

THERMAL DECOMPOSITION BEHAVIOR OF PRECURSORS FOR YTTRIUM ALUMINUM GARNET

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Precursor powders for yttrium aluminum garnet (YAG) were synthesized by solution combustion reactions (nitrate–glycine reaction with stoichiometric and sub-stoichiometric amount of fuel) and simple decomposition of nitrate solution. The TG-DTA, FTIR and XRD analyses of the precursors and the typical heat-treated samples were carried out to understand the processes occurring at various stages during heating to obtain phase pure YAG. Precursors from all the reactions exhibited dehydration of adsorbed moisture in the temperature range of 30 to 300°C. The precursor from nitrate–glycine reaction with stoichiometric amount of fuel (precursor-A) contained entrapped oxides of carbon (CO and CO₂) and a carbonaceous contaminant. It exhibited burning away of the carbonaceous contaminant and crystallization to pure YAG accompanied by loss of oxides of carbon in the temperature ranges of 400 to 600 and 880 to 1050°C. The precursor from simple decomposition of nitrates (precursor-B) exhibited denitration cum dehydroxylation and crystallization in the temperature ranges of 300 to 600 and 850 to 1050°C. The precursor from nitrate–glycine reaction with sub-stoichiometric amount of fuel (precursor-C) contained entrapped carbon dioxide and exhibited its release during crystallization in the temperature range of 850 to 1050°C. This study established that, in case of metal nitrate–glycine combustion reactions, crystalline YAG formation occurs from an amorphous compound with entrapped oxides of carbon. In case of simple decomposition of metal nitrates, formation of crystalline YAG occurs from an amorphous oxide intermediate.

Keywords: combustion synthesis, FTIR analysis, TG-DTA, XRD analysis, yttrium aluminum garnet (YAG)

Introduction

Yttrium aluminum garnet (YAG) powders possessing controlled characteristics find a wide variety of applications in making transparent laser components, advanced engineering material and composites, refractory coatings, etc. [1]. Formation of YAG by solid-state reaction requires temperature of the order of 1600°C and long duration of heat treatment. There are various solution based methods reported (such as sol–gel process, homogeneous and heterogeneous precipitation, solution combustion and simple decomposition of nitrates) in which YAG phase forms at a much lower temperature due to mixing of the reactants in molecular scale in solutions [1–14]. Solution combustion and nitrate decomposition are the simplest techniques that involve only heating the concentrated solution of the nitrates with or without a fuel. The powders formed by the above reactions are generally agglomerates (soft or hard) of fine crystallites, may or may not contain volatiles and need to be calcined to form phase pure oxide compound. Also they need to be ground appropriately as the presence of agglomerates introduces defects in the fabricated ceramic bodies. Solution combustion process is preferred over simple decomposition as most of the gases evolved

in the former process are environmental friendly neutral gases with minimum amount of acidic nitrogen dioxide. Also this process results in formation of powder of soft agglomerate that can be very easily ground.

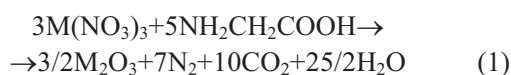
In solution combustion technique, from a very concentrated solution of the metal nitrates (oxidizer) and urea or glycine etc., (fuel) a very porous mass of the oxide compound is formed. Evolution of large amount of gases during the process makes the powder agglomerates to be soft (i.e., easy to be ground to finer size). The heat evolved during combustion makes the reaction self-sustaining to form the compound directly. However, one of the limitations of the process is the problem encountered in scaling up due to the vigorous nature of the combustion reaction accompanied by flame formation. Also generation of excessively high a temperature could lead to formation of harder agglomerates that would be more difficult to be ground. Thus in preparing soft agglomerated powders it is required to use the fuel that would provide more amount of gases with just required amount of heat.

The nitrate–urea reaction for formation of YAG was found to result in phase pure YAG accompanied by formation of a bright flame (flame temperature measured by a two-color pyrometer was about

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1600°C) [15]. In this reaction, the exothermicity, fast reaction kinetics and evolution of large amount of gases make the reaction violent and pose major problems in scaling up of the process. One way of exercising control over the reaction kinetics is by way of using the fuel for which the heat of combustion is sufficient but not excessively high. Another way is using sub-stoichiometric amount of fuel in which case the amount of heat evolved is less but enough gases are evolved so as to make the agglomerates sufficiently soft for grinding. However, these processes result in incomplete reaction and the powder has to be calcined to form into phase pure compound. Using glycine as fuel for YAG led to evolution of lesser amount of heat (compared to using urea as fuel) making the reaction less vigorous. However, the precursor formed was an amorphous intermediate, which exhibited volatile loss upon calcination [16, 17].

The stoichiometric amount of glycine (fuel) required for combustion can be calculated using the reported combustion reactions [13, 18].



where M is the aluminium and yttrium ions in 5:3 ratio i.e., $M_2\text{O}_3$ can be represented as $(Y_{3/8}\text{Al}_{5/8})_2\text{O}_3$. For every mole of $M_2\text{O}_3$ formed 20 moles of gases are evolved for reaction (1). The gaseous products formed are environment friendly (nonpolluting) and make the powder agglomerates soft enough to be easily ground.

