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# Processing and characterization of combustion synthesized YAG powders

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## Abstract

Precursor powders for yttrium aluminum garnet ($Al_5Y_3O_{12}$—YAG) were prepared by combustion of the solution of nitrates (oxidizer) of yttrium and aluminum containing lean amount of glycine (fuel–molar ratio of glycine to nitrate 0.18). The precursor formed by this reaction was a porous mass and was dry ground to a powder. Its thermal decomposition and crystallization behavior was studied using TG-DTA and XRD. The as formed precursor heated up to 880 °C was amorphous. It underwent volatile loss and crystallization into YAP and YAG at 920 °C which transformed to pure YAG at 1050 °C. The crystallization stage was characterized by two exotherms associated with loss of weight. The morphological features of the as formed and 1100 °C calcined precursor by SEM revealed that they were porous agglomerates consisting of fine particle network with fissures and cracks. The ideal conditions for grinding of the agglomerated powder into a fine one were fixed from the results of a combined study of zeta potential and viscosity evaluations. The zeta-potential variation with pH for the suspensions of the 1100 °C calcined powder exhibited a value of $\sim$35 mV at a pH of 3, a required condition for good dispersion stability for grinding. A study of the rheological behavior with shear rate for slurries containing various amount of solid concentration at this pH exhibited lower and strain rate independent viscosity for solid concentrations of about 20 vol.% (about 25 mPa s), showing absence of flocculates at this concentration, which is essential for effective grinding. Grinding conditions were optimized to obtain powder with size ($D_{50}$)$\sim$1.5 μm using the aqueous slurry containing 22.5 vol.% of solid concentration at a pH 3. A study of the role of calcination temperature on final sintered densities of the compacts showed that translucent bodies with a maximum sintered density $>$ 98% of the theoretical value could be obtained at 1600 °C in 5 h for the 1300 °C calcined powder.

*Keywords:* A. Powders; D. $Al_2O_3$; D. $Y_2O_3$; Chemical preparation

## 1. Introduction

YAG powders possessing controlled characteristics find application in the synthesis of advanced engineering material, composites and optically transparent solid state laser components etc. There are various solution based methods reported for the synthesis of the powder-simple decomposition of mixed nitrates, hydrolysis of organo-metallic precursors, co-precipitation from inorganic salt solutions (both homogeneous and heterogeneous precipitations) and solution combustion of nitrates with a fuel (urea, glycine, carbohydrazide) etc. [1–11]. In solution combustion technique, from a very concentrated solution of the metal nitrates a very porous mass of the oxide compound is formed due to the large amount of gaseous products formed. The combustion reaction is exothermic and self-sustaining. Due to the fast kinetics of the reaction, the heat evolved increases the reactant temperature and activates the process of product formation. However the oxide formed is porous agglomerate of finer particles and needs to be ground into agglomerate free finer powder and appropriately calcined to form dense particles for the synthesis of ceramic bodies. The precondition for formation of phase pure powder is that there should not be any compositional segregation in the solution during combustion and the exothermicity should be just enough to sustain the reaction and not be excessively too high so as to enable scaling up of the process. This is

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achieved by appropriately choosing the fuel and its amount. Using lean (substoichiometric) amount of fuel reduces the amount of heat evolved and offers an excellent method of controlling the vigorousness of the reaction.

In case of substoichiometric amount of fuel, the reaction is expected to take place by two mechanisms namely both solution combustion (an exothermic process) and simple decomposition of nitrates (an endothermic process). The combustion reaction can be represented as

$$3\ \mathrm{M(NO_3)_3} + 5\ \mathrm{NH_2CH_2COOH}$$

$$\rightarrow\ 3/2\mathrm{M_2O_3} + 7\ \mathrm{N_2} + 10\ \mathrm{CO_2} + 25/2\ \mathrm{H_2O}$$

in which the products are $CO_2$, $H_2O$, $N_2$ and the oxide [10,14]; where M is the aluminum and yttrium ions in 5:3 ratio [i.e. $M_2O_3$ is $(Y_{3/8}Al_{5/8})_2O_3$].

The number of moles of gases produced per mole of oxide ($M_2O_3$) formation is about 20 and the ideal molar ratio of glycine (fuel) to nitrate ion (oxidizer) to be used is 0.56.

