Journal of Rare Earths 36 (2018) 49–57

Contents lists available at ScienceDirect

Journal of Rare Earths

journal homepage: http://www.journals.elsevier.com/journal-of-rare-earths

Influence of reaction parameters on the luminescence properties of monodisperse $NaGd_{(1-x-y)}(WO_4)_2$:xEu^{3+},yTb^{3+} phosphor by molten salt synthesis☆

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ARTICLE INFO

Article history:
Received 1 April 2017
Received in revised form
11 July 2017
Accepted 14 July 2017
Available online 18 August 2017

Keywords:
$NaGd_{(1-x-y)}(WO_4)_2$:xEu^{3+}
yTb^{3+}
Molten salt method
Single component
WLEDs
White light

ABSTRACT

Eu^{3+} activated and Eu^{3+}, Tb^{3+} co-activated monodisperse sodium double tungstates $NaGd(WO_4)_2$ phosphors were prepared by molten salt method at 750 °C for 10 h using NaCl as a flux. The crystal structure and morphology of the as-synthesized phosphors were measured by XRD and SEM, respectively. The photoluminescence properties were characterized by PL spectra, decay lifetime and CIE. The presence of NaCl plays an important role in the morphology and luminescence properties. In this work, NaCl and one of the raw material Na_2CO_3 in a certain proportion will form a low eutectic salt to decrease the reaction temperature and benefit the formation of monodisperse $NaGd(WO_4)_2$ crystals. The color of Eu^{3+} and Tb^{3+} co-doped $NaGd(WO_4)_2$ phosphors can be tuned from creamy white to orange, red and green by adjusting the doping concentration of rare earth ions, since the emission contain the broad blue-green emission origin from $NaGd(WO_4)_2$ host and characteristic red and green emission origin from Eu^{3+} and Tb^{3+} ions. The electroluminescent spectra and CIE measurement shows that the LED device with $NaGd_{(1-x)}(WO_4)_2$:xEu^{3+} ($x = 0.24$) phosphor can be excited by 365 nm and 380 nm LED chip, and their CIE coordinate is ($x = 0.45$, $y = 0.45$) and ($x = 0.36$, $y = 0.37$), *Ra* is 80.3 and 86.3, T_c is 3196 and 4556 K, respectively. As a single-component phosphor, $NaGd(WO_4)_2$:Eu^{3+},Tb^{3+} have potential application in UV-pumped WLEDs.

1. Introduction

Tungstate compounds have attracted great attention in many fields for their optical,[1–5] photocatalytic,[6–8] photosensitizer,[9] thermal,[10,11] photoelectrochemical[10] properties, and so on. As the hosts of luminescence materials, they show great potentiality for the characteristic host absorption in UV region. Usually, tungstate phosphors as a kind of self-activating phosphors can emit a broad blue-green emission under the UV excitation. So the emission spectra of rare earth ions doped tungstate phosphors contain the broad and intense charge-transfer (CT) absorption bands in the UV region and 4f–4f sharp lines origin from rare earth ions. Based on this luminescent properties, we believe that full color white light phosphors can be designed from these kinds of tungstate phosphors. There are a great many tungstate compounds suitable for the host of luminescent materials, such as AWO_4 (A = Ca, Sr, Ba),[12] $LiLn(MO_4)_2$:Eu^{3+} (Ln = La, Eu, Gd, Y; M = W, Mo),[13] Bi_2WO_6,[14] $Gd_{(2-x)}MO_6$:Eu_x^{3+} (M = W, Mo),[15] $ZnWO_4$:Eu^{3+}.[16] Among them, rare earth alkali metal double tungstate with tetragonal (I4) structure and formula $ARE(WO_4)_2$ (A = Li, Na, K; RE = Y, La, Gd and Lu) have attracted great attention in optical field.[17–20] Wang et al. reported $NaLu(WO_4)_2$:Eu^{3+} microcrystal and investigated its luminescence properties for LED, and they also indicated the efficient energy transfer from the host matrix to the localized states of lanthanide ions.[21] Huang et al. investigated the effect of alkali-metal ions on the local structure and luminescence properties for

☆ **Foundation item**: Project supported by the National Natural Science Foundation of China (21301115) and the Shanghai University Innovation Fund (sdcx2012005), Funding scheme for training young teachers in Colleges and Universities (Grant ZZSD12025), and Opening Foundation of the Key Laboratory for Advanced Displays and System Application, Ministry of Education (Shanghai University) (P201602).

