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5 **Fabrication of transparent Ce³⁺-doped (Gd,Lu)₃Al₅O₁₂ ceramics by two-step spark**
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7 **plasma sintering**
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5 **Abstract**
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8 Transparent $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ with microstructure control were fabricated by two-step
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10 spark plasma sintering. In the two-step profile, the heating rate was changed from 50 to 5°C/min
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12 at the first-step temperatures. During the initial stage of shrinkage, the holding time of the first-
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14 step sintering could induce densification by suppressing the microstructure coarsening. As
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16 compared to the single-step profile, the two-step profile showed smaller grain size, which
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18 decreased with a decrease in the first-step temperature. The porosity of the two-step profile was
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20 lower than that of the single-step profile, and the lowest porosity was obtained at the first-step
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22 temperature of 1000°C, which was the starting point of shrinkage. The TS-1000 specimen
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24 showed the highest transmittance among all the specimens because of the microstructure control
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26 offered by the two-step profile. Thus, by employing the two-step profile, the transmittance could
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28 be increased from 50.1% (SS-1250) to 56.5% (TS-1000).
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37 **Keywords:** Two-step spark plasma sintering; Optical property; Photoluminescence
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39 characteristics; Microstructure; Gadolinium and lutetium aluminum garnet
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1. Introduction

Lanthanide aluminum garnets ($\text{Ln}_3\text{Al}_5\text{O}_{12}$, LnAG), represented by $\text{Gd}_3\text{Al}_5\text{O}_{12}$ (GdAG) and $\text{Lu}_3\text{Al}_5\text{O}_{12}$ (LuAG), have high theoretical densities, and are attractive candidates for scintillator applications. LnAGs exhibit unique properties, such as wide bandgaps, high chemical and thermal stability, and wide transparent range, which make them suitable for scintillator applications [1–4]. Scintillators should possess high theoretical density to stop X-rays. YAG shows relatively X-ray low stopping power owing to its low density (4.53 g/cm^3). Among the lanthanide elements with atomic weights higher than Y (89), Gd (157), and Lu (174) are considered as suitable candidates for increasing the density of the garnet structure. However, Gd (0.21 ppm) and Lu (0.02 ppm) are less abundant in the earth's crust as compared to Y (1.39 ppm) [5]. As Gd is more abundant than Lu, it is considered as a more suitable substitute for Y. Recently, transparent Gd-based LnAGs have been extensively investigated for scintillator applications. However, GdAGs thermally decompose into GdAlO_3 perovskite and Al_2O_3 above 1300°C ($\text{Gd}_3\text{Al}_5\text{O}_{12} \rightarrow 3\text{GdAlO}_3 + \text{Al}_2\text{O}_3$) [6]. In addition, GdAGs are doped with Ce^{3+} as an activator of yellow-emitting phosphors. The larger Ce^{3+} ions cause the destabilization of the garnet structure, thereby reducing its thermal decomposition temperature. In order to suppress their thermal decomposition, Ce-doped GdAGs are doped with Lu^{3+} ions, which are much smaller than Gd^{3+} ions [7]. These Lu^{3+} ions reduce the average Ln^{3+} size, and hence stabilize the garnet structure. In addition, Lu^{3+} doping retains the photoluminescence (PL) characteristics of Ce^{3+} and increases the theoretical density of $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$, thus enabling the development of advanced yellow-emitting phosphors [7].

Decreasing the sintering temperature can prevent the thermal decomposition of GdAG above 1300°C and improve its mechanical properties while providing a dense microstructure.

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5 Among the various sintering techniques, spark plasma sintering (SPS) controlled by an electric
6 field and mechanical pressure is considered as an efficient sintering approach for GdAG [8,9].
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8 In the SPS process, the electric field rapidly heats the mold and powder compact, facilitating
9 the rapid densification by several microscopic mechanisms, including increased atom
10 diffusivity and softening of the particle surfaces, so that excessive grain growth is suppressed
11 at low temperatures [8,10]. Therefore, high densities and fine microstructures, which are the
12 advantages of SPS, improve the mechanical and optical properties of ceramics. Recently, the
13 fabrication and characterization of LuAG ceramics, such as Nd:YAG [11], LuAG [12], and
14 $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ [13], using the SPS process have been reported [11–13]. Sufficient
15 transparency can be obtained by conventional sintering, hot pressing (HP), and hot isostatic
16 pressing (HIP) [14–16]. However, the fabrication of transparent LnAG using the SPS process
17 has not been sufficiently studied. In our previous work [13], a $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ powder was
18 fully densified using the SPS process, but a transparent compact was not obtained. Therefore,
19 further research is required to improve the transparency of SPS-prepared ceramics while
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42 Various studies have reported the application of a two-step sintering profile to the
43 conventional sintering, HP, and HIP techniques to improve the optical properties and control
44 the microstructure of ceramics [16–19]. Previous studies on the two-step sintering profile
45 suggested that preliminary experiments on microstructure control should be conducted to
46 improve the optical properties of ceramics [18,19]. Although the two-step sintering profile is
47 applied in different ways, the main objective is to achieve primary densification without
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49 residual pores during the second step sintering. As a result, full densification can be effectively
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5 achieved by dividing the sintering process into two steps with different objectives. In addition,
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7 some researchers have reported that a two-step profile can be applied to improve the optical
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9 properties of ceramics while retaining the intrinsic merits of the SPS process [20–24]. In the
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11 SPS process, the two-step profile is applied in a slightly different way, because the amount of
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13 carbon contamination and residual pores inevitably increases with an increase in the sintering
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15 time. Considerable research [22,23] has been carried out on the microstructure and optical
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17 properties of each step of the two-step profile. After primary densification without excessive
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19 microstructure coarsening when the first step temperature is lower than the second step
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21 temperature, sufficient densification and excellent transparency could be achieved by removing
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23 the residual defects at the second-step temperature. In our previous work [24], in transparent
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25 Y_2O_3 fabricated with a lower first-step temperature, microstructural control and improved
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27 optical properties could be achieved. On the basis of the previously reported results on the two-
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29 step profile, it can be stated that by suppressing excessive microstructure coarsening and
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31 separating the primary densification and full densification processes, the microstructure of
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33 LnAG can be made fine and dense and its transmittance can be improved.
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42 In this study, a two-step SPS profile was employed to improve the optical properties of
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44 transparent $\text{Ce}^{3+}:(\text{Gd},\text{Lu})_3\text{Al}_5\text{O}_{12}$ ceramics while controlling their microstructure. The two-step
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46 profile involved first-step sintering at 900, 1000, and 1200°C and second-step sintering at
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48 1250°C. The first-step sintering provided primary densification and suppressed excessive
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50 microstructure coarsening. The second-step sintering on the other hand, provided full
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52 densification and the removal of the residual pores along with microstructure control. The
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54 microstructure and optical properties of the ceramics were evaluated by focusing on the
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56 microstructure control by varying the first-step temperature.
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2. Experimental Procedure

2.1. Preparation of $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ powder

The rare-earth and aluminum sources used in this study were Ln_2O_3 ($\text{Ln} = \text{Gd}$ and Lu , 99.99%, Huizhou RUIER Rare-Chem. Hi-Tech, China), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%, Huizhou Ruier Rare-Chem. Hi-Tech, China), and alum ($\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, > 99%, Zhenxin Chemical Reagent Factory, China). A $\text{Ln}(\text{NO}_3)_3$ stock solution was prepared by dissolving the oxide powders in an optimum amount of nitric acid. To precipitate the carbonate precursor, a mixed solution containing the stoichiometric amounts of the nitrates and alum was added dropwise to the ammonium bicarbonate solution. The precipitated carbonate precursor was dried in an oven for 24 h. The $[(\text{Gd}_{0.6}\text{Lu}_{0.4})_{0.99}\text{Ce}_{0.01}]_3\text{Al}_5\text{O}_{12}$ powder was obtained by the thermal decomposition of the precursor *via* calcination at 1100°C for 4 h in air. To suppress the oxidation of Ce^{3+} , a second calcination process was performed at 1000°C for 4 h in Ar/H_2 (5 vol% of H_2) [7,25].

2.2. Consolidation of $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ compacts using SPS process

The $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ powder was consolidated using SPS equipment (LABOX-315, Sinter Land, Japan) under a vacuum atmosphere of 10 Pa. The powder was directly sintered without any pre-treatment, using a graphite mold with a diameter of 10 mm. Heating was performed using a pulse pattern of 5:5 (on:off) in the AC mode, and temperature was measured by installing a pyrometer in the non-through hole of the mold. The entire SPS process was divided into single-step and two-step profiles. For the single-step profile, the powder compact was heated to a sintering temperature of 1250°C at a heating rate of $50^\circ\text{C}/\text{min}$, and held for 20 min. In the case of the two-step profile, to achieve primary densification without excessive microstructure coarsening, the first-step sintering was performed at 900, 1000, and 1200°C with

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5 heating rate of 50°C/min and the sintering temperature was held for 30 min. In the single-step
6 profile, shrinkage started at approximately 1000°C. Thus, the first-step temperature for the two-
7 step profile was considered to be 1000°C. To achieve full densification and the removal of the
8 residual pores, further heating was conducted to reach the second-step temperature of 1250°C
9 at 5°C/min. This temperature was held for 20 min. In the entire SPS process, a mechanical
10 pressure of 6.5 kN (80 MPa) was applied from the beginning and was maintained until before
11 cooling. In addition, cooling was sequentially performed at 1100°C for 10 min, 800°C for 5 min,
12 and 25°C for 5 min. The SPS conditions and specimen names are listed in Table 1.
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27 2.3. Characterization

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29 The annealing process was conducted at 1250°C for 10 h in air to remove the carbon
30 contamination and oxygen vacancies. Both the surfaces of the $\text{Ce}^{3+}:(\text{Gd},\text{Lu})_3\text{Al}_5\text{O}_{12}$ compacts
31 were mirror polished with 9, 3, and 1 μm diamond pastes. The transmittance of the compacts
32 were measured using a double-beam spectrophotometer (SolidSpec-3700DUV, Shimazu, Japan)
33 equipped with an integrating sphere. PL measurements were conducted using a
34 spectrofluorometer (FP-6500, JASCO, Japan) equipped with a 60 mm diameter-integrating
35 sphere (Model ISF-513, JASCO, Japan) and a 150 W Xe lamp as the excitation source. The X-
36 ray photoelectron spectroscopy (XPS, AXIS-165, Shimadzu, Japan) profiles of the samples
37 were recorded at room temperature with $\text{Al-K}\alpha$ radiation for excitation. The binding energy was
38 referenced to the C-1 s line of adventitious carbon. The mirror-polished surfaces were thermally
39 etched at 1100°C for 2 h in air. The polished and fracture surfaces of the specimens were
40 examined using scanning electron microscopy (SEM, SU-8000, Hitachi, Japan). The porosity
41 of the specimens was determined by measuring their porous areas from the SEM images. The
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grain and pore sizes of the specimens were calculated by measuring their average cross-sectional areas per grain and pore sizes. The grain size was apparent in the cross-section; therefore, it was multiplied by 1.225 to determine the actual grain size [26].

3. Results and Discussion

3.1. Shrinkage behavior and microstructure

In our previous work, we successfully developed a stable $(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ garnet structure, which could be well indexed to the cubic structure of GdAG [13]. Single-step and two-step SPS profiles were applied to fabricate transparent $(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ ceramics with structural stabilization. The SPS curves (temperature, displacement, and pressure over time) of the single-step profile (SS-1250) are shown in Fig. 1 (a). As can be observed from the displacement curve, the ceramics showed thermal expansion when heated to approximately 1000°C . In addition, shrinkage began to occur at this temperature. No further shrinkage occurred during the holding period at 1250°C , and the shrinkage was sufficient. Based on the SPS curves of the single-step profile (SS-1250), a two-step profile (TS-1000) was designed, as shown in Fig. 1 (b). At a relatively low first-step temperature of 1000°C , the powder compact was rapidly heated at $50^\circ\text{C}/\text{min}$ to suppress excessive microstructure coarsening, and primary densification was performed for 30 min [20,22,24]. In addition, during the first-step holding time, as the shrinkage began and did not occur rapidly, a small amount of the residual pores could be expected. Owing to the achievement of the primary densification, including a small amount of the residual pores in the first-step sintering, the shrinkage of the two-step profile was completed at 1200°C , which is approximately 50°C lower than that 1250°C of the single-step profile, although the amount of shrinkage was almost the same. This improvement in the sintering behavior of the compacts by the two-step profile not only enabled microstructure control but can also improve the optical properties.

Fig. 2 shows the SEM images of the cross-sections of the SPSed $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ compacts after annealing. All the specimens densified at the final sintering temperature of

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5 1250°C. However, the microstructures for the two SPS profile differed in terms of the grain size,
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7 pore size, and porosity. The microstructural parameters (grain size, pore size, and porosity)
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9 calculated from the SEM images are summarized in Table 2. By applying the two-step profile,
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11 it was possible to significantly lower the porosity at the same sintering temperature. All the two-
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13 step SPSed specimens showed lower porosity than the single-step SPSed specimen (SS-1250)
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15 (3.74%). In particular, TS-1000 exhibited a porosity of 1.63%, indicating that significant
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17 reduction in the porosity was possible by applying the two-step SPS profile. A significant
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19 decrease in the porosity of the two-step SPSed specimens was due to the improvement in their
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21 shrinkage behavior, i.e., the smaller amount of residual pores and the lower shrinkage
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23 completion temperature, as shown in Fig. 2. In addition, as the first-step temperature in the two-
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25 step profile was reduced, the grain size decreased gradually from 207 to 139 nm, and the pore
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27 size decreased from 72 to 43 nm. This microstructural change was due to the microstructure
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29 control of the two-step profile [18,19]. In this study, the microstructure control using the two-
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31 step profile was expected to improve the optical properties as well.

3.2. Optical appearance and transmittance

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42 The optical appearances of the $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ compacts after annealing are shown
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44 in Fig. 3. The optical appearances and transparency of the annealed specimens placed on the
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46 grid can be easily compared. SS-1250 exhibited the lowest optical transparency among all the
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48 specimens. The application of the modified two-step profile improved the optical appearance of
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50 the compacts. For the two-step SPSed specimens, the optical appearance improved with a
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52 decrease in the heating rate at second-step. However, the most significant improvement was
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54 observed at the first-step temperature of 1000°C. This indicates that a decrease in the heating
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5 rate at the critical temperature for densification had more significant effect than simply reducing
6 the heating rate to improve the optical appearance. Therefore, at the first-step temperature of
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8 1000°C, the porosity was the lowest and the optical appearance also improved the most. The
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10 microstructure and optical appearance analysis results indicate that the TS-1000 specimen
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12 showed the highest transmittance among all the specimens investigated in this study.
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17 Fig. 4 shows the in-line transmittance (ILT) curves of the sintered $\text{Ce}^{3+}:(\text{Gd},\text{Lu})_3\text{Al}_5\text{O}_{12}$
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19 compacts after annealing. Significant light absorption was in the range of 420–500 nm. Owing
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21 to the light absorption due to the $4f \rightarrow 5d_2$ and $4f \rightarrow 5d_1$ transitions of Ce^{3+} at 340 nm and over
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23 the wavelength range of 420–500 nm, respectively, strong absorption occurred at these
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25 wavelengths [27]. The optical transmittance of the specimens showed the same trend as that
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27 shown by their optical appearance. At the same sintering temperature of 1250°C, all the two-
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29 step SPSed specimens showed improved transmittance as compared to the single-step SPSed
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31 specimen. The TS-1000 specimen showed the most improved ILT of 56.5% at 1000 nm as
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33 compared to that (50.1%) of the SS-1250 specimen. In transparent ceramics, the area of the
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35 grain boundary also affects the transmittance; however, the porosity is the most critical factor
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37 [28]. In the case of the TS-1000 specimen, the first-step temperature was 1000°C, at which the
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39 shrinkage began, and the porosity decreased significantly from 3.74% (SS-1250) to 1.63% (TS-
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41 1000). This decrease in the porosity had a significant effect on the transmittance of the ceramic.
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43 In addition, as can be observed from Table 2, the porosity of the specimens showed a trend
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45 similar to that shown by the optical transmittance. The TS-1000 specimen showed slightly
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47 reduced grain and pore sizes and significantly reduced porosity as compared to the SS-1250
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49 specimen. The decrease in the porosity, which had the most critical effect on the transmittance,
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51 resulted in the most noticeable improvement in the transmittance of the TS-1000 specimen.
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5 (Gd,Lu)₃Al₅O₁₂:Ce ceramics with a composition similar to that of the ceramics prepared in this
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7 study were fabricated by conventional sintering at 1750°C for 4 h under a vacuum atmosphere
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9 after cold isostatic press at 240 MPa [14]. As a result, an ILT of approximately 72% was
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11 achieved at 1000 nm, showing excellent optical properties. Although there have been reports of
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13 preparing garnet materials with full densification and high transmittance by conventional
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15 sintering, it is difficult to achieve high transmittance with the SPS method. In a previous study,
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17 Nd:YAG ceramics were fabricated using the reactive-SPS method by applying a two-step
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19 heating profile [29]. The Nd:YAG powder was heated at 100°C/min to the first-step temperature
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21 of 1000°C with an applied pressure of 70 MPa and at 15°C/min to the second-step temperature
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23 of 1350°C, which was maintained for 5 min. However, an ILT of approximately 36% was
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25 obtained at 1000 nm, and excellent optical properties were not achieved. In this study, although
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27 the ILT was not close to the theoretical value, the transmittance could be improved through the
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29 application of the two-step profile and microstructure control.
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40 3.3. Oxidation state and PL characteristic

