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Energy-efficient green synthesis of Nd:Y_2O_3 nanopowder by microwave gel combustion

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Abstract A novel method for the synthesis of nanocrystalline neodymium-doped yttria (Nd:Y_2O_3) by gel combustion in microwave without long period of calcination at high temperature is described. The method leads to rapid formation of phase pure product with saving of time and energy. Gels were prepared by selecting citrate to nitrate (C/N) ratios of 0.5:1 & 1:1 followed by combustion in microwave for drying of gel leading to precursor formation. Thermogravimetric-differential thermal analysis (TG-DTA) of precursor with (C/N) ratios of 1:1 exhibited a total loss in weight of about 31.7% up to 1300 °C and did not show M–O bonds characteristic of yttria by FTIR indicating requirement of calcination at high temperature. Crystallization to phase pure yttria took place only on thermal treatment at 1000 °C for 4 h in oxygen atmosphere confirmed by XRD with particle size 40 nm. While the microwave combusted precursor with C/N ratio of 0.5:1 exhibited a weight loss of only 4.7% up to 1300 °C and showed M–O bonds characteristic of yttria in FTIR spectrum without calcinations at higher temperature. This microwave combustion precursor with C/N ratio of 0.5:1 was found to be crystalline phase pure yttria by X-ray diffraction (XRD) with primary particle size 28 nm by Scherrer's equation and 30–50 nm of uniform morphology by transmission electron microscopy (TEM). In the present work the ratio of citric acid to nitrates is playing a crucial role in terms of saving time and energy involved in calcinations of microwave combusted precursor for the composition with higher citrate content.

Introduction

Y_2O_3 is an important material used in advanced ceramics as a laser host material, as well as phosphors and selective catalysts. Nd:Y_2O_3 is a promising laser material. A number of methods explored to synthesize Y_2O_3 nanopowders are coprecipitation [1], hydrothermal [2], emulsion precipitation [3], electro spray pyrolysis [4], sol–gel [5] and combustion [6–8]. Desirable powder characteristics for advanced ceramics are fine mono dispersed particles with size less than 100 nm of high phase purity with spherical or equiaxial shape [9].

Microwave heating is being increasingly used to prepare high purity nano particles [10]. Traditional methods take long processing time to synthesize such materials. On the other hand microwave heating is efficient, economical and synthesis can be scaled up from lab scale to industrial scale efficiently [11]. The advantage of using a microwave is that the energy interacts at molecular level as compared to conventional heat treatment which just applies heat to the whole system. Earlier reports on microwave assisted synthesis of Y_2O_3 [12] and YAG (Yttrium Aluminium Garnet) [13] nanoparticles led to precursor formation in microwave which required calcination at higher temperatures for formation of phase pure products. But in the present work, synthesis of phase pure yttria is described during gel combustion in microwave itself without calcinations at higher temperature.

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In the present work citrate nitrate gel combustion synthesis of Nd:Y_2O_3 nanoparticles in domestic microwave oven having frequency 2.45 GHz, modified for flow of oxygen is described. Amorphous carbon from the decomposition of citric acid provides high microwave susceptibility for the faster formation reaction of product [14].

Experimental

Yttrium nitrate, $Y(NO_3)_3 \cdot 6H_2O$ (99.9% purity Alfa Aesar), neodymium nitrate, Nd $(NO_3)_3 \cdot 6H_2O$ (99.9% purity Alfa Aesar) and citric acid anhydrous (99.5+% purity Alfa Aesar) were used as the starting materials. The metal precursors

