

Preparation of YAG Nanoparticles and their Characteristics

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Abstract. The nanosized yttrium aluminium garnet powders doped with rare earth oxides are prepared by combustion synthesis using several organic fuel. Dense materials are manufactured by conventional sintering and spark plasma sintering (SPS). The combustion synthesis provides preparation of pure crystalline YAG nanopowders at ratio $Y/Al = 3/5$ after additional calcination at 1000 °C. The relative density of the SPS sintered samples at 1500 °C for 2 min is in the range of 95.4–98.5% depending on dispersity of powders.

Introduction

Recently $Y_3Al_5O_{12}$ (YAG) nanoparticles and nanostructural materials have received much attention because of their interesting physical and mechanical characteristics. Polycrystalline $Y_3Al_5O_{12}$ ceramic exhibits excellent creep resistance and it ought to be used as matrix or reinforcing material, for example, for fabrication YAG–SiC nanocomposites with fine microstructures [1]. Nanosized YAG powder finds application for manufacture transparent ceramics [2]. YAG doped with rare-earth elements are promising phosphors for displays and for development of dye lasers [3, 4]. Characteristics of these phosphors have critical dependence of their particle size. At present, nanosized oxide powders can be prepared mainly by soft-solution routes [5] such as hydrothermal, sol-gel, co-precipitation, combustion synthesis, etc.

Each preparation method has its own advantages and disadvantages which mainly relate to the particle size distribution, purity of the products, its production rate and cost. Among soft-solution preparation methods, the combustion synthesis due to simplicity, energetic efficiency is very promising. The nitrate–citrate process was realized for preparation of Eu:YAG [6], Nd:YAG [7, 8] but formation temperature of crystalline powders and their phase composition differs. Pure crystalline Eu:YAG nanoparticles have been prepared by nitrate–citrate process at calcination temperature in the range of 900–930 °C by direct crystallization from amorphous material and without formation of intermediate phases [6]. From data [7] followed that crystallization of amorphous Nd:YAG prepared by nitrate–citrate route occurred at the range of 800–850 °C depending on the nitrate–citrate ratio. Addition of isopropyl alcohol to citric acid promoted crystallization of Nd:YAG and as-prepared at 300 °C powder besides amorphous part contained also YAG phase [8]. The crystallization of the amorphous part included formation of YAP phase and pure crystalline Nd:YAG powder was obtained by calcination at 900 °C for 3 h.

In the present work the influence of the organic fuel used in the combustion synthesis on the phase formation, crystallite size, specific surface area (SSA) and densification of prepared powders is studied.

Experimental

The combustion synthesis was based on the exothermic reaction between the solution of aluminium and yttrium nitrates, and Eu, Ce, Nd nitrates (Treibacher GmbH), and organic fuel [8]. The citric acid, glycerin, and ethylene glycol were used as organic fuel in order to determine their influence on the produced particle size. The solution of components was concentrated by evaporation at 150 °C. The obtained gel was combusted at temperature 380–400 °C. The as-prepared grey powder was calcined at 650–1000 °C in order to obtain well crystalline pure YAG particles. Chemical and phase

composition of the products was determined by conventional chemical and X-ray diffraction (Bruker AXS) analysis. The specific surface of powders was determined by argon adsorption-desorption method. The particle size, shape and microstructure of bulk materials were studied by SEM. The crystallite size and lattice parameters were studied by using program Topas3 (Bruker AXS).

The nanoparticles were consolidated by using pressureless sintering at 1500–1700 °C and by using spark plasma sintering (SPS, Sojitz Corp.) technique at 1400–1600 °C. The nanoparticles were filled up into cylindrical graphite die (inner diameter of 20 mm, outer diameter of 40 mm and height of 40 mm). The applied pressure of 30 MPa was selected and maintained constant during the whole consolidation process in SPS apparatus. The density of the sintered bodies was determined by the Archimedes method.

