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Microwave assisted combustion synthesis of nanocrystalline yttria and its powder characteristics

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ABSTRACT

Microwave assisted combustion synthesis is used for fast and controlled processing of advanced ceramics. Single phase and sinter active nanocrystalline cubic yttria powders were successfully synthesized by microwave assisted combustion using the organic fuels urea, citric acid and glycine as reducing agents. The precursor powders were investigated by thermogravimetry (TG) and differential scanning colorimetry (DSC) analyses. The as-prepared precursors and the resulting oxide powders calcined at 1100 °C in oxygen atmosphere were characterized for their structure, particle size and morphology. The thermal analyses (TG/DSC), X-ray diffraction (XRD) and Fourier transform infra red (FT-IR) results demonstrate the effectiveness of the microwave assisted combustion synthesis. The scanning electron microscopy (SEM) observations show the different morphologies of as-prepared powders and transmission electron microscopy (TEM) shows the particle sizes in the range of 30–100 nm for calcined powders for different fuels. The results confirm that the homogeneous, nano scale yttria powders derived by microwave assisted combustion have high crystalline quality and the morphology of the as-prepared precursor powders depends on the nature of organic fuel used.

1. Introduction

Yttria is a promising ceramic material, has attractive properties like high chemical and thermal stability, and optical transparency over a wide wavelength region from violet to infrared light. It finds applications as high temperature chemical-resistant substrates, crucibles for melting reactive metals and nozzles for jet-casting molten, rare-earth-iron magnetic alloys [1–4]. As an optical ceramic, it transmits well in the infrared range of 1 to 8 µm wavelength. Such a high infrared transmission together with good resistance to erosion and thermal shock make the material ideal for developing protection missile domes as well as infrared sensors and lasers. It is already a known refractory material, because of its high melting point (2683 K) and low thermal expansion coefficient (4×10^{-7} K^{-1}) [4–8]. There are several methods reported for the processing of yttria ceramic powders. They include precipitation, hydrothermal, co-precipitation, glycothermal treatment, electro-spray-pyrolysis and sol-gel processing [2,9–15]. Each one of these methods has their merits and demerits. Combustion synthesis is one of the simple techniques and a less time consuming process well recognized for preparing various oxide materials [7,16,17]. But in the normal combustion synthesis, the heat is generated by external heating elements and the heat energy is transferred through conduction mechanism to the material surfaces to bulk. In this study, we have utilized microwaves for the combustion synthesis yttria nanopowders. Microwave assisted combustion synthesis of ceramic oxides is fundamentally different from the conventional combustion in which heat is generated within the reactants material itself by absorbing the microwaves in the microwave oven. Microwaves interact with the matter from bulk to the surface and the heat generation is governed by the rapid kinetics of the dipole moments of the molecules. It is better known for its voluminous heating within few minutes of the reaction and advantages such as early phase formation, fine particle size and low temperature densification are seen in many ceramic systems. It is also possible to achieve reactive fine powders within a short duration of the reaction. The application of microwave heating irradiation in the preparation of nanocrystalline advanced ceramics can be seen in many recent works [18–25].

2. Experimental

Microwave induced combustion synthesis involves the dissolution of metal (yttrium) nitrate as an oxidizer and fuel (urea, citric acid and glycine, respectively) as a reducer in water, and then heating the resulting solution in a microwave oven. The starting solution

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containing yttrium nitrate and fuel (urea or citric acid or glycine) was prepared based on the total oxidizing and reducing valencies of the oxidizer and reducer using the concepts of propellant chemistry [17,26]. The amount of fuel needed was calculated and taken to prepare 1 mol of yttrium oxide by combustion reaction. The equivalence ratio, i.e., the ratio of the oxidizing valency and reducing valency (O/F) was maintained at unity. The valency of nitrogen was not considered because of its conversion to molecular nitrogen (N_2) during combustion. Accordingly, in a typical experiment, the molar ratio of yttrium nitrate and urea, citric acid and glycine was maintained at 1:5, 1:1.667 and 1:3.33, respectively. The desired amounts of yttrium nitrate and the fuel were dissolved in a required amount of doubled distilled water in order to form a clear and homogeneous solution. The solution was thoroughly stirred to ensure a molecular level mixing. The yttrium nitrate and the fuel mixture was transferred to a alumina crucible (250 ml) and subsequently introduced into a microwave oven and applied microwave field of 2.45 GHz to undergo decomposition. The solution reaches the point of spontaneous combustion few two minutes, and the precursor starts burn. The combustion completes in three minutes and a foamy porous precursor powder was left out as residue. The foamy nature of the powders is varied in its morphology with respect to the fuels used. The foamy porous precursor was collected and crushed for further processing. During combustion, the gaseous products released were N_2, CO_2 and H_2O as water vapour. We assume that the brown fumes (NO_2) observed during combustion was released in the form of above gaseous products. The theoretical reaction of the assumed complete combustion for different fuels can be written as follows:

$$2Y(NO_3)_3 + 5NH_2CONH_2 \rightarrow Y_2O_3 + 5CO_2 + 10H_2O + 8N_2(\text{urea as a fuel})$$

$$6Y(NO_3)_3 + 5CH_2COOH\ COH\ COOH\ CH_2COOH \rightarrow 3Y_2O_3 + 30CO_2 + 20H_2O + 9N_2(\text{citric acid as a fuel})$$

$$6Y(NO_3)_3 + 10NH_2CH_2COOH \rightarrow 3Y_2O_3 + 20CO_2 + 25H_2O + 14N_2(\text{glycine as a fuel})$$

