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Synthesis of nanocrystalline lutetium aluminum garnet powders by co-precipitation method

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Abstract

Lutetium aluminum garnet (LuAG) precursor was co-precipitated from a mixed solution of aluminum and lutetium nitrates using ammonia water as precipitant. Phase evolution and thermal decomposition of the precursor during calcination was studied by TG-DSC and XRD. The particle size and morphology of the synthesized powders were determined by TEM. It was found that the precursor was amorphous and transformed to pure LuAG at about 900 °C. The crystallization stage was characterized by an exothermic peak of DSC curve at 1032 °C. The resultant LuAG powders were loosely agglomerated with an average particle size 50 nm. The addition of small amount of ammonia sulfate to mixed solution reduces the agglomeration and produces more uniform spherical particle.

Keywords: A. Calcination; A. Powders: chemical preparation; LuAG

1. Introduction

Inorganic scintillator plays an important role in radiation detection in many sectors of research concerning almost all medical diagnostic imaging modalities that use X-ray or gamma rays, dosimetry, nuclear medicine, high energy physics and also in many industrial measuring systems [1,2]. In the different applications, the scintillator is essentially a luminescent material that absorbs the high-energy photons and then emits visible light [3]. The relationship between absorption coefficient of X-rays (η_{abs}), the density (ρ) and the effective atomic number of material (Z_{eff}) is: $\eta_{\mathrm{abs}} = \rho Z_{\mathrm{eff}}^4$ [4]. So the usual scintillator requirements are fast response time (10–100 ns), high light out, high density and high atomic number [5].

Recently, lutetium aluminum garnet ($Lu_3Al_5O_{12}$, hereinafter referred to as LuAG), due to its high density (6.73 g/cm^3, 94% of BGO) and other physical properties such as shock resistivity and chemical radiation stability, is known to be quite promising host crystal for scintillating materials. This host lattice containing rare earth ions as luminescent activators, in special cerium (Ce^{3+}), yields fast decay and is an efficient high response scintillator [6]. However, LuAG single crystals are almost entirely grown from the melt (Czochralski method) by slow cooling in an expensive iridium crucible. As an alternative, polycrystalline LuAG can be used if high density and transparency are made possible by synthesizing LuAG powder and using ceramic processing techniques. To achieve high density and transparent polycrystalline LuAG, nanoscaled LuAG powder with no or little agglomeration is necessary.

LuAG is usually synthesized by solid-state reaction using the component oxides [7–9]. To achieve desired phase purity, the process of solid-state reaction usually needs lengthy high temperature treatment (>1400 °C for 20–30 h) and extensive mechanical mixing, which generally introduces additional impurities and defects. In general wet-chemical route is a good way to solution it. Several kinds of wet-chemical methods have been developed and successfully used in recent years for low-temperature production of phase-pure yttrium aluminum garnet (YAG) powders. These

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methods include sol–gel processing [10,11], hydroxide co-precipitation [12–15], homogeneous precipitation [16–18], glycothermal treatment [19], and combustion synthesis [20–22]. However, to date, there has not been reported for LuAG host in the literature.

In this work, LuAG powders were synthesized by co-precipitation from a mixed solution of aluminum and lutetium nitrates using ammonia water as precipitant. Phase evolution of the precursors and particle size and morphologies of the resultant LuAG powders were investigated.

2. Experimental

2.1. Materials

Aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$, analytical grade), lutetium oxide (Lu_2O_3, 99.99%), nitric acid (HNO_3, excellent grade), 25% ammonia water (analytical grade) and ammonia sulfate ($(NH_4)_2SO_4$, analytical grade) were used as starting materials in the present work.

The stock solution of mother salts was made by dissolving Lu_2O_3 in HNO_3 and then dissolved in deionized water with a stoichiometric amount of aluminum nitrate. Concentration of the stock solution was 0.15 M for Al^{3+}. A 2N ammonia water, obtained by diluting the 25% ammonia water, was used as the precipitant for co-precipitation.

