands were determined from the area under the absorption curve using the formula [5]

$$f_{\mathrm{exp}} = \frac{mc^2}{N\pi e^2} \int \alpha(\nu)\mathrm{d}\nu \qquad (1)$$

where $\alpha(\nu)$ is the measured absorption coefficient at a given energy ν (cm^{-1}) and N is the number of absorbing ions determined from the starting glass composition. These experimentally measured 'f' values are presented in Table 1

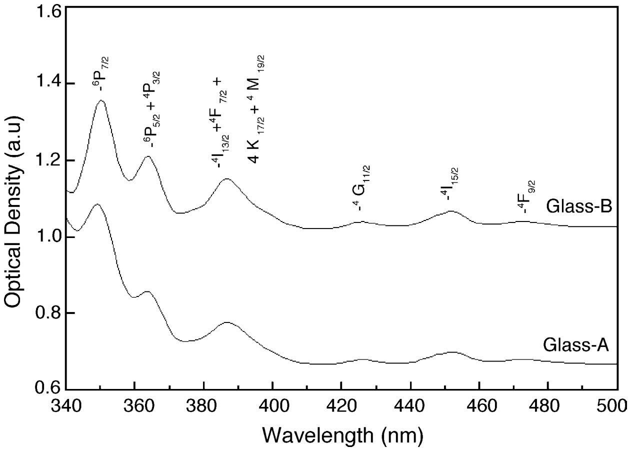

Fig. 1. UV–VIS absorption spectra of Dy^{3+} ions in glasses A and B.

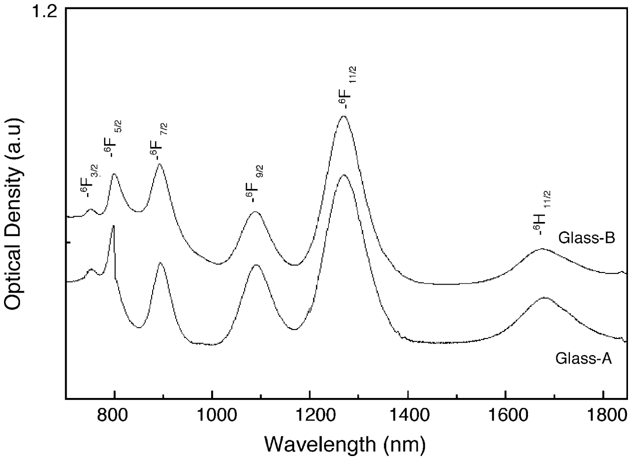

Fig. 2. NIR absorption spectra of Dy^{3+} ions in glasses A and B.

Table 1
Energies (cm^{-1}) of the observed bands, experimental (f_{exp}) and calculated (f_{cal}) oscillator strengths ($\times 10^{-6}$) for Dy^{3+}-doped glasses A and B

Transition from $^6H_{15/2}$	Glass-A			Glass-B		
	Energy	f_{mes}	f_{cal}	Energy	f_{mes}	f_{cal}
$^6H_{11/2}$	5972	0.6350	0.8960	5947	0.8250	1.0545
$^6F_{11/2}$	7891	5.3010	5.2683	7878	5.1960	5.1654
$^6F_{9/2}$	9197	1.9560	2.0194	9163	2.4660	2.6710
$^6F_{7/2}$	11,195	1.7120	1.4754	11,170	2.3980	1.9705
$^6F_{5/2}$	12,528	1.0000	0.6347	12,528	1.1930	0.8541
$^6F_{3/2}$	13,294	0.1630	0.1193	13,294	0.1630	0.1606
$^4F_{9/2}$	21,091	0.1120	0.1142	21,180	0.1520	0.1537
$^4I_{15/2}$	22,069	0.4290	0.3032	22,069	0.3640	0.3677
$^4G_{11/2}$	23,523	0.1580	0.0740	23,523	0.1130	0.0948
$^4I_{13/2}$, $^4F_{7/2}$, $^4K_{17/2}$, $^4M_{19/2}$	25,899	2.1300	1.6447	25,899	2.2300	2.0965
$^6P_{5/2}$, $^4P_{3/2}$	27,465	0.9341	0.4899	27,465	1.1420	0.6592
$^6P_{7/2}$	28,645	2.8850	3.0348	28,465	4.2650	3.9797
δ_{rms} ($\times 10^{-6}$)		±0.249			±0.246	

and are comparable to those reported for Dy^{3+} in different glasses [6,14]. One can see from Table 1 and Fig. 2 that the band at 1270 nm in both the glasses A and B is the most intense among all the absorption bands representing the hypersensitive transition $^6H_{15/2} \rightarrow {}^6F_{11/2}$.

