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Single-phase $LiY(MoO_4)_{2-x}(WO_4)_x:Dy^{3+}$, Eu^{3+} phosphors with white luminescence for white LEDs

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ABSTRACT

Single-phase and Dy^{3+}/Eu^{3+} co-doped novel phosphor $LiY(MoO_4)_{2-x}(WO_4)_x:Dy^{3+},Eu^{3+}$, emitting white luminescence under near ultraviolet (NUV) light, was prepared through sol-gel method. The preparation and characterization of this phosphor were systematically studied by X-ray diffraction and spectrofluorophotometric measurements. The molar ratio of metal ions and citric acid ($R_{m/c}$) and calcination temperature greatly influenced the phase purity of sample, revealing that the pure phase could be obtained by using $R_{m/c}$ = 1:2.5 and calcination temperature = 800 °C. Under NUV excitation, the as-prepared phosphor exhibited the emissions of 485, 572 and 612 nm, which intensities could be affected by the pH and the concentrations of molybdenum and tungsten ions. By doping appropriate concentrations of Dy^{3+} and Eu^{3+}, white light emitting phosphor $LiY(MoO_4)_{1.2}(WO_4)_{0.8}$:6%$Dy^{3+}$,7%$Eu^{3+}$ with good responsiveness to NUV light was obtained. The Commission Internationale de L'Eclairage chromaticity coordinates were calculated to be (x = 0.334, y = 0.322), close to the D_{65} illuminant (x = 0.313, y = 0.329), indicating the potential application for NUV WLEDs.

1. Introduction

White light-emitting diodes (WLEDs) have been considered as the next generation of solid state light sources, due to their superior properties such as lower energy consumption, more efficient output and environmental friendliness [1,2]. Currently, combining blue LED chip with YAG:Ce yellow-emitting phosphor or coating ultraviolet (UV) LED with red/green/blue emission phosphors is the main approach to obtain WLEDs [3–5]. So far, amounts of investigations have been made to develop novel phosphors for WLEDs. However, some challenges, which still exist in WLEDs, are to realize high luminescent efficiency, high chromatic stability, excellent color-rending properties, and competitive price against traditional implemented fluorescent lamps [6,7]. Hence, the single-phase phosphor has become the necessary pre-requisite for the fabrication of WLEDs to solve these above challenges [6–8].

In the recent years, a great number of efforts have been made to develop single-phase white-light-emitting phosphors for near ultraviolet (NUV) WLEDs [6,9,10]. It is well known that rare-earth (RE) doped materials can emit different colors of luminescence such as red, green and blue or yellow which cover the whole visible light range [1,3]. Therefore, there are some different methods to realize white light emission from a single-phase host lattice including: (i) doping a single RE ion (Eu^{3+}, Dy^{3+}) into single phase hosts; (ii) co-doping two or more RE ions with different emissions simultaneously, such as Ce^{3+}/Eu^{2+}, Tm^{3+}/Dy^{3+}, $Tm^{3+}/Tb^{3+}/Eu^{3+}$; (iii) co-doping different ions to control emission through energy transfer processes (EPT); and (iv) controlling the concentration of the defect and reaction conditions of defect-related luminescent materials [6,8,9,11,12].

Compared with other host lattices, molybdates and tungstates have drawn much attention for WLEDs, due to their good chemical and physical stability, high density and low phonon threshold energy. What's more, the $(MoO_4)_2$ and $(WO_4)_2$ groups have strong absorption in the NUV region. These groups can transfer their absorbed energy to the dopant ions, making these phosphors exhibiting strong and broad absorption in the UV region. Therefore, these materials have been considered as excellent hosts for phosphor materials [13–16]. In the past years, these above scheelite-type crystalline structures (such as $LiEu(MoO_4)_2$ [14], $LiLn(MO_4)_2$:Eu [1], $Tb_2(WO_4)_3$:Eu) [13] have attracted a great of

