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Article

Synthesis and Properties of a Red $\text{Na}_5\text{Zn}_2\text{Gd}_{1-x}(\text{MoO}_4)_6: x\text{Eu}^{3+}$ Phosphor

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Abstract: The novel phosphor Eu^{3+} doped $\text{Na}_5\text{Zn}_2\text{Gd}(\text{MoO}_4)_6$ triple molybdate were prepared by the sol-gel method. The structure, morphology, and luminescent properties have been characterized by X-ray diffraction, thermogravimetry-differential thermal analysis, scanning electron microscopy, FTIR spectroscopy and Luminescence spectroscopy. The results indicated that the synthesized $\text{Na}_5\text{Zn}_2\text{Gd}_{1-x}(\text{MoO}_4)_6: x\text{Eu}^{3+}$ phosphor consisted of a pure phase with monoclinic structure. Under excitation at 465 nm, the $\text{Na}_5\text{Zn}_2\text{Gd}_{1-x}(\text{MoO}_4)_6: x\text{Eu}^{3+}$ phosphor exhibits intensive red emission band around 610 nm corresponding to the transition of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ is much higher than that $^5\text{D}_0 \rightarrow ^7\text{F}_1$ at 594 nm, which was appropriate for blue LED. According to the influence of the synthesis conditions, the phosphors show the highest emission intensity as the doping concentration of Eu^{3+} was 25 mol.% and the molar ratio of citric acid to metal ions was 2:1. $\text{Na}_5\text{Zn}_2\text{Gd}_{0.75}(\text{MoO}_4)_6: 0.25 \text{Eu}^{3+}$ with the color coordinates ($x = 0.658$, $y = 0.341$) is a stable red phosphor for blue-based white LEDs due to it is closer to the NTSC standard values (0.670, 0.330) comparing with the color coordinates (0.48, 0.50) of the commercial $\text{Y}_2\text{O}_2\text{S}: \text{Eu}^{3+}$ red phosphor.

Keywords: $\text{Na}_5\text{Zn}_2\text{Gd}_{1-x}(\text{MoO}_4)_6: x\text{Eu}^{3+}$; red phosphor; luminescent properties

1. Introduction

White light-emitting diode (WLED) has attracted wide attention due to its advantages of high luminous efficiency, long lifetime and low power consumption and environmental friendliness [1,2]. The red phosphors can be excited by blue and near-ultraviolet in particular. The commercial sulfide phosphors $\text{CaS}: \text{Eu}^{2+}$, $\text{Y}_2\text{O}_2\text{S}: \text{Eu}^{3+}$ show limitations, such as being chemically unstable and having a short lifetime under ultraviolet radiation, thus hindering the development of a highly efficient white LED [3–5]. Therefore, more interest is being focused on the search for a stable red phosphor with intense absorption in the near-UV to the blue spectral region [6,7]. With strong physical and chemical stability, molybdates have been investigated as potential red emitting phosphors. It is well known that Eu^{3+} is an rare earth ion generating red light and can be effectively stimulated by blue light and UV light to achieve red emission [8–12]. Molybdates have been widely used as host materials to phosphors based on their low phonon energy, outstanding chemical and physical properties, good thermal stability, and strong charge transfer zone in the ultraviolet region [13,14]. Eu^{3+} -doped molybdates are red-emitting phosphors due to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ spin and parity-forbidden transition. Currently, some ternary molybdate compounds have emerged as promising laser materials [15–18]. Based on relevant studies, the triple molybdates have a layered structure which is tetrahedral, and four O^{2-} ions are positioned in four corners of the tetrahedron [19]. The MoO_4^{2-} isolated island-like tetrahedron was distributed in the crystal, in which the compounds of divalent ions (such as Zn, Ba, Mg, and Sr) were coordinated by six oxygen atoms, and the O^{2-} were from the MoO_4^{2-} tetrahedral group [20]. In this work, a new kind of triple molybdate compound $\text{Na}_5\text{Zn}_2\text{Gd}_{1-x}(\text{MoO}_4)_6: x\text{Eu}^{3+}$ ($0.03 \leq x \leq 0.35$) red phosphor with scheelite structure was prepared, and its luminescent properties were studied in detail for the first time. The obtained phosphor compared with commercial red phosphor $\text{Y}_2\text{O}_2\text{S}: \text{Eu}^{3+}$ is closer to

standard color coordinate values by the color coordinate calculated, indicating that the red phosphor has high color purity.

