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The effects of processing parameters on formation of nano-spinel ($MgAl_2O_4$) from LiCl molten salt

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Abstract

Nano-$MgAl_2O_4$ particles were successfully synthesized at 850 °C using the molten-salt method, and the effects of processing parameters, such as temperature, holding time and amount of salt on the crystallization of $MgAl_2O_4$ were investigated. Nano-alumina, magnesia and lithium chloride were used as starting materials. LiCl molten salt provided a liquid medium for reaction of Al_2O_3 and MgO to form $MgAl_2O_4$. The results demonstrated that $MgAl_2O_4$ started to form at about 650 °C and that, after the temperature was increased to 1000 °C, the amounts of $MgAl_2O_4$ in the resultant powders increased with a concomitant decrease in Al_2O_3 and MgO contents. After washing with hot-distilled water, the samples heated for 3 h at 850 °C were single-phase $MgAl_2O_4$ with 30–50 nm particle size. Furthermore, the synthesized $MgAl_2O_4$ particles retained the size and morphology of the Al_2O_3 powders, which indicated that a template formation mechanism dominated the formation of $MgAl_2O_4$ by molten-salt method.

Keywords: Molten salt method; Nano-materials; Nano-spinel; Template growth

1. Introduction

Magnesium aluminate, $MgAl_2O_4$ (MA), is an important candidate as a refractory raw material because of its superior physical and chemical properties such as high melting point (2135 °C), low thermal conductivity, high strength at room and elevated temperatures and good corrosion resistance [1]. This material has potential to be used as catalyst support in petrochemical industries for alkane dehydrogenation [2,3], methane oxidation [4] and catalyst support [5]. Solid-state synthesis is the conventional route to produce the $MgAl_2O_4$ spinel from reaction between MgO and Al_2O_3 as primary materials. This reaction occurs by the diffusion of Al^{3+} toward MgO and Mg^{2+} toward Al_2O_3, forming a spinel layer which acts as a barrier layer against the diffusion agents [1,6,7]. Therefore, the formation of spinel by solid-state reaction requires high temperature (~1400 °C) and long time firing conditions. Other synthesis techniques like sol–gel of metal alkoxides, co-precipitation and combustion synthesis have also been applied for synthesis of MA spinel [8–10]. However, these routes suffer from complexity, unfriendly environment, reproducibility and expensive precursors [11–13].

Molten-salt synthesis (MSS) is appreciated as a straightforward method for the preparation of ceramic powders with whisker-like, needle-like or plate-like morphologies [14–17]. This synthesis technique is a well-established process of forming a target compound in a flux with a low melting point [18–20]. MSS offers a significant reduction in the formation temperature compared to a conventional solid-state reaction. It also provides noticeable control of the particle size and morphology of the resulting powders [21,22].

The molten-salt synthesis method is based on the use of salts with low melting points that are water soluble, such as alkali chlorides and sulfates, for the synthesis of ceramics. This method avoids leaving high levels of impurities in the final product powder [18,20,23]. Numerical studies of the MSS technique are available in the literature that involve the preparation of ferroelectrics, dielectrics, piezoelectrics, pyroelectrics, spinel and mullite using various alkali salts [24–26].

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The selection of an appropriate salt significantly influences the ability of the reaction to produce desirable powder morphologies and characteristics. The selection of the salt is highly dependent on two criteria: the melting point of the salt should be low and appropriate for the synthesis of the required phase, and the salt should exhibit sufficient aqueous solubility to be easily eliminated by a simple washing after the synthesis [20]. In the present paper, the molten-salt synthesis method was used for preparation of nano-crystalline $MgAl_2O_4$. Also, the effects of processing parameters such as temperature, holding time and amount of salt on the synthesis of nano-crystalline $MgAl_2O_4$ were studied.

