Enhanced Photoluminescent Properties and Crystalline Morphology of LiBaPO$_4$:Tm$^{3+}$ Phosphor through Microwave Sintering Method

Hsuan-Lin Lai $^1$, Min-Hang Weng $^2$, Ru-Yuan Yang $^{3,*}$ and Shoou-Jinn Chang $^1$

$^1$ Institute of Microelectronics, Department of Electrical Engineering, Advanced Optoelectronic Technology Center, National Cheng Kung University, Tainan 701, Taiwan; shiuannlin@hotmail.com (H.-L.L.); changsj@mail.ncku.edu.tw (S.-J.C.)

$^2$ Medical Devices and Opto-Electronics Equipment Department, Metal Industries Research and Development Center, Kaohsiung County 811, Taiwan; mhweng@mail.mirdc.org.tw

$^3$ Graduate Institute of Materials Engineering, National Pingtung University of Science and Technology, Pingtung County 912, Taiwan

* Correspondence: ryyang@mail.npust.edu.tw; Tel.: +886-8-7703202; Fax: +886-8-7740552

Academic Editor: Dinesh Agrawal
Received: 4 March 2016; Accepted: 4 May 2016; Published: 12 May 2016

Abstract: An investigation of the photoluminescent properties and crystalline morphology of blue emitting LiBa$_{1-x}$PO$_4$:xTm$^{3+}$ phosphors with various concentrations ($x = 0.005$–$0.030$) of Tm$^{3+}$ ions were synthesized by microwave sintering. For comparison, the LiBa$_{1-x}$PO$_4$:xTm$^{3+}$ powders sintered at the same sintering condition but in a conventional furnace were also investigated. LiBaPO$_4$ without second phase was formed no matter which furnace was used. More uniform grain size distributions are obtained by microwave sintering. When the concentration of Tm$^{3+}$ ion was $x = 0.015$, the luminescence intensity reached a maximum value, and then decreased with the increases of the Tm$^{3+}$ concentration due to concentration quenching effect. The microwave sintering significantly enhanced the emission intensity of LiBa$_{1-x}$PO$_4$:xTm$^{3+}$ phosphors. Additionally, the d-d interaction is the key mechanism of concentration quenching for LiBaPO$_4$:Tm$^{3+}$. The chromaticity ($x$, $y$) for all LiBa$_{1-x}$PO$_4$:xTm$^{3+}$ phosphors are located at (0.16, 0.05), which will be classified as a blue region.

Keywords: phosphors; LiBaPO$_4$; microwave; luminescence

1. Introduction

Several advantages of white light-emitting diodes (WLEDs) such as high luminous efficiency, energy-saving, maintenance as well as environmental protection, lead the WLEDs to be called the next-generation solid-state light and to replace traditional incandescent and fluorescent lamps. The combination of blue LED with yellow luminescence from Y$_3$Al$_5$O$_{12}$:Ce$^{3+}$ is the present strategy to make white light (YAG:Ce$^{3+}$) phosphor materials [1]. Another method to make white light is to combine ultraviolet LED and different colors of phosphors obtained from excitation by ultraviolet LED. Therefore, many red, green and blue phosphors that can be excited by UV light should be developed [2]. Also, phosphors with high luminescent efficiency, stability and low cost are in demand for application in WLEDs.

Phosphates with a general formula like ABPO$_4$, where A is a mono-valent cation and B is a divalent cation, are interesting because of their optical, ferroelectric properties, excellent thermal and hydrolytic stability [2–7]. Therefore, many studies have concentrated on ABPO$_4$ phosphate by solid-state reaction for WLEDs [2–7]. Among them, Tm$^{3+}$-doped materials have been widely adopted as blue emitting phosphors because of their intense $^1D_2 \rightarrow ^3F_4$ emission. The investigation from Li et al. materials 2016, 9, 356; doi:10.3390/ma9050356 www.mdpi.com/journal/materials
has shown that \( \text{Tm}^{3+} \)-doped NaCaPO\(_4\) phosphor exhibits relatively strong absorption in near-UV region of 356 nm and intense blue emission of 451 nm with excellent color purity [7].