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http://dx.doi.org/10.1016/j.jre.2017.07.007
1002-0721/

alkali-metal europium double tungstate compounds $AEu(WO_4)_2$ (A = Li, Na, K), and they found that alkali-metal ions not only modify the crystal structure but also distort the metal oxide polyhedron and disturb the sublattice structure around the luminescent center ions.[20] Zaldo et al. prepared Yb^{3+} doped $NaGd(WO_4)_2$ crystalline layers on Y modified $NaGd(WO_4)_2$ Czochralski grown single crystal substrates; their purpose of the work is to study strategies to compensate these crystallographic modifications in double tungstate crystals and to determine a viable layer substrate combination for the development of Yb-doped layers.[17] Cascales et al. provide the crystallographic information required to select the most suited Yb-doped layer and optically inert substrate combination.[19] To our knowledge, most of the reported double tungstate $ARE(WO_4)_2$ (A = Li, Na, K; RE = Y, La, Gd and Lu) are focused on single crystal and their laser properties, only few of them are about the powder synthesis and luminescence properties for LEDs.[22]

In our work, we synthesized a series of monodisperse $NaGd_{(1-x-y)}(WO_4)_2$:xEu^{3+}, yTb^{3+} phosphor by molten salt method using NaCl as the flux, and found sodium gadolinium double tungstate $NaGd(WO_4)_2$ (NGW) is an excellent host for rare earth doped phosphors. There are many synthesis routes for synthesizing morphology controlled monodisperse micro- and nano-structured inorganic compounds, such as hydrothermal method,[21] sol–gel method,[23] coprecipitation method,[24] spray deposition method,[25] microwave method,[26,27] molten salt method,[28,29] ultrasonic method[30,31] and so on. Molten salt synthesis (MSS) is one of the simplest, most versatile, environmentally friendly, and cost effective routes for the synthesis of uniform crystalline and single phase powder.[28,32–34] This paper was focused on the synthesis of $NaGd(WO_4)_2$:Eu^{3+},Tb^{3+} phosphors via molten salt method and the investigation of the effect of synthetic method on the crystal size, morphology and luminescence properties. By adjusting the reaction parameters, such as the amount of molten salt, reaction time and temperature, and doping concentration of rare earth ions, the size, morphology and luminescence properties can be controlled. And the emission color can be tuned by adjusting the doping concentration of Eu^{3+} and Tb^{3+} ions in the $NaGd(WO_4)_2$ host, which is due to the combination of the emission of NGW host and characteristic 4f–4f transition of rare earth ions.

2. Experiment and measurement

Powder samples of $NaGd_{(1-x-y)}(WO_4)_2$:xEu^{3+},yTb^{3+} phosphor were prepared by molten salt synthesis. The starting materials were Na_2CO_3 (AR), WO_3 (AR), Gd_2O_3 (99.99%), Eu_2O_3 (99.99%) and Tb_4O_7 (99.99%), respectively. In addition, NaCl (AR) was added as a flux. The raw materials were mixed homogeneously in an agate mortar for about 30 min and then calcined in an alumina boat at a certain temperature (400–900 °C) for about 10 h. The obtained powder was washed completely with deionized water for several times and detected the upper clear solution by $AgNO_3$ solution to ensure the Cl ions have been totally removed, then the final product was dried in an oven at 80 °C for 12 h.

For the prototype LED device, the LED chip (λp = 365 and 380 nm) was attached on the ceramic substrate by silver paste, and gold wires were bonded for electrical connection. Then the phosphor/silicone mixture was encapsulated on the top of the LED chip. After the baking processes (150 °C for 1 h) of the mixture, the electroluminescence performances were tested.

