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Ceramics International 37 (2011) 1521–1524
CERAMICS INTERNATIONAL
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# The effects of sintering method on crystalline morphology and photoluminescent properties of $BaY_2ZnO_5:Tb^{3+}$

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Received 5 November 2010; received in revised form 26 November 2010; accepted 7 January 2011
Available online 3 February 2011

**Abstract**

This paper describes the effects of microwave assisted sintering on the crystalline morphology and photoluminescent properties of $BaY_2ZnO_5$ doped with 4 mol% Tb powder. For comparison, the properties of $BaY_2ZnO_5$:Tb powders sintered at 1250 °C in conventional furnace for 12 h were also investigated. X-ray powder diffraction analysis showed the enhanced crystallinity of orthorhombic $BaY_2ZnO_5$ without second phase or phases of starting materials as $BaY_2ZnO_5$:Tb powders sintered at 1250 °C in microwave furnace for 1 h. In the PL studies, the emission spectra of $BaY_2ZnO_5$:Tb powders excited at 237 nm exhibits a maximum peak assigned to $^5D_4 \rightarrow {}^7F_5$ transition. In addition, the emission intensity of the prepared powder is slightly enhanced, compared to that sintered at 1250 °C/12 h in a conventional sintering furnace.


*Keywords:* A. Sintering; Phosphors; Microwave; Luminescence

## 1. Introduction

Oxide phosphors recently gained much attention for applications such as screens in field-emission displays [1], plasma display panels [2,3], and for white light-emitting diodes (LEDs) [4]. The most common and convenient method of generating white light is the combination of blue LED with yellow emitting phosphor materials such as YAG:Ce phosphor [5–7]. However, there are problems for such white LED, such as higher color temperature due to lack of a red emitting component and lower color-rendering index. Employing UV-LED with three phosphors of various colors (red, green, and blue), is another approach to solving these problems [8]. Recently, high efficiency UV-LED based on III-nitride compound semiconductors was demonstrated [9–11], which can provide a lighting source for UV-LED converted phosphors for solid-state lighting.

In the past, the phosphor based on $BaY_2ZnO_5$ system has been prepared by solid-state reaction using a conventional sintering furnace [12]. However, a long sintering time (~12 h), is required to synthesize the $BaY_2ZnO_5$ based phosphor with single phase and high enough luminance intensity. Many investigations suggest that heat treatment is an important factor for controlling size and crystalline structure of the materials. Microwave heating has been becoming a novel synthesis method and rapidly developing research field [13]. In contrast to conventional furnace sintering, the material sintered in a microwave furnace interacts with microwaves in stead of radiant heat. Because heat is generated within the material itself, heating is more volumetric and can be very rapid, selective, and uniform [13]. 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 [14–16] and achieve a rapid heating rate [17].

In this study, we synthesized the $BaY_2ZnO_5$:Tb phosphor materials using a microwave assisted sintering technique and discussed its microstructure and photoluminescent properties.

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0272-8842/$36.00. 
doi:10.1016/j.ceramint.2011.01.014

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 procedures

### 2.1. Samples preparation

The raw materials, $BaCO_3$, ZnO, $Y_2O_3$, and $Tb_4O_7$ with a purity of 99.9%, were mixed in a ball mill and ground for 1 h with zirconia balls. After drying, a conventional solid-state reaction method is used to synthesis $BaY_2ZnO_5$ doped with 4 mol% $Tb^{3+}$ ions, including microwave assisted sintering and conventional furnace sintering. The flow chart of the red phosphors prepared by the solid-state reaction method is shown in Fig. 1. 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), which has a very strong heating response to 2.45 GHz microwaves, was used as a susceptor to provide indirect heating of the powders [18]. The material sample was placed on an $Al_2O_3$ crucible surrounded by four silicon carbide susceptors in a microwave cavity and encapsulated by a ceramic fiber insulating material. The samples were sintered at 1250 °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 in a conventional furnace at 1250 °C for 12 h under an air atmosphere with the heating and cooling rate controlled at 5 °C/min.

### 2.2. Characterization

In order to know the effects of sintering method on the crystallization of the phosphors, the crystalline phases of the phosphors were identified by X-ray diffraction (Bruker D8 Advance) analysis with CuKα radiation of λ = 1.5406 Å using a Ni filter, and with a secondary graphite monochromator. 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. Particle morphology was observed using scanning electron microscopy (SEM; HORIBA EX-200). The excitation and emission spectra were analyzed using spectrofluorimeter (PL, JASCO FP-6000) equipped with a 150 W xenon lamp as the light source. To obtain comparative phosphor performance data, specimens were prepared within an identical loading of phosphor in a sample holder. The amount of phosphor materials was thus identical in all samples in this study.

