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Microwave-flash combustion synthesis of yttria nanopowders

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Single phase yttria nanopowders for transparent ceramics were successfully prepared by using a novel approach called microwave-flash combustion technique. This technique involves the reaction of yttrium nitrate and urea in microwave oven for few minutes. The as-prepared precursor powder was later calcined at 1100 °C for 4h to form cubic crystalline yttria nanopowders. The as-prepared and calcined powders were analysed by such methods as thermogravimetry, Brunauer–Emmett–Teller surface area measurement, X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The results confirmed that the yttria powder synthesized by microwave-flash combustion was homogeneous and the particles size was in the range of 50–120 nm for calcined powders.

Key words: *synthesis; microwave-flash combustion; yttria nanopowders; transparent ceramics*

1. Introduction

Transparent yttria ceramics find applications in IR windows in heat seeking rockets, luminous pipes for high-intensity discharge lamps and as laser host materials [1–3]. Their properties include high thermal conductivity, high thermal stability, low thermal expansion, high melting point, chemical stability and good transparency to infrared radiation [1–5]. In order to fabricate a transparent polycrystalline yttria ceramic by sintering, there are several requirements like fine particle size and its distribution, purity, homogeneity and low agglomeration that the starting powder must meet. The method of processing yttria powder is an important factor to provide uniform and high density ceramics. Several methods have been used to produce ultrafine yttria powders such as precipitation [3], hydrothermal method [6], electro spray pyrolysis [7], sol-gel [5] and combustion [2, 8, 9] methods. However, flash combustion technique is an unconventional technique reported earlier [10] in which heat is gener-

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ated by heating elements. Microwave-assisted process is a novel technique, used for rapid and controlled processing of advanced ceramic materials. Many researchers used microwave-assisted method for different types of ceramic materials [11–17]. In the microwave heating process, heat is generated internally within the material instead of originating from external heating sources and hence is fundamentally different from other heating processes. Microwave-flash combustion technique is the modified combustion technique and is reported for the synthesis of Ni–Zn ferrite nanopowders [18] in which the combustion process takes place by heating the reactant mixture using the absorption of microwaves. This microwave assisted flash-combustion process is simple and inexpensive due to energy savings and shorter processing times. Furthermore, the synthesized powder is generally more homogeneous, and the uniformity and yield are high. The present work reports the synthesis and characterization of yttria nanopowders under microwave-assisted flash combustion technique for transparent ceramics.

2. Experimental

The microwave assisted flash-combustion technique for synthesizing yttria nanopowders involves dissolving yttrium nitrate (oxidizer) and urea (fuel) in water by mixing thoroughly and then heating the solution in a microwave oven. It was calculated that 5 mol of urea was needed to prepare 1 mol of yttria by complete combustion. The oxidizer to fuel ratio (O/F) plays a crucial role in determining the exothermicity of the combustion product. The equivalence ratio, i.e. the ratio of the oxidizing valency to 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. The solution mixture of yttrium nitrate, urea and water were transferred to an alumina crucible and later introduced into a microwave oven followed by the application of microwave field at 2.45 GHz to undergo decomposition. When the solution reaches the point of spontaneous combustion, it starts to burn in solid form at high temperature. After few minutes, the combustion was completed and a foamy porous precursor powder was left out as a residue. The foamy porous precursor was then collected and crushed for further processing. During combustion, the only gaseous products released were N_2, CO_2 and H_2O. The theoretical reaction of the assumed complete combustion can be written as:

$$2Y(NO_3)_3 + 5NH_2CONH_2 \rightarrow Y_2O_3 + 5CO_2 + 10H_2O + 8N_2$$

The as-prepared precursor powder was calcined at 1100 °C for 4 h [4, 5, 10, 19, 20] soaking in oxygen atmosphere to get pure crystalline powder. The as-prepared precursor powder was characterized by thermogravimetry (TG) and differential scanning colorimetry (DSC) techniques using a Netzsch-STA 449C equipped with a mass spectrometer (Netzech-QMS 403C) for the identification of evolving gases. The as-prepared precursor powder and calcined powder were studied by X-ray diffractometry (XRD) to establish the formation of crystalline phases and to determine the crystalline size of fine powders. The diffraction patterns 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 formula [21]:

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

Where D is the crystallite diameter (nm), $\lambda = 1.54$ Å, θ is the diffraction angle, β_{sample} is the full width at half maximum (FWHM) of the diffraction peak and β_{ref} corresponds to the instrumental FWHM. The powder morphology and the particle size of the crystalline powder were studied by using a scanning electron microscope (SEM -JEOL 6460 LV) and a transmission electron microscope (TEM-JEOL JEM 2000 EX), respectively.

