EFFECTS OF PREPARATION PROCESS ON DECAY LIFETIME OF $LaPO_4$:Ce,Tb PHOSPHORS

YUNXIA YANG, CHEN LI, SHUANGLONG YUAN, BIN FANG, GUORONG CHEN

Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

E-mail: grchen@ecust.edu.cn

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A two-step reaction method was used to prepare superfine $LaPO_4$:Ce,Tb phosphor particles under two set of conditions. The crystallinity and particle morphology of the product were characterized by using XRD, SEM and particle size analysis, and decay lifetime was investigated as a function of preparation conditions. Results highlighted that an appropriate preparation process leads to less-aggregated $LaPO_4$:Ce,Tb phosphor with greatly improved decay lifetime.

INTRODUCTION

High quality tricolor luminescent lamps are based on introduction of rare earth ions, where the green emitting phosphor plays an important role in improving luminescent efficiency and luminous flux. As reported previously, $LaPO_4$:Ce,Tb is mainly used as a green emitting phosphor for fluorescent lamp because of its advantages over other phosphors such as high quantum efficiency, thermal stability at high temperature and sharp emission around 544 nm with high intensity [1].

Several reports have dealt with the conventional or alternative methods of preparation of phosphors. For examples, $LaPO_4$:Ce,Tb particles could be prepared by solid state method [2-3], the spray-drying method [1,4], or firing the precursor of LaCeTb oxalate [5]. The solid state route requires high reaction temperatures, long heating time, and milling to obtain the pure phase and small particles. Therefore, phosphor particles produced by this route tended to be agglomerated, of an irregular shape, and the reduced brightness due to the destruction of surface structure. The other reported methods also had the disadvantages such as incomplete crystallinity or little stability of elemental composition.

In this work, a new method was introduced to prepare $LaPO_4$:Ce,Tb phosphor, that is, via coprecipitation of a rare earth nitrate solution with diammonium hydrogen phosphate to form a lanthanum cerium terbium phosphate. Advantages of this method over others include the lower firing temperature, an easy control of the reaction, and furthermore, the stable elemental composition. The latter is due to the fact that the $(LaCeTb)PO_4$ was insoluble in the aqueous solution so that it could be precipitated completely.

In the compact lamp, the decay lifetime of phosphor is one of the most important properties affecting application of the lamp. Furthermore, it is closely related to the intrinsic characteristics of phosphor, especially, the quenching temperature, VUV radiation resistance, and resistance against ion-bombardment. These properties are influenced by the composition, structure, and crystal morphology of phosphor [6-7]. In this paper the effects of preparation process on decay lifetime of $LaPO_4$:Ce,Tb phosphors are investigated.

EXPERIMENTAL

In the present work $LaPO_4$:Ce,Tb phosphors with the formula of $La_{0.55}Ce_{0.30}Tb_{0.15}PO_4$ were prepared by using two-step reaction method. The rare earths (La, Ce, Tb) doped phosphate was first coprecipitated from a solution of rare earth nitrates by adding diammonium hydrogen phosphate; the pre-prepared phosphate was then calcined at high temperature under the reducing atmosphere [8]. Two kinds of $LaPO_4$:Ce,Tb phosphors were prepared in the similar way except for adjusting nitrates concentration, pH value and reaction temperature in the course of preparation in order to control the reaction. The details of product preparation are given below.

Method 1: The used solution of rare-earth nitrates (500 ml) with an overall concentration of 0.5mol/l has the following composition: 0.275 mol/l of $La(NO_3)_3$, 0.15 mol/l of $Ce(NO_3)_3$, and 0.075 mol/l of $Tb(NO_3)_3$.

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It was added in one hour to diammonium hydrogen phosphate solution which was provided in an excess amount to react with the rare earth compounds. This is because diammonium hydrogen phosphate decomposes at a relatively low temperature, and its excess provides sufficient phosphate for a complete reaction with the rare earth ions. The pH value during the precipitation was adjusted to 1.4 by adding ammonia solution. The coprecipitation took place at about 10°C. After the precipitation, the reaction medium was further digested from 10°C to 80°C for 8 hours. Then the precipitate was recovered by filtration, washed with deionized water and dried. The dried phosphate was thoroughly blended with 0.5 wt.% of a fluxing compound (H_3BO_3) and then fired to form the product. Firing occurred in covered corundum crucible in a slightly reducing atmosphere at 1100°C for 2 hours. The fired phosphor was cooled, crushed, and rinsed in hot deionized water for final usage.