The simple decomposition reaction of nitrates to form the oxide compound can be represented as

$$2\ \mathrm{M(NO_3)_3}\ \rightarrow\ \mathrm{M_2O_3} + 6\ \mathrm{NO_2} + 3/2\ \mathrm{O_2}$$

The number of moles of gases produced per mole of oxide ($M_2O_3$) formation is about 7.5.

In our previous studies it was found that the stoichiometric amount of glycine as fuel yielded carbon contamination (black powder with 8 wt.% carbon) and there was a large amount of volatile loss at the crystallization stage (12%) [11].

Formation of amorphous precursors for compounds of yttria–alumina by the nitrate–glycine reaction and evolution of crystalline phases upon heat treatment has been studied using XRD by Hess et al. [9]. The formation of precursors by direct decomposition of nitrates has been studied in our laboratory [12]. It was found that the agglomerates from this reaction were harder than that from the combustion reaction.

A detailed study of the thermal decomposition and phase evolution behavior of the precursor formed by TG-DTA, EGA and XRD is essential to obtain the optimum conditions of calcination to form well-crystallized pure YAG. A study of the morphological features of the agglomerates by SEM throws light on the mechanism of their formation and their grinding behavior. A systematic study of the grinding behaviour of the agglomerated mass formed is important as the presence of agglomerates influences sinterability and introduces microstructural heterogeneities in the product formed. This is an aspect, which has not been reported for combustion-synthesized powders. Recently, Houivet et al. have studied and reported the importance of dispersion conditions (variation of zeta-potential with pH and viscosity with shear rate of the suspensions) on the grinding behaviour of the oxide powders [13]. The role of calcination temperature on the sinterability of the fine ground powder is another aspect which has not been reported for combustion synthesized YAG.

Hence a detailed study of the TG-DTA, EGA and XRD characterization of the precursors formed with lean amount of fuel (glycine to nitrate ratio of 0.18) has been carried out. SEM was used to study the morphological features of the precursor and that calcined. The optimum conditions of dispersion (zeta potential and viscosity) for the effective grinding of agglomerated YAG powder have been obtained. The role of calcination temperature on the green and sintered densities of the fine ground powder has been studied. Results of all these studies have been presented in this paper.

## 2. Experimental

Concentrated stock solutions of aluminum nitrate (1.54 M) and yttrium nitrate (1.17 M) were prepared and standardized for exact concentration by gravimetric technique. Glycine (amino acetic acid—$NH_2CH_2COOH$) was used as a fuel. The stock solutions of aluminum and yttrium nitrates in the required ratio for a batch size of 40 g of YAG were taken in a pyrex beaker and desired amount of glycine was added (molar ratio of glycine to nitrate ion used was 0.18). It was heated gently on a laboratory nicrome wire heater till the viscous liquid fumed and combustion reaction set in, resulting in the evolution of bubbles of gaseous product without violent bursting and spilling over of the product. The temperature of the solution was monitored by a thermocouple dipped in it. The viscous liquid foamed and formed the precursor. It was dry ground for 30 min in the planetary mill (M/s Fritsch) to form into a less voluminous homogeneous powder and the grinding parameters used are given in Table 1.

The powder thus obtained was subjected to TG-DTA-EGA studies in Netzsch Thermal Analyser (Model STA 409) in air for volatile loss and heat effects and evolved gas analysis. XRD studies for the as formed and typical heat-treated precursors were carried out in a Philips

Table 1
Mill parameters used for planetary grinding

| Type of grinding and sample name | Mill (rev/min) | Pot size (cc) | Ball diameter (mm) | No. of balls | Time (h) |
|---|---|---|---|---|---|
| Dry (A) | 200 | 250 | 20 | 2 | 1/2 |
| Wet (B) | 200 | 80 | 20 | 2 | 3 |
| Wet (C) | 200 | 80 | 10 | 10 | 3 |
| Wet (D) | 200 | 80 | 6 | 20 | 3 |

