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Analysis of energy transfer based emission spectra of (Sm^{3+}, Dy^{3+}): Li_2O–LiF–B_2O_3–CdO glasses

V. Naresh*, S. Buddhudu

Department of Physics, Sri Venkateswara University, Tirupati-517502, India

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ABSTRACT

The present paper brings out the results concerning the preparation and optical properties of Sm^{3+} and Dy^{3+} each ion separately in four different concentrations (0.1, 0.5, 1.0 and 1.5 mol%) and also together doped (1 mol% $Dy^{3+}+x$ mol% Sm^{3+}): Li_2O–LiF–B_2O_3–CdO (where $x=0.1$, 0.5, 1.0 and 1.5 mol%) glasses by a melt quenching method. Sm^{3+} doped base glasses have displayed an intense *orange* emission at 602 nm ($^4G_{5/2}\rightarrow{}^6H_{7/2}$) with an excitation at 403 nm and Dy^{3+} doped glasses have shown two emissions located at 486 nm ($^4F_{9/2}\rightarrow{}^6H_{15/2}$; *blue*) and 577 nm ($^4F_{9/2}\rightarrow{}^6H_{13/2}$; *yellow*) with $\lambda_{exci}=387$ nm. The co-doped ($Dy^{3+}+Sm^{3+}$) lithium fluoro-boro cadmium glasses have been excited with an excitation at 387 nm of Dy^{3+} which has resulted in with a significant reduction in Dy^{3+} emission, at the same time there exists an increase in the *reddish-orange* emission of Sm^{3+} due to an energy transfer from Dy^{3+} to Sm^{3+}. The non-radiative energy transfer from Dy^{3+} to Sm^{3+} is governed by dipole–quadrupole interactions as is explained in terms of their emission spectra, donor lifetime, energy level diagram and energy transfer characteristic factors.

1. Introduction

Trivalent rare earth ions doped glasses have generated a great deal of interest in studying their luminescence, lasing and sensing properties because of their wide range of applications like opto-electronic devices, fibre optics, fibre amplifiers, Q-switched devices, solid state lasers and multicolour emitting devices [1,2]. Though rare earth ions possess unique nature of exhibiting sharp and distinct spectral lines of absorption and emission, sometimes they fail to absorb the excitation energy and result in exhibiting low emission intensity. In order to overcome this, the host matrix containing a luminescent rare earth ion (acts as activator/acceptor) has been co-doped with another luminescent rare earth ion (acts as sensitiser/donor). Co-dopant ion as sensitiser absorbs excitation energy and transfers it to the acceptor ion in enhancing its luminescence performance [3]. The energy transfer based luminescence has quite significant applications in research and development of novel materials by means of pumping schemes in enhancing luminescence for achieving lasing action with an improved efficiency at a reduced threshold energy of laser oscillations in solid state lasers, in producing multicolour emitting devices, and in up-converters (IR to visible) [4,5]. Host plays a vital role in exhibiting efficient and intense luminescence, thus in the present study, alkali fluoro-borate glass with a divalent oxide (CdO) has been considered because of its combined optical advantages of fluorides and oxides. Fluorides having low phonon energy (300–600 cm^{-1}) reduce non-radiative decay losses due to multiphonon relaxations and increase the quantum efficiencies of rare earth ions related emission and do possess higher IR cutoff edge towards higher wavelength side, which can have transmission ability from UV to IR, low non linear refractive index and also decreases the OH absorption because fluorine might react with OH group and forms HF and oxides impart high mechanical and thermal stability and chemical durability [6–8]. Samarium (Sm^{3+}) ion has been chosen here to analyse its luminescence properties in visible region (*orange*) with potential applications in high-dose measurements in medical radiation dosimetry, spectral hole burning, high-density optical storage, colour displays, under sea communication and alongside samarium ion doped glasses can also be used as a cladding for Nd-glass laser rods [9–11]. Dysprosium (Dy^{3+}) ion possesses emission in visible (*yellow/blue*) and NIR regions, its visible emission is used in white light emitting diodes, possible with mixing good ratio of blue and yellow colours, blue emission can be used in the development of blue laser diodes and mid-infrared (1.3 μm) emission of Dy^{3+} ion for the optical amplification telecommunication systems and its visible up-conversion emission can be used as a solid state lasers [11–13]. In the present work, we have undertaken both the Dy^{3+} and Sm^{3+} ions glass alongside single ion doped glasses, to understand the energy transfer based emission and also the interaction which governs energy migration in terms of their emission spectra, emission transition decay-curves in evaluating their lifetimes.

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* Corresponding author. Tel.: +91 8790198658.
E-mail addresses: varna.naresh@gmail.com (V. Naresh), profsb_svuniv@hotmail.com (S. Buddhudu).

