

Research Article

Transparent Yttrium Aluminium Garnet Obtained by Spark Plasma Sintering of Lyophilized Gels

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Lyophilized YAG gel, synthesized by the coprecipitation technique, has been sintered to transparency by spark plasma sintering method at 1500°C. Whereas conventionally dried gels show large agglomerates, over 1 μm, powders from lyophilized gels show no agglomeration with an average particle size below 100 nm. The absence of agglomerates affects on the optical properties of the sintered materials: conventionally dried powders are opaque after sintering, whereas 0.8 mm thick transparent YAG materials with in-line transmittances close to 60% at 680 nm and over 80% in the infrared range have been obtained for the lyophilized gels.

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1. Introduction

Yttrium aluminates are optically interesting materials as they are not absorbent between 300 nm and 4 μm and show no birefringence. Traditionally, Yttrium Aluminium Garnet (YAG) has been prepared as single crystals by the Czochralski method, but this production method shows two main drawbacks: on one hand, it is very expensive, and, on the other hand, it is difficult to produce large size pieces. In recent years, more attention has been paid to fabrication of polycrystalline YAG ceramics [1–3] since they have shown optical and high-temperature mechanical properties comparable to those of single crystalline systems, but with a much easier processing and therefore, low price, ease of manufacture, and mass-production.

In order to produce polycrystalline YAG materials with high optical transmittance levels, it is mandatory to start with fine deagglomerated powders with chemical and phase purity and, very importantly, a narrow particle size distribution. For this reason, different synthesis routes have been explored in literature. For example, conventional solid-state reaction [4, 5] between the component oxides requires high calcination temperatures (over 1600°C) and prolonged burning time

in order to obtain the pure YAG phase, but it often leads to large powders with a broad grain size distribution. In recent years, several wet chemical synthesis methods have been developed and successfully used for low-temperature production of pure phase powders. These methods include solvothermal synthesis [6, 7], sol-gel route [8, 9], nitrate-citrate combustion [10], and coprecipitation methods [11–14]. These chemical processes achieve intimate mixing of reactant cations at the atomic level, leading to an increase in the reaction rate and lowering the synthesis temperature. In particular, reverse-strike precipitation [15] has the advantage to assure higher cations homogeneity in the precipitate precursor in the case of multication materials [16]. However, for all the synthesis routes cited above the formation of coarse agglomerates during the drying process is a common problem that reduces sinterability and homogeneity of the microstructure in the formed product. It is the aim of this work to show that lyophilization of the amorphous gel is an efficient process to produce submicrometer deagglomerated powders after the drying process, and finally, the obtention of transparent YAG by spark plasma sintering (SPS) of these powders is studied.

2. Experimental Procedure

Nanosized YAG powder has been obtained by the reverse-strike precipitation method [15–18]. $\text{AlCl}_3 \cdot 9\text{H}_2\text{O}$ (98%) and $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%) with a 5 : 3 molar ratio were mixed with ammonium hydroxide solution (28% in water). Keeping a constant pH value during the process is critical for the control of chemical homogeneity within the particles [15]. After 24 hours of aging, a gelatinous precipitate was obtained. Then, solvent was removed by centrifugation, and subsequently the amorphous gel was placed on a plate in a lyophilizer (CryoDos, Telstar) under vacuum (0.1 mbar) and held to -50°C for 100 hours in order to remove the water by sublimation of the frozen gel. Thermogravimetric and differential temperature analyses (SDT 2960, TA Instruments) were carried out under air atmosphere on the dried gel at a heating rate of $5^\circ\text{C}/\text{min}$ up to 1000°C . The particle size and the morphology of the YAG nanopowders were investigated by TEM (2000FX, JEOL). The phase transitions of the heat-treated samples as a function of the temperature were followed by Raman spectroscopy (Jobin Yvon, HORIBA). Sintering was performed in a spark plasma sintering (SPS) apparatus (HPD 25/1, FCT) under low vacuum (10^{-1} mbar). Crystalline powders were placed into a graphite die with an inner diameter of 20 mm and sintered at 1500°C for 3 minutes under an applied pressure of 50 MPa and a heating rate of $100^\circ\text{C}/\text{min}$. The density of the samples was measured by the Archimedes method using distilled water as the immersion liquid and a theoretical density of $4.55\text{ g}/\text{cm}^3$. Microstructure was studied by scanning electron microscopy (DSM 950, Zeiss). The SEM samples were prepared by using mechanical polishing with a diamond spray down to $1\ \mu\text{m}$, followed by a thermal etching. The samples were gold covered before observations. The average final grain size was measured using the intercept analysis of Smith and Guttman [19], using 1.56 as the stereological correction factor. The transmission spectrum was recorded on VIS (AvaSpec-2048, Avantes) and IR (IR-560, Nicolet Magna) equipments.

