The Effect of Pretreatment of Raw Powders on the Photoluminescence of Ca- α -SiAlON:Eu²⁺ Phosphor

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ABSTRACT

The effect of calcination treatment of raw powders prior to high temperature synthesis of Ca- α -SiAlON:Eu²⁺ phosphor was investigated. Based on data acquired from thermogravimetric analysis, calcination temperatures were set at 600, 750, and 900°C. Compared to the photoluminescence (PL) intensity of direct synthesis without calcination, a similar intensity was found for the 600°C treatment, a 19% increased PL intensity was found for the 750°C treatment, and a 23% decreased PL intensity was found for the 900°C treatment. Observation of the particle morphology of the synthesized phosphors revealed that the material transport promoted through the agglomerates formed by the 750°C treatment led to enhanced PL intensity. On the other hand, the oxidation of the starting AlN particles during the 900°C treatment resulted in decreased photoluminescence.

Key words : Nitrides, Oxynitrides, Sialon, Phosphor, Calcination

1. Introduction

The SiAlON ceramics are modifications of silicon nitride (Si₃N₄) ceramics; they are made from the main ingredient Si₃N₄ and such additives as AlN, rare earth oxides, and alkaline earth oxides.^{1,2)} On top of their excellent thermal quenching property, Eu²⁺-doped SiAlON phosphors are attractive due to their wide emission range, which covers band from green to red.³⁻¹¹⁾ The fabrication and analysis of both the green-emitting β -SiAlON:Eu²⁺ phosphor^{3,4)} and the yellow-emitting Ca- α -SiAlON:Eu²⁺ phosphor⁵⁻¹¹⁾ were well documented.

It is conventional to employ wet milling to take advantage of homogeneous mixing for the majority of the ceramic fabrication process. However, dry milling is preferred for the fabrication of SiAlON phosphors because this process reduces oxygen gathering from the milling and drying processes. In the case of dry milling, a metal blade is usually coated with Teflon to prevent metallic contamination, which is harmful to the luminescence efficiency. However, there has so far been no research on the effect of the incorporation of polymer coating materials in the starting materials. In the research laboratory as well as in the industry, chemically stable CaCO₃ is frequently adopted as a source of Calcium for α -SiAlON phosphors.⁵⁻⁹⁾ Therefore, the formation of agglomerates by CaO-containing eutectics and the decomposition of CaCO₃ to CaO is expected to occur in the course of heating.

Calcination at an intermediate temperature is frequently used as a pretreatment prior to high temperature ceramic processes such as sintering and synthesis. Enhancement of material properties via the employment of calcination is attributed to the elimination of volatile components and the crystallization of raw materials. In this study, the effect of calcination treatment conducted at various temperatures on the photoluminescence (PL) characteristics of synthesized Ca- α -SiAlON:Eu²⁺ phosphors was investigated. The focus was put on the effects of Teflon contamination and of the decomposition of CaCO₃ on the optical properties.

2. Experimental Procedure

The starting materials used for the synthesis of Ca- α -SiAlON:Eu²⁺ phosphor were Si₃N₄ (SN-E10, Ube Industries, Ltd.), AlN (99.99%, H. C. Starck), CaCO₃ (99.9%, Kanto Industries, Ltd.), and Eu₂O₃ (99.99%, Aldrich). The composition employed in this research was (m, n, x, y) = (2, 1, 0.895, 0.07) located on the m = 2n line in the so-called SiAlON phase plane,¹²⁾ where the nominal composition is expressed as Ca_xSi_{12-m-n}Al_{m+n}O_nN_{16-n}:Eu_y. Weighed starting powders were mixed using a Teflon-coated blade in dry state. Thermogravimetric analysis under flowing air atmosphere was conducted to determine the calcination temperature for the mixed powder. Based on the data acquired from thermogravimetric analysis, calcination was conducted at 600, 750, and 900°C for 30 minutes using a box-type furnace. Each 10 g of the as-mixed powder and the calcined powder was loosely poured into BN crucibles and fired at 1800°C for 4 h under nitrogen pressure of 0.5 MPa. Heating up to 900°C was conducted under vacuum in order to ventilate the decomposed CO₂ gas. Then, nitrogen gas was introduced

