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Photoluminescence studies of red-emitting $NaEu(WO_4)_2$ as a near-UV or blue convertible phosphor

Qiyue Shao *, Huijuan Li, Kewei Wu, Yan Dong, Jianqing Jiang *

Jiangsu Key Laboratory of Advanced Metallic Materials, School of Materials Science and Engineering, Southeast University, Nanjing 211189, China

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ABSTRACT

Sodium europium double tungstate $[NaEu(WO_4)_2]$ phosphor was prepared by the solid-state reaction method. Its crystal structure, photoluminescence properties and thermal quenching characteristics were investigated aiming at the potential application in the field of white light-emitting diodes (LEDs). The influences of Sm doping on the photoluminescence properties of this phosphor were also studied. It is found that this phosphor can be effectively excited by 394 or 464 nm light, which nicely match the output wavelengths of near-ultraviolet (UV) or blue LED chips. Under 394 or 464 nm light excitation, this phosphor exhibits stronger emission intensity than the $Y_2O_2S:Eu^{3+}$ or Eu^{2+}-activated sulfide phosphor. The introduction of Sm^{3+} ions can broaden the excitation peaks at 394 and 464 nm of the $NaEu(WO_4)_2$ phosphor and significantly enhance its relative luminance under 400 and 460 nm LEDs excitation. Furthermore, the relative luminance of $NaEu(WO_4)_2$ phosphor shows a superior thermal stability compared with the commercially used sulfide or oxysulfide phosphor, and make it a promising red phosphor for solid-state lighting devices based on near-UV or blue LED chips.

1. Introduction

White light-emitting diodes (LEDs), as the promising solid-state lighting sources to replace conventional incandescent and fluorescent lamps, have attracted much attention due to their high reliability, long lifetime, low energy consumption and environment-friendly characteristics [1]. Phosphor-converted LED technique is an important approach to produce solid-state illumination devices. An excellent approach using the combination of a GaN-based blue LED and a cerium-doped yttrium aluminum garnet (YAG:Ce) phosphor was first proposed in 1996 [2], and nowadays it is still the most widely used method to realize the white LEDs. However, such white LEDs have low color-rendering index (CRI) because of their weak emission intensity in red spectral region. As a possible solution, a separate red-emitting phosphor can be used to compensate the red deficiency in light output. The red phosphor for blue LED chips is commercially still limited to Eu^{2+}-activated alkaline-earth sulfide, which has poor chemical stability and low luminescence efficiency [3,4]. Another type of phosphor-converted white LEDs can be fabricated by employing blue/green/red tricolor phosphors excited by a near-ultraviolet (UV) (360–410 nm) InGaN-based LED, which can compete for applications requiring high quality of light. The commonly used red-emitting phosphor for near-UV LED is $Y_2O_2S:Eu^{3+}$. The $Y_2O_2S:Eu^{3+}$ phosphor is chemically unstable and not desirable in efficiency, compared with blue ($BaMgAl_{10}O_{17}:Eu^{2+}$) and green ($ZnS:Cu^+$, Al^{3+}) phosphors [5]. Hence, there is an urgent need to search a suitable red phosphor for fabrication of phosphor-converted white LEDs. The promising red phosphor should be excited efficiently by the blue light around 460 nm or the near-UV light around 400 nm.

As interesting candidates for red-emitting phosphors, Eu^{3+}-activated double molybdates or tungstates $ALn(MO_4)_2$ ($A = Li^+$, Na^+, K^+; Ln = trivalent rare-earth ions; M = Mo,W) have attracted much attention [5–11]. $ALn(MO_4)_2$ materials adopt a scheelite-like ($CaWO_4$) structure, exhibit excellent thermal and chemical stability, and therefore are considered to be efficient host candidates. Eu^{3+} ions were frequently used as activators for the red phosphors, which mainly show very sharp $^5D_0$–$^7F_2$ red emission lines around 612 nm as Eu^{3+} ions occupy the lattice sites without inversion symmetry. In $ALn(MO_4)_2$ materials, Mo^{6+}or W^{6+} is coordinated by four oxygen atoms in a tetrahedral site, and the rare-earth/sodium ions occupy eight-coordinated sites. The tetrahedral Mo^{6+} and W^{6+} have similar ionic radius (0.41 and 0.42 Å), and make it possible to prepare solid solutions of the type $ALn(WO_4)_{2-x}(MoO_4)_x$ [5]. The photoluminescence properties of scheelite-type $NaLn_{0.95}Eu_{0.05}(WO_4)_{2-x}(MoO_4)_x$ (Ln = Gd, Y, Bi)

* Corresponding authors. Tel.: +86 25 52090630; fax: +86 25 52090634.
E-mail addresses: qiyueshao@seu.edu.cn (Q. Shao), jqjiang@seu.edu.cn (J. Jiang).

