



Luminescence Properties of Dy³⁺-Doped CaLaP₃O₁₀ White-Light Phosphors Under Vacuum Ultraviolet Excitation†

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New Dy³⁺-doped CaLaP₃O₁₀ white light phosphors were satisfactorily synthesized by solid phase reaction. The luminescence properties of the CaLa_{1-x}P₃O₁₀:xDy³⁺ under vacuum ultraviolet (VUV) excitation were investigated. The emission spectra show that the phosphors can efficiently emit blue light and yellow light and finally obtain white light. The excitation spectrum monitored at 572 nm indicates that the samples can efficiently absorb vacuum ultraviolet light from 100 to 300 nm with the strongest peak at about 172 nm and the energy can transfer to the levels of Dy³⁺ ion from the host materials. Moreover, the white light phosphors materials are activated by a Dy³⁺ ion and the luminescence of CaLa_{1-x}P₃O₁₀:xDy³⁺ under vacuum ultraviolet excitation was effective. Therefore, it may have the promising of being applied to mercury-free fluorescence lamp.

Keywords: White light, Vacuum ultraviolet, Phosphors, Phosphate.

INTRODUCTION

In recent years, luminescence materials doped with Dy³⁺ have attracted broad attention due to its white emission under vacuum ultraviolet excitation¹⁻⁴. As a rule, Dy³⁺ has two prominent bands in the emission spectra in many host matrices. The yellow band (572 nm) corresponds to the hypersensitive transition ⁴F_{9/2}→⁶H_{13/2} (ΔL = 2, ΔJ = 2) and the blue band (478 nm) corresponds to the ⁴F_{9/2}→⁶H_{15/2} transition. To obtain near-white emission with only a Dy³⁺-activated phosphors is possible by suitably adjust the yellow-to-blue intensity ratio(Y/B) value. So Dy³⁺-activated phosphors materials are potential white light materials and can use in mercury-free fluorescence lamp. Furthermore, for mercury-free fluorescence lamp, the excitation energy was mainly consisted of vacuum ultraviolet radiation, however most of vacuum ultraviolet radiation energy is absorbed by the host materials, if the energy can be transferred from host materials to rare-earth ions, the rare-earth-ions can emit visible light. Therefore the effectiveness of the host absorption and the energy transfer play very important role in vacuum ultraviolet-excited phosphors materials being applied to mercury-free fluorescence lamp.

Rare-earth-ions-doped phosphate-based luminescence materials have been applied in various fields, such as colour

televisions, mercury-free fluorescence lamp and visible light¹⁻⁵. So it can be inferred that orthophosphates are potential host crystal for its application in vacuum ultraviolet range^{6,7}. ARP₃O₁₀ (A = Ba or Ca; R = La, Ce or Sm) is one of complex polyphosphates and ARP₃O₁₀ with a monazite type monoclinic crystal structure^{8,9}. The results show that the P₃O₁₀⁵⁻ groups can efficiently absorb the excited energy and transfer the energy. Thus we confirm that monoclinic P₃O₁₀⁵⁻ may be a potential host materials under vacuum ultraviolet excitation. In this paper, we synthesized CaLa_{1-x}P₃O₁₀:xDy³⁺ crystal phosphors by the solid phase reaction and investigated the luminescence properties of CaLa_{1-x}P₃O₁₀:xDy³⁺ crystal phosphors in vacuum ultraviolet range.

EXPERIMENTAL

CaLa_{1-x}P₃O₁₀:xDy³⁺ are prepared by solid phase reaction. first, starting materials are prepared by (NH₄)₂HPO₄ (AR), La₂O₃ (99.99 %), Dy₂O₃ (99.99 %) and CaCO₃ (99 %). The doping amount x of Dy₂O₃ is from 0.04-0.15 %. Starting materials are mixed and grounded together, then the resulting mixture is heated at 400 °C for 1 h and the resulting mixture is heated again at 700 °C for 1 h, reground and reheated at 1000 °C for 8 h.

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The powder X-ray diffraction (XRD) patterns of samples is collected in the 2θ range $10\text{--}80^\circ$ by XRD using Rigaku D/MAX-2400 X-ray diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation. The vacuum ultraviolet excitation and emission spectra are measured by an Edinburgh Instruments FLS920T. The emission and excitation spectra are measured by a VM504-type the vacuum monochromator using a 150W Deuterium lamp as the vacuum ultraviolet lighting source of the spectrometer system. The vacuum ultraviolet excitation spectrum are corrected by dividing the excitation intensity of sodium salicylate.

RESULTS AND DISCUSSION

The powders of $\text{CaLa}_{1-x}\text{P}_3\text{O}_{10}:x\text{Dy}^{3+}$ are all white coloured. Fig. 1 shows the XRD pattern of the $\text{CaLa}_{0.94}\text{P}_3\text{O}_{10}:0.06\text{Dy}^{3+}$, the XRD pattern of the other samples were also similar and were very similar to the XRD pattern of $\text{CaLaP}_3\text{O}_{10}$ ⁸. Because all the peaks of samples are indexed to the monazite-type structure. Therefore, all the powders of $\text{CaLa}_{1-x}\text{P}_3\text{O}_{10}:x\text{Dy}^{3+}$ are a single phase with the monoclinic phase monazite-type structure.