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Fig. 1. Thermogravimetric analysis results of (a) Teflon and (b) powder mixture of phosphor composition.

into the chamber at 900°C and gas pressure was maintained at 0.5 MPa throughout the synthesis process. The phases of the synthesized samples were identified using an X-ray diffractometer (D/Max 2200, Rigaku) with Cu K α radiation operating at 36 kV and 26 mA. The PL spectra were measured using a fluorescent spectrophotometer (Darsa Pro-5200, PSI Ltd.) equipped with a 200 W Xe-lamp as an excitation source. The particle morphology was examined by scanning electron microscopy (JSM-6700F, Jeol).

3. Results and Discussion

The thermogravimetric analysis conducted on the Teflon and powder mixture is plotted in Fig. 1. The exothermal decomposition of Teflon, the coating material on the mixing blade, starts at around 500°C and continues until the residual mass reaches zero before the temperature reaches 600°C (Fig. 1(a)). The weight loss of the powder mixture, corresponding to the endothermic decomposition of CaCO₃, initiates at around 600°C. Then, maximum weight loss was seen at around 700°C and gradual weight gain was detected over the subsequent heating period. Assuming a contamination-free state of the volatile components and complete thermal decomposition of CaCO₃, the theoretical weight loss for the powder mixture with (m, n, x, y) = (2, 1, 0.895, 0.07) composition is 6.1%. The following are considered as presumable reasons for the excessive weight loss of 7.4% during the TG experiment that is shown in Fig. 1(b): 1) evaporation of physically absorbed vapor, 2) thermal decomposition of contaminated organics, and 3) vaporization of starting materials. The oxidation of the starting nitride materials by the following equations is postulated as the cause of weight gain from 700°C, which will be discussed later. The nitridation of the starting oxides is discarded as a reason because the nitridation reactions entail weight loss.

Temperatures for the calcination treatment were set at

600, 750, and 900°C based on the results shown in Fig. 1. That is, calcination at 600°C was expected to eliminate Teflon contamination, while complete decomposition of CaCO₃ was expected to be the result of 750°C calcination. Calcination at 900°C may lead to oxidation of the starting nitride materials in the powder mixture. The measured weight loss values due to calcination when using a box furnace were 0.2, 3.4, and 3.9% for 600, 750, and 900°C temperature treatments, respectively. The negligibly small amount of weight loss at 600°C (0.2%) implies both the trivial contamination of volatile components and the stability of CaCO₃ up to this temperature. It should be noted that the measured weight loss values for the 750°C treatment (3.4%) and 900°C treatment (3.9%) using box furnace were quite a lot smaller than those from the TG experiment.

In order to figure out the discrepancy between the TG experiment and the calcination experiment, the phases of the XRD patterns of the samples calcined using the box furnace were analyzed, with results shown in Fig. 2. The pattern for the 600°C treatment (600 Cal) is similar to that of the as-mixed powder mixture (NoCal), which supports the idea of the sturdiness of CaCO₃ at 600°C. Contrary to expectations for the TG experiment done at 750°C, however, peaks for the reactant CaCO₃ were still detected during the 750°C calcination (750 Cal). That is, incomplete decomposition of CaCO₃ explains the lower than expected weight loss value. It is postulated that calcination of 10 g of powder mixture using a box furnace requires more than 30 minutes to complete the decomposition of CaCO₃. Further, an only 3.9% weight loss was measured for the 900°C calcination (900 Cal), with complete decomposition of CaCO₃ (no X-ray peaks of CaCO₃). This odd phenomenon is related to the weight gain behavior pointed out in the TG data shown in Fig. 1(b).

