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Pore-existing $Lu_3Al_5O_{12}$:Ce ceramic phosphor: An efficient green color converter for laser light source

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ABSTRACT

$Lu_3Al_5O_{12}$:Ce (LuAG:Ce) ceramic - a super-duper green color converter was fabricated by a solid-state reaction method under vacuum. The sintering temperature was adjusted to control the pore characteristics, which would cause different degrees of scattering. Microstructures of ceramics sintered at different temperatures were observed by scanning electronic microscopy (SEM). Photoluminescence (PL) of the ceramics was characterized by a fluorescent spectrophotometer. It was found that the micro-sized pores inside the ceramics play a key role in optimizing the PL intensity. Under the blue laser (450 nm) excitation, the optimized sample with a porosity of 2.88% showed high luminous efficiency of over 200 lm/W and high thermal stability of luminescence. The light conversion efficiency was 50.2% and 44.4% in the dynamic and static mode, respectively. The results highlighted that the prepared ceramics had great potentials for application in solid state laser light source (LLS).

1. Introduction

The laser light source (LLS) which promises wide color gamut, super-high brightness and long lifetime is becoming more popular in display applications, such as data projectors, TV, cinema and home theaters. One of the most effective ways to obtain LLS is using the laser-activated remote phosphor (LARP) technology [1]. The LARP system primarily includes laser diodes (LDs), optical modules and phosphor wheels. Typically, the pumping light from blue LD array is collimated and focused onto a rotating phosphor wheel with green, yellow and red phosphors. The properties of phosphors would eventually determine the performance of the LARP system. At present, phosphors for the LARP technology are generally nano or micron-sized powders, and they are usually dispersed in silicone matrix. The low heat-resistance and low thermal conductivity of silicon resins would eventually cause the degradation of luminous intensity and the change of color chromaticity [2]. To improve the long term reliability of phosphors, glass phosphors [3–7] and ceramic phosphors [8–10] are widely studied. However, despite their much higher thermal stability, the glass phosphors fall a big problem of comparatively low quantum efficiency (QE) [11,12]. In contrast, QE of Y(Lu)AG:Ce ceramic phosphors can easily reach up to 90% or even higher, comparable to that of powder phosphors. Another characteristic of phosphors for LARP technology should be the luminous efficiency at high laser power. Xie et al., reported that the luminous flux of β-Sialon: Eu phosphor-in-glass reached saturation as the incident laser power was around 1 W/mm^2 [13]. In contrast, the luminous flux of YAG:Ce ceramic phosphors increased without saturation up to 13.5 W/mm^2 [14]. Therefore, ceramic phosphors are better alternatives for LARP technology.

Transparent ceramics are generally expected to be fully dense for IR window or laser applications, pores inside the ceramics will cause serious scattering loss and lead to a degradation of optical quality. However, for luminescence applications, scattering is found to be one of the most interesting and important factors that greatly affects the luminescence properties [15,16]. Optimized scattering centers can not only increase the absorption efficiency, allow lower dopant concentrations, but also enhance the extraction of partial converted light trapped by the total inner reflection (TIR). As is well known, transparent LuAG:Ce ceramics are good candidates for green color converters, they show large absorption coefficient and high QE [17,18]. In the past decades, LuAG:Ce ceramics have been widely discussed and applied in the fields of WLEDs [19,20] and scintillators [21–23], but their performance in the LARP technology has rarely been studied. LuAG:Ce ceramics are cubic phase, they are optically isotropic,

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scattering does not occur from grain boundaries but in residual pores. Therefore, in the present work, LuAG:Ce ceramics are fabricated for LARP system, pores are introduced as scattering centers in the ceramics by changing the sintering temperature. The effects of porosity and pore size on luminous performance are discussed.

2. Experimental procedure

$(Lu_{.999}Ce_{.001})_3Al_5O_{12}$ ceramics were prepared via a solid-state reactive sintering method under vacuum. Lu_2O_3 (99.99%), Al_2O_3 (99.99%), CeO_2 (99.99%) were used as raw materials, 0.5 wt% tetraethyl orthosilicate (TEOS) and 0.1 wt% MgO were added as sintering aids. After stoichiometrically weighed, the raw materials were uniformly mixed by ball milling for 12 h in ethanol, dried in the oven at 60 °C for 24 h. Then the powders were pulverized and sieved, pressed to pellets (Φ20 mm) and cold isotactic pressed at 200 MPa. The green bodies were firstly pre-sintered in a muffle furnace at 800 °C for 6 h then sintered at different temperatures (from 1600 °C to 1750 °C) for 3 h under vacuum. After being annealed at 1400 °C for 3 h in air to remove oxygen vacancy, all the samples were finally double-surface polished to 0.28 mm for characterization.

The crystalline phase of the prepared ceramics was characterized in the 2θ range from 10° to 80° with a step of 0.02° by X-ray diffraction (XRD, D/MAX 2200PC, Rigaku, Japan) with Cu Kα radiation. The microstructures of the ceramics were characterized by scanning electron microscopy (SEM, TM3000, Hitachi, Tokyo, Japan). The bulk porosities of the ceramics were measured by Archimedes method in distilled water. The PL spectra and temperature-dependent luminescence in a temperature range from 300 K to 500 K with a step size of 50 K were measured with a fluorescent spectrophotometer (FLS920, Edinburgh, UK) equipped with a 200 W Xe lamp as the excitation source. Optical properties of the ceramic phosphors under the laser excitation were tested by a reflection mode. Luminous flux was recorded under the irradiation of 450 nm blue LDs with various incident powers.

