Advanced Powder Technology xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Multifunctional broad-band excited Eu^{3+}-activated fluorescent materials for potential warm white light-emitting diodes (w-LEDs) and temperature sensor applications

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ARTICLE INFO

Article history:
Received 12 May 2017
Received in revised form 26 September 2017
Accepted 10 October 2017
Available online xxxx

Keywords:
Broad-band excitation
Warm white light-emitting diodes
Temperature sensor

ABSTRACT

Discovery of novel multifunctional fluorescent materials are of great concern to the development of disciplinary crossing and integration. In this work, we prepared a broad-band Eu^{3+}-activated Lu_2MoO_6 multifunctional material for potential warm white light-emitting diodes (*w*-LEDs) and temperature sensor applications. $Lu_{1.9}MoO_6$:0.1Eu^{3+} phosphor was synthesized by high-temperature solid-state reaction method, and the structure characterization was investigated for the first time. The excitation spectrum of this phosphor exhibits the intense broad band ranging from 250 nm to 440 nm assigned to the O^{2-}-Mo^{6+} charge transfer band (CTB) transition, and a strong red emission centered at 610 nm corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ions were detected under 365 nm excitation. Importantly, warm white light composite material was hybridized via blending commercial green, blue and the present red phosphors, which under 365 nm excitation exhibited a high color rendering index (CRI) of 78 at a correlated color temperature of 4271 K with CIE coordinates of x = 0.351, y = 0.308. Furthermore, a strong temperature sensitization phenomenon was found, where the results show that the emission intensities and chromaticity coordinates are sensitive to the temperature, which can provide guidance for the potential application in temperature sensing.

1. Introduction

Phosphor-converted w-LEDs have attracted much attention as promising next-generation solid state lighting devices due to superior efficiency, low energy consumption, and long lifetime etc [1–4]. Nowadays, combining a blue LED chip emitting at 465 nm with a broad band yellow $Y_3Al_5O_{12}$:Ce^{3+} (YAG:Ce^{3+}) phosphor has become mainstream. However, white light obtained by this method exhibits low CRI due to lack of red light in the emission spectra [5]. Another new strategy is to mix a near-ultraviolet (UV) InGaN-based LED chip (350–420 nm) with red, green and blue phosphors, which is a better strategy to produce white light with superior characteristics, such as good CRI and appropriate light temperature [6,7]. Unfortunately, the efficiency of currently commercially used red phosphors, such as Y_2O_2S:Eu^{3+} or Y_2O_3:Eu^{3+}, is relatively lower [8,9]. Therefore, the exploration of novel efficient red phosphors excited by near-UV or blue light is an urgent task.

Recently, Eu^{3+} doped molybdate and tungstate has been intensively investigated due to their broad and strong CTB in near-UV-blue region [10–12]. Several works have focused on Eu^{3+} doped molybdates Ln_2MoO_6 (Ln = Y, Gd, La, etc.) owing to the higher excitation efficiency of CTB from W/Mo-O than that of WO_4/MoO_4 [13–15]. For example, Y_2MoO_6:Eu^{3+} as a host red phosphor materials have been reported with strong red light emission under NUV excitation [14]. Moreover, a g-C_3N_4/Y_2MoO_6:Eu^{3+} composite phosphor was synthesized and characterized, under the excitation of 360 nm near ultraviolet light, these composite phosphors show tunable emission from blue to red region [15]. Recently, Peng Du synthesized a series of Eu^{3+}-activated Gd_2MoO_6 phosphors and a *w*-LED device was fabricated by integrating a blue-light chip and YAG:Ce^{3+} and Gd_2MoO_6: Eu^{3+} phosphor. [13] But the features of the red Gd_2MoO_6: Eu^{3+} phosphor did not stand out, which could be further improved. Attributed to charge transfer from O ligands to the Mo central ions in Eu^{3+} doped Ln_2MoO_6 phosphors, the strong broad excitation bands are usually located in a UV or near-UV region [15–17]. The luminescent properties and luminescence enhancement of Lu_2MoO_6:Eu^{3+} phosphors were studied by the

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https://doi.org/10.1016/j.apt.2017.10.008
0921-8831/

previous work [18,19]. However, the detailed structure refinement and promising application on warm *w*-LEDs and temperature sensor have not yet been investigated so far. What is more, these work remains to be further investigated.