SEM micrographs of the as-mixed powder (NoCal) and the calcined powders (600 Cal, 750 Cal, 900 Cal) are provided in Fig. 3. Similar morphology was observed regardless of the powder treatment condition, except for a few agglomerates that were found for the calcined powders; these agglomerates were absent from the as-mixed powder.

Fig. 2. XRD patterns of the powder mixture for the various calcination treatments prior to phosphor synthesis. (a) as-mixed (NoCal), (b) 600°C calcination (600 Cal), (c) 750°C calcination (750 Cal), and (d) 900°C calcination (900 Cal).

The PL emission spectra of synthesized Eu²⁺-doped Ca- α -SiAlON phosphors excited by 450 nm source are plotted in Fig. 4. All of the phosphors were synthesized by firing at 1800°C for 4 h; the legend of the figure indicates the calcination condition prior to high temperature synthesis. The PL intensity value in the legend in Fig. 4(a) was normalized by the intensity of the phosphor made from 'NoCal'. Compared to PL intensity of 'NoCal' phosphor, similar intensity was acquired for '600 Cal' phosphor and about 20% increased intensity was measured for '750 Cal' phosphor. However, '900 Cal' phosphor yielded decreased intensity by approximately 23%. The contamination effect of impurity organics including blade coating Teflon is safely excluded by the similar PL intensity between the NoCal phosphor and the 600 Cal phosphor. Along with the blue-shift of the PL spectra with increased calcination temperatures, as shown in Fig. 4(b), the positive effect due to the 750°C calcination and the negative effect due to the 900°C calcination are related to the synthesized phosphor morphology and the compositional change. The morphology of the SiAlON phosphors synthesized at 1800°C is compared in Fig. 5. Analogous to the similar PL intensity, a similar particle morphology was observed between the NoCal and the 600 Cal specimens. It should be noted that the size of the agglomerates increased with the calcination temperatures from 750°C (Fig. 5(c)) to 900°C (Fig. 5(d)). The formation of agglomerates in the calcination stage accelerated material transport during high temperature synthesis, which eventually led to an increased PL property due to enhanced crystallinity for the 750 Cal phosphor. However, the most extended formation of agglomerates, due to 900°C calcination, resulted in the dramatically decreased PL intensity.

The drawback of calcination treatment at high temperature (900 Cal) is that it resulted in decreased PL intensity,

Fig. 3. SEM micrographs of the powder mixture for the various calcination treatments prior to phosphor synthesis: (a) as-mixed, (b) 600°C calcination, (c) 750°C calcination, and (d) 900°C calcination.

Fig. 4. PL characteristics of the synthesized phosphors after firing at 1800°C: (a) as-acquired PL spectra and (b) normalized PL spectra. Legend of the figure indicates the calcination conditions.

as shown in Fig. 4(a). The mechanism was investigated. The XRD pattern of the broad band ($10^\circ \leq 2\theta \leq 50^\circ$) and that in the vicinity of the major peak ($26^\circ \leq 2\theta \leq 35^\circ$) for the synthesized phosphors are plotted in Fig. 6(a) and Fig. 6(b), respec-

Fig. 5. SEM micrographs of the synthesized phosphors after firing at 1800°C. The calcination temperatures prior to phosphor synthesis were (a) as-mixed, (b) 600°C, (c) 750°C, and (d) 900°C.

Fig. 6. XRD patterns of the synthesized phosphors after firing at 1800°C: (a) broad band pattern and (b) selected band pattern. (thick arrow: (201) peak of α -SiAlON, thin arrow: (201) peak of α -Si₃N₄).

tively. Silicon was partially coated onto the surface of the XRD samples as a standard material for the correction of the peak position.⁹⁾ A single phase α -SiAlON, free from sec-

Fig. 7. Thermogravimetric analysis of the starting nitride materials under flowing air atmosphere.