2.2. Powder synthesis

Precipitation processes were performed at room temperature on a magnetic stirrer. Chemical precipitation can be performed by the normal-strike co-precipitation method (adding precipitant solution to the salt solution) or by the reverse-strike co-precipitation technique (adding salt solution to the precipitant solution). The main difference between the two methods is the rate at which of the salt solution changes as a function of time. For multi-cation materials, the latter technique has the advantage of higher cation homogeneity in the precursor [23,24], and was used in this study.

The precursor precipitate was produced by adding the salt solution at a speed of 3 ml/min from a burette into 2N ammonia water contained in a beaker under mild agitation, which a pH value of 8 was constant. The slurry was filtered using a suction filter after being stirred for another 30 min for homogenization. The resultant precipitate cake was then stirred and dispersed into deionized water and the suspension was filtered again. The above dispersing and filtering processes were repeated to completely remove by-products of the precipitation reaction until a pH value of 7 was reached. Finally, the precipitate was rinsed with anhydrous ethanol to replace water in the precipitate and prevent severe agglomeration of the particles during drying, and dried at 120 °C for 24 h. The dried cake was crushed with an alumina pestle and mortar and calcined at various temperatures for 2 h in air.

To investigate the effect of sulfate anion (SO_4^{2-}) on the morphology and agglomeration of the resultant powders, for some specimens, 1.98 g ammonia sulfate was added to a 500 ml of salt solution.

2.3. Powder characterization

Phase identification was performed by the X-ray diffraction analysis (XRD, Model D/MAX-2550 V) using nickel-filtered Cu Kα radiation in the range of $2\theta = 10–80°$.

Differential scanning calorimetry and thermal gravimetric (DSC/TG) analysis of the original precursors were made on a TG-DSC analyzer (Model NETZSCH STA 449C, Germany) in air atmosphere with a heating rate 10 °C/min. The sample pot was platinum and the reference material was alpha alumina.

The particle sizes and morphologies of the precursor and the heat-treated powders were examined by transmission electronic microscope (TEM, Model 200CX, JEOL, Tokyo, Japan).

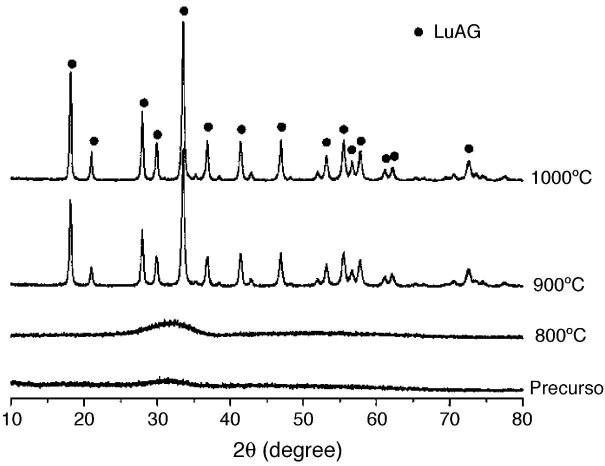

Fig. 1. XRD spectra of the precursor and powders heat-treated at various temperatures for 2 h.

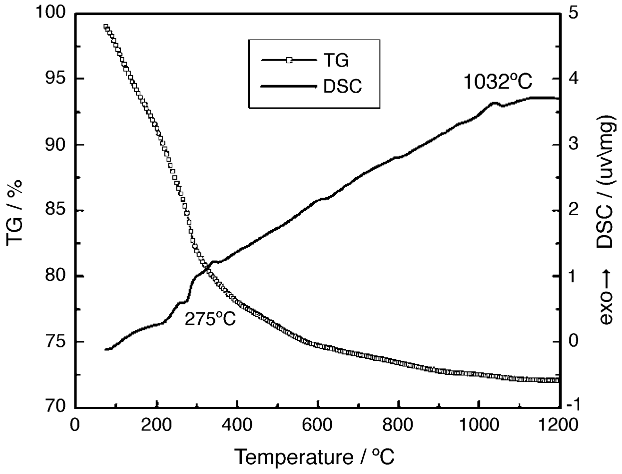

Fig. 2. DSC/TG curves of the precursor.

