Materials Research. 2013; 16(4): 844-849
DOI: 10.1590/S1516-14392013005000062

Thermal Stability and Microstructure Characterization of $MgAl_2O_4$ Nanoparticles Synthesized by Reverse Microemulsion Method

***Ping Fu*[a,b,c], *Wenzhong Lu*[a,c]*, *Wen Lei*[a,c], *Ke Wu*[b], *Yong Xu*[b], *Jiamin Wu*[a,c]**

[a]*Department of Electronic Science and Technology,*
HuaZhong University of Science & Technology – HUST, Wuhan 430074,China
[b]*Department of Materials Science and Engineering,*
Wuhan Institute of Technology – WIT, Wuhan 430073,China
[c]*Key Lab of Functional Materials for Electronic Information(B) MOE,*
HuaZhong University of Science & Technology – HUST, Wuhan 430074,China

Received: May 25, 2012; Revised: January 3, 2013

Magnesium aluminate ($MgAl_2O_4$) spinel nanoparticles were synthesized by reverse microemulsion process in cyclohexane by using two kinds of surfactants, n-amyl alcohol as cosurfactant and mixture of aluminic/magnesic salt aqueous solution as basic reagents. The effects of surfactant types and titration methods on the morphologies and sizes of the $MgAl_2O_4$ nanoparticles were characterized by TEM, TGA-DTA, XRD, HR-TEM and FT-IR. TEM images show that the particles prepared by forward-titration method with SPAN-80/Triton X-100 compound emulsifier have uniform spherical shape and good monodispersity with an average size of 9.5 nm. However, the average size of the particles prepared by reverse-titration method was about 10 nm and some particles have irregular platelike appearance. The products prepared with NP-40 surfactant and forward-titration method were agglomerated with an average size of 13 nm. TGA and XRD results show that the reverse microemulsion method has dramatically lowered the calcination temperature of $MgAl_2O_4$ with a degree of 700 °C, and the precursor can transform to single spinel phase at 900 °C.

Keywords: *$MgAl_2O_4$, spinel nanoparticles, reverse microemulsion, microstructure analysis*

1. Introduction

Due to the excellent refractoriness (melting point ~2135 °C), good thermal shock resistance, high-mechanical strength at elevated temperatures, and chemical inertness, $MgAl_2O_4$ become gradually the first choice in many structural, chemical and electrical applications[1,2]. Besides, it also has a very important application in transparent ceramic fabrication. Transparent $MgAl_2O_4$ ceramic has been considered as a high-quality optical material and attracted a growing interest from both defense and civil industries such as infrared domes and window for high temperature, optical lenses, laser host materials and optical heat exchangers[3,4].

In the preparation of the high-performance transparent ceramic, the qualities of starting powders are very important. The successful fabrication of dense transparent ceramics needs powders with the following features: highly dispersed, no hard agglomeration, small particle size with narrow distribution and high sinterability[4]. The preparation of $MgAl_2O_4$ powders by classical solid-state reaction requires a high calcination temperature (~1600 °C) and long reaction time, so that the powders suffer from low sinterability and agglomeration, which makes it difficult to fabricate transparent ceramics[5]. Therefore, some wet-chemical methods like co-precipitation[6], mechanochemical method[7], molten salt method[8], citrate-nitrate combustion[9,10] and sol-gel process[11,12] have been used for the synthesis of nanosized $MgAl_2O_4$. Although nanosized particles could be produced by means of these synthesis routes, it is hard to achieve the falicity of tuning particle size and morphology. Besides, most of the methods described above need use expensive equipment.

