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The enhancement of thermal properties of phosphor ceramic plate as sintering aids

Min Ji Lee, Yoon Ah Roh, Usama Bin Humayoun, Young-Hyun Song and Dae-Ho Yoon*
School of Advanced Materials Science & Engineering, Sungkyunkwan University, Suwon 440-746, Korea

Cerium doped $Lu_3Al_5O_{12}$ phosphor ceramic plate was fabricated by solid state reaction and electric furnace reactive sintering method using commercial Lu_2O_3, α-Al_2O_3, and CeO_2 powders as the starting materials, AlN or Al_2O_3 were used as sintering additives. When Al_2O_3 was used as sintering aid, the optimum dosage was 2 wt%. Although plate optical characteristics was slightly reduced and the difference was very small, whereas the thermal properties exhibited appreciable increase of more than 5%. The excellent feature of using compound additives is to make the intensified liquid sintering begin at a lower temperatures in electric furnace, promoting the densification rate and resulting in uncontaminated crystalline grains.

Key words: $Lu_3Al_5O_{12}$:Ce^{3+} Phosphor Ceramics Plate, AlN, Al_2O_3 as sintering aid.

Introduction

While light typically is generated by blue-emitting InGaN LED combined with $Y_3Al_5O_{12}$: Ce^{3+} yellow phosphor packed with organic resin, the human eye perceives white light by combination of blue and yellow emission [1]. Since, organic resins have poor heat-resistance and are easily subjected to deterioration at high temperatures, resulting in the degradation of luminous efficacy and the alteration of emission color [2, 3]. The temperature of LED chip is increases with the increase of its output power. Hence, the traditional encapsulation of white LED becomes less suitable in this field. Recently, it has been demonstrated that a large separation between the phosphor and the primary LED emitter, which Luo *et al*., referred to as remote phosphor arrangement, enhances the phosphorescence extraction by reducing the optical power absorbed by the LED chip [4, 5]. Based on these previous studies, we try to fabricate a new type LED using phosphor ceramic plate instead of organic resins has been reported. Many studies involving remote phosphor have been carried out, in which primary target is to increase output power of LEDs [6-8]. This makes it possible to increase luminous flux per of the LED, but the chip temperature of the blue LED for the excitation.

In previous research, Liu *et al*., reported that there is a reduction in emission intensity at higher temperature for all phosphors but a larger reduction in $Y_3Al_5O_{12}$-based versus $Lu_3Al_5O_{12}$-based phosphor, therefore we used $Lu_3Al_5O_{12}$: Ce^{3+} phosphor for out experiment. Until now, many reports have been made focused on the luminescence of Ce^{3+}-activated $Lu_3Al_5O_{12}$ phosphor [9]. Many previous studies have explained the beneficial role and function mechanism of AlN, Al_2O_3 as sintered aids. The beneficial role of silica in sintering kinetics has been reported for many time, i.e. an increase of the grain-boundary diffusion coefficient and the decrease of grain-boundary surface energy in the presence of secondary phases [10].

In this paper, $Lu_3Al_5O_{12}$: Ce^{3+} phosphor ceramics plates were fabricated by solid state reaction and electric furnace sintering method, different quantity AlN, Al_2O_3. The optimum dosages of the series of additive were provided and the through what action mechanism the additives efficient, especially the compound additives, was analyzed.

Experimental

The commercial high-purity Lu_2O_3 (99.99%, Sigma-Aldrich), α-Al_2O_3 (99.99%, High Purity Chemicals), and CeO_2 (99.99%, Sigma-Aldrich) powders were mixed according to the stoichiometric $Lu_{2.95}Ce_{0.05}Al_5O_{12}$ (LuAG: Ce) with various additives and ball milled in alcohol for 24 h. The mixture of powders was dried at 90 °C for 24 hrs. after that, the powders were pressed with 250 MPa pressure into disks and cold isostatic pressing consolidated at 140 MPa for 10 min. pre-sintering of the green body was conducted at 800 °C under oxygen atmosphere to remove organic substances. Subsequently, the $Lu_3Al_5O_{12}$:Ce^{3+} polycrystalline ceramics were obtained through sintering under reduction atmosphere (H_2 9 %/N_2 95 %) at 1700 °C for 24 hrs. Finally, the specimens were annealed at 1500 °C for 6 hrs in air. Eventually, ceramic phosphor formed in the cylinder type using a laser or wire saw and cut the plate type. Abrasive cutting a ceramic phosphor plate type with a soft cloth and an abrasive such as sand paper, CeO_2 to go through a process of controlled thickness. The polished ceramic phosphor plate was then packaged

*Corresponding author:
Tel : +82-31-291-7388
Fax: +82-31-290-7410
E-mail: dhyoon@skku.edu

over LED chip.