Method 2: It is similar as the method 1 except for the following different points. Firstly, the overall concentration of rare-earth nitrates solution was adjusted to 1.5 mol/l, correspondingly with the resulting composition as 0.825 mol/l of $La(NO_3)_3$, 0.45 mol/l of $Ce(NO_3)_3$, and 0.225 mol/l of $Tb(NO_3)_3$. Secondly, the pH value was maintained to 2.0 by adding ammonia solution. Thirdly, the reaction was carried out at the temperature of 80°C throughout the precipitation process.

Crystallinity of the prepared powders were characterized with XRD (D/max 2550 VB/PC, CuKα, $\lambda = 1.54056$ Å, 40 mA/30 kV, filter Ni, scanning speed 5 degree/min). The surface morphology of powders was examined under a scanning electron microscope (JSM-6360LV). The size distribution of particles was measured by a Particle Size Analyzer (BT-9300H). The degradation time of brightness was determined using Brightness Meter (Topcon BM-7, λ_{exc} = 254 nm) by applying phosphors into a fluorescent lamp tube (1.8 mm in diameter) and then lighting at 6 mA current for 45,000 hours.

RESULTS AND DISCUSSION

XRD spectra and data recorded on products prepared using methods 1 and 2 are shown in figure 1 and table 1 and SEM photographs of these two products in figures 2 and 3 shows measured the size distribution of phosphor particles prepared by the two methods. As shown in table 1, d-spacings of the products synthesized by the different methods are both similar with those of the standard monoclinic $LaPO_4$. The latter is appreciably larger at each diffraction degree probably owing to the substitution of smaller Ce^{3+} and Tb^{3+} ions for the larger La^{3+} ions. It can be seen from figures 2 and 3 that both phosphors have also similar average particle size of about 5 μm and a similar size distribution. However, the particles prepared in the method 2 (figure 2b) present the shape of congregation, while those prepared by the method 1 (figure 2a) display the less-aggregated shape.

Comparison of SEM photographs between these two products suggests that greater concentration of nitrates, greater pH value and higher temperature during precipitation process favored fast emergence of crystal nuclei. In this case, the speed of nucleation was far greater than that of crystal growth, so that large numbers of crystal nucleus aggregated compactly. On the other hand, the appropriate conditions in the method 1 controlled the speed of nucleation which matched that of crystal growth so that less-aggregated particles were obtained.

Table 1. XRD data of phosphors prepared by two methods.

Serial No.	2θ (°)		*d*-spacing (Å)			Intensity [I/I_1 (%)]	
	(a)*	(b)*	$LaPO_4$**	(a)	(b)	(a)	(b)
1	18.94	19.08	4.70	4.6817	4.6477	21	24
2	21.26	21.40	4.19	4.1758	4.1488	40	43
3	26.98	27.18	3.31	3.3021	3.2782	72	59
4	28.78	29.00	3.12	3.0995	3.0765	100	100
5	31.16	31.36	2.88	2.8680	2.8501	79	87
6	34.48	34.64	2.61	2.5990	2.5874	20	22
7	37.34	37.02	2.45	2.4063	2.4263	7	20
8	41.10	41.38	2.21	2.1944	2.1802	26	21
9	42.16	42.68	2.15	2.1416	2.1167	28	20
10	46.02	46.34	2.04	1.9706	1.9577	32	27
11	51.76	52.74	1.774	1.7647	1.7342	23	21

