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Crystalline morphology and photoluminescent properties of $YInGe_2O_7$: Eu^{3+} phosphors prepared from microwave and conventional sintering

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Abstract

This paper describes an investigation of the crystalline morphology and photoluminescent properties of $YInGe_2O_7$:Eu^{3+} powders using microwave assisted sintering. For comparison, the properties of $YInGe_2O_7$:Eu^{3+} powders sintered at 1200 °C in conventional furnace for 10 h were also investigated. X-ray powder diffraction analysis confirmed the formation of monoclinic $YInGe_2O_7$ without second phase or phases of starting materials as $YInGe_2O_7$:50 mol% Eu powders sintered at 1200 °C in microwave furnace for 1 h. Scanning electron microscopy showed smaller particle size and more uniform grain size distributions are obtained by microwave assisted sintering. In the PL studies, both microwave sintered and conventionally sintered powders emitted a maximum luminescence centered at 620 nm under excitation of 393 nm with similar luminescent intensity. The results show that microwave processing has the potential to reduce the time and required energy input for the production of $YInGe_2O_7$:Eu^{3+} phosphors without sacrificing the photoluminescence.

Keywords: A. Sintering; Phosphors; $YInGe_2O_7$; Microwave; Luminescence

1. Introduction

White light emitting diodes (LEDs) are candidates for new lighting systems in the future due to their advantages of high brightness, reliability, long life time, environment-friendly and low maintenance [1,2]. Recently, considerable efforts have been devoted to study on rare earth luminescent materials used for white LEDs [3–5]. Oxide phosphors have attracted a lot of attention because of high chemical stability relative to that of sulfide phosphors [6]. Many studies have been conducted to develop new oxide phosphors with high performance for phosphor applications [7,8].

In the past, $YInGe_2O_7$:Eu^{3+} phosphor has been prepared by solid-state reaction using a conventional sintering furnace [9]. However, a long sintering time (∼10 h), is required to synthesize the $YInGe_2O_7$:Eu^{3+} phosphor with single phase and high enough luminance intensity. The conventional synthesis of phosphors usually needs high temperature solid-state reactions to generate agglomerate powders, which can permit to easily change the structural characteristics of the powders [10]. Since the luminescent efficiency decreases as the size of the phosphor particles reduces, the preparation process of phosphor powders becomes an important issue in the technological procedure [11]. To achieve a better quality of small particle size powders an alternative sintering method, microwave assisted sintering, was proposed using different heat generation mechanisms. In contrast to conventional furnace sintering, the material sintered in a microwave furnace interacts with microwaves instead of radiant heat. Because heat is generated within the material itself, heating is more volumetric and can be very rapid and selective [12]. Microwave assisted sintering was observed to lower the activation energy significantly and thus enhance substantially the diffusion rate of the species. Microwave assisted sintering of materials has generally been found to reduce required sintering time and temperatures [13–15] and achieve a rapid heating rate [16].

In the present study, we synthesized the $YInGe_2O_7$ doped with Eu^{3+} phosphor materials using a microwave sintering

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technique and discussed its microstructure and photoluminescent properties. The results showed that microwave sintering improves the crystalline properties and then enhances the emission intensity of phosphor, even in a shorter sintering time.

2. Experimental procedure

2.1. Samples preparation

The raw materials, Y_2O_3, In_2O_3, GeO_2, and Eu_2O_3 with a purity of 99.9%, were mixed in a ball mill and ground for 1 h with zirconia balls. After drying, Eu^{3+} doped $YInGe_2O_7$ phosphors were synthesized by means of a solid-state reaction method, using microwave furnace and conventional furnace, to form $YInGe_2O_7$ doped with 50 mol% Eu^{3+} powders ($YInGe_2O_7$:Eu^{3+}). Fig. 1 shows the flow chart of the $YInGe_2O_7$:Eu^{3+} phosphors prepared by the solid-state reaction method. As in the case of microwave sintering, a microwave furnace (Therm Wave Mod. III), with a continuously variable power of 2.45 GHz microwaves up to 1.3 kW was used. Silicon carbide (SiC), having a very strong heating response to 2.45 GHz microwaves, was used as a susceptor to provide indirect heating of the powders [17]. The material sample was placed on an Al_2O_3 crucible in a microwave cavity surrounded by four silicon carbide susceptors and encapsulated by a ceramic fiber insulating material. The samples were sintered at 1200 °C for 1 h under an air atmosphere with a power of 900 ± 20 W, which produced an average heating rate greater than 100 °C/min. For comparison, the sample was also sintered at 1200 °C for 10 h under an air atmosphere with the heating and cooling rate controlled at 5 °C/min.

