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The effect of flux materials on the physical and optical properties of Eu^{3+}-activated yttrium oxide phosphors

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ABSTRACT

A flux fusion method was used to obtain the various sizes of Eu^{3+}-activated Y_2O_3 red phosphors. The flux material was selected as an independent variable to control the physical properties of phosphor particles and their effects on the morphology and size distribution of phosphors were examined by scanning electron microscopy. The concentration of the flux materials and synthetic temperature were optimized for maximal photoluminescence intensity. Fluoride-based flux materials were found to work for the crystal formation of Eu^{3+}-activated Y_2O_3. In particular, when a BaF_2 flux was used during the reaction at 1450 °C for 3 h, the photoluminescence (PL) intensity of Eu^{3+}-activated Y_2O_3 was 25% higher than that without a flux and spherical phosphors had a mean particle size of 4–5 μm. The morphology and size distribution of the synthesized Eu^{3+}-activated Y_2O_3 phosphor were predominantly dependent upon the type and concentration of flux material and synthetic temperature.

1. Introduction

The development of new types of high resolution and high efficiency planar displays has created a need for high efficiency phosphor materials with novel or enhanced properties including mono-disperse crystalline fine particles [1,2]. The shape and size of phosphor particles are critical factors to be considered when fabricating high quality display screens. For instance, the use of phosphor particles with a uniform size distribution (3–7 μm) yields the best result in case of CRT and X-ray screen surface [3]. Reducing the particle size typically results in a higher resolution due to the higher packing density of the phosphor layers and spherical particles are known to give a high packing density and small minimized light-scattering coefficients [4–6]. Recently, Cho et al. [7] reported that a smaller phosphor particle size can contribute to an improvement in panel efficiency through the synergistic effect of an increase in the photon extraction efficiency via layer reflectivity control and an increase in the plasma efficiency via discharge space control. In their study, an even bimodal size distribution was used to maximize light extraction. That is, optimizing powder morphology and size distribution are important for successful applications. However, these factors are difficult to control because phosphor materials have an intrinsic crystal structure and will grow according to their own natural characteristics during synthesis.

One of the techniques to solve this problem is to use the flux. The addition of flux to the reactants in solid-state reactions is the most popular way to accelerate sintering and/or crystal growth [8,9]. Adding a flux not only increases the reaction rate but also aids in the formation of well crystallized particles of appropriate size. Besides, by using the flux material, one of the big advantages to be taken is known to reduce the processing temperature, which can lead to reduce the production cost. That is, a flux material that has a melting point below the solid-state reaction temperature dissolves one or more of the reaction components and allows the material to enter the reaction zone, without entering the solid state [10]. Kottaisamy et al. [11] confirmed that flux agents can influence the phosphor product particle size distribution and growth conditions. Recently, halide fluxes have been used as additives to increase the luminescence characteristics of particles [12,13].

Here, yttrium oxide phosphor is taken as a sample to understand the role of flux. It is well-known and used in tricolor fluorescent lamps and field emission displays because of its atmospheric stability and safety. The purpose of this work is to use a flux fusion method to control the phosphor size of the europium-activated yttrium oxide phosphors with improved luminescence properties and to understand the effects of various fluoride compound fluxes on the crystal formation of Eu^{3+}-activated yttrium oxide phosphor. Our specific aims in this study were to select an appropriate flux for the synthesis of yttrium oxide phosphor and to understand the effect of the flux on the optical and mechanical properties of the product. We

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concentrated on controlling the particle size, morphology and luminescence intensity by combining a firing technique with the appropriate flux, which is an important factor from the applicability point of view. We believe that this systematic approach can be applicable to find a proper flux material to fit a given host material and contribute to develop a new phosphor for a specific application.

2. Experimental

2.1. Preparation of Eu^{3+}-activated yttrium oxide

Phosphor samples were synthesized by a conventional flux fusion method. The principal raw material was Y_2O_3, which functioned as a host material, while Eu_2O_3 was used as an activator. We used various raw materials within a particle size range of 1–5 μm.

$$_{(1-x)}Y_2O_3 + {}_xEu_2O_3 + \text{flux} \rightarrow Y_{2-x}Eu_{2x}O_3 + \text{flux residue}$$

Barium fluoride, calcium fluoride, alumina fluoride, ammonium fluoride, ammonia chloride and boric acid were used as fluxes in the temperature range of 1300–1450 °C for 1–5 h in air. Each of these flux components can act as a solvent in the solid-phase reaction by creating a very small amount of melt that enhances the reaction. The amount and type of flux materials in the reactants were used as independent variables in this work. The final samples were washed in warm water to remove the flux residue from the reactants. The reaction time and temperature were optimized for maximum PL intensity.

2.2. Characterization of physical and optical properties

To identify the phase and crystal structure of the prepared phosphors, the particles were characterized by X-ray diffractometry (XRD, Scintag Co., USA, 35 kV and 30 mA) with a CuKα wavelength of λ=1.5406 nm. We also used scanning electron microscopy (SEM, Hitachi S-3400 N) to investigate particle size and morphology. Optical measurements were obtained using a photoluminescence (PL) instrument with a Xe lamp at room temperature. The samples were excited with 254 nm radiation, and a scanning emission wavelength of 550–700 nm was used at a rate of 100 nm/min. The photoluminescence properties of the particles prepared with and without flux were also compared. All of the data were referenced against a commercial product (Nichia, Co., Ltd.).

