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STUDY OF PREPARATION AND PHOTOLUMINESCENCE PROPERTY OF MOLYBDATE PHOSPHORS FOR WHITE LED

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ABSTRACT

Eu³⁺ doped SrMoO₄ phosphors were synthesized through the high-temperature solid-state reaction method and characterized with X-ray diffraction, photoluminescence emission and photoluminescence excitation spectra. The color coordinates is calculated. The optimum concentration of 30% is determined by adjusting the concentration of Eu³⁺. The effects of charge compensator type and concentration on the luminescent properties of phosphor are studied. The result shows that the addition of Na₂CO₃ can significantly enhanced the luminescence intensity by about 4.7 times when the best concentration is 9%. This phosphor is a red phosphor that can be matched with the blue LED. And it can be doped in traditional white LED (blue LED + yellow phosphor YAG: Ce) to increase the red-light emission to compensate for the low color rendering defects.

KEYWORDS

White LED, Phosphor, Molybdate.

1. INTRODUCTION

White LEDs, because of the excellent properties, *eg.* small size, low power consumption, high efficiency, long durability, fast response and lack of toxic mercury, are considered as next generation solid-state lighting resource [1-3]. Currently, there are two methods for synthesizing white LEDs: one is that using a blue LED chip and a yellow-emitting Y₃Al₅O₁₂:Ce³⁺ (YAG: Ce³⁺) phosphor to combine white light, but in this way, white light emission spectrum lack of red light, and at high current yellow light changes slower than blue light changes, so color rendering performance is not good, and it has limitations in the application; Another way is that use near ultraviolet (UV) InGaN chip excite three-color phosphors. the disadvantage of the method is that the phosphor has lower luminous efficiency in the near ultraviolet and color rendering index [4].

Based on these, the study of highly efficient and stable red phosphors has become an important task. Because of their attractive chemical, optical and structural properties, molybdates as hosts for luminescence material have received extensive interests. For example, Ana Paula A have reported the luminescence of Eu³⁺ doped SrMoO₄ by complex polymerization (CP) method [5]. The effect of Eu³⁺ ion doping on the luminescence properties was studied. Eu³⁺ ions doped tungsten or molybdate oxides are representative red-emitting phosphors for basic luminescent materials in LED because of its high brightness and high efficiency. In this work, aiming to improve the emission intensity of the phosphor, we have prepared a new type of molybdate phosphor successfully. And the influence of charge compensating agent was investigated systematically.

2. EXPERIMENTAL

Eu³⁺ doped molybdate SrMoO₄ was prepared through conventional solid-state reaction. Firstly, the starting materials SrCO₃, H₂MoO₄, Eu₂O₃ were analytical grade reagents, thoroughly mixed in light of stoichiometric ratio of SrMoO₄ formula. Furthermore, Li₂CO₃, Na₂CO₃, and K₂CO₃ as the charge compensators reagents were added to the raw materials for the sample synthesis reaction [6]. The stoichiometric raw materials were thoroughly mixed in an agate mortar, then the mixture was transferred to a corundum crucible and heated at different temperatures and different times in air atmosphere.

X-ray diffraction (XRD) patterns were collected on a XRD-7000 powder diffractometer with CuKα radiation ($\lambda = 0.15405\text{nm}$) at 45 kV and 40 mA, and the data were recorded in the range $2\theta = 10 - 80^\circ$ to analyze the crystal structure and phase purity of samples [7]. The photoluminescence (PL) and excitation (PLE) spectra were measured using an RF-5301PC fluorescence spectrophotometer assembled with 150 W Xe lamp. The measuring range is 220~750nm. 340nm and 420nm filters were used, and the test was performed with a slit EX = 1.5 and EM = 1.5.

3. RESULTS AND DISCUSSION

3.1 Powder X-ray diffraction

Figure 1 (a) shows the wide-angle powder X-ray diffraction patterns of SrMoO₄ phosphors with 30% Eu³⁺ doped, and the sample was prepared through the solid-state reaction fired at 900°C for 4h. All the positions of the diffraction peaks of the sample were agree well with the standard pattern (JCPDS File No. 08-0482), which is shown in Figure 1a. The Eu³⁺ ion has been incorporated into the Sr²⁺ ion in the host lattice of SrMoO₄. The intense diffraction peaks confirmed the formation of single phase compounds [8].

