Synthesis of Nano-sized Yttrium-Aluminum Garnet in a Continuous-Flow Reactor in Supercritical Fluids

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Z. Naturforsch. **2008**, *63b,* 756 – 764; received February 7, 2008

Dedicated to Professor Gérard Demazeau on the occasion of his 65th birthday

The conditions for obtaining pure yttrium-aluminum garnet (YAG) in a one-step process starting from components soluble in supercritical (SCR) liquids in a flow reactor have been studied. The powders were characterized using XRD, BET, SEM and helium pycnometry. Favorable conditions for YAG production were achieved using acetates (and acetylacetonates) in aqueous-alcoholic solutions as starting materials. Aqueous and alcoholic solutions of nitrates and aqueous solutions of acetates were found not appropriate as precursors for YAG production. The powders obtained had the shape of nano-sized cubes with diameters in the range 80 – 120 nm. After annealing at 600 °C the powders have comparable density as those made *via* a conventional precipitation-calcination route but differ from the calcinated products form soft agglomerates.

Key words: YAG, Supercritical Fluids, Nanopowders

Introduction

Synthetic yttrium-aluminum garnet $Y_3Al_5O_{12}$ (YAG) is one of the most important materials used since the 60's for the production of optoelectronic devices. Doped in the monocrystallization process with a number of the lanthanide-family metals it is used, among others, for the production of lasers. The neodymium laser has particularly useful properties with an emission wavelength of 1063 nm and an efficiency of up to 53 %, operating at temperatures up to 200 °C [1]. Despite many years of development, monocrystallization of YAG is still an expensive process. The shape and size of the forms offered as well as the level of their doping are limited [2]. Therefore, studies were undertaken to find alternative routes to YAG monocrystals, particularly ceramic specimens of YAG of high quality [3, 4]. The production of YAG ceramics for laser purposes was finally established in 1995 [5]. The starting material is a nano-sized YAG powder made using a precipitation process followed by calcination and grinding. Free sintering leads to transparent ceramics with micrometric grain size and a number of properties superior to the monocrystals, including higher levels of doping [6]. Production of YAG nanopowders is possible using a range of techniques, such as co-precipitation and calcination [7 – 9], sol-gel and Pechini's method with many modifications [10 – 16], and hydrothermal methods [17].

Obtaining a ternary compound, such as YAG, requires a precise maintenance of the reaction conditions. Even careful control of the stoichiometry of the precursors does not guarantee success, since YAG formation is known to be a multi-step process [18] with intermediate stages connected with the formation of the related compounds $Y_4Al_2O_9$ (YAM) and $YAlO_3$ (YAP). Subsequent reaction steps for these materials require higher production temperatures (exceeding even 1500 °C) which leads to partial sintering of the material and the formation of aggregates. Co-precipitation and further calcination of stoichiometric gels containing aluminum and yttrium hydroxides permit to obtain pure nanometric YAG powder at a surprisingly low temperature of *ca.* 900 °C [18]. Nanocrystalline YAG powders doped with rare-earth ions made using the sol-gel and coprecipitation [19] methods show interesting new optical properties as compared to microcrystalline samples [13], and can be sintered to translucent ceramics under extreme pressures exceeding 2 GPa [20, 21]. Such high pressures are needed to break hard aggregates that form during the calcination process.

Solvothermal synthesis seems particularly promising to lower the synthesis temperature [22], and powders obtained in a one-step process may have a narrow grain-size distribution and should form only weak agglomerates. Therefore a technology where the calcination and grinding processes are eliminated, and non-aggregated YAG nanoparticles are produced in one step show real promise. Approximate calculations by Piticescu [23] have shown that YAG production by decomposition of salts containing Y^{3+} and Al^{3+} in aqueous solutions proceeds above 500 ℃, and that a high rate of heating is necessary, otherwise intermediate reaction products would segregate. The feasibility of a continuous synthesis process of metal oxide nanoparticles in supercritical water was demonstrated by Adschiri *et al.* [24] as well as by Cabanas *et al.* [25]. The particular advantage of the reactor used by the latter group was that its special design prevents clogging of the equipment with nanopowders and allows shorter reaction times.

