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Effect of Mn^{2+} ions on the enhancement upconversion emission and energy transfer of $Mn^{2+}/Tb^{3+}/Yb^{3+}$ tri-doped transparent glass-ceramics

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ABSTRACT

The effect of Mn^{2+} on the enhancement upconversion (UC) emission and energy transfer of $Mn^{2+}/Tb^{3+}/Yb^{3+}$ tri-doped SiO_2–AlF_3–BaF_2–TiO_2–LaF_3 transparent glass-ceramics under excitation 980 nm LD were successfully investigated. The UC emission intensity bands centered at 493, 548, 593 and 622 nm corresponding to $(^5D_4 \rightarrow {}^7F_{J(J=6,\ 5,\ 4\ \text{and}\ 3)})$ transitions of Tb^{3+} were significantly increased with the increase of the Mn^{2+} concentrations and reaches its maximum at 2.0 mol%, then decreases due to the self-quenching effect. Particularly, the UC emission intensity bands centered at 656 nm $(^5D_4 \rightarrow {}^7F_{J(J=2,\ 1\ \text{and}\ 0)})$ of Tb^{3+} was strongly increased about 15-fold with the increase of Mn^{2+} concentration up to 2.0 mol%. The upconversion mechanism and the energy transfer processes from $(^4T_1 \rightarrow {}^6A_1)$ transition of Mn^{2+} to $^5D_4 \rightarrow {}^7F_{J(J=6,\ 5,\ 4,\ 3,\ 2,\ 1\ \text{and}\ 0)}$ transitions of Tb^{3+} were discussed.

1. Introduction

In the recent decades, UC and energy transfer (ET) processes of rare earths (RE) doped glass-ceramics have been widely investigated [1–5], because of their potential applications such as laser materials and optoelectronic devices [6–11]. Among RE ions, Tb^{3+} deserves special attention due to its distinctive energy level structure, which can deploy a number of promising applications [12,13]. In the field of lasers, the long lifetime of excited state $^5D_4$ make it very attractive, since the long lifetime can allow substantial and efficient energy storage, which is convenient for the population inversion and realize highpower UC lasers [14,15]. Besides, the blue, green and red emissions of Tb^{3+} have been obtained recently by utilizing a co-operative effect of two Yb^{3+} ions. Cooperative sensitization between Yb^{3+} and Tb^{3+} were first independently investigated by Livanova, Saitkulov and Stolov [16–18], and theoretically proposed by Miyakawa and Dexter [19].

Recently, ET processes between RE ions and metals transition have been also investigated, such as: ET processes between Mn^{2+} with Eu^{2+}, Nd^{3+} and Tb^{3+} [20–22]. However, enhancement UC emission intensity and ET processes between Tb^{3+}, Yb^{3+} and Mn^{2+} in transparent glass-ceramics have not been reported up to now. On the other hand, Tb^{3+} emission bands are located in range about from 450 to 700 nm. While the Mn^{2+} luminescent can give broad emission band from green to red, which strongly depends on the crystal environment of host materials and located in the region about from 460 to 700 nm [23]. Therefore, the possibility of ET between Tb^{3+} and Mn^{2+} is expected occur.

Based on the above considerations, in the present work, we mainly investigated effect of Mn^{2+} on the enhancement UC emission and the ET process of $Mn^{2+}/Tb^{3+}/Yb^{3+}$ transparent glass-ceramics. At same time, the UC mechanism and ET processes between Mn^{2+} and Tb^{3+} ions were proposed.

2. Experimental

Glasses were prepared according to a conventional melt-quenching method. High purity SiO_2, AlF_3, TiO_2, BaF_2, LaF_3, TbF_3,

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$MnCO_3$ and YbF_3 were used as the starting materials. Compositions chosen in present study are presented in Table 1. The mixtures (about 10 g), which compacted into a platinum crucible, were set in an electric furnace. After holding at 1450 °C for 45 min under air atmosphere in an electric furnace, the melts were quenched by putting it onto a polished plate of stainless steel. All the glasses were annealed at 495 °C for 6 h to remove thermal strains. The samples were cut into the size of 10 mm × 10 mm × 2 mm and polished for optical measurements.

Thermograms, differential thermal analysis (DTA) was carried out in a nitrogen atmosphere with a rate of 10 °C/min on DTA-60AH SHIMADZU. To identify the crystallization phase, XRD analysis was carried out with a powder diffractometer (BRUKER AXS GMBH) using CuKα radiation. The sizes, shape, structure and component compositions of the asprepared nanocrystals were characterized by transmission electron microscopy (TEM, JEM–2100) at 200 kV. Absorption spectrum in wavelength range of 350–1200 nm was measured on a HITACHI U–4100 spectrophotometer. UC luminescence spectra of $Mn^{2+}/Tb^{3+}/Yb^{3+}$ under 980 nm LD excitation was measured by using a HITACHI F–7000 fluorescence spectrophotometer in wavelength range of 450–750 nm. Fluorescence decay curves were recorded on an Edinburgh Instruments FLS980 time-resolved fluorescence spectrometer by using a μF920 microsecond flash lamp as the excitation source. All measurements were performed at the ambient temperatures.

Table 1
Chemical composition of analyzed glasses from SiO_2–AlF_3–BaF_2–TiO_2–LaF_3–$MnCO_3$–TbF_3–YbF_3 system (in mol %).

