

Luminescence Properties of $\text{LaMgAl}_{11}\text{O}_{19}:\text{Mn}^{2+}$ and $\text{LaMgAl}_{11}\text{O}_{19}:\text{RE}, \text{Mn}^{2+}$ ($\text{RE}=\text{Eu}^{2+}, \text{Gd}^{3+}$) under UV/VUV Excitation

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Abstract: Using H_3BO_3 as a flux, $\text{LaMgAl}_{11}\text{O}_{19}:\text{Mn}^{2+}$ and $\text{LaMgAl}_{11}\text{O}_{19}:\text{RE}, \text{Mn}^{2+}$ ($\text{RE}=\text{Eu}^{2+}, \text{Gd}^{3+}$) were synthesized by solid state reaction at 1150 °C for 4 h. The effect of Mn^{2+} on the luminescent properties excited by vacuum ultraviolet (VUV) was investigated. The strong emission spectrum excited by 147 nm is composed of peaks from Eu^{2+} and Mn^{2+} luminescence in $\text{LaMgAl}_{11}\text{O}_{19}:(\text{Eu}^{2+}, \text{Mn}^{2+})$ and only Mn^{2+} luminescence in $\text{LaMgAl}_{11}\text{O}_{19}:\text{Mn}^{2+}$ and $\text{LaMgAl}_{11}\text{O}_{19}:(\text{Gd}^{3+}, \text{Mn}^{2+})$. The results show that the green emission of Mn^{2+} becomes stronger because of efficient energy transferring from Eu^{2+} and Gd^{3+} to Mn^{2+} .

Key words: flux; luminescence; $\text{LaMgAl}_{11}\text{O}_{19}$ (LMA); phosphor

As a commercial green phosphor for plasma display panel (PDP), $\text{Zn}_2\text{SiO}_4:\text{Mn}$ has been restricted in its application because of lacking long-time persistence. Until now, great efforts have been made to develop high efficient luminescent materials, by finding new luminescent materials and improving luminescent properties of the existing phosphors. Among these, a number of activities have been carried out on the investigation of the optical properties of $\text{LaMgAl}_{11}\text{O}_{19}$ (LMA) which has a distorted magnetoplumbite structure and consists of spinal-like blocks separated by mirror planes. It has particular performances: (1) Eu^{3+} , Tb^{3+} and Eu^{2+} can replace La^{3+} on the mirror planes and establish red, green and blue-emitting luminescent center, respectively; (2) Mn^{2+} replacing Mg^{2+} which is located centrally in Al-O tetrahedron can lead to the green emission of about 520 nm. In addition, high level excited state of the active ion, energy-band structure of the host and the energy transfer among active ions can be researched through the study of spectra of rare-earth-doped LMA to supply an important academic guidance to the design and synthesis of new efficient PDP phosphors^[1].

Previously some studies on photoluminescence properties of LMA-based phosphors were mainly focused on UV region and

few on VUV region^[1,2]. In order to explore novel green PDP phosphors, we investigated the luminescent properties of $\text{LMA}:\text{Mn}^{2+}$ with different Mn^{2+} -content by means of VUV excited. Eu^{2+} or Gd^{3+} is co-doped with fixed Mn^{2+} -content for enhancing the Mn^{2+} luminescence.

1 Experimental

The phosphor samples were prepared by solid-state reaction. Stoichiometric amount of the starting materials, La_2O_3 (purity: 99.95%), MgO (purity: 98.0%), Al_2O_3 (purity: 99.99%), Eu_2O_3 (purity: 99.99%), Gd_2O_3 (purity: 99.99%) and MnCO_3 (purity: 98.0%) were weighed accurately, and H_3BO_3 was added as a flux. The starting materials were thoroughly mixed in agate mortar; $\text{LaMgAl}_{11}\text{O}_{19}$ was heated at 1200 °C for 4 h in atmosphere; $\text{LaMgAl}_{11}\text{O}_{19}:\text{xMn}^{2+}$, $\text{LaMgAl}_{11}\text{O}_{19}:\text{xEu}^{2+}$, 0.05Mn^{2+} and $\text{LaMgAl}_{11}\text{O}_{19}:\text{xGd}^{3+}, \text{Mn}^{2+}$ were heated at 1150 °C for 4 h in a reducing agent atmosphere (95% N_2 +5% H_2). After they were cooled down, the samples were taken out and triturated to obtain phosphor powder.

