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Growth of $YAG:Ce^{3+}$-Al_2O_3 eutectic ceramic by HDS method and its application for white LEDs

Yang Liu[a], Mingfu Zhang[a,*], Ying Nie[a], Jin Zhang[a], Jiazhi Wang[b]

[a] National Key Laboratory of Science and Technology on Advanced Composites in Special Environments, Harbin Institute of Technology, Harbin, 150001, PR China
[b] Oles Honchar Dnipropetrovsk National University, Dnipropetrovsk, Gagarin 72, Ukraine

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The resin-free $YAG:Ce^{3+}$-Al_2O_3 eutectic ceramic phosphor for white light emitting diodes (WLEDs) was successfully grown in vacuum by Horizontal Directional Solidification method (HDS). X-ray diffraction and scanning electron microscopy indicate that this material has a typical eutectic structure of interpenetrating sapphire and garnet phases. The excitation spectra, emission spectra and temperature characteristics of the eutectic show that it is characterized by a wide excitation band and it has good stability in high temperature. In X-ray photoelectron spectroscopy, annealing in an air atmosphere could eliminate the oxygen vacancies and didn't change the Ce^{3+} valence in the eutectic. The $YAG:Ce^{3+}$-Al_2O_3 eutectic ceramic with different thickness was fixed in COB (chip on board) element for researching the performance of the WLEDs with the phosphor. The electroluminescence characterization of the WLEDs show that the WLEDs with the eutectic ceramic are more excellent than the common commercial WLEDs.

1. Introduction

With the advantages of high luminous efficiency, long life, better energy-saving and environmental protection, white LEDs have gradually become the important productions in the lighting industry. Currently, one of the white LEDs synthetic methods on the market is to combine yellow light-emitting $Y_3Al_5O_{12}:Ce^{3+}$ ($YAG:Ce^{3+}$) phosphors with blue InGaN chips [1–4]. However, due to poor thermal conductivity of the epoxy resin, it will produce thermal aging problems, which seriously affected the life and light efficiency of white LEDs [5]. In order to solve those problems, researchers are working to develop a new type of fluorescent materials to replace the phosphor and epoxy resin used in the traditional LEDs [6–9].

YAG-Al_2O_3 eutectic ceramic has been widely applied because of its excellent performance at high temperature [10]. In the eutectic ceramic, Al_2O_3 phase and YAG phase interspersed with each other and there is no grain boundary [11–14], so it makes Ce^{3+} dispersed in the eutectic ceramic more uniform than phosphor dispersed in the epoxy resin. The refractive index (1.83 and 1.78 for YAG and Al_2O_3, respectively) of the two phases are similar, which allows light to have better communication in the eutectic ceramic than that in the epoxy resin [15,16].

In the study, we prepared large plate-like $YAG:Ce^{3+}$-Al_2O_3 eutectic ceramic successfully by horizontal directional solidification method under different growth parameters and annealed in an air atmosphere. We characterized the basic performances of eutectic ceramic by X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) and so on. We packaged the eutectic ceramic into white LEDs whose power is 9W and tested the white LEDs' light color electrical parameters.

2. Experiment

2.1. Growth of $YAG:Ce^{3+}$-Al_2O_3 eutectic ceramic

CeO_2, Al_2O_3 and Y_2O_3 with 99.999% purity were used as raw materials in growing the $YAG:Ce^{3+}$-Al_2O_3 eutectic ceramic. YAG-Al_2O_3 binary phase diagram shows that coupled growth occurs only in the composition range of 18.5mol% to 20.5mol% Y_2O_3. In the current experiment, the mole ratio of Y_2O_3/Al_2O_3 was 18.5/81.5, and the dopant of CeO_2 was a mole ratio of Ce/Y = 0.25-1.0%.

The homogeneous slurry was obtained by wet ball mill with a certain proportion of raw materials, a small amount of PVA (0.5mol%) and amounts of absolute ethanol, and then dried (70 °C for 120 min). They were pressed into column by cold isostatic press-

* Corresponding author.
E-mail addresses: mfzhang1@hit.edu.cn, mfzhangpsu@gmail.com (M. Zhang).

