Microwave-assisted combustion synthesis of nanocrystalline MgAl$_2$O$_4$ spinel powder

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Abstract

A stoichiometric MgAl$_2$O$_4$ spinel powder was synthesized by a microwave-assisted combustion synthesis (MWCS) route. For the purpose of comparison, another stoichiometric MgAl$_2$O$_4$ spinel powder was also prepared following the conventional combustion synthesis (CCS) method. The batch size had a strong influence on the specific surface area of the material, which in turn is highly dependent on the preparation method adopted. The surface areas of these synthesized powders were found to decrease from 36.78 to 0.1 m^2/g for MWCS and 126 to 8.06 m^2/g for CCS samples, respectively, when the batch size was increased from 2 to 100 g. This could be attributed to sintering of the samples due to high adiabatic temperature generated as a result of increased heat accumulation with bigger batch quantities. Between the two powders synthesized by the two different routes, the powders obtained by MWCS and CCS routes were found to contain grains/crystals in range of 20–50 and 100–250 nm size, respectively. The thermogravimetry/differential thermal analysis (TG-DTA) and X-ray diffraction (XRD) studies reveal that microwave-assisted combustion synthesis route yields materials with higher degree of compositional stability and phase purity as compared to the conventional combustion synthesis method.
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1. Introduction

Magnesium aluminate spinel (MgAl$_2$O$_4$) has received a great deal of attention as a technologically important material on account of its attractive properties such as high melting point, high mechanical strength at elevated temperatures, high chemical inertness, and good thermal shock resistance [1–3]. Because of these properties, the MgAl$_2$O$_4$ spinel has been extensively used for various purposes such as refractory material, humidity sensor [4], and so on. Recently, the MgAl$_2$O$_4$ spinel has also been employed as an excellent transparent ceramic material for high-temperature arc-enclosing envelopes and alkali-metal vapor discharge devices [5]. However, making such a high-purity transparent spinel body from a powder obtained by conventional

solid-state reaction routes is very difficult, since this technique requires repeated grinding and calcination steps to get the desired properties, which invariably contaminate the powders. Though, methods such as hydrothermal synthesis, plasma spray decomposition of oxides, sol–gel, etc., could be used to produce high-purity oxide powders, however these techniques have not received much commercial importance because of the use of expensive raw materials and many processing steps [6–9]. Recently, combustion synthesis has emerged as an attractive technique for the production of homogeneous, high-purity, and crystalline oxide powders at significantly lower temperatures than the conventional synthesis methods requiring shorter time periods and using less amount of external energy as well [10–12]. Further, it has also been observed that the combustion-synthesized powders retain their nanocrystalline structure even after sintering, which is extremely useful in making superplastic deformation materials [13].

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Of late, it has been realized that microwave energy can be used to synthesize ceramic powders where reactions of component oxides at elevated temperatures are involved [14–17]. Recently, microwave-assisted combustion synthesis technique has been effectively used to produce powders in shorter times in comparison with the conventional synthesis carried out in an electric furnace at 500 °C [14]. Microwave synthesis of materials is fundamentally different from the conventional synthesis in terms of its heating mechanism. In a microwave oven, heat is generated within the sample volume itself by the interaction of microwaves with the material [15–17]. Microwave energy heats the material on a molecular level, which leads to uniform heating, whereas, conventional heating systems heat the material from outer surface to interior, which results into steep thermal gradients. In fact, microwave energy has became an essential tool in the processing of some of the technologically important products such as ceramic honeycombs, where thermal gradients have to be minimized in order to avoid the formation of cracks which occur during drying [18].

In this paper, an attempt has been made to synthesize $MgAl_2O_4$ spinel powders from aluminum nitrate, magnesium nitrate and urea precursors by microwave-assisted combustion synthesis route using a modified domestic microwave oven. For the purpose of comparison, a stoichiometric $MgAl_2O_4$ spinel powder was also prepared following conventional combustion synthesis route and compared with the one synthesized by the microwave route.