In a previous paper [26] we have demonstrated that YAG powders with a diameter in the range 50 – 150 nm can be obtained in a one-step process from water – ethanol solutions of acetates and acetylacetonates of yttrium and aluminum. It has to be noted that contrary to the work of Zhang *et al.* [22] the solutions of the reactants were processed and not hydroxyl gel precipitates. The grain size of the powders depends mainly on the process temperature, and the finest grains (about 50 nm) with a narrow grain-size distribution were obtained in supercritical conditions at temperatures in the range 380 – 385 ℃, while upon a decrease of temperature to 350 – 354 ℃ particles of 150 nm (in average) with a wider size range were obtained.

In the present paper we compare the results of syntheses using nitrates and acetates of yttrium and aluminum dissolved in water and ethanol. We also compare the properties of YAG nanopowders obtained in the supercritical process with those obtained using the traditional co-precipitation method.

Experimental Section

Apparatus

The syntheses were carried out at the University of Nottingham (UK) utilizing a flow reactor for synthesis in supercritical water at pressures up to 24 MPa and temperatures up to 460 ℃. The description of the reactor and methods for obtaining the metal and metal oxide powders were presented in detail in ref. [27]. In short, salts of metals are injected in a stream of SC water using a specially designed nozzle ensuring short reaction times. The construction prevents clogging of the reactor with nanopowders. Constant parameters of the process were maintained. The temperature of the SC water was 450 ℃ at its source, 380 ℃ in the center of the reactor, and about 45 ℃ in the cooler part (Table 1).

Denley BS400 and MPW 350 centrifuges were used for phase separation. For comparison, part of the material obtained was subjected to drying in a vacuum sublimation drier (cryodesiccator).

Studies of physicochemical properties and structure of the products were carried out by means of a Siemens D 5000 diffractometer utilizing $CuK_{\alpha1}$ radiation, an ACCU PYC 1330 helium pycnometer, a GEMINI 2360 apparatus for measuring the specific surface of powders by the BET method, and a LEO 1530 electron microscope.

Chemicals used and mode of their preparation

$Y(NO_3)_3 \cdot 6H_2O$ (Aldrich 23,795-7), $Al(NO_3)_3 \cdot 9H_2O$ (Aldrich 23,797-3), hydrated yttrium acetate ($Y(ac)_3 \cdot H_2O$, Aldrich), aluminum acetylacetonate ($Al(acac)_3$, 99 %, Aldrich), basic aluminum acetate (Aldrich), aquaeous ammonia 35 % (Fisher Scientific, A/3240/PB17), acetic acid CH_3COOH 100 % (BDH AnalaR EC-No200-580-7), ethyl alcohol C_2H_5OH (UN1170), and demineralized water were used as reactants.

The following solutions were prepared:

Solution A

24.0 g of $Y(NO_3)_3 \cdot 6H_2O$ and 39.020 g of $Al(NO_3)_3 \cdot 9H_2O$ in 1 L of deionized water, which corresponds to the stoichiometric composition Al : Y = 5 : 3 (by mole) and concentration of 0.02 M (with respect to $Y_3Al_5O_{12}$).

Solution B

Half of the prepared solution A was dropped into a solution of 3 % aqueous ammonia maintaining a constant pH of 9. The precipitate obtained was subjected to two-fold centrifugation, was washed with deionized water and centrifuged. Dissolution in 15 mL of 100 % acetic acid gave 120 mL of an acetate solution.

Solution C

12.0 g of $Y(NO_3)_3 \cdot 6H_2O$ and 19.51 g of $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in 500 mL of pure ethanol (concentration of *ca.* 0.02 M with respect to YAG).

Table 1. Methods of manufacturing and characterization of the investigated samples.

