

Photoluminescence Properties of (Gd_{1-x}, Eu_x) Doped Tungsten Oxide Red Phosphors Synthesized using Solution Chemistry

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Gd_{1-x}-Eu_x ($x = 0.2, 0.3, 0.4, 0.5$) doped tungsten oxide red-emitting phosphor was prepared using solution chemistry. The phase, morphology, and luminescence characteristics of the obtained phosphors were compared with those of oxide obtained from general solid-state reaction processes. The suitability of the 600°C calcination temperature for producing W-Eu-Gd-O mixtures was confirmed by TG weight loss measurements. The results show that the phase development behaviors and morphologies differ from those of general solid-state processes. Whereas the general process developed only one phase, the solution process produced various phases, such as Gd₂WO₆, Gd₂W₂O₉, and Gd₂(WO₄)₃, from the heat treatment of the oxide mixture at 1000°C. The phosphor grain size can be controlled by this solution chemistry process. The emission behaviors of the synthesized phosphors strongly depend on the phase structures.

Key words: solution chemistry, red emitting, phosphors.

Introduction

The increasing demand for phosphors has promoted researchers to develop various phosphors for use as luminescent materials. Various phosphor inorganic host materials are used in the fabrication of white-light emitting diodes (WLED), field emission displays, fluorescent lamps, electroluminescent materials, plasma display panels, laser materials, etc. These inorganic phosphors have many desirable luminescence properties, such as high brightness, high efficiency, high stability, and low energy consumption. [1].

A number of materials activated by trivalent rare earth ions, which can exhibit light-emitting properties, have been used as phosphors. As host materials for red-emitting phosphors, rare earth oxides such as WO₃, which is commonly used in tricolor fluorescent lamps and color displays because of its efficient luminescence under ultraviolet and electron beam excitation, have been extensively investigated. The crystal structure typical of Gd doped tungsten oxide produces a suitable host material for red-emitting phosphors [2]. However, conventional solid-state reaction processes require complex thermal treatment to realize high-performance red phosphors. In this study, a solution chemistry process was applied to fabricate Gd_{1-x}-Eu_x doped tungsten oxide phosphors [3]. The properties of the phosphors obtained from the solid-state reaction and solution chemistry approaches are compared.

Experimental Procedures

The solution chemistry method was adopted to obtain the powder mixtures used for composites. High-purity Gd(NO₃)₃·6H₂O (Aldrich Chem.) and Eu(NO₃)₃·5H₂O (Aldrich Chem.) were selected as source materials for Gd and Eu, respectively. The Eu(x) content in the specimen was set to $x = 0.2, 0.3, 0.4, 0.5$ for the synthesis of Gd_{1-x}-Eu_x doped tungsten oxide phosphors. Weighted nitrates were dissolved in ethyl-alcohol at 60°C for 2 hrs, and WO₃ powder (100 nm, Aldrich Chem.) was mixed into the solution. The slurry mixtures were dried in a vacuum oven, and the dehydrated mixtures were calcined at 600°C in air flow to obtain the WO₃-GdO-EuO oxide mixture. The calcination behavior of the nitrate mixture powders was studied using thermogravimetry (TG). The calcinated powders were heat-treated at 1000°C for 10 hrs in air to obtain the red phosphors.

The sample composition and characteristics were determined by X-ray diffractometry (XRD) in the region of 2θ from 20 to 70° using Cu K α radiation ($\lambda = 0.15406$ nm). The surface morphologies of the synthesized composite powders were observed by field emission scanning electron microscopy (FE-SEM, JSM-7001F, Jeol). The optical properties were measured by photoluminescence (PL).

Results and Discussion

The TG results for the solution-chemistry-processed WO₃, Gd-nitrate, and Eu-nitrate mixture powder ($x = 0.5$) are shown in Fig. 1. Rapid weight loss is

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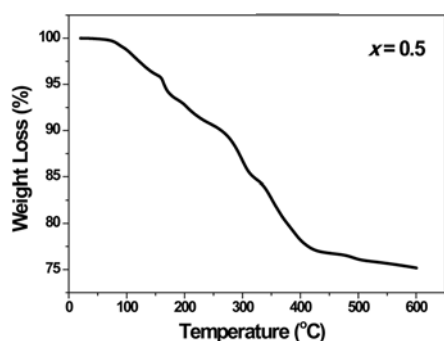


Fig. 1. TG curve of the Eu-nitrate, Gd-nitrate and WO_3 mixture for $Gd_{1-x}Eu_x$ doped tungsten oxide phosphors.

observed from 100 to 150°C, which is attributed to the loss of water and the burnout of the impurities in the reaction mixture. The weight loss is saturated at 600°C after two significant weight loss events. The weight loss ranges from 250 to 400°C and 320 to 450°C are related to Eu-nitrate and Gd-nitrate calcination, respectively, as determined in a previous experiment. Finally, the oxide mixtures (W-Eu-Gd-O) were synthesized via calcination. The Eu-nitrate and Gd-nitrate weight losses were approximately 12% and 7%, respectively, which are similar to the theoretical calculation results. Thus, the calcination temperature of 600°C was chosen for preparing $Gd_{1-x}Eu_x$ doped tungsten oxide phosphors using a high-temperature solid-state reaction.

