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Upconversion luminescence, optical thermometric properties and energy transfer in Yb^{3+}/Tm^{3+} co-doped phosphate glass

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ABSTRACT

Yb^{3+}/Tm^{3+} co-doped transparent phosphate glasses were successfully synthesized by conventional melt-quenching method. The upconversion (UC) emission spectra, fluorescence lifetime and transmission spectra were characterized by using UV–visible spectrophotometer and Fluorescence Spectrometer. The results show that the Yb^{3+}/Tm^{3+} co-doped phosphate glasses are highly transparent with a transmittance of about 90% in the visible light range, and the energy transfer between Yb^{3+} and Tm^{3+} occurs. Furthermore, the temperature dependent luminescence of the glasses was systematically investigated to explore the possible application as optical temperature sensors. Using the fluorescence intensity ratio (FIR) technique, the FIR of the UC emissions from 693 nm (Tm^{3+}: $^1G_4 \rightarrow {}^3H_5$) and 658 nm ($Tm^{3+}$: $^3F_2 \rightarrow {}^3H_6$) was studied as a function of temperature in the range of 303–653 K, under 980 nm laser excitation. Impressively, the high relative temperature sensitivity of 3.94% K^{-1} was obtained at 303 K in the Yb^{3+}/Tm^{3+} co-doped phosphate glass, which is a very promising candidate for optical temperature sensors.

1. Introduction

Recently, the rare earth (RE) ion doped upconversion (UC) materials have attracted considerable interest owing to the potential applications, such as light emitting diodes, biomedical imaging, sensor, laser and so on [1–5]. Especially, non-contact optical temperature sensors have been investigated widely due to their excellent sensitivity and convenience [6–8]. Er^{3+}, Pr^{3+}, Ho^{3+}, Tm^{3+} ions are widely used as an activator, with its superior optical properties [9]. UC is multi step optical process that energy absorbed at low energy near-infrared (NIR) wavelengths converts to the high energy visible wavelengths. The combination of Yb^{3+} and Tm^{3+} form one of the most attractive energy transfer UC system [9–12]. In this system, the Yb^{3+} as an efficient sensitizer possess large absorption band at 975 nm [3] and increases the intensity of UC luminescence [13–15]. Tm^{3+} level can be populated by two or three steps energy transfer from Yb^{3+}, under the excitation of 980 nm, and then generates intense shorter wavelength emission at 793 nm originating from $^3H_4 \rightarrow {}^3H_6$ transition. The Tm^{3+} and Yb^{3+} co-doped materials have been considered as one of the typical energy transfer donor-acceptor systems for UC material [9,16].

Recently, phosphate glass materials with stable thermal properties and high rare earth doping concentration are promising hosts for UC luminescence material and optical temperature sensing [3,17–20]. There are some reports focusing on UC luminescence in Yb^{3+}/Tm^{3+} co-doped oxyfluoride [21,22]. However, there are little reports on the Yb^{3+}/Tm^{3+} co-doped phosphate glass materials. It is well known that the Yb^{3+}/Tm^{3+} co-doped phosphate glass has the near infrared emission (793 nm), and the energy transfer processes the donors and acceptors. Importantly, it has a strong temperature dependence emissions and a wide range of potential applications in optical temperature sensing. The direct energy transfer from donor to acceptor is ineffective, but the donor can be efficiently energy transfer to the acceptor. Through the energy absorption of the acceptor ground state or excitation state, the energy from the non radiative transition of excited state to ground state of the donor [9,23,24]. As a result, the energy transfer in Yb^{3+}/Tm^{3+} co-doped systems is notable, for example, the upconverted near infrared emission (793 nm) is performed by two step energy transfers and the upconverted blue emission is performed by three or four step energy transfers [23]. It has been observed that the energy transfer of the Yb^{3+}/Tm^{3+} co-doped samples are efficient even for low Tm^{3+} doping in some materials [9,24,25]. This means that the energy transfer may play an important role in the phosphate glass. Presently, Er^{3+} is one of the most investigated elements on the UC optical thermometric material. However, its small energy gap (~800 cm^{-1}) of Er^{3+} ions usually makes the actual FIR deviate from the real one and thus causes large detecting error [26,27]. Therefore, it is highly

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Table 1
Chemical composition of the glasses added RE ions (in mol%).

