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Energy transfer, tunable emission and optical thermometry in Tb^{3+}/Eu^{3+} co-doped transparent $NaCaPO_4$ glass ceramics

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ABSTRACT

Tb^{3+}/Eu^{3+} co-doped glass ceramics containing $NaCaPO_4$ nanocrystals were successfully synthesized via traditional melt-quenching route with further heat-treatment and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and photoluminescence spectroscopy. The energy transfer process of $Tb^{3+} \rightarrow Eu^{3+}$ was confirmed by excitation and emission spectra and luminescence decay curves, and the energy transfer efficiency was also estimated. The results indicated that the efficient emission of Eu^{3+} was sensitized by Tb^{3+} under the excitation of 378 nm, realizing tunable emission in the transparent bulk glass ceramics containing $NaCaPO_4$ nanocrystals. Furthermore, optical thermometry was achieved by the fluorescence intensity ratio between Tb^{3+}:$^5D_4 \rightarrow {}^7F_5$ (~542 nm) and Eu^{3+}:$^5D_0 \rightarrow {}^7F_2$ (~612 nm). The maximum absolute sensitivity of 4.55% K^{-1} at 293 K and the maximal relative sensitivity of 0.66% K^{-1} at T=573 K for Tb^{3+}/Eu^{3+} co-doped transparent $NaCaPO_4$ glass ceramic are obtained. It is expected that the investigated transparent $NaCaPO_4$ glass ceramics doped with Tb^{3+}/Eu^{3+} have prospective applications in display technology and optical thermometry.

1. Introduction

Recently, materials doped with rare earth (RE^{3+}) ions have been drawing significant attention for their potential application in laser, plasma display panels (PDP), solid-state lighting and temperature sensors [1–6]. Due to the radiative/nonradiative energy transfer of RE^{3+} ions are highly dependent on the environment surrounding them, the host materials, where RE^{3+} ions reside, should be appropriately selected [7–9]. Single crystal and transparent ceramics as a part of transparent inorganic materials have been widely used as the host of RE^{3+} ions due to their suitable crystalline environment and high ability to transmit light [10–13]. However, there still have some inescapable disadvantages such as complicated and time-consuming procedures to avoid porosity, limited compositions, segregation of doping agents, etc. [14]. Actually, glass-ceramic (GC) technology can be used to avoid these obstacles of both single crystals and transparent ceramics. GCs are a multiphase material that consists of a glassy phase and a nanocrystalline phase, which are generally obtained by the high temperature melting followed by subsequent heat-treatment technique. High transparent GCs can be realized by controlling crystallization of the precursor glass with specially designed chemical compositions [15]. More recently, the selection of Tb^{3+} and Eu^{3+} as activators has recently received considerable interests for possible applications in white light emitting diodes (WLEDs) and temperature sensors because of their tunable luminescence with the help of energy transfer from Tb^{3+} to Eu^{3+} [16].

Hence, GCs were verified to have another promising application in non-invasive temperature sensors as it can overcome the weakness of long response time and inaccuracy of conventional contact temperature sensors. And it can be used in harsh environment such as electromagnetically surroundings with an extreme temperature [17,18].

In this work, the luminescence spectroscopic characterization of Tb^{3+}, Eu^{3+} and Tb^{3+}/Eu^{3+} doped transparent bulk GCs containing $NaCaPO_4$ nanocrystals are fully conducted by the excitation and emission spectra and decay curves measurements, in order to verify the occurrence of $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer process. Furthermore, tunable emission and optical temperature sensing can be realized in Tb^{3+}/Eu^{3+} codoped transparent $NaCaPO_4$ GCs. The purpose of this work is to systematically discuss the energy transfer process from $Tb^{3+} \rightarrow Eu^{3+}$, and its potential multi-functional applications.