No.	Details of sample preparation	SEM ig. No.	Density [g cm^{-3}]	Specific surface BET [m^2 g^{-1}]	Equivalent grain size calculated from BET [nm]	XRD evaluation, average grain size by XRD analysis
1	Solution A diluted with water 1 : 10, initial pH = 3.5, pH after reaction 0.8, pH after 24 h 1.2, precipitate centrifuged, dried at ambient temperature, small amount useless for further studies					Mixture
2	Solution A diluted with ethanol 1 : 4, initial pH = 3.5, pH after reaction 4.5, precipitate centrifuged, dried at ambient temperature, small amount useless for further studies					YAG+ YAP+ AlOOH
3	Solution C, initial pH = 3.9, pH after reaction 4.5, precipitate centrifuged, dried at ambient temperature, small amount useless for further studies					YAG+ YAP+ YOOH
4	Solution B diluted with ethanol 1 : 30, initial pH = 5, pH after reaction 3.3, dried at ambient temperature	5		11.79	120	YAG 80 nm
5	Solution B diluted with ethanol 1 : 30, initial pH = 5, pH after reaction 3.3, dried in a cryodesiccator	1 – 4				YAG 100 nm
6	Solution D	6	3.59	21.36	80	YAG 60 nm
7	Solution E 415/355 °C,	7 – 8	3.95	13.41	110	YAG 70 nm
8	Comparative Sample Co-precipitation from Solution A NH_3aq, pH = 9, washing with distilled water and isopropanol, centrifugation, calcination 5 h at 900 °C	9	4.27	72.76	18	YAG 30 nm

Solution D

Hydrated yttrium acetate and basic aluminum acetate at a 3 : 5 molar ratio were dissolved in deionized water to give a 0.0025 M solution (with respect to YAG).

Solution E

Hydrated yttrium acetate was dissolved in a small amount of deionized water, and independently aluminum acetate was dissolved in ethanol. The solutions were mixed to give the molar ratio Al : Y = 5 : 3, 0.01 M with respect to YAG, and 40 % of water in alcohol.

The above described solutions were used directly or diluted with deionized water or ethanol at proportions presented in Table 1.

Syntheses

The solutions prepared for the reaction were introduced into the reactor at a flow rate of 10 mL min^{-1}. The supercritical water was heated to a temperature of 450 °C at a pressure of 24 MPa and a flow rate of 20 mL min^{-1} (see details of operation [26 – 28]). The temperature at the reactor's center reached 380 °C. The reaction conditions were identical in all experiments, except experiment no. 7 (Table 1), where the actual reaction temperature was somewhat lower (415/355 °C).

The products obtained after the reaction were separated by means of a centrifuge (4000 rpm, 20 min). Drying was carried out in the air at r. t. (12 h). One of the samples (Table 1, entry 5) was dried under vacuum of the order of 2 hPa at −50 °C (for 10 d) by placing it in a sublimation drier (cryodesiccator) together with the parent liquid.

Reaction products

YAG was produced in the form of a fine white powder suspended in the parent liquid. After centrifuge separation and drying under vacuum at reduced temperature, the products appeared as white, agglomerated powders. The powders were characterized using various methods, and the results are presented in Table 1.

The grain size and shape of selected powders was evaluated on the basis of microscopic observations carried out with an electron microscope LEO 1530 (Figs. 1 – 10). The X-ray powder patterns of the products are shown in Fig. 11.

The powders from entry 8 and entry 7 were investigated for mass losses by thermogravimetric analysis. Comparing the obtained curves we found that a powder made by the SC process loses weight mainly in the temperature range 300 – 600 °C, while powders made by coprecipitation-calcination lose mass mainly in the temperature range below 250 °C (Fig. 12).

Discussion

YAG nanopowders were obtained from alcoholic solutions of mixtures of yttrium and aluminum acetates.

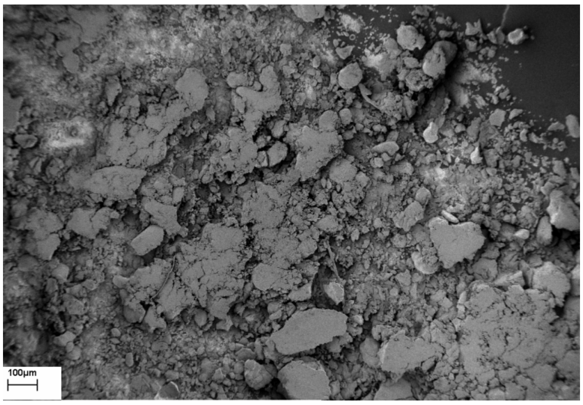

Fig. 1. Entry 5. Agglomerates of 100 μm, easily destroyed under the pressure of tweezers.