In recent years, reverse microemulsion method has been widely used to synthesize inorganic oxide nanoparticles owing to its inherent advantages such as demanding no extreme pressure or temperature control, easy handling, no requiring for special equipment, and achieving products with a characteristic of good dispersion with controlled size and narrow size distribution[13-15]. However, the synthesis of $MgAl_2O_4$ nano-powders by the microemulsion technology has seldom been reported. Recently, Christy et al.[16] synthesized $MgAl_2O_4$ nanoparticles using normal microemulsion method and adjusted the metal cation concentration to control nanoparticles size. Chandradass et al.[17] prepared $MgAl_2O_4$ nanoparticles *via* reverse microemulsion process and studied the influence of water to surfactant molar ratio (R) on the particle size of $MgAl_2O_4$ powder. In the present work, nanosized $MgAl_2O_4$ powders were synthesized *via* reverse microemulsion method and the effects of different surfactants and titration methods on the particle size and morphology were investigated. The influences of particle size and morphology on the sinterability of $MgAl_2O_4$ transparent ceramics were further studied.

---

*e-mail: lwz@mail.hust.edu.cn

2. Material and Experimental Method

2.1. *Preparation of $MgAl_2O_4$ nanopowders*

Two types of microemulsion were used to prepare $MgAl_2O_4$ nanoparticles. The experimental process is shown in Figure 1. All chemicals were of analytic reagent and used as received. Magnesium nitrate and aluminum nitrate salts with molar ratio (Mg^{2+}/Al^{3+}) of 1:2 were dissolved in deionized water to a concentration of 1M. Two types of surfactant system were used: one was a mixture of SPAN-80 (Sorbitan monooleate) and Triton X-100 (polycthylene glycol octylphenyl ether) as compound emulsifier with a hydrophile-lipophile balance value (HLB) of 8.2, the other was NP-40 (nonyl phenoxypolyethoxylethanol, HLB is 17.5). Cyclohexane and n-amyl alcohol were used as oil phase and cosurfactant, respectively. The surfactant and cosurfactant were mixed in cyclohexane by vigorous stirring until the mixture became light yellow transparent liquid. Two parts of microemulsions were prepared. In part A, 15 mL mixture of aqueous solution of Al $(NO_3)_3$ and Mg $(NO_3)_2$ were added into one part of the mixture and stirred to form a transparent microemulsion and the molar ratio (R) of water to surfactant was maintained at 4. In the same way, the adequate ammonia was added into the other part of mixture and stirred to form a transparent microemulsion (part B). Subsequently, forward-titration or reverse-titration method were adopted to mix these two kinds of microemulsions (Figure 1). During the mixing a continuous stirring was used to keep the solution clear. After being aged for 48h, the microemulsion was centrifuged to extract the particles, which were then washed fully by deionized water and ethanol to remove residual surfactant and dried in a vacuum oven at 300 °C for 2h, subsequently ground and calcined at 500-1000 °C for 2h.

2.2. *Characterization of $MgAl_2O_4$ nanopowders*

The TGA-DTA analysis was carried out on thermal gravimetric analyzer (STA 409 PC, Netzsch) at a temperature range from 40 °C to 1200 °C with a heating rate of 5 °C/min. The phase identification of precursor and calcined $MgAl_2O_4$ powders was recorded by X-ray diffractometer (MAXima_x XRD-7000, Shimadzu) working at 40kV, 30mA. HR-TEM observation was carried out on high resolution transmission electron microscopy (JEM-2100F, JOEL) operating at 200 kV to characterize the details about the microstructures of the powders. The FT-IR spectra was measured on a Fourier transform infrared spectrophotometer (VERTEX 70, Bruker) using the KBr pellet method. The grain sizes of the nanoparticles were estimated from the XRD pattern using Scherer's formula and confirmed by HR-TEM observation.

3. Results and Discussion

3.1. *Thermal stability and phase-transition*

The TGA and DSC curves of the precursor obtained from forward-titration process are shown in Figure 2. The endothermic peak at 110 °C in DSC curve corresponds to the evaporation of adsorbed water. The exothermic peak between 300 °C and 500 °C may be associated with the burning of the residual surfactant, cosurfactant and dehydroxylation, which results in about 20% loss of the mass. Such a mass loss was accompanied by the disappearance of hydroxide phase and hydroxyl after annealing at 500 °C, which is consistent with the X-ray diffraction results (Figure 3b). The weak exothermic peak at 560 °C with a slight mass loss is likely corresponding to the crystallization of amorphous oxide powder to nanocrystals, as shown in Figure 3, very weak and obviously broadened diffraction peaks were finally observed from 500 °C to 700 °C. The exothermic peaks with almost no mass loss at 810 °C, 1026 °C and 1131 °C are corresponding to the processes of incomplete crystallization of spinel to full crystallization. The similar TGA-DSC results could be observed from the powders synthesized by reverse-titration process.

