Journal of Alloys and Compounds 488 (2009) 331–333

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Luminescence properties of a novel red emitting phosphor, $Mg_2GeO_4:Sm^{3+}$

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ARTICLE INFO

Article history:
Received 4 February 2009
Received in revised form 22 August 2009
Accepted 25 August 2009
Available online 31 August 2009

Keywords:
Mg_2GeO_4:Sm
Luminescence
Phosphor

ABSTRACT

A novel red emitting phosphor, Sm^{3+} doped Mg_2GeO_4 was prepared by the traditional solid state reaction. The luminescence properties were investigated in details. Diffuse reflection spectra of undoped and Sm^{3+} doped Mg_2GeO_4 were measured. The excitation spectra present a broad band and are consistent with the diffuse reflectance spectra. The emission bands which peak at 631 and 659 nm are due to the $^4G_{5/2}$–$^6H_{9/2}$ transition. The CIE coordinates of the phosphor $Mg_2GeO_4:Sm^{3+}$ is $x = 0.626$ and $y = 0.323$ which are close to the NTSC standard values for red. The dependence of the emission intensity on the Sm^{3+} dopant concentration was studied: the optimum doping levels for Sm^{3+} is $x = 0.03$ molar ratio. The luminescence properties suggest it is a good novel red emitting phosphor.

1. Introduction

Recently, field emission displays (FEDs) have been developed as a next-generation flat-panel display, which are the most promising candidate to replace some cathode-ray tubes (CRTs) [1–4]. Its advantages include portable size with low power consumption, broad viewing angle and wide operating-temperature range. At low-voltage operation, high current density is required to maintain constant power in FEDs [5], so high luminescent efficiency, good stability and reasonable electric conductivity are necessary for promising FEDs phosphors.

The properties of a phosphor are strongly dependent on the host materials. The compound composed of elements with small differences in electronegativity (X) should have a narrower band gap which leads to higher conductivity [6]. The electronegativity difference between Ge and O ($\Delta X = 1.43$) is lower than that between Si and O ($\Delta X = 1.54$) or Al and O ($\Delta X = 1.83$) [7]. Then germanates have attracted much attention as new host materials for application in FEDs. $Gd_2GeO_5:M^{3+}$, $Y_2Ge_2O_7:M^{3+}$, $Y_2GeO_5:M^{3+}$and $Y_4GeO_8:M^{3+}$ ($M^{3+} = Eu^{3+}$, Tb^{3+} and Bi^{3+}) were studied as possible phosphors for FEDs applications [6,8]. Under the excitation of cathode ray, the brightness of $Y_{0.94}Tb_{0.06}GeO_5$ is about 90%, compared with Nichia YAG:Tb [9]. This suggests that germanates may be useful host materials with reasonable conductivity and high stability. Therefore, in order to search for high efficient FEDs phosphors, germanates can be selected as promising host material candidates. So we chose Mg_2GeO_4 as a novel host material.

In this article we prepared the novel red emitting phosphor $Mg_2GeO_4:Sm^{3+}$ by the traditional solid state reaction. Sm^{3+} is an excellent activator with high lumen output, good color purity and great radiation stability [10–12]. Germanates are good host materials because of their high stability and reasonable conductivity. The novel phosphor $Mg_2GeO_4:Sm^{3+}$ presents red emission at 631 and 659 nm when excited at 287 nm. The CIE coordinates of the phosphor $Mg_2GeO_4:Sm^{3+}$ is $x = 0.626$ and $y = 0.323$ which is better than the red emission of Eu^{3+} ions at about 610 nm. The luminescence properties suggested it a good candidate for application in FEDs.

2. Experimental

2.1. Preparation of $Mg_{2-x}Sm_xGeO_4$ ($x = 0.01$–0.09) samples

All the Sm^{3+} doped Mg_2GeO_4 phosphors were synthesized using the solid state technique. Mixtures of appropriate amount of $(Mg_2CO_3)_4Mg_2(OH)_2\cdot5H_2O$ (analytical grade), GeO_2 (analytical grade) and Sm_2O_3 (99.99%) were thoroughly mixed in an agate mortar adding ethanol and then were triturated for a good mixing. The dried powders were obtained after baked in an oven at 80 °C for 20 min. Then the powders were treated in a corundum crucible at 1250 °C for 3 h in an oven with air atmosphere.

2.2. Apparatuses and measurements

X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (D/max-IIIA diffractometer, RIGAKU Corporation of Japan. 40 kV and 20 mA, Cu $K\alpha = 1.5406$ Å, Rigaku/Dmax-IIIA) for crystal phase identification.

