Journal of Luminescence 197 (2018) 153–158

Contents lists available at ScienceDirect

Journal of Luminescence

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

Spectroscopic characterization and temperature-dependent upconversion behavior of Er^{3+} and Yb^{3+} co-doped zinc phosphate glass

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ARTICLE INFO

Keywords:
Zinc phosphate glass
Er^{3+} and Yb^{3+} co-doped
Spectroscopic properties
Upconversion
Temperature-dependent

ABSTRACT

The zinc phosphate glass co-doped with Er^{3+} and Yb^{3+} ions was prepared by melt-quenching method. The Judd-Ofelt theory has been applied to analyze the absorption spectrum and estimate the spectroscopic parameters of Er^{3+} ions. Upconversion luminescence of the glass was investigated under the excitation at 976 nm. The red and green emissions of Er^{3+} ions were observed. The energy transfer processes between Yb^{3+} and Er^{3+} ions responsible for the upconversion emissions were discussed based on their dependences on pump power. The fluorescence decays of the relevant energy levels were measured for evaluating the energy transfer efficiency. Furthermore, the influence of temperature on upconversion emission in this glass was carried out at temperatures from 323 to 573 K. The result indicates that the glass has a potential application in the construction of optical temperature sensors based on the self-referenced FIR technique.

1. Introduction

Recent years, rare earth (RE) ions doped upconversion (UC) glasses have drawn much attention because of their extensive potential applications in many fields such as solid-state lasers, multicolor displays, high-density optical data storage, solar cells, remote temperature sensing, and so on [1–5]. Zinc phosphate glasses are desired to develop optical materials due to their low ultraviolet (UV) cut-off wavelength, high solubility for RE ions, and high chemical durability and thermal stability [6]. Some researchers have reported that the RE doped zinc phosphate glasses have potential advantages for white LED lighting and laser applications [7–10], However, to the best of our knowledge, little attention has been devoted to the study of zinc phosphate glass as UC host apart from the observation of UC emission in a Dy^{3+} doped sodium zinc phosphate glass [11].

Among the trivalent RE ions, Er^{3+} is one of the best candidates for converting infrared light into visible in the green and red regions. However, single Er^{3+} doped glasses exhibit small absorption cross section which results in weak UC luminescence [12]. In order to improve the UC intensity of Er^{3+}, the Yb^{3+} ions with huge absorption cross section at around 980 nm are the most commonly used as sensitizers to enhance the pumping absorption. Finally, the enhanced UC luminescence of Er^{3+} ions is produced, usually consisting of the green emissions from $^4S_{3/2}$ and $^2H_{11/2}$ energy levels and the red emission from $^4F_{9/2}$ level [13]. Since the energy gap between $^4S_{3/2}$ and $^2H_{11/2}$ is only about 700 cm^{-1}, varying with the host matrix, these two energy levels should be thermally coupled, and thus their relative emission intensities are temperature-dependent. Such temperature-dependent emissions of the Er^{3+} ion can be utilized for optical remote temperature sensing based on the fluorescence intensity ratio (FIR) technique [14].

In this article, the zinc phosphate glass co-doped with Er^{3+} and Yb^{3+} was prepared. The Judd-Ofelt (J-O) theory has been applied to calculate the phenomenological intensity parameters and the various radiative spectroscopic parameters. When excited at around 980 nm, the intense UC luminescence was observed and the possible energy transfer mechanism was analyzed. The UC green emissions at varying temperatures were measured. Based on the FIR of the two thermally coupled levels, $^4S_{3/2}$ and $^2H_{11/2}$, of Er^{3+}, this glass has potential application in the construction of optical temperature sensor.

