

Low-temperature crystallization at 700 °C of magnesium aluminate nanospinel Using nitrate precursors by masking-gel calcination process

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Nanoparticles MgAl_2O_4 spinel with the cubic crystal structure was successfully prepared through masking-gel calcination process, using aluminum and magnesium nitrates as spinel precursors and sugar as a masking-gel agent. Calcination treatment was performed at 600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C. X-ray diffraction analysis, transmission electron microscopy and scanning electron microscopy studies were conducted to identify the crystalline phase and the microstructure of the spinel product. The metal nitrate precursors were found to crystallize completely as MgAl_2O_4 spinel at a low temperature of 700 °C having crystallite sizes below 15 nm. The average particle sizes of the spinel powder at that temperature were less than 75 nm. The microstructure analysis of the spinel sample at the calcination temperature of 1000 °C shows the particle sizes below 100 nm and high formation of agglomerates.

Key words: Nanospinel MgAl_2O_4 , Metal nitrate precursors, Sugar, Masking-gel calcination, Low-temperature crystallization.

Introduction

Magnesium aluminate (MgAl_2O_4) is a spinel-type oxide having chemical formula AB_2O_4 and consisting of 8 of 64 tetrahedral sites that occupied by Mg^{2+} and 16 of 32 octahedral sites which occupied by Al^{3+} [1]. It is a promising material for ceramics or advanced products due to excellent properties such as, high melting point, high hardness, relatively low density, excellent transmittance, high strength at room and at elevated temperatures, excellent chemical resistance, relatively low thermal expansion coefficient and high thermal shock resistance [1, 2, 3, 4, 5, 6, 7, 8]. Therefore, MgAl_2O_4 spinel finds applications on the metallurgical, electrochemical, and chemical industrial fields [9] such as refractory materials [10, 11], humidity sensors [11], glass tank furnaces, optical devices and ultrafiltration membrane [12]. Recently, the spinels are also now being developed as transparent ceramics for armor applications [13, 14, 15, 16]. Since, sapphire, the most mature transparent ceramic window material has the highest cost production due in part to the processing temperatures involved [17], MgAl_2O_4 spinel is used to make transparent windows because of its better ballistic efficiency, and a lower predicted cost of production compared with sapphire [18].

Nanomaterials exhibit superior properties, compared to their normal, bulk counterparts, due to the small size. Since their properties can be engineered during synthesis and processing steps, they show great technological

potential due to their grain size dependent properties [19].

Many synthesis methods have been reported for micron and nano powder MgAl_2O_4 preparation, such as self-heat-sustained (SHS) technique [20], a combustion route [3, 11], reverse micelle processing [4], co-precipitation and sol-gel techniques [5, 10, 12, 21, 22, 23], molten salts [24], mechanical activation with subsequent annealing [9], the aqueous chemical synthesis [25], thermal decomposition of an organometallic compound [26], etc. Most of the methods commonly reported the formation or the crystallization MgAl_2O_4 nanospinel at temperatures equal or above 800 °C [1, 3, 4, 12, 21, 24, 25]. In this work, the preparation of nano powder MgAl_2O_4 spinel is reported using aluminum and magnesium nitrates as spinel precursors by masking-gel calcination process [27, 28]. This work aims to prepare nanopowder MgAl_2O_4 from the precursors of aluminum and magnesium salts using sugar as a gelling agent at a lower temperature than 800 °C of about 700 °C; and to investigate the phase transformation and crystal sizes of the MgAl_2O_4 formed. Sugar weight ratio to total metal precursor applied in this work referred to previous researches [29, 30].

Experimental Procedure

Materials and instruments

Materials used in this research were aluminum nitrate nonahydrates ($\text{Al}_2(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), magnesium nitrate hexahydrates ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), which obtained from Merck Inc., Germany and commercial sugar from a local market, consisting of sucrose as a major constituent and the other organic constituents [29]. The instruments

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used were an IKA speed mixer with the maximum speed of 2000 rpm, a Heraus electrical furnace, a Phillips PANalytical X-ray diffractometer, a JEOL JSM-35C scanning electron microscope (SEM), and a JEM-1400 120 kV transmission electron microscope (TEM).

Synthesis of MgAl_2O_4 spinel from metal nitrate precursors

MgAl_2O_4 spinel precursors were initially prepared by mixing and dissolving aluminum and magnesium precursors in a stoichiometric proportion into demineralized water to obtain a homogenous solution. An appropriate amount of sugar added slowly to the solution and stirred vigorously. Sugar to total the aluminum and magnesium precursors weight ratios had to be maintained at 1 : 6 [29, 30]. The mixture was constantly stirred and slowly heated until a yellowish foam gel was formed at 100 °C. The yellowish foam gel was continuously heated at about 200 °C until a fine brownish yellow precursors formed. The fine precursors were successfully calcined at 600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C for 5 hrs in an Heraus electric furnace. The final product was then characterized.

