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Microwave-assisted solvothermal preparation and photoluminescence properties of Y_2O_3:Eu^{3+} phosphors

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Abstract

Europium doped yttrium oxide phosphors were synthesized by a rapid microwave-assisted solvothermal method. The microwave processing time for synthesizing the precursors of Y_2O_3:Eu^{3+} powders was as short as 5 min. After calcination at 600 °C, a well-crystallized pure phase of Y_2O_3:Eu^{3+} was obtained. The morphology of the precipitated powders was spherical and composed of nano-sized grains. As the microwave irradiation time was increased, the average particle size of the spherical powders increased, and the crystallinity of heat-treated powders was also enhanced. The synthesized powders retained the spherical morphology after heating treatments. An intense red emission at 611 nm was assigned to the $^5D_0$–$^7F_2$ transition of Eu^{3+}.

Keywords: D. Y_2O_3; Microwave; Solvothermal; Spherical; Methanol

1. Introduction

Field emission displays (FEDs) are considered to be one of the promising flat panel displays (FPDs) due to the superior properties, such as high brightness, high contrast, wide viewing angle, and fast response time [1–3]. For improving the performance of color purity in FEDs, developing phosphors with sufficient brightness and high chemical stability is required. Recently, oxide-based phosphors for FEDs have been intensively searched because of the good stability under high current density [4]. Among oxide-based phosphors, europium activated yttrium oxide (Y_2O_3:Eu^{3+}) is known as one of the promising phosphors, due to its short decay time, high luminescence, long-term thermal stability, and sharp red emission [5–7].

Y_2O_3:Eu^{3+} phosphors have been synthesized via different methods. In the solid-state method, the required temperature is higher than 1000 °C [8–10]. The high-temperature heating usually results in unfavorable coarsening of particles and serious aggregation. In the conventional solvothermal and hydrothermal processes, the processing temperature is reduced. However, the required heating time is relatively long (4–72 h) [5,11–14]. In order to overcome the drawbacks of these methods, it is necessary to develop a new process for synthesizing Y_2O_3:Eu^{3+} phosphors.

The microwave-hydrothermal method allows the formation of several oxides with controlled particle sizes and well-defined morphologies [15–18]. The microwave-hydrothermal process presents interesting advantages when compared to the conventional methods, such as (a) low synthesis temperatures, (b) short processing durations, and (c) formation of different morphologies [19].

A facile microwave-assisted solvothermal route has been used to synthesize ceramic powders, such as SnO_2, ZnO, ZrO_2, Sr_2CeO_4 and $Y_3Al_5O_{12}$, in a short processing time [20–23]. The advantages of the microwave process are attributed to the rotation of the dipolar molecules in the solution under the influence of an applied microwave electric field. During this process, molecules lose energy in the form of heat by molecular friction [22,24–26]. Thus, the heat is produced within the liquid and not transferred from the vessel as in the other conventional system [27]. Therefore, the microwave-assisted process can provide uniform heating and shorten the reaction time for synthesizing ceramic powders. In addition, the morphology and size of formed particles can be well controlled by changing solvents and reaction time [20,26,28]. Compared with conventional methods, the microwave-assisted process is found to be a convenient and

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energy efficient route to produce ceramic powders [29,30]. In the present study, the microwave-assisted solvothermal process was utilized to synthesize spherical Y_2O_3:Eu^{3+} phosphors. The effects of microwave irradiation time on the structure and morphology of Y_2O_3:Eu^{3+} powders were investigated. The effects of calcination temperature on the photoluminescence properties of Y_2O_3:Eu^{3+} phosphors were also studied.

2. Experimental

Y_2O_3:Eu^{3+} powders were prepared via the rapid microwave-assisted solvothermal route. The molar ratio of Y^{3+}:Eu^{3+}:O^{2-} was set to 1.86:0.14:3. Stoichiometric oxides of each element were dissolved in HNO_3, and the mixed solution was stirred at room temperature for 3 h. Methanol was added with threefold volume of the above solution. The microwave-assisted solvothermal reaction was treated in a double walled vessel. The microwave system (MLS 1200 Mega) was operated at a frequency of 2.45 GHz and a fixed power of 500 W at 180 °C. The mixed solution was heated with microwave irradiation for 5, 10, 15 and 20 min. Under microwave irradiation, white precipitates were immediately formed. The formed precipitates were dried at 70 °C in an oven for 2 h. Microwave-derived precursors were further calcined in a regular box furnace at 600 °C for 2 h in air. In order to investigate the effects of calcination temperature on the microstructural and photoluminescence properties of Y_2O_3:Eu^{3+} powders, the precursor obtained after microwave irradiation for 15 min was further calcined at 800 °C, 1000 °C, 1200 °C and 1400 °C for 2 h in air.

