Optik 124 (2013) 5517–5519

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

A new self-activated yellow-emitting phosphor $Zn_2V_2O_7$ for white LED

Shao-Ping Kuang[a,b,*], Yan Meng[a], Jie Liu[a], Zhan-Chao Wu[a,b,*], Lai-Shi Zhao[b]

[a] State Key Laboratory Base of Eco-chemical Engineering, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, PR China
[b] State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan 430074, PR China

ARTICLE INFO

Article history:
Received 2 November 2012
Accepted 30 March 2013

Keywords:
WLED
Self-activated
Yellow emission
$Zn_2V_2O_7$
Phosphor

ABSTRACT

A new self-activated yellow-emitting $Zn_2V_2O_7$ phosphor was synthesized by high temperature solid-state reaction. X-ray powder diffraction (XRD) analysis confirmed the sample with monoclinic formation of $Zn_2V_2O_7$. The excitation and emission spectra indicated the phosphor can be efficiently excited by near ultraviolet (NUV) light in 220–400 nm range and exhibit a bright broad yellow emission with the highest emission intensity at 531 nm. The broad emission band from 400 to 650 nm can be attributed to the charge transfer transition in the VO_4 tetrahedra, which suggests that the phosphor is a promising yellow phosphor applied for white light-emitting diodes (WLED).

1. Introduction

White light-emitting-diodes (WLEDs) are called the novel generation solid-state light sources for several advantages such as high luminous efficiency, low power consumption, maintenance and environmental protection [1–4]. WLED can be generated by two main ways. One is the combination of a blue (450–460 nm) chip with a yellow phosphor (YAG: Ce). The other is to mix the red/green/blue tricolor phosphors with a near ultraviolet (NUV, 350–410 nm) chip. As we all know, the available phosphors which can be excited by blue light are scarce. Therefore, development of the former fabrication process is restricted. NUV chips can offer a more efficient excitation source than blue chips [5], and the number of phosphors selectable excited by near ultraviolet chip is much larger than those applied on blue chips. So WLEDs fabricated with NUV chips and red/green/blue tricolor phosphors become a new research hotspot.

At present, the main tricolor phosphors for NUV InGaN-based LEDs are some classical phosphor, such as $BaMgAl_{10}O_{17}$: Eu^{2+} for blue, ZnS: (Cu^+, Al^{3+}) for green, and Y_2O_2S: Eu^{3+} for red [6]. Especially, the red and green phosphors are sulfide-based phosphors which exhibit low chemical stabilities against strong irradiation from InGaN chip and cause some environmental problems both in preparation and in application as they contain toxic elements. Therefore, it is urgent to search for new green and red phosphors or a new yellow phosphor with high efficiency, low cost, no environmental hazards.

Recently, vanadates (vanadium oxide) based materials have attracted a special attention due to their unique structural, optical, and magnetic properties [7]. Among these compounds, it has been found that some metavanadates have a rare luminescent property: they show a quite broad band emission from 400 to 700 nm. Metavanadates as self-activated phosphors have several advantages. Firstly, compared with the rare-earth-doped phosphor, vanadate self-activated phosphors are cheaper. Secondly, the broad band luminescence in the visible light range is effective to obtain a good color rendering property for illumination devices. Thirdly, vanadate was prepared at lower sintering temperatures (600 °C) compared with conventional phosphors, which is consistent with the requirements of energy saving for products in today's society. During the past few years, a number of broad-band-emitting vanadate phosphors have been synthesized and studied extensively which can be used for fabricating WLEDs [8–14]. However, to the best of our knowledge, there is no report about the broad-band-yellow-emitting phosphor $Zn_2V_2O_7$ for potential application on WLEDs.

In this paper, a new self-activated yellow phosphor $Zn_2V_2O_7$ was synthesized by solid stated reaction technique and its photoluminescent properties were investigated.

2. Experimental

2.1. Samples preparation

The powder sample $Zn_2V_2O_7$ was synthesized by the solid-state reaction method. $5ZnO{\cdot}2CO_3{\cdot}4H_2O$(AR) and V_2O_5(AR) as raw

* Corresponding authors at: State Key Laboratory Base of Eco-chemical Engineering, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, PR China. Tel.: +86 532 84023653; fax: +86 532 84023927.
E-mail addresses: qustksp@126.com (S.-P. Kuang), wuzhan_chao@163.com (Z.-C. Wu).

0030-4026/$ – see front matter © 2013 Elsevier GmbH. All rights reserved.
http://dx.doi.org/10.1016/j.ijleo.2013.03.172

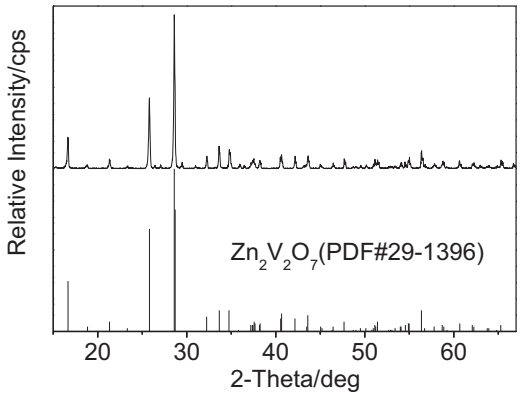

Fig. 1. XRD patterns of $Zn_2V_2O_7$ prepared at 600 °C.

materials were mixed with stoichiometric molar ratio, obtaining homogeneous mixtures by thorough grinding in an agate mortar and burned in an electric furnace at the temperature of 600 °C for 6 h.