The simple decomposition of the aqueous solution of nitrates of aluminum and yttrium can be represented as



This reaction is endothermic and the number of moles of gases evolved per mole of $M_2\text{O}_3$ formed is only 7.5. A constant supply of heat is required till the powder mass is formed during decomposition. Acidic nitrogen dioxide gas polluting the atmosphere is evolved in this reaction. Even though this reaction is endothermic and hence expected to result in lesser reaction temperature, the aggregates formed were found to be hard and difficult to be ground [15].

The thermal decomposition, chemical characterization and phase evolution behavior of the precursors formed in novel powder preparation techniques (such as solution sol-gel, decomposition of inorganic and organo-metallic compounds, solution combustion, etc. for synthesis of various oxide compounds used in advanced applications) is widely studied in the recent years as it helps not only in optimizing the calcination conditions but also in understanding the mechanism of formation of phase pure compounds through various reaction intermediates [19–25]. Such

a study brings out the basic differences in phase evolution behavior of precursors formed by different reactions. The characterization of the intermediates (amorphous/crystalline) formed at various stages of thermal analysis by FTIR exhibits the changes occurring in their chemical composition and salient features of their structure (fingerprint of the chemical entity), characteristic of each precursor. In solution combustion technique, such a study can bring out whether the fuel simply reacts with the oxidizer in solution or it interacts/complexes with the metal ion in the solution and forms into intermediates before formation of the final compound.

A comparative study of the characterization of the intermediates formed at various temperature ranges during thermal analysis by FTIR spectra and XRD for the precursors of YAG formed by nitrate-glycine solution combustion (with stoichiometric and sub-stoichiometric amount of fuel) and simple decomposition of nitrates has not been reported yet and hence has been carried out. The differences in their crystallization behavior have been brought out in this study.

Experimental

Aqueous stock solutions of aluminum nitrate (1.9 M) and yttrium nitrate (1.1 M) required for YAG composition (batch size ~40 grams) were mixed and concentrated to a viscous liquid (metal ion concentration ~10 M) by evaporation at 70°C in an air oven for three batches. Required amount of glycine (glycine/nitrate ion molar ratio ~5/9 for stoichiometric and ~2/9 for sub-stoichiometric) was dissolved in two batches of the concentrated liquid of nitrates in two pyrex beakers. The precursors were formed by heating the viscous solutions in the beakers gently on a laboratory assembled nicrome wire heater till the combustion reaction set in accompanied by the evolution of a large amount of gaseous product with heat (called precursor-A and -C; time of heating was about 10 min for both reactions). The third batch of the nitrate solution in the beaker was decomposed on the same heater till the viscous liquid formed into granular powder mass accompanied by the evolution of reddish fumes of nitrogen dioxide (precursor-B; time of heating was about 10 min). The so formed precursors-A, -B and -C were dry ground separately in the planetary mill (Fritsch) for half an hour to form into a homogeneous powder mass (mill parameters used – mill r.p.m. 200, pot size 250 cc, number of balls 2 and ball diameter 20 mm). The carbon content of the precursors was determined using an elemental analyzer (Elltra, Model CS800) by the combustion followed by IR detection technique. The powders thus obtained were subjected to TG-DTA studies

in Netzsch Thermal Analyser (Model STA 409) in air for volatile loss and heat effects (heating rate $-10^{\circ}\text{C min}^{-1}$). The evolved gas analysis of the precursor-A was carried out by a mass spectrometer (Balzers, Model QMG 311) coupled to the thermal analyzer through a heated capillary in argon atmosphere. Powder samples for the Fourier transformed infrared spectra were prepared by heating the precursors to various temperatures in a programmed laboratory Kanthal furnace followed by air quenching. The spectra of the precursors and those heated to desired temperatures were recorded using pellets of the mixture of the sample and KBr powders using the spectrophotometer (JASCO 610 Model) at 4 cm^{-1} resolution. The XRD studies were carried out for the same typical heat-treated samples in a X-ray diffractometer (Philips).

The average crystallite size of the precursors heated to different temperatures was determined from the line broadening observed for the peak corresponding to the 420 reflection using the Scherer formula.

$$G = \lambda/\beta\cos\theta$$

where G is the average crystallite size (\AA), λ is the wavelength of X-ray used (1.54 \AA), θ is the angle of diffraction (16.7° in this case), $\beta = (B^2 - b^2)^{1/2}$ where B and b are full widths (in radian) at half maximum observed for the sample and the instrument, respectively. The instrumental broadening was assumed to be the width exhibited by a standard well-crystallized YAG powder obtained by heating to 1600°C .