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42 XPS measurements were conducted to investigate the oxidation states of the Ce dopant,
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44 and the results of the powder, single-step profile (SS-1250), and two-step profile (TS-1000) are
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46 summarized in Fig. 5. The red lines represent the spectra of Ce³⁺ ions and the blue lines
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48 represents the spectra of Ce⁴⁺ ions. The fractions of the Ce³⁺ and Ce⁴⁺ ions were calculated from
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50 the areas of their spectra. For comparing the as-synthesized powder with the compacts sintered
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52 in the single-step and two-step profiles, the fraction of Ce³⁺ in the as-synthesized powder was
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54 required. The fraction of Ce³⁺ in the powder was 61.42%, as shown in Fig. 5 (a). The Ce³⁺
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56 fraction of the SS-1250 specimen was 61.73%, which is almost the same as that of the
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5 synthesized powder. However, the TS-1000 specimen showed a Ce^{3+} fraction of 60.66%
6 because of slight oxidation. As the SPS process provides an oxidizing atmosphere of graphite
7 components, oxidation occurred in the two-step profile with a long sintering time, and the
8 fraction of Ce^{3+} decreased slightly. The slightly decreased Ce^{3+} fraction of the two-step profile
9 affected its PL characteristics along with the microstructure.
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17 Fig. 6 (a) shows the PL excitation spectra of the $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ compacts after
18 annealing. PL excitation measurements were performed to investigate the wavelength-
19 dependent excitation when 571 nm light was emitted. Excitation bands were detected at
20 approximately 342, 453, and 506 nm, which correspond to the excitation of Ce^{3+} [30,31]. The
21 excitation peak at approximately 342 nm corresponded to the transition of Ce^{3+} from the ground
22 state ($2F_{5/2}$) to the T_{2g} state. The excitation peaks at approximately 453 and 506 nm
23 corresponded to the transition from the ground state to the E_{2g} state [30,31]. The SS-1250
24 specimen exhibited significantly higher PL excitation intensity than the two-step profile
25 specimens. Independent of the first-step temperature, the PL excitation of the TS-1000 specimen
26 intensity was the lowest. The transmittance of the specimens was strongly influenced by their
27 porosity, and the two-step profile showed better results than the single-step profile. However,
28 the PL excitation characteristics showed an opposite trend. First, the fraction of Ce^{3+} (Fig. 5)
29 directly affected the PL excitation characteristics of the specimens. Because the PL excitation
30 was caused only by Ce^{3+} [30,31], the fraction of Ce^{3+} present in the $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$
31 ceramics was a very important factor. Next, the grain size of the SS-1250 specimen was the
32 largest at 221 nm, which decreased gradually from 207 to 139 nm with a decrease in the first-
33 step temperature. Owing to its large grain size and small grain boundary area, the single-step
34 profile affected the PL excitation characteristics of the compacts more than the two-step profile
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5 [32,33]. Fig. 6 (b) shows the PL emission spectra of the $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ compacts after
6 annealing. The wavelength-dependent emission of the compacts under excitation by a
7 wavelength of 453 nm was investigated. The PL emission characteristics of the compacts
8 showed the same trend as that shown by the PL excitation characteristics. The full width at half
9 maximum values were almost the same for all the specimens. This indicates that the crystallinity
10 and light clarity of all the specimens were almost the same and that the two-step profile did not
11 affect the PL emission characteristics.
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4. Conclusions

In this study, a two-step SPS profile was employed to improve the optical properties of $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ ceramics as attractive yellow-emitting phosphors. The shrinkage curve of the two-step profile showed a significant reduction in the porosity from 3.74% to 1.63% at the first-step temperature of 1000°C, at which the shrinkage began. As the first-step temperature decreased, the microstructure control of two-step profile refined the microstructure of the compacts by reducing the grain and pore sizes. As a result of the significant reduction in the porosity in the two-step profile, the transmittance improved from 50.1% to 56.5% at 1000 nm. On the other hand, owing to the long sintering time of the two-step profile, oxidation occurred and the fraction of Ce^{3+} decreased slightly. Therefore, the two-step profile did not affect the PL excitation and emission characteristics of the ceramics.

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6 **Figure captions**
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10 Figure 1. Fig. 1. SPS curves of the SPSed $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ ceramics (a) single-step SPS
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12 (SS-1250) and (b) two-step SPS (TS-1000).
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17 Figure 2. SEM images of the cross-sections of the SPSed $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ ceramics.
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22 Figure 3. Optical appearances of the SPSed $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ ceramics under the
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24 conditions listed in Table 1.
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29 Figure 4. (a) Transmittance curves of the SPSed $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ ceramics after annealing.
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31 (b) is the curve magnified over the wavelength of 750–1050 nm.
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36 Figure 5. XPS profiles of the (a) $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ powder, (b) single-step SPSed compact
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38 (SS-1250), and (c) two-step SPSed Compact (TS-1000).
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43 Figure 6. (a) PL excitation and (b) PL emission spectra of the $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ ceramics
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45 with different SPS conditions after annealing.
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Figures

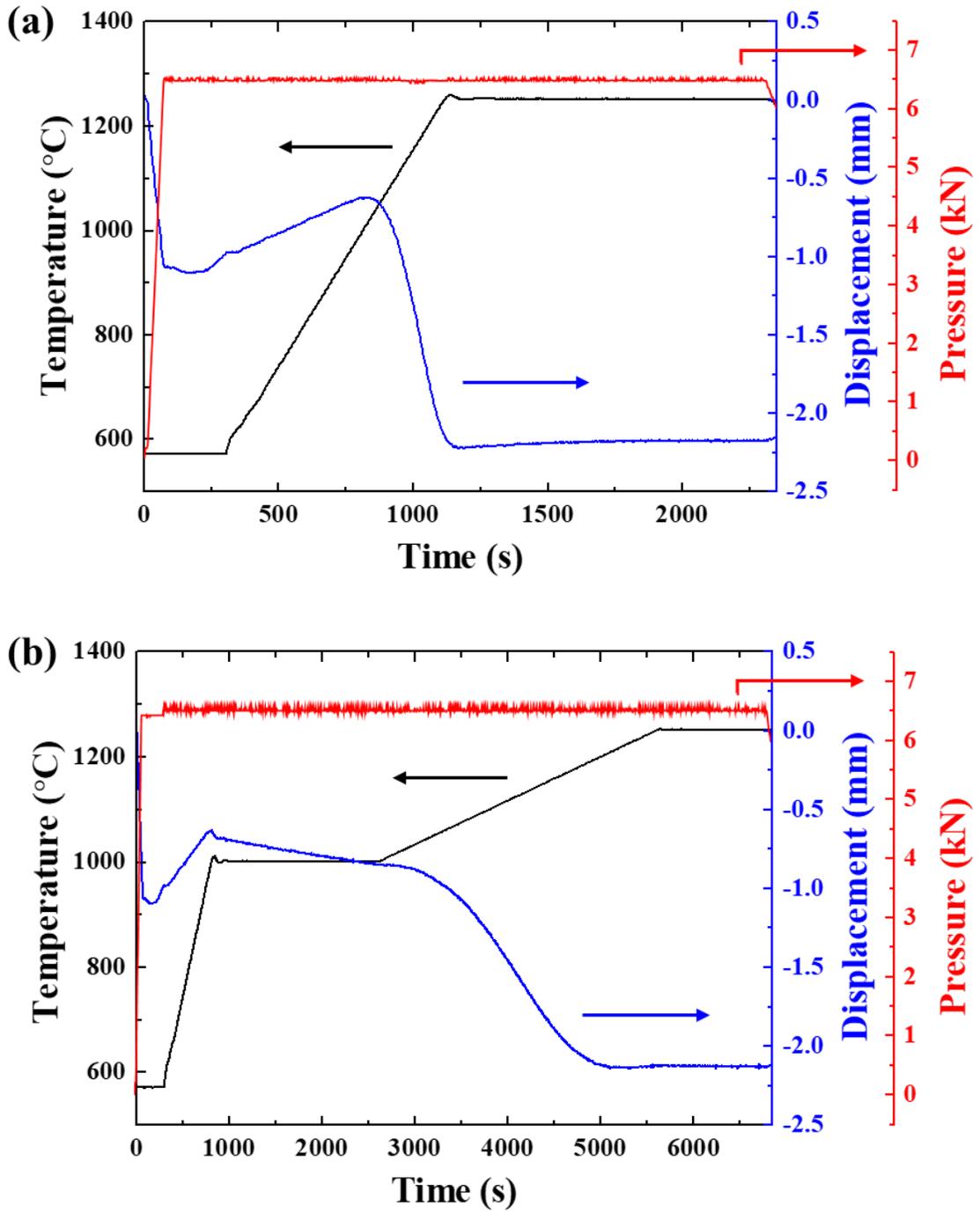


Fig. 1

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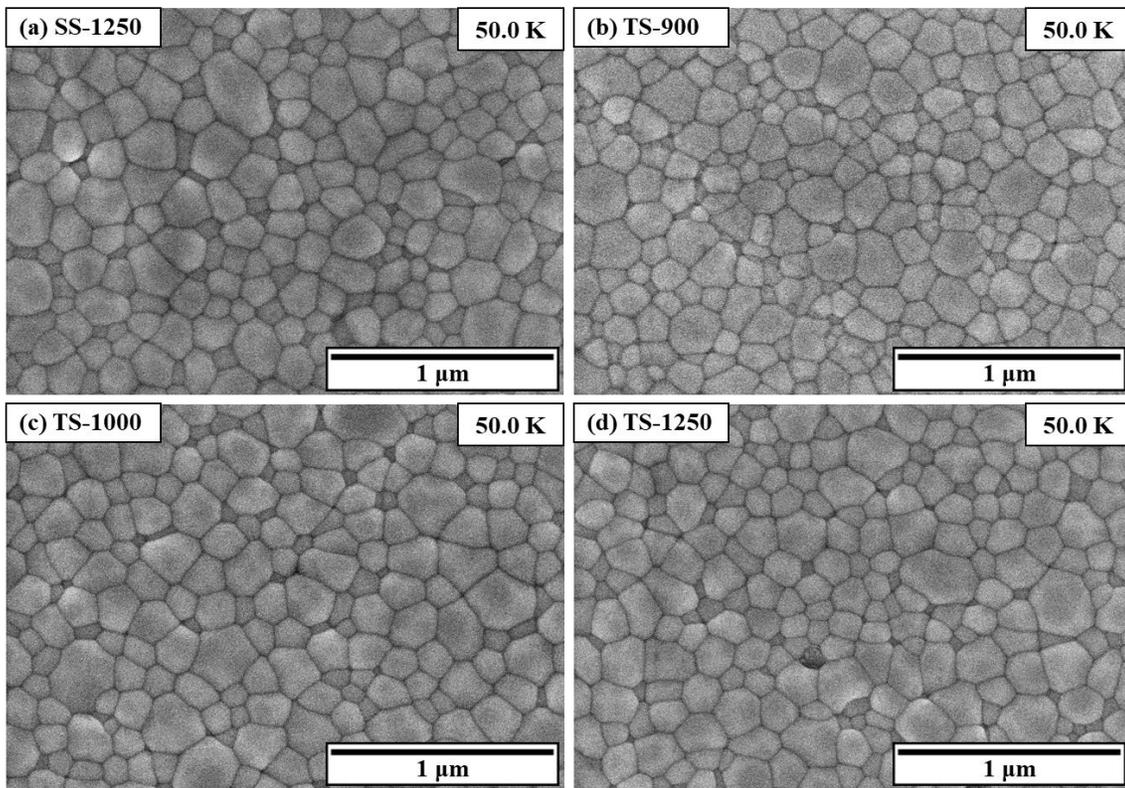


Fig. 2

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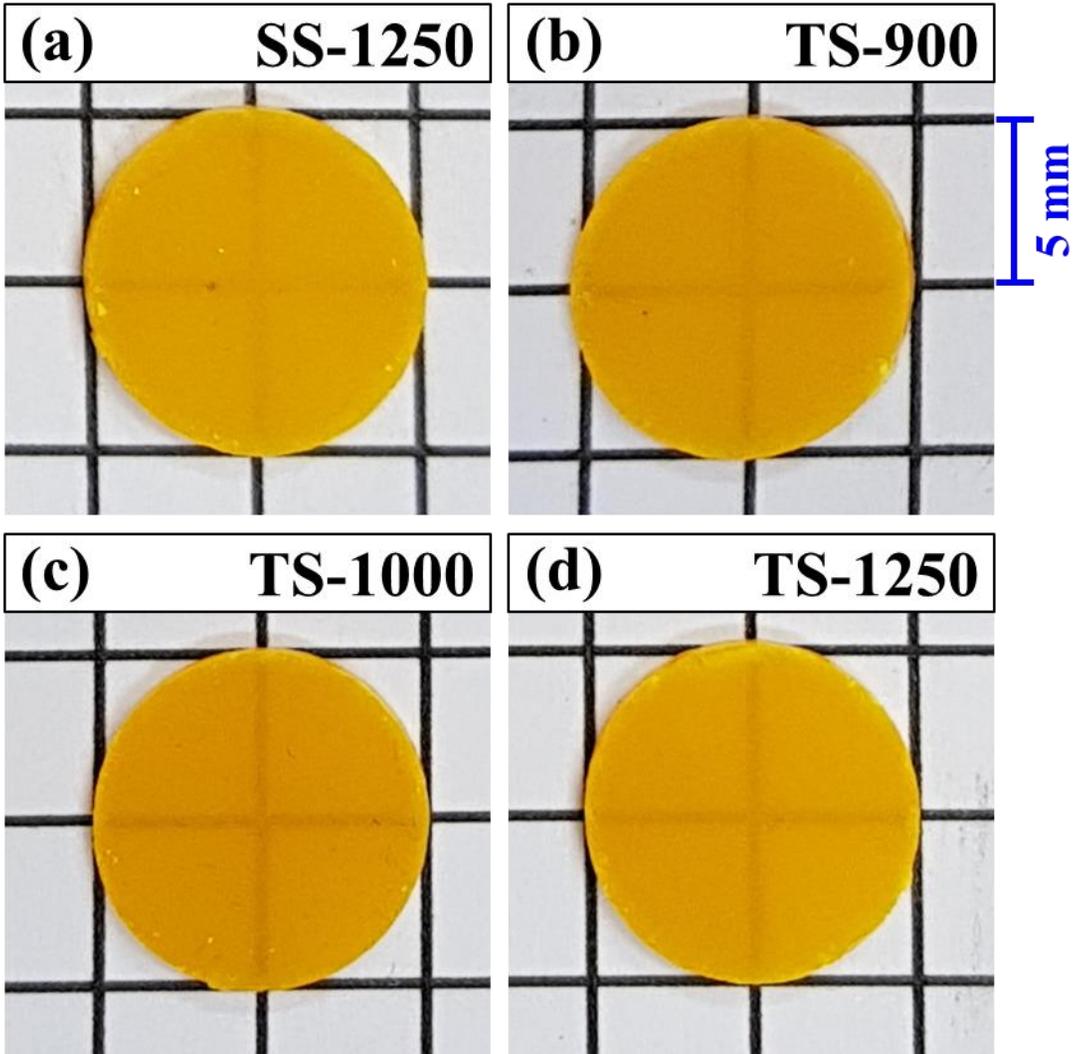
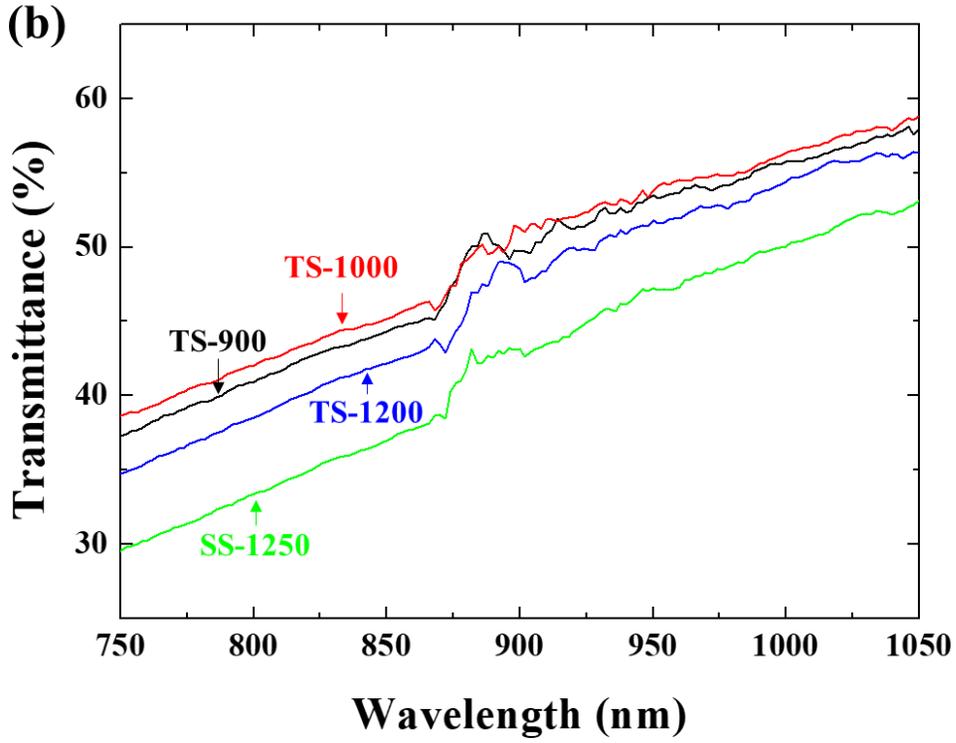
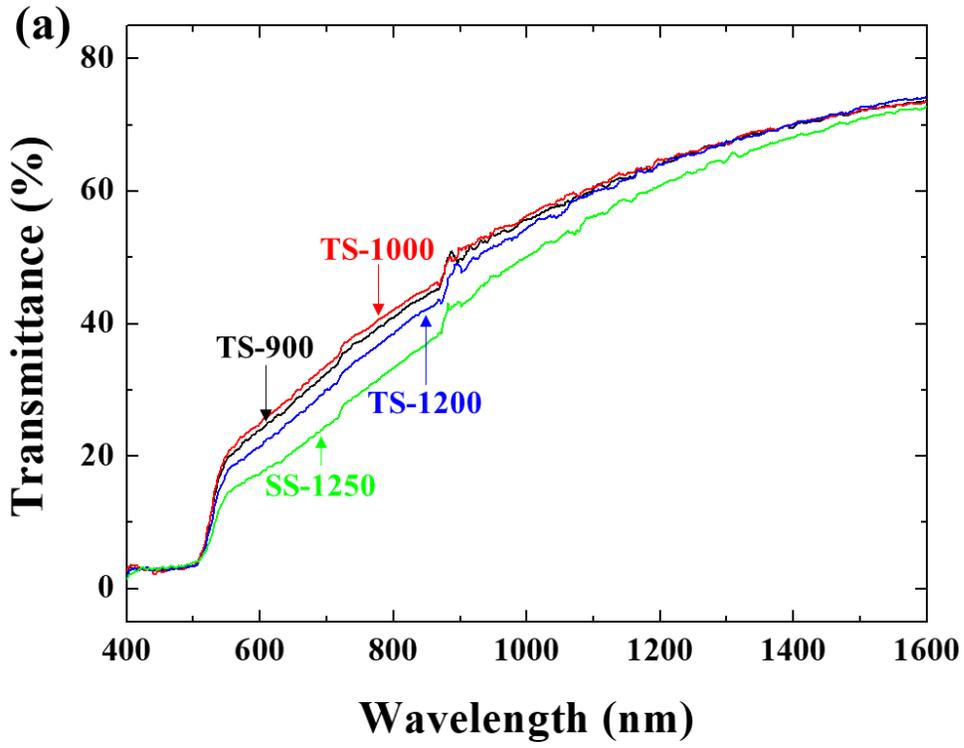


