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Original article

The effect of SiC addition on photoluminescence of YAG:Ce phosphor for white LED

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ABSTRACT

An effective way of improving photoluminescence (PL) of YAG:Ce by addition of small amount of SiC and sintering in air was described. The breakdown of SiC during sintering process in air was employed to provide the presence of SiO_2 and CO both of which are known to be beneficial in enhancing the PL of YAG:Ce phosphor. SiC in the form of a fine powder was added to YAG:Ce powder and sintered to densities of > 99% of theoretical density. The highest luminescence was measured in sample containing 0.08 wt% SiC. The effect of the formed SiO_2 and CO was discussed and their contribution to the emission intensity was assessed. The enhancement of PL intensity is attributed to the formation of vacancies, both on Y sub-lattice and on oxygen sub-lattice and their ability to release the electrons for subsequent reduction of Ce^{4+} to Ce^{3+} which plays a role of luminescence activator.

1. Introduction

Over the past two decades, the white light emitting diodes (LEDs) have been displacing the incandescent and fluorescent lamps owing to their low energy consumption, high brightness and long life time [1,2]. Most commonly used white LEDs are the combination of blue LED and yellow phosphor which converts one part of blue light into yellow [3–5].

The obtained yellow emission complements the transmitted blue light to yield the white light. Yttrium aluminium garnet (YAG) doped with trivalent Ce^{3+} is the most important phosphor for the conversion of blue to yellow light. The broad emission band around 550 nm is the result of 5d→4f transition of 4f electron of Ce^{3+} excited by blue LED [6,7]. However, cerium easily changes between Ce^{3+} and Ce^{4+} states [8,9] which can result in reduction or even complete disappearance of yellow emission. For this reason, the formula of cerium oxide is normally given as CeO_{2-x} where x ranges from 0 to 0.5, meaning that the composition of cerium oxide varies between Ce_2O_3 and CeO_2, i.e., there is a mix of Ce^{3+} and Ce^{4+} ions. It is, thus, essential to keep Ce^{3+}/Ce^{4+} ratio as high as possible in order to achieve high photoluminescence effect. One way to reduce Ce^{4+} to Ce^{3+} is to treat the phosphor material in reducing atmosphere such as CO [10] or to subject to high temperature and vacuum [11,12]. It is well known that relatively large number of oxygen vacancies can be created in CeO_{2-x} when the surface oxygen atoms react with CO to form CO_2 [13]. Each vacancy is a donor of two electrons available for reduction of two Ce^{4+} ions to Ce^{3+}. There is also a similar effect of vacuum on vacancy formation except that two oxygen atoms recombine to make oxygen molecule [14].

Besides atmosphere, it was also found that doping with SiO_2 can increase the Ce^{3+}/Ce^{4+} ratio and thus improve luminescence [15]. The mechanism responsible for this involves formation of Y^{3-} vacancies which act as electron donor.

This paper describes an effective way to improve photoluminescence of YAG:Ce by doping it with SiC which oxidises during sintering in air according to the following reaction:

$$2SiC + 3O_2 \rightarrow 2SiO_2 + 2CO\uparrow \quad (1)$$

The oxidation of SiC provides simultaneous presence of two reducing agents, SiO_2 and CO both of which are effective in increasing the intensity of light emission. It is shown in this paper that the photoluminescence of YAG:Ce containing SiC is higher than that of samples containing equivalent amount of SiO_2 added in the form of silica sol.

2. Material and methods

YAG powders containing different concentrations of Ce were prepared by glycine-nitrate combustion synthesis. High purity nitrates (> 99.99%): $Al(NO_3)_3{\cdot}9H_2O$, $Y(NO_3)_3{\cdot}6H_2O$ and $Ce(NO_3)_3{\cdot}6H_2O$ were supplied by Stanford Advanced Materials, California, USA. The nitrates were dissolved in water along with glycine which served as a fuel. The

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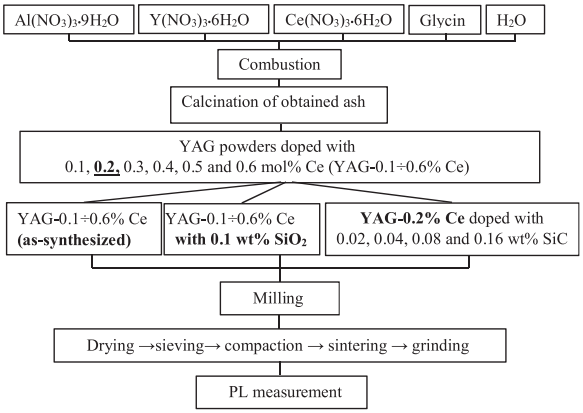

Fig. 1. Schematic diagram of the experimental procedure.

