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A novel approach to synthesis of nanosize $MgAl_2O_4$ spinel powder through sol–gel citrate technique and subsequent heat treatment

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Abstract

This paper summarizes a study on the influence of heat-treatment atmosphere in synthesis of nanosize $MgAl_2O_4$ spinel powder employing sol–gel citrate route. Based on measurement of BET specific surface area, crystallite size, simultaneous thermal analysis, and microscopic observation, it was clarified that the argon atmosphere used for heat treatment of precursor reduced the particle size of synthesized ceramic powder significantly. Comparing with heat treatment in air atmosphere, it was elucidated that the carbonaceous material remaining from citrates has an important role in hindering the particle sintering. Also the slower heat generation in argon atmosphere creates a chance to achieve a nanocrystalline $MgAl_2O_4$ spinel powder with crystallite size in the range of 5–7 nm. The present novel approach shows that the argon treatment confronts the problem of sudden heat generation in sol–gel citrate method to synthesize nanosize $MgAl_2O_4$ spinel particles in the range of 20–100 nm.

Keywords: Chemical preparation; Calcination; X-ray methods; Electron microscopy

1. Introduction

Due to the excellent refractoriness (melting point ≈2135 °C), good thermal shock resistance, high-mechanical strength at elevated temperatures, and chemical inertness $MgAl_2O_4$ spinel is widely used in the metallurgical, electrochemical, and chemical industrial fields [1–3].

The production of high purity and reactivity of $MgAl_2O_4$ spinel is influenced by synthesis technique. In addition to the solid-state synthesis which suffers from the inhomogeneity and high-synthesis temperatures, many unconventional techniques like co-precipitation, sol–gel, citrate-nitrate combustion, and freeze-drying have been used for the synthesis of $MgAl_2O_4$ spinel [4–8].

Because of cheapness, easy-setup, and good chemical homogeneity of synthesized powder thorough sol–gel citrate technique, this method has be frequently used for the synthesis of single and multi-oxide powders [9]. The effects of pH and the amount of citric acid on citrate-nitrate process parameters such as crystallization temperature, crystallite size, and particle size of synthesized powder have been reported [10–14]. Most of these investigations, however, were carried out in air atmosphere and less attention has been paid to atmospheric effect.

We have recently reported the synthesis of $MgAl_2O_4$ spinel powder via sol–gel citrate route where the combustion reactions were studied [15]. It was found despite of nanosize particle yield, the enormous liberated heat of combustion reactions caused the partial sintering of synthesized particles. This phenomenon necessitated controlling synthesis parameters during citrate-nitrate process.

In the present study, a novel heat-treatment regime was employed to control the combustion heat generated during the synthesis which yielded smaller particle size in the range of 20–100 nm.

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Table 1
The products notation and the utilized heat-treatment schedules

Denotation	A-3	A-42	A-9	B-7	D-3	D-4	D-7	D-9
Starting sample	P	P	P	A-9	P	P	P	P
Atmosphere	Argon	Argon	Argon	Air	Air	Air	Air	Air
Maximum temperature (°C)	300	420	700	900	300	400	700	900

P: precursor; dwelling time = 1 h; heating rate = 10 °C/min; gas flow = 40 ml/min.

2. Experimental procedure

The general description of preparation of precursor and synthesis of $MgAl_2O_4$ spinel has been reported in a previous article [15]. Briefly, the precursor was obtained by dissolving stoichiometric amount of aluminum and magnesium nitrates in distilled water and subsequent introduction of citric acid and ammonia solution. This solution was gelled while heating the primary sol at 120 °C and with further heating at 180 °C in an electric oven the gel was converted to a pale yellowish mass. The produced mass, hereinafter referred to as precursor, was ground into the powder by a mortar and pestle and subsequently heat-treated in an atmosphere controlled furnace in dynamic air. The precursor was also heat-treated in argon and subsequently in the flowing air. The samples notation and their treatment condition are demonstrated in Table 1. The schematic flowchart of the synthesis process used is shown in Fig. 1.

