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Effects of NaCl flux on microstructure and luminescent characteristics of $KSrPO_4:Eu^{2+}$ phosphors

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ABSTRACT

$KSr_{0.99}PO_4:0.01Eu^{2+}$ phosphors were synthesized in succession by adding different NaCl flux concentrations (0, 2, 4 and 6 wt.%). The sintering condition was set at 1300 °C for 3 h under 97% N_2/3% H_2 atmosphere. The effect of NaCl flux on the microstructural and luminescent characteristics of $KSr_{0.99}PO_4:0.01Eu^{2+}$ phosphors were investigated and discussed. The XRD results showed that the phase purity of $KSr_{0.99}PO_4:0.01Eu^{2+}$ phosphors could be improved after adding NaCl flux. The EDS data showed that the peaks of NaCl flux were not detected. The SEM images showed that the particle size became bigger when more NaCl flux was added. It was also observed that many little fragments on the surface appeared as the NaCl flux increased to 4 wt.% and 6 wt.%. Additionally, all of the $KSr_{0.99}PO_4:0.01Eu^{2+}$ phosphors emitted blue luminescence under UV excitation. The use of the NaCl flux in $KSrPO_4$ may cause the change the crystal field of $KSrPO_4$ but not the change in the energy transfer mechanism among Eu^{2+} ions.

1. Introduction

Because of high luminous efficiency, energy-saving, long lifetime and environmental protection properties, white light-emitting diode (WLED) has attracted a significant attention over the past few years as a potential replacement for incandescent and fluorescent light sources [1]. At present, the most popular method to generate white light is to use a blue LED chip and a yellow-emitting phosphor, usually made of cerium doped yttrium aluminum garnet (YAG:Ce^{3+}) [2]. However, the WLED produced using this method have the following problems: variation of white emitting color with different input powers and low color rendering index due to two-color mixing. Recently, a new approach that uses the red/green/blue tricolor phosphors excited by ultraviolet (UV) or near UV chips to generate white light was suggested [3]. The two advantages in this approach include, high color tolerance and excellent color rendering index.

Because of UV excited phosphors, phosphate compounds such as $ABPO_4$ (A: Li. Na and K; B: Mg. Ca and Sr) have become an important family of luminescent materials. The rigid tetrahedral three dimensional matrix of phosphate is thought to be ideal for charge stabilization [3–10]. It is known that the Eu^{2+} ion is an activator having a f–d broadband transitions. Therefore, the emission and absorption spectra of Eu^{2+} ion usually consist of broad band (UV to red range) due to the transitions between the $^8S_{7/2}$ ($^4f_7$) ground state and the crystal field components of the $4f^65d$ excited state configuration. Since the involved 5d orbital is external, the positions of the excitation and emission wavelength of Eu^{2+} strongly depend on the host crystal [1,3]. Moreover, the advantage of using Eu_2O_3 in phosphors is that its quantum efficiency can approach unity in a suitable crystalline environment [1]. Thus, in recent years there have been many reports on Eu^{2+}-doped phosphate phosphors applied not only on WLED, but also plasma display panels, medical devices, and others [4–6]. There are many methods for preparing the phosphate series phosphors, such as solid-state reaction [3–7], co-precipitation [8] and combustion method [9]. However, the co-precipitation and combustion methods have disadvantages of large energy loss for the removal of organic elements during calcining process and difficulties in controlling powder morphology, thus reducing the ease of industrial mass production. Although the solid-state reaction also has some disadvantages of high firing temperature, long duration time and low chemical uniformity, it can be improved by adding different flux additions [10–14]. A flux method is well-known to accelerate the kinetics of the formation of the desired materials by enhancing diffusion coefficients. Therefore, the flux method has potential advantages such as the mass productivity and the ability to obtain fine particle morphology as well as the control of the particle size of products and so on [13,14]. Moreover, it was reported that in the

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high temperature sintering, the fluxes affected the ionic diffusions, the crystallite size distribution, crystallization and the formation of the phosphors [15]. In order to improve the drawback of the solid-state reaction, a flux addition has been developed in research [13–20]. Kottaisamy et al. and Lee et al. confirmed that flux method could affect the particle size distribution of phosphor as well as growth condition [16,17]. Additionally, Park et al. also found that the AlF_3 and H_3BO_3 fluxes of alkali- or alkaline earth metals not only improved the particle morphology but also reduced the sintering temperature [18]. Lee et al. reported that the phosphor powder prepared without the flux BaF_2 had irregular morphologies and aggregated structure [19]. Additionally, with adding the flux such as BaF_2, the photoluminescence intensities of phosphor can be improved [20]. Thus, the application of phosphor in WLED leads to an optimized particle size distribution due to a better packing density. However, there has been no study on the effect of the addition of NaCl flux on the microstructure and luminescent characteristics of $KSrPO_4:Eu^{2+}$ phosphors.

In this paper, the $KSrPO_4:Eu^{2+}$ phosphors were synthesized via the solid-state reaction. The effects of different concentrations of NaCl flux on the microstructure and luminescent characteristics of the $KSrPO_4:Eu^{2+}$ phosphors were investigated by using X-ray diffraction (XRD), energy dispersive spectrometer (EDS), scanning electron microscopy (SEM) and photoluminescence (PL) measurement.

