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Short Communication

Chemical substitution effects of elements on photoluminescence properties of YAG:Ce phosphors using orthogonal experimental design

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ABSTRACT

In this paper, the chemical substitution effects of elements on photoluminescence properties of YAG:Ce phosphors were studied by orthogonal experimental design. The controllable factors used in this design consisted of Tb^{3+}, Ga^{3+}, and Si^{4+} substitution in YAG:Ce host. Emission intensities and wavelengths of as-obtained phosphors were regarded as the indexes of orthogonal experiment. The experimental results show that the emission spectra are blue-shifted by Si^{4+} replaced Al^{3+} and red-shifted by Tb^{3+} substituted Y^{3+}; meanwhile, the emission intensity visibly depends on the addition of Si^{4+} and Ga^{3+}. The luminous efficiency is improved by proper elements substitution in YAG:Ce and the optimum composition ($Y_{2.74}Tb_{0.2}Al_{4.7}Si_{0.1}Ga_{0.2}$:0.06Ce) shows good optical properties and has a great potential to substitute the commercial phosphors.

1. Introduction

White light-emitting diodes (LEDs) are excellent candidates for general lighting because of their rapidly improving efficiency, durability, reliability, and their environmentally friendly constituents. Effective lighting devices can be realized by combining one or more phosphor materials with chips. Accordingly, it is very important that the architecture of phosphors can be developed. Although numerous phosphors have been proposed in the past several years, the range of phosphors that are suitable for LEDs is limited [1].

Nowadays, the majority of white LEDs use a blue InGaN chip pumped with yellow-emitting $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce) phosphors [2]. YAG is a host with excellent structural compatibility. Inner Y^{3+} and Al^{3+} can be partly substituted by many kinds of cations with different sizes and valence in a certain extent [3]. With the replacement of Al^{3+} by a small amount of Si^{4+}, the emission spectrum shows a blue shift due to a decrease of the splitting of 5d levels of Ce^{3+} ion. The thermal stability is greatly improved by adding Si^{4+} because the activation energy ΔE increases from 0.1836 eV to 0.2401 eV [4]. Similarly, the Ce^{3+} emission is blue-shifted by Ga^{3+} substitution into YAG:Ce and the red-shift effect is observed for Y^{3+} as Tb^{3+} substituted due to a modified crystal field splitting [5,6]. These spectral variations caused by a co-dopant and substituents can lead to the manipulation of photoluminescence properties. This tunability would contribute to improve color gamut and luminous efficiency of white LEDs. However, chemical substitution effects of multi-elements on photoluminescence properties of YAG:Ce phosphors are seldom investigated using orthogonal experimental design. This fact is the main motivation for this study. In this report, Tb^{3+}, Ga^{3+}, and Si^{4+} ions were used as the controllable factors. The substitution effects and optimum combination of these elements for improving YAG:Ce phosphors with better emission intensity and longer emission wavelength were studied by the orthogonal experiment.

2. Experimental

The orthogonal experiment design was adopted to optimize the design parameters because this approach can minimize the testing time and the experimental costs. The optimum experimental parameters can easily be determined using the orthogonal array. This paper considers three controllable factors (Tb^{3+}, Ga^{3+}, and Si^{4+} ions substitution in YAG:Ce), and each factor has three level. An L9(3^4) orthogonal array is chosen, so the factors and levels are given in Table 1.

In this experiment, all reagents were of analytical grade purchased from Chengdu Kelong Chemical Corporation and used in this work without any further purification. According to Table 1, precursors were synthesised for acquiring the target composition of $Y_{(2.94-x)}Tb_xAl_{(5-y-z)}Si_yGa_zO_{12}:Ce_{0.06}$ by a simple co-precipitation method. The detailed process was as follows: firstly, a stoichiometric amount of $Y(NO_3)_3\cdot 6H_2O$, $Al(NO_3)_3\cdot 9H_2O$, $Ce(NO_3)_3\cdot 6H_2O$, $Na_2SiO_3\cdot 9H_2O$, $Ga(NO_3)_3\cdot 6H_2O$ and $Tb(NO_3)_3\cdot 6H_2O$, were dissolved

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Table 1
Factors and levels of orthogonal experiment.

Factors	Description	Level 1 (mol)	Level 2 (mol)	Level 3 (mol)
A	n_{Si} (y), the y value of Si^{4+} substitution in $Y_{(2.94-x)}Tb_xAl_{(5-y-z)}Si_yGa_zO_{12}$:$Ce_{0.06}$	0	0.1	0.2
B	n_{Ga} (z), the z value of Ga^{3+} substitution	0	0.1	0.2
C	n_{Tb} (x), the x value of Tb^{3+} substitution	0	0.1	0.2
D	Blank	0	0	0

in distilled water. 1 mol/L of NH_4HCO_3 was slowly dropped in above solution under stirring until a white precipitate formed. Secondly, the precipitate was filtered, washed three times with distilled water and dried at 80 °C for 24 h. Finally, the dried precipitate was calcined at 1500 °C for 4 h in a N_2 (95%)–H_2 (5%) atmosphere.