Fig. 3



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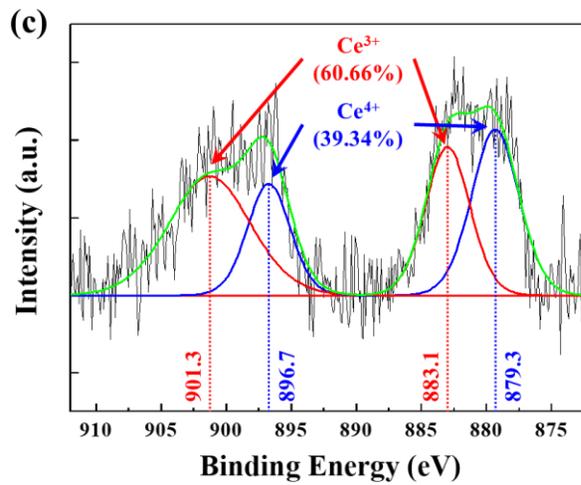
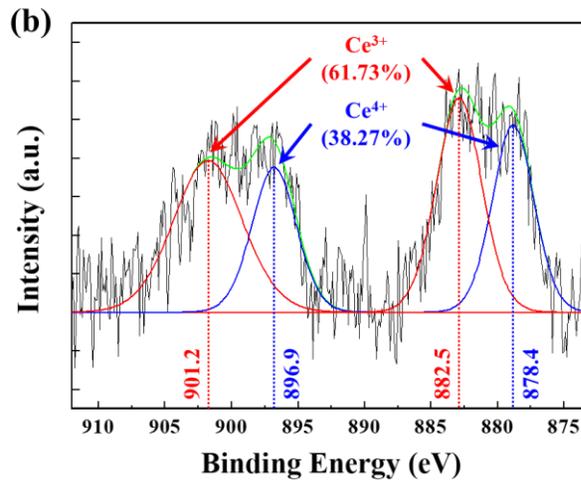
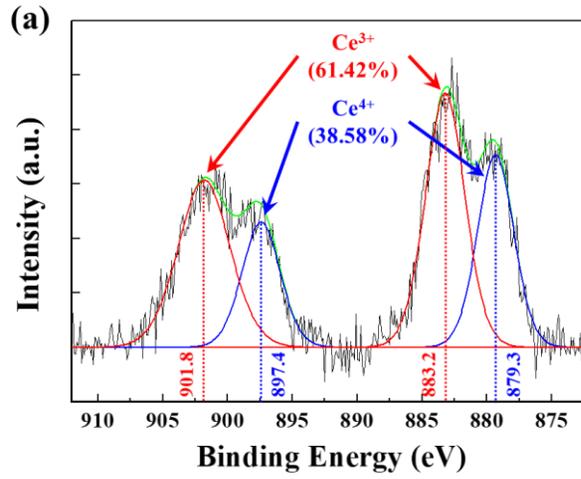
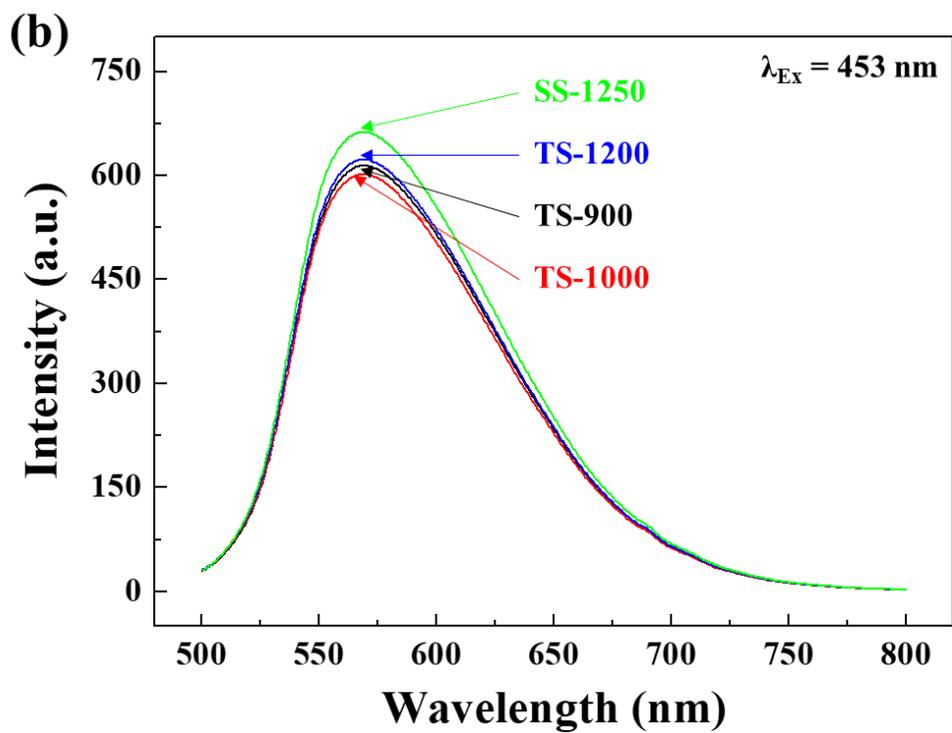
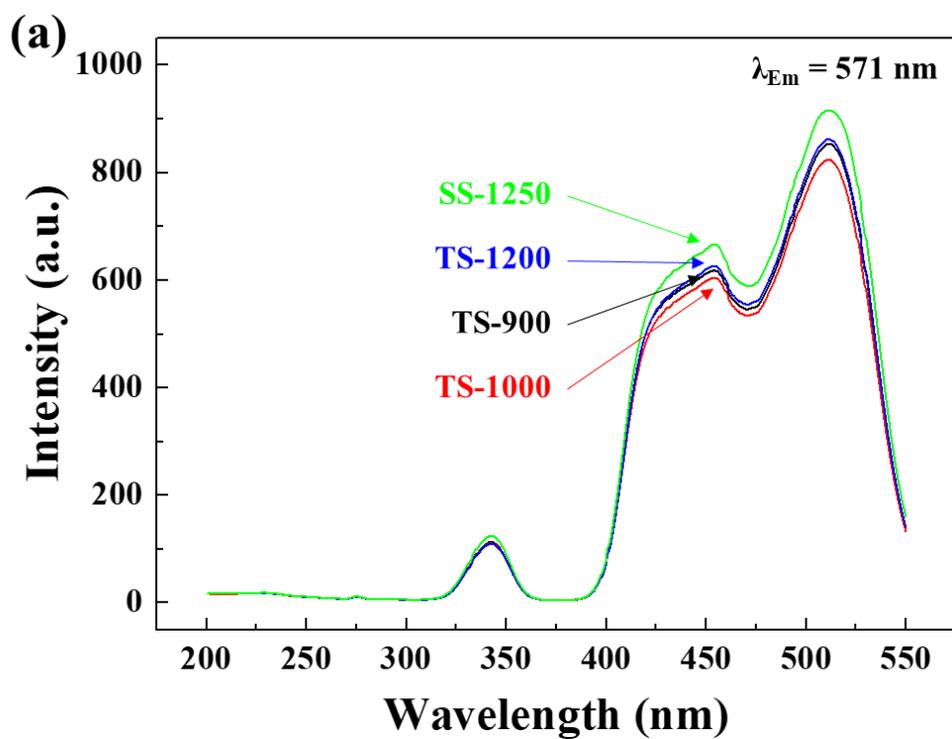


Fig. 5



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Tables

Table 1. SPS conditions of the $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ ceramics.

No.	Specimen name	SPS profile	Heating rate	Range (°C)	Holding stage
1	SS-1250	Single-step profile	50°C/min	600–1250	@ 1250°C for 20 min
2	TS-900	1 st step	50°C/min	600–900	@ 900°C for 30 min
		2 nd step	5°C/min	900–1250	@ 1250°C for 20 min
3	TS-1000	1 st step	50°C/min	600–1000	@ 1000°C for 30 min
		2 nd step	5°C/min	1000–1250	@ 1250°C for 20 min
4	TS-1200	1 st step	50°C/min	600–1200	@ 1200°C for 30 min
		2 nd step	5°C/min	1200–1250	@ 1250°C for 20 min

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Table 2. Microstructure parameters of the SPSed $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ ceramics.

No.	Specimen name	Grain size	Pore size	Porosity
1	SS-1250	221 nm	81 nm	3.74%
2	TS-900	139 nm	43 nm	2.29%
3	TS-1000	163 nm	69 nm	1.63%
4	TS-1200	207 nm	72 nm	2.96%

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5 **1 Fabrication of transparent Ce³⁺-doped (Gd,Lu)₃Al₅O₁₂ ceramics by two-step spark**
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7 **2 plasma sintering**
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12 **3**
13 **4 Ji-Hwoan Lee^a, Byung-Nam Kim^a, Ji-Guang Li^a, and Byung-Koog Jang^{b,*}**
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1 **Abstract**

2 Transparent $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ with microstructure control was fabricated by two-
3 step spark plasma sintering. In the two-step profile, the heating rate was changed from 50 to
4 5°C/min at the first step temperatures. During the initial stage of shrinkage, the holding time
5 of the first step sintering could induce densification by suppressing the microstructure
6 coarsening. As compared to the single-step profile, the two-step profile showed a smaller
7 grain size, which decreased with a decrease in the first step temperature. The porosity of the
8 two-step profile was lower than that of the single-step profile, and the lowest porosity was
9 obtained at the first step temperature of 1000°C, which was the starting point of shrinkage.
10 The TS-1000 specimen showed the highest transmittance among all specimens because of
11 the microstructure control offered by the two-step profile. Thus, by employing the two-step
12 profile, the transmittance could be increased from 50.1% (SS-1250) to 56.5% (TS-1000).

13
14 **Keywords:** Two-step spark plasma sintering; Optical property; Photoluminescence
15 characteristics; Microstructure; Gadolinium and lutetium aluminum garnet

1. Introduction

Lanthanide aluminum garnets ($\text{Ln}_3\text{Al}_5\text{O}_{12}$, LnAG), represented by $\text{Gd}_3\text{Al}_5\text{O}_{12}$ (GdAG) and $\text{Lu}_3\text{Al}_5\text{O}_{12}$ (LuAG), have high theoretical densities, and are attractive candidates for scintillator applications. LnAGs exhibit unique properties, such as wide bandgaps, high chemical and thermal stability, and a wide transparent range, which make them suitable for scintillator applications [1–4]. Scintillators should possess high theoretical density to stop X-rays. Yttrium aluminum garnet (YAG) shows relatively low X-ray stopping power due to its low density (4.53 g/cm^3). Among lanthanide elements with atomic weights higher than Y (89), Gd (157), and Lu (174) are considered suitable candidates for increasing the density of the garnet structure. However, Gd (0.21 ppm) and Lu (0.02 ppm) are less abundant in the earth's crust as compared to Y (1.39 ppm) [5]. As Gd is more abundant than Lu, it is considered to be a more suitable substitute for Y. Recently, transparent Gd-based LnAGs have been extensively investigated for scintillator applications. However, GdAGs thermally decompose into GdAlO_3 perovskite and Al_2O_3 above 1300°C ($\text{Gd}_3\text{Al}_5\text{O}_{12} \rightarrow 3\text{GdAlO}_3 + \text{Al}_2\text{O}_3$) [6]. In addition, GdAGs are doped with Ce^{3+} as an activator of yellow-emitting phosphors. The larger Ce^{3+} ions cause the destabilization of the garnet structure, thereby reducing its thermal decomposition temperature. In order to suppress their thermal decomposition, Ce-doped GdAGs are doped with Lu^{3+} ions, which are much smaller than Gd^{3+} ions [7]. These Lu^{3+} ions reduce the average Ln^{3+} size, and hence stabilize the garnet structure. In addition, Lu^{3+} doping retains the photoluminescence (PL) characteristics of Ce^{3+} and increases the theoretical density of $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$, thus enabling the development of advanced yellow-emitting phosphors [7].

Decreasing the sintering temperature can prevent the thermal decomposition of GdAG

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1 above 1300°C and improve its mechanical properties while providing a dense microstructure.
2 Among the various sintering techniques, spark plasma sintering (SPS) controlled by an
3 electric field and mechanical pressure is considered to be an efficient sintering approach for
4 GdAG [8,9]. In the SPS process, the electric field rapidly heats the mold and powder compact,
5 facilitating rapid densification by several microscopic mechanisms, including increased atom
6 diffusivity and softening of the particle surfaces, so that excessive grain growth is suppressed
7 at low temperatures [8,10]. Therefore, high densities and fine microstructures, which are the
8 advantages of SPS, improve the mechanical and optical properties of ceramics. Recently, the
9 fabrication and characterization of LuAG ceramics, such as Nd:YAG [11], LuAG [12], and
10 $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ [13], using the SPS process have been reported [11–13]. Sufficient
11 transparency can be obtained by conventional sintering, hot pressing (HP), and hot isostatic
12 pressing (HIP) [14–16]. However, the fabrication of transparent LnAG using the SPS process
13 has not been sufficiently studied. In our previous work [13], a $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ powder
14 was fully densified using the SPS process; however, a transparent compact was not obtained.
15 Therefore, further research is required to improve the transparency of SPS-prepared ceramics
16 while retaining the intrinsic merits of the SPS technique.

17 Various studies have reported the application of a two-step sintering profile to
18 conventional sintering, HP, and HIP techniques to improve the optical properties and control
19 the microstructure of ceramics [16–19]. Previous studies on the two-step sintering profile
20 suggested that preliminary experiments on microstructure control should be conducted to
21 improve the optical properties of ceramics [18,19]. Although the two-step sintering profile is
22 applied in different ways, the main objective is to achieve primary densification without
23 excessive coarsening at the higher first step temperature and full densification and removal

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1 of residual pores during the second step sintering. As a result, full densification can be
2 effectively achieved by dividing the sintering process into two steps with different objectives.
3 In addition, some researchers have reported that a two-step profile can be applied to improve
4 the optical properties of ceramics while retaining the intrinsic merits of the SPS process [20–
5 24]. In the SPS process, the two-step profile is applied in a slightly different way, because
6 the amounts of carbon contamination and residual pores inevitably increase with increased
7 sintering time. Considerable research [22,23] has been carried out on the microstructure and
8 optical properties of each step of the two-step profile. After primary densification without
9 excessive microstructure coarsening when the first step temperature is lower than that of the
10 second step, sufficient densification and excellent transparency could be achieved by
11 removing the residual defects at the second step temperature. In our previous work [24], in
12 transparent Y₂O₃ fabricated with a lower first step temperature, microstructural control and
13 improved optical properties could be achieved. On the basis of the previously reported results
14 regarding the two-step profile, it can be stated that by suppressing excessive microstructure
15 coarsening and separating the primary densification and full densification processes, the
16 microstructure of LnAG can be made fine and dense and its transmittance can be improved.