Figure 3 shows XRD pattern of the precursor and its calcined products. The precursor (Figure 3a) was identified as a mixture of $Al(OH)_3$ (JCPDS card 20-0011)

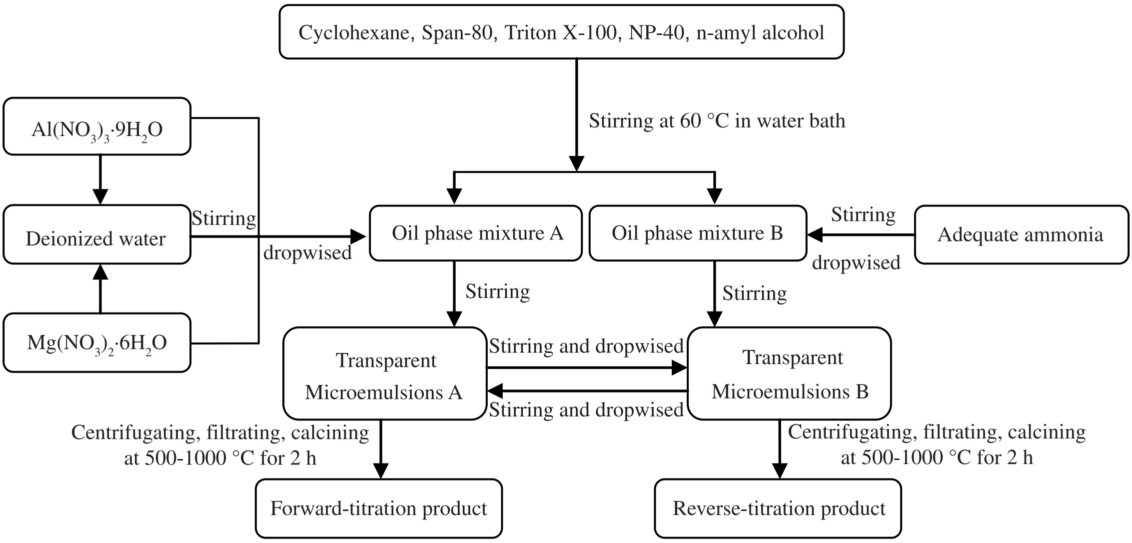


Figure 1. Schematic diagram of synthesize of $MgAl_2O_4$ nanoparticles by reverse microemulsion method.

and $MgAl_2(OH)_8$ (JCPDS card 35-1274) phases. Between 500 °C and 700 °C, the broadened peaks are corresponding to the amorphous precursor of spinel structure. With the calcination temperatures increasing, the XRD peaks become sharper and the crystal structure is improved gradually. The diffraction peaks at 800 °C, 900 °C and 1000 °C correspond to $MgAl_2O_4$ with a spinel structure (JCPDS card 77-0435). Further heating only increases the intensity of the diffraction peaks and no characteristic peak of impurity or other compound is observed. Table 1 shows the average grain size of the powders calcined at different temperatures. The grain size is calculated from full width at half maximum (FWHM) of the main intense peak of spinel (311) using Scherer' formula. It can be seen that the temperature range from 700 °C to 800 °C is the transition zone that spinel crystallites grow up quickly. All together, the TGA-DSC and XRD analysis suggest that the synthesized nanopowders show a lower crystallization temperature to spinel structure and have good high-temperature stability.

Table 1. The average grain sizes of powders calcined at different temperatures.

