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Short communication

Single step synthesis of yttrium aluminum garnet ($Y_3Al_5O_{12}$) nanopowders by mixed fuel solution combustion approach

Kiranmala Laishram *, Rekha Mann, Neelam Malhan

Laser Materials Division, Laser Science and Technology Centre, DRDO, Metcalfe House, Civil Lines, Delhi 110054, India

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Abstract

A single step synthesis of single-phase $Y_3Al_5O_{12}$ (YAG) nanopowders via solution combustion using a fuel mixture (urea + glycine) approach, without high temperature calcinations, is being reported for the first time. Solution combustion was carried out in furnace pre-heated at 700 °C. The use of individual fuels did not lead to the formation of YAG directly from the combustion reaction. FTIR of combusted product showed peaks characteristic of YAG in case of mixed fuel. TGA revealed negligible weight loss indicating that reaction mixture containing the stoichiometric ratio of metal nitrates, urea and glycine triggered a vigorous combustion reaction forming single-phase nanocrystalline YAG. X-ray diffraction of combusted powder confirmed formation of phase pure YAG. Nanometric particles with size range from 40 nm to 60 nm were obtained with uniform morphology by TEM.

Keywords: Solution combustion; Mixed fuel; Single step synthesis; YAG nanopowder

1. Introduction

YAG is a very useful window material that can be used for both UV and IR optics. As YAG is not birefringent it has very high optical homogeneity. It has excellent thermal and opto-mechanical properties and very high thermal conductivity [1]. Moreover it is extremely hard and durable. It is particularly useful for high temperature and high energy applications.

YAG when doped with different rare earth elements has many medical as well as military applications. Er doped YAG laser has very important clinical application in periodontology [2] and Nd doped YAG laser have shown its applications in dental clinics [3]. Rare earth ion doped $Y_3Al_5O_{12}$ nanopowders are very important materials because of their solid state laser applications, luminescence systems, fibre-optic telecommunication systems and as window materials [4–6]. Various researchers have been synthesizing nano sized YAG powders using different techniques such as, co-precipitation [7], freeze drying [8], solvothermal process [9] sol-gel method [10] to name a few. But all these methods require high temperature calcinations.

Solution combustion (SC) is a newly evolved technique for synthesizing oxide nanopowders in which a solution containing metal nitrates with a fuel is allowed to undergo a rapid combustion [11–13]. Fuels can be selected based on their reactive groups such as amino, hydroxyl or carboxyl group. The reaction between these reactive groups and the decomposition products, containing oxygen, initiates a self-sustaining high temperature rapid interaction. Since the initial reaction medium is an aqueous solution it allows molecular level intermixing, leading to the desired composition on nano level in the combusted oxide powder. The high combustion temperature not only ensures high phase purity and crystallinity in case of multi-component systems but also ends the need of high temperature calcinations to form oxide products which are mandatory in case of other techniques mentioned above [14]. Further, because there is no room for particle size growth due to the very short process duration, at the same time rapid evolution of large volume of gases, the process always gives very fine nano-sized powders [15]. Since the concept of fuel mixture approach was published in 2004 [16], many researchers have successfully exploited the advantages of SC using fuel mixtures for the synthesis of single/multicomponent oxide nanoparticles [11,13,17,18].

Though direct synthesis of YAG has been reported by inductively coupled R–F plasma system, only ~62% of the

* Corresponding author. Tel.: +91 11 23907513.
E-mail address: kiranmala@lastec.drdo.in (K. Laishram).

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product is YAG with contamination of other phases [19]. For the first time we are reporting, the direct synthesis of phase pure YAG without high temperature calcination using a fuel mixture of urea and glycine in stoichiometric ratio where ratio of oxidizing valency to reducing valency is equal to unity in accordance with the equivalence theory [20]. The concept of using this fuel mixture comes from the individual reactivity of aluminum nitrate and yttrium nitrate with respect to urea and glycine [16,21]. In this work the formation of single phase YAG was achieved because of the strong exothermic self-propagating redox reaction between the metal nitrates and the fuel mixture. The combustion reaction was initiated by rapidly heating the homogeneous solution in a furnace preheated at 700 °C. Combustion product was found to be phase pure YAG and additional annealing at higher temperature was no longer required.

2. Experimental

Yttrium nitrate, $Y(NO_3)_3.6H_2O$ (99.9%, Alfa Aesar), Aluminum nitrate, $Al(NO_3)_3{\cdot}9H_2O$ (98–102%, Alfa Aesar), glycine (99%, Sigma), and urea (99–100.5%, Merck) were used as the starting materials. The metal nitrates were taken in the molar ratio of Y^{3+} to Al^{3+} as 3:5. Three routes using different types of fuels were carried out (Fig. 1).

Route 1: A total metal nitrate to glycine in the stoichiometric ratio of 1:1.666 was taken. The weighed chemicals were dissolved in deionized water to make a sol. This mixture was warmed at ∼65 °C to dissolve all the contents and to get a clear transparent sol. This sol was transferred into an alumina crucible and treated for 10 min in a furnace (Make Nebertherm, Model LH 60/13) preheated at 700 °C. Brown flaky powders were obtained on combustion.