3. Results and discussion

XRD patterns of LuAG:Ce ceramics sintered at various temperatures are shown in Fig. 1. It is obvious that the obtained ceramics are well indexed as cubic garnet structure of LuAG (PDF#73-1368). The ceramic is highly crystalized even at a comparatively low sintering temperature of 1600 °C.

Fig. 2 shows the PL spectra of LuAG:Ce ceramics prepared at different temperatures under the excitation of 450 nm. The typical broad emission bands from 470 nm to 650 nm are ascribed to the electron transitions from the lowest crystal-field splitting component of the 5d level to the ground state of Ce^{3+} ($^2F_{5/2}$, $^2F_{7/2}$). The luminous intensity first increased as the sintering temperature increased from 1600 °C to 1650 °C, and then decreased at higher sintering temperatures. Obviously, the sintering temperature has a great influence on the luminous efficiency of the LuAG:Ce ceramic phosphors.

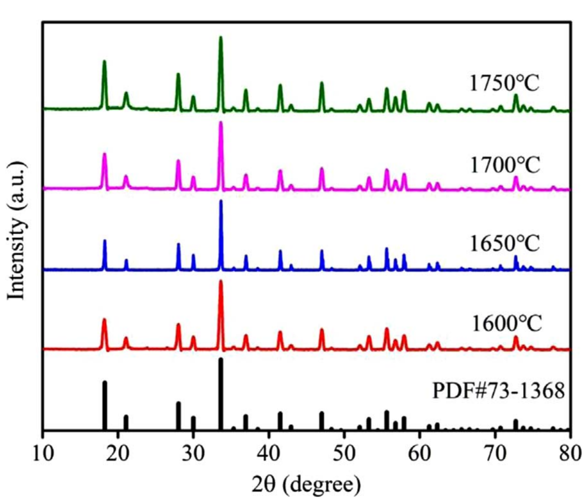

Fig. 1. XRD patterns of the LuAG:Ce ceramics sintered at different temperatures.

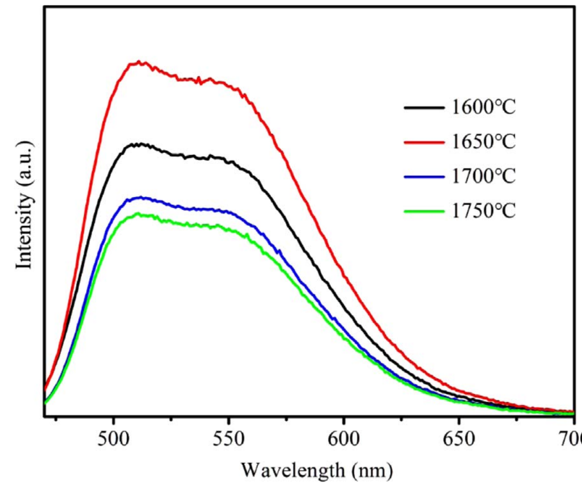

Fig. 2. Emission spectra of LuAG:Ce ceramics sintered at different temperatures under the excitation of 450 nm.

Microstructures of the double polished surface of LuAG:Ce ceramics were observed by SEM, showing in Fig. 3(a)-(d). It is found that the grain size increased with increasing sintering temperature. However, the number of micron-pores decreased with sintering temperature, which means the porosity of the ceramics decreased monotonously as the sintering temperature increased, as shown in Fig. 4. Pores were gradually eliminated at high temperatures, but most pores stayed in the triangular junction of grains or inside grains at low sintering temperatures. The pores were micron-sized, and acted as scattering centers in the ceramics.

The effects of scattering on the luminous efficiency should be considered from both aspects of incident light and converted light, which have drawn a lot of attentions [24–26]. Researchers found that it was important for scattering centers to enhance light absorption as well as light extraction in the applications of phosphors. For LuAG:Ce ceramic phosphors, in the circumstance that the transmittance is high (sintered at or above 1700 °C), the incident light, as shown in the left of Fig. 5, would directly pass through the bulk phosphor with less absorption by luminescence center. On the other hand, as the refractive index of LuAG:Ce ceramic ($n \approx 1.84$) is much larger than that of air ($n_0 = 1$), the converted light would be easily trapped by TIR, only light emits within the critical angle cone $\theta_{crit} \approx 33°$ will escape, according to the formula $\theta_{crit\ =}$ arcsin (n_0/n). As a result, the ceramics sintered at high temperatures exhibited high optical quality but low conversion efficiency. As pores were introduced in the ceramics, the situation became different (see the right part of Fig. 5). A proper amount of scattering increased the interaction between incident blue light and the LuAG:Ce ceramic phosphor, which resulted in more blue light being absorbed. In addition, scattering improved extraction of light, due to that part of the converted lights generated beyond critical angle had some probabilities of being scattered back into the critical angle cone. Even failed, TIR continued to reflect the lights until they were scattered again and eventually escaped from the ceramic phosphors. However, as the porosity was high enough in ceramics, light had little chance to pass through the ceramics. Therefore, the luminous intensity of the ceramic with a porosity of 2.88% (sintered at 1650 °C) was the highest (Fig. 2). Further lowering sintering temperature (such as1600 °C), the luminous intensity started to decrease. Thus, the ceramic sintered at 1650 °C was adopted for following measurements.

The temperature-dependent PL spectra of LuAG: 0.1 at% Ce ceramic