Differential scanning calorimetry (DSC) and thermogravimetric (TG) analyses of precursor were carried out using a Netzsch STA 449C from room temperature to 1000 °C with a heating rate of 10 °C/min in a continuous air or argon flow (40 ml/min). Phase evaluation of the heat-treated precursor at different temperatures and atmosphere was studied using a Philips (PW 3040) diffractometer with Cu Kα radiation. JCPDS cards 21-1152 and 47-0867 were used for identification of $MgAl_2O_4$ spinel and ammonium nitrate, respectively. The details of crystallite size measurement by XRD were as explained in previous study [15]. Field emission scanning electron microscope (LEO® 1530, FE-SEM) and transmission electron microscope (LIBRA® FE-200, TEM) were used for microscopical observation. The surface area of synthesized powders was measured with an ASAP 2010, Gimini according to BET technique.

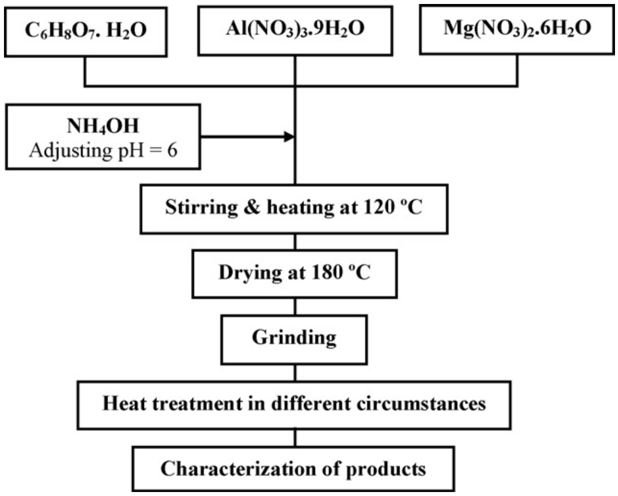

Fig. 1. Schematic flowchart for the synthesis of nanosize $MgAl_2O_4$ spinel powder.

3. Results and discussion

Fig. 2(a) presents the DSC–TG curves of heated precursor in argon atmosphere. The initial broad endothermic peak at around 150 °C which accompanied with 17% weight loss is assigned to dehydration of precursor. This material despite of being dried at 180 °C, has apparently absorbed some environmental moisture due to its hygroscopic nature. The sharp exothermic peak at 294 °C with 56% weight loss in TG curve is attributed to decomposition of NH_4NO_3. This heat generation also happens in air atmosphere as explained in the previous study [15]. Looking at Fig. 2(a), one may notice that the heat release according to DSC curve is about 2.5 mW/mg