3. Results and discussion

The phase formation of as-prepared yttria powder was studied using TG/DSC measurement analysis. Figure 1 shows the results of thermal analysis of the as-prepared precursor yttria powder. The weight loss of about 35% was obtained, which corresponds to the evolution of absorbed moisture (water molecules), burn out of carbon dioxide and excess nitrate gases present in the as-prepared precursor yttria powder.

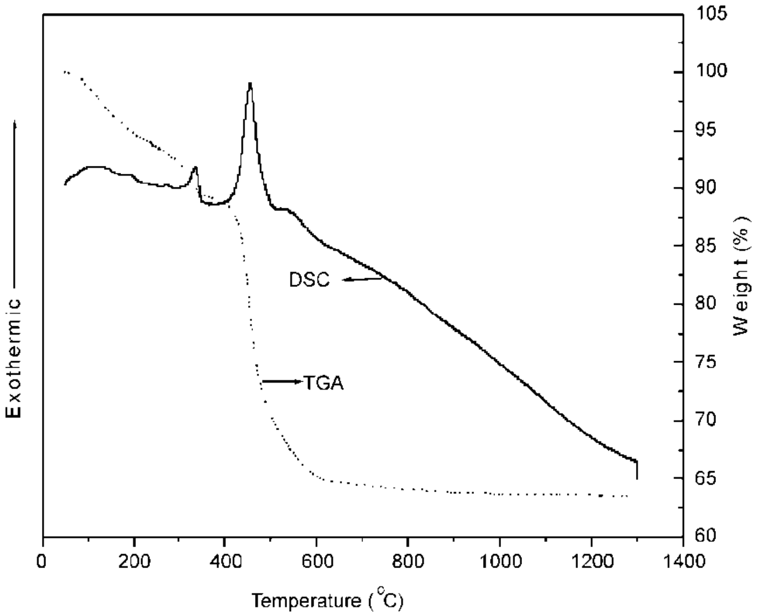

Fig. 1. TGA and DSC curves of yttria precursor powders as-prepared by microwave-flash combustion technique

The DSC curve shows three steps decomposition behaviour of exothermic peaks between 100 and 530 °C. First small broad peak between 100 and 120 °C corresponds to desorption of moisture from precursor powder and the second peak corresponds to removal of water molecules from the hydroxyl group. Third peak corresponds to the evolution of nitrate gases due to the presence of excess nitrate in the precursor powder. There is also a small amount of carbon dioxide gas evolution at this stage.

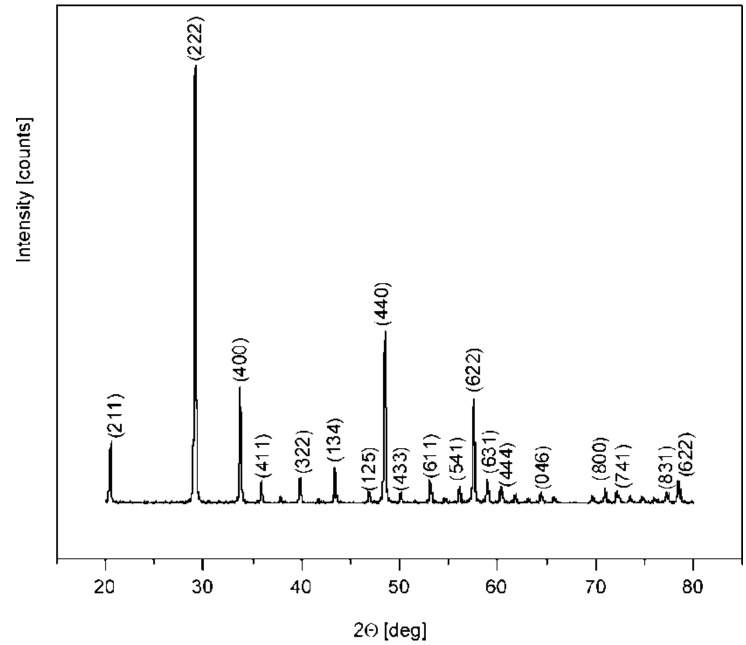

Fig. 2. XRD pattern of yttria powders calcined at 1100 °C

Figure 2 shows the X-ray diffraction pattern of calcined at 1100°C yttria nanopowders prepared by microwave assisted flash combustion technique. The XRD pattern confirms the formation of single-phase cubic crystalline yttria nanopowders. The formation of a single phase is attributed to high in-situ temperature generated during microwave absorbed combustion and rapid cooling. The peaks observed in the XRD pattern for the powder calcined at 1100 °C were found to match well with those reported earlier [8, 9, 22]. The average diameter of the crystallite size was 7 and 90 nm for as-prepared precursor and calcined yttria powders, respectively. The Brunauer –Emmett–Teller (BET) surface area of the as-prepared and calcined powders was 15.42 and 4.56 m^2/g, respectively.