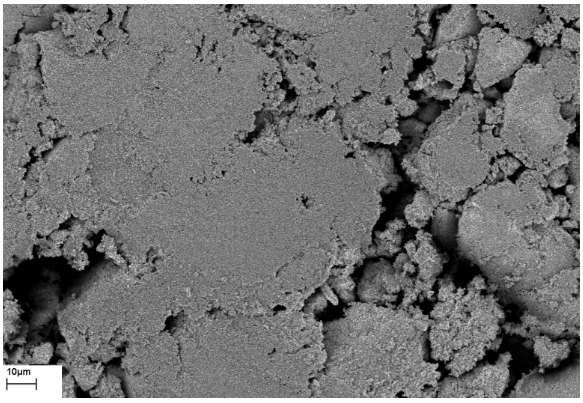

Fig. 2. Entry 5. Structure of agglomerates after squeezing with tweezers.

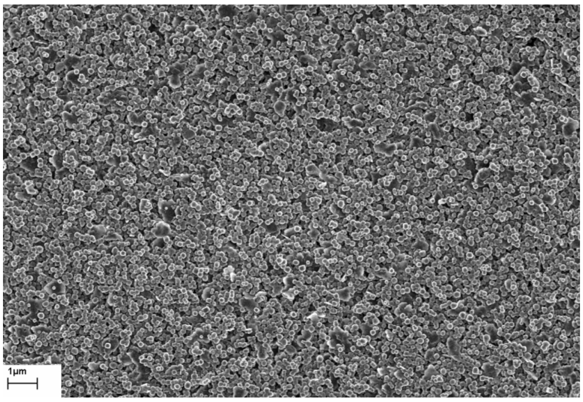

Fig. 3. Entry 5. Structure of the agglomerates.

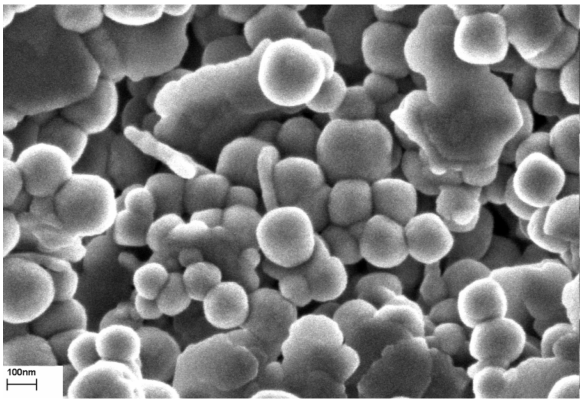

Fig. 4. Entry 5. Morphology of the crystallites.

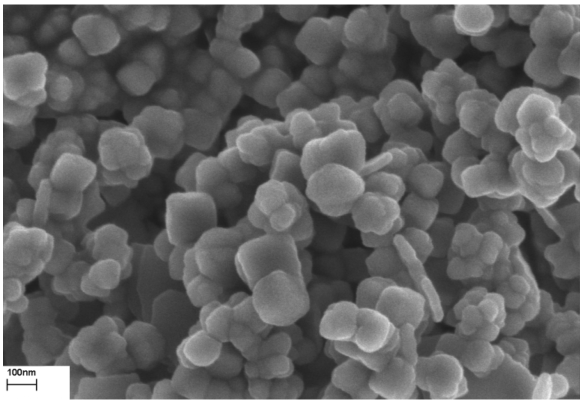

Fig. 5. Entry 4. Morphology of the crystallites and agglomerates.

