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Microstructure, and luminescence properties of $LiBaPO_4:Dy^{3+}$ phosphors with various Dy^{3+} concentrations prepared by microwave assisted sintering

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ABSTRACT

$LiBaPO_4:Dy^{3+}$ phosphors were synthesized by microwave-assisted and conventional sintering. XRD analysis confirmed the phase formation of all the $LiBaPO_4:Dy^{3+}$ phosphors. PL results showed that the optimum concentration of Dy^{3+} for $LiBaPO_4:Dy^{3+}$ prepared by microwave-assisted sintering is 7 mol%. The phosphors were efficiently excited by the UV–vis light region from 300 to 400 nm, and exhibited blue (483 nm), yellow (576 nm) and red (671 nm) emission corresponding to $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^6H_{13/2}$, and $^6H_{11/2}$ transitions, respectively. The microwave-assisted sintering improves the sintering behavior and provides a more uniform particle morphology of $LiBa_{0.03}PO_4:0.07Dy^{3+}$ phosphors so as to obtain a luminescence intensity greater than that obtained by conventional sintering even at the same sintering temperature. Moreover, all the chromaticity (x, y) of the $LiBa_{0.03}PO_4:0.07Dy^{3+}$ phosphors are located in the white region (0.33, 0.37) even on using microwave-assisted sintering as the heat treatment did not influence the purity of $LiBa_{0.03}PO_4:0.07Dy^{3+}$ phosphors.

1. Introduction

White light-emitting diodes (WLEDs) are widely seen as being the next generation of solid-state lighting, and have attracted considerable attention because of their energy efficiency, high brightness, long lifetime, harmlessness and environment friendliness [1]. The present strategy for generating white light is to combine blue LEDs with yellow luminescence from $Y_3Al_5O_{12}:Ce^{3+}$ (YAG) phosphor materials. However, due to the lack of a red light component, white light generated by this method usually renders color poorly. A novel approach has been suggested in which red/green/blue tricolor phosphors are pumped by near UV-LED chips (350–410 nm) to produce white light [2,3], but there are currently insufficient references on the use of phosphors for converting near UV-LEDs as illumination sources. Therefore, it is important to study phosphors for near UV-LEDs.

As an important family of luminescent materials, orthophosphates have attracted intense attention, In particular, researchers have concentrated on the phosphate series of phosphors with an $ABPO_4$ structure, where A is a monovalent cation (Li^+, Na^+, K^+, Rb^+, and Cs^+) and B is a divalent cation (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) due to their large band gap, along with the high absorption of $PO_4{}^{3-}$ in UV region, their moderate phonon energy, high thermal and chemical stability, and exceptional optical damage threshold [4–6]. For example, $KSrPO_4$, $NaCaPO_4$, and $LiBaPO_4$, have been reported to act as new phosphor materials for potential applications in WLEDs [4–6].

Recently, Dy^{3+} ions have attracted considerable attention because of their white light emission. It is well known that a Dy^{3+} ion with a $4f^9$ electronic configuration generally has two dominant emission bands. One is the blue band (470–500 nm) due to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition. Another is the yellowish band (570–600 nm) due to the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition [7–9]. White light can be observed not only by mixing the appropriate ratio of the red/green/blue tricolors, but also by creating the appropriate mixture of blue and yellowish emissions. In the past, Dy^{3+} doped orthophosphates and $ABPO_4$ phosphors have been prepared by solid-state reaction using a conventional sintering furnace [7]. However, the phosphors usually produced agglomerate powders, which would alter the structural characteristics of the powders, and these powders were produced in non-uniform sizes, which would make the properties uncontrollable. It has been reported that, when the phosphors were sintered using the microwave energy as the heating sources, the energy can be absorbed immediately and uniformly compared to results from a conventional solid state sintering process [10]. This technique has been applied recently to prepare various oxide phosphors, such as $YInGe_2O_7:Eu^{3+}$ [11], $Y_2BaZnO_5:Eu^{3+}$ [12], and $Sr_2SiO_4:Eu^{3+}$ [13]. However, to our knowledge, Dy^{3+} ions doped $LiBaPO_4$ phosphors prepared by microwave-assisted sintering or conventional sintering

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have not yet been reported. Thus, the aim of the present work is to investigate the effects on the microstructure and luminescence properties of $\text{LiBaPO}_4\text{:Dy}^{3+}$ phosphors prepared by using microwave-assisted sintering.

2. Experimental procedure

2.1. Samples preparation

Li_2CO_3, BaCO_3, $\text{NH}_4\text{H}_2\text{PO}_4$ and Dy_2O_3 powders, all with a purity of 99.9%, were used as the staring materials for the $\text{LiBa}_{1-x}\text{PO}_4\text{:}x\text{Dy}^{3+}$ phosphors with different concentrations of Dy^3 ions ($x=0.05$, 0.07, 0.1, and 0.15). The powders were mixed in alcohol as a solvent and ball-milled for 1 h with zirconia balls. After drying, the mixed powders were sintered by microwave-assisted sintering in a microwave furnace to form the $\text{LiBa}_{1-x}\text{PO}_4\text{:}x\text{Dy}^{3+}$ phosphor. A Therm Wave Mod. III microwave furnace with controllable microwave powers up to 1.3 kW at 2.45 GHz was used in this study. Silicon carbide (SiC) was used as a susceptor to provide the indirect heating of the powders because of a very strong heating response to 2.45 GHz microwaves [10]. The material sample was placed on an Al_2O_3 crucible surrounded by four silicon carbide susceptors and encapsulated by a ceramic fiber insulating material in a microwave cavity. The mixed powders were sintered at 900 °C for 3 h under an air atmosphere with a power of 900 ± 20 W, producing an average heating rate greater than 100 °C/min. For comparison purposes, a sample of $\text{LiBa}_{1-x}\text{PO}_4\text{:}x\text{Dy}^{3+}$ phosphor ($x=0.07$) was prepared using the same procedures with the conventional sintering method.