X-ray diffractometer for phase formation. The shape and surface morphology of the as formed and calcined powders were observed by SEM (M/s Jeol). The zeta potential variation with pH for 1100 °C calcined powder was found by the Zetasizer 3000 (M/s Malvern). Viscosity variation with shear rate for slurries with varying solid concentration was evaluated using a cone and plate viscometer (M/s Bohlin). Wet grinding studies were carried out for the aqueous suspension containing about 22.6 vol.% of the YAG powder (20 g of powder in 15 cc of water) at a pH of 3. Wet grinding was carried out in the planetary mill and grinding parameters used are given in Table 1. The pot size and the number of balls used were decided judiciously by considering volume of the slurry of the powder to be ground. Progress of grinding was monitored by measuring the particle size distribution using Mastersizer 2000 (M/s Malvern). Measuring the loss of weight of the balls after grinding monitored the amount of contamination by the grinding media. Compacts of ground powders calcined at temperatures in the range of 1100–1500 °C were formed by uni-axial pressing at 150 MPa and sintered at 1600 °C for 5 h in air in a super kanthal furnace. The green and sintered densities were calculated by the measurement of geometrical dimensions and water displacement method (Archimedes' method), respectively. The grain structure of the thermally etched sintered specimen was obtained by optical microscopy.

## 3. Results and discussion

### 3.1. Formation of precursor

Precursors were formed with varying amount of fuel (fuel to oxidizer ratio in the range of 0.1–0.56). The precursors formed with the value of molar ratio of glycine to nitrate ion more than 0.2 appeared black. This is attributed to contamination with carbonaceous material formed by partial charring of the fuel. Hence the white precursor formed by the reaction with glycine to nitrate ratio 0.18 was selected for characterization and processing studies. The reaction to form the precursor was carried out on a heater in open, as the heat output of the heater can be controlled so that the reaction did not become excessively vigorous and the gases evolved could easily escape (a primary requirement for scaling up of the process). Upon heating the solution containing nitrates and glycine, the temperature increased gradually to about 200 °C accompanied by faster rate of increase of the temperature. The reaction proceeded with foaming of the viscous liquid due to the evolution of a large amount of gases. Foaming resulted in a porous solid. Using concentrated solution of aluminum nitrate and yttrium nitrate before adding glycine was necessary to reduce the reaction time. It appears that there is no local segregation of fuel with this composition as powder is white in color.

In the present study, as the amount of fuel used was less than the amount required for full combustion of the nitrate, direct decomposition of the nitrates formed an alternative path for the oxide formation. The gases evolved by both combustion and simple decomposition of nitrates (nitrogen, carbon-di-oxide and water evolved due to partial solution combustion reaction; brownish acidic nitrogen-di-oxide evolved due to partial simple decomposition of nitrates) led to the formation of porous agglomerated mass while the evolution of lesser amount of heat offered safe operation of the process especially for larger size batches. In this lean fuel composition, the combustion was slower, no glow noticed with in the porous product mass and controlling the process for larger batch size was easier. The combustion reaction was complete in a few minutes. The loosely agglomerated porous precursor formed was easily dry ground into a less voluminous homogeneous powder in about 30 min.

### 3.2. TG-DTA, XRD and morphology studies on precursor

TG-DTA pattern of the precursor formed exhibited loss of weight and absorbtion/evolution of heat effects (Fig. 1). It exhibited an endotherm in the temperature range of 25–300 °C accompanied by a weight loss of ~3%. This is attributed to the dehydration of absorbed moisture in the powder. The salient observation of this study was that there was a sharp and strong exotherm in the range of 880–950 °C followed by a very shallow exotherm in the range of 980–1050 °C accompanied by a total weight loss of ~6%. The EGA data has shown that the gas evolved around these exotherms to be carbon dioxide (Fig. 2). A comparison of the TG-DTA pattern of this precursor with those for the precursors formed by solution combustion with stoichiometric

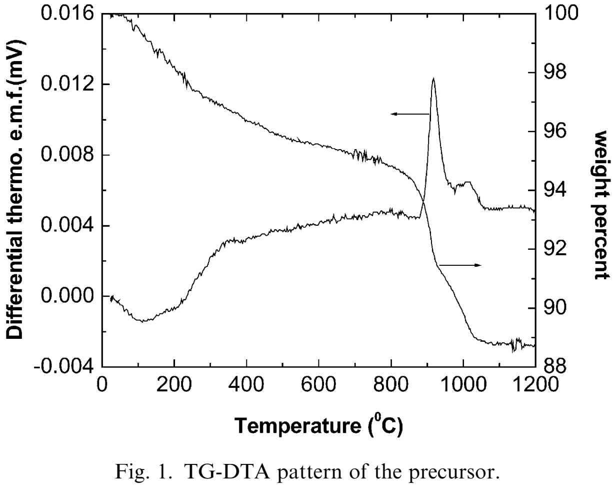

Fig. 1. TG-DTA pattern of the precursor.

