Materials Research Bulletin 73 (2016) 357–361

Contents lists available at ScienceDirect

Materials Research Bulletin

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

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

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ARTICLE INFO

Article history:
Received 30 March 2014
Received in revised form 6 August 2015
Accepted 15 September 2015
Available online 18 September 2015

Keyword:
A. Ceramics
A. Glasses
A. Optical materials
B. Luminescence
C. X-ray diffraction

ABSTRACT

The effects of Mn^{2+} ions on the enhancement red upconversion emission intensity of $Mn^{2+}/Tm^{3+}/Yb^{3+}$ tri-doped transparent glass-ceramics were investigated. The ratio I_{698nm}/I_{478nm} significantly increases about ten-fold with the increase of Mn^{2+} concentrations up to 4.0 mol.%. The red upconversion emission of $Mn^{2+}/Tm^{3+}/Yb^{3+}$ tri-doped transparent glass-ceramics is greatly enhanced, due to constitution of the energy transfer bridge. The upconversion mechanism, the energy transfer and back energy transfer processes between the ($^1G_4 \rightarrow {}^3H_6$), ($^3F_2 \rightarrow {}^3H_6$) transitions of Tm^{3+} ions and the $|^2F_{7/2},{}^4T_1\rangle \rightarrow |^2F_{7/2},{}^6A_1\rangle$ transitions of Mn^{2+}–Yb^{3+} dimer were discussed.

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1. Introduction

In the recent decades, the demand for development of novel rare-earth (RE) doped materials based on the infrared to visible frequency upconversion (UC) has been increased considerably, because of their potential applications such as multicolor display, energy solar cells, optoelectronic devices, etc. [1–7]. Among the RE ions, the Tm^{3+} ions is great interest because it exhibits strong fluorescence in the ultra-visible color regions [8,9]. Furthermore, the efficiency UC of Tm^{3+} ions could be substantially improved, if appropriate sensitizer and energy transfer (ET) between the RE ions are implemented [10]. There has been a significant interest in the research due to the attractive emissions of Tm^{3+} ions in the visible and infrared regions [11,12]. Recently, the ET processes between the Tm^{3+} ions and the RE ions have been also investigated, such as the ET processes between the Tm^{3+} ions with Ho^{3+}, Er^{3+}, Tb^{3+} and Yb^{3+} ions [13–16]. And the effects of the metals transition on the enhancement UC emission intensity of Tm^{3+} ions have been studied [17–19]. However, the effect of Mn^{2+} ions on the enhancement red UC emission and the ET process between the Tm^{3+} ions and Mn^{2+}–Yb^{3+} dimer in the glass-ceramics has not been reported up to now. On the other hand, the emission bands of Tm^{3+} ions are located in the range about 450–850 nm, corresponding to $^1G_4 \rightarrow {}^3H_6$, $^1G_4 \rightarrow {}^3F_4$, $^3F_2 \rightarrow {}^3H_6$ and $^3H_4 \rightarrow {}^3H_6$ transitions. While the bands of Mn^{2+} emission ions are located in the range about 460–700 nm [20]. Therefore, the possibility of the ET between the Tm^{3+} and Mn^{2+} ions is expected.

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

2. Experimental

The glasses were prepared according to a conventional melt-quenching method. High purity SiO_2, AlF_3, TiO_2, BaF_2, LaF_3, TmF_3, $MnCO_3$ 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

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http://dx.doi.org/10.1016/j.materresbull.2015.09.019
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Table 1
Chemical composition of analysed glasses from SiO_2–AlF_3–BaF_2–TiO_2–LaF_3–$MnCO_3$–TmF_3–YbF_3 system (in mol.%).