2. Experimental

The precursor glass with the following chemical composition (in mol%): $25Na_2O$-$23CaO$-$6\ P_2O_5$–$44B_2O_3$–$2ZrO_2$–$0.5Tb_4O_7$-xEu_2O_3 (x=0,

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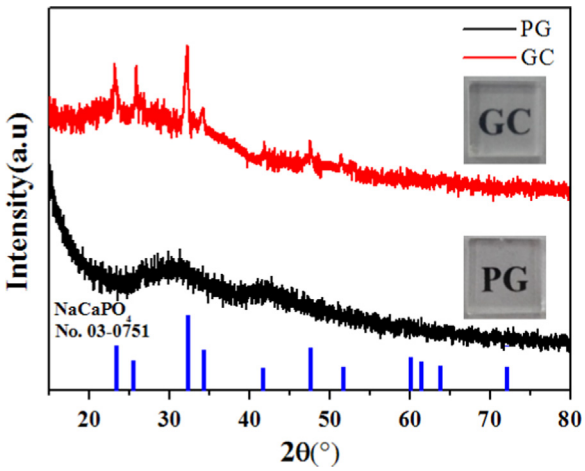

Fig. 1. XRD patterns of Tb^{3+}/Eu^{3+} (2.0/0.5 mol%) co-doped precursor glass (PG) and glass ceramic (GC). Insets show the photographs of PG and GC samples doped with Tb^{3+}/Eu^{3+} (2.0/0.5 mol%).

0.25, 0.5, 1.0) were prepared by a conventional melting-quenching technique. Powders of analytical reagent grade, comprising Na_2CO_3, $CaCO_3$, $NH_4H_2PO_4$, H_3BO_3, ZrO_2 ($\geq$99.5%), and high purity Tb_4O_7, Eu_2O_3 ($\geq$99.95%), were used as the starting materials. About 20 g of the mixtures were calcined at 500 °C for 60 min to remove vapor and then were melted in a corundum crucible at 1250 °C in air for 100 min in an electric furnace. The glass melts were poured into a preheated copper mold for quenching and annealed in a muffle furnace at 450 °C for 3 h to relinquish thermal stress and then cooled to room temperature slowly. Then the precursor glasses were cut and polished into $10 \times 10 \times 2$ mm^3. Afterwards, the precursor glasses were heat-treated to 600 °C with a heating rate of 5 K/min, and hold for 120 min to form glass ceramics by glass crystallization.

The structural analysis of the glass and GC samples was identified by a model D8-Advance X-ray powder diffractometer with Cu Kα radiation at room temperature. The microstructure of GCs sample was studied using a transmission electron microscopy (TEM, JEM-2010). TEM specimen was prepared by directly drying a drop of a dilute ethanol dispersion solution of GC particles on the surface of a carbon coated copper grid. The emission and excitation spectra, fluorescence lifetimes of the Tb^{3+}, Eu^{3+} ion doped glass and GCs were recorded on an Edinburgh Instruments FS5 spectrofluorometer with a Xenon lamp as the excitation source. The temperature dependent emission spectra were recorded on an Edinburgh Instruments FS5 spectrofluorometer equipped with a homemade temperature controlling stage.

3. Results and discussion

XRD patterns of Tb^{3+}/Eu^{3+} (2.0/0.5 mol%) co-doped precursor glass (PG), glass ceramic (GC) and the standard diffraction peaks of $NaCaPO_4$ are shown in Fig. 1. The PG is structurally amorphous characterized by diffused humps and absence of sharp peaks. After glass crystallization, intense diffraction peaks assigned to the $NaCaPO_4$ crystals (JCPDS No. 030751) are detected. The mean size of the crystals can be estimated by Scherer's equation [19].