2. Experimental procedure

2.1. Samples preparation

$SrCO_3$, KH_2PO_4 and Eu_2O_3 powders all with a purity of 99.9% were used as the starting materials for the $KSrPO_4:Eu^{2+}$ phosphors. The molar ratios for $SrCO_3$, KH_2PO_4 and Eu_2O_3 powders were kept at 0.99: 1: 0.01 to form a $KSr_{0.99}PO_4:0.01Eu^{2+}$ phosphor. The powders were mixed with alcohol for the solvent and ball-milled for 1 h with zirconia balls and different concentrations (0, 2, 4 and 6 wt.%) of NaCl flux were added. The addition of the NaCl flux is expected to lower the melting temperature, thus dissolving one or more of the components in the reaction region without entering into the solid-state reaction [10,11]. After drying, the mixed powders were placed on an Al_2O_3 crucible in a tube furnace and then sintered in a tube furnace to form the $KSr_{0.99}PO_4:0.01Eu^{2+}$ phosphors. For most phosphate series phosphors, the sintering temperature is set as 1300 °C for 3 h with an average heating rate of 2 °C/min [4,5]. The sintering atmosphere is 97% N_2/3% H_2, a reduction atmosphere used to reduce Eu^{3+} to Eu^{2+}. After sintering, the phosphor samples were cooled to room temperature and then characterized.

2.2. Characterization

The crystalline phases of the phosphors were identified using X-ray diffraction (XRD, Bruker D8 Advance) analysis with Cu Kα radiation of $\lambda = 1.54$ Å using a Ni filter, and with a secondary graphite monochromator. A scan range of $2\theta = 10–70°$ with a step of 0.03° and 0.4 s as a count time per-step were used. The constituent elements of the phosphors were detected by energy dispersive spectrometer (EDS, JSM-6400F. JEOL, Japan) analysis. The scanning electron microscopy (SEM; HORIBA EX-200) was used to observe particle morphology of the phosphors. The excitation, emission spectra and fluorescence decay time were obtained using photoluminescence measurement (PL, JASCO FP-6000), which was equipped with a 150 W Xenon lamp as the light source. For accuracy of data, the specimens were measured within the same sample holder to ensure the consistent amount of phosphor materials in all samples.

3. Results and discussion

3.1. Structure

Fig. 1 shows the X-ray diffraction patterns of $KSr_{0.99}PO_4:0.01Eu^{2+}$ phosphors with different concentrations of NaCl flux sintered at 1300 °C for 3 h. The XRD result shows that the $KSr_{0.99}PO_4:0.01Eu^{2+}$ phosphor without NaCl flux contains an impurity phase "$Sr_3(PO_4)_2$" This indicates that starting materials sintered at 1300 °C for 3 h fail to convert completely into the $KSrPO_4$ lattice. Thus, the sintering temperature should be higher than 1300 °C. It is clearly observed that the phase purity could be improved with the addition of NaCl flux. All the $KSr_{0.99}PO_4:0.01Eu^{2+}$ phosphors prepared with addition of NaCl flux sintered at 1300 °C for 3 h show a single phase. This is according to the data reported for $KSrPO_4$ powder in JCPDS #33-1045, which demonstrate that the $KSr_{0.99}PO_4:0.01Eu^{2+}$ phosphors is an orthorhombic structure with space group Pnma and lattice constants $a \sim 7.35$ Å, $b \sim 5.56$ Å, $c \sim 9.64$ Å and $\alpha = \beta = \gamma = 90°$. The NaCl flux addition speeds up the kinetics of the formation of the desired $KSrPO_4$ phosphors by enhancing diffusion coefficients, dissolving one or more of the components and then permitting material transport to the reaction region to enhance the sintering [12].

3.2. Element analysis

Fig. 2 shows the EDS data of $KSr_{0.99}PO_4:0.01Eu^{2+}$ phosphors sintered at 1300 °C for 3 h with NaCl flux of (a) 0 wt.%, (b) 2 wt.%, (c) 4 wt.% and (d) 6 wt.%. It showed the existence of Eu^{2+} element in the $KSrPO_4:Eu^{2+}$ powders after combining with the XRD results. Moreover, it is also found that K, Sr, Eu, P, and O elements are well maintained in the $KSr_{0.99}PO_4:0.01Eu^{2+}$ phosphor powders. On the other hand, the peaks of NaCl were not detected. These results are consistent with the reports from Lo et al. [21], because the flux materials are unable to enter the solid-state reaction to form the end-product [13].

3.3. Morphology

Fig. 3 shows the SEM images of $KSr_{0.99}PO_4:0.01Eu^{2+}$ phosphors sintered at 1300 °C for 3 h with NaCl flux of (a) 0 wt.%, (b) 2 wt.%, (c) 4 wt.% and (d) 6 wt.%. It is clearly with addition of NaCl flux, the particle size of the sintered $KSr_{0.99}PO_4:0.01Eu^{2+}$ phosphors can be enhanced. The average particle sizes of the $KSr_{0.99}PO_4:0.01Eu^{2+}$ phosphors with NaCl flux of 0, 2, 4 and 6 wt.% are around 2, 4, 6 and 8 μm, respectively. In the case of 2 wt.% NaCl flux, as

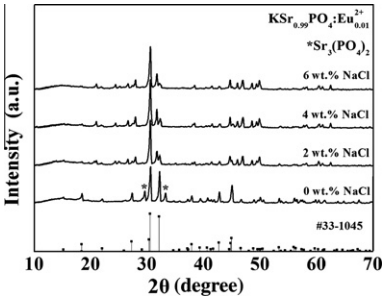

Fig. 1. XRD pattern of $KSr_{0.99}PO_4:0.01Eu^{2+}$ phosphors with different concentrations of NaCl flux sintered at 1300 °C for 3 h.