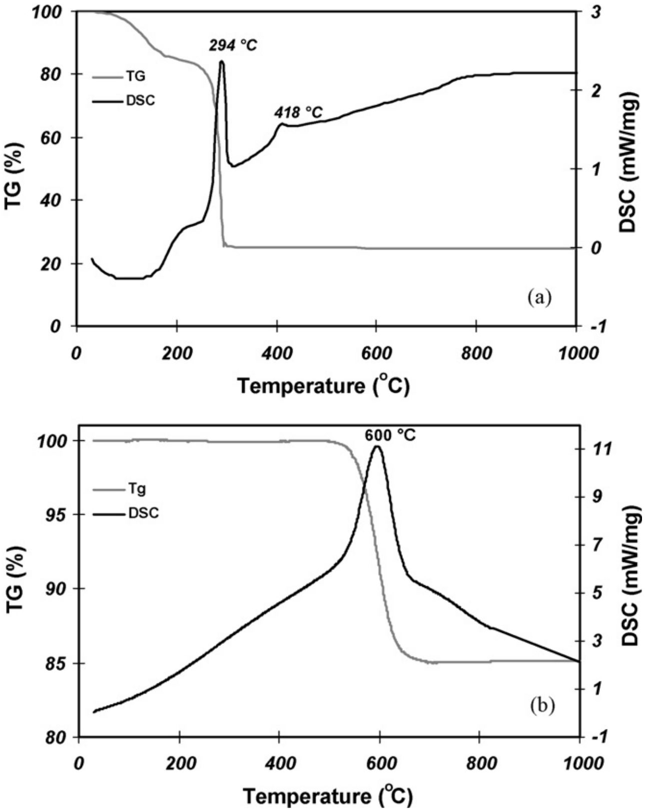

Fig. 2. DSC–TG results of precursor in argon (a) and the thermal analysis of argon heat-treated sample in air (b).

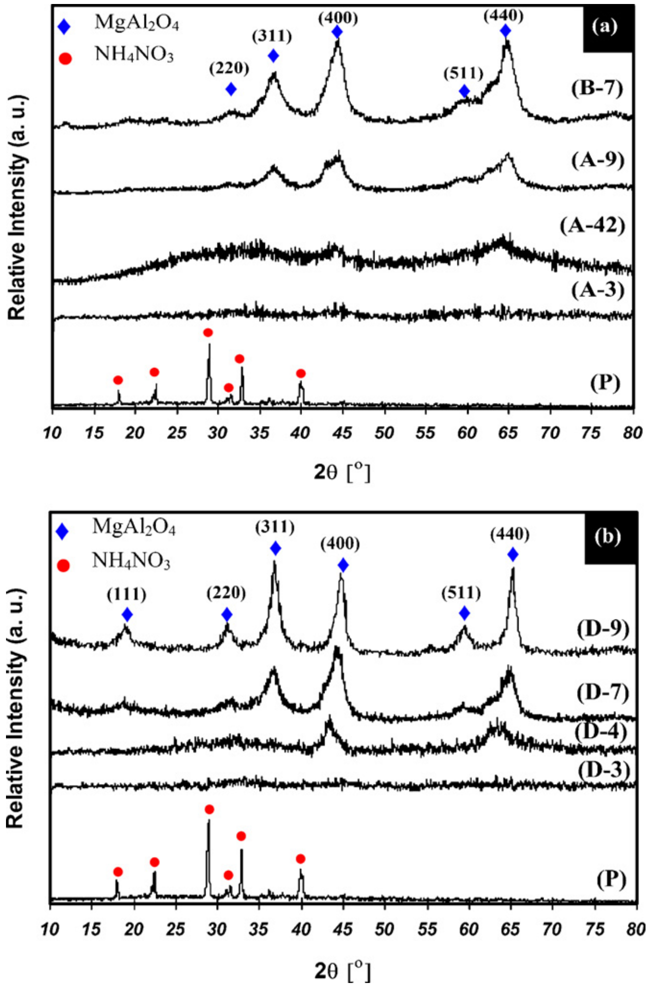

Fig. 3. XRD patterns of the dried precursor and samples A-3, A-42, A-9, and B-7 (a), and X-ray diffraction patterns of the samples directly calcined in air atmosphere at different temperatures (b).

which in comparison with previously related decomposition of the same material in air is much lower (at stated in Ref. [15] the heat release was about 6 mW/mg). The significant difference in decomposition rate has the implication that the decomposition reactions are different in nature in air and argon atmospheres. Despite of the heat treatment of precursor in air atmosphere where ammonium nitrate and citrates take part in redox reaction, in inert atmosphere however, only ammonium nitrate participates in combustion reaction. Further heating causes a small and broad exothermic peak at 418 °C, which is assigned to the crystallization of $MgAl_2O_4$ spinel (Fig. 2(a)). No significant changes were observed in further heating up to 1000 °C. The sample cooled in DSC–TG chamber had a black and fluffy appearance which shows the unburned carbonaceous residual.