2.2. Measurements

Crystal phase identification was carried out on an X-ray diffractometer (D-MAX2500/PC, RIGAKU Corporation of Japan) using 40 kV, 20 mA, and Cu *K*α radiation (1.5406 Å). Morphology and size of the calcined particles were observed by field-emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL Corporation of Japan). Excitation and emission spectra of the powdered phosphors were measured by a fluorescence spectrometer (F-2700, HITACHI High-Technologies Corporation) and a 450 W xenon lamp was used as the excitation source. All measurements were made at room temperature unless otherwise stated.

3. Results and discussion

3.1. XRD of phosphor powders

The XRD pattern of $Zn_2V_2O_7$ prepared at 600 °C is shown in Fig. 1. All the diffraction peaks can be attributed to $Zn_2V_2O_7$ (PDF#29-1396) which is monoclinic with lattice parameters $a = 7.429(5)$ Å, $b = 8.340(3)$ Å, $c = 10.098(3)$ Å, $\beta = 111.37(5)°$, $Z = 4$ and space group C2/c. The result shows that the sample obtained is the target product.

3.2. FE-SEM images of phosphor powders

The SEM images of $Zn_2V_2O_7$ sintered at 600 °C are shown in Fig. 2, which reveals the phosphor microstructure consisted of irregular grains with smooth surface. The particles are agglomerated slightly and the average diameter size of the grain is in the range of 3–7 μm. The results show that $Zn_2V_2O_7$ phosphor has a good crystallinity and a relatively low sinter temperature.

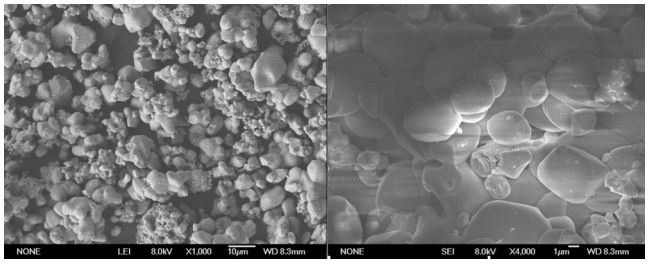

Fig. 2. SEM images of $Zn_2V_2O_7$ sintered at a 600 °C.

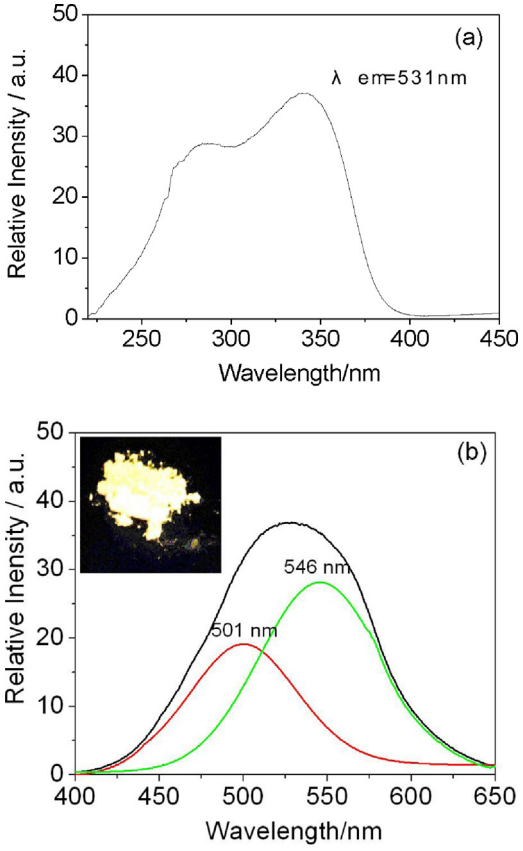

Fig. 3. Photoluminescence spectra of $Zn_2V_2O_7$: (a) excitation spectra ($\lambda_{em} = 531$ nm); (b) emission spectra ($\lambda_{ex} = 340$ nm). Inset: the photograph of $Zn_2V_2O_7$ under ultraviolet light irradiation.

3.3. Photoluminescence properties

The photoluminescence spectra of $Zn_2V_2O_7$ are shown in Fig. 3. A broad excitation band ranged from 220 to 400 nm is observed (Fig. 3(a)), which implies that this phosphor may be suitable for application on white LEDs excited by NUV chips. The maximum excitation intensity at 340 nm ($^1A_1 \rightarrow {}^1T_1$) is attributed to the charge transfer (CT) transition from oxygen ligands (O^{2-}) to the central vanadium ions (V^{5+}) in the VO_4 tetrahedra. Fig. 3(b) shows an emission spectrum of ZnV_2O_7 phosphor excited by 340 nm NUV light. It can be seen that ZnV_2O_7 exhibits a broad band emission from 400 to 650 nm with a maximum intensity at 531 nm without adding any other activators. The CIE chromaticity coordinates are calculated from the emission spectrum to be $x = 0.276$, $y = 0.499$. The inset in Fig. 3b shows photograph of $Zn_2V_2O_7$ under ultraviolet light irradiation. Bright yellow light is observed by naked eyes.

In the sample of $Zn_2V_2O_7$, the host lattice complex (tetrahedral VO_4) operates as the luminescence center. The CT transition from the 2p orbitals of O^{2-} to the 3d orbitals of V^{5+} in the VO_4 tetrahedra is the main reason for their luminescence properties. The V^{5+} ion has a closed-shell electronic structure with no *d* electron. Considering the electronic structure of the $VO_4{}^{3-}$ ion in T_d symmetry, the electron charge transfer process from the 2p orbital of O^{2-} to 3d orbital of V^{5+} ion is involved in the excitation and luminescence phenomena. Fig. 4 is the vanadium-oxygen (pyro) units in $Zn_2V_2O_7$ [15]. The bridging oxygen atom (O_1) connects the two four-coordinate vanadium atoms in a bent arrangement (bond angle (V—O_1—V) is 150°). Because of the structure, V_2O_7 become the