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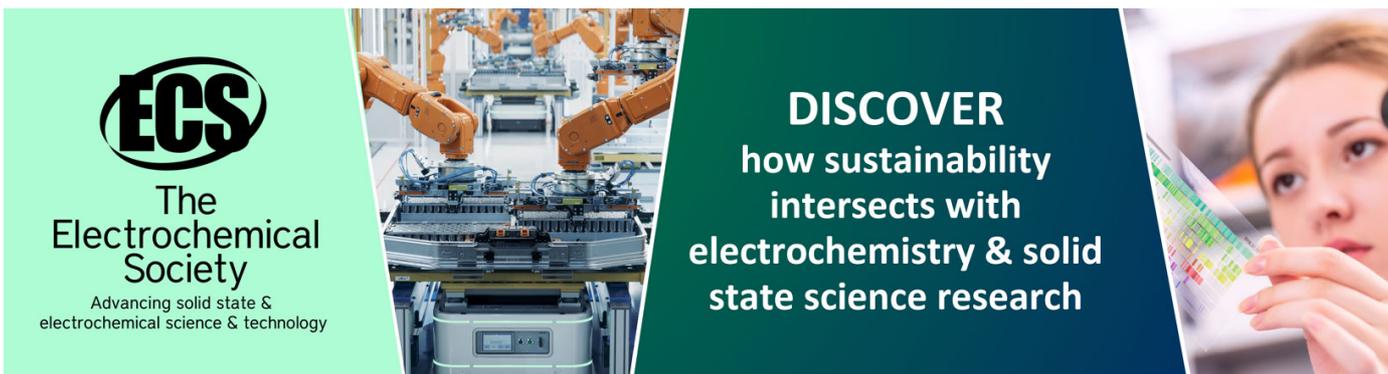
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Synthesis and Luminescence Properties of Orange-Red Phosphors Na Y (WO₄)₂: Eu³⁺, Sm³⁺

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Abstract. Orange-red phosphors NaY(WO₄)₂:Eu³⁺, Sm³⁺ were successfully synthesised by hydrothermal synthesis method. The photoluminescence (PL) properties were investigated. The PL emission spectrum of Na Y (WO₄)₂: Eu³⁺ shows good luminous properties under 398 nm, which mainly located at 596 and 615 nm, with the additional of Sm³⁺ could broaden and increase emission intensity of Eu³⁺, which could be suitable for the excitation of UV light emitting diodes (LEDs) (~400 nm). The PL results indicated that Na Y (WO₄)₂: Eu³⁺, Sm³⁺ may be a promising red phosphor candidate for use in white LEDs.

1. Introduction

White light emitting diodes (WLEDs) as the next generation solid state lighting, have attracted much attention attribute to their advantage, such as quite low power consumption, high efficiency, low maintenance, and so on. Commonly, we use the yellow phosphor YAG: Ce³⁺ coated on the blue In GaN chip, while, such a combination exhibits a poor colour rendering index (<80) as the result of the lack of a red-light component (above 600 nm). To overcome these disadvantages, WLEDs based on red, green and blue primary colours have been studied [1-3]. The WLEDs can be achieved by combining red, green and blue light emitting diodes (LEDs), precoating those three phosphor colours onto a UV LED or precoating green and red phosphors onto a blue LED [4-7]. Efficient red emitting phosphors are necessary for both of these methods. Y₂O₂S:Eu³⁺ for red phosphor is generally used, unfortunately, it is inefficient under the excitation of 370-410 nm, and its decomposition products are harmful to the environment. Therefore, it is an attractive and challenging research task to develop novel, stable red phosphors that can be excited effectively in the near UV (n-UV).

Tungstate compounds have been extensively studied as host material for phosphors when doped by lanthanide ions, and tungstate NaY(WO₄)₂ was chosen as the host material as it is easily obtained and has lower cost, expediently synthesise condition, good stabilization and good luminescence properties. Tungstate NaY(WO₄)₂ as the host material to synthesise phosphors has been investigated by some researchers and represents good luminescence properties when doped by rare earth ions. Eu³⁺ is a preferable choice as an activator ion which has been used in most red phosphors. In order to increase and broaden the emission region, adding codoped ions in phosphors is an effective method, and