2. Experimental procedure

2.1. Powder preparations

In a typical experiment, a solid mixture containing requisite quantities of aluminum nitrate (Loba-Chemie, GR grade), magnesium nitrate (Loba-Chemie, GR grade), and urea (Loba-Chemie, GR grade) was taken in a Pyrex glass dish (150 mm diameter and 80 mm height) and was irradiated with microwaves in a modified domestic microwave oven (BPL India Limited, Bangalore, India, Model No. BMO-700T, microwave 700 W, input range 210–230 V-ac 50 Hz, microwave frequency 2.45 GHz) to produce $MgAl_2O_4$ spinel material [14]. A provision was made for the escape of combustion gases by providing an exhaust opening at the top of the microwave oven as shown in Fig. 1. Within a few minutes of irradiation, reaction mixture was converted into a clear solution and started boiling, and after about 20 min of irradiation white fumes started coming out from the exhaust opening provided on the top. After about 45 min of irradiation, the concentrated mixture solution burst into flames and resulted into a foamy white powder (termed as MWCS spinel). In a separate experiment, the same reaction mixture containing aluminum nitrate, magnesium nitrate and urea was treated in an electrically operated conventional furnace (Hind Furnaces, India,

Fig. 1. Modified domestic microwave oven used for the powder synthesis.

12 kW, having Kanthal A_1 heating elements and maximum operating temperature of 1100 °C) at 500 °C for 5 min and thus resulted powder was collected (termed as CCS spinel) [11,12].

2.2. Material characterization

Both the combustion-synthesized spinel powders were milled separately in a planetary ball mill (Fritsch, Pulverisette-5, containing alumina vessel and balls, 12 mm diameter) for about 1 h under identical conditions using 1:1 charge to balls ratio. Phase analysis of the samples was carried out by X-ray diffraction (XRD; Bruker's D8 advance system, Bruker's AXS, GmbH, Germany) using Cu Kα radiation. The crystallite size of $MgAl_2O_4$ spinel was estimated with the help of Debye–Scherrer equation ($\langle L \rangle_{hkl} = K\lambda/\beta_{hkl} \cos\theta$, where K is a constant taken as 1 and β is the integral breadth that depends on the width of the particular hkl plane, $\lambda = 1.5406$ Å, the wavelength of the Cu Kα source, and θ is the Bragg's angle) using the XRD data of the spinel (3 1 1) reflection [19]. Particle sizes of all powders synthesized were measured according to the Laser diffraction technique on a particle size analyzer (Granulometer G 920, Cilas, France). Both differently synthesized spinel powders in the 100-g batches (CCS-100 and MWCS-100) were subjected to thermogravimetric/differential thermal analysis (TG-DTA) on a Netzch (Luxx, STA, 409 PC, Germany) analyzer using α-Al_2O_3 as the reference material in the temperature range of 25–1200 °C with a heating rate of 10 °C min^{-1} in air atmosphere. Transmission electron microscope (Tecnai 12, Netherlands) working at 120 kV was used to identify the particle morphology of the synthesized and ground (planetary ball mill) spinel powders. A Gemini Micromeritics analyzer (Micromeritics Instrument Corporation, Norcross, USA) was used for Brunauer–Emmett–Teller (BET) surface area measurements. The BET surface area was measured by nitrogen physisorption at liquid nitrogen temperature (−196 °C) by considering 0.162 nm^2 as the area of cross

Table 1
Physical properties of $MgAl_2O_4$ powders produced by various methods

S. No.	Method	Code	Batch quantity (g)	Median particle size (μm)	BET surface area (m^2/g)	Crystallite size[a] (nm)	Amount of spinel formation (%)
1	Microwave combustion	MWCS-2	2	4.58	36.78	47	80
2	Microwave combustion	MWCS-100	100	9.61	0.1	55	>99
3	Conventional combustion	CCS-2	2	3.61	126	–	Poor crystallinity
4	Conventional combustion	CCS-100	100	6.80	8.06	43	>99

[a] $MgAl_2O_4$ crystallite size, (3 1 1) plane was considered for crystallite size calculation [19].

section of N_2 molecule. Prior to measurements, the samples were evacuated (up to 1×10^{-3} Torr) at 180 °C for 2 h.