*Note: (a) method 1; (b) method 2

** Reference: Carron et. al. U.S.GEOL. Survey Bull. 1036-N,253)

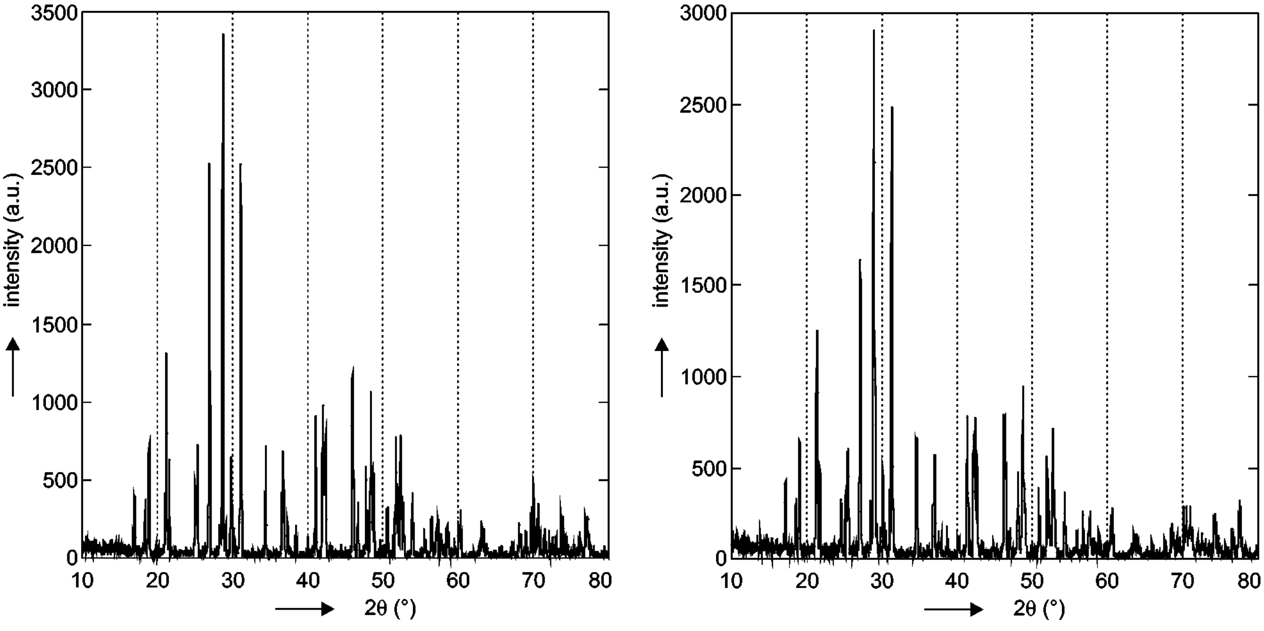
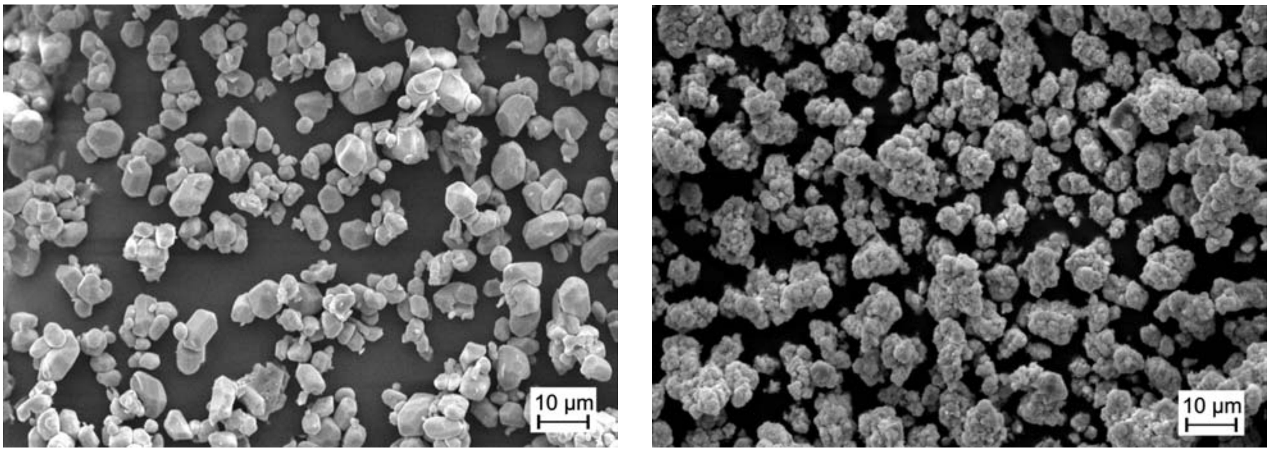


Figure 1. XRD diffraction pattern of phosphors prepared by two methods (a) method 1; (b) method 2.