The photoluminescence (PL) excitation and emission spectra were examined using a fluorescence spectrometer (SINCO, FluroMate FS-2, Korea) with a 150 W xenon lamp as the excitation source at room temperature.

Results and Discussion

Table 1 shows the value of the optical characteristics and thermal characteristics of the phosphor ceramic plate according to different quantities of AlN as a sintering aid (2, 4, 6, 8, and 10 wt%). The photoluminescence (PL) spectra of $Lu_3Al_5O_{12}$: Ce^{3+} added AlN as sintering aid are presented in Fig. 1(a-b). As demonstrated in Fig. 1(a) the optical properties of the samples in this group, representing a decrease with the increasing AlN quantity. Fig. 1(b) shows thermal properties of the samples in this group decrease with increasing AlN quantity.

The AlN added phosphor ceramic plate was lowered pure ceramic phosphor plate optical characteristics compared to 3, 4, 8, 11, and 19%, respectively. At 6 wt% of additive the decrease in emission intensity was about 10%, concluding to the ineffectiveness of AlN additive in improving thermal stability of the phosphor plate. This can be explained by oxygen atoms replacing nitrogen atoms resulting in a decrease of thermal conductivity [11]. In AlN, powders oxygen is a typical contaminant, located at the surface of the AlN grains as aluminum oxide or oxynitride. During the sintering, oxygen reacts with the additive to form aluminates [12]. Dissolved oxygen ions in AlN occupy the nitrogen site, and they generate Al vacancies to compensate the electric charge balance. Commercially available AlN powders have around 1 wt% of oxygen

Table 1. Optical properties and thermal properties of the fluorescent ceramic plate according to the AlN content (2, 4, 6, 8, 10 wt%).

	Optical property (%)	Thermal property (%)
Pure	100	100
AlN 2 wt%	97.2	98.7
AlN 4 wt%	95.9	95.3
AlN 6 wt%	91.7	91.5
AlN 8 wt%	88.5	88.5
AlN 10 wt%	81.3	84.6

Table 2. Optical properties and thermal properties of the fluorescent ceramic plate according to the Al_2O_3 content (1, 3, 5, 10 wt%).

	Optical property (%)	Thermal property (%)
Pure	100	100
Al_2O_3 1 wt%	98.9	100.2
Al_2O_3 3 wt%	93.5	100.3
Al_2O_3 5 wt%	88	101.1
Al_2O_3 10 wt%	79	101.6

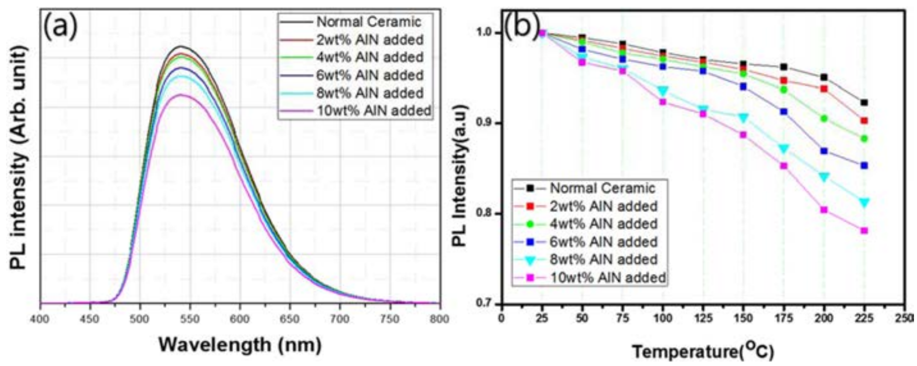

Fig. 1. Optical properties and thermal properties of the fluorescent ceramic plate according to the AlN content (2, 4, 6, 8, 10 wt%).

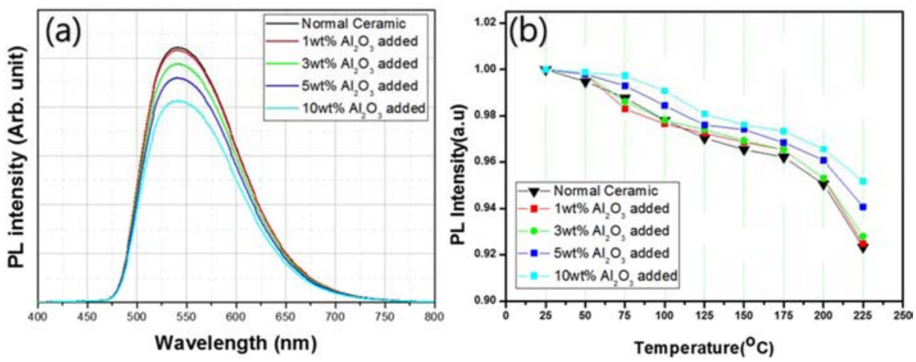

Fig. 2. Optical properties and thermal properties of the fluorescent ceramic plate according to the Al_2O_3 content (1, 3, 5, 10 wt%).

