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Development and Characterization Properties of Non Stoichiometric Al-Mg Spinel by Sol-Gel Process

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Abstract—*$MgAl_2O_4$ is the most important compound in the MgO–Al_2O_3 system which can be produced through various methods. In the present work, synthesis and sintering behavior of nano-sized spinel powder produced through sol-gel process were studied. For this purpose, Mg $(NO_3)_2$, $9H_2O$ and Al $(NO_3)_3$, $6H_2O$ and Citric acid reagent altogether with a small amount of water were mixed. The homogeneous mixture was dried at 80 °C for 8-10 hours followed by sonication for 2 to 5 hours. Obtained gel was characterized by DTA/TGA. Sol gel calcined at various temperature 650 °C, 700 °C, 800 °C, 900 °C, 1000 °C with soaking time 5 hours. The heated powders were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, Field Emission Scanning electron microscopy techniques. It was found that pure nano-sized spinel phase, with 20–25 nm mean particle size. Morphological study displays that the particles are agglomerated and layered. Solid state bond formed at higher temperature.*

1. INTRODUCTION

The Magnesia Alumina spinel ($MgAl_2O_4$) is being used from the traditional ceramic industry for shaped and unshaped refractory materials [1] and also now a days in petrochemical industry [2,3], armor and domes materials ,humidity sensor, dentist materials, photo catalyst materials, electro ceramic materials and porous materials for withstanding high-temperature applications. The Magnesia is

a common example of basic refractory material stable to alkaline but can react to acidic.On the other hand the alumina is a acidic refractory material not affected by acidic material but can easily affected by the basic material. So to combine them both here we try to make a refractory material which can withstand both the above materials either acidic or basic materials. Sol gel synthesis is the most economical process for combining the Magnesia Alumina Spinel. Many variety of methods have been used throughout the years for the synthesis of $MgAl_2O_4$ such as combustion synthesis, mechanical milling, mechano chemical processing ,hydrothermal route etc have been proposed for the synthesis of $MgAl_2O_4$.The mechano chemical synthesis of $MgAl_2O_4$have been reported by several researcher using different raw materials along with also fuel agent.

Abdi et. Al [1] shows that $MgAl_2O_4$ nanoparticles were successfully synthesized by mechanically activated solid-phase exchange reaction of magnesium chloride with aluminum chloride in the presence of sodium hydroxide altogether with a small amount of water followed by subsequent heating at 800°C. Gilvan et al.[4] indicate that $MgAl_2O_4$nanoparticles were synthesized using Magnesium Nitrate and Aluminum nitrate as precursor and Gelatin as organic precursor. Lucience et al shows that $MgAl_2O_4$were successfully synthesized using stoichiometric mass of the Magnesium Nitrate and Aluminium Nitrate with urea as precursor.

Here in the present work we use sol gel synthesis method for making the magnesia alumina spinel more homogeneous. In the sol gel route for fast reaction we can use citric acid, thiourea, ethanol etc. as a fuel agent.In the present work we use Citric Acid as fuel agent and Magnesium Nitrate, Aluminium Nitrates a precursor mixes together along with DI water for hydrolysis and condensation. After synthesized the material, characterization was done on DTA analysis .After calcined the material at different temperature 650,700,800,900 and 1000°C.Then grinded the material using Agate mortar pester. Then by XRD, FTIR and FESEM analysis different characterization of the spinel material has been evaluated.

2. EXPERIMENTAL PROCEDURE

2.1 Preparation of $MgAl_2O_4$

The Magnesia Alumina spinel powder were prepared by sol gel synthesis procedure using $Mg(NO_3)_2$,$9H_2O$ and $Al(NO_3)_3$, $6H_2O$ as the precursor mixes together along with 5-7 ml DI water and Citric Acid as fuel agent .The $Mg(NO_3)_2$,$9H_2O$ and $Al(NO_3)_3$, $6H_2O$ and

Citric Acid were mixes in the ratio of molar weight in 1:2.25:1.5.

The formation of the sol gel route happened by heating at 80°C for 8 to 10 hr and then when the gas unable to evaporate i.e. turns in little bit reddish colour heat it in ultra sonicator for 5-8 hr at temperature in 50°C .After the removal of pore liquid further heat treatment is required to convert xerogel into a catalytically useful form[10]. Heating is done in the presence of flowing air in order to burn off any residual organics or oxide of the sample.