2. Experimental procedure

Nano-alumina (γ-Al_2O_3, Ionic Liquid Technologies, 99.9% pure, $D_{50}=20$ nm), magnesia (MgO, Merck, Germany, 99% pure, $D_{50}=3$ μm) and lithium chloride (LiCl, Merck, 99% pure) were used as starting materials. Firstly, stoichiometric compositions of MgO and LiCl were completely mixed and then heated at 150 °C for 12 h to dry. Agglomerated nano-Al_2O_3 particles were dispersed in distilled water and its pH was controlled at 9.5 using nitric acid. To increase dispersion, the suspension was placed for 1 h in ultrasonic probe. Then, MgO–LiCl mixture was added to completely dispersed nano-Al_2O_3 and the obtained mixture was stirred 1 h to homogenize extremely. The mixture was fully dried at 120 °C for 12 h. Agglomerations of obtained powder' that is a completely homogeneous mixture, were broken using an agate mortar and then sifted to pass through a 325 mesh screen (45 μm). Finally, the mixture (20 g) was placed in an alumina crucible covered with an alumina lid, heated to 650, 700, 850 and 1000 °C and held for 0.5, 1, 3 and 5 h. For investigation of the effect of salt to oxide ratio on the synthesis process, the samples were heated at optimum temperature with 3:1, 5:1 and 7:1 salt to oxide ratios. The heating and cooling rates were 3 °C/min and 5 °C/min, respectively. After cooling to room temperature, the solidified mass was washed and filtered in hot-distilled water five times to remove the salts. Then, the obtained powder was dried at 120 °C for 4 h. The phase formation, morphology and elemental analysis of the synthesized powders were characterized via X-ray diffraction (XRD, Philips pw3710), scanning electron microscopy (SEM, Tescan Vega II) and X-ray fluorescence (XRF, Philips 2404), respectively.

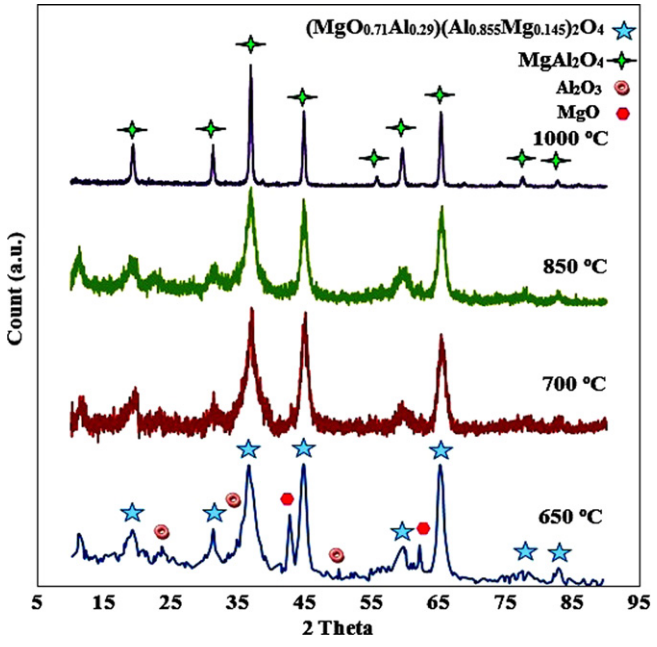

Fig. 1. XRD patterns of the samples (water washed) heated for 3 h at different temperatures.

3. Results and discussion

3.1. Effect of temperature

Fig. 1 shows XRD patterns of the samples heated for 3 h at different temperatures. It is obviously observed that the optimum temperature for these samples is 850 °C. At this temperature, the samples were single-phase $MgAl_2O_4$ and Al_2O_3 and MgO peaks were not observed. In other words, Al_2O_3 and MgO were completely transformed to $MgAl_2O_4$. At temperatures above 850 °C, the samples were likewise single-phase $MgAl_2O_4$ and just their crystallinity was increased. This object was confirmed by means of increase in peaks intensity. At 1000 °C, the peaks intensity was insignificantly decreased and peaks became partly wider that can be attributed to acceding decomposition temperature of $MgAl_2O_4$. Thus, increase in temperature was a very effective factor for completion of synthesis process.

Energy dispersive X-ray spectroscopy (EDS) micrograph of the samples heated at 850 °C for 3 h shown in Fig. 2 confirms

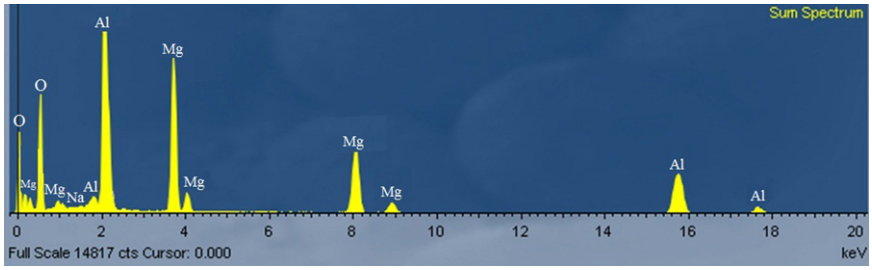

Fig. 2. EDS micrograph of the samples heated at 850 °C for 3 h.

that optimum temperature for synthesized samples is 850 °C. As seen, almost only [Mg], [Al] and [O] elements were observed and other elements were eliminated.