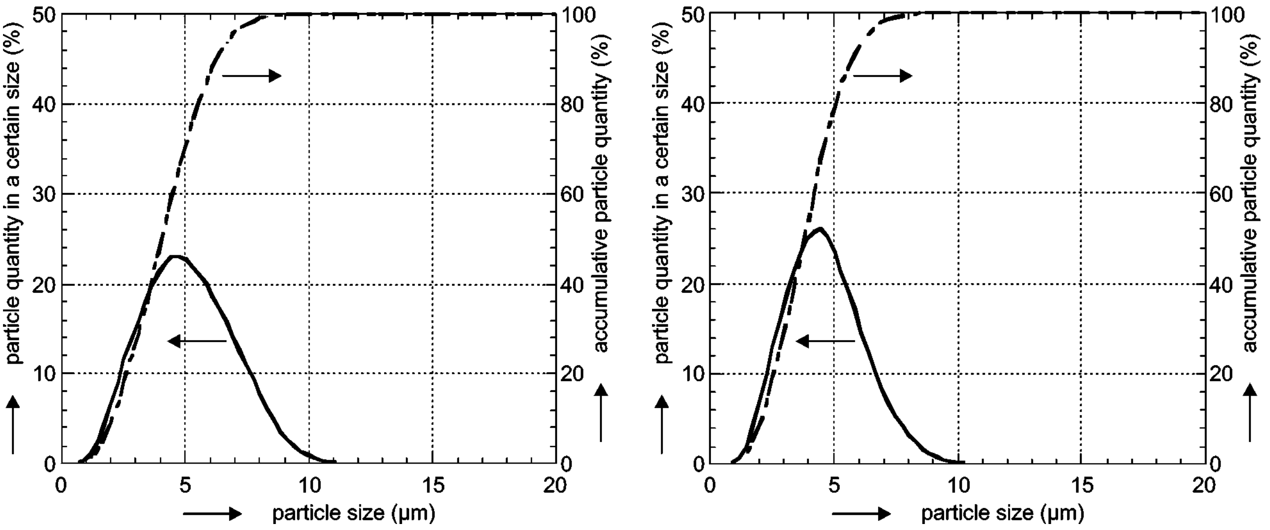
a)

b)

Figure 2. SEM photograph of phosphors prepared by two methods (a) method 1; (b) method 2.

Table 2 shows the original brightness data of phosphors prepared by two methods while the curves of surface brightness as a function of lighting time (decay lifetime) are plotted in figure 4. By comparison, it can be found that initial (time 0) brightness of the phosphor prepared in method 2 was only as much as 94.3% of that of the phosphor prepared in method 1. Although the observed crystal sizes by SEM did not show an obvious difference between these two phosphors, XRD pattern did exhibit the discrepancy in intensity of their characteristic diffraction peaks. As shown in figure 1, the intensity of main diffraction peak at about 29.0 degree for particles prepared in method (a) is greater than that for particles in method (b), indicating that the crystal integrity of the former is better. In other word, the aggregated particles might possess more surface defects than that of less-aggregated particles. This suggestion is partially supported by the fact that the brightness attenuation of aggregated particles in 500 hours (5.5 %) is twice higher than that of less-aggregated particles (2.1 %), as shown in figure 4. This was most likely due to the higher concentration of color centers associated with surface defects on the aggregated phosphors which caused the remarkable degradation of luminescence at the beginning of lighting.