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solid solutions were studied by Neeraj et al. [5]. These materials show intense red emission by exciting at 394 nm using the sharp $^7F_0 \rightarrow {}^5L_6$ line of Eu^{3+} ions, and could be used as red phosphors for white lighting devices utilizing near-UV LED chips. Wang et al. [6] studied double molybdates $NaLa_{1-x}Eu_x(MoO_4)_2$ with various Eu content, and no concentration quenching of Eu^{3+} ions was observed in the series of samples. Furthermore, Wang et al. prepared composition-optimized double molybdate $(Li_{0.333}Na_{0.334}K_{0.333})Eu(MoO_4)_2$, which shows broadened excitation band in near-UV range and intense red emission with appropriate CIE chromaticity coordinates [7]. Sivakumar and Varadaraju [8] reported a red-emitting tungstomolybdate phosphor with composition of $AgGd_{0.95}Eu_{0.05}(WO_4)_{2-x}(MoO_4)_x$, and this material can be excited efficiently by near-UV and blue (i.e., 394 and 465 nm) light. The tungstomolybdate phosphors with the composition of $KEu(WO_4)_{2-x}(MoO_4)_x$ [9] and $LiEu(WO_4)_{2-x}(MoO_4)_x$ [10] have also been reported recently, and are considered to be potential red-emitting phosphors for white LEDs.

Motivated by the above-stated studies and the attempts to develop suitable red phosphors for white LEDs, sodium europium double tungstate $(NaEu(WO_4)_2$ phosphor was prepared by the solid-state reaction method in this paper. Its crystal structure and photoluminescence properties were investigated aiming at the potential application in the field of phosphor-converted white LEDs. The influences of sintering temperature, Sm doping and atmosphere temperature on the photoluminescence properties of $NaEu(WO_4)_2$ phosphor were also studied.

2. Experimental

The $NaEu(WO_4)_2$ samples were prepared by the solid-state reaction technique at high temperature. The starting materials $NaHCO_3$ (A. R. grade), WO_3 (99.9% purity), Eu_2O_3 (99.99% purity) and Sm_2O_3 (99.99% purity) were weighted by stoichiometric ratio. NaF (A. R. grade) at a certain mass ratio was added as the flux to improve the chemical reaction. After these powders were mixed thoroughly, the homogeneous mixture was filled into a little alumina crucible and calcined in a muffle furnace for 4 h at the temperature from 700 to 1200 °C. The crystal structure of the final products was examined by powder X-ray diffraction (XRD) using Cu K_α radiation. Photoluminescence excitation and emission spectra were recorded by a Hitachi F-7000 fluorescence spectrophotometer at room temperature. The temperature-dependent luminance of the phosphors was recorded by a self-made measuring system, which includes a temperature-controlled heating plate and a fluo-brightness meter (Zhejiang University Sensing Instruments Co., Ltd., China). Two near-UV LEDs ($\lambda_{em} = 385$, 400 nm) and a blue LED ($\lambda_{em} = 460$ nm) were used as excitation sources for temperature-dependent luminance measurements.

3. Results and discussion

3.1. Crystal structure and photoluminescence properties of $NaEu(WO_4)_2$

The XRD patterns of the $NaEu(WO_4)_2$ phosphors fired at different temperature are shown in Fig. 1. After being sintered at 700 °C for 4 h, a white product can be obtained. XRD data indicate that the product sintered at 700 °C is not a single phase. In addition to strong diffraction peaks corresponding to scheelite-like phase, a peak at $2\theta = 33.02°$ ascribed to cubic Eu_2O_3 phase and two unidentifiable peaks at $2\theta = 21.86°$ and 36.56° can also been observed. It indicates that the formation of scheelite-like