Calcination temperature/°C	Average grain size/nm
500	1.2
600	3.0
700	3.2
800	7.9
900	9.6
1000	14.1

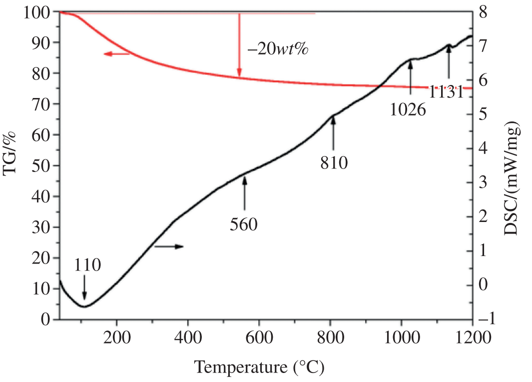


Figure 2. TGA–DSC curves of the precursor synthesized from forward-titration process.

3.2. *Effects of preparation conditions on microstructures of products*

In order to compare the difference of the microstructure of powders prepared by different process, $MgAl_2O_4$ powders calcined at 900 °C were taken as samples for further discussion.

The XRD patterns of products calcined in air at 900 °C for 2h are shown in Figure 4. The results show clearly that the peaks are well consistent with the standard X-ray diffraction pattern of spinel (JCPDS Card 77-0435). The powders show good crystallinity indicating that the reverse microemulsion process could dramatically lower the crystallization temperature of $MgAl_2O_4$ with a degree of 700 °C comparing to the classical solid-state reaction sintering. The shape of diffraction peaks are broadened, which suggests the formation of nanosized crystals. The average grain size of the $MgAl_2O_4$ powder synthesized from forward-titration and reverse-titration processes are 9.5 nm and 10.5 nm respectively when compound emulsifier of SPAN-80/Triton X-100 are used, while the powder synthesized by forward-titration process with NP-40 surfactant is 11.8 nm. The average crystallite size is smaller than that of 26 nm prepared by co-precipitation method reported by Rashad et al.[18].

Figure 5 shows HR-TEM images of the $MgAl_2O_4$ nanopowders synthesized under different conditions and calcined at 900 °C for 2h. The HR-TEM images (Figure 5a-f) show polycrystalline nanoparticles with the lattice spacing about 0.466, 0.286, 0.244 and 0.202 nm,

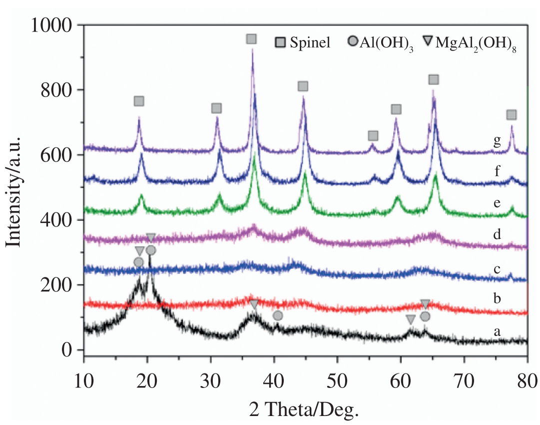


Figure 3. XRD patterns of the precursor synthesized from forward-titration process and powders calcined at different temperatures for 2h (a. as-prepared; b. 500 °C; c. 600 °C; d. 700 °C; e. 800 °C; f. 900 °C; g. 1000 °C).