Phase purity of the samples was examined by power X-ray diffraction (XRD) performed on a XRD-6000 (Shimadzu, Japan) diffractometer by using Cu Kα1 radiation. The XRD data were collected by a scanning mode in the 2θ range from 10° to 70° with a scanning step of 0.02° and a scanning rate of 2.0° min^{-1}. The particle morphology was acquired using a JSM-5900LV (JEOL, Japan) scanning electron microscopy (SEM) with accelerating voltage of 10 kV. Photoluminescence spectra and quantum yields were recorded with an F-7000 (Hitachi, Japan) spectrophotometer equipped with a 60 mm integrating sphere and a 150 W xenon lamp as excitation source. luminous efficiency, color-rendering index, and the Commission Internationale de l'Eclairage (CIE) color coordinates were characterized using a HSP3000 high accuracy LED photo-color and electron test system (Hangzhou Hongpu Optoelectronics Technology Co. Ltd., China), and evaluated under a current of 350 mA. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Characterization of as-prepared phosphors

Fig. 1 shows the XRD patterns of different samples (the numbers are same as those in Table 2). It is observed that all the prepared samples are pure cubic phases and coincide well with the standard data of $Y_3Al_5O_{12}$ (JCPDS No. 82-0575). No obvious peak shift or other phase can be detected, indicating that the substitution elements, such as Ce^{3+}, Tb^{3+}, Ga^{3+}, and Si^{4+} ions, have been dissolved successfully in $Y_3Al_5O_{12}$ host. The corresponded peaks for YAG are mainly identified as (2 1 1), (4 0 0), (4 2 0), and (6 4 0) planes.

SEM images of the YAG:Ce phosphor powders after annealed at 1500 °C and ground for 4 h are shown in Fig. 2. The as-prepared particles of YAG:Ce shows a very smooth surface and an almost spherical shape with a uniform size ranging from 1.5 to 2.5 μm. In appearance, samples 1–3 are loose yellow powders, samples 4–6 become compact and hard, but samples 7–9 are changed into solid bulk and difficultly to be broken. The possible reason is the addition of Si^{4+} ions. As we can see in Fig. 2, the size of grains in sample 9 is similar to that in sample 1, but their shapes are distinctly different, owing to the surfaces closely squeezed with other grains. So it can be suppose the interaction force of grains increases with increasing the amount of Si^{4+} ions.

The excitation and emission spectra of samples are showed in Fig. 3. Upon 450 nm excitation, all the emission spectra correspond to the excitation into the lowest energy d-level of Ce^{3+}. The emission intensity continuously increases from sample (a) to sample (d). Further, most of the prepared YAG:Ce phosphor powders show higher photoluminescence intensity and the maximum emission intensity is sample 6. The excitation spectra obtained upon 530 nm emission show two excitation bands that are assigned to transitions to the two lowest energy levels and are centered at around 450 nm and 340 nm. It is worth noting two weak excitation bands with peaks at about 375 nm (see Fig. 4b and c) are ascribed to f–f transition of Tb^{3+} ions; this is in agreement with the report in the literature [7].

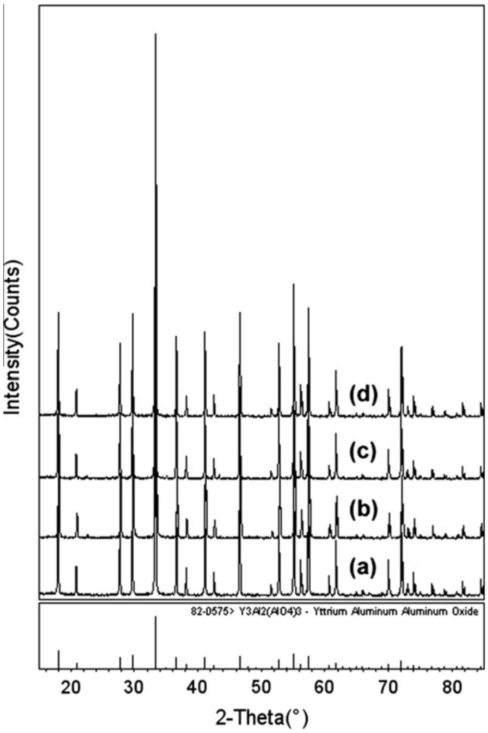

Fig. 1. XRD patterns of samples 1(a), 4(b), 9(c), and 6(d).

3.2. Analysis of results in the orthogonal experiment and chemical substitution effects

Nine experimental trials were designed according to the L9(3^4) orthogonal array, and the corresponding emission intensities and wavelengths were obtained and listed in Table 2. Here, k_{Ii} and k_{wi} are the average output of response intensity and wavelength for certain factor at level i, respectively. R_I and R_W are the related range. The results of intuitive analysis displays that the effect of A factor (Si^{4+}) is greater than others, the emission intensity increase but wavelength decrease with increasing the amount of A. Moreover, the effect of B factor (Ga^{3+}) on intensity is obvious and C factor (Tb^{3+}) has a relative impact on wavelength. Effects of other factors are near to or less than D factor (blank), so those are negligible. Therefore, the optimum combination is $A_2B_3C_3$, and then the corresponding formula is $Y_{2.74}Tb_{0.2}Al_{4.7}Si_{0.1}Ga_{0.2}$:0.06Ce. Attributed to the different splitting of 5d levels of Ce^{3+} ion in YAG, the emission wavelength is blue-shifted by Si^{4+} replacement, but the red-shift effect is indicated as Y^{3+} substituted by Tb^{3+}. According to the value of K_{Ii}, the emission intensity has visible dependence on