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

where k=0.89, θ is the Bragg angle of the X-ray diffraction peak, β represents the corrected half width of diffraction peak and λ (=0.154056 nm) represents the wavelength of Cu Ka radiation. The mean crystalline size is estimated to be about 13 nm for $NaCaPO_4$:Tb^{3+}/Eu^{3+} GC. Fig. 2 depicts TEM and HRTEM images for GC sample. TEM image of the Tb^{3+}/Eu^{3+} co-doped GC sample (Fig. 2a) demonstrates that particles with size of about 13 nm are homogeneously dispersed among glass matrix with their selected area electron diffraction (SAED) rings well indexed to the $NaCaPO_4$ crystals. The associated interplanar spacing d value is about 0.21 nm, which can be attributed to the (201) crystal plane of $NaCaPO_4$ nanocrystals ($d_{(201)}$=0.22 nm), as shown in Fig. 2b.

The room temperature photoluminescence (PL) and photoluminescence excitation (PLE) spectra of Tb^{3+}, Eu^{3+} single-doped and Tb^{3+}/Eu^{3+} co-doped GCs are shown in Fig. 3. The PLE of Tb^{3+} doped GC is obtained by monitoring the emission with 542 nm (Fig. 3a). The excitation spectrum contains five peaks at 339, 351, 368, 378 and 621 nm which are attributed to the transitions of the Tb^{3+} ions: $^7F_6 \rightarrow {}^5L_8$, $^7F_6 \rightarrow {}^5D_2$, $^7F_6 \rightarrow {}^5G_6$, $^7F_6 \rightarrow {}^5D_3$ and $^7F_6 \rightarrow {}^5D_4$, respectively. The emission spectrum of Tb^{3+} doped GC under 378 nm excitation shows several bands centered at 488, 542, 585 and 621 nm assigned to $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$ (seen in Fig. 3a). Fig. 3b exhibits the PLE monitoring the emission with 542 nm and PL under 393 nm of Eu^{3+} doped GC. The excitation spectrum has five peaks located at 362, 383, 393, 464 and 532 nm corresponding to the transitions from the ground state ($^7F_0$) to $^5D_4$, $^5L_7$, $^5L_6$, $^5D_2$ and $^5D_1$ excited states. The emission

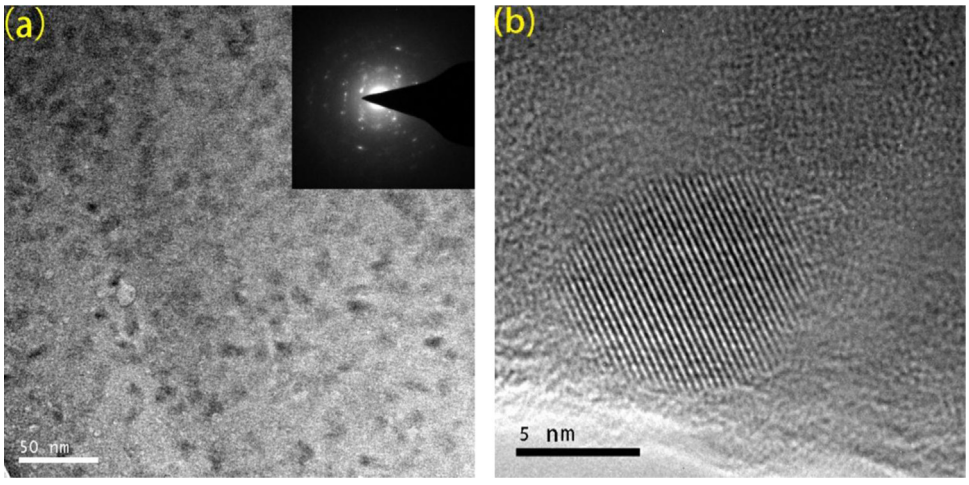

Fig. 2. (a) TEM image and the corresponding SAED pattern (inset) of Tb^{3+}/Eu^{3+} (2.0/0.5 mol%) co-doped GC sample and (b) high resolution TEM (HRTEM) image of Tb^{3+}/Eu^{3+} (2.0/0.5 mol%) co-doped GC sample.