The XRD analysis shows that the corresponding lattice constants of SrMoO₄ are calculated to be $a = 0.5394\text{nm}$, $c = 1.202\text{nm}$, $\alpha = \beta = \gamma = 90^\circ$, I41/a (88) space group, which is attributed to scheelite SrMoO₄ structure, In SrMoO₄:Eu³⁺, each Sr²⁺ atom was bonded to eight O atoms to form [SrO₈] unit [9]. And the Eu³⁺ atoms substitute partly the lattice sites of the Sr²⁺ ions, which are coordinated with eight O atoms. Meanwhile, also, the Mo atoms were coordinated by four O atoms [MoO₄] clusters. The structure of SrMoO₄ is shown in Figure 1(b).

Figure 1: (a) XRD patterns of SrMoO₄:Eu³⁺ phosphors and (b) the standard data for SrMoO₄ (JCPDS 08-0482); (b) The crystal structure of SrMoO₄:Eu³⁺

3.2 Photoluminescence Properties of SrMoO₄:Eu³⁺ Phosphors

Figure 2 shows the excitation and emission spectra of SrMoO₄ phosphor. The PL spectrum with a peak at 615 nm was recorded by monitoring the excitation spectrum 464 nm, which was assigned as the transition originating from the allowed ⁵D₀-⁷F₂ level of Eu³⁺. The corresponding PLE spectra bands at 464 nm from the ⁷F₀→⁵D₂ transition of Eu³⁺ when monitored at 615 nm.

Figure 2: (a) PL excitation and (b) emission spectra of SrMoO₄ red phosphor

As can be seen from the figure 3(a) and (b), when the concentration of Eu³⁺ ions is 3%, the luminescence intensity of the Sr_{1-x}MoO₄:xEu³⁺ sample is the weakest. The light intensity of the sample increases with the increase of the molar concentration of Eu³⁺ ions. When the concentration of Eu³⁺ ions is 30%, the peak intensity of the sample peaks. If you continue to increase the proportion of Eu³⁺ ions, the emission peak intensity of the sample will tend to decrease. This is due to the concentration quenching effect between Eu³⁺ ions as the molar concentration of Eu³⁺ ions continue to increase. The proportion of Eu³⁺ ions in the host crystal lattice gradually increases, resulting in a constant reduction in the distance between Eu³⁺ ions. And as well as the distance between the luminescent center Eu³⁺ ions decreases, Eu³⁺ ions begin to interact with each other. As a result, no radiation energy transfer occurs Eu³⁺ ions each other, which is considered that the energy is consumed between Eu³⁺ ions. The energy is not released in the form of light, which results in the loss of energy. This phenomenon also shows the energy transfer between Eu³⁺ ions in Sr_{1-x}MoO₄:xEu³⁺.

Figure 3: (a) the linear graph of emission intensity vs. Eu³⁺ concentrations, (b) the linear graph of excitation intensity vs. Eu³⁺ concentrations

3.3 Effect of Charge Compensator on Luminescence Properties of Phosphors

The excitation and emission spectra of Sr_{0.94}MoO₄:0.03Eu³⁺, 0.03A (A=Li⁺, Na⁺, K⁺, Cl⁻) samples are shown in Figure 4 (a) and (b), which is similar to Sr_{0.97}MoO₄:0.03Eu³⁺. However, as well as charge compensating agent was not added, the spectral intensity of the synthesized sample was relatively weak. The intensity of the emitted light of the synthesized sample was significantly enhanced on adding the charge compensating agent. The effect of several charge compensators on the spectral intensity enhancement is Li⁺<Cl⁻<K⁺<Na⁺. Because of the similar radius of Na⁺ ions (0.102 nm) and that of Sr²⁺ ions (0.118 nm) compared with Cl⁻ (0.181 nm), K⁺ (0.138 nm), and Li⁺ (0.076 nm), Na⁺ ion has the best enhancement effect on the spectrum, which could effectively fit into the lattice sites of Sr. In this case, the emission probability of Eu³⁺ ions is significantly increased, and the luminescence intensity of phosphor Sr_{0.97}MoO₄:0.03Eu³⁺ is significantly enhanced, also.

Figure 4: (a) Photoluminescence excitation spectra of SrMoO₄:Eu³⁺ phosphor codoped with different alkali-metal ions (Li⁺, Na⁺, and K⁺) for charge compensation, at an emission wavelength of 615 nm. (b) Emission spectra of SrMoO₄:Eu³⁺ phosphor codoped with different alkali-metal ions (Li⁺, Na⁺, K⁺) for charge compensation at excitation wavelengths of 464 nm.