2. Experimental

2.1. Phosphors Preparation

The red phosphors $\text{Na}_5\text{Zn}_2\text{Gd}_{1-x}(\text{MoO}_4)_6: x\text{Eu}^{3+}$ ($0.03 \leq x \leq 0.35$) were prepared using citrate method with raw materials of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (AR), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (AR), $\text{C}_6\text{H}_8\text{O}_7 \cdot 2\text{H}_2\text{O}$ (AR), NaOH (AR), Eu_2O_3 (99.99%) and Gd_2O_3 (99.99%). The detailed experimental process is similar to that in Refs. [8,9]. Firstly, rare-earth oxides (Eu_2O_3 , Gd_2O_3) were dissolved in 1:1 HNO_3 under vigorous stirring, and the excess HNO_3 was removed under heating. Then a stoichiometric amount of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, NaOH, and $\text{Zn}(\text{NO}_3)_2$ solution was obtained by dissolving in deionized water. Subsequently, $0.1 \text{ mol L}^{-1} \text{Gd}(\text{NO}_3)_3$ and $0.1 \text{ mol L}^{-1} \text{Eu}(\text{NO}_3)_3$ solution added to the $\text{Zn}(\text{NO}_3)_2$ solution mix well and then citric acid dissolved in a round-bottomed flask. NaOH was added to the other in the $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ solution stirring to dissolve and poured into a round bottom flask and stirred uniformly, and 60°C for 4 h after the pH of the solution was adjusted to 7-8 (with white precipitate). The resulting sample was placed in a drying oven at 120°C for 10h, after the water was gradually reduced to give a brown powder precursor, then calcined in the furnace at 800°C for 2 h, and cooled. As a result of the last process, white powders of the $\text{Na}_5\text{Zn}_2\text{Gd}(\text{MoO}_4)_6: \text{Eu}^{3+}$ were synthesized.

2.2. Characterizations

X-ray powder diffractions (XRD) of the samples were examined using the Bruker D8-Advance diffractometer. The crystallization processes of the complex precursors were examined by thermogravimetry differential thermal analysis (TG-DTA, DTG-60H, Harriet Island ferry), using a heating rate of $10^\circ\text{C}/\text{min}$ in an air atmosphere. The infrared spectrum was measured on a Nicolet-6700 Fourier transform infrared spectrometer, KBr pellet. The morphology of the samples was characterized by Japan's Hitachi S-3400N scanning electron microscopy. Luminescent properties of the samples were carried out using a Japan's Hitachi F-4500 fluorescence spectrometer with a 150W-Xenon lamp under working voltage 400V, scan rate $1200 \text{ nm}/\text{min}$, and the excitation and emission slits were set at 2.5 nm. All the measurements were performed at room temperature.

3. Results and Discussion

3.1. TG-DTA Analysis of $\text{Na}_5\text{Zn}_2\text{Gd}_{1-x}(\text{MoO}_4)_6: x \text{Eu}^{3+}$

To choose the best thermal decomposition temperature for the samples, the TG-DTA curves of the $\text{Na}_5\text{Zn}_2\text{Gd}(\text{MoO}_4)_6: \text{Eu}^{3+}$ precursors were studied, as shown in Figure 1. The TG curve shows two distinct weight loss steps upto 500°C and no further weight loss was registered between 500 and 1000°C . The weight loss is related to the decomposition of the organic matrix. The DTA curve consist of three exothermic peaks at 220 , 331 , 420°C . The peak at 220 and 331°C indicate that the thermal events can be associated with the exhaustion of organic species of surface absorbed water and citric acid, and the third exothermic peak at 420°C is due to the crystallization of $\text{Na}_5\text{Zn}_2\text{Gd}(\text{MoO}_4)_6$ powder from the amorphous component. However, the particle size distribution of the sample was more uniformity at 800°C than at other thermal decomposition temperature.