2.2 Characterization of MgAl2O4 Powder:

From the decomposition of xerogel were characterized by DTA [5] analysis with a heating rate of 10°c/min under nitrogen flow from 30°C to 1000°C. From the data of DTA analysis as shown in figure 1 we are able to find out that the crystal formation of the spinel structure happened after around 550-600°C. According to the data shown in the graph we have chosen five separate temperatures to calcine the sample. The sample is calcined at 650, 700, 800, 900, 1000 degree in furnace for 5 hours. After that grind the powdered material using Agate Mortar Pester for decreasing its grain size which eventually increases its surface morphology and also density increases and apparent porosity decreases of that material.

From the XRD analysis shown in figures 2,we seen that most intense peak we got from the material is (311) while given aluminum contents in 2.25 molar ratio from the Scherer formula i.e.,

$d = k\lambda / \beta \cos \theta$

Where d represents the crystallite size in nm, k =

0.9 is a correction factor, λ is the wavelength = 0.15406 nm and β = full width at half maximum[4] and θ is the Braggs angle. After calcinations and grinding of the synthesized materialfrom the Fourier Transform Infrared Spectroscopy analysis we able to find out the bonding of Magnesia Alumina happened at 400-600 cm^{-1}at the temperature of 900°C and 1000°C as shown in figures 6. The surface morphology and particle size were characterized by Filled Emission Scanning Electron Microscope as shown in figures.

3. RESULT AND DISCUSSION

3.1 Formation of Gel:

The synthesized procedure is done by the sol gel route synthesis. The time required for the gel formation is depends on the amount of material used for synthesis. Generally it takes 4-6 hour at 80°C at heating thereby ultra sonication for 5 -8 hours.

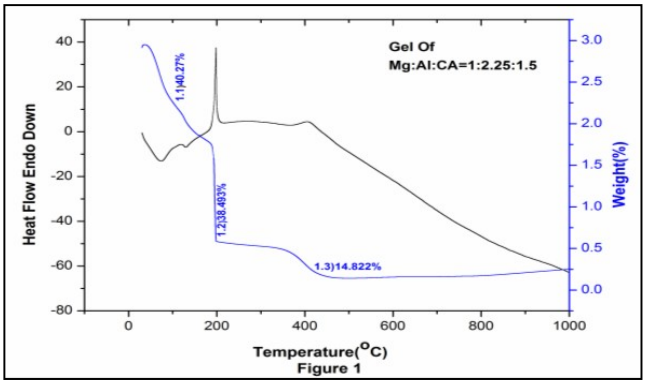

Fig. 1: TG-DTA analysis of homogeneous mixture within the temperature range 0°C to 1000°

The gel substance is then used for DTA and TGA analysis. The graph is shown in figure 1 By analysis the graph we can see that the weight % loss in 1.1) 31°C - 188°C the weight loss is 40.267% which is associated with water

.1.2)188°C-198.68°C the weight loss is 38.493% which is also associated of OH [5] molecules. 1.3) 198.68°C- 595°C the weight loss is 14.822% regarding elimination of amino acid and also reaction agent citric acid compounds. The higher temperature is required to break the bonds between the citric acid and the spinel.

3.2 X-Ray Diffraction: Structural Characterization

The crystal structure of the 3 different sample of $MgAl_2O_4$ at different temperature of 650,700 800, 900 and 1000°C has been done using the Cu Ka radiation which are shown in figure 2. The diffraction peaks are recorded [5] from 10 degree to 80 degree.

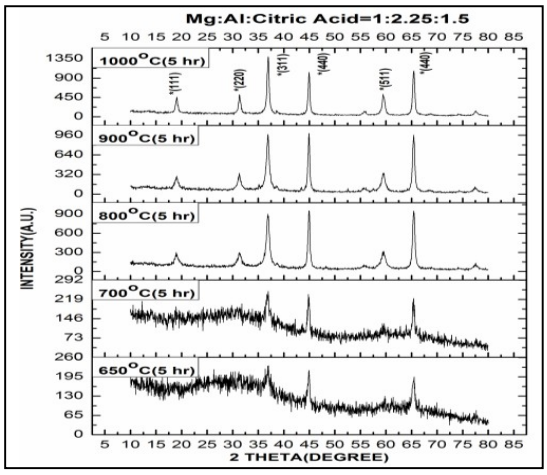

Fig. 2: $MgAl_2O_4$ after calcinations in different temperature for 5 hour

All the planes are (111), (220), (311), (440), (511), (440) which are corresponds to the Magnesia alumina crystal compound has been recorded from JCPDS card no. 77-0435, 77 1193, 77-1203 and 75-1799 of $MgAl_2O_4$ those have same structure and the crystalline size in 1000°C is closer in 0.35 to 0.61 nanometer by using Scherer formula as compare to 900°C.

