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Molten salt synthesis and luminescent properties of nearly spherical YAG:Ce phosphor

Yujun Liang [a,b,*], Dongyan Yu [b], WenZhu Huang [b], Mengfei Zhang [b], Guogang Li [a,b], Chunjie Yan [a,b]

[a] Engineering Research Center of Nano-Geomaterials of Ministry of Education, China University of Geosciences, Wuhan 430074, People's Republic of China

[b] Faculty of Materials Science and Chemistry, China University of Geosciences, Wuhan 430074, People's Republic of China

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ABSTRACT

Nonaggregated YAG:Ce phosphor with a nearly spherical morphology was successfully synthesized using the mixtures of Na_2SO_4–BaF_2 as the molten salt and the oxides (Y_2O_3, CeO_2 and Al_2O_3) as raw materials via a molten salt method. The $Y_3Al_5O_{12}$ phase can be well crystallized at a temperature as low as 1350 °C. By varying the mass ratios of molten salt/raw materials and Na_2SO_4/BaF_2, the average diameter of the particles can be controlled in a range of 10–40 μm. The as-prepared YAG:Ce phosphor showed a characteristic yellow emission of Ce ions in a range of 480–650 nm under excitation of 460 nm blue light. What's more, the phosphor showed the strongest emission when the mass ratio of the molten salt/raw materials was 1.8:1 and the dosage of BaF_2 in Na_2SO_4–BaF_2 was 5 wt%.

1. Introduction

While many strategies have been proposed for more efficient general lighting, including polymer and small-molecule organic and inorganic light-emitting diodes (LEDs), down conversion strategies based on inorganic light sources and phosphor conversion is one of the mot widespread strategies [1–3]. Phosphor converted inorganic light-emitting diodes possess many advantages, including durability, long life, color stability and environmental friendliness, specifically in their being free of toxic heavy metals [4]. The oxide garnet $Y_3Al_5O_{12}$ (YAG), when substituted with a few percent of the activator ion Ce^{3+}, is a luminescent material that has nearly ideal photoluminescence properties for excitation by a blue solid-state light source [5]. YAG:Ce continues to be a canonical phosphor with widespread use in solid-state lighting due to high quantum efficiency, excellent chemical and thermal stability, high mechanical strength and excellent optical properties [6,7]. A fine YAG:Ce phosphor consisting of spherical, high-efficiency and mono-distributed particles is very important in a remote phosphor technology, which offers a low glare system capable of higher system efficiency, increased reliability and less color shift over time [7–9]. In general, the commercial YAG:Ce phosphor is prepared by solid-state reaction method at a high temperature (> 1600 °C in general) with long soaking time (> 5 h) to obtain pure YAG, which leads to a waste of energy and contamination of impurities and results in inhomogeneous composition and irregular morphology for the final product [10,11]. In recent years, a series of wet chemical synthesis methods including sol–gel [12], co-precipitation

* corresponding author at: Engineering Research Center of Nano-Geomaterials of Ministry of Education,China University of Geosciences, Wuhan 430074, People's Republic of China. Tel.: +86 27 67884814; fax: +86 27 67883731.

E-mail address: yujunliang@sohu.com (Y. Liang).

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[13], combustion method [8], spray pyrolysis [14] and solvothermal [15,16] have been developed to synthesize the YAG:Ce phosphor with uniform and well-distributed morphology. However, these methods still suffer from lots of disadvantages, such as expensive equipment, complicated synthesis processes, environment-unfriendly precursors and solvents and especially surface trap sites, which always induce in these materials and result in the decreased emission intensity [17,18]. Compared to the above methods, the molten salt synthesis (MSS) method has attracted increasing interest and it has been successfully used in the synthesis of a number of ceramic powders and phosphors, such as Y_2O_3:Eu [19], $ZnTiO_3$ [20], $CaMoO_4$:Eu^{3+}, Li^+ [21]. Very recently, Yang et al. [17] and Wu et al. [22] reported MSS of the YAG:Ce phosphor using the nitrate hydrates or chloride hydrates of Y, Ce and Al as the starting materials. However, harmful gases including nitrogen oxides and hydrogen chloride will be released during the heating process. Lin et al. [6] successfully prepared the YAG:Ce phosphor by MSS from oxide raw materials. But it is a pity that the alumina source must be nano-Al_2O_3 (γ phase) or submicron-Al_2O_3 (α phase).

In this paper, we reported a MSS method to synthesize the YAG phosphor using the mixtures of Na_2SO_4–BaF_2 as the molten salt and the general oxides (Y_2O_3, CeO_2 and Al_2O_3) as raw materials. Influences of the experimental factors including the mass ratio of the molten salt/raw materials and the dosage of BaF_2 in Na_2SO_4–BaF_2 molten salt on the crystallization, morphology and photoluminescence properties were investigated.