This blackish loose mass may indicate the presence of carbonaceous derivatives from citrates. When this powder was reheated in DSC–TG apparatus under air flow, the curves shown in Fig. 2(b) were recorded. The exothermic peak at 600 °C accompanied with a 15% weight loss in TG curve indicates the oxidation of carbonaceous ingredient.

Fig. 3 exhibits the XRD patterns of different samples which heat-treated in different circumstance as described in Table 1. The precursor converts to an amorphous mass when heated at 300 °C in argon atmosphere (sample A-3). This shows that ammonium nitrate could undergo a combustion reaction even in an inert atmosphere. Also from this figure we may notice that the crystallization initiates at 420 °C (sample A-42). Comparison of Fig. 3(a) and (b) shows the thermal behavior of heat-treated precursors are more or less the same in either air or inert atmospheres up to 420 °C. At higher temperatures, however, there are some differences. For instance heat treatment at 900 °C in air yields a well-crystallized $MgAl_2O_4$ spinel powder with sharp XRD peaks (sample D-9), while the inert atmosphere product at same temperature (sample A-9) possesses low crystallinity with small and broad XRD peaks.

Sample B-7 which has been treated in argon up to 900 °C and subsequently heated up in air at 700 °C shows an improvement in crystallinity compared to sample A-9. Indeed, the removal of carbonaceous material in oxidized atmosphere has accelerated the crystallization of sample A-9.

All the above discussions have the indication that the less heat generation in argon compared to air atmosphere hinders the grain growth of synthesized $MgAl_2O_4$ spinel and leaves a product of virtually nanosize particles. It seems that the primary carbonaceous material left in the batch after decomposition at 294 °C is a source of heat sink to slow down the heat transfer to $MgAl_2O_4$ spinel particles. Also the carbonaceous material has a role of separating the primary nanoparticles of spinel from each other and hence hindering their sintering at higher temperatures.

Table 2 presents the approximate crystallite size of the synthesized $MgAl_2O_4$ spinel powders under different heat-treatment circumstances. Three diffraction peaks (3 1 1), (4 0 0), and (4 4 0), which have the advantages of being well separated and having high intensities, where taken for measuring the crystallite size. The crystallite size of product of argon treatment at 900 °C (sample A-9) is in the range of 5–6 nm and is less than the crystallite size of product directly heat-treated at 700 °C in air atmosphere (sample D-7) which is in the

Table 2
The approximate crystallite size of samples A-9, B-7, D-7, and D-9

Sample	$d_{3\,1\,1}$ (Å)	D (nm)	$d_{4\,0\,0}$ (Å)	D (nm)	$d_{4\,4\,0}$ (Å)	D (nm)	Average crystallite size (nm)
A-9	2.474	5	2.039	5	1.460	6	5.4
B-7	2.449	7	2.032	8	1.440	9	8
D-7	2.449	9	2.063	10	1.464	10	9.7
D-9	2.438	19	2.028	21	1.432	18	19.4