The X-ray diffraction data were obtained with a Rigaku D/max-2400 X-ray diffractionmeter. The excitation and emission spectra of the phosphor powders were measured by

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FLS920T fluorescence spectrophotometer and VM504 VUV monochromator with a deuterium lamp. The excitation spectra were corrected with sodium salicylate powder. All measurements were carried out at room temperature.

2 Results and Discussion

The XRD pattern of the phosphor using H_3BO_3 as a flux calcined at $1200\text{ }^\circ\text{C}$ for 4 h is shown in Fig.1a. The result indicates that as the flux varies from 7.5wt% to 12.5wt%, the LaAlO_3 diffraction peak reduces gradually until it disappears. At the same time, LaBO_3 and $\text{LaMgB}_5\text{O}_{10}$ diffraction peak is absent. Only when H_3BO_3 content exceeds to 15.0wt%, we can find LaBO_3 and $\text{LaMgB}_5\text{O}_{10}$ diffraction peak.

The other group is B_2O_3 used as a flux in the same circumstances. After a comparative study, we find H_3BO_3 is better than B_2O_3 , because H_3BO_3 has a lower melting point.

Using 12.5wt% H_3BO_3 as a flux, $\text{LMA}:x\text{Mn}^{2+}$ ($0 \leq x \leq 0.125$) was synthesized by solid state reaction at $1150\text{ }^\circ\text{C}$ for 4 h. The temperature was a little lower than that of the single phase of LMA, because the melting point of MnCO_3 is far lower than MgO . Fig.1b is the XRD patterns of $\text{LMA}:x\text{Mn}^{2+}$ ($0 \leq x \leq 0.125$), which show the LMA prepared with different Mn^{2+} -contents of 0.025, 0.050, 0.075, 0.100, and 0.125 mol/mol, respectively. It is indicated that the phosphor is a single-phase of LMA, because the peak positions in the Fig.1b correspond to those of the standard patterns reported by the Joint Committee on Powder Diffraction Standards (JCPDF260873) for LMA.

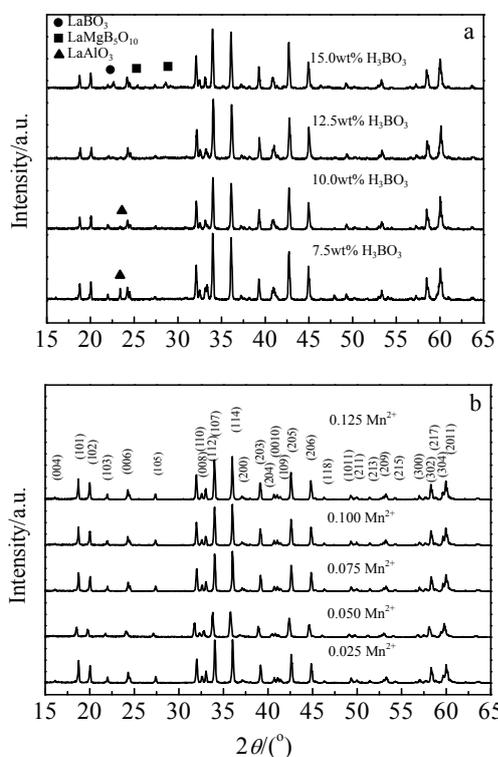


Fig.1 XRD patterns of LMA: (a) LMA, using H_3BO_3 as a flux and (b) $\text{LMA}:x\text{Mn}^{2+}$ ($0 \leq x \leq 0.125$), using 12.5wt% H_3BO_3 as a flux