Results and discussion

The X-ray diffraction and chemical analysis of the powders prepared by combustion synthesis indicates that phase composition and purity of the products depends on an organic fuel used and calcination temperature employed (Table 1).

Accordingly to XRD patterns the yttria–alumina powders produced by glycerine route at ratio $Y/Al = 3/5$ and calcined at 650 °C contain traces of crystalline $Y_3Al_5O_{12}$ but the higher calcination temperature results in the increasing intensity and narrower diffraction maxima. Besides $Y_3Al_5O_{12}$ phase small amount of hexagonal $YAlO_3$ phase is presented at calcination temperature below 1000 °C. The quantitative analysis shows that powders calcined at 800, 900 and 1000 °C contain 85%, 95%, and 100% of $Y_3Al_5O_{12}$ phase respectively.

The as-prepared yttria–alumina compounds prepared by citric acid and ethylene glycol routes are fully X-ray amorphous.

Table 1. Dependence of the phase composition of prepared powders on calcination temperature and used organic additives.

Calcination temperature [°C]	Phase composition		
	Powders prepared by citric acid route	Powders prepared by glycerine route	Powders prepared by ethylene glycol route
650	X-ray amorphous	$Y_3Al_5O_{12}$ (tr.)	X-ray amorphous
800	$Y_3Al_5O_{12}$ (tr.)	$Y_3Al_5O_{12}$ (85%), $YAlO_3$ (15%)	X-ray amorphous
850	$Y_3Al_5O_{12}$ (80%), $YAlO_3$ (20%)	$Y_3Al_5O_{12}$ (94%), $YAlO_3$ (6%)	$Y_3Al_5O_{12}$ (14%), $YAlO_3$ (16%)
900	$Y_3Al_5O_{12}$ (92%), $YAlO_3$ (8%)	$Y_3Al_5O_{12}$ (95%), $YAlO_3$ (5%)	$Y_3Al_5O_{12}$ (71%), $YAlO_3$ (29%)
1000	$Y_3Al_5O_{12}$ (100%)	$Y_3Al_5O_{12}$ (100%)	$Y_3Al_5O_{12}$ (100%)

The crystallization of the powders prepared by using citric acid starts at 800 °C. XRD patterns of yttria–alumina powders prepared by ethylene glycol route and calcined at 850 °C show only weak traces of crystalline YAG phase. Calcination at 900 °C promotes crystallization of $Y_3Al_5O_{12}$ and $YAlO_3$ phases. All samples calcined at 1000 °C contain only well crystalline YAG phase.

The dependence of crystallization temperature of yttria–alumina compounds on used fuel can be explained by different combustion temperatures of mixtures.

Formation of YAG phase at high temperature influences the specific surface area of the particles (Fig. 1). The specific surface area of the YAG powders calcined at 1000 °C depends on the starting temperature of their crystallization. The YAG powder prepared by using ethylene glycol has higher specific surface area as that of powders prepared by glycerin or citric acid route. Obviously partial formation of YAG crystallites at the lower temperature promotes growth of the formed particles during the further calcination process.