The crystalline phase of MgAl_2O_4 spinel was identified by an X-ray diffraction (XRD) instrument. Crystallite sizes were estimated from XRD peak widths using the Scherrer equation after correction for instrumental broadening [29].

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where D is the crystallite size, K is a shape factor with a value of 0.9-1.4, λ is the wavelength of the X-rays (1.54056 Å), is the Bragg angle and β is the value of the full width at half maximum (FWHM). XRD patterns were identified using the PDF2 CD-ROM (JCPDS-International Centre for Diffraction Data). Meanwhile, a JEOL JSM-35C SEM was used to observe the morphology of Spinel particles. A transmission electron microscopy was also performed to measure the particle sizes of the synthesized MgAl_2O_4 spinel using a JEM-1400 120 kV TEM.

Results and Discussion

Qualitative and quantitative analysis on the mineral phase transformation of MgAl_2O_4 spinel using XRD method

Fig. 1 shows XRD patterns of the spinel transformation from the metal nitrate precursors with sugar as a gelling agent at the elevation temperatures of 600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C. The spinel powders are amorphous after calcination at 600 °C for 5 h. Nevertheless, since sugar was used as a gelling agent in the spinel preparation, the metal nitrate precursors were found to crystallize completely at the lower temperature of

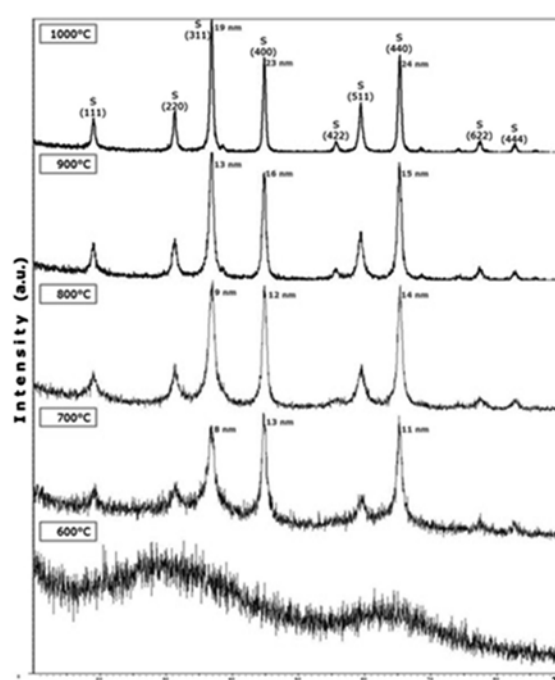


Fig. 1. XRD patterns of the spinel transformation from the metal nitrate precursors with sugar as a gelling agent at temperatures of 600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C.

700 °C, with broadening peaks of cubic MgAl_2O_4 spinel at diffraction angles 2θ of 36.873 °, 44.899 °, 65.307 ° ($2\theta\text{-CuK}\alpha$), corresponding to the (3 1 1), (4 0 0) and (4 4 0) crystal planes of the MgAl_2O_4 spinel structures, respectively. On further increasing the temperature to 800 °C, cubic MgAl_2O_4 spinel peaks increased and no other phases were detected in the spinel sample. The profiles of phase changes of the minerals with the elevated temperature are mostly similar to those indicated by Fig. 1 after calcination for 5 h at 800 °C, the cubic MgAl_2O_4 spinel was identified as the only existing phases in the spinel sample; showing strong peaks at the higher calcination temperature of 1000 °C.

However, the results of the present work are significantly different from Ding's finding [25]. They prepared ultrafine MgAl_2O_4 spinel powder using metal nitrates as precursors and oxalic acid as a chelating agent through the aqueous chemical synthesis. Ding *et al.* [25] observed that the crystallization or the growth of MgAl_2O_4 started at a higher temperature of 800 °C. This confirms the effect of the additive presence such as sugar or oxalic acid on the spinel preparation, which significantly gives different phase transformation route from metal nitrate precursors to MgAl_2O_4 spinel. However, this different phenomenon demands further study, which is currently under way.

A quantitative analysis of diffractogram patterns for spinel sample at the elevated temperatures of 700 °C, 800 °C, 900 °C, 1000 °C such as crystallite sizes of spinel phase formed was applied and assisted using XRD software. PDF 2 No. 730559, 751796, 770435,

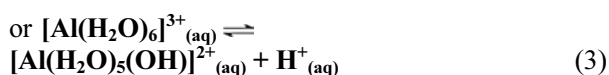
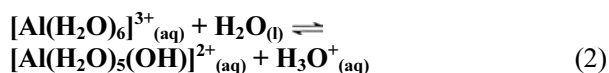
and 822424 (MgAl_2O_4) were used as references or standards in determining crystallite sizes mineral phases formed. The Scherrer's equation from a line broadening technique, which measures the full width at half-intensity of the largest intensity reflection of XRD pattern was used to estimate the spinel crystallite sizes [25].