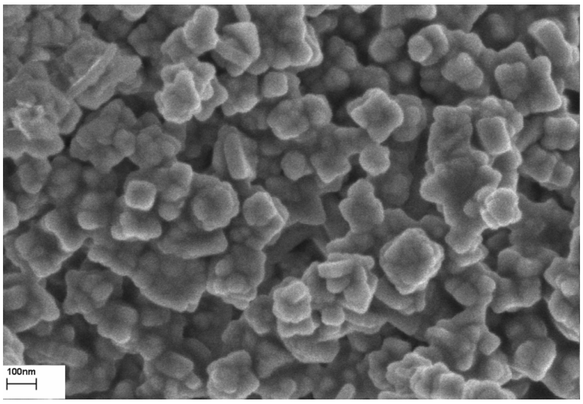

Fig. 6. Entry 6. Morphology of the crystallites and agglomerates.

The finest powders with a mean grain diameter of about 80 nm were obtained from highly diluted aqueous solutions (entry 6). However, they also appeared to have a density below that of a well-crystallized oxide such as that obtained using the precipitation-calcination route. From our previous experience [19, 28], fine YAG powders suitable for luminescence studies are characterized by a density above 4.1 g cm^{-3} (compared to the density of a single crystal: 4.56 g cm^{-3}). Annealing the powders leads to evapo-

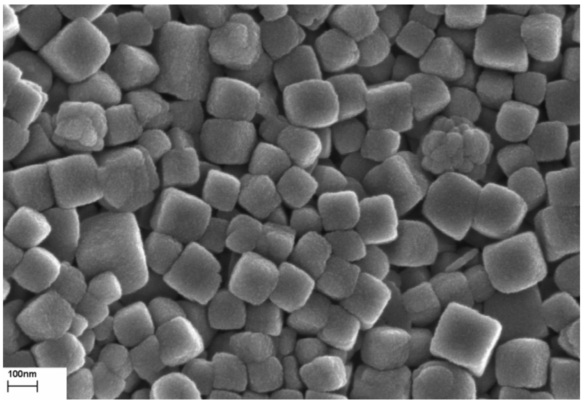

Fig. 7. Entry 7. Structure of the powder and agglomerates.

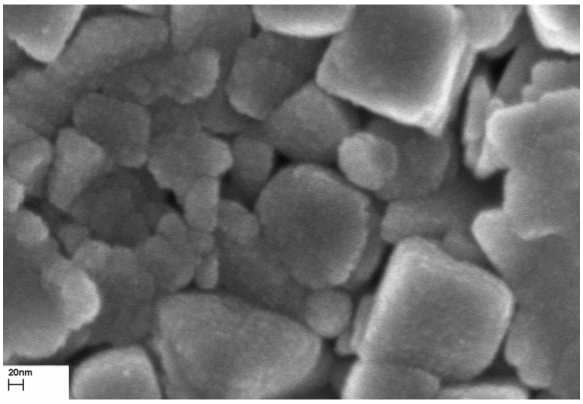

Fig. 8. Entry 7. Details of the YAG powder morphology.

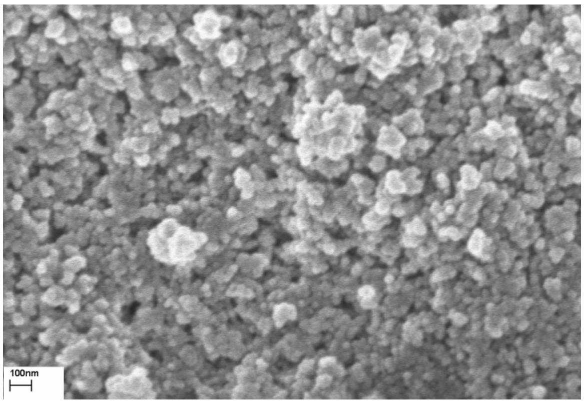

Fig. 9. For comparison, YAG powders obtained from Solution A in the entry 8. The crystallites are less than 100 nm in diameter and form hard agglomerates.