3.3 FTIR Analysis

FTIR spectra were captured from 400- 4000 cm^{-1} Range for $MgAl_2O_4$ at 1000°C after calcinations for 5 hour. Here at 535 and 683 wave number the Mg-O-Al [6,7] corresponds to stretching vibration ,1400cm^{-1} is stretching vibration of NO_3^- group,2200 ,2350and 2380 cm^{-1} is bending vibration for C-N [5,6] group and 3480 cm^{-1} is bending vibration for OH group.

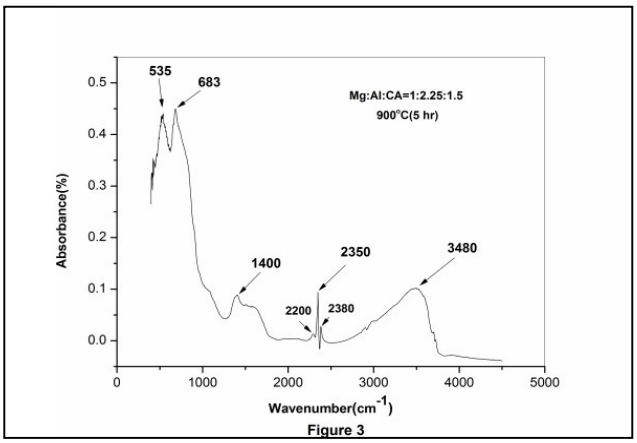

Fig. 3: FTIR-spectroscopy of the $MgAl_2O_4$ precursor powders at 900°C (5 hrs.)

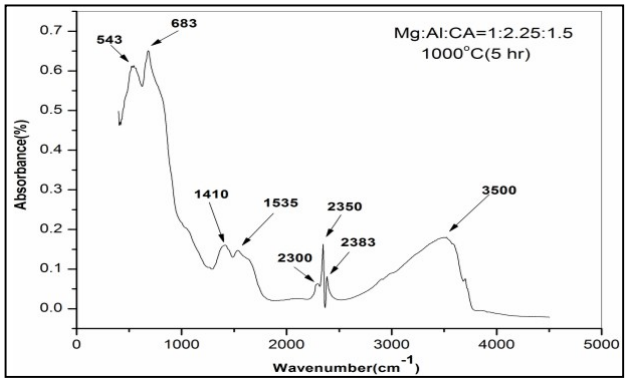

Fig. 4: FTIR-spectroscopy of the $MgAl_2O_4$ precursor powders at 1000°C (5 hrs.)

Also from 1000°C after calcinations for 5 hour at 543 and 683 wave number the Mg-O-Al [6,7] corresponds to stretching vibration ,1410 cm^{-1} is stretching vibration of NO_3-group,1535 cm^{-1} is stretching vibration of organic group[8] including CH_2 and CH_3[9], 2300, 2350 and 2383 cm^{-1} is bending vibration of C-N[5,6] group and 3500 cm^{-1} is bending vibration of OH group. From the both FTIR data the molecular vibration almost remains same but for very less bending vibration in Mg-O-Al. I have chosen best sample at 1000°C which is calcined for 5 hour.

3.4 FESEM Analysis:

In Field Emission Scanning Electron Microscope analysis the scanning of surface is mainly done by high energy electron beam. When a high energy electron beam incident on a sample surface various signal is produced and this signals contain information about the surface of the sample.

By FESEM we can achieve information whose resolution is better than 1 nm. Due to high energy electron beam there is secondary electron generated from the sample and we can produce FESEM images by detecting these secondary electrons.

In my project I have chosen the best possible samples which analysis discussed below: From figure 5 it is clearly seen that there is flakes like structure with particle size of 25nm to 35nm. The particles are not separate. They are stuck to each other and making an agglomerated structure.

