Journal of Alloys and Compounds 663 (2016) 545–551

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Optical transition properties, energy transfer mechanism and luminescent thermal stability of Sm^{3+}-doped silicate glasses

Zhongli Wu [a, b], Baojiu Chen [a, *], Xiangping Li [a], Jinsu Zhang [a], Jiashi Sun [a], Hua Zhong [a], Hui Zheng [a], Lili Tong [a], Haiping Xia [c, **]

[a] Department of Physics, Dalian Maritime University, Dalian, Liaoning, 116026, PR China
[b] School of Science, Liaoning University of Technology, Jinzhou, 121001, PR China
[c] Key Laboratory of Photo-electronic Materials, Ningbo University, Ningbo, 315211, PR China

ARTICLE INFO

Article history:
Received 15 September 2015
Received in revised form
15 December 2015
Accepted 18 December 2015
Available online 21 December 2015

Keywords:
Judd-Ofelt theory
Energy transfer
Crossover
I–H model

ABSTRACT

Sm^{3+} doped silicate glasses were synthesized via a conventional melt-quenching and annealing technique. Optical transition properties of Sm^{3+} in the studied silicate glass were evaluated in the framework of Judd–Ofelt theory. The radiative transition rates, fluorescence branching ratios and intrinsic lifetime for interested transitions or level were obtained. Concentration quenching, energy transfer and thermal stability were studied by fluorescence spectra and decay curves. It was found that the main reason for concentration quenching was nonradiative energy transfer through cross-relaxation mechanism due to dipole–dipole interaction. The temperature-dependent fluorescence emission was studied in detail, and it was found that crossover mechanism based on the Arrhenius model can well explain the fluorescence temperature quenching behavior of $^4G_{5/2}$ level.

1. Introduction

Rare Earth (RE) doped luminescence materials have attracted much attention since they have been discovered owing to their practical and potential applications in many fields such as lighting, displays, optical information processing, energy sources and environments [1–8]. Recently, the RE activated luminescence materials which can be effectively excited by near ultraviolet (NUV) or blue light have become a key researched and developed target driven by the demand of white light illumination in which the light-emitting diodes (LEDs) and photon-conversion fluorophors are used [9–12]. The white LEDs first designed and developed by combining blue GaN-based LED and YAG:Ce^{3+} phosphor are thought to be the mainstream product in the commercial market [13–15] and have showed many advantages over the traditional light source, such as high brightness, long serving lifetime, quick response time, high electro-optic conversion efficiency and excellent environmental security [5–9]. Despite the above mentioned advantages, however, there still exist some defects such as poor color rendering index (CRI), highly correlated color temperature, poor heat-release from the devices. In addition, epoxy resin tends to deteriorate after long time operation, which limits the application of white LED [16–18].

In order to further improve and enhance the performance of the white LEDs, many efforts have been devoted to the luminescence materials amongst which the glasses doped with RE^{3+} were also specially concerned, for example, Sm^{3+}-doped silicate or borate glass [19–23], Ce^{3+}/Sm^{3+} co-doped silicate glasses [24], Sm^{3+} doped phosphate glasses [25,26], Sm^{3+} doped tellurite glasses [27] and so on. In comparison with all these glass hosts, the silicate glasses exhibit excellent mechanical performance, low cost, outstanding optical and thermal properties [28–33]. Thereby, the preparation and spectroscopic properties of Sm^{3+} doped silicate glasses will be the main task of this work. Moreover, compared to conventional phosphors, the fluorescent glass materials show more advantages, such as excellent thermal stability, simple synthesis procedure, high transparency, low production cost, convenient mechanical treatment, and easy epoxy-resin assembly process. What is more, the fluorescent glasses can directly replace both the powder phosphors and epoxy resin in the white LED devices, meanwhile the far-field packing for the white LEDs can be easily realized. In addition, the Sm^{3+} glass may be used in the presently main-streamed white LEDs, which combining the YAG:Ce^{3+} phosphor and blue emitting chip, as a red emitting fluorophor to

---

* Corresponding author.
** Corresponding author.
E-mail addresses: chenmbj@sohu.com (B. Chen), hpxcm@nbu.edu.cn (H. Xia).

http://dx.doi.org/10.1016/j.jallcom.2015.12.140

compensate red component of the output light. Therefore, the RE doped glasses have been widely studied [34–43].

In this paper, a series of silicate glasses with various Sm^{3+} concentrations were prepared. Judd–Ofelt (J–O) analysis was carried out for quantitatively characterizing the optical transition properties of the Sm^{3+}-doped silicate glasses. The spectroscopic properties and energy transfer behavior of the glass fluorophors were examined by inspecting the excitation and emission spectra as well as the fluorescence decays. Finally, the temperature quenching of the glasses was also investigated.

2. Experimental and theoretical procedures

2.1. Sample preparation and characterization

The glass samples with the composition of $65SiO_2$–$16K_2CO_3$–$16BaF_2$–$3La_2O_3$–xSm_2O_3 (in molar, where $x = 0.1$, 0.5, 1, 3 and 5) were synthesized via a traditional melt-quenching method in air atmosphere, and named as SKBL-$x$$Sm^{3+}$. Silicon oxide ($SiO_2$, 99.99%), potassium carbonate (K_2CO_3, 99.99%), barium fluoride (BaF_2, 99.99%), lanthanum oxide (La_2O_3, 99.99%) and samarium oxide (Sm_2O_3, 99.99%) were used as starting materials. According to the designed composition, total 5 g of starting materials were weighed and mixed, then grinded thoroughly in an agate mortar for 5 min. After that, the mixture was transferred to an alumina crucible and directly heated in a high-temperature electric muffle furnace at around 1250 °C for 6 min to melt the raw materials completely. Subsequently, the homogeneous molten both was then quickly quenched by pouring onto a preheated brass plate, and then the transparent sample was immediately transferred into another furnace at 400 °C for 4 h for annealing. After annealing the transparent glass sample was polished carefully for subsequent optical measurements.