Route 2: A similar process was carried out by taking metal nitrates and urea in the stoichiometric ratio of 1:2.5. When the sol was treated for 10 min in a furnace preheated at 700 °C a white porous powder was obtained.

Route 3: Again a similar process was carried out by taking molar ratio of urea to Al^{3+} as 2.5:1 and glycine to Y^{3+} as 1.666:1 and treated for 10 min in a preheated furnace at 700 °C. Very fine white powder was obtained.

The combusted powders were characterized by Thermo Gravimetric Analysis (TGA) in air at the heating rate of 10 °C/min from room temperature to 1000 °C, on Perkin Elmer Diamond Simultaneous TGA/DTA. Fourier transform infra-red spectroscopy (FTIR) of powders was carried out by Bruker, Vector 22 Spectrophotometer. Evolution of the crystalline phases was monitored by X-ray diffraction (XRD) on X'PERT PRO PANalytical PW 3050/60 standard resolution Goniometer, 2θ range from 15° to 75°. The crystallite size was determined by using Scherrer's equation [22]:

$$t = \frac{0.9\lambda}{(\beta^2_{\text{sample}} - \beta^2_{\text{inst}})^{1/2} \cos\ \theta}$$

where t is the crystallite diameter, $\lambda = 1.54056$ Å, θ is the diffraction angle, β_{sample} is the FWHM of the diffraction peak and β_{inst} is characteristic of the instrument. Transmission electron microscopy (TEM) was done on FEI Philips Morgagni-268 by preparing samples on copper grids.

3. Results and discussion

The TGA (Fig. 2) of the powders using mixed fuel showed negligible weight loss of only ∼3.7% which indicates that the combustion between the oxidizer and reducer is so exothermic that almost all the organic contents got converted into H_2O and CO_2. The result suggests that using this mixed fuel approach the powder obtained is almost free from organic residues. Further evolution of such a huge amount of gases led to the formation of highly porous and fine powder during the combustion process as observed by TEM.

The FTIR (Fig. 3) of the furnace combusted powder of Route 1 gave slightly broad bands at 1530 cm^{-1} and 1411 cm^{-1} that may be assigned to carbonates [23] which remained after the combustion. This strongly indicates that glycine alone is not acting as a good fuel for combustion. Further broad bands in the region of 850–450 cm^{-1} suggest incomplete formation of Y–O

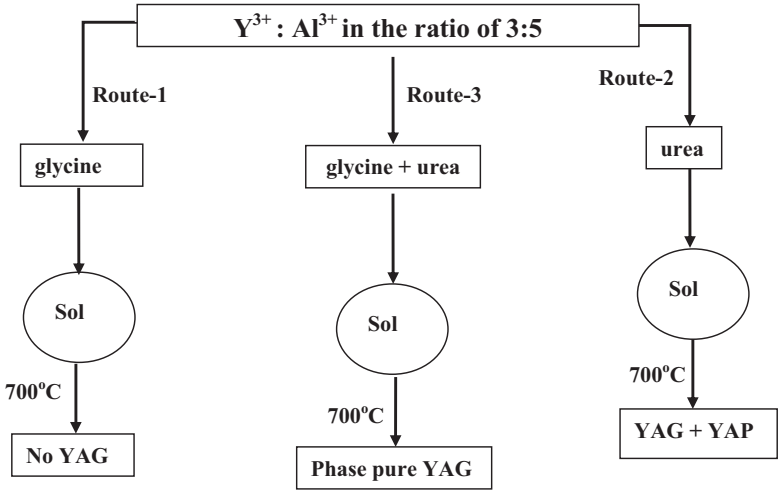

Fig. 1. Schematic representation of synthesis using different fuels.

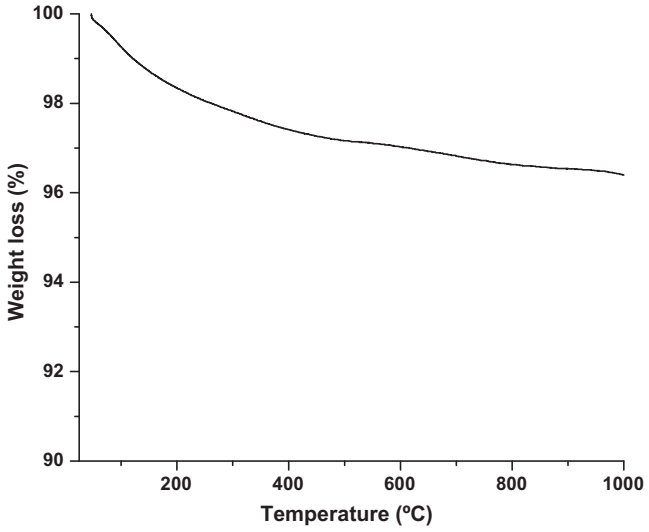

Fig. 2. TGA of furnace combusted powder of Route-3.