Regarding the sintering process, 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 [8]. This technique has been applied recently to prepare various oxide phosphors, such as YInGe\(_2\)O\(_7\):Eu\(^{3+}\) [9], BaY\(_2\)ZnO\(_5\):Eu\(^{3+}\) [10], and Sr\(_2\)SiO\(_4\):Eu\(^{3+}\) [11] and LiBaPO\(_4\):Dy\(^{3+}\) [12].

However, to our knowledge, \( \text{Tm}^{3+} \) ions doped LiBaPO\(_4\) phosphors prepared by microwave-assisted sintering or conventional sintering have not yet been reported. In addition, the luminescent characteristics of \( \text{Tm}^{3+} \) ions doped LiBaPO\(_4\) and the mechanism of energy transfer of \( \text{Tm}^{3+} \)-doped LiBaPO\(_4\) phosphor has been little-reported until now. Therefore, in this paper, the luminescent characteristics, microstructure properties and mechanism of energy transfer of LiBaPO\(_4\):Tm\(^{3+}\) phosphors prepared using different sintering processes are investigated.

2. Results and Discussion

2.1. Structure

Figure 1 shows the X-ray diffraction patterns of LiBa\(_{0.985}\)PO\(_4\):0.015Tm\(^{3+}\) sintered at 1200 °C for 3 h in different furnace, respectively. According to the Joint Committee on Powder Diffraction Standards (JCPDS #14-0270), the LiBaPO\(_4\) has a hexagonal crystal structure with a space group P\(\text{6}_3\) [12], and all patterns of LiBa\(_{0.985}\)PO\(_4\):0.015Tm\(^{3+}\) phosphors with different sintering furnace can be indexed and match the reference [13] and no other second phase or starting material is observed. The XRD result implied that the full-width at half-maximum (FWHM) of LiBa\(_{0.985}\)PO\(_4\):0.015Tm\(^{3+}\) phosphors prepared using microwave sintering is smaller than that prepared using the conventional one, indicating that the crystallinity of LiBa\(_{0.985}\)PO\(_4\):0.015Tm\(^{3+}\) was improved by microwave sintering. It is known that a long sintering time causes grain growth, resulting in good crystallinity. However, at the same sintering condition (1200 °C, 3 h) with a different sintering method, the heat through conventional method is indirect, but in a microwave furnace, the material is rapidly heated both internally and externally. The heat generated within the material, and the susceptors provided the heat to the specimen externally by thermal conduction [9]. High sintering efficiency could be obtained through microwave sintering, resulting in good crystallinity.

![Figure 1. X-ray diffraction patterns X-ray diffraction patterns of LiBa\(_{0.985}\)PO\(_4\):0.015Tm\(^{3+}\) compared by sintered at 1200 °C for 3 h in different furnace.](image)

Figure 2a,b shows typical SEM micrographs for LiBa\(_{0.985}\)PO\(_4\):0.015Tm\(^{3+}\) sintered in microwave furnace and in conventional furnace at 1200 °C for 3 h, respectively. The microstructures of the LiBa\(_{0.985}\)PO\(_4\):0.015Tm\(^{3+}\) powders changed significantly through different sintering processes. The shapes of the particles are not very different from one another, but the grain size distribution from
microwave sintered powder is uniform. The grain distribution of conventionally sintered powder reveals the agglomeration of particles. Additionally, the particle sizes of LiBa$_{0.985}$PO$_4$:0.015Tm$^{3+}$ phosphors are in the range of 9–11 μm.

Figure 2. (a) SEM image of LiBa$_{0.985}$PO$_4$:0.015Tm$^{3+}$ phosphor sintered at 1200 °C for 3 h in microwave furnace; (b) SEM image of LiBa$_{0.985}$PO$_4$:0.015Tm$^{3+}$ phosphor sintered at 1200 °C for 3 h in conventional furnace.