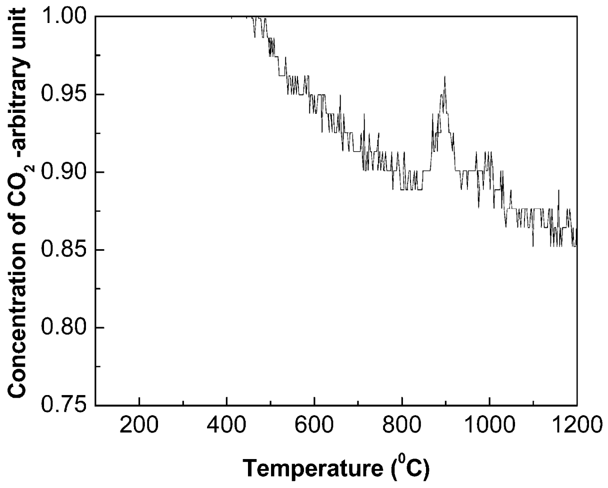

Fig. 2. EGA plot for carbondioxide evolution from the precursor at the crystallization stage.

amount of glycine and simple decomposition of nitrates would confirm the existence of both mechanisms during the formation of this precursor. The TG-DTA pattern for the precursor formed by solution combustion with stoichiometric amount of glycine exhibited an exotherm accompanied by a loss of weight of 5% around 400–600 °C (which was attributed to the burning of the carbonaceous material) [11]. The pattern of the precursor by simple decomposition of nitrates exhibited an endotherm accompanied by 10% weight loss around 300 to 400 °C (which was attributed to the decomposition of the undcomposed nitrate) [12]. Both these features were absent in the present precursor showing the absence of both the undecomposed nitrates and carbonaceous material. Thus the amount of fuel used is just enough to give sufficiently high temperature to decompose completely the nitrates without formation of any carbonaceous material. In the range of 870–1050 °C, the precursor formed by combustion reaction with stoichiometric amount of fuel exhibited two shallow endotherms accompasnied by 12% weight loss (attributed to crystallization accompanied by the release of trapped carbon dioxide or carbon present in the amorphous oxide structure) while the precursor formed by the decomposition of nitrates exhibited one sharp and one very shallow exotherm with no weight loss (attributed to crystallization from pure amorphous oxide possessing YAG composition) [11,12]. The precursor from the present reaction exhibited a sharp and a shallow exotherm in the range of 880–950 and 980–1050 °C accompanied by 6% weight loss. Thus the heat and weight loss effects at this stage are in between those corresponding to those found for precursors formed by solution combustion with stoichiometric amount of glycine and simple decomposition of nitrates. This shows that the precursor formed by the solution combustion of nitrates with lean amount of glycine is a mixture of both the above-mentioned precursors. The carbon analysis data by vacuum fusion technique for the precursor formed in the present study was 2.5 wt.% which was evolved as carbon-di-oxide in the 880–1050 °C temperature range during crystallization.

The XRD patterns of the precursor heat treated to different temperatures decided from TG-DTA studies are shown in Fig. 3. The as formed precursor heated to 880 °C was amorphous, that heated to 920 °C was a mixture of hexagonal YAP and cubic YAG and that heated to 1050 °C was pure cubic YAG. It has been reported, based on the XRD results, that intermediate YAP phase formed which subsequently transformed into the stable YAG phase[9]. The salient feature of this study is that the amorphous precursor at 880 °C is not chemically pure YAG compound and it releases volatiles during crystallization, which is a new observation in this study. The formation of hexagonal YAP as an intermediate showed the closeness of its structure to that of the amorphous precursor. It could be said that the kinetically favored YAP phase formed that finally transformed into the thermodynamically stable cubic YAG. The EGA result led to the conclusion that the carbon dioxide gas evolved at the crystallization stage was either the trapped one inside the amorphous oxide structure or the carbon was a part of the complex amorphous structure of the precursor powder. The occurrence of a sharp exotherm in the range of 880–950 °C accompanied by loss in weight and XRD results could be attributed to the formation of YAG via the intermediate YAP phase. The shallow exotherm in the range of 980–1050 °C is attributed to the further growth of crystallites.

