



# A comparative study of the synthesis of nanocrystalline Yttrium Aluminium Garnet using sol-gel and co-precipitation methods

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## Abstract

Nanocrystalline yttrium aluminium garnet (nYAG) powder has been synthesized via sol-gel and co-precipitation methods using nitrate precursors. Thermal evolution and crystallisation kinetics of both the methods were investigated. The optimised calcination condition for the formation of nYAG was also examined. It was found that a complete transformation to nYAG was observed at 925 °C/2 h and 1000 °C/1 h for the coprecipitation and sol-gel samples respectively. An intermediate  $YAlO_3$  phase was formed at 900 °C in all powders regardless of the synthesis methods. The powder morphologies obtained from TEM revealed very similar particle sizes for the two routes (20–30 nm); whilst the extent of agglomeration was higher for the sol-gel method. It was also observed that by controlling the pH in a narrow range, maintaining the precipitate processing temperature and dehydrating excess OH<sup>-</sup> ions in the precipitates using n-butanol treatment, the extent of agglomeration was further reduced in the co-precipitated nYAG powder.

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## 1. Introduction

Ceramic powder processing within the  $Y_2O_3$ - $Al_2O_3$  system has largely been intended for optical and structural applications. In this system, three stable yttrium aluminates exist with different polymorphs, perovskite-based orthorhombic  $YAlO_3$  (YAP), monoclinic  $Y_4Al_2O_9$  (YAM) and garnet  $Y_3Al_5O_{12}$  (YAG) [1]. The latter is rich in  $Al_2O_3$  and crystallises with cubic symmetry. It does not exhibit any birefringence effects at the grain boundaries and hence results in high in-line transparency. A hexagonal  $YAlO_3$  (YAH) has also been identified as an intermediate metastable phase during the processing of YAG [2].

The choice of powder synthesis route has a significant effect on powder characteristics such as size, shape, distribution and the extent of agglomeration, each of which greatly influences the

microstructural homogeneity of the resulting ceramics [3]. Each factor has the potential to introduce an adverse effect on densification and microstructure of the ceramics. The presence of particle agglomeration, for example, is a well-known source of inhomogeneity, and hence defects, in the final microstructure of ceramic components [4]. Therefore, efforts have been made to produce high quality ceramic powders by a range of synthesis routes.

The conventional method for preparing YAG involves mixing  $Y_2O_3$  and  $Al_2O_3$  in a 3:5 M ratio and then calcining at 1600 °C for prolonged times together with repeated grinding [5]. Wet chemical routes such as sol-gel [6], co-precipitation [7], solvo-thermal [8] and combustion [9,10] routes are promising methods for synthesising high purity single phase YAG at relatively low temperatures, though there are some disadvantages. Solvo-thermal synthesis, for example, requires the use of an autoclave and pressures of about 70–175 MPa, whilst combustion synthesized powders result in chemical inhomogeneities and particle agglomeration due to the intense local heating. In contrast, sol-gel and co-precipitation synthesis can be low cost and are more likely to yield homogenous YAG powders. The use of alkoxide precursors [11] leads to crystallisation from 700–1000 °C and

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the resultant powder consequently exhibits particle sizes of about 60–80 nm with heavy agglomeration. In contrast, nitrate [12] and chloride [13] precursors lead to crystallisation at about 950 °C, although chlorine ions are more difficult to rinse from the hydroxide precipitate, even with washing. The presence of chlorine ions results in hard agglomerates in the nanopowder [14] and hence has negative effects on the mechanical properties of the subsequent ceramic. To reduce the level of agglomeration, several complexing and precipitating agents have been examined for both sol-gel and co-precipitation methods using nitrate precursors. Nanocrystalline YAG was synthesised using citric acid as a chelating ligand in sol-gel method, [15]. This resulted in rod shaped particle morphology with particle sizes in the range of 20–70 nm and significant agglomeration was still observed. Recently, Yang et al. [16] optimised the solvent concentration and calcination conditions to achieve nano YAG with soft agglomerates using a sol-gel method. This work also confirmed that the molar concentration ratio of the  $Y^{3+}$  and  $Al^{3+}$  ions in the precursor solution has a significant effect on particle size. Wang et al. [17] also studied the effect of different concentrations of precursor solution for the co-precipitation synthesis of YAG nano powder. They achieved 20–30 nm particles using a precursor solution ratio of  $< 1$  and calcination for 2 hours at 900 °C. The uses of different precipitants [18] and pH conditions [19–21] have also been studied; these are also considered to be very important factors governing particle morphology with the co-precipitation method. Li [18] studied the effect of precipitants using ammonium hydroxide and ammonium hydrogen carbonate (AHC) with a precursor solution ratio of about 1.5 at pH 9. Their comparative study suggests that the YAG powder synthesized using AHC resulted in less agglomeration with crystallite size of about 52 nm. However, neither the precursor concentration, nor the control over the pH was optimized. Apte and Vrolijk [19,22] investigated the best pH range for the precipitating YAG using ammonium hydroxide was investigated and suggested that it was pH 7–9. Palmero et al. [20] investigated the influence of calcination temperature on the phase evaluation of YAG from 800–1100 °C, but omitted 950 and 1000 °C/1 h, the powders were over calcined at 1100 °C and resulted in large particles with heavy agglomeration.