As shown in figure 4, the curve a tends to parallel X axis after 500 hours when the curve b continues to decline. This demonstrates that the preparation process has tremendous effect on the decay lifetime of $LaPO_4$:Ce,Tb phosphors. It is known that the aggregated phosphors have a larger specific surface compared with the less-aggregated phosphors. The possible consequence is that more luminescent centers (Tb^{3+}) will be exposed to the surface of particles so that the distortion force of electron cloud is weakened greatly. As a result, the number of electrons above the valence band becomes less with respect to the aggregated phosphors under the high-energy ultraviolet radiation. Tb^{3+} ions thus neutralize only as common impurity ions, leading to the shortened decay time [9]. On the contrary, the less-aggregated morphology of phosphors creates more Tb^{3+} ions that act as the luminescent centers, and therefore effectively prolongs the luminescent decay time. The latter was demonstrated by the luminescent decay curves that correspond to the lamp lighting continuously for 20,000 hours after which its brightness still kept 90% of initial brightness.



a) b)

Figure 3. Particle size distribution curves of phosphors prepared by two methods (a) method 1; (b) method 2.

Table 2. Lighting data of phosphors prepared by two methods.

Lighting time (h)	Surface brightness (cd/m^2)	
	a (method 1)	b (method 2)
0	11844	11173
200	11760	10870
300	11718	10805
500	11596	10558
1000	11282	10099
2500	11089	9416
10000	10806	9050
22500	10623	8492
33750	10402	7897
45000	10368	7225

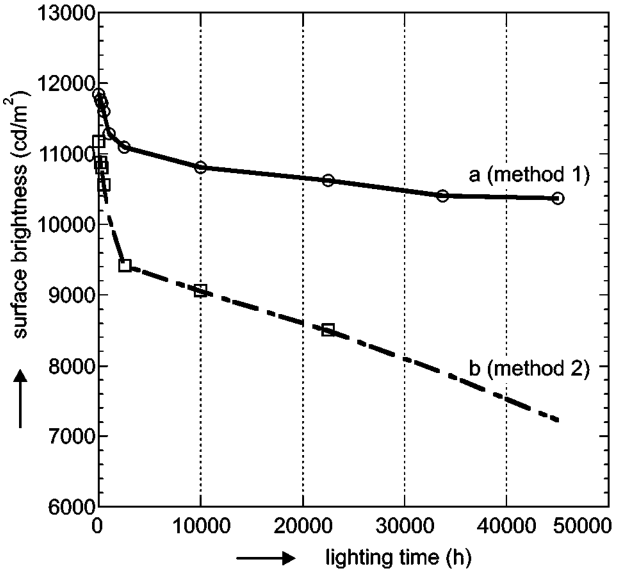


Figure 4. Surface brightness of phosphors prepared by two methods as a function of lighting time.

CONCLUSIONS

The LaPO$_4$:Ce,Tb phosphor particles were prepared by a two-step reaction method. Two set of preparation parameters were compared with respect to morphology of phosphor particles, that is closely related to the brightness and decay lifetime of phosphors. The less-aggregated phosphor particles were shown preferable to the aggregated phosphor particles. They were synthesized through controlling reaction conditions in the liquid phase so that the speed of crystal nucleation matched that of the crystal growth. The lamp lighting test was carried out on the less-aggregated phosphor particles for continuous 20,000 hours after which their brightness may still maintain more than 90 % of their initial brightness.

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VLIV POSTUPU PŘÍPRAVY NA POLOČAS ROZKLADU LUMINOFORU LAPO$_4$:Ce, Tb

YUNXIA YANG, LI CHEN, SHUANGLONG YUAN,
BIN FANG, GUORONG CHEN

*Key Laboratory for Ultrafine Materials of Ministry
of Education, School of Materials Science and Engineering,
East China University of Science and Technology,
Shanghai 200237, China*

Byla použita dvoustupňová metoda přípravy velmi malých částic luminoforu LaPO$_4$:Ce,Tb za dvou různých podmínek. Krystalinita a tvar částic produktu byly charakterizovány pomocí rtg difrakce, řádkovací elektronové mikroskopie SEM a analýzy velikosti částic; poločas rozkladu byl zkoumán v závislosti na podmínkách jejich přípravy. Výsledky ukázaly, že vhodné podmínky přípravy vedou k méně agregovanému luminoforu LaPO4:Ce,Tb, čímž se jeho poločas rozkladu značně zlepší.