3. Results and discussion

3.1. Combustion reactions

The high temperatures required for the formation of ceramic powders are usually accomplished by the exothermicity of the redox reactions occurring between the decomposition products of metal nitrate (oxidizer) and urea/carbohydrazide/sucrose (fuel) during combustion [11–13,20]. Stoichiometric compositions of the metal nitrates and urea were calculated using the total oxidizing and reducing valencies of the components which provide as numerical coefficients for stoichiometric balance so that the equivalent ratio is unity and the energy generated by the combustion is at a maximum. According to the concepts used in propellant chemistry, the elements Al, Mg, C, and H have reducing valencies of +3, +2, +4, and +1, respectively. Oxygen has an oxidizing valency of −2 and the valency of nitrogen is zero [14,20,21]. Thus, the oxidizing and the reducing valencies of aluminum nitrate, magnesium nitrate, and urea become −15, −10, and +6, respectively.

To synthesize the magnesium aluminate spinel by combustion route, crystalline $Al(NO_3)_3 \cdot 9H_2O$ (total valencies −15) and $Mg(NO_3)_2 \cdot 6H_2O$ (total valencies −10) can be
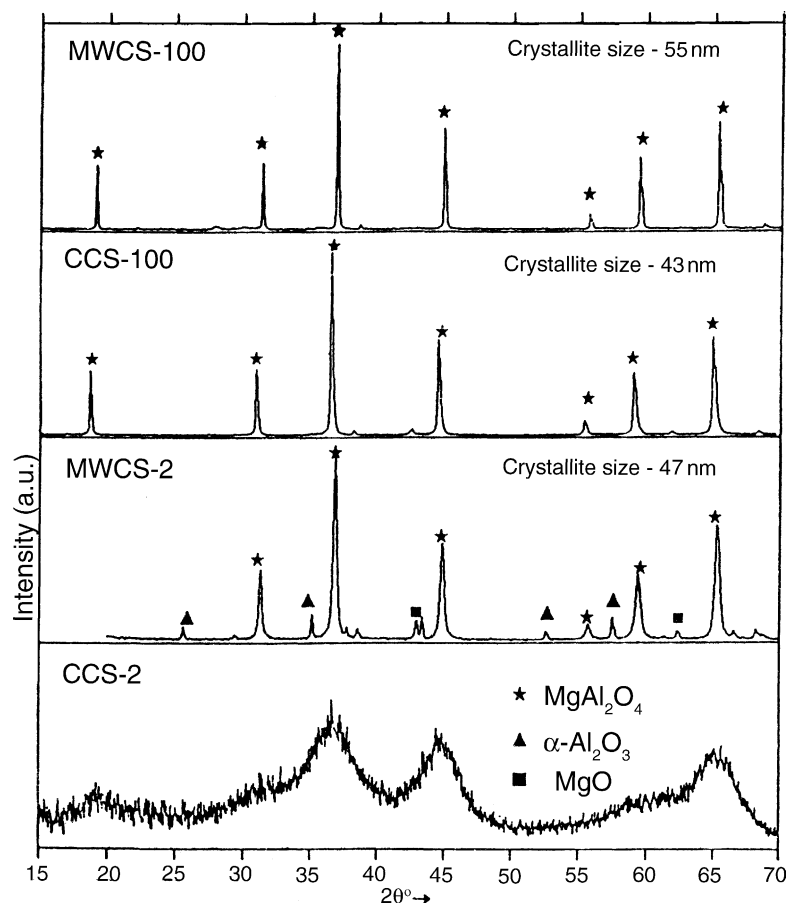

Fig. 2. X-ray diffraction patterns of conventional combustion-synthesized-(CCS-2 and -100) and microwave-assisted combustion-synthesized (MWCS-2 and -100) spinel powders.