## 3. Results and discussion

Fig. 2 shows the X-ray diffraction patterns of $BaY_2ZnO_5$ doped with 4 mol% Tb powder prepared by microwave sintering at 1250 °C for 1 h and conventional sintering at 1250 °C for 12 h, respectively. All of the peaks can be attributed to the orthorhombic $BaY_2ZnO_5$ phase, which are in excellent agreement with the standard card (PDF#89-5856). Trivalent terbium ions (0.98 Å) [20] were introduced to substitute trivalent yttrium ions (0.96 Å) [20] in the $BaY_2ZnO_5$ system. No other second phase or starting material is observed, implying that the formation time of $BaY_2ZnO_5$ phase using microwave assisted sintering is rather low, demonstrating only 1 h is needed, as compared to conventional sintering. The full-width at half-maximum (FWHM) of these peaks seemed to decrease and the crystallinity of $BaY_2ZnO_5$:Tb phosphors became better as sintered in microwave furnace at 1250 °C for 12 h, which indicates microwave assisted sintering does not only shorten the progress time, but also improves the sintering behaviors. Moreover, 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, this result indicates the better degree of crystallinity can be produced with a significantly shorter formation time due to fast heating rate and shorter sintering time using microwave assisted processing.

Fig. 3 shows typical SEM micrographs for $BaY_2ZnO_5$ doped with 4 mol% Tb powders for the microwave-sintered and conventionally sintered samples. The microstructures of the $BaY_2ZnO_5$:Tb powders change significantly with the different sintering process. From the figures, it is obvious that the microwave sintered powders comprised particles with diameters in the range of 2–3 μm (Fig. 3a), whereas the conventionally sintered powders comprised particles with

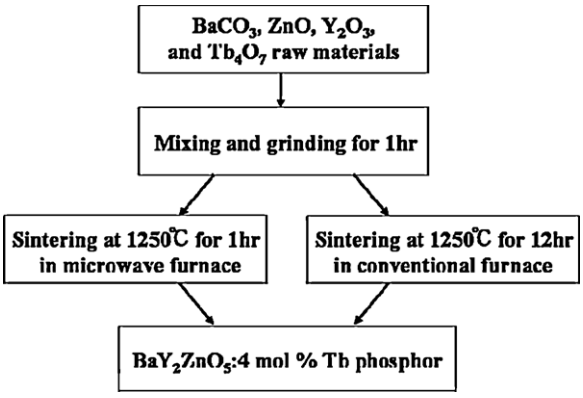


Fig. 1. Flow chart for the preparation of $BaY_2ZnO_5$:Tb phosphors prepared by microwave assisted sintering and conventional sintering.

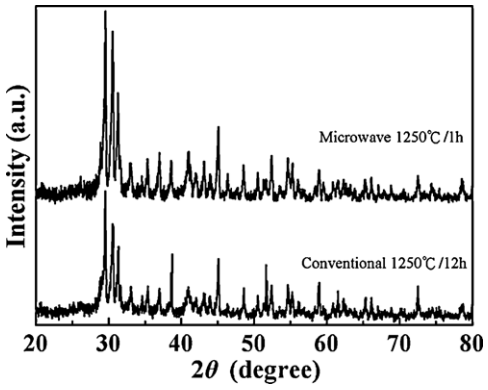


Fig. 2. XRD pattern of $BaY_2ZnO_5$:Tb phosphors prepared by microwave assisted sintering and conventional sintering.

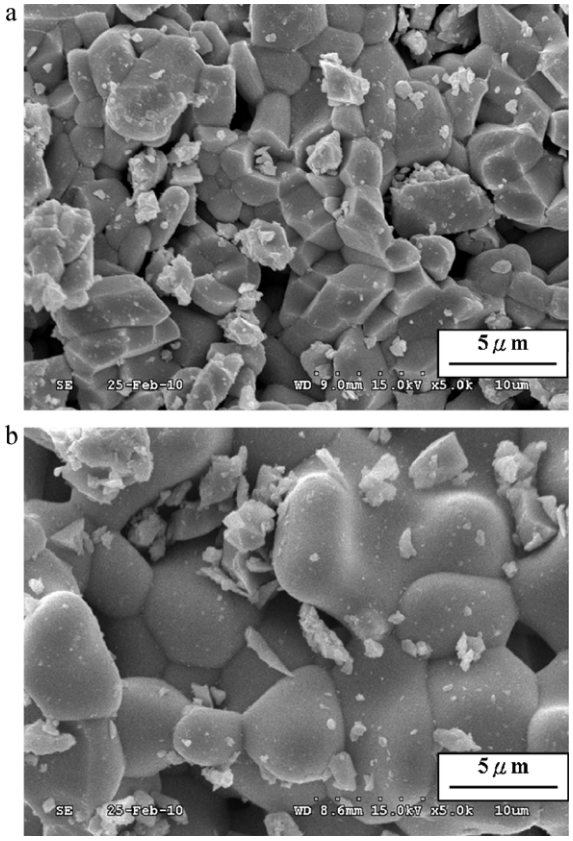


Fig. 3. SEM images of $BaY_2ZnO_5$:Tb phosphors prepared by (A) microwave assisted sintering at 1250 °C for 1 h and (B) conventional sintering at 1250 °C for 12 h.