The Judd-Ofelt [10,11] method was used to analyze the measured absorption intensities and to estimate the intensity parameters, radiative transition rates and branching ratios for certain excited Dy^{3+} multiplets. According to the JO model the calculated oscillator strength of an induced electric dipole transition between the states ψJ and $\psi' J'$ is

$$f_{cal}(\psi J, \psi' J') = \frac{8\pi^2 mcv}{3h(2J+1)} \frac{(n^2+2)^2}{9n} \times \sum_{\lambda=2,4,6} \Omega_\lambda (\psi J || U^\lambda || \psi' J')^2 \tag{2}$$

where n is the refractive index of the glass, v is the wavenumber of the absorption peak, Ω_λ ($\lambda = 2$, 4, 6) are the host dependent intensity parameters, $||U^\lambda||$ are the square reduced matrix-elements which are not sensitive to the host. By equating the measured and calculated values of the oscillator strength ($f_{exp} = f_{cal}$) and solving the system of equations by the method of least squares, the J-O intensity parameters Ω_λ ($\lambda = 2$, 4, 6) have been evaluated numerically. To do this, we used the reduced matrix elements reported by Jayasankar and Rukmini for Dy^{3+} in sulphate glasses [9]. The resulting Ω_λ ($\times 10^{-20}$ cm^2) parameters for glasses A and B are found to be $\Omega_2 = 4.620$, $\Omega_4 = 2.706$, $\Omega_6 = 2.087$ and $\Omega_2 = 5.306$, $\Omega_4 = 2.027$, $\Omega_6 = 1.511$, respectively. Generally these J-O parameters provide information on the bonds between rare earth ion and surrounding ligands, as well as the symmetry of the rare earth's environment [13]. The decreasing trend: $\Omega_2 > \Omega_4 > \Omega_6$ in the magnitudes of J-O parameters in both the glasses may be explained by the fact that the Dy^{3+} ions are surrounded by similar environment and consequently it can evidence the good quality of the glasses. The calculated oscillator strengths obtained using these intensity parameters are listed in Table 1 along with measured f values. A measure of the accuracy of the fit is given by the root-mean-square deviation between the measured and calculated oscillator strengths. The small rms deviations of ±0.249 and $\pm 0.246 \times 10^{-6}$ for the glasses A and B, respectively, indicate a fairly good agreement between the measured and calculated oscillator strengths.

The intensity parameters Ω_λ, thus determined were used to calculate the radiative transition rates of various excited states using the relation

$$A(\psi J; \psi' J') = \frac{64\pi^4 v^3}{3h(2J+1)} \left[\frac{n(n^2+2)^2}{9} S_{ed} + n^3 S_{md} \right] \tag{3}$$

Table 2
Comparison of predicted radiative lifetimes τ_R (ms) for various excited levels of Dy^{3+} ions in glasses A and B with different glasses and crystals

Host	$^4F_{9/2}$	$^6F_{5/2}$	$^6H_{9/2}$	$^6F_{11/2}$	$^6H_{11/2}$	$^6H_{13/2}$
Glass-A[a]	1.159	1.093	14.705	1.280	12.211	28.944
Glass-B[a]	1.111	0.873	11.757	1.331	10.980	27.122
Fluorozirconate [5]	1.600	–	–	–	13.500	51.200
Fluoroindate [14]	–	–	–	2.690	14.530	56.080
Silicate [15]	1.531	–	–	–	–	–
YLF [16]	–	1.000	–	5.200	14.800	62.500
KPB_2Cl_5 [17]	–	–	–	1.090	4.240	11.800
YAB [18]	0.572	–	–	–	5.958	16.714