Diffuse reflectance spectra were taken on a Cary 5000 UV-Vis-NIR spectrophotometer. Photoluminescence (PL) and PL excitation (PLE) spectra of the samples were taken on an FLS920 luminescence spectrometer at room temperature. In all

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doi:10.1016/j.jallcom.2009.08.123

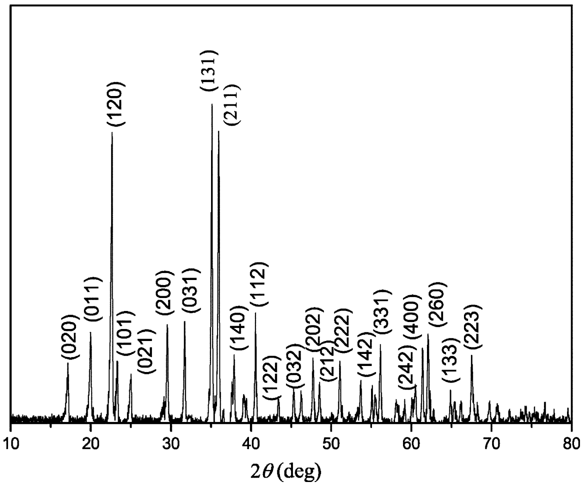

Fig. 1. The XRD pattern of the sample $Mg_{1.97}Sm_{0.03}GeO_4$ calcined at 1250 °C for 3 h.

experiments, both excitation and emission slits were 5 nm.

3. Results and discussion

Fig. 1 shows the XRD pattern of the sample $Mg_{1.97}Sm_{0.03}GeO_4$ calcined at 1250 °C for 3 h. All the diffraction peaks match very well with the standard values from the Joint Committee on Powder Diffraction Standards (JCPDS) data card No. 36-1479, which can be assigned to orthorhombic structures. And the samarium doping does not introduce any detectable impurity phases.

Fig. 2 presents the diffuse reflection spectra of $Mg_{2-x}Sm_xGeO_4$ ($x = 0$–0.09). We found that the undoped sample ($x = 0$) present an absorption edge band at 330 nm, which may correspond to the host material absorption. There is a strong absorption band at 260–330 nm in the diffuse reflection spectra of the doped samples. A stronger absorption band at 200–230 nm and many sharp peaks at 346, 361, 376, 403, 414, 424, 441, 466, 477, 499, 528 and 565 nm are found in the diffuse reflection spectra of the Sm^{3+} doped samples. The absorption intensities of the band at 200–230 nm and the sharp peaks increase with the increment of Sm^{3+} concentration. The sharp peaks are due to the 4f–4f inner shell transitions of Sm^{3+} [13]. The broad band at 200–230 nm corresponds to the charge transfer band (CTB) of $O^{2-} \rightarrow Sm^{3+}$ [14]. With the increasing of Sm^{3+} concentration the absorption of Sm^{3+} become stronger.

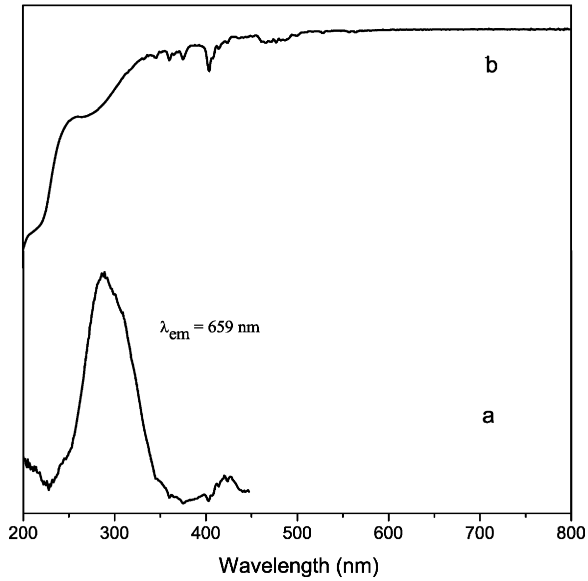

Fig. 3. The diffuse reflection spectrum (b) and excitation spectrum (a) of $Mg_{1.97}Sm_{0.03}GeO_4$.

Fig. 3 shows the diffuse reflection spectrum and excitation spectrum of $Mg_{1.97}Sm_{0.03}GeO_4$. The UV excitation spectrum is obtained by monitoring the emission at 659 nm as Fig. 3a shows. The excitation spectrum presents a dominating broad band at 250–340 nm which can be due to the host material absorption and which is consistent with the diffuse reflectance spectrum as presented in Fig. 3b. As f–f transitions of the rare earth ions are electric dipolar transitions which are forbidden by the parity selection rules but forced by the crystal field configuration mixing due to the odd terms of the crystal field Hamiltonian development, they are difficult to observe because the f–f intra-configuration transitions of Sm^{3+} in this range are weak and hidden by other stronger broad band transitions. The weak broad band under 230 nm is attributed to both the host material absorption and the charge transfer band (CTB) of Sm^{3+}. There is an effective energy transfer from the host material to the Sm^{3+} ions. It is favorable to the red emission of Sm^{3+}.