3. Results and Discussion

In Figure 1, the differential thermal analysis curve obtained from the precipitated gels after the lyophilization process is shown. In this thermogram, an endothermic peak in the $50\text{--}300^\circ\text{C}$ range corresponding to the dehydration of aluminium mono and trihydrates [20] and of yttrium hydroxides [21] can be observed. The exothermic peak at 525°C is due to the evaporation of NH_4Cl which appears during the synthesis as a subproduct, and finally, the exothermic peak close to 900°C is attributed to powders crystallization. Simultaneously, the thermogravimetry curve shows an overall weight loss of approximately 40% until the final transformation at 915°C .

The TEM images of the YAG powders directly obtained after lyophilization and dried in an oven are shown in Figures 2(a) and 2(b), respectively. Figure 2(a) reveals that the lyophilized YAG powders are well dispersed with an average grain size below 50 nm consisting of structural units of approximately 10 nm. On the other hand, Figure 2(b)

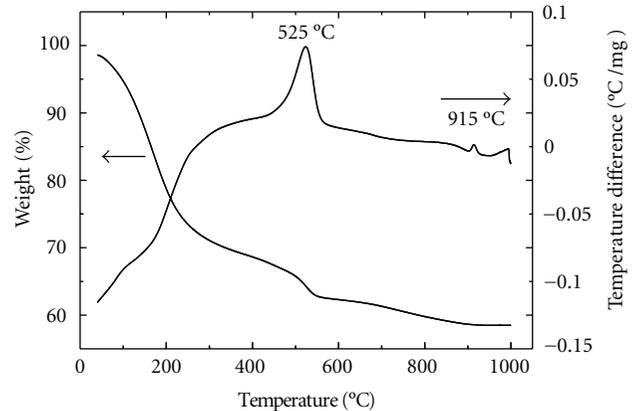


FIGURE 1: TG/DTA plot of amorphous YAG powder.

shows the presence of large agglomerates with an average particle size much larger than $4\ \mu\text{m}$. By comparing the morphology and the agglomeration level in both cases, it can be concluded that lyophilization is an efficient drying method in order to prevent the formation of agglomerates and that it allows obtaining a material with a homogeneous distribution of grain sizes.

Figure 3 shows Raman spectroscopy spectra of the material fired for 2 hours at different temperatures in the $800\text{--}1300^\circ\text{C}$ range. Although the TG results show that YAG crystallization takes place around 900°C , at moderately low temperatures, 800°C , it is already possible to identify the characteristic peaks of crystalline YAG as compared in other works where the calcined powders are still amorphous at this low temperature [22]. However, at these temperatures there is still a noticeable amount of amorphous material as indicated by the background. When the temperature is raised, the peaks become sharper and the background disappears. Pure YAG with a high degree of crystallization is obtained at 1200°C . It is important to note that no other phases such as YAM (monoclinic) or YAP (perovskite) have been obtained along the process. The grain size of YAG obtained after calcination at 1300°C remains in the nanometer range, 100 nm approximately, as it can be seen in the TEM images (Figure 4), and, most importantly, grains are completely deagglomerated. Therefore, deagglomerated homogeneous nanometric crystalline YAG powders have been obtained by reverse strike precipitation followed by gel lyophilization.

In order to determine the sintering conditions, a dilatometric analysis was performed in the Spark Plasma apparatus up to 1700°C . The linear shrinkage curve and its derivative are shown in Figure 5. It can be seen that the material starts shrinking at 1250°C and the final sintering temperature is 1580°C . The maximum speed is reached at 1400°C . According to Chaim et al. [23] to eliminate the residual porosity, it is more efficient to sinter at a temperature lower than the final sintering temperature with a holding time. For this reason, the powders were sintered at 1500°C for 3 minutes. During the entire sintering cycle, a pressure of 50 MPa was applied, and the heating rate was $100^\circ\text{C}/\text{min}$.

