Available online at www.sciencedirect.com
SCIENCE DIRECT®
Spectrochimica Acta Part A 61 (2005) 431–436
SPECTROCHIMICA ACTA PART A
www.elsevier.com/locate/saa

Optical properties of Dy^{3+} doped in oxyfluoroborate glass

K.K. Mahato [b], Anita Rai [a], S.B. Rai [b,*]

[a] *Department of Chemistry, Jagatpur P.G. College, Varanasi, India*
[b] *Department of Physics, Banaras Hindu University, Varanasi 221005, India*

Received 2 December 2003; accepted 24 February 2004

Abstract

Optical absorption, fluorescence and photoacoustic spectra of Dy^{3+} doped in oxyfluoroborate glass has been studied. Lifetime of $^4F_{9/2}$ level has been measured for different concentration of Dy^{3+}. Effect of concentration quenching on the lifetime and the fluorescence yield has been observed and the mechanism of energy transfer discussed. The energy transfer from Pr^{3+} to Dy^{3+} has been observed and explained in a codoped glass containing $Pr^{3+} + Dy^{3+}$.

Keywords: Photoacoustic spectrum; Concentration quenching; Lifetime; Energy transfer

1. Introduction

Dy^{3+} is known to give lasing transition in the NIR region at 1.35 and 3.0 μm in several crystals and glass hosts since long time [1]. Lasing has also been observed at 570 and 661 nm when this ion is doped in tungstate glass [2] though the efficiency is poor. The lasing in visible region in solid hosts has great technological applications in commercial displays, optical science, etc. and efforts are constantly being made to develop host materials which can give better efficiency. The absorption and fluorescence spectra of Dy^{3+} has been a subject of investigations [2–23] for several decades. Raghuvanshi et al. [7] studied the spectra of this ion in several hosts and noted that phosphate host shows better emissive efficiency. These workers also measured the lifetime of $^4F_{9/2}$ level of this ion in different hosts at different temperatures. The effect of host on the absorption characteristics of Dy^{3+} in lead borate glass has been reported by Carnall et al. [15]. The energy transfer from Dy^{3+} to other rare earth ions has also been studied by several workers [14–21]. Thus, Cabezas and Deshazer [16] noted a radiative energy transfer from Dy^{3+} to Tb^{3+} and from Dy^{3+} to Nd^{3+} ions in borosilicate glass, while a non-radiative energy transfer was observed from Dy^{3+} to Tb^{3+} in tungstate glass by Van Uitert et al. [17]. Joshi et al. [18–21] reported non-radiative energy transfer from Dy^{3+} to Pr^{3+}, Ho^{3+}, Er^{3+} etc. in several hosts and the mechanism of energy transfer was attributed to be dipole–dipole interaction. Crystals belonging to molybdate and tungstate families of MXO_4 (where M is Ca, Sr, Ba and X is Mo and W) type doped with Dy^{3+} have been reported recently by Kaminskii et al. [2], Basiev et al. [22] and Cavalli et al. [23] as better host materials for laser and Raman lasers. In this paper, we have studied the absorption, fluorescence and photoacoustic spectra and measured the lifetime of the $^4F_{9/2}$ level of Dy^{3+} doped in oxyfluoroborate glass. A concentration-dependent study of the fluorescence and lifetime of $^4F_{9/2}$ level has also been made. The energy transfer from Dy^{3+} to Pr^{3+} has been studied by doping Pr^{3+} and Dy^{3+} together. The mechanism of energy transfer has been discussed.

2. Experimental

Following chemical composition has been used to make Dy^{3+} doped oxyfluoroborate glass:

$$(70 - X)H_3BO_3 + 20Li_2CO_3 + 10LiF + XDy_2O_3$$

where X is 0.5, 1.0, 1.5, 2.0 and 2.5 mol%. Several sets of glasses were made for each composition. The method of preparation is discussed in our earlier work [24]. We have also prepared glasses with 1 mol% Pr^{3+} + 1 mol% Dy^{3+} doped simultaneously. The absorption spectra of the

* Corresponding author. Tel.: +91-542-2307308; fax: +91-542-368468.
E-mail address: sbrai49@yahoo.co.in (S.B. Rai).

1386-1425/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2004.02.038

glasses were recorded in the spectral region 300–2000 nm using Cary 2390 UV-Vis-NIR Varian double beam spectrophotometer. The fluorescence spectra were recorded using 457.9 nm line with 100 mW power and 0.01 nm bandwidth from Ar^+ laser. A Spex 0.5 m monochromator was used to record the spectra in the 460–750 nm region.

The photoacoustic spectra of glasses were recorded in the spectral region 360–700 nm using a single beam photoacoustic spectrometer. For lifetime measurements we have used an excimer laser radiating at 308 nm. The gate width and the delay of the box car used was varied to optimize the signal and the decay profile was scanned using a recorder. Several scans were made for each measurements to avoid any artefact. All the measurements were made at room temperature.