[a] Present work.

where S_{ed} and S_{md} are the linestrengths of the electric dipole and magnetic dipole transitions, respectively. The total spontaneous emission probability A_{T} (ψJ) is related to the τ_{R} of an excited state by

$$\frac{1}{\tau_{\mathrm{R}}} = A_{\mathrm{T}}(\psi J) = \sum_{\psi' J'} A(\psi J; \psi' J') \tag{4}$$

The branching ratio β_{R} corresponding to the emission from an excited ψJ level to the lower $\psi' J'$ may be defined as

$$\beta_{\mathrm{R}}(\psi J; \psi' J') = \frac{A(\psi J; \psi' J')}{\sum_{\psi' J'} A(\psi J; \psi' J')} \tag{5}$$

The calculated lifetimes τ_{R} presented in Table 2 for certain excited luminescent transitions of Dy^{3+} ions in glasses A and B are comparable with those of other crystals and glasses reported in literature [5,14–18]. From these results, it is noted that there are several transitions namely $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (483 nm), $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (575 nm), $^4F_{9/2} \rightarrow {}^6H_{11/2}$ (663 nm), $^4F_{9/2} \rightarrow {}^6H_{9/2}$ (750 nm) in Dy^{3+} ions, which can be eventually used for laser applications in the visible region.

Room temperature emission spectra recorded in the UV–VIS region clearly show thermalization process. The assignment of the emission peaks has been made in accordance with the previous studies reported for Dy^{3+} ion [6,15]. The two most intense bands at 483 and 575 nm are assigned to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions, respectively. Two weak emissions at 420 and 440 nm on the high energy side of $^4F_{9/2} \rightarrow {}^6H_{15/2}$ band are undoubtedly assigned to $^4G_{11/2} \rightarrow {}^6H_{15/2}$ and $^4I_{15/2} \rightarrow {}^6H_{15/2}$ transitions respectively. These emissions are probably due to thermalization of higher lying sublevels of the $^4F_{9/2}$ state [18]. The observed emissions may be explained in the following way. After the excitation of Dy^{3+} ions to levels at energies higher than 21,200 cm^{-1}, fast nonradiative cascade decay to the $^4F_{9/2}$ level occurs. Since this state is separated from the next lower lying level $^6F_{3/2}$ by about 7800 cm^{-1}, which makes the multiphonon relaxation rate (W_{NR}) negligible even for the host materials with high phonon energies ($\hbar\omega \approx 1200\ \mathrm{cm}^{-1}$). Therefore, the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ yellow emission is the strongest band in the luminescence spectra and it could be of more interest for laser applications.

The most important parameter influencing the potential laser performance of a material is the emission cross-section σ_{em} that is usually determined by the following formula:

$$\sigma_{\mathrm{em}}(\psi J; \psi' J') = \frac{\lambda_{\mathrm{p}}^4}{8\pi c n^2\, \Delta\lambda_{\mathrm{eff}}} A(\psi J; \psi' J') \tag{6}$$

where λ_{p} is the wavelength of the emission peak, $\Delta\lambda_{\mathrm{eff}}$ is its effective linewidth (nm). Good laser transitions are generally characterized by large stimulated emission cross-sections. The evaluated peak emission cross-sections for $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition are $\sigma_{\mathrm{em}} = 0.198 \times 10^{-20}$ and $0.216 \times 10^{-20}\ \mathrm{cm}^2$ for the glasses A and B, respectively.

4. Conclusions

In conclusion, our experimental results obtained from the absorption and emission spectra of Dy^{3+} in alkali borate and fluoroborate glasses are in good agreement with the Judd-Ofelt theory. The radiative parameters τ_{R}, β_{R} and σ_{em} obtained in the glasses are similar to other Dy^{3+}-doped systems. From the magnitudes of these parameters one can conclude that the glasses A and B may to found to be more attractive for laser host materials in the blue–green region. In addition the first excited $^6H_{13/2}$ multiplet located at about 3500 cm^{-1} above the $^6H_{15/2}$ ground state seems to be highly favourable for a desired four-level laser operation associated with most intense $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition at 575 nm.

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