Excited by 254 nm, the emission spectrum of $\text{LMA}:x\text{Mn}^{2+}$ ($0 \leq x \leq 0.125$) is very weak, because either the host lattice or Mn^{2+} cannot absorb energy effectively in UV region^[3]. Excited by 147 nm, the excitation and emission spectra of $\text{LMA}:x\text{Mn}^{2+}$ ($0 \leq x \leq 0.125$) phosphor are similar with x which varies from 0 to 0.125; when $x=0.05$, the emission intensity reaches the maximum. As shown in Fig.2a, the excitation spectrum reveals that the host lattice absorption peak appears at 167 nm and the activator Mn^{2+} absorption peak occurs at 188 nm which is originated from the $3d^5 \rightarrow 3d^4 4s$ transition of Mn^{2+} . Moreover, the host lattice absorption overlaps with the activator Mn^{2+} absorption, which indicates that the energy transfers from the host lattice to the activator Mn^{2+} . From Fig.2b, the emission spectrum shows a wide band at 516 nm which is attributed to the ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ transition of Mn^{2+} ^[3,4].

Upon fixing Mn^{2+} -content at 0.05 mol/mol, the excitation and emission spectra (Fig.3) of the $\text{LMA}: (x\text{Eu}^{2+}, 0.05\text{Mn}^{2+})$ ($0 \leq x \leq 0.20$) and $\text{LMA}: (x\text{Gd}^{3+}, 0.05\text{Mn}^{2+})$ ($0 \leq x \leq 0.20$) phosphor were investigated in UV region. $\text{LMA}: (0.1\text{Eu}^{2+}, 0.05\text{Mn}^{2+})$ was chosen as an example for its strongest emission intensity. The excitation spectra with two wide bands at about 263 nm and 294 nm are attributed to the $4f \rightarrow 5d$ transition of Eu^{2+} , which has a split crystal field^[5]. The emission spectrum excited by 254 nm consists of Eu^{2+} characteristic emission and Mn^{2+} feature emission. Two wide bands at 454 nm and 516 nm correspond to transitions of Eu^{2+} from the highest excited state

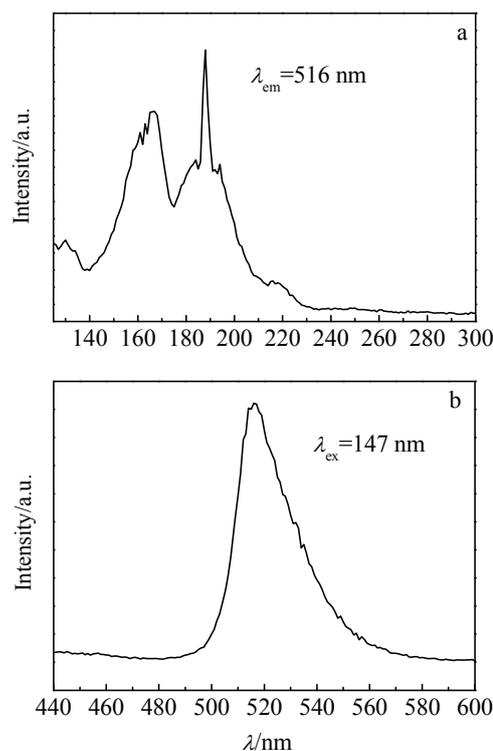


Fig.2 Excitation(a) and emission(b) spectrum of $\text{LaMgAl}_{11}\text{O}_{19}:0.05\text{Mn}^{2+}$ under VUV excitation