The quantitative results show that the phases in calcined spinel powder at temperatures of at temperatures of 700 °C, 800 °C, 900 °C, and 1000 °C consisting of only the MgAl_2O_4 spinel phase having crystallite sizes below 25 nm, as according to the three main peaks of spinel phase, as shown in the diffractogram in Fig. 1.

The nanocrystallite sizes of spinel sample might be produced by the presence of commercial sugar in the preparation, which reduces the tendency toward agglomeration in the as-synthesized nanoparticle spinel. The concentration of Al^{3+} and Mg^{2+} ions of the nitrate precursors with amount of sugar will be lower during the course of the phase transformation. As the calcination temperature is increased, the material is considered to be deficient in Al^{3+} and Mg^{2+} content so that this retards the crystallite grain growth [31]. When sugar used as a gelling agent in the preparation, it also performed as a masking compound. The compound covered on the surfaces of the metal precursors to generate a wider molecule binding distance, restricting the contact among the nucleated Al_2O_3 MgO and restraining the spinel crystallite growth [29, 31].

The role of sugar in the synthesis of MgAl_2O_4 spinel precursors

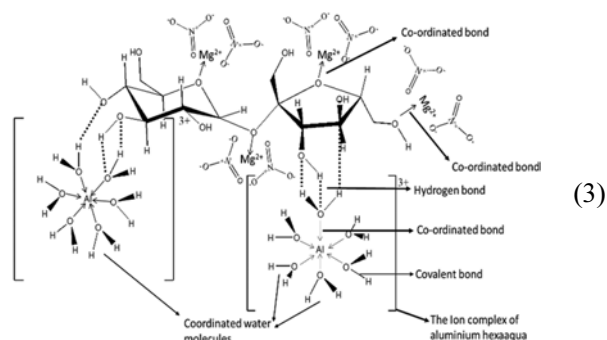
Since the metal salt of aluminium nitrate nonahydrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is a type of salts of strong acids and weak bases, when dissolved in water, produce a solution, which reacts acidic. Thus, when the salt is dissolved in distilled water, a hydrated aluminium ion would be produced from aqueous aluminium nitrate in the ion complex form of aluminium hexaaqua ion, where the reaction is as follows [27, 32]:



Whereas a salt of strong acid and strong base, magnesium nitrate hexahydrates ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), is hydrolyzed in water, the salt is completely ionized in the water solvent to form Mg^{2+} and NO_3^- [32].

However, the presence of sugar in the preparation reduces the tendency toward agglomeration in the as-synthesized MgAl_2O_4 spinel particles. The sugar has a sucrose structure consisting of a disaccharide molecule namely glucose and fructose. The structure contains hydroxyl and ether groups, whose hydrogen bond with

the hydroxyl groups of coordinated water molecules from the aluminum ion complex surfaces. As a result, the surface hydroxyl groups get capped with the sugars [29, 30]. Meanwhile, the magnesium ions of magnesium nitrates are coordinated bond to ether groups or free hydroxyl groups of sucrose molecules. The coordinated bond occurs due to the shared use of the free electron pair of the oxygen atom from the ether and free hydroxyl groups of sucrose with the magnesium ions. The sugar molecule coating on Al_2O_3 MgO particle surfaces results in reduced particle aggregation due to the steric hindrance provided by the sugars [27, 29]. All those bonding and reactions that occurred between metal nitrates with sugar in water medium are quite complex, however, can be assumed as follows:



Sugar, having a sucrose structure molecule, starts to decompose into glucose and fructose at 180 °C. When fructose and glucose start to break down into smaller during caramelization, more volatile compounds with different aroma are produced and detected by our sense of smell. They are the furans (have a nutty aroma), diacetyl (smells like butter), maltol (toasty), and ethyl acetate (fruity) [33]. Almost all the compounds contain the -OH and -COOH groups helping in binding the metal ions in the precursor mixture, which reduces the chances of agglomeration in the as-synthesized MgAl_2O_4 spinel particles [34, 35]. When the precursors of magnesium-aluminum-sugar were heated at higher temperatures of 200 °C, the precursors were being decomposed; leaving residual carbonaceous material, which undergone a combustion reaction in further heating and produced carbon dioxide and water vapor; and a large amount of heat was generated. [27, 29, 34, 35]. The outgoing gases prevent agglomeration, and form fine particles with high surface area in the final products [34].