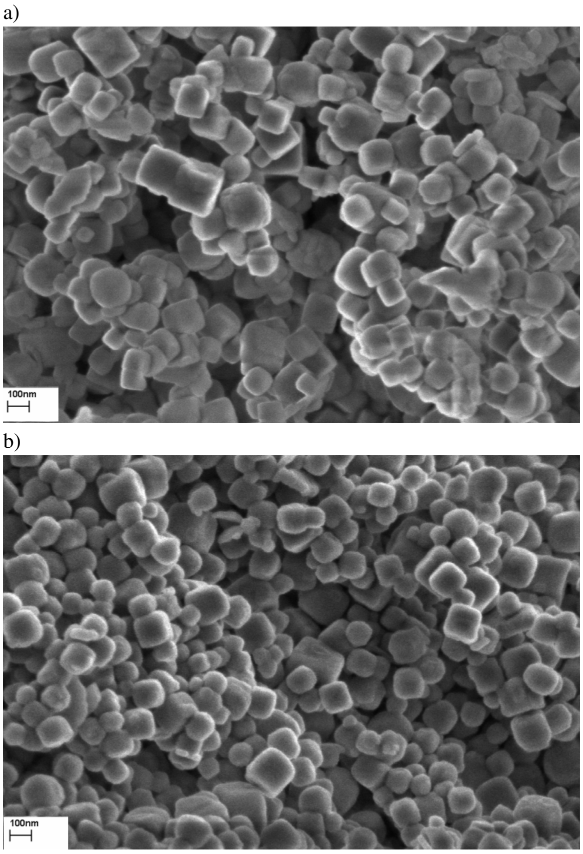

Fig. 10. Structure of the powder from entry 7, after TG measurements up to temperatures a) 500 °C, and b) 1000 °C, respectively.

ration of some volatile components in the temperature range 300 – 600 °C (Fig. 12). After a loss of 7 % of the weight the density of this powder reaches a value close to the density of co-precipitated – calcinated samples. During TG analysis the shape of the grain powders does not change, and grain growth is not observed (Fig. 10). For comparison, the calcined powder (entry 8) shows a weight loss of only about 2 % up to 300 °C. Calcination at temperatures above 900 °C is required after coprecipitation to eliminate intermediate products and leads to the formation of hard aggregates [18]. The weight loss of 2 % is connected with evaporation of water absorbed from air.

A similar behavior was recently observed by us for nanopowders of zirconia [20]. If the temperature of the hydrothermal synthesis was below 230 °C at 5 MPa, the density of the powders was relatively low and the TG loss relatively high. If the synthesis was carried out above 5 MPa, the density was relatively high and the TG loss relatively low, limited only to the evaporation of water absorbed from air during powder storage. We interpreted this result in terms of unreacted hydroxides remaining on the surface of nanopowders if the synthesis temperature was too low. By analogy, in the present