3.2. Effect of holding time

Fig. 3 provides XRD patterns of the samples heated for different holding times at 850 °C. It is seen that optimum holding time for these samples is 3 h. In this holding time, synthesis process was completed and the samples were single-phase $MgAl_2O_4$ and Al_2O_3 and MgO peaks were not observed. In holding times 0.5 h and 1 h, Al_2O_3 and MgO peaks were seen in addition to $MgAl_2O_4$ peaks. In other words, synthesis process was not completed. In holding time 5 h, the samples were likewise single-phase $MgAl_2O_4$ and only their peaks intensity was insignificantly increased compared with holding time 3 h, which means that their crystallinity was venially increased. Thus, increase in holding time before optimum holding time was an effective factor for completion of synthesis process and after this holding time did not have a significant effect.

3.3. Effect of salt amount

XRD patterns of the samples heated with different salt to oxide ratios at 800 °C and for 3 h have been shown in Fig. 4. It can be deduced that the optimum salt to oxide ratio is 5:1, because synthesis process was completed in this salt to oxide ratio. In salt to oxide ratio 3:1, the samples still did not become single-phase $MgAl_2O_4$ and it is necessary to increase salt to oxide ratio for completion of the synthesis. With increase in salt to oxide ratio 5:1 to higher values, the samples remained single-phase $MgAl_2O_4$ and further increase in salt to oxide ratio caused more increase in peaks intensity and crystallinity property. Thus, the increase in salt to oxide ratio was a very effective factor for completion of synthesis process.

3.4. Particle size

Fig. 5 shows SEM micrographs of the samples synthesized for 3 h at different temperatures. As seen, the particle size of $MgAl_2O_4$ synthesized at 650, 700 and 850 °C was in the range of 30–50 nm, whereas the particle size of $MgAl_2O_4$ synthesized at 1000 °C was in the range of 70–80 nm which can be attributed to acceding grain growth phenomenon that starts at above 1000 °C.

3.5. Salt assembly and molten salt synthesis of $MgAl_2O_4$

According to the thermodynamic prediction, reaction 1 starts at about 648 °C [27]. At above this temperature, LiCl salt melts and provides a liquid medium for reaction 1. With increase in temperature to 850 °C, LiCl salt completely melts and rate of reaction 1 becomes maximum. Due to very high reactivity of nano-size Al_2O_3, synthesis of $MgAl_2O_4$ was completed at 850 °C.

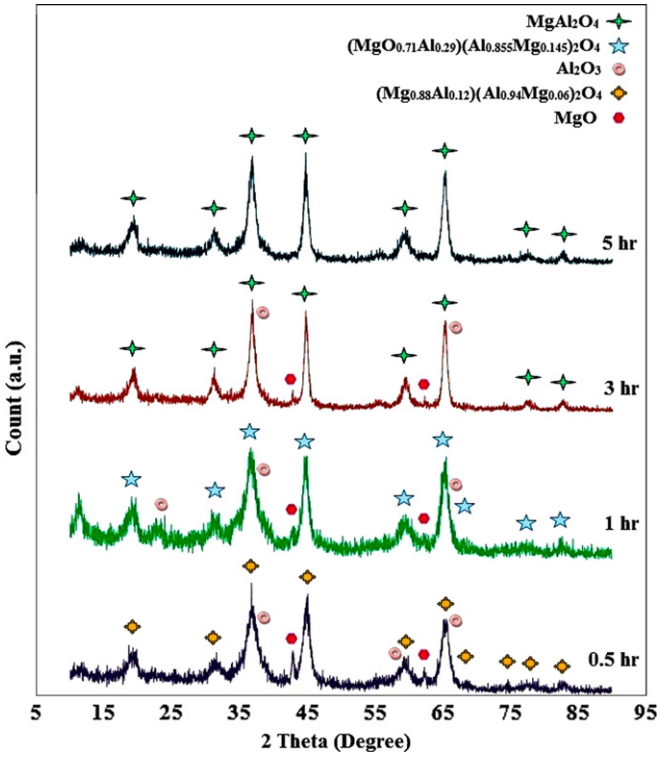

Fig. 3. XRD patterns of the samples (water washed) heated at 850 °C with different holding times.

