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Statistical design for the optimization of the red to orange ratio in $YBO_3:Eu^{3+}$ phosphors

Xianwen Zhang[a,*], Yixuan Fu[a], Zhi Zhao[b], Jing Yang[c], Na Li[d], Maofeng Zhang[e]

[a] School of Automobile and Transportation Engineering, Hefei University of Technology, Hefei, Anhui 230009, China
[b] Hefei National Laboratory for Physical Sciences at the Microscale, University of Science & Technology of China, Hefei, Anhui 230009, China
[c] School of Mechanical Engineering, Hefei University of Technology, Hefei, Anhui 230009, China
[d] Department of Chemical and Chemical Engineering, Hefei Normal University, Hefei, Anhui 230601, China
[e] School of Mechanical Engineering, Hefei University of Technology, Xuancheng, Anhui 242000, China

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ABSTRACT

In this study, response surface methodology (RSM) is applied for the optimization of red/orange ratio of $YBO_3:Eu^{3+}$ phosphors synthesized via hydrothermal process. The influence of various process parameters namely borate/yittrium ratio (1, 2, 3), Eu^{3+} concentration (5%, 10%, 15%), and ethanol concentration (20%, 40%, 60%) were taken into consideration. A total of 15 experimental runs were carried out based on Box-Behnken design. Response surface plots were used to determine the interaction effects of the process parameters and optimum conditions of hydrothermal process. Regression analysis shows good fitting of the experimental data to the quadratic polynomial model with *P-value* of 0.025, *F-value* of 6.73 and coefficient of determination of 0.924. The optimum experimental conditions were as follows: borate/yittrium ratio at 1.928, Eu^{3+} concentration at 15%, ethanol concentration at 20%. The predicted R/O ratio under the optimum conditions is in good agreement with the R/O ratio obtained from the experiment under the same optimum conditions. The results indicate Box-Behnken design can help for the searching of optimum factors and improve R/O ratio. Moreover, the quadratic model from the Box-Behnken design can quantitatively describe the inherent relationships between the process factors and R/O ratio of $YBO_3:Eu^{3+}$ phosphors.

1. Introduction

Solid state lighting on basis of white light emitting diodes (W-LEDs) has attracted more and more attentions, owing to their long lifetimes, high rendering indices, high luminous efficiencies, and safety over conventional incandescent and fluorescent lamps [1]. The fabrication of W-LEDs by combing YAG: Ce^{3+} yellow phosphors on blue-light emitting GaN chip is one of the most convenient methods. However, the yellow phosphors lack sufficient red emission component leading to white light with a poor color rendering index (CRI). Recent works reported that Eu^{3+}-doped red phosphors were used to improve the CRI and conversion efficiency in W-LEDs. YBO_3 as the host materials of red phosphors has aroused great interest due to excellent vacuum ultraviolet absorption, high chemical stability, and exceptional optical damage threshold [2–4]. Therefore, YBO_3 is readily doped with red Eu^{3+} ion, which can be activated in the deep (200–250 nm) and near (300–400 nm) UV [5]. In YBO_3: Eu^{3+}, Eu^{3+} color center generates narrow emission at 591 nm (orange, abbreviated as O) due to magnetic dipole transition ($^5D_0$–$^7F_1$) and at 611 and 627 nm (red, abbreviated as R) ascribed to the electric dipole transition ($^5D_0$–$^7F_2$). High value of the R/O intensity ratio is desirable to improve red chromaticity of YBO_3: Eu^{3+} by optimizing experimental factors. One-variable-at-a-time technique is widely used by fixing one factor, then varying the other factors to optimize result. The major drawback of this technique is that it does not consider interactive effects among the variables, thus it cannot explain the complete effects of the parameters in the experiment [7].

Mathematics is expected to play an important role in tackling the challenges and boosting the development of materials science [6]. In most existing scientific literatures, synthesis of micro/nanomaterials lacks of theoretical guidance for obtaining high quality and reproducible materials. It is important to improve the performance of the experiments and to increase the yield or quality of the processes without increasing the cost and time. The strategy used for this purpose is called optimization [7]. Statistical techniques have made considerable impacts in many fields in the past. Furthermore these methods allow the development of mathematical models that permit assessment of the relevance as well as statistical significance of the factor effects and evaluate the interaction effects between the factors. The first step of

* Corresponding author.
E-mail address: nali2017@163.com (X. Zhang).

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multivariate optimization is to complete screening the factors (full factorial or fractional factorial design) in order to obtain the significant effects of the experimental system. After determining the significant factors, statistical optimization studies can be carried out using response surface methodology (RSM), such as central composite designs (CCD) and Box-Behnken design (BBD) [8–11].

RSM is a collection of mathematical and statistical techniques useful for modeling and analysis of problems in which a response of interest is influenced by several variables and the objective is to determine the optimum operating conditions. Box and Behnken (1960) proposed BBD for fitting response surfaces [12]. For three factors its graphical representation can be seen in two forms: a cube that consists of a central point and the middle points of the edges and a figure of three interlocking factorial designs and a central point. A comparison between the response surface methods and factorial designs has demonstrated that BBD is more efficient than the CCD and full factorial designs. Another advantage of BBD is that it does not contain combinations for which all factors are simultaneously at their highest or lowest levels. So BBD is useful in avoiding experiments performed under extreme conditions, where unsatisfactory results might occur [13]. Recently, the BBD approach has been applied for the optimization of the production of carbon nanotubes, hydroxyapatite, ZnO nanoparticles and copper(II) complex for chemiluminescence. [14–17].