Sm^{3+} could be a good sensitizer. As the result of Sm^{3+} ions displaying strong linear absorption peak, it makes the phosphor match well with the LED (InGaN based) emission (~400 nm); it indicates that Eu^{3+} and Sm^{3+} co-doped phosphors could increase the absorption near 400 nm. In most reports, the emission intensity of the Eu^{3+} emission is enhanced by additional Sm^{3+} doping, e.g. $\text{SrIn}_2\text{O}_4: \text{Sm}^{3+}, \text{Eu}^{3+}$, $\text{LaOCl}: \text{Sm}^{3+}, \text{Eu}^{3+}$, $\text{Lu}_2\text{O}_3: \text{Sm}^{3+}, \text{Eu}^{3+}$. Nevertheless, a few reports about Eu^{3+} and Sm^{3+} co-doped in silicates phosphors are found, and no report about the investigation of Eu^{3+} and Sm^{3+} co-doped $\text{NaY}(\text{WO}_4)_2$ orange-red phosphors is found. In this study, a novel red phosphor $\text{NaY}(\text{WO}_4)_2: \text{Sm}^{3+}, \text{Eu}^{3+}$ sample was synthesised by the solid-state reaction method. The luminescence properties and energy transfer between Sm^{3+} and Eu^{3+} were also discussed. The phosphor could be effectively excited by n-UV, which could be suitable for use in WLEDs.

2. Experimental

All the samples were prepared by hydrothermal synthesis method. Analytical reagent grade $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and spectrographically pure $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were employed as reactants. All samples were characterized by X-ray powder diffraction (XRD). The XRD measurements were performed on a Bruker/D8-Advance with Cu K α radiation ($\lambda=0.1518$ nm). The operation voltage and current were maintained at 40 kV and 40 mA, respectively. A scan rate of 2 ($^\circ$)/min was applied to record the patterns in the range of $2\theta=10^\circ-80^\circ$. The excitation and emission spectra were measured by a Hitachi F-7000 fluorescence spectrofluorometer equipped with a 150W Xe lamp. All the experiments were performed at room temperature.

3. Result and discussion

The phase purities and the crystal structures of the as-prepared powder samples were characterized by XRD at room temperature. The XRD patterns of $\text{NaY}(\text{WO}_4)_2$, $\text{NaY}(\text{WO}_4)_2:0.05\text{Eu}^{3+}$, $\text{NaY}(\text{WO}_4)_2:0.05\text{Eu}^{3+}/0.03\text{Sm}^{3+}$ phosphor samples are seen in Figure 1. All of the diffraction peaks are accord with $\text{NaY}(\text{WO}_4)_2$ (JCPDS card No.48-0886). All these samples are of single phase without any impurities. This indicates that doping of rare earths in $\text{NaY}(\text{WO}_4)_2$ host with such a small concentration has no other phase specific changes. The radius of Eu^{3+} (0.095 nm) and Sm^{3+} (0.096 nm) nearly to the radii of Y^{3+} ion, the doping ions replace the Y^{3+} ions and unchanged the structure of $\text{NaY}(\text{WO}_4)_2$.

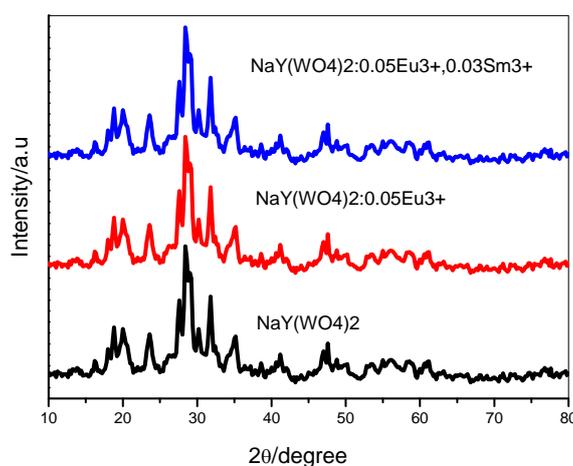


Figure 1. Typical XRD patterns of $\text{NaY}(\text{WO}_4)_2$, $\text{NaY}(\text{WO}_4)_2:0.05\text{Eu}^{3+}$, $\text{NaY}(\text{WO}_4)_2:0.05\text{Eu}^{3+}/0.03\text{Sm}^{3+}$

Figure 2 shows the photoluminescence (PL) emission spectra of Eu^{3+} doped $\text{NaY}(\text{WO}_4)$ phosphor samples with different concentration under 398 nm. As shown in Figure 2, the emission spectrum excited by 398 nm covers the region from 550 to 700 nm, consisting of lines in the orange and red spectral range exhibit exclusively the characteristic f-f transitions of Eu^{3+} , mainly, ${}^5\text{D}_0\text{-}{}^7\text{F}_1$ (596 nm), ${}^5\text{D}_0\text{-}{}^7\text{F}_2$ (615 nm), respectively. Inset of Figure 2 shows the emission intensity of $\text{NaY}(\text{WO}_4)_2:\text{xEu}^{3+}$ ($\text{x} = 0.01\text{--}0.09$) with different concentrations. From figure 2 we can see that the intensity of all of the emissions are enhanced significantly with the Eu^{3+} concentration increasing and gradually decreases as the doping concentration becomes higher than $\text{x}=0.05$. Therefore, the optimum doping concentration of Eu^{3+} is fixed at 5 mol%.