Fig. 8. XRD pattern of AlN after oxidation at 900°C for 1 h in air ($\diamond$ AlN, $\blacktriangledown$ Al₂O₃).

ond phases, was confirmed regardless of the calcination temperature (Fig. 6(a)). It can be seen in Fig. 6(b) that the degree of peak shift of the SiAlON phosphors (thick arrow) from that of the starting material Si₃N₄ (thin arrow) decreased with increasing calcination temperature. The deduced 'm' values by empirical equations suggested by Rutten *et al.* from the detected peak position are 1.73, 1.62, and 1.11 for the phosphors made of 600 Cal, 750 Cal, and 900 Cal, respectively.¹³⁾ The deviation from the designed stoichiometric value ($m = 2.0$) became larger with increased calcination temperature. This tendency is directly related to the blue-shift of the PL spectra, which can be seen in Fig. 4(b)). Xie *et al.* reported in their experimental data that the blue-shift of the yellow emission occurred due to a decreasing 'm' value for Eu²⁺-doped Ca- α -SiAlON phosphors.¹¹⁾

TG analysis for the nitride materials in the starting powder mixture, Si₃N₄ and AlN, was conducted to investigate the effect of oxidation for 900°C calcination (Fig. 7). It was

found that Si₃N₄ and AlN behave in different ways. Compared to the result of no weight change for Si₃N₄ during the isothermal soaking, there was a significant degree of weight gain for AlN. The phases of the oxidized AlN powder were analyzed, with results shown in Fig. 8. In this research, the peaks for Al₂O₃ are indexed as a minor phase beside the major peaks of AlN, which supports the previous reasoning that the weight gain during the 900°C calcination was caused by the oxidation of nitride materials, specifically AlN, in the starting powder mixture. Together with the SiO₂ layer on the surface of Si₃N₄ and CaO from CaCO₃, the supply of Al₂O₃ due to oxidation induces eutectic melting at 1170°C. Therefore, the increased amount of eutectic liquid phase due to the oxidation of AlN is a cause of severe agglomeration for the 900 Cal sample due to accelerated liquid phase sintering. Further, deviation of the stoichiometry from the designed composition ($m = 2.0$) became larger as the converted amount of Al₂O₃ increased. The substantially lowered PL intensity for the 900 Cal phosphor was partially affected by the decreased 'm' value because the PL intensity is known to be inversely proportional to the 'm' value, in the range of $m \leq 3$, for Eu²⁺-doped Ca- α -SiAlON phosphors.¹¹⁾ Besides this negative 'm' value effect, surface defects in the form of ingot-like agglomerates imposed during the grinding of the synthesized phosphor by the promoted liquid phase sintering deteriorated the PL intensity.

4. Conclusions

The PL property of Eu²⁺-doped Ca- α -SiAlON phosphor was enhanced by employing calcination treatment prior to high temperature synthesis. It was revealed that the calcination temperature substantially affected the crystallinity of the SiAlON phosphors, as summarized below;

(1) Calcination at 600°C: The weight loss was trivial, which result agrees with the idea of the stability of CaCO₃ up to 600°C; this was confirmed by both TG and XRD analysis. A PL intensity similar to that of the non-calcined sample implies that the contamination by the Teflon coating during the milling process does not affect the PL property.

(2) Calcination at 750°C: The partial decomposition of CaCO₃ was confirmed by the degree of weight loss and by the results of XRD analysis. Compared to the non-calcined phosphor, the calcined sample's PL intensity increased by 19%. Improved crystallinity was attributed to both lowered oxygen content in the powder mixture due to the thermal decomposition of CaCO₃ and promoted material transport due to the formation of agglomerates.

(3) Calcination at 900°C: The raw material CaCO₃ decomposed completely and surface oxidation of the starting material AlN resulted in the formation of Al₂O₃ on the surface of

AlN. The PL intensity value, which decreased by 23%, is attributed to both the decreased 'm' value and the surface defects generated during the grinding of the synthesized phosphor.

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