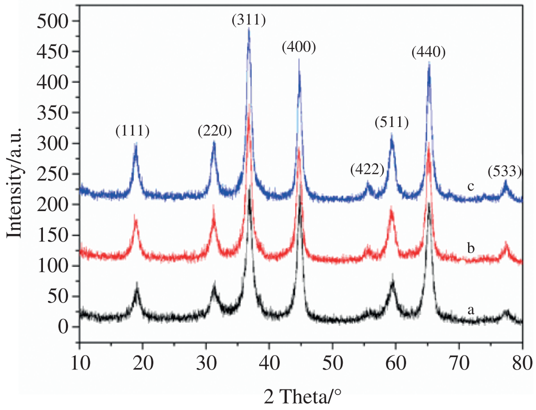
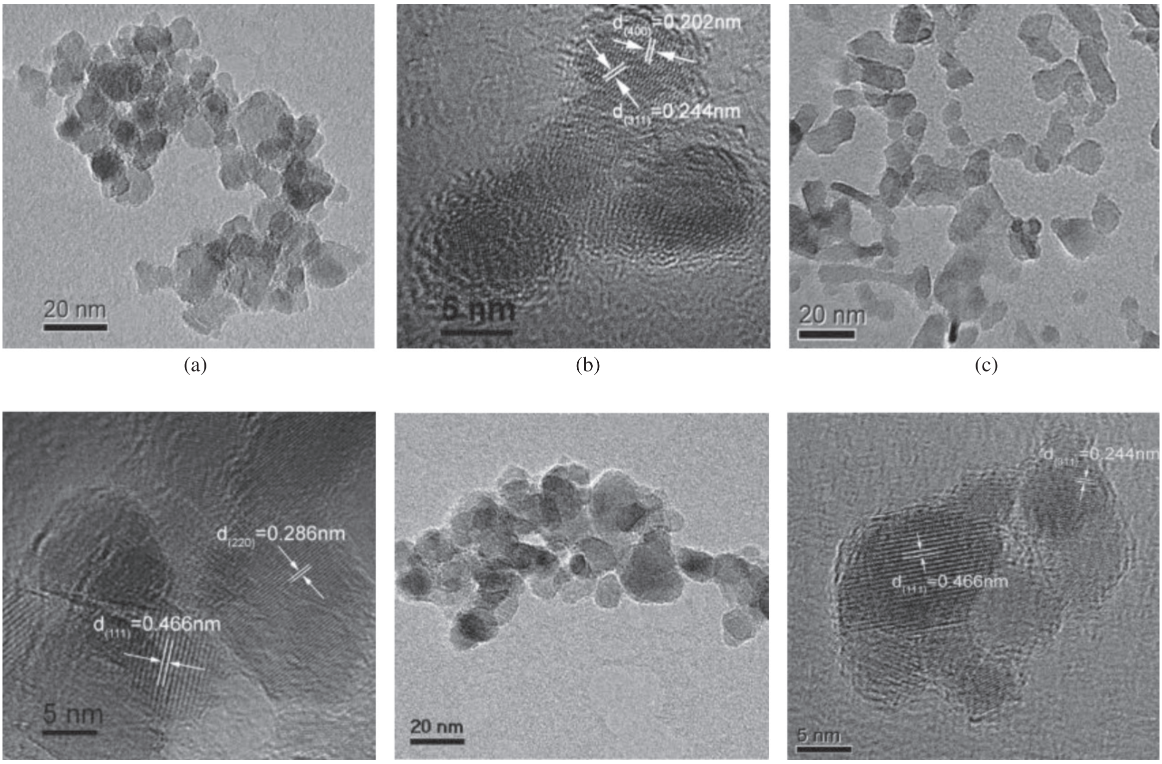


Figure 4. X-ray diffraction patterns of $MgAl_2O_4$ samples calcined at 900 °C for 2h (a. SPAN-80 + Triton X-100, forward-titration; b. SPAN-80 + Triton X-100, reverse-titration; c. NP-40, forward-titration).



(a) (b) (c)

(d) (e) (f)

Figure 5. HR-TEM images of $MgAl_2O_4$ nanoparticles calcined at 900 °C for 2h (a,c,e.morphology image of nanoparticles, which synthesized conditions of SPAN-80 + Triton X-100, forward-titration, and SPAN-80 + Triton X-100, reverse-titration, and NP-40, forward-titration, respectively; b, d, f. lattice fringe image of nanoparticles from a, c, e, respectively).

