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

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CERTIFICATE

This is to certify that the thesis entitled " Development and Characterization Properties of Non Stoichiometric Spinel of Al-Mg Spinel By Sol-Gel Process" has been carried out under the guidance of **Dr. Sathi Banerjee, Dept. of Metallurgical and Material Engineering, Jadavpur University** by **Saikat Biswas** during the academic session 2018-2019 in partial fulfillment of the requirement for the award of the degree of **Master of Technology** in **Material Engineering** in the **Department of Metallurgical and Material Engineering, Jadavpur University**, **Kolkata- 700032**. In our opinion the work fulfils the requirement for which it is submitted. It is further certified that materials obtained from other sources have been acknowledged in the thesis.

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CERTIFICATE OF EXAMINATION

The forgoing thesis is hereby approved as credible study of engineering subject carried out and represented in a manner of warrants its acceptance as a prerequisite to the degree for which it has been submitted. It is to be understood that by the approval of the undersigned does not necessarily endorse any statement made, opinion, opinion expressed or conclusion drawn there in but approved the thesis only for the purpose for which it has been submitted.

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CONTENTS

ABSTRACT

Magnesium Aluminium Oxide,$MgAl_2O_4$ spinel is being used in many field for its high temperature application as a refractory material, good mechanical strength, high resistance to chemical attacks, good thermal shock resistance, good dielectric and catalytic properties. The spinel ($MgAl_2O_4$) is a mineral which has been found due to the process called metamorphism in igneous grade rocks. Its high melting point (2135^oC) and chemically inertness make it possible for use as refractory material. $MgAl_2O_4$ 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 behaviour 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 ^oC 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 ^oC, 700 ^oC, 800 ^oC, 900 ^oC, 1000 ^oC 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.

CHAPTER 1

INTRODUCTION

1. Refractory Material

1.1 Basic Concept:

Refractory material having high melting points, with properties that make them suitable to act as heat- resisting barriers between high and low temperature zones. These are non-metallic inorganic materials. The basic function are

- They act as a thermal barrier between a hot medium (e.g., flue gases, liquid metal, molten slags, and molten salts) and the wall of the containing vessel.
- They insure a strong physical protection, preventing the erosion of walls by the circulating hot medium.
- They represent a chemical protective barrier against corrosion.
- They act as thermal insulation, insuring heat retention.
- The principal raw materials used in the production of refractories are: the oxides of silicon, aluminium, magnesium, calcium and zirconium and some non-oxide refractories like carbides, nitrides, borides, silicates and graphite

Refractory materials due to these high quality properties has find its role in various industrial application such as the production of ferrous and non-ferrous metals, cement, glass, ceramics, chemicals, etc. in the following areas the refractory materials find its role majorly.

- furnaces
- kilns
- Boilers
- Incinerators

1.2 Definition of Refractory:

According to ASTM C71 defines refractory as "non-metallic materials having those chemical and physical properties that make them applicable for structures or as components of systems that are exposed to environments above 1000ºF (538ºC)".The iron and steel making industry has improved themselves by selecting proper refractory materials. This has resulted in remarkable changes in the operating practice such as furnace capacity, operating temperature, physio-chemical condition of reactor etc. To cope up with this there is requirement of refractory material selection according to working atmosphere at which these refractory materials are working upon .In present industry there are various types of refractories are used such as silica brick, fire clay brick, spinel group etc.

1.3 Types of Refractories:

Refractories can be classified in following ways:

I.   On the Basis of Chemical nature Materials:
- ➢ Acid Refractories (silica, Alumina silicate, zirconia etc.)
- ➢ Neutral Refractories (Graphite, Chromite etc.)
- ➢ Basic Refractories (Dolomite, Magnesite, Frosterite etc.)

II. On the basis of method of manufacturing:
- ➢ Shaped Refractories (available in the form of different brick shapes including the oxides and non- oxides systems)
- ➢ Unshaped Refractories (includes mortars, castable and other monolithic)

1.4 Required Characteristics of the refractory Material:

The type of refractory we will be using is depending upon on the nature of working condition. The refractory materials which are used in the iron and steel industry have to pass through very strict environment. This strict can environment can be of several types and these are discussed below

- Very high amount of load of molten metal
- Refractories have to withstand very high temperature which can be more than 1600°C.
- There can be slag attack which are corrosive in nature

Such an operating environment becomes even more challenging due to continuous improvement of technology for better results. Some of these ever changing features are:

- ➢ In the metal extraction technology there is further improvement and upgradation.
- ➢ Operation temperature is getting higher.
- ➢ Challenge of having longer service life

To cope up with the above mentioned barriers there is requirement of certain characteristics which must prevail in refractory materials nature and these are discussed below

- Corrosion resistance must be very high
- High thermal shock resistance
- Considerable mechanical strength even at high temperature
- Ease of application
- Prolonged lining life
- Less down time and environmental friendly.

2. Crystal Structure:

The crystalline structure of spinel ($MgAl_2O_4$) has been derived by the application of Hartman –Perdok analysis [1]. The Magnesia Alumina spinel is a cubic crystal structure. The general chemical composition of spinel is AB_2O_4 ,where A represent as a divalent cation such as Mg^{2+}, Fe^{2+}, Ni^{2+}, Zn^{2+} etc. and B represent as a trivalent anion such as Al^{3+},Cr^{3+}etc.
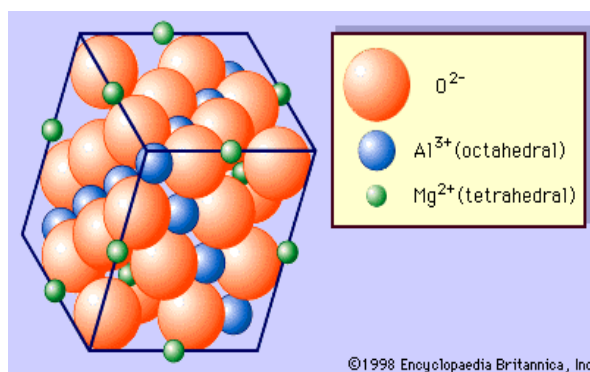
Figure 1.1 Crystal Structure of MgAl₂O₄

From the above figure, the divalent cation i.e. Mg^{+2} here took one eighth of the tetragonal sites and the trivalent cation which is Al^{+3} took one-half of octahedral sites. There are 8 $MgAl_2O_4$ units per unit cell. So a unit cell of $MgAl_2O_4$can be expressed in the form of $Mg_8Al_{16}O_{32}$ in which the structure of the anion oxide having face centered cubic packing. The space group space and lattice parameter of MgAl2O4 is having Fd3m and 'a' is 8.08435 Å.

3. Spinel:

In the early literature survey on 1960, the magnesia aluminate spinel as the basic refractory were produced[2] .The spinel ($MgAl_2O_4$) is a type of mineral had found due to the process called Metamorphism in existing rocks. The term spinel was derived from the latin word 'spina' in reference to its pointed octahedral crystal habit .The spinel series were evolved from the classification of Spinel, Magnesite and Chromite. They are usually very hard, various coloured minerals and occurring in carbonate and ignition rocks. Spinels are very attractive subjects for material research purpose and also in engineering applications. The magnesia alumina spinel are highly refractory and it varies from translucent to transparent and from colourless to blue, brown and black.

The magnesia alumina spinel offers high melting point, excellent resistance against chemical attack [3], low thermal expansion, considerable hardness [4] and outstanding dielectric optical properties [5].

3.1 Normal Spinel:

- In spinel the general expression is AB_2O_4.

- The cation A^{+2} occupies tetrahedral sites whereas B^{+3} occupies octahedral sites.
- The common example belongs to aluminate such as $MgAl_2O_4$,$CoAl_2O_4$, $FeAl_2O_4$and also ferrite such as $ZnFe_2O_4$,$CdFe_2O_4$.

3.2 Inverse Spinel:

- The general expression is $B(AB)O_4$
- The structure is opposite to the normal spinel i.e. the A^{+2} occupies in octahedral sites and B^{+3} cations occupies tetrahedral sites.
- Most of the ferrite are fallen in inverse spinel category such as Fe_3O_4,$NiFe_2O_4$, $CoFe_2O_4$.

3.3 Physical Properties:

The physical property has been described below:

a) High Melting Point:
   The fusion melting point is 2135ºC, so it can withstand in a very high range of temperature. We know that melting point of all kind of steel is below 2000ºC, so it can be used as refractory purpose for steel making.

b) Hardness:
   As natural occurrence is little, the $MgAl_2O_4$ spinel is artificially synthesized, the hardness value measured for nano crystalline $MgAl_2O_4$ spinel the hardness varied within 2.89-7.79 GPa[6, 7]

c) High Electric Resistivity:
   The energy bandgap is greater than 7.5 eV, so it is highly electrical resistivity, so it is beneficiary to use as a refractory[7]

d) Low Thermal Expansion:
   It has relatively low thermal expansion coefficient which is 9×10^{-6} c^{-1} between 30 and 1400ºC [8].

e) Chemically Inertness:
   It has higher chemical resistance in higher temperature, so the $MgAl_2O_4$ has been replaced traditional chromite based refractories in cement rotary kilns and steel ladles [9, 10].
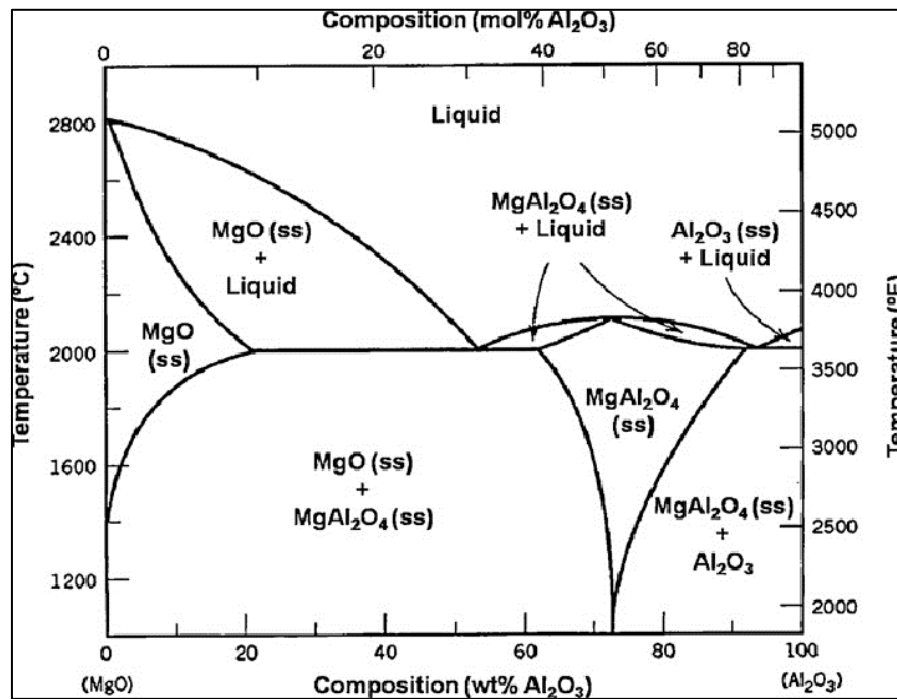
f) Mechanical Strength:
   It has high mechanical strength at room temperature as well as in higher temperature. In room temperature its strength ranges in between 135 MPa to 216 MPa and in elevated temperature (1300º C) it is between 120MPa to 205 MPa [7].

g) Density:
   It has relatively low density as 3.93gm/cc.

3.4 Phase Diagram Of MgAl₂O₄:

Figure 1.2: Phase Diagram in the system MgO-Al₂O₃ spinel (MgAl₂O₄) is the only intermediate compound, with a congruent melting point at 2135°C

From the figure 1.2

- The melting temperature of pure magnesia is 2800°C.
- The melting temperature of pure alumina is2054°C.
- Magnesia can be solvable in 2% alumina and at 2000°C and also it has the maximum solubility. The solid solution of alumina in magnesia is called "periclase."
- The Magnesia cannot be dissolved into alumina.
- Magnesium aluminate (MgAl2O₄) is a major figure when we are considering about spinel group. In the phase diagram it is the binary system consisting of magnesia and alumina. From the figure it has been observed that the solubility of alumina is varying from 40% to 84% within the temperature range 1800°C to 2000°C. The spinel which consist 50% of alumina melts at 2200°C.
- 82% of partial solidification of magnesia alloy starts at 2200 °C with equal parts of periclase and liquid.
- In 2000°C, there is transformation of 68% magnesia alloys from liquid phase to two solid phase by cooling. Periclase is one of the solid phase which contains 2% alumina and MgAl2O4 is the other one with 40% alumina content.
- In 2000°C, it has been seen 73% alumina consist of half liquid and half MgAl₂O₄.

- In 1800°C, transformation of phase occurs from liquid to 2 solid phase at the composition of 95% alumina alloy and one of them is spinel of 84% alumina and the other one is pure alumina.
- In 1000°C, there is an equal amount of alumina phase and spinel phase of 74% of alumina, the latter with a composition of 54% alumina.

CHAPTER 2

LITERATURE REVIEW

2.1 MgAl₂O₄ Spinel as a Refractory Material:

Refractories play an important role in metallurgical, glassmaking and ceramic industries [11, 12]. The main problems faced in steel ladle refractories are corrosion by steel slags, thermal spalling, oxidation of carbon layer, abrasion by liquid metal, deterioration of strength at high temperature and molten steel penetration. The basic problems in the technology of highly refractory ceramics include of increasing the thermal shock resistance, reducing creep at elevated temperatures and improving the sintering ability of the materials. The performance of refractories greatly depends on the selection of raw materials. It is now well established that magnesia-spinel refractories derived from pure raw materials with a high degree of direct bonding of MgO-MgO and MgO-spinel grains exhibit high hot temperature strength, an improved resistance to slag attack, and dimensional stability at high temperatures [13]. In this study Magnesium Nitrate Nona Hydrate and Aluminium Nitrate Nona Hydrate with Citric acid (as a fuel) were used as starting materials for preparation of magnesia-alumina spinel $MgAl_2O_4$ ceramics.

The Magnesium-Aluminate spinel structure offers some attractive combination of properties such as high mechanical strength at high temperature, high melting point (2135ºC), high chemical inertness and thermal stability [14-15]. Due to these properties, it is greatly desired as a refractory material [16]. Humidity sensor [17], catalyst or catalyst support and recently as an excellent transparent ceramic material for high temperature arc-enclosing envelopes and alkali-metal vapour discharge devices [18]. Nowadays this spinel has owned many applications in metallurgical, chemical, electro technical, catalysis, electronic and glass industries [19]. Over the last few decades various novel techniques have been applied for the synthesis of $MgAl_2O_4$ spinel including Sol-Gel [20], spray drying [21], freeze-drying [22], mechanical activation [23], and organic gel-assisted citrate process [24]. Although wet-chemical techniques have successfully been used for the preparation of pure spinel nano particles at relatively low temperatures, but have not received much commercial attention because of the expensive raw materials and multiple processing steps. The conventional preparation method of $MgAl_2O_4$ spinel is to calcine the mixture of metal oxides at elevated temperatures (1625ºC for 2hours), which has disadvantages of large aggregates and inhomogeneous compositions [25]. Recent works show combustion synthesis for preparation of binary oxides has many advantages including homogeneity, high purity, formation of crystalline oxide powders in shorter time periods and lower amount of external energy [26-27]. Magnesium aluminate spinel, which is the only stable compound in the $MgO-Al_2O_3$ system, has long been considered an important ceramic material. Many studies have reported its properties, applications and different processing methods [28]. Magnesium aluminate spinel ($MgAl_2O_4$) is an excellent refractory oxide of immense technological importance as a structural ceramic. It possess successful physical, chemical and thermal properties, both at normal and elevated temperatures. It melts congruently at 2135ºC, shows high resistance to attack by most of the acids and alkalis and has low electrical losses. Due to these desirable properties, it has a wide range of application in structural, chemical, optical, and electrical industry. It is used as a refractory in lining of steel-making furnaces, transition and burning zones of cement rotary kilns, checker work of the glass furnace regenerators, sidewalls and

bottom of the steel ladles, glass furnaces and melting tanks. Synthesis and fabrication of spinel $MgAl_2O_4$ is known since long. A number of techniques such as conventional solid-state-reaction (SSR), sol-gel, spray drying (atomization) and organic gel-assisted citrate complexation have been extensively employed [29].

2.2 Various Route of Synthesis of MgAl₂O₄ Spinel:

Abdi et. Al [30] shows that MgAl2O4 nanoparticles were successfully synthesized by mechanically activated solid-phase exchange reaction of magnesium chloride with aluminium chloride in the presence of sodium hydroxide altogether with a small amount of water were mixed and subjected to high energy ball milling for a short time. After that milled powder heated from 400°C to 1200°C for 2 hour. After characterization pure nano phase with 8-12 nm mean particle size obtained. Then sintered at 1500°C and obtained 93.8% theoretical density.

Gilvan et al. [31] indicate that $MgAl_2O_4$ nanoparticles were synthesized using Magnesium Nitrate and Aluminum nitrate as precursor and Gelatin as organic precursor and to verify the influence the temperature and time of calcination on the structural and morphological properties of obtained materials. The Aluminum Nitrate and Magnesium Nitrate were used as metal precursor of 2:1 ratio. The obtained crystalline size was 12.4 to 55.5 nm.

Vahid et al.[32] shows that $MgAl_2O_4$ nanoparticles were synthesized by using combustion method Magnesium Nitrate ($Mg(NO_3),6H_2O$) Aluminium Nitrate($Al(NO_3)_3,9H_2O$) and urea (NH_2CONH_2) were used without further purification .For the production of biodiesel, sunflower oil and methanol were used as reactants of transesterification.

Viacheslav et al[33] prepared the $MgAl_2O_4$ nanoparticle using raw amorphous magnesite and γ-Al_2O_3 as nanopowders were used as starting materials for preparation of periclase-magnesium aluminate spinel ceramics. Magnesite was annealed at a temperature of 800°C with an exposure of 2 hours. A nanosized γ - Al_2O_3 powder was obtained by hydrothermal method. The resulting nanopowders were mixed and milled in a ball mill during 30 min. Specimens of periclase-magnesium aluminate spinel ceramics were compacted by a bi-directional axial compression and sintered at 1500°C with an exposure 2 hours at the maximum temperature. The microstructure and mechanical properties of the ceramics were evaluated. Dense periclase-magnesium aluminate spinel ceramics with density of 3.3 g/cm^3 and compressive strength of more than 300 MPa were obtained.

Li et al. [34] shows that for the synthesis of $MgAl_2O_4$,the anhydrous aluminium chloride ($AlCl_3$) and anhydrous magnesium chloride ($MgCl_2$) were used as aluminium and magnesium precursors, respectively. Anhydrous ethanol (C_2H_5OH) was used as an oxygen donor and dichloromethane (CH_2Cl_2) was used as solvent, respectively. All the raw materials were analytically pure and used without further purification. After characterization results showed that the $MgAl_2O_4$ spinel possessed mesoporous structure with the pore diameter between 3-50 nm and it also exhibit superior sintering properties.

Ganesh et al.[35] shows in there experiment that by different types of dense stoichiometric and nonstoichiometric magnesium aluminate ($MgAl_2O_4$) spinel ceramics were prepared

following a conventional double-stage firing process using different commercially available alumina such as Aluminium trioxide and aluminium oxide and magnesia raw materials such as Magnesium hydroxide and caustic MgO prepared from sea water magnesia. During preparation of spinel all the calcined powder were milled using rotary mill till average particle size was reached. After that Stoichiometric, magnesia-rich, and alumina-rich spinels were sintered at 1500°–1800^oC for 1–2.5 h. The influence of the different processing parameters on the densification behavior of MAS was assessed by measuring the bulk density, apparent porosity, and water absorption capacity, and microstructural observations. Most of the MAS compositions tested exhibited excellent sintering properties.

Padmaraj et al. [36] shows in there experiment that by sol gel combustion method nano crystalline spinel type magnesium aluminate ($MgAl_2O_4$) ceramic material was synthesized. The synthesis was done using Magnesium Nitrate ($Mg(NO_3)_2, 6H_2O$), Aluminium Nitrate ($Al(NO_3)_2 ,9H_2O$) and glycine ($NH_2.CH_2.COOH$) for the preparation of nano crystalline $MgAl_2O_4$ spherical particle by glycine assisted gel combustion method, where Magnesium and Aluminium (1:2) and fuel as glycine were dissolved separately with the required quantity of distilled water. The specific surface area of the prepared nanocrystalline $MgAl_2O_4$ powder was measured by adsorption method and is found to be $162.704 m^2/gm$. The calculated conductivity value of nanocrystalline $MgAl_2O_4$ pellet at 573K is found to be 4.9213×10^{13} S cm^{-1}. The activation energy of magnesium aluminate sample was estimated in two different temperature dependent conductivity regions and are found to be $E_1 = 0.1828$ eV (<503 K) and $E_2 = 0.8791 eV$ (>503K).The conductivity, dielectric constant and dielectric loss of the nanocrystallineMgAl2O4 sample were obtained from the analysed impedance data and the observed results are analysed and explained using the existing theoretical models

2.3 Selection Of Citric Acid as the fuel agent:

Golyeva et al[37] in their work of preparation of nanocrystalline aluminium magnesite spinel doped with europium ions powders were synthesized via modified Pechini method. So for that Eu_2O_3 ,$Al(NO_3)_3 \cdot 9H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ crystalline hydrates were chosen as starting reagents. Eu_2O_3 was dissolved in concentrated nitric acid to form the nitrate solution Eu(NO3)3, whereas Al(NO3)3·9H2O and Mg(NO3)2·6H2O were dissolved in a distilled water. Then both solutions were mixed and heated, then citric acid was subsequently added (volume ratio 1:1) to the resulting mixture, that led to the citric metal complexes $[Me(C_6H_8O_7)_3](NO_3)_3$ formation. After adding the ethylene glycol to citric acid solution in ratio of 1:4 and this mixture was heated to remove excess water. Polymeric gel was obtained due to poly esterification process. Then resulting gel was calcined at temperature 500,600 and 700^oC with soaking time 1.5 hour Then, the obtained powder was mixed with potassium chloride in weight ratio 1:1 and calcined the second time at higher temperature (800, 850, 900,950, 1000, 1100, 1200 °C) for the period of time (1, 2, 3, 4 h). After the second calcination stage the powder was centrifuged, washed with distilled water three times to remove potassium chloride and then dried. So, MgAl2O4: Eu3+ nanocrystalline powders with different temperatures and durations of calcination stages were synthesized.

Miroliaee et al[38] had shown in their work by ion pair complex precursor approach to fabricate high surface area nanopowder of $MgAl_2O_4$ spinel, the synthesization of $MgAl_2O_4$ using thermal decomposition of $[Mg(H_2O)_6]$ $[Al(dipic)]_2.6H_2O$ as an ion-pair complex precursor. For comparing, 2 other samples were fabricated by co-precipitation and citrate sol-gel methods. Among these three routes to obtain $MgAl_2O_4$ spinel, the ion-pair complex precursor approach exhibits the smallest crystallite size (8.7 nm) and the by that the highest BET surface area (203.4 m2/g), indicating fabrication method influence.

Sanjabi et al[39] has shown in their experiment that by modified sol gel method nanocrystalline $MgAl_2O_4$ spinel were successfully synthesized using Aluminium Nitrate $(Al(NO_3)_3,9H_2O)$ and Magnesium Nitrate $(Mg(NO_3)_2.6H_2O)$ .The Magnesium Nitrate
At first dissolved in diethyl glycol monoethyl ether and anhydrous citric acid was slowly added to this solution and then sintered .After fully synthesized and also after calcination by FESEM analysis the spherical nanoparticle is in the range of 12 nanometer.

Rahmat et al[40] has shown in their experiment that by single stage solid state fusion is done of Magnesium aluminate ($MgAl_2O_4$) with citric acid as a fuel agent .The samples were prepared at different annealing condition such as temperature and duration .The stoichiometric ratio of $Mg(NO_3)_2.6H_2O$, $Al(NO_3)_3.9H_2O$, and $C_6H_8O_7.H_2O$ are in the ratio of 1:2:3 were mixed using a mortar and a pestle, and rigorously pulverized for at least 1 hour.
The pulverized mixture was then transferred into a crucible and placed in an oven at 100 °C for 2 hours. Then as calcination temperature increases it also increased the crystallite size, but decreased the specific surface area of the $MgAl_2O_4$ spinel. Its catalytic activity in the steam reforming of methane has revealed that the $MgAl_2O_4$ spinel, with a high surface area, small crystallite size, and low aggregations could result in a high conversion of methane (57%) in the first 180 minutes of reaction. Meanwhile, sample annealed at 1000 °C exhibited low catalytic activity due to the thermal sintering at high temperatures.

CHAPTER 3

EXPERIMENTAL WORK

3.1PREAMBLE:

In this experiment the Magnesium Alumina spinel powder were prepared by the sol gel synthesis procedure. For preparation of $MgAl_2O_4$ the Magnesium Nitrate Hexahydrate $(Mg(NO_3)_2 .6H_2O)$ and Aluminium Nitrate Nonahydrate $(Al(NO_3)_3 . 9H_2O)$ used as precursor mixes with Citric Acid Anhydrous$(C_6H_8O_7)$ as fuel agent with 5-7 ml DI water. The $Mg(NO_3)_2 .6H_2O$ and $Al(NO_3)_3 . 9H_2O$ and $C_6H_8O_7$ were mixed in the ratio of non-stoichiometric ratio by increasing $Al(NO_3)_3.9H_2O$ in 1:2.25:1.5,1:2.5:1.5 and 1:2.75:1.5 molar ratio and also by decreasing $Al(NO_3)_3 . 9H_2O$ in 1:1.5:1.5 and 1:1.75:1.5 in molar weight ratio.So the ratio of different sample were synthesized for $MgAl_2O_4$ spinel .Not only varying aluminium nitrate nonahydrate ratio but also attempted to manage lowering the temperature of obtaining spinel.

3.2 SAMPLE PREPARATION:

3.2.1Preparation Of Solution:

The $MgAl_2O_4$ spinel was prepared by the sol gel route using the Magnesium Nitrate Hexahydrate $(Mg(NO_3)_2 .6H_2O)$ and Aluminium Nitrate Nonahydrate$(Al(NO_3)_3 . 9H_2O)$ as the precursor mixes with Citric Acid Anhydrous$(C_6H_8O_7)$ as fuel agent along with 5-7 ml DI water and by varying aluminium nitrate nonahydrate in the 5 different ratio of molar weight in 1:2.25:1.5, 1:2.5:1.5 and 1:2.75:1.5 and also by decreasing aluminium nitrate nonahydrate in 1:1.5:1.5 and 1:1.75:1.5.

3.2.2 Heating and Drying Of Solution:

After mixing them together in the above molar ratio heated at 80^oC for the formation of the sol gel route for around 8 to 10 hours in each of the given ratio sample. The very small amount of water is added because of the gel formation, which happened faster due to the fuel were used. In the gel formation the solution undergoes rapid rise of viscosity that corresponds to the transition from a viscous fluid to an elastic gel. So in that gel formation when the gas unable to evaporate, heated in the Ultra sonicator for 5-8 hour at a temperature in 50^oC which helps the formation of synthesis more homogeneous. Though the time is required is much higher but due the vibration of the molecules it can easily separated and it helps to evaporate the vapour.
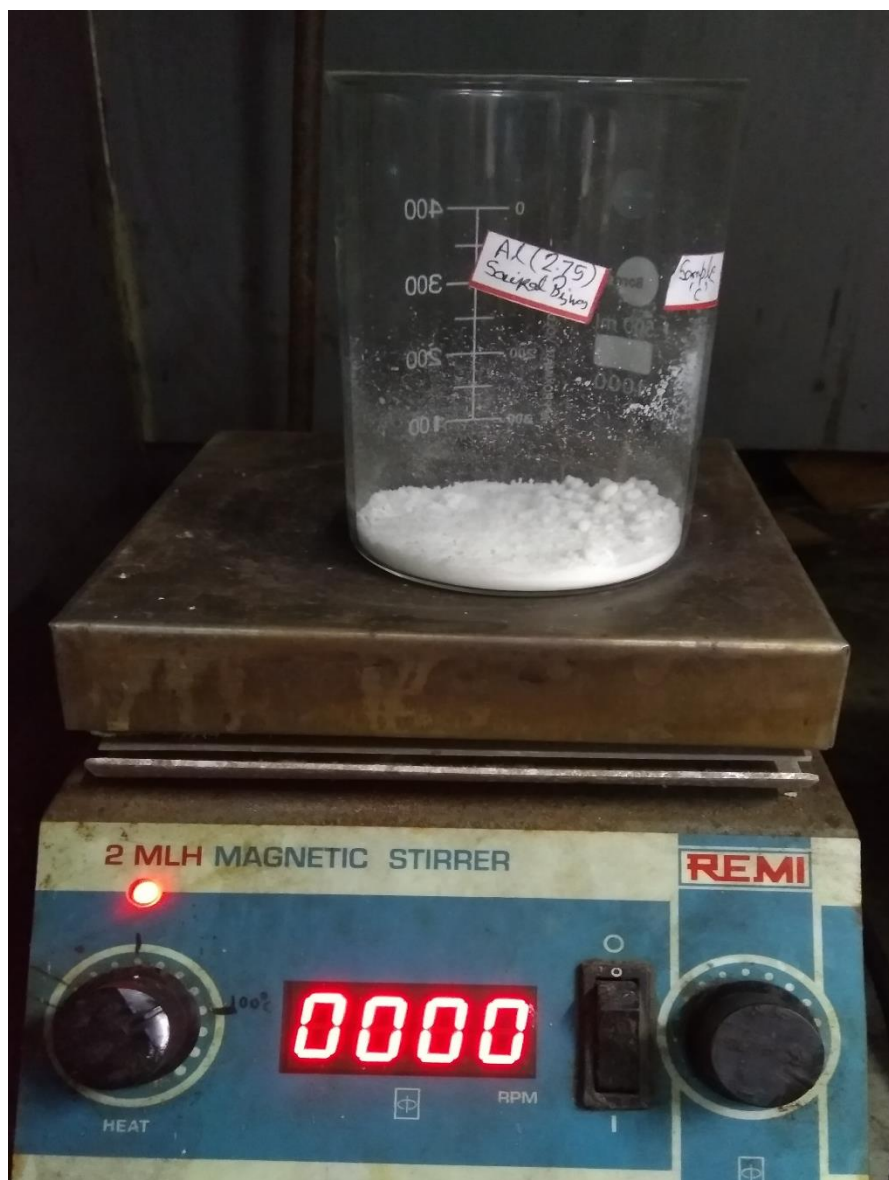
Figure 3.1: Heating the material at 80ºC until the gel is formed

Figure 3.2: Ultrasonic Cleaner is used for heating and drying after formation of gel

3.2.3 Calcination:

After the removal of pore liquid further heat treatment is necessary to convert into a catalytically useful form. The heating is done in the presence of a reactive gas (here flowing air) in order to burn off any residual organics.

The collected sample were taken in a ceramic boat for calcination in the furnace.

- At first sets the temperature at which calcination will be done and it would be fixed throughout the whole curing process. Here the temperature were set at 650°C,700°C, 800°C, 900°C and 1000°C.And the rate of rising the temperature is 5°C/minute.
- Then the holding time is set which remains same in every sample i.e. 5 hours. As electric furnace is used, so the programme is set at first.
- Then the cooling is done which is not in controlled programme. So certain time is required to cool the furnace.

Figure 3.3: Electric Cord Furnace

3.2.4 Hand Grinding Of Ceramic Powder:

After calcination at different temperature, the materials were grinded using Agate Mortar Pestle for its better characterization.

Figure 3.4: Nanopowder were grinded using Agate Mortar Pestle

3.3 PRESSING AND COMPACTING FOR MICROHARDNESS TEST:

After calcination the powder mixes with PVA(Polyvinyl Alcohol) for the binding of the material, which were taken in 1.9 wt% ratio of PVA along with 98:1 ratio of water and PVA. The water: PVA was heated at $50^{o}C$ until it dissolved and then the powder $MgAl_2O_4$ were heated and sonicated until it completely dissolved. Then the powder mixture were poured in a 50 mm diameter mould cavity in a die system and pressed by applying uniaxial pressure of approximately 200 MPa .Then cylindrical pellets of spinel of different ratio of materials were obtained.

Figure 3.5: Hydraulic Controlled high pressure Pressing Machine

3.4 CURING:

The compacted sample were cured at first 400°C for removal of PVA for about 1 hour. But the formation of sintering of spinel was not remain proper at lower temperature, so in different temperature analyse the 2 sample denoting S and T which corresponds to $Al(NO_3)_3.9H_2O$ molar ratio in 1.75 and 1.5, well sintered at 1200^0C with holding time for 2 hour. And for sample A, B and C which corresponds to $Al(NO_3)_3.9H_2O$ molar ratio are in 2.25, 2.5 and 2.75 they were well sintered at 1400^0C with holding time for 2 hours. This was done for

- Elimination of residual water, volatile matters if presence in the sample.

- Development of sufficient strength and proper binding of the constituents so that pellets can be used for micro hardness test.
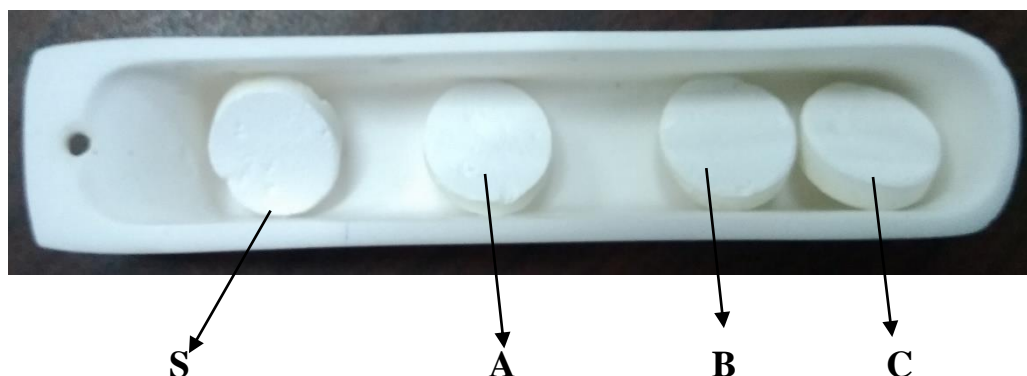
Figure 3.6: Sintered Spinel Material in different ratio of Al

1.3 CHARACTERIZATION:
1.3.1 DTA/DSC-TGA Analysis:

The DTA stands for Differential Thermal Analysis and the TGA stands for Thermo Gravimetric Analysis. In that analysis in DTA part, heat a sample in crucible and a reference in another simultaneously. DTA give signal in the temperature difference between the sample and refrence.From that we can easily see the exothermic reaction or endothermic reaction. In TGA it measures accurately the mass and its change with respect to increase in temperature. Diamond DT-TGA can also analyse DSC by suitable software to measure heat flow Vs temperature plot. This system can measure simultaneously both weight change and heat flow and accordingly any phase change can be identified precisely as most of the phase change occurs without change in weight. Below the schematic view and the image of DT-TGA instrument are given below-

Figure 3.7:DTA/DSC-TGA Instrument

MODEL NO. : Pyris Diamond TG/DTA

MAKE : PerkinElmer (SINGAPORE)

Nitrogen Atmosphere (150ml/min) Platinum crucible used with alpha alumina powder as reference.

3.5.2 XRD Analysis:

After synthesized of material there is needed of characterization in order to determine the phase of the material. The XRD analysis is an analytical technique designed to provide more in depth information about the crystalline compound including identification and quantification of crystalline phases. This is a useful tool when we want to identify a contaminant for additive identification of foreign phases for purity analysis of crystalline powders.

The X-Ray are generated by a cathode ray tube filter to produce monochromatic radiation collimated to concentrate and directed towards the sample. The interaction of the incident rays with the sample produce constructive interference when condition satisfied Bragg's Law

$$n\lambda = 2dSin\theta$$

The information which we get from diffraction patterns are

i.   Phase Identification
ii. Crystal Size
iii. Crystal Quality
iv. Texture to some extent
v.   Crystal Structure.

From the XRD analysis data got a graph which is in a form of intensity v/s 2θ. There would be peaks in the graph which indicates about a certain phase which has been crystallized. Every peak's information (angle, intensity, flex width, d-value) has to be compared with JCPDS data. The JCPDS stands for Joint Committee on Powder Diffraction Standards. This is a database of standard XRD reference patterns.

Figure 3.8: X-Ray Diffraction Machine

For the synthesized sample X-Ray Diffraction analysis was carried out with Bruker D8 Advance of all the samples under identical conditions with Cu Kα radiation whose-
- Tube voltage is 40 kV
- Tube current is 40 mA.
- Scan Range: 10º-90º
- Scan Mode: Continuous
- Speed: 1º/min

3.5.3 FTIR Analysis:

In FTIR (Fourier Transform Infrared Spectroscopy) the resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like fingerprint no two unique molecular structures produce the same infrared spectrum. From the FTIR analysis we can identify

- Unknown material in the sample
- Determine the quality or consistency of the sample
- Determine the amount of components in the mixture.

The size of the peaks in the spectrum is a direct indication of the amount of material present and the position indicates typical bonds. For FTIR spectroscopy the sample was prepared by adding KBr to the sample to make a pellet by hydraulic pressure. One KBr pellet was also made for the reference material.

From the FTIR analysis by plotting the signal and wavelength graph we can evaluate the vibration is either bending or stretching. Generally it is easier to bend than stretch so bending vibration are of low energy than stretching vibration for the same bond.
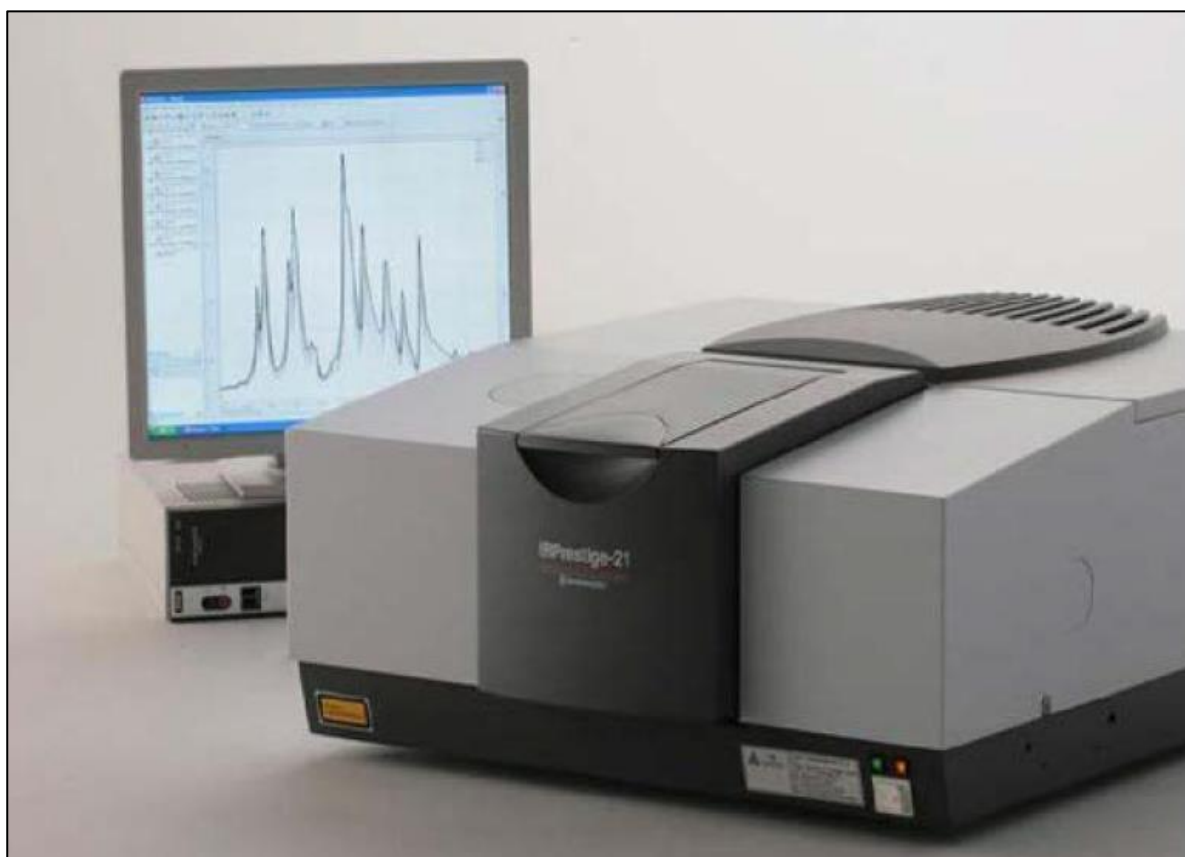
Figure 3.9: Shimadzu IRPrestige-21 FTIR spectrometer

3.5.4 FESEM Analysis:

The field emission scanning electron microscope (FESEM) images a sample
Surface by raster scanning over it with a high-energy beam of electrons. The electrons interact with the atoms comprising the sample to produce signals that contain information about surface topography, composition and other properties, such as electrical conductivity. The function of the electron gun is to provide a large and stable current in a small beam.
FE source is about 1000 times smaller than that in a standard microscope with a thermal electron gun, the image quality will be markedly improved; for example, resolution is on the order of ~2 nm at 1 keV and ~1 nm at 15 keV. The size range in Nanoscience is typically from hundreds of nanometers down to the atomic level (approximately 0.2 nm), in which the materials (nano materials) can have different or enhanced chemical/physical properties compared to the same ones at a bulk size [41-43].
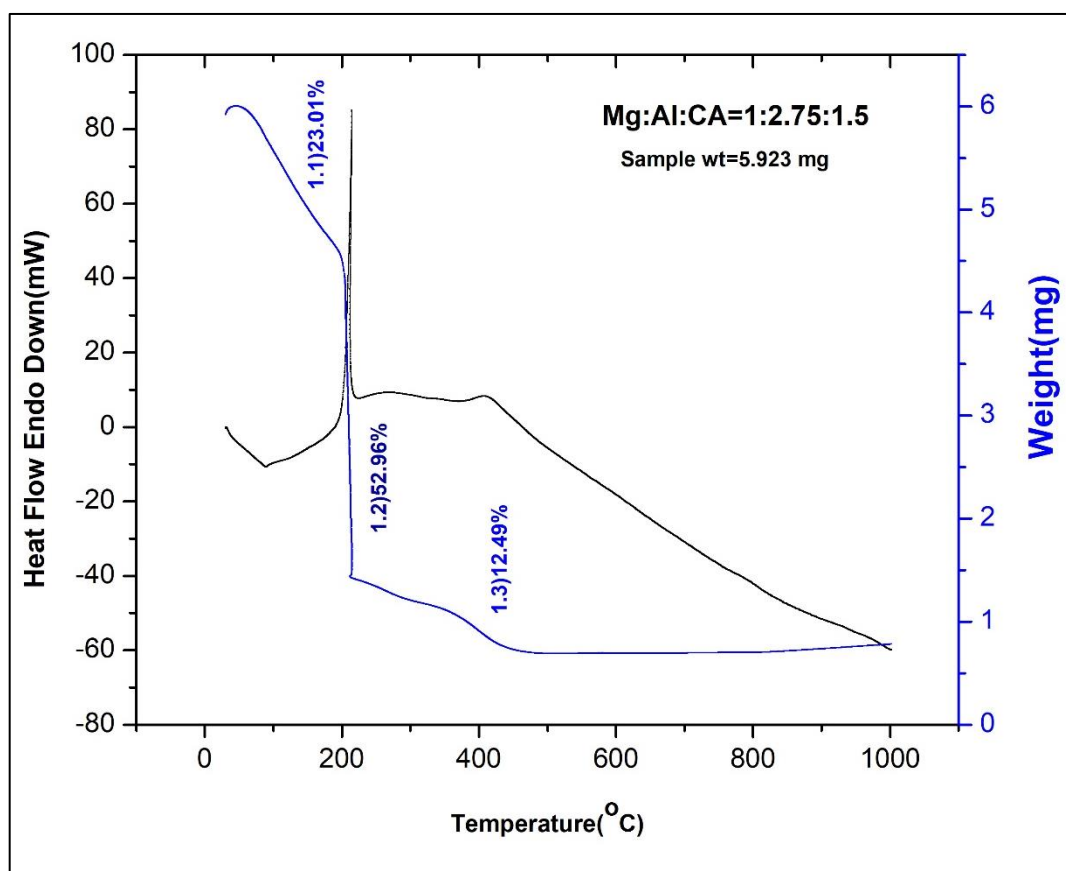

Figure 3.10:FESEM Machine ZEISS

CHAPTER 4

RESULT AND DISCUSSION

4.1 DTA/DSC-TGA Analysis of Various Ratio:

4.1.1 DTA/TGA Analysis of $MgAl_2O_4$ Spinel ($Al(NO_3)_3.9H_2O$ in 2.75 molar ratio):

Figure 4.1:DTA/TGA analysis of mixture of Mg:Al:CA=1:2.75:1.5 within the temperature range 0°C-1000°C at the rate of 10°C/min

Thermal analysis of the prepared gel of substance is used for DTA/TGA analysis .The graph is shown in figure 4.1 .Analysing the graph we can see that the weight % loss is 23.01% which is associated with water molecules in temperature range 30.05°C-199.8°C. The weight loss is 52.96% in temperature 199.8°C-213.65°C which is associated with OH molecules [34]. The weight loss is about 12.49% in temperature range 213.65°C-535.84°C, corresponds to elimination of amino acids and also reaction agent citric acid compounds. The higher temperature is required to break the bonds between the citric acid and spinel. As per the DTA plot the endothermic reaction occurred at 89.2°C.The sharp exothermic reaction occurs at 210.46°C which corresponds to release of chemically held moisture. The small exothermic reaction occurs at 407.93°C which corresponds to the reaction agent citric acid and decomposition of nitrate. As from the graph we have seen the loss of weight remains stable from above 600°C which refers to the formation of crystalline structure.

4.1.2 DTA/TGA Analysis of MgAl2O$_4$ Spinel(Al(NO$_3$)$_3$.9H$_2$O in 2.25 molar ratio):
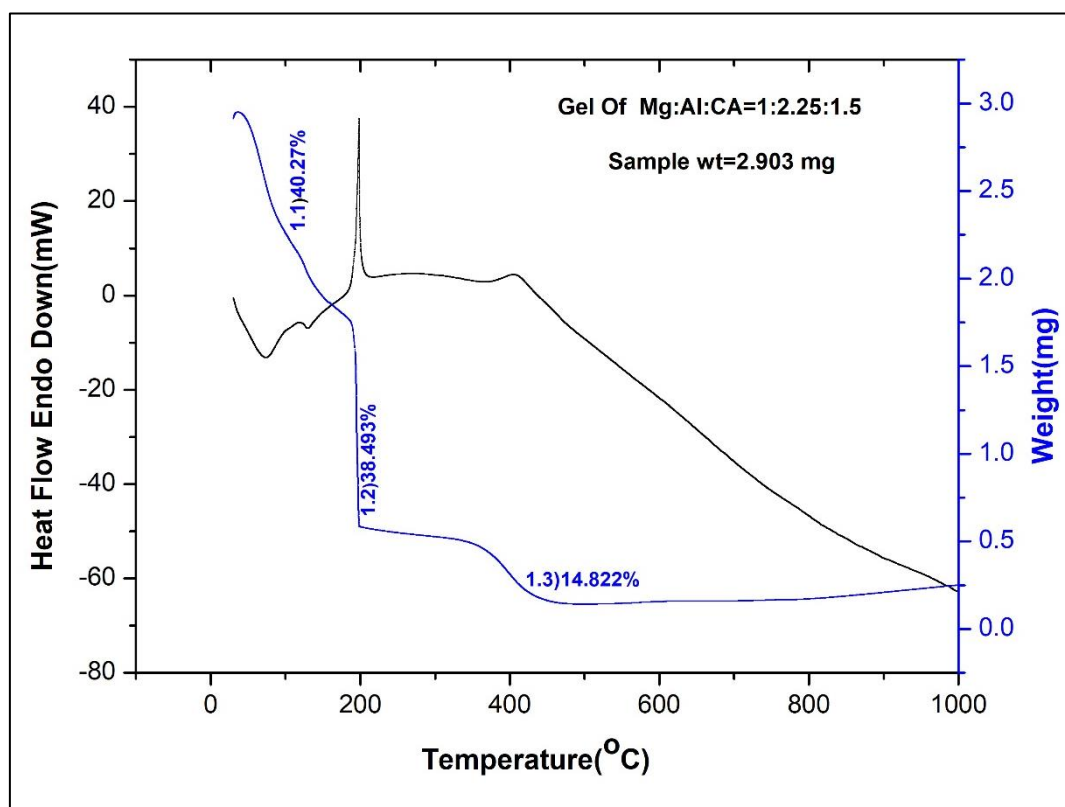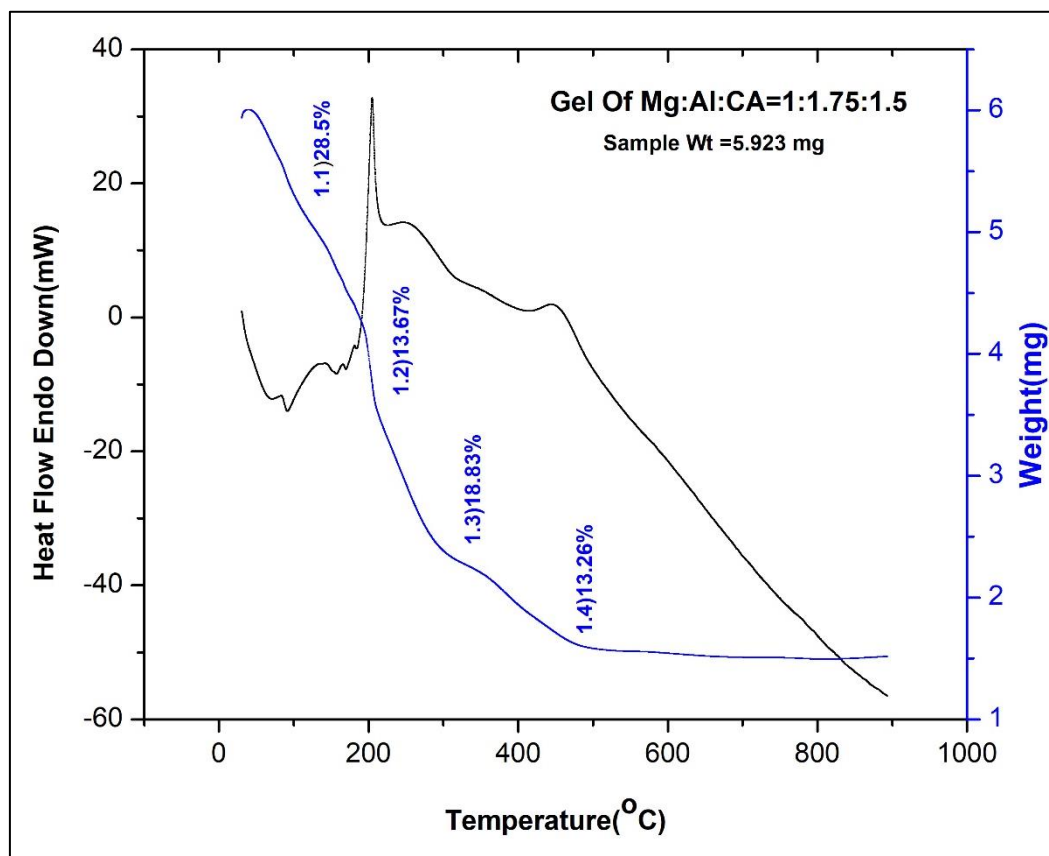

Figure 4.2:DTA/TGA analysis of mixture of Mg:Al:CA=1:2.25:1.5 within the temperature range 0ºC-1000ºC at the rate of 10ºC/min

Thermal analysis of the prepared gel of substance is used for DTA/TGA analysis .The graph is shown in figure 4.2 .Analysing the graph we can see that the weight % loss is 40.267% which is associated with water molecules in temperature range from 31ºC-188ºC. The weight loss is 38.493% which is associated with OH molecules [34] in the temperature range 188ºC-198.68ºC.The weight loss is about 14.822% regarding elimination of amino acid and also reaction agent citric acid compounds in the temperature range 198.68ºC-595ºC. The higher temperature is required to break the bonds between the citric acid and spinel. As per the DSC plot the endothermic reaction the drop at 75ºC and 129ºC.The sharp exothermic reaction occurs at 197.8ºC which corresponds to release of chemically held moisture. The small exothermic reaction occurs at 404ºC which corresponds to the reaction agent citric acid. From the graph the loss of weight remains almost stable after around 600ºC which refers the formation of crystalline structure of the material.

4.1.3 DTA /TGA Analysis of MgAl$_2$O$_4$ spinel(Al(NO$_3$)$_3$.9H$_2$O in 1.75 molar ratio):

Figure 4.3:DTA/TGA analysis of mixture of Mg:Al:CA=1:1.75:1.5 within the temperature range 0ºC-1000ºC at the rate of 10ºC/min

Thermal analysis of the prepared gel of substance is used for DSC-TGA analysis .The graph is shown in figure 4.3 .By analysis the graph we can see that the weight % loss is 28.5% which is associated with water molecules in the temperature range 30.48ºC-191.95ºC. The weight loss is 13.67% which is associated with OH molecules [34] molecules in the temperature range 191.95ºC-216.1ºC. The weight loss is about 18.83% and 13.26% both are corresponds to elimination of amino acids and also reaction agent citric acid compounds in the range of temperature 216.1ºC-314.55ºC and 314.55ºC-585.12ºC The higher temperature is required to break the bonds between the citric acid and spinel. As per the DTA plot the endothermic reaction occurred at 142ºC.The sharp exothermic reaction occurs at 205.35ºC which corresponds to release of chemically held moisture. The small exothermic reaction occurs at 245.35ºC and 445.97ºC which corresponds to the reaction agent citric acid and decomposition of nitrate. As from the graph we have seen the loss of weight remains stable from above 600ºC which refers to the formation of crystalline structure.

4.2 XRD Analysis of Various Ratio:

For the XRD analysis using Citric Acid as fuel agent the composition were varied for 5 different samples which corresponds to Mg:Al:CA are in the ratio of 1:2.75:1.5, 1:2.5:1.5, 1:2.25:1.5, 1:1.75:1.5 and 1:1.5:1.5.The samples at different temperature from 650ºC,700ºC,800ºC,900ºC and 1000ºC, at first XRD data were obtained in 2.75,2.5 and 2.25 $Al(NO_3)_3.9H_2O$ molar ratio. Because of showing too much vibration of $MgAl_2O_4$, proper crystalline structure is not formed at 650ºC and 700ºC,so the next 2 molar ratio of $Al(NO_3)_3.9H_2O$ at 1.75 and 1.5 were taken XRD data on 800ºC,900ºC and 1000ºC.So total 21 sample were undergone for XRD analysis.

4.2.1 XRD Analysis of $MgAl_2O_4$ spinel in $Al(NO_3)_3.9H_2O$ at molar ratio 2.75:

Here for MgAl2O4 spinel,$Mg(NO_3)_2 .6H_2O$ and $Al(NO_3)_3.9H_2O$ were mixed using Citric Acid as fuel agent in the ratio of 1:2.75:1.5 by sol gel route. After calcination at different temperature ranging from 650ºC, 700ºC, 800ºC, 900ºC and 1000ºC for 5 hour the graph of Intensity (Arbitrary Unit) versus 2θ (Degree) is given below.
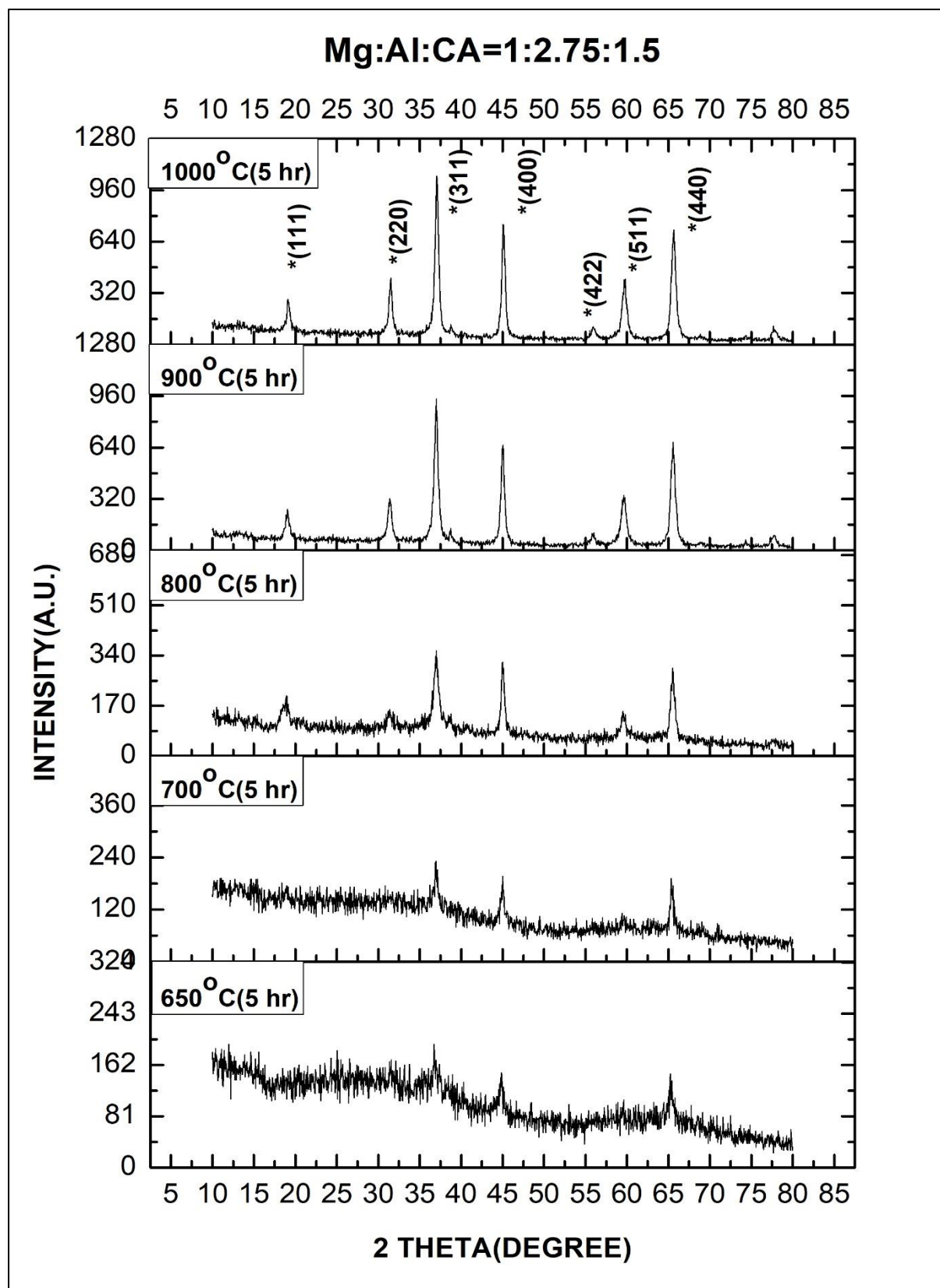
Figure 4.4: XRD of MgAl₂O₄ spinel(Al(NO₃)₃.9H₂O in 2.75 molar ratio) heat treated for 5 hour at various temperature

Main diffraction spectra shows the planes corresponding to these peaks indexed with the help of the standard JCPDS data which suggests that all the peaks are of $MgAl_2O_4$ spinel. Detail of each peaks are listed below.

Table 4.1:XRD Analysis of Spinel($Al(NO_3)_3.9H_2O$ in 2.75 molar ratio) at 650^oC(5 hour):

Peak No	d-value of corresponding peak	2Ɵ value of corresponding peak	Standard d-value	Planes	Chemical formula of compound	JCPDS Card No	Crystallite size(using schhere's formula) nm
1	2.4467	36.70	2.4478	(111)	Al_2O_3	86-1410	49.10
2	2.4276	37.00	2.4363	(311)	$MgAl_2O_4$	84-0377	49.10
3	1.4287	65.25	1.4298	(440)	$MgAl_2O_4$	82-2424	55.29

The planes corresponding to these peaks indexed with the help of the standard JCPDS data. 3 peaks are there and out of which 2 peak suggests that at 650°C is pure phase of spinel ($MgAl_2O_4$) and in plane(111) find that phase is Al_2O_3.As from the figure shown because of molecule vibration the peak search is abruptly changes. The crystallite size of the material has been derived from the Scherrer formula

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

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 and θ is the Braggs angle. The approximate crystallite size of the material is 49 nm.

Table 4.2:XRD Analysis of Spinel($Al(NO_3)_3.9H_2O$ in 2.75 molar ratio) at 700^oC(5 hour):

Peak No	d-value of corresponding peak	2Ɵ value of corresponding peak	Standard d-value	Planes	Chemical formula of compound	JCPDS Card No	Crystalline size(using schhere's formula) nm
1	2.4339	36.90	2.4371	(111)	$MgAl_2O_4$	86-1410	49.10
2	2.0128	45.00	2.0201	(400)	$MgAl_2O_4$	84-0377	30.183
3	1.4268	65.35	1.4298	(440)	$MgAl_2O_4$	84-0377	55.35

The planes corresponding to these peaks indexed with the help of the standard JCPDS data. 3 peaks are there and each peak suggests the phase at 700°C are in pure phase of spinel ($MgAl_2O_4$).The crystallite size of the material is different which are 49.1 nm,30.18 nm and 55.35 nm.

Table 4.3:XRD Analysis of Spinel(Al(NO$_3$)$_3$.9H$_2$O in 2.75 molar ratio) at 800ºC(5 hour):

Peak No	d-value of corresponding peak	2Ꙩ value of corresponding peak	Standard d-value	Planes	Chemical formula of compound	JCPDS Card No	Crystallite size(using schhere's formula) nm
1	4.7038	18.85	4.7192	(111)	MgAl$_2$O$_4$	77-0436	35.36
2	2.8160	31.75	2.8204	(110)	Al$_2$O$_3$	86-1410	36.27
3	2.4629	36.45	2.4645	(311)	MgAl$_2$O$_4$	77-0436	36.73
4	2.015	44.95	2.0201	(400)	MgAl$_2$O$_4$	77-0435	30.18
5	1.4229	65.55	1.4284	(440)	MgAl$_2$O$_4$	77-0435	41.49

The planes corresponding to these peaks indexed with the help of the standard JCPDS data. 5 peaks are there and 4 peak suggests the phase at 800°C are in pure phase of spinel (MgAl$_2$O$_4$) and peak (110) are in Al$_2$O$_3$ phase. The crystallite size of the material is remains in closer size from 30nm to 41 nm.

Table 4.4:XRD Analysis of Spinel(Al(NO$_3$)$_3$.9H$_2$O in 2.75 molar ratio) at 900ºC(5 hour):

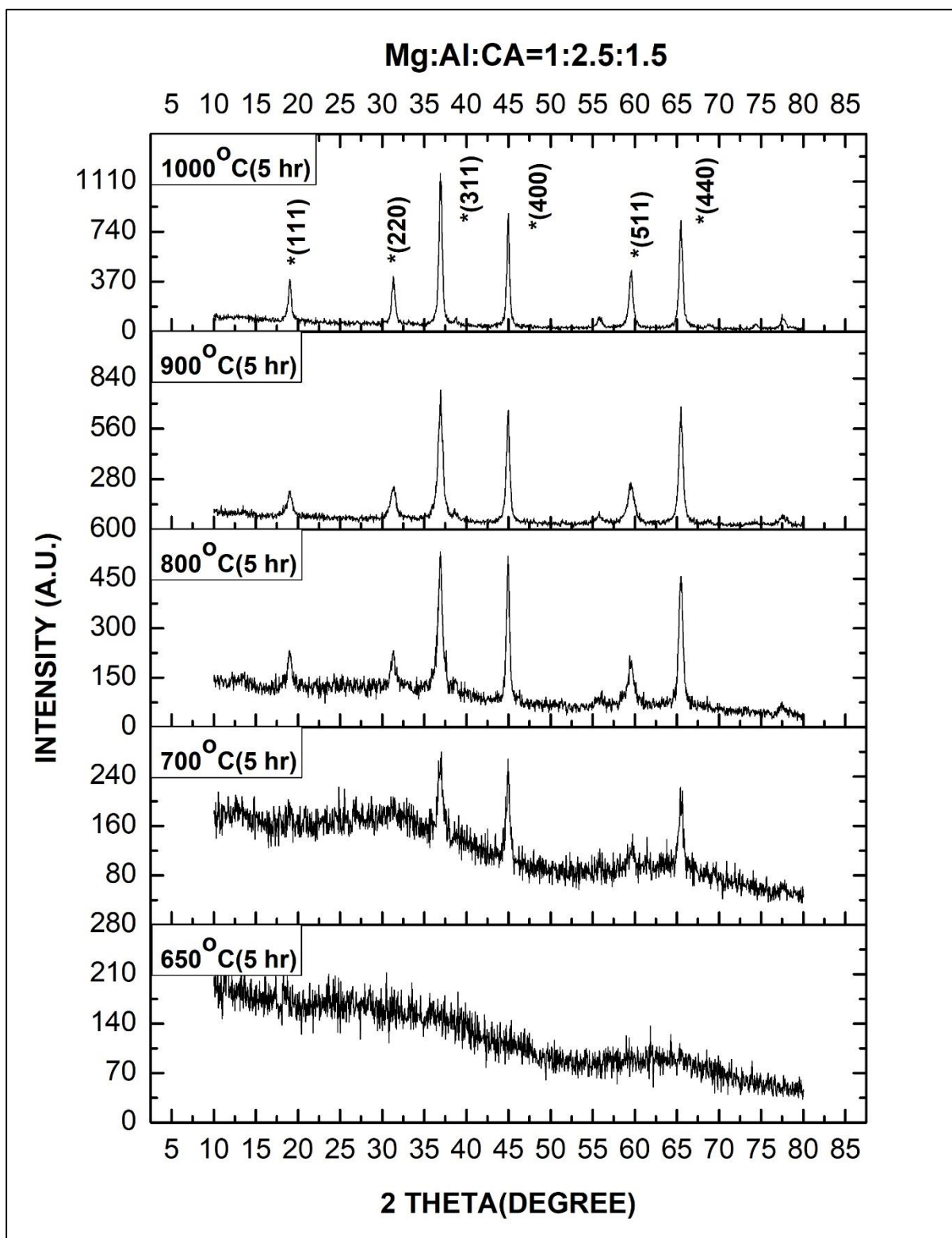| Peak No	d-value of corresponding peak	2Ꙩ value of corresponding peak	Standard d-value	Planes	Chemical formula of compound	JCPDS Card No	Crystalline size(using schhere's formula) nm
1	4.6670	19.000	4.6653	(111)	MgAl$_2$O$_4$	77-1203	22.81
2	2.8466	31.400	2.8569	(220)	MgAl$_2$O$_4$	77-0435	15.60
3	2.4307	36.950	2.4363	(311)	MgAl$_2$O$_4$	77-0435	20.317
4	2.3248	38.700	2.3326	(222)	MgAl$_2$O$_4$	77-0435	28.625
5	2.0128	45.000	2.0201	(400)	MgAl$_2$O$_4$	77-0435	18.24
6	1.6434	55.900	1.6494	(422)	MgAl$_2$O$_4$	77-0435	21.82
7	1.5499	59.600	1.5551	(511)	MgAl$_2$O$_4$	77-0435	15.56
8	1.4239	65.500	1.4284	(440)	MgAl$_2$O$_4$	77-0435	16.05

Now after calcined at 900ºC for 5 hour the planes corresponding to these peaks indexed with the help of the standard JCPDS data. 8 peaks are there and each peak suggests the phase at 900°C is in pure phase of spinel (MgAl$_2$O$_4$). The crystallite size of the material is remains in closer size and they are much smaller in size from 15 nm to 28 nm.

Table 4.5:XRD Analysis of Spinel($Al(NO_3)_3.9H_2O$ in 2.75 molar ratio) at 1000^oC(5 hour):

Peak No	d-value of corresponding peak	2θ value of corresponding peak	Standard d-value	Planes	Chemical formula of compound	JCPDS Card No	Crystallite size(using schhere's formula) nm
1	4.6308	19.150	4.6653	(111)	$MgAl_2O_4$	77-0435	22.81
2	2.8422	31.450	2.8569	(220)	$MgAl_2O_4$	77-0435	20.025
3	2.4244	37.050	2.4363	(311)	$MgAl_2O_4$	77-0435	17.78
4	2.0107	45.050	2.0201	(400)	$MgAl_2O_4$	77-0435	18.25
5	1.6448	55.850	1.6494	(422)	$MgAl_2O_4$	77-0435	30.57
6	1.5488	59.650	1.5551	(511)	$MgAl_2O_4$	77-0435	22.21
7	1.4229	65.550	1.4284	(440)	$MgAl_2O_4$	77-0435	16.06

Now from the table as shown the planes corresponding to these peaks indexed with the help of the standard JCPDS data. 7 peaks are there and each peak suggests the phase at 1000°C is in pure phase of spinel ($MgAl_2O_4$). The crystallite size of the material is remains in closer size and they are much smaller in size from 17 nm to 30 nm.

4.2.2 XRD Analysis of MgAl₂O₄ Spinel in Al(NO₃)₃.9H₂O molar ratio 2.5:

Figure 4.5: XRD of MgAl₂O₄ spinel(Al(NO₃)₃.9H₂O in 2.5 molar ratio) heat treated for 5 hour at various temperature

Table 4.6:XRD Analysis of Spinel (Al(NO$_3$)$_3$.9H$_2$O in 2.5 molar ratio) at 650°C(5 hour):

Peak No	d-value of corresponding peak	2Θ value of corresponding peak	Standard d-value	Planes	Chemical formula of compound	JCPDS Card No	Crystalline size(using schhere's formula) nm
1	2.9332	30.45	2.9014	(220)	MgAl$_2$O$_4$	75-1803	72.02

The plane obtained here indexed with the help of the standard JCPDS data. Because of too much vibration the peaks are unable to find properly. The obtained peak is spinel (MgAl$_2$O$_4$). The only crystallite size of the material obtained is 72 nm.

Table 4.7:XRD Analysis of Spinel (Al(NO$_3$)$_3$.9H$_2$O in 2.5 molar ratio) at 700°C(5 hour):

Peak No	d-value of corresponding peak	2Θ value of corresponding peak	Standard d-value	Planes	Chemical formula of compound	JCPDS Card No	Crystallite size(using schhere's formula) nm
1	2.372	37.90	2.369	(222)	MgAl$_2$O$_4$	75-1803	29.51
2	2.0386	44.40	2.0327	(400)	MgAl$_2$O$_4$	75-1800	30.14
3	1.4258	65.40	1.4289	(440)	MgAl$_2$O$_4$	77-1193	30.14

The planes corresponding to these peaks indexed with the help of the standard JCPDS data. 3 peaks are there and each peak suggests the phase at 700°C is pure phase of spinel (MgAl$_2$O$_4$).The crystallite size of the material is remains in closer size in 30 nm approximately..

Table 4.8:XRD Analysis of Spinel ($Al(NO_3)_3.9H_2O$ in 2.5 molar ratio) at 800°C(5 hour):

Peak No	d-value of corresponding peak	2θ value of corresponding peak	Standard d-value	Planes	Chemical formula of compound	JCPDS Card No	Crystallite size(using schhere's formula) nm
1	2.4339	36.90	2.4371	(311)	$MgAl_2O_4$	77-1193	29.40
2	2.015	44.95	2.0215	(112)	Al_2O_3	86-1410	30.18
3	1.5547	59.40	1.555	(511)	$MgAl_2O_4$	77-1193	32.09
4	1.4248	65.45	1.4289	(440)	$MgAl_2O_4$	77-1193	33.23

The planes corresponding to these peak search indexed with the help of the standard JCPDS data. 4 peaks are there out of that 3 peaks suggests the phase at 800°C is in pure phase of spinel ($MgAl_2O_4$) and in plane (112) it corresponds to phase of Al_2O_3.The crystallite size of the material is approximately 30 nm.

Table 4.9:XRD Analysis of Spinel ($Al(NO_3)_3.9H_2O$ in 2.5 molar ratio) at 900°C(5 hour):

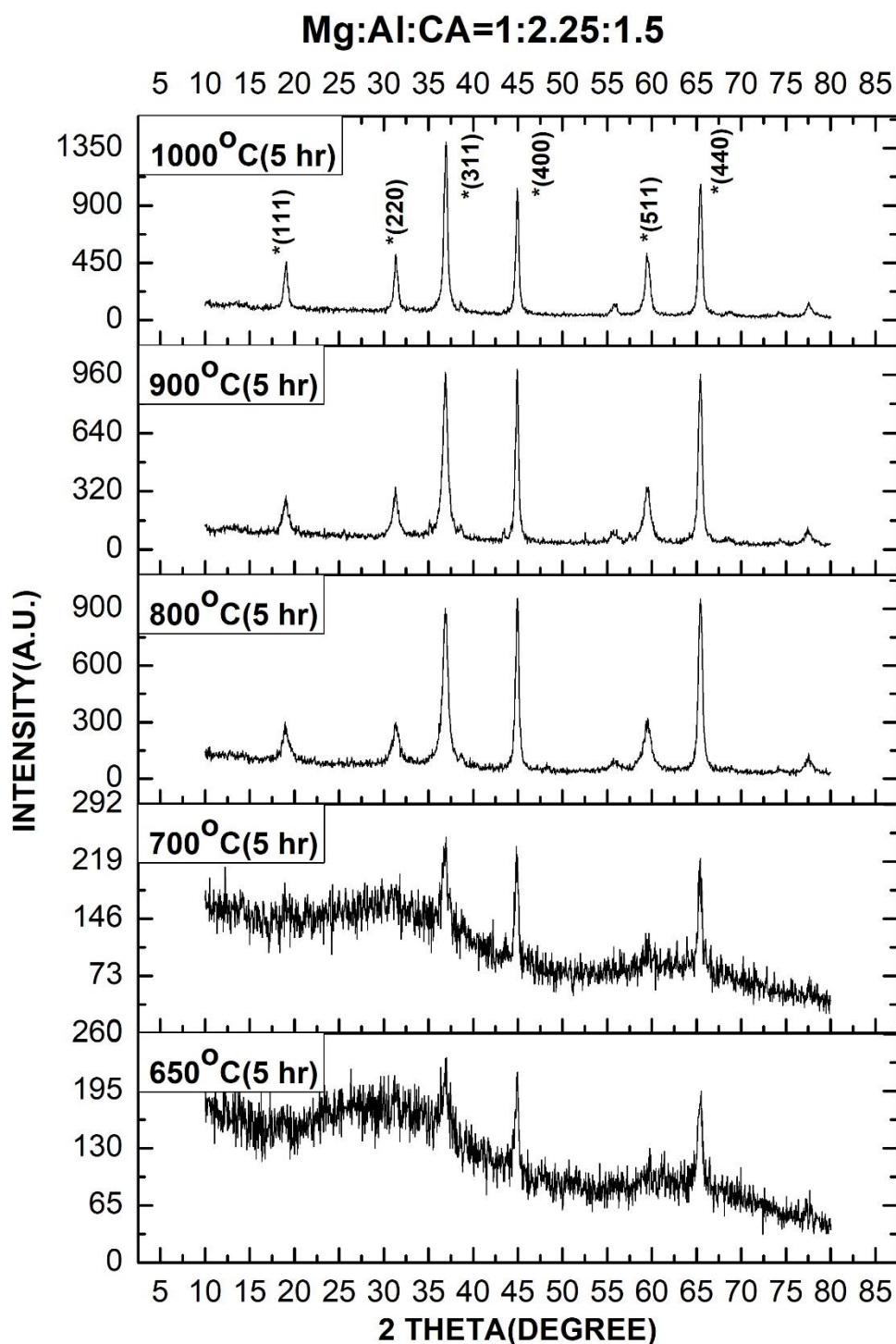| Peak No	d-value of corresponding peak	2θ value of corresponding peak	Standard d-value	Planes	Chemical formula of compound	JCPDS Card No	Crystallite size(using schhere's formula) nm
1	4.6670	19.00	4.6653	(111)	$MgAl_2O_4$	77-0435	38.90
2	2.8510	31.350	2.8569	(220)	$MgAl_2O_4$	77-0435	12.75
3	2.4339	36.90	2.4363	(311)	$MgAl_2O_4$	77-0435	17.77
4	2.0150	44.950	2.0201	(400)	$MgAl_2O_4$	77-0435	24.35
5	1.6489	55.70	1.6494	(422)	$MgAl_2O_4$	77-0435	25.44
6	1.5547	59.40	1.5551	(511)	$MgAl_2O_4$	77-0435	25.90
7	1.4248	65.450	1.4284	(440)	$MgAl_2O_4$	77-0435	17.84

From the table, the planes corresponding to these peaks indexed with the help of the standard JCPDS data. 7 peaks are there and each peak suggests the phase at 900°C is in pure phase of spinel ($MgAl_2O_4$). The crystallite size of the material is ranges from 12 nm to 38 nm.

Table 4.10:XRD of Spinel (Al(NO$_3$)$_3$.9H$_2$O in 2.5 molar ratio) at 1000°C(5 hour):

Peak No	d-value of corresponding peak	2θ value of corresponding peak	Standard d-value	Planes	Chemical formula of compound	JCPDS Card No	Crystallite size(using schhere's formula) nm
1	4.6549	19.05	4.6653	(111)	MgAl$_2$O$_4$	77-0435	23.55
2	2.8510	31.35	2.8569	(220)	MgAl$_2$O$_4$	77-0435	18.10
3	2.4339	36.90	2.4363	(311)	MgAl$_2$O$_4$	77-0435	20.97
4	2.0150	44.950	2.0201	(400)	MgAl$_2$O$_4$	77-0435	30.16
5	1.5523	59.50	1.5551	(511)	MgAl$_2$O$_4$	77-0435	20.05
6	1.4248	65.450	1.4284	(440)	MgAl$_2$O$_4$	77-0435	23.66
7	1.2313	77.45	1.2322	(533)	MgAl$_2$O$_4$	77-0435	44.69

From the table as shown the planes corresponding to these peaks indexed with the help of the standard JCPDS data. 7 peaks are there and each peak suggests the phase at 1000°C is in pure phase of spinel (MgAl$_2$O$_4$). The crystallite size of the material are much smaller in size from 18 nm to 44 nm.

4.2.3 XRD Analysis of MgAl$_2$O$_4$ Spinel in Al(NO$_3$)$_3$.9H$_2$O molar ratio 2.25:

Figure 4.6: XRD of MgAl$_2$O$_4$ spinel(Al(NO$_3$)$_3$.9H$_2$O in 2.25 molar ratio) heat treated for 5 hour at various temperature

Table 4.11:XRD Analysis of Spinel (Al(NO$_3$)$_3$.9H$_2$O in 2.25 molar ratio) at 650°C(5 hour):

Peak No	d-value of corresponding peak	2Θ value of corresponding peak	Standard d-value	Planes	Chemical formula of compound	JCPDS Card No	Crystallite size(using schhere's formula) nm
1	2.3963	37.50	2.3820	(110)	Al$_2$O$_3$	75-1865	73.34
2	2.0171	44.90	2.0207	(400)	MgAl$_2$O$_4$	77-1203	75.06

As shown the plane obtained here indexed with the help of the standard JCPDS data. Because of too much vibration peaks are unable to find properly. The obtained 2 peak one is spinel (MgAl$_2$O$_4$) and the other one is Al$_2$O$_3$. The crystallite size of the material obtained is 73 nm and 75 nm.

Table 4.12:XRD Analysis of Spinel (Al(NO$_3$)$_3$.9H$_2$O in 2.25 molar ratio) at 700°C(5 hour):

Peak No	d-value of corresponding peak	2Θ value of corresponding peak	Standard d-value	Planes	Chemical formula of compound	JCPDS Card No	Crystallite size(using schhere's formula) nm
1	2.4794	36.20	2.4780	(111)	MgAl$_2$O$_4$	75-1803	72.76
2	2.0235	44.75	2.0207	(400)	MgAl$_2$O$_4$	77-1803	75.114
3	1.4258	65.40	1.4289	(440)	MgAl$_2$O$_4$	77-1193	82.50

The planes corresponding to these peak search indexed with the help of the standard JCPDS data. 3 peaks suggests the phase at 700°C is completely pure phase of spinel (MgAl$_2$O$_4$).The crystallite size of the material is ranging from 72 nm to 82nm.

Table 4.13:XRD Analysis of Spinel ($Al(NO_3)_3.9H_2O$ in 2.25 molar ratio) at 800°C(5 hour):

Peak No	d-value of corresponding peak	2θ value of corresponding peak	Standard d-value	Planes	Chemical formula of compound	JCPDS Card No	Crystallite size(using schhere's formula) nm
1	4.6915	18.90	4.6910	(111)	$MgAl_2O_4$	75-1799	45.74
2	2.7945	32.00	2.8569	(220)	$MgAl_2O_4$	84-0377	69.96
3	2.4403	36.80	2.4406	(311)	$MgAl_2O_4$	75-1797	70.87
4	2.0171	44.90	2.0201	(400)	$MgAl_2O_4$	84-0377	48.81
5	1.5559	59.350	1.5551	(511)	$MgAl_2O_4$	84-0377	77.35
6	1.4258	65.40	1.4284	(440)	$MgAl_2O_4$	84-0377	53.57

The planes corresponding to these peaks indexed with the help of the standard JCPDS data. 6 peaks are there and each peak suggests the phase at 800°C is in pure phase of spinel ($MgAl_2O_4$).The crystallite size of the material is ranging from 45 nm to 77 nm.

Table 4.14:XRD Analysis of Spinel ($Al(NO_3)_3.9H_2O$ in 2.25 molar ratio) at 900°C(5 hour):

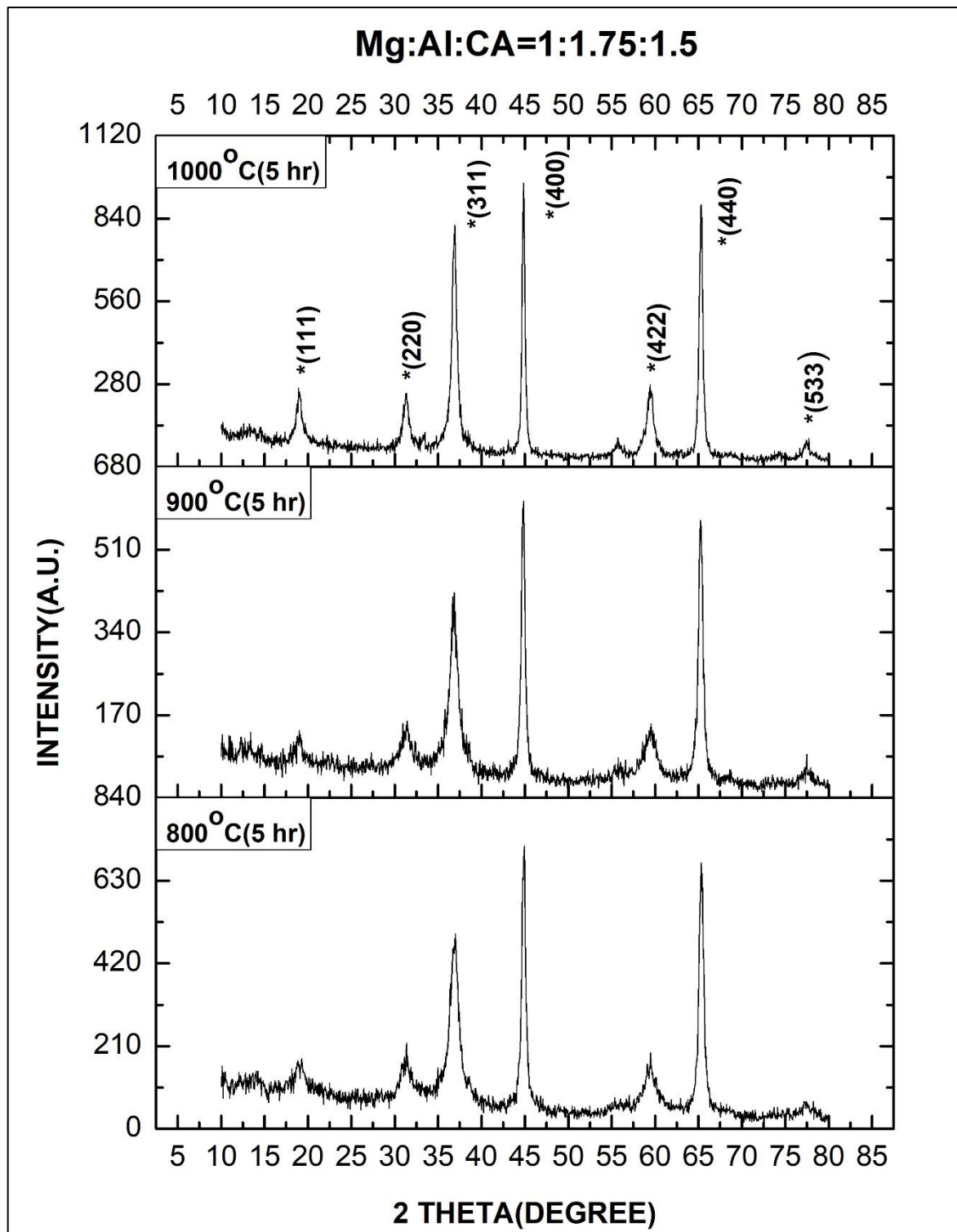| Peak No	d-value of corresponding peak	2θ value of corresponding peak	Standard d-value	Planes	Chemical formula of compound	JCPDS Card No	Crystallite size(Using Schherer's formula) nm
1	4.6670	19.00	4.6667	(111)	$MgAl_2O_4$	77-1193	68.18
2	2.8510	31.350	2.8578	(220)	$MgAl_2O_4$	77-1193	44.50
3	2.4339	36.90	2.4371	(311)	$MgAl_2O_4$	77-1193	48.82
4	2.0171	44.90	2.0207	(400)	$MgAl_2O_4$	77-1203	50.42
5	1.5547	59.40	1.5555	(511)	$MgAl_2O_4$	77-1203	77.47
6	1.4258	65.40	1.4284	(440)	$MgAl_2O_4$	77-0435	53.61

From the table as shown the planes corresponding to these peaks indexed with the help of the standard JCPDS data. 6 peaks are there and each peak suggests the phase at 900°C is in pure phase of spinel ($MgAl_2O_4$). The crystallite size of the material is remains in closer size ranging from 44 nm to 77 nm.

Table 4.15:XRD Analysis of Spinel (Al(NO$_3$)$_3$.9H$_2$O in 2.25 molar ratio) at 1000°C(5 hour):

Peak No	d-value of corresponding peak	2Ɵ value of corresponding peak	Standard d-value	Planes	Chemical formula of compound	JCPDS Card No	Crystallite size(Using Schherer's formula) nm
1	4.6549	19.05	4.6653	(111)	MgAl$_2$O$_4$	77-0435	27.39
2	2.8554	31.30	2.8569	(220)	MgAl$_2$O$_4$	77-0435	35.09
3	2.4307	36.95	2.4307	(311)	MgAl$_2$O$_4$	77-0435	20.32
4	2.0171	44.90	2.0201	(400)	MgAl$_2$O$_4$	77-0435	24.34
5	1.5535	59.45	1.5551	(511)	MgAl$_2$O$_4$	77-0435	38.91
6	1.4258	65.40	1.4284	(440)	MgAl$_2$O$_4$	77-0435	26.73

Now from the table as shown the planes corresponding to these peaks indexed with the help of the standard JCPDS data. 6 peaks are there and each peak suggests the phase at 1000°C is in pure phase of spinel (MgAl$_2$O$_4$). The crystallite size of the material is remains in closer size and they are much smaller in size from 20 nm to 38 nm.

4.2.3 XRD Analysis of MgAl₂O₄ Spinel in Al(NO₃)₃.9H₂O molar ratio 1.75:

Figure 4.7: XRD of MgAl₂O₄ spinel(Al(NO₃)₃.9H₂O in 1.75 molar ratio) heat treated for 5 hour at various temperature

Table 4.16:XRD Analysis of Spinel ($Al(NO_3)_3.9H_2O$ in 1.75 molar ratio) at $800^{\circ}C$(5 hour):

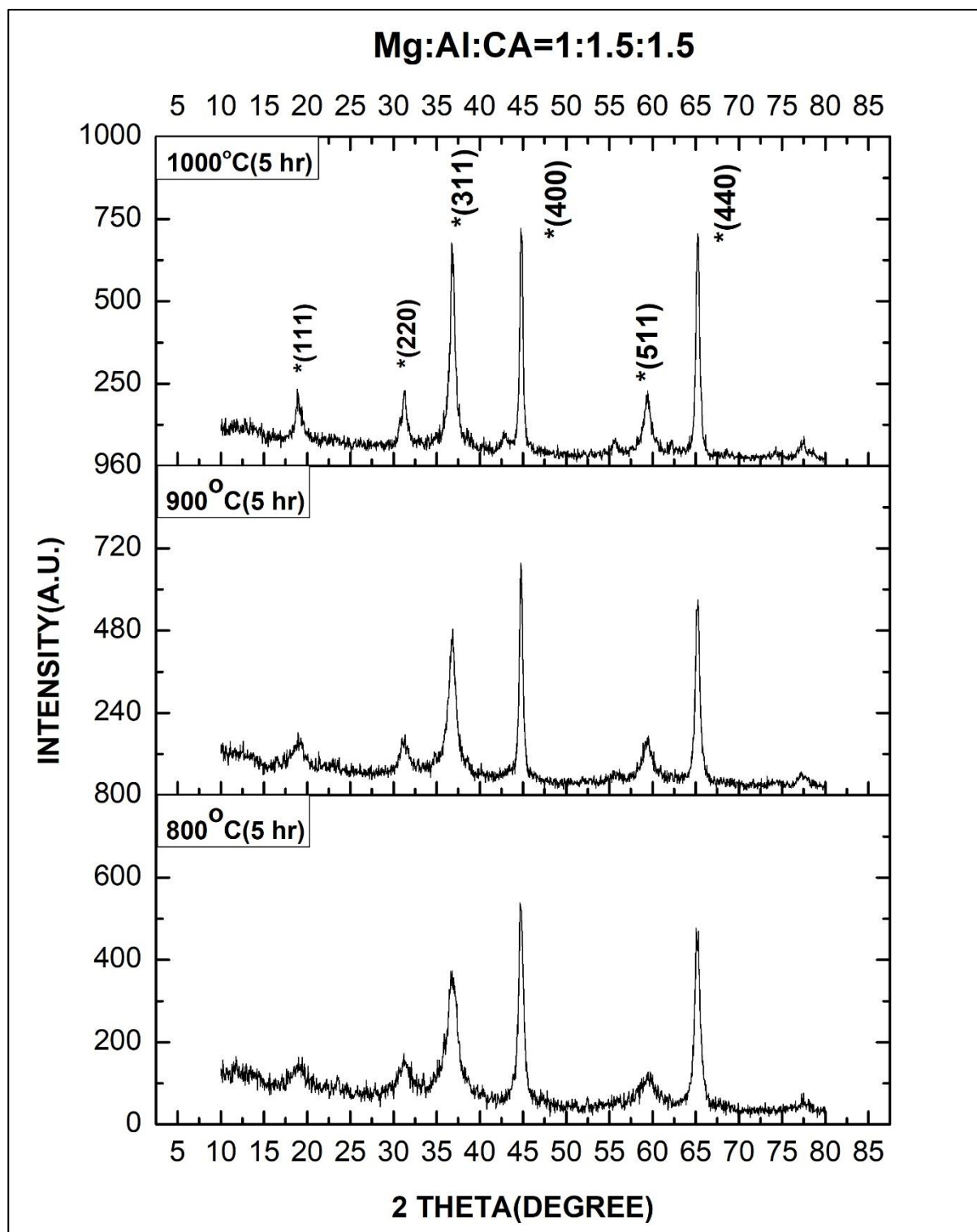| Peak No	d-value of corresponding peak	2Θ value of corresponding peak	Standard d-value	Planes	Chemical formula of compound	JCPDS Card No	Crystallite size(using schhere's formula) nm
1	2.8510	31.35	2.8569	(220)	$MgAl_2O_4$	77-0435	24.12
2	2.3335	38.55	2.3326	(222)	$MgAl_2O_4$	77-0435	24.64
3	2.0192	44.85	2.0201	(400)	$MgAl_2O_4$	77-0435	20.05
4	1.5631	59.05	1.5730	(511)	$MgAl_2O_4$	77-0436	32.08
5	1.4278	65.30	1.4284	(440)	$MgAl_2O_4$	77-0435	14.90

From the diffracted peaks recorded form 10 $^{\circ}$-80° the planes corresponding to these peaks indexed with the help of the standard JCPDS data. 5 peaks are there and each peak suggests the phase at $800^{\circ}C$ is in pure phase of spinel ($MgAl_2O_4$) nanopowder. The crystallite size of the material is remains in closer size and they are much smaller in size from 20nm to 32 nm.

Table 4.17:XRD Analysis of Spinel ($Al(NO_3)_3.9H_2O$ in 1.75 molar ratio) at $900^{\circ}C$(5 hour):

Peak No	d-value of corresponding peak	2Θ value of corresponding peak	Standard d-value	Planes	Chemical formula of compound	JCPDS Card No	Crystallite size(using schhere's formula) nm
1	2.8422	31.451	2.8569	(220)	$MgAl_2O_4$	77-0435	20.68
2	2.4403	36.801	2.4363	(311)	$MgAl_2O_4$	77-0435	14.67
3	2.0235	44.75	2.0201	(400)	$MgAl_2O_4$	77-0435	18.91
4	1.5559	59.35	1.5551	(511)	$MgAl_2O_4$	77-0435	20.05
5	1.4297	65.20	1.4297	(440)	$MgAl_2O_4$	77-0435	16.61

From the diffracted peaks recorded form 10 $^{\circ}$-80° the planes corresponding to these peaks indexed with the help of the standard JCPDS data. 5 peaks are there and each peak suggests the phase at $900^{\circ}C$ is in pure phase of spinel ($MgAl_2O_4$) nanopowder. The crystallite size of the material are remains in very closer range and they are much smaller in size ranging from 14 nm to 21 nm.

Table 4.18:XRD Analysis of Spinel ($Al(NO_3)_3.9H_2O$ in 1.75 molar ratio) at 1000^oC(5 hour):

Peak No	d-value of corresponding peak	2Θ value of corresponding peak	Standard d-value	Planes	Chemical formula of compound	JCPDS Card No	Crystallite size(using schhere's formula) nm
1	4.6670	19.00	4.6653	(111)	$MgAl_2O_4$	77-0435	14.32
2	2.8510	31.35	2.8569	(220)	$MgAl_2O_4$	77-0435	20.63
3	2.4371	36.85	2.4363	(311)	$MgAl_2O_4$	77-0435	16.04
4	2.0214	44.80	2.0201	(400)	$MgAl_2O_4$	84-0377	25.21
5	1.6489	55.70	1.6494	(422)	$MgAl_2O_4$	84-0377	23.50
6	1.4287	65.25	1.4284	(440)	$MgAl_2O_4$	77-0435	23.49
7	1.2300	77.55	1.2322	(533)	$MgAl_2O_4$	77-0435	22.34

The recorded peaks of diffracted pattern from 10 ^{o}-80° the planes corresponding to these peaks indexed with the help of the standard JCPDS data. 7 peaks are there and each peak suggests the phase at 1000°C is in pure phase of spinel ($MgAl_2O_4$) nanopowder. The crystallite size of the material are remains in very closer range and they are much smaller in size from 14 nm to 25 nm.

4.2.3 XRD Analysis of MgAl₂O₄ Spinel in Al(NO₃)₃.9H₂O molar ratio 1.75:

Figure 4.8: XRD of MgAl₂O₄ spinel(Al(NO₃)₃.9H₂O in 1.5 molar ratio) heat treated for 5 hour at various temperature

Table 4.19:XRD Analysis of Spinel (Al$(NO_3)_3$.9H_2O in 1.5 molar ratio) at 800ºC(5 hour):

Peak No	d-value of corresponding peak	2Ө value of corresponding peak	Standard d-value	Planes	Chemical formula of compound	JCPDS Card No	Crystallite size(using schhere's formula) nm
1	2.8688	31.15	2.8685	(220)	MgAl$_2$O$_4$	75-1798	28.93
2	2.4532	36.60	2.4498	(311)	MgAl$_2$O$_4$	75-1799	14.67
3	2.026	44.65	2.0207	(400)	MgAl$_2$O$_4$	77-1193	12.55
4	1.5547	59.80	1.5555	(511)	MgAl$_2$O$_4$	77-1193	32.14
5	1.4317	65.101	1.4363	(440)	MgAl$_2$O$_4$	75-1799	13.75

From the table as shown the planes corresponding to these peaks indexed with the help of the standard JCPDS data. 5 peaks are there and each peak suggests the phase at 800°C is in pure phase of spinel (MgAl$_2$O$_4$). The crystallite size of the material is remains in closer size and they are much smaller in size from 14 nm to 32 nm.

Table 4.20:XRD Analysis of Spinel (Al$(NO_3)_3$.9H_2O in 1.5 molar ratio) at 900ºC(5 hour):

Peak No	d-value of corresponding peak	2Ө value of corresponding peak	Standard d-value	Planes	Chemical formula of compound	JCPDS Card No	Crystallite size(using schhere's formula) nm
1	4.5834	19.35	4.6843	(111)	MgAl$_2$O$_4$	75-1798	20.05
2	2.8869	30.95	2.8899	(220)	MgAl$_2$O$_4$	75-1801	28.93
3	2.4403	36.80	2.4463	(311)	MgAl$_2$O$_4$	75-1798	14.67
4	2.0235	44.75	2.0284	(400)	MgAl$_2$O$_4$	75-1798	21.54
5	1.5607	59.15	1.5614	(511)	MgAl$_2$O$_4$	75-1798	32.08
6	1.4307	65.15	1.4309	(440)	MgAl$_2$O$_4$	78-1797	20.68

From the table shown that the planes corresponding to these peaks indexed with the help of the standard JCPDS data. Here each of 6 peak suggests the phase at 900°C is in pure phase of spinel (MgAl$_2$O$_4$). The crystallite size of the material is remains in closer size and they are much smaller in size from 14 nm to 32 nm.

Table 4.21:XRD Analysis of Spinel (Al(NO$_3$)$_3$.9H$_2$O in 1.5 molar ratio) at 1000°C(5 hour):

Peak No	d-value of corresponding peak	2Ө value of corresponding peak	Standard d-value	Planes	Chemical formula of compound	JCPDS Card No	Crystallite size(using schhere's formula) nm
1	4.6792	18.95	4.6735	(111)	MgAl$_2$O$_4$	75-1797	20.17
2	2.8599	31.25	2.8619	(220)	MgAl$_2$O$_4$	75-1797	20.68
3	2.4403	36.80	2.4406	(311)	MgAl$_2$O$_4$	75-1797	16.33
4	2.0214	44.80	2.0207	(400)	MgAl$_2$O$_4$	77-1193	21.54
5	1.5523	59.50	1.5555	(511)	MgAl$_2$O$_4$	77-1193	40.10
6	1.4297	65.20	1.4289	(440)	MgAl$_2$O$_4$	77-1193	23.60

The recorded peaks of diffracted pattern from 10 ^{o}-80° the planes corresponding to these peaks indexed with the help of the standard JCPDS data. 6 peaks are there and each peak suggests the phase at 1000°C is in pure phase of spinel (MgAl$_2$O$_4$) nanopowder. The crystallite size of the material are remains in very closer range and they are much smaller in size from 16 nm to 40 nm.

4.3 FTIR Analysis of Various Ratio:

For the analysis of FTIR spectroscopy 2 best possible samples of each molar ratio of Al(NO$_3$)$_3$.9H$_2$O (i.e. at 2.75, 2.5, 2.25 ,1.75 and 1.5) chosen at 900ºC and 1000ºC shown from figure 4.9 to 4.18 .Those are discussed below:

4.3.1 FTIR of MgAl$_2$O$_4$ Spinel (Al(NO$_3$)$_3$.9H$_2$O in 2.75 molar ratio):

The FTIR sepctra were captured from 400-4000 cm^{-1} range for MgAl$_2$O$_4$ at 900ºC after calcination for 5 hours followed by grinding using Agate Mortar Pestle.
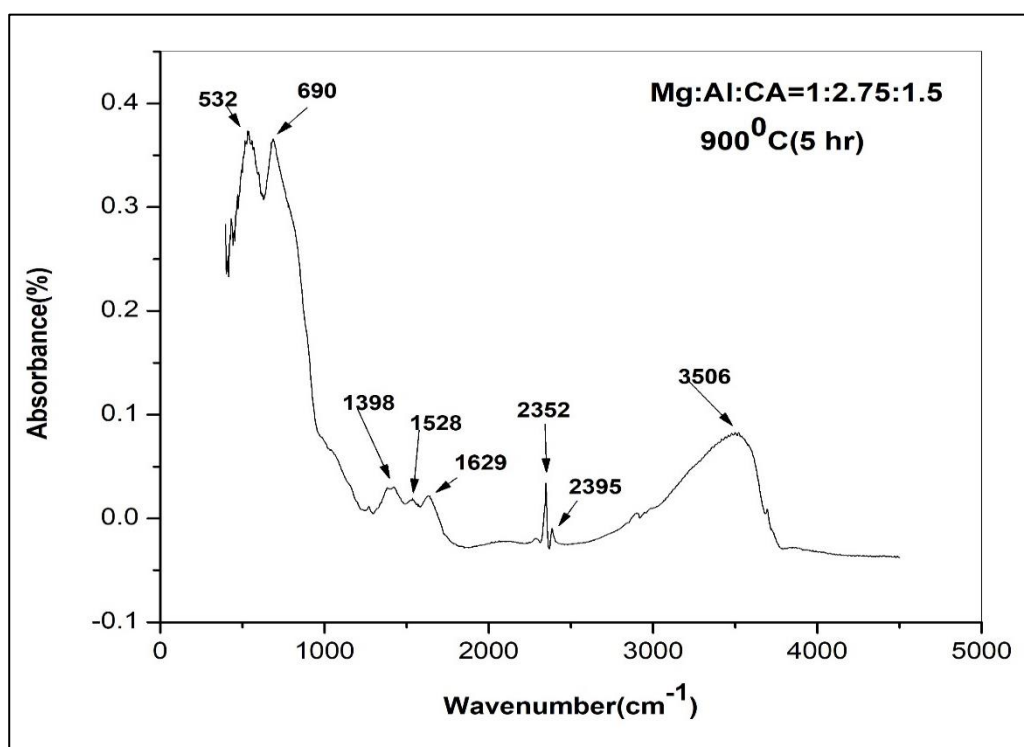
Figure 4.9:FTIR of MgAl$_2$O$_4$ Spinel(Al(NO$_3$)$_3$.9H$_2$O in 2.75 molar ratio) heat treated for 5 hour at 900ºC

Table 4.22:FTIR of Spinel(Al(NO$_3$)$_3$.9H$_2$O in 2.75 molar ratio) at 900ºC(5 hr)

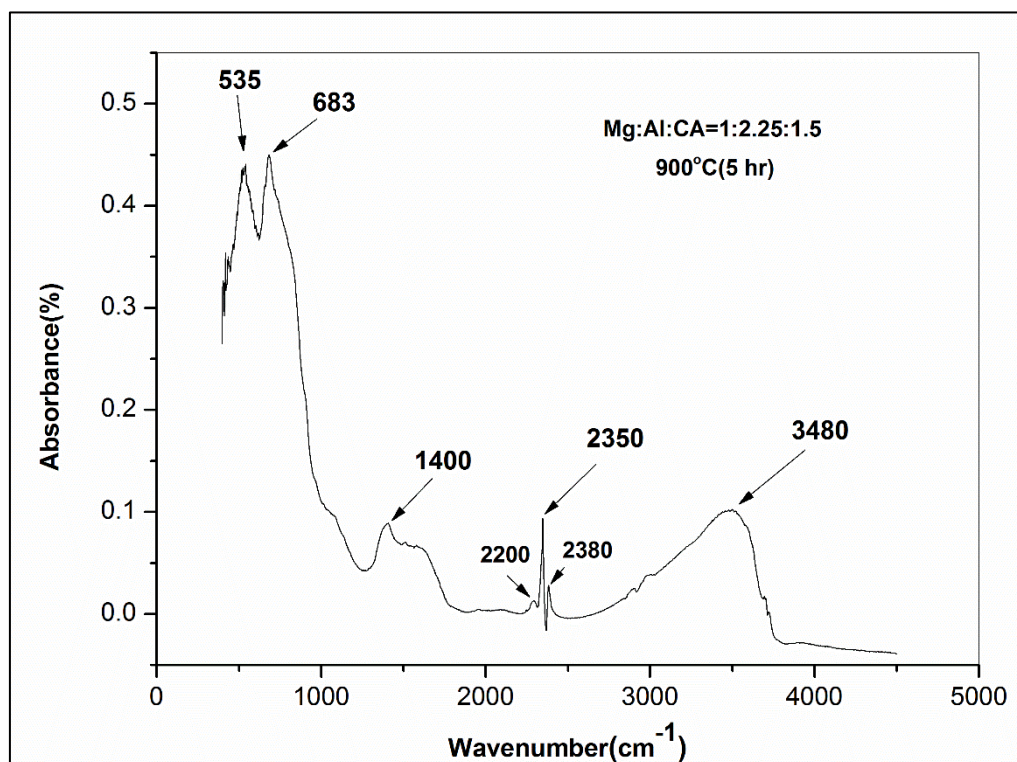| Wavenumber(cm^{-1})	Assignment
532	Mg-O-Al stretching vibration[39,45]
690	Mg-O-Al stretching vibration[39,45]
1398	NO$_3^-$ bending vibration[34,39]
1528	Aromatic Nitrate bending vibration[44]
1629	H-O-H stretching vibration[46]
2352	C-N group stretching vibration[34,39]
2395	C-N group stretching vibration[34,39]
3506	OH group bending vibration
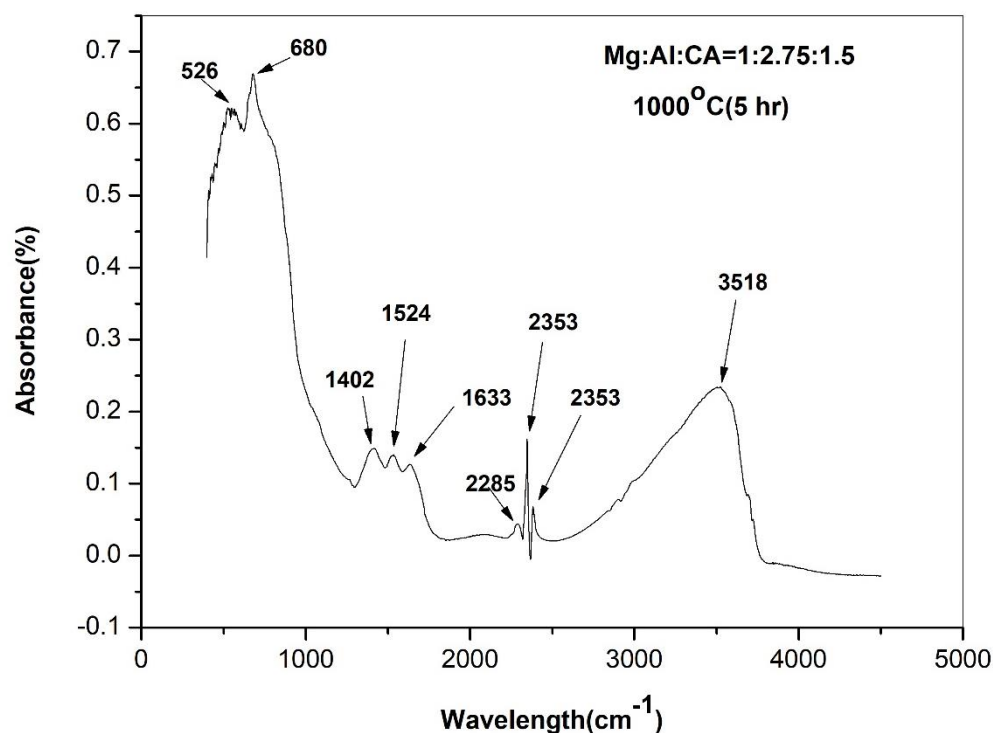
Figure 4.10:FTIR of MgAl₂O₄ Spinel(Al(NO₃)₃.9H₂O in 2.75 molar ratio) heat treated for 5 hour at 1000ºC

Table 4.23:FTIR of Spinel(Al(NO₃)₃.9H₂O in 2.75 molar ratio) at 1000ºC(5 hr):

Wavenumber(cm^{-1})	Assignment
526	Mg-O-Al stretching vibration[39,45]
680	Mg-O-Al stretching vibration[39,45]
1402	NO_3^- bending vibration[34,39]
1524	Aromatic Nitrate bending vibration[44]
1633	H-O-H stretching vibration[46]
2285	C-N group stretching vibration[34,39]
2352	C-N group stretching vibration[34,39]
3518	OH group bending vibration

4.3.2 FTIR of MgAl$_2$O$_4$ Spinel (Al(NO$_3$)$_3$.9H$_2$O in 2.5 molar ratio):
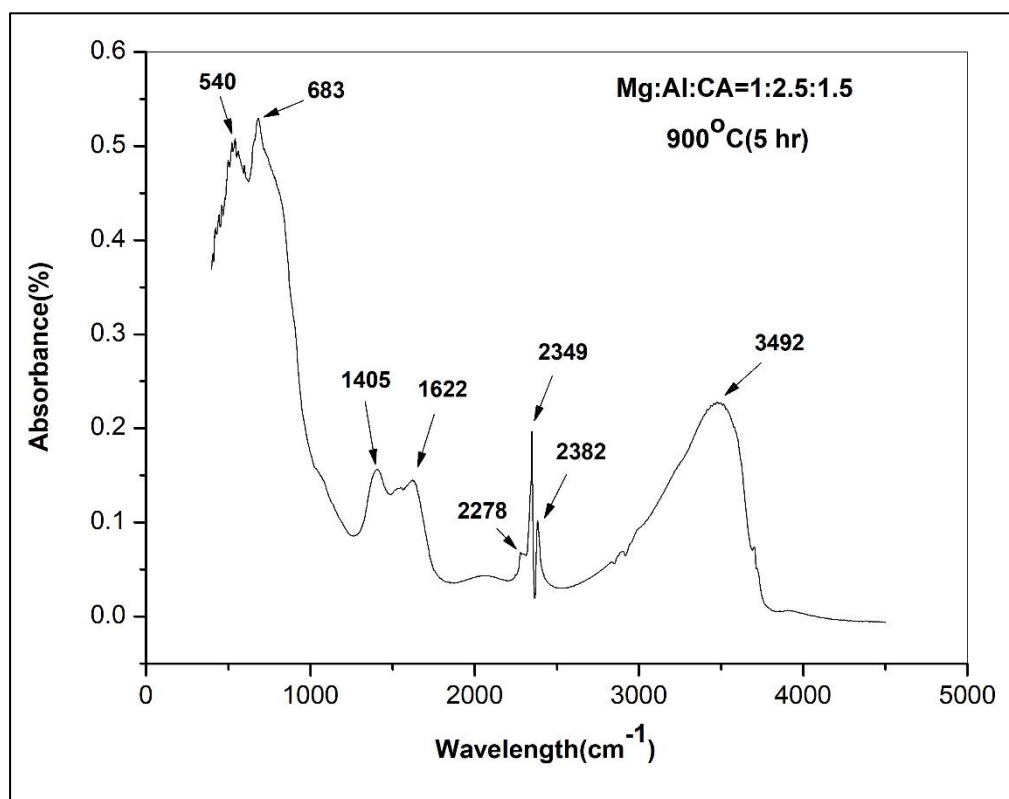
Figure 4.11:FTIR of MgAl₂O₄ Spinel(Al(NO₃)₃.9H₂O in 2.5 molar ratio) heat treated for 5 hour at 900ºC

Table 4.24:FTIR of Spinel(Al(NO$_3$)$_3$.9H$_2$O in 2.5 molar ratio) at 900ºC(5 hr):

Wavenumber(cm^{-1})	Assignment
540	Mg-O-Al stretching vibration[39,45]
683	Mg-O-Al stretching vibration[39,45]
1405	NO$_3^-$ bending vibration[34,39]
1622	H-O-H stretching vibration[46]
2278	C-N group bending vibration[34,39]
2349	C-N group stretching vibration[34,39]
2382	C-N group stretching vibration[34,39]
3518	OH group bending vibration
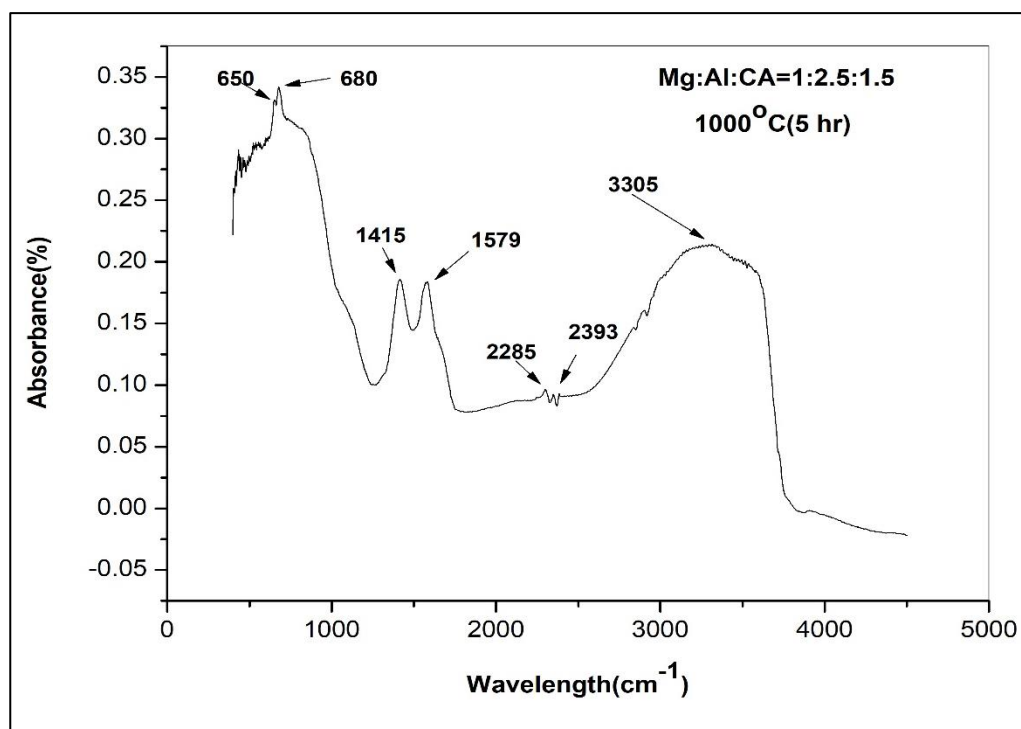
Figure 4.12:FTIR of MgAl₂O₄ Spinel(Al(NO₃)₃.9H₂O in 2.5 molar ratio) heat treated for 5 hour at 1000°C

Table 4.25:FTIR of Spinel(Al in 2.5) at 1000°C(5 hr):

Wavenumber(cm^{-1})	Assignment
650	Mg-O-Al stretching vibration[39,45]
680	Mg-O-Al stretching vibration[39,45]
1415	NO$_3^-$ bending vibration[34,39]
1579	H-O-H stretching vibration[46]
2285	C-N group bending vibration[34,39]
2393	C-N group stretching vibration[34,39]
3518	OH group bending vibration

4.3.3 FTIR of MgAl$_2$O$_4$ Spinel (Al(NO$_3$)$_3$.9H$_2$O in 2.25 molar ratio):

Figure 4.13:FTIR of MgAl$_2$O$_4$ Spinel(Al(NO$_3$)$_3$.9H$_2$O in 2.25 molar ratio) heat treated for 5 hour at 900ºC

Table 4.26:FTIR of Spinel(Al(NO$_3$)$_3$.9H$_2$O in 2.25 molar ratio) at 900ºC(5 hr):

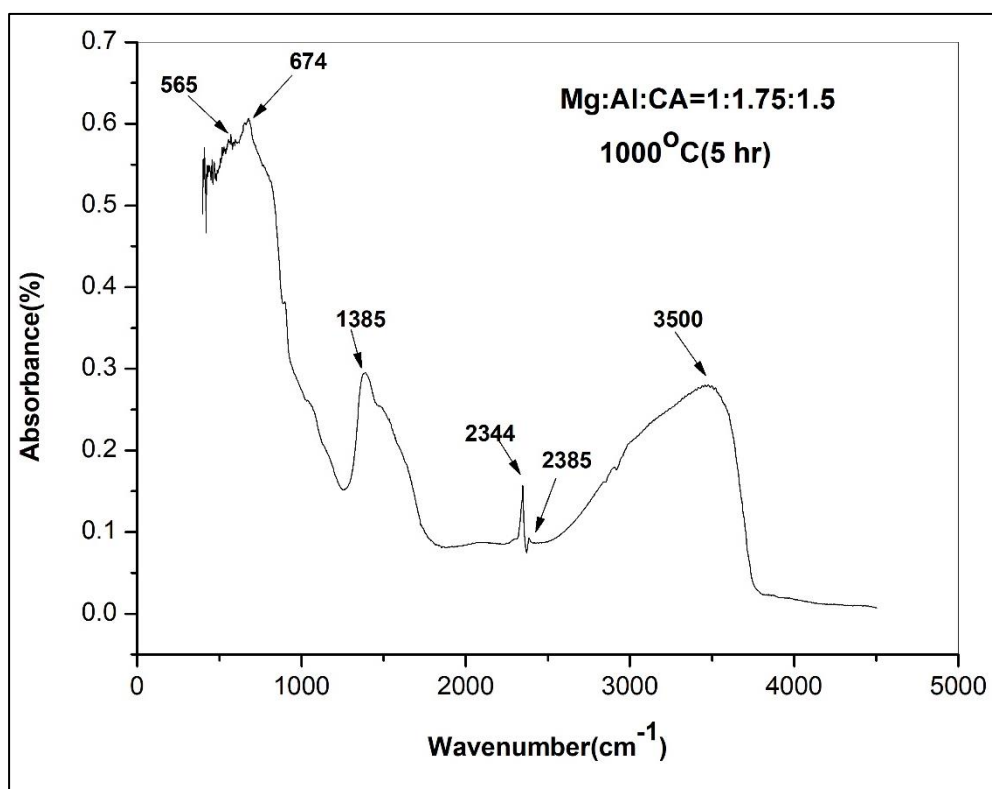| Wavenumber(cm^{-1})	Assignment
535	Mg-O-Al stretching vibration[39,45]
683	Mg-O-Al stretching vibration[39,45]
1400	NO$_3^-$ bending vibration[34,39]
2200	C-N group bending vibration[34,39
2350	C-N group stretching vibration[34,39]
2380	C-N group stretching vibration[34,39]
3518	OH group bending vibration
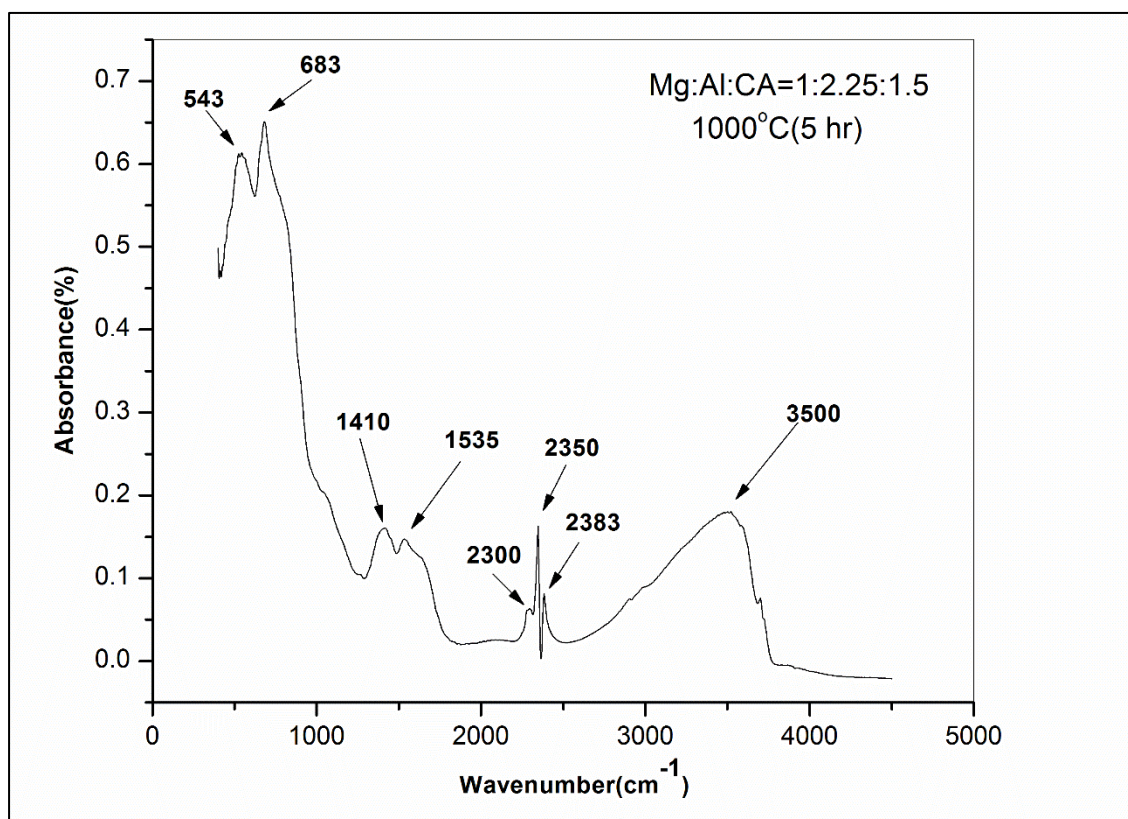
Figure 4.14:FTIR of MgAl₂O₄ Spinel(Al(NO₃)₃.9H₂O in 2.25 molar ratio) heat treated for 5 hour at 1000ºC

Table 4.27:FTIR of Spinel(Al(NO₃)₃.9H₂O in 2.25 molar ratio) at 1000ºC(5 hr):

Wavenumber(cm^{-1})	Assignment
543	Mg-O-Al stretching vibration[39,45]
683	Mg-O-Al stretching vibration[39,45]
1410	NO₃$^-$ bending vibration[34,39]
1535	H-O-H stretching vibration[46]
2300	C-N group bending vibration[34,39]
2350	C-N group stretching vibration[34,39]
2380	C-N group stretching vibration[34,39]
3518	OH group bending vibration

4.3.4 FTIR of MgAl$_2$O$_4$ Spinel (Al(NO$_3$)$_3$.9H$_2$O in 1.75 molar ratio):
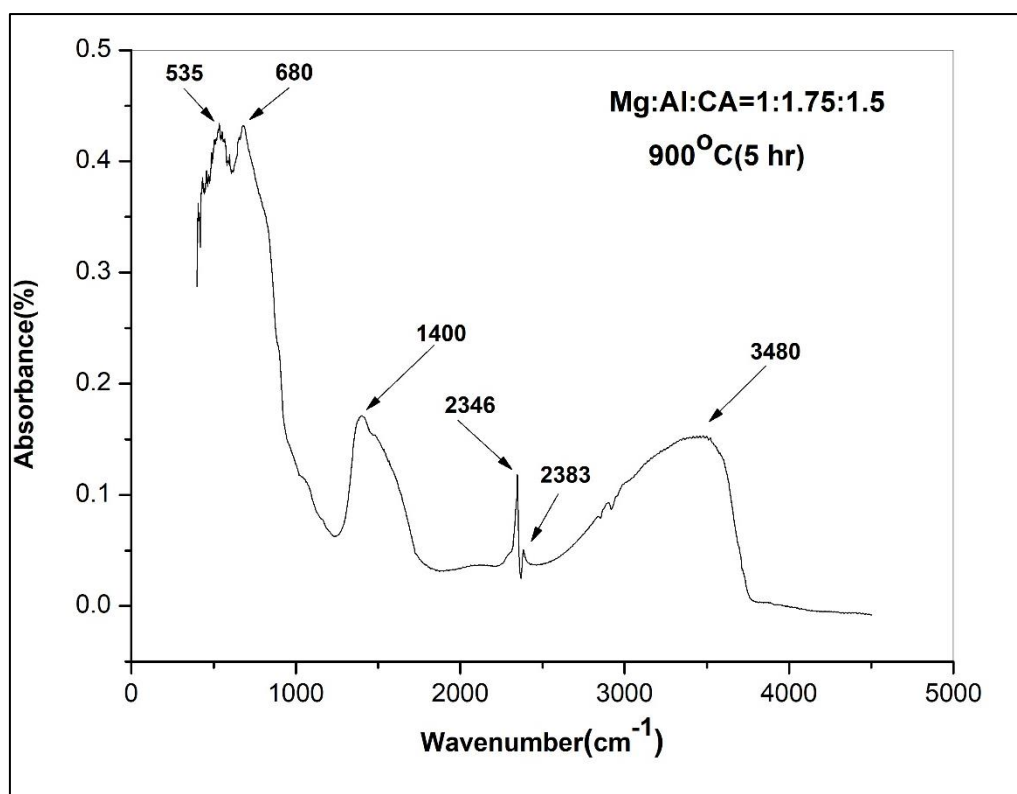
Figure 4.15:FTIR of MgAl₂O₄ Spinel(Al(NO₃)₃.9H₂O in 1.75 molar ratio) heat treated for 5 hour at 900ºC

Table 4.28:FTIR of Spinel(Al in 1.75) at 900ºC(5 hr):

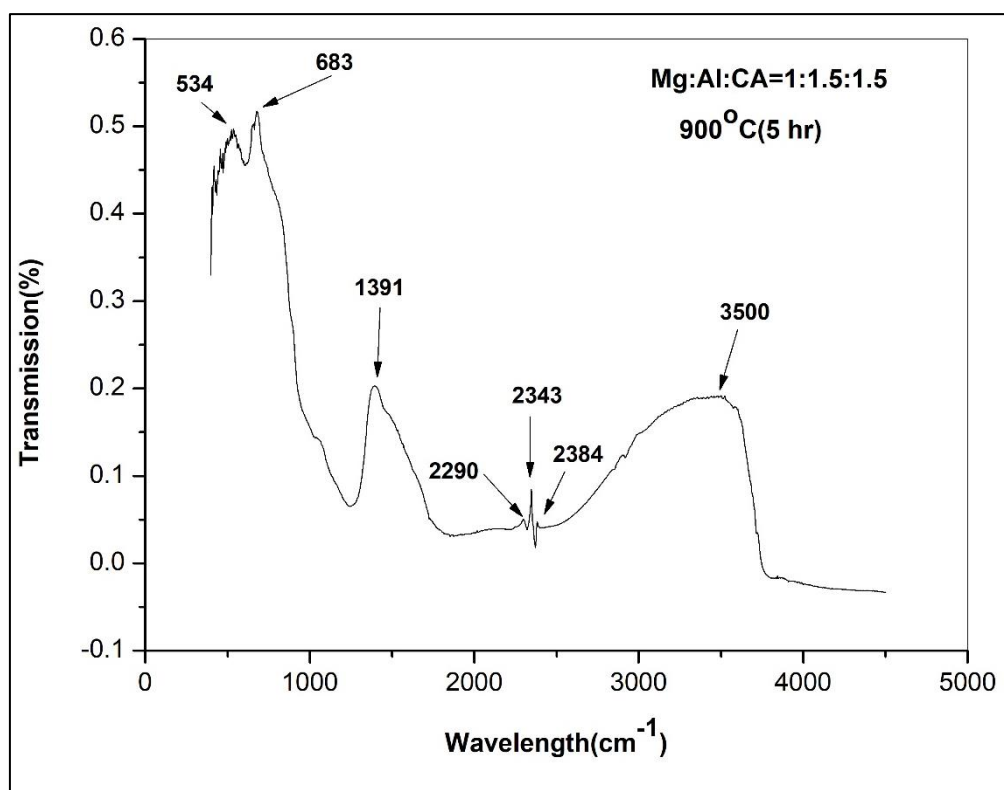| Wavenumber(cm^{-1})	Assignment
535	Mg-O-Al stretching vibration[39,45]
680	Mg-O-Al stretching vibration[39,45]
1400	NO$_3^-$ bending vibration[34,39]
2346	C-N group stretching vibration[34,39]
2383	C-N group stretching vibration[34,39]
3480	OH group bending vibration

Figure 4.16: FTIR of MgAl$_2$O$_4$ Spinel(Al(NO$_3$)$_3$.9H$_2$O in 1.75 molar ratio) heat treated for 5 hour at 1000ºC

Table 4.29:FTIR of Spinel(Al(NO$_3$)$_3$.9H$_2$O in 1.75) at 1000ºC(5 hr):

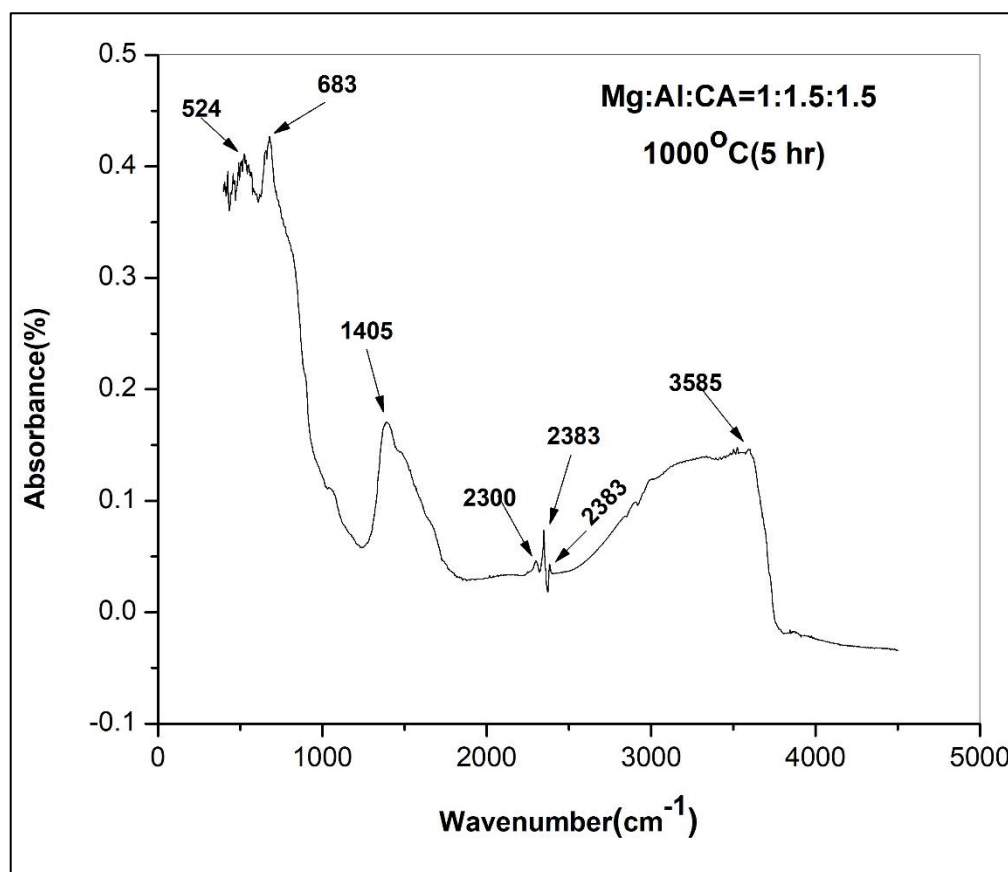| Wavenumber(cm^{-1})	Assignment
565	Mg-O-Al stretching vibration[39,45]
674	Mg-O-Al stretching vibration[39,45]
1385	NO$_3^-$ bending vibration[34,39]
2344	C-N group stretching vibration[34,39]
2385	C-N group stretching vibration[34,39]
3500	OH group bending vibration

4.3.5 FTIR of MgAl$_2$O$_4$ Spinel (Al(NO$_3$)$_3$.9H$_2$O in 1.5 molar ratio):

Figure 4.17: FTIR of MgAl$_2$O$_4$ Spinel(Al(NO$_3$)$_3$.9H$_2$O in 1.5 molar ratio) heat treated for 5 hour at 900°C

Table 4.30:FTIR of Spinel(Al(NO$_3$)$_3$.9H$_2$O in 1.5 molar ratio) at 900°C(5 hr):

Wavenumber(cm^{-1})	Assignment
534	Mg-O-Al stretching vibration[39,45]
683	Mg-O-Al stretching vibration[39,45]
1391	NO$_3^-$ bending vibration[34,39]
2290	C-N group bending vibration[34,39]
2343	C-N group stretching vibration[34,39]
2384	C-N group stretching vibration[34,39]
3500	OH group bending vibration

Figure 4.18: FTIR of MgAl$_2$O$_4$ Spinel(Al(NO$_3$)$_3$.9H$_2$O in 1.5 molar ratio) heat treated for 5 hour at 1000ºC

Table 4.31:FTIR of Spinel(Al(NO$_3$)$_3$.9H$_2$O in 1.5 molar ratio) at 1000ºC(5 hr):

Wavenumber(cm^{-1})	Assignment
524	Mg-O-Al stretching vibration[39,45]
683	Mg-O-Al stretching vibration[39,45]
1405	NO$_3^-$ bending vibration[34,39]
2300	C-N group bending vibration[34,39]
2358	C-N group stretching vibration[34,39]
2383	C-N group stretching vibration[34,39]
3585	OH group bending vibration

4.4 FESEM Analysis of Various Ratio:

For the analysis of FESEM 3sample have been choosen from the 5 different samples which have $Al(NO_3)_3.9H_2O$ contents of 2.75, 2.25 and 1.75 molar ratio.The analysis are discussed below:

4.4.1 FESEM Image of $MgAl_2O_4$($Al(NO_3)_3.9H_2O$ in 2.75molar ratio):
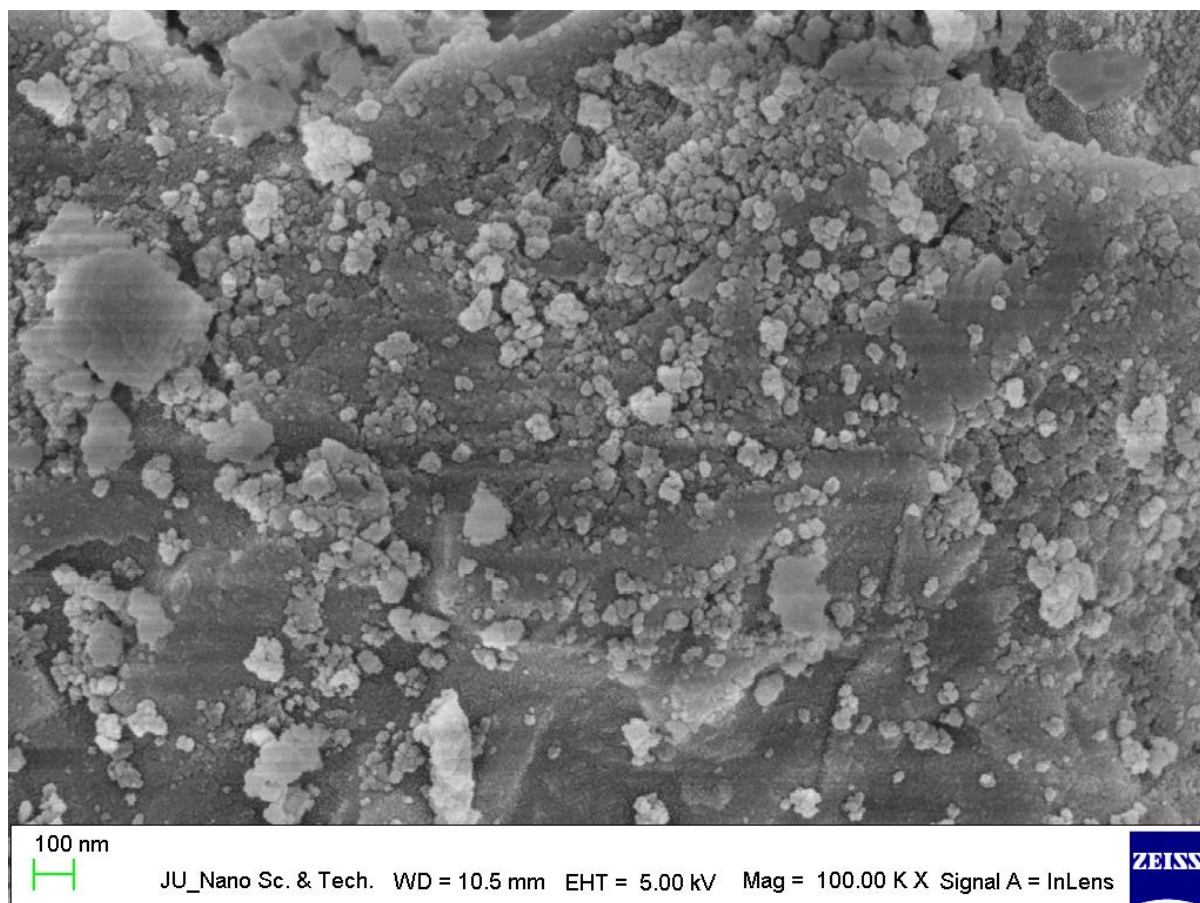
Figure 4.19: FESEM Image of $MgAl_2O_4$ Spinel($Al(NO_3)_3.9H_2O$ in 2.75 molar ratio) heat treated for 5 hour at 1000ºC

From the figure 4.19 it is clearly seen that there is flake like structure with particle size 20 to 30 nm. They are not separated .They are stuck to each other and make agglomerated structure.

4.4.2 FESEM Image of $MgAl_2O_4(Al(NO_3)_3.9H_2O$ in 2.25 molar ratio):
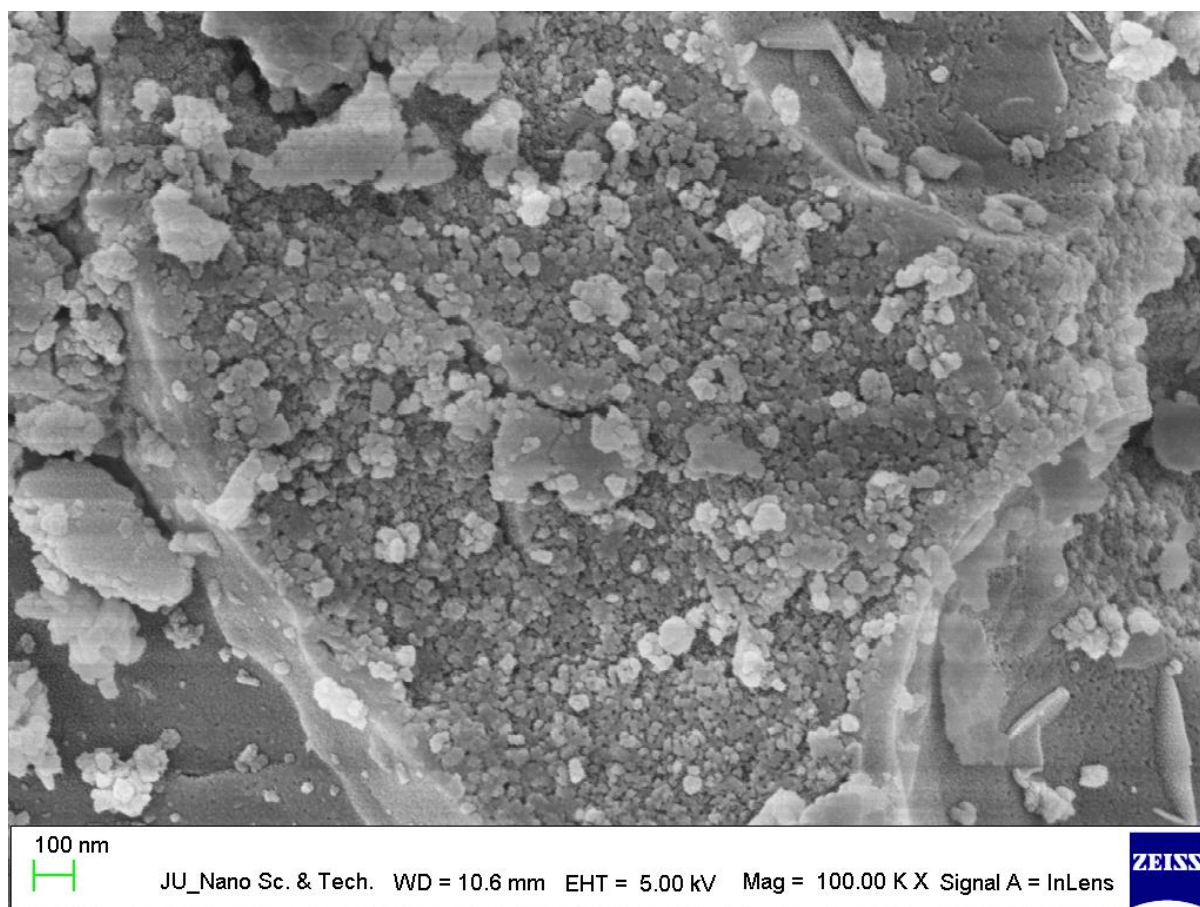
Figure 4.20: FESEM Image of $MgAl_2O_4$ Spinel$(Al(NO_3)_3.9H_2O$ in 2.25 molar ratio) heat treated for 5 hour at 1000ºC

From the figure 4.20 it is clearly seen that there is flake like structure with particle size 25nm to 35 nm. They are not separated .They are stuck to each other and make agglomerated structure.
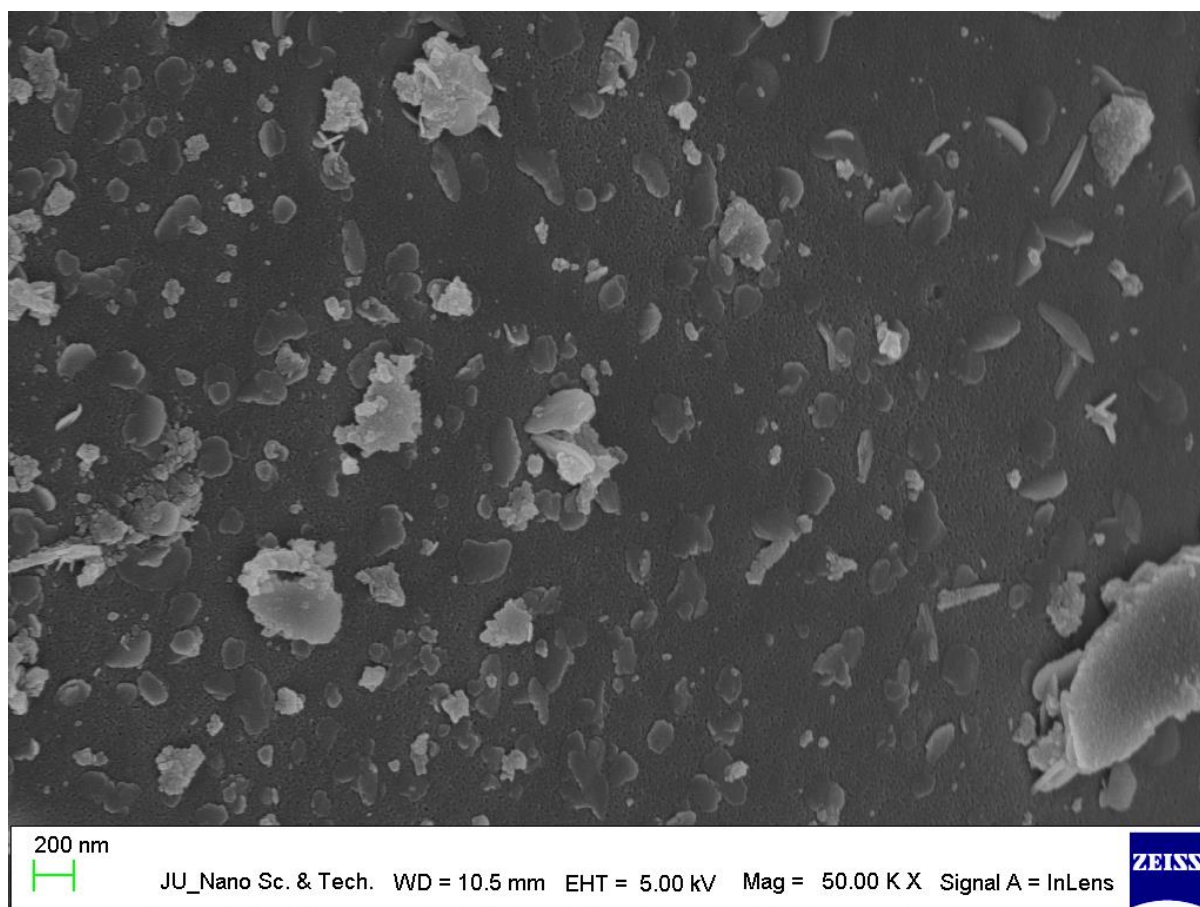
4.4.3 FESEM Image of $MgAl_2O_4$(Al(NO$_3$)$_3$.9H$_2$O in 1.75molar ratio):

Figure 4.21: FESEM Image of MgAl$_2$O$_4$ Spinel(Al(NO$_3$)$_3$.9H$_2$O in 1.75 molar ratio) heat treated for 5 hour at 1000ºC

From the figure 4.21, some flake like structure with particle size 20nm to 25 nm have been observed. They make agglomerated structure.

Morphology obtained in this case to exhibits agglomeration without interconnected pores. Individual particulates are flake like shape to be around 25 nanometer while the agglomerates are in irregular shapes. Thus, the spinel formed by using the 3 different Al(NO$_3$)$_3$.9H$_2$O molar ratio exhibit agglomeration tendency with reducing surface area.

CHAPTER 5

CONCLUSION

Here MgAl$_2$O$_4$ spinel has been prepared with the help of sol-gel method using Magnesium Nitrate Hexahydrate and Aluminium Nitrate Nonahydrate as the precursor were used for the formation of MgAl$_2$O$_4$. The homogeneous spinel with enhanced structural change is successfully synthesized by molecular level mixing process followed by sintering. From literature review, it has been concluded that the stoichiometric ratio of Mg/Al is 1:2. For the non-stoichiometric ratio by varying Aluminium Nitrate Nonahydrate in 2.75,2.5,2.25,1.75 and 1.5 molar ratio using citric acid as fuel agent various conclusions discussed below:

❖ As compare to urea and glycine the duration of synthesis process using citric acid is much more time consuming. Due to use of ultrasonic cleaner there is chance of less moisture absorption.

❖ From the DTA/TGA data as shown it is clear that crystallization of the MgAl$_2$O$_4$ spinel formation happened after 600°C.The weight loss in formation of spinel in sample of Al(NO$_3$)$_3$.9H$_2$O in 2.75 molar ratio is around 88.47% ,in 2.25 molar ratio it is around 93.582% and in 1.75 molar ratio it is around 74.72% .It is because of gel of spinel given and also OH molecules presence in there.

❖ From the XRD data in different temperature ranging from 650°C to 1000°C it is clear that the pure spinel structure of the material appears from 800°C.In 650°C and 700°C XRD data showed that there was peak shift occurred between Al$_2$O$_3$ and spinel.

❖ For FTIR analysis of different sample at 900°C and 1000°C it is seen that stretching vibration of spinel is very much stable at 900°C and 1000°C.

❖ From the FESEM images it is observed that there is formation of MgAl$_2$O$_4$ with flake like structure which are agglomerated to each other.

❖ For the sintering of material ,best sample have chosen in each of 5 different ratio of spinel. The choosen sample is 1000°C(5 hour heat treated) in each sample.Among the different ratio of Al(NO$_3$)$_3$.9H$_2$O, the result have been observed for 1.75 and 1.5 molar ratio. The pellet is well sintered at 1200°C followed by 2 hour soaking time. For the molar ratio of 2.75,2.5 and 2.25 of Al(NO$_3$)$_3$.9H$_2$O the result have been observed that pellet is well sintered at 1400°C followed by 2 hour soaking time.

FUTURE SCOPE

Author will study the sintering process for measuring its microhardness property. The material is not completely sintered for few ratio so the particles are not properly stuck so further investigation is required. Semiconducting properties are needed to be studied. The band gap evaluation for optical studies are to be carried out in future .For dielectric analysis dopants using transition metal ion are to be carried out in the future.

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

At Jawaharlal Nehru University (J.N.U.), New Delhi

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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 (NO3)2, 9H2O and Al (NO3)3, 6H2O and Citric acid reagent altogether with a small amount of water were mixed. The homogeneous mixture was dried at 80 ºC 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 ºC, 700 ºC, 800 ºC, 900 ºC, 1000 ºC 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 800ºC. 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 1000ºC.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 $Mg(NO_3)_2$,9H2O and $Al(NO_3)_3$, 6H2O as the precursor mixes together along with 5-7 ml DI water and Citric Acid as fuel agent .The $Mg(NO_3)_2$,9H2O and $Al(NO_3)_3$, 6H2O 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 80ºC 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 50ºC .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 10ºc/min under nitrogen flow from 30ºC to 1000ºC. 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 550-600ºC. 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 900ºC and 1000ºC 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 80ºC at heating thereby ultra sonication for 5 -8 hours.
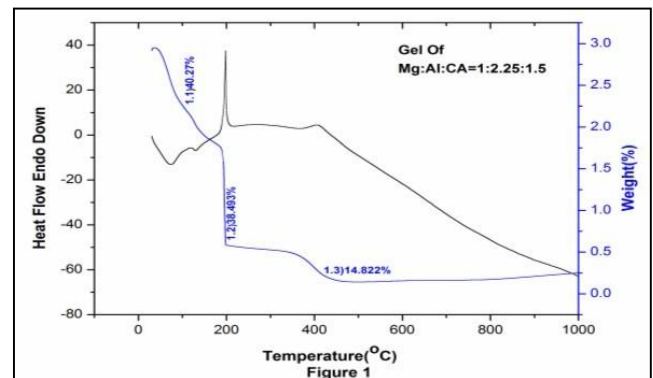

Fig. 1: TG-DTA analysis of homogeneous mixture within the temperature range 0ºC to 1000º

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) 31ºC - 188ºC the weight loss is 40.267% which is associated with water

.1.2)188ºC-198.68ºC the weight loss is 38.493% which is also associated of OH [5] molecules. 1.3) 198.68ºC- 595ºC 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$_2$O$_4$ at different temperature of 650,700 800, 900 and 1000ºC 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.
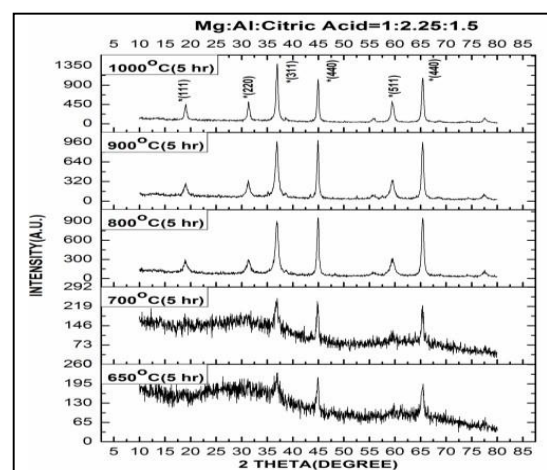

Fig. 2: MgAl$_2$O$_4$ after calcinations in different temperature for 5 hour

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 1000ºC is closer in 20 nanometer to 40 nanometer by using Scherer formula as compare to 900ºC.

3.3 FTIR Analysis

FTIR spectra were captured from 400- 4000 cm^{-1} Range for $MgAl_2O_4$ at 1000ºC 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
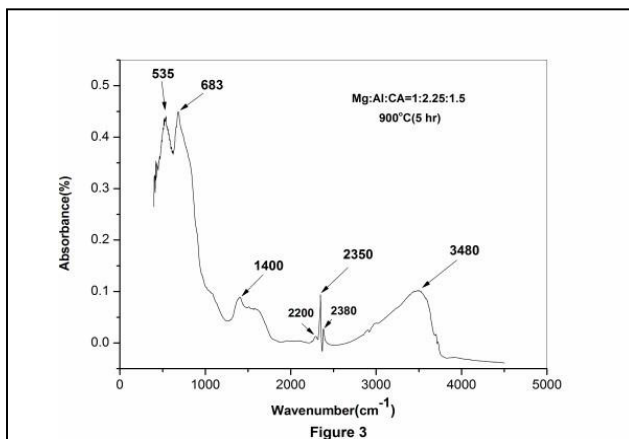
3480 cm^{-1} is bending vibration for OH group.

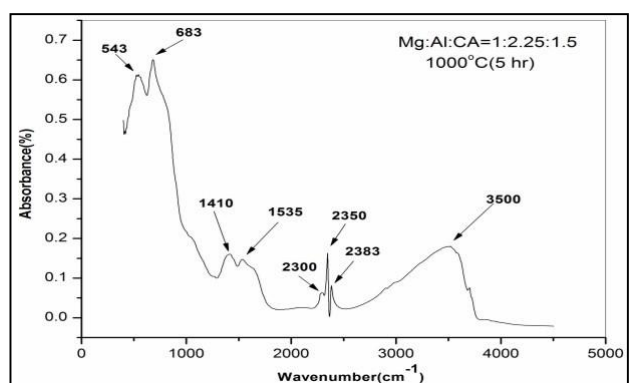Fig. 3: FTIR-spectroscopy of the $MgAl_2O_4$ precursor powders at 900ºC (5 hrs.)

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

Also from 1000ºC 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 1000ºC 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.
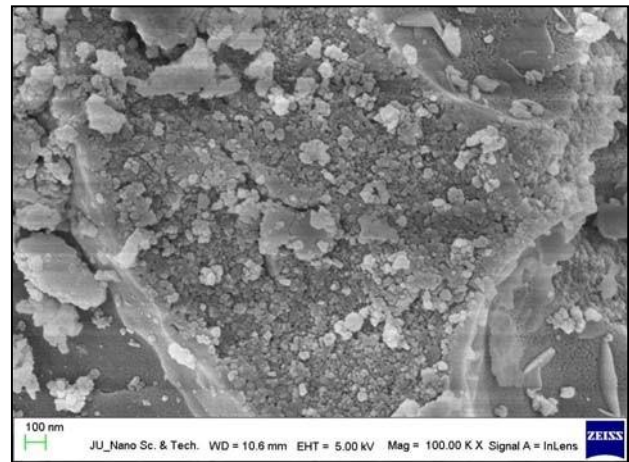

Fig 5: FESEM image of $MgAl_2O_4$ after calcinations at 1000ºC

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.

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