2. Experimental

2.1. Glass preparation

The zinc phosphate glass with compositions of $42P_2O_5$-35ZnO-$9Al_2O_3$-$5Li_2O$-$3.5Na_2O$-$5Yb_2O_3$-$0.5Er_2O_3$ (in mol%) was prepared by

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https://doi.org/10.1016/j.jlumin.2018.01.029
Received 15 May 2017; Received in revised form 10 December 2017; Accepted 18 January 2018
Available online 02 February 2018

melt-quenching method. The 5% of Yb_2O_3 was chosen for achieving sufficient NIR absorption, and a lower concentration 0.5% of Er_2O_3 is helpful in avoiding the energy migration between different Er^{3+} ions, which is considered to be unfavorable for improving the FIR of green emissions [15]. The high pure Yb_2O_3 (99.99%) and Er_2O_3 (99.99%) and the other chemicals of P_2O_5, ZnO, Al_2O_3, Li_2CO_3, and Na_2CO_3 with the purity of reagent grade (> 98%) were used as raw materials. The well-mixed stoichiometric chemicals were melted at 1200 °C for 1 h in an electric furnace in air atmosphere, and then the melt was cast into a preheated brass mold and annealed at 400 °C for 4 h to release the internal stress. Finally, a transparent glass was obtained for experiments.

2.2. Measurements

The density of the glass was measured to be 3.06 g/cm^3, based on the Archimedes method. The refractive index was measured to be 1.54 at 638 nm, using a prism coupler (Model 2010, Metricon). The differential scanning calorimetry (DSC) thermogram was carried out by using a DSC apparatus (STA409PC, Netzsch) and the linear thermal expansion behavior was recorded by a dilatometer (DIL 402CL, Netzsch). Both of the thermal measurements were carried out at a heating rate of 5 K/min. The absorption spectrum in the wavelength range of 250–1600 nm was measured by a UV/VIS/NIR spectrophotometer (Cary 5000, Agilent). The UC emission spectra were recorded on a spectrometer (LS 55, PerkinElmer) with a power-tunable laser diode (LD) centered at 976 nm as pump source. The fluorescence decay curves were measured by a spectrometer (FLS980, Edinburgh) equipped with a tunable optical parametric oscillator (OPO) pulsed laser (NT242-1K-SH/SFG-SCU-H/2 H, Ekapla, pulse duration ~ 5 ns) as the excitation source. For the temperature-dependent UC measurements, the sample was heated in a small furnace in the temperature range from 323 K to 573 K, and measured with a thermocouple located in-situ with the sample. The heating and cooling rates were controlled during test so that the sample temperature did not vary substantially from the desired measurement temperature.

3. Results and discussion

3.1. Thermal analysis

Fig. 1 shows the DSC thermogram and linear thermal expansion curve of the zinc phosphate glass. It can be seen from the DSC thermogram that the T_g and T_x, which represent the temperatures of glass transition and the onset of crystallization, are 397 and 575 °C, respectively. The maximum crystallization temperature, T_c, is about 597 °C. In

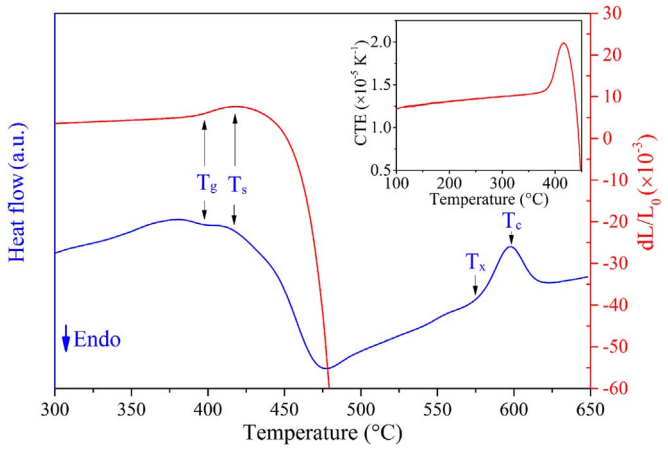

Fig. 1. DSC thermogram and thermal expansion curve of the zinc phosphate glass recorded at a heating rate of 5 K/min. The inset displays the curve of coefficient of thermal expansion versus temperature.