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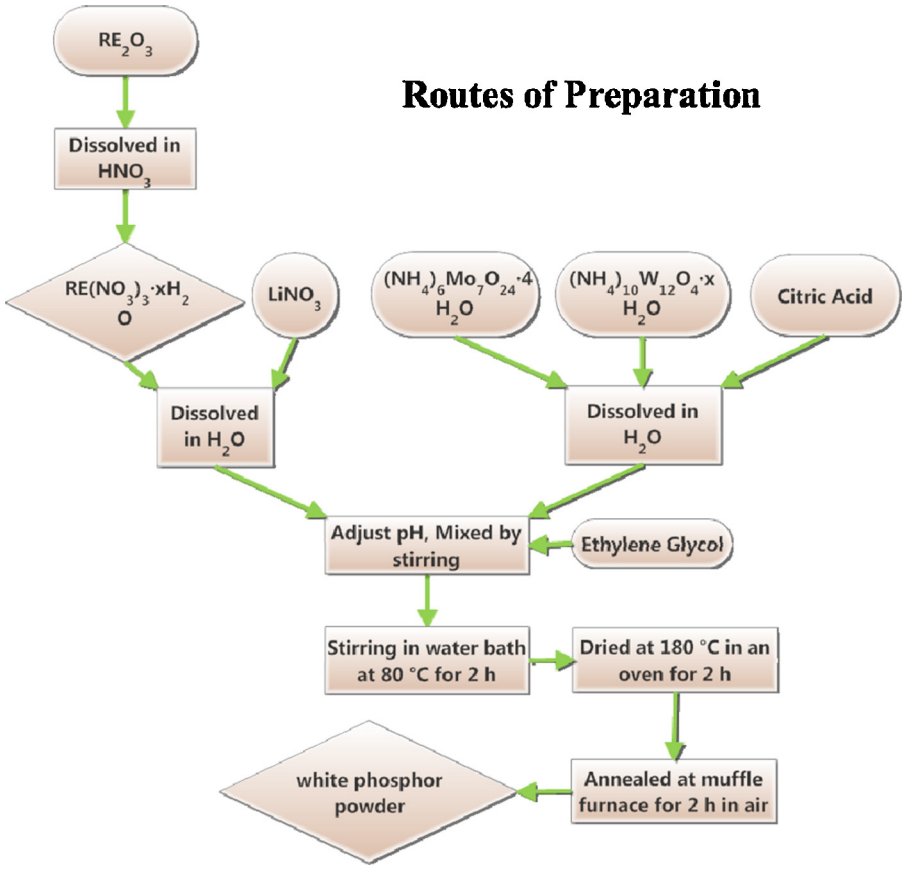

Scheme 1. The brief synthetic process of white phosphor powder $LiY(MoO_4)_{2-x}(WO_4)_x:Dy^{3+}$, Eu^{3+}.

attentions. A number of papers have been reported about molybdates/tungstates phosphors activated by RE ions. However, only a few of papers have been investigated on the complex molybdate–tungstates phosphors, in which luminescence can be affected by the ratio of molybdate and tungstate ions [15]. Because that Mo^{6+} and W^{6+} ions have similar ionic radii and can be substituted for each other, introducing changes in the energy transitions and luminescence intensities of RE ions. Hence, it is of scientific importance to investigate this influence systematically.

Motivated by the above-stated studies and attempts to develop phosphors excitable by NUV light for the applications of WLEDs, herein we have successfully synthesized a single-phase and white emitting phosphor $LiY(MoO_4)_{2-x}(WO_4)_x:Dy^{3+}$, Eu^{3+} through a simple sol-gel method, based on the consideration that Li-based tungstate/molybdate materials exhibit more promising luminescence performance than other K and Na-based counterparts [1]. Furthermore, we have systematically studied the preparation, luminescence and color chromaticity properties of a series of phosphors $LiY(MoO_4)_{2-x}(WO_4)_x:Dy^{3+}$, Eu^{3+}. The influence of citric acid and calcination temperature on crystal structure is studied by XRD measurement. The pH of solution and the concentrations of molybdenum and tungsten ions are adjusted to realize the highest luminescent intensities under NUV light. Moreover, the appropriate doping concentrations of Dy^{3+} and Eu^{3+} make white light emitting phosphor well responsive to NUV light.

2. Experimental section

Europium oxide (Eu_2O_3, 99.99%), dysprosium oxide (Dy_2O_3, 99.99%), ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot4H_2O$,

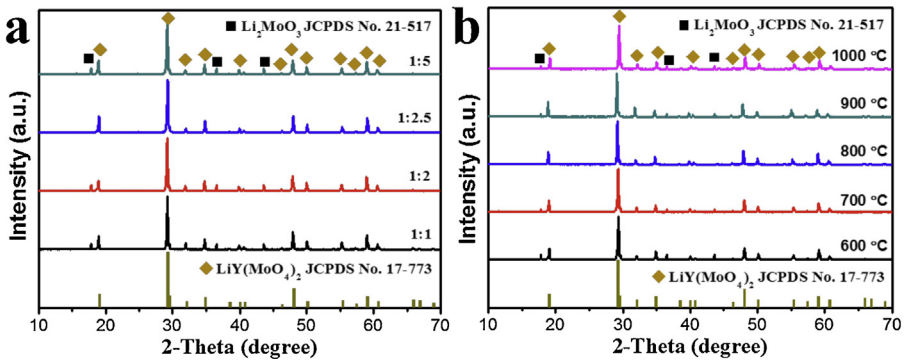

Fig. 1. XRD patterns of $LiY(MoO_4)_2$ synthesized with (a) different $R_{m/c}$ (1:1, 1:2, 1:2.5, 1:5); and (b) different calcination temperature (600, 700, 800, 900 and 1000 °C).