2.2. Photoluminescence Properties

Figure 3a,b shows the emission spectra of LiBa$_{0.985}$PO$_4$:0.015Tm$^{3+}$ phosphors with different concentrations of Tm$^{3+}$ ions using different sintering process, respectively. LiBa$_{0.985}$PO$_4$:0.015Tm$^{3+}$ phosphors can be effectively excited by NUV LED because all the LiBa$_{0.985}$PO$_4$:0.015Tm$^{3+}$ phosphors are excited by a xenon lamp at a wavelength of 359 nm. The inset of Figure 3a shows the tendency of the blue emission intensity (454 nm) for LiBa$_{1-x}$PO$_4$:xTm$^{3+}$ at 0.005 < x ≤ 0.030 sintered in a microwave furnace. The inset of Figure 3b shows the tendency of the blue emission intensity (454 nm) for LiBa$_{1-x}$PO$_4$:xTm$^{3+}$ at 0.010 < x ≤ 0.030 sintered in conventional furnace. Both of the emission spectra of the LiBa$_{1-x}$PO$_4$:xTm$^{3+}$ phosphors display four emission bands at 454, 476, 513, and 660 nm, respectively corresponding to the $^1D_2 \rightarrow ^3F_4$, $^1G_4 \rightarrow ^3H_{6}$, $^1D_2 \rightarrow ^3H_5$ and $^1G_4 \rightarrow ^3F_4$ transitions of Tm$^{3+}$ ions.

Figure 3. (a) Emission spectra of LiBa$_{1-x}$PO$_4$:xTm$^{3+}$ phosphors with different concentrations of Tm$^{3+}$ ions sintered at 1200 °C for 3 h in microwave furnace ($\lambda_{ex} = 359$ nm). The inset on the top right is the tendency of the blue emission intensity (454 nm) for LiBa$_{1-x}$PO$_4$:xTm$^{3+}$ at 0.005 < x ≤ 0.030; (b) Emission spectra of LiBa$_{1-x}$PO$_4$:xTm$^{3+}$ phosphors with different concentrations of Tm$^{3+}$ ions sintered at 1200 °C for 3 h in conventional furnace ($\lambda_{ex} = 359$ nm). The inset on the top right is the tendency of the blue emission intensity (454 nm) for LiBa$_{1-x}$PO$_4$:xTm$^{3+}$ at 0.010 < x ≤ 0.030.
Figure 4 shows the emission spectra of LiBa$_{0.985}$PO$_4$:0.015Tm$^{3+}$ phosphors with different sintering processes. It is shown that LiBa$_{0.985}$PO$_4$:0.015Tm$^{3+}$ phosphor prepared by microwave sintering has much higher luminescent intensity than that of a conventionally sintered one. Referring to Figure 1, the crystallinity of LiBa$_{0.985}$PO$_4$:0.015Tm$^{3+}$ phosphors prepared by microwave sintering is better than that using conventionally sintering so that higher luminous intensity is expected. As the concentration of Tm$^{3+}$ ion increased, the probability of the energy transfer among Tm$^{3+}$ ions also increased. The luminescence intensity reached a maximum when the concentration of Tm$^{3+}$ ion was at 0.015, and then decreased with the increases of the Tm$^{3+}$ concentration due to the concentration quenching effect.

Blasse proposed the critical transfer distance ($R_c$) to realize the mechanism of energy transfer in phosphors whereby $R_c$ is about equal to twice the radius of a sphere with the volume as shown in Equation (1) [14–16].

$$R_c = 2\left[\frac{3V}{4\pi x_c N}\right]^{1/3}$$  \hspace{1cm} (1)