Results and discussion

Formation of precursors

The precursors were formed by conducting the combustion and decomposition reactions on a heater in open, as the heat output of the heater could be easily controlled so that the reaction did not become excessively vigorous and the gases evolved could easily escape. This procedure is always desired in case of reactions involving decomposition of liquid reactants exhibiting very large percentage of loss in mass during product formation. In case of formation of precursor by glycine–nitrate reaction (precursor-A), as the temperature reached about 200°C , the viscous liquid foamed vigorously with the evolution of a larger amount of bubbles of gaseous product of fuel – oxidizer reaction with no flame formation. The reaction was smooth without any spilling and the product appeared glowing for a minute. In case of formation of precursor by simple decomposition of nitrates (precursor-B), the solution decomposed smoothly with the evolution of bubbles of reddish brown nitrogen dioxide gas (major acidic pollutant to the atmosphere)

forming granules of aggregated powder. In the sub-stoichiometric fuel composition (precursor-C), as the amount of fuel used was less than the amount required for full combustion of the nitrate, direct decomposition of the nitrates also formed an alternative path for the oxide formation. The combustion was slower and reddish brown nitrogen dioxide gas was also evolved. All these reactions were complete in 10 min. The precursor-A was black while precursors-B and C were white. The black color of precursor-A was attributed to segregation of some amount of glycine and its charring at lower reaction temperature ($\sim 600^{\circ}\text{C}$). This was confirmed by the formation of a black product in the initial stage of decomposition of the aqueous solution of pure glycine.

TG-DTA-EGA, FTIR and XRD characterization

Precursor from nitrate–glycine reaction with stoichiometric amount of fuel (precursor-A)

The precursor was found to contain 8 mass% carbon by elemental analysis. The TG-DTA-EGA patterns, FTIR spectra and XRD profiles of the precursor and that heated to desired temperatures are shown in Fig. 1a–d. The FTIR spectra of the so formed precursor exhibited absorption peaks at 2350 and 2200 cm^{-1} which could be attributed to the presence of trapped carbon dioxide and carbon monoxide respectively [26]. Also a broad band of absorption was noticed in the range of 3000 to 3700 cm^{-1} , characteristic of adsorbed moisture. Absorption peaks characteristic of presence of carbonate were noticed at 1540 , 1390 (attributed to split anti-symmetrical carbonate stretching) and 840 cm^{-1} (attributed to out of plane bending of carbonate) [27]. Thus presence of carbon dioxide, carbon monoxide, adsorbed moisture and some amount of carbonate in the precursor of this combustion reaction is established. The precursor was found to be amorphous to X-ray.

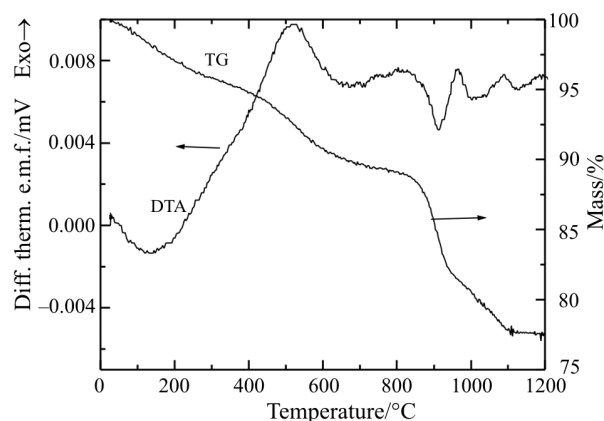


Fig. 1a TG-DTA pattern for precursor-A

During thermal analysis, it exhibited a broad endotherm accompanied by a loss of mass of 5% in the temperature range of 30 to 300°C, attributed to the dehydration of adsorbed moisture in the powder. This