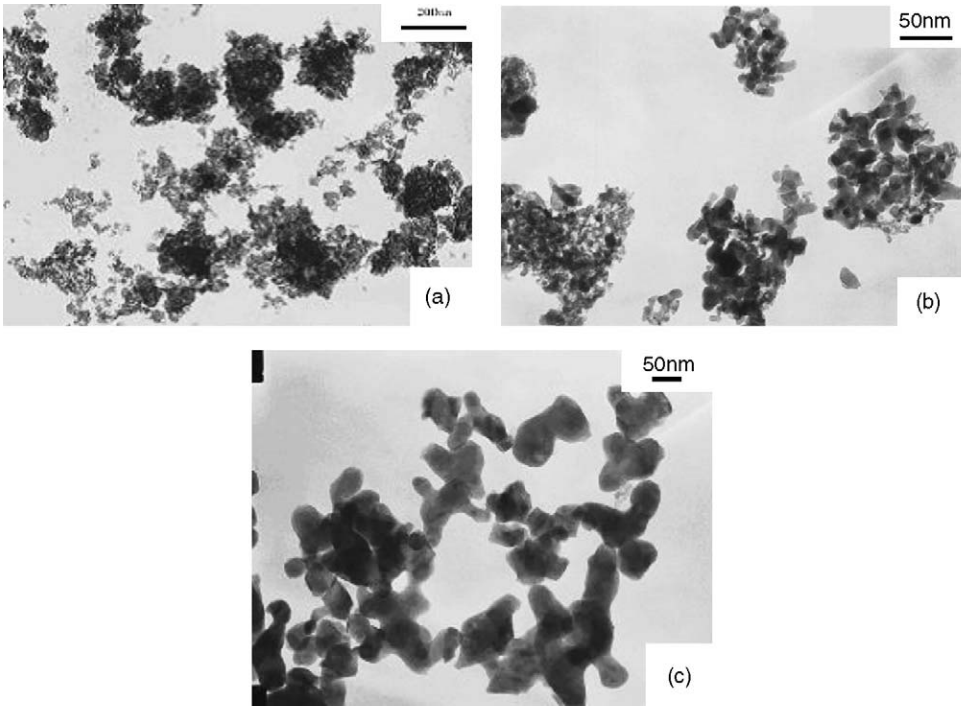

Fig. 3. TEM morphologies of the powders synthesized with ammonia water: (a) the precursor, (b) calcined at 900 °C for 2 h, (c) calcined at 1000 °C for 2 h.

3. Results and discussion

XRD spectra of the precursor and powders heat-treated at various temperatures for 2 h are shown in Fig. 1. The co-precipitated powders were found to be amorphous until about 800 °C. At 900 °C, however, all of the characteristic peaks of LuAG phase appeared without the formation of any other phases, indicating high cation homogeneity of the precursor. Above 900 °C, continued refinement of peak shapes and intensities were observed, indicating crystallite growth of the LuAG powder as temperature increases.

DSC/TG curves of the precursor are given in Fig. 2. Two major peaks were identified on the DSC curve. The endothermic peak centered at 275 °C was assigned to the removal of molecular water. The exothermic peak around 1032 °C resulted from the crystallization of LuAG, which is evidenced by the XRD results in Fig. 1 where no other phases were found. The crystallization temperature (1032 °C) measured by TG-DSC analyzer is higher than that (900 °C) given by XRD results, which is caused by the different soaking time and the hysteresis of the TG-DSC analyzer.