3. Results and discussion

3.1. The selection of flux material for Eu^{3+}-activated yttrium oxide powder

3.1.1. Morphology of Y_2O_3:Eu^{3+} synthesized with various kinds of flux materials

Eu^{3+}-activated Y_2O_3 phosphors are generally elaborated from oxides or carbonates by a conventional solid state process. Typically, efficient control of chemical homogeneity or morphology of the phosphor particles cannot be achieved without the use of a flux. The selection of an appropriate flux material is one of the most important factors to consider for the control of particle morphology and optical characteristics, such as PL intensity. In this experiment, we used a variety of fluoride materials and other well-known flux materials such as boric acid and ammonium chloride to understand the effects of the flux on the properties of the phosphor particles produced. Fig. 1 shows the SEM images of phosphor samples prepared at 1350 °C for 3 h and constant europium concentration with different types of fluxes. The mole fraction of the flux material in the reactants was fixed at 5 mol% in each case. Also, the mole fraction of Eu^{3+} ions in $Y_{2-x}Eu_{2x}O_3$ was fixed at x=0.1. A phosphor sample was also synthesized with the same conditions without flux for comparison. The SEM image of a commercial product (Nichia Co., Ltd.) was used as a reference (Fig. 1). The particle size and morphology of the final products were found to be largely dependent on the type of flux used. A flux is known to act as a solvent in the solid-phase reaction; while it does not react with the target oxide, it induces reactant movement by creating a very small amount of melt and thereby enhances the reaction. The compounds are preferably introduced into or coated on the individual particles of the starting material powder [9]. All of the reactions with flux promoted better particle growth than the reaction without flux, due to the effect of the flux as a reaction enhancer. But, flux selection is not generally known and relies on the experience of the investigator. In Fig. 1, the effect of each flux type on particle formation was demonstrated. SEM images show a small particle size (less than 0.5 μm) from the preparation without flux. On the other hand, samples prepared with fluoride materials and common fluxes such as NH_4Cl or H_3BO_3 show a larger particle size (0.5–6 μm). This implies that all of the flux materials tested enhanced particle growth. In the particle growth model, the rate of particle growth ($d\varphi/dt$) in the

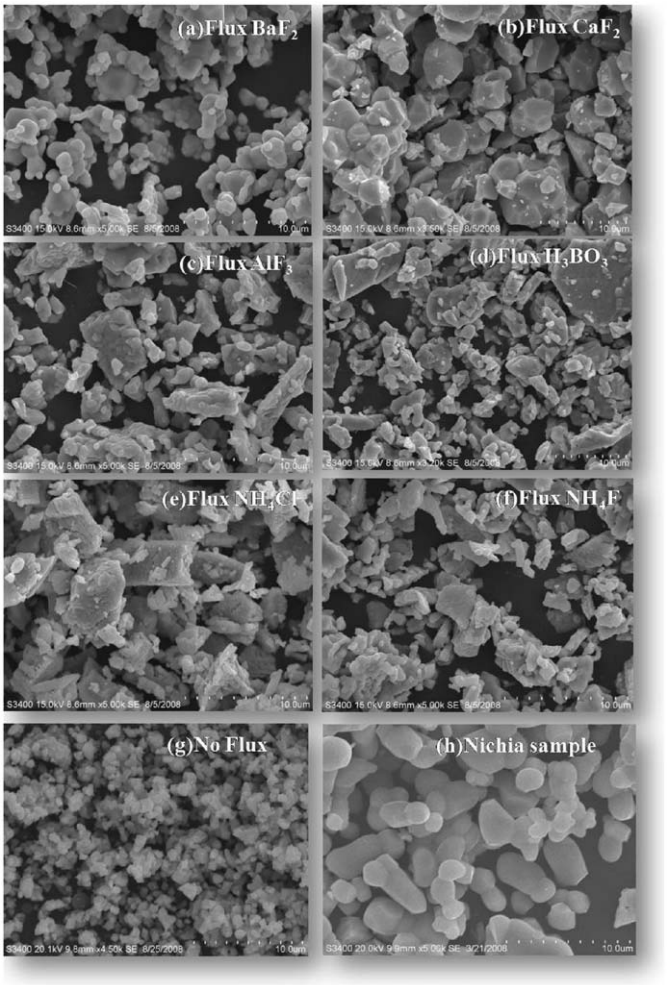

Fig. 1. SEM images of phosphor samples prepared at 1350 °C for 3 h by a solid state reaction with the following flux materials: (a) BaF_2, (b) CaF_2, (c) AlF_3, (d) H_3BO_3, (e) NH_4Cl, (f) NH_4F and (g) no flux. As a reference, the SEM image of commercial product (Nichia, Co., Ltd.) is shown.