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2. Experimental studies

Glasses in general composition of Li_2O–LiF–B_2O_3–CdO (LFBCd) doped individually with Sm^{3+} and Dy^{3+} in different concentrations (0.1, 0.5, 1, 1.5 mol%) and also co-doped with fixed 1 mol% concentration of Dy^{3+} and Sm^{3+} concentration varied from 0.1 to 1.5 mol% were prepared by a quenching method as listed out here:

i. $30Li_2O$–20LiF–$46B_2O_3$–4CdO (reference glass)
ii. $30Li_2O$–20LiF$(46-x)B_2O_3$–4CdO–xSm_2O_3 (where $x=0.1$, 0.5, 1.0, 1.5 mol%)
iii. $30Li_2O$–20LiF–$(46-y)B_2O_3$–4CdO–yDy_2O_3 (where $y=0.1$, 0.5, 1.0, 1.5 mol%)
iv. $30Li_2O$–20LiF–$(46-x-y)B_2O_3$–4CdO–xDy_2O_3–ySm_2O_3 (where $x=1.0$ mol% and $y=0.1$, 0.5, 1.0, 1.5 mol%)

Reagent grade chemicals of H_3BO_3, Li_2CO_3, LiF, CdO, Sm_2O_3, and Dy_2O_3 were used in the preparation of both host and rare-earth ions doped glasses. All these chemicals were weighed separately in 10 g batch each, thoroughly mixed and finely powdered using an agate mortar and pestle. Each batch of chemicals mix was transferred into porcelain crucibles and each of those was sintered separately in electric furnace for an hour at 950 °C in order to ensure homogenous melts and then these melts were quenched in between two smooth surfaced brass plates to obtain circular glass discs of 2–3 cm in diameter and 0.3 cm as thickness. By incorporating the rare earth ions (Sm^{3+} and Dy^{3+}), each ion separately and also together in (LFBCd) glasses have exhibited orange, blue/yellow and reddish-orange colours under UV lamp illumination of these glasses.

3. Measurements

Glass densities were measured using xylene as an immersion liquid from Archimedes' principle. Abbe refractometer was used to measure the glass refractive indices with a sodium (589.3 nm) lamp. The values of density are found to be in the range of 3.288–3.672 (g/cm^3) with an error of ± 0.001 and refractive index values are found to be in the range of 1.652–1.653 with an error of ± 0.001 for Dy^{3+} (1.0 mol%) and Sm^{3+} (0.1–1.5 mol%) co-doped glasses. The XRD profiles of rare-earth ions (Sm^{3+} and Dy^{3+}) doped LFBCd glasses were measured on a *Seifert X-ray Difractometer* (*model 3003TT*) with CuK_α radiation ($\lambda=1.5406$ Å) at 40 KV as the applied voltage and 20 mA as the anode current using a Si detector in the range of $2\theta=10$–$60°$ at the scanning rate of 2°/min. The optical absorption spectra of LFBCd glasses doped with ($Sm^{3+}+Dy^{3+}$) were recorded on a *Varian-Cary-Win* Spectrometer (*JASCO V-570*). The excitation and emission spectra of singly doped Sm^{3+}, Dy^{3+} and co-doped Sm^{3+} and Dy^{3+} glasses were recorded at room temperature on a *SPEX Flurolog-3* (*Model-II*) spectrophotometer, attached with an Xe-arc lamp (450 W) as the excitation source. This system is employed with a Datamax software package for acquiring the spectral data and emission decay-curve (lifetime measurement) data using a phosphorimeter attached with a Xe-flash lamp.

4. Results and discussion

4.1. XRD spectrum

The measured XRD features of LFBCd glasses with dopant ions clearly reveal the amorphous nature as shown in Fig. 1.

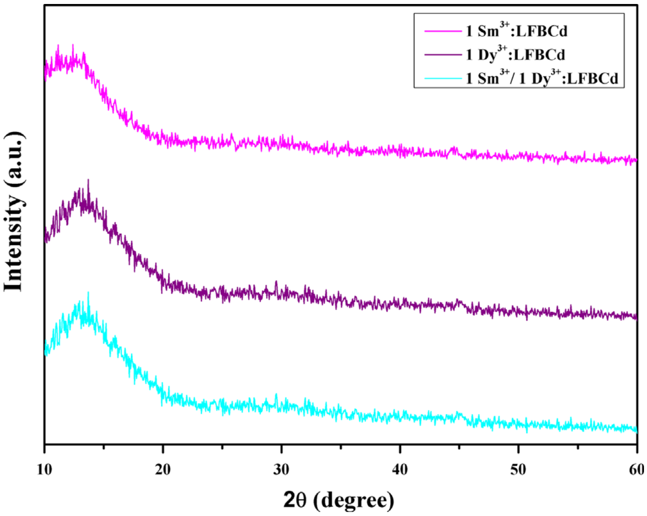

Fig. 1. XRD profiles of singly doped $1Sm^{3+}$, $1Dy^{3+}$: Li_2O–LiF–B_2O_3–CdO glasses, and together doped (1 mol%) Sm^{3+}+(1 mol%) Dy^{3+}: Li_2O–LiF–B_2O_3–CdO glasses.