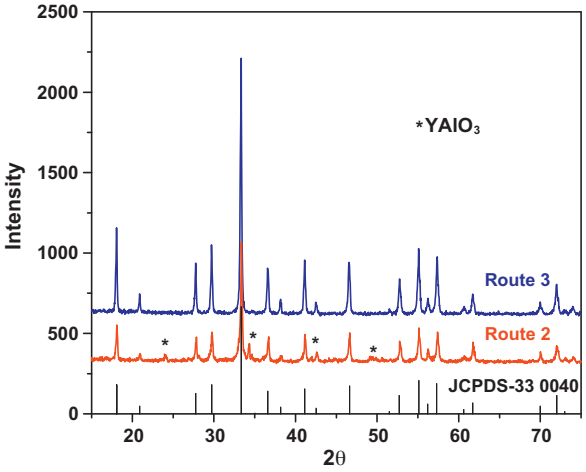

Fig. 4. Depiction of phase evolution by XRD.

and Al–O bonds in YAG. But in case of the FTIR of Routes 2 and 3 combusted powders, peaks at 1530 cm^{-1} and 1411 cm^{-1} have almost gone and the broad band at 850–450 cm^{-1} has been replaced by several well defined peaks at 790, 722, 691, 568, 512, 463 and 426 cm^{-1} which are characteristic of Y–O and Al–O stretching frequencies [23,24]. It indicates that both urea and the mixed fuel are very good fuels for combustion. But for confirming complete crystallization of YAG the combusted powders were monitored by XRD.

XRD (Fig. 4) of Route 1 combusted powder shows no well defined peaks showing amorphous nature of the powder. This result is consistent with the FTIR results confirming that glycine is not a very good fuel for the direct synthesis of YAG, because the heat evolved during the exothermic reaction was not enough for the crystallization of YAG. But in case of Route 2 the combusted powder shows sharp and well defined peaks corresponding to YAG (JCPDS-33 0040) with additional peaks corresponding to yttrium aluminum pervoskite (YAP, $YAlO_3$). This implies that some metal nitrates could not be completely converted to YAG. But in case of Route 3 combusted powder, only characteristic peaks of YAG were detected by XRD. The use of fuel mixture selected according to the combustion characteristics of glycine with yttrium nitrate and urea with aluminum nitrate played its role in contributing the sufficient energy during combustion for the complete crystallization of YAG. Crystallite size as calculated by Scherrer's equation was 30 nm.

The morphology of particles as observed by TEM was found to be mono disperse and uniform with size range of 40–60 nm (Fig. 5).

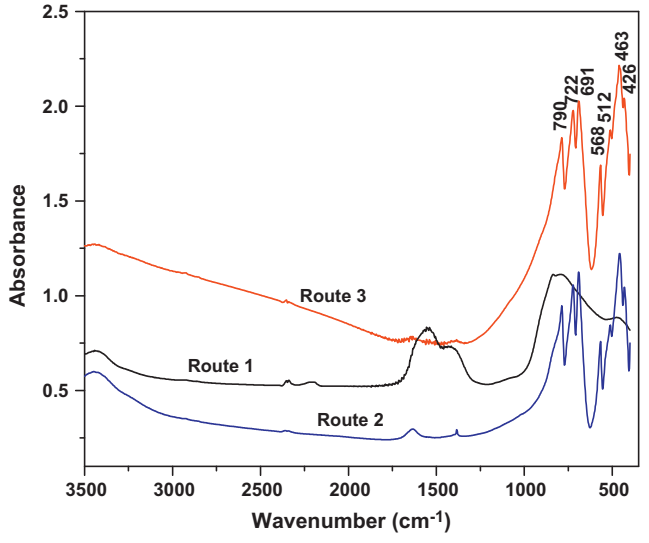

Fig. 3. FTIR of combusted powders.

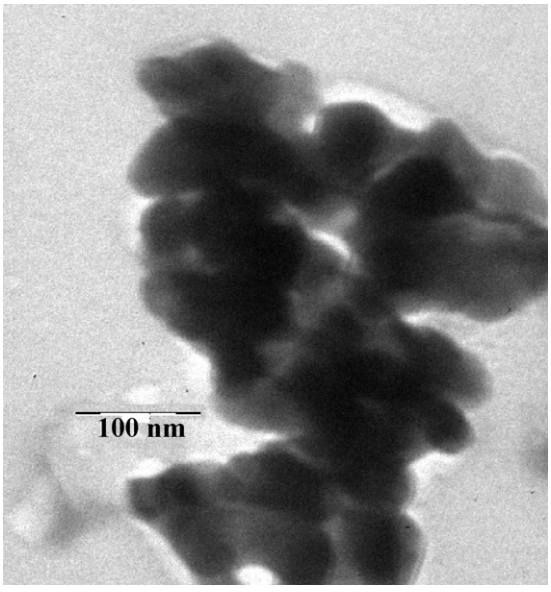

Fig. 5. TEM of YAG obtained from Route-3.

4. Conclusions

An efficient route for the synthesis of phase pure YAG in a single step was achieved by solution combustion technique. By using the mixture of two fuels urea and glycine in their stoichiometric ratios with respect to Al^{3+} and Y^{3+}, single phase YAG was formed directly from the combustion process, without any further calcination. Phase pure, fine particles in size range 40–60 nm obtained. The process is fast and easily scalable.

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