2. Experimental

In this paper, YAG:Ce phosphor was prepared by a molten salt synthesis method. Y_2O_3 (99.99%), CeO_2 (99.99%), Al_2O_3 (A.R.), Na_2SO_4 (A.R.) and BaF_2 (A.R.) were used as raw materials. In a typical synthesis, Y_2O_3, CeO_2, Al_2O_3 were weighted in stoichiometric ratio and mixed in an agate mortar with the Na_2SO_4–BaF_2 mixture. The salt/oxide mass ratio was kept as 0.8:1, 1:1, 1.2:1, 1.4:1, 1.6:1 and 1.8:1, and the dosage of BaF_2 in Na_2SO_4–BaF_2 molten salt was kept as 1 wt%, 5 wt%, 7 wt%, 11 wt% and 13 wt%. The mixture was placed in a corundum crucible with a lid and heated in a tube furnace for 2 h at 1350 °C under flowing N_2–H_2 (5%) atmosphere. After being heated, the furnace cooled down naturally to room temperature. Then the reacted powders were washed in hot deionized water followed by filtration for five times to remove the salts. Finally, the powders were oven-dried at 80 °C before further characterization.

The crystal structure of the phosphors was characterized by X-ray powder diffractometer (XRD) (Bruker D8 Focus) with Ni-filtered Cu-kα ($\lambda = 1.540598$ Å) radiation at 40 kV tube voltage and 40 mA tube current. The XRD data were collected in a 2θ range from 10° to 70°, with the continuous scan mode at the speed of 0.05 s per step with step size of 0.01°. The morphology and microstructure were characterized with Japan SU8010 field emission scanning electron microscope (FESEM) at 15 kV. Elemental analysis of the samples was carried out using an Electron Dispersive Spectrometer unit attached to Japan SU8010 at 15 kV. Excitation (PLE) and emission (PL) spectra were measured by fluorescence spectrometer (FLUOROMAX-4) equipped with a 150 W xenon lamp as the excitation source. The spectral resolution of both excitation and emission spectra was set up to be 1.0 nm with the width of the monochromator slit adjusted as 0.50 nm. The other measurement conditions (PMT detector sensitivity, scan peed) were kept consistent from sample to sample in measurements. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Structural characterization

The YAG structure looking down the *a* axis is presented in Fig. 1(A). It suggests that Y ions locate at the dodecahedral sites (co-ordination number (CN=8)), and Al ions occupy the octahedral sites (CN=6) or tetrahedral sites (CN=4) in the YAG structure. It crystallizes in the most symmetric space group, *Ia*-3*d*, of the cubic crystal system [23]. When the Ce^{3+} ions replace the Y^{3+} ions in the YAG

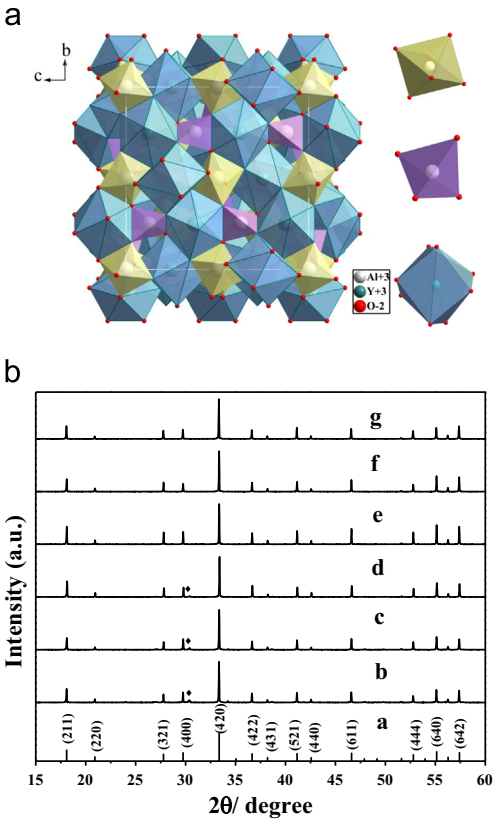

Fig.1. (A) The YAG structure looking down the *a* axis, with gray, yellow and blue polyhedron representing four-co-ordinate Al (Al^{IV}), six-co-ordinate Al (Al^{VI}), Y, and O atoms, respectively. (B) The standard data JCPDS card no.88-2048 (a) and X-ray diffraction patterns of YAG synthesized by MSS with different mass ratios of the salt/oxide materials is kept as (b) 0.8:1, (c) 1:1, (d) 1.2:1, (e) 1.4:1, (f) 1.6:1 and (g)1.8:1. (BaF_2 is kept as 5 wt% in the mixture molten salt) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)