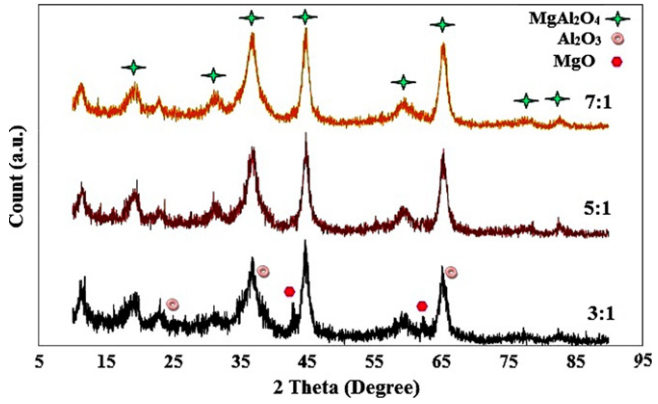

Fig. 4. XRD patterns of the samples (water washed) heated at 850 °C for 3 h with different salt to oxide ratios.

$$Al_2O_3 + MgO = MgAl_2O_4 \quad (1)$$

$$\Delta G^0 = 283,700 - 438T$$

To understand the reaction mechanisms, the whole synthesis process of $MgAl_2O_4$ discussed above has schematically been illustrated in Fig. 6.

3.6. $MgAl_2O_4$ synthesis mechanism

Two main mechanisms, "template-growth" and "dissolution–precipitation", were involved in MSS. Solubility of reactants in the molten salt plays an important role in MSS.

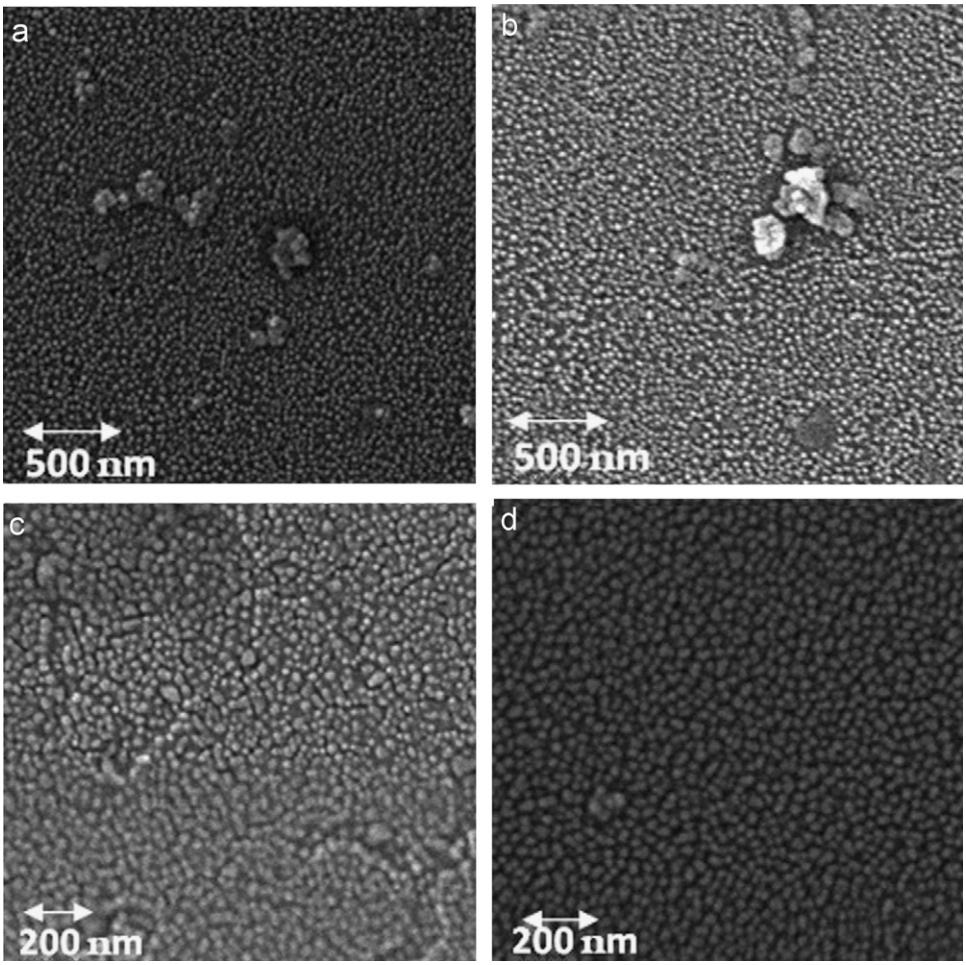

Fig. 5. SEM micrographs of the samples synthesized for 3 h at (a) 650 °C, (b) 700 °C and (c) 850 °C and (d)1000 °C.