To understand the phase developments in the solution chemistry process, the general solid-state reaction was used to prepare a WO_3 -GdO-EuO oxide mixture as a reference. Both $Gd_{1-x}Eu_x$ doped tungsten oxide specimens

contained $x = 0.2, 0.3, 0.4$ and 0.5 . Fig. 2 shows the phase studies for the general oxide solid-state reaction process Fig. 2(a) and the solution chemistry process Fig. 2(b) after heat treatment at 1000°C for 10 hrs. The diffraction peak positions of all general solid-state reaction samples reveal that only the well reported Gd_2WO_6 phase [JCPDS card no. 78-1704] is present in the solid-state reaction product shown in Fig. 2(a). Thus, the phase development with composition is difficult to determine in this material system and the doping concentration does not influence the crystal structure of the resultant phosphors [4]. However, the XRD patterns of the sample prepared by the solution chemistry process, shown in Fig. 2(b), reveal three phosphor phases. The Eu^{3+} ion (0.95 Å) and Gd^{3+} ion (0.94 Å) have similar radii, making their doped phases difficult to distinguish. With increasing Eu^{3+} content (x), the initial Gd_2WO_6 phase developed clearly into the $Gd_2W_2O_9$ and $Gd_2(WO_4)_3$ phases. The diffraction peak of $x = 0.2$ can be mainly indexed to the Gd_2WO_6 phase. The doping concentration of the Eu^{3+} ($x = 0.3, 0.4$) produces $Gd_2W_2O_9$ as the dominant phase, whereas the $Gd_2(WO_4)_3$ phase is dominant in the condition of $x = 0.5$.

Fig. 3(a) shows the morphology developments for the general oxide solid-state reaction. Although the Eu^{3+} contents (x) increased, the grain size remained at approximately 100 nm. Thus, the Eu^{3+} concentration does not affect the crystal structure of Gd_2WO_6 , as shown in Fig. 2(a), and the grain growth in the general process. However, the solution chemistry processed $Gd_{1-x}Eu_x$ doped tungsten oxide powders in Fig. 3(b)

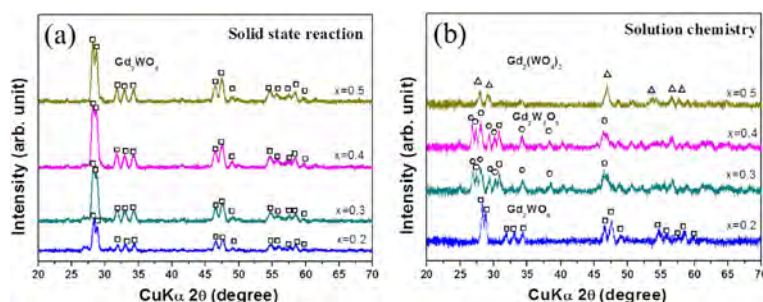


Fig. 2. XRD patterns for different powder preparation processes: (a) general solid-state reaction and (b) solution chemistry.

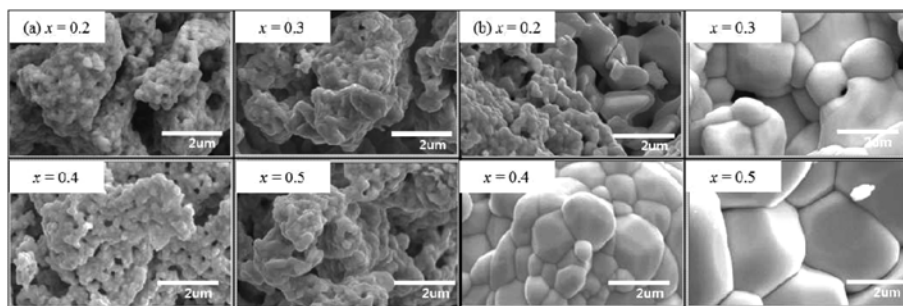


Fig. 3. Morphologies of samples prepared with different powder preparation processes: (a) general solid-state reaction and (b) solution chemistry.

