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Luminescent properties of $(Ce_{0.67}Tb_{0.33})Mn_xMg_{1-x}Al_{11}O_{19}$ phosphor in VUV region

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Abstract

$(Ce_{0.67}Tb_{0.33})Mn_xMg_{1-x}Al_{11}O_{19}$ phosphor powder was synthesized using a simple sol–gel process. The chemical state and location of the Mn ion in the phosphor were investigated using X-ray photoelectron spectroscopy (XPS) and electron spin resonance (ESR). Effect of Mn ion on the luminescent properties excited by VUV (vacuum ultraviolet) was studied. The Mn ion exists as Mn^{2+} in the phosphor and is located at a tetrahedrally surrounded site. The emission spectrum excited by VUV is composed of lines from Tb^{3+} and Mn^{2+}. The emission intensity of Tb^{3+} decreases while that of Mn^{2+} increases when the content of Mn^{2+} increases and concentration quenching occurs when $x > 0.05$. Doping Mn^{2+} in the phosphor increases the brightness of the phosphor.

Keywords: A. Sol–gel processes; Fluorescence spectra; XPS

1. Introduction

$(Ce_{0.67}Tb_{0.33})MgAl_{11}O_{19}$ as a type of efficient green emission phosphor has been used in fluorescent lights (FL). Recently, it has been widely employed in plasma display panels (PDP) [1–5].

AC color PDPs are one of the most promising candidates for large flat panel displays. As a main green-emitting phosphor used for PDP, the emission light of $(Ce_{0.67}Tb_{0.33})MgAl_{11}O_{19}$ phosphor with a peak at about 542 nm is not ideal [1,2]. Luminescent efficiency and emission color of this phosphor should be improved in order to enhance the performance of PDP, one way is to obtain fine particles without milling or grinding, and another way is to dope other elements to change the emission spectra [2,3].

In the former paper, $(Ce_{0.67}Tb_{0.33})Mn_xMg_{1-x}Al_{11}O_{19}$ phosphor was synthesized by a simple sol–gel process in our laboratory [6]. In this paper, the valence and location of Mn ion in the phosphor were investigated by XPS and ESR spectra. The excitation and emission characterization were studied in the VUV region, and the brightness was also obtained to measure the luminescent property of the phosphor.

2. Experimental procedure

$Ce_{0.67}Tb_{0.33})Mn_xMg_{1-x}Al_{11}O_{19}$ phosphor was synthesized by a simple sol–gel process described by Zhang et al. [6].

XPS measurement was performed on a HI5300 ESCA/610SAM spectrometer with Mg Kα radiation (300 W, 15 KeV) from Mg/Al twin anode to measure the chemical state of Mn ion. ESR spectra of Mn ion were obtained with a Bruker ER200-SRC-10/12 X-band (ν≈9.75 GHZ) spectrometer at room temperature. The excitation and emission spectra of the phosphor powders in the UV (ultraviolet) region were recorded by a spectrofluorometer (Model 850, Hitachi Instruments). The excitation characterization of the phosphor in VUV

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region was studied using synchrotron radiation from the BSRF storage ring at the Institute of High Energy (Chinese Academy of Sciences, China). The electron energy of the storage ring is 2 GeV, and the beam current is about 100 mA. Excitation spectra were corrected for spectral distribution of the light source and the instrumental response by using sodium salicylate as a standard. The emission spectra and brightness of the phosphor was measured by the SPR-920 Spectra Radiometer at the Institute of Chinese Nonferrous Metal (China), using a VUV excitation light source.

3. Results and discussion

Fig. 1 shows the XPS spectrum of the phosphor in $2p_{3/2}$ and $2p_{1/2}$ region of Mn. The binding energy of 640.9 eV and 653.1 eV indicates that the Mn ion has +2 oxidation state.