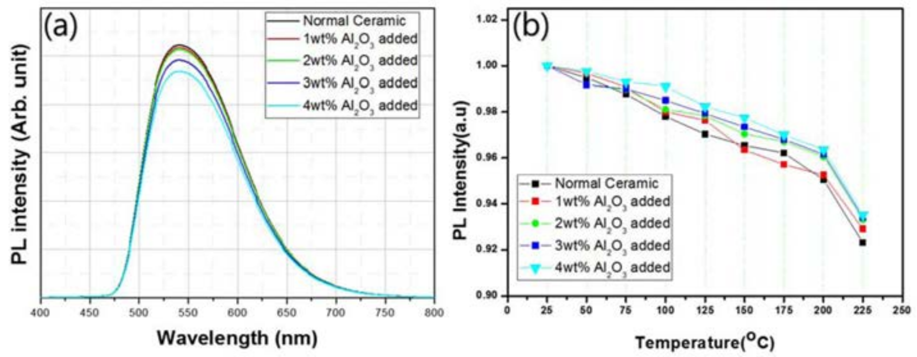

Fig. 3. Optical properties and thermal properties of the fluorescent ceramic plate according to the Al_2O_3 content (1, 2, 3, 4 wt%).

Table 3. Optical properties and thermal properties of the fluorescent ceramic plate according to the Al_2O_3 content (1, 2, 3, 4 wt%).

	Optical property (%)	Thermal property (%)
Pure	100	100
Al_2O_3 1 wt%	98.9	100.2
Al_2O_3 2 wt%	98.1	101.0
Al_2O_3 3 wt%	94.0	101.1
Al_2O_3 4 wt%	89.5	101.3

as a surface layer of oxide or oxy-nitride of aluminum. Without any oxygen getter, the oxygen in the surface layer dissolves in to AlN sintering [13].

Table 2 shows the value of the optical characteristics and thermal characteristics of the phosphor ceramic plate according to different quantities of Al_2O_3 as a sintering aid (1, 3, 5 and 10 wt%).

The photoluminescence (PL) spectra of $Lu_3Al_5O_{12}$: Ce^{3+} with Al_2O_3 as sintering aid are presented in Figs. 2(a-b). Fig. 2(a) shows the optical properties of the samples in this group decrease with the increasing Al_2O_3 quantity. Fig. 2(b) shows a decrease in photoluminescence properties of the plate with increase temperature.

The optical properties were greatly reduced compared to conventional ceramics, the sample containing 5 wt% or more exhibited a decrease of more than 20% in comparison to the sample fabricated without sintering aid. On the other hand, plate fabricated with the sintering and of Al_2O_3 showed an increased thermal stability, though the increase was very small as mentioned in Table 2 and shown in Fig. 2(b). Keeping in view slight increase in thermal stability and high degree of decrease i.e. more than 20% in optical properties in samples with higher additive amounts, we proceeded our experiments with lower amounts of Al_2O_3. In further experiments, the content of Al_2O_3 additive studied was 1, 2, 3 and 4 wt%.

Table 3 shows the value of the optical characteristics and thermal characteristics of the phosphor ceramic plate according to lowered quantities of Al_2O_3 as a sintering aid (1, 2, 3 and 4 wt%).

The photoluminescence (PL) spectra of $Lu_3Al_5O_{12}$: Ce^{3+} with lowered amount Al_2O_3 as sintering aid are presented in Figs. 3(a-b), presenting a decrease in optical and thermal properties of the sample.

It can be seen light that with 2 wt% of Al_2O_3 the decrease in optical properties was very small i.e. less than 5%, but the photoluminescence properties decrease sharply at higher quantity. All of the samples demonstrated a slight increase in thermal stability with increasing amount of Al_2O_3. Considering a sharp decrease in optical properties and a very small increase in thermal properties we determined 2 wt% of Al_2O_3 as the optimum sintering aid.

Summary

LuAG: Ce phosphor ceramic plates were fabricated by reactive sintering method and electric furnace sintering using commercial powders as raw materials with both AlN and Al_2O_3 as sintering aids. The sample with 2 wt% Al_2O_3 demonstrated the best optical and thermal properties. When we added AlN as sintering aid, all results of the optical and thermal properties was lowered. On the other hand, experimental results of Al_2O_3, displayed a minimal decreased in optical properties and improved thermal properties.

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