17 In the present work, the main objective is to control the microstructure and improve the
18 optical properties by fabricating transparent Ce³⁺:(Gd,Lu)₃Al₅O₁₂ ceramics by applying a
19 two-step SPS profile. The two-step SPS profile is divided into first step (@ 900, 1000, and
20 1200°C) and second step (@ 1250°C) sintering, and the goals to be achieved in each step are
21 as follows. At a relatively low temperature of first step sintering, primary densification can
22 be achieved, which is effective in suppressing excessive microstructure coarsening. Next, in
23 second step sintering, full densification and the removal of residual pores can be

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1 accomplished. The microstructure and optical properties of the $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$
2 ceramics were evaluated by focusing on the improvement of in-line transmittance by varying
3 the first step temperature.

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2. Experimental Procedure

2.1. Preparation of $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ powder

The rare-earth and aluminum sources used in this study were Ln_2O_3 ($Ln = Gd$ and Lu , 99.99%, Huizhou RUIER Rare-Chem. Hi-Tech, China), $Ce(NO_3)_3 \cdot 6H_2O$ (99.99%, Huizhou RUIER Rare-Chem. Hi-Tech, China), and alum ($NH_4Al(SO_4)_2 \cdot 12H_2O$, > 99%, Zhenxin Chemical Reagent Factory, China). A $Ln(NO_3)_3$ stock solution was prepared by dissolving the oxide powders in an optimum amount of nitric acid. To precipitate the carbonate precursor, a mixed solution containing stoichiometric amounts of the nitrates and alum was added dropwise to the ammonium bicarbonate solution. The precipitated carbonate precursor was dried in an oven for 24 h. The $[(Gd_{0.6}Lu_{0.4})_{0.99}Ce_{0.01}]_3Al_5O_{12}$ powder was obtained by the thermal decomposition of the precursor *via* calcination at 1100°C for 4 h in air. To suppress the oxidation of Ce^{3+} , a second calcination process was performed at 1000°C for 4 h in Ar/H_2 (5 vol% of H_2) [7,25].

2.2. Consolidation of $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ compacts using the SPS process

The $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ powder was consolidated using SPS equipment (LABOX-315, Sinter Land, Japan) under a vacuum atmosphere of 10 Pa. The powder was directly sintered without any pretreatment, using a graphite mold with a diameter of 10 mm. Heating was performed using a pulse pattern of 5:5 (on:off) in the AC mode, and the temperature was measured by installing a pyrometer in the non-through hole of the mold. The entire SPS process was divided into single-step and two-step profiles. For the single-step profile, the powder compact was heated to a sintering temperature of 1250°C at a heating rate of 50°C/min, and held for 20 min. In the case of the two-step profile, to achieve primary

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1 densification without excessive microstructure coarsening, first step sintering was performed
2 at 900, 1000, and 1200°C with a heating rate of 50°C/min and the sintering temperature was
3 held for 30 min. In the single-step profile, shrinkage started at approximately 1000°C. Thus,
4 the first step temperature for the two-step profile was considered to be 1000°C. To achieve
5 full densification and the removal of residual pores, further heating was conducted to reach
6 the second step temperature of 1250°C at 5°C/min. This temperature was held for 20 min. In
7 the entire SPS process, a mechanical pressure of 6.5 kN (80 MPa) was applied from the
8 beginning and was maintained until cooling. In addition, cooling was sequentially performed
9 at 1100°C for 10 min, 800°C for 5 min, and 25°C for 5 min. The SPS conditions and specimen
10 names are listed in Table 1.

12 2.3. Characterization

13 The annealing process was conducted at 1250°C for 10 h in air to remove the carbon
14 contamination and oxygen vacancies. Both of the surfaces of the $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$
15 compacts were mirror polished with 9, 3, and 1 μm diamond pastes. The transmittance of the
16 compacts was measured using a double-beam spectrophotometer (SolidSpec-3700DUV,
17 Shimadzu, Japan) equipped with an integrating sphere. PL measurements were conducted
18 using a spectrofluorometer (FP-6500, JASCO, Japan) equipped with a 60 mm diameter-
19 integrating sphere (Model ISF-513, JASCO, Japan) and a 150 W Xe lamp as the excitation
20 source. The X-ray photoelectron spectroscopy (XPS, AXIS-165, Shimadzu, Japan) profiles
21 of the samples were recorded at room temperature with $Al-K_{\alpha}$ radiation for excitation. The
22 binding energy was referenced to the C-1 s line of adventitious carbon. The mirror-polished
23 surfaces were thermally etched at 1100°C for 2 h in air. The polished and fractured surfaces

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1 of the specimens were examined using scanning electron microscopy (SEM, SU-8000,
2 Hitachi, Japan). The porosity of the specimens was determined by measuring their porous
3 areas from the SEM images. The grain and pore sizes of the specimens were calculated by
4 measuring their pore sizes and average cross-sectional areas per grain. The grain size was
5 apparent in the cross section; therefore, it was multiplied by 1.225 to determine the actual
6 grain size [26].

3. Results and Discussion

3.1. Shrinkage behavior and microstructure

In our previous work, we successfully developed a stable $(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ garnet structure, which could be well indexed to the cubic structure of GdAG [13]. Single-step and two-step SPS profiles were applied to fabricate transparent $(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ ceramics with structural stabilization. The SPS curves (temperature, displacement, and pressure over time) of the single-step profile (SS-1250) are shown in Fig. 1 (a). As can be observed from the displacement curve, the ceramics showed thermal expansion when heated to approximately 1000°C . In addition, shrinkage began to occur at this temperature. No further shrinkage occurred during the holding period at 1250°C , and the shrinkage was sufficient. Based on the SPS curves of the single-step profile (SS-1250), a two-step profile (TS-1000) was designed, as shown in Fig. 1 (b). At a relatively low first step temperature of 1000°C , the powder compact was rapidly heated at $50^\circ\text{C}/\text{min}$ to suppress excessive microstructure coarsening, and primary densification was performed for 30 min [20,22,24]. In addition, during the first step holding time, as the shrinkage began and did not occur rapidly, a small amount of residual pores could be expected. Owing to the achievement of primary densification, including a small amount of residual pores in the first step sintering, the shrinkage of the two-step profile was completed at 1200°C , which is approximately 50°C lower than that 1250°C of the single-step profile. However, the amount of shrinkage was almost the same. This improvement in the sintering behavior of the compacts by the two-step profile enabled microstructure control and improved the optical properties.

Fig. 2 shows the SEM images of the cross sections of the SPSed $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ compacts after annealing. All specimens were densified at the final sintering temperature of

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1 1250°C. However, the microstructures for the two SPS profiles differed in terms of grain size,
2 pore size, and porosity. The microstructural parameters (grain size, pore size, and porosity)
3 calculated from the SEM images are summarized in Table 2. Applying the two-step profile
4 made it possible to significantly lower the porosity at the same sintering temperature. All
5 two-step SPSed specimens showed lower porosity than that of the single-step SPSed
6 specimen (SS-1250) (3.74%). In particular, the TS-1000 exhibited a porosity of 1.63%,
7 indicating that a significant reduction in porosity was possible by applying the two-step SPS
8 profile. The significant decrease in the porosity of the two-step SPSed specimens was due to
9 improvement in their shrinkage behavior, i.e., fewer residual pores and a lower shrinkage-
10 completion temperature, as shown in Fig. 2. In addition, as the first step temperature in the
11 two-step profile was reduced, the grain size decreased gradually from 207 to 139 nm, and the
12 pore size decreased from 72 to 43 nm. This microstructural change was due to the
13 microstructure control of the two-step profile [18,19]. In this study, microstructure control
14 using the two-step profile was expected to improve the optical properties as well.

15
16 3.2. Optical appearance and transmittance

17 The optical appearances of the $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ compacts after annealing are shown
18 in Fig. 3. The optical appearances and transparency of the annealed specimens placed on the
19 grid can be easily compared. SS-1250 exhibited the lowest optical transparency among all
20 specimens. Applying the modified two-step profile improved the optical appearance of the
21 compacts. For two-step SPSed specimens, the optical appearance improved with a decrease
22 in the heating rate at the second step. However, the most significant improvement was
23 observed at the first step temperature of 1000°C. This indicates that a decrease in the heating

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1 rate at the critical temperature for densification had a more significant effect than simply
2 reducing the heating rate to improve the optical appearance. Therefore, at the first step
3 temperature of 1000°C, porosity was lowest and the optical appearance also improved the
4 most. The microstructure and optical appearance analysis results indicate that the TS-1000
5 specimen showed the highest transmittance among all specimens investigated in the present
6 work.

7 Fig. 4 shows the in-line transmittance (ILT) curves of the sintered $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$
8 compacts after annealing. Significant light absorption was in the range of 420–500 nm.
9 According to the reported results [27], well-fabricated $Lu_{2.7}Gd_{0.3}Al-O_{12}$ ceramics exhibited
10 excellent transmittance above 250 nm. In the present work, since light absorption by Ce^{3+}
11 occurred at less than 500 nm, transmittance decreased rapidly. Owing to the light absorption
12 due to the $4f \rightarrow 5d_2$ and $4f \rightarrow 5d_1$ transitions of Ce^{3+} at 340 nm and over a wavelength range
13 of 420–500 nm, respectively, a strong light absorption band was detected [28]. The optical
14 transmittance of the specimens showed the same trend as that of their optical appearance. At
15 the same sintering temperature of 1250°C, all two-step SPSed specimens showed improved
16 transmittance as compared to the single-step SPSed specimen. The TS-1000 specimen
17 showed the most improved ILT of 56.5% at 1000 nm as compared to that (50.1%) of the SS-
18 1250 specimen. In transparent ceramics, the area of the grain boundary also affects
19 transmittance; however, porosity is the most critical factor [29]. In the case of the TS-1000
20 specimen, the first step temperature was 1000°C, at which shrinkage began, and porosity
21 decreased significantly from 3.74% (SS-1250) to 1.63% (TS-1000). This decrease in porosity
22 had a significant effect on the transmittance of the ceramic. In addition, as can be observed
23 from Table 2, the porosity of the specimens showed a trend similar to that shown by the

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1 optical transmittance. The TS-1000 specimen showed slightly reduced grain and pore sizes
2 and significantly reduced porosity as compared to the SS-1250 specimen. The decrease in
3 porosity, which had the most critical effect on transmittance, resulted in the most noticeable
4 improvement in the transmittance of the TS-1000 specimen. (Gd,Lu)₃Al₅O₁₂:Ce ceramics
5 with a composition similar to that of the ceramics prepared in this study were fabricated by
6 conventional sintering at 1750°C for 4 h under a vacuum atmosphere after cold isostatic press
7 at 240 MPa [14]. As a result, an ILT of approximately 72% was achieved at 1000 nm,
8 showing excellent optical properties. Although there have been reports of preparing garnet
9 materials with full densification and high transmittance by conventional sintering, it is
10 difficult to achieve high transmittance with the SPS method. In a previous study, Nd:YAG
11 ceramics were fabricated using the reactive-SPS method by applying a two-step heating
12 profile [30]. The Nd:YAG powder was heated at 100°C/min to the first step temperature of
13 1000°C with an applied pressure of 70 MPa and at 15°C/min to the second step temperature
14 of 1350°C, which was maintained for 5 min. However, an ILT of approximately 36% was
15 obtained at 1000 nm, and excellent optical properties were not achieved. In this study,
16 although the ILT was not close to the theoretical value, the transmittance could be improved
17 through the application of the two-step profile and microstructure control.

18
19 3.3. Oxidation state and PL characteristic

20 XPS measurements were conducted to investigate the oxidation states of the Ce dopant,
21 and the results of the powder, single-step profile (SS-1250), and two-step profile (TS-1000)
22 are summarized in Fig. 5. The red lines represent the spectra of Ce³⁺ ions and the blue lines
23 represent the spectra of Ce⁴⁺ ions. The fractions of the Ce³⁺ and Ce⁴⁺ ions were calculated

1 from the areas of their spectra. For comparing the as-synthesized powder with the compacts
2 sintered in the single-step and two-step profiles, the fraction of Ce^{3+} in the as-synthesized
3 powder was required. The fraction of Ce^{3+} in the powder was 61.42%, as shown in Fig. 5 (a).
4 The Ce^{3+} fraction of the SS-1250 specimen was 61.73%, which is almost the same as that of
5 the synthesized powder. However, because of slight oxidation, the TS-1000 specimen
6 showed a Ce^{3+} fraction of 60.66%. As the SPS process provides an oxidizing atmosphere of
7 graphite components, oxidation occurred in the two-step profile with a long sintering time,
8 and the fraction of Ce^{3+} decreased slightly. The slightly decreased Ce^{3+} fraction of the two-
9 step profile affected its PL characteristics along with the microstructure.

10 Fig. 6 (a) shows the PL excitation spectra of the $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ compacts after
11 annealing. PL excitation measurements were performed to investigate the wavelength-
12 dependent excitation when 571 nm light was emitted. Excitation bands were detected at
13 approximately 342, 453, and 506 nm, corresponding to the excitation of Ce^{3+} [31,32]. The
14 excitation peak at approximately 342 nm correspond to the transition of Ce^{3+} from the ground
15 state ($2F_{5/2}$) to the T_{2g} state. Excitation peaks at approximately 453 and 506 nm corresponded
16 to the transition from the ground state to the E_{2g} state [31,32]. The SS-1250 specimen
17 exhibited significantly higher PL excitation intensity than did the two-step profile specimens.
18 Independent of the first step temperature, the PL excitation of the TS-1000 specimen intensity
19 was the lowest. Their porosity strongly influenced the transmittance of the specimen, and the
20 two-step profile showed better results than did the single-step profile. However, the PL
21 excitation characteristics showed an opposite trend. First, the fraction of Ce^{3+} (Fig. 5) directly
22 affected the PL excitation characteristics of the specimens. Because the PL excitation was
23 caused only by Ce^{3+} [31,32], the fraction of Ce^{3+} present in the $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ ceramics

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1 was a very important factor. Next, the grain size of the SS-1250 specimen was the largest at
2 221 nm, which decreased gradually from 207 to 139 nm with a decrease in the first step
3 temperature. Owing to its large grain size and small grain boundary area, the single-step
4 profile affected the PL excitation characteristics of the compacts more than the two-step
5 profile did [33,34]. Fig. 6 (b) shows the PL emission spectra of the $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$
6 compacts after annealing. The wavelength-dependent emission of the compacts under
7 excitation by a wavelength of 453 nm was investigated. The PL emission characteristics of
8 the compacts showed the same trend as that shown by the PL excitation characteristics. The
9 full widths at half maximum values were almost the same for all specimens. This indicates
10 that the crystallinity and light clarity of all specimens were almost the same and that the two-
11 step profile did not affect the PL emission characteristics.

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1 **4. Conclusions**

2 In this study, a two-step SPS profile was employed to improve the optical properties of
3 $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ ceramics as attractive yellow-emitting phosphors. The shrinkage curve
4 of the two-step profile showed a significant reduction in porosity from 3.74% to 1.63% at the
5 first step temperature of 1000°C, at which shrinkage began. As the first step temperature
6 decreased, the microstructure control of the two-step profile refined the microstructure of the
7 compacts by reducing the grain and pore sizes. As a result of the significant reduction in
8 porosity in the two-step profile, transmittance improved from 50.1% to 56.5% at 1000 nm.
9 On the other hand, oxidation occurred owing to the two-step profile's long sintering time,
10 and the fraction of Ce^{3+} decreased slightly. Therefore, the two-step profile did not affect the
11 ceramics' PL excitation and emission characteristics.

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1 **Figure captions**

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Figure 1. SPS curves of the SPSed $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ ceramics (a) single-step SPS (SS-1250) and (b) two-step SPS (TS-1000).

Figure 2. SEM images of the cross sections of the SPSed $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ ceramics.

Figure 3. Optical appearances of the SPSed $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ ceramics under the conditions listed in Table 1.

Figure 4. (a) Transmittance curves of the SPSed $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ ceramics after annealing; (b) the curve magnified over the wavelength of 750–1050 nm.

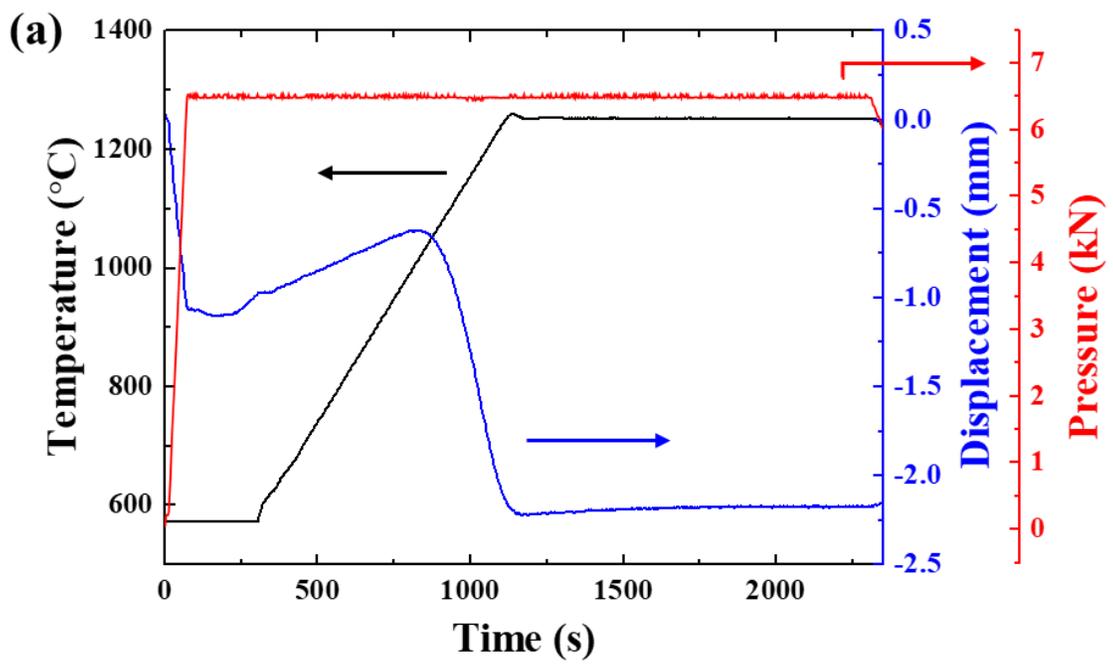
Figure 5. XPS profiles of the (a) $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ powder, (b) single-step SPSed compact (SS-1250), and (c) two-step SPSed compact (TS-1000).