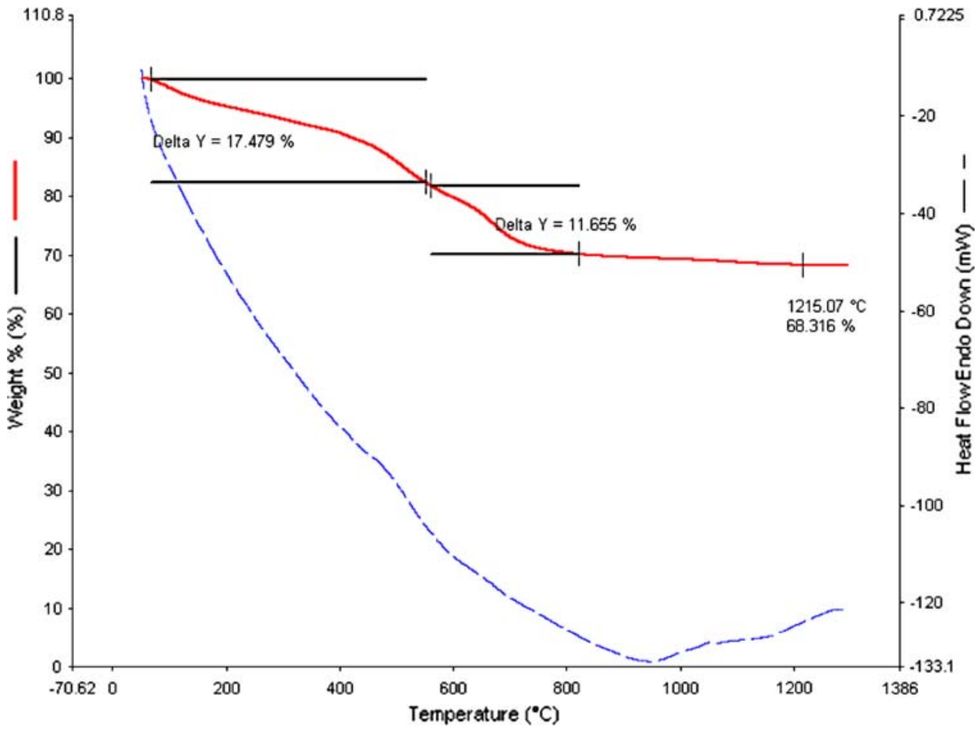


Fig. 1 TG-DTA of C/N 1:1 microwave combusted gel

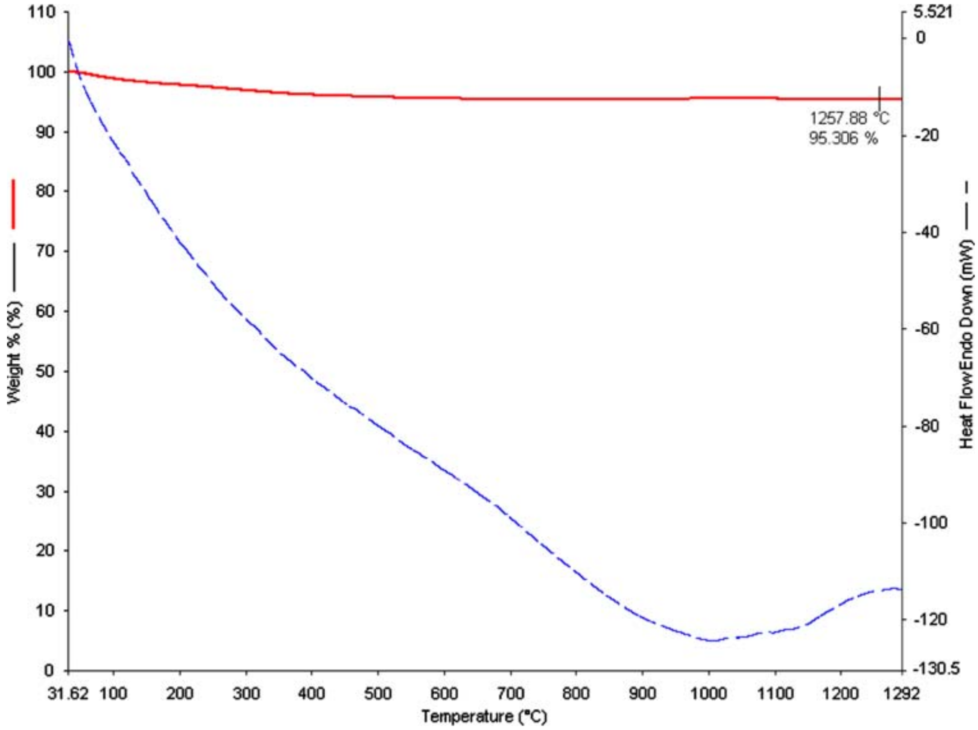


Fig. 2 TG-DTA of C/N 0.5:1 microwave combusted gel

were taken in the molar ratios of $Y_{2.94}Nd_{0.06}$. Citric acid was used as the chelating agent. The total citric acid to metal nitrate (C/N) was taken in the ratios 0.5:1 and 1:1. The citrate nitrate-sol was prepared in high purity water of resistivity >5 MΩ cm. Gelation took place at 80 °C for 16 h. Drying of the gel was carried out in domestic microwave modified for the supply of oxygen. The gel underwent rapid combustion with red glow giving white powder in case of C/N composition 0.5:1 and grey powder in case of C/N composition 1:1. This precursor powder thus obtained was calcined at 1000 °C for 4 h. The crystallization took place at 1000 °C for 4 h with oxygen supply.

TG/DTA of microwave combusted powder was carried out in air at the heating rate of 10 °C/min from room temperature to 1300 °C, on Perkin Elmer Diamond Simultaneous TGA/DTA. FTIR spectra were recorded on FTIR Spectrometer (Bruker, model Vector 22) using KBr pellets. XRD was carried out using Philips X-Ray Diffractometer, PW 3020 in 2θ range from 15 to 80° keeping