Glass	1	2	3	4	5	6	7	8	9
Host	$20Na_2O–42ZnO–28P_2O_5–10B_2O_3$								
Yb^{3+}(fromYb_2O_3)	0	1	2	3	4	3	3	3	3
Tm^{3+}(from Tm_2O_3)	0.15	0.15	0.15	0.15	0.15	0.05	0.1	0.15	0.2

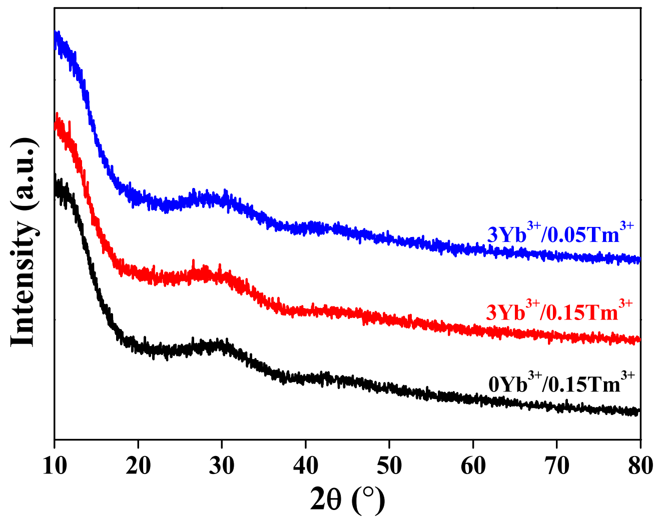

Fig. 1. XRD spectra of the typical glass samples with Yb^{3+}/Tm^{3+} (mol %).

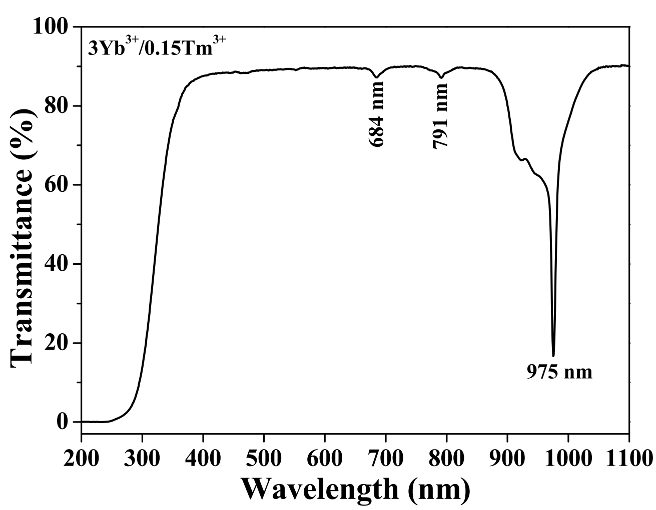

Fig. 2. Transmittance spectrum of the typical glass (3 mol % Yb^{3+}/0.15 mol % Tm^{3+}).

desirable to explore a new route to solve this intrinsic drawback. And the Yb^{3+}/Tm^{3+} co-doped phosphate glasses may be a good choice.

In the present work, Yb^{3+}/Tm^{3+} co-doped phosphate glass was successfully prepared by conventional melt-quenching method and characterized by XRD. The transmittance, UC emission, lifetime and the energy transfer process of the glass samples were investigated. Furthermore, under the 980 nm laser excitation, the temperature dependent UC emission behaviors of Yb^{3+}/Tm^{3+} co-doped phosphate glasses were systematically investigated. The theoretical maximal relative sensitivity S_{Rmax} of 3.94% K^{-1} was achieved at 303 K based on the FIR technique. The results show that the Yb^{3+}/Tm^{3+} co-doped phosphate glasses have greatly possible application in UC luminescence and optical thermometric material.