The crystallization of pure YAG phase at 1050 °C established the presence of compositional homogeneity of metal atoms in the precursor intermediate. The ease of formation of YAG phase from the YAP phase showed that the chemical composition of the YAP phase is $Y_3Al_5O_{12}$ (i.e. it is a solid solution of $Al_2O_3$ in

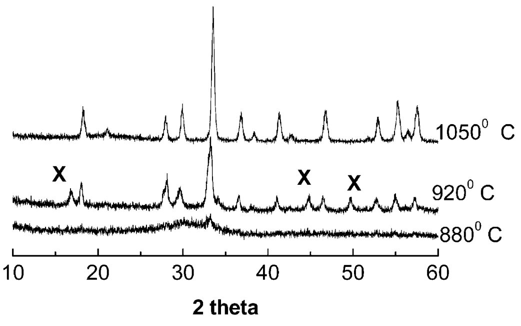

Fig. 3. XRD pattern of the precursor heated to different temperatures at 10 °C/min and quenched (peaks marked as 'X' are due to YAP phase).

$AlYO_3$ and not a mixture of $Al_2O_3$ and $AlYO_3$). As the formation of YAG was complete at 1050 °C, the precursor powder was calcined at 1100 °C for 2 h to eliminate volatiles and formation of crystalline compound.

The SEM study showed that the as formed precursor powder consisted of irregularly shaped agglomerates possessing a wide size distribution. The typical agglomerates were made up of fine particles with big voids (Fig. 4A). Upon calcination at 1100 °C, the porous network structure made up of fine particles of the agglomerates was retained (Fig. 4B).

### 3.3. Zeta-potential, viscosity and grinding studies on 1100 °C calcined precursor

The as formed dry ground precursor calcined at 1100° C was found to possess particle size with a $D_{50}$ (size below which 50 vol.% of the powder exist) of about 4 µm but still contained substantial amount of coarser agglomerates (20 vol.% in the range of 10–100 µm) as shown by the broader size distribution (Fig. 5A). Presence of these agglomerates are detrimental to final stage of sintering. They introduce heterogeneities in the microstructure of the sintered ceramics that can not be eliminated and act as defect centers. Thus these agglomerates need to be got rid off by grinding. Reduction of size to finer range is effective by wet grinding. The precondition for efficient wet grinding is that the powder should be well dispersed in the slurry. The zeta potential of the suspension is a measure of the amount of charge on the particle, which offer stability to its dispersion through electrostatic repulsion. The variation of zeta-potential of the suspension of the powder with pH