taken as Al and Mg sources, respectively. Direct use of propellant chemistry criterion, with the metal precursors in a 1:2 molar proportion, to determine the urea required to balance the total oxidizing and reducing valencies in the mixture, leads to: $1(-10) + 2(-15) + n(+6) = 0$. The stoichiometric redox mixture of the metal nitrates and urea, to release the maximum energy for the spinel reaction would require that $n = 6.66$ mol. Reaction involved in urea combustion process is exothermic (-382.48 kcal (ΔH°, 25 °C)) and since, a significant amount of heat is generated, it would help in sustaining the necessary reactions. The corresponding chemical reaction is as follows: $2Al(NO_3)_3 \cdot 9H_2O$ (C) $+ Mg(NO_3)_2 \cdot 6H_2O$ (C) $+ 6.66$ NH_2CONH_2 (C) $\Rightarrow MgAl_2O_4$ (C) $+ 6.66CO_2$ (g) $+ (4 + 6.66)N_2$ (g) $+ (24 + 6.66 \times 2)H_2O$ (g). The net enthalpy (ΔH°, 25 °C) of the reaction was calculated from the standard enthalpy of formation (ΔH_f°, 25 °C) of products–reactants using the following thermodynamic data: $Al(NO_3)_3 \cdot 9H_2O$ (C): -897.57 kcal/mol; $Mg(NO_3)_2 \cdot 6H_2O$ (C): -622.21 kcal/mol; $CO(NH_2)_2$ (C):-79.7 kcal/mol; $MgAl_2O_4$ (C):-547.38 kcal/mol; H_2O (g):-57.796 kcal/mol; CO_2 (g):-94.051 kcal/mol; N_2 (g): 0 and O_2: 0, where (C) is a crystalline material and (g) is a gas [22,23].

3.2. Powder properties

Various powders prepared in this study are listed in Table 1 along with their median particle size, BET surface area, degree of spinel formation, and crystallite size calculated
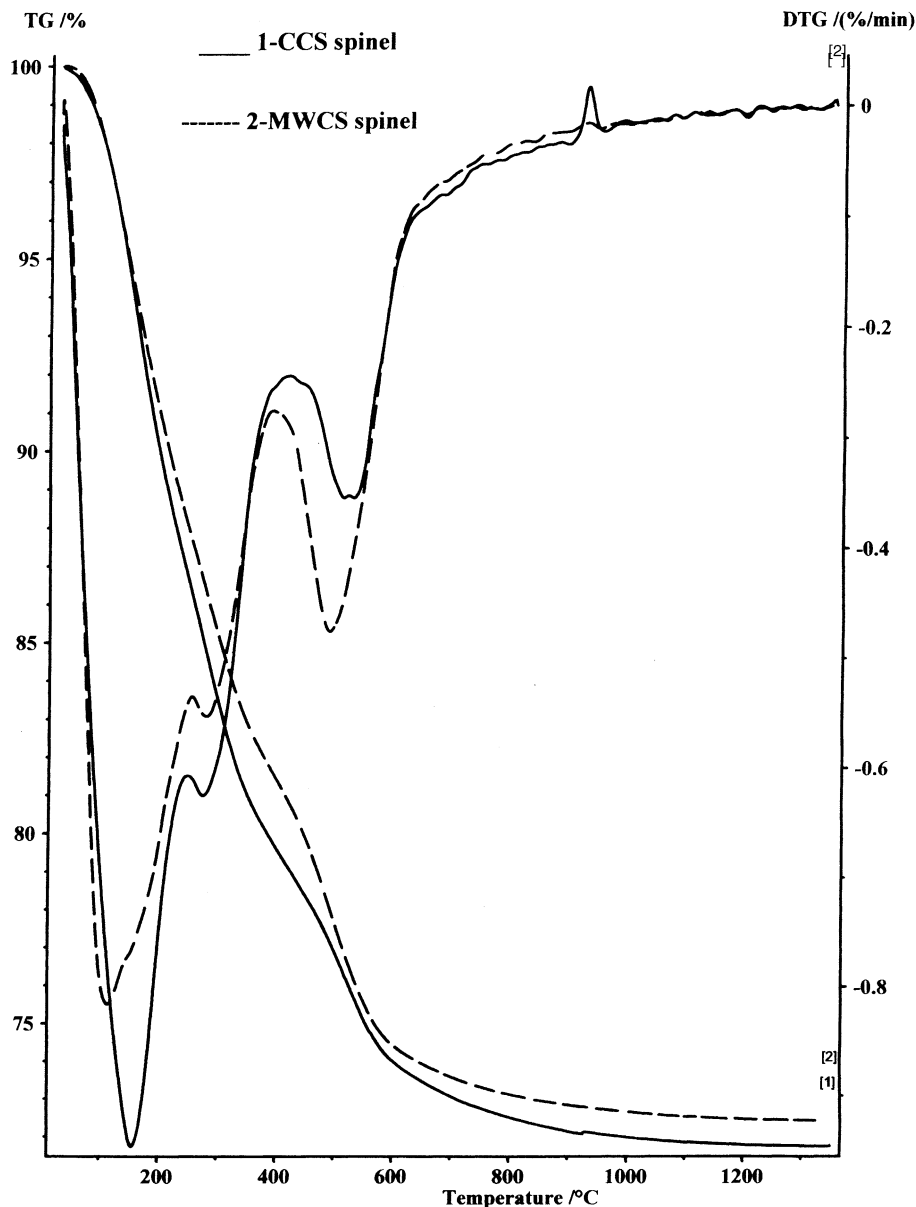