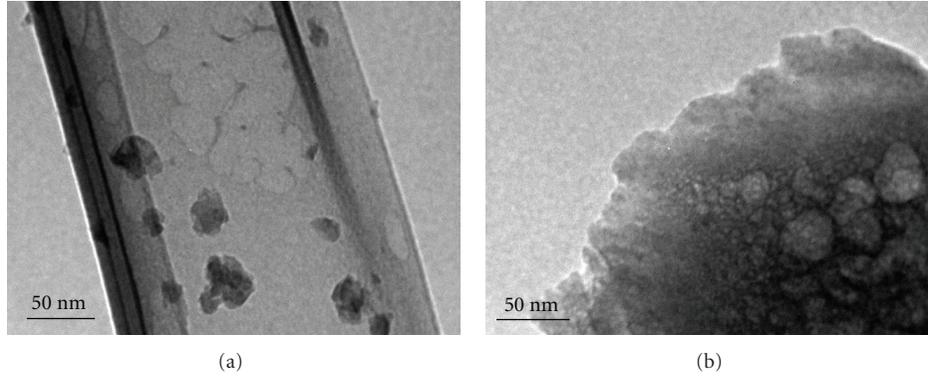


FIGURE 2: Morphology of the amorphous YAG powder: (a) lyophilized; (b) dried in oven.

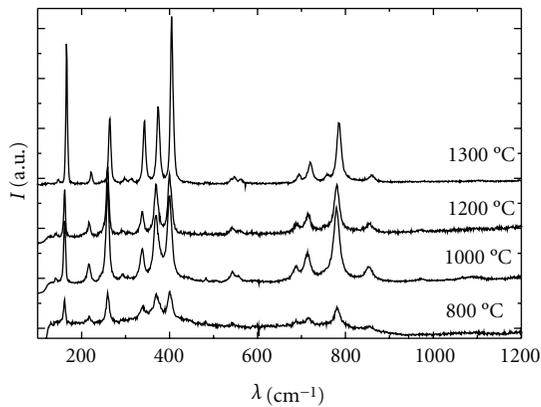


FIGURE 3: Raman spectra showing phases at different calcination temperatures plus 2 hours of holding time.

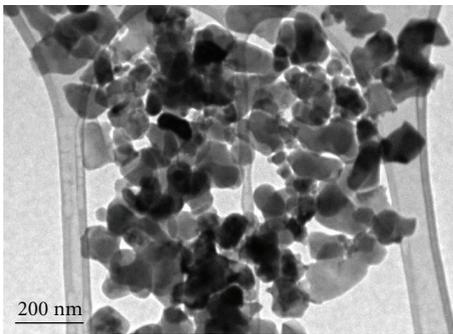


FIGURE 4: TEM image showing the morphology of the crystalline YAG powder.

The samples prepared by SPS exhibited relative densities >99.5%.

Figure 6 shows the microstructures of YAG materials sintered from lyophilized powders (Figure 6(a)) and dried in an oven (Figure 6(b)) after thermal etching at 1275°C for 1 hour. Whereas Figure 6(a) shows a dense and perfect pore-free structure with equiaxed polyhedral-shape (tetrakaidekahedra) grains with an average grain size of 380 (± 100) nm, in the case of YAG sintered from powders dried in a furnace

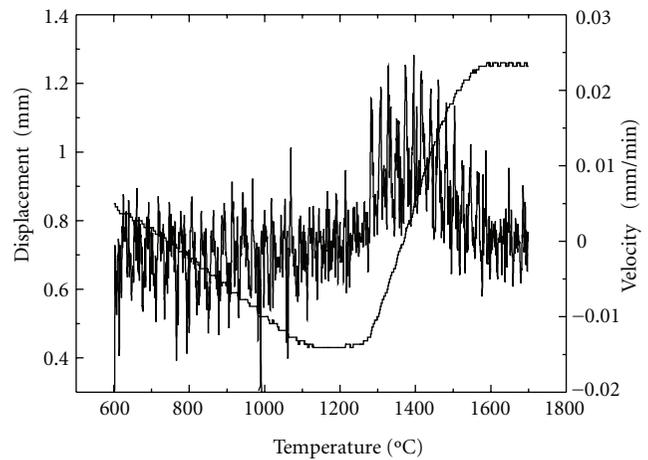


FIGURE 5: Dilatometric linear shrinkage and velocity curve of YAG powder at 1700°C with a 4°C/min heating rate and no holding time.

(Figure 6(b)) a porous microstructure with an average grain size of 420 (± 90) nm is obtained.