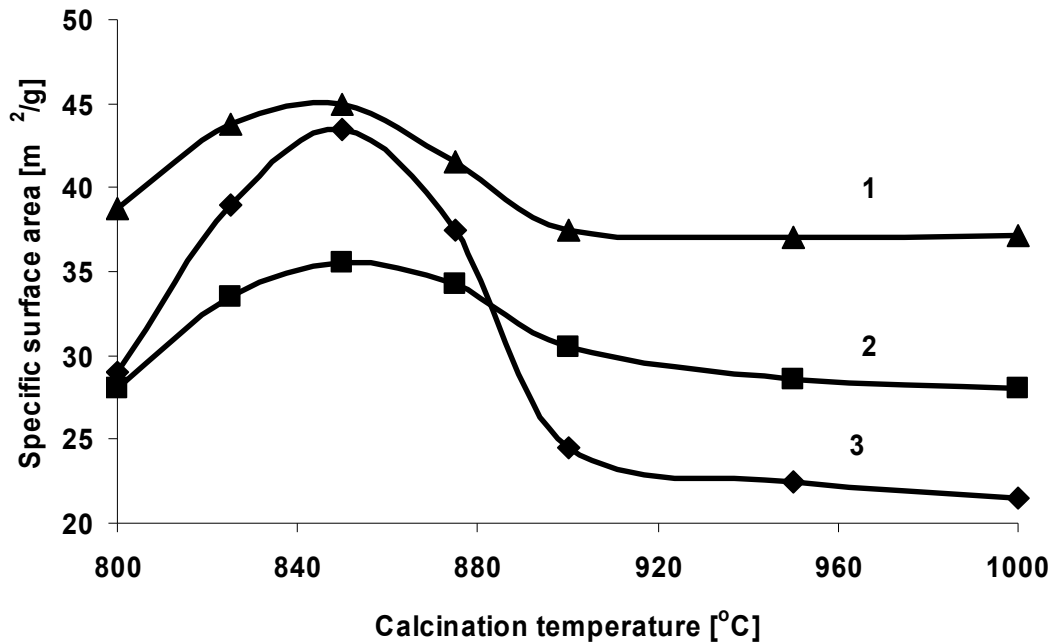


Fig. 1. Dependence of specific surface area of samples prepared by ethylene glycol (1), citric acid (2), and glycerine (3) route on calcination temperature.

The calculated average particle size of YAG prepared by ethylene glycol route is about 36 nm but for particles prepared by citric acid and glycerine route – about 49 and 78 nm respectively. Determined crystallite size of YAG is close to calculated average particle size (Fig. 2).

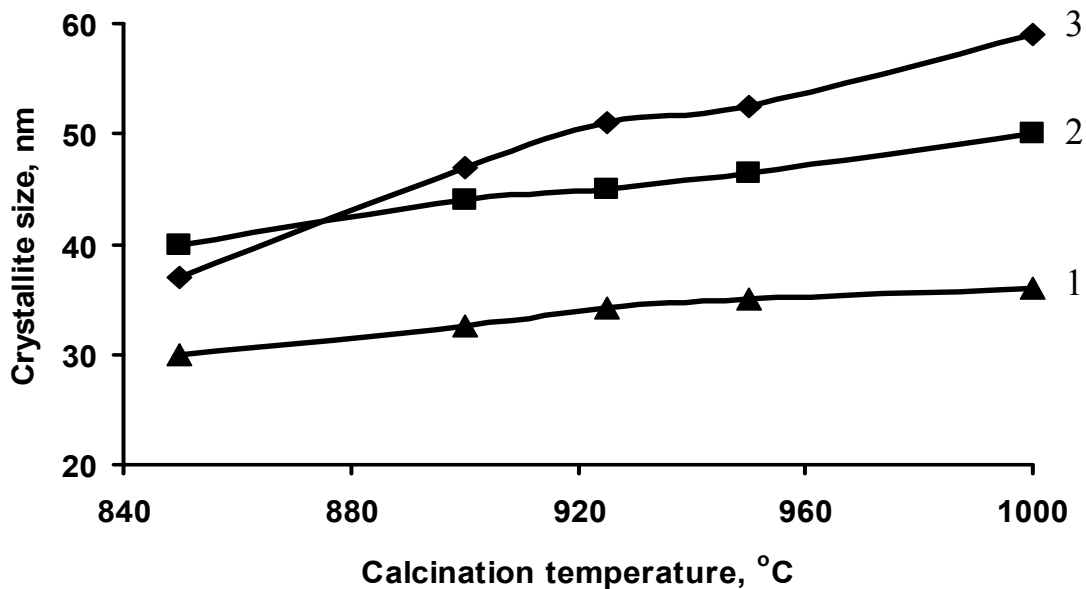


Fig. 2. Dependence of crystallite size of $Y_3Al_5O_{12}$ on calcination temperature and organic additive: ethylene glycol (1), citric acid (2), glycerine (3).

