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Reaction mechanism for the solid state synthesis of $LaPO_4$:Ce,Tb phosphor

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Abstract

$LaPO_4$:Ce,Tb is an efficient green component of trichromatic lamp phosphors. It is usually prepared by solid state reaction of a blend of $(NH_4)_2HPO_4$, Tb_4O_7 and CeO_2 with or without Li_2CO_3 flux. This reaction mechanism has been investigated by differential thermal analysis, thermogravimetric analysis, X-ray diffraction and scanning electron microscopy. Experimental results show that at ~200 °C $(NH_4)_2HPO_4$ decomposes to form syrupy $P_2O_5 \cdot xH_2O$. As the firing temperature is increased to 600 °C (in the presence of Li_2CO_3) and 800 °C (in the absence of Li_2CO_3) syrupy P_2O_5 begins to react with rare earth oxides to form mixed rare earth orthophosphates. Up to 1000 °C and 1400 °C, respectively, these two reactions go to completion. Their reaction rates change linearly as the reciprocal temperature and with different slopes, from which activation energies are estimated to be 22 and 35 kcal mol^{-1}, respectively. Reactions appear to be diffusion-limited. Thermal quenching of luminescence of $LaPO_4$:Ce,Tb can be minimized by the addition of Li_2CO_3 in the reaction mixture.

1. Introduction

$LaPO_4$:Ce,Tb is an efficient green component of trichromatic lamp phosphors. Much work has been devoted to its synthesis by solid state reaction, but few of them are concerned with the reaction mechanism [1–3]. Moreover, $LaPO_4$:Ce,Tb is a chemically stable compound, but it undergoes serious luminescence depression at higher temperature, which is detrimental for its use in narrow tube lamps. We have studied the reaction mechanism for the solid state synthesis of $LaPO_4$:Ce,Tb in order to improve its luminescence thermal stability, and have obtained positive results.

2. Experimental details

Li_2CO_3 was selected as the best flux for obtaining better phosphors both in crystallinity and luminosity. Two mixture with the following compositions were used for the study of reaction mechanism: Blend I, $0.65La_2O_3+0.40CeO_2+0.10Tb_4O_7+2.10(NH_4)_2HPO_4$; Blend II, $0.65La_2O_3+0.40CeO_2+0.10Tb_4O_7+2.10(NH_4)_2HPO_4+0.04Li_2CO_3$. All the materials (analytical grade) were weighed according to the above mole ratios, ground and mixed thoroughly. Small samples of these blends were treated by DTA-TGA on a CK-G model thermal analyser and some thermal effects were observed. Larger samples taken from these blends were fired at definite different temperatures from 25 to 1400 ° for 2 h in a CO atmosphere formed by igniting active carbon granules covered on the samples. Morphology and phase analysis of the fired samples were studied with a JSM 35-CF scanning electron microscope and Siemens D 500 automatic X-ray powder diffractometer, respectively. Luminescence studies of $LaPO_4$:Ce,Tb were performed on a Hitachi M-850 fluorescence spectrophotometer ($\lambda_{EX}=254$ nm).

3. Results and discussion

3.1. DTA and TGA

DTA and TCA results up to 1300 °C of samples from blends I and II are shown in Fig. 1. Both samples underwent two endothermic and weight-loss steps around 200 °C. This corresponds to the decomposition of $(NH_4)_2HPO_4$ first to give off NH_3 and then to form syrupy $P_2O_5 \cdot xH_2O$ in these two samples. There is a small exothermic effect at 300 °C of unidentified nature in sample II. The decomposition of Li_2CO_3 is not seen by TGA, maybe because of the small amount. As the temperature is raised higher, no further obvious thermal effect was observed. Thus the reaction proceeded progressively through interdiffusion between rare earth oxides and syrupy phosphorous oxide.