2.2. Characterization

The crystalline phases of the phosphors were identified using X-ray diffraction (XRD, Bruker D8 Advance) analysis with CuKα radiation of $\lambda=1.54$ Å using a Ni filter, and with a secondary graphite monochromator. A scan range of $2\theta=10$–$60°$ with a step of 0.03° and 0.4 s as a count time per-step were used. 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), using a 150 W Xenon lamp as the light source. To ensure measurement accuracy, specimens were measured within the same sample holder to preserve a consistent amount of phosphor materials in all samples.

3. Results and discussion

3.1. Structure

It is well known that pure LiBaPO_4 has a tetragonal structure with space group $P6_3$. Fig. 1 shows the X-ray diffraction patterns of $\text{LiBa}_{1-x}\text{PO}_4\text{:}x\text{Dy}^{3+}$ phosphors with various concentrations of Dy^{3+} ions prepared by microwave-assisted sintering at 900 °C for 3 h in an air atmosphere. All the samples are found to belong to a single phase, which agrees well with the Joint Committee on Powder Diffraction Standards JCPDS (No. 14-0270) except for little shift of diffraction peak positions due to the doping effect. Therefore, the substitution Dy^{3+} ions were incorporated into the LiBaPO_4 host lattice without any significant structural change or observed impurity phase. Additionally, from energy saving, this synthesis temperature is much lower than that of commercial phosphor YGB, BAM, and ZSM. They are usually prepared at temperature above 1000 by the conventional high temperature solid state reaction technique.

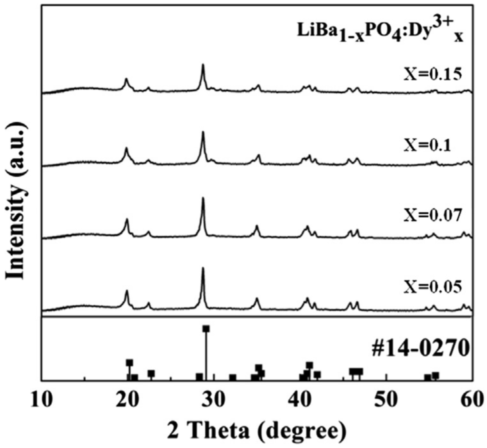

Fig. 1. XRD pattern of $\text{LiBa}_{1-x}\text{PO}_4\text{:}x\text{Dy}^{3+}$ phosphors with various concentrations of Dy^{3+} ions prepared by microwave assisted sintering at 900 °C for 3 h in an air atmosphere.

Table 1
Lattice parameters and unit cell volume of $\text{LiBa}_{1-x}\text{PO}_4\text{:}x\text{Dy}^{3+}$ phosphors with various concentrations of Dy^{3+} ions.

Value (x)	Lattice parameters (Å)			Unit cell volume (Å^3)
	a	b	c	
0.05	8.633	8.735	5.211	392.958
0.07	8.632	8.735	5.210	392.837
0.1	8.630	8.732	5.210	392.611
0.15	8.629	8.731	5.208	392.370

From the Bragg′s equation (1), the cell parameters for orthorhombic structure can be expressed as

$$2\text{d} \times \sin\theta = \lambda \tag{1}$$

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \tag{2}$$

wherein h, k and l are Miller indices, λ is the wavelength of CuKα radiation radiation (1.54 Å), and θ is the diffraction angle which is determined from the XRD results. Compared with pure LiBaPO_4, the lattice constants of $\text{LiBa}_{1-x}\text{PO}_4\text{:}x\text{Dy}^{3+}$ a little decrease by the introduction of Dy^{3+} ions as shown in Table 1, indicating that the rare earth ions have doped into the lattices of the LiBaPO_4 host. The ion radius of Dy^{3+} (0.912 Å) is smaller than that of Ba^{2+} (1.350 Å) so that Ba^{2+} ion in LiBaPO_4 can be replaced by Dy^{3+} ion to form $\text{LiBa}_{1-x}\text{PO}_4\text{:}x\text{Dy}^{3+}$ phosphor.

3.2. Morphology

The particle size distribution of the phosphor is an important factor for its application in WLEDs. Fig. 2 shows the SEM images of $\text{LiBa}_{1-x}\text{PO}_4\text{:}x\text{Dy}^{3+}$ phosphors with various concentrations of Dy^{3+} ions prepared by microwave-assisted sintering at 900 °C for 3 h in an air atmosphere. The particle morphology of $\text{LiBa}_{1-x}\text{PO}_4\text{:}x\text{Dy}^{3+}$phosphors sintered by microwave-assisted sintering are not obviously different, and found to be fine and uniform since the heat energy is generated within the material itself as the materials interact with the microwave power, and are then dispersed uniformly within the material [10–13]. On the other hand, the particle size is seen to gradually decrease from 3 μm to 1 μm as the concentration of Dy^{3+} ions is increased. This may indicate that the doping ions act as nucleation catalyst, and the nucleation density of the micro-crystallites increased in LiBaPO_4 powders as the number of Dy^{3+} ions increased. It has been reported that the