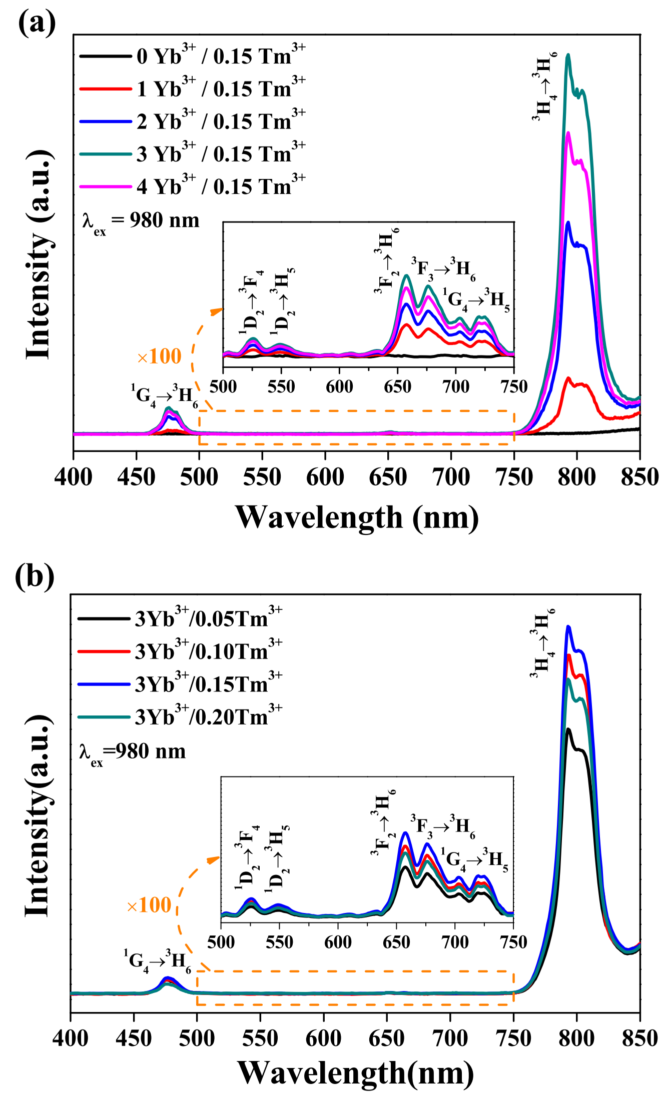

Fig. 3. Up-conversion emission spectra of (a) (0, 1, 2, 3, 4) Yb^{3+}/0.15 Tm^{3+} mol % co-doped phosphate glasses and (b) 3 Yb^{3+}/Tm^{3+} (0.05, 0.10, 0.15, 0.20) mol % under 980 nm excitation. The inset shows the enlarged weak emission in the range of 500–750 nm.

2. Experimental

The as-made glasses with chemical composition (in mol %) listed in Table 1 were prepared by melt-quenching method. The analytical reagents comprising Na_2CO_3, ZnO, $NH_4H_2PO_4$, H_3BO_3, (≥99.5%) and high purity Yb_2O_3 and Tm_2O_3 (≥99.99%) (Guo-Yao Co. Ltd, Shanghai, China) were used as starting materials. About 20 g batches of the starting materials were appropriately weighed and thoroughly mixed, the mixtures were calcined at 600 °C for 60 min to remove vapor, then melted in a covered corundum crucible at 1250 °C in air for 100 min in an electric furnace. The glass melts were poured into a preheated copper mold and immediately quenching and annealed in a muffle furnace at 400 °C for 10 h to release thermal stress and then cooled to room temperature. Subsequently, the obtained glasses were cut and polished into 10 × 10 × 1 mm^3 for spectral measurement and a part of samples were smashed into powder for other property measurement. In order to obtain accurate optical characterization, all the glass samples were polished carefully to form a mirror surface.

The structure of the glasses was identified via X-ray powder diffractometer (D8-Advance, BRUKER) with CuKα radiation at room temperature. The optical transmission spectra were recorded on