Fig. 3. Thermogravimetric profiles of CCS-100 (1: —) and MWCS-100 (2: - - -) spinel powders.
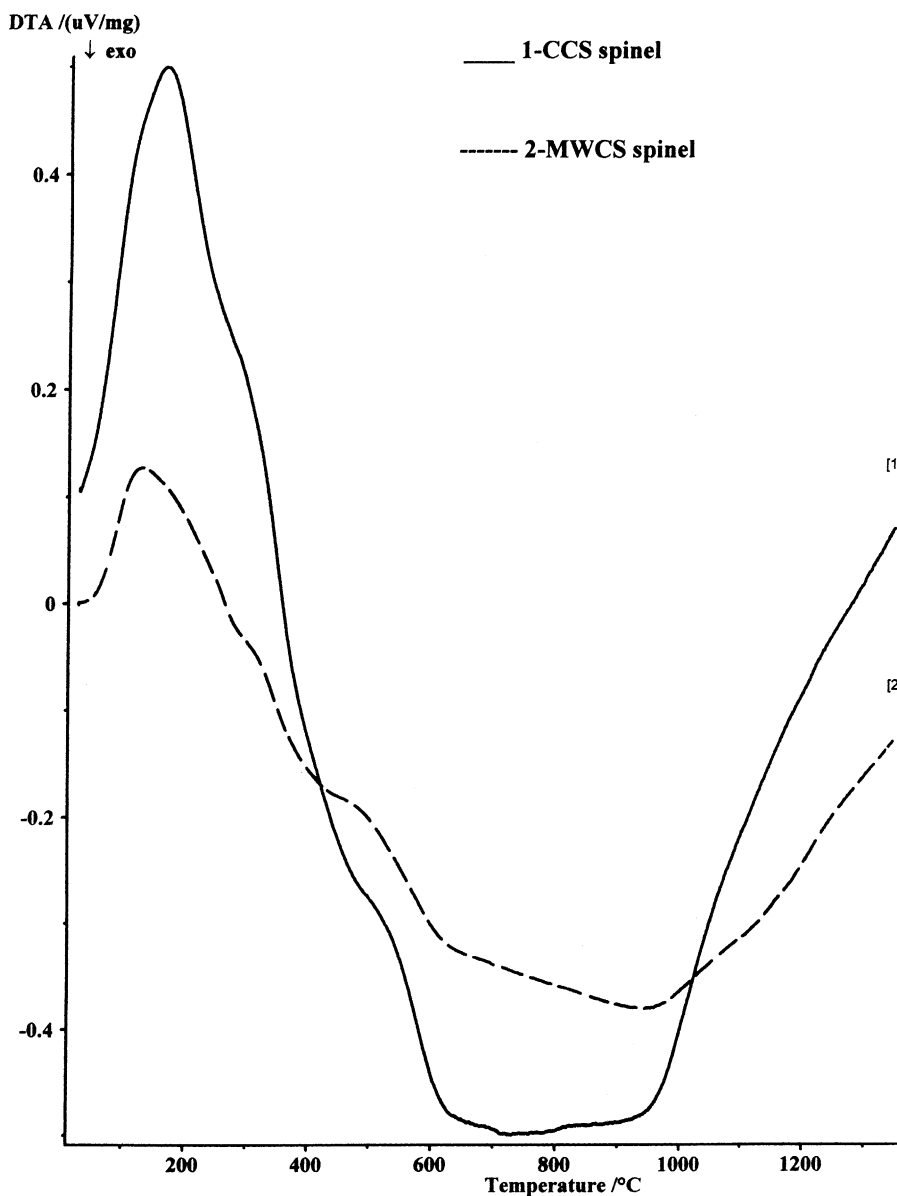
Fig. 4. Differential thermal analysis profiles of CCS-100 (1: —) and MWCS-100 (2: - - -) spinel powders.