The X-band ESR spectrum of an Mn^{2+} ion (S = 5/2, I = 5/2) in a distorted state consists of six major lines due to the $m_S = |-1/2> \leftrightarrow |+1/2>$ transition, which is split into six lines due to hyperfine interaction with the manganese nucleus. The other transitions are usually not resolved due to a large anisotropy, and they contribute to the background upon which the six major hyperfine lines are superimposed. When the zero field splitting is non-negligible, small peaks in between the six major hyperfine lines appear [7]. Fig. 2 shows the X-band ESR spectra for the phosphors with different contents of Mn^{2+} ion. When the content of Mn^{2+} ion was small, the spectrum showed six resolved hyperfine features at $g \approx 2.039$. The separation between the adjacent hyperfine lines, indicated by the average hyperfine coupling constant (A_{Mn}), are not equal, and increase when the concentration of Mn^{2+} increases as shown in Table 1. When the concentration of Mn^{2+} is higher than 2%, the spectrum forms a single broad line.

As known, the $(Ce_{0.67}Tb_{0.33})MgAl_{11}O_{19}$ phosphor has a distorted magnetoplumbite structure, and there are two sites for Mn^{2+}, one is tetrahedrally surrounded by oxygen, and the other is octahedrally surrounded by oxygen atoms [8]. The hyperfine coupling constant is between 65 G and 74 G in this phosphor, which is typical for Mn^{2+} ion in a tetrahedral environment [9]. Increase of the hyperfine coupling constant with the Mn^{2+} content is attributed to the stronger spin-spin interaction. At high Mn^{2+} content ($\geq 2\%$), no hyperfine structure was observed, consistent with the spin-spin interaction being too strong at this concentration.

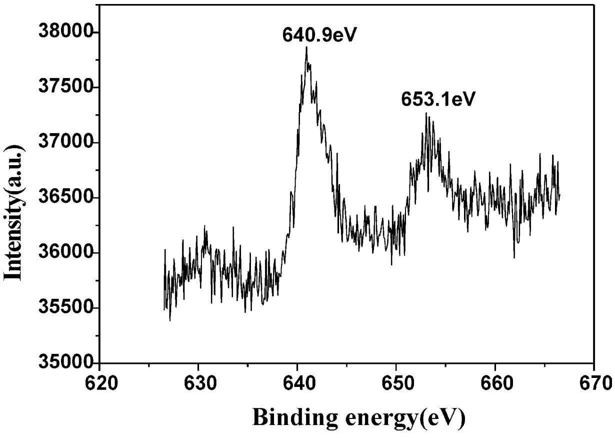

Fig. 1. XPS spectrum of Mn ion in the phosphor.

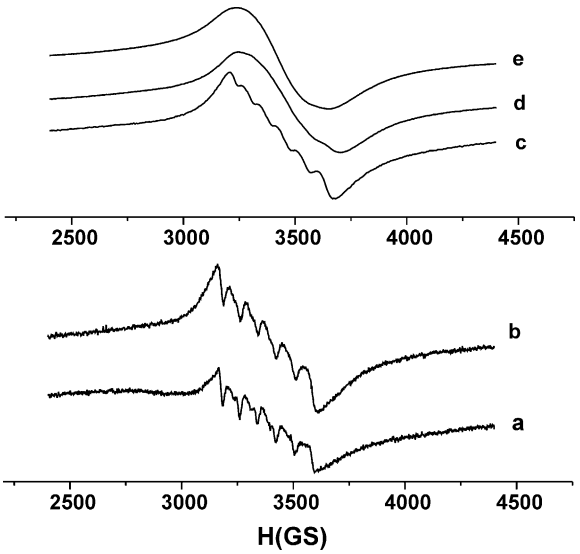

Fig. 2. ESR spectra of $(Ce_{0.67}Tb_{0.33})Mn_xMg_{1-x}Al_{11}O_{19}$ phosphor: (a) $x = 0.002$ (b) $x = 0.005$ (c) $x = 0.02$ (d) $x = 0.08$ (e) $x = 0.2$.

