Optik - International Journal for Light and Electron Optics 169 (2018) 118–124

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.com/locate/ijleo

Original research article

Optical properties and upconversion in rare earth doped oxyfluoride glasses

Li Feng[a,*], Liang Bian[b,*], Jianan Nie[b], Huichao He[b], Chao Liu[a]

[a] College of Gemmology and Material Technics, Hebei GEO University, Shijiazhuang 050031, China
[b] Key Laboratory of Solid Waste Treatment and Resource Recycle, Ministry of Education, South West University of Science and Technology, Mianyang 621010, Sichuan, China

ARTICLE INFO

Keywords:
Judd–Ofelt
Upconversion
Oxyfluoride glass

ABSTRACT

Ho^{3+} and Er^{3+}-singly doped and Ho^{3+}/Yb^{3+} and Er^{3+}/Yb^{3+}-codoped SiO_2–Al_2O_3–MgO–MgF_2 glasses were developed. Ho^{3+} and Er^{3+}-singly doped glasses were analyzed by the Judd–Ofelt theory, and the intensity parameters obtained by Judd–Ofelt theory and by the linear relationship reported by Su were contrasted. Upconversion luminescence was observed in Ho^{3+}/Yb^{3+} and Er^{3+}/Yb^{3+}-codoped glasses under 980 nm excitation.

1. Introduction

Rare earth doped transparent materials have been widely researched due to their practical applications in upconversion lasers, color displays, optical amplifiers and temperature sensors, etc. [1–9]. Among transparent materials, glasses are very attractive hosts because they have unique advantages such as large rare earth ions doping concentration with uniform distribution, large optical transparency from ultraviolet to infrared region, easily developed in different sizes and shapes, high mechanical strength, simple and low cost manufacturing process [2,5,10]. Generally, oxyfluoride glasses are one of promising hosts for infrared to visible upconversion luminescence since they combine the advantages of oxide and fluoride glasses. They possess low cut off phonon energy of fluoride glasses which can reduce the nonradiative relaxation and enhance the efficiency of upconversion luminescence, and good thermal and chemical stability, high mechanical strength and ease of fabrication of oxide glasses which are favorable for practical applications.

Among the trivalent rare earth ions, Ho^{3+} and Er^{3+} ions are very effective active ions for upconversion luminescence due to their abundant energy levels from near-infrared to ultraviolet region. Recently, upconversion luminescence of Ho^{3+} and Er^{3+} ions doped materials has been studied by several researchers [11–18]. In order to enhance upconversion luminescence, Yb^{3+} ions are usually used as sensitizers due to large absorption around 980 nm and quick and efficient energy transfer from Yb^{3+} ions to Ho^{3+} and Er^{3+} ions [19,20].

Generally, spectroscopic properties of rare earth doped glasses can be estimated by Judd–Ofelt theory [21,22]. In this study, absorption spectra of Ho^{3+} and Er^{3+}-singly doped SiO_2–Al_2O_3–MgO–MgF_2 glasses were analyzed by the Judd–Ofelt theory, and Judd–Ofelt intensity parameters, radiative transition probabilities, fluorescence branching ratios and radiative lifetimes were obtained. Upconversion luminescence properties of Ho^{3+}/Yb^{3+} and Er^{3+}/Yb^{3+}-codoped SiO_2–Al_2O_3–MgO–MgF_2 glasses under 980 nm excitation were also investigated.

* Corresponding authors.
E-mail addresses: fengli5435@hgu.edu.cn, fengli5435@sina.com (L. Feng), bianliang555551@126.com (L. Bian).

https://doi.org/10.1016/j.ijleo.2018.05.042
Received 22 March 2018; Accepted 10 May 2018