Figure 6. (a) PL excitation and (b) PL emission spectra of $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ ceramics with different SPS conditions after annealing.

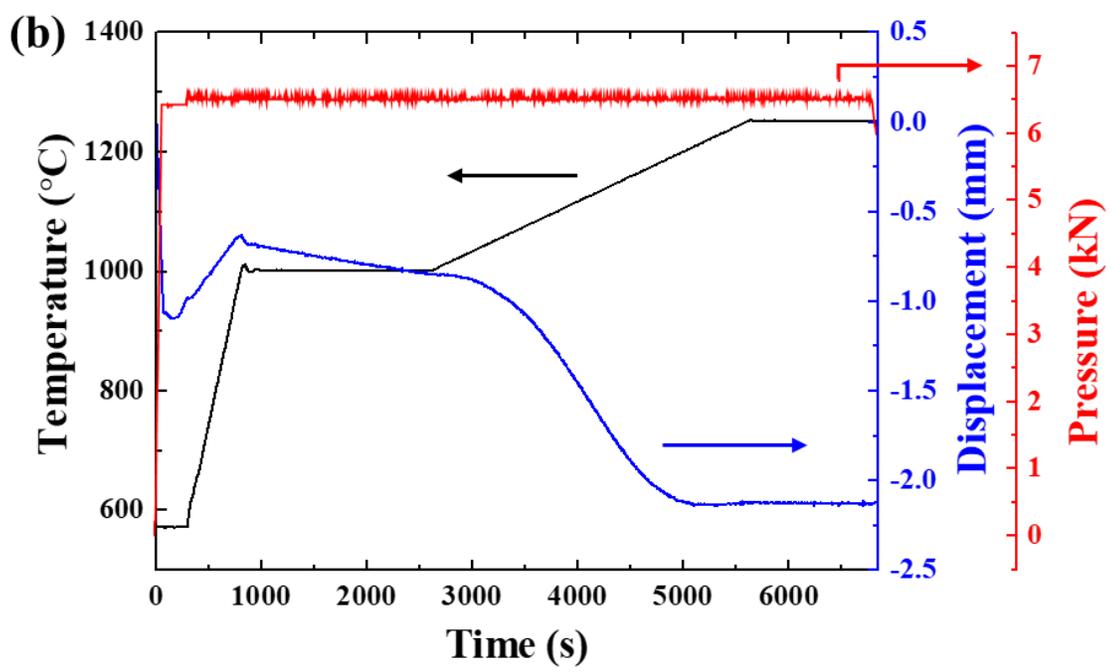
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1 **Figures**

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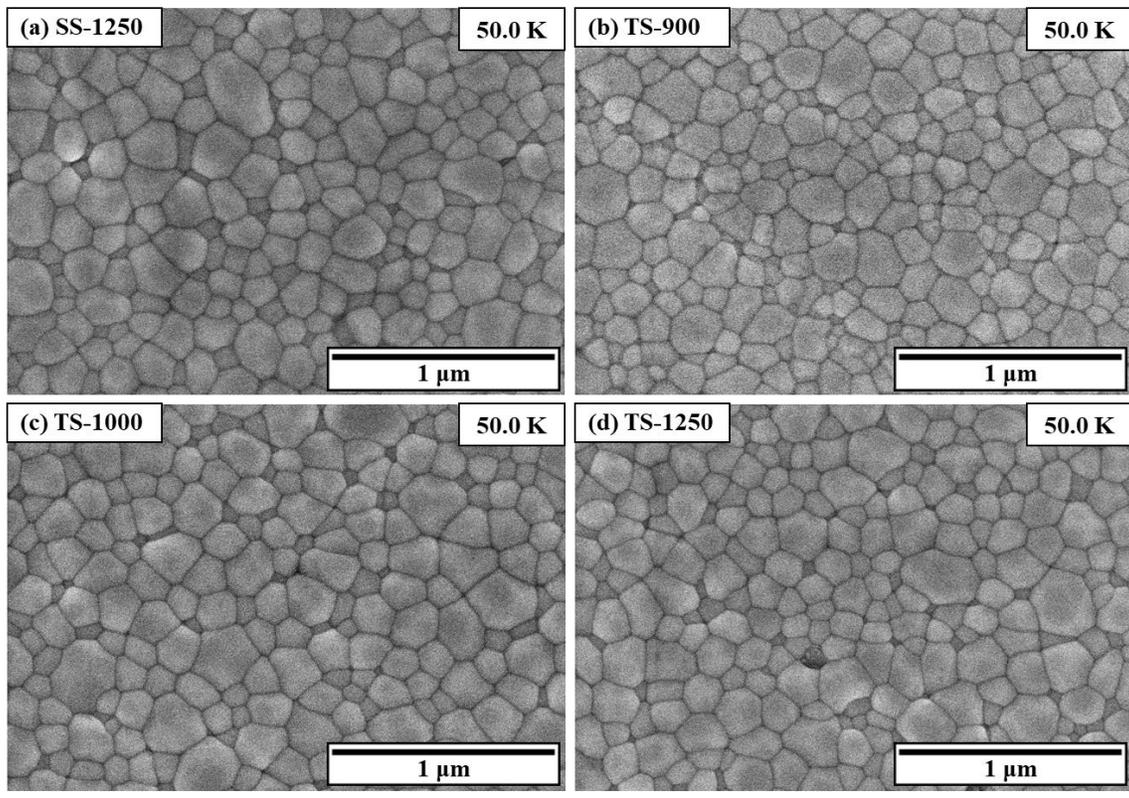


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Fig. 1

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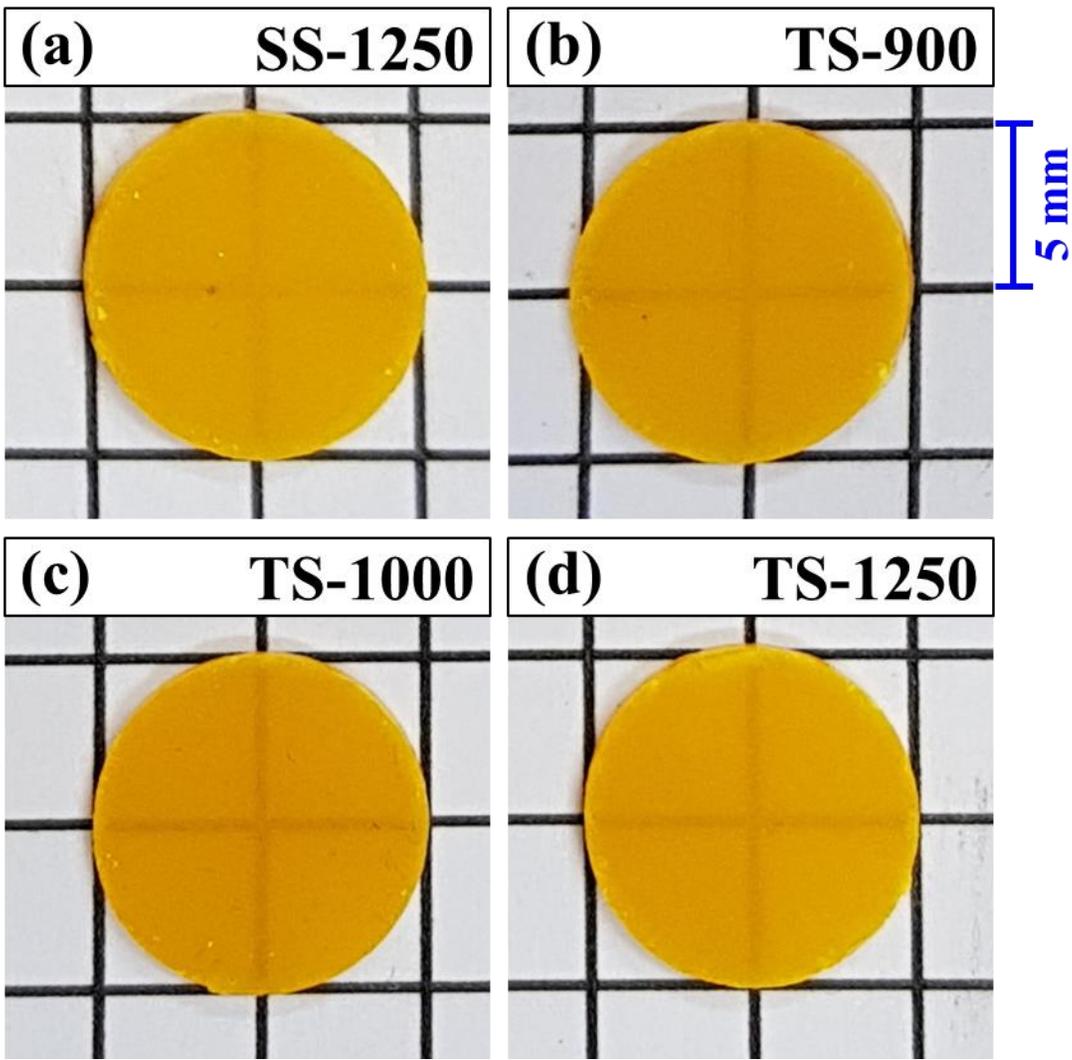


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Fig. 3

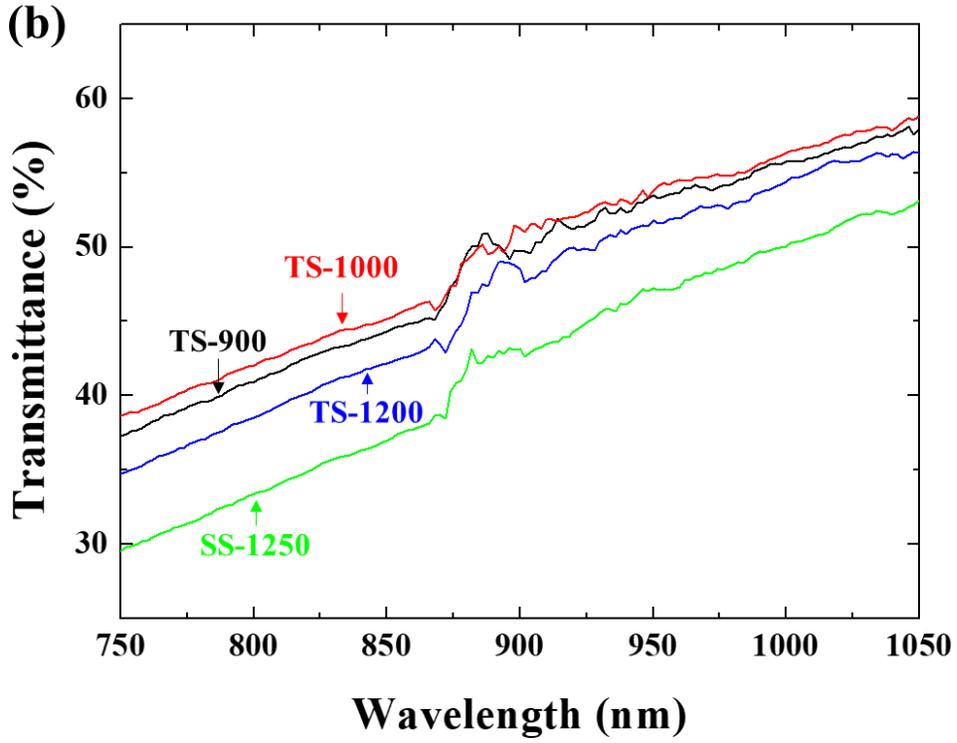
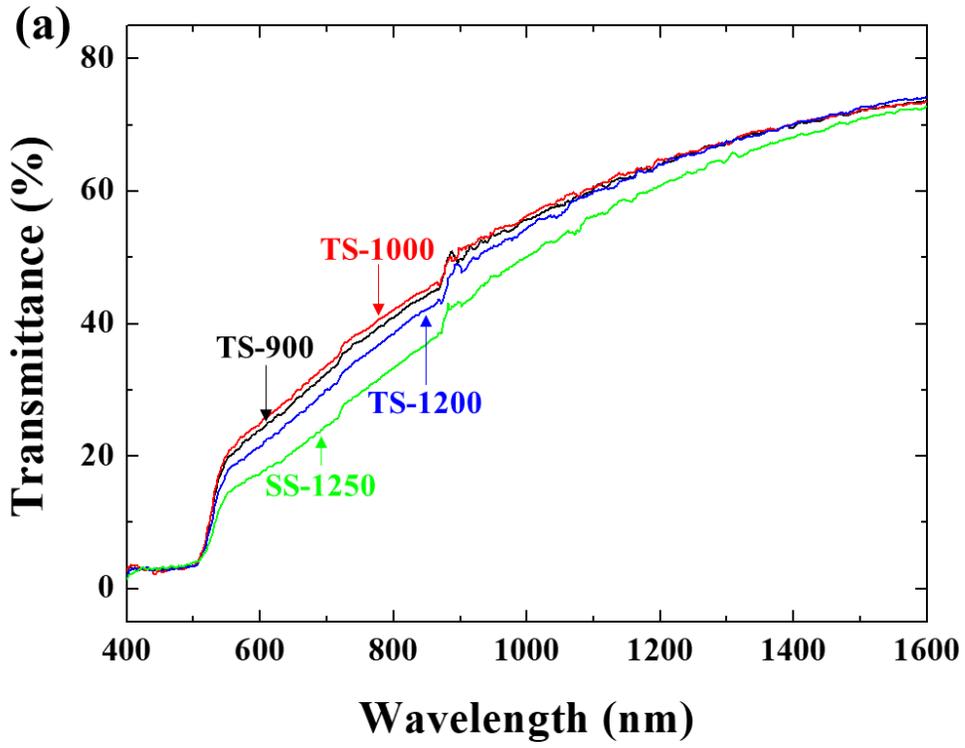
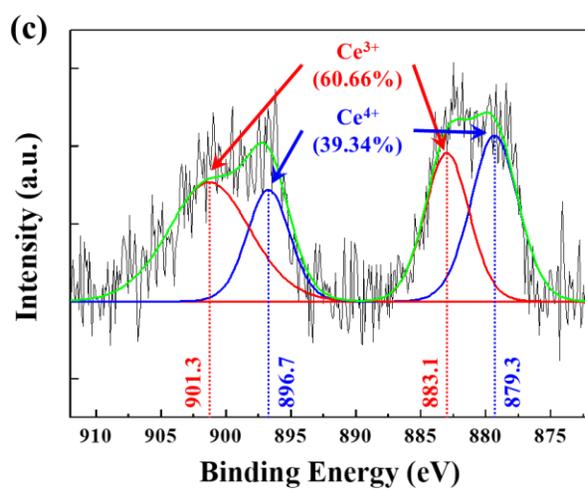
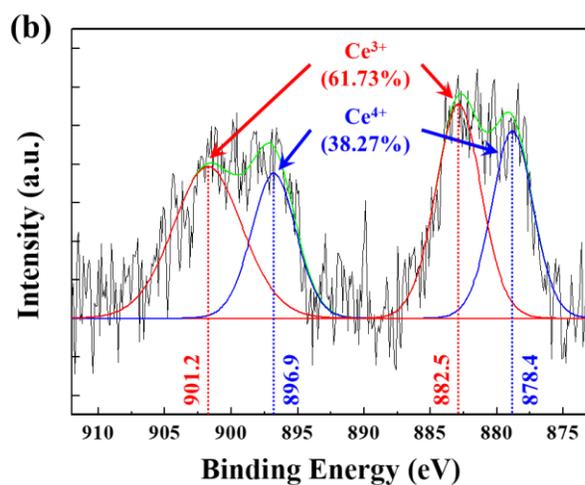
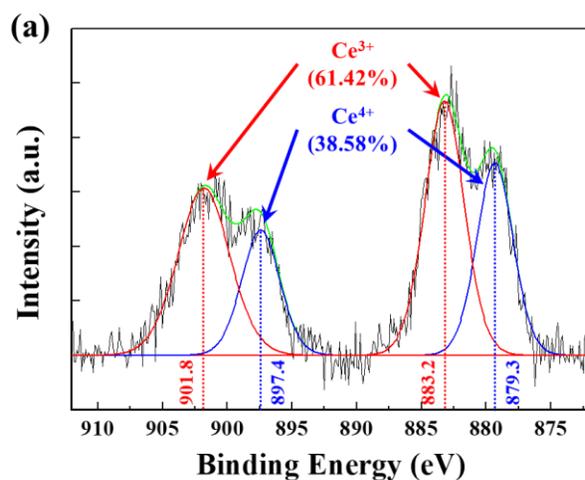