XRD analyses were recorded with a Rigaku D\max-2550 X-ray diffractometer equipped with a Cu-Kα radiation. The morphology of product was investigated by a Philips XL-30 Scanning electronic microscope (SEM). PL excitation and emission spectra were obtained using a fluorescence spectrophotometer (RF-5301PC) at room temperature. The luminescence decay profile was examined at ambient temperature on a spectrofluorometer (FLSP920, Edinburgh Instruments) under excitation of 246 nm and emission of 613 nm. The CIE color coordinates was calculated using the CIE1931xy.v1.5 freeware program. Electroluminescence performances were measured by integrating sphere (HAAS-2000). All the measurements were performed at room temperature.

3. Results and discussion

3.1. Influence of the amount of molten salt, reaction temperature, doping concentration on structure

In order to investigate the influence of the amount of molten salt on the structure, we carried out a series experiments of different molar ratios of raw material and NaCl. Fig. 1 shows the XRD patterns of $NaGd_{0.96}Eu_{0.04}(WO_4)_2$ obtained by molten salt synthesis at 750 °C for 10 h in the presence of NaCl with the molar ratio of (a) 0, (b) 1:6, (c) 1:12 and (d) 1:18, respectively. All the diffraction peaks of the samples (a, b, c and d) can be indexed to tetragonal sodium gadolinium tungstate $Na_{0.5}Gd_{0.5}WO_4$ (JCPDS card No. 25-0829) with space group $I41/a(88)$, and a lattice parameter of $a = b = 0.5243$ nm, $c = 1.1368$ nm, and $\alpha = \beta = \gamma = 90°$(Fig. 1a–d). With increasing the molar ratio of NaCl and raw material, there are not much difference from the XRD patterns. So in these experiments, the amount of NaCl has little influence on the phase purity of the product.

Fig. 2 shows the XRD patterns of the prepared powders obtained at different calcining temperatures for 10 h by molten salt synthesis in the presence of NaCl with molar ratio of 1:12, respectively. The diffraction peaks of the products obtained at 650, 700 and 750 °C can be indexed to $Na_{0.5}Gd_{0.5}WO_4$ phase (Fig. 2(a)–(c)), with space group of $I41/a$[88], corresponding to the JCPDS card 25-0829. When the temperature is higher than 800 °C, the other phase came into being (Fig. 2(d) and (e)). In this work, though NaCl was used as the flux and its melt point is 801 °C, we obtain the pure NGW phase at 650–750 °C, this may be due to the melting point of the eutectic salt of NaCl and Na_2CO_3 is 637 °C.[35,36] So in this reaction, above 637 °C, the reaction medium has already been in a liquid environment, which promoted the completion of the reaction. And the Na_2CO_3 salt came from the raw material. The results indicate that molten salt synthesis can reduce the synthesized temperature to

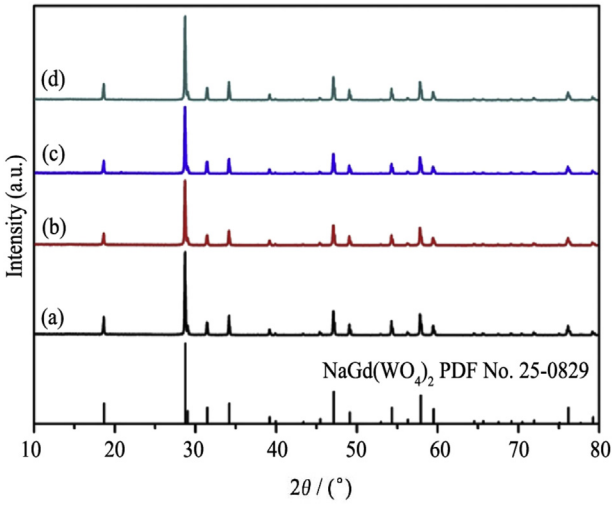

Fig. 1. XRD patterns of $NaGd_{0.94}Eu_{0.06}(WO_4)_2$ obtained by molten salt synthesis at 750 °C for 10 h in the presence of NaCl with the molar ratio of (a) 0, (b) 1:6, (c) 1:12 and (d) 1:18.