composition of the obtained powders can be expressed as $(Y_{1-x}Ce_x)_3Al_5O_{12}$ where **x** indicates the fraction of Y atoms replaced by Ce and ranges from 0.001 to 0.006 with 0.001 increment. In terms of mole concentration, the level of Ce was kept between 0.1 mol% and 0.6 mol %. The prepared mix was first slowly heated to high temperature to evaporate excess water after which the resulted viscous liquid was ignited and underwent combustion process producing a mass in the form of ash. The ash was subsequently calcined at 900 °C when it changed the color from brown to pale yellow powder. In order to determine the effect of SiO_2, the synthetized YAG powders containing different amount of Ce were doped with 0.1 wt% SiO_2 (Fig. 1). The silica dopant was added to YAG:Ce powders in the form of a silica sol, i.e., 40 wt% SiO_2 suspended in H_2O (LUDOX® HS-40 colloidal silica, Aldrich, Germany). Series of samples consisted of YAG with 0.2 mol% Ce (no SiO_2) were doped with a small amount of SiC: 0.02, 0.04, 0.08 and 0.16 wt%. Commercially available, high purity α-SiC powder (HSC490 N) produced by Superior Graphite, Illinois, USA was use as a source of carbon and silica. It will be shown that the YAG powder with 0.2 mol% of Ce had the best optical properties and for that reason it was used to examine the effect of SiC dopant. The synthetized YAG powders containing different amount of Ce (undoped), the YAG powders doped with silica sol as well as those doped with SiC were subsequently milled for 6 h in ball mill using Al_2O_3 balls as milling media and deionized water as liquid vehicle. The powders were afterwards sieved and mechanically pressed into thin pellets with 9 mm diameter. After subsequent cold isostatic pressing at 200 MPa, the pellets were sintered at 1600 °C for 10 h in air.

X-ray diffraction (XRD) patterns of powders and sintered samples were recorded by Rigaku diffractometer with CuK_α radiation, in the 2θ range from 15 to 80° Particle size distribution was measured by laser diffraction using Horiba LA-920. The relative density of sintered samples was determined by the water displacement method assuming that the theoretical density (TD) of YAG is 4.56 g/cm^3. The microstructure of YAG ceramics was observed by Scanning electron microscopy (SEM). The photoluminescence (PL) spectra of 200 µm thin plates were measured at room temperature by Ocean Optics fluorescence spectrophotometer with 450 nm diode laser as the excitation source.

3. Results and discussion

3.1. Powder characterization

Fig. 2 shows the XRD pattern of YAG powder containing 0.2 mol% Ce obtained after 2 h of calcination at 900 °C. All peaks are assigned to the cubic garnet structure of the YAG crystal indicating that temperature of 900 °C is sufficient to complete the crystallization of the YAG. The presence of secondary phases was not detected even after sintering at 1600 °C (Fig. 2).

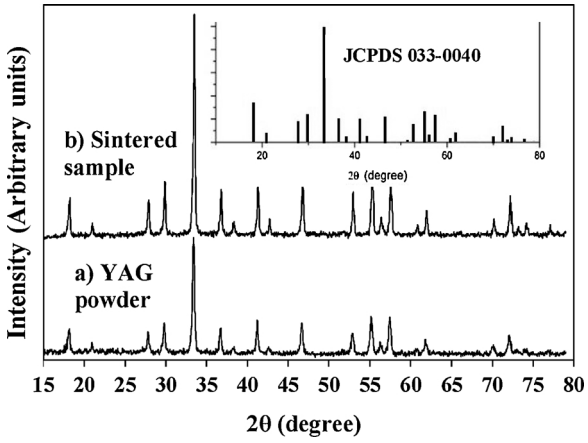

Fig. 2. XRD patterns of a) YAG powder containing 0.2 mol% Ce calcined at 900 °C for 2 h and b) compacted calcined powder containing 0.2 mol% Ce sintered at 1600 °C for 10 h. The YAG phase was indexed by JCPDS Card. No. 033-0040.

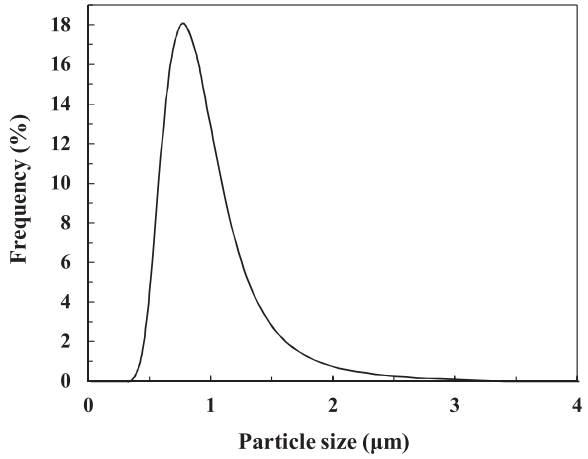

Fig. 3. Particle size distribution of YAG powder containing 0.2 mol% Ce after 6 h milling.

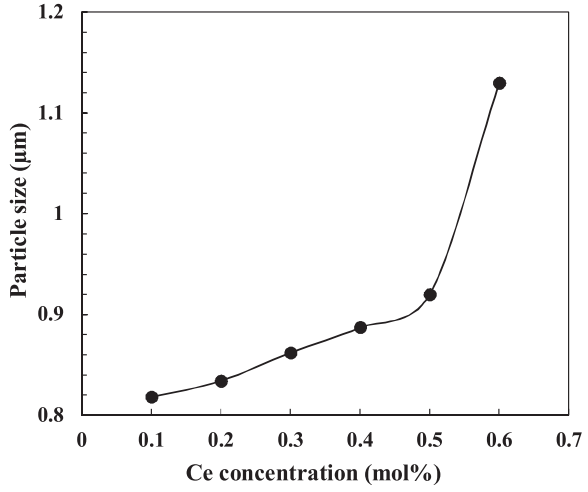

Fig. 4. Effect of Ce concentration on the mean particle size of the synthesized Ce-doped YAG powders after 6 h milling.

The particle size distribution of YAG powder containing 0.2 mol% Ce is presented in Fig. 3, which shows that the majority of particles have diameter between 0.5 and 1.5 µm. The mean particle size values for all compositions are given in Fig. 4 which shows that the mean