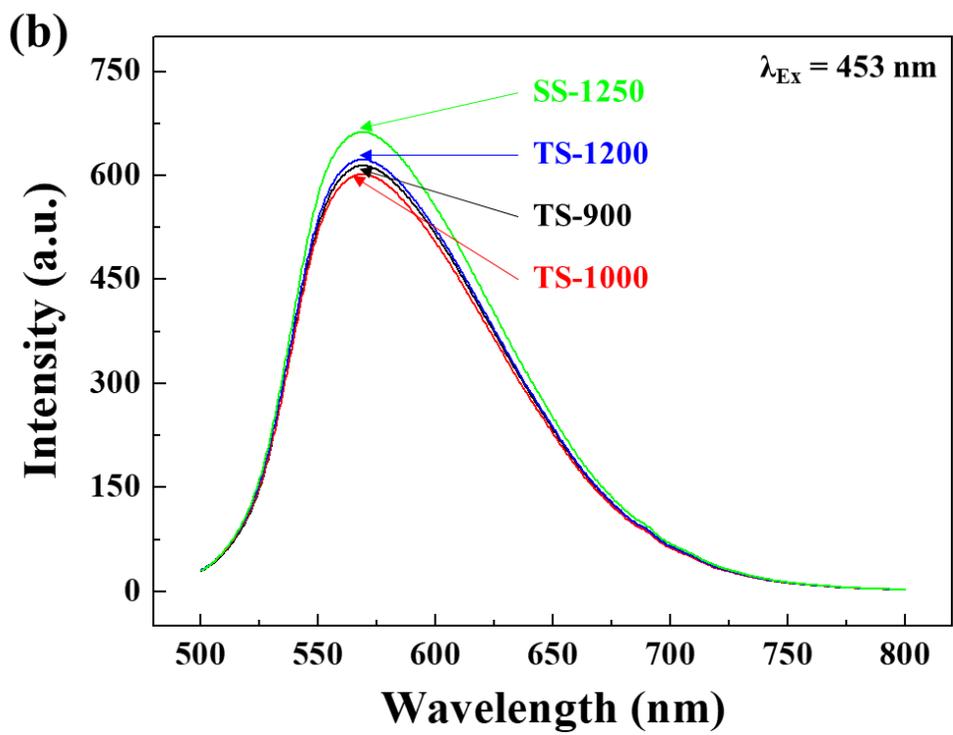
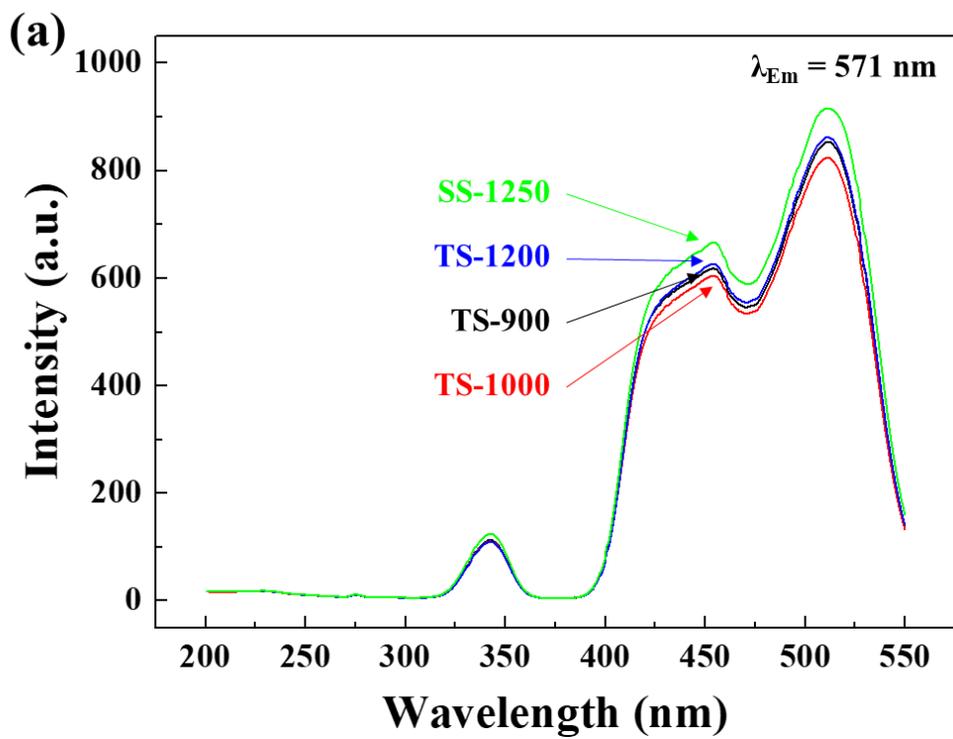
Fig. 4



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Fig. 5



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1 **Tables**

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9 Table 1. SPS conditions of Ce³⁺:(Gd,Lu)₃Al₅O₁₂ ceramics.

No.	Specimen name	SPS profile	Heating rate	Range (°C)	Holding stage
1	SS-1250	Single-step profile	50°C/min	600–1250	@ 1250°C for 20 min
2	TS-900	1 st step	50°C/min	600–900	@ 900°C for 30 min
		2 nd step	5°C/min	900–1250	@ 1250°C for 20 min
3	TS-1000	1 st step	50°C/min	600–1000	@ 1000°C for 30 min
		2 nd step	5°C/min	1000–1250	@ 1250°C for 20 min
4	TS-1200	1 st step	50°C/min	600–1200	@ 1200°C for 30 min
		2 nd step	5°C/min	1200–1250	@ 1250°C for 20 min

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Table 2. Microstructure parameters of SPSed $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ ceramics.

No.	Specimen name	Grain size	Pore size	Porosity
1	SS-1250	221 nm	81 nm	3.74%
2	TS-900	139 nm	43 nm	2.29%
3	TS-1000	163 nm	69 nm	1.63%
4	TS-1200	207 nm	72 nm	2.96%

1. Introduction

Lanthanide aluminum garnets ($\text{Ln}_3\text{Al}_5\text{O}_{12}$, LnAG), represented by $\text{Gd}_3\text{Al}_5\text{O}_{12}$ (GdAG) and $\text{Lu}_3\text{Al}_5\text{O}_{12}$ (LuAG), have high theoretical densities, and are attractive candidates for scintillator applications. LnAGs exhibit unique properties, such as wide bandgaps, high chemical and thermal stability, and a wide transparent range, which make them suitable for scintillator applications [1–4]. Scintillators should possess high theoretical density to stop X-rays. Yttrium aluminum garnet (YAG) shows relatively low X-ray stopping power due to its low density (4.53 g/cm^3). Among lanthanide elements with atomic weights higher than Y (89), Gd (157), and Lu (174) are considered suitable candidates for increasing the density of the garnet structure. However, Gd (0.21 ppm) and Lu (0.02 ppm) are less abundant in the earth's crust as compared to Y (1.39 ppm) [5]. As Gd is more abundant than Lu, it is considered to be a more suitable substitute for Y. Recently, transparent Gd-based LnAGs have been extensively investigated for scintillator applications. However, GdAGs thermally decompose into GdAlO_3 perovskite and Al_2O_3 above 1300°C ($\text{Gd}_3\text{Al}_5\text{O}_{12} \rightarrow 3\text{GdAlO}_3 + \text{Al}_2\text{O}_3$) [6]. In addition, GdAGs are doped with Ce^{3+} as an activator of yellow-emitting phosphors. The larger Ce^{3+} ions cause the destabilization of the garnet structure, thereby reducing its thermal decomposition temperature. In order to suppress their thermal decomposition, Ce-doped GdAGs are doped with Lu^{3+} ions, which are much smaller than Gd^{3+} ions [7]. These Lu^{3+} ions reduce the average Ln^{3+} size, and hence stabilize the garnet structure. In addition, Lu^{3+} doping retains the photoluminescence (PL) characteristics of Ce^{3+} and increases the theoretical density of $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$, thus enabling the development of advanced yellow-emitting phosphors [7].

Decreasing the sintering temperature can prevent the thermal decomposition of GdAG

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1 above 1300°C and improve its mechanical properties while providing a dense microstructure.
2 Among the various sintering techniques, spark plasma sintering (SPS) controlled by an
3 electric field and mechanical pressure is considered to be an efficient sintering approach for
4 GdAG [8,9]. In the SPS process, the electric field rapidly heats the mold and powder compact,
5 facilitating rapid densification by several microscopic mechanisms, including increased atom
6 diffusivity and softening of the particle surfaces, so that excessive grain growth is suppressed
7 at low temperatures [8,10]. Therefore, high densities and fine microstructures, which are the
8 advantages of SPS, improve the mechanical and optical properties of ceramics. Recently, the
9 fabrication and characterization of LuAG ceramics, such as Nd:YAG [11], LuAG [12], and
10 $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ [13], using the SPS process have been reported [11–13]. Sufficient
11 transparency can be obtained by conventional sintering, hot pressing (HP), and hot isostatic
12 pressing (HIP) [14–16]. However, the fabrication of transparent LnAG using the SPS process
13 has not been sufficiently studied. In our previous work [13], a $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ powder
14 was fully densified using the SPS process; however, a transparent compact was not obtained.
15 Therefore, further research is required to improve the transparency of SPS-prepared ceramics
16 while retaining the intrinsic merits of the SPS technique.

17 Various studies have reported the application of a two-step sintering profile to
18 conventional sintering, HP, and HIP techniques to improve the optical properties and control
19 the microstructure of ceramics [16–19]. Previous studies on the two-step sintering profile
20 suggested that preliminary experiments on microstructure control should be conducted to
21 improve the optical properties of ceramics [18,19]. Although the two-step sintering profile is
22 applied in different ways, the main objective is to achieve primary densification without
23 excessive coarsening at the higher first step temperature and full densification and removal

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1 of residual pores during the second step sintering. As a result, full densification can be
2 effectively achieved by dividing the sintering process into two steps with different objectives.
3 In addition, some researchers have reported that a two-step profile can be applied to improve
4 the optical properties of ceramics while retaining the intrinsic merits of the SPS process [20–
5 24]. In the SPS process, the two-step profile is applied in a slightly different way, because
6 the amounts of carbon contamination and residual pores inevitably increase with increased
7 sintering time. Considerable research [22,23] has been carried out on the microstructure and
8 optical properties of each step of the two-step profile. After primary densification without
9 excessive microstructure coarsening when the first step temperature is lower than that of the
10 second step, sufficient densification and excellent transparency could be achieved by
11 removing the residual defects at the second step temperature. In our previous work [24], in
12 transparent Y₂O₃ fabricated with a lower first step temperature, microstructural control and
13 improved optical properties could be achieved. On the basis of the previously reported results
14 regarding the two-step profile, it can be stated that by suppressing excessive microstructure
15 coarsening and separating the primary densification and full densification processes, the
16 microstructure of LnAG can be made fine and dense and its transmittance can be improved.

17 **In the present work, the main objective is to control the microstructure and improve the**
18 **optical properties by fabricating transparent Ce³⁺:(Gd,Lu)₃Al₅O₁₂ ceramics by applying a**
19 **two-step SPS profile. The two-step SPS profile is divided into first step (@ 900, 1000, and**
20 **1200°C) and second step (@ 1250°C) sintering, and the goals to be achieved in each step are**
21 **as follows. At a relatively low temperature of first step sintering, primary densification can**
22 **be achieved, which is effective in suppressing excessive microstructure coarsening. Next, in**
23 **second step sintering, full densification and the removal of residual pores can be**

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1 accomplished. The microstructure and optical properties of the $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$
2 ceramics were evaluated by focusing on the improvement of in-line transmittance by varying
3 the first step temperature.

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2. Experimental Procedure

2.1. Preparation of $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ powder

The rare-earth and aluminum sources used in this study were Ln_2O_3 ($Ln = Gd$ and Lu , 99.99%, Huizhou RUIER Rare-Chem. Hi-Tech, China), $Ce(NO_3)_3 \cdot 6H_2O$ (99.99%, Huizhou RUIER Rare-Chem. Hi-Tech, China), and alum ($NH_4Al(SO_4)_2 \cdot 12H_2O$, > 99%, Zhenxin Chemical Reagent Factory, China). A $Ln(NO_3)_3$ stock solution was prepared by dissolving the oxide powders in an optimum amount of nitric acid. To precipitate the carbonate precursor, a mixed solution containing stoichiometric amounts of the nitrates and alum was added dropwise to the ammonium bicarbonate solution. The precipitated carbonate precursor was dried in an oven for 24 h. The $[(Gd_{0.6}Lu_{0.4})_{0.99}Ce_{0.01}]_3Al_5O_{12}$ powder was obtained by the thermal decomposition of the precursor *via* calcination at 1100°C for 4 h in air. To suppress the oxidation of Ce^{3+} , a second calcination process was performed at 1000°C for 4 h in Ar/H_2 (5 vol% of H_2) [7,25].

2.2. Consolidation of $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ compacts using the SPS process

The $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ powder was consolidated using SPS equipment (LABOX-315, Sinter Land, Japan) under a vacuum atmosphere of 10 Pa. The powder was directly sintered without any pretreatment, using a graphite mold with a diameter of 10 mm. Heating was performed using a pulse pattern of 5:5 (on:off) in the AC mode, and the temperature was measured by installing a pyrometer in the non-through hole of the mold. The entire SPS process was divided into single-step and two-step profiles. For the single-step profile, the powder compact was heated to a sintering temperature of 1250°C at a heating rate of 50°C/min, and held for 20 min. In the case of the two-step profile, to achieve primary

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1 densification without excessive microstructure coarsening, first step sintering was performed
2 at 900, 1000, and 1200°C with a heating rate of 50°C/min and the sintering temperature was
3 held for 30 min. In the single-step profile, shrinkage started at approximately 1000°C. Thus,
4 the first step temperature for the two-step profile was considered to be 1000°C. To achieve
5 full densification and the removal of residual pores, further heating was conducted to reach
6 the second step temperature of 1250°C at 5°C/min. This temperature was held for 20 min. In
7 the entire SPS process, a mechanical pressure of 6.5 kN (80 MPa) was applied from the
8 beginning and was maintained until cooling. In addition, cooling was sequentially performed
9 at 1100°C for 10 min, 800°C for 5 min, and 25°C for 5 min. The SPS conditions and specimen
10 names are listed in Table 1.

12 2.3. Characterization

13 The annealing process was conducted at 1250°C for 10 h in air to remove the carbon
14 contamination and oxygen vacancies. Both of the surfaces of the $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$
15 compacts were mirror polished with 9, 3, and 1 μm diamond pastes. The transmittance of the
16 compacts was measured using a double-beam spectrophotometer (SolidSpec-3700DUV,
17 Shimadzu, Japan) equipped with an integrating sphere. PL measurements were conducted
18 using a spectrofluorometer (FP-6500, JASCO, Japan) equipped with a 60 mm diameter-
19 integrating sphere (Model ISF-513, JASCO, Japan) and a 150 W Xe lamp as the excitation
20 source. The X-ray photoelectron spectroscopy (XPS, AXIS-165, Shimadzu, Japan) profiles
21 of the samples were recorded at room temperature with $Al-K_{\alpha}$ radiation for excitation. The
22 binding energy was referenced to the C-1 s line of adventitious carbon. The mirror-polished
23 surfaces were thermally etched at 1100°C for 2 h in air. The polished and fractured surfaces

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1 of the specimens were examined using scanning electron microscopy (SEM, SU-8000,
2 Hitachi, Japan). The porosity of the specimens was determined by measuring their porous
3 areas from the SEM images. The grain and pore sizes of the specimens were calculated by
4 measuring their pore sizes and average cross-sectional areas per grain. The grain size was
5 apparent in the cross section; therefore, it was multiplied by 1.225 to determine the actual
6 grain size [26].

7

3. Results and Discussion

3.1. Shrinkage behavior and microstructure

In our previous work, we successfully developed a stable $(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ garnet structure, which could be well indexed to the cubic structure of GdAG [13]. Single-step and two-step SPS profiles were applied to fabricate transparent $(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ ceramics with structural stabilization. The SPS curves (temperature, displacement, and pressure over time) of the single-step profile (SS-1250) are shown in Fig. 1 (a). As can be observed from the displacement curve, the ceramics showed thermal expansion when heated to approximately 1000°C. In addition, shrinkage began to occur at this temperature. No further shrinkage occurred during the holding period at 1250°C, and the shrinkage was sufficient. Based on the SPS curves of the single-step profile (SS-1250), a two-step profile (TS-1000) was designed, as shown in Fig. 1 (b). At a relatively low first step temperature of 1000°C, the powder compact was rapidly heated at 50°C/min to suppress excessive microstructure coarsening, and primary densification was performed for 30 min [20,22,24]. In addition, during the first step holding time, as the shrinkage began and did not occur rapidly, a small amount of residual pores could be expected. Owing to the achievement of primary densification, including a small amount of residual pores in the first step sintering, the shrinkage of the two-step profile was completed at 1200°C, which is approximately 50°C lower than that 1250°C of the single-step profile. However, the amount of shrinkage was almost the same. This improvement in the sintering behavior of the compacts by the two-step profile enabled microstructure control and improved the optical properties.

