Strong thermal stability of Lu₃Al₅O₁₂:Ce³⁺ single crystal phosphor for laser lighting

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A B S T R A C T
Green-yellow single crystal Lu₃Al₅O₁₂:Ce³⁺ (LuAG:Ce) as a color conversion phosphor for high-power laser lighting was grown through a floating zone method by an image furnace. It showed an excellent thermal stability, a lower quantum efficiency (QE), and a broader photoluminescence excitation (PLE) spectrum compared with the polycrystalline powder phosphor. The thermal stability was explained by a decrease of intrinsic defects and a less phonon generation at high temperature, confirmed by PLE spectra and temperature-dependent Raman spectra, respectively. To evaluate its feasibility for high-power laser lighting, the single crystal LuAG:Ce was applied to a 5 W blue laser diode with a remote-phosphor structure, and thus it reached a lower equilibrium temperature at 62 °C after 40 min operating in comparison with the polycrystalline powder phosphor (95 °C). Thus, the single crystal LuAG:Ce phosphor can achieve the extremely stable light emission without an efficiency loss under the high-power density of blue laser diode.

1. Introduction
Solid-state white lighting devices such as phosphor-conversion white-laser diodes (pc-WLDs) [1–3] and white-light-emitting diodes (pc-WLEDs) [4] are considered to be good general lighting devices due to the brightness, high efficiency, long-term reliability, and low applied voltage. For the two types, the devices based on the blue LEDs currently suffer a loss in external quantum efficiency (EQE), a shift in the peak emission wavelength, and a broadening of the emission spectrum due to an increase in the temperature of the device as increasing the operating current [5,6]. They make high-power devices difficult to achieve using single LEDs as the excitation source. On the other hand, the output power and EQE of LDs increase linearly with the operating current, so that LDs are capable of droop-free light emission, and maintain the color stability of the laser emission with higher power density by a factor of 2.5 and more visibility range of 600 m than the LEDs under much higher operating current [7–10]. Thus, the blue LDs are more attractive as an excitation source for new high-power white lighting applications than the blue LEDs. In the white-laser lightings combining the blue LD and one or more phosphor compositions, the extremely intense laser irradiation is focused on the phosphor and excites it, so that the phosphor-converted visible light and the scattered blue light generate white light. The focused laser irradiation on the mixture of phosphor powders and organic silicon resin causes a significant decrease in luminous efficacy due to the oxidation of silicon resin and surface of phosphor powders, shift in the peak emission wavelength and broadening of the emission spectrum due to the locally-generated high heat. Herein, it should be noted that a thermally stable phosphor material and a thermal designed structure are extremely important to maintain the EQE and the color stability of white-laser lighting devices under much higher operating current.

Our previous work has shown that the single crystal Y₃Al₅O₁₂:Ce³⁺ (YAG:Ce) garnet phosphor showed a higher thermal stability at 200 °C of about 97% and a lower heating temperature of 79 °C under a 5 W blue laser diode compared with those of the polycrystalline powder phosphor (89% and 153 °C, respectively) [11]. The high thermal conductivity of single crystal YAG:Ce garnet phosphors (> 10 W/m-K) [12] prevents a local heating from an intense blue irradiation and provides a good thermal stability at a higher temperature. Thus, the single crystal garnet phosphor is suggested as an alternative to the polycrystalline powder phosphor for the high-power white-laser lighting. To make full-spectral white light, the green LuAG:Ce was used as a color compensator for poor green region in the yellow YAG:Ce phosphor. The drawbacks of the green LuAG phosphor are poor yellow-red spectral region and expensive raw material.
Nevertheless, there are few alternatives for high green emission and blue absorption: \( \text{BaSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+} \) with lower thermal stability, \( \beta\)-\( \text{SiAlON}:\text{Eu}^{2+} \) sintered in much higher nitrogen pressure of about 5 bar and temperature of about 2000 °C.

In this work, we presented a single crystal \( \text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+} \) (LuAG:Ce) with an excellent thermal stability and an enhanced quantum efficiency as a color conversion phosphor for the high-power white-laser lighting. The reason on the positive thermal stability was investigated in terms of a decrease of intrinsic defects and a less phonon generation at high temperature, confirmed by PLE spectra and temperature-dependent Raman spectra, respectively. Furthermore, its feasibility for the high-power white-laser lighting was evaluated with remote-phosphor structure under a 5 W blue LD in comparison with the polycrystalline powder phosphor.

2. Experimental details

The single crystal LuAG:Ce phosphor was grown through a floating zone method by an image furnace. To prepare the single crystal, the seed rods were formed by a uniaxial press under 350 kgf/cm² with the stoichiometric mixture ratio of starting materials with a high purity of 99.99%: \( \text{Lu}_2\text{O}_3, \text{Al}_2\text{O}_3 \) and \( \text{Ce}_2\text{O}_3 \) with a molar concentration of 1 mol% with respect to one of Lu mole. To increase the packing density of primarily formed rods, they were secondly pressed by using a cold isostatic press under 2000 kgf/cm². The feed rods were then sintered at 1500 °C for 5 hours under a reducing atmosphere (5% \( \text{H}_2/\text{N}_2 \) mixture gas).