The absorption spectra for all the Sm^{3+}-doped samples were obtained using a UV-3600 double beam spectrophotometer (shimazu, Japan) in the range of 300–2000 nm. The emission spectra, excitation spectra and fluorescence decays of all the samples were measured by using a F-4600 fluorescence spectrophotometer (Hitachi, Japan) equipped with a 150 W xenon lamp as the excitation source. The emission spectra were well intensity-corrected by using a sub-standard light source provided by the manufacturer of the spectrophotometer. The density of the studied samples was obtained by Archimedean method using distilled water as the immersion medium. The sample temperature was controlled and measured by using temperature control system assembled in our lab.

2.2. Calculation procedures

The experimental oscillator strengths for absorption transitions from ground state $^6H_{5/2}$ to the various excited states of Sm^{3+} were calculated using the following formula,

$$f_{\exp} = \frac{mc^2}{\pi e^2}\int \alpha(v)dv \tag{1}$$

where m stands for the mass of a electron, c represents the velocity of light in vacuum, e is quantity of electric charge, π the circumference ratio, $\alpha(v)$ is the absorption cross section at wavenumber v and can be calculated by using corresponding the absorption band in the absorption spectrum from following equation,

$$\alpha(\lambda) = \frac{2.303\lg[I_0(v)/I(v)]}{Nd} \tag{2}$$

In Eq. (2), N stands for the number of rare earth ions in unit volume, $I_0(v)$ and $I(v)$ are, respectively, the intensity of incident and outgoing light, d is the thickness of the measured sample. According to Eqs. (1) and (2), the experimental oscillator strengths for all the absorption transitions can be determined.

Based on J-O theory [44,45], the theoretical oscillator strength for a transition within $4f^n$ electronic configuration of trivalent RE ions from the initial state ϕj to the final state$\phi j'$, can be expressed by following formulas,

$$f_{th} = f_{th}^{ed} + f_{th}^{md} \tag{3}$$

$$f_{th}^{ed} = \frac{8\pi^2 mcv}{3h(2J+1)}\frac{(n^2+2)^2}{9n}\sum_{\lambda=2,4,6}\Omega_\lambda\left|\left\langle f^N\phi j\|U^\lambda\|f^N\phi' j'\right\rangle\right|^2 \tag{4}$$

$$f_{th}^{md} = \frac{hvn}{6mc(2J+1)}\left|\left\langle f^N\phi j\|L+2S\|f^N\phi' j'\right\rangle\right|^2 \tag{5}$$

In the above Eqs. (4) and (5), n is refractive index of the glass, h is Planck's constant, J and J' are quantum numbers of the total angular momentums for the initial and final states, $|\langle f^N\phi j\|U^\lambda\|f^N\phi' j'\rangle|^2$ and $|\langle f^N\phi j\|L+2S\|f^N\phi' j'\rangle|^2$ are the square of doubly reduced square matrix element for the electric dipole transition and magnetic dipole transition, respectively, and are independent of the host, Ω_λ ($\lambda = 2$, 4 and 6) are the J-O intensity parameters, and the other physical variables in Eqs. (4) and (5) have the same meanings as in the Eq. (1), S and L are quantum numbers of spin angular momentum and orbital angular momentum quantum for the initial state. According to Eqs. (1)–(5), the J–O parameters Ω_λ can be calculated by using least squares fitting approach.

Once the Ω_λ parameters are known, the spontaneous transition rate $A_{JJ'}$ (including electric dipole transition rate $A_{JJ'}^{ED}$ and magnetic dipole transition rate $A_{JJ'}^{MD}$) for a transition between any two states within $4f^n$ configuration of trivalent rare earth ion can be calculated from following equations [46],

$$A_{JJ'}^{ED} = \frac{64\pi^4 e^2 v^3 n(n^2+2)^2}{27h(2J+1)}\sum_{\lambda=2,4,6}\Omega_\lambda|\langle\Psi J\|U^\lambda\|\Psi' J'\rangle|^2 \tag{6}$$

$$A_{JJ'}^{MD} = \frac{16\pi^4 e^2 n^3}{3h(2J+1)m^2c^2}|\langle\psi J\|L+2S\|\psi' J'\rangle|^2 \tag{7}$$

Then the fluorescence branching ratio $\beta_{JJ'}$ for the emission from state J to state J' can be calculated from following equation,

$$\beta_{JJ'} = \frac{A_{JJ'}}{\sum_{J'} A_{JJ'}} \tag{8}$$

The intrinsic radiative lifetime τ_J for a certain level J is given by the reciprocal of the sum of all the transition rates from initial level J to final level J' (J' runs over all the possible levels lower than J), thus writing as,

$$\tau_J = \frac{1}{\sum_{J'=1}^{n} A_{JJ'}} \tag{9}$$

3. Results and discussion

3.1. Optical transition calculation

As a rare earth doped glass fluorophor for LED devices, optical