Table 1
ESR parameters assigned for Mn^{2+} ion in $(Ce_{0.67}Tb_{0.33})Mn_xMg_{1-x}Al_{11}O_{19}$ phosphor

	Content of Mn^{2+}, x				
	0.002	0.005	0.02	0.08	0.20
g	2.0393	2.0390	2.0390	2.0038	2.0095
A_{Mn}(G)	67.595	68.538	74	–	–

Fig. 3 gives the excitation and emission spectra of the $(Ce_{0.67}Tb_{0.33})MgAl_{11}O_{19}$ phosphor in the UV region. The excitation spectrum with a wide band at about 280 nm is attributed to the 4f–5d transition of Ce^{3+}. The emission spectrum of the sample excited by 280 UV nm is composed of bands at 487 nm, 542 nm, 584 nm and 625 nm, which correspond to transitions of Tb^{3+} from ${}^5D_4$ to ${}^7F_J$ ($J = 6,5,4,3$) [10]. The strongest peak of ${}^5D_4$-${}^7F_5$ transition appears at 542 nm.

The excitation and emission spectra of $(Ce_{0.67}Tb_{0.33})Mn_{0.10}Mg_{0.90}Al_{11}O_{19}$ are shown in Fig. 4. Compared with that in Fig. 3, the excitation spectrum remains unchanged, whereas the emission spectrum significantly changes. Besides the four bands ascribed to Tb^{3+}, a strong band at about 518 nm appears, which originates from the ${}^4T_1(t_{2g}^4e_g^1)$–${}^6A_1(t_{2g}^3e_g^2)$ transition of

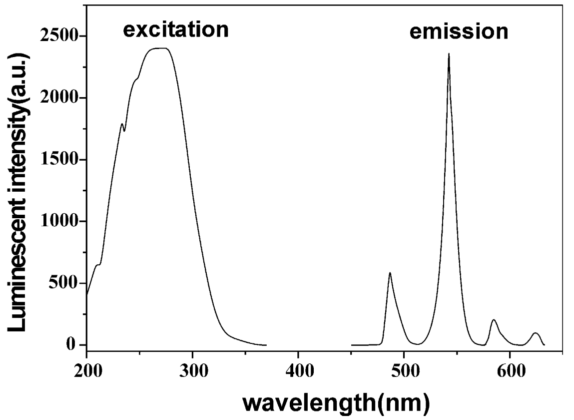

Fig. 3. Excitation and emission spectra of $(Ce_{0.67}Tb_{0.33})MgAl_{11}O_{19}$ phosphor in the UV region.

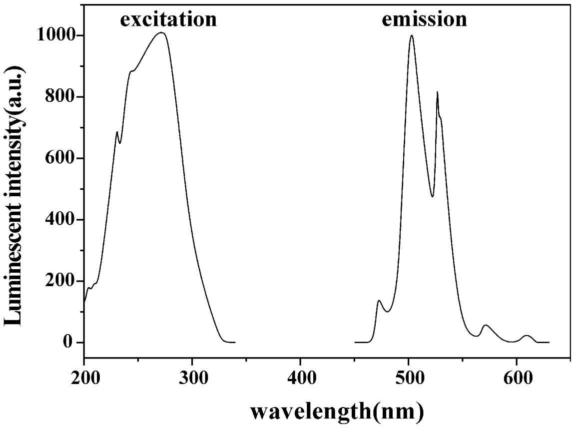

Fig. 4. Excitation and emission spectra of $(Ce_{0.67}Tb_{0.33})Mn_{0.10}Mg_{0.90}Al_{11}O_{19}$ in the UV region.

Mn^{2+}. Due to this additional band, the color of the emitting light shifts to a deeper green. Excitation of the phosphor is due to 4f–5d transition of Ce^{3+} while emission is originated from Tb^{3+} and Mn^{2+}, so there is energy transfer from Ce^{3+} to Tb^{3+} and Mn^{2+}.