The as-prepared precursor powders were calcined at 1100 °C for 4 h soaking in oxygen atmosphere to get single phase crystalline yttria powders. This calcination temperature is usually required for obtaining highly sinterable yttria powder [1,4,27]. Also, yttria powders calcined at this temperature show reduced weight loss during sintering. In fact, the calcination of yttria powders at 1100 °C is preferred because it is possible to obtain transparent yttria under vacuum sintering [1,14,18]. The crushed precursor powders corresponding to the fuels urea, citric acid and glycine are designated as U-YO-MW, C-YO-MW and G-YO-MW, respectively and the calcined powders are noted as U-YO-MW-1100, C-YO-MW-1100 and G-YO-MW-1100, respectively.

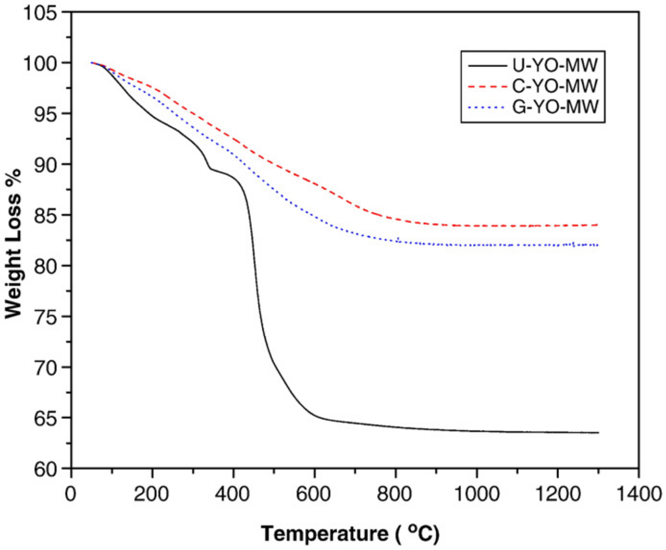

Fig. 1. TGA curves of as-prepared yttria powders.

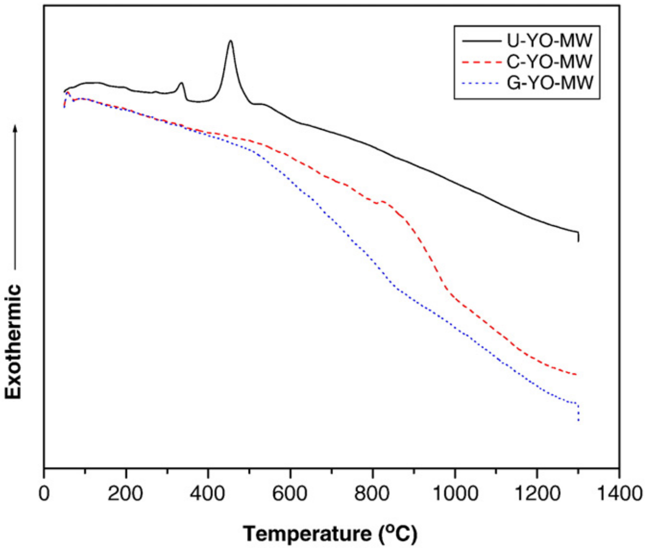

Fig. 2. DSC curves of as-prepared yttria powders.

The as-prepared powders were characterized into thermogravimetry (TG) and differential scanning colorimetry (DSC) analyses using a Netzsch-STA 449C equipped with a mass spectrometer (Netzech-QMS 403C) for the identification of evolving gases. The as-prepared precursors and calcined powders were studied by X-ray diffractometry (XRD) to establish the formation of crystalline phases and to determine the crystalline size of the fine powders. The diffractions were recorded by a Philips X'Pert X-ray diffractometer using CuK_α radiation. The crystallite sizes were calculated from the X-ray broadening technique as per the Scherrer's formula [28]:

$$D = 0.9\lambda / \left(\beta^2_{\text{sample}} - \beta^2_{\text{ref}}\right)^{1/2} \cos\theta$$

Where D is the crystallite size diameter (nm), $\lambda = 1.54$ Å, q is the diffraction angle, β_{sample} is the full width at half maximum (FWHM) of a diffraction peak and β_{ref} corresponds to the instrumental FWHM. The surface area was measured by Brunauer–Emmett–Teller (BET) method in (Micromeritics ASAP 2010) using nitrogen adsorption–desorption isothermic measurements at 77 K for as-prepared and calcined powders. All the samples were degassed at 100 °C before the actual measurements. The Fourier transform infra red spectroscopy (FT-IR) spectra were recorded using Nicolet–Nexus spectrometer with

Table 1
BET-surface area values of as-prepared and calcined (1100 °C) yttria powders

Sample	Specific surface area in m^2/g
U-YO-MW	15.42
C-YO-MW	24.20
G-YO-MW	45.95
U-YO-MW-1100	4.56
C-YO-MW-1100	6.50
G-YO-MW-1100	4.06