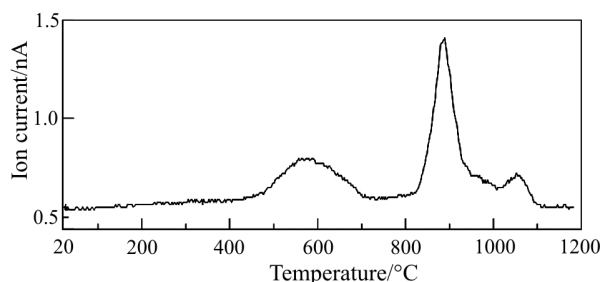


Fig. 1b EGA pattern for the evolution of CO₂ gas for precursor-A

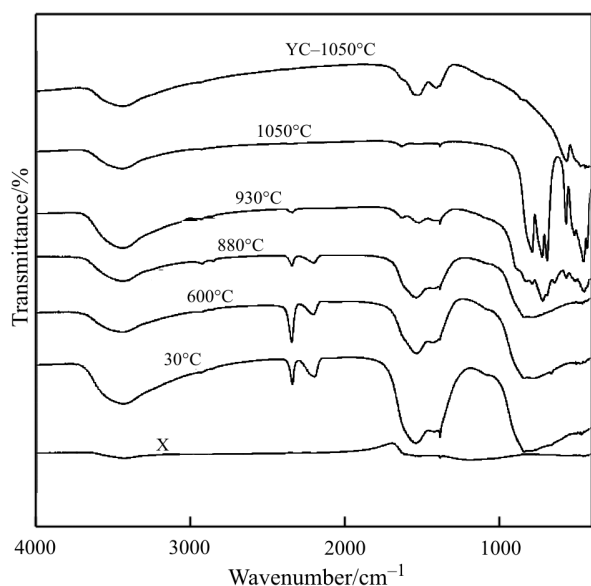


Fig. 1c FTIR spectra of precursor-A heated to various temperatures

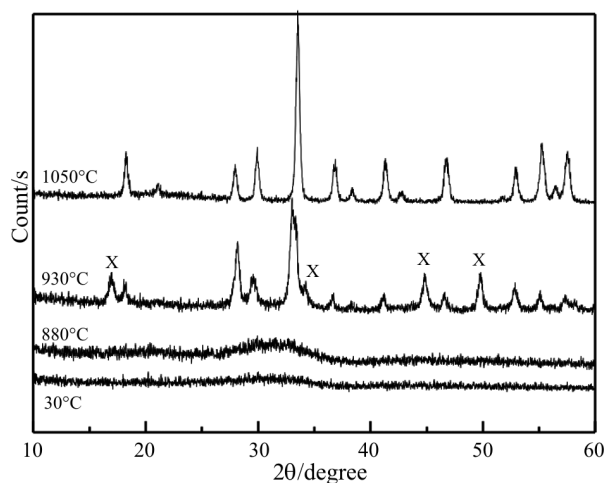


Fig. 1d XRD patterns for the precursor -A heated to different temperatures (peaks marked as 'X' denote YAP structure)

was followed by a broad exotherm accompanied by a loss of mass of about 5% in the temperature range of 400 to 600°C which could be attributed to the burning of a carbonaceous contaminant formed due to some amount of segregated glycine. This was confirmed by the partial burning off of the black product formed in the initial stages of decomposition of pure glycine in this temperature range. The EGA pattern (Fig. 1b) exhibited loss of carbon dioxide in this temperature range, which shows presence of trace amount of oxygen in the argon atmosphere. The FTIR spectra of this carbonaceous intermediate did not exhibit any characteristic absorption peaks (marked in Fig. 1c as 'X') and hence could not be detected by this technique. In the temperature range of 880 to 1100°C, mass loss occurred in two stages (about 8 and 4% in the ranges of 880 to 930 and 930 to 1050°C) accompanied by corresponding heat effects. The evolved gas analysis data exhibited loss of carbon dioxide in these two temperature ranges. The DTA peaks were found to be ill-defined in shape possibly because of overlapping processes. The FTIR spectra of the precursor intermediates heated up to 880°C exhibited presence of trapped carbon dioxide, carbon monoxide and some amount of carbonate while that of the precursor heated to 930°C exhibited substantial reduction in the content of entrapped oxides of carbon and carbonate (i.e., reduction in the intensity of absorption at 2200, 2350 and 1530, 1385, 850 cm⁻¹), in agreement with the TG and EGA results. New peaks at 790, 720, 690, 640 and 570 cm⁻¹ started appearing in the FTIR spectra of the sample heated to 930°C. The XRD pattern of the sample heated to 880°C was amorphous while that heated to 930°C exhibited the powder to be predominantly crystalline cubic YAG with some amount of hexagonal YAP (PC-PDF: 33–40; 16–219). Thus the loss of carbon dioxide observed from TG and EGA curves in the temperature range of 880 to 930°C is seen to be overlapping with the crystallization of YAG and a small amount of YAP. The distortion in shape of the DTA peak in the temperature range of 880 to 930°C is indicative of the overlap between the exothermic crystallization process and an endothermic event like a simple decomposition reaction or a desorption process releasing carbon dioxide from the precursor. Since the carbonates of yttrium and aluminum are not stable above 700°C, the endothermicity is most likely due to release of oxides of carbon entrapped in the amorphous precursor during combustion reaction.

The intensity of absorption peaks corresponding to oxides of carbon and carbonate further reduced in the FTIR spectra of the sample heated to 1050°C, indicating completion of the reaction. It exhibited absorption bands with peaks around 790, 720, 690 and

560 cm^{-1} and there was no peak at 640 cm^{-1} . The peaks at 790, 720, 690 and 570 cm^{-1} have been attributed to be characteristic of the lattice modes of vibrations of crystalline YAG [28–30]. Thus the absorption peak observed at 640 cm^{-1} , in the case of 930°C heated sample, could be attributed to the presence of some amount of the YAP phase while the rest of the peaks are due to YAG. Presence of small amount of YAP phase indirectly indicates presence of a corresponding amount of amorphous alumina. The XRD pattern of the sample heated to 1050°C was pure cubic YAG free of the YAP phase. The TG and EGA curves showed a loss in mass accompanied by release of carbon dioxide in the range of 930 to 1050°C which could be due to the loss of entrapped oxides of carbon present in the amorphous alumina, during its reaction with YAP to form YAG. The exothermicity of the reaction between YAP and alumina was partly compensated by the endothermicity of the process involving release of entrapped carbon dioxide and hence the DTA curve in the temperature range of 930 to 1050°C exhibited a broad and weak exothermic peak. Thus the present set of observations establishes the formation of an amorphous intermediate containing trapped oxides of carbon during the combustion process.

