

Synthesis and characterization of YAG : Eu spray dried powders

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YAG compounds doped with Eu have been successfully synthesized by spray drying a solution of precursor nitrates. Aluminum and yttrium nitrates, europium oxide, ethylene glycol and citric acid were used as reagents. The resultant solution was fed to a spray dryer to obtain precursor powders, which were in turn heat treated at 800, 850 and 900°C and characterized by X-ray diffraction. Morphology of the synthesized powders was observed by scanning and transmission electron microscopy. Results showed that the crystallization temperature of the powders is below 850°C without the presence of intermediate phases. The powders consist of spherical agglomerates constituted of primary particles of 40 nm diameter approximately.

Key words: YAG, powder technology, spray-dried, crystallization, ceramics.

Introduction

Yttrium Aluminum Garnet (YAG) has a cubic structure that belongs to space group *Ia3d* with a lattice parameter of 12.01 Å, where metallic ions occupy *d*, *a* and *c* positions (tetrahedral, octahedral and dodecahedral sites, respectively). The aluminum atoms occupy 24 *d* sites and 16 *a* sites and yttrium is typically reported in 24 *c* sites [1]. This compound has several applications, either as a pure phase or doped with some elements such as Nd⁺³, Eu⁺³, Tb⁺³, Cr⁺³ [2] in laser systems production, coating of electronic devices, such as a phosphor for cathode ray tubes. Lately this compound has been considered as a good material for structural applications at high temperatures [3, 4] and as a ceramic matrix reinforcement. These applications are intimately related to their optical properties, chemical stability at high temperatures, excellent corrosion resistance and good mechanical properties. The conventional solid state reaction method of powders [5] for the synthesis of YAG requires high temperatures (1600°C) and a prolonged time of calcination for YAG formation. This causes grain growth and a decrease of mechanical properties of the final products. Several wet methods of synthesis have been developed [6-9] to diminish the crystallization temperature and increase the purity of YAG materials. Liu and Gao [7] reported synthesis of YAG from a polymeric precursor that includes a calcination step at different temperatures. These authors observed the formation of YAG phase at 950°C with a previous formation of metastable YAlO₃ phase. Han et al. [9] synthesized YAG by dissolving

Y₂O₃ powders in alumina sol. This route reports the formation of the metastable hexagonal YAlO₃ phase, and the powders have to be burned at temperatures higher than 950°C for full the formation of YAG. The presence of intermediate phases has also been observed in other synthesis routes such as precipitation with urea [10], where other phases were observed such as Y₄Al₂O₉, Y₂O₃ and Y₂O₂SO₄. Recently, Zhang et al. [11] reduced considerably the temperature of crystallization, obtaining the YAG crystalline phase at approximately 300°C for 2 hours, using a pressurized reactor. However, even when the temperature of crystallization is much lower than those reported before, it is necessary to have a high pressure (from 10.6 to 12.5 MPa) to achieve the reaction, which is a limiting condition. The addition of dopant elements has the purpose of producing powders with optical applications [12]. There are also some reports in the literature on the synthesis and characterization of YAG with dopant elements. [13, 14]. Zhou et al. [15] reported YAG:Eu doped powders using spray-pyrolysis with poly ethylene glycol (PEG) and rare earth oxides as reactants. Although, we use a spray drying process in the present study, we react rare earth nitrates and ethylene glycol. Furthermore, we crystallized the powders for different times in contrast to Zhou and colleagues, who calcined the samples for four hours. Additionally, we carried out different analyses. Thus, a simple route of obtaining YAG phase with Eu⁺³ addition is proposed using spray drying, where reagents keep a high degree of dispersion avoiding segregation of the components leading to a narrow size distribution of powders in the nanometre range.

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Experimental

Aluminum nitrate (99.9% J.T. Baker), yttrium nitrate (99.9% Aldrich), europium oxide (99.99% ALPHA-AESAR), citric acid (J. T. Baker), ethylene glycol (99.9% J. T. Baker) and deionized water were used as raw materials. Aluminum and yttrium nitrates were dissolved into deionized water in adequate quantities to obtain a final mixture with a 2.94 : 5 yttrium/aluminum molar ratio. The resultant concentrations of Al^{+3} and Y^{+3} were 0.10 and 0.060 molar, respectively. Once the aluminum and yttrium solutions were dissolved separately, both were mixed forming a nitrates solution. Citric acid and europium oxide were dissolved separately with some drops of nitric acid and added to the mixture of nitrates (concentration of the citric acid in the final solution was 0.05 M). Finally, ethylene glycol was added to the solution (molar ratio 1 : 1 of ethylene glycol with the citric acid). The resultant solution was stirred for 15 minutes to assure homogeneous mixing of the components. Two solutions with compositions YAG:2 mol%Eu and YAG: 5 mol%Eu were fed separately into the Spray Dryer (Mini Spray-Dryer, ADL-31), to eliminate the solvent and lead to precursor powders. These powders were thereafter calcined at 800, 850 and 900°C to promote the crystallization of YAG phase. Heat treated powder samples were characterized by X-ray diffraction using a SIEMENS D5000 diffractometer with Cu-K α radiation of 1.54056Å operated at 20 kV. Several micro- graphs of the samples were obtained by scanning electron microscopy (SEM, JEOL JSM-6400) to measure the size of agglomerates and their morphology as well as by trans- mission electron microscopy (TEM, Phillips TECNAI super Twin) with an acceleration voltage of 200 kV to measure the particle size and representative unit cell parameters of crystallites.