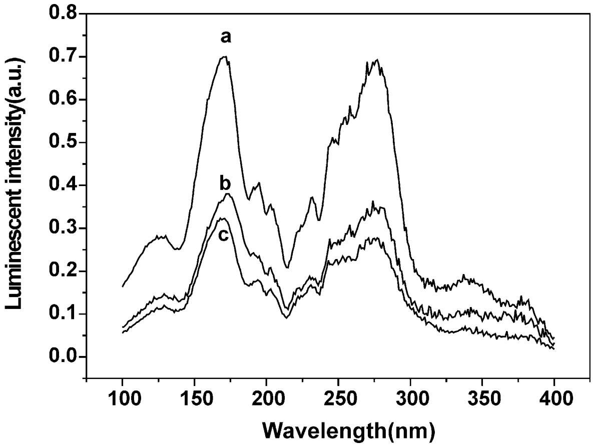

Fig.5. Excitation spectra of phosphor s in the VUV region: (a) $(Ce_{0.67}Tb_{0.33})MgAl_{11}O_{19}$ monitored by 542 nm emission; (b) $(Ce_{0.67}Tb_{0.33})Mn_{0.10}Mg_{0.90}Al_{11}O_{19}$ phosphor monitored by 542 nm emission; (c) $(Ce_{0.67}Tb_{0.33})Mn_{0.10}Mg_{0.90}Al_{11}O_{19}$ phosphor monitored by 518 nm emission.

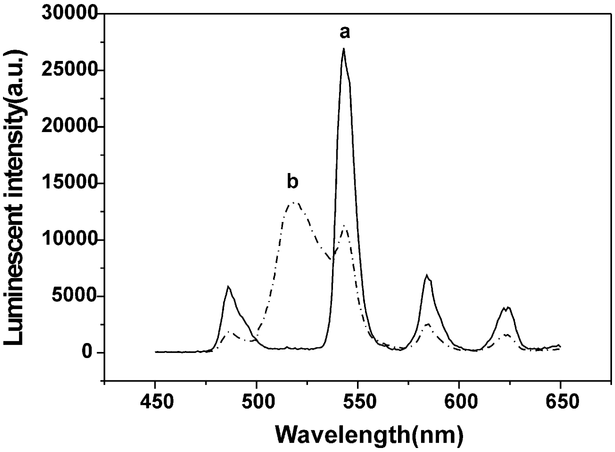

Fig. 6. Emission spectra of the phosphor excited by 147 nm VUV: (a) $(Ce_{0.67}Tb_{0.33})MgAl_{11}O_{19}$; (b) $(Ce_{0.67}Tb_{0.33})Mn_{0.10}Mg_{0.90}Al_{11}O_{19}$.

Use of phosphors in PDP requires efficient excitation in the VUV region, especially near the Xe resonance line (147 nm) and/or the Xe_2 molecular emission band (172 nm). Fig. 5 shows the excitation spectra of $(Ce_{0.67}Tb_{0.33})MgAl_{11}O_{19}$ and $(Ce_{0.67}Tb_{0.33})Mn_{0.10}Mg_{0.90}Al_{11}O_{19}$ phosphor by monitoring the green emission at 542 nm and 518 nm. The shape of the excitation in the UV region is similar to that in Figs. 3 and 4, and the wide band in the VUV region with peaks at about 171 nm corresponds to the band-to-band excitation of the host crystal, i.e., the electrons are promoted from the valence band to the electron band. The emission spectra of $(Ce_{0.67}Tb_{0.33})MgAl_{11}O_{19}$ and $(Ce_{0.67}Tb_{0.33})Mn_{0.10}Mg_{0.90}Al_{11}O_{19}$ phosphors excited by 147 nm VUV are shown in Fig. 6. For $(Ce_{0.67}Tb_{0.33})MgAl_{11}O_{19}$, the spectra consist mainly of a wide band with the peak at about 542 nm, which corresponds to emission of the Tb^{3+}ion. For $(Ce_{0.67}Tb_{0.33})Mn_{0.10}Mg_{0.90}Al_{11}O_{19}$, besides the emission bands ascribed to Tb^{3+}, a strong band at about 518 nm appears, which originates from emission of Mn^{2+} ion.

