Synthesis of yttrium aluminum garnet (Y₃Al₅O₁₂, YAG) powder with nano and submicro size and high infrared transmittance using flame aerosol synthesis method

Hui Tian¹, Lei Wang², Taisheng Yang³ and Zili Zhang

¹ School of Environment, Tsinghua University, Beijing 100084, People’s Republic of China
² Institute of Electrical Engineering, Chinese Academy of Sciences, Beijing 100190, People’s Republic of China
³ China Building Materials Academy, Beijing 100024, People’s Republic of China

E-mail: zhangzili@mail.iee.ac.cn

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Abstract

In this study, the flame aerosol synthesis (FAS) method was used to synthesize a yttrium aluminum garnet (Y₃Al₅O₁₂, YAG) nanopowder. The dominant reaction route in the FAS method is the liquid route; this shaped the primary morphology of the YAG nanopowder into hollow and solid spheres. The effects of precursor concentration and annealing parameters were systematically investigated. At a precursor concentration of 0.4 mol L⁻¹ and an annealing temperature of 1400 °C, the YAG nanopowder exhibited excellent infrared transmittance. Compared to other conventional synthesis methods, the FAS method has the advantages of high yield, low cost, and ease of obtaining a nanosized powder. The FAS method is thought to be one of the best choices for the large-scale production of YAG powders.

1. Introduction

In 1962, Dr Coble of the General Electric Company successfully prepared translucent alumina ceramics, breaking the traditional concept of opaque ceramics. Subsequently, various transparent ceramics, including Y₂O₃, MgO, BeO, CaO, ThO₂, and other oxide and non-oxide transparent ceramics, have emerged [1]. Transparent ceramics must have the following characteristics: (1) high density, exceeding 99.5% of the theoretical density; (2) absence of voids in the grain boundary, or the voids are much smaller than the wavelength of the light wave; (3) a grain boundary without impurities and glass phases, or there is a very small difference between the optical properties of the grain boundaries and the microcrystals; (4) small crystal grains that are uniform and have no gaps; (5) a small selective absorption of incident light for the crystal; (6) absence of optical anisotropy, a preferably cubic crystal structure, and a high surface finish [1–4].

Yttrium aluminum garnet (Y₃Al₅O₁₂, YAG) is a cubic crystal system with stable physical and chemical properties. Consequently, it is widely used as a structural and functional material; a typical example is YAG ceramics with their unique light transmittance. The cubic crystal system of YAG ceramics exhibits no birefringence loss due to optically isotropic light at the grain boundary. The main factors that determine the transparency of a ceramic are the porosity and impurity content. Ordinary ceramics do not transmit light owing to defects, such as a large number of pores and impurities. The relatively high diffusion rate of the nanopowder during the annealing process can discharge microscopic pores in the material, bestowing transparency on the ceramic. Additionally, high-purity nanopowders can reduce the generation of second phases and defects during the annealing process and further improve the light transmittance of ceramics [5]. Therefore, the preparation of nano-YAG powder is a key step in realizing its application in manufacturing high-performance functional and structural ceramics. The ideal powder should be uniform with fine particle size, regular and consistent shape (isotropic), no agglomeration, high purity, and controllable phase composition.
To date, multiple methods have been used in the synthesis of YAG powder, including solid [6–9], coprecipitation [10, 11], sol-gel [12, 13], and hydrothermal reactions [14, 15]. However, few studies have attempted the flame aerosol synthesis (FAS) method, which is not a conventional technique but has the significant advantage of scale-up capability [5]. The FAS method has been proved to successfully synthesize multiple metal oxides such as Al₂O₃ [16], SiO₂ [17], TiO₂ [18], V₂O₅ [19], Mn₂O₃ [20], Fe₂O₃ [21] and ZnO [22]. In this study, we used the FAS method for the synthesis of YAG powder and systematically investigated the phase formation, morphology, and infrared transmittance properties of the YAG powder.

