Journal of Alloys and Compounds 719 (2017) 264–270

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Synthesis of yttrium aluminum garnet nanoparticles in confined environment II: Role of the thermal treatment on the composition and microstructural evolution

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ARTICLE INFO

Article history:
Received 18 March 2017
Received in revised form
4 May 2017
Accepted 16 May 2017
Available online 18 May 2017

Keywords:
YAG nanoparticles
Water in oil bicontinuous microemulsion
Transmission Electron Microscopy
Phase evolution

ABSTRACT

Nanoparticles of *yttrium aluminum garnet* (YAG, $Y_3Al_5O_{12}$) have been obtained by thermal treatments, at several temperature in the range 400–950 °C, of the precursors synthetized via co-precipitation in water in oil microemulsion.

The obtained nanoparticles have been characterized by means of X-ray Diffraction and Transmission Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (EDS) and Select Area Electron Diffraction (SAED).

Results show the phase evolution occurring to obtain not aggregated nanoparticles of YAG phase.

A possible growth mechanism of YAG nanoparticles is discussed on the basis of observed particle microstructure and morphology. The results indicate that, applying this sequence of thermal treatments, the formation of the garnet phase takes place with the formation of yttria nuclei that grow preferentially in one direction. The growth takes place via two processes: at low temperature the nuclei evolve to the garnet phase by following the oriented attachment mechanism, at higher temperatures by the Kirkendall effect accounting for the morphological modification. The proposed synthesis and thermal treatments, by favoring one or the other growth mechanisms, allowed attaining a fine control on nanoparticles features thus making it useful for similar mixed oxides preparations.

1. Introduction

The interesting technological applications of *Yttrium Aluminum Garnet* (YAG, $Y_3Al_5O_{12}$), whose cubic structure is in the space group Ia-3d, doped with lanthanides ions, in inorganic electroluminescence displays, X-ray scintillators, lasers, and white light LED are nowadays well consolidated [1]. Notwithstanding, the interest of researchers is still growing because the optical properties of nanocrystals are expected to be dependent on the properties of doping agent and on the synthesis route that may influence particle size and its distribution and morphology [2–4]. As a consequence, several chemical routes such as coprecipitation [5–10], sol-gel [11–13], Pechini method [14,15], solvo-thermal synthesis [16,17] and others have been used. All methods, unless the solvo-thermal synthesis, involve a post-synthesis treatment at high temperature, necessary to obtain the garnet phase avoiding the formation of secondary crystalline phases. Since the thermal treatment induces the growth of the particles and can carry out to the formation of big agglomerated and/or aggregated particles, this step has to be controlled and monitored.

Many authors have investigated the evolution of YAG precursors to the formation of the YAG nanoparticles [18–21] showing that the evolution underwent by the precursors can be influenced by synthesis procedure and by the relative experimental parameters such as nature of reactants, temperature and pH. Sang at al. explored the

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http://dx.doi.org/10.1016/j.jallcom.2017.05.174

influence of pH on the evolution of the chemical composition and the morphology of the precipitate, and on the variation of phase composition during the calcination process [22]. The results of this study indicated that during the synthesis of the YAG precursor, the pH and aging duration should be carefully controlled. Palmero et al. observed the crystalline evolution at several temperature (from 450 to 1350 °C) of precursors obtained by coprecipitation, showing the effect of the counterion type on the phase formation, in fact the chlorine induces the formation of the secondary hexagonal phase while the nitrate avoids it [19]. Qin et al. studied the grain growth and microstructural evolution of YAG nanocrystallites during the calcination process of precursors obtained by urea method combined with supercritical CO_2 fluid drying technique [14]. They observed the formation of the garnet phase explaining the growth of the crystallite in terms of oriented attachment and Ostwald ripening. Li et al. compared the phase evolution during calcination of the precursors obtained by coprecipitation by using two different precipitants: aqueous ammonia and ammonium hydrogen carbonate. The aqueous ammonia precursor transformed to pure YAG at about 1000 °C via perovskite YAP intermediate phase while the ammonium hydrogen carbonate precursor is directly converted to pure YAG at about 900 °C [21].

Recently, the YAG nanoparticles have been obtained by using a bicontinuous microemulsion [23,24] to synthesize precursors. The thermal treatment, performed in one step at 900 °C for 1 h, allowed to obtain nanoparticles monodispersed in size, with well-defined shape, not agglomerate and of smaller size (10–45 nm) respect to those obtained by using other synthetic procedures. A close relationship between the microstructure of the confined environment and the nanoparticles features has been found.