These results suggest that identification of the most suitable processing conditions is still required for the production of fine, nanocrystalline YAG displaying little agglomeration. In the present work, the syntheses of nano YAG by sol-gel and co-precipitation methods are compared with a view to optimising the processing conditions and determining the formation mechanisms.

## 2. Experimental

### 2.1. Materials

99.9%  $Y(NO_3)_3 \cdot 6H_2O$  and  $\geq 98\%$   $Al(NO_3)_3 \cdot 9H_2O$ , both from Sigma Aldrich, Dorset, UK were used as the source of  $Y^{3+}$  and  $Al^{3+}$  ions. 99.9% citric acid, also from Sigma Aldrich, was used as the complexing agent for the sol-gel synthesis. 35% ammonium hydroxide and 99% *n*-butanol, both

from Fisher Chemicals, Loughborough, UK were used as the precipitating agent for the cations and for dehydrating them in the co-precipitation method, respectively.

### 2.2. Synthesis

#### 2.2.1. Sol-gel

A solution containing the stoichiometric ratio of 3:5 (Y:Al) was prepared by mixing calculated amounts of 0.6 M  $Y(NO_3)_3 \cdot 6H_2O$  and 1 M  $Al(NO_3)_3 \cdot 9H_2O$  aqueous solutions in 1 M citric acid solution. The schematic representation of the sol-gel process is shown in Fig. 1a. Homogenous mixing was achieved in a round bottom (RB) flask equipped with a magnetic stirrer and a refluxing condenser. The reaction flask was immersed in a thermostatic oil bath and refluxed at  $90 \pm 10$  °C for 24 h. During mixing, the transparent precursor sol underwent substitution and polymerization reactions to form a transparent gel, which was then dried in an oven at 100 °C for 24 h. The fluffy mass obtained after drying was subsequently ground using an agate pestle and mortar for further characterisation.

#### 2.2.2. Co-precipitation

The reverse strike co-precipitation method used involved mixing the same 0.6 M  $Y(NO_3)_3 \cdot 6H_2O$  and 1 M  $Al(NO_3)_3 \cdot 9H_2O$  aqueous solutions for 2 h. The schematic representation of the co-precipitation process is shown in Fig. 1b. This precursor solution was placed in a burette and added drop-wise to 200 ml of the aqueous  $NH_4OH$  precipitant solution whilst simultaneously stirring and maintaining the pH at  $8.20 \pm 0.05$ . The first few drops of the precursor solution were found to decrease the pH rapidly to 4; therefore excess ammonia solution of 5 M concentration was added concurrently to maintain the pH. Continuous monitoring of the pH allowed it to be controlled to  $\pm 0.05$  pH units. The resultant precipitate was filtered, washed three times with dilute ammonia solution of pH 8.2 to remove nitrate residues, and then the filtered precipitate was dispersed with 20 ml of *n*-butanol using ultrasound for two minutes.

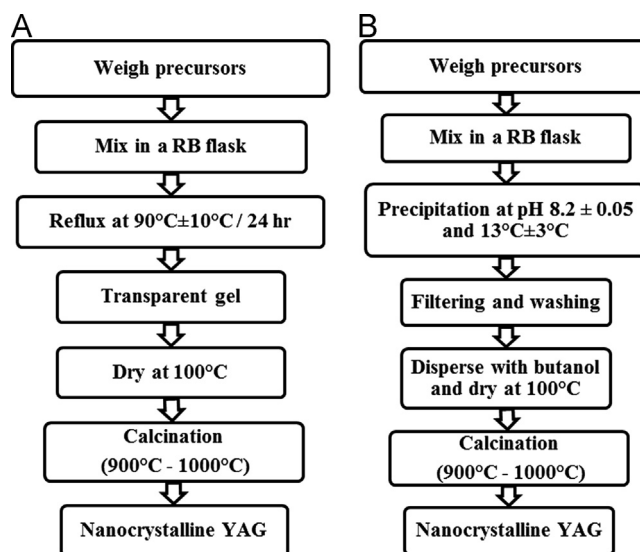


Fig. 1. Flow chart of (a) Sol-gel and (b) Co-precipitation process.

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