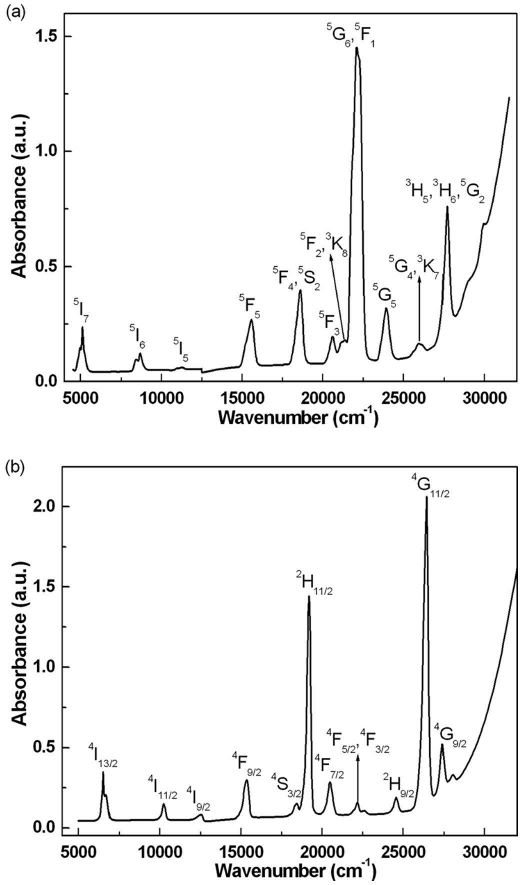

Fig. 1. Absorption spectra of Ho^{3+} and Er^{3+}-singly doped glasses: (a) Ho^{3+}; (b) Er^{3+}.

2. Experimental

The oxyfluoride glasses with composition (mol%) of $45SiO_2$–$12Al_2O_3$–(13–x)MgO–$30MgF_2$–$x$$Yb_2O_3$–$y$$RE_2O_3$ (where x = 0, 0.5, 1.5, 3, 5, 7; y = 0.005, 0.015, 0.05, 0.1, 0.3, 0.5; RE_2O_3 = Ho_2O_3, Er_2O_3) were prepared by the melt quenching method. The raw materials (high purity reagent grade) were thoroughly mixed in an agate mortar and then melted at 1440 °C for 45 min in an electric furnace. The melts were poured on a preheated stainless steel plate in an electric furnace and then cooled down to the room temperature. The obtained samples were carefully polished to make the thickness around 2 mm for optical measurements.

The optical absorption spectra of the samples were recorded by using Cary 5000 UV–vis–NIR spectrophotometer in the range of 4000–32,000 cm^{-1}. The upconversion spectra were monitored by using SPEX Fluorolog-3 spectrofluorometer and a 980 nm laser diode with a maximum power of 1 W was used as excitation light source. The densities of the glasses were measured by Archimedes method using distilled water as an immersion liquid. The refractive indices of the glasses were measured by using an Abbe refractometer.

3. Results and discussion

3.1. Absorption spectra and the Judd–Ofelt analysis

Absorption spectra of 1 mol% Ho^{3+} ions and 1 mol% Er^{3+} ions doped glasses are shown in Fig. 1(a) and (b), respectively. The absorption bands can be attributed to 4f–4f transitions of Ho^{3+} ions from the ground state $^5I_8$ to the excited states ^5I_J, ^5F_J, ^5S_J, ^3K_J, ^5G_J and ^3H_J, and Er^{3+} ions from the ground state $^4I_{15/2}$ to the excited states ^4I_J, ^4F_J, ^4S_J, ^2H_J and ^4G_J. The intensities of the absorption bands can be utilized to estimate their optical properties on the basis of Judd–Ofelt analysis. The density, refractive index and thickness of glasses are required for Judd–Ofelt analysis. For 1 mol% Ho^{3+} ions and 1 mol% Er^{3+} ions doped glasses, the density, refractive index and thickness are 2.6997 g/cm^3, 1.574 and 4.04 mm, and 2.4897 g/cm^3, 1.575 and 4.44 mm, respectively. The experimental (P_{exp}) and calculated (P_{cal}) oscillator strengths along with Judd–Ofelt intensity parameters (Ω_λ(λ = 2, 4, 6)) are obtained and the results are presented in Table 1. The magnetic dipole oscillator strengths (P_{md}) of $^5I_8 \rightarrow {}^5I_7$ and $^4I_{15/2} \rightarrow {}^4I_{13/2}$ transitions are not negligible and the results are also shown in Table 1. The root mean square (rms) deviations are calculated and the