Figure 3 shows the morphologies of the as-prepared precursor foam and powder, respectively. The as-prepared foam (Fig. 3a) is a fluffy foam with porous structure. The crispy foam with pores and voids is due to the evolution of gases during combustion. This porous structure is highly friable and fine particles are easy to obtain by grinding [23]. The crushed precursor powder (Fig. 3b) shows the flaky and thin platelet type of loosely agglomerated particles.

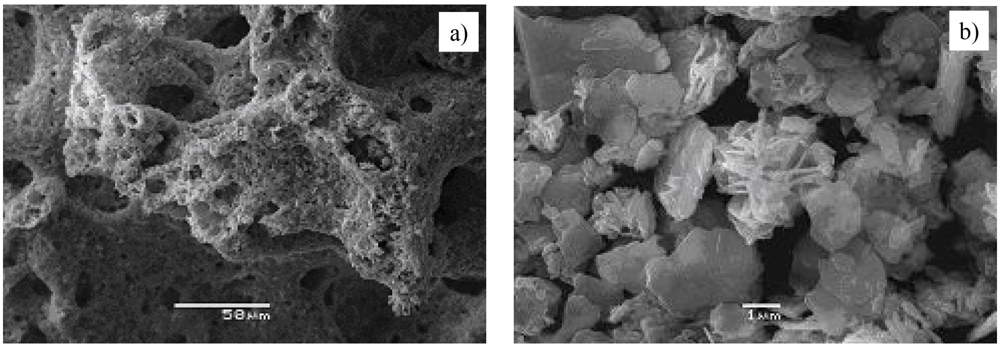

Fig. 3. SEM photographs of as-prepared yttria precursor: a) foam, b) powder

The morphologies of the as-prepared precursor foam and powder depend on the nature and the concentration of organic fuel. During combustion, yttrium nitrate impregnates into the polymeric product and gets ignited. Heat dissipates by the evolution of gaseous products in minimization and thus it leads to a localization of heat due to the polymeric nature of the fuel [24]. After calcination at 1100 °C, flaky agglomerated particles break into smaller pieces of nanometric, non-agglomerated and regular shape particles.

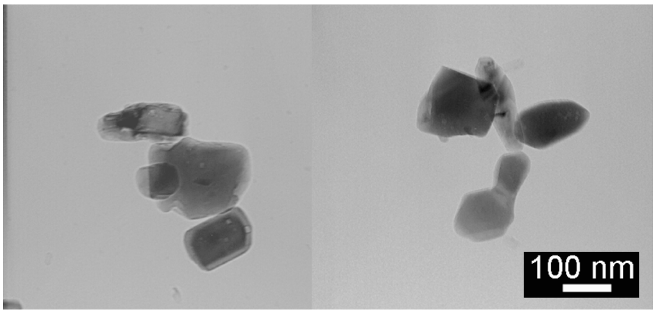

Fig. 4. TEM photograph of yttria powder calcined at 1100°C

The TEM photograph of the yttria powder calcined at 1100 °C for 4h is shown in Fig. 4. The particle sizes were observed to be in the range 50–120 nm. The shape of the particles in the calcined powder was the mixture of rectangular and spherical. This is in fair agreement with the crystallite size measured by XRD broadened peak. The use of these nanosized and more homogeneous calcined powder leads to low sintering temperature, fast densification, and maximum density with improved microstructure which are essential for the fabrication of transparent yttria ceramics.

4. Conclusions

Yttria nanopowders were synthesized by microwave assisted flash combustion technique using yttrium nitrate and urea. The synthesized powders reveal the formation of single-phase cubic nanocrystalline yttria. For powders calcined at 1100 °C for 4 h, the particle sizes were in the range 50–120 nm. Homogeneous yttria powders with nanodimensions are suitable for the fabrication of transparent ceramics, which finds applications in the fields of optics and opto-electronics.

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