step size 0.02 for characterization of phase purity, particle size and cell parameters. Nd^{+3} doping was confirmed by EDX of carbon coated compacts of powder sample using scanning electron microscope (ZEISS EVO Series 50). Transmission Electron Microscopy (TEM) was done on (FEI Philips Morgagni 268D, AC Voltage 100 kV and Magnification up to 2,80,000×).

Results and discussion

Thermo gravimetric–differential thermal analysis (TG-DTA) of precursor with (C/N) ratios of 1:1 (Fig. 1) exhibited a total loss in weight of about 31.7% in stages 50–430 °C and 430–750 °C indicating dehydration of absorbed moisture and decomposition of residual organics due to decomposition of nitrates. The microwave combusted precursor with C/N ratio of 0.5:1 (Fig. 2) exhibited a very small total weight loss of 4.7% up to 1300 °C.

From the FTIR spectra of microwave combusted gel precursor (Fig. 3), it is seen that the composition with C/N ratio 1:1 showed peaks at 1530 cm^{-1} and 1384 cm^{-1} due to residual organic in addition to broad band between 600 and 400 cm^{-1} indicating incomplete formation of $Nd{:}Y_2O_3$. However, in the composition with C/N ratio 0.5:1, peaks are observed at 559, 465, 419 cm^{-1} quite consistent with metal