2. Materials and methods

The YAG powders were synthesized using the FAS method on a custom-built co-flow diffusion flame burner. Figure 1 shows a sketch map of the equipment, in which the carrier gas oxygen and the fuel methane flowed along the same path. The solution precursor was prepared by dissolving Y(NO₃)₃ · 6H₂O (Aladdin, purity 99.9%) and Al(NO₃)₃ · 9H₂O (Aladdin, purity 99%) in deionized water. The total metal concentrations of the precursor solution were between 0.16 mol L⁻¹ and 0.8 mol L⁻¹. The water-based precursor solution was then nebulized using a medical nebulizer and transported by oxygen. The flow rate of the oxygen and methane were set as 1.6 l min⁻¹ and 4.8 l min⁻¹, respectively. The flame was enclosed in a 40 cm long quartz glass tube with an inner diameter of 100 mm. After synthesis, the powder attached to the quartz tube was scraped off. The YAG powder was pressed into a pellet form using a hydraulic press machine at a pressure of 30 MPa. Both the powder and pellet were sintered using a tube furnace in the air at temperatures between 1000 °C and 1400 °C for 2 to 8 h.

X-ray diffraction (XRD, Bruker Advanced D-8) was used to detect the phase formation of the product powder. The crystallite size of the powders was calculated using the Debye–Scherrer formula. The morphology of the powder was measured using scanning electron microscopy (SEM, FEI QUANTA FEG450) and transmission electron microscopy (TEM, FEI, G2 F20). To obtain the particle size distribution, a size exceeding 200 particles was counted for each sample from the SEM images. The infrared transmittance was measured using a Fourier transform infrared spectrometer (IR, Gangdong, FTIR-850). The IR samples were prepared by mixing the YAG powder with KBr. After sufficiently drying, the mixed powder was pressed into pellet.

![Figure 1. Schematic diagram of the co-flow diffusion flame burner.](image-url)
3. Results

Figure 2 shows the typical morphology of the YAG powder synthesized using the FAS method. It is clear that there are two distinct morphologies in figure 2(a). In the middle of this TEM image is a large hollow sphere of size 325 nm. The thickness of the hollow spheres was approximately 50 nm. There were multiple small particles with sizes between 20 and 50 nm attached to this large hollow sphere. According to the reaction mechanism described in Ref. 5, there are two main reaction routes in the FAS method: the gas reaction route and the liquid reaction route, as shown in figure 2(b). The primary difference between the two routes is the evaporation of the precursor during the initial reaction stage. The gas precursor yields dispersed small nanoparticles or aggregates consisting of nanoparticles. By contrast, the liquid route results in a core–shell structure, namely a hollow sphere. Because both small particles and large hollow spheres existed in the sample, the synthesis of the YAG powder included both the liquid and gas routes. Whether a FAS reaction is liquid or gas depends on multiple factors, and two of them are the most important. The first is the ratio between the boiling point temperature of the solvent and the decomposition or melt point temperature of the solute. When the ratio is higher than 1.05, there is more possibility that the system is in the gas reaction route. If the ratio is less than 1.05, it is more complicated, both liquid and gas can exist. The second important factor is the combustion enthalpy. The higher combustion enthalpy can cause complete decomposition and evaporation of precursor solution and finally cause small particles.

Based on the statistical data from all the TEM images, the hollow sphere morphology dominated the YAG samples, which indicates that the liquid route was the primary reaction mechanism in the synthesis of the YAG powder.