from XRD data. Different codes are given for each powder for the sake of clarity. Initially, combustion reaction experiments were conducted in order to yield 2-g powders and to carry out the feasibility study for the scale-up and its effect on powder properties. Later on experiments were conducted to yield 100-g powders by both microwave-assisted combustion (MWCS) and conventional combustion synthesis (CCS) routes. As can be noted from Table 1, when the batch quantity increased from 2 to 100 g, the surface area values decreased drastically and this reduction is more in the case of MWCS powders. Further the median particle size and crystallite size of the powders increased. Among various powders synthesized (Table 1), the MWCS powders show large crystallite size. In general, the crystallite sizes of powders increase with the increasing treatment temperature due to sintering. Therefore, it gives an impression that

MWCS powders are exposed to higher temperatures than in the case of CCS powders.

X-ray diffraction patterns of various powders synthesized in this study are shown in Fig. 2. As can be observed from Fig. 2, the smaller 2 g (CCS-2) batch powders obtained by the combustion of aluminum nitrate, magnesium nitrate and urea mixture in an electric furnace at 500 °C for 5 min exhibit a few broad XRD peaks indicative of very fine crystallite size. The 100-g batch powders (CCS-100) produced under identical conditions exhibit the presence of well defined crystalline $MgAl_2O_4$ spinel phase. It can also be noted from Fig. 2 that the 2-g batch material (MWCS-2) obtained from the identical reaction mixture in a domestic microwave oven shows about 80% spinel formation with the presence of small quantities of un-reacted corundum and periclase in contrast to CCS-2 powder (very fine crystallite size). As the batch

quantity increased from 2 to 100 g (MWCS-100), a complete spinel (ICDD File No. 211152) formation is occurred as in the case of CCS-100 sample. As far as thermodynamics is concerned, the same amount of heat is expected to be evolved in the processes of combustion of aluminum nitrate, magnesium nitrate and urea in both CCS-2 and MWCS-2 reactions, and thus obtained powders are supposed to show similar properties. The anomaly exhibited by the powders synthesized in this study may be due to the enhanced reactions under the influence of microwaves as discussed below.