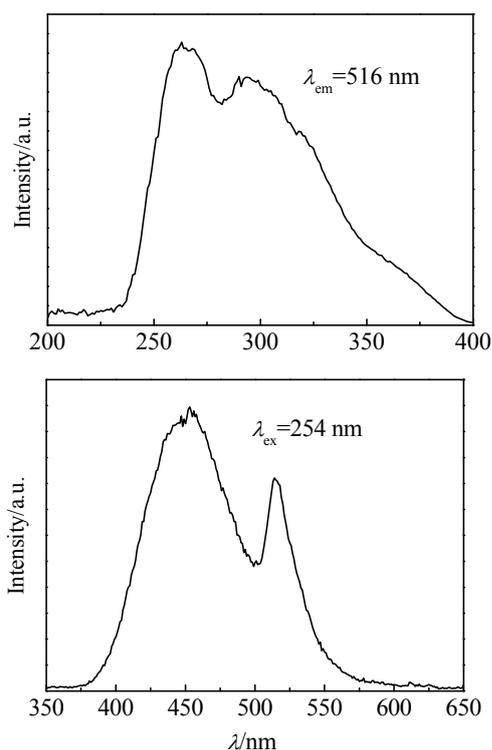


Fig.3 Excitation(a) and emission(b) spectra of LMA:0.10Eu²⁺, 0.05Mn²⁺ under UV excitation

5d to the ground state 4f⁷ and Mn²⁺ from ⁴T₁ to ⁶A₁ respectively. LaMgAl₁₁O₁₉:Mn's emission is very weak, so following finding can be drawn that there occurred an energy transfer effectively from Eu²⁺ to Mn²⁺ in LMA: xEu²⁺, Mn²⁺ under UV excitation. Similar with LMA:Mn²⁺, the emission spectrum of LMA:(xGd³⁺, 0.05Mn²⁺) (0 ≤ x ≤ 0.20) indicates that there was no effective energy transfer from Gd³⁺ to Mn²⁺ in LMA: x Gd³⁺, Mn²⁺ under UV excitation.

Excited by 147 nm, the excitation spectra of the LMA: (xEu²⁺, 0.05Mn²⁺) (0 ≤ x ≤ 0.20) and LMA: (xGd³⁺, 0.05Mn²⁺) (0 ≤ x ≤ 0.20) phosphor consist of host lattice absorption and the activator Mn²⁺ absorption with different Eu²⁺ or Gd³⁺ doping contents. Fig.4 gives the excitation and emission spectra of the LMA:(0.10Eu²⁺, 0.05Mn²⁺) and LMA:(0.15Gd³⁺, 0.05Mn²⁺) phosphor with maximum emission intensity in the VUV region. The excitation spectra of the LMA: (0.10Eu²⁺, 0.05Mn²⁺) are monitored by means of the green emission at 516 nm. The host lattice absorption includes the peaks at 129, 158, 167 nm and the activator absorption peak at 189 nm which is originate from the 3d⁵ → 3d⁴4s transition of Mn²⁺[6-8]. Between 230-300 nm, LMA:(0.10Eu²⁺, 0.05Mn²⁺) with two wide bands with the peaks at about 262 nm and 294 nm attributes to the 4f → 5d transition of Eu²⁺. The emission spectrum of the sample LMA:(0.10Eu²⁺, 0.05Mn²⁺) excited by 147 nm consist of bands at 453 nm and 517 nm, which correspond to transitions of Eu²⁺ from the highest excited state 5d to 4f⁷ ground state