In which $x_c$ is the critical concentration, $N$ is the number of cations in the unit cell and $V$ is the volume of the unit cell. The unit cell volume $V$ of LiBaPO$_4$ is 0.391577 nm$^3$ and the critical concentration $x_c$ is 0.015, resulting from the maximum intensity of LiBa$_{1-x}$PO$_4$:$x$Tm$^{3+}$ at $x = 0.015$. The number of host cations in the unit cell of LiBaPO$_4$ is 4. Based on the above values, the critical distance of energy transfer $R_c$ is calculated as 2.3186 nm. Exchange interaction, radiation reabsorption, or multipole-multipole interaction and so-called non-radiative energy transfer between different Tm$^{3+}$ ions may have happened. When the typical critical distance is approximately 5 Å, the exchange interaction is generally responsible for the energy transfer of forbidden transitions [16]. When the sensitizer and activator coexist in phosphor system, the mechanism of radiation reabsorption occurs due to broad overlap between excitation and emission spectra. In this study, there is no overlap between excitation and emission spectra of LiBa$_{1-x}$PO$_4$:$x$Tm$^{3+}$ phosphor. Besides, the critical distance $R_c$ (2.3186 nm) of LiBa$_{1-x}$PO$_4$:$x$Tm$^{3+}$ phosphor is larger than 5 Å. Therefore, the energy transfer mechanism between Tm$^{3+}$ ions in LiBaPO$_4$ phosphor could be suggested by multipole-multipole interaction from Dexter’s theory [16]. If the energy transfer takes place between the same sorts of Tm$^{3+}$ ions, the multipole-multipole interaction effect can be determined from of the difference of the emission intensity according to the emitting level with multipolar interaction. The emission intensity ($I$) per Tm$^{3+}$ ion can be calculated by the Equation (2) [14–16]:

$$I/x = K[1 + \beta(x)^{Q/3}]^{-1}$$  \hspace{1cm} (2)
where $x$ is the activator concentration; $Q = 6, 8$ or 10 for dipole–dipole ($d$-$d$), dipole-quadrupole ($d$-$q$) or quadrupole-quadrupole ($q$-$q$) interaction, respectively; and $K$ and $\beta$ are constants for a given host crystal with the same excitation condition. The doped Tm$^{3+}$ concentration, which is not less than the critical concentration ($i.e., x = 0.02, 0.025, 0.03$), is used to determine the dependence of the emission intensity of LiBaPO$_4$:Tm$^{3+}$ phosphor excited at 359 nm. As shown in Figure 5, the dependence of log ($I/x$) on log ($x$) in microwave sintering is linear and the slope is $-2.231$. The value of $Q$ can be calculated as 6.693. In addition, the dependence of log ($I/x$) on log ($x$) in conventional sintering is linear and the slope is $-2.186$. The value of $Q$ can be calculated as 6.558. Both are approximately equal to 6 based on Equation (2). Therefore, the $d$-$d$ interaction is the major mechanism for concentration quenching of the LiBaPO$_4$:Tm$^{3+}$ phosphor no matter what sintering method was used.

![Figure 5](image1.png)

**Figure 5.** The curve of log ($I/x$) vs. log ($x$) in LiBa$_{1-x}$PO$_4$:xTm$^{3+}$ phosphors with doped Tm$^{3+}$ concentration at $x = 0.02, 0.025, 0.03$ using different sintering process.

It is known that color coordinates could be established by Commission International de l’Eclairage (CIE) 1931 according to a two-dimensional graphical representation of any color perceptible by the human eye. The CIE coordinates could be obtained through commercial software by converting the data of photoluminescence emission spectrum. Figure 6 shows all LiBa$_{0.985}$PO$_4$:0.015Tm$^{3+}$ phosphors having the same chromaticity ($x$, $y$) coordinates located in the blue region (0.16, 0.05). Therefore, if we choose appropriate green and red phosphors mixed with the LiBaPO$_4$:Tm$^{3+}$ onto the ultraviolet LED chip, the goal to form WLEDs could be achieved.