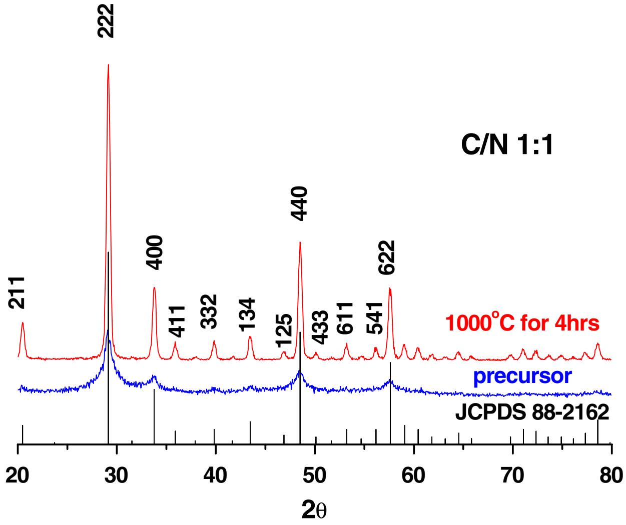


Fig. 4 XRD of composition with C/N 1:1 at different stages

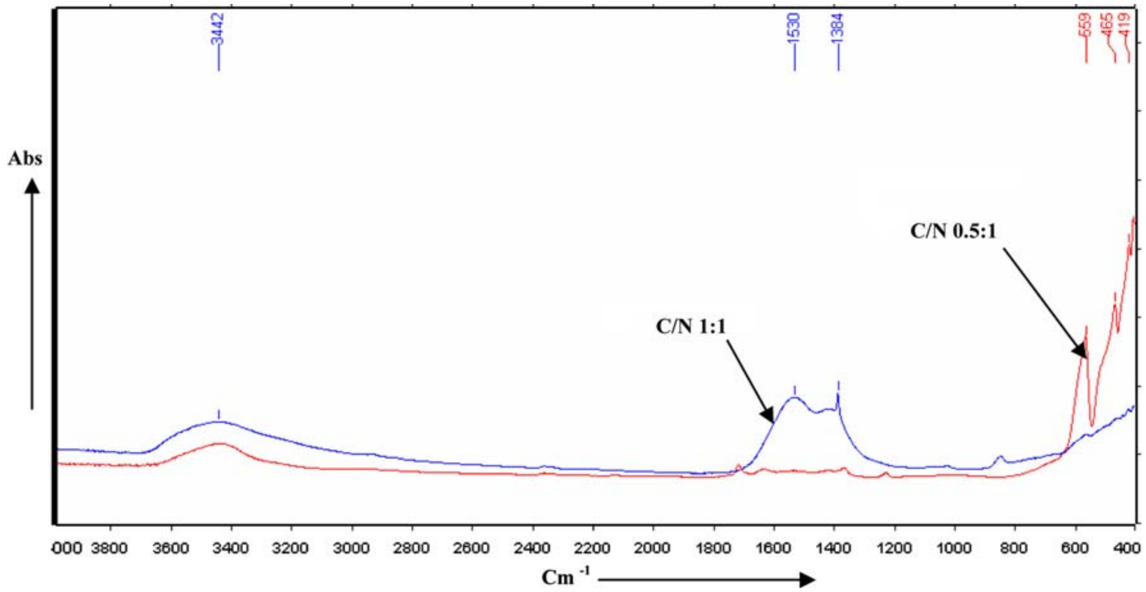


Fig. 3 FTIR of microwave combusted gels

oxygen bond in Y_2O_3 [15, 16]. This indicates formation of Nd:Y_2O_3 by microwave treatment only.

The XRD pattern of microwave combusted gel with C/N ratio 1:1 (Fig. 4) showed amorphous background indicating incomplete crystallization of yttria. On calcination at 1000 °C for 4 h in oxygen atmosphere X-ray diffractogram showed all the peaks consistent with yttria (JCPDS 88-2162). However microwave combusted gel with C/N ratio 0.5:1 (Fig. 5) showed all the peaks corresponding to phase pure yttria indicating complete crystallization of phase pure yttria without calcinations at higher temperature for a long time. Due to lesser amount of organics to be removed in composition with C/N ratio 0.5:1 formation of single-phase cubic crystalline yttria nanopowders is facilitated in microwave itself. TEM images indicated grain growth through calcination at 1000 °C for 4 h in oxygen atmosphere (Fig. 7). Particle size was calculated using Scherrer's equation [17]