2.2. Characterization

The crystalline phases of the phosphors were identified by X-ray diffraction (Bruker D8 Advance) analysis with Cu Kα radiation of $\lambda = 1.5406$ Å using a Ni filter, and with a secondary graphite monochromator so as to realize the effect of sintering process on the crystallization of the phosphors. A scan range of $2\theta = 20$–80° with a step of 0.03° and 0.4 s as a count time per-step were used. The scanning electron microscopy (SEM; HORIBA EX-200) was used to observe particle morphology of phosphors. The excitation and emission spectra were obtained using spectrofluorimeter (PL, JASCO FP-6000) equipped with a 150 W xenon lamp as the light source. To compare phosphor performance data accurately, specimens were tested within the same sample holder to ensure consistent amount of phosphor materials in all samples in this study.

3. Result and discussions

3.1. Structure

Fig. 2 shows the X-ray diffraction patterns of $YInGe_2O_7$:Eu^{3+} sintered at 1200 °C for 1 h in microwave furnace and at 1200 °C for 10 h in conventional furnace, respectively. The XRD analysis reveals that pure monoclinic phase diffraction peaks of $YInGe_2O_7$ are predominant in the XRD patterns and no other second phase or starting material is observed. The XRD result implied that the formation time of $YInGe_2O_7$ phase using microwave assisted sintering is rather low (~1 h), whereas 10 h is required to prepare $YInGe_2O_7$ powder by conventional sintering [9]. However, the full-width at half-maximum (FWHM) of $YInGe_2O_7$:Eu^{3+} phosphors prepared using microwave assisted sintering is higher than that prepared using conventional sintering, which describes the crystallinity of $YInGe_2O_7$:Eu^{3+} phosphors prepared using conventional sintering better than that prepared using microwave assisted sintering. It is known that a long sintering time causes grain growth, resulting in good crystallinity. Since microwave assisted sintering used a power level of 900 W, corresponding to a heating rate about 100 °C/min, and conventional sintering used a heating rate of 10 °C/min, indicating the formation time of $YInGe_2O_7$:Eu^{3+} phosphors can be reduced due to fast heating rate so as to shorten sintering time using microwave assisted processing.

3.2. Morphology

Fig. 3 shows typical SEM micrographs for $YInGe_2O_7$:Eu^{3+} sintered at 1200 °C for 1 h in microwave furnace and at 1200 °C

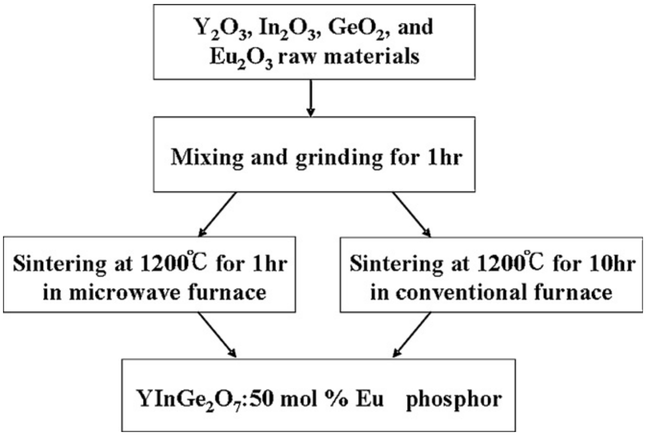

Fig. 1. Flow chart for the preparation of $YInGe_2O_7$:50 mol% Eu phosphors prepared by microwave assisted sintering and conventional sintering.

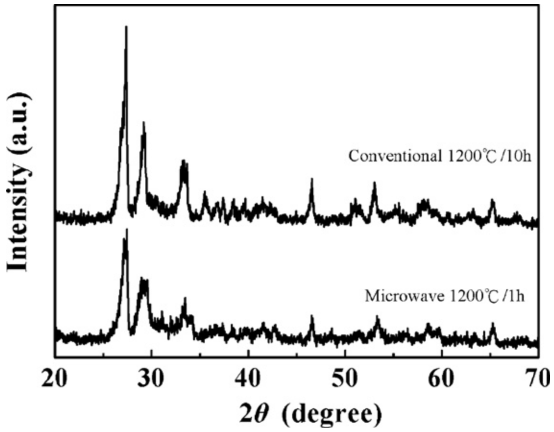

Fig. 2. XRD pattern of $YInGe_2O_7$:50 mol% Eu phosphors prepared by microwave assisted sintering and conventional sintering.

for 10 h in conventional furnace, respectively. The microstructures of the $YInGe_2O_7:Eu^{3+}$ powders change significantly with the different sintering process. The shape of the particles is not much different from each other, but the particle size increases significantly as sintering for longer time due to grain growth. The grains are relatively small for microwave sintered powders (<1 μm, Fig. 3A), and are large for the conventionally sintered powders (2–5 μm, Fig. 3B). In other materials system, it also been observed that the samples sintered by microwave have smaller grains than that by conventional process [18]. In the grain growth process, the ions jump from the convex to the concave side of the grain boundaries, but microwave sintering seems not to facilitate such a process, resulting in smaller grain microstructure [18]. Additionally, the grain size distribution of microwave sintered powder is uniform but that of conventionally sintered powder reveals the agglomeration of particles. When interacting with microwaves, the heat is generated within the material itself then dispersing the heat uniformly within the material [12].