Formation of a carbonate intermediate (stable up to 700°C) from the precursor formed by the thermal decomposition of yttrium–aluminum isobutrylates and yttrium–aluminum malonates has been reported [4, 27]. Based on XRD studies on isothermal heat treated samples prepared by nitrate–glycine reaction, Hess *et al.* [11], reported that an intermediate YAP phase formed which subsequently transformed into the stable YAG phase. Vietch *et al.* [27], have proposed formation of YAG occurring from the reaction of YAP with amorphous alumina. However, in the present thermal analysis study, there is a loss of carbon dioxide in the temperature range of 930 to 1050°C accompanying the formation of pure YAG from the YAP and amorphous alumina. This indicates that the amorphous alumina contains entrapped oxides of carbon. These two phases (YAP and amorphous Al_2O_3) appear to be mixed in nano-scale as shown by their reactivity at this relatively lower temperature (930 to 1050°C). However, the amount of YAP is very less.

The entrapped gases are released only when the ordering in the lattice takes place during the crystallization process. Generally, the release of carbon dioxide occurring in two steps could be attributed to two different reactions. No carbonates of yttrium and aluminium stable above 700°C are known. Yttrium hydroxy-carbonate prepared in our laboratory was found to attain mass stability around 700°C (i.e., completely decomposed) while the FTIR of the same heated to 1050°C exhibited

presence of some amount of carbonate (marked in Fig. 1c as YC–1050°). Also yttria exposed to atmosphere in ambient conditions has been found to contain carbonate which has been attributed to pick up of carbon dioxide from atmosphere [31]. Aluminium carbonate, being easily hydrolysable to the hydroxide, has not been studied for its thermal stability. Although Liu *et al.* [4], have reported formation of some forms of aluminium carbonate during the thermal decomposition of aluminium isobutrylate, it was seen to be unstable above 300°C. Hence the absorption bands corresponding to carbonate in the FTIR spectra of the precursor at 880°C appears to be formed by the reaction of moisture and carbon dioxide adsorbed/present in the precursor. The decrease in intensities of these infrared absorption peaks with increasing temperature of heat treatment could be attributed to the decreasing surface activity of the powder. The evolution of carbon dioxide observed in EGA curves above 800°C, therefore, is most likely due to the release of entrapped oxides of carbon.

The FTIR spectra of the precursor heated to varying temperatures up to 1050°C exhibited a broad absorption band in the range of 3000 to 3700 cm^{-1} , attributed to presence of water absorbed from atmosphere. However, the intensity reduced with increasing temperature due to the reduction in specific surface area.

The point to be noted is that the reaction (1) does not go to completion and stops at an intermediate stage due to lesser amount of heat evolved in this combustion reaction. This provides feasibility of larger batch sizes of soft agglomerated powders.

Precursor from simple decomposition of nitrate (precursor-B)

The TG-DTA patterns, FTIR spectra and XRD profiles of the precursor-B formed by the simple decomposition of nitrates and that heated to different temperatures are shown in Fig. 2a–c. The TG-DTA curves exhibited an endotherm in the range of 30 to 300°C accompanied by a mass loss of about 5% attributed to the loss of adsorbed moisture in the powder. The FTIR spectra of the precursor exhibited presence of nitrate and hydroxide as shown by the characteristic bands with the peaks of absorption at 1470, 1385, 1350, 1050 cm^{-1} (characteristic of nitrate) and at 1640 cm^{-1} (characteristic of hydroxide) [30]. Also a broad absorption band was noticed in the range of 3000 to 3700 cm^{-1} , characteristic of adsorbed moisture. An endotherm occurred in the range of 300 to 600°C accompanied by a mass loss of about 12%. The spectra for sample heated to 600°C showed a drastic reduction in the intensity of all the peaks of absorption corresponding to nitrate and hydroxide. Thus the process occurring at this stage is decomposition of left over nitrate and hydroxide in the precursor. This