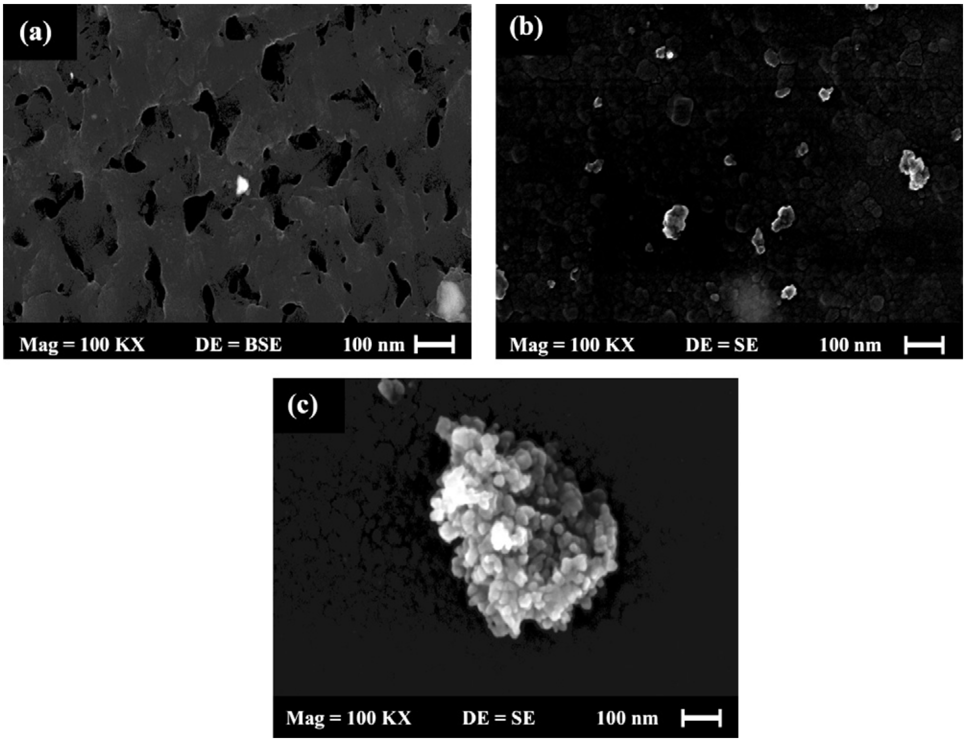

Fig. 4. FE-SEM micrographs of A-9 (a), B-7 (b), and D-7 (c).

range of 9–10 nm. The comparison between the crystallite size of sample B-7 and the sample D-9 clarifies that the new approach hinders the exaggerated grain growth. However, the crystallite size of sample B-7 is almost the same as the sample directly heat-treated at 700 °C in air (sample D-7).

Fig. 4(a)–(c) illustrates the FE-SEM micrographs of samples A-9, B-7, and D-7, respectively. The backscattered electron mode (BSE) of sample A-9 shows the formed $MgAl_2O_4$ spinel particles, visible as white particles, inside a carbonaceous matrix (Fig. 4(a)). By calcination of sample A-9 in air at 700 °C, the carbonaceous matrix was completely oxidized (Fig. 4(b)). According to the FE-SEM micrograph the particles size of sample B-7 are in the range of 20–100 nm. Fig. 4(c) shows the powder obtained by direct heat treatment of precursor at 700 °C in air atmosphere (sample D-7). The particles of sample D-7 are sintered and much bigger compared to sample B-7 shown in Fig. 4(b).

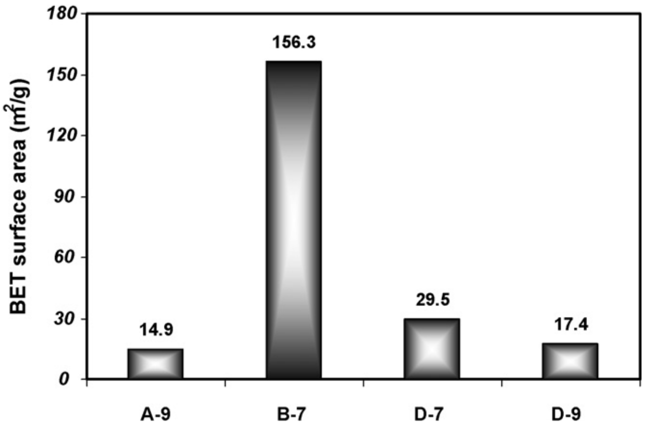

Fig. 5. BET surface area of the synthesized $MgAl_2O_4$ spinel powders in different heat-treatment circumstances.

Fig. 5 demonstrates the BET surface area values of samples treated in different circumstances. Powder B-7 which has been prepared by heating in argon (900 °C) and subsequent air treatment (700 °C) shows a surface area of almost five times more than sample D-7.