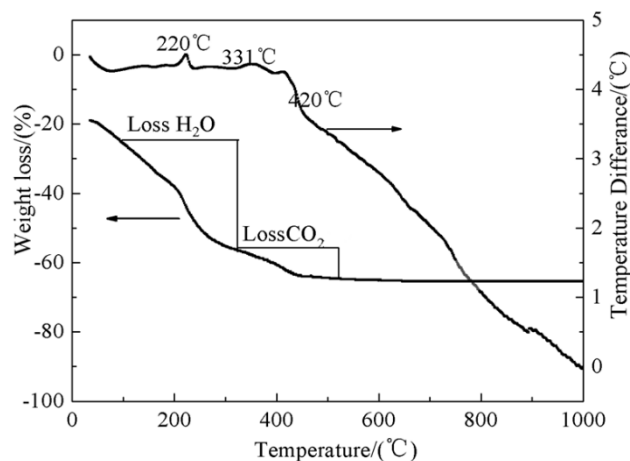


Figure 1. TG-DTA curves of the $\text{Na}_5\text{Zn}_2\text{Gd}(\text{MoO}_4)_6: \text{Eu}^{3+}$.

3.2. Structure and Morphology of $\text{Na}_5\text{Zn}_2\text{Gd}_{1-x}(\text{MoO}_4)_6: x \text{Eu}^{3+}$

Figure 2(a) shows the XRD patterns of $\text{Na}_5\text{Zn}_2\text{Gd}_{1-x}(\text{MoO}_4)_6: x \text{Eu}^{3+}$ ($x = 0.0, 0.25$) annealed at 800°C . All of the diffraction peaks coincide well with the standard data of $\text{Na}_{2.2}\text{Zn}_{0.9}(\text{MoO}_4)_2$ (JCPDS NO. 49-0898) and no extra peaks from any impurities are detected, which indicates that all the phosphors adopt a monoclinic powellite structure of $\text{Na}_{2.2}\text{Zn}_{0.9}(\text{MoO}_4)_2$ and Eu^{3+} doping do not impact the crystal structure of the host matrix. The diffraction peaks at $2\theta = 12.94^\circ$ is almost invisible caused by the preferred orientation of the sample, which is no crystal growth along the (020) plan orientation. The diffraction peak intensity at 30.28° is significantly weaker than that in the standard card, thus indicating that the existence of an incomplete crystal structure on the $\text{Na}_5\text{Zn}_2\text{Gd}_{1-x}(\text{MoO}_4)_6: x \text{Eu}^{3+}$ surface can interfere with the diffraction of the X-rays, resulting to a reduced intensity of the diffraction peak.

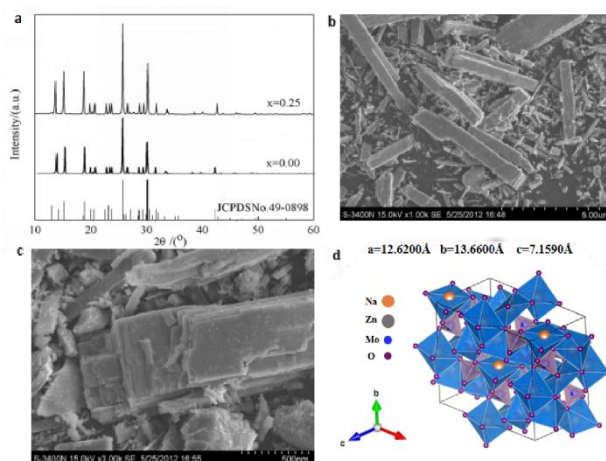


Figure 2. Structure and Morphology of $\text{Na}_5\text{Zn}_2\text{Gd}_{1-x}(\text{MoO}_4)_6: x \text{Eu}^{3+}$: (a) XRD patterns; (b) and (c) SEM images of $\text{Na}_5\text{Zn}_2\text{Gd}_{0.75}(\text{MoO}_4)_6: 0.25 \text{Eu}^{3+}$; (d) Crystal structure.