Finally, the influence of these microstructural characteristics on the final optical properties of the material was evaluated. Then, the in-line transmittance in the infrared and visible ranges for, lyophilized (solid line) and dried in a furnace (dashed line), YAG powders was measured and they are shown in Figure 7. The in-line transmittance of the sample was measured and then normalized to a thickness of 0.8 mm according to (1).

$$T = (1 - R_s) \cdot \left\{ \frac{T_{\text{measured}}}{(1 - R_s)} \right\}^{t/d}, \quad (1)$$

where, T is the normalized transmittance; $R_s = (n - 1)^2 / (n^2 + 1)$; n is the refractive index; t is the 0.8 mm; d is the actual thickness of the sample.

As shown in the transmittance curve in Figure 7 while the YAG material lyophilized and sintered under the conditions above described presents transmittance values of 82% in the infrared region and 56% at 680 nm, the transmittance of the material dried in a furnace does not reach 40% in the IR range, and it is negligible at 680 nm. The lower

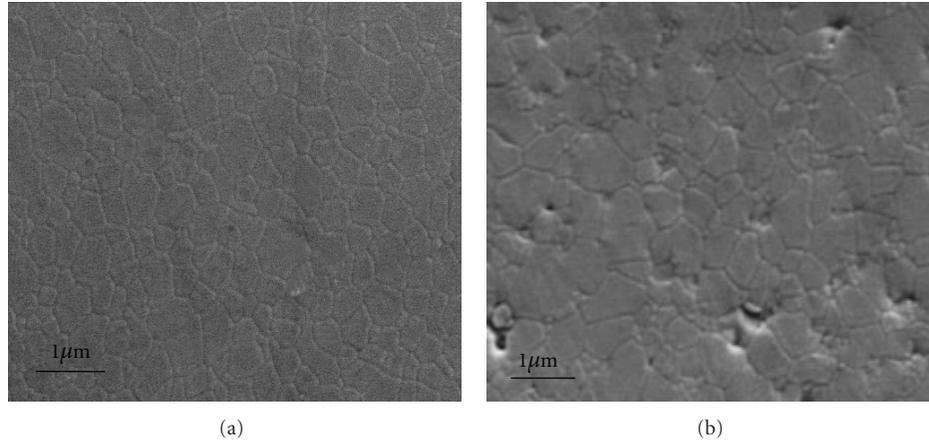


FIGURE 6: SEM observations of sintered samples (1500°C, 3 hours under vacuum) made from powder oxidized at 1300°C thermal etching sample; (a) lyophilized; (b) dried in an oven.

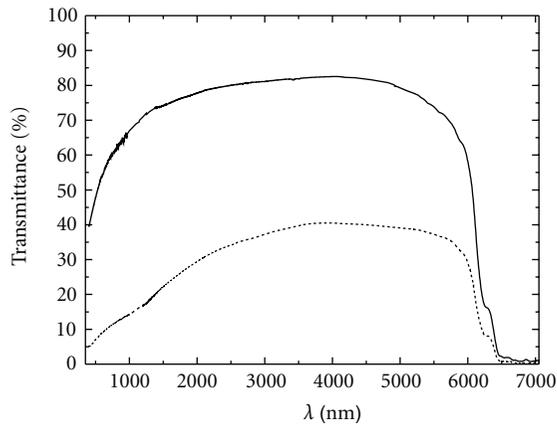


FIGURE 7: Optical transmittance of the pure YAG ceramic dried in an oven (dashed line) and lyophilized (solid line).

transmitted intensity of YAG not dried in a lyophilizer is due to a larger residual porosity in the sintered microstructure that originates a scattering of light, decreasing the value of transmittance. The agglomerates shown in Figure 2(b) lead to the presence of large pores in the green body that cannot be completely closed during sintering [24]. It is important to note that, in [23], transparent YAG was obtained by SPS under much more strict conditions: 100 MPa of applied pressure, a high vacuum: 10^{-6} mbar, and heating rates over $100^{\circ}\text{C}/\text{min}$. It is shown here that an adequate processing of the powders, mainly, avoiding the formation of agglomerates allows relaxing the conditions during sintering.

4. Conclusions

In conclusion, a direct lyophilization of the gel avoids the formation of agglomerates. The lyophilized powders have been sintered into 0.8 mm thick transparent YAG materials with in-line transmittances close to 60% at 680 nm and over 80% in the infrared range by spark plasma sintering.

However, conventionally dried gels show agglomerates with sizes over $1\ \mu\text{m}$ and turn to be opaque after sintering. Although proved for a particular system such as YAG, this result is extensible to any other material in which agglomerates need to be avoided and/or densities over 99.5% are required.

Acknowledgments

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