diameters in the range of 5–10 μm (Fig. 3b) due to longer sintering time. The phenomenon of microwave sintered samples having smaller grains than the conventional sintered ones has also been observed in other materials system [19]. The explanation for this phenomenon is that in the grain growth process the ions jump from the convex to the concave side of the grain boundaries. The presence of microwave seems not to facilitate such a process, resulting in smaller grain microstructure [19]. The particles of both powders are aggregated, and the conventional sintered one shows the smooth surface.

Fig. 4 shows the emission spectra of $BaY_2ZnO_5$ doped with 4 mol% Tb phosphors prepared by microwave sintering at 1250 °C for 1 h and conventional sintering at 1250 °C for 12 h, respectively, under excitation at 237 nm. Samples with different sintering process have similar emission spectra patterns. When $\lambda_{ex} = 237$ nm, the emission wavelength for $BaY_2ZnO_5$:Tb are located at 491, 546, 589, and 625 nm correspond to the $Tb^{3+}$ intra-4f transition from the excited levels to lower levels, which are $^5D_4 \rightarrow {}^7F_J$ ($J = 6, 5, 4, 3$) transitions [21], respectively. It indicates that the $BaY_2ZnO_5$:Tb phosphor exhibits a green emission, revealing that $BaY_2ZnO_5$:Tb phosphor prepared by microwave assisted sintering is luminescent even if only 1 h of sintering time is used, and has a higher luminous intensity than that of conventionally sintered phosphor. As seen in Fig. 3, $BaY_2ZnO_5$:Tb powders sintered in microwave furnace at 1250 °C for 1 h have stronger crystalline intensity, which appears that the phosphor with better crystallinity results in better photoluminescent properties. Moreover, the strong and narrow emission feature is indicative of the presence of terbium ions in the orthorhombic structure of $BaY_2ZnO_5$. Armellinin et al. have suggested that the increase of quantum yield of $Tb^{3+}$ is attributed to the reducing of the Tb–Tb cross-relaxation processes [22], thus it is possible that microwave assisted sintering prevents clustering of Tb ions, causing higher luminescence. Accordingly, microwave sintering for 1 h not only yields homogeneous phosphor powder, but also gives itself to substituting $Tb^{3+}$ for $Y^{3+}$ ions.

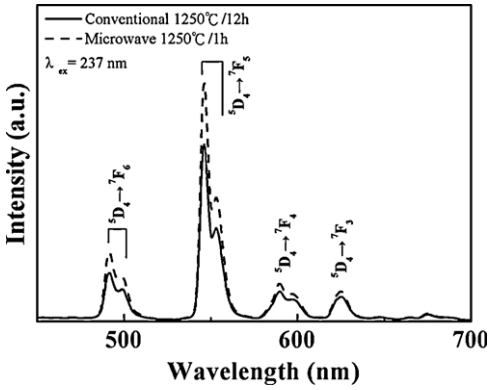


Fig. 4. Photo emission spectra of $BaY_2ZnO_5$:Tb phosphors prepared by different sintering methods under excitation of 237 nm.

## 4. Conclusion

In this paper, characteristics of $BaY_2ZnO_5$ doped with 4 mol% Tb phosphor prepared by microwave assisted sintering are investigated and compared to those prepared by conventional sintering. It is found that at the same sintering temperature of 1250 °C, sintering time using microwave assisted sintering is rather low compared with conventional sintering, requiring only 1 h to form the single phase of $BaY_2ZnO_5$ with higher crystallinity. The microwave sintered $BaY_2ZnO_5$:Tb phosphors have a pronouncedly smaller and more uniform grain size in the range of 2–3 μm, as compared with 5–15 μm from the conventionally sintered $BaY_2ZnO_5$:Tb phosphors. Furthermore, the emission intensity of $BaY_2ZnO_5$:Tb phosphors is enhanced slightly. Microwave processing therefore has the potential to reduce the time, cost, and required energy for the high quality production of $BaY_2ZnO_5$:Tb phosphor.

## Acknowledgements

The authors would like to acknowledge funding support from Nation Science Council of Taiwan, under Grant NSC 98-2221-E-020-017, and would also like to acknowledge National Nano Device Laboratories for supporting the experimental equipment.

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