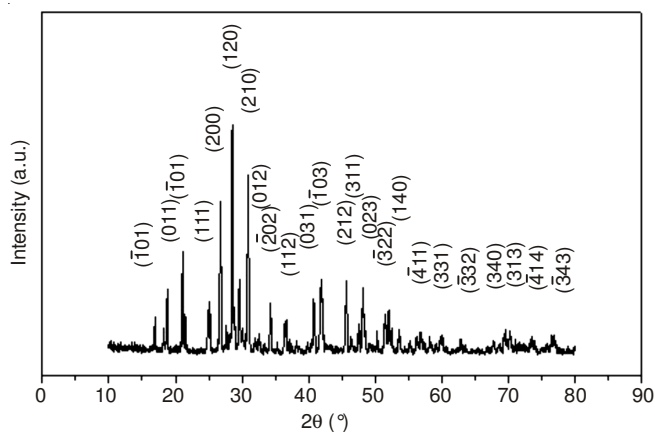


Fig. 1. X-Ray powder diffraction pattern of $\text{CaLa}_{0.94}\text{P}_3\text{O}_{10}:0.06\text{Dy}^{3+}$

The emission spectrum of $\text{CaLa}_{1-x}\text{P}_3\text{O}_{10}:x\text{Dy}^{3+}$ under 172 nm excitation was shown in Fig. 2. The peaks at 404, 458, 478, 572 and 660 nm correspond to ${}^4\text{F}_{7/2} \rightarrow {}^6\text{H}_{15/2}$, ${}^4\text{F}_{7/2} \rightarrow {}^6\text{H}_{13/2}$, ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$, ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{11/2}$ transitions of Dy^{3+} , respectively^{10,11}. ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ transition corresponds to the hypersensitive transition, the hypersensitive transition is strongly influenced by the environment^{12,13}. It is clear that the intensities of the peaks at 478 and 572 nm are gradually enhanced along with increasing of x and become strongest when $x = 0.06$, then decrease when $x > 0.06$. Therefore, by suitable adjusting the Y/B ratio, the chromaticity coordinates of $\text{CaLa}_{1-x}\text{P}_3\text{O}_{10}:x\text{Dy}^{3+}$ phosphors can be adjusted to white light zone and can be used for the mercury-free lamp.

The influence for luminescence materials intensity of the main emission peaks at 572 nm with the increasing of the concentration x of $\text{CaLa}_{1-x}\text{P}_3\text{O}_{10}:x\text{Dy}^{3+}$ was shown in Fig. 3. It is obvious that the luminescence materials intensities of $\text{CaLa}_{1-x}\text{P}_3\text{O}_{10}:x\text{Dy}^{3+}$ increase along with the increasing of x , the luminescence materials intensity is the strongest at $x = 0.06$ and gradually decrease due to the concentration quenching when $x > 0.06$.

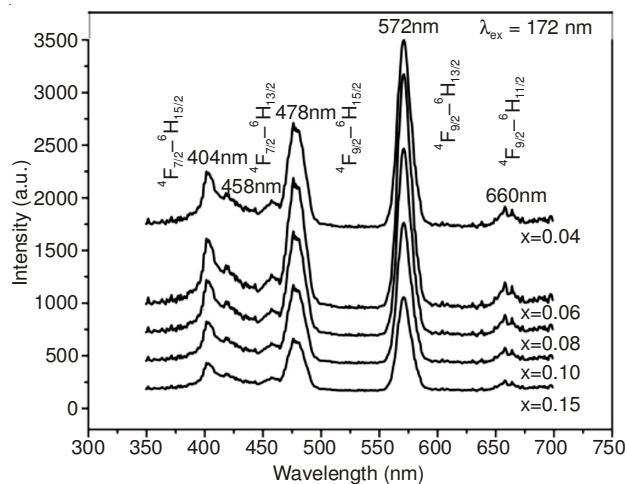


Fig. 2. Emission spectra of $\text{CaLa}_{1-x}\text{P}_3\text{O}_{10}:x\text{Dy}^{3+}$ ($0 < x \leq 0.15$)

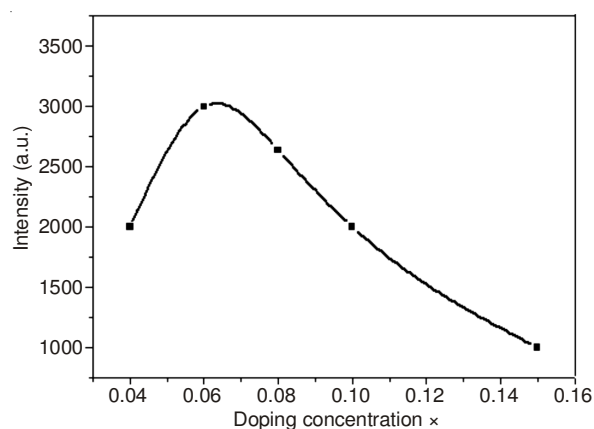


Fig. 3. Influence for luminescence intensity of the main emission peaks at 572 nm along with the increase in doping amount x