The morphology of the $\text{Na}_5\text{Zn}_2\text{Gd}_{0.75}(\text{MoO}_4)_6: 0.25 \text{Eu}^{3+}$ samples annealed at 800°C was determined using SEM analysis. Figure 2 (b) and (c) shows the different magnification scanning electron images. It can be seen that the $\text{Na}_5\text{Zn}_2\text{Gd}_{0.75}(\text{MoO}_4)_6: 0.25 \text{Eu}^{3+}$ samples with the layered monoclinic structure are substantially rectangular, the length from 1 to $4 \mu\text{m}$, and the width between $0.5\sim 1 \mu\text{m}$ larger individual particles. Furthermore, VESTA software was used to simulate its unit cells, as shown in Figure 2 (d). The crystal structure contains MoO_4^{2-} tetrahedral and $(\text{Zn}, \text{Gd})\text{O}_6$ octahedrons, a three-dimensional structure, and Na atoms in a cavity formed in the polyhedron. The tetracoordination of molybdate connects with the sides of the layer by the oxygen vertex, and $(\text{Zn}, \text{Gd})\text{O}_6$ octahedra are connected between the common edge. Each layer consists of passing corner-

connected GdO_6 octahedrons and MoO_4^{2-} tetrahedra. Adjacent layers connected through ZnO_6 octahedral form $\text{Na}_5\text{Zn}_2\text{Gd}(\text{MoO}_4)_6$ scheelite layered structure, which is consistent with the information conveyed by XRD.

3.3. FTIR spectra of $\text{Na}_5\text{Zn}_2\text{Gd}_{0.75}(\text{MoO}_4)_6: 0.25 \text{Eu}^{3+}$

Figure 3 shows the IR spectra of $\text{Na}_5\text{Zn}_2\text{Gd}(\text{MoO}_4)_6: \text{Eu}^{3+}$, the peaks of the precursor at 3431 cm^{-1} is the stretching vibration of $-\text{OH}$ group from water and citric acid and the absorption peak at 1396 cm^{-1} is attributed to stretching vibration of $\text{C}-\text{O}$ bond. The peak at 1630 cm^{-1} belong to $-\text{C}=\text{O}$ bond, and the carbonyl group red-shifts due to the formation of complex [21]. The absorption peak of H_2O and CO_2 decreased significantly after the precursor was sintered at 800°C for 2 h. The absorption peak of citric acid was almost vanishing. As for the calcined samples, a series of strong absorption bands, corresponding to the appearance of MoO_4^{2-} , can be observed in the region of $500\text{--}1000 \text{ cm}^{-1}$, indicating the formation of $\text{Na}_5\text{Zn}_2\text{Gd}_{0.75}(\text{MoO}_4)_6: 0.25 \text{Eu}^{3+}$. The absorption peaks at $702, 899, 1000 \text{ cm}^{-1}$ were should be attributed to the bending vibration and asymmetric stretching modes of $\text{Mo}-\text{O}$ bond asymmetric stretching vibrations of MoO_4^{2-} . And there is the stretching vibration of the $\text{Eu}-\text{O}$ bond at 549 cm^{-1} .

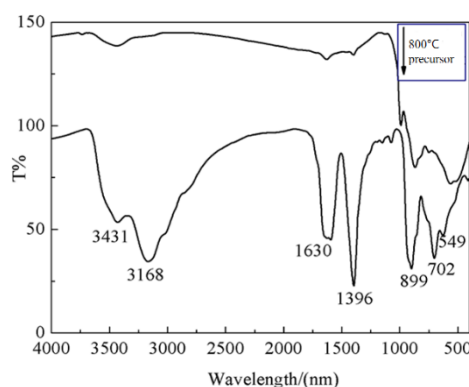


Figure 3. IR spectra of the precursor and $\text{Na}_5\text{Zn}_2\text{Gd}_{0.75}(\text{MoO}_4)_6: 0.25\text{Eu}^{3+}$ phosphor calcined at 800°C .

3.4. Luminescent Properties of $\text{Na}_5\text{Zn}_2\text{Gd}(\text{MoO}_4)_6: \text{Eu}^{3+}$

Figure 4 shows the excitation spectrum of $\text{Na}_5\text{Zn}_2\text{Gd}(\text{MoO}_4)_6: \text{Eu}^{3+}$ phosphor calcined at 800°C by monitoring the emission wavelength at 614 nm . It can be seen that the excitation spectrum consists of broad band from $250\text{--}350 \text{ nm}$ which corresponds to the charge transfer transition $\text{O}^{2-} \rightarrow \text{Eu}^{3+}$ and narrow excitation peaks from 360 to 500 nm , which is attributed to the intra-configurational $f-f$ transitions of Eu^{3+} ions [22]. The absorption peak at 395 nm and 465 nm is attributed to the $f-f$ transition of Eu^{3+} ions, corresponding to ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ and ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ electronic transition, respectively. The new triple molybdate $\text{Na}_5\text{Zn}_2\text{Gd}(\text{MoO}_4)_6: \text{Eu}^{3+}$ can be excited by blue light 465 nm prepared by the method, indicating that the phosphor matching with a wide output wavelength of the blue LED chip.