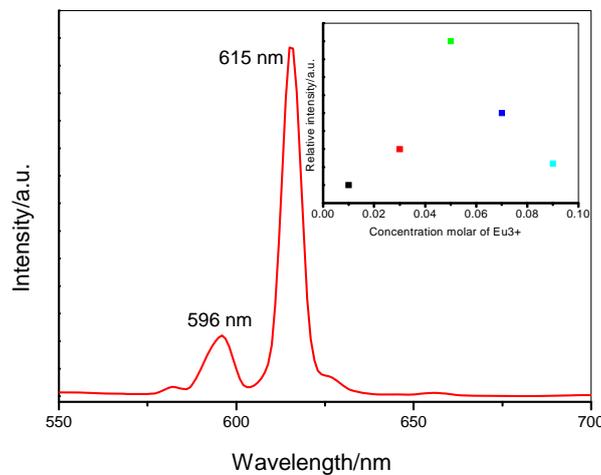


Figure 2. Photoluminescence excitation and emission spectra of $\text{NaY}(\text{WO}_4)_2:\text{Eu}^{3+}$

The excitation spectrum of $\text{NaY}(\text{WO}_4)_2: 0.05\text{Eu}^{3+}, 0.03\text{Sm}^{3+}$ samples monitored at 615 nm are shown in Figure 3, it can be seen clearly that the excitation spectrum of $\text{NaY}(\text{WO}_4)_2:0.05\text{Eu}^{3+}, 0.03\text{Sm}^{3+}$ consists of the excitation peaks of in n-UV region (~ 400 nm), it is found that the excitation wavelength of the co-doped phosphors matches well with the emission wavelength of the UV LEDs (~ 400 nm).

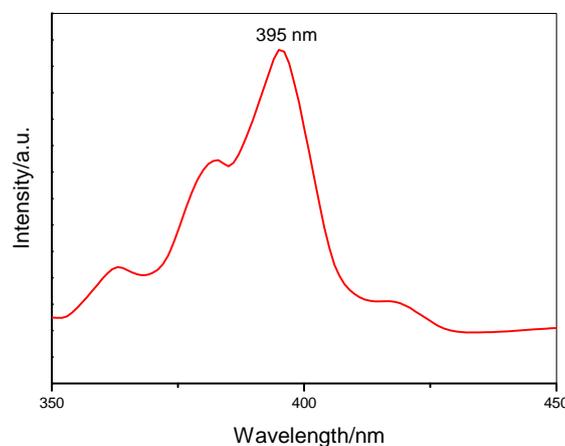


Figure 3. Photoluminescence excitation spectrum of $\text{NaY}(\text{WO}_4)_2:0.05\text{Eu}^{3+}, 0.03\text{Sm}^{3+}$

Figure 4 shows the emission spectra of $\text{NaY}(\text{WO}_4)_2:0.05\text{Eu}^{3+}, y\text{Sm}^{3+}$ phosphor samples under the excitation of 395 nm. From Figure 4, the characteristic emission peaks of both Eu^{3+} and Sm^{3+} under the excitation of Sm^{3+} at 395 nm can be observed. Comparing figure 4 and figure 5, it indicates that additional Sm^{3+} co-doped in $\text{NaY}(\text{WO}_4)_2:0.05\text{Eu}^{3+}$ phosphors could increase the emission intensity of Eu^{3+} , it is proof that the energy transfers from Sm^{3+} to Eu^{3+} . From Figure 4, it can be seen that the optimum doping concentration of Sm^{3+} is fixed at 3mol%. The emission intensity is the maximum as the doping concentration of Sm^{3+} becomes higher than 3mol%, and the emission intensity decreases as the result of the effect of concentration quenching in the host. Such behavior also strongly indicates that energy transfer exists.

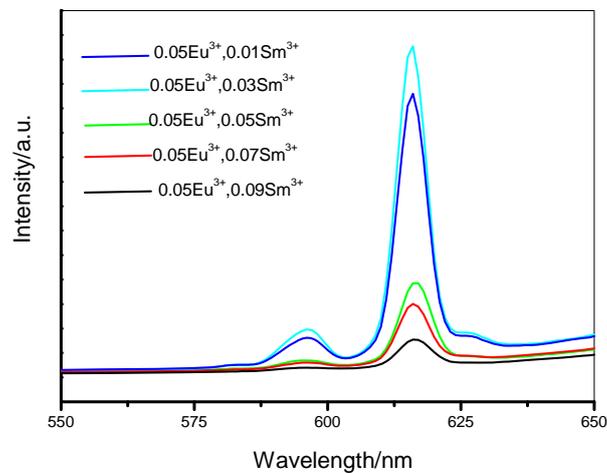


Figure 4. Photoluminescence emission spectra of $\text{NaY}(\text{WO}_4)_2:0.05\text{Eu}^{3+}, y\text{Sm}^{3+}$