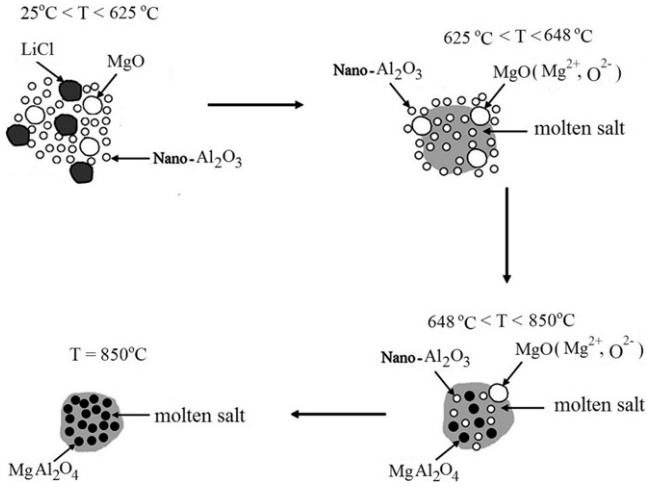

Fig. 6. Schematic diagram illustrating the synthesis of $MgAl_2O_4$ powder by heating nano-Al_2O_3, MgO and LiCl.

This not only affects the reaction rate but also the morphologies of the synthesized particles. If both of the reactants are soluble in the molten salt, then the product phase will be readily synthesized via precipitation from the salt containing the dissolved reactants (dissolution–precipitation mechanism). In this case the morphologies of the product grains will generally be different from those of the reactants. On the other hand, if one of the reactants is much more soluble than the other, the more soluble reactant will dissolve into the salt first and then diffuse onto surfaces of the less soluble reactant and react in situ to form the product phase. In this case, the morphology of the synthesized grain will retain the less soluble reactant (template-growth mechanism) [28].

According to Refs. [29,30], solubility of MgO in a chloride molten salt is higher than that of Al_2O_3. Therefore, during the MSS process, MgO would be dissolved more in the LiCl molten salt and react with Al_2O_3 templates to form $MgAl_2O_4$. This explains the similarity between the grain shapes of the synthesized $MgAl_2O_4$ and original Al_2O_3 powder. The morphology and particle size of the synthesized $MgAl_2O_4$ grains were similar to Al_2O_3 grains which means that the "template-growth" mechanism has played a dominant role in the low temperature molten salt synthesis of $MgAl_2O_4$ particles (Fig. 7).

The particle size distributions of Al_2O_3 and $MgAl_2O_4$ measured via the DLS method have been illustrated in

Figs. 8 and 9, respectively. Since particle size distributions of Al_2O_3 and $MgAl_2O_4$ have been centralized in the range of 20–30 nm and 40–50 nm, respectively, "template-growth" mechanism was confirmed.

The chemical composition of product powders determined via XRF analysis has been shown in Table 1. As seen, only minor salt components remained in the synthesized $MgAl_2O_4$ powders after washing. The main objective of this table is to illustrate the feasibility of the molten-salt method for the synthesis of pure ceramic powders.