Therefore, in this work, we prepared a broad-band excited Eu^{3+}-activated Lu_2MoO_6 multifunctional material for potential warm white light-emitting diodes (*w*-LEDs) and temperature sensor applications. The as-prepared $Lu_{1.9}MoO_6$:$0.1Eu^{3+}$ phosphor was investigated in detail including the structure refinement, luminescent properties, and decay kinetics, etc. Warm white light composite material was hybridized via blending commercial green, blue and the present red phosphors, which under 365 nm excitation exhibited a high color rendering index (CRI) of 78 at a correlated color temperature of 4271 K. In addition, a strong temperature sensitization phenomenon was found, where the results show that the emission intensities and chromaticity coordinates are sensitive to the temperature. All the results demonstrate that the multifunctional broad-band excited Eu^{3+}-activated fluorescent materials can be used for potential warm white light-emitting diodes (w-LEDs) and temperature sensor applications.

2. Experimental details

2.1. Sample preparation

The $Lu_{1.9}MoO_6$:$0.1Eu^{3+}$ phosphor was synthesized by the high-temperature solid-state method. Analytical reagent (A.R.) grade molybdenum trioxide (MoO_3), lutetium oxide (Lu_2O_3) (99.99%) and europium oxide (Eu_2O_3) (99.99%) were obtained from Sinopharm Chemical Reagent, Co. Ltd., Shanghai, China. The stoichiometric amounts of reactants were ground thoroughly in an agate mortar and preheated at 600 °C for 1 h. Subsequently, the products were removed from the muffle furnace, cooled, finely ground and sintered at 1200 °C for 4 h in air. Finally, the products were cooled to room temperature and ground into powder to form the final sample.

2.2. Characterization

The powder X-ray diffraction (XRD) data were collected on a PANalytical X'pert diffractometer equipped with a PIXcel 1D detector (Cu K_α, 1.5406 Å). The crystal structure refinement was performed using JANA2006 program [20]. The morphology of phosphors was examined by a Hitachi S3700N scanning electron microscope. The excitation, emission spectra and the decay curve were measured by a FLS920 (Edinburgh Instrument Ltd, Livingston, UK) fluorescence spectrophotometer equipped with a 450 W xenon (Xe) lamp as the light source and Shimidazu R9287 (Hamamatsu Photonics K.K., Hamamatsu, Japan) photomultiplier (200–900 nm) as the detector. The temperature-dependent luminescence properties were measured by the same spectrophotometer combined with a computer-controlled electrical furnace.

3. Results and discussions

3.1. Structure analysis

In order to obtain the crystallographic data for the Eu^{3+} ions, the structure refinement of $Lu_{1.9}MoO_6$:$0.1Eu^{3+}$ compound was firstly performed using JANA2006 program. All the diffraction peaks are in good consistent with JCPDS card 25-0972 (Tm_2MoO_6). Therefore, the structural parameters of Tm_2MoO_6 are used as initial parameters in the Rietveld analysis. Fig. 1 shows the observed (black points), calculated (red solid lines), and difference (gray lines) results for the Rietveld refinement at room temperature. Lu_2MoO_6 can be assigned to the monoclinic structure with space group *C*12/*c*1. The final refinement is stable and convergent well with low residual factors R_{wp} = 8.67%, R_p = 7.33% and χ^2 = 3.789, indicating the single phase with no unidentified diffraction peaks from impurity. The final refined crystallographic data are summarized in Table 1. The cell parameters are determined to be *a* = 16.2195 Å, *b* = 10.8871 Å, *c* = 5.27853 Å and *V* = 882.78 Å^3. Furthermore, the fractional atomic coordinates, isotropic displacement parameters (Å^2), as well as the main bond lengths (Å) are listed in Table 2. According to Table 2, Eu^{3+} ions can occupy Lu^{3+} site in the crystal lattice of Lu_2MoO_6. The crystal structure of Lu_2MoO_6 are given in Fig. 2. It can be seen that all the Lu^{3+} occupy three non-centrosymmetric crystallographic sites, namely, 4e, 4e (with C_2 site symmetry) and 8f (with C_1 site symmetry), which could favor the luminescence properties and will be further discussed below [21]. All Lu atoms are coordinated to eight O atoms, while Mo atoms are coordinated to five O atoms. Fig. 3 presents typical FE-SEM image of $Lu_{1.9}MoO_6$:$0.1Eu^{3+}$ phosphor. The obtained $Lu_{1.9}MoO_6$:$0.1Eu^{3+}$ phosphor are aggregated, and have irregular morphology. The average diameter is approximately micrometer range, which is in favor of its application in w-LEDs [22].