Glasses name		Composition ratios of reagents							
		SiO_2	AlF_3	BaF_2	TiO_2	LaF_3	TmF_3	$MnCO_3$	YbF_3
STM-1	STM-0Mn	50	12.5	25	5	4.8	0.2	0	2.5
	STM-0.6Mn	49.4	12.5	25	5	4.8	0.2	0.6	2.5
	STM-0.8Mn	49.2	12.5	25	5	4.8	0.2	0.8	2.5
	STM-1.0Mn	49	12.5	25	5	4.8	0.2	1.0	2.5
	STM-1.2Mn	48.8	12.5	25	5	4.8	0.2	1.2	2.5
	STM-1.4Mn	48.6	12.5	25	5	4.8	0.2	1.4	2.5
	STM-1.8Mn	48.2	12.5	25	5	4.8	0.2	1.8	2.5
	STM-4.0Mn	46	12.5	25	5	4.8	0.2	4.0	2.5
STM-2	STM-0Tm	49.2	12.5	25	5	5	0	0.8	2.5
	STM-0.2Tm	49.2	12.5	25	5	4.8	0.2	0.8	2.5
	STM-0.3Tm	49.2	12.5	25	5	4.7	0.3	0.8	2.5
	STM-0.4Tm	49.2	12.5	25	5	4.6	0.4	0.8	2.5
	STM-0.5Tm	49.2	12.5	25	5	4.5	0.5	0.8	2.5

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 545 °C for 6 h to remove thermal strains. The glasses samples were then heat-treated at temperature 680 °C for 10 h to form transparent glass-ceramics. The samples were cut into the size of 10 mm × 10 mm × 2 mm and polished for optical measurements. To identify the crystallization phase, XRD analysis was carried out with a powder diffractometer (BRUKER AXS GMBH) using CuKα radiation. The optical absorption spectrum in the wavelength range of 350–1800 nm was measured on a HITACHI U-4100 spectrophotometer. The UC luminescence spectra of Mn^{2+}/Tm^{3+}/Yb^{3+} tri-doped samples under 980 nm laser diode (LD) excitation was measured by using a HITACHI F-7000 fluorescence spectrophotometer in the wavelength range of 450–850 nm. The X-ray photoelectron spectroscopy (XPS) analysis was carried out on a PHI5500 ESCA spectrometer. All measurements were performed at the ambient temperatures.

3. Results and discussion

The XRD patterns of STM-1 glass and glass-ceramics samples are shown in Fig. 1(a). From this figure, the prominent diffraction peak of Mn^{2+} is not observed in all four patterns. Moreover, the increase of XRD peaks is very small. These results may indicate that the Mn^{2+} ions are dispersed in to the glass matrix. The average of Ba_2LaF_7 crystallite size of the sample were about 15 nm, by using Scherrer's formula [21]. At the same time, the X-ray photoelectron spectroscopy indicated the existence of Si 2s, Si 2p, Al 2p, Ba 3d3, Ba 3d5, Ba 4d, La 3d5, La 4d, C 1s, O 1s, F 1s, Ti 2s, Ti 2p3, Mn 2p1, Mn 2p3, Tm 4d and Yb 4p3 on the specimen surface as shown in Fig. 1(b).

The absorption spectra of Mn^{2+}/Tm^{3+}/Yb^{3+} tri-doped glass and glass-ceramics samples in the 350–1800 nm regions are shown in Fig. 2. The absorption spectra of Tm^{3+}/Yb^{3+} co-doped glass sample are shown in curve (a) of Fig. 2. It consisted five absorption band peaks at around 461, 680, 784, 1209 and 1644 nm, each of which were corresponding to the transitions from the $^3H_6$ ground-state to the excited states: $^1G_4$, $^3F_3$, $^3H_4$, $^3H_5$ and $^3F_4$ transitions of Tm^{3+} ions, respectively. The absorption spectrum of Mn^{2+}/Yb^{3+} co-doped glass-ceramics sample is shown in curve (b) of Fig. 2, it can be assigned to the transition of $^6A_{1g} \rightarrow {}^4T_{1g}$. And the band centered at about 975 nm can be identified by transitions that originated from the Yb^{3+} ions ground multiple $^2F_{7/2}$ to the excited multiple $^2F_{5/2}$ [21]. The absorption spectrum of Mn^{2+}/Tm^{3+}/Yb^{3+} tri-doped glass-ceramics sample is shown in curve (c) of Fig. 2. Compared with the