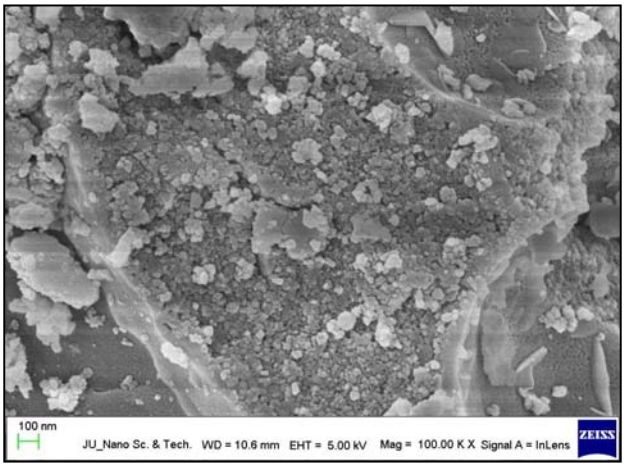

Fig 5: FESEM image of $MgAl_2O_4$ after calcinations at 1000°C

4. CONCLUSION

Spinel ($MgAl_2O_4$) nanoparticles were successfully synthesized by solgel process using Magnesium Nitrate and Aluminium Nitrate as a precursors followed by TG/DTA analysis of the homogeneous solution. The calcined powder was characterised by XRD, FTIR, and FESEM. From Sherrer's equation the crystallite size is found out to be in the range 0.31

to 0.69 nm. From FESEM image it can be observed that flakes like structure with agglomeration of particle is predominant on the surface. Average particle size of the spinel is 25nm to 35nm.

REFERENCES

[1] Abdi, Md., Ebadzadeh,T., Ghaffari, A. and Feli,M., "Synthesis of nano-sized spinel (MgAl2O4) from short mechanochemically activated chloride precursors and its sintering behavior", *Advanced Powder Technology*, xxx, 2014, pp xxx-xxx.

[2] R. Ianos_, I. Laza˘u, C. Pa˘curariu and P. Barvinschi in "Solution combustion synthesis ofMgAl2O4 using fuel mixtures", Mater. Res. Bull. 43 (2008) 3408–3415.

[3] Duraes, L., Matias,T., Segadaes, A.M., Campos, J. and A. Portugal in "MgAl2O4 spinel synthesis by combustion and detonation reactions: a thermochemical evaluation", J. Eur. Ceram. Soc. 32 (2012) 3161–3170.

[4] Gilvan Per.de F.,AlexanderF.M.C.,Francisco M.S.,Heloisa,Marcus and Dulce in "Synthesis of MgAl2O4 by Gelation Method:effect of Temperature and time of calcination in Crystalline Structure."July 6,2017,ISSN 1980-5373

[5] Hui LI, Heng-Yong WEI., Yi CUI, Rong-Li SANG, Jing-Long BU,Ying-Na WEI, Jian LIN and Jun-Hong ZHAO., "Synthesis and characterisation of MgAl2O4 spinel nanopowdersvia nonhydrolytic sol–gel route" Journal of the Ceramic Society of Japan 125 [3] 100- 104 2017

[6]S.Sanjabi, A.Obeydavi in "synthesis and characterization of nano crystalline MgAl2O4 Spinel via modified sol-gel method" in Journal of Alloys and Compounds 645 (2015) 535 -540

[7] Behgam Rahmani Vahid, Mohammad Haghighi in " Urea-Nitratecombustion synthesis of MgO- MgAl2O4 Nano catalyst used in biodiesel production from sunflower oil: Influence of fuel ratio on catalytic properties and performance" in 'Energy Conservation and Management' in 2016 362-372.

[8] Narges Habibi, Yuan wang, Hamidreza Arendiyan, Mehran Rezaei in "Low-temperature synthesis of mesoporous nano crystalline magnesium aluminate(MgAl2O4) spinel with high surface area using a novel modified sol-gel method" in 'Advanced Powder Technology' in Feb 23,2017.APT 1534

[9]P. H. Mutin and A. Vioux, J. Mater. Chem. A Mater. EnergySustain.,1, 1150411512(2013).

[10]E. Navaei Alvar, M. Rezaei, H. Navaei Alvar, H. Feyzallahzadeh and Zi-Feng Yan in " Synthesis of Nanocrystalline MgAl2O4 spinel by using ethylene diamine as precipitation agent". ISSN: 0098-6445 (Print) 1563-5201

[11]Ghosh S.R.,Mukherjee S.,Banerjee S."Solution Combustion Synthesis of Alumina Spinel and its Characterization", *Interceram 2018,*67th Volume ,Page no 34-41