3.3. Excitation and emission spectrum

Fig. 4 shows the excitation spectra of the red emission at 620 nm of $YInGe_2O_7:Eu^{3+}$ phosphors prepared by microwave sintering at 1250 °C for 1 h and conventional sintering at 1250 °C for 10 h, respectively, in the spectral region from 200 to 450 nm. The spectrum of $YInGe_2O_7:Eu^{3+}$ phosphors exhibit a broad band in the UV region centered at about 270 nm, and several sharp lines between 300 and 450 nm. The broad absorption band is called charge transfer state (CTS) band due to the europium-oxygen interactions, which is caused by an electron transfer from an oxygen 2p orbital to an empty 4f shell of europium. The sharp excitation peaks located at 299, 321, 363, 382, 395, and 416 nm are related to the intraconfigurational 4f–4f transitions of Eu^{3+} ions in the host lattices, which can be assigned to $^7F_0 \rightarrow {}^5F_3$, $^7F_0 \rightarrow {}^5H_6$, $^7F_0 \rightarrow {}^7D_4$, $^7F_0 \rightarrow {}^5L_7$, $^7F_0 \rightarrow {}^5L_6$, and $^7F_0 \rightarrow {}^5D_3$ transitions, respectively. The peak positions are in good agreement with the excitation spectra reported in Refs. [9,19]. The CTS intensity of the conventional sintered sample is stronger than that of the microwave sintered one, because a strong coupling interaction between the Eu^{3+} ions and the $YInGe_2O_7$ host matrix resulting from longer sintering time. However, the intensities of intra-4f transition are similar for $YInGe_2O_7:Eu^{3+}$ phosphors under microwave or conventional condition. The intensities of 363 nm and 382 nm are slightly over, when phosphors are prepared by microwave assisted sintering.

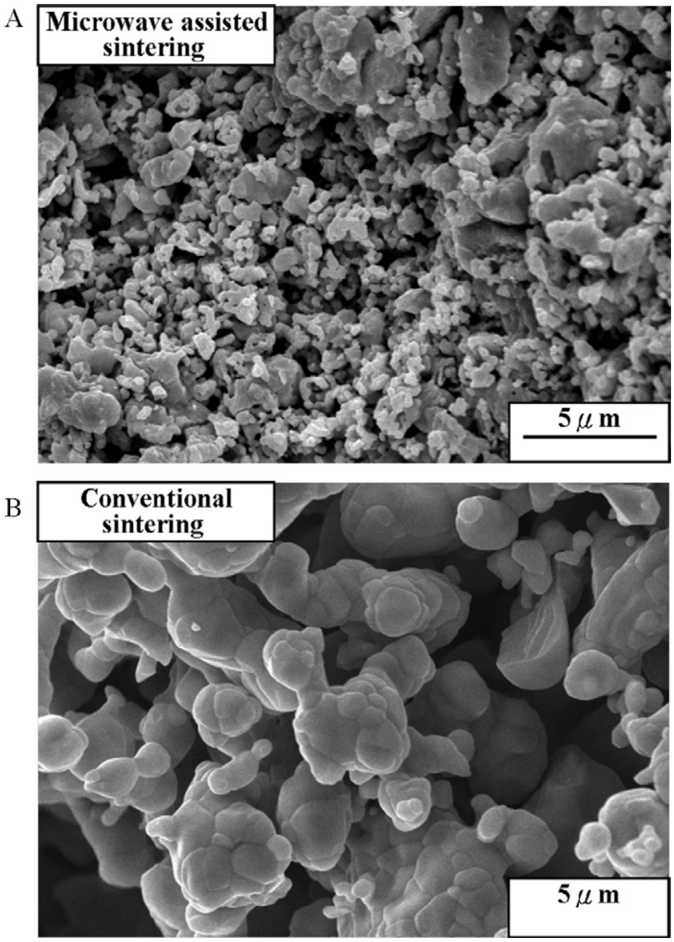

Fig. 3. SEM images of $YInGe_2O_7$:50 mol% Eu phosphors prepared by (A) microwave assisted sintering at 1200 °C for 1 h and (B) conventional sintering at 1200 °C for 10 h.