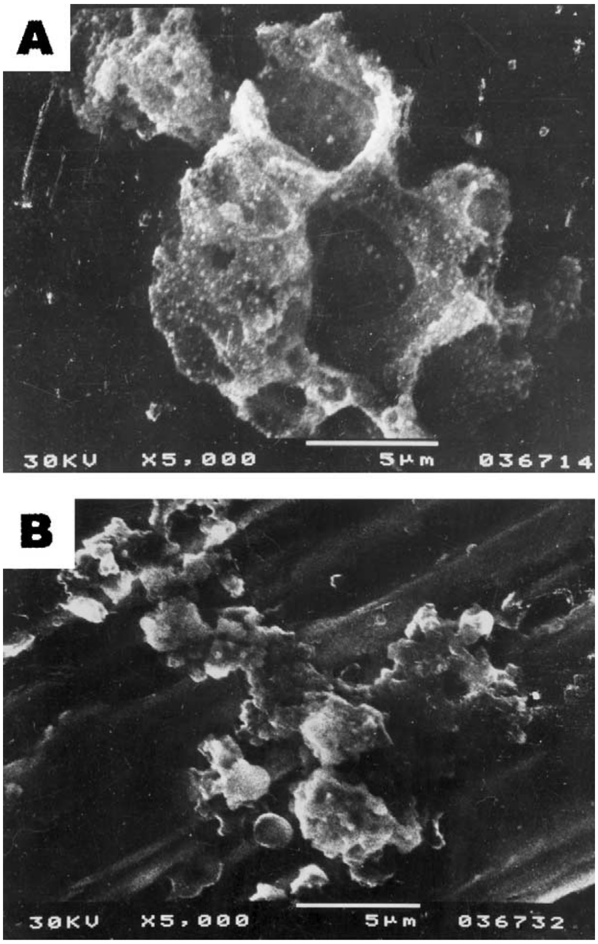

Fig. 4. Scanning electron micrographs of precursor and calcined powders: (A) as formed precursor: (B) precursor calcined at 1100 °C.

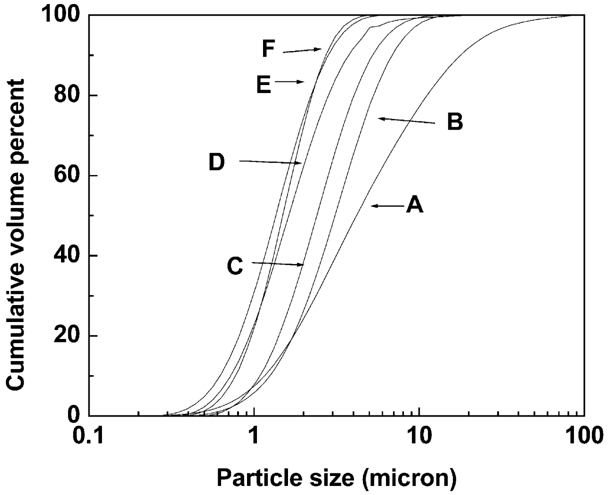

Fig. 5. Particle size distribution of 1100 °C calcined and wet ground powders from combustion reaction of nitrate-glycine (molar ratio of glycine/nitrate 0.18). (A) precursor dry ground with two balls of 20 mm diameter for 1/2 h and calcined at 1100 °C. (B) Powder 'A' wet ground with 2 balls of 20 mm diameter for 3 h. (C) Powder 'B' wet ground with 10 balls of 10 mm diameter for 3 h. (D) Powder 'C' wet ground with 30 balls of 6 mm diameter for 3 h. (E, F) Powder 'D' calcined at 1300 and 1500 °C and wet ground for 1/2 h.

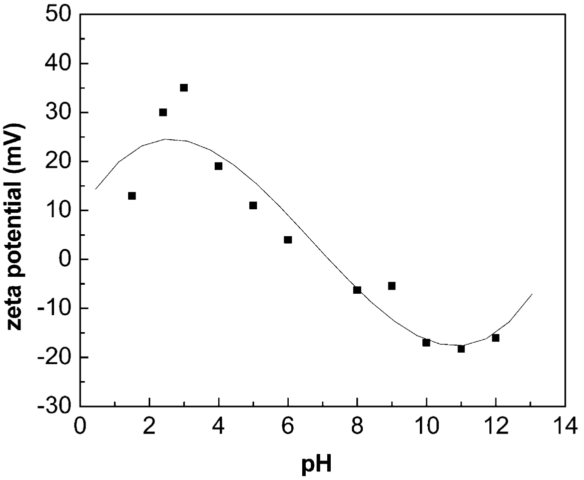

Fig. 6. Zeta-potential variation with pH for 1100 °C calcined powder.

