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A STUDY ON THE SYNTHESIS OF $MgAl_2O_4$ SPINEL BY STARCH ASSISTED SOL-GEL PROCESS

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ABSTRACT

In this paper, the synthesis of ceramic spinel $MgAl_2O_4$ by starch assisted sol - gel process is presented. The gel mixture was prepared by using $Mg(NO_3)_2.6H_2O$, $Al(NO_3)_3.9H_2O$ as precursors and starch as a gel agent. The study focused on relevant components of gel mixture and the calcinating temperature. The results showed that suitable molar proportion of Mg^{2+}/Al^{3+}; starch/(Mg^{2+} + Al^{3+}) and H_2O/starch were 0.5, 0.4 and 60, respectively. The calcination at 1100 ^oC for 60 minutes was suitable for forming phase of spinel. The product was a single phase of spinel $MgAl_2O_4$ with excellent crystallinity and uniform size in the range of 300 to 400 nm.

Keywords: spinel $MgAl_2O_4$, ceramic material, metal-starch precursor.

1. INTRODUCTION

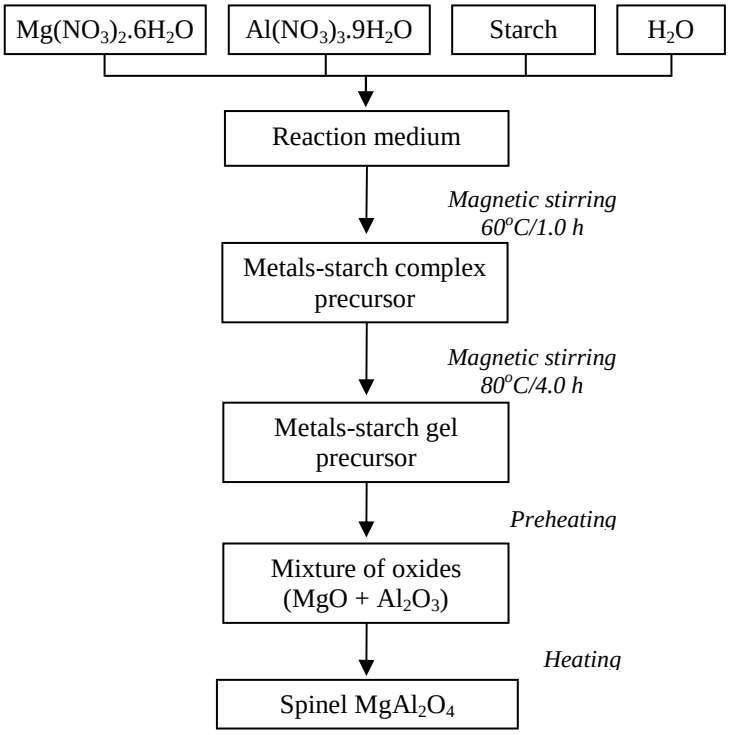
Spinel $MgAl_2O_4$ is stable compound consisted of MgO and Al_2O_3 constituents and has the face-centred cubic (FCC) lattice formed by oxygen ions. While Mg^{2+} cations occupy at centre of tetrahedron holes and Al^{3+} cations occupy at the centre of octahedron holes. Spinel $MgAl_2O_4$ has many wonderful chemical and physical properties such as mechanical endurance, chemical stability, thermal and electrical durability. In the past, spinel $MgAl_2O_4$ was an important ceramic material used for lining unburnable material, as substrate for thermal durable pigments in ceramic industry [1, 2].

Nowadays, spinel has many applications in manufacturing of filter-super ceramic membrane, electrical insulator and optical material. So, many studies have reported chemical and physical properties and applications of $MgAl_2O_4$ material paying special attention on its synthesis methods. There are some different ways to synthesize this material such as traditional ceramic method, coprecipitation, sol-gel and Pechini method [2, 3, 4, 5, 6, 9]. Among them, starch assisted sol-gel method exhibits such important advantage that Al^{3+}, Mg^{2+} cations are dispersed highly thanks to the formation of complex between these cations and -OH group from starch, and as a result, the spinel phase formation will take place at low temperature. This paper presents the synthesis of spinel $MgAl_2O_4$ by starch assisted sol-gel process.