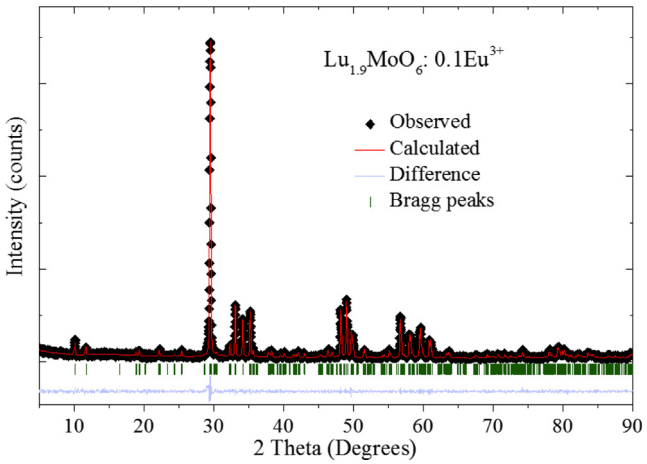

Fig. 1. The observed (◆) and calculated (upper solid line) X-ray diffraction patterns, the peak position (|), the difference between observed and calculated patterns (lower solid line) for $Lu_{1.9}MoO_6$:$0.1Eu^{3+}$ compound.

3.2. Photoluminescence properties

Fig. 4 shows the excitation (a) and emission (b) spectra of $Lu_{1.9}MoO_6$:$0.1Eu^{3+}$ phosphor. As can be seen from Fig. 4, the excitation spectrum shows the intense broad band ranging from 250 nm to 440 nm, which was assigned to the O^{2-}-Mo^{6+} CTB transition. It is worthwhile mentioning that the $Lu_{1.9}MoO_6$: $0.1Eu^{3+}$ phosphor can efficiently absorb the emission (370–400 nm) from NUV LED chips. Thus, it can be a potential candidate for application in near-UV excited w-LEDs. Moreover, observation of the O^{2-}-Mo^{6+}

Table 1
Crystallographic and Rietveld refinement data of $Lu_{1.9}MoO_6$:$0.1Eu^{3+}$ compounds.

Formula	$Lu_{2.9}MoO_6$: $0.1Eu^{3+}$
	C 1 2/*c* 1-monoclinic
Cell parameters	*a* = 16.2195(6) Å, *b* = 10.8871(4) Å, *c* = 5.27853(19) Å, *β* = 108.7201(19)°, *V* = 882.78(7) Å^3, *Z* = 8
Reliability factors	R_{wp} = 8.67% R_p = 7.33% χ^2 = 3.789 $R^2_{\beta F}$ = 6.71%

Please cite this article in press as: L. Li et al., Multifunctional broad-band excited Eu^{3+}-activated fluorescent materials for potential warm white light-emitting diodes (w-LEDs) and temperature sensor applications, Advanced Powder Technology (2017), https://doi.org/10.1016/j.apt.2017.10.008