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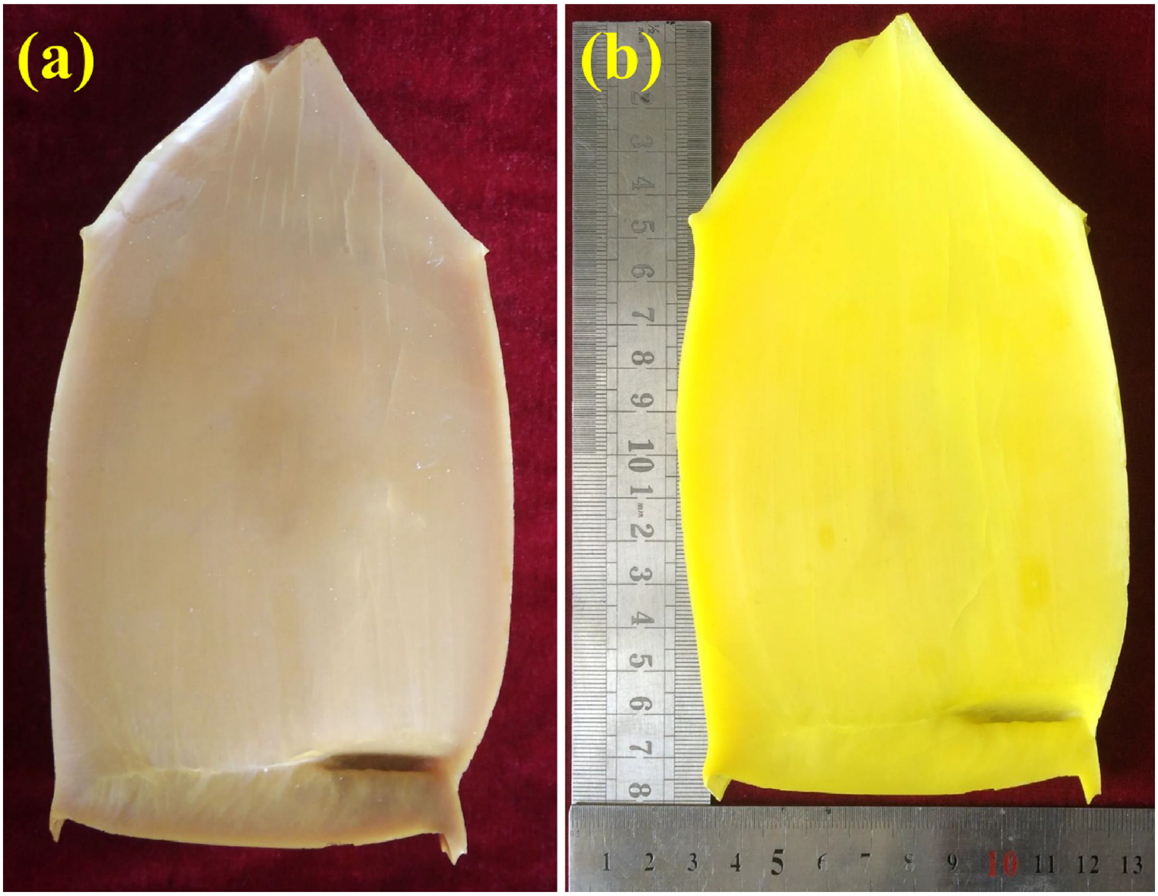

Fig. 1. The photographs of YAG:Ce^{3+}-Al_2O_3 eutectic ceramic: (a) as-grown and (b) annealed at 1473 K for 12 h.

ing and calcined at 1500 °Cfor 5 h. The calcined materials shows faint yellow. The reaction during calcining process is as follows:

$$3(1\text{-}x)Y_2O_3 + 6\,xCeO_2 + 5Al_2O_3 \rightarrow\ 2(Y_{1-x}Ce_x)_3Al_5O_{12} + 1.5\,xO_2$$

The x represented 0.01, 0.005 and 0.0025 in the reaction, respectively. In the calcining process, Y_2O_3 and Al_2O_3 will be reacted and synthesized YAG ($Y_3Al_5O_{12}$). After reaction, the calcined material comprised YAG and excess Al_2O_3. It should be Al_2O_3/YAG = 4.1:1 in mole, 0.7:1 in weight, and 0.82:1 in volume, calculated according to their molecular weight and density.

The calcined materials were charged into a particular boat-shaped molybdenum crucibles (200mm × 85mm × 45 mm), and then loaded two crucibles into the IKAK-2 type crystal growth furnace which is produced by Ukraine Donets company. In accordance with the growth furnace's application flow sheet, the loading link was finished [17]. The optimal pulling rate by high precision program controller was found to be as follows after a series of gropes: 10–20 mm/h. After growth, the eutectic ceramic was cooled down to 1000 °C at the rate of 25 °C/h, and further down to room temperature at the rate of 50 °C/h. The total experiment procedure including installation, heating up, growth operation and eutectic ceramic cooling took about four days and we could get two plate-like eutectic ceramics with the dimension of 170 mm × 90 mm × 20 mm. One of the as-grown eutectic ceramics was placed in a muffle furnace, which was heated up to 1200 °C and kept for 12 h in an air atmosphere. Fig. 1 (a) shows the photograph of the as-grown YAG:Ce^{3+}-Al_2O_3 eutectic ceramic and (b) shows the one after annealing. We could find that the color of the annealed YAG:Ce^{3+}-Al_2O_3 eutectic ceramic becomes brighter compared to the as-grown one.

2.2. Sample preparation

The processes that the as-grown and the annealing eutectic ceramics were processed into pieces included cutting into rods (the diameter of 9.3 mm), rounding, slicing (the thickness d = 0.4 mm and 0.8 mm) and polishing. Some pieces which the Al_2O_3 phase excluded by hydrothermal method (8.0 mol/L of KOH solution, 250 °C, 12 h) [18] were selected in order to observe its three-dimension structure. Some of them were used for processing into 9W WLEDs with the blue LED chips (30 V, 300 mA, emitted 470 nm blue light). Fig. 2 shows the photograph of (a) the YAG:Ce^{3+}-Al_2O_3 eutectic ceramic piece and (b) the COB with YAG:Ce^{3+}-Al_2O_3 eutectic ceramic. We can find that the eutectic ceramic appears translucent.

2.3. Sample measurement methods

Fine ground powder from the as-grown eutectic ceramics was used as the sample for XRD analysis with Cu Kα1 radiation at a scan width of 0.02° within 2θ=10°–90°. The microstructure was studied on aurum coated samples using a Quanta 200FEG Scanning Electron Microscope (SEM) equipped with Energy Dispersive Spectrometry (EDS). The XPS spectra, which were used for analyzing the valence change of the Ce in the whole experiment and the effect of annealing in the air for eutectic ceramics, were obtained using a Thermo Fisher Scientific ESCALAB250Xi Photoelectron Spectrometer by Al Kα radiation. A pass energy (ΔE) was 20.0 eV for elements with an energy resolution of 0.05 eV. The C 1 s binding energy was fixed at 284.6 eV of adsorbed adventitious carbons. Temperature characteristics, emission and excitation spectra of the eutectic pieces were recorded with a spectrophotometer equipped with a xenon