which correspond to (111), (220), (311) and (400) plane of $MgAl_2O_4$, respectively. The result is consistent with the XRD pattern. From the HR-TEM images, it can be clearly seen that individual particle prepared by forward-titration method with SPAN-80/Triton X-100 compound emulsifier is near spherical in shape with average particle size of about 9.5 nm (Figure 5a), which agrees with the result calculated from XRD pattern. In addition, the powder shows good dispersity. The particle size of the spinel powder prepared from surfactant NP-40 is about 13 nm (Figure 5e), and is larger than that calculated from XRD pattern, which caused by the agglomeration of particles. The choice of surfactant plays a very important role in the preparation of nanoparticles. In order to prevent aggregation of microemulsion particles in reaction process, the film formation performance of selected surfactant must be suitable, otherwise interfacial film formed by surfactants is easily opened when two microemulsion particles collide and results in substance exchange between particles in different water pond. The result shows that the size uniformity and dispersity of nanoparticles are affected by the surfactant type. This may be related to the strength and toughness of oil/water interfacial film formed by different surfactants on the surface of water pond in microemulsion. On the other hand, the powders prepared by reverse-titration method have platelike and spherical shape and the average size of the particles is about 10 nm (shown in Figure 5c). The shape of the particle is controlled by interaction of two micelles, and it can also be affected by phase behavior and solubility, average occupancy of reacting species in the aqueous medium and dynamic behavior of the reverse micellar solution[19].

In the reverse microemulsion process, when forward-titration method is adopted, the microemulsion of ammonia is dribbled into the one of salt solution, the reactions could be described as follows:

$$Mg^{2+} + Al^{3+} + 5OH^- = Mg(OH)_2 + Al(OH)_3 \quad (1)$$

$$Mg(OH)_2 + Al(OH)_3 \rightarrow 1/2MgO + 1/2Al_2O_3 + 3H_2O \quad (2)$$

$$1/2MgO + 1/2Al_2O_3 \rightarrow MgAl_2O_4 \quad (3)$$

Reaction (1) takes place in the microemulsion droplets. The surfactant and cosurfactant adhere to the surface of the nanoparticles serve as a protective layer to prevent collision and amalgamation of the droplets, which results in the monodispersed spherical $MgAl_2O_4$ nanoparticles. With reverse-titration method, however, $Al(OH)_3$ is an amphoteric hydroxide and dropping titration is conducted under an alkaline condition, which may induce the reactions as follows:

$$Al^{3+} + 3OH^- = Al(OH)_3 \quad (4)$$

$$Al(OH)_3 + OH^- = AlO_2^- + 2H_2O \quad (5)$$

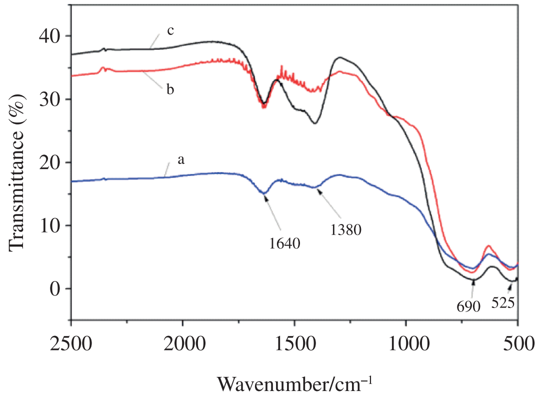


Figure 6. FT-IR spectra of $MgAl_2O_4$ nanoparticles calcined at 900 °C for 2h (a. SPAN-80 + Triton X-100, forward-titration; b. SPAN-80 + Triton X-100, reverse-titration;c. NP-40, forward-titration).

$$Al^{3+} + 3AlO^{2-} + 6H_2O = 4Al(OH)_3 \quad (6)$$

Because $Al(OH)_3$ is a kind of weak electrolyte, Al^{3+} and AlO^{2-} can not coexist in an aqueous solution. Dual hydrolysis reaction could take place and the products are all $Al(OH)_3$. The shape of water pools may be destroyed by these reactions and platelike particles are finally obtained. Therefore, the advantage of our procedure is that a well nanocrystalline spinel phase can be obtained at low calcination temperature of 800 °C with fine crystallite size and uniform morphology when appropriate surfactant and titration methods are used.