2. EXPERIMENTS

The chemicals used in this work were $Mg(NO_3)_2.6H_2O$, $Al(NO_3)_3.9H_2O$ and dissolved starch (QuangZu, China). The molar ratio of Mg^{2+}/Al^{3+} in the synthesized mixture was fixed at 0.5. Two other ratios of starch/(Mg^{2+} + Al^{3+}) and H_2O/starch would be changed in the survey. The heating process included two stages: the first step was at 60 – 70 ^oC for 1 hour with the aim of hydrolyzing starch, and the second one was at 80 – 90 ^oC for 3 - 4 hours and stirred in order to evaporate water slowly until the mixture became viscous and gel of metal-starch precursor was formed. The gel was dried at 105^oC till stable mass. For the purpose of completely burning starch, the gel after drying was preheated. After that, the obtained mixture was grinded and pressed into cylinder shape with the diameter of 30 mm and the thickness of 5 mm by hydraulic press with the compression of 300 $kG.cm^{-2}$ (Danir, Denmark). Then, the sample was sintered in furnace (Lennton, England) at suitable temperature.

The synthesis of pigment was processed as shown in Schema 1.



Schema 1. The diagram of the synthesis of pigment by starch assisted sol-gel process.

The obtained material was characterized by thermal analysis (TG-DSC) using Labsys TG/DSC Setaram (France) in ambient atmosphere with the maximum temperature of 800 ^oC, heating rate of 10 $^oC.min^{-1}$.

Crystal phase of the sample was determined by X-ray diffraction (XRD) using Brucker D8 Advance with $\lambda_{CuK\alpha}$ = 1,5406 Å.

The crystallite size, D of spinel was calculated by Scherrer's equation [6]:

$$D = \frac{0,9\lambda}{FWHM \times \cos\theta}$$

where λ is the X wavelength (Å), θ is the diffraction angle (rad) of the (311) peak with highest intensity and FWHM is the abbreviation of full width at half maximum of diffraction peak.

IR spectrum of the sample was analyzed on IRPrestige-21 (Shimadzu, Japan). Morphology of obtained sample was observed by scanning electron microscope (SEM) using Hitachi S4800 (Japan).

3. RESULTS AND DISCUSSION

As the ratio of H_2O/starch was too high the gel would be dilute resulting a long time for evaporation of water, reverse the gel would be too viscous to stir.

Four samples with the molar ratio of Mg^{2+}/Al^{3+} = 0.5; starch/(Mg^{2+} + Al^{3+}) = 0.4 and H_2O/starch increased from 50 to 80 corresponding with the notations from A1 to A4 were prepared as shown in Table 1.

Table 1. The initial composition of samples with different molar ratio of H_2O/starch.

Notation	Starch/M^{n+}	H_2O/starch	Percentage composition (w/w)			
			$Mg(NO_3)_2.6H_2O$	$Al(NO_3)_3.9H_2O$	Starch	H_2O
A1	0.4	50	11.2	32.9	8.5	11.2
A2	0.4	60	10.3	30.0	7.8	10.3
A3	0.4	70	9.5	27.7	7.2	9.5
A4	0.4	80	8.8	25.6	6.6	8.8

(M^{n+} = Mg^{2+} + Al^{3+}).

The results showed that as the molar ratio of H_2O/starch was 50, the obtained gel was too viscous to stir, whereas it was rather dilute if this ratio increased to 70 and 80, so, it took a long time to evaporate water. Therefore, the molar ratio of H_2O/starch = 60 was to select for further surveys.

Table 2. The initial composition of samples with different molar ratio of starch/(Mg^{2+} + Al^{3+}).

Notation	Starch/M^{n+}	H_2O/starch	Percentage composition (w/w)			
			$Mg(NO_3)_2.6H_2O$	$Al(NO_3)_3.9H_2O$	Starch	H_2O
B1	0.3	60	12.1	35.3	6.9	45.8
B2	0.4	60	10.3	30.0	7.8	51.9
B3	0.5	60	8.9	26.1	8.5	56.5
B4	0.6	60	7.9	23.1	9.0	60.0
B5	0.7	60	7.1	20.8	9.4	62.7

The molar ratio of starch/(Mg^{2+} + Al^{3+}) could effect on the formation of precursor. So, in order to determine the most suitable value, five samples possessed the molar ratio of Mg^{2+}/Al^{3+} = 0.5, H_2O/starch = 60 and starch/(Mg^{2+} + Al^{3+}) increased from 0.3 to 0.7 corresponding with the notations from B1 to B5 were prepared. The initial compositions of the samples are shown in Table 2.

The images of samples after preheating at 500 ^oC shown in Figure 2 indicate that the samples of B3, B4 and B5 were gray. The reason is because starch was burned uncompletely, so there was a large amount of starch existed in precursor. On the contrary, samples of B1 and B2 after being sintered at 1100 ^oC were light white. However, we chose the molar ratio of starch/M^{n+} = 0.4 corresponding with B2 sample because the gel from this sample was more viscous than B1 sample.