Results and discussion

Fig. 1 and 2 show XRD patterns of powders thermally treated at 800, 850 and 900°C (a, b and c) with 2 and 5% additions of europium, respectively. Powders calcined at 800°C are in an amorphous state. Powder crystallization occurs between 800 and 850°C, irrespective of the europium content and without the formation of intermediate phases. The crystalline phase, as observed in patterns b and c, corresponds to YAG (JCPDS card 33-0040). Samples prepared with 2% of europium showed a higher intensity from all the diffracted planes. Considering that the Eu^{+3} ions enter in solid solution occupying dodecahedral sites that are originally occupied by Y^{+3} ions and that the ionic radii of Y^{+3} and Eu^{+3} are 1.015 and 1.25Å respectively one can expect that europium ions would need a longer time for diffusion than yttrium ions during arrangement. Thus, increasing the Eu^{+3} content seems to produce a decrease in intensity of the diffraction peaks. This behavior suggests that at higher dopant

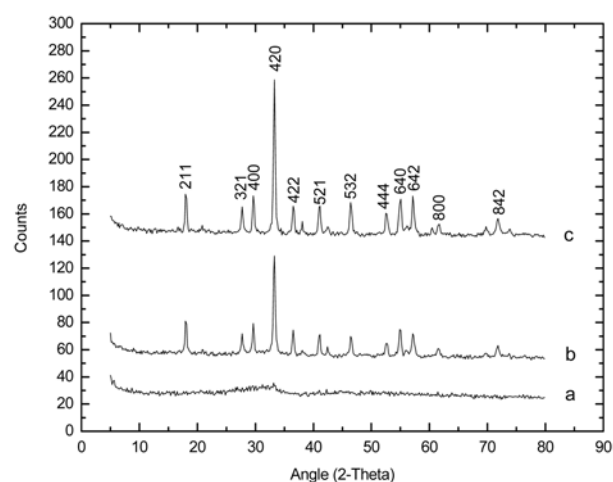


Fig. 1. XRD patterns of YAG : Eu 2% calcined at: a) 800, b) 850 and c) 900°C.

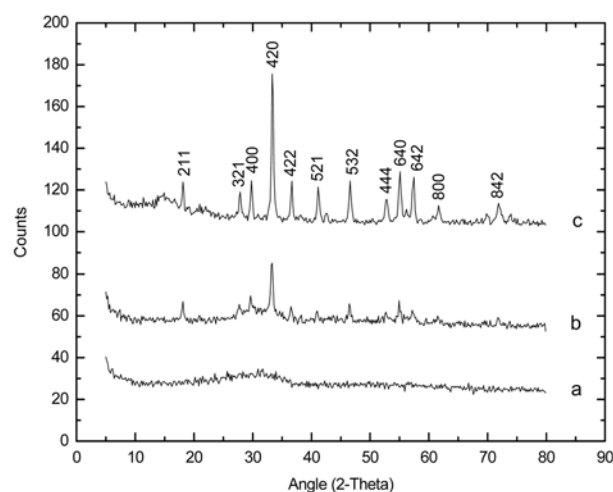


Fig. 2. XRD patterns of YAG:Eu 5% calcined at, a) 800, b) 850 and c) 900°C.

concentrations, a longer time of diffusion is required, which can in turn be related to the difference in diffusion coefficients between yttrium and europium, electronegativities and atomic sizes.

Fig. 3 shows SEM images of powders with 2% and 5% additions of europium. Image analysis of these images reveals agglomerates with a spherical morphology and average diameter of 1 μm . A spherical morphology is characteristic of agglomerates obtained by spray drying [16]. This morphology does not seem to be influenced with the composition of the feed solution. This current method also allowed obtaining agglomerates of controlled size, this being an important advantage comparing with other methods. [1, 10, 15] Further on, the spherical morphology of agglomerates with a narrow size distribution in the range of 3 μm benefits the emissivity of materials for phosphor applications, as is reported elsewhere [13, 15]. An additional advantage of spherical agglomerates is its excellent fluidity, which is beneficial for the elaboration of pressed bodies.