4.2. Optical spectra of Sm^{3+}: LFBCd and Dy^{3+}: Li_2O–LiF–B_2O_3–CdO glasses

In Fig. 2(a) and (b), vis–NIR absorption spectra of 1.0 mol% Sm^{3+}: LFBCd and 1.0 mol% Dy^{3+}: LFBCd glasses are shown. In Sm^{3+} doped glass the intra-configurational transitions in the absorption spectrum originate from ground state $^6H_{5/2}$ to various excited states. The bands are assigned to $^6H_{5/2}\rightarrow{}^4F_{7/2}$ (402 nm), $^6H_{5/2}\rightarrow{}^4I_{11/2}$ (471 nm), $^6H_{5/2}\rightarrow{}^6F_{11/2}$ (942 nm), $^6H_{5/2}\rightarrow{}^6F_{9/2}$ (1078 nm), $^6H_{5/2}\rightarrow{}^6F_{7/2}$ (1228 nm), $^6H_{5/2}\rightarrow{}^4F_{5/2}$ (1374 nm), $^6H_{5/2}\rightarrow{}^4F_{3/2}$ (1449 nm), $^6H_{5/2}\rightarrow{}^6H_{15/2}$ (1524 nm), $^6H_{5/2}\rightarrow{}^6F_{1/2}$ (1584 nm), and $^6H_{5/2}\rightarrow{}^6H_{13/2}$ (1920 nm) respectively. Most of the absorption transitions of Sm^{3+} originate based on the selection rules of $|\Delta L|\geq 0$, $|\Delta J|\geq 0$ and $|\Delta S|=0$ [14]. The high intense transitions in the infrared region are spin allowed ($\Delta S=0$) and the transitions in the visible region are spin-forbidden. In case of the absorption spectrum of Dy^{3+} doped glass, the transitions originate from the ground state $^6H_{15/2}$ to various excited states $^4K_{17/2}$ (376 nm), $^4I_{13/2}$ (386 nm), $^4G_{11/2}$ (425 nm), $^4I_{15/2}$ (452 nm), $^4F_{9/2}$ (476 nm), $^6F_{3/2}$ (742 nm), $^6F_{5/2}$ (801 nm), $^6F_{7/2}$ (898 nm), $^6F_{9/2}$, $^6H_{7/2}$ (1088 nm), $^6F_{11/2}$, $^6H_{9/2}$ (1261 nm), $^6H_{11/2}$ (1325 nm), and $^6H_{13/2}$ (1674 nm) respectively. The transitions $^6H_{5/2}\rightarrow{}^6F_{1/2}$, $^6F_{3/2}$ of Sm^{3+} and $^6H_{15/2}\rightarrow{}^6F_{11/2}$, $^6H_{9/2}$ of Dy^{3+} are hypersensitive transitions as they follow the selection rules, $|\Delta S|=0$, $|\Delta L|\leq 2$, and $|\Delta J|\leq 2$ and are found to be more intense than other transitions [11,15].

4.3. Photoluminescence of Sm^{3+}: Li_2O–LiF–B_2O_3–CdO glasses

The excitation spectrum of (1 mol%) Sm^{3+}: LFBCd glass is shown in Fig. 3(a). From this figure we could notice the presence of excitation bands $^6H_{5/2}\rightarrow{}^4H_{9/2}$ (345 nm), $^4D_{5/2}$,$^6P_{5/2}$ (363 nm), $^4D_{1/2}$ (376 nm), $^4F_{7/2}$ (403 nm), $^4M_{19/2}$ (418 nm), $^4G_{9/2}$ (439 nm), $^4I_{13/2}$ (463 nm), $^4I_{11/2}$ (471 nm), $^4G_{7/2}$ (501 nm), $^4F_{3/2}$ (528 nm), $^4G_{5/2}$ (563 nm) attributed to 4f–4f transitions of Sm^{3+}. Of all the transitions, the prominent excitation 403 nm ($^6H_{5/2}\rightarrow{}^4F_{7/2}$) has been chosen for the measurement of emission spectra of Sm^{3+} glasses as shown in Fig. 3(b) for four concentrations (0.1, 0.5, 1, and 1.5 mol%) of Sm^{3+} (inset figure shows the dependence of emission intensity as a function of Sm^{3+} concentration). At 403 nm, Sm^{3+} ions are excited to upper energy state $^4H_{9/2}$ and from where those decay to $^4F_{7/2}$ state and these excited ions cascades rapidly to the $^4G_{5/2}$ metastable state by populating it. The energy states between $^4F_{7/2}$ and $^4G_{5/2}$ are very close and their energy differences are small, which encourages an efficient and fast non-radiative relaxation to $^4G_{5/2}$ state. Upon reaching $^4G_{5/2}$ state these unstable ions relaxes radiatively by emitting fluorescence to the