The crystal structure of as-synthesized and calcined powders was investigated using an X-ray diffractometer (XRD, Philips X'Pert/MPD) operated at 45 kV and 40 mA. The morphology of powders was examined using a scanning electron microscope (SEM, Hitachi, S-800) and a transmission electron microscope (TEM, Hitachi H-7100). The photoluminescence properties of the prepared powders were analyzed using a fluorescence spectrometer (Hitachi, F-4500). A 150 W Xe lamp was used as a multi-wavelength light source. The equipped photomultiplier tube (PMT) (Hamamatsu R928) was operated at 400 V. The excitation spectra for samples were monitored by an emission wavelength at 611 nm, and the emission spectra were recorded by exciting the sample at 254 nm.

3. Results and discussion

3.1. Effects of microwave irradiation time on structure and morphology of Y_2O_3:Eu^{3+} powders

Fig. 1(a) illustrates the XRD patterns of the microwave-derived Y_2O_3:Eu^{3+} powders after microwave irradiation for 5 min. No characteristic diffraction peaks were observed, implying that the as-prepared powders were in an amorphous phase. Fig. 1(b)–(e) illustrates the XRD patterns of 600 °C-calcined powders obtained after microwave irradiation for 5, 10, 15 and 20 min, respectively. These XRD patterns exhibited well-resolved diffraction peaks, indicating that well-crystallized powders were formed. No impurity phases were detected

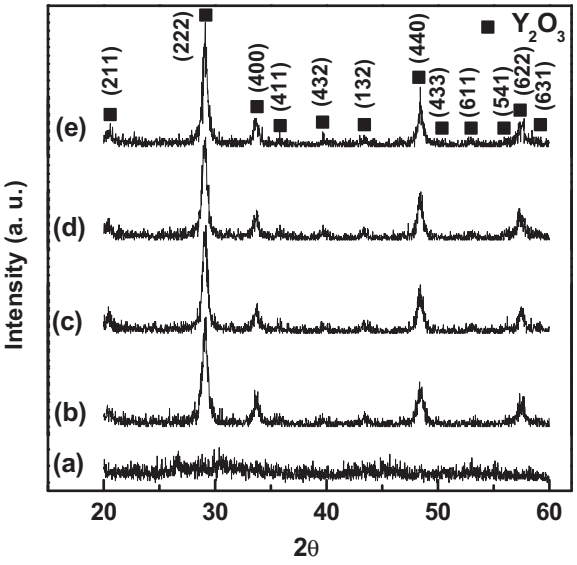

Fig. 1. X-ray diffraction patterns of as-prepared Y_2O_3:Eu^{3+} powders obtained under microwave irradiation for (a) 5 min, and 600 °C-calcined Y_2O_3:Eu^{3+} powders obtained under microwave irradiation for (b) 5 min, (c) 10 min, (d) 15 min and (e) 20 min.

in the diffraction patterns. The obtained diffraction patterns were consistent with the data reported in ICCD No. 89-5592 [31]. It was confirmed that the single cubic phase of Y_2O_3:Eu^{3+} powders was obtained. The reaction temperature for synthesizing single phase of Y_2O_3:Eu^{3+} powders is above 1000 °C in the solid state method [9,32]. However, in the microwave-assisted solvothermal process, the reaction temperature for synthesizing pure phase of Y_2O_3:Eu^{3+} powders is reduced to 600 °C. This is attributed to the improved compositional homogeneity and the enhanced reactivity in the microwave-derived precursors, thereby reducing the required heating temperature for preparing Y_2O_3:Eu^{3+} powders.

The crystallite sizes of the calcined powders were calculated from the FWHM (full width of half maximum) of the (2 2 2) diffraction peak in the XRD patterns using Scherrer's equation. The crystallite size of 600 °C-calcined Y_2O_3:Eu^{3+} powders obtained after microwave irradiation for 5 min was 18.7 nm. When the microwave irradiation time was increased to 20 min, the crystallite size of formed powders increased to 20.8 nm. It was found that the crystallite size of Y_2O_3:Eu^{3+} powders increased with an increase in the microwave irradiation time.

Fig. 2 shows the TEM micrograph and the selected area electron diffraction (SAED) pattern of the powders obtained by microwave irradiation for 5 min. The TEM micrograph shows that the as-prepared powders had a spherical shape with an average diameter of 1–2 μm and were softly agglomerated. Some nano-sized grains may be clearly observed on the surface of the spherical particles. The SAED pattern showed diffused halo rings, indicating the amorphous nature. When the microwave irradiation time was prolonged to 10, 15 and 20 min, the as-prepared powders SAED pattern did not change.

The SEM images of as-prepared powders obtained by under 5, 10, 15 and 20 min irradiation are shown in Fig. 3(a)–(d), respectively. In Fig. 3(a), the microwave-derived powders