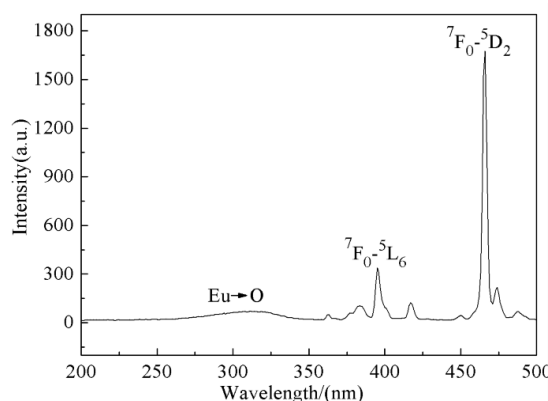


Figure 4. The excitation spectrum of $\text{Na}_5\text{Zn}_2\text{Gd}(\text{MoO}_4)_6: \text{Eu}^{3+}$ sample monitored at $\lambda_{\text{em}}=614 \text{ nm}$.

The emission spectrum of $\text{Na}_5\text{Zn}_2\text{Gd}(\text{MoO}_4)_6: \text{Eu}^{3+}$ phosphor is obtained under the excitation wavelength at 465 nm as shown in Figure 5. The emission band is observed at 614 nm, which is $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} , much higher than at 595 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_1$), the ratio of intensity $I_{5\text{D}_0-7\text{F}_2}/I_{5\text{D}_0-7\text{F}_1}$ is about 10. It indicates that Eu^{3+} occupies a site or sites without an inversion center, and low symmetry. In addition, another emission peak at 580 nm are attributed to $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition of Eu^{3+} ions. Therefore, $\text{Na}_5\text{Zn}_2\text{Gd}(\text{MoO}_4)_6: \text{Eu}^{3+}$ phosphors is a phosphor that is excited by blue light and emits strong red light. The $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition is mainly magnetic allowed (magnetic dipole transition) in the spectra of Eu^{3+} . At the same time, the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ is the only center in the absence of inversion symmetry conditions have low sensitivity to mandatory electric dipole transition. Thus Eu^{3+} was asymmetrically occupied in the $\text{Na}_5\text{Zn}_2\text{Gd}(\text{MoO}_4)_6$ lattice sites [23–25].

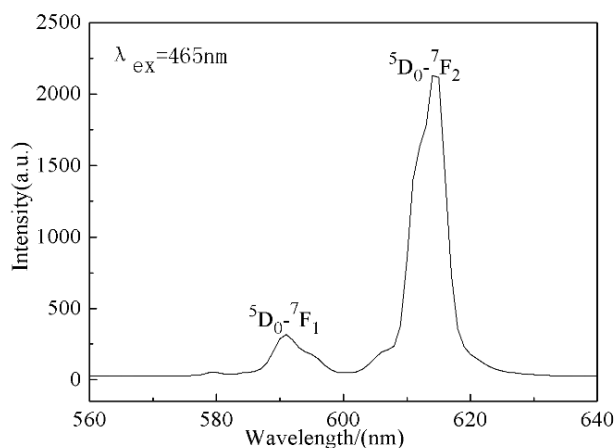


Figure 5. The emission spectra of $\text{Na}_5\text{Zn}_2\text{Gd}_{1-x}(\text{MoO}_4)_6: x \text{Eu}^{3+}$.