Figure 3 shows the morphologies of the YAG powder at different concentrations synthesized using the FAS method. The TEM images show that more than half of the spherical particles were hollow in the low-concentration sample. As the concentration reached 0.8 mol L⁻¹, nearly all the spherical particles were solid. In addition, more than 200 spherical particles were counted in each sample from the SEM images. The particle size distribution shows a clear trend of increasing particle size with increasing concentrations. The average particle sizes of the samples with 0.16 mol L⁻¹, 0.4 mol L⁻¹, and 0.8 mol L⁻¹ concentrations were 719 ± 290 nm, 851 ± 313 nm, and 1369 ± 694 nm, respectively. It is worth mentioning that the size distribution in the
0.8 mol L^{-1} sample doesn’t fit the Gaussian distribution, which needs further research. Combined with the increase in particle size and the transformation from hollow to solid, it can be concluded that the precursor concentration has a significant effect on the morphology of the YAG powder.

The synthesis of the YAG phase is complicated. As shown in the reaction equations, there are multiple stages in the formation of YAG. Superior infrared transmittance entails a pure YAG phase with high crystallinity. The YAG phase requires a high-temperature reaction at approximately 1400 °C–1600 °C. Although the FAS method can support a flame with a temperature exceeding 2000 °C, the reaction time is only a few milliseconds; hence, there is a possibility that the reaction to form YAG remains incomplete. Moreover, the short reaction time of the FAS method can cause poor crystallinity. Therefore, XRD was used to analyze phase formation and crystallinity.

\[
\begin{align*}
2Y_2O_3 + Al_2O_3 & \rightarrow Y_2Al_2O_3(YAM)(900 – 1100 °C) \\
Y_4Al_2O_9 + Al_2O_3 & \rightarrow 4YAlO_3(YAP)(1100 – 1250 °C) \\
3YAlO_3 + Al_2O_3 & \rightarrow Y_2Al_2O_12(YAG)(1400 – 1600 °C)
\end{align*}
\]

Figure 4 shows the XRD results of the YAG powders fabricated using different precursor concentrations. It can be observed that all the initial samples were in the YAlO_3 (YAP) phase instead of the target YAG phase. Moreover, the crystallinity of the phase was quite poor. This proves that annealing is necessary to obtain a pure YAG phase with high crystallinity. We performed annealing on the different powders at 1000 °C–1400 °C for 4 h. In the 0.16 mol L^{-1} and 0.4 mol L^{-1} samples, after annealing at 1000 °C for 4 h, the powder changed to a pure YAG phase with excellent crystallinity. However, in the 0.8 mol L^{-1} sample, only a very weak YAG peak was observed after annealing at 1000 °C for 4 h. As the temperature reached 1200 °C, a strong YAG peak appeared. This shows that a higher concentration requires a higher annealing temperature to obtain a pure YAG phase. This is because a higher concentration yields larger, solid particles, which require more energy to complete the phase transformation.

The crystallite sizes were calculated from the XRD results (table 1). It is worth mentioning that the value of the 0.8 mol L^{-1} sample at 1000 °C is not accurate because of the very poor crystallinity and weak peak intensity. It can be observed that all the samples retained a small crystallite size, even after long-term high-temperature heat treatment. Although the primary morphology of all the samples is a large sphere, the crystallite size value shows that the large sphere consisted of small grains, which fit the reaction mechanism reported in Ref [5]. Clearly, the low-concentration sample had a larger crystallite size. This is because there are two processes during heat treatment: phase transformation from YAP to YAG and grain growth. As analyzed here, the higher concentration caused larger and solid spherical particles, which required more energy to complete the phase transformation. Because the total energy available is the same under the same heat treatment process, the higher energy taken to complete the phase transformation corresponds to the lower energy available to support the grain growth. Therefore, the crystallite size in the higher-concentration sample is smaller.

Figure 5 shows the infrared transmittance results of the YAG powders with different concentrations after synthesis. It is shown that the infrared transmittance increased with increasing precursor concentration. Infrared transmittance is relevant to the package density of the sample. There are many hollow spherical particles in the low-concentration sample, which results in low package density in the sample. As the concentration increased, most of the spherical particles became solid, and the infrared transmittance increased significantly. Notably, there are multiple peaks of low infrared transmittance in figure 5. This could be relevant to the fact that either the poor crystallinity or the phase was not YAG. Because the 0.16 mol L^{-1} sample has a low
density and the 0.8 mol L\(^{-1}\) sample requires a higher temperature and longer annealing time, the precursor solution concentration of 0.4 mol L\(^{-1}\) was chosen in the following research.