On theoretical grounds, formation of $MgAl_2O_4$ spinel material from aluminum nitrate, magnesium nitrate and urea (2:1:6.66 mole ratio, respectively) involves the generation of –382.487 kcal (ΔH°, 25 °C) heat [11,12]. According to Merzhanov's [24,25] empirical criterion for self-propagating high-temperature synthesis (SHS), if T_{ad} (adiabatic temperature) <1227 °C, combustion does not occur, and if T_{ad} > 2227 °C, self-propagating combustion occurs. If the T_{ad} is in the range, i.e., 1227 °C < T_{ad} < 2227 °C, a combustion wave cannot propagate but can be made to do so by special techniques such as heating of the reactants. It is a well-known fact that heat generation takes place in the microwave oven on account of constant rotation of dipolar molecules (H_2O) under the influence of microwave radiation. Since, uniform heating is taking place in the microwave oven, which in turn helps in enhancing the reaction rate in contrast to the reaction occurring in the conventional heating systems [14]. This might be the reason, for enhanced reactions in the microwave-synthesized powders in comparison with the powders produced in an electric furnace (Fig. 2). As batch quantity increases, the amount of heat generated in a particular reaction also increases because of the accumulation of heat [25]. An important point to be emphasized here is that as the accumulation of heat increases, the adiabatic temperature that generated also increases with the increased batch size, which ultimately deteriorates the powder properties in terms of decrease in surface area and increase in crystallite size [26], which would result in the poor sinterability of the powders.

In order to assess the degree of reaction occurred and stability of the powders with respect to thermal as well as chemical composition, two differently synthesized spinel powders (CCS-100 and MWCS-100) were subjected to thermogravimetric (TG) (Fig. 3) and differential thermal analysis (DTA) (Fig. 4) in the temperature range of 25–1200° C with a heating rate of 10 °C min^{-1}. As can be noted from TG and DTA profiles (Figs. 3 and 4), though the degree of weight and heat changes exhibited by the CCS-100 is relatively more, in general, both the powders exhibit a similar kind of thermal and weight changes upon heat treatment. The major endothermic (Fig. 4) and weight loss peaks (Fig. 3) observed below 400 °C are mainly due to the evaporation of physisorbed moisture. The next major change occurs in the temperature range 400–550 °C, which could be attributed to the combustion of un-reacted metal nitrates that are not consumed during the reactions [13,14]. The higher compositional and
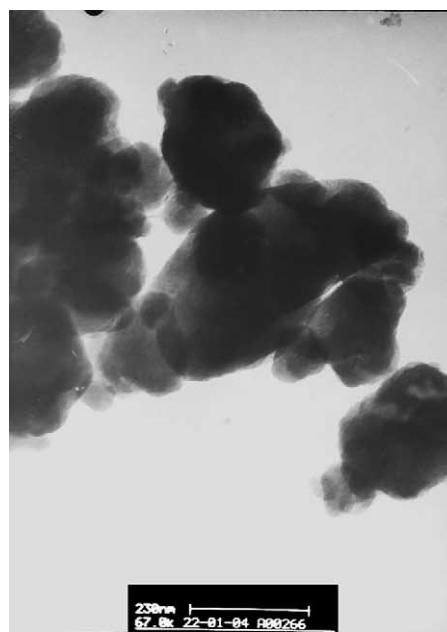
(a)
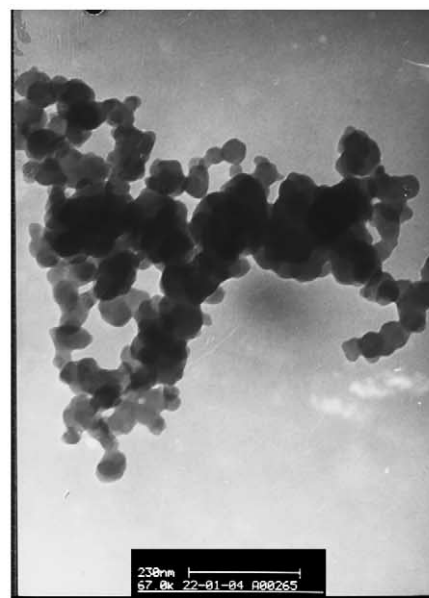
(b)

Fig. 5. Transmission electron microscope of CCS-100 (a) and MWCS-100 (b) spinel powders.

thermal stability of MWCS powders as compared to CCS powders (Figs. 3 and 4) upon heat treatment indicates that microwave synthesis yields materials with superior powder properties. Kiminami et al. also made similar observations in their study of microwave synthesis of alumina powders [14].