Presence of small amounts of rare-earth dopants (1.5 wt.%) has insignificant influence on the phase composition and specific surface area of the prepared powders but change of the lattice parameters indicating that dopants are incorporated in lattice (Table 2).

Table 2. Specific surface area (SSA), phase composition of doped YAG nanoparticles prepared by ethylene glycol route and calcined at 1000 °C.

Sample	Specific surface area [m ² /g]	Phase composition	Lattice parameters [nm]
YAG	36.0	Y ₃ Al ₅ O ₁₂	1.20067
Ce:YAG	36.5	Y ₃ Al ₅ O ₁₂	1.20412
Eu:YAG	40.6	Y ₃ Al ₅ O ₁₂	1.20411
Nd:YAG	41.2	Y ₃ Al ₅ O ₁₂	1.20408

Densification of Y₃Al₅O₁₂ nanopowders by using SPS process starts at 1000 °C and maximal density of materials is reached at 1400 °C during 2 min (Fig. 3).

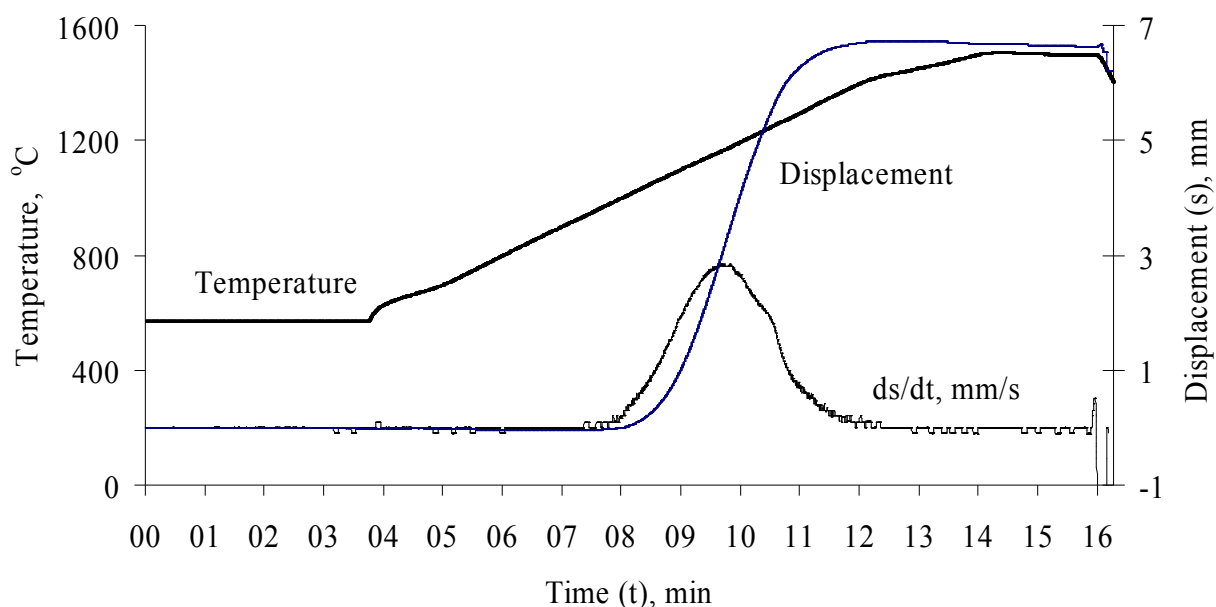


Fig. 3. Parameters of spark plasma sintering process of the YAG nanopowders.

The increase of holding time or temperature has insignificant influence on the density of manufactured samples. The relative density of samples in the range of 95.5-98.9% is depending on the specific surface area of the used powders (Table 3).

Table 3. Relative density of YAG samples sintered by pressureless and spark plasma sintering (SPS) methods in dependence of the preparation route.