Figure 6 shows the FT-IR spectra of $MgAl_2O_4$ nanoparticles calcined at 900 °C for 2h . As shown in Figure 6, the three samples exhibited similar absorption bands in the recorded spectra. The bands at 1640 cm^{-1} appeared in all the samples are contributed to the deformation vibration of the water molecules. Absorption bands centered at 1380 cm^{-1} are assigned to the presence of nitrate groups. Besides, broad band presented at the range of 900 cm^{-1}~500 cm^{-1} are related to the inorganic network, and may be identified to be the existence of Al-O stretching frequency in the AlO_6 octahedral and AlO_4 tetrahedral units[20,21]. Among these, the two high-frequency bands, appeared at around 525 cm^{-1} and 691 cm^{-1} may be related to the Al-O stretching vibration in the AlO_6 octahedra, indicateing the formation of $MgAl_2O_4$ spinel in all the calcined powders synthesized by using different surfactants and emulsifiers[21,22].

4. Conclusions

Based on the experimental results, the following conclusions can be drawn:

1. $MgAl_2O_4$ nanoparticles can be prepared through reverse microemulsion method. Pure spinel phase were completely formed when the precursor were calcined at 900 °C for 2 h. The calcination temperature is dramatically lowered by a degree of 700 °C comparing to the classical solid-state reaction sintering method;
2. The $MgAl_2O_4$ nanoparticles obtained from SPAN-80/Triton X-100 compound emulsifier using forward-titration process have spherical shape, narrow size distribution, little agglomeration and small particle size of 9.5 nm, while reverse-titration process is difficult to control the shape of nanoparticles and is subject to producing platelike and spherical particles.

Acknowledgements

This work was supported by National Natural Science Foundation of China through Grant No.61172004 and No.50902055. The provided supports are gratefully acknowledged.

References

1. Salmones J, Galicia JA, Wang GA, Valenzuela MA and Aguilar-Rios G. Synthesis and characterization of nanocrystalline $MgAl_2O_4$ spinels as catalysts support. *Journal of Materials Science Letters*. 2000; 19(12):1033-1037. http://dx.doi.org/10.1023/A:1006734902538
2. Smith R, Bacorisen D, Uberuaga BP, Sickafus KE, Ball JA and Grimes RW. Dynamical simulations of radiation damage in magnesium aluminate spinel $MgAl_2O_4$. *Journal of Physics*: Condensed Matter. 2005; 17(6):875-891. http://dx.doi.org/10.1088/0953-8984/17/6/008
3. Naum F, Shahar C, Shay M, Sergei K and Moshe PD. Spark plasma sintering (SPS) of transparent magnesium-aluminate spinel. *Journal of Materials Science*. 2007; 42(9):3273-3275. http://dx.doi.org/10.1007/s10853-007-1672-0
4. Shukla P, Chernatynskiy A, Nino JC, Sinnott SB and Phillpot SR. Effect of inversion on thermoelastic and thermal transport properties of $MgAl_2O_4$ spinel by atomistic simulation. *Journal of Materials Science*. 2011; 46(1):55-62. http://dx.doi.org/10.1007/s10853-010-4795-7
5. Domanski D, Urretavizcaya G, Castro FJ and Gennari FC. Mechanochemical Synthesis of Magnesium Aluminate Spinel Powder at Room Temperature. *Journal of the American Ceramic Society*. 2004; 87(11):2020-2024. http://dx.doi.org/10.1111/j.1151-2916.2004.tb06354.x
6. Zawrah MF, Hamaad H and Meky S. Synthesis and characterization of nano $MgAl_2O_4$ spinel by the co-precipitated method. *Ceramics International*. 2007; 33(6):969-978. http://dx.doi.org/10.1016/j.ceramint.2006.02.015
7. Mackenzie KJD, Temuujin J, Jadambaa T, Smith ME and Angerer P. Mechanochemical synthesis and sintering behaviour of magnesium aluminate spinel. *Journal of Material Science*. 2000; 35(22):5529-5535. http://dx.doi.org/10.1023/A:1004839108758
8. Zhang SW, Daniel DJ, Goutam B and William EL. Molten Salt Synthesis of Magnesium Aluminate ($MgAl_2O_4$) Spinel Powder. *Journal of the American Ceramic Society*. 2006; 89(5):1724-1726. http://dx.doi.org/10.1111/j.1551-2916.2006.00932.x
9. Ganesh I, Johnson R, Rao GVN, Mahajan YR, Madavendra SS and Reddy BM. Microwave-assisted combustion

synthesis of nanocrystalline $MgAl_2O_4$ powder. *Ceramics International*. 2005; 31(1):67-74. http://dx.doi.org/10.1016/j.ceramint.2004.03.036

10. Ianos R and Lazau R. Combustion synthesis, characterization and sintering behavior of magnesium aluminate ($MgAl_2O_4$) powders. *Materials Chemistry and Physics*. 2009;115(2-3):645-648. http://dx.doi.org/10.1016/j.matchemphys.2009.01.028
11. Lepkova D, Batarjav A, Samuneva B, Ivanova Y and Georgieva L. Preparation and properties of ceramics from magnesium spinel by sol-gel technology. *Journal of Material Science*. 1991; 26(18):4861-4864. http://dx.doi.org/10.1007/BF00549861
12. Ye GT and Troczynski T. Mechanical activation of heterogeneous sol-gel precursors for synthesis of $MgAl_2O_4$ Spinel. *Journal of the American Ceramic Society*. 2005; 88(10):2970-2974. http://dx.doi.org/10.1111/j.1551-2916.2005.00533.x
13. Tian ZQ, Huang WJ and Liang YJ. Preparation of spherical nanoparticles of $LaAlO_3$ via the reverse microemulsion process. *Ceramics International*. 2009; 35(2):661-664. http://dx.doi.org/10.1016/j.ceramint.2008.01.020
14. Chandradass J and Ki HK. Solvent effects in the synthesis of $MgFe_2O_4$ nanopowders by reverse micelle processing. *Journal of Alloys and Compounds.* 2011; 509(5):L59-L62. http://dx.doi.org/10.1016/j.jallcom.2010.10.090
15. Huang KL, Yin LG, Liu SQ and Li CJ. Preparation and formation mechanism of $A1_2O_3$ nanoparticles by reverse microemulsion. *Transactions of Nonferrous Metals Society of China.* 2007; 17:633-637. http://dx.doi.org/10.1016/S1003-6326(07)60147-2
16. Vestal CR and Zhang ZJ. Normal micelle synthesis and characterization of $MgAl_2O_4$ spinel nanoparticles. *Journal of Solid State Chemistry*. 2003; 175(1):59-62. http://dx.doi.org/10.1016/S0022-4596(03)00143-9
17. Chandradass J, Balasubramanian M, Dong SB, Jongryoul K and Ki HK. Effect of water to surfactant ratio (R) on the particle size of $MgAl_2O_4$ nanoparticle prepared via reverse micelle process. *Journal of Alloys and Compounds.* 2010; 491(1-2):L25-L28. http://dx.doi.org/10.1016/j.jallcom.2009.10.213
18. Rashad MM, Zaki Z I and EI-Shall H. A novel approach for synthesis of nanocrystalline $MgAl_2O_4$ powders by co-precipitation method. *Journal of Materials Science.* 2009; 44(11):2992-2998. http://dx.doi.org/10.1007/s10853-009-3397-8
19. Petit C, Lixon P and Pileni MP. In situ synthesis of silver nanocluster in AOT reverse micelles. *Journal of Physical Chemistry*. 1993; 97(49):12974-12983. http://dx.doi.org/10.1021/j100151a054
20. Parmentier J, Richard PM and Vilment S. Influence of the sol-gel synthesis on the formation of spinel $MgAl_2O_4$. *Materials Research Bulletin*. 1998; 33(12):1717-1724. http://dx.doi.org/10.1016/S0025-5408(98)00169-X
21. Guo J, Lou H, Zhao H, Wang X and Zheng X. Novel synthesis of high surface area $MgAl_2O_4$ spinel as catalyst support. *Materials Letter*. 2004; 58(12-13):1920-1923. http://dx.doi.org/10.1016/j.matlet.2003.12.013
22. Adak AK, Saha SK and Pramanik P. Synthesis and characterization of $MgAl_2O_4$ Spinel by PVA evaporation technique. *Journal of materials science letters*. 1997; 16(3):234-235. http://dx.doi.org/10.1023/A:1018512025919