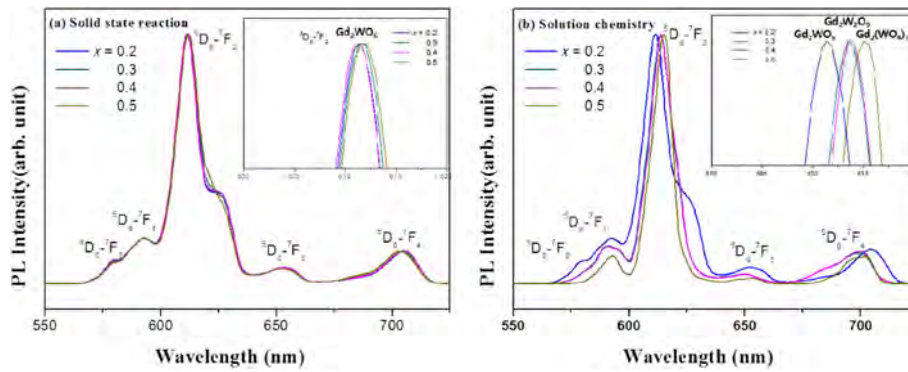


Fig. 4. Emission spectra of $Gd_{1-x}Eu_x$ doped tungsten oxide phosphors prepared by (a) general solid-state reaction and (b) solution chemistry.

exhibit a strong interdependence between the Eu^{3+} content (x) and grain size. The grain size of the particles increased from the initial 100 nm to 5 μm when the Eu^{3+} contents increased from 0.2 to 0.5. Thus, the Eu^{3+} concentration strongly affects the phases, shown in Fig. 2(b), and the grain size in the solution chemistry process.

Fig. 4 presents the emission spectra for both specimen groups, which were annealed at 1000°C. The $Gd_{1-x}Eu_x$ doped tungsten oxide phosphors prepared at various Eu^{3+} concentrations ($x = 0.2, 0.3, 0.4$ and 0.5) were excited at 325 nm. As shown in Fig. 4(a), the Gd_2WO_6 structures from the general solid-state reaction have similar photoluminescence spectra. The dominant dipole transition was $^5D_0 \rightarrow ^7F_2$ at 611 nm. With increasing Eu^{3+} concentration, the luminescent peaks exhibited almost no shift.

The emission spectra can be described by the $^5D_0 \rightarrow ^7F_J$ ($J = 0, 1, 2, 3, 4$) emission line of the strong emission line for $J = 2$ by excitation with 325 nm UV irradiation, which indicates that the host lattice involves a center of asymmetry for Eu^{3+} [5]. According to the Judd-Ofelt theory, the magnetic dipole transition was permitted. However, the electric dipole transition is can use without inversion center, which occupies the site only of the Eu^{3+} ions. The intensity is strongly influenced by the environment surrounding the Eu^{3+} ions [6]. In the emission spectra, the $^5D_0 \rightarrow ^7F_2$ transition is stronger than the $^5D_0 \rightarrow ^7F_1$ transition, signifying that the majority of Eu^{3+} ions lack an inversion center. The electric dipole transition is the dominant $^5D_0 \rightarrow ^7F_2$ of the host lattice. According to the electronic transitions Eu^{3+} ion, when the Eu^{3+} ions are situated such that there is no inversion centers lattice or the deviation. $^5D_0 \rightarrow ^7F_2$ is the main emission peak, corresponding to the dipole transition [7].

Fig. 4(b) shows the emission spectra of the products of the solution chemistry method. The photoluminescence behaviors of solution chemistry strongly depend on the developed phases ($x = 0.2: Gd_2WO_6$, $x = 0.3, 0.4: Gd_2W_2O_9$ and $x = 0.5: Gd_2(WO_4)_3$ in Fig. 2(b)). The solution chemistry process presented herein can be used to control the emission spectra by varying the morphologies and grain size.

Conclusions

A solution chemistry process was applied to the synthesis of $Gd_{1-x}Eu_x$ doped tungsten oxide phosphors. To understand the properties of the phosphors, we studied the phase, morphology, and luminescence of these phosphors relative to the products of general oxide solid-state reaction processes. The oxide mixtures (W-Eu-Gd-O) were synthesized by the calcination of nitrate mixtures at a calcination temperature of 600°C, selected using the results of TG measurements. The present technique produces various phase structures, such as Gd_2WO_6 , $Gd_2W_2O_9$, and $Gd_2(WO_4)_3$, whereas the solid-state reaction process synthesizes only the Gd_2WO_6 phase. Remarkable grain growth from 100 nm to 5 μm was observed with increasing Eu^{3+} content for the solution chemistry process only. When the solution chemistry process is applied to phosphor synthesis, the various emission spectra can be controlled by setting the particle sizes and phases.

Acknowledgments

This research was conducted under the industrial infrastructure program for fundamental technologies (N000600001), which is funded by the Ministry of Knowledge Economy (MKE, Korea).

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