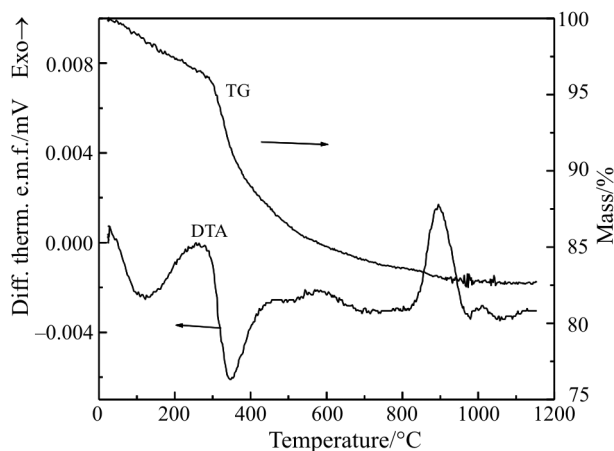


Fig. 2a TG-DTA pattern for the precursor-B

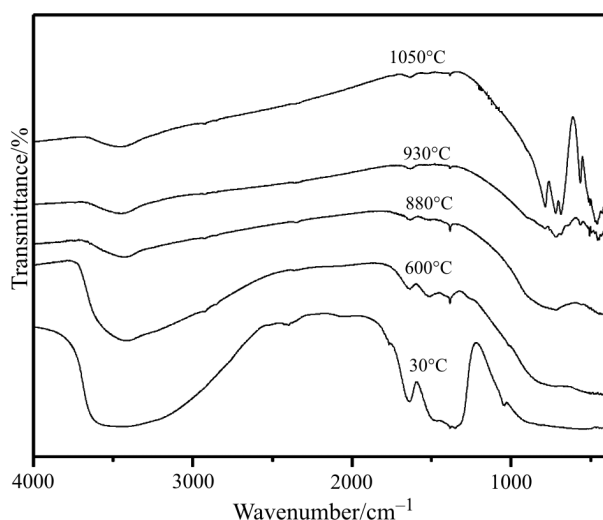


Fig. 2b FTIR spectra of precursor-B heated to various temperatures

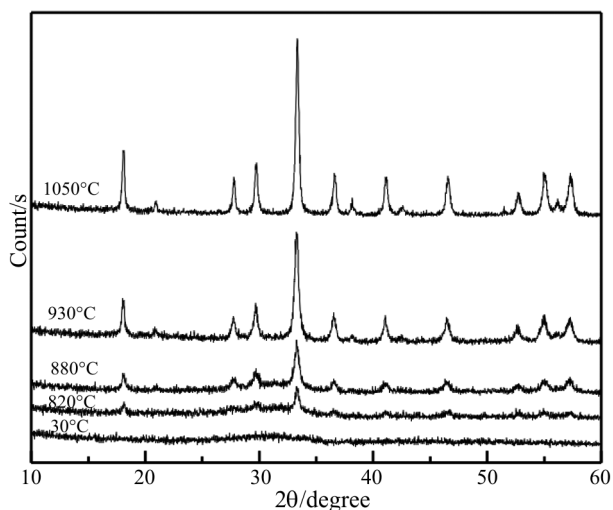


Fig. 2c XRD patterns for the precursor-B heated to different temperatures

was confirmed by the evolution of the pungent and red color nitrogen dioxide gas upon the calcination of the precursor powder up to 600°C. There was a gradual loss of mass of about 3% in the temperature range of 600 to 800°C with no detectable heat effect. There was a little reduction in the intensities of the absorption peaks in the FTIR spectra indicating loss of trace amount of left over volatiles. The precursor remained X-ray amorphous till 820°C. There was a sharp exotherm in the temperature ranges of 850 to 950°C followed by a small broad peak in the range of 950 to 1050°C. There was a very little loss in mass at these stages. This indicated the chemical composition of the precursor before and after the exotherms was the same. The FTIR spectra of the sample heated to 880°C did not exhibit any absorption characteristic of YAG while that heated to 930°C developed bands with weak absorption peaks at 790, 720, 690, 570 cm^{-1} characteristic of lattice modes of vibration in crystalline YAG. The XRD profile also exhibited formation of crystalline cubic YAG at 930°C. The point to be noted is that the crystallization is a sharp exothermic process as there was no loss of mass involved at this stage. The FTIR and XRD patterns of sample heated to 1050°C remained the same but became more intense and sharp indicative of increased degree of crystallinity. This was confirmed by the increase in the average crystallite size values obtained by line broadening method. The average crystallite size values for the precursor heated to 880 and 930°C were exactly the same (~ 280 Å) while that for the precursor heated to 1050°C were 350 Å. This observation showed that in the temperature range of 880 to 930°C only the progress of crystallization from amorphous precursor took place while further growth of crystallites occurred in the range of 950 to 1050°C. As there was no YAP phase found during formation of YAG at 930°C in this precursor and the crystallite size increased in the range of 950 to 1050°C, the small and broad exothermic peak around 1000°C could be attributed to growth of crystallites. Thus well-crystallized YAG formed from this precursor at 1050°C. The point to be noted here is crystalline YAG formed directly from amorphous oxide compound of the same chemical composition without any detectable YAP phase. Eventhough crystallization of YAG phase occurred from amorphous precursor intermediates in the range of 850 to 1050°C for both precursors-A and -B, their chemical composition and mechanism of crystallization differed. Thus the presence of fuel modified the reaction path resulting in different composition for the precursor and hence its decomposition behavior.