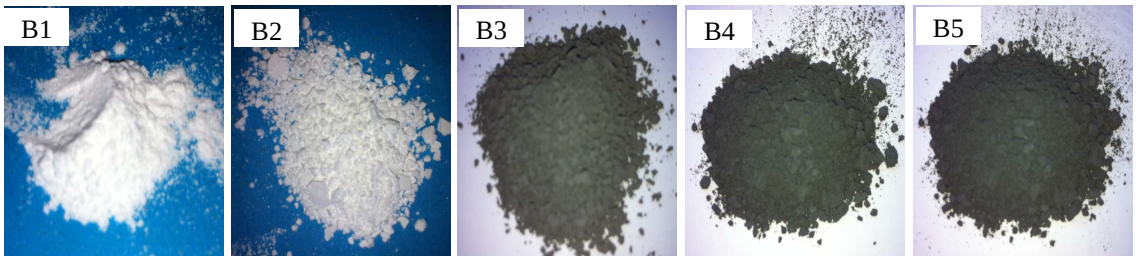


Figure 2. Samples images after preheating at 500 ^oC for 1 hour.

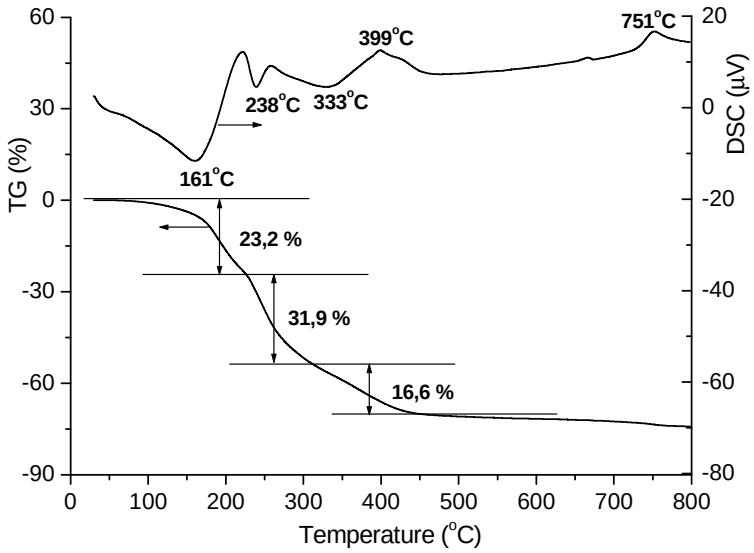


Figure 3. TG-DSC diagram of metals-starch gel precursor.

DSC-TG diagram of B2 sample is presented in Figure 3. As can see, there was a strong endothermic peak in the range from room temperature to 160 ^oC with the weight loss of 23.2 %. This corresponded with the physical-water evaporation and the water seperation from -OH groups on the surface of material [7, 9]. Next, there were endothermic peaks at 238^oC and 333^oC and exothermic peak at 399 ^oC with the total weight loss of 32 %. This might be originated from the decomposition of nitrate salts, the burning of precursor and abundant starch, respectively. In the temperature range from 450 ^oC to 800 ^oC, we could see an exothermic peak at 751 ^oC

corresponding with spinel formation from MgO and Al_2O_3 creating from the decomposition of precursor. The weight loss in this period was negligible, about 2.4 % and we predict that nitrate salt continued to decompose, precursor and abundant starch continued to combust completely. From above-mentioned, we chose the preheating and spinel forming temperatures to be of 500 ^oC and 800 ^oC.

With the aim of determination of suitable sintering temperature, we calcinated the sample at various temperatures 900, 1000 and 1100 ^oC for 1.5 hours with the heating rate of 10 $^oC.min^{-1}$. The notations of samples were PTB900, PTB1000 and PTB1100. XRD patterns are shown in Figure 4. The characteristic peaks of spinel at $2\theta = 19.03^o$ (d_{111}); 31.32^o (d_{220}); 36.87^o (d_{113}); 44.83^o (d_{400}); 59.43^o (d_{115}); 65.29^o (d_{440}) were observed with high intensity at 900^{o}C while characteristic peaks of MgO and Al_2O_3 were not appeared, indicating that the formation of spinel took place completely. The values of FWHM, I and D of samples are shown in Table 3. As the calcinated temperature increases from 900 to 1100 ^oC the intensity of diffraction peaks of spinel increases significantly, the value of FWHM reduced rapidly from 0.652^o to 0.175^o and the value of D increased promptly from 13 to 47 nm.

