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ScienceDirect
Spectrochimica Acta Part A 70 (2008) 577–586
SPECTROCHIMICA ACTA PART A
www.elsevier.com/locate/saa

Photoluminescence and energy transfer studies of Dy^{3+}-doped fluorophosphate glasses

R. Praveena, R. Vijaya, C.K. Jayasankar*

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

Received 17 April 2007; received in revised form 25 July 2007; accepted 2 August 2007

Abstract

Dy^{3+}-doped fluorophosphate glasses with composition (in mol%) $(56-x/2)P_2O_5 + 17K_2O + (15-x/2)BaO + 8Al_2O_3 + 4AlF_3 + xDy_2O_3$, $x = 0.01$, 0.05, 0.1, 1.0 and 2.0, have been prepared by melt quenching technique. The luminescence spectra and lifetimes of $^4F_{9/2}$ level of Dy^{3+} ions in these glasses have been measured using the 457.9 nm line of argon ion laser as an excitation source. The free-ion calculation and Judd–Ofelt analysis have been performed. The room temperature emission spectra corresponding to $^4F_{9/2} \rightarrow {}^6H_J$ ($J = 7/2$, 9/2, 11/2, 13/2 and 15/2) transitions of Dy^{3+} ions were measured. The fluorescence decay from $^4F_{9/2}$ level have been measured by monitoring the intense $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition. The lifetime of the decay is obtained by taking the first e-folding times of the decay curves and is found to decrease with increase in Dy^{3+} ions concentration due to concentration quenching. The decay curves are found to be perfectly single exponential for samples with low Dy^{3+} ion concentration. The non-exponential decay curves observed for higher concentrations are well fitted to the Inokuti–Hirayama model for $S = 6$, which indicates that the energy transfer between the donor and acceptor is of dipole–dipole nature. The energy transfer parameter and donor to acceptor interaction increases with Dy^{3+} ions concentration due to increase of energy transfer from Dy^{3+} (donor) to unexcited Dy^{3+} (acceptor) ions.
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Keywords: Dysprosium; Phosphate glasses; Optical properties; Judd–Ofelt analysis

1. Introduction

Recent innovations in special photonic glasses and fibers are pushing fiber lasers to the forefront of solid-state laser applications and consequently an on-going reshaping of the laser industry [1]. Glasses doped with rare earth (RE) ions are the material foundation for fiber lasers and amplifiers. In past studies, Dy^{3+} ($4f^9$) doped crystals or glasses have been considered as promising laser active materials able to emit radiation associated with the $^6H_{13/2} \rightarrow {}^6H_{15/2}$ transition of Dy^{3+} ion around 3 μm [2–4]. Little attention was paid to the visible emission originating in the $^4F_{9/2}$ state situated at about 21,000 cm^{-1} [5,6]. This was due to the fact that the spectral region between the emitting state and the UV absorption edge of matrices is too narrow to ensure efficient population on the higher laser level with classical broad-band pumping sources. However, tremendous progress in development of laser diodes is going on to overcome this disadvantage. Commercialization of blue laser diodes opens new possibilities of optical pumping and therefore potential laser transitions in the visible region are very interesting to be investigated.

The active Dy^{3+} ion provides two typical emission transitions that correspond to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (magnetic dipole) in blue (~480 nm) and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (electric dipole) in yellow (~570 nm) regions, which are necessary for full primary color displays [7–9]. Also it is well known that the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition is hypersensitive ($|\Delta L| \leq 2$ and $|\Delta J| \leq 2$) and therefore, its intensity strongly depends on the host, whereas intensity of the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition is less sensitive to the host. In addition, the emission probability of electric dipole transition is greatly affected by the crystal-field (CF) and radial integral of 4f and 5d electrons [8].

The optical properties of RE ions in glasses depend on the chemical composition of the glass matrix, which determines the structure and nature of the bonds. Among different host materials, fluorophosphate (FPh) glasses are promising hosts because these glasses can bring together the advantages of both fluoride and phosphate glasses such as low phonon energy, good moisture resistance, physical and chemical stability, low nonlinear refractive index and high transparency from near UV to

* Corresponding author. Tel.: +91 877 2248033; fax: +91 877 2225211.
E-mail address: ckjaya@yahoo.com (C.K. Jayasankar).

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doi:10.1016/j.saa.2007.08.001

mid IR spectral range [10–12]. It was also found that a relatively higher degree of line broadening and smoother line shapes can be obtained [13] with an FPh glass. These properties contribute to the applications of FPh glasses as RE-doped fiber laser matrix. Many researchers have showed that RE-doped FPh glasses have promising features as laser matrix [14–16]. It is well known that the spectroscopic parameters such as absorption cross-section, emission cross-section, and fluorescence decay time of RE ions depend on the local environment in the glass structure [17,18]. For FPh glasses, the local structure of RE ions can be modified over a large extent by varying P/F ratio and/or introducing other special ions [19,20]. The infrared optical properties of Dy-doped KPb_2Br_5 are discussed and evaluated for possible applications in solid-state lasers by Hommerich et al. [21]. Therefore, in the present work, the optical and fluorescence properties of different concentrations of Dy^{3+} ions in the FPh glasses in the UV to IR region have been reported.

