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# **Rapid synthesis of nanocrystalline YAG via microwave assisted solvothermal process**

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## **1. Abstract**

A rapid synthesis procedure for the preparation of nanocrystalline yttrium aluminium garnet (nYAG) particles has been developed, for the first time, using the combination of subcritical conditions and microwave irradiation. It is believed that the use of butanediol delayed the onset of pressure rise due to its low partial pressure, whilst the microwaves facilitated a selective crystallisation of nanocrystalline YAG particles in the solvent medium. This methodology was found to encourage rapid bulk nucleation with minimal particle growth or agglomeration of nYAG particles. The resultant powder characteristics, examined using XRD and TEM analyses, revealed that a narrow window of pressure and temperature conditions needed to be maintained to achieve spherical particles in the size range 60-80 nm without any intermediate phases being formed. The STEM/EDX and FTIR results obtained suggested that the nucleated YAG particles were masked by carbon clouds until they were completely crystallised into single phase YAG particles; this allowed them to be dispersed in water with little agglomeration.

## 2. Introduction

Yttrium aluminium garnet is an excellent structural and functional material that is used in many applications<sup>1</sup>. Single crystal YAG is a known laser host material owing to its excellent optical properties; however, due to the enhanced availability of high purity powders and advanced processing technologies, the use of single crystal YAG is being replaced by the polycrystalline material, which typically contains up to 4 atomic percent of dopant to achieve transparency. Since YAG has cubic symmetry, it does not exhibit birefringence at the grain boundaries<sup>2</sup>. This results in a high in-line transmittance of about 84%, which makes polycrystalline YAG ceramics desirable for laser applications and IR domes<sup>2-4</sup>.

Submicron yttrium aluminium garnet powders have been synthesised via a range of different chemical<sup>5-7</sup> and mechanical routes<sup>8-10</sup>. The former has also been successful in achieving single phase nanopowders<sup>5, 11</sup> and used to tailor the particle characteristics to adapt them for different applications. However, these process routes typically suffer from the need to use elevated temperature calcination to achieve a high degree of crystallinity, thus rendering the use of surfactants to avoid agglomeration ineffective since they are decomposed by the exposure to heat. As a result, researchers continue to investigate rapid and cost-effective routes to the synthesis of YAG nanoparticles, with the major challenge being the agglomeration issue. The underlying principle of the current work has been the need to crystallise the nanoparticles in a fluid medium, where the fluid acts as an interfacial barrier and thus isolates each individual particle, inhibiting agglomeration during the crystallisation process. Continuous flow hydrothermal synthesis<sup>12</sup> is currently the fastest route for the synthesis of YAG nanoparticles with little agglomeration, however, the process requires quite aggressive conditions, ~340°C and ~27 MPa, which makes it expensive. The solvothermal route, however, opens up the

opportunity to utilise different solvents to reduce the severity of the supercritical conditions required <sup>13-16</sup> and also offers greater control over particle characteristics by acting as an interfacial barrier between the crystallites during the process<sup>1</sup>.

Our previous study on the conventional solvothermal synthesis of YAG nanoparticles suggested that a minimum of 270°C and 2 MPa was required for 2 h to initiate the onset of formation of YAG <sup>15</sup>. The degree of crystallinity was poor under these conditions, however, and hence even higher temperatures and pressures, of 300°C and 8.5 MPa, were required, again for 2 h, to achieve highly crystalline nanopowders<sup>2</sup>. In related work, 1 kW of 2.45 GHz microwave energy was used to synthesis YAG nanopowder in a multimode cavity; the results revealed that 600°C for 30 minutes was required to crystallise the precursors into single phase YAG <sup>17</sup>. In the present work, microwave irradiation was used to reduce the time and to achieve rapid nucleation in a low vapour pressure solvent <sup>18, 19</sup> at lower temperatures and pressures. Here, the influence of microwaves on temperature, pressure and time were investigated and the effects that these factors had on the YAG particle characteristics were studied.

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<sup>1</sup> [A hydrothermal process uses water as a medium to facilitate the heterogeneous reaction of nanoparticles under supercritical conditions, whilst a solvothermal process uses alcohols and glycols to crystallise in both super or /subcritical conditions and typically yields have a greater control of a particle morphology via the by wisely manipulations of the physical and chemical-characteristics conditions \[Ref required\].](#)

<sup>2</sup> [In order to avoid defects arising from intermediates structures such as YAP, YAM and YAH, it is highly beneficial to start with highly crystalline particles. \[Ref required\].](#)