3.2. Scanning electron microscopy

Samples fired at 600, 800, 1000, 1200 and 1400 °C do not show different morphologies. This implies that

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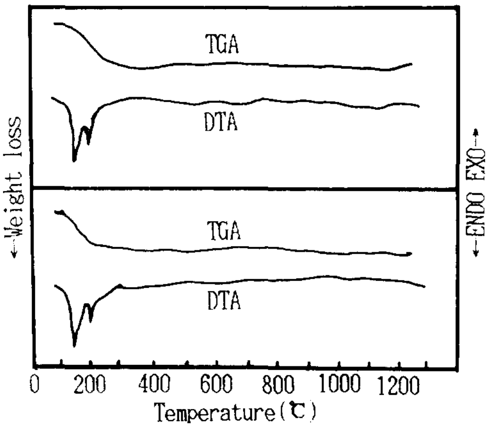

Fig. 1. DTA and TGA of samples up to 1400 °C.

the particle size and surface condition for the intermediate as well as for the final products do not change significantly.

3.3. Phase analysis

Typical XRD patterns of the fired samples I and II show that there existed phases of the product $REPO_4$ and still unreacted RE_2O_3. Based upon the diffraction peak intensities of the phases in the samples fired at different definite temperatures, we have estimated the relative phase composition in the reaction mixture (Table 1). Amounts of non-crystalline phases were estimated by the diffraction background intensity. Li_2CO_3, Li_2O and P_2O_6 could not be detected because of the light elements contained or because of the existence of non-crystalline state.

We found that the main diffraction peak intensity of $\{h\,k\,l\}$ 120 and $2\theta=36.511$ (expressed in common logarithmic value) of the $REPO_4$ product in the reaction blends fired above the formation temperature and in the range 1000–1250 K, changed linearly against reciprocal temperature as shown in Fig. 2.

3.4. Luminescence property

Referring to the literature [4,5], we have improved the luminescence thermal stability of $LaPO_4$:Ce,Tb phosphors by doping with a certain amount of Li_2CO_3 in the reaction blend. It is well known that luminescence efficiency and thermal stability of phosphors are related to their crystallinity which is dependent on the firing condition for their preparation. Therefore we prepared the phosphors of composition $La_{0.8}Ce_{0.1}Tb_{0.1}PO_4$ with or without 0.2 mol Li_2CO_3 flux by firing the mixture of starting materials at different temperatures and for different times. Experimental results show that doping with 0.2 mol Li_2CO_3 in the mixtures enables the reaction to go to completion and the crystallinity (judged by XRD peak intensity) as well as luminescence intensity of the product $LaPO_4$:Ce,Tb to reach their maximum at a greater rate and lower temperature during the firing process (Fig. 4). However, prolonged firing time somewhat lowers the luminescence intensity, perhaps due to the oxidation of Tb^{3+} and Ce^{3+} to tetravalent in the phosphors. There is a little change in the excitation spectra of $La_{0.8}Ce_{0.1}Tb_{0.1}PO_4$ prepared under various conditions; this will be discussed in detail elsewhere. Doping with Li^+ ions by firing with Li_2CO_3 flux in the preparation of $LaPO_4$:Ce,Tb not only improves its luminescence intensity at room temperature but at higher temperature (Fig. 3). That means that thermal quenching of this phosphor can be minimized by the addition of Li_2CO_3 in the reaction mixture (Fig. 5).

4. Discussion

From the results of DTA, TGA and XRD we know that below 300 °C $(NH_4)_2HPO_4$ gradually decomposed into syrupy $P_2O_5 \cdot H_2O$. As the temperature is increased, P_2O_5 begins to react with RE_2O_3. Since the morphology of the reaction blends did not change significantly and there was no obvious thermal effect, we presume that the reaction should proceed further by diffusion of

TABLE 1. XRD phase analysis on the reaction blend samples fired at different temperatures[a]

Phases	T (°C)											
	400		600		800		1000		1200		1400	
	I	II	I	II	I	II	I	II	I	II	I	II
La_2O_3	+ + +	+ + +	+ + +	+ +	+ +	+	+	–	+	–	–	–
Ce_2O_3	+ + +	+ + +	+ + +	+ +	+ +	+	+	–	–	–	–	–
Tb_4O_7	+ + +	+ + +	+ + +	+ +	+ +	+	+	–	–	–	–	–
$REPO_4$	–	–	–	+	+	+ +	+ +	+ + +	+ +	+ + +	+ + +	+ + +
Non-crystalline phase	+ + +	+ + +	+ + +	+ +	+ +	+	+	+	+	–	–	–

[a]+ + +, large; + +, medium; +, small; –, none.