The FTIR spectra of the precursor heated up to 1050°C exhibited a broad absorption band in the range

of 3000 to 3700 cm^{-1} with reduced intensity, as compared with samples obtained from precursor-A. It is obvious that the amount of moisture present in samples reduced with increasing temperature of heating. Lesser tendency to pick up moisture by these samples could be attributed to the lesser specific surface area of these powders formed by simple decomposition of nitrates. Still some amount of water is present in all samples due to the absorption-taking place during their preparation as discussed for precursor-A.

Precursor from nitrate-glycine reaction with sub-stoichiometric amount of fuel (precursor-C)

TG-DTA, FTIR and XRD patterns of the precursor-C (glycine/nitrate ratio $\sim 2/9$) are shown in Fig. 3a-c. As powders formed by reactions with fuel to oxidizer ratio higher than 2/9 were black, due to carbon contamination, this composition was studied. This precursor was white in color. It exhibited an endotherm in the temperature range of 30 to 300°C accompanied by a mass loss of $\sim 5\%$, attributed to the dehydration of adsorbed moisture in the powder. There was no heat effect in the temperature range of 300 to 800°C indicating the absence of carbonaceous contaminant. There were two exotherms (one sharp and another shallow) in the temperature range of 850 to 950 and 950 to 1050°C accompanied by a total mass loss of about 6%. The FTIR spectra of the precursor exhibited absorption peaks at 2350 cm^{-1} characteristic of entrapped carbon dioxide and at 1540, 1380, 750 cm^{-1} characteristic of carbonate. The intensity of the peaks corresponding to carbonate and carbon dioxide were lesser than that observed for the precursor formed from stoichiometric amount of fuel, indicating lesser amount of these constituents in this powder. The broad band observed in the range of 3000 to 3700 cm^{-1} is characteristic of adsorbed water. Even though there was a gradual, small loss in mass and decrease in intensity of peaks in FTIR spectra with increasing temperature in the range of 300 to 880°C, the kinetics of the decomposition of the amorphous compound accompanied by the release of carbon dioxide became enhanced above 880°C. The precursor remained X-ray amorphous up to 880°C.

A comparison of the TG-DTA pattern of this precursor with those for the precursor formed by solution combustion with stoichiometric amount of glycine and simple decomposition of nitrates brings out the advantages in this precursor formed from lean amount of fuel. The absence of heat effects and mass losses in the temperature range of 300 to 880°C in TG-DTA curves for this precursor-C formed with lean amount of fuel showed absence of the carbonaceous contaminant observed in precursor-A and left behind nitrate, hydroxide observed in precursor-B in

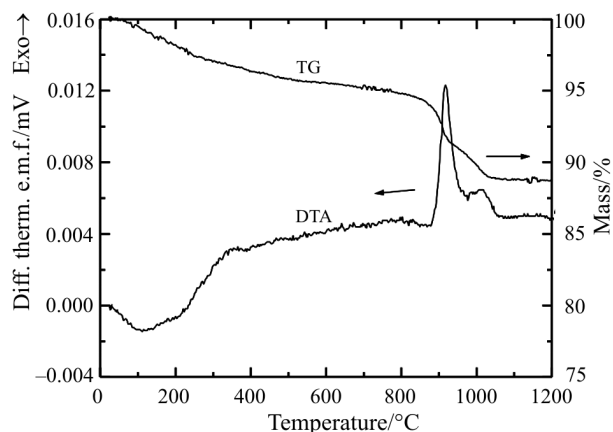


Fig. 3a TG-DTA pattern for the precursor-C

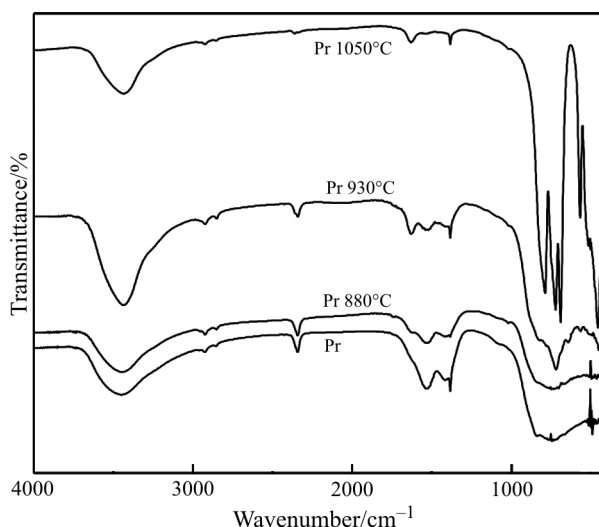


Fig. 3b FTIR spectra of precursor-C heated to different temperatures

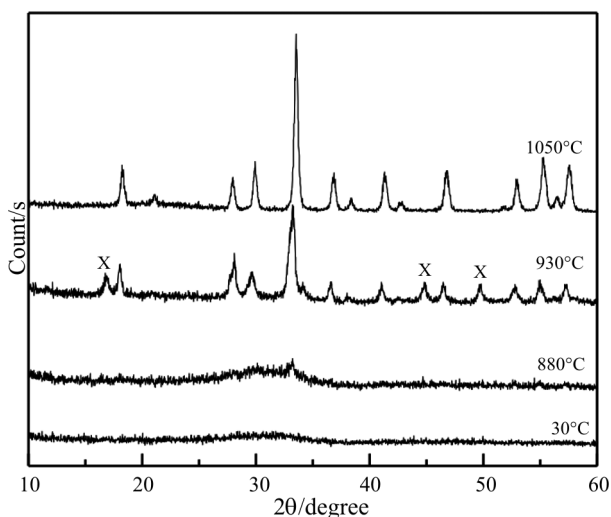


Fig. 3c XRD pattern of the precursor-C heated to different temperatures (peaks marked as 'X' denote YAP structure)