Fig. 4 shows the excitation spectrum and the emission spectrum of the phosphor $Mg_{1.97}Sm_{0.03}GeO_4$. The emission spectrum of $Mg_{1.97}Sm_{0.03}GeO_4$ is dominated by red emission at 631 and 659 nm due to intra-atomic $4f \rightarrow 4f\,(^4G_{2/5} \rightarrow {}^6H_{9/2})$ transition of Sm^{3+} when the sample is excitated at 287 nm [15]. The two peaks at 631 and 659 nm show Stark levels due to the crystal field [16]. The red emission of the Sm^{3+} doped Mg_2GeO_4 phosphor excited by UV lamp is visible to naked eyes. A novel phosphor which has a good CIE of luminescence is thus suggested. Excitation spectra obtained by

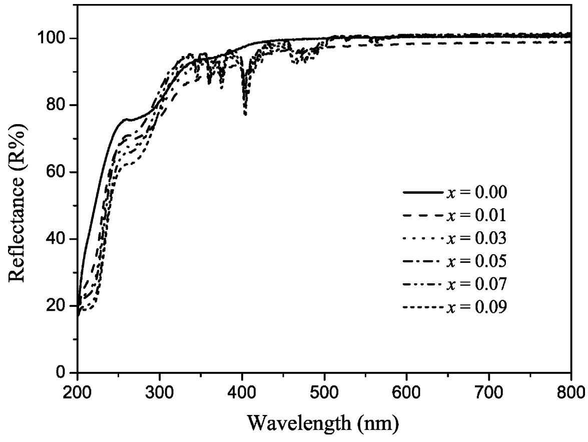

Fig. 2. The diffuse reflection spectra of $Mg_{2-x}Sm_xGeO_4$ ($x = 0$–0.09).

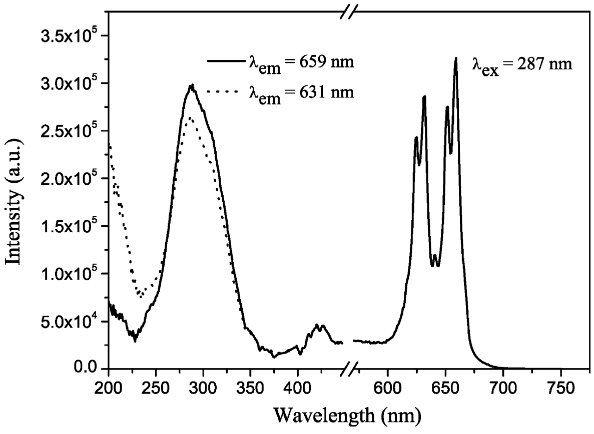

Fig. 4. The excitation and emission spectra of $Mg_{1.97}Sm_{0.03}GeO_4$.

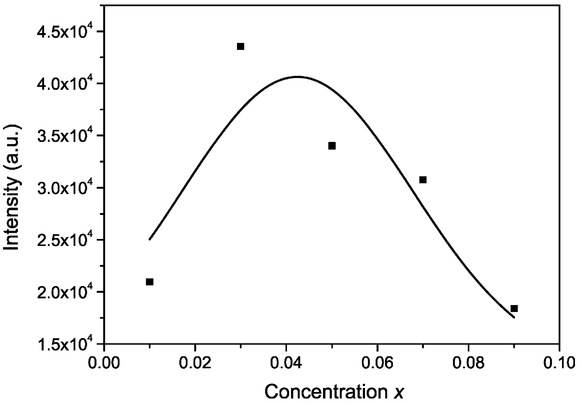

Fig. 5. The emission intensity dependence on the Sm^{3+} concentration x.

monitoring the emission at 631 and 659 nm, respectively, present a broad band at 250–340 nm which peak at 287 nm which belongs to the host absorption band. This suggests an effective energy transfer from the host material to Sm^{3+} ions.

The emission intensity dependence on Sm^{3+} concentration x is depicted in Fig. 5. A series of phosphors $Mg_{2-x}Sm_xGeO_4$ with $x = 0–0.09$ was prepared. We found that the PL emission intensity of Sm^{3+} will increase with the increasing x up to 0.03. However, the emission intensity of Sm^{3+} drops down rapidly with any further increase of Sm^{3+} above $x = 0.03$. It suggests that concentration quenching happened above $x = 0.03$ of Sm^{3+}.

4. Conclusion

A new red emitting Sm^{3+} doped Mg_2GeO_4 phosphor was synthesized for the first time and its luminescence properties were investigated. The phosphor presents a bright red emission peaking at 631 and 659 nm. The CIE coordinates of the phosphor $Mg_2GeO_4:Sm^{3+}$ is $x = 0.626$ and $y = 0.323$ which is pure red. The diffuse reflection spectra and the excitation spectra measurements suggest that there is an effective energy transfer from the host material to Sm^{3+} ions which is favorable to the red emission. The optimum concentration of Sm^{3+} corresponding to the highest emission intensity is $x = 0.03$. The phosphor shows promising luminescence properties and suggests an attractive oxide phosphor for FEDs applications.

Acknowledgements

This work was financially supported by grants from the Foundation of the 211 Project and the Research Fund for the Doctoral Program of Guangdong University of Technology.

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