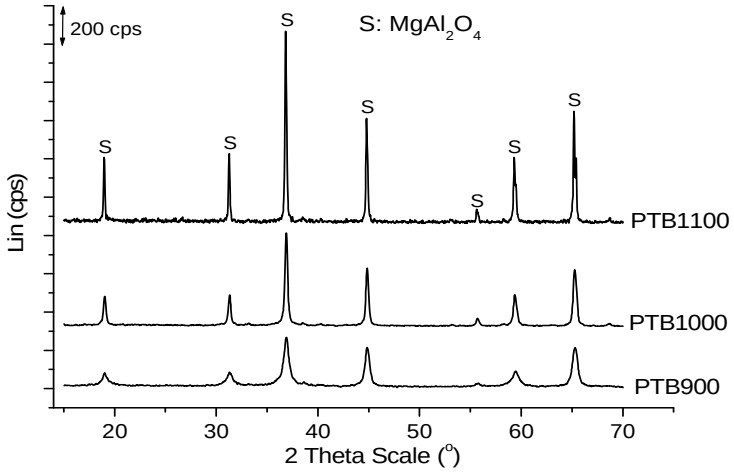


Figure 4. XRD diagram of spinel $MgAl_2O_4$.

Table 3. The value of FWHM, diffraction intensity (I) and crystallite size (D) of spinel samples.

Notations	FWHM (^{o})	I (cps)	D (nm)
PTB900	0.652	268	13
PTB1000	0.311	493	27
PTB1100	0.175	743	47

When increasing the temperature from 900 to 1100 ^oC, the crystalization of spinel took place strongly, Mg^{2+} and Al^{3+} cations diffused contrariwise through spinel layer according to Wagner mechanism [1]. At 1100 ^oC, the single phase of spinel $MgAl_2O_4$ was obtained with high crystalinity.

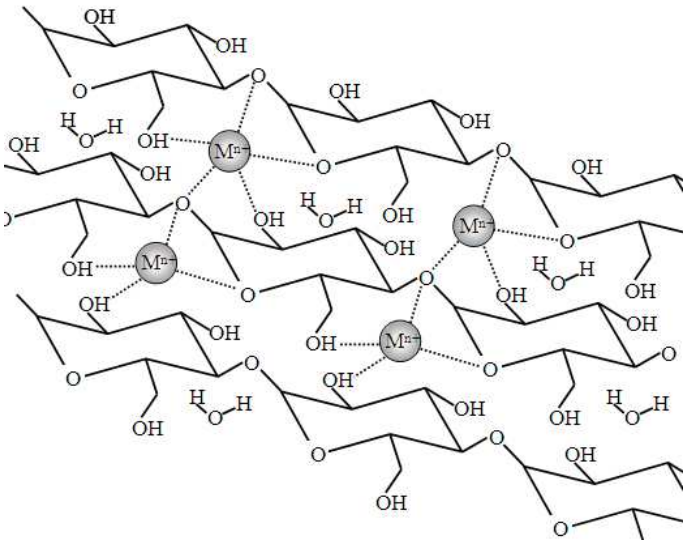


Figure 5. The structure of metals-starch gel precursor [9].

According to traditional ceramic method in study of Kong and coworkers [5], the initial mixture contained MgO and Al_2O_3 were sintered at the temperature from 900 to 1300 ^oC for 120 minutes, the obtained material was multi-phase including spinel and corundum. Only with the sinterned temperature higher than 1400^oC, the sample exhibited single phase of spinel.