it. Thus the amount of fuel used was just enough to give sufficiently high temperature to decompose completely the nitrates without formation of any carbonaceous material. In the temperature range of 880 to 1050°C, the precursor-A formed by combustion reaction with stoichiometric amount of fuel exhibited a two-stage loss in mass amounting to a total of 12% (attributed to release of entrapped oxides of carbon). The precursor formed by the decomposition of nitrates exhibited one sharp exotherm followed by another small, broad one with no loss of mass (attributed to crystallization from pure amorphous oxide possessing YAG composition and growth of crystallites). The precursor from the present reaction exhibited a two-stage loss in mass (6%) accompanied by a sharp and a small exotherm in the temperature range of 880 to 930 and 950 to 1050°C. Thus the mass loss and heat effects at this stage were in between those found for precursors formed by solution combustion with stoichiometric amount of glycine and simple decomposition of nitrates. This showed that the precursor formed by the solution combustion of nitrates with lean amount of glycine is similar to precursor-A free of the carbonaceous contaminant and contains lesser amount of entrapped oxides of carbon. As the amount of fuel used is less than stoichiometric amount required, part of the precursor is formed by the reaction of direct decomposition of nitrate also. It appears that the temperature of combustion was just enough to get rid of the nitrate and hydroxide which were otherwise observed in precursor-B. The carbon analysis data for the precursor formed in the present study was 2.5 mass percent which was evolved as carbon-dioxide in the temperature range of 880 to 1050°C during crystallization. In case of this precursor also, evolution of carbon dioxide in the temperature range of 880 to 1050°C by evolved gas analysis (EGA) technique has been observed in our previous study [17].

The FTIR spectra of the precursor heated to 930°C exhibited weak intensity absorption peak due to presence of some amount of carbon dioxide and carbonate. The peaks corresponding to crystalline YAG appeared (790, 720, 690, 530 cm^{-1}) indicating setting in of crystallization. The peaks became more intense with increasing calcination temperature to 1050°C indicating improvement in the crystallinity of the powder. The XRD data indicated the precursor heated to 930°C was a cubic YAG with some amount of hexagonal YAP. The precursor heated to 1050°C exhibited FTIR absorption bands at 790, 720, 690, 530 cm^{-1} characteristic of crystalline YAG. The XRD data also confirmed it to be pure cubic YAG (average crystallite size ~ 330 Å). Again, the peak observed at 640 cm^{-1} in the precursor heated to 930°C could be attributed to presence of YAP phase. The point to be

noted here again is that the amorphous precursor at 880°C was not chemically pure YAG compound and it released volatiles during crystallization, similar to precursor-A, but in lesser amount. The average crystallite size values in the temperature range of 880 to 930°C for precursors-A and -C could not be calculated due to overlapping of both YAP and YAG peaks increasing the broadening.

The FTIR spectra of the precursor heated to varying temperatures up to 1050°C exhibited a broad absorption band in the range of 3000 to 3700 cm^{-1} attributed to the presence of adsorbed water in all of them as seen in case of precursor-A.

The crystallization of pure YAG phase in all these precursors at a temperature less than 1100°C established the presence of required amount of compositional homogeneity of metal atoms in the precursor intermediates.

Conclusions

The nitrate–glycine reaction yielded an amorphous precursor. The amorphous precursor contained a carbonaceous contaminant and entrapped oxides of carbon. Upon subsequent heat treatment, it exhibited volatile loss in stages due to dehydration, carbon burning, loss of oxides of carbon and crystallization. Loss of carbon dioxide during crystallization is an important observation in this study. The reaction of simple decomposition of nitrates yielded an amorphous precursor containing nitrate. Upon further heat treatment, it evolved volatile gases in stages due to dehydration and de-nitration forming into an amorphous oxide. Crystalline YAG phase formed directly from the amorphous oxide without loss of any volatile. The precursor from the reaction with sub-stoichiometric amount of fuel contained lesser amount of trapped oxides of carbon and was free of carbonaceous contaminant, nitrate and hydroxide. This study establishes that metal nitrate–glycine combustion reaction proceeds through formation of an amorphous metal oxide intermediate with entrapped oxides of carbon while simple decomposition reaction of metal nitrates proceeds through an amorphous oxide intermediate to form crystalline YAG.

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