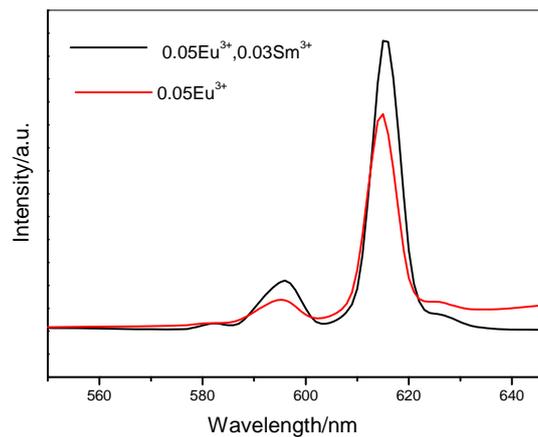


Figure 5. Photoluminescence emission spectra of $\text{NaY}(\text{WO}_4)_2:0.05\text{Eu}^{3+}$ and $\text{NaY}(\text{WO}_4)_2:0.05\text{Eu}^{3+}, y\text{Sm}^{3+}$

4. Conclusion

In summary, a series of NaY (WO₄)₂:0.05Eu³⁺ and NaY (WO₄)₂:0.05Eu³⁺, ySm³⁺ phosphors have been synthesized by hydrothermal synthesis method. The phosphors NaY (WO₄)₂:0.05Eu³⁺, 0.03Sm³⁺ excited under the UV region and show orange-red emitting light extended from 550 to 700 nm. The addition of Sm³⁺ could increase and broaden the absorption in the n-UV region (-400 nm), it makes the phosphor match well with LED (In GaN based) emission (-400 nm) and attractive for application in LEDs. additional Sm³⁺ co-doped in NaY (WO₄)₂: 0.05Eu³⁺ phosphors could increase the emission intensity of Eu³⁺, it is proof that the energy transfers from Sm³⁺ to Eu³⁺. Therefore, the NaY(WO₄)₂:0.05Eu³⁺, 0.03Sm³⁺ phosphor could act as a potential orange-red emitting phosphor for UV LEDs.

Acknowledgments

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References

- [1] Z.J. Wang, P.L. Li, Q.L. Guo, Z.P. Yang, Luminescent property of a novel yellow emitting phosphor Sr₂ZnMoO₆:Dy³⁺, *Optik*. 126 (2015) 731-734.
- [2] S. Schmiechen, M. Siegert, A. Tücks, P.J. Schmidt, W. Schnick, Narrow-band green emitting nitridolithoalumosilicate Ba [Li₂ (Al₂Si₂) N₆]:Eu²⁺ with framework topology whj for LED/LCD-backlighting applications philipp strobel, *Chem.Mater.* 27 (2015) 6109-6115.
- [3] A.J. Carrión, M. Ocaña, J.G. Sevillano, E. Cantelar, A.I. Becerro, New single-phase, white-light-emitting phosphors based on δ-Gd₂Si₂O₇ for solid-state lighting, *J.Mater.Chem.C.* 118 (2014) 18035-18043.
- [4] H. Yu, W.W. Zi, S. Lan, S.C. Gan and H.F. Zou, Photoluminescence properties and energy transfer in Ce³⁺/Dy³⁺ co-doped Sr₃MgSi₂O₈ phosphors for potential application in ultraviolet white light-emitting diodes, *Luminescence.* 28 (2013) 679-684.
- [5] P.J. Wang, X.H. Xu, D.C. Zhou, X. Yu and J.B. Qiu, Sunlight activated long-lasting luminescence from Ba₅Si₈O₂₁: Eu²⁺, Dy³⁺ phosphor, *Inorg. Chem.* 54 (2015) 1690-1697.
- [6] F.X. Liu, Q.H. Liu, Y.Z. Fang, N. Zhang, B. Yang and G.Y. Zhao, White light emission from NaLa(PO₃)₄: Dy³⁺ single-phase phosphors light-emitting diodes, *Ceram. Int.* 41 (2015) 1917-1920 .
- [7] K. Li, X.M. Liu, Y. Zhang, X.J. Li, H.Z. Lian and J. Lin, Host-Sensitized luminescence properties in CaNb₂O₆:Ln³⁺ (Ln³⁺ =Eu³⁺/Tb³⁺/Dy³⁺/Sm³⁺) phosphors with abundant colors, *Inorg. Chem.* 54 (2015) 323-333.