Figure 6 shows the SEM images of the YAG pellet with 0.4 mol L\(^{-1}\) concentration sintered at different temperatures and times. In figures 6(a) and (b), it is clear that there is no apparent change in the morphology.
after heat treatment at 1200 °C for 2 and 4 h. By contrast, after annealing at 1400 °C, a sintering neck appeared, as indicated by the red arrow. As shown in figure 4, annealing at 1200 °C and 1400 °C can produce a pure YAG phase with high crystallinity. However, the morphology did not reveal this. Only the annealing at 1400 °C

Figure 5. Infrared transmittance results of the YAG powders with different concentrations after synthesis.

Figure 6. SEM images of the YAG pellet with 0.4 mol L⁻¹ concentration annealled at (a) 1200 °C for 2 h; (b) 1200 °C for 4 h; (a) 1400 °C for 2 h; (a) 1400 °C for 4 h.

Table 1. Crystallite size data was calculated from the XRD results.

| Concentration (mol L⁻¹) | Annealing Temperature (°C) | Crystallite size (nm) |
|-------------------------|---------------------------|-----------------------|
| 0.16                    | 1000                      | 21.07                 |
|                         | 1200                      | 37.54                 |
|                         | 1400                      | 48.60                 |
| 0.4                     | 1000                      | 11.87                 |
|                         | 1200                      | 19.45                 |
|                         | 1400                      | 32.05                 |
| 0.8                     | 1000                      | 10.74                 |
|                         | 1200                      | 13.85                 |
|                         | 1400                      | 27.60                 |
resulted in an apparent connection between the spherical particles. Because the pressure of the pellet was the same, it can be concluded that temperature is the key to the enhancement of the connection.

To further explore the connection process of the YAG powder, different annealing times at 1400 °C were tested. Figure 7 shows the SEM images of the YAG pellet with 0.4 mol L\(^{-1}\) concentration sintered at 1400 °C for different times. At 2 h, the small particles started to connect, and an annealing neck appeared. From 4 h to 6 h, small particles nucleated in the large spherical particles. Furthermore, after 8 h, the small particles were connected again. Based on the analysis in figure 1, both the liquid and gas routes occurred in the synthesis, resulting in two kinds of morphologies: small nanoparticles and large spherical particles. The connection processes of the two morphologies were different. Small nanoparticles were directly connected and formed an annealing neck, which required a short time. By contrast, the large spherical particles could not connect directly. As shown in table 1, the large spherical particles also consisted of small grains. During annealing, these small grains grew initially. With increasing time, the large grains started to connect. These connections first exist in their own sphere and subsequently connect to other particles out of the sphere.

Figure 8 shows the infrared transmittance results of the YAG pellet with 0.4 mol L\(^{-1}\) concentration sintered at different temperatures for 4 h. Compared to the infrared transmittance result of the as-synthesized powder shown in figure 5, the curves are smoother without any significant peak. This indicates that after annealing, the YAG pellet exhibited better infrared transmittance over all wavelengths. This could be attributed to the pure YAG phase and better crystallinity. As the annealing temperature increased, the infrared transmittance
Table 2. Summary of the different synthesis methods for YAG powders.