The excitation spectrum of $\text{CaLa}_{0.94}\text{P}_3\text{O}_{10}:0.06\text{Dy}^{3+}$ monitored at 572 nm was shown in Fig. 4. The broad band ranging from 115 to 160 nm correspond to the host absorption of polyphosphate and the similar observations in other system have been also corresponded to previous work^{9,14,15}. The band at around 172 nm should correspond to $f-d$ transition of Dy^{3+} ^{16,17}. The strongest excitation at near 172 nm indicates that the $\text{CaLa}_{1-x}\text{P}_3\text{O}_{10}:x\text{Dy}^{3+}$ phosphors might be applied at the mercury-free fluorescence lamp.

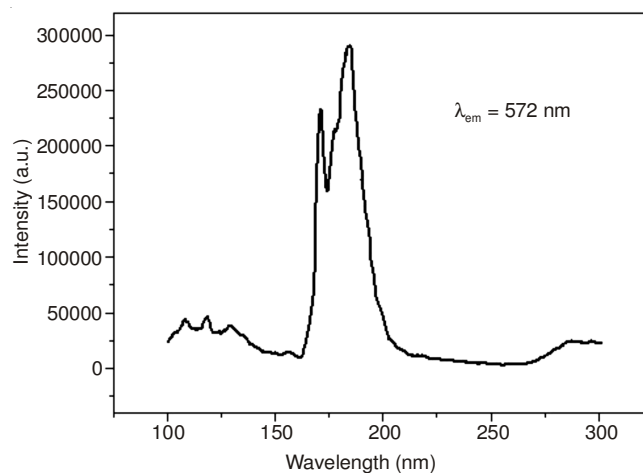


Fig. 4. Excitation spectrum of $\text{CaLa}_{1-x}\text{P}_3\text{O}_{10}:x\text{Dy}^{3+}$ ($x = 0.06$)

The chromaticity coordination (x, y) of CaLa_{1-x}P₃O₁₀:xDy³⁺ phosphors excited under 172 nm in the CIE 1931 chromaticity diagram was shown in Fig. 5. It is obvious that the chromaticity coordinates of CaLa_{1-x}P₃O₁₀:xDy³⁺ phosphors gradually moves to the warm white area along with decreasing concentration x; when x < 0.06, it moves to the cold white zone in contrary orientation. Listed chromaticity coordinates are in Table-1, which are all located in white light range.

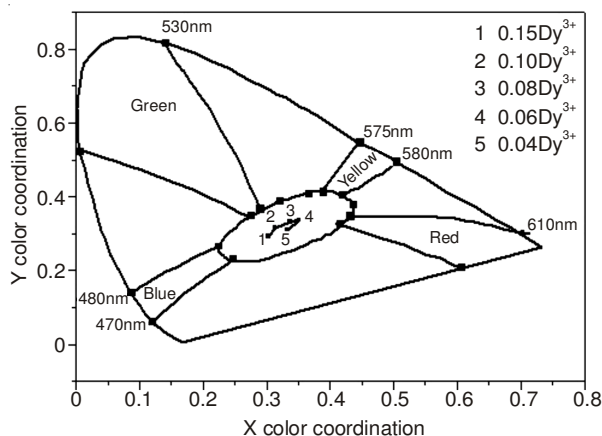


Fig. 5. Chromaticity coordinates (x, y) of CaLa_{1-x}P₃O₁₀:xDy³⁺ (0 < x ≤ 0.15) under 172 nm excitation in the CIE 1931 chromaticity diagram

TABLE-1
CHROMATICITY COORDINATION OF
CaLa_{1-x}P₃O₁₀:xDy³⁺ (0 < x ≤ 0.15)

Amount of doping x	Chromaticity	
	Coordination x	Coordination y
x = 0.04	0.321	0.310
x = 0.06	0.339	0.338
x = 0.08	0.328	0.328
x = 0.10	0.305	0.318
x = 0.15	0.296	0.290

Conclusion

New CaLa_{1-x}P₃O₁₀:xDy³⁺ white light phosphors with monoclinic crystal structure were synthesized by solid phase

reaction. The *f-d* transition of Dy³⁺ ion was observed locating at about 172 nm. Two strong emission bands locating at 478 and 572 nm under 172 nm excitation were observed and the optimal concentration of Dy³⁺ is x = 0.06. The chromaticity coordinates of CaLa_{1-x}P₃O₁₀:xDy³⁺ phosphors are located in the white-light region. Thereby, we obtained the white light by a single activated ion in a single system. Therefore, CaLa_{1-x}P₃O₁₀:xDy³⁺ may have a potential application for mercury-free fluorescence lamp.

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