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Solution-combustion synthesis of Tb^{3+}-doped $Y_3Al_5O_{12}$ nanoparticles

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ABSTRACT

Nano-sized YAG:Tb powder phosphors were prepared by a solution-combustion method, using the general inorganic salts as starting materials. The X-ray diffraction (XRD) measurements showed that the precursor can be well-crystallized at 900 °C. As-prepared particles have sizes mostly in the range between 30 and 100 nm as obtained by scanning electron microscope (SEM) and transition electron microscope (TEM). Selected area electron diffraction (SAED) patterns proved that the larger particles are monocrystalline. The effects of annealing temperature and Tb-doping concentration on the luminescence intensity were studied.

1. Introduction

The yttria-alumina system includes three crystalline phases: (1) yttrium aluminum perovskite (YAP), $YAlO_3$; (2) yttrium aluminum monoclinic (YAM), $Y_4Al_2O_9$ and (3) yttrium aluminum garnet (YAG), $Y_3Al_5O_{12}$ [1]. The most important of these compositions is YAG, which exists in the cubic form with a garnet structure. It is an advanced ceramic which has stable physical and chemical properties and is being used as a host material in many applications [2,3]. When doped with a transition metal or lanthanide element, YAG can be widely used as an active medium in solid-state lasers and in fiber-optic telecommunication systems. The rare-earth-doped YAG oxides are also widely used as phosphors in cathode-ray tubes, field emission, vacuum fluorescent, electroluminescent displays and as scintillations in X-ray and positron emission tomographs [4,5]. Among rare-earth ions, trivalent terbium (Tb^{3+}) ion is well-known as an active dopant for many different inorganic lattices. YAG:Tb has luminescence properties fairly insensitive to temperature variation and shows a little tendency to saturate at high current excitations. Furthermore, it is a characteristic narrow-band phosphor suitable for contrast-enhanced display application in high ambient illumination conditions [6].

YAG phosphors doped with activators are conventionally synthesized by solid-state reaction techniques. These techniques require long reaction times (10–20 h), high sintering temperatures (>1600 °C) and extensive ball milling, introducing additional impurities such as YAP and YAM [7]. However, the size of YAG:Tb particles are in the order of 5–20 μm as produced by conventional solid-state reactions. It is difficult to control phase homogeneity and purity for these methods at the high temperature. Therefore, improved chemical routes have been developed to achieve high-quality materials [8–11]. Some researchers have successfully synthesized $Y_3Al_5O_{12}$:Tb^{3+} phosphors using wet chemical methods [12–14]. In this paper, solution-combustion method is applied to synthesize YAG:Tb (0.5, 2.0, 7.0 and 9.0 at%) using the general inorganic salts as starting materials. The phase developments, morphology, as well as the photoluminescence properties of the resulting powders are studied. The luminescent properties of YAG:Tb have been examined as a function of annealing temperature and Tb-doping concentration.

2. Experimental procedures

2.1. Materials and powder synthesis

A facile solution-combustion method was used for preparing the precursors of Tb-activated YAG nanoparticles. The concentra-

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tions of Tb vs. Y were 0.5, 2.0, 7.0 and 9.0 at%. The starting materials were: yttrium nitrate, $Y(NO_3)_3 \cdot 6H_2O$ (99.99% Shanghai Yuelong Non-Ferrous Metals Co., Ltd.); aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$ (99.99 Shanghai Chemical Reactant Co., Ltd.); terbium oxide, Tb_4O_7 (99.99% Sinopharm Chemical Reagent Co., Ltd.); hydrated citric acid, $C_6H_8O_7 \cdot H_2O$ (analytical grade) and diluted nitric acid, HNO_3. The ratio of nitrate to citrate used in this experiment was 1:1.

Y $(NO_3)_3 \cdot 6H_2O$, Al $(NO_3)_3 \cdot 9H_2O$ and $C_6H_8O_7 \cdot H_2O$ were dissolved in dionized water. Aqueous solution of Tb $(NO_3)_3$ was prepared by dissolving high-purity Tb_4O_7 with HNO_3 and some deionized water. After mixing stoichiometric amounts of the above solutions, the solution was initially heated to 60 °C and continuously stirred for several hours. The resulting solution was then heated at 80 °C and stirred constantly until it was transferred into transparent sticky gel. The gel was rapidly heated to 190–220 °C and an auto-combustion process took place yielding a yellowish precursor. The precursor was placed in an alumina boat located in an alumina tube and mounted in a traditional resistance-heated furnace, then calcined at different temperatures, 700, 750, 800, 900, 1000 and 1100 °C for 5 h in air.

2.2. Powder characterization

The crystal structures of as-prepared samples were characterized by using X-ray diffraction (XRD), collected by Y-2000 Automated X-ray diffractometer (D/max-RB) using Cu Kα radiation ($\lambda = 0.154078$ nm) in the 2θ range of 10–70°, with a counting time of 1 s for each step size of 0.06°. Scanning electron microscope (SEM) images were taken on a JEOL JSM-6700F field-emission scanning electron microscope. Sample powders were also ultrasonically dispersed in ethyl alcohol (C_2H_5OH) solution and dropped onto a carbon-coated copper grid for TEM using a JEOL-2010 (HT) electronic microscope, with a micro-analysis system of energy-dispersive X-ray spectrum (EDX). The luminescence spectra of Tb^{3+} substituted for Y^{3+} in YAG have been measured on samples sintered at different (1000, 1100 and 1200 °C) temperatures and different (0.5, 2.0, 7.0 and 9.0 at%) Tb concentrations. The spectra were recorded with a Perkin Elmer (LS 55) fluorescence spectrometer at room temperature using an excitation wavelength of ~244 nm.

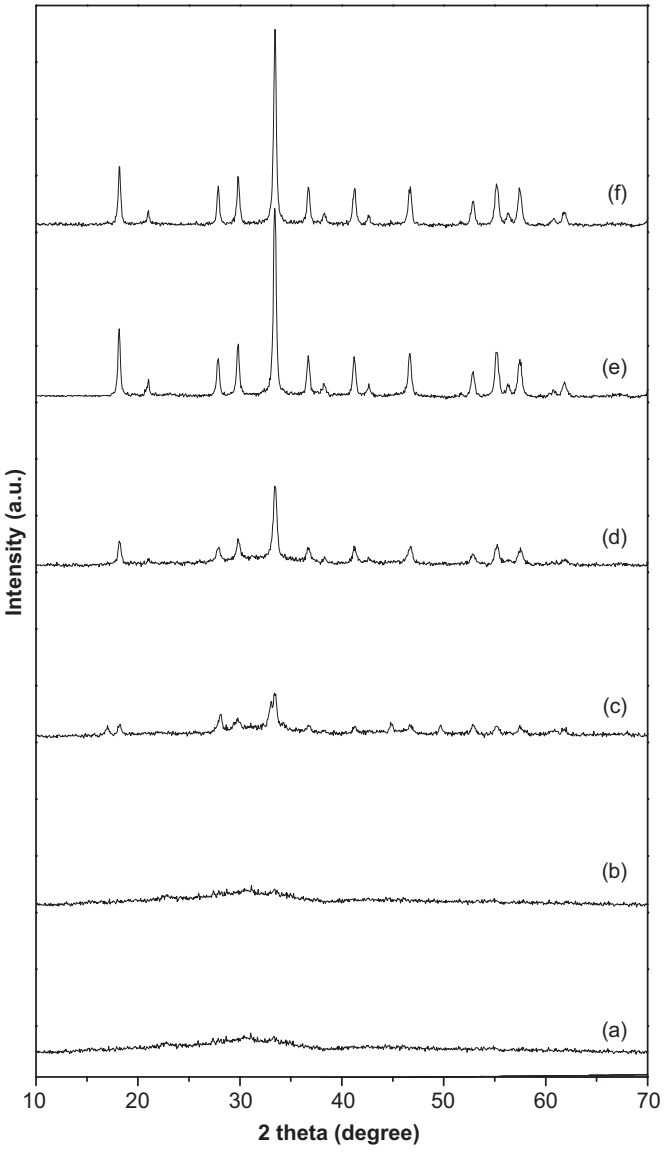

Fig. 1. XRD spectra of Tb^{3+}-activated YAG samples sintered at different temperatures for 5 h in air: (a) $T = 700$ °C, (b) $T = 750$ °C, (c) $T = 800$ °C, (d) $T = 900$ °C, (e) $T = 1000$ °C and (f) $T = 1100$ °C.

3. Results and discussion

3.1. Formation process of crystalline YAG:Tb^{3+} particles

3.1.1. XRD analysis

XRD measurements were carried out on the precursors and powders of YAG:Tb (7.0 at%) sintered at various temperatures from 700 to 1100 °C. As shown in Fig. 1, no obvious diffraction peaks are observed at 700 and 750 °C. This indicates that the precursor is amorphous at these temperatures. However, when the annealing temperature reached 800 °C, the characteristic peaks of YAG phase appeared with rather weak peaks. The obtained diffraction peak of the sample sintered at 900 °C is in good agreement with the reference data for $Y_3Al_5O_{12}$ (JCPDS file card 33–40) and no other crystalline phases such as YAM or YAP can be detected. The most prominent peak at $2\theta = 33.30°$ is the crystal plane with Miller indices of {4 2 0} in YAG. This indicates that the single-phase YAG:Tb was successfully prepared at a temperature as low as 800 °C using solution-combustion method, which is rather low as compared with the conventional solid-state reaction. Further heating treatment in the range 900–1100 °C leads to an increase of diffraction peak intensity and a decrease of peak full-width at half-maximum. The explanation of this observation is that the crystallinity improves and crystallite size increases with thermal treatment. The average crystallite size was determined from the broadening of the peak corresponding to the {4 2 0} reflection, using the Scherrer formula [15]. The obtained values are 19, 23, 29 and 34 for samples treated at 800, 900, 1000 and 1100 °C, respectively.

3.1.2. Morphology of as-prepared particles

Fig. 2a shows the SEM micrograph of the crystalline YAG:Tb (7.0 at%) samples derived from the solution-combustion method prepared at 1000 °C for 5 h in air. Most of the particles appear to be irregularly semi-spherical or elliptical in shape. The size of the particles measured from SEM photograph varies from ~30 to 100 nm. It is known that the luminescence characteristics of phosphorous particles depend on the morphology of the particles such as shape, size, crystallinity and defects. Thus, the solution-combustion process used in the present study provides a novel