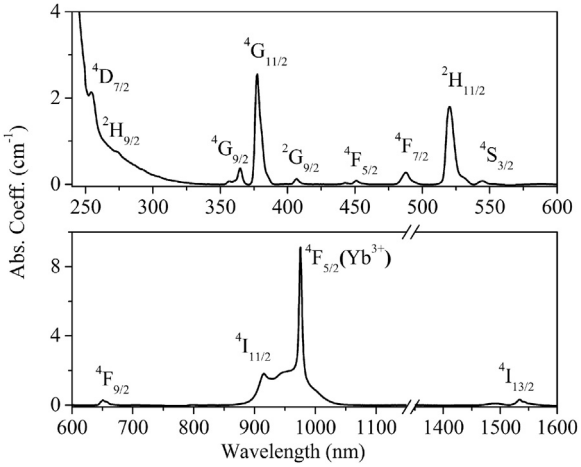

Fig. 2. Room-temperature absorption spectrum of the zinc phosphate glass from 250 to 1600 nm.

general, the difference between these two temperatures, $T_x - T_g$, is used as the criterion of the stability against crystallization of glass [16]. It is noted that the difference is as high as 178 °C, which indicates that the glass is relatively stable against crystallization and thus is promising for the construction of optical fibers. In addition, the thermogram shows a broad endothermic hump at around 475 °C and it can be attributed to the glass softening which is well verified in the thermal expansion curve. The onset temperature of the glass softening, T_s, can be determined to be about 417 °C, according to the change of thermal expansion. The coefficient of thermal expansion (CTE) is also determined and displayed in the inset of Fig. 1. The CTE at temperatures from 100 °C to T_g keeps well linear increase from 1.22 × 10^{-5} to 1.40 × 10^{-5} K^{-1} and significantly grows at the point of T_g. This enormous growth trend has been maintained until the glass becomes soft.

3.2. Absorption spectrum and J-O analysis

Fig. 2 shows the absorption spectrum of the zinc phosphate glass, ranging from 250 to 1600 nm. It can be seen that the tail of the UV absorption edge appears at around 300 nm. All the absorption bands can be assigned to the transitions of Er^{3+} except the intense absorption band around 980 nm, which is mainly assigned to the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of Yb^{3+}. The peak absorption of Yb^{3+} is located at 976 nm and its absorption cross section (σ_{Abs}) is 1.19 × 10^{-20} cm^2, calculating from $\sigma_{Abs} = \alpha/N_{Yb}$, where α = 9.10 cm^{-1} is the absorption coefficient and N_{Yb} is the ion concentration of Yb^{3+} (7.65 × 10^{20} cm^{-3}) in the glass. The full width at half maximum (FWHM) of the band is about 7 nm. The peak absorption cross section of Yb^{3+} in this glass is larger than those in some other phosphate glasses [17,18], which indicates that the glass has a relatively strong ability to absorb the NIR light.

Twelve well-resolved absorption bands of Er^{3+} ions, due to the transitions from the ground energy level of $^4I_{15/2}$ to the excited energy levels of $^4D_{7/2}$, $^2H_{9/2}$, $^4G_{9/2}$, $^4G_{11/2}$, $^2G_{9/2}$, $^4F_{5/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$, were recorded in the spectrum. The spectroscopic parameters of Er^{3+} in the glass were evaluated based on the J-O theory [19,20]. Six intense absorption bands, from the $^4I_{15/2}$ to the $^4I_{13/2}$, $^4F_{9/2}$, $^2H_{11/2}$, $^4F_{7/2}$, $^4G_{11/2}$, and $^4G_{9/2}$, were used in the J-O analysis to determine the three phenomenological intensity parameters Ω_t (t = 2, 4, 6) by a least-square fitting approach [21,22], and then the spontaneous emission rates, fluorescence branching ratios, and radiative lifetimes of the excited energy levels can be estimated. The values of the reduced matrix elements of unit tensor operators and the coefficients of intermediate coupling wavefunctions of Er^{3+} used in the calculation were taken from Refs. [23] and [24], respectively. The refractive index was supposed practically unchanged with the wavelengths. It is worth