Preparation route	Relative density [%]		Phase composition
	Pressureless sintering, 1700 °C, 2 h	SPS, 1500 °C, 2 min	
Glycerin route	78.0	95.4	Y ₃ Al ₅ O ₁₂
Citric acid route	81.3	95.8	Y ₃ Al ₅ O ₁₂
Ethylene glycol route	91.3	98.5	Y ₃ Al ₅ O ₁₂

The similar relationship is characteristic for samples sintered at 1700 °C by pressureless sintering but these samples have lower relative density with respect to SPS samples. This can be explained by low green density (40-43%) of used samples of nanoparticles.

The SEM image of fracture surface shows that SPS sintered YAG samples have dense microstructure with shaped grains with size in the range of 1.5-5 μm (Fig. 4a) but crystallite size is in the range of 135-144 nm.

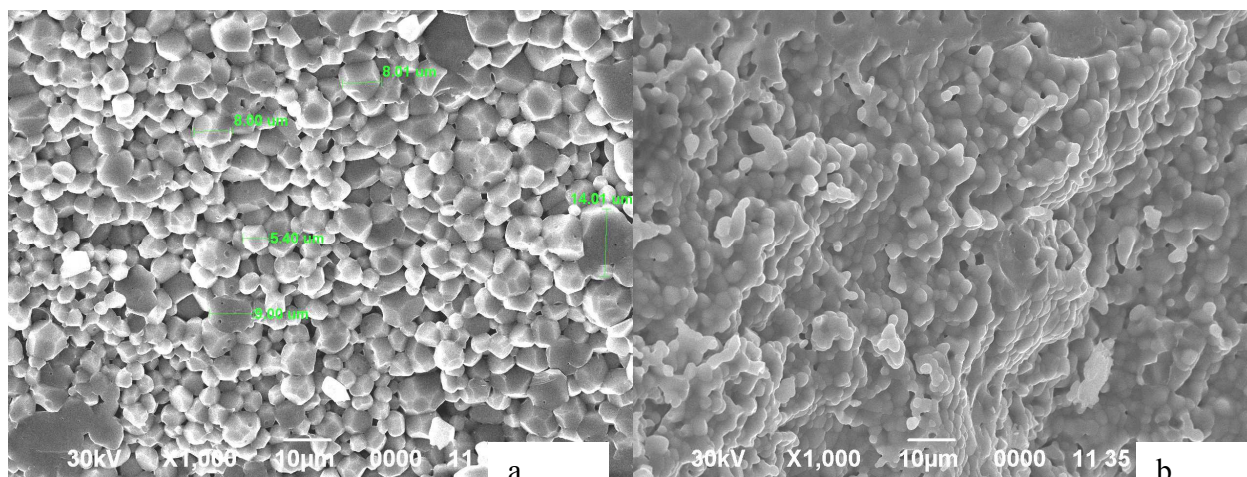


Fig. 4. SEM images of the fracture surface of the $\text{Y}_3\text{Al}_5\text{O}_{12}$ samples manufactured by spark plasma (a) and pressureless sintering (b) technique.

The fracture surface of the sample manufactured by pressureless sintering exhibits round grains with size in the range of 3-6 μm (Fig. 4b). The relatively high grain size of the samples manufactured by SPS technique can be explained by presence of agglomerates of nanoparticles. According to [9] the size of agglomerates determines the final grain size of sintered samples in the SPS process.

Summary

1. The developed combustion synthesis after calcinations at 1000 $^{\circ}\text{C}$ provides preparation of nanocrystalline YAG powder with specific surface area in the range of 22–36 m^2/g and average particle size in the range of 36–78 nm. The presence of rare-earth dopants (1.5wt.%) increases the lattice parameter without change of phase composition.
2. The crystallization temperature and average particle size strongly depend on used organic fuel. The use of ethylene glycol can be recommended as organic fuel for preparation of fine YAG nanoparticles.
3. Spark plasma sintering provides manufacture of dense YAG bodies with crystallite size in the range of 135-144 nm at 1400-1500 $^{\circ}\text{C}$ during 2 min.

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