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Up-conversion luminescent properties of Er^{3+}/Yb^{3+} co-doped transparent glass ceramics containing $Na_{3.6}Y_{1.8}(PO_4)_3$ crystals

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ABSTRACT

Er^{3+}/Yb^{3+} co-doped transparent glass ceramics containing $Na_{3.6}Y_{1.8}(PO_4)_3$ crystals were prepared by high-temperature melting and subsequent heat treatment the precursor glass, and their up-conversion luminescent properties were investigated. The optimum heat treatment condition of glass at 630 °C for 2 h were determined by a series of experimental results, and confirmed the existence of $Na_{3.6}Y_{1.8}(PO_4)_3$ crystals in glass ceramics. The up-conversion luminescence spectra of the glass ceramic samples under pulsed excitation at 980 nm revealed luminescence bands corresponding to Er^{3+} ion transitions in the green ($^4F_{7/2}$-$^4I_{15/2}$, $^2H_{12/2}$-$^4I_{15/2}$,$^4S_{3/2}$-$^4I_{15/2}$) and red ($^4F_{9/2}$ - $^4I_{15/2}$) spectral regions. The fluorescence spectra reaches a maximum when the molar ratio of Er_2O_3 to Yb_2O_3 is 1:7. Luminescence quantum yield of the samples was measured by using an integrating sphere. The transmission spectra proved that the glass ceramics sample still maintained a high transparency up to 83% in the visible region.

1. Introduction

Recently great attention has been paid to investigation of rare earth (RE) doped glass ceramics (GC) for up-conversion luminescence (UCL), an anti-Stokes process in which low-energy photons are converted to photons with higher energy [1]. UCL GC have demonstrated many potential applications such as optical temperature sensors [2,3], up-conversion lasers [4], optical amplifiers [5], white light-emitting diode (WLED) [6,7], color display [8] and others.

Er^{3+} is one of the most widely investigated luminescence center for the UCL [9–11] due to specific electronic configuration, particularly, unfilled 4f shell. Optically active 4f-4f electronic transitions responsible for the UCL are effectively shielded by the outer 5s and 5p electrons thus minimizing the impact of the host material [12]. Nevertheless, the impact of the host material is crucial for the efficiency of the UCL because the rate of nonradiative transitions in the incorporated Er^{3+} ion strongly depends on the phonon energy of the medium [13]. The low-phonon energy materials are required in order to maximize the efficiency of the UCL [14,15]. Phosphate matrix glass has moderate phonon energy, excellent solubility of Er^{3+} ions, good spectral properties and a series of great characteristics, which make the Er^{3+} doped phosphate GC become a research hotspot at present [16].

One of the most important quantities to describe the efficiency of luminescent materials is the luminescence quantum yield (LQY) which is defined as the ratio of emitted to absorbed photons and thus describes the UCL efficiency of a given GC [17]. Jiasong Zhong et al. prepared the red-emitting $CaLa_4(SiO_4)_3O:Eu^{3+}$ phosphor with superior high LQY for warm white LEDs [18]. Franziska Steudel et al. prepared Sm^{3+}, Eu^{3+}, and Tb^{3+} single-doped barium borate glasses with high LQY values of more than 80% for white LEDs [19]. T.W. Kang et al. presented a single crystal $Lu_3Al_5O_{12}:Ce^{3+}$ with an excellent thermal stability and an enhanced LQY as a color conversion phosphor for the high-power white-laser lighting [20]. Shaoan Zhang et al. reported a series of phosphate phosphors $Ca_9Ce(PO_4)_7:xTb^{3+}/yMn^{2+}$, exhibiting much efficient energy transfer, stable thermal stability and high LQY [21]. However, GC with high LQY have not been studied extensively.

In this article, we successfully prepared Er^{3+}/Yb^{3+} co-doped transparent glass ceramics containing $Na_{3.6}Y_{1.8}(PO_4)_3$ crystals, analyzed the crystal phases and micrographs of the samples by X-

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ray diffraction (XRD) patterns and scanning electron microscopy(SEM) images, measured the transmittance and refractive index, and investigated their luminescent properties and quantum yield under 980 nm light excitation.

2. Experimental

The as-made glasses with composition listed in Table 1 were prepared by high-temperature melting method. Batches of about 20 g materials were well mixed in covered corundum crucibles under air atmosphere, the mixed materials were heated at 1200 °C for 1 h in a resistance furnace with the heating rate of 2 °C/min, and then the system was heated up to 1400 °C for 2 h under stirring. Subsequently, the glass melts were poured into a preheated steel mold for quenching and annealed in a muffle furnace at 450 °C for 2 h to relinquish thermal stress and then cooled to room temperature slowly. After proper heat treatment the glasses were transformed into glass ceramics. The glass ceramic samples were cut into small pieces with the size of 10 mm × 10 mm × 3 mm and polished.