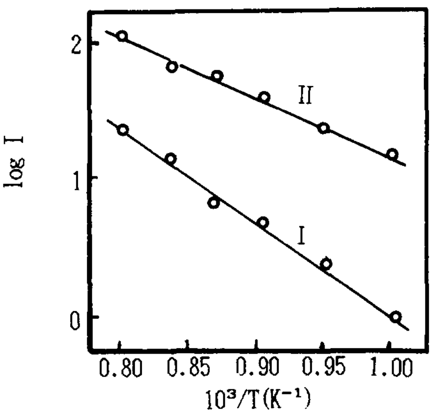

Fig. 2. Firing temperature dependence of $REPO_4$ main diffraction peak intensity in the reaction blends.

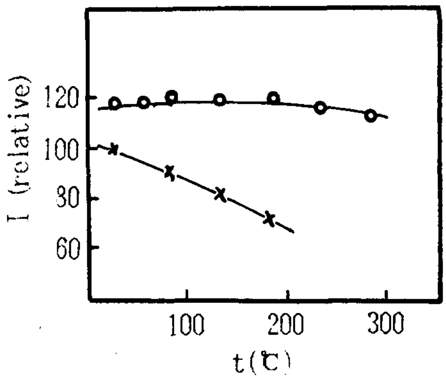

Fig. 3. Temperature dependence of the emission intensity of $(La_{0.8}Ce_{0.1}Tb_{0.1})PO_4$. Undoped (×); 0.105 mol Li^+-doped (○).

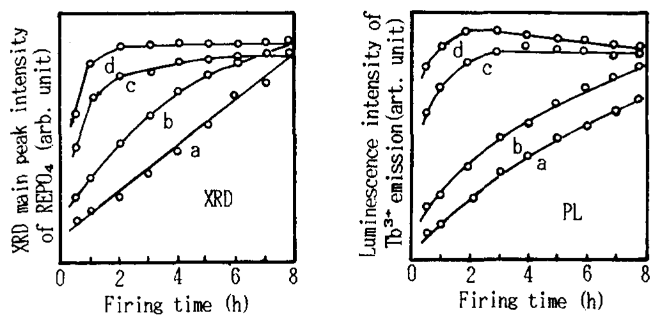

Fig. 4. Firing temperature and time dependence of $REPO_4$ main diffraction peak intensity and of Tb^{3+} $^5D_4$-$^7F_4$ transition emission intensity. (a) 1300 °C, without flux; (b) 1100 °C, with Li_2CO_3 flux; (c) 1350 °C, without flux; (d) 1150 °C, with Li_2CO_3 flux.

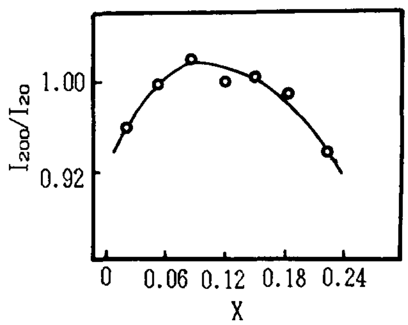

Fig. 5. Emission intensity ratio at 200 °C and 20 °C of $(La_{0.8-x}Ce_{0.1}Tb_{0.1}Li_{3x})PO_4$ versus amount of Li^+

P_2O_5 into RE_2O_3 particles through the $REPO_4$ layer formed. The relative XRD peak intensities expressed as log*I* of the $REPO_4$ formed are proportional to the reciprocal reaction temperatures in the range 1000–1250 K as shown in Fig. 2. XRD peak intensity of $REPO_4$ might be considered to represent its relative amount in the reaction blend. Therefore, the activation energy of the formation reaction of $REPO_4$ taking place in blends I and II can be estimated to be 35 and 22 kcal mol^{-1}, respectively by the following equation:

$$A = Jt \propto \exp(-E/kT)$$

where A is the relative amount of $REPO_4$ formed in the period t by diffusing a mass flux J of P_2O_5 into RE_2O_3 at temperature T.

Acknowledgment

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