In this study, the experiments for optimizing R/O ratio of YBO_3:Eu^{3+} red phosphors synthesized via hydrothermal method were carried out based on BBD with three factors (Eu^{3+} doping concentration, borate(B)/yittrium(Y) ratio and ethanol concentration). The effects of these factors on R/O ratio and the relationships between the factors were statistically analyzed with response surfaces, and the synthesis conditions using mathematical equations and response surface plots were optimized.

2. Materials and methods

2.1. Preparation of YBO_3: Eu^{3+} red phosphors

All the 15 experiments designed by BBD were conducted using hydrothermal synthesis through the reaction of $Y(Eu)(NO_3)_3$•$6H_2O$ and $K_2B_4O_7$•$4H_2O$ in the mixture of water and ethanol. All chemicals were analytical grade and used directly without any treatment. In a typical synthesis, an aqueous solution of 0.2 M $Y(NO_3)_3$•$6H_2O$ and $Eu(NO_3)_3$•$6H_2O$ with three different ion molar ratio of Y^{3+}/Eu^{3+} (95/5, 90/10 and 85/15) was dropped into the mixture of ethanol solution (20%, 50%, and 80%) under vigorous stirring. An aqueous solution of 0.2 M $K_2B_4O_7$•$4H_2O$ with different volumes was added into the former solution and stirred. Three different Y/B molar ratios (1/1, 1/2 and 1/3) were used. A white precipitate appeared immediately. After stirring for about 10 min, the solution was rapidly adjusted to a designated pH at 9 using 1 M ammonia water. Both the solution and the precipitate were then transferred into a 60 mL autoclave, sealed, and heated to 180 °C for 12 h. The system was then cooled to room temperature. The final product was collected by filtration, washed with deionized water and ethanol to remove any possible ionic remnants, and then dried in a vacuum at 60 °C for 4 h.

2.2. Characterization

The scanning electron microscope (SEM) micrograph of the YBO_3:Eu^{3+} phosphor was obtained using Zeiss (Model SU8020, Japan). X-ray powder diffraction (XRD) measurement was carried out by using a Bruker D5005 X-ray diffractometer furnished with Cu Kα radiation (λ = 1.54406 Å) under 40 kV. Finally, the value of red (R) and orange (O) was obtained by integrating the red and orange emission peaks in photoluminescence spectra of the 15 samples. The crystal phases and crystallized quality of as-prepared nano/micro powders will be identified using X-ray diffraction with Cu Kα radiation. The morphology and primary particle size were observed using field emission SEM. The photoluminescence spectra of the samples excited at 363 nm were measured by a steady-state/lifetime spectrofluorometer (JOBIN YVON, FLUOROLOG-3-TAU) with a 450 W monochromatized xenon lamp. Fine powdered phosphor samples were pressed into a square cell, volume of which is approximately 14 × 7 × 2 mm^3 to ensure uniform thickness and distribution of powders.

Table 1
Independent variables and their coded levels for the BBD.

Factor	Code	Coded variables levels		
		−1	0	+1
Eu^{3+} percentage	X_1	5%	10%	15%
B/Y ratio	X_2	3	2	1
Ethanol volume percentage	X_3	20%	50%	80%

2.3. Design of experiments

The response surface is a curved surface that can indicate the relation between the independent variables X_i and the response. Both independent variables and the coded levels are shown in Table 1.

A polynomial to represent the function can be generally applied for simplicity. The experimental design, data analysis and modeling were performed by Minitab 16.0 (Minitab Inc, USA). A multiple regression analysis was conducted on basis of the second-order response function with the independent variables, and the model can be expressed by the following equation:

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \sum_{j=1}^{n} \beta_{ij} X_i X_j + \sum_{i=1}^{k} \beta_{ii} X_{ii}^2 + \varepsilon$$

where Y is the response value; β_0, β_i, and β_{ij}, obtained by the technique of least squares are regression coefficients for intercept, linear and interactions among variables, respectively. X_i and X_j are the independent factors to be studied and ε is the error term. β_i, β_{ij} can measure the effects of the variables X_i and X_j. The extent of fitting the experimental results to the polynomial model equation was evaluated by coefficient of determination (R^2). Meanwhile, *F-test* was used to estimate the significance of all terms in the regression equation within 95% confidence interval.

The BBD of YBO_3:Eu^{3+} R/O optimization is a three-level experimental design that allows prediction of the combined effects of three controlled factors of 15 runs. Run 13, 14, and 15 have been performed with the variable parameters in the middle level (center point runs). Three levels were attributed to each factor, coded as −1 (low), 0 (medium), and +1 (high). The response values R/O were observed ranging from 1.58191 to 2.30323 in Table 2.

3. Results and discussion

3.1. Development of regression model equation

The mathematical model predicts the optimum point between the three variables in the coded levels. The response can be expressed as follows:

$$Y = 1.33277 - 0.0659883X_1 + 0.974050X_2 - 0.538504X_3 + 0.00718068X_1^2 - 0.132935X_2^2 - 0.0301087X_1 * X_2$$

This equation reveals how the individual factors or double interaction affect R/O of the red phosphors at the excitation of 363 nm. Coefficients of single factor in the equation indicate the effect of the specific factor, while coefficients of two factors and second-order terms indicate the interaction between the two factors and a quadratic effect, respectively. The positive sign represents a synergistic effect, while a