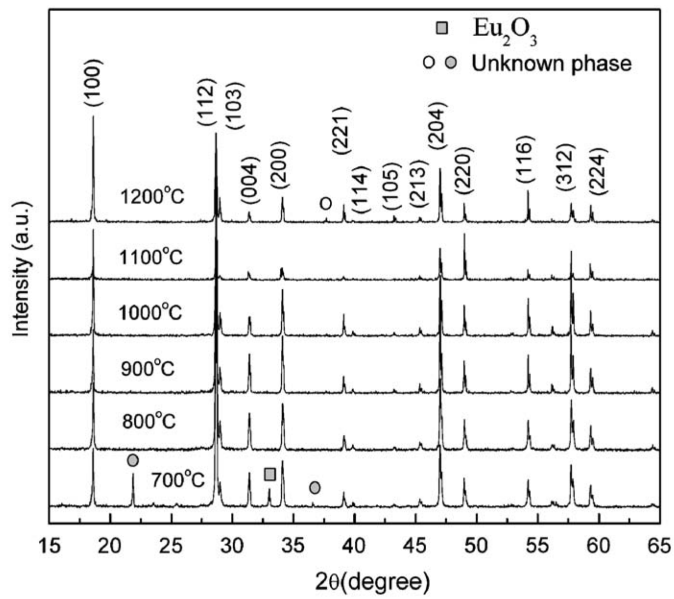

Fig. 1. XRD patterns of $NaEu(WO_4)_2$ sintered at different temperature from 700 to 1200 °C.

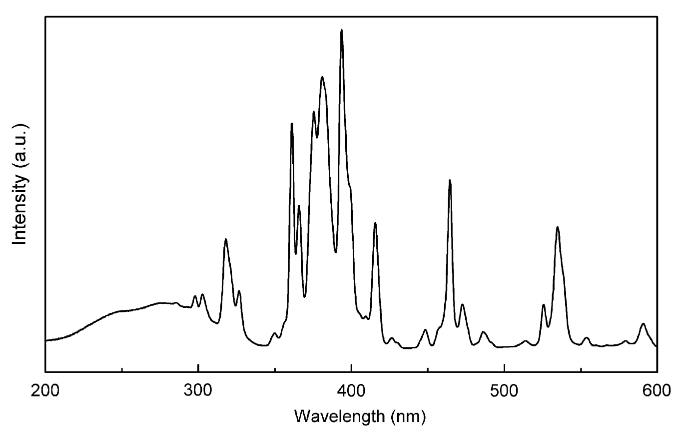

Fig. 2. Excitation spectrum for the 615 nm emission of the $NaEu(WO_4)_2$ phosphor sintered at 1100 °C for 4 h.

$NaEu(WO_4)_2$ is incomplete at this temperature. With the sintering temperature increasing, the obtained products vary from white to pink in color. The samples sintered at 800–1100 °C have a single crystalline phase with scheelite-like structure, and their XRD patterns are consistent with that given in JCPDS card 25–0828 $[Na_{0.5}Gd_{0.5}MoO_4]$. When the firing temperature increases up to 1200 °C, a weak diffraction peak related to an unknown phase can be observed at $2\theta = 37.70°$. It indicates that an excessively high sintering temperature ($\geqslant$1200 °C) is unfavorable for the formation of $NaEu(WO_4)_2$ with scheelite-like structure.

Fig. 2 represents the excitation spectrum of the $NaEu(WO_4)_2$ phosphor sintered at 1100 °C for 4 h. The excitation spectrum for monitoring the $^5D_0 \rightarrow {}^7F_2$ emission (~615 nm) of Eu^{3+} ions consists of a broad band and some sharp lines. The broad excitation band centered at ~280 nm can be attributed to the charge-transfer transition arising from oxygen to tungsten [5,10]. In the range from 325 to 550 nm, the sample shows characteristic intra-configurational 4f–4f transitions of Eu^{3+}: sharp $^7F_0 \rightarrow {}^5L_6$ transition for 394 nm, $^7F_0 \rightarrow {}^5D_2$ transition for 464 nm and the $^7F_1 \rightarrow {}^5D_1$ transition for 535 nm [10]. So the $NaEu(WO_4)_2$ phosphor can be excited efficiently by near-ultraviolet (394 nm) or blue (464 nm)