| Method          | Precursor                                                     | Synthesis parameter                                      | Phase purity       | Yield        | Particle size                  |
|-----------------|---------------------------------------------------------------|-----------------------------------------------------------|--------------------|--------------|-------------------------------|
| FAS             | Y(NO$_3$)$_3$ · 6H$_2$O Al(NO$_3$)$_3$ · 9H$_2$O               | Instantaneous high temperature with 1000 °C–1400 °C annealing | High (Above 1000 °C) | Very high   | Tens to hundreds of nanometers |
| Coprecipitation | Al(NO$_3$)$_3$ · 9H$_2$O Y$_2$O$_3$ HNO$_3$ (NH$_4$)$_2$SO$_4$ NH$_3$ · H$_2$O | Room temperature with 700 °C–1150 °C annealing             | High (Above 900 °C) | Medium      | N/A                           |
| Solid reaction  | AlY$_2$O$_3$                                                  | 1750 °C at 7 × 10$^{-7}$ Pa                               | High (Above 1200 °C) | High        | Sub-micrometer to micrometers |
| Sol-Gel [12]    | Y(NO$_3$)$_3$ · 6H$_2$O Al(NO$_3$)$_3$ · 9H$_2$O Isopropanol Citric acid | 200 °C with 1000 °C annealing                             | High (Above 1000 °C) | Low         | Hundreds of nanometers        |
| Hydrothermal [14]| Al(NO$_3$)$_3$ · 9H$_2$O Y$_2$O$_3$ HNO$_3$ NH$_4$HCO$_3$     | 300 °C for 1 h under 10 MPa                               | Low                | Low         | Tens of Nanometers            |
increased. The 1200 °C sample showed only a slight improvement over the 1000 °C sample. By contrast, the 1400 °C sample was significantly enhanced. This corresponds to the morphology evolution shown in figure 6. High infrared transmittance requires a high pellet density. The 1400 °C pellet had an apparent annealing neck, which indicated a definite improvement in the density.

4. Discussion

As shown in the results section, the FAS method can be used to successfully synthesize YAG nanopowders with high infrared transmittance. In this section, we briefly compare the FAS method with other reported methods. Table 2 summarizes the FAS and four other synthesis methods for YAG powders. The most significant advantage of the FAS method is its yield. Among the synthesis methods, the chemical methods, including co-precipitation, sol-gel, and hydrothermal methods, can only produce powders on a scale of grams, even milligrams, per hour. The solid reaction method has a larger yield per heat treatment, such as tens or hundreds of grams. The FAS method can easily produce tens of grams per hour in a small-scale laboratory and kilograms per hour in large facilities, according to our previous results [18]. An overwhelmingly high yield can dramatically decrease the production cost. Because it uses almost the simplest precursor among all the synthesis methods, FAS could have the lowest production cost. In terms of morphology control, the solid reaction method cannot control particle morphology. All chemical methods require an extra dispersant to obtain nano- or sub-micrometer powders. However, FAS can directly obtain nanopowders owing to its unique reaction mechanism. In summary, the FAS method is one of the most promising methods for synthesizing YAG nanopowders with a high yield and low cost.

However, the FAS method also has its own disadvantages. It requires a custom-built flame burner. Such equipment is the most significant barrier to the application of the FAS method. Safety is also an issue because flammable gases are necessary for the FAS method. Moreover, although the basic reaction mechanism of the FAS method is known, the synthesis process still occurs within milliseconds and at a temperature exceeding 2000 °C. Therefore, the entire reaction process has not yet been clearly elucidated, making delicate morphology control unavailable.

5. Conclusions

In this study, YAG nanopowders were synthesized using the FAS method. The precursor concentration and annealing parameters were systematically optimized. Both gas and liquid reaction routes occurred during the FAS method, which resulted in two distinct morphologies: large hollow or solid spheres and small nanoparticles. As the precursor concentration increased, the spherical particles became more solid and larger. At the same time, an increase in the precursor concentration caused the nanopowders to require a higher temperature to complete the phase transformation and crystallinity. After the pressing and annealing processes, the YAG pellet with 0.4 mol L⁻¹ precursor concentration and 1400 °C, 4 h annealing parameters had a high infrared transmittance. Compared to other conventional methods, the FAS method has the advantage of producing YAG nanopowders with a low cost and high yield.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Zili Zhang https://orcid.org/0000-0001-9836-2138
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