Fig. 6 shows the TEM micrographs and selected area electron diffraction (SAED) patterns for sample B-7 and D-9. As it is observed, the crystallite size of sample B-7 (Fig. 6(a)) is in the range of 5–7 nm which is significantly smaller than the sample D-9 (Fig. 6(b)). Although both samples experienced 900 °C, the difference in crystallite size can be attributed to their heat treatment and environmental differences. We may note that the SAED patterns of the samples B-7 and D-9 are different. While in sample B-7 there are only three diffraction circle, in sample D-9 five groups of planes are diffracting. This indicates the lower crystallinity of sample B-seven compared to sample D-9.

4. Conclusion

Nanosize $MgAl_2O_4$ spinel powder in the range of 20–100 nm was prepared via sol–gel citrate route and subsequent heat treatment in argon atmosphere. The heat treatment in argon atmosphere slows down the heat generation during the combustion reactions and yields a fluffy loose product in which the carbonaceous matrix separates the ceramic particles

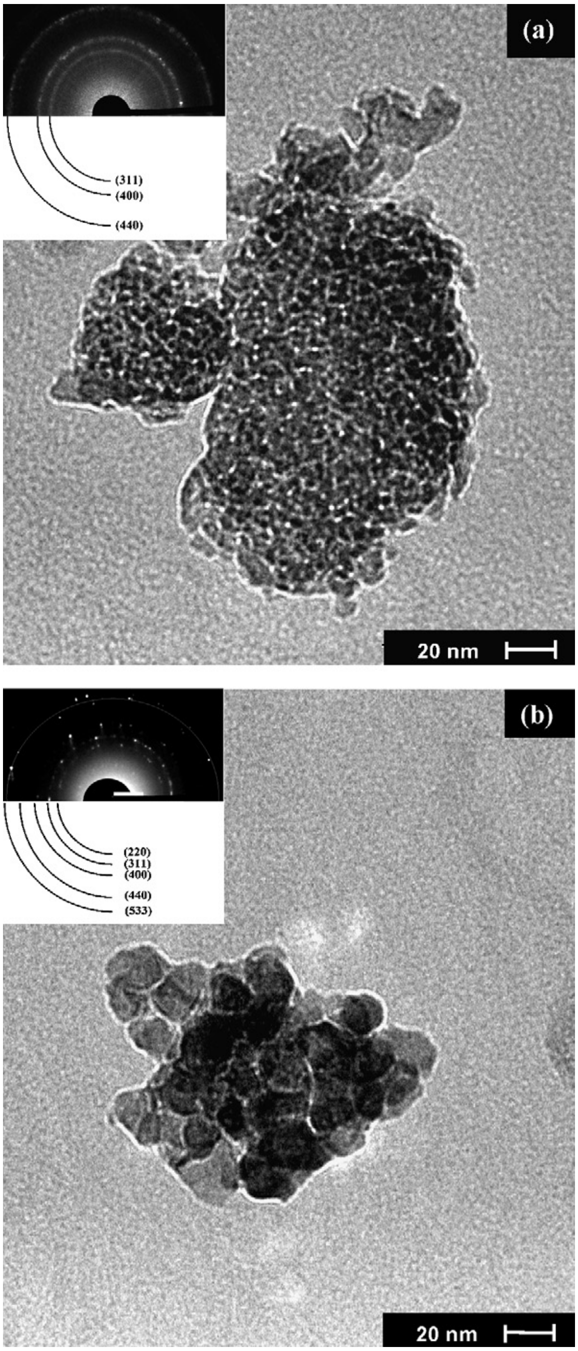

Fig. 6. TEM micrographs with inserted SAED patterns of $MgAl_2O_4$ spinel powders which heated in different heat-treatment circumstances: sample B-7 (a) and sample D-9 (b).

from each other. The results of XRD, SEM, TEM, and BET surface area measurement all confirmed the formation of nanosize $MgAl_2O_4$ spinel powder with crystallite size in the range of 5–7 nm. It was demonstrated that applying argon atmosphere in sol–gel citrate route process is a useful method for reducing the particle size of synthesized ceramic powder.

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