Microstructures

Typical TEM bright field images of nanoparticles MgAl_2O_4 spinel after thermal treatment at 700 °C using a JEM-1400 120 kV TEM are shown in Fig. 2, showing an appreciable formation of agglomerates and the particle growth. The sizes of MgAl_2O_4 spinel particles are found to be less than 75 nm at a calcination temperature of 700 °C. Fig. 3 shows SEM micrographs

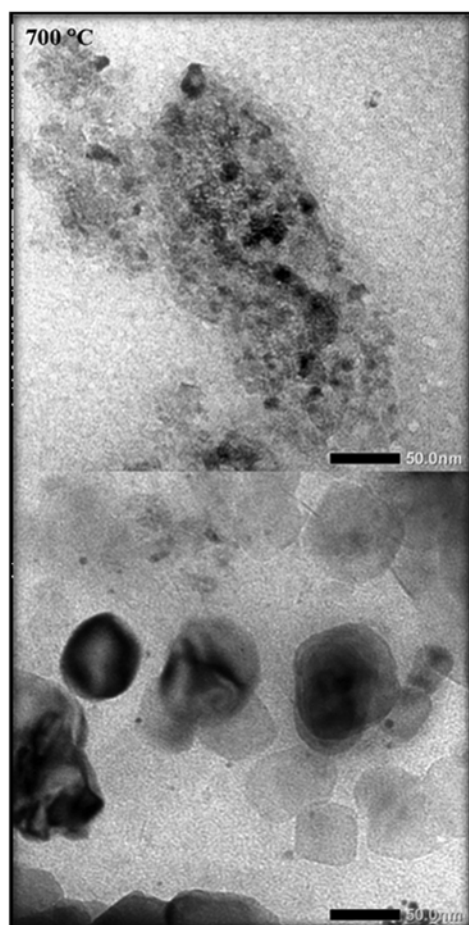


Fig. 2. Typical TEM bright field images of calcined MgAl_2O_4 spinel at a temperature of 700 °C

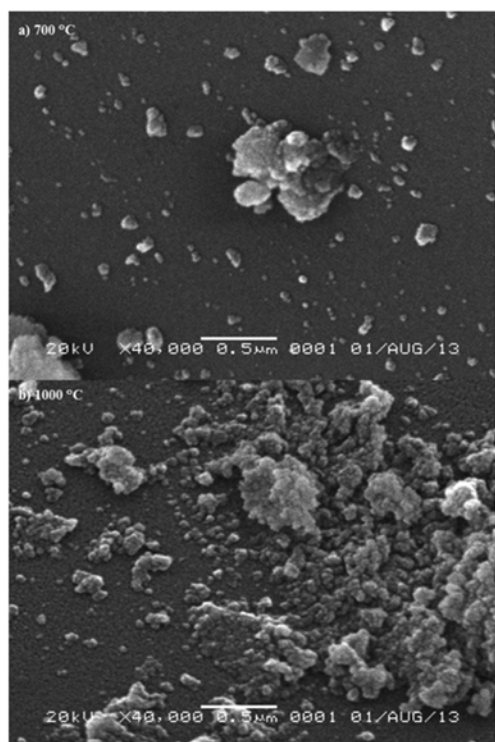


Fig. 3. SEM micrographs of calcined MgAl_2O_4 spinel at temperatures of 700 °C (a) and 1000 °C (b).

of calcined MgAl_2O_4 spinel at temperatures of 700 °C and 1000 °C using a JEOL JSM-35C SEM. High formation of agglomerates can be found in both calcined MgAl_2O_4 spinel particles at temperatures of 700 °C and 1000 °C. Nevertheless, according to the SEM results in Fig. 3, the particle sizes of the spinel sample at a calcination temperature of 1000 °C are below 100 nm. Nanoparticles with very tiny particle sizes, allow them to have large surface areas. Hence, they often agglomerate to form either lumps or secondary particles, in which refers to adhesion of the particles to each other. This phenomenon is due to *van der Waals* forces of attraction, which is significantly higher in nanoparticles. The agglomeration of nanoparticles occurs in order to minimize the interfacial energy of the system [36].

Conclusions

Nanoparticles MgAl_2O_4 spinel was successfully prepared using metal nitrate precursors and sugar as a masking-gel agent at a low temperature of 700 °C. Since sugar was used as a gelling agent in the spinel preparation, the metal nitrate precursors were found to crystallize completely as MgAl_2O_4 spinel at a low temperature of 700 °C having crystallite sizes below 15 nm. The microstructure analysis shows that the spinel powder after calcination at temperatures of 700 °C and 1000 °C having particle sizes less than 75 nm and 100 nm, respectively.

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