Two sintered LuAG:Ce rods were mounted by using a platinum wire so as to be perfectly aligned in the image furnace, and then each rod was located on the top and bottom, respectively. Two halogen lamps with 3500 W maximum power were used as a heating source, and the intense lights were focused on the center of image furnace by a gold-coated ellipsoidal mirror. The top feed rod was heated and melted by the focused lights under an operating power of 1900 W for each lamps, and then single crystal was grown on the bottom rod under the following growth conditions: (1) growth rate of 1 mm/hour, (2) clockwise rotation speed of 15 RPM for the top feed rod, (3) counterclockwise rotation speed of 10 RPM for the bottom rod, (4) ambient gas of nitrogen. The obtained as-grown LuAG:Ce single crystal sample showed a cylindrical morphology with approximately 8 mm in diameter and 30 mm in length. The single crystal was cut perpendicularly to the growth orientation with a thickness of 5 mm, and then the surfaces were polished.

The obtained single crystal were identified through X-ray diffraction (XRD) technique (Cu Kα, D/Max 2500) with Ni-filtered Cu Kα radiation, scanning from 10° to 80° with 20 step of 0.02°. The XRD patterns of single crystal and powder phosphors were measured, the powder sample showed the same with the standard powder diffraction pattern, and the single showed the only [100] growing orientation consistent with JCPDS Card (No. 73-1368) [13,14]. The photoluminescence (PL), photoluminescence excitation (PLE), temperature-dependent PL spectra, quantum efficiencies (QE) and absorbances were obtained using an integrating sphere attached DARS\( \text{A} \) PRO-5200 fluorescence spectrophotometer equipped with a 200 W xenon lamp as an excitation light source. To determine the cause of positive thermal stability for the single crystal, temperature-dependent Raman spectra were measured by H-Peak Seeker Pro-785 Raman systems with 300 mW InGaAs line laser with 785 nm wavelength. The temperature-dependent PL and Raman spectra were measured on the same heater. To evaluate its feasibility for high-power laser lighting, it was mounted at a distance of 24 mm far from the laser source, and then irradiated by a 5 W blue LD with an emission peak wavelength of 445 nm. The output optical power of blue LD was measured by a RM-6600 optical power meter of Laser Probe Inc. at 25 °C, and thus it showed the output power of 5 W under an operating voltage 4.7 V and forward-bias current of 3.6 A. All transmitted lights were collected in an integrated sphere, and their correlated color temperatures (CCT) were fixed at 5700 K by adjusting phosphor thickness, and then thermograph spectra were measured by IR-TCM 384 thermograph camera (JENOPTIK).

3. Results and discussion

Fig. 1 shows 520 nm-monitored PLE and 445 nm-excited PL spectra of (a) the single crystal and (b) the polycrystalline powder phosphor, and the inset images show the photographs of single crystal LuAG:Ce with a diameter (Ø) of 8 mm and a thickness (T) of 5 mm. The fundamental excitation bands of Ce³⁺ are known to be up to five bands at much lower temperature than room temperature. Our both single and powder samples showed only two broad bands at higher temperature. It results from the spectral overlap of peaks broadened by light scattering or thermal effects. The broad PL spectra in green spectral region are originated from a close overlap of two transition peaks from the first lowest excited 5d¹ level to two spin-orbit split \( ^2\text{F}_{7/2} \) and \( ^2\text{F}_{5/2} \) levels of 4f⁰ ground state [15,16]. The outer 5d¹ orbitals have a large crystal-field splitting: the first lowest and the second lowest levels [17]. Thus, the PLE spectra consist of two PLE peaks at 460 nm and 345 nm: the 460 nm peak from the \( ^2\text{F}_{5/2} \) level of 4f⁰ ground state to the first lowest 5d¹ excited state and the 345 nm peak from the \( ^2\text{F}_{5/2} \) level of 4f⁰ ground state to the second lowest 5d¹ excited state. The PLE intensity of single crystal LuAG:Ce phosphor at the 345 nm peak is increased by a factor of 3.7 compared with that of the reference. The 345 nm excitation peak is well known to be originated from the proximity of the second lowest 5d¹ level close to the conduction band edge. Our single crystal showed higher 345 nm peak intensity than that of the powder, which indicates that the single crystal has less defects at the proximity of the second lowest 5d¹ level close to the conduction band edge than those of the reference. It indicates that the single crystal has less defects at the proximity of the second lowest 5d¹ level close to the conduction band edge than those of the reference.