2. Experimental details

Dy^{3+} ions doped fluorophosphate glasses with composition $(56-x/2)P_2O_5+17K_2O+(15-x/2)BaO+8Al_2O_3+4AlF_3+xDy_2O_3$ for $x=0.01$, 0.05, 0.1, 1.0 and 2.0 mol% (referred as PKBAFD001, PKBAFD005, PKBAFD01, PKBAFD10 and PKBAFD20, respectively) have been prepared by the conventional melt quenching technique [4,22].

The selected glass compositions were thoroughly mixed in an agate mortar and melted in a platinum crucible by using an electric furnace at 1075 °C for 1 h to get a homogenized melt. The melt was then air-quenched by pouring it on a thick brass plate. In order to remove thermal strains, the glass samples were annealed for 10 h at 350 °C. Finally, these glass samples were polished to obtain smooth surfaces for optical measurements.

The refractive index, n, is measured on an Abbe refractometer at sodium wavelength (589.3 nm) with 1-bromonapthalene as a contact liquid. The glass density is measured by Archimedes principle using water as an immersion liquid. All these measurements were measured at room temperature. The glass samples were excited by the 457.9 nm line of Ar^+ laser and the resulting fluorescence was collected at right angle to the excitation source and recorded using a 0.85 m double grating monochromator equipped with a cooled photomultiplier. Decay curves were obtained using a mechanical chopper with a multi-channel scalar interfaced to a personal computer that recorded and averaged the signal at room temperature.

3. Theory

3.1. Energy level analysis

The model Hamiltonian expressed in terms of free-ion or atomic parameters are used to analyse the free-ion energy levels involved in f-f transitions. The free-ion Hamiltonian (H_{FI}) that was used to study the energy level structure of Dy^{3+} ion may be written as [23],

$$\hat{H}_{FI} = E_{AVG} + \sum_k F^k \hat{f}_k + \xi_{4f}\hat{A}_{SO} + \alpha\hat{L}(\hat{L}+1) + \beta\hat{G}(G_2) + \gamma\hat{G}(R_7) + \sum_i T^i \hat{t}_i + \sum_k P^k \hat{p}_k + \sum_j M^j \hat{m}_j \quad (1)$$

where $k=2$, 4, 6, $i=2$, 3, 4, 6, 7, 8 and $j=0$, 2, 4. The operators ($\hat{f}_k$, $\hat{A}_{SO}$, $\hat{L}$, $\hat{G}$, $\hat{t}_i$, $\hat{p}_k$ and $\hat{m}_j$) and their associated parameters (central field, E_{AVG}; two body electro static repulsion, F^k; spin–orbit coupling, ξ; two-body configuration, α, β and γ; three-body configuration, T^k; spin-other-orbit, M^j; and electrostatically correlated spin-orbit, P^k, are written according to conventional notation and meaning. The operators represent angular integrals and their associated parameters represent radial integrals, where the former can be evaluated exactly and the latter can be determined by a semi-empirical approach [23,24].

The fitting procedure between experimental and calculated energy level values was carried out similar to earlier analysis for Dy^{3+}:glass systems [24] using the standard least-square fit method along with the minimum values of root-mean-square (r.m.s.) deviation, σ, (deviation between the experimental and calculated energies) as a figure of merit in describing the quality of the fit. The quality of the parametric fit is generally defined as

$$\sigma = \sqrt{\frac{\sum_{i=1}^{N}(E_i^{exp} - E_i^{cal})^2}{N}} \quad (2)$$

where E_i^{exp} and E_i^{cal} are the experimental and calculated energies, respectively, for level i and N denotes the total number of levels included in the energy-level fit.

3.2. Oscillator strengths: Judd–Ofelt analysis

Quantitative analysis for f-f transition of REs is provided by the Judd–Ofelt (JO) theory [25,26]. The experimental oscillator strengths (f_{exp}) of absorption band intensities are determined using the relation [27],

$$f_{exp} = 4.32 \times 10^{-9} \int \varepsilon(\nu)\, d\nu \quad (3)$$

where $\varepsilon(\nu)$ is the molar absorptivity at a frequency ν in cm^{-1}.

According to JO theory the spectral intensity (f_{cal}) of the absorption band corresponding to transitions from the ground state (ΨJ) to an excited state ($\Psi' J'$) depends on the three parameters Ω_λ ($\lambda=2$, 4, 6) known as the JO intensity parameters and is given by

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

where n is the refractive index of the medium, J the ground state total angular momentum, ν the energy of the transition in cm^{-1} and $||U^\lambda||^2$ are the squared doubly reduced matrix elements of the unit tensor operator of the rank $\lambda=2$, 4 and 6 which are calculated from the intermediate coupling approximation for

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