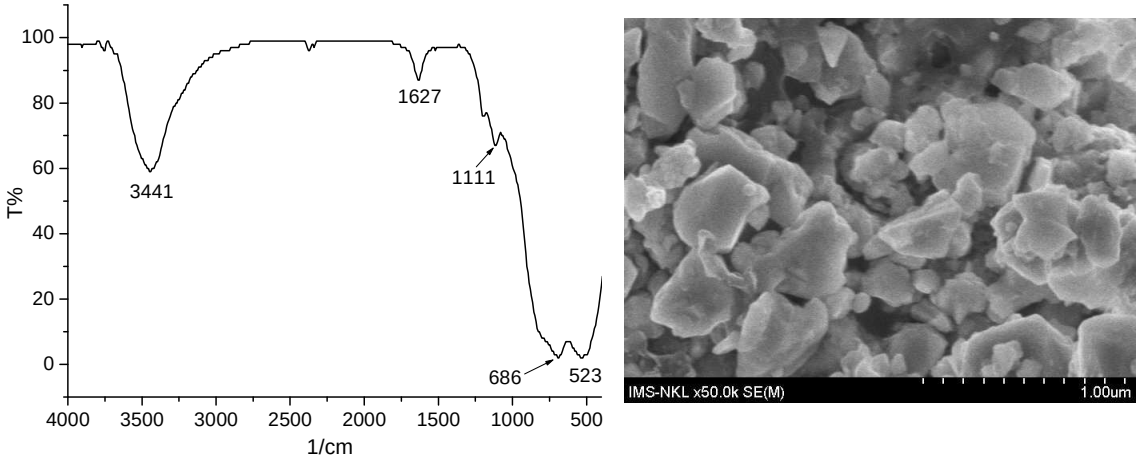


Figure 6. FTIR spectrum and SEM image of spinel $MgAl_2O_4$.

As can see, by starch assisted sol-gel method, solid phase reaction between MgO and Al_2O_3 took place favourably, the formation of spinel phase occured at low temperature. Hence, the sintering temperature could be lower in comparison with that by traditional ceramic method. This could be explained by the fact that dissolved state (amilose) of starch had kinky polymer chain structure with 3 –OH group for each link and they played three main roles: (i) ligand of the complex formation bewteen OH group and metal cations, (ii) structure directing agent and (iii) formed gel when heating because it could dissolve in water completely. This helped metal

cations disperse highly and the surface area bewteen MgO and Al_2O_3 was increased resulting solid phase reaction took place favourably (Figure 5) [4, 6, 7, 9].

IR spectrum of spinel $MgAl_2O_4$ is demonstrated in Figure 6. The band around wave numbers of 3441 and 1627 cm^{-1} corresponds to stretching and bending variations of water molecule adsorped on the surface of sample. Besides, the bands around wave number of 686 and 523 cm^{-1} corresponding with symmetrical valence variation inside octahedrons [AlO_6] and lattice variation of Mg-O bond extension. This met well with the study of Nassar and coworkers [6]. SEM image of $MgAl_2O_4$ is shown in Figure 6. That particles were agglomerated and formed large particle with the size in the range of 300 - 400 nm. This size is larger used in comparision with crystallite size calculated from Scherrer's equation (about 47 nm) suggesting that particles on SEM image may consists of many crystallite particles.

4. CONCLUSION

Spinel $MgAl_2O_4$ material was synthesized successfully by starch assisted sol-gel method. Main advantage of this way was the sintering temperature was much lower than that used in traditional ceramic method. The suitable conditions were the molar ratio of Mg^{2+}/Al^{3+} = 0.5; starch/(Mg^{2+}+Al^{3+}) = 0.4; H_2O/starch = 60; hydrolyzing temperature was 60 – 70 ^oC; gelation temperature was 80 – 90 ^oC. The gel was preheated at 500 ^oC for 1.0 hour and sintered at 1100 ^oC for 1.0 hour. The obtained product was characterized by modern method such as XRD, TG-DSC, FTIR and SEM. The results showed that spinel $MgAl_2O_4$ material consists of particles in nanoscale. The obtained spinel is of single phase with high crystallinity.

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TÓM TẮT

NGHIÊN CỨU TỔNG HỢP VẬT LIỆU GỐM SPINEL $MgAl_2O_4$ BẰNG PHƯƠNG PHÁP SOL-GEL CÓ SỰ HỖ TRỢ CỦA TINH BỘT

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Bài báo trình bày kết quả tổng hợp vật liệu gốm spinel $MgAl_2O_4$ bằng phương pháp sol-gel có sự hỗ trợ của tinh bột. Hỗn hợp gel được chuẩn bị từ $Mg(NO_3)_2.6H_2O$, $Al(NO_3)_3.9H_2O$ và tinh bột tan. Các điều kiện tổng hợp bao gồm: tỷ lệ mol H_2O/tinh bột; tỷ lệ mol tinh bột/(Mg^{2+} + Al^{3+}) và nhiệt độ nung đã được khảo sát. Kết quả cho thấy với thành phần phối liệu có các tỷ lệ mol Mg^{2+}/Al^{3+} = 0,5; tinh bột/(Mg^{2+} + Al^{3+}) = 0,4; H_2O/tinh bột = 60 và nhiệt độ nung thiêu kết 1100 ^oC trong 60 phút, sản phẩm thu được hoàn toàn đơn pha tinh thể spinel $MgAl_2O_4$, kích thước hạt cỡ 300 - 400 nm.

Từ khóa: spinel $MgAl_2O_4$, vật liệu gốm, tiền chất kim loại - tinh bột.