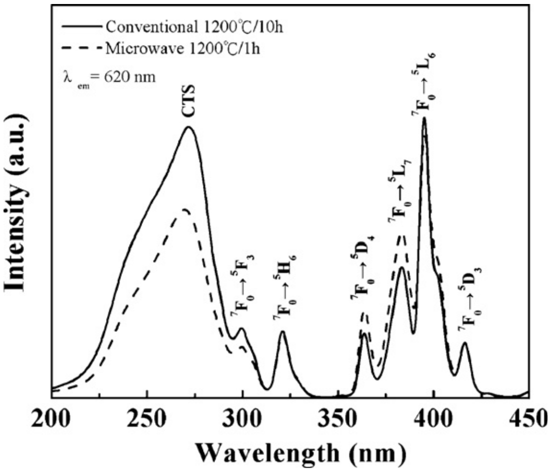

Fig. 4. Photoluminescence excitation spectra of $YInGe_2O_7$:50 mol% Eu phosphors prepared by different sintering methods (λ_{em} = 620 nm).

Fig. 5 shows the emission spectra of $YInGe_2O_7:Eu^{3+}$ phosphors prepared by microwave sintering at 1200 °C for 1 h and conventional sintering at 1200 °C for 10 h, respectively. $YInGe_2O_7:Eu^{3+}$ phosphor is excited with 393 nm wavelength from a xenon lamp. The emission wavelengths are all in the red region, which corresponds to 592 nm ($^5D_0 \rightarrow {}^7F_1$), 620 nm ($^5D_0 \rightarrow {}^7F_2$), and 654 nm ($^5D_0 \rightarrow {}^7F_3$) [9], respectively. Even if only 1 h sintering time is used, it is shown that $YInGe_2O_7:Eu^{3+}$ phosphor prepared by microwave assisted sintering has a similar luminescent intensity to that of conventional sintered one. Refer to Fig. 2, the crystallinity of $YInGe_2O_7:Eu^{3+}$ phosphors prepared by conventionally sintering is better than that using microwave sintering, which higher luminous intensity is expected. However, the emission spectra of both under an excitation wavelength of 393 nm are similar, which

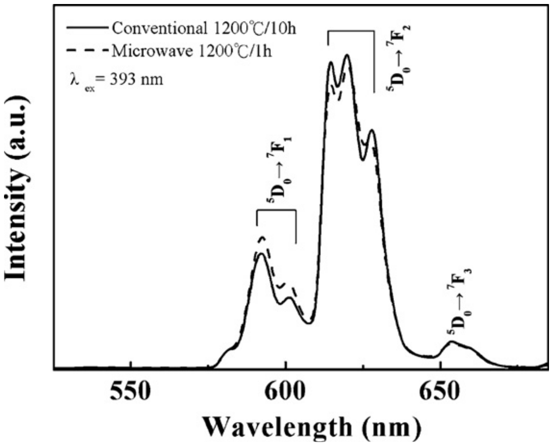

Fig. 5. Photoluminescence emission spectra of $YInGe_2O_7$:50 mol% Eu phosphors prepared by different sintering methods (λ_{ex} = 393 nm).

may be attributed to the non-uniform grain size distribution and agglomeration under conventionally sintering. Moreover, the strong and narrow emission feature is indicative of the presence of europium ions in the monoclinic structure of $YInGe_2O_7$. It is well-known that the $^5D_0 \rightarrow {}^7F_1$ transition is magnetic dipole in character and is independent of the crystal fields, unlike the $^5D_0 \rightarrow {}^7F_0$, which is a weak electric dipole transition. Although the $^5D_0 \rightarrow {}^7F_0$ transition is forbidden in a centrosymmetric environment, it is allowed in low-symmetry sites. This effect is evidenced by the complete disappearance of the $^5D_0 \rightarrow {}^7F_0$ transition in the emission spectra of Fig. 5. Furthermore, the ratio of the relative intensities of the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transitions, understood to be reliable spectroscopic probe for the degree of symmetry around the Eu^{3+} ion, is around 2.4 to be compared with the typical value higher than 3 characteristic of low-symmetry sites [20]. These observations constitute a further demonstration that the Eu^{3+} ions are embedded in their crystalline surroundings [21].

4. Conclusion

In this paper, we compared the characteristics of $YInGe_2O_7:Eu^{3+}$ phosphors prepared by microwave assisted sintering and by conventional sintering. It is exposed that at the same sintering temperature of 1200 °C, the sintering time of only 1 h required to form the single phase of $YInGe_2O_7$ under microwave sintering is rather low compared with conventional sintering. Since $YInGe_2O_7:Eu^{3+}$ phosphors are sintered under microwave, a pronouncedly smaller and more uniform grain size of less than 1 μm are obtained. Furthermore, the emission intensity of $YInGe_2O_7:Eu^{3+}$ phosphors are similar. Microwave sintering was able to reduce the sintering time and cost to get high-quality $YInGe_2O_7:Eu^{3+}$ phosphors.

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