Considering the importance of nanoparticle physical features on optical properties and by taking into account the importance of temperature and duration of thermal treatment on the final properties of nanoparticles, in this paper the effect of the thermal treatment on the evolution of precursors, synthesized in the microemulsion toward the formation of YAG nanoparticles, has been investigated. The samples have been prepared in the bicontinuous microemulsion constituted by water/Cetyltrimethylammonium bromide (CTAB)/1-butanol/n-heptane. The formation and the evolution of the crystalline phase have been investigated by using X-ray Diffraction (XRD). The morphology and particles size, the elemental composition and the crystalline habit have been investigated by using Transmission Electron Microscopy (TEM) coupled with Energy Dispersive X-ray Spectroscopy (EDS) and Select Area Electron Diffraction (SAED).

2. Materials and methods

2.1. Materials

Cetyltrimethylammonium bromide (CTAB) (Aldrich ≥98%), 1-butanol (Aldrich, 99.8%), n-heptane (Sigma-Aldrich, 99%), deionized water, $Y(NO_3)_3\cdot 6H_2O$ (Sigma-Aldrich, 99.8%), $Al(NO_3)_3\cdot 9H_2O$ (Sigma-Aldrich, 99.8%) and ammonia solution (Sigma-Aldrich 28%) were used as received. The conductance of deionized water was <1.5 μS/m.

2.2. Preparation of the nanoparticles

The precursor synthesis of YAG nanoparticles has been performed following the procedure already reported [24]. The microemulsion containing ammonia solution was added dropwise to the microemulsion containing the solution of nitrates, maintained under constant stirring at room temperature. The two microemulsions were prepared at the same composition ($R = 70$) and by following the same procedure already reported [24]. A white hue sol was instantaneously observed, indicating the formation of hydroxides. A complete precipitation occurred in 12 h. The precipitate was filtered and repeatedly washed with water to remove residual ammonia, nitrate ions, and surfactant molecules.

The obtained white precipitate was over-night dried at 100 °C, then treated at 400 °C for 24 h to remove the CTAB by complete oxidation. The obtained material was subsequently subjected to cumulative stages of thermal treatment at 500, 600, 700, 750, 800, 850, 900 and 950 °C for 1 h each. After each treatment, an aliquot was taken to be analyzed.

2.3. Characterization techniques

XRD patterns were acquired by a Philips PW 1050/39 diffractometer in the Bragg-Brentano geometry using Ni-filtered Cu Kα radiation ($\lambda = 1.54056$ Å) in the 2θ range 5–90° with a step of 0.05° and a time for step of 5 s. The X-ray generator worked at power of 40 kV and 30 mA, and the resolution of the instrument (divergent and antiscatter slits of 0.5°) was determined using R-SiO_2 and R-Al_2O_3 standards free from the effect of reduced crystallite size and lattice defects. The phase identification has been performed by using the X'pert HighScore® Software.

Transmission Electron Microscopy (TEM) micrographs were acquired by using a JEM-2100 (JEOL, Japan) operating at 200 kV accelerating voltage, equipped with an energy dispersive X-ray spectrometer (EDS, Oxford, UK) suitable for element identification. Each treated powder was homogeneously dispersed in isopropanol by sonication. A small drop was deposited on a lacey-carbon grid of 300 mesh, and after complete solvent evaporation the nickel-copper grid was introduced into the TEM chamber analysis. The Selected Area Electron Diffraction (SAED) pattern was collected by using a CCD camera (Gatan MSC KAF1000).

3. Results and discussion

The phase evolution process of the powder treated at various temperatures was followed by X-ray diffraction. The XRD patterns of the samples treated at 400, 600, 800, 850 and 950 °C are reported in Fig. 1. The XRD patterns of the samples treated at 500, 700, 750 and 900 °C are reported in Fig. SI1 of the Support Information (S.I.).

The sequence of patterns reported in Fig. 1 and Fig. SI1 shows that the sample is completely amorphous up to 500 °C. The crystallization seems to occur at 600 °C for the thermal treatment conditions adopted.

In detail, the XRD pattern of the sample treated at 600 °C show a tiny peak at 29.1° ascribed to the (222) plane of the cubic yttrium oxide (Y_2O_3, yttria) phase. This peak, superimposed to the amorphous pattern of the hydroxides, indicates that, at this temperature small yttria crystallites are formed. The XRD pattern of the samples treated at 700 and 800 °C does not significantly change: an increase of the (222) yttria peak is observed together with the appearance of other tiny peaks at higher angles. The XRD pattern of the sample treated at 850 °C show a sequence of peaks superimposed to a fading amorphous band, thus indicating that the process of conversion of hydroxides into crystalline phases is effective in the range 750–800 °C. The crystalline pattern can be described in terms of three crystalline phases: yttria, yttrium aluminum garnet YAG and hexagonal yttrium aluminum oxide ($YAlO_3$, YAH).

The subsequent thermal treatment at 900 °C favors the complete crystallization process, since no discernible amorphous contribution can be detected above the background base line. Also in this case, the crystalline pattern is described in terms of yttria, YAG and YAH.

The XRD pattern of the sample treated at 950 °C is described by