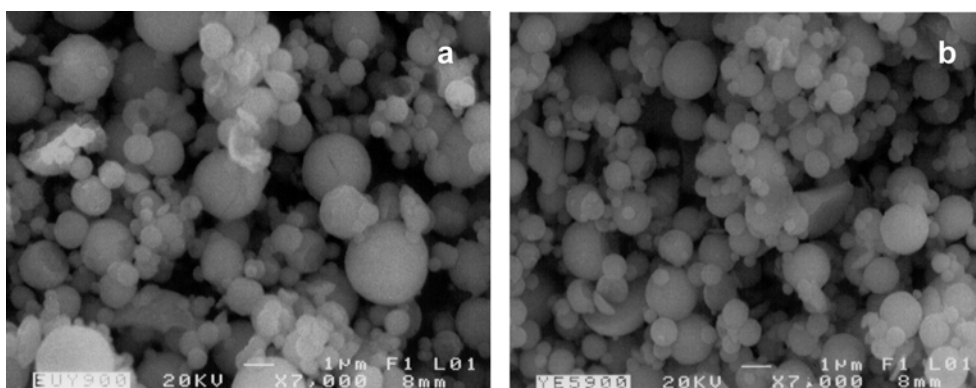


Fig. 3. SEM images of YAG with 2% (a) and 5 % (b) of europium annealed at 900°C for 1 h.

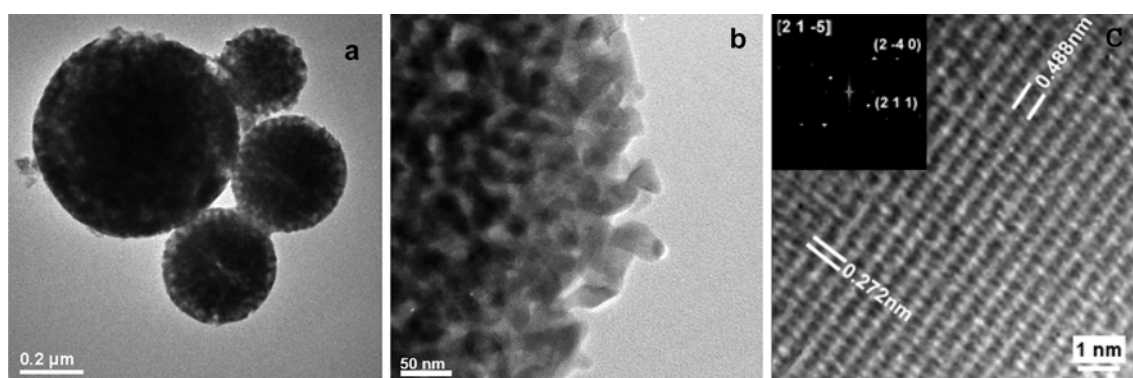


Fig. 4. TEM micrographs of YAG powders doped with 5 % of Europium calcined at 900°C for 1 h, (a) bright field image, (b) dark field image and c) High resolution image and the corresponding experimentally observed diffraction pattern.

Transmission electron micrographs of typical spherical particles as well as a high resolution TEM image of a single particle are shown in Fig. 4. Agglomerates are clearly composed of particles with an average size of 40 nm as shown in figure 4b. Formation of agglomerates also occurs irrespective of the europium content only being influenced by the spray drying procedure. A nanometre and homogeneous size of particles is very important, since they are the determining factors for good densification behavior and thus mechanical properties. Figure 4c shows experimentally the observed diffraction pattern showing the central beam and an array of diffraction spots from the crystallographic planes (2 $\bar{4}$ 0) and (211) of the cubic YAG phase. This crystallographic array shows interplanar distances of 0.272 and 0.488 nm which correspond to those of the crystalline planes of the YAG phase with a relative intensity of 100 and 27% and can be used as evidence to verify the crystallinity of the calcined powders at 900°C.

These results clearly demonstrate that the here proposed route of synthesis of YAG doped with Eu using spray drying reduces considerably the crystallization temperature of precursor powders to a temperature close to 850°C. Reduction of the crystallization temperature is possible because of the reduction in effective diffusion distances of the components.

Conclusions

Yttrium aluminum garnet with 2% and 5% of europium were successfully synthesized by spray drying of precursor nitrates leading to spherical agglomerates of nanometric sized particles with a narrow size distribution. This morphology is mainly attributed to homogeneous mixing of reagents and a decrease of the effective distances during component diffusion. The temperature of crystallization occurs below 850°C without the presence of any intermediate phases.

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