3.5. Effect of Doped- Eu^{3+} Concentration

The different intensity of emission spectra under 465 nm excitation corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of $\text{Na}_5\text{Zn}_2\text{Gd}_{1-x}(\text{MoO}_4)_6: \text{Eu}_x^{3+}$ ($x = 0.03, 0.04, 0.05, \dots, 0.35$) phosphor after annealing at 800 °C for 2 h is shown in Figure 6. It can be seen that the shapes and positions of all the $\text{Na}_5\text{Zn}_2\text{Gd}_{1-x}(\text{MoO}_4)_6: \text{Eu}_x^{3+}$ samples are the same in addition to their relative luminescence intensity. Thus, with the increased concentration of Eu^{3+} in the host, the luminescent intensity has enhanced and reached a maximum at a concentration of $x=0.25$. Rare earth ion itself has a lot of energy levels. Thus, with the increased concentration of Eu^{3+} in the host, the luminescent intensity has enhanced and reached a maximum at a concentration of $x=0.25$. As the Eu^{3+} doping is further increased, the distance between Eu^{3+} ions decreases. The concentration quenching phenomenon occurs during excitation, thus the luminous intensity decreases. The energy loss at the emission level initiated by the cross-relaxation between the excited ions might be the main reason causing the concentration quenching [26]. The fluorescent emission of Eu^{3+} was mainly due to the transitions from metastable level $^5\text{D}_0$ to level $^7\text{F}_2$. Considerable excited ions on the $^5\text{D}_0$ level were transferred from the $^5\text{D}_0$ level to the $^7\text{F}_2$ level due to the cross-relaxation process; therefore, several useful excited ions were consumed through the radiation and relaxation processes and the fluorescence emission was thereby reduced lead to the luminous intensity decrease. The optimum molar concentration of 25 mol% in Eu^{3+} ions doped $\text{Na}_5\text{Zn}_2\text{Gd}_{1-x}(\text{MoO}_4)_6: \text{Eu}_x^{3+}$ phosphor.

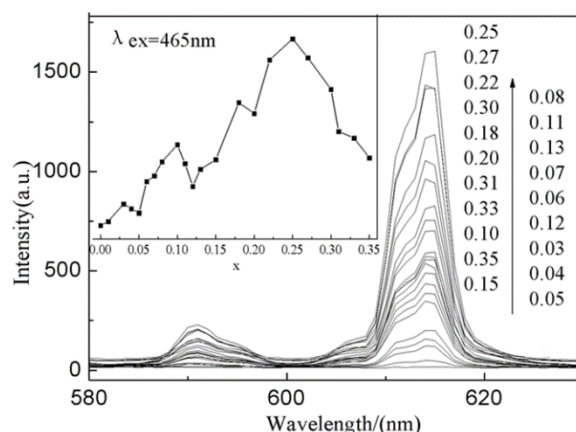


Figure 6. Emission spectra of different Eu^{3+} concentration doped $\text{Na}_5\text{Zn}_2\text{Gd}_{1-x}(\text{MoO}_4)_6: x\text{Eu}^{3+}$.

The emission spectra of $\text{Na}_5\text{Zn}_2\text{Gd}_{0.75}(\text{MoO}_4)_6: 0.25\text{Eu}^{3+}$ samples with different ratios of citric acid with metal ions (C: M = 0.5:1, 1:1, 1.5:1, 2:1, 2.5:1 and 3:1) at 800 °C annealing temperature were measured, as shown in Figure 7. The luminescent intensity of samples increased with the trend of first increases and then decreased with the rise in the ratio of citric acid and metal ions. Thus, it can be seen that the luminous intensity reaches a maximum when the ratio of citric acid and metal ion at 2:1. The pH values with a constant molar ratio of citric acid to metal ions effect the emission intensities of $\text{Na}_5\text{Zn}_2\text{Gd}_{1-x}(\text{MoO}_4)_6: x\text{Eu}^{3+}$ due to the luminescent performance at different pH value should be ascribed to the different morphology of the products.