showed that it was maximum at a pH of 3 (Fig. 6), indicating the ideal pH for the dispersion stability. Hence the suspension for grinding was prepared at a pH of 3. Even at this pH, flocculates are reported to be present in concentrated slurries, which are destroyed at higher shear rates during measurement of viscosity, resulting in thixotropic flow behavior. Presence of these flocculates hinder grinding efficiency and hence optimum solid loading in the slurry has to be just the point below which thixiotropic flow behavior is absent. However the batch size decreases with slurries containing decreasing amount of solid and always an optimum condition need to be arrived at from the required level of fineness of the powder and time of grinding. The study of variation of viscosity of the slurries with strain rate depicted thixotropic behavior confirming the presence of flocculates at solid concentration of 30 vol.% (Fig. 7). It is seen that the thixotropic effect reduced drastically with decreasing solid content of the slurry (30 to 20 vol.%). Shear rate independent flow (~25 mPa s) behavior was exhibited by the slurry with 20 vol.% solid. Hence, in this study, the calcined powders were wet ground at a pH of 3 with 22.5 vol.% of solid in water (20 g of powder in 15 cc of water). The particle size distribution of powders ground with balls of graded sizes was found to be more uniform in our previous studies [11] and hence the same procedure was followed. The size ($D_{50}$) reduced from ~4 to 1.6 μm (Fig. 5B–D) with a substantial amount of reduction in the coarse fraction. It was found that the bigger balls were efficient in grinding coarser agglomerates while smaller balls were efficient in finer size range. Under the same conditions of grinding, the particle size distribution data ($D_{50}$) of the powder formed by combustion reaction with stoichiometric amount of fuel was ~1.5 μm while the powder from simple decomposition of nitrates was much higher (~3.6 μm) [11,12]. Thus the grindability of the powder formed with lean amount of fuel is found to be same as that of the powder formed with stoichiometric amount of fuel, thereby indicating no additional advantage by using more fuel (glycine to nitrate ion ratio >0.18). After calcination at 1300 and 1500 °C, the powders were ground for about 30 min to break the weak agglomerates that could have formed. The particle size distribution of these ground calcined powders remained essentially the same with a slight reduction ($D_{50}$ ~1.4 μm; Fig. 5E,F). The contamination by the grinding media (as seen by the total loss in weight of balls) was ~0.3% by following the above grinding schedule.

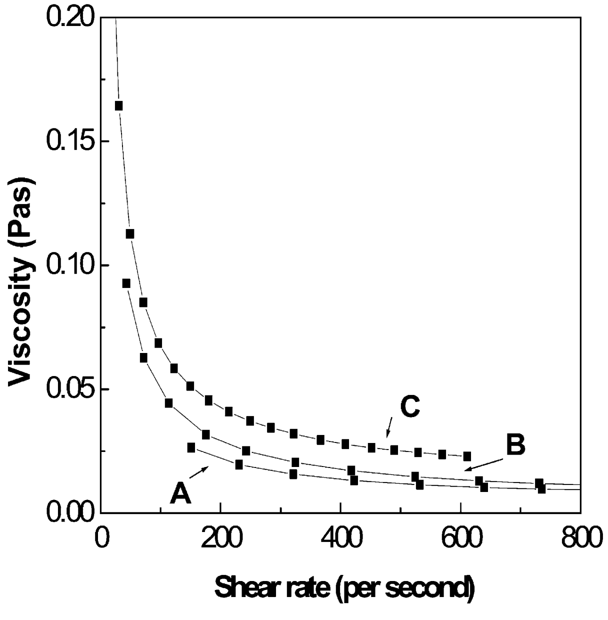

Fig. 7. Viscosity variation for slurries of the 1100 °C calcined powders with different solid content as a function of shear rate at a pH of 3. (A–C) Slurries with solid concentration 20, 25 and 30 vol.%.

### 3.4. Calcination and sintering studies

With increasing the calcination temperature from 1100 to 1500 °C, the green density of the compacts formed by uniaxial pressing at 150 MPa increased from ~45 to 56% T.D. (Fig. 8). It can be said that the porous fine particles individually undergo sintering at higher calcination temperatures leading to improvement in the green compact density. The bulk density data of the pellets sintered at 1600 °C for 5 h showed that it was maximum for the compact formed with 1300 °C calcined powder (>98% T.D.), indicating the particles from this powder are sufficiently dense and is still sinteractive. The typical microstructure of the translucent sintered specimen exhibited a uniform fine grain size distribution (Fig. 9).