### 3. Experimental

Organic precursors,  $Y(CH_3CO_2)_3 \cdot xH_2O$ , 99.9% purity, and  $Al(OCH(CH_3)_2)_3$ ,  $\geq 98\%$  purity, from Sigma Aldrich, Dorset, UK, were used as the source of  $Y^{3+}$  and  $Al^{3+}$  ions, respectively. 99.9% pure 1-4 butanediol, also from Sigma Aldrich, was used as the solvent medium for the solvothermal synthesis. A stoichiometric ratio of 3 Y to 5 Al was prepared by mixing appropriate amounts of the two precursors, weighed to two decimal places in the butanediol solvent<sup>15</sup>. 10.5 ml of the mixture was sealed in a 60 ml glass autoclave vessel and processed at different temperatures in an Anton Paar monowave 300 microwave reactor, which operated at 2.45 GHz. The vessel for the latter had a Teflon lining and was rated to 290°C (this was found to limit the autogenous pressure to 3.0 MPa). The temperature and the pressure were both controlled by the output power of the microwave reactor. To obtain different autogenous pressures at a constant temperature, the volume of the precursors was varied between 10.5 to 15 ml, without changing the concentration. The resultant white suspension was centrifuged at 5000 rpm for 5 minutes, washed three times using ethanol to remove the precursor residues and then dried at 60°C for 24 hours before being ground using an agate pestle and mortar for at least 1 min.

All the powder samples were analysed by scanning  $2\theta$  angles from 25° to 65° at a step size of 0.02° using XRD. TEM (JEOL JEM 1200FX, JEOL Ltd. Tokyo, Japan) was used to study the particle size of the powders; the samples were prepared by dispersing the powders in isopropanol using ultrasound (SoniPrep, MSE Ltd, London, UK) and then a drop of the suspension was deposited on a carbon film (AGS160H, Agar Scientific, Stansted, UK). The TEM samples were dried in a laboratory oven at 60°C for 15 minutes and loaded into a single tilt holder. The TEM was operated at 80 kV and the images were obtained under different magnifications from 50 to 200 thousand times. STEM images were also obtained from a different TEM (Tecnai F20, FEI, Hillsboro, OR, USA) using a CCD camera, whilst elemental mapping was performed using an Oxford EDX system (X-Max 80 mm<sup>2</sup>, Oxford Instruments,

UK). FTIR (8400S, Shimadzu, Maryland, USA) was used to identify the functional groups present in the samples; the as-prepared YAG sols were dropped in between two NaCl crystals to form a thin film for analysis. After initialising the equipment, the sample holder was fixed and a background correction performed to avoid the CO<sub>2</sub> peak in the resultant spectrum.

## 4. Results and discussion

### Crystallisation and growth kinetics of YAG particles

In this work, 1,4 butanediol has been used a solvent due to its higher boiling point, 235°C<sup>20</sup> and lower vapour pressure, ~35 Pa<sup>21</sup>, when compared to water and other alcohols. Otherwise, high pressure and high temperature autoclaves are needed for the reaction to occur. Also, it is a polar solvent and exhibits a high dielectric loss tangent,  $\tan \delta$  of 0.783 at 2.45 GHz<sup>22</sup> and facilitates microwave absorption. Note that for better microwave absorption the  $\tan \delta$  of a solvent should be >0.5 and possess permanent dipoles<sup>23</sup>. The aforementioned thermodynamic characteristics govern the rate of autogenous pressure rise and the microwaves help rapid heating of the solvents and hence the precursors to synthesis YAG under subcritical conditions. The initial experiments were carried out to identify the desired reaction time required to obtain single phase YAG at 290°C. Figure 1a shows the results; after up to 15 mins the precursors remained unreacted and the XRD spectrum displayed only the phases of Al(O)OH and Y(OH)<sub>3</sub>. When the duration was increased to 30 minutes, however, the precursors crystallised into single phase YAG without intermediates such as YAM, YAP and YAH being formed. This shows good agreement with our previous study on the microwave synthesis of YAG<sup>17</sup> and indicates the importance of reaction time in crystallising multi-cation materials such as YAG.

Since hydro/solvothermal synthesis involves both temperature and pressure in combination, the effects of these two factors over a constant reaction time of 30 minutes were also investigated.

When the temperature was increased from 250°C to 290°C, crystalline peaks were seen only above 270°C, figure 1b, which is consistent with conventional solvothermal synthesis<sup>15</sup>. As an aside, it is worth comparing the XRD spectra obtained after 5 and 15 minutes at 290°C with those obtained after 30 mins at 250 and 260°C, Figures 1a and b. The former reveals unreacted precursors, as mentioned, whilst the latter shows that complete dissolution had occurred. When the autogenous pressure was varied at 270°C by adjusting the volume of the precursors without changing their concentration, Figure 1c, the XRD results showed that the primary effect was to increase the degree of crystallinity. These results indicated that the crystallisation and particle growth kinetics of YAG could be tailored by adjusting the pressure and temperature during microwave heating.