Fig. 2 shows the SEM images of the cross sections of the SPSed $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ compacts after annealing. All specimens were densified at the final sintering temperature of

1 1250°C. However, the microstructures for the two SPS profiles differed in terms of grain size,
2 pore size, and porosity. The microstructural parameters (grain size, pore size, and porosity)
3 calculated from the SEM images are summarized in Table 2. Applying the two-step profile
4 made it possible to significantly lower the porosity at the same sintering temperature. All
5 two-step SPSed specimens showed lower porosity than that of the single-step SPSed
6 specimen (SS-1250) (3.74%). In particular, the TS-1000 exhibited a porosity of 1.63%,
7 indicating that a significant reduction in porosity was possible by applying the two-step SPS
8 profile. The significant decrease in the porosity of the two-step SPSed specimens was due to
9 improvement in their shrinkage behavior, i.e., fewer residual pores and a lower shrinkage-
10 completion temperature, as shown in Fig. 2. In addition, as the first step temperature in the
11 two-step profile was reduced, the grain size decreased gradually from 207 to 139 nm, and the
12 pore size decreased from 72 to 43 nm. This microstructural change was due to the
13 microstructure control of the two-step profile [18,19]. In this study, microstructure control
14 using the two-step profile was expected to improve the optical properties as well.

15 16 3.2. Optical appearance and transmittance

17 The optical appearances of the $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ compacts after annealing are shown
18 in Fig. 3. The optical appearances and transparency of the annealed specimens placed on the
19 grid can be easily compared. SS-1250 exhibited the lowest optical transparency among all
20 specimens. Applying the modified two-step profile improved the optical appearance of the
21 compacts. For two-step SPSed specimens, the optical appearance improved with a decrease
22 in the heating rate at the second step. However, the most significant improvement was
23 observed at the first step temperature of 1000°C. This indicates that a decrease in the heating

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1 rate at the critical temperature for densification had a more significant effect than simply
2 reducing the heating rate to improve the optical appearance. Therefore, at the first step
3 temperature of 1000°C, porosity was lowest and the optical appearance also improved the
4 most. The microstructure and optical appearance analysis results indicate that the TS-1000
5 specimen showed the highest transmittance among all specimens investigated in the present
6 work.

7 Fig. 4 shows the in-line transmittance (ILT) curves of the sintered $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$
8 compacts after annealing. Significant light absorption was in the range of 420–500 nm.
9 According to the reported results [27], well-fabricated $Lu_{2.7}Gd_{0.3}Al-O_{12}$ ceramics exhibited
10 excellent transmittance above 250 nm. In the present work, since light absorption by Ce^{3+}
11 occurred at less than 500 nm, transmittance decreased rapidly. Owing to the light absorption
12 due to the $4f \rightarrow 5d_2$ and $4f \rightarrow 5d_1$ transitions of Ce^{3+} at 340 nm and over a wavelength range
13 of 420–500 nm, respectively, a strong light absorption band was detected [28]. The optical
14 transmittance of the specimens showed the same trend as that of their optical appearance. At
15 the same sintering temperature of 1250°C, all two-step SPSed specimens showed improved
16 transmittance as compared to the single-step SPSed specimen. The TS-1000 specimen
17 showed the most improved ILT of 56.5% at 1000 nm as compared to that (50.1%) of the SS-
18 1250 specimen. In transparent ceramics, the area of the grain boundary also affects
19 transmittance; however, porosity is the most critical factor [29]. In the case of the TS-1000
20 specimen, the first step temperature was 1000°C, at which shrinkage began, and porosity
21 decreased significantly from 3.74% (SS-1250) to 1.63% (TS-1000). This decrease in porosity
22 had a significant effect on the transmittance of the ceramic. In addition, as can be observed
23 from Table 2, the porosity of the specimens showed a trend similar to that shown by the

1 optical transmittance. The TS-1000 specimen showed slightly reduced grain and pore sizes
2 and significantly reduced porosity as compared to the SS-1250 specimen. The decrease in
3 porosity, which had the most critical effect on transmittance, resulted in the most noticeable
4 improvement in the transmittance of the TS-1000 specimen. (Gd,Lu)₃Al₅O₁₂:Ce ceramics
5 with a composition similar to that of the ceramics prepared in this study were fabricated by
6 conventional sintering at 1750°C for 4 h under a vacuum atmosphere after cold isostatic press
7 at 240 MPa [14]. As a result, an ILT of approximately 72% was achieved at 1000 nm,
8 showing excellent optical properties. Although there have been reports of preparing garnet
9 materials with full densification and high transmittance by conventional sintering, it is
10 difficult to achieve high transmittance with the SPS method. In a previous study, Nd:YAG
11 ceramics were fabricated using the reactive-SPS method by applying a two-step heating
12 profile [30]. The Nd:YAG powder was heated at 100°C/min to the first step temperature of
13 1000°C with an applied pressure of 70 MPa and at 15°C/min to the second step temperature
14 of 1350°C, which was maintained for 5 min. However, an ILT of approximately 36% was
15 obtained at 1000 nm, and excellent optical properties were not achieved. In this study,
16 although the ILT was not close to the theoretical value, the transmittance could be improved
17 through the application of the two-step profile and microstructure control.

19 3.3. Oxidation state and PL characteristic

20 XPS measurements were conducted to investigate the oxidation states of the Ce dopant,
21 and the results of the powder, single-step profile (SS-1250), and two-step profile (TS-1000)
22 are summarized in Fig. 5. The red lines represent the spectra of Ce³⁺ ions and the blue lines
23 represent the spectra of Ce⁴⁺ ions. The fractions of the Ce³⁺ and Ce⁴⁺ ions were calculated

1 from the areas of their spectra. For comparing the as-synthesized powder with the compacts
2 sintered in the single-step and two-step profiles, the fraction of Ce^{3+} in the as-synthesized
3 powder was required. The fraction of Ce^{3+} in the powder was 61.42%, as shown in Fig. 5 (a).
4 The Ce^{3+} fraction of the SS-1250 specimen was 61.73%, which is almost the same as that of
5 the synthesized powder. However, because of slight oxidation, the TS-1000 specimen
6 showed a Ce^{3+} fraction of 60.66%. As the SPS process provides an oxidizing atmosphere of
7 graphite components, oxidation occurred in the two-step profile with a long sintering time,
8 and the fraction of Ce^{3+} decreased slightly. The slightly decreased Ce^{3+} fraction of the two-
9 step profile affected its PL characteristics along with the microstructure.

10 Fig. 6 (a) shows the PL excitation spectra of the $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ compacts after
11 annealing. PL excitation measurements were performed to investigate the wavelength-
12 dependent excitation when 571 nm light was emitted. Excitation bands were detected at
13 approximately 342, 453, and 506 nm, corresponding to the excitation of Ce^{3+} [31,32]. The
14 excitation peak at approximately 342 nm correspond to the transition of Ce^{3+} from the ground
15 state ($2F_{5/2}$) to the T_{2g} state. Excitation peaks at approximately 453 and 506 nm corresponded
16 to the transition from the ground state to the E_{2g} state [31,32]. The SS-1250 specimen
17 exhibited significantly higher PL excitation intensity than did the two-step profile specimens.
18 Independent of the first step temperature, the PL excitation of the TS-1000 specimen intensity
19 was the lowest. Their porosity strongly influenced the transmittance of the specimen, and the
20 two-step profile showed better results than did the single-step profile. However, the PL
21 excitation characteristics showed an opposite trend. First, the fraction of Ce^{3+} (Fig. 5) directly
22 affected the PL excitation characteristics of the specimens. Because the PL excitation was
23 caused only by Ce^{3+} [31,32], the fraction of Ce^{3+} present in the $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ ceramics

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1 was a very important factor. Next, the grain size of the SS-1250 specimen was the largest at
2 221 nm, which decreased gradually from 207 to 139 nm with a decrease in the first step
3 temperature. Owing to its large grain size and small grain boundary area, the single-step
4 profile affected the PL excitation characteristics of the compacts more than the two-step
5 profile did [33,34]. Fig. 6 (b) shows the PL emission spectra of the $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$
6 compacts after annealing. The wavelength-dependent emission of the compacts under
7 excitation by a wavelength of 453 nm was investigated. The PL emission characteristics of
8 the compacts showed the same trend as that shown by the PL excitation characteristics. The
9 full widths at half maximum values were almost the same for all specimens. This indicates
10 that the crystallinity and light clarity of all specimens were almost the same and that the two-
11 step profile did not affect the PL emission characteristics.

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1 **4. Conclusions**

2 In this study, a two-step SPS profile was employed to improve the optical properties of
3 $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ ceramics as attractive yellow-emitting phosphors. The shrinkage curve
4 of the two-step profile showed a significant reduction in porosity from 3.74% to 1.63% at the
5 first step temperature of 1000°C, at which shrinkage began. As the first step temperature
6 decreased, the microstructure control of the two-step profile refined the microstructure of the
7 compacts by reducing the grain and pore sizes. As a result of the significant reduction in
8 porosity in the two-step profile, transmittance improved from 50.1% to 56.5% at 1000 nm.
9 **On the other hand, oxidation occurred owing to the two-step profile's long sintering time,**
10 **and the fraction of Ce^{3+} decreased slightly.** Therefore, the two-step profile did not affect the
11 ceramics' PL excitation and emission characteristics.

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1 **Figure captions**

2
3 Figure 1. SPS curves of the SPSed $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ ceramics (a) single-step SPS (SS-
4 1250) and (b) two-step SPS (TS-1000).

6 Figure 2. SEM images of the cross sections of the SPSed $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ ceramics.

8 Figure 3. Optical appearances of the SPSed $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ ceramics under the
9 conditions listed in Table 1.

11 Figure 4. (a) Transmittance curves of the SPSed $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ ceramics after
12 annealing; (b) the curve magnified over the wavelength of 750–1050 nm.

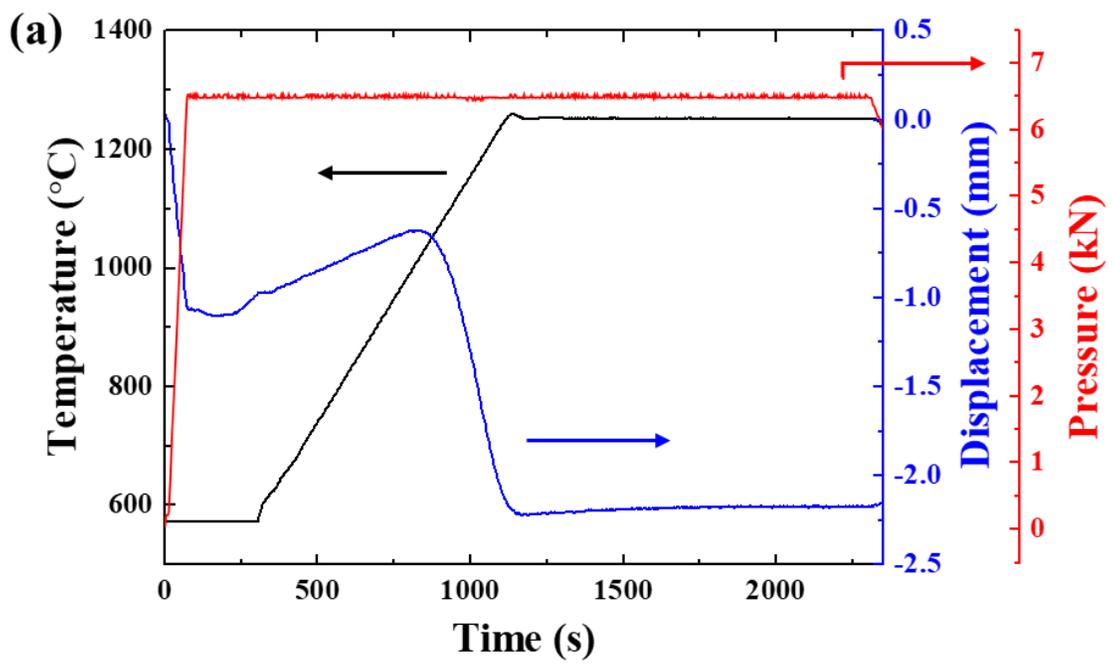
14 **Figure 5. XPS profiles of the (a) $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ powder, (b) single-step SPSed
15 compact (SS-1250), and (c) two-step SPSed compact (TS-1000).**

17 Figure 6. (a) PL excitation and (b) PL emission spectra of $\text{Ce}^{3+}:(\text{Gd,Lu})_3\text{Al}_5\text{O}_{12}$ ceramics
18 with different SPS conditions after annealing.

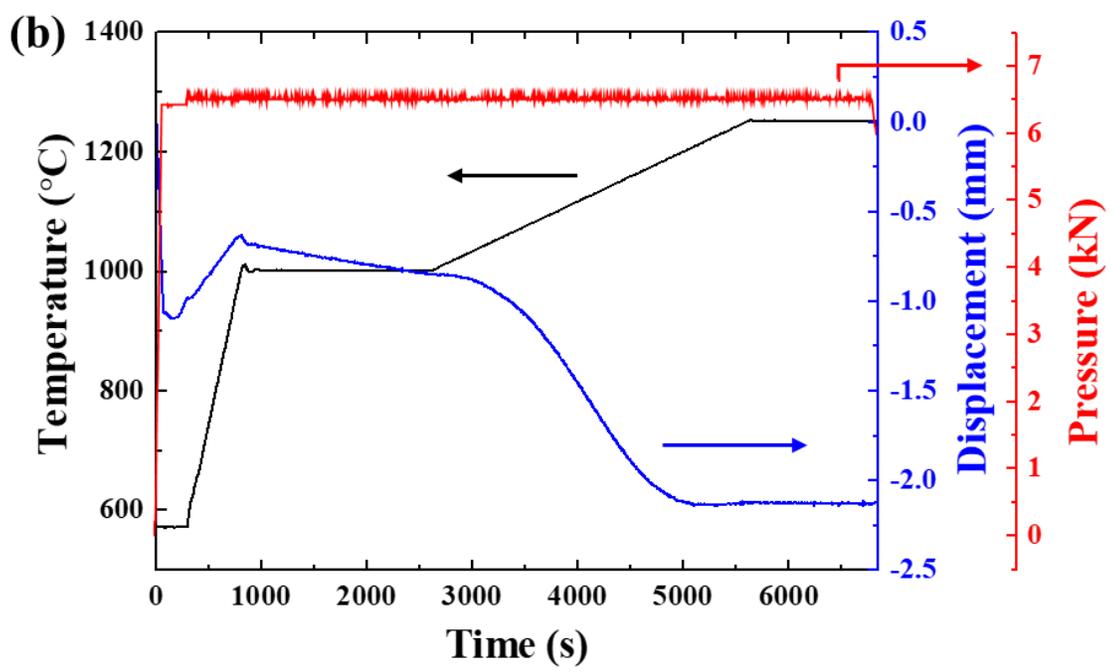
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1 **Figures**

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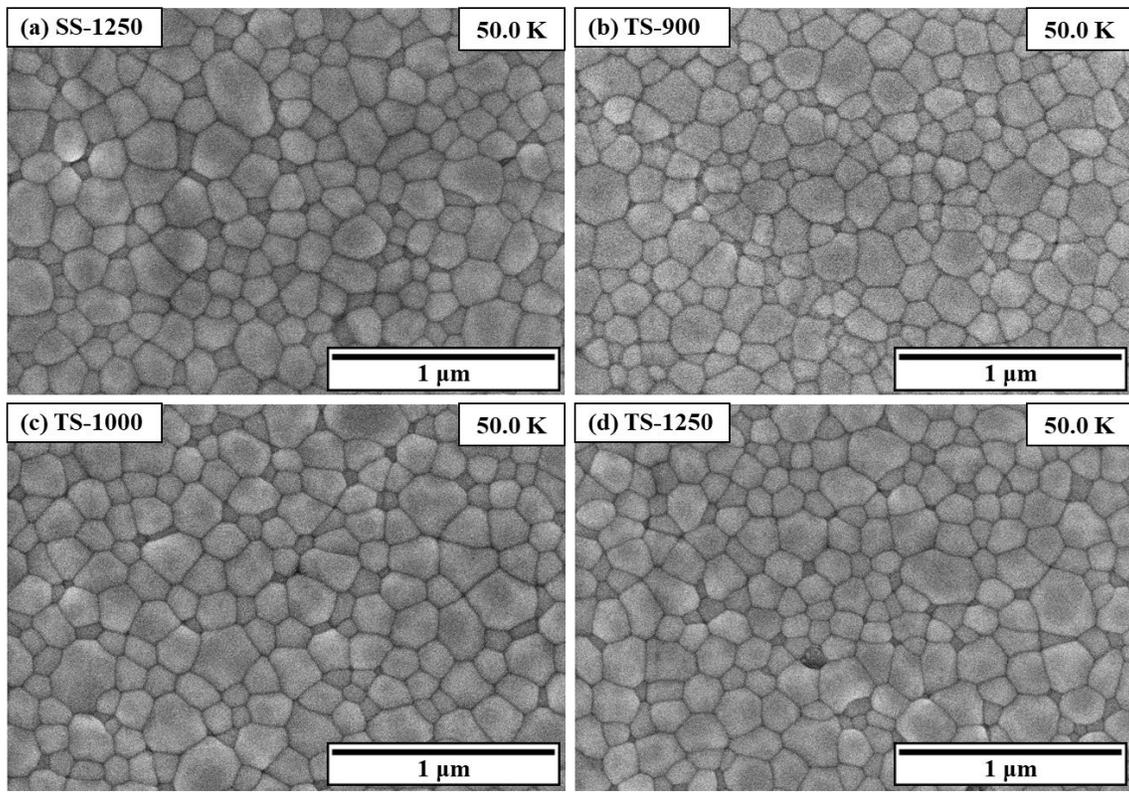