The TG curves showed that complete decomposition of the precursor into oxides was achieved at about 900 °C with a total weight loss of 27.8%, which is higher than the value (20.2%) expected for a precursor of pure hydroxide. Chemical analysis was not performed on this precursor, however, previous work [25] revealed that Y^{3+} usually precipitates as basic salt of approximate formula $Y_2(OH)_5X{\cdot}nH_2O$ (where X is NO_3^- or Cl^- depending on the type of starting salts, and $n = 1$–2) instead of pure hydroxide when ammonia water or sodium hydroxide was used as precipitant. Lu and Y have identical valence (+3), similar radius ($r_{Lu^{3+}} = 85.0$ pm, $r_{Y^{3+}} = 89.2$ pm) and properties. So the precursor contains NO_3^- ions, too. In fact, the mass loss of the present precursor is very

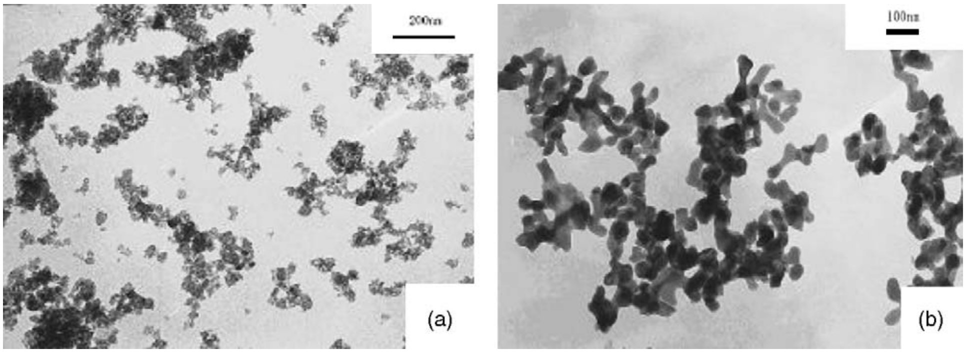

Fig. 4. TEM morphologies of the powders with the addition of SO_4^{2-}: (a) the precursor, (b) calcined at 1000 °C for 2 h.

close to the theoretical value (28.4%) calculated for $Al(OH)_3 \cdot 0.3[Lu_2(OH)_5(NO_3) \cdot 2H_2O]$.

Fig. 3 shows TEM morphologies of the precursor and powders calcined at 900 °C and 1000 °C for 2 h. The precursor (Fig. 3a) mainly consists of sub-micrometer sized loose aggregates of nano-sized primary particles. The resultant LuAG powders (Fig. 3b and c) showed much lower agglomeration and better dispersity. Although appreciable particle/crystallite growth occurred at higher calcined temperature, relatively good dispersity persisted. The particle size is about 50 nm after calcining at 1000 °C for 2 h.

It is well known that sulfate ions tie up flocks of inorganic fine particles in an aqueous solution [26]. This role of sulfate ions has been successfully applied in a quasi-alkoxide method to fabricate bulky powders [27]. Fig. 4 shows the morphologies of the ammonia sulfate doped precursor and LuAG powders calcined at 1000 °C for 2 h. It can be seen that the dispersity of the sulfate-doped precursor (Fig. 4a) is much better than that of the undoped precursor (Fig. 3a). Moreover, the particle size of the LuAG powders calcined at 1000 °C for 2 h (Fig. 4b) is more uniform and the morphologies are spherical. These phenomena are attributed to a higher decomposition temperature of the SO_4^{2-} than hydroxide, and its existence at comparatively high temperature may reduce element diffusion between particles, which is beneficial for the dispersion of powder [28].

4. Conclusions

LuAG powders were produced via co-precipitation from a mixed solution of aluminium and lutetium nitrates using ammonia water as precipitant. The precursor converted directly to pure LuAG at 900 °C. No other phase occurred. The precursor after drying and the resultant LuAG powders were loosely agglomerated. The addition of small amount of ammonia sulfate to mixed solution can reduce the agglomeration and produce more uniform spherical particle.

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