TEM, STEM/EDX and FTIR analyses were used to obtain valuable information about the chemical species and to gain more insight into the underpinning mechanism(s) that lead to the formation of the YAG nanoparticles. Figure 1d shows the FTIR spectra with the corresponding peak assignments of the as-synthesised YAG sol after 270°C & 2 MPa and 280°C & 2.7 MPa, both for 30 minutes. The broad peaks around  $\sim 3450\text{ cm}^{-1}$  are attributed to the hydroxyl vibrations,  $\nu(\text{OH})$ , which are dissociated from the 1, 4 butanediol in both cases<sup>24</sup>. The doublets near  $\sim 2940\text{ cm}^{-1}$  are the symmetric and asymmetric modes of  $\text{CH}_2$ , which are believed to be the stretching and bending vibrations formed after the dehydration of 1, 4 butanediol. Note that these peaks are very well defined in the spectrum obtained at 280°C, meaning that these functional groups are terminated from the precursors and thus became free radicals.

This belief is substantiated by the decrease in the peak at  $2140\text{ cm}^{-1}$ , representing C-C bonds, and the formation of another doublet at  $1400\text{ cm}^{-1}$ , followed by a characteristic YAG peak of strong metal–oxygen bonding from  $400 - 750\text{ cm}^{-1}$ <sup>7</sup>. It is interesting to note that the former is from the symmetric and asymmetric vibrations of carboxylate ions cleaved from the yttrium acetate precursor, which was also noticed following conventional solvothermal synthesis but at

conditions of 300°C and 8.0 MPa for 2 h<sup>15</sup>. Thus, the use of microwaves appears to have reduced the magnitude of the temperature, pressure and time required. This suggests that the microwaves influenced the activation energy needed for the formation of oxide bonding with the metal ligands during synthesis. This suggestion was supported by the wagging of the CH<sub>2</sub> groups observed at 1340 and 900 cm<sup>-1</sup><sup>25</sup>, which were the weakly bonded functional groups detached from the aluminium iso-propoxide. Figure 2 shows the morphologies of the single phase YAG particles obtained under the different conditions discussed above. The powders obtained at 270°C exhibited sizes ranging between 20 – 80 nm with clouds of residual precursor surrounding the nanoparticles. These residues were very hard to separate from the particles, even after centrifuging at 5000 rpm for 5 minutes. This suggested that there was a degree of chemical bonding present. In order to identify the chemical composition of the residue a detailed STEM/EDX analysis was carried out. The data revealed that they were some form of carbon species, Figure 3, which were chemically co-ordinated with the metal cations, Y<sup>3+</sup> and Al<sup>3+</sup>, in the form of complex ions. The FTIR results obtained at 270°C showed good agreement with this conclusion.

This suggests that the increase in pressure at 270°C helped to increase the degree of crystallinity present, whilst the carbon residue appears to have retarded clustering/agglomeration between the nYAG particles. Note that these are yet the most moderate conditions used to produce single phase YAG nanoparticles to the best of our knowledge. However, these chemically bound carbon residues will have a negative influence on the stoichiometry and remain as oxycarbides in the ceramic parts after sintering.

When the temperature was increased to 280°C, the autogenous pressure increased to 2.7 MPa in 30 minutes and the approximately spherical particles were subsequently grown to 60 – 80 nm. From the TEM images, it is also clear that the particles were free from the carbon chains



and it is believed that the surface chemistry will have changed due to the formation of YAG crystals with high crystallinity. This claim is further supported by the FTIR spectrum obtained at 280°C; note the decrease in free carbon peaks at 2040 and 1550  $\text{cm}^{-1}$  in Figure 1d. Further increase in temperature continued to increase the particle size and the degree of crystallinity. Note that the particles produced at 280°C and 290°C were easily separated from the carbon residues using the centrifuge, yielding single phase YAG nanoparticles.

## 5. Conclusions

A rapid microwave assisted solvothermal route has been demonstrated for the first time to be capable of synthesising unagglomerated nanocrystalline YAG particles and the crystallisation kinetics and reaction pathways have been investigated. The XRD results suggested that the crystallisation begins when the condition was 270°C / 30 min at 2.2 MPa when using microwave heating, however the powders produced were difficult to separate from the residual carbon species. When the temperature was increased to 280°C, the residues were able to be removed easily from the particles using a centrifuge and the resultant approximately spherical nanopowders exhibited a size ranging between 60 – 80 nm with a high degree of crystallinity. Increasing the temperature further to 290°C, and hence the autogenous pressure to 3 MPa for 30 mins, yielded nanoparticles measuring approximately 140 nm in diameter. This work suggests that to obtain unagglomerated, single phase YAG nanoparticles of 60 – 140 nm in size involves utilising a narrow operating window of 280 – 290°C at 2.7 – 3.0 MPa for 30 mins and 2.45 GHz microwave heating.

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