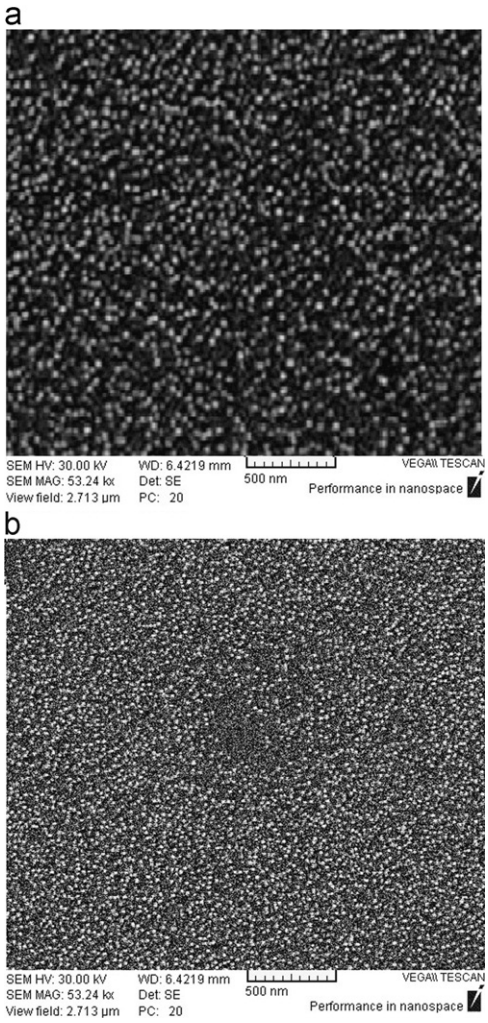

Fig. 7. SEM micrographs of (a) nano-Al_2O_3 and (b) synthesized $MgAl_2O_4$.

4. Conclusions

1. Nano-size magnesium aluminate powders were synthesized via the molten salt method. MgO, LiCl and nano-Al_2O_3 were used as starting materials.

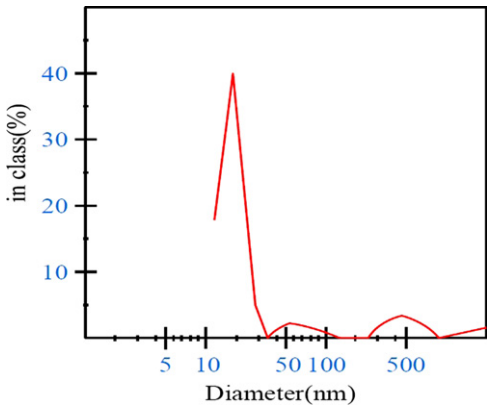

Fig. 8. Particle size distribution curve of nano-Al_2O_3.

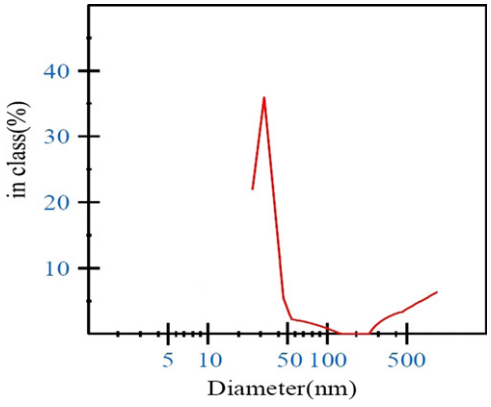

Fig. 9. Particle size distribution curve of synthesized nano-$MgAl_2O_4$.

Table 1
Chemical composition of synthesized $MgAl_2O_4$ in different reaction conditions.

Weight percent					Reaction condition		
Cl	Li	O	Al	Mg	Salt to oxide ratio	Time (h)	Temperature (°C)
0.12	0.09	57.02	28.51	14.26	5:1	3	650
0.10	0.07	57.23	28.84	13.76	5:1	3	700
0.13	0.09	57.14	28.73	13.91	5:1	3	850
0.09	0.08	56.88	28.92	14.03	5:1	3	1000
0.11	0.07	57.18	29.05	13.59	5:1	0.5	850
0.10	0.08	57.17	29.03	13.62	5:1	1	850
0.13	0.09	57.20	29.05	13.53	5:1	5	850
0.15	0.12	57.15	29.01	13.57	3:1	3	850
0.16	0.12	57.13	28.98	13.61	7:1	3	850

2. Optimum temperature for samples was 850 °C that was significantly lower than that required by the solid state method. Increase in temperature was a very effective factor for completion of synthesis process.
3. Optimum holding time for samples was 3 h. Increase in holding time significantly did not affect synthesis process.
4. Optimum salt to oxide ratio for samples was 5:1 (stoichiometry ratio). Increase in salt to oxide ratio resulted in increase in the crystallinity property. Also, increase in salt to oxide ratio was an effective factor for completion of synthesis process.
5. Particle size of synthesized $MgAl_2O_4$ was 30–50 nm. At above 1000 °C, grain growth phenomenon caused increase in particle size.
6. Similarity of morphology and particle size of synthesized $MgAl_2O_4$ to Al_2O_3 grains showed that ''template-growth'' was the dominant mechanism in synthesis process.
7. Very minor salt components remained in the synthesized powders showing that very pure nano-$MgAl_2O_4$ was formed from LiCl molten salt.

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