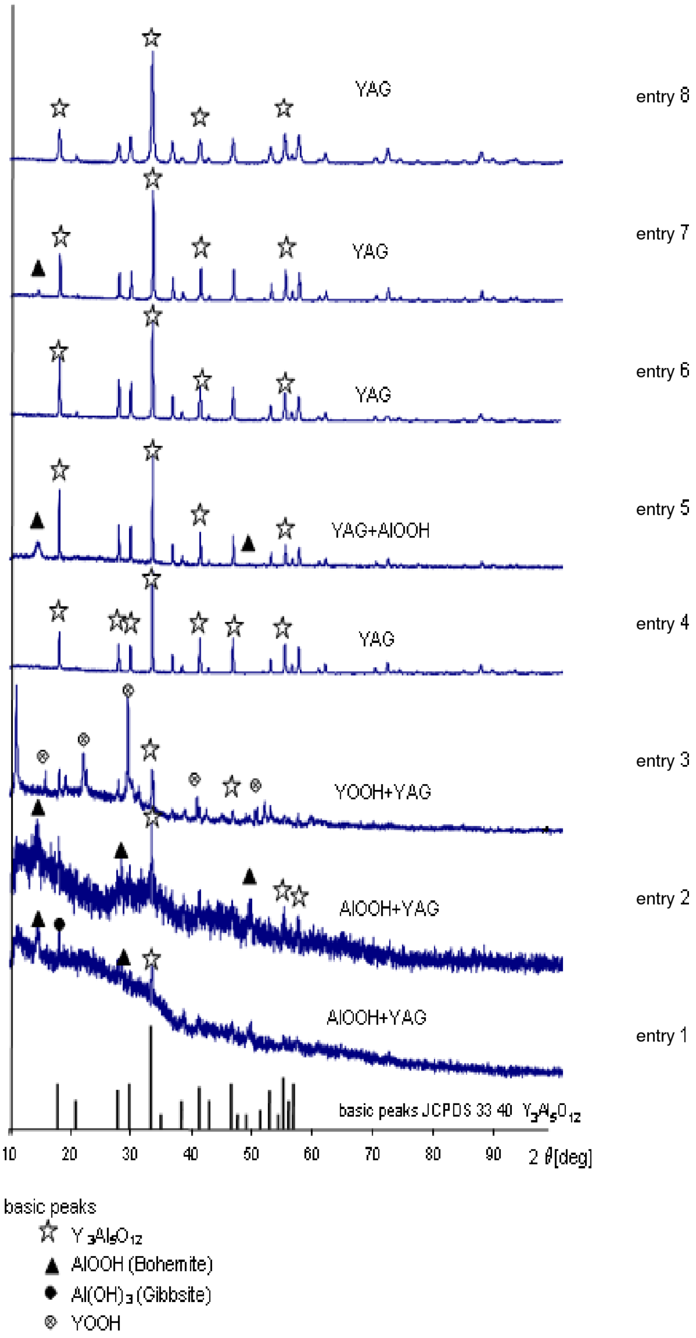

Fig. 11. X-Ray powder patterns of the SCR reaction products (together with the pattern of the co-precipitation product entry 8).

case we may assume that a temperature of 415 °C was still too low to obtain fully crystalline YAG nanopowders. To reach fully crystalline powders an additional annealing at 600 °C is necessary.

The results presented in this paper confirm the earlier thermodynamic calculations of Piticescu [23]. His work also suggests that YAG formation from soluble salts proceeds at lower temperatures when running the process in an anhydrous or partially anhydrous medium, and that the decomposition of the solution of salts such as nitrates requires a temperature close to 500 °C.

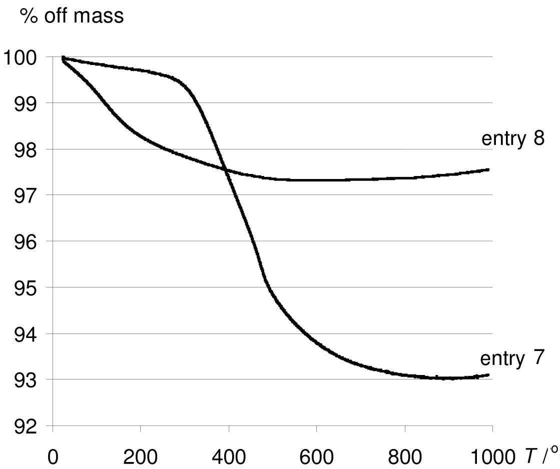

Fig. 12. TG curves for powders from entry 7 and entry 8.

It is interesting to compare agglomerates formed in powders prepared by using the solvothermal and the calcination method. Figs. 1 – 3 show the agglomerates of powders made using the solvothermal method. As seen in Fig. 2, under the pressure of tweezers the agglomerates easily deform and form flat surfaces. This is a striking difference to powders made by calcination [8], where aggregates are hard and resistant to milling (Fig. 9).

The best results of the solvothermal synthesis were obtained when using a solution of the mixture of Al^{3+} and Y^{3+} acetates, at a concentration of about 0.02 M, in a mixture of water and ethanol (entry 4, 7). Acetates appear to undergo complete decomposition in the reaction in supercritical water (to CO_2) with only stable products remaining in the parent liquid.