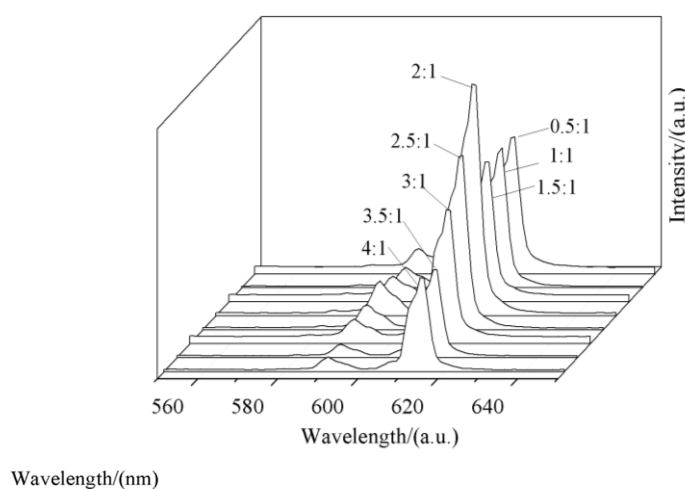


Figure 7. Emission spectra of different citric acid concentration in $\text{Na}_5\text{Zn}_2\text{Gd}_{1-x}(\text{MoO}_4)_6: \text{Eu}^{3+}$.

3.6. CIE Color Coordinates of $\text{Na}_5\text{Zn}_2\text{Gd}_{0.75}(\text{MoO}_4)_6: 0.25 \text{Eu}^{3+}$

According to the emission spectrum data of $\text{Na}_5\text{Zn}_2\text{Gd}_{0.75}(\text{MoO}_4)_6: 0.25 \text{Eu}^{3+}$ (the ratio of citric acid and the metal cation is 2:1) samples under 465 nm excitation, the CIE chromaticity diagram shown in Figure 8. The color coordinates of the emission spectra of the sample (0.658, 0.341) was located in the red region. It is closer to the NTSC standard values (0.670, 0.330) after comparing with the U.S. National Television Standards Committee (NTSC) and the color coordinates (0.48, 0.50) of the commercial $\text{Y}_2\text{O}_3\text{S}: \text{Eu}^{3+}$ red phosphor, which means the $\text{Na}_5\text{Zn}_2\text{Gd}_{0.75}(\text{MoO}_4)_6: 0.25 \text{Eu}^{3+}$ is a stable red phosphor for white LEDs.

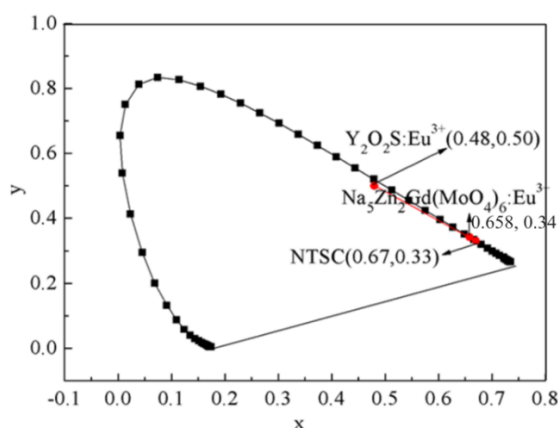


Figure 8. CIE of the $\text{Na}_5\text{Zn}_2\text{Gd}_{0.75}(\text{MoO}_4)_6: 0.25 \text{Eu}^{3+}$.

4. Conclusions

The novel $\text{Na}_5\text{Zn}_2\text{Gd}_{1-x}(\text{MoO}_4)_6: x\text{Eu}^{3+}$ ($x = 0.03, 0.04, 0.05, \dots, 0.25, \dots, 0.35$) series red phosphors successfully prepared with sol-gel method, and the optimal synthesis condition was investigated based on luminescent relative intensity. The results of XRD and SEM show samples with scheelite layered structure, the length from 1 to 4 μm , and wide with between 0.5~1 μm . The strongest emission peaks was located at 614 nm under the 465 nm excitation, which is corresponding to $^5D_0 \rightarrow ^7F_2$ transition of Eu^{3+} indicated that the $\text{Na}_5\text{Zn}_2\text{Gd}(\text{MoO}_4)_6: \text{Eu}^{3+}$ crystal has a strong and pure red emission. The red phosphor with the color coordinate values (0.658, 0.341) was almost close to the international standard color coordinate values (0.670, 0.330) and thus it is a promising red light material candidate for creating near UV light and blue light in phosphor-converted white LEDs.

Data Availability Statement: Data will be made available on reasonable request.

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Conflicts of Interest: The authors declare no conflict of interest. The authors declare no competing financial interest.

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