TEM micrographs of 1 h ground CCS-100 and MWCS-100 spinel powders are given in Fig. 5a and b, respectively. As can be seen from Fig. 5, both CCS and MWCS powders show the presence of similar kind of grains/crystals having equiaxed shape with different crystal sizes. The MWCS powder is found to have crystals/grains in the size range of 20–50 nm, whereas CCS powder has in the range of
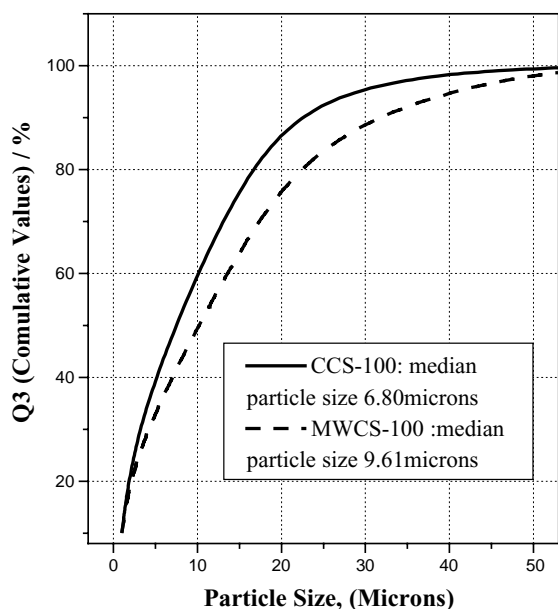
Fig. 6. Particle size distribution of CCS-100 (1: —) and MWCS-100 (2: - - -) spinel powders.

100–250 nm. As MWCS powder is expected to be exposed to higher flame temperature during its synthesis, the degree of agglomeration of grains/crystals is less probably owing to its higher crystalline nature as compared to CCS powder, which has relatively poor crystalline particles. The crystallite sizes calculated from XRD data using Debye–Scherrer formula for CCS-100 and MWCS-100 samples were found to be 43 and 55 nm, respectively, which are different from TEM observations. At this point it is important to mention on the differences between the XRD and TEM results. The difference may be due to the fact that XRD represents a global picture while TEM depicts a local feature. Nonetheless, the trend observed (Table 1; Fig. 6) in the median particle sizes of powders measured by Laser Diffraction Technique correlate well with the trend observed in the crystallite sizes calculated from XRD study. The particle size distributions as well as median particle size of both ground (1 h planetary ball mill) spinel powders are given in Fig. 6. As can be observed from Fig. 6, MWCS-100 sample has a wide range of particle size distribution in contrast to CCS-100, which has a narrow particle size distribution. The presence of different median particle sizes and particle size distributions for both differently synthesized powders even after grinding under identical conditions for 1 h further support that the microwave combustion-synthesized spinel powders are different from the conventional combustion-synthesized spinel powders.

4. Conclusions

Single-phase nanocrystalline $MgAl_2O_4$ spinel powder can be prepared in a domestic microwave oven by solu-

tion combustion reaction of a mixture of aluminum nitrate, magnesium nitrate and urea. As the batch quantity increases, the specific surface area of combustion-synthesized $MgAl_2O_4$ spinel powder decreases and their crystallite size increases. This can be attributed to the higher adiabatic temperature generated as a result of increased accumulation of heat with bigger batch quantities. Powders obtained by the microwave-assisted combustion synthesis route posses higher compositional and thermal stability when compared to the powders generated by the conventional combustion synthesis route. Microwave-synthesized powders were found to have crystals in the range of 20–50 nm, whereas conventional combustion-synthesized powders have aggregates of fine crystals in the size range of 100–250 nm.

Acknowledgements

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