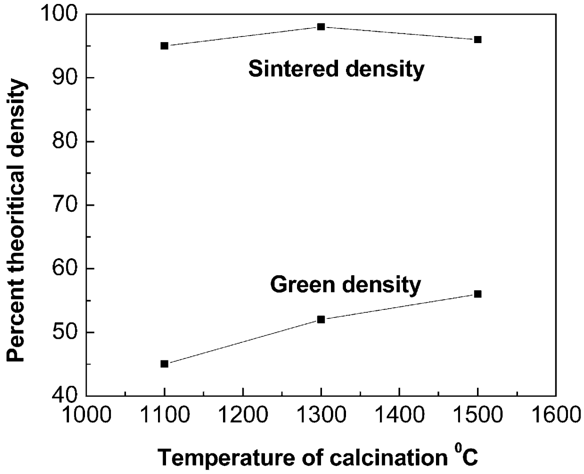

Fig. 8. Green and sintered density variation for pellets from powders calcined at varying temperatures. Compaction pressure, 150 MPa; sintering temperature, 1600 °C for 5 h).

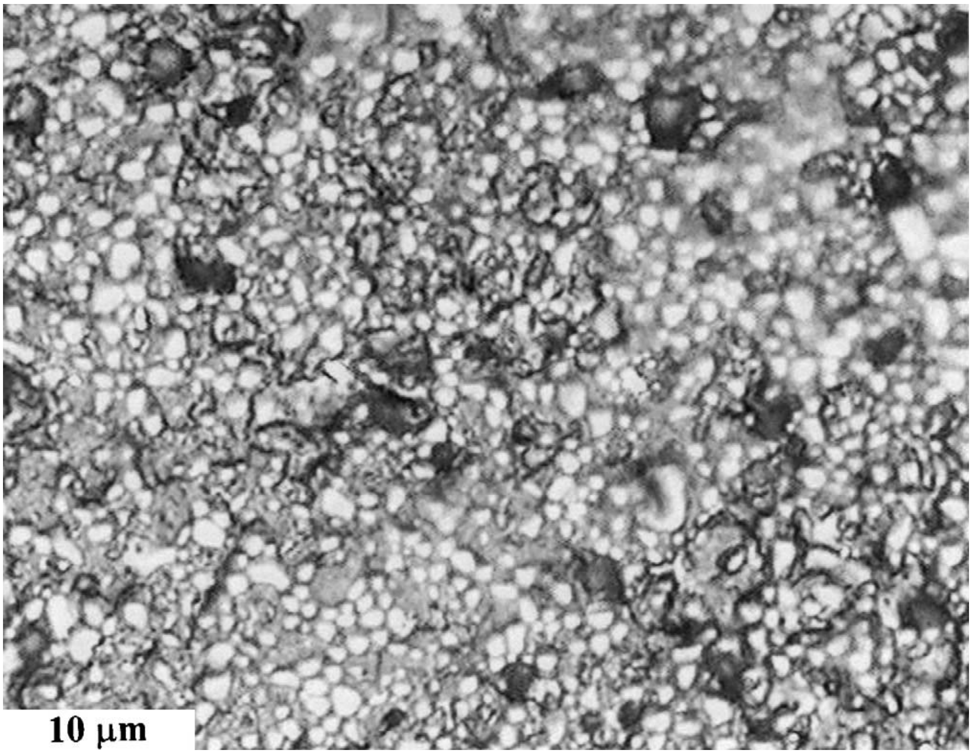

Fig. 9. Microstructure of YAG compact sintered at 1600 from 1300 °C calcined powder.

## 4. Conclusions

Amorphous precursor powder for YAG was obtained by the solution combustion method with lean amount of glycine (fuel). The powder formed underwent crystallization to YAG and loss of weight upon calcination up to 1100 °C evolving volatiles—water, carbon dioxide and this step was a solid state reaction resulting in little change in the size and shape of the particle. The important finding of this study was that the crystallization stage was exothermic characterized by carbon dioxide loss. The calcined powder particles were porous agglomerates that could be planetarily wet ground to finer size with their $D_{50}$ less than 1.5 μm using an aqueous slurry of concentration of 22.5 vol.% of solid (least thixiotropic fluid) in the pH range of 3–4 (zeta potential $>20$ mV). Another important finding of this study, by comparison with the results of our previous study, was that the powder formed by the combustion reaction with lean amount of glycine was as soft as that formed with stoichiometric amount of glycine. Calcination at higher temperature of the powder improved the green density of the compacts. Compacts from powder calcined at 1300 °C sintered to 98% T.D. at 1600 °C in 5 h exhibiting a uniform and fine grain structure.

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