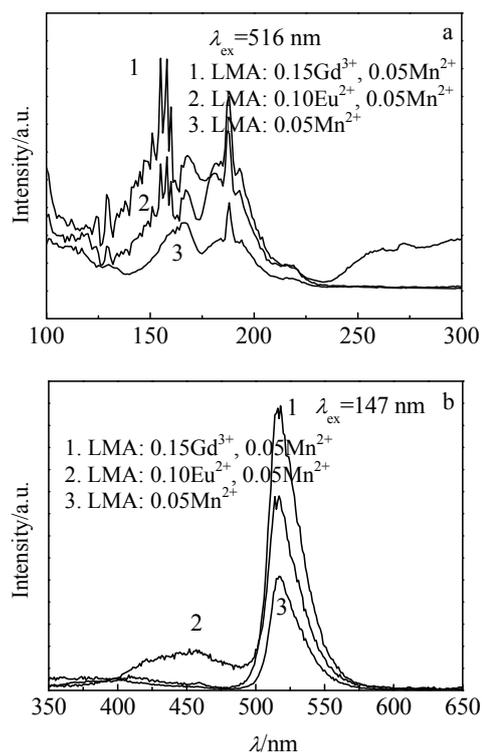


Fig.4 Excitation(a) and emission(b) spectrum of LMA

and Mn²⁺ from ⁴T₁ to ⁶A₁. Here, the emission at 453 nm is so weak that most energy absorbed by Eu²⁺ must be transferred to Mn²⁺. The emission spectrum of the sample LMA:(0.15Gd³⁺, 0.15Mn²⁺) in VUV region has a peak only at 516 nm originated from the ⁴T₁ → ⁶A₁ transition Mn²⁺ ion, the emission intensity is much strengthened because the energy transfers from Gd³⁺ to Mn²⁺. While comparing the excitation spectra of LMA:0.05Mn²⁺ with the excitation spectra of LMA:(0.10Eu²⁺, 0.05Mn²⁺) and LMA:(0.15Gd³⁺, 0.05Mn²⁺), the following result can be shown that Eu²⁺ or Gd³⁺ replaces La³⁺ on the mirror planes and the host lattice absorption is enhanced, which confirms the existence of energy transformation from Eu²⁺ or Gd³⁺ to the activator Mn²⁺. while comparing the emission spectra of LMA:0.05Mn²⁺ with the emission spectra of LMA:(0.10Eu²⁺, 0.05Mn²⁺) and LMA:(0.15Gd³⁺, 0.05Mn²⁺), the another result can be shown that the emission peak at 516 nm becomes about 75% stronger in LMA: (0.10Eu²⁺, 0.05Mn²⁺) and 154% stronger in LMA: (0.15Gd³⁺, 0.05Mn²⁺) than that in LMA:0.05Mn²⁺, which confirms the existence of energy transformation from Eu²⁺ or Gd³⁺ to the activator Mn²⁺ too.

3 Conclusions

- 1) As a flux, H₃BO₃ is better than B₂O₃.
- 2) In the case of the emission spectrum of LMA: x Mn²⁺ (0 ≤ x ≤ 0.125), a wide band at about 516 nm is originated from the ⁴T₁ → ⁶A₁ transition of Mn²⁺ ion.

3) LMA:($x\text{Eu}^{2+}$, 0.05Mn^{2+}) ($0 \leq x \leq 0.20$) and LMA:($x\text{Gd}^{3+}$, 0.05Mn^{2+})($0 \leq x \leq 0.20$) give the result that Mn^{2+} emission is enhanced greatly for the energy transferring from Eu^{2+} and Gd^{3+} to Mn^{2+} efficiently.

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LaMgAl₁₁O₁₉: Mn²⁺和 LaMgAl₁₁O₁₉:RE, Mn²⁺(RE=Eu²⁺, Gd³⁺)的发光特性

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摘 要: 以 H₃BO₃ 作助熔剂, 用高温固相法在 1150 °C、保温 4 h 的条件下成功制备了 LaMgAl₁₁O₁₉:Mn 的单相粉末样品并研究了其真空紫外光激发下的一系列发光特性。在紫外光(254 nm)激发下, LaMgAl₁₁O₁₉: Mn 不发光; 真空紫外光(147 nm)激发下, 观察到 Mn²⁺ 很强的 3d⁵→3d⁴4s 的跃迁发光, 峰值位于 516 nm, 结果表明, Mn²⁺ 的掺杂浓度在 0.05 mol/mol 时发光最强。为了继续增强 LaMgAl₁₁O₁₉ 中 Mn²⁺ 的发光强度, 在固定 Mn²⁺ 的浓度为 0.05 mol/mol 的条件下又合成了 LaMgAl₁₁O₁₉:(Eu²⁺, Mn²⁺)与 LaMgAl₁₁O₁₉:(Gd³⁺, Mn²⁺), 利用 (Eu²⁺, Mn²⁺)和(Gd³⁺, Mn²⁺)间存在有效的能量传递的特性, 很好的达到了增强 Mn²⁺ 的发光的目的。

关键词: 助熔剂; 发光; LaMgAl₁₁O₁₉; 荧光粉

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