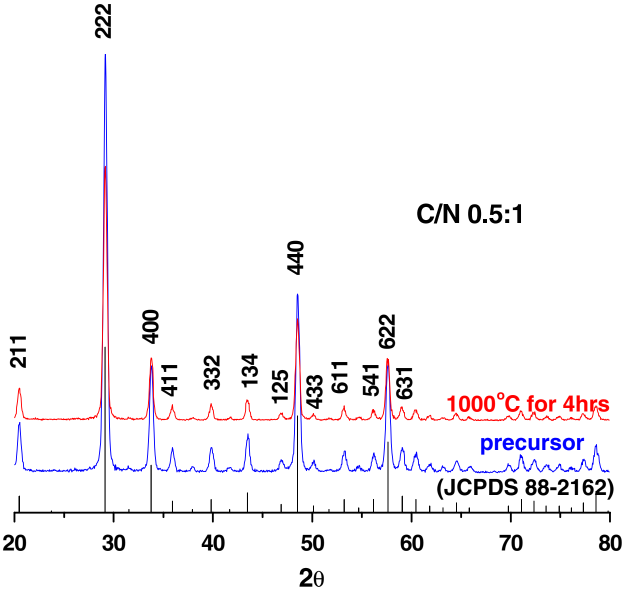


Fig. 5 XRD of composition with C/N 0.5:1 at different stages

$$t = \frac{0.9\,\lambda}{\left(\beta_{\text{sample}}^2 - \beta_{\text{inst}}^2\right)^{1/2}\cos\theta}$$

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. Primary particle size was found to be 28 nm for microwave precursor with C/N ratio of 0.5:1. For both the compositions calcined at 1000 °C for 4 h the primary particle size was found to be 40 nm.

The lattice constant for Nd-doped yttria calculated by least square method was found to be 10.604 Å (for undoped Y_2O_3 $a = 10.60$ Å from JCPDS 88-2162 [18]) indicating substitution of Y^{+3} ions by Nd^{+3} ions. Increase of lattice

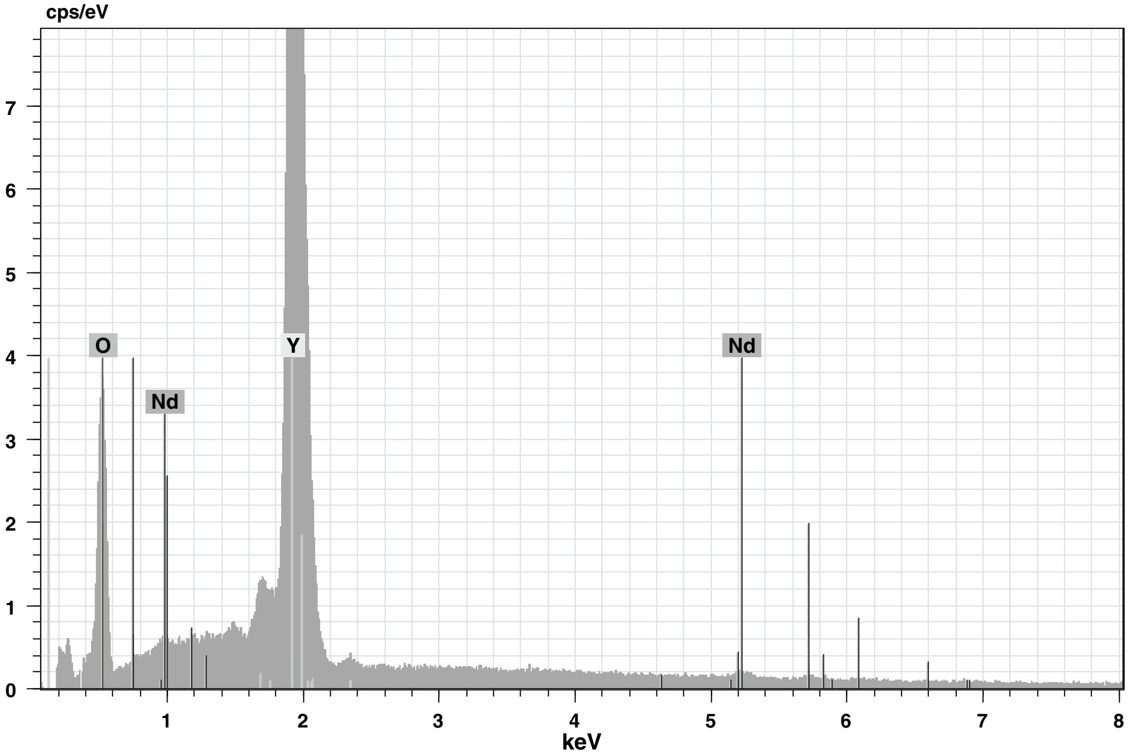
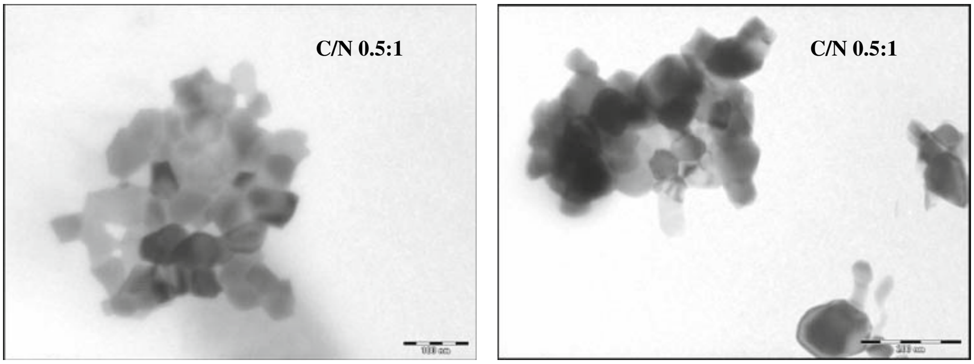