3. Results and discussion

3.1. Absorption spectrum

The absorption spectrum of 1 mol% concentration of Dy^{3+} doped oxyfluoroborate glass is shown in Fig. 1. The spectrum shows nine bands in the 300–2000 nm region. The electronic configuration of Dy^{3+} is $4f^9\ 5S^2Sp^6$ which gives large number of states with $^6H_{15/2}$ as the ground state. Some of the other states arising from this configuration are $^4G_{7/2,9/2,11/2}$, $^4I_{11/2,13/2,15/2}$, $^4F_{9/2}$, $^4M_{15/2}$, etc. The bands observed in the absorption spectrum could be easily assigned on the basis of earlier work [7–14,25]. The assignment of the bands along with their energies are given in Table 1. The bands due to $^6P_{3/2}$ and $^6H_{9/2}$ as upper state are very intense. Our spectrum is similar to the one reported by Orera et al. [14] for Dy^{3+} in fluorozirconate lattice. The oscillator strength for absorption band is given as

$$f_{\text{exp}} = 4.32 \times 10^{-9} \int \xi(\nu)\, \mathrm{d}\nu$$

where $\xi(\nu)$ is the molar absorptitivity and is equal to $(1/c\ell)\log(I_0/I)$ from Beer–Lambert law; c is the molar concentration of the rare earth ion and ℓ is the optical path length in the glass. The values of oscillator strengths for different transitions thus obtained are given in Table 1. The Judd–Ofelt intensity parameters were calculated using the measured values of oscillator strengths and the reduced matrix elements for Dy^{3+} given by Carnall et al. [15]. The Ω_λ parameters thus obtained are also given in Table 1. In the present case Ω_λ values follow the trend $\Omega_2 > \Omega_4 > \Omega_6$ which is similar with the trend followed in fluorozirconate glass [14] (see Table 1). The Ω_λ values thus obtained has been used to calculate theoretical oscillator strength:

$$f_{\text{cal}} = \frac{8\pi^2 mc\nu}{3he^2(2J+1)} \frac{(n^2+2)^2}{9n} \sum_{\lambda=2,4,6} \Omega_\lambda (\psi_J \| \nu^\lambda \| \psi' J')^2$$

and are given in Table 1.

3.2. Photoacoustic spectrum

Dy^{3+} doped oxyfluoroborate glass gives a poor photoacoustic spectrum (see Fig. 2). This is not surprising as rare earth ions give very poor photoacoustic spectrum in glass lattices [26,27] perhaps due to its poor heat conducting nature. Only three absorption bands at 432, 460 and 480 nm are observed in between 400 and 700 nm region. These bands were assigned to arise due to $^4G_{11/2} \leftarrow {}^6H_{15/2}$, $^4I_{15/2} \leftarrow H_{15/2}$ and $^4F_{9/2} \leftarrow {}^6H_{15/2}$ transitions, respectively.

3.3. Fluorescence spectrum

The fluorescence spectrum of Dy^{3+} doped in oxyfluoroborate glass obtained on excitation with 457.9 nm laser line is shown in Fig. 3. The energy of 457.9 nm line is 21 832 cm^{-1} which is only slightly smaller than the en-

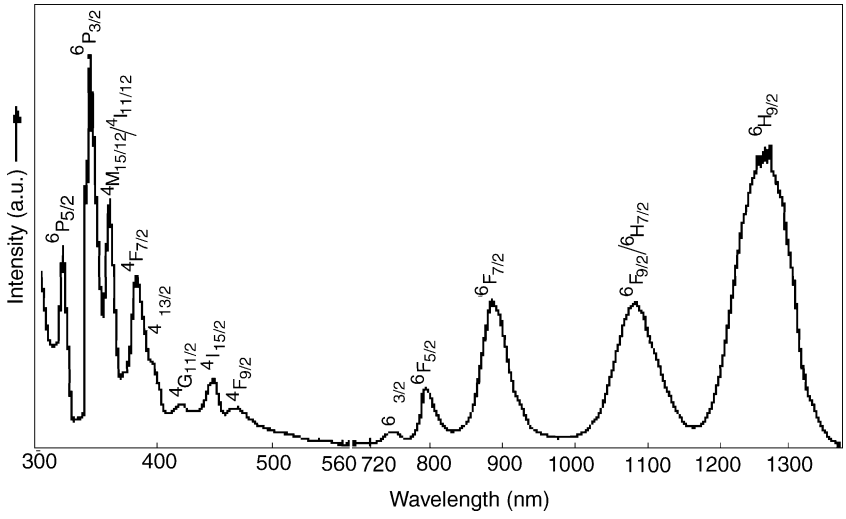

Fig. 1. Absorption spectrum of Dy^{3+} doped in oxyfluoroborate glass.