The differential thermal analysis (DSC) was carried out in a differential thermal analyzer (NETZSCH STA 449F3) at a heating rate of 10 °C/min with Al_2O_3 as a reference. To confirm the crystallization phase, X-ray diffraction(XRD) date was obtained by Rigaku2500PCX(Japan) X-ray powder diffractometer using Cu Kα tube operated at 40 kV and 30 mA. The microstructure of GCs were characterized by scanning electron microscopy (SEM, JEOL, JSM-7610F) operated at 10 kV. The optical transmittance of the samples were measured by UV-VIS spectrophotometer (SHIMADZU, UV mini-1240). The refractive index of samples were measured by Abbe refractometer (2WAJ). The up-conversion luminescence spectra were measured by a Hitachi F-4500 spectrometer. The luminescence quantum yield of samples were measured by a Absolute PL Quantum Yield Measurement System (C9920-02G, Hamamatsu Photonics K.K., Japan).

3. Result and discussion

3.1. Heat treatment condition

Fig. 1 shows the DSC curve of the precursor glass. As seen in Fig. 1, the onset temperature of crystallization T_x is around 600 °C and the crystallization peak is situated at 630 °C. According to this, heat treatment temperature and time, glass ceramic samples photo are listed in Table 2.

Fig. 2 shows the XRD patterns of the glass ceramic samples heat treated under different conditions. The XRD patterns of glass ceramics (heat treated at 610 °C, 630 °C, 650 °C and 670 °C for 1 h) are shown in Fig. 2(a). After heat treatment at 610 °C for 1 h, no discrete diffraction peaks are observed in the XRD patterns. The XRD patterns of glass ceramics heat treated at 630 °C, 650 °C and 670 °C for 1 h show intense and sharp diffraction peaks. These peaks fit well with the standard data of JCPDS card No.47-0972 for

Table 1
Material composition of different glass samples.

Samples number	Material composition (mol%)						
	Na_2CO_3	Y_2O_3	SiO_2	H_3BO_3	P_2O_5	Er_2O_3	Yb_2O_3
GEr	15	3	45	31.5	6.4	0.1	0
GEr-Yb	15	3	45	31.4	6.4	0.1	0.1
GEr-3Yb	15	3	45	31.2	6.4	0.1	0.3
GEr-5Yb	15	3	45	31.0	6.4	0.1	0.5
GEr-7Yb	15	3	45	30.8	6.4	0.1	0.7
GEr-9Yb	15	3	45	30.6	6.4	0.1	0.9
GEr-11Yb	15	3	45	30.4	6.4	0.1	1.1

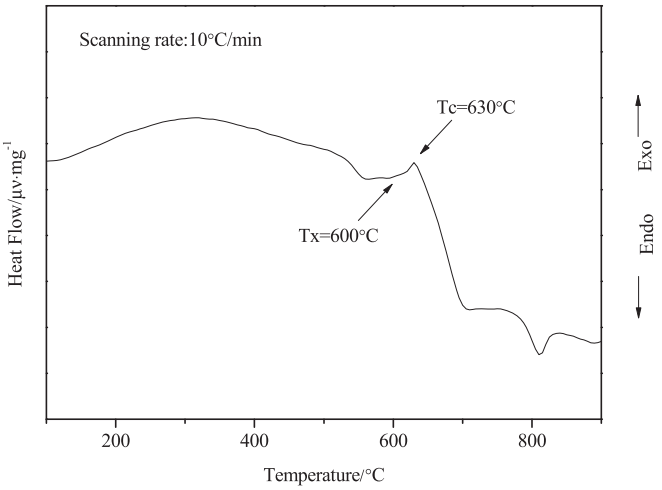
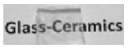


Fig. 1. DSC curve of glass sample.

Table 2
Heat treatment condition of different glass ceramic samples.

Heat treatment Temperature (°C)	Heat treatment Time (h)	Sample photo
610	1	
630	1	
650	1	
670	1	
630	1.5	
630	2	
630	2.5	
630	3	

$Na_{3.6}Y_{1.8}(PO_4)_3$, directly confirming the formation of $Na_{3.6}Y_{1.8}(PO_4)_3$ crystals in glass ceramic sample as the treatment temperature rises. Samples become translucent (shown in Table 2) at 670 °C due to reunion phenomenon when the heat treatment temperature is too high.

Fig. 3(a), (b), (c) and (d) show the SEM images of glass ceramics (heat treated at 610 °C, 630 °C, 650 °C and 670 °C for 1 h). There are few grains in the SEM image (a). The obvious phenomenon of reunion in SEM image (c) and (d) show that the growth of grains is rather quick and heterogeneous when the temperature is too high. In order to obtain small and uniform size grain, the lower temperature 630 °C is chosen as the best heat treatment temperature.

The XRD patterns of glass ceramics (heat treated at 630 °C for 1.5 h, 2 h, 2.5 h and 3 h) are shown in Fig. 2(b). The XRD results indicated that the crystal phase has no change and the diffraction peaks become sharper with increasing duration of heat treatment, which reveals that a gradual growth of $Na_{3.6}Y_{1.8}(PO_4)_3$ crystals occurs within the glass matrix.

Fig. 3(e), (f), (g) and (h) show the SEM images of glass ceramics (heat treated at 630 °C for 1.5 h, 2 h, 2.5 h and 3 h). The SEM results