Fig. 6 EDX spectra showing Nd^{+3} ion doping in Y_2O_3

Fig. 7 TEM of C/N 0.5:1 microwave precursor at different stages



Microwave precursor **Calcination at 1000^{0}C for 4 hrs.**

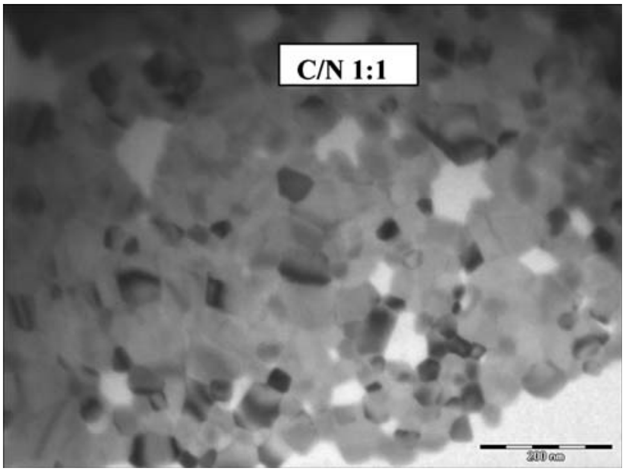


Fig. 8 TEM of C/N 1:1 microwave combusted gel after calcinations at 1000 °C for 4 h

constant is due to introduction of neodymium ion with larger atomic radius ($R_{Nd} = 1.821$ Å, $R_Y = 1.803$ Å) [19].

Powder EDX spectra (Fig. 6) confirmed the doping of Nd^{3+} ions. Peaks of all constituent elements Y, Nd and O are observed in the EDX spectrum of $Nd{:}Y_2O_3$ nanopowders.

The transmission electron micrograph (TEM) of microwave precursor with C/N ratio of 0.5:1 (Fig. 7) shows that particles are homogeneous with particle size distribution of 30–50 nm. Shape of the particles is mixture of polyhedral and spherical. These nanosized particles are highly sinterable. On calcination at 1000 °C for 4 h grain growth takes place as shown with size distribution of 40–70 nm for both the compositions (Figs. 7, 8).

Conclusions

- Composition with C/N ratio of 0.5:1 underwent rapid and energy-efficient synthesis to $Nd{:}Y_2O_3$ nanoparticles in microwave with supply of oxygen without requirement of calcination at high temperature thus making it a energy-efficient process.
- Homogeneous uniform sized particles of polyhedral and spherical shapes with particle size distribution of 30–50 nm were obtained which showed grain growth on annealing at higher temperature for composition with C/N ratio of 0.5:1.

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