The degree of conversion when nitrates were used was low. After centrifuging the reaction products from the parent liquid and alkalization with ammonia, the isolated white precipitate indicated the presence of unreacted starting materials. The relatively poor degree of conversion of the nitrates in YAG production is probably due to the formation of nitric acid according to Eq. 1.

$$\begin{aligned}&5\,Al(NO_3)_3 + 3\,Y(NO_3)_3 + 12\,H_2O\\&\rightarrow Y_3Al_5O_{12} + 24\,HNO_3\end{aligned} \tag{1}$$

The initial pH of the stable nitrate solution was kept at 3.5 (above this value hydrolysis of the reactants and isolation of precipitates will begin), but, as it was found that after reaction in supercritical water the pH drops to 1.2, and even as low as 0.7, which inevitably causes dissolution of the freshly precipitated YAG. The quality of the YAG product appears to improve somewhat with the use of ethanol as a solvent (entry 3, Fig. 10). The initial pH of the acetate solution reaches approximately 4.5, but increases to 5.0 after the reaction is completed. At such a relatively high pH the weak acetic acid cannot dissolve the YAG formed. Unfortunately, aqueous aluminum acetate solutions are not stable and can be used only directly after preparing the solutions (*e. g.* Solution B), Therefore aluminum acetylacetonate or basic aluminum acetate, which are commercial products, were also used in these studies. An increase of the reaction temperature and pressure to a higher level than described by Hakuta [17] might enable the formation of pure YAG from an alcoholic solution of nitrates in a one-step process, but using nitrate precursors cause the additional problem to remove nitric acid from the reaction products.

The decomposition of acetic acid from solutions D and E may produce CO_2 and/or CO. Systematic control of the atmosphere carried out (using a CO indicator) during the synthesis in our case did not show the presence of CO, and in the reaction products no trace of carbonates was found indicating that these decomposition products do not provide a threat for the personnel, apparatus or course of synthesis.

The use of alcohols as components of the reaction medium is one of the basic factors enabling a one-step reaction of YAG formation from aluminum and yttrium salt solutions. The simple reaction notion according to [23] suggests that a decrease in the hydrogen ion concentration in the reaction medium shifts the equilibrium towards the products (Eq. 2).

$$3\,Y^{3+} + 5\,Al^{3+} + 12\,OH^- \rightleftarrows Y_3Al_5O_{12} + 12\,H^+ \tag{2}$$

At high temperatures the dissociation constant of water is lower than that at r. t. [29], reaching a minimum of 1.3×10^{-12} at 120 °C and 5×10^{-13} at 350 °C, which probably favors the reaction course in the step of solution cooling.

In the medium containing alcohol the equilibrium is shifted still more in the required direction (YAG formation). Summarizing, the advantageous reaction course according to Eq. 2 is favored by:

- a high process temperature,
- a high pH of the solution of the starting materials,
- a lack of products of an acidic character,

- a proper stoichiometry of the starting materials, and
- a high process rate.

These conditions can be achieved in the supercritical process, of course with the consideration of natural restrictions, connected with the permissible pressures and use of suspensions. Additional possibilities could be provided in the future by the use of other supercritical fluids than water (*e. g.* high-boiling stable mono- and polyalcohols). However, it seems that some amount of water is necessary for the reaction course (dissociation of aluminum and yttrium salts). It is worth noting that even in entry 4 with solution B (where a 30-fold dilution of the starting materials with pure ethanol was applied) the stream of superheated water was double the weight of the alcohol solution stream carrying the precursor.

After the first attempts it is difficult to present an explicit evaluation of the role of cryodesiccation. The comparison of the microscopic images of the reaction product dried after centrifugation and washing (Fig. 5), and of that dried by sublimation in a cryodesiccator (Fig. 4) suggests that after centrifugation of the parent liquid, the purest product of more regular structure is obtained. In the X-ray pattern of the sample of entry 5 (Fig. 11) a peak of an unidentified impurity at about $2\theta = 15^\circ$ exists. The microscopic image does not show clear differences in the degree of agglomeration of the dried powders with respect to that of other samples.

Summary

The work presented in this paper shows that YAG nanopowders can be produced continuously in supercritical water and ethanol mixtures using only soluble precursors. Acetate (or acetylacetonate) precursors appear to be best for that purpose. The powder obtained was composed of very well formed cubic grains with an average diameter smaller than 100 nm. Further annealing at 600 °C leads to a powder with a density comparable with that obtained in a high-temperature calcination process, but without the negative effect of sintering or forming hard aggregates.

Acknowledgement

The work was financed with support of COST action D30 and network WITNANO.

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