As summarized in Table 1, the LuAG:Ce single crystal phosphor
has a higher absorbance of 92% and a lower quantum efficiency (QE) of 63% under 445 nm excitation wavelength compared with the polycrystalline reference sample with 88% and 90%, respectively. This is the reason why the single crystal has no light-scattering sources such as grain boundary or surface roughness, so that the emission lights suffer from severe internal reflections within the single crystal due to a large refractive index (n=1.85 at 520 nm) [18,19].

The single crystal sample has a broader PLE spectrum with a band width of 83 nm around 445 nm excitation wavelength than that of the reference sample (51 nm). It can be explained by more internal reflections of the incident excitation lights within the single crystal. The more internal reflections cause the increase in Raman scattering of the incident lights so as to generate more phonons. Thus, the generated phonons can be more coupled with excited electrons, so that the PLE spectra are broadened [11]. In addition, this broadened PLE spectrum gives rise to larger spectral overlap between excitation and emission bands. It results in the increase of the reabsorption rate of emission lights so as to quench the QE of LuAG:Ce single crystal. Nevertheless, the QE of LuAG:Ce single crystal (63%) still shows a higher value than that of a YAG:Ce single crystal (47%) [11]. The LuAG single crystal sample showed the broader PLE spectrum than that of the powder. The same phenomenon was also observed in the YAG:Ce single crystal and its pulverized sample as reported in our previous work [11]. We can simply suggest that the broadened PLE spectrum results from higher photon-photon coupling due to larger internal reflections of the excitation light. The deep research on the PLE broadening of the single crystal is required in the future.

Fig. 2 shows temperature-dependent PL spectra of (a) the LuAG:Ce single crystal phosphor and (b) the polycrystalline powder phosphor under 445 nm excitation wavelength. The insets show the thermal stability (PL intensity at high temperature to that at low temperature (I25/I200°C)) of the LuAG:Ce phosphor under 445 nm excitation wavelength. The insets show the each thermal stability with increasing the temperature from 25 to 200 °C with an interval of 25 °C.

Table 1: Absorbance, quantum efficiency, and thermal stability (I200°C/I25°C) of the LuAG:Ce single crystal and reference sample under 445 nm excitation wavelength. The maximum temperatures after 40-minute operating of the blue LD.

<table>
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<tr>
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<th>Single crystal</th>
<th>Reference</th>
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<tr>
<td>Absorbance (%)</td>
<td>92</td>
<td>88</td>
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<tr>
<td>Quantum efficiency (%)</td>
<td>63</td>
<td>90</td>
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<tr>
<td>Thermal stability (%)</td>
<td>103</td>
<td>90</td>
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<tr>
<td>Maximum temperature (°C)</td>
<td>62</td>
<td>95</td>
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Fig. 2. Temperature dependent PL spectra of (a) the single crystal LuAG:Ce phosphor and (b) the reference powder under 445 nm excitation wavelength. The insets show the each thermal stability with increasing the temperature from 25 to 200 °C with an interval of 25 °C.
condition. The air gaps among particles of the reference interrupt the heat dissipation leading to an increase of temperature at the laser-irradiated spot. On the contrary, the locally-generated heat at the focused laser-irradiation spot for the single crystal can be effectively dissipated to the surrounding without any interruption within the bulky single crystal. High-power LDs heated the powder more than the single crystal. As shown in the temperature-dependent PL spectra (Fig. 2), the more heated powder showed more redshift and more increase in the longer-wavelength side compared with the single crystal phosphor. As a result, the emission spectrum of the powder seems to be different from the single crystal. As summarized in Table 1, the single crystal reached the lower equilibrium temperature at 62 °C after 40 min operating of the blue LD than that of the reference powder sample (95 °C). Thus, laser lighting using the single crystal LuAG:Ce as a color conversion phosphor can achieve the stable light emission without an efficiency loss under much higher operating current.

4. Conclusion

Green-emissive single crystal LuAG:Ce as a color conversion phosphor for high-power laser lighting was grown through a floating zone method by an image furnace. It showed an excellent thermal stability of 103%, a lower QE of 63%, and a broader PLE spectrum with 83 nm band width around 445 nm excitation wavelength compared with the polycrystalline reference powder with 96%, 90%, and 51 nm, respectively. For the single crystal, the defect-sensitive PLE intensity at 345 nm was by a factor of 3.7 increased, and the $K_1$ are decreased down to 78% at 200 °C. Therefore we determined that the positive thermal stability of the single crystal was caused by the decrease of intrinsic defects and the less phonon generation at higher temperature. The higher heat dissipation rate of single crystal causes a lower equilibrium temperature at 62 °C after 40 min operating of the 5 W blue LD in comparison with the reference with 95 °C. Thus, the single crystal LuAG:Ce phosphor can achieve the extremely stable light emission without an efficiency loss under the high-power density of blue laser diode. Nevertheless, further work is required to improve the low QE of single crystal phosphor in order to realize a commercially available high-power laser lighting devices.

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