As the content of Mn^{2+} increases in $(Ce_{0.67}Tb_{0.33})Mn_xMg_{1-x}Al_{11}O_{19}$, the emission intensity of Tb^{3+} at 542 nm and Mn^{2+} at 518 nm under 147 nm VUV excitation changes, as shown in Fig. 7. The emission intensity of Tb^{3+} emission decreases when the content of Mn^{2+} increases while the emission intensity of Mn^{2+} increases to a maximum at Mn^{2+} content of $x=0.05$, and decreases at higher Mn^{2+} content due to concentration quenching. When doping $(Ce_{0.67}Tb_{0.33})MgAl_{11}O_{19}$ with Mn^{2+} content of $x=0.05$, the phosphor emits green light with strong peaks at 518 nm and 542 nm.

As the content of Mn^{2+} increases in $(Ce_{0.67}Tb_{0.33})Mn_xMg_{1-x}Al_{11}O_{19}$, the emission brightness of the phosphor excited by 147 nm VUV changes as

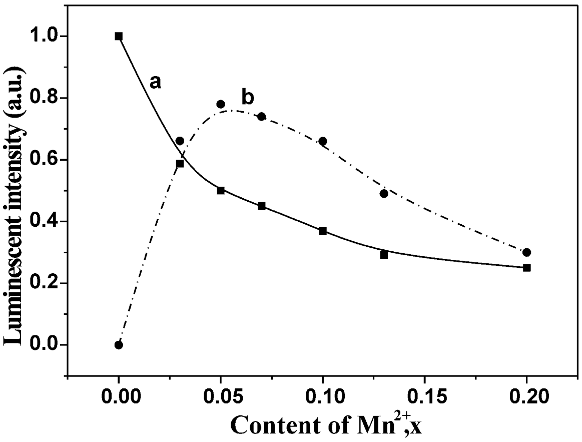

Fig. 7. Emission intensity of Tb^{3+} and Mn^{2+} in $(Ce_{0.67}Tb_{0.33})Mn_xMg_{1-x}Al_{11}O_{19}$ phosphor excited by 147 nm VUV as a function of Mn^{2+} content: (a) Tb^{3+} emission; (b) Mn^{2+} emission.

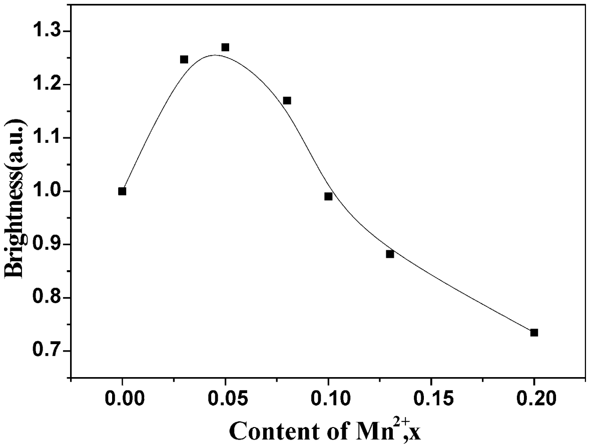

Fig. 8. Brightness of $(Ce_{0.67}Tb_{0.33})Mn_xMg_{1-x}Al_{11}O_{19}$ phosphor excited by 147 nm VUV as a function of Mn^{2+} content.

indicated in Fig. 8. The brightness of the phosphor increases when the content increase and reaches a maximum when $x = 0.05$, so doping Mn^{2+} in the phosphor can improve the emission brightness.

4. Conclusions

In green-emitting $(Ce_{0.67}Tb_{0.33})Mn_xMg_{1-x}Al_{11}O_{19}$ phosphor, Mn ions has +2 oxidation state and is located in tetrahedral coordination. The phosphor without Mn^{2+} doping shows Tb^{3+} emission and the emitting light is yellow-green. Mn^{2+} can dramatically change the luminescent properties. The emission intensity of Tb^{3+} excited by VUV decreases when Mn^{2+} is doped in the phosphor, and the Mn^{2+} emission intensity increases to a maximum when x is about 0.05. The brightness of the phosphors improves when Mn^{2+} is doped in the phosphor.

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