Figure 5 shows the effect of Na⁺ ions with different concentrations on the luminescence intensity of Sr_{0.97}MoO₄:0.03Eu³⁺ phosphors. The luminescence intensity of the sample increases with the increasing of Na⁺ ion. And on the addition amount of Na⁺ ion is 9%, the enhancement effect of the emission peak intensity is best. It is considered that the volume of Na⁺ is smaller than other ions, which occupying the position in the crystal lattice, and it fill in the gap, also. Crystal field environment around Sr²⁺ ions and Eu³⁺ ions has been changed. The luminescence intensity (973.258 a.u.) of Sr_{0.88}MoO₄:0.03Eu³⁺, 0.09Na⁺ is about 4.7 times larger than that of Sr_{0.97}MoO₄:0.03Eu³⁺ (200.482 a.u.). The above results show that adding a suitable charge compensator could greatly improve the performance of phosphor Sr_{0.97}MoO₄:0.03Eu³⁺. In addition, the color coordinate of the sample Sr_{0.97}MoO₄:0.03Eu³⁺ was changed from (0.495, 0.484) with no charge compensating agent added to (0.552, 0.435) with 9% Na₂CO₃ added, and the color coordinate shifted significantly to the red light region.

Figure 5: Luminous intensity comparison chart of Sr_{0.97-x}MoO₄:0.03Eu³⁺, x Na⁺ (x=0.03, 0.05, 0.07, 0.09, 0.11)

Figure 6: CIE 1931 chromaticity diagram for $\text{SrMoO}_4:\text{Eu}^{3+}$ phosphor

REFERENCES

- [1] Shivakumara, C., Saraf, R. 2015. Eu^{3+} -activated SrMoO_4 phosphors for white LEDs applications: Synthesis and structural characterization [J]. Optical Mater., 42, 178-186.
- [2] Chen, J.Y., Guo, C.F., Yang, Z. 2016. $\text{Li}_2\text{SrSiO}_4:\text{Ce}^{3+}, \text{Pr}^{3+}$ Phosphor with blue, red, and near-infrared emissions used for plant growth LED [J]. J. Am.

Ceram. Soc., 99 (1), 218-225.

[3] Qin, L., Huang, Y. 2012. The red-emitting phosphors of Eu^{3+} -activated $\text{MR}_2(\text{MoO}_4)_4$ ($\text{M} = \text{Ba}, \text{Sr}, \text{Ca}; \text{R} = \text{La}^{3+}, \text{Gd}^{3+}, \text{Y}^{3+}$) for light emitting diodes [J]. Materials Research Bulletin, 47, 4498-4502.

[4] Marques, A.P.A., Tanaka, M.T.S., Longo, E., Leite, E.R., Rosa, I.L.V. 2011. The Role of the Eu^{3+} Concentration on the $\text{SrMoO}_4:\text{Eu}$ Phosphor Properties: Synthesis, Characterization and Photophysical Studies [J]. Journal of Fluorescence, 21 (3), 893-899.

[5] Talewar, R.A., Joshi, C.P. 2016. Near infrared emission and energy transfer in $\text{Eu}^{2+} - \text{Nd}^{3+}$ co-doped $\text{Ca}_2\text{B}_3\text{O}_8\text{Cl}$ [J]. Optical Materials, 55, 44-48.

[6] Gupta, S.K., Sudarshan, K. 2018. Deciphering the Role of Charge Compensator in Optical Properties of $\text{SrWO}_4:\text{Eu}^{3+}:\text{A}$ ($\text{A} = \text{Li}^+, \text{Na}^+, \text{K}^+$): Spectroscopic Insight Using Photoluminescence, Positron Annihilation, and X-ray Absorption [J]. Inorganic chemistry, 57, 821-832.

[7] Cho, T. 2017. Innovative Micro-Dust Reduction Technologies. Acta Chemica Malaysia, 1 (1), 04-07.

[8] Bao, X., Zhou, S. 2013. Color tunable phosphor $\text{CaMoO}_4:\text{Eu}^{3+}, \text{Li}^+$ via energy transfer of $\text{MoO}_4^{2-} \rightarrow \text{Eu}^{3+}$ dependent on morphology and doping concentration [J]. Materials Research Bulletin, Mater. Res. Bull., 48 (3), 1034-1039.

[9] Zhang, N., Wang, D.J., Li, L. 2006. $\text{YAG}:\text{Ce}$ phosphors for WLED via nano-pseudoboehmite sol-gel route [J]. J. Rare Earths, 24 (3), 294-297.