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Fig. 1

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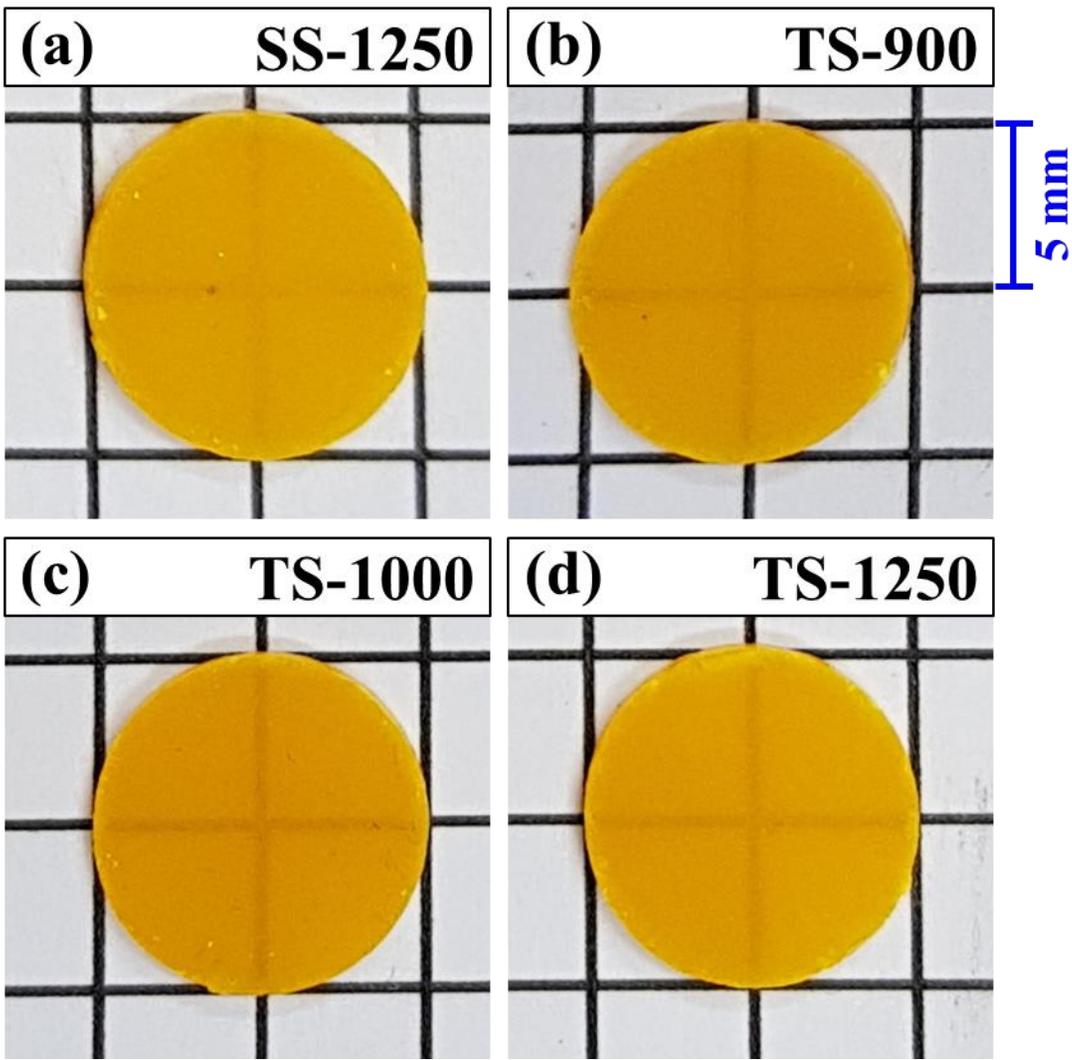


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Fig. 2

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Fig. 3

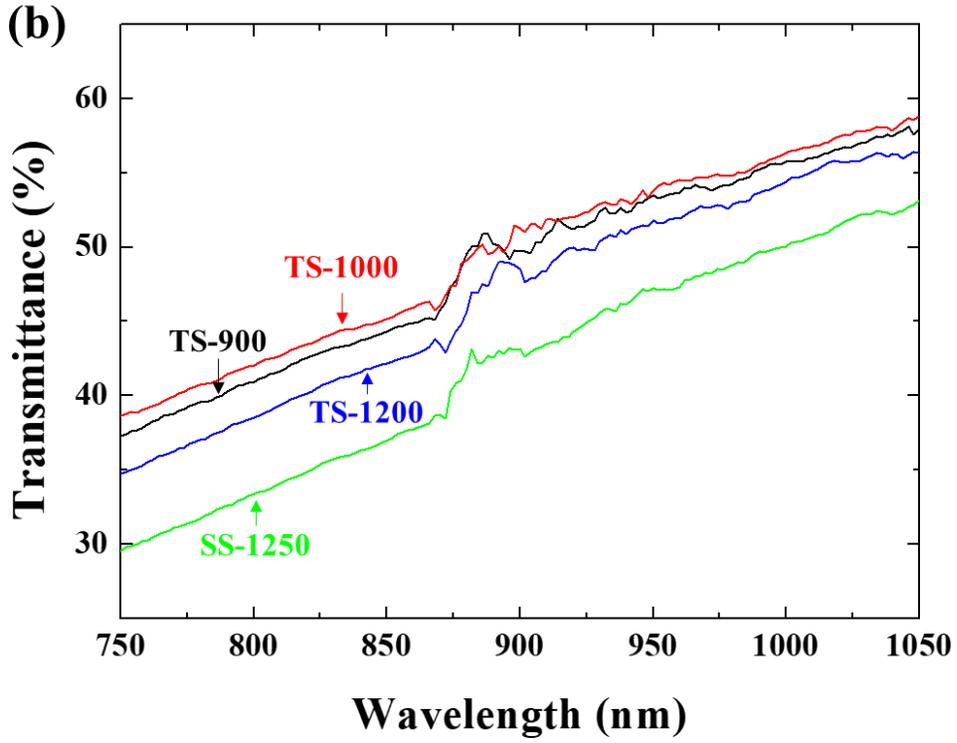
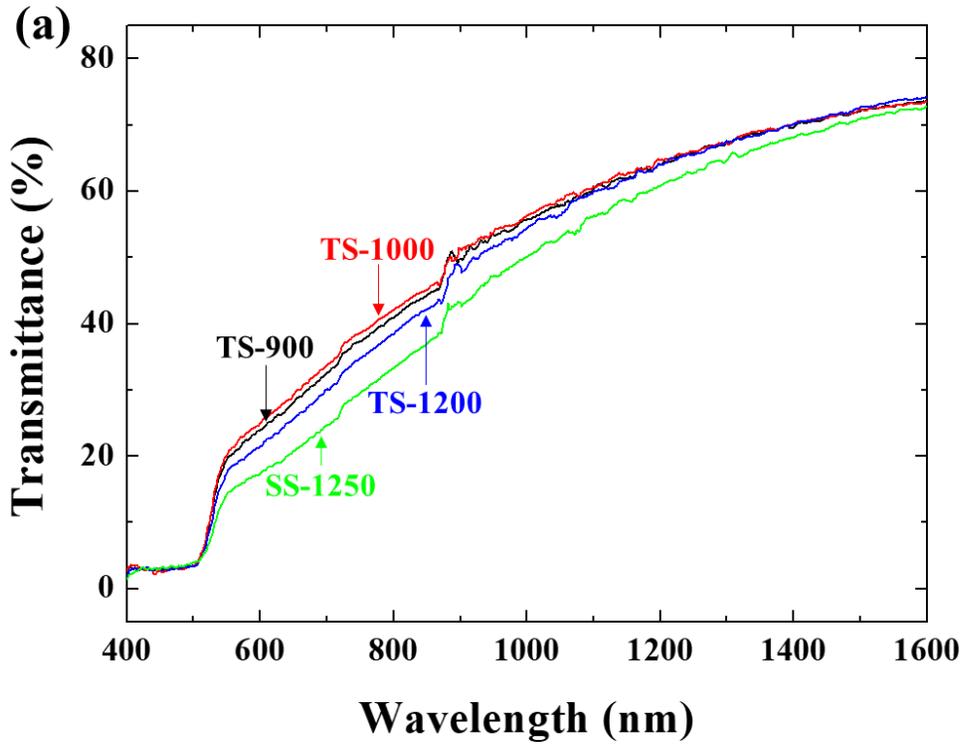
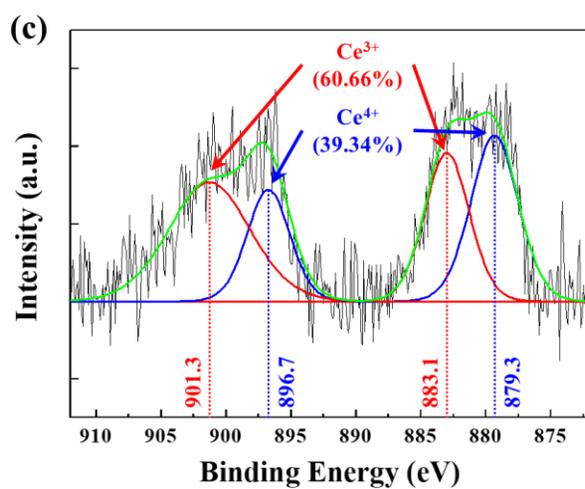
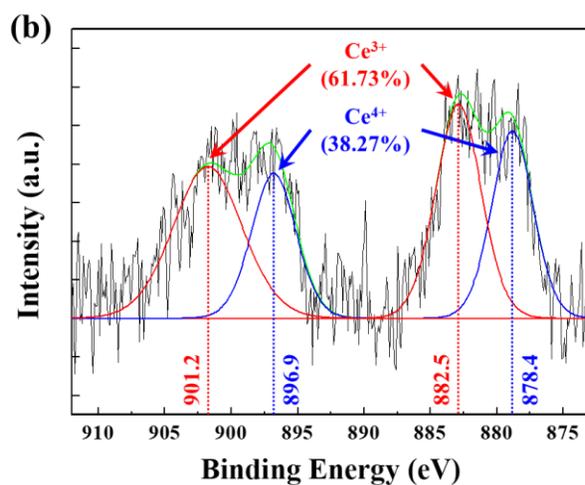
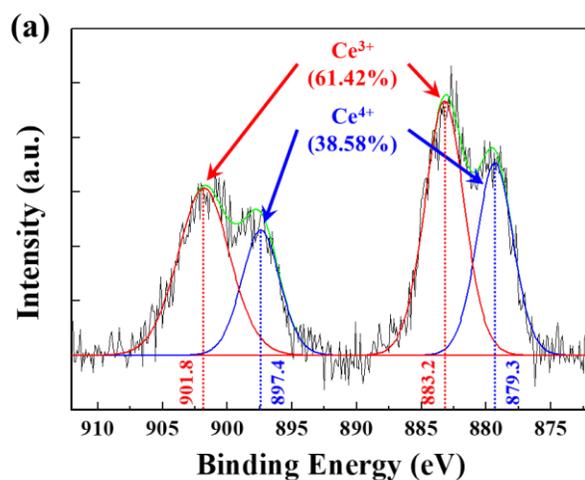


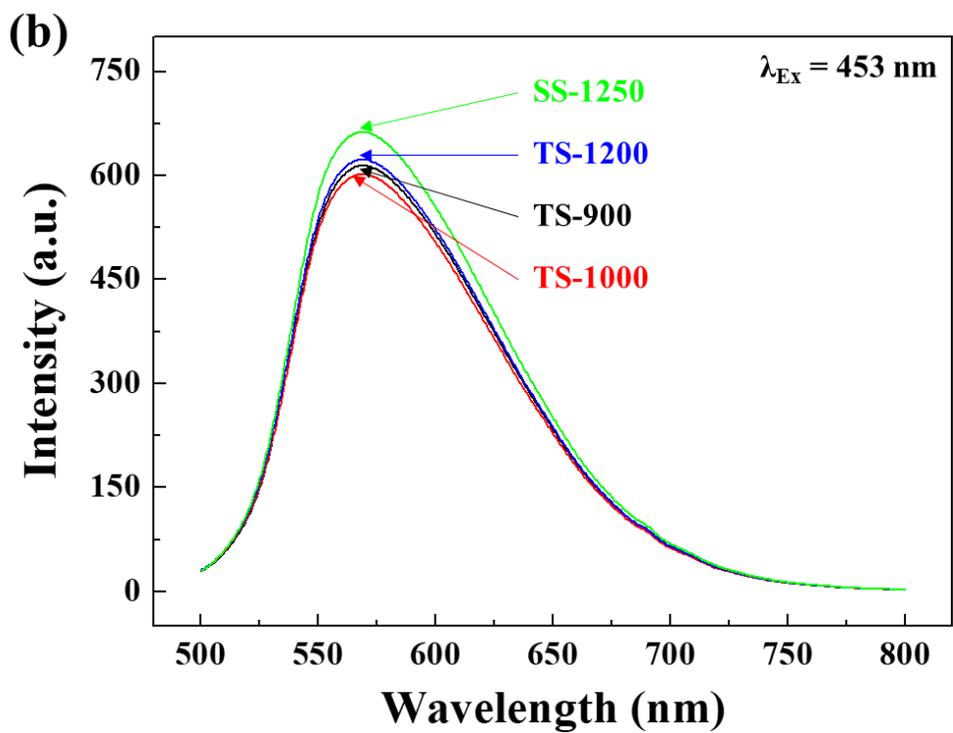
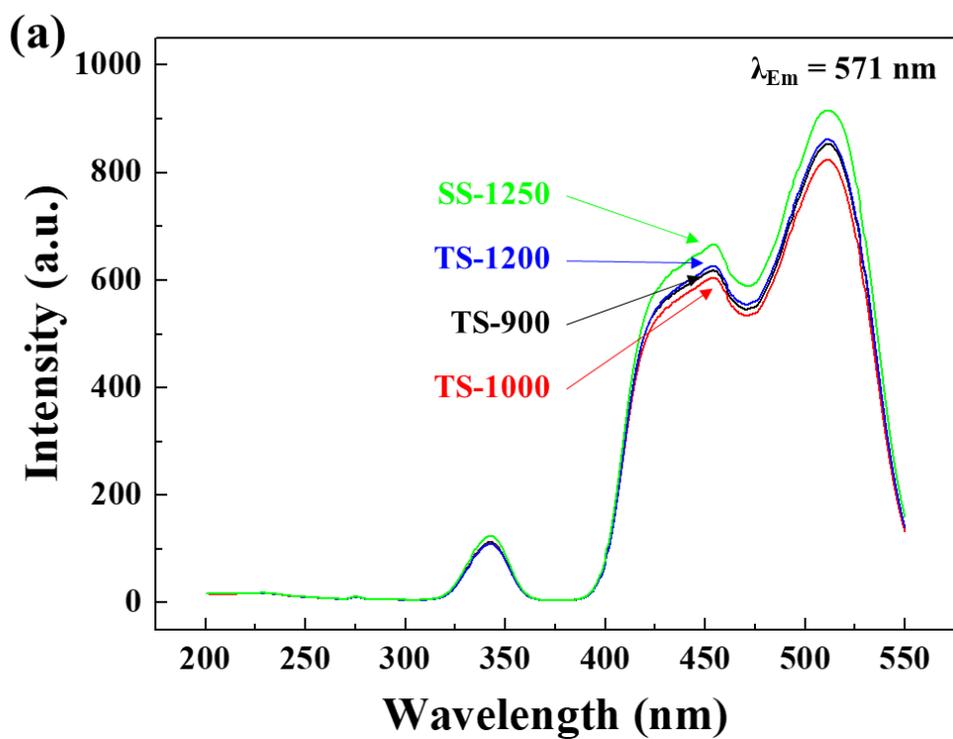
Fig. 4



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Fig. 5



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1 **Tables**

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9 Table 1. SPS conditions of $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ ceramics.

No.	Specimen name	SPS profile	Heating rate	Range (°C)	Holding stage
1	SS-1250	Single-step profile	50°C/min	600–1250	@ 1250°C for 20 min
2	TS-900	1 st step	50°C/min	600–900	@ 900°C for 30 min
		2 nd step	5°C/min	900–1250	@ 1250°C for 20 min
3	TS-1000	1 st step	50°C/min	600–1000	@ 1000°C for 30 min
		2 nd step	5°C/min	1000–1250	@ 1250°C for 20 min
4	TS-1200	1 st step	50°C/min	600–1200	@ 1200°C for 30 min
		2 nd step	5°C/min	1200–1250	@ 1250°C for 20 min

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Table 2. Microstructure parameters of SPSed $Ce^{3+}:(Gd,Lu)_3Al_5O_{12}$ ceramics.

No.	Specimen name	Grain size	Pore size	Porosity
1	SS-1250	221 nm	81 nm	3.74%
2	TS-900	139 nm	43 nm	2.29%
3	TS-1000	163 nm	69 nm	1.63%
4	TS-1200	207 nm	72 nm	2.96%

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: