Preparation of $MgAl_2O_4$ Spinel Through Different Wet Chemical Methods and Study of Its Densification Behavior

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Preparation of $MgAl_2O_4$ Spinel Through Different Wet Chemical Methods and Study of Its Densification Behavior

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by

Subrat Dash

(Roll Number: 711CR1144)

based on research carried out

under the supervision of

Prof. Ritwik Sarkar

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Prof. Ritwik Sarkar
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May 31, 2016

Supervisor's Certificate

This is to certify that the work presented in the dissertation entitled *Preparation of $MgAl_2O_4$ Spinel Through Different Wet Chemical Methods and Study of Its Densification Behavior* submitted by *Subrat Dash*, Roll Number 711CR1144, is a record of original research carried out by him under my supervision and guidance in partial fulfillment of the requirements of the degree of *Masters of Technology* in *Ceramic Engineering*. Neither this thesis nor any part of it has been submitted earlier for any degree or diploma to any institute or university in India or abroad.

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Ritwik Sarkar

Dedication

To my friends and my family ... .

Subrat Dash

Declaration of Originality

I, *Subrat Dash*, Roll Number *711CR1144* hereby declare that this dissertation entitled *Preparation of $MgAl_2O_4$ Spinel Through Different Wet Chemical Methods and Study of Its Densification Behavior* presents my original work carried out as a postgraduate student of NIT Rourkela and, to the best of my knowledge, contains no material previously published or written by another person, nor any material presented by me for the award of any degree or diploma of NIT Rourkela or any other institution. Any contribution made to this research by others, with whom I have worked at NIT Rourkela or elsewhere, is explicitly acknowledged in the dissertation. Works of other authors cited in this dissertation have been duly acknowledged under the sections ``Reference" or ``Bibliography". I have also submitted my original research records to the scrutiny committee for evaluation of my dissertation.

I am fully aware that in case of any non-compliance detected in future, the Senate of NIT Rourkela may withdraw the degree awarded to me on the basis of the present dissertation.

May 31, 2016

Subrat Dash
NIT Rourkela

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May 27, 2016 *Subrat Dash*

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Abstract

Magnesium aluminate spinel offers a wide range of properties. It has very high thermal stability, excellent mechanical strength both at ambient and at elevated temperatures, resistances against chemical environment and thermal fluctuations, etc. These properties have made spinel as one of most the effective refractory materials and used in steel ladles, cement rotary kilns, vacuum induction furnaces, continuous casting tundishes, glass industries, etc. Spinel-based materials are also used in various applications, such as: humidity sensors, dentistry, nuclear technique, catalyst support, reinforcing fibers, photo luminescent materials, and ceramic pigments.

The preparation of high purity $MgAl_2O_4$ is influenced by the synthesis method. The conventional method, based on the mechanical oxide and/or salt mixtures calcination is the most used for the $MgAl_2O_4$ synthesis. Modified Sol-Gel method is the most widely used for production of high purity spinel. In the present study magnesium aluminate spinel was prepared by various wet chemical routes, namely auto combustion, citrate sol-gel and co-precipitation methods using aluminium and magnesium nitrates as precursors. 0.5M both $Al(NO_3)_3.9H_2O$ and $Mg(NO_3)_2.6H_2O$ aqueous solution was prepared. Glycine and citric acid were used as fuel in Auto-combustion and Sol-gel method respectively. Spinel powders prepared through these three different methods were calcined at various temperatures to optimize the calcination temperature. Small amount of all the samples (prepared through 3 different methods) were taken in different clean and dry alumina crucibles & put in furnace and calcined at various temperatures (600° C & 700° C) for 2 hours soaking period at heating rate of 3° C/minute. By increasing the calcination temperature, quality of the crystallinespinelphaseincreases, sowegethighpurityatelevatedtemperature. Thecalcined powders were then characterized for different characterizations. Calcine powders were then uni-axially pressed to pellets for densification studies in the temperature range of 1450 to 1550° C. for all the preparation routes,TiO_2 was added to the spinel and the sintering was done in a chamber furnace at various temperatures like 1450° C, 1500° C & 1550° C.The heating rate in the furnace was 5° C/minute. The samples were held for 2 hours at these temperatures.

The powders obtained from the different preparation routes were characterized by DSC-TG at constant heating rate of 10° C/min. Powder produced by auto combustion method shows a gradual weight loss upto 600° C which indicates that there is huge amount of organic volatile materials present in the samples or in glycine. The weight loss may also be due to decomposition of nitrates. Powder prepared by co-precipitation method shows DSC peak 120° C due to the evaporation of water or/and removal of residual ammonia, peak about 280° C and 380° C may be due to the decomposition of the different hydroxide phases formed during the preparation procedure. Above 550° C, the TGA profile is relatively flat.

Powder prepared by citrate sol-gel method shows an exothermic peak at 300° C, indicates the oxidation of carbonaceous ingredient. Further heating causes a broad exothermic peak at 500° C, which is due to the crystallization of spinel phase. No significant changes were observed on increasing the temperature.

Phase analysis study of the citrate sol-gel and auto combustion routes shows diffused, and very poorly crystalline material on calcination at 600° C and does not show the formation of spinel phase. Increase in calcination temperature to 700° C and above confirms the spinel phase for these routes and 700° C calcined products were selected for sintering study. Whereas powders prepared by co-precipitation route showed phase pure spinel powder on calcination at 600° C.

Dilatometry study was done on dried samples using a dilatometer. The heating rate used was 5° C/min up to 1450° C (equipment's limitation) in an argon atmosphere. The onset temperature for all three routes was in between 890 and 990° C. Sintering starts at a temperature as low as 896° C in case of the spinel powder prepared by Auto-combustion method.

The bulk density and apparent porosity of the sintered spinel pellets were calculated by using Archimedes principle using DI water. Densification study shows the conventional sintering trend of increasing density values with increasing sintering temperatures.Higher density values were obtained for the citrate sol gel method. A highest density of 3.23g/cc was obtained for this samples sintered at 1550° C. TiO_2 addition enhances the densification of spinel prepared through all three routes at 1550° C with the highest density observed in citrate sol gel method i.e. 3.3g/cc.

***K*eywords: Mag-Al spinel, Advance refractory, Modified sol-gel process, Densification.**

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Chapter 1

Introduction

Chapter 1

Introduction

Magnesium Aluminate in spinel structure offers a wide range of properties .It has very good mechanical strength at room and at elevated temperature (MP-2135° C) with high thermal stability, which makes it an essential refractory material. Apart from this, it has normal spinel structure with high amount of tetrahedral and octahedral vacancies, which enables it to provide high chemical inertness in both acidic and basic environment. low expansion values at elevated temperatures, and is an ecologically benign refractory material [1] and [2]. It has been recognized as one of the effective refractory materials and used in steel ladles, cement rotary kilns, vacuum induction furnaces, continuous casting tundishes, glass industries, etc. [3], [4] and [5]. Along with those properties, Spinel has relatively low thermal expansion coefficient, thermal shock resistance and a low dielectric constant. It has a wide range of applications, such as structural, chemical, optical and electrical applications. These Spinel-based materials are generally used in variety of applications, such as: humidity sensing instruments, dentistry, nuclear technology, catalytic support, reinforcement fibers, photo luminescent products, and ceramic pigments.

1.1 Characteristic properties of magnesia alumina spinel

Spinel shows a very high melting temperature (2135° C, which is higher than Al_2O_3 (2054° C) but lower than that of MgO (2850° C). The thermal expansion coefficient (8.4×10^{-6}/K) of spinel is somehow close to that of alumina (8.8×10^{-6}/K), but very much lower than that of MgO (13.5×10^{-6}/K). Additionally, it has greater hydration resistance than MgO , so it can also be used in water-based castables.

1.2 Crystallographic Structure

The mag-al spinel crystallographic structure was determined by Bragg [6] and Nishikawa [7] independently1.1.It has a characteristic compositions of AB_2O_4 where A is a divalent cation like Mn, , Fe, Mg and Zn whereas B is a trivalent cation like Fe^{+2}, Al^{+3} . The space group from which spinel belong is Fd3m with 16 no of octahedral and 08 no of tetrahedral sites

[8]. The highest number of sites possible for octahedral and tetrahedral sites are 32 and 64, respectively. Generally trivalent cations are positioned in octahedral and divalent are located in tetrahedral sites. Generally, Spinels are represented by the B(AB)O formula whereas inverse spinels are denoted by the formula of $B(AB)O_4$. The in-between Distribution of cations has a general formula of $(A_{1-x}Bx)\,[B_{2-x}A_x]O_4$, where x is an inversion parameters with values in between 0 to 4.

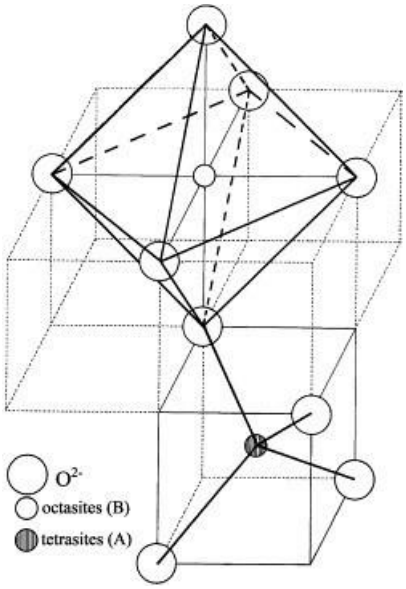

Figure 1.1: Position of cations and anions in spinel

1.3 Phase Diagram of $MgO\text{-}Al_2O_3$

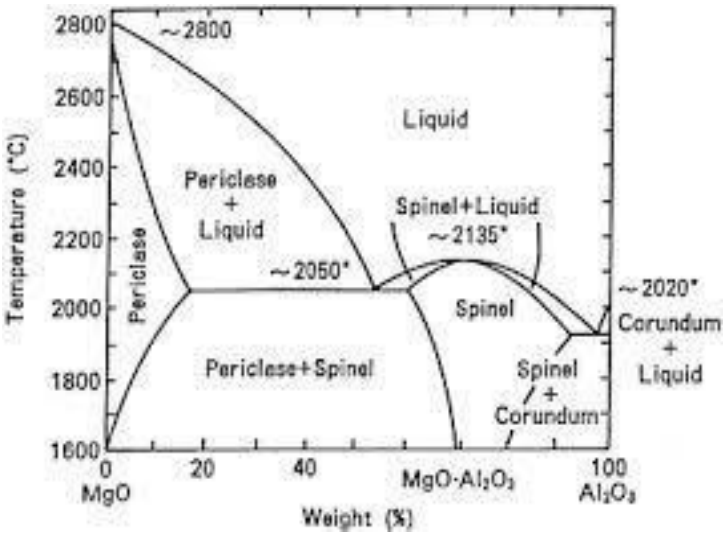

Figure 1.2: Phase diagram of Spinel

The phase diagram of Magnesia and Alumina is shown above 1.2. At 50:50 molar compositions of MgO and Al_2O_3 the spinel phase formation takes place. It can be seen that the melting point of MgO is 2800°C and that of Al_2O_3 is 2020°C. The $MgAl_2O_4$ spinel made is an eutectic compound, which is a congruently melting compound. The M.P of spinel is found to be around 2135°C. The spinel distributes the entire system into two different eutectic systems where the first one is given by MgO-$MgAl_2O_4$ and the second one is $MgAl_2O_4$-Al_2O_3 as shown in the diagram. So if a stoichiometric composition of MgO and Al_2O_3 is taken, and heated and cooled down subsequently slowly then at eutectic point, we can find pure spinel. The MgO.Al_2O_3 system is interesting to the refractory technologists, because spinel MgO.Al_2O_3 itself is a refractory and there is no liquid formation.

Mag-al spinel has a wide series of stoichiometry, noticeable by the phase field in the above phase diagram. Stoichiometric Mag-al spinel has 28.3 wt.% MgO and 71.7 wt. % Al_2O_3. but, with increasing temperature, a wide variety of non-stoichiometry will form in the system. The solid solubility of alumina in the Mag-al spinel is higher than that of magnesia at the same temperature. It can be evident from the fact that, the solid solubility of MgO and $Al2O_3$ at 1600°C are only 2.0 and 6.0 wt.%, respectively, but the solubility increase to almost 3.0 and 10.0 wt.%, respectively, at 1700°C. Hence, it can be concluded that a single-phase mag-al spinel will be very alumina-rich, which can be specified by MgO. nAl_2O_3, where n is the no. of moles of Al_2O_3. Magnesia-rich spinels (n<1), according to the above binary phase diagram, can be achievable Al_2O_3 by quick cooling it from an elevated temperatures (>1600°C), but usually MgO-rich spinel grains has high amount of periclase which is situated at the MgO-spinel binary phase field. n can be as high as 7.3 [9].

1.4 Normal spinel and Inverse spinel

In case of normal spinels the octahedrals can be occupied with B (trivalent atoms) whereas the tetrahedral voids can be filled with A (divalent atoms). The total no. of octahedral voids are double than that of the tetrahedral voids and the normal spinel has a formula of AB_2O_4 .In the case of inverse spinel structure all the divalent cations are located in the tetrahedral void place where some of the trivalent cations are placed in the tetrahedral voids and rest are located in the octahedral voids [10]1.3. The example of inverse spinel is magnetite whereas chromite is a normal spinel[8].

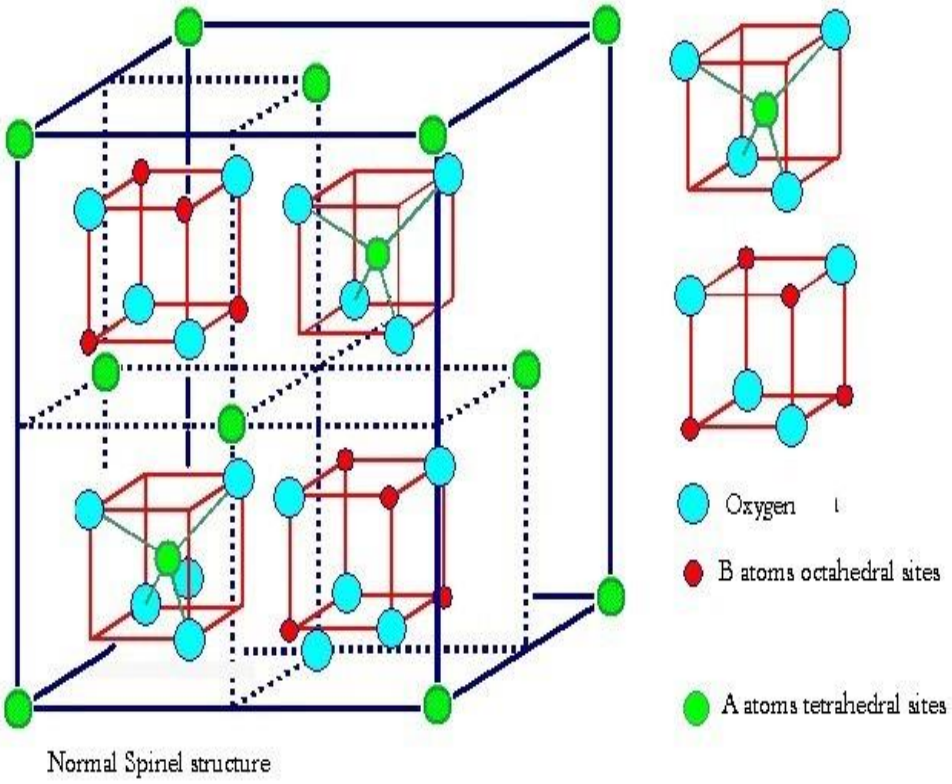

Figure 1.3: Normal and inverse spinels

Chapter 2

Literature Review

Chapter 2

Literature Review

2.1 Spinel as an advanced ceramic material

Advanced ceramic materials magnesium aluminate spinel has the following characteristic features i.e. even under extreme temperature mechanical properties are quite remarkable,. Excellent mechanical strength at room and at elevated temperature. It also shows good corrosion resistance, erosion and abrasion resistance. This spinel has excellent fire-resistant property due to its very high M.P. and thermal spalling resistance, which makes it an excellent refractories. This spinel is generally used as a refractory material as well as for structural applications. This compound has the highest stability in the $MgO\text{-}Al_2O_3$ system. It is structurally and chemically attuned with a wide range of refractory materials such as Al_2O_3, ZrO_2 and mullite, therefore spinel phase can be used in the composition of ceramic matrix composite [11]. The primary application fields of spinel refractory are generally sidewalls and the bottom part of steel ladles , burning zones of cement rotary kilns [12], and it is also used in checker tiles of the glass tank furnace generators due to its of its good corrosion resistant to slag. Depending upon the temperature and environment zone where it is used, Alumina rich or magnesia rich matrix is suitable for spinel. Thus Mg rich and Al rich are widely used in refractory applications. Compounds with a structure similar to that of the Spinel are used for electrochemical uses, semi conductor devices for semi conduction like in solar cell and in the biological applications and electrical applications. Magnesia alumina Spinel can also be used broadly as an excellent replacement for the chrome ore in basic brick manufacture. It enhances the thermal shock resistance which is generally associated with the additions of chrome, but without the critical problem of hazardous waste disposal associated with it. Spinel also upgraded the thermal shock resistance due to the formation of internal micro cracks and voids due to the thermal expansion mismatched rates. The reversible thermal expansion of this Spinel is approximately half that of the magnesia. The most used area of magnesia spinel bricks is in cement rotary kilns where they have demonstrated superior properties compared to that of previously used mag-chrome bricks. This reversible thermal expansion of spinel is approximately half of the magnesium oxide. The most common

area of magnesia spinel brick compared to the traditional prove the excellent performance of the previously used magnetic chrome brick for cement kiln. The extended life has been attributed to the coating retention property of spinel brick without excessive penetration and peeling capabilities. The mag-Al spinel can also replace chrome where disposal of chromium is a big problem in some other applications, such as lime and glass tank regenerators checkers. alternatives. Spinel-alumina refractory freedom for designing a small amount of magnesium oxide. Free magnesia and free alumina measured by technical sintering, is 5 percent. Therefore, in addition to aluminum spinel agency will give some of the volume expansion. Free MgO in spinel may also be used as a coagulant for the phosphate bond, to produce a cold setting monolithic refractory or mortar[13].

Spinel can be widely used alternative to the basic brick production of chromium ore use. It gives its typically added to chromium associated with improved thermal shock resistance, but without its potential problems of hazardous waste disposal. The improved thermal shock resistance, due to the development of internal microcracks and voids, due to the mismatch of the thermal expansion rate achieved. . Being an important refractory material it is also used in advanced applications like domes and armour material , humidity and infrared sensors, transparent windows, high-temp arc-enclosing envelops, [14]. Additives are intentionally added foreign substances to provide good promotion effects in microstructural processing and subsequently enhances the final properties. Additives are added to form a solid solution, or a new compound or its own or liquid composition or compositions with the new batch reaction. both the interstitial and/or substitutional effects may occur In a solid solution, causing lattice vacancies or strain, which ultimately facilitated diffusion-dependent process. The addition of a lower valence cation leads to a creation of anion vacancy or cation interstitial, which subsequently increases the diffusivity and the other dependent processes like Li_2O doping in case of MgO[15]. However by adding higher valence cations, cation vacancies are formed rather than anionic interstitial [16].

Hence the cation diffusion rate and other related processes are enhanced. Liquid phase formation occurs, which works as a lubricant, hence it provides higher diffusivity than that of the solid phase. Wet solid particles come together by the action of capillary force of attraction that leads in a way better compaction. Additive in magnesium aluminate spinel systems may affect the synthesis and formation, sintering, growth, and other characteristics of the formation. and the sintering additive is magnesium aluminate spinel is the most important. Sintering additives are essential for ease in formation and sintering of Mag-Al spinel.

This present work deals with the processing and sintering of phase pure Mag-Al spinel synthesized by three various wet chemical process. Magnesium and aluminium nitrates have been used as the oxidizers for all the methods. Glycine and Citric acid are used as the fuel in case of Auto-Combustion and Citric sol-gel method. Addition of fuel to the mixture of magnesium and aluminium nitrates leads to a series of redox reactions to form a glycine – nitrate or a citrate-nitrate complex which ultimately crystallizes to form spinel at a lower temperature. TiO_2 is used as a sintering additive and its effect on powder sinterability have been reported.

2.2 Wet Chemical Methods to Prepare Spinel

The preparation of high purity $MgAl_2O_4$ is influenced by the synthesis method. The conventional method, based on the mechanical oxide and/or salt mixtures calcination is the most used for the $MgAl_2O_4$ synthesis. Modified Sol-Gel method is the most widely used for production of high purity spinel. Here Citric acid is used as a fuel to produce Nano crystalline spinel. Nano crystalline $MgAl_2O_4$ with average crystal size of 400nm were produced at 700° C. In this process spinel phase formation began around 600° C. The formation process of $MgAl_2O_4$ spinel is most likely to contain two stages, first, the decomposition of the compound of nitric and citric to γ-Al_2O_3 and MgO, and finally, the solid-state reaction between γ-Al_2O_3 and MgO to $MgAl_2O_4$ spinel. The isoelectric point of the $MgAl_2O_4$ spinel is about pH 11.8.It is also observed that the calcined powder contained two kinds of particles: plate-like particles with about 30–50 nm in size and relatively spherical particles with about 200 nm in diameter [5].By increasing the calcination temperature, quality of the crystalline spinel phase increases, so we get high purity at elevated temperature. Here the cations are mixed in the atomic level, which results in a low path of diffusion and high volume diffusivity.Other research papers show that In order to get the complete homogeneity of magnesium and aluminum ions at atomic level in the starting material, it is required to increase the relative concentration of magnesium and aluminum citrate complexes ((Mg(HCit), Al(Cit) and Al(OH)Cit−))[17]. the concentration

of Mg_2+ and Al(Cit) ions decreases with increasing pH values, the concentration of Mg(HCit) and Al(OH)Cit− ions increases with pH values increase;the concentration of citric acid shows a little influence on the concentration of Mg_2+and Mg(HCit) ions, however, it has almost no effect on the concentration of Al(Cit) and Al(OH)Cit− ions;the concentration of Mg(OH)+, Al_3+, $Al(OH)_2$+, $Al(OH)_2$+, Al(HCit)+ ions is lower with a value about 0 comparing with that of Mg(HCit), Al(Cit), Al(OH)Cit− at all conditions;at pH>5, all magnesium and aluminum ions completely form magnesium citrate complex Mg(HCit) and aluminum citrate complex Al(OH)Cit−.[18]

The formation process of high density spinel products has evolved over the years. The preparation of spinel by different routes has been reported in different years [19]. Phase pure homogeneous powders of single phase spinel are useful in case low temperature densification. Combustion synthesis process [20] is very much suitable for producing powders for advanced ceramic applications. The fuels used are source of C and H and liberate heat which help in the formation of metal ion complexes facilitating mixing of the cations in solution. The advantages of combustion synthesis being:

1. Relatively simple instruments are required
2. Phase pure products are formed
3. Stabilized Metastable phases are formed
4. Practically any size and shape product are formed

Both the stoichiometric and non-stoichiometric Mag-Al spinel has been prepared by combustion synthesis route using Glycine as fuel source and metal nitrates as the oxidizers. By adding glycine as a fuel it reacts with the nitrate precursors, which led to a series of redox reactions to form a complex structure that finally crystalizes to form spinel at lower temperature. Two actions that occur during combustion are

1. Generation of heat during combustion
2. Gas evolution

Generation of heat during combustion results in the formation and the crystallization of the desired phases. Very High flame temperature generally has various affects on powder characteristics such as formation of hard agglomerates and increase in crystal size, so the surface area and sinterability decreases . heat of combustion monitors the Powder characteristics and the evolution of gas which are reliant on ratio of oxidant to fuel and the fuel nature.

The phase pure spinel was formed at 700° C. Calcination done at an elevated temperatures did not change the peak position but sharpened the peaks in terms of intensity, indicating higher crystallite size [21]. By varying the metal to glycine ratio, bulk density of the final sintered product is also varied.

The magnesium-alumina spinels can be produced by wet mixing of magnesium oxide and aluminum hydrogel, coprecipitation and sol-gel techniques with the calcination temperatures between 1200° C and 1600° C, resulting in a bulk-sintered body with very small surface area [21–24].Another modified Sol-Gel technique by combining gelation and co-precipitation is also used to produce high purity spinel. The formation temperature is quite low compared to other conventional process. Here we get well crystallized and high pure spinel phase at 600° C. It is found that the samples prepared through this process show high thermal stability and uniform pore size distribution. The average particle size is around 800 nm, which is higher than other conventional processes. Other papers suggest that with the sample prepared at pH = 7 with ammonia as precipitating agent, a uniform pore centered at about 86$\mathring{A}$ was formed. When the pH value was increased to 12, quite a different pore size distribution was observed [25].

There is not much research articles available doing the comparative study of densification behavior of spinel produced through different methods. In this present work, $MgAl_2O_4$ was synthesized through 3 different routes i.e. Citrate Sol-Gel, Auto-Combustion and Co-Precipitation process and their densification behavior is compared.

2.3 Objective

1. To synthesize phase pure Mag-Alspinel at low temperature using various wet chemical methods.

2. Optimization of these synthesis routes to get phase pure spinel at lowest calcination temperature possible

3. Use of Citric acid as fuel in the Citrate sol-gel synthesis and Glycene for Auto-Combustion process.

4. Study of Densification of these spinel prepared through different routes at various sintering temperatures (1450° C,1500° C, 1550° C).

5. Use of TiO_2 as a sintering additive and study of its effect on the densification behavior of the spinel sintered at various temperatures (1450° C,1500° C, 1550° C).

Chapter 3

Experimental Details

Chapter 3

Experimental Details

3.1 Batch Preparation

3.1.1 Citrate Sol-Gel process

Raw Materials used are

1. Magnesium nitrate hex-hydrate($Mg(NO_3)_2.6H_2O$), AR (MERCK LTD.)
2. Aluminium nitrate nona-hydrate($Al(NO_3)_3.9\ H_2O$) (LOBA CHEMIE PVT. LTD)
3. Citric acid($C_6H_8O_7.H_2O$)
4. NH_4OH solution

The aqueous solution of Aluminium and magnesium nitrates(0.5M each) are prepared in stotiometric amounts. Stotiometric amount (1:1 metal ratio) of Citric acid is added to the solution. PH of the solution is maintained at 5 using NH_4OH solution. This solution is properly mixed and slowly evaporated until a highly viscous gel is formed, which was then dried at 1400° C for 24 hrs. The dried gel is then calcined at 600° C and 700° C for 2 hrs to get the spinel powder.

3.1.2 Auto-Combustion process

Raw Materials used are

1. Magnesium nitrate hex-hydrate($Mg(NO_3)_2.6H_2O$), AR (MERCK LTD.)
2. Aluminium nitrate nona-hydrate($Al(NO_3)_3.9\ H_2O$) (LOBA CHEMIE PVT. LTD)
3. Glycene($C_2H_5NO_2$)

0.5 M both $Al(NO_3)_3.9H_2O$ and $Mg\ (NO_3)_2.6H_2O$ aqueous solution was prepared. 150 ml of these solution was taken in a 250 ml. beaker and 14.06 gm(1:2.22 fuel to metal ratio). of glycine as a fuel was added, a magnetic needle (for stirring) was put into the beaker. The beaker was placed on a hot plate (spinot) & both stirring and heating were done

simultaneously. After continued heating for 2-3 hours, the solution converted to gel like liquid and finally combustion took place leaving behind a black mass. After cooling, the black mass was calcined at 600° C and 700° C for 2 hrs to get the spinel powder.

Oxidizer to Fuel Ratio Calculation

Oxidation/reduction valency of

1. Aluminium Nitrate Nonahydrate ($Al(NO_3)_3.9H_2O$) = +3+3(0+(-6)) = +3-18 =-15
2. GLYCINE = $C_2H_5NO_2$= 2 ×(+4)+5+0-4 = 8+5-4 = +9
3. $Mg(NO_3)_2.6H_2O$ = +2+2(0+(-6)) = +2-12 = -10

In spinel Mg : Al = 1:2
Hence total valency of oxidiser = (-15)+(-5) =-20
Fuel valency = +9
Stoichiometric(where complete combustion takes place) oxidiser to fuel ratio is = 20/9 = 2.22

3.1.3 Co-Precipitation process

Raw Materials used are

1. Magnesium nitrate hex-hydrate($Mg(NO_3)_2.6H_2O$), AR (MERCK LTD.)
2. Aluminium nitrate nona-hydrate($Al(NO_3)_3.9\ H_2O$) (LOBA CHEMIE PVT. LTD)
3. NH_4OH solution

The aqueous solution of Aluminium and magnesium nitrates are prepared in stotiometric amounts(0.5M each). PH of the solution is maintained at 9.5 using NH_4OH solution. This solution is properly mixed until a highly viscous gel is formed, which was then dried at 140° C for 24 hrs. The dried gel is then calcined at 600° C for 2 hrs to get the spinel powder.

3.1.4 Characterization

Differential Scanning Calorimetry and Thermogravimetry Test

The samples with different preparation routes were characterized by DSC-TG (NETZSCH, GERMANY)atconstantheatingrateof10° C/mininthetemperaturerangeof30° Cto600° C.
Data was collected and graphs were plotted.

Figure 3.1: DSC-TG (NETZSCH, GERMANY)

Calcination at Various Temperatures

Small amount of all the samples (prepared through 3 different methods) were taken in different clean and dry alumina crucibles & put in furnace and calcined at various temperatures (600° C & 700° C) for 2 hours soaking period at heating rate of 3° C/minute.

Figure 3.2: DSC-TG (High Temperature electric furnace)

XRD Analysis of Calcined Powders

After Calcination X-Ray Diffraction was performed using Philips X-Ray diffractometer PW 1730 with nickel filtered Cu Kα (λ=1.5406) 40kV and 30mA. The scanning rate was 3^0/min scanned continuously in the range of 15° C to 65° C.

Figure 3.3: Philips X-Ray diffractometer PW 1730

Particle size distribution

Particle size distribution test of the Calcined spinel powders from 3 different routes was done using Malvern PSD instrument. Data was collected and graphs were plotted.

Figure 3.4: Malvern Zetasizer Nano ZS

Dilatometry study

Dilatometrystudywasdoneondriedsamplesusingadilatometer(modelDIL402C,Netzsch, Germany make). The heating rate used was 5° C/min up to 1450° C (equipment's limitation) in an argon atmosphere. Samples for dilatometry study were pressed at 150 MPa using a rectangular stainless steel mold (Sample dimensions: 25 mm×6 mm×6 mm).

Figure 3.5: DIL 402C, Netzsch, Germany

Pelletization

Mag-al Spinel prepared by 3 wet chemical routes were mixed with with 3 vol% PVA, an organic binder and ground with the help of a mortar and pestle. The three different powders were weighed differently and uniaxially pressed (CARVER, USA) at 200 MPa with 90 sec. dwelling time.

The very same process was repeated with the three spinel samples prepared by various methods with TiO_2 as sintering additive.

Figure 3.6: Hydraulic Press

Sintering

The sintering was done in a chamber furnace at various temperatures like 1450° C, 1500° C & 1550° C.The heating rate in the furnace was 5° C /minute. The samples were held for 2 hours at these temperatures.

Figure 3.7: High Tempereture Raising Hearth Furnace

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2 wt % of TiO_2 was mixed with the magnesia alumina spinel prepared through three different process by wet mixing using ethanol. It is then dried up and three sample powders were made.

Apparent Porosity and Bulk Density Calculation

The bulk density and apparent porosity of the sintered spinel pellets were calculated by using Archimedes principle using DI water. Dry Weight was measured first and then the pellets were kept in water and vacuuming was done for about 2 hrs. Then that suspended weight is measured using apparatus in which pellet is suspended in water. After the suspended weight, soaked weight was taken accurately. The bulk density and apparent porosity were calculated by using the formulas:

Bulk density = Soaked weight / Dry weight−Suspended weight

Apparent porosity = Soaked weight- Dry weight / Soaked weight- Suspended weight

Microstructure Study (FESEM)

Field emission scanning electron microscopy (FESEM) offers provides morphological as well as elemental facts at a wide range of high amplifications of 10×to 300,000×, with practically any depth of field. As compared to Scanning Electron Microscopy (SEM), Field Emission SEM (FESEM) gives less electrostatically distorted and clearer, images with a very good spatial resolution down to 1-1/2 nanometers – roughly three to six times better than SCM [26].

Figure 3.8: FESEM Setup

So one from eachof three spinel powders of the batch of the pellets sintered at 1550° C were broken down and sent for FESEM (Field Effect Scanning Electron Microscope) to do the microstructure study.

Table 3.1: Details of the Instruments used

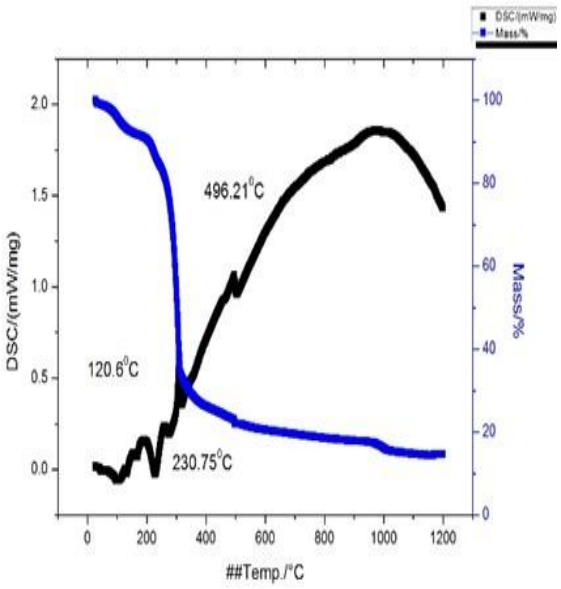
Instrument Name	**Used for**	**Company/Supply Name**
Dilatometer	Shrinkage analysis	NETZSCH TASC 414/4 Controller
X-Ray Diffractometer	Phase analysis	Philips PW 1730
FESE Microscope	Microstructure analysis	Nova NanoSEM
Muffle Furnace	Thermal etching	Testing Instruments
High-temperature Furnace	Firing/Sintering	OKAY Electric Furnace
Weighing machine	Weighing	OHAUS Pioneer Balance
Hydraulic Pressing Machine	Compaction	Carver Laboratory Press
Magnetic Stirrer	Mixing of batches	SPINOT Magnetic Stirrer
Drying oven	Drying	YORCO OVEN

Chapter 4
Results and Discussion

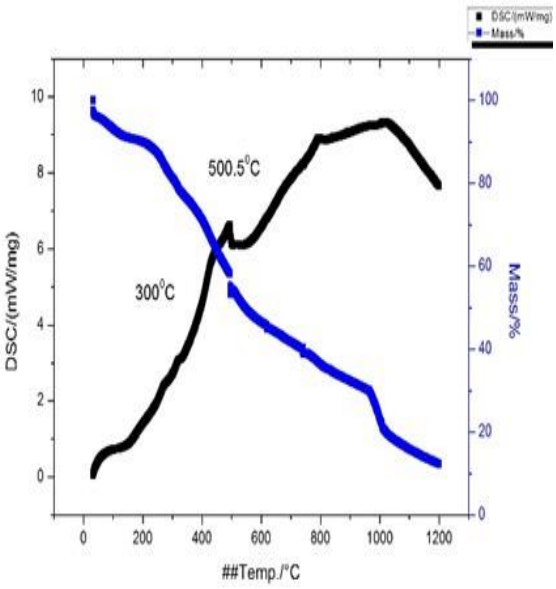
Chapter 4

Results and Discussion

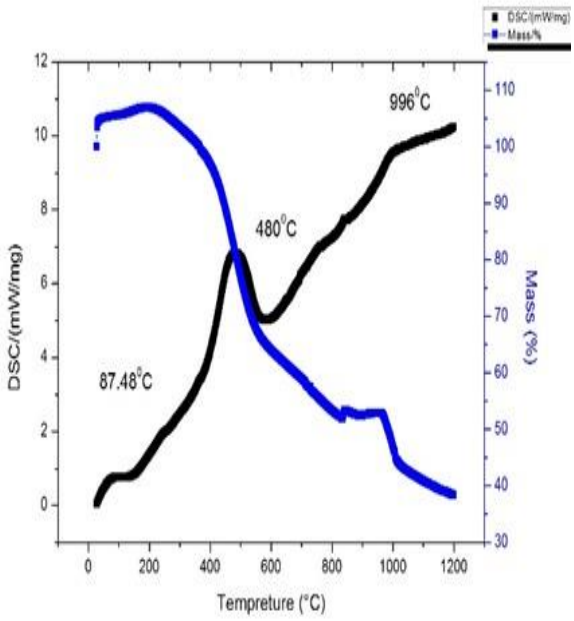
4.1 DSC/TG



(a) DSC/TG-Co-precipitation method



(b) DSC/TG- Citrate Sol-Gel method



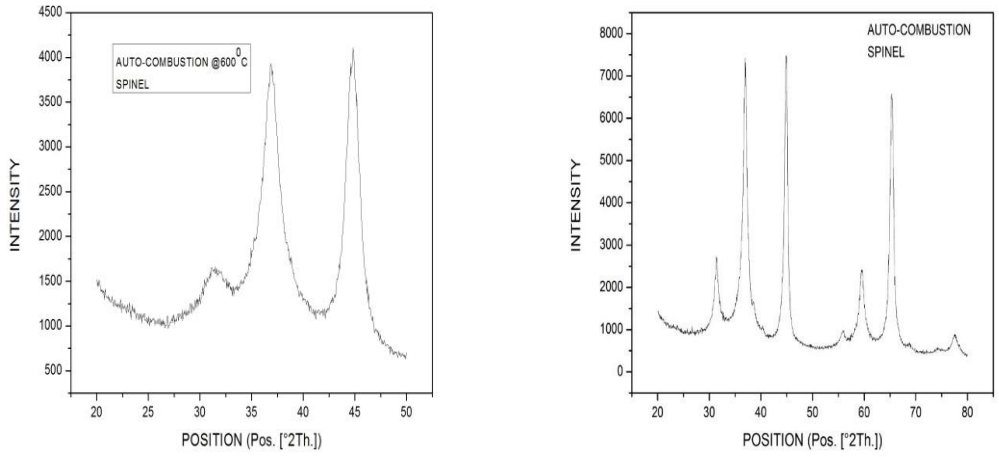
(c) DSC/TG- Auto Combustion Method

In case of Auto combustion method,4.1(c). There is a gradual weight loss upto 600◦ C which indicates that there is huge amount of organic volatile materials present in the samples or in glycine. The weight loss may also be due to decomposition of nitrates

In case of Co precipitation method,4.1(a), first peak is positioned at about 120◦ C due to the evaporation of water or/and a small amount of residual ammonia adsorbed on the surface of samples as ammonia solution was used as precipitating agent and the peaks appeared at about 280◦ C and 380◦ C may be due to the decomposition of the different phases(i.e. hidrotalcite, bayerite and boehmite) formed during the preparation procedure. When the samples were fired at 600◦ C, these phases were decomposed and finally spinel crystals were producedathightemperature. Above550◦ C,theTGAprofileisrelativelyflat. Thisindicates that solid state reaction to form $MgAl_2O_4$ spinel may occur above 500◦ C. Here in we chose 600◦ C as calcination temperature.

In case of citrate sol-gel method,4.1(b), The exothermic peak at 300◦ C indicates the oxidation of carbonaceous ingredient. Further heating causes a broad exothermic peak at 500◦ C, which is due to the crystallization of mag-al spinel. No significant changes were observed in further heating up to 1200◦ C.

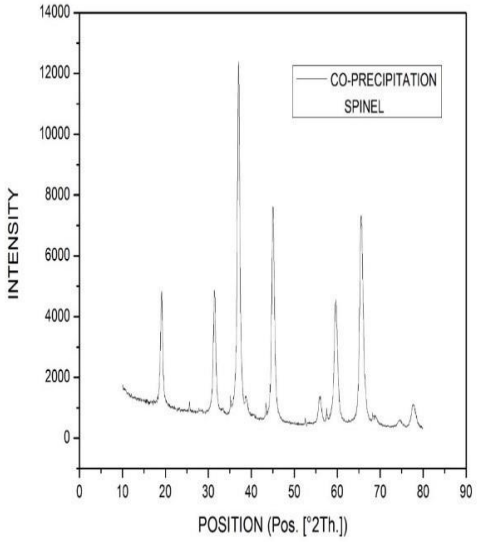
4.2 XRD



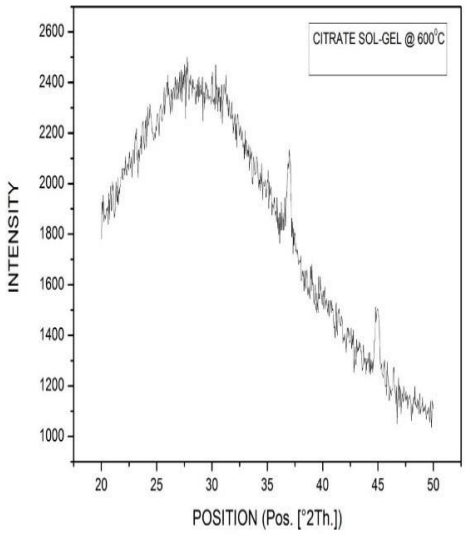
(a) XRD-Auto Combustion process at 600◦ C (b) XRD-Auto Combustion process at 700◦

Figure 4.2: The figures 4.2(a) to 4.2(b) give the results of XRD Procees at various temperatures.

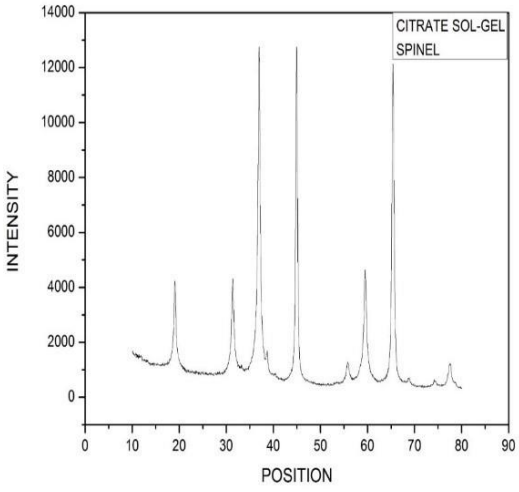
In case of citrate sol-gel.(4.3(b) &4.3(c)). and auto combustion route (4.2(a)&4.2(b)), 600◦ C calcination shows diffused, and very poorly crystalline material and does not show the formation of spinel phase. Increase in calcination temperature to 700◦ Cand above confirms the spinel phase for these routes and 700◦ C calcined products were selected for sintering study. Spinel powder prepared through co-precipitation route showed 100% spinel phase at 600◦ C.4.3(a).



(a) XRD-Co-precipitation process at 600◦



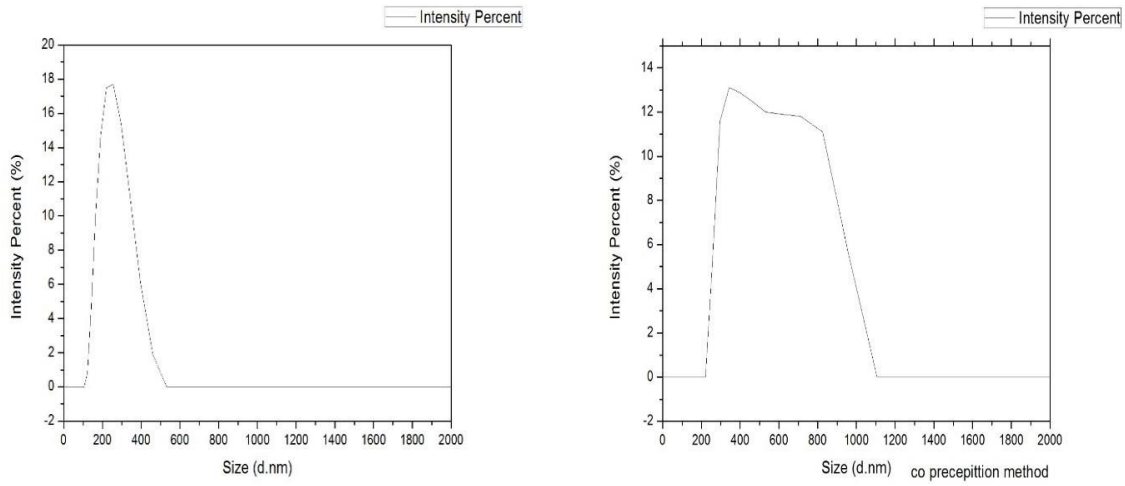
(b) XRD-Citrate sol-gel process at 600◦



(c)XRD-Citrate sol-gel process at 700^0 C

4.3 Particle size distribution

In case spinel powders of citrate sol-gel(4.5) and auto combustion(4.4(a)) route, average particle size was found around 300nm and for the co-precipitation process it was around 800nm(4.4(b)) which is higher than other conventional processes due to the formation of relatively large agglomerates in the spinel.



(a) Intensity %(Auto-Combustion process) (b) Intensity (co-precipitation process)

Figure 4.4 : The figures 4.4(a) to 4.4(b) give the intensity variation as per the particle size distribution in different methods involved.

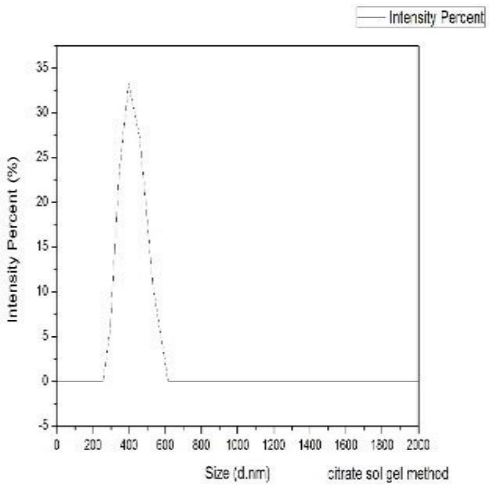
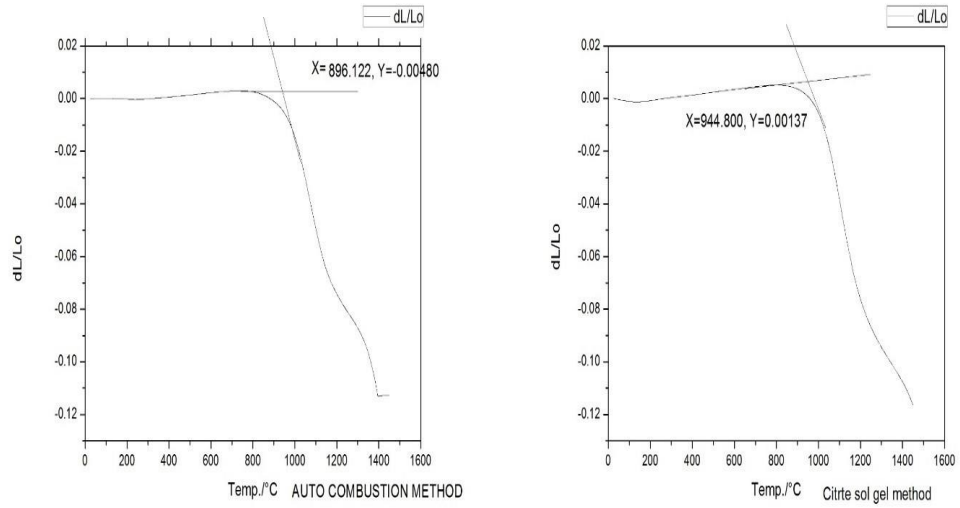


Figure 4.5: Intensity (Citrate Sol-gel process)

4.4 Dilatometry study

The onset temperature for all three routes was in between 890° C and 990° C.(4.6(a),4.6(b) &4.7). In this dilatometry study there are two major different phenomena occurring, i.e. the expansion due to the formation of spinel phase and shrinkage due to the sintering. This study shows that there is an increase in length with increase in temperature initially and an expansion of sample associated with spinel formation so an increase in length is observed. At an elevated temperature there is also sintering of the spinel. Onset temperature is the temperature beyond which sintering takes place. Onset temperature of the spinel powders



(a) Dilatometer-Auto-Combustion process (b) Dilatometer-Citrate Sol-gel process

Figure 4.6: The figures 4.6(a) to 4.6(b) give the results obtauned in Dialometry study.

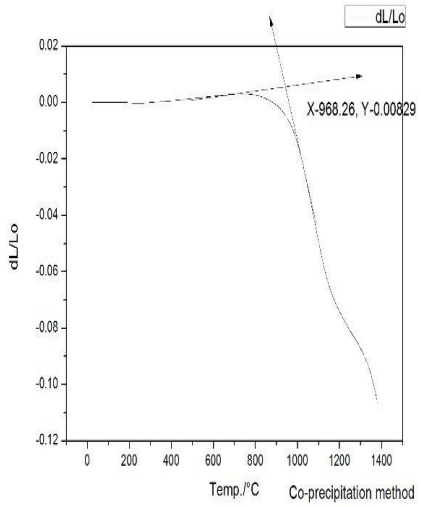


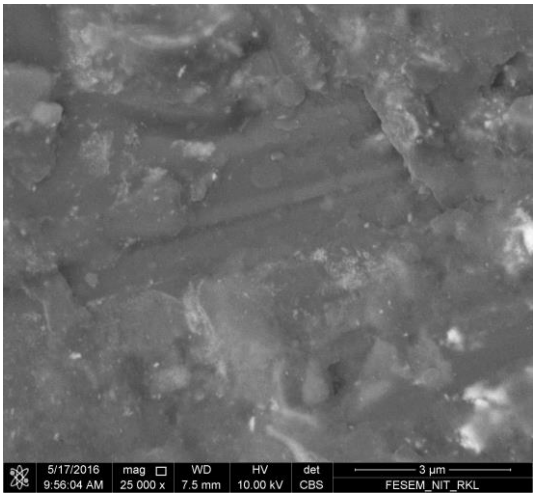
Figure 4.7: Dilatometer-Co-precipitation process

prepared through three different processes was calculated by using tangential method. By further increasing the temperature the effect of sintering overcome the expansion effect of the spinel samples. Sintering starts at a temperature as low as 896° C in case of the spinel powder prepared by Auto-combustion method.

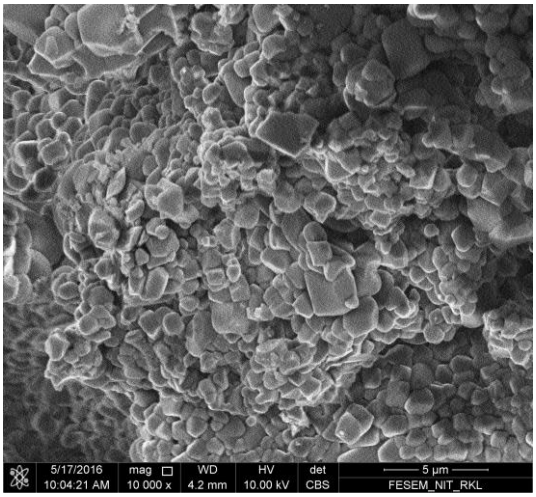
4.5 Microstructure study

4.5.1 Auto-Combustion Process

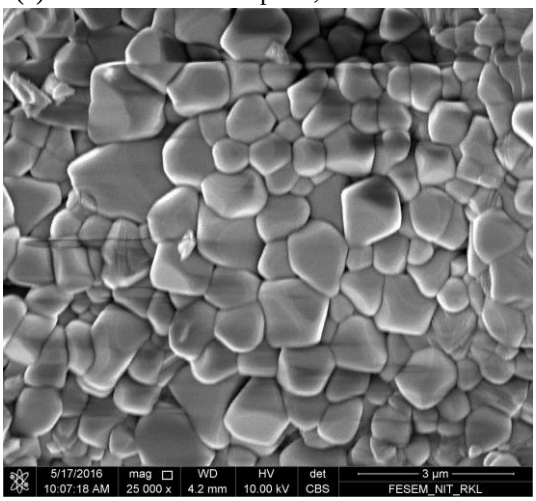
From the 4.8(a),4.8(b),4.8(c) & 4.8(d)(prepared by Auto-Combustion process), we can find very fine grain structure as compared to other routes, hence it gives high spinel formation but due to small size of spinel grains, it has a porous structure.



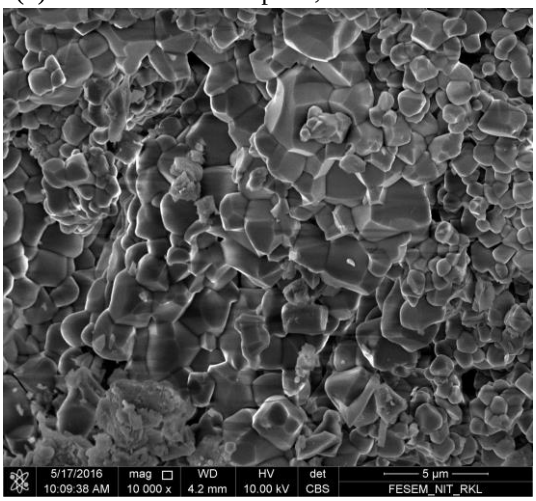
(a) Microsturcture of Spinel, Auto-Combustion



(b) Microsturcture of Spinel, Auto-Combustion



(c) Microsturcture of Spinel, Auto-Combustion

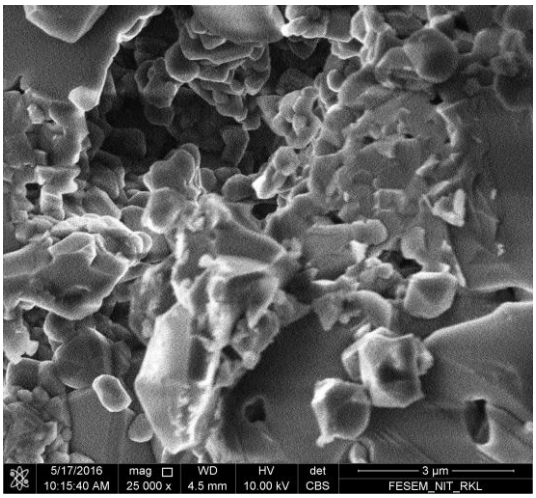


(d) Microsturcture of Spinel, Auto-Combustion

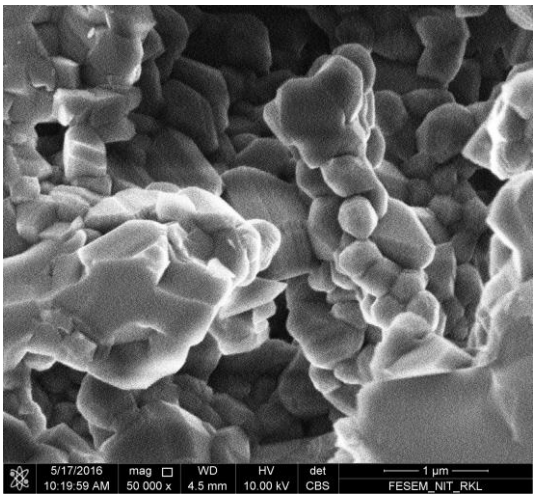
Figure 4.8: The figures 4.8(a) and 4.8(d) give the results obtained in Microstructure study of Auto-Combustion Process.

4.5.2 Co-precipitation Process

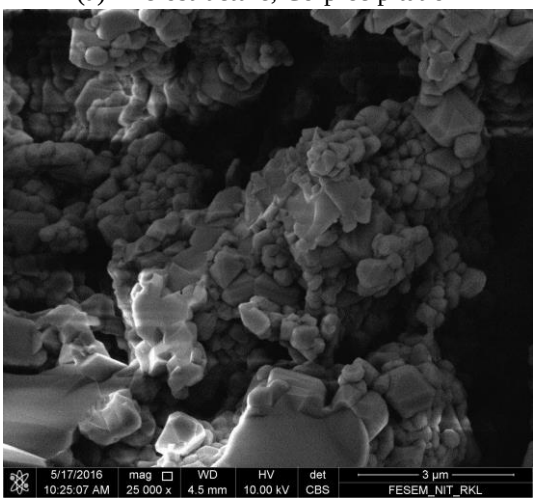
36 From the figures 4.9(a),4.9(b), 4.9(c) & 4.9(d),(Sample prepared by Co-precipitation process) It is observed that the spinel powders show irregular morphology. It shows definite distribution in the size range of microns. The size of most of the particcles are below 1.5 micron,however some of the grains are larger than 2 micron. This is due to the aggregation phenomenon which is originated from high temperature sintering conditions.



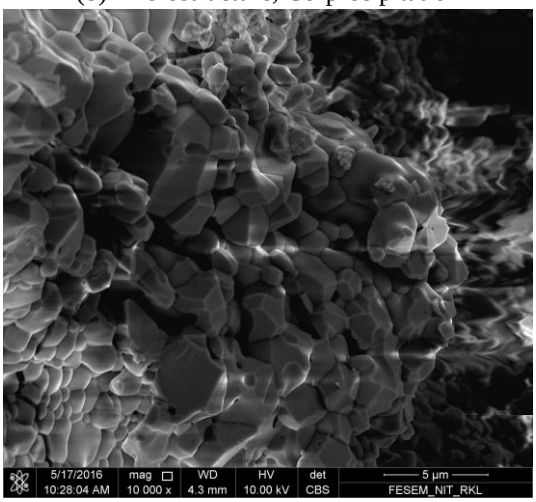
(a) Microstructure, Co-precipitation



(b) Microstructure, Co-precipitation



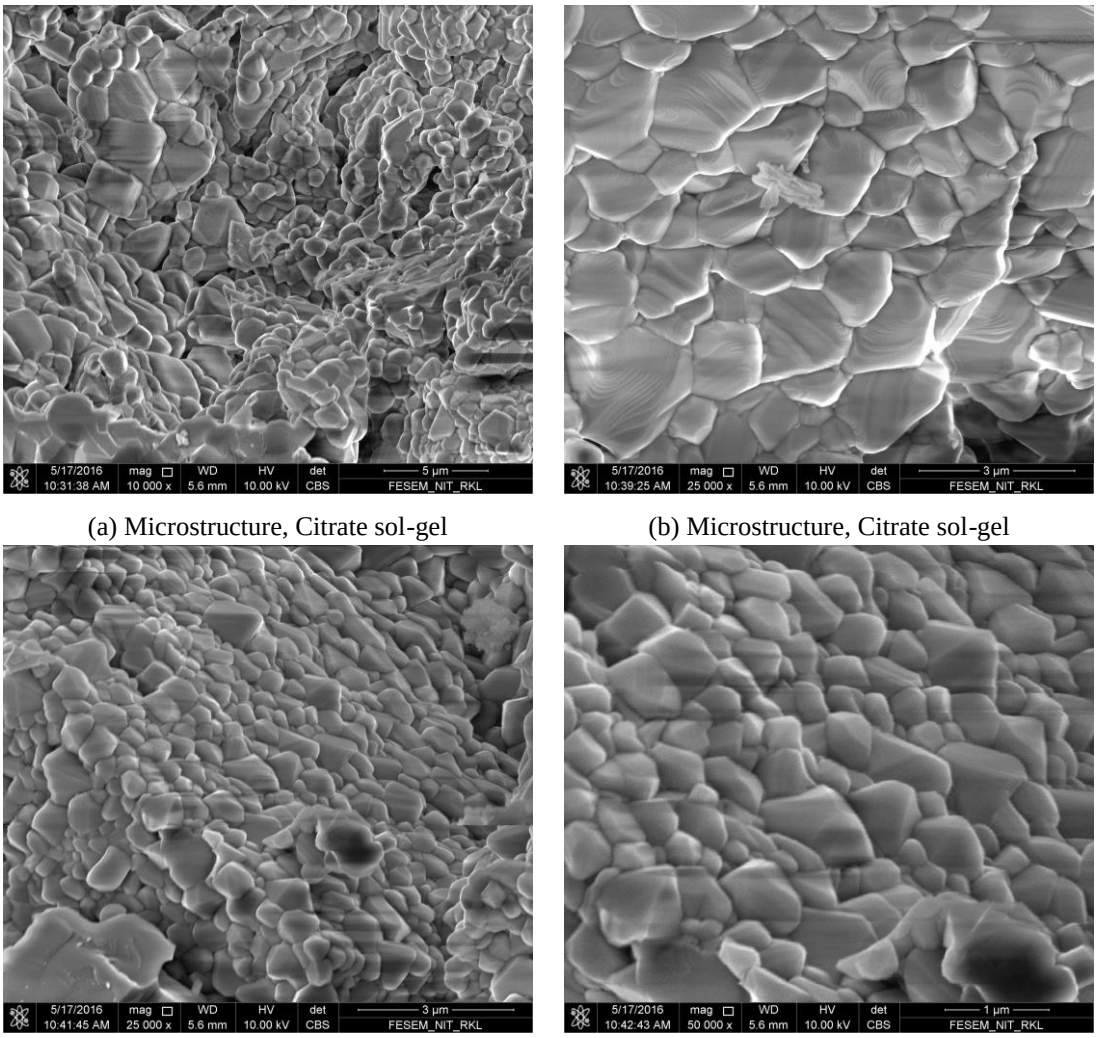
(c) Microstructure, Co-precipitation



(d) Microstructure, Co-precipitation

Figure 4.9: The figures 4.9(a) to 4.9(d) give the results obtained in Microstructure study of Co-precipitation.

4.5.3 Citrate sol-gel process



(a) Microstructure, Citrate sol-gel

(b) Microstructure, Citrate sol-gel

(c) Microstructure, Citrate sol-gel

(d) Microstructure, Citrate sol-gel

Figure 4.10: Microstructure study of Citrate sol-gel.

From the figures 4.10(a),4.10(b),4.10(c) & 4.10(d)(Sample prepared by citrate sol-gel process).In this case Citric acid was added as a fuel which is also a source of carbon. It made the dry gel more porous and enforced the combustion process to advance rapidly after it was added. The excess of the fuel may act as a space filling agent, which leave empty spaces after the burning of the fuel during the reaction.

4.6 Densification Study

4.6.1 Calculation of Bulk Density (without additive)

The bulk density and apparent porosity of the sintered spinel pellets were calculated by using Archimedes principle using DI water.

Table 4.1: Bulk Density Variation (Without additive)

Temperature	**Auto-Combustion**	**Co-precipitation**	**Citrate Sol-Gel**
1450	2.68	2.88	2.79
1500	2.72	2.97	3.18
1550	2.87	3.06	3.23

4.6.2 Calculation of Bulk Density(With TiO_2 as additive)

Table 4.2: Bulk Density Variation(With additive)

Temperature	**Auto-Combustion**	**Co-precipitation**	**Citrate Sol-Gel**
1450	2.74	2.93	2.87
1500	2.94	3.08	3.19
1550	3.03	3.13	3.3

4.6.3 Calculation of Apparent Porosity(Without additive)

Table 4.3: Apparent porosity calculation (Without additive)

Temperature	**Auto-Combustion**	**Co-precipitation**	**Citrate Sol-Gel**
1450	36.57	27.37	35.73
1500	25.17	19.04	29.28
1550	21.35	14.05	25.34

4.6.4 Calculation of Apparent Porosity (With TiO_2 as additive)

It is commonly assumed that the final density of any powder compact primarily depends on the reactivity of the powder along with the compaction uniformity of green body. In the

Table 4.4: Apparent porosity calculation (With additive)

Temperature	Auto-Combustion	Co-precipitation	Citrate Sol-Gel
1450	31.47	23.64	24.01
1500	28.96	18.60	19.32
1550	28.48	13.53	18.77

present study, the most important reason for the high reactivity and ultimately high density of the ultrafine powders is the large specific surface area. We also observe the agglomeration of the spinel powders prepared by co-precipitation process, but the agglomeration is significantly reduced in case of the spinel powders prepared through Auto-Combustion and Citrate Sol-Gel process. As we know that the agglomeration is inescapable for nanosized powder for practically any chemical methods. Furthermore the ultra high purity of the spinel powders, which is a characteristic feature of wet chemical preparation route or modified sol-gel process may also responsible for the higher sinterability of these spinel powders.To improve the densification behavior of the spinel powder, sintering additive(TiO_2) is added. This additive actually resides at the grain boundaries and restricts grain growth during the sintering, which ultimately leads to the improved packing hence, we get higher BD by using a sintering additive. Densification study shows the conventional sintering trend of increasing density values with increasing sintering temperatures. Higher density values were obtained for the citrate sol gel method. A highest density of 3.23 g/cc was obtained for this samples sintered at 1550° C. TiO_2 addition enhances the densification of spinel prepared through all three routes at 1550° C with the highest density observed again for the citrate sol gel method i.e. 3.3g/cc.

Chapter 5

Conclusion

Chapter 5

Conclusion

1- $MgAl_2O_4$ spinel was prepared through three different routes, i.e. Auto-Combustion process, Citrate sol-gel process and Co-precipitation process.

2- Spinelization was studied at three different temperatures (600° C, 700° C, 800° C) for Auto-Combustion process and Citrate sol-gel process and two different temperature (600° C, 700° C) for Co-precipitation process.

3- Optimization was done for all the three routes to achieve phase pure spinel at lowest possible calcination temperature.

4- Phase pure spinel was achieved at 600° C in Co-precipitation process, whereas 700° C was required to prepare phase pure spinel in case of Auto-Combustion process and Citrate sol-gel process.

5- Spinel powders prepared by Co-precipitation process shows relatively high average particle size(800nm).whereas spinel powders prepared by citrate sol-gel and auto combustion route, have an average particle size of around 300 nm.

6- Higher density values were obtained for the citrate sol gel method. A highest density of 3.23 g/cc was obtained for this samples sintered at 1550° C.

7- TiO_2 addition enhances the densification of spinel prepared through all three methods.

8- Highest density achieved were 3.13 and 3.03 for Co-precipitation and Auto-combustion methods respectively.

9- Again Higher density values were obtained for the citrate sol gel method. A highest density of 3.3 g/cc was obtained for this samples sintered at 1550°C.

Chapter 6
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