![Figure 6](image2.png)

**Figure 6.** The CIE1931 chromaticity diagram of LiBa$_{0.985}$PO$_4$:0.015Tm$^{3+}$ phosphors using different sintering process.
3. Experimental Procedure

3.1. Sample Preparation

The LiBa$_{1-x}$PO$_4$:xTm$^{3+}$ phosphors used Li$_2$CO$_3$ (99.94%), BaCO$_3$ (99.9%), NH$_4$H$_2$PO$_4$ (98%), and Tm$_2$O$_3$ (99.9%) powders as starting materials and different concentrations of Tm$^{3+}$ ions ($x = 0.005$–$0.03$) were chosen as a variable parameter. The starting materials were mixed using alcohol as a solvent and then ball-milled for 1 h with zirconia balls. After drying, the mixed powders were sintered in a microwave furnace and conventional furnace to form LiBa$_{1-x}$PO$_4$:xTm$^{3+}$ phosphors. 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. For comparison, the sample was also sintered at 1200 °C for 3 h in conventional furnace under an air atmosphere with the heating rate controlled at 10 °C/min. The average heating rate of microwave furnace was greater than 100 °C/min. After sintering, the phosphor samples were cooled to room temperature and then characterized.

3.2. Characterization

The crystalline phases of the phosphors were identified by X-ray diffraction (XRD, model D8 Advance, Bruker Axs Gmbh, Karlsruhe, Germany) with CuKα radiation of $\lambda = 1.54$ Å using a Ni filter, and a secondary graphite monochromator. A scanning range of 2$\theta$ = 10°–60° was used with a step of 0.03° and 0.4 s as a per-step count time. The particle morphology of phosphors was identified by scanning electron microscopy (SEM; model S-3000N, Hitachi, Ltd., Tokyo, Japan). Additionally, the excitation, emission spectra and the color coordinates and the Commission International de l’Eclairage (CIE) information were obtained using a photoluminescence spectrophotometer (PL, model FP-6000, JASCO Corporation, Tokyo, Japan) with a 150 W xenon lamp as the light source.

4. Conclusions

In this paper, LiBa$_{0.985}$PO$_4$:0.015Tm$^{3+}$ phosphors with various sintering process were successively synthesized at 1200 °C for 3 h. XRD results indicate that pure LiBa$_{0.985}$PO$_4$:0.015Tm$^{3+}$ phosphor phase was formed. The major emission peak centered at 454 nm corresponds to the $^1D_2 \rightarrow ^3F_4$ transition and the maximum photoluminescence intensity appeared at the Tm$^{3+}$ concentration of 0.015. Under the microwave sintering, good crystallinity and uniform grain size distributions are obtained because microwave energy provides the material rapidly heated both internally and externally. The $d$-$d$ interaction plays a major role in the mechanism of concentration quenching of LiBaPO$_4$:Tm$^{3+}$ phosphor based on the theoretical calculation no matter what sintering method was used. Additionally, WLEDs could be achieved by mixing appropriate green and red phosphors with the LiBaPO$_4$:Tm$^{3+}$ onto the ultraviolet LED chip.

Acknowledgments: This study was funded by the Ministry of Science and Technology, under contracts NSC 101-2628-E-020-002-MY3 and Metal Industries Research and Development Center, Taiwan. The authors would also like to thank the National Nano-Device Laboratories, and the Precision Instrument Center of National Pingtung University of Science and Technology for supplying experimental equipment.

Author Contributions: Hsuan-Lin Lai conducted the experiment and completed the manuscript writing; Min-Hang Weng supported the electrical and optical measurements and provided suggestions for the manuscript; Ru-Yuan Yang supplied the laboratory and revised the manuscript; Shoou-Jinn Chang supervised this work.

Conflicts of Interest: The authors declare no conflict of interest.
References

1. Sheu, J.K.; Chang, S.J.; Kuo, C.H.; Su, Y.K.; Wu, L.W.; Lin, Y.C.; Lai, W.C.; Tsai, J.M.; Chi, G.C.; Wu, R.K. White-light emission from near UV InGaN-GaN LED chip precoated with blue/green/red phosphors. *IEEE Photonics Technol. Lett.* **2003**, *15*, 18–20. [CrossRef]

2. Su, Y.K.; Peng, Y.M.; Yang, R.Y.; Chen, J.L. Effects of NaCl flux on microstructure and luminescent characteristics of KSrPO₄:Eu³⁺ phosphors. *Opt. Mater.* **2012**, *34*, 1598–1602. [CrossRef]

3. Peng, Y.M.; Su, Y.K.; Yang, R.Y. The charge transfer transition phenomenon and microstructure of Eu³⁺-doped NaCaPO₄ phosphors sintered with NH₄Cl flux via solid-state reaction. *Mater. Res. Bull.* **2013**, *48*, 1946–1951. [CrossRef]

4. Yang, R.Y.; Peng, Y.M.; Su, Y.K. Novel red-emitting microwave-assisted-sintered LiSrPO₄:Eu³⁺ phosphors for application in near-UV white light-emitting diodes. *J. Electron. Mater.* **2013**, *42*, 2910–2914. [CrossRef]

5. Yang, R.Y.; Peng, Y.M.; Lai, H.L.; Chu, C.J.; Chiou, B.; Su, Y.K. Effect of the different concentrations of Eu³⁺ ions on the microstructure and photoluminescent properties of Zn₂SiO₄:xEu³⁺ phosphors and synthesized with TEOS solution as silicate source. *Opt. Mater.* **2013**, *35*, 1719–1723. [CrossRef]

6. Peng, Y.M.; Su, Y.K.; Yang, R.Y. Improving thermal stability of KSrPO₄:Tb³⁺ phosphors prepared by microwave assisted sintering. *Opt. Mater.* **2013**, *35*, 2102–2106. [CrossRef]

7. Li, Y.Z.; Wang, Y.H.; Wang, Z.F.; Zhang, Z.Y. UV–VUV-excited photoluminescence of Tm³⁺ substituted β-rhenanite as a blue-emitting phosphor. *J. Lumin.* **2010**, *130*, 1225–1229. [CrossRef]

8. Weng, M.H.; Yang, R.Y.; Peng, Y.M.; Chen, J.L. Yellowish green-emitting KSrPO₄:Tb³⁺ phosphors with various doping concentrations prepared by using microwave assisted sintering. *Ceram. Int.* **2012**, *38*, 1319–1323. [CrossRef]

9. Yang, R.Y.; Chen, H.Y.; Hsiung, C.M.; Chang, S.J. Crystalline morphology and photoluminescent properties of YInGe₂O₇:Eu³⁺ phosphors prepared from microwave and conventional sintering. *Ceram. Int.* **2011**, *37*, 749–752. [CrossRef]

10. Chen, H.Y.; Yang, R.Y.; Chang, S.J. Improving crystalline morphology and photoluminescent properties of BaY₂ZnO₅:Eu³⁺ phosphors prepared using microwave assisted sintering. *Mater. Lett.* **2010**, *64*, 2548–2550. [CrossRef]

11. Chen, H.Y.; Yang, R.Y.; Chang, S.J.; Yang, Y.K. Microstructure and photoluminescent properties of Sr₂SiO₄:Eu³⁺ phosphors with various NH₄Cl flux concentrations. *Mater. Res. Bull.* **2012**, *47*, 1412–1416. [CrossRef]

12. Yang, R.Y.; Lai, H.L. Microstructure, and luminescence properties of LiBaPO₄:Dy³⁺ phosphors with various Dy³⁺ concentrations prepared by microwave assisted sintering. *J. Lumin.* **2014**, *145*, 49–54. [CrossRef]

13. Sun, J.; Zhang, X.; Xia, Z.; Du, H. Luminescent properties of LiBaPO₄:RE (RE = Eu²⁺, Tb³⁺, Sm³⁺) phosphors for white light-emitting diodes. *J. Appl. Phys.* **2012**, *111*, 013101. [CrossRef]

14. Van Uitert, L.G. Characterization of energy transfer interactions between rare earth ions. *J. Electronchem. Soc.* **1967**, *114*, 1048–1053. [CrossRef]

15. Ozawa, L.; Jaffe, P.M. The mechanism of the emission color shift with activator concentration in +³ activated phosphors. *J. Electronchem. Soc.* **1971**, *118*, 1678–1679. [CrossRef]

16. Dexter, D.L. A theory of sensitized luminescence in solids. *J. Chem. Phys.* **1953**, *21*, 836–850. [CrossRef]