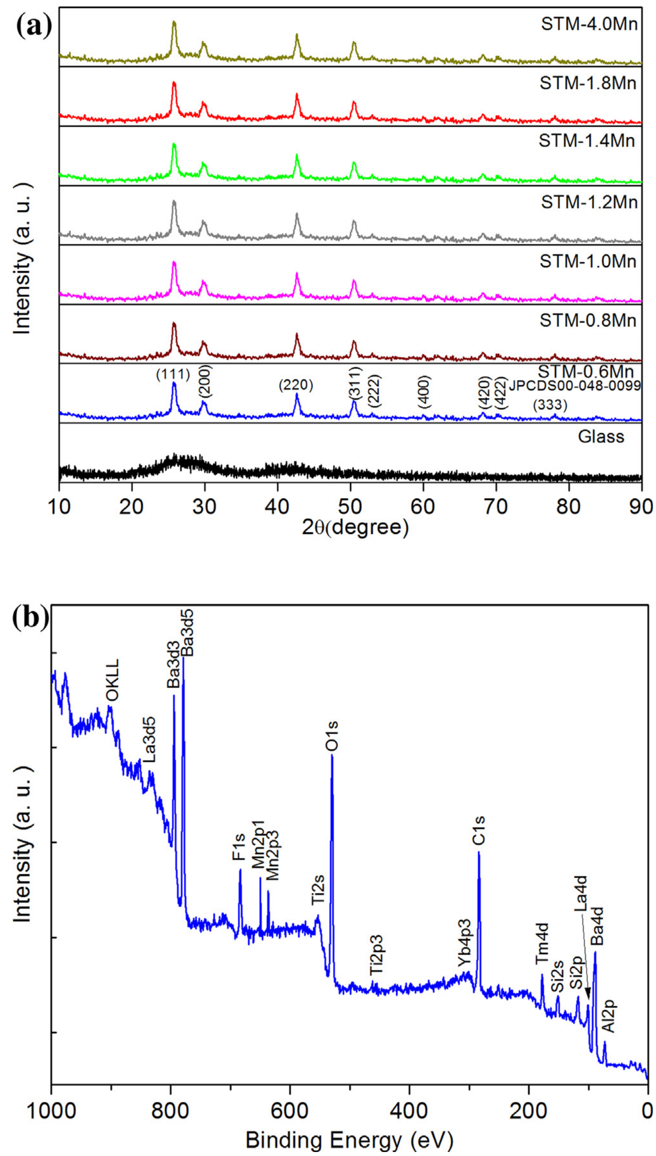

Fig. 1. (a) The XRD patterns of the STM-1 glass and glass-ceramics samples. (b) The XPS of the STM-0.6Mn glass-ceramics sample.

precursor glass, the absorption spectra of Mn^{2+}/Tm^{3+}/Yb^{3+} tri-doped glass-ceramics were showed a significant increase at $^1G_4$, $^3F_3$, $^3H_4$, $^3H_5$ and $^3F_4$ absorption band peaks of Tm^{3+} ions and at $^4T_{1g}$ absorption band peaks of Mn^{2+} ions, respectively. The optical image of glass-ceramic's STM-0.6Mn sample, it display good transparency in the visible wavelength range (see inset of Fig. 2).

Fig. 3 shows the UC emission spectra of STM-0Tm, STM-0Mn and STM-0.6Mn glass-ceramics samples under excitation 980 nm LD, which were heat-treated at 680 °C for 10 h. As can be observed, the Tm^{3+}/Yb^{3+} co-doped glass-ceramics there were three well-known emission bands centered at 478, 651 and 798 nm was consistent with $^1G_4 \rightarrow {}^3H_6$, $^1G_4 \rightarrow {}^3F_4$ and $^3F_2 \rightarrow {}^3H_6$ transitions of Tm^{3+} ions, respectively [22–23]. The UC of Mn^{2+}/Yb^{3+} co-doped in the STM-0Tm glass-ceramics there were two well-known emission bands centered at 588 and 612 nm corresponding to the with the transition from $^4T_2(^4G)$ and $^4T_1(^4G)$ levels to ground-state $^6A_1(^6S)$ of Mn^{2+} ions [24]. Simultaneously, compared with the precursor glass, the strong UC emission intensity of Mn^{2+}/Tm^{3+}/Yb^{3+} tri-doped at 478 and 698 nm were observed in the STM-0.6Mn glass-ceramics sample. The reasons contributing to the increase UC

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