Glasses name		Composition ratios of reagents							
		SiO_2	AlF_3	BaF_2	TiO_2	LaF_3	TbF_3	$MnCO_3$	YbF_3
SMY		49	17	20	5	5	0	1	3
SMTY-1	SMTY-0Mn	50	16	20	5	5	1	0	3
	SMTY-1.0Mn	49	16	20	5	5	1	1	3
	SMTY-1.5Mn	48.5	16	20	5	5	1	1.5	3
	SMTY-2.0Mn	48	16	20	5	5	1	2.0	3
	SMTY-2.5Mn	47.5	16	20	5	5	1	2.5	3
SMTY-2	SMTY-0.3Tb	50	14.7	20	5	5	2	0.3	3
	SMTY-0.5Tb	50	14.5		5	5	2	0.5	3
	SMTY-0.8Tb	50	14.2	20	5	5	2	0.8	3
	SMTY-1.0Tb	50	14	20	5	5	2	1	3
	SMTY-1.5Tb	50	13.5	20	5	5	2	1.5	3

3. Results and discussion

DTA curve of SMTY-1 glass is shown in Fig. 1(a). As can be seen in this figure, three temperature parameters: glass transition temperature (T_g), crystallization onset temperature (T_x) and crystallization peak temperature (T_p) were located at 495, 606, and 665 °C, respectively. Therefore, transparent glass-ceramics can be prepared by heat-treat in first crystallization peak near 606 °C. Difference ΔT between T_x and T_g is used as a rough indicator of glass thermal stability, and $\Delta T = T_x - T_g = 111$ °C > 100 °C indicating the prepared glass is stable and suitable for applications such as fiber amplifiers, lasers materials, and energy solar cells, etc. [24]. According to the DTA results analysis, in this study, all the prepared glasses were heat-treated at 665 °C for 5 h.

XRD patterns of SMTY-1 glass-ceramics are shown in Fig. 1(b). The precursor glass sample presents a broad diffraction curve characteristic of amorphous state, while in the patterns of glass-ceramics, five intense diffraction peaks are clearly observed, indicating that micro-crystallites are successfully precipitated during thermal treatment. Diffraction pattern of crystalline element is typical of a face-centered-cubic and these diffraction peaks around $2\theta = 26°$, 30°, 43° and 50° can be assigned respectively to (111), (200), (220) and (311) planes of Ba_2LaF_7 cubic phase. Average of Ba_2LaF_7 crystallite size of samples were estimated about 13 nm by using Scherrer's formula [25–27].

TEM images of SMTY-2.0Mn glass-ceramics are shown in Fig. 2. Results of Fig. 2(a)–(c), it demonstrates that Ba_2LaF_7 nanocrystals were distributed homogeneously among the glass matrix, and the mean sizes of nanocrystals were about 13 nm, which was similar to those calculated by the Scherrer equation. Fig. 2(d) shows absorption spectra of SMY, SMTY-0Mn and SMTY-2.0Mn glass-ceramics in the 350–1200 nm regions. The band centered at ~973 nm can be identified by transitions that originated from Yb^{3+} ground multiple $^2F_{7/2}$ to the excited multiple $^2F_{5/2}$. Absorption spectra of Tb^{3+} can be assigned to transition of $^7F_6 \rightarrow {}^5D_4$ at 486 nm, and absorption spectra of Mn^{2+} can be assigned to $^6A_{1g} \rightarrow {}^4T_{2g}$ and $^6A_{1g} \rightarrow {}^4T_{1g}$ transitions.

UC emission spectra of SMY and SMTY-1 glass-ceramics are shown in Fig. 3. Clearly, from the Fig. 3, UC emissions intensity

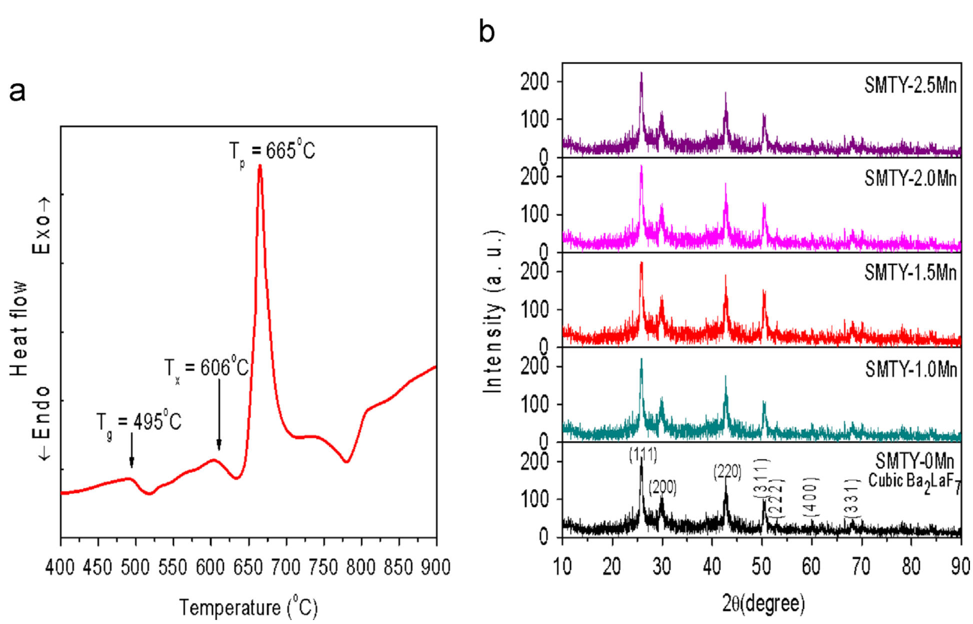

Fig. 1. (a) DTA curve of SMTY-1 glass, (b) XRD patterns of SMTY-1 glass-ceramics.