Synthesis And Characterization Of Spinel By Solution Combustion Route

A thesis submitted in partial fulfillment of the requirement for the award of the degree of

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CERTIFICATE

This is to certify that the thesis entitled "Synthesis and characterization of alumina & spinel by solution combustion route" has been carried out under the guidance of **Prof. Siddhartha Mukherjee, Dept. of Metallurgical and Material Engineering, Jadavpur University and Dr. Soumya Mukherjee, AMITY University, Kolkata** by **Srinath Ranjan Ghosh** during the academic session 2015-2016 in partial fulfillment of the requirement for the award of the degree of **Master of Metallurgical Engineering in Industrial Metallurgy** 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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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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DECLARATION OF ORIGINALITY AND COMPLIANCE OF ACADEMIC ETHICS

I hereby declare that the thesis contains literature survey and original research work by the undersigned candidate as a part of his Master of Metallurgical Engineering curriculum.

All information in this document have been obtained and presented in accordance with the academic rules and ethical conducts.

I also declare that as required by these rules and conducts, I have cited and referenced all the materials and results which are not original to this work.

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ABSTRACT

Refractories are a very integral part of today's emerging science and technology of high temperature materials. These play a very important role in many technological advances all over the world. The iron and steel sector in particular benefits a lot from these refractories. The production of good quality iron and steel (whose consumption is an index of the technological development of a country) depends on the quality and performance of refractories. This study was aimed towards examination of various properties of $MgAl_2O_4$ spinel and compare with standard refractory material. $MgAl_2O_4$ spinel has several important limitations. To take care of the drawbacks people doing research in this field are trying to incorporate more MgO in the Alumina matrix. Aluminum nitrate, magnesium nitrate and thiorea are mixed with proper proportion. The mixture were then dried and heat treate in different temperature. Experimented temperature were 650ºC, 700ºC, 800ºC. obtained heat treated material were then sent to various testing such as XRD, FTIR, SEM, Micro hardness test. By these testing we have came to an conclusion that even at low temperature spinel can be formed and this material can be used as a refractory material.

CHAPTER I

INTRODUCTION

1.Refractory materials

1.1.Basic concepts

Refractory materials are plays an important in various scientific and technological applications. Refractories are non metallic inorganic materials. Refractories are capable of withstanding very high temperatures. Melting temperatures are extremely high of these materials. The most striking features of refractory materials are as follows:

- Excellent room temperature and high temperature mechanical properties.
- Very high melting temperature.
- Capability of withstanding frequent fluctuations of temperature due to repeated heating and cooling in service environment.
- Ability to resist corrosion and erosion due to molten metal, glass, slag, hot gases, etc
- Good thermal stability

Refractory materials have contributed significantly towards many industrial applications such as the production of ferrous and non-ferrous metals, cement, glass, ceramics, chemicals, etc. Some of the major application areas of refractories are:

- Kilns
- Furnaces
- Boilers
- Incinerators

1.2 Definition of refractories

According to the ASTM C71 the definition of the refractories is “nonmetallic materials having those chemical and physical properties that make them applicable for structures or as components of systems that are exposed to environments above 10000F (5380ºC). The iron and steel industry has undergone a drastic technological improvement. This has resulted in significant changes in the operating practice. These changes include increase of the furnace capacity, operating temperature, physico-chemical condition of reactors, etc. To cope with these changes in the manufacturing and application environment the refractories used in these applications must be upgraded accordingly in terms of better properties and life. Over and above these materials should be environment friendly.

1.3 Classification of refractories:

Refractories, in general can be categorized in different ways as follows:

(a) Based on raw materials:

- Acidic refractories (e.g. zircon, fireclay and silica)
- Basic refractories (e.g. dolomite, Magnesite, magnesia-carbon, alumina-magnesia – carbon, chrome-Magnesite and Magnesite- chrome)
- Neutral refractories (e.g. alumina, chromites, Silicon carbide , carbon)

(b)Based on manufacturing process:

- Shaped refractories (available in the form of different brick shapes ,and includes the oxide and non-oxide systems)
- Unshaped refractories (includes mortars, castables and other monolithics).

1.4 Required features

The type of the refractory to be used is dictated by the conditions prevailing in the application area. The refractories used in the iron and steel industry have to endure a very stringent and precise set of operating conditions. The most important features of such a strict environment are:

- heavy load of molten metal
- very high temperature (>1600ºC)
- corrosive slag attack
- abrasion and thermal/mechanical spalling caused by molten metal and slag
- Such an operating environment becomes even more challenging due to continuous improvement
- of technology for better results. Some of these ever changing features are:
- further improvement and upgradation in the metal extraction technology
- higher temperature of operation
- longer service life
- In order to be able to withstand the above effects it is mandatory to make use of superior
- refractory lining with the following characteristics:

- very high corrosion resistance
- good thermal spalling resistance
- excellent mechanical characteristics even at high temperature
- ease of application
- enhanced lining life
- less down time and environmental friendliness

2. Alumina (Corundum)

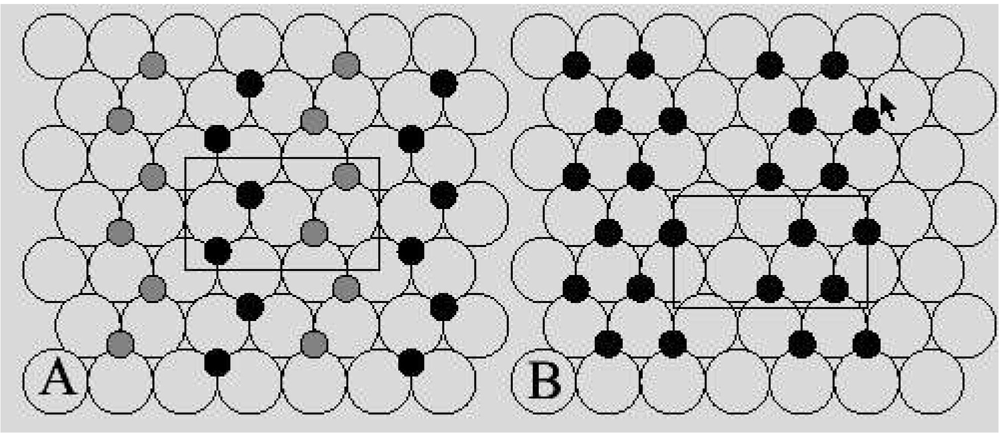
Corundum is the most common naturally-occurring crystalline form of aluminum oxide(alumina). Much less-common rubies and sapphires are gem-quality forms of corundum with their characteristic colours due to trace impurities in the corundum structure. Rubies are given their characteristic deep red color and their laser qualities by traces of the metallic element chromium. Sapphires come in different colors given by various other impurities, such as iron and titanium.

2.1 Crystal Structure

The most common form of crystalline alumina, α-alumina oxide, is known as corundum. Corundum has a trigonal Bravais lattice with a space group of R-3c. The primitive cell contains two formula units of aluminum oxide. The oxygen ions nearly form a hexagonal close-packed structure with aluminum ions filling two-thirds of the octahedral interstices. Alumina also exists in other phases, namely eta, chi, gamma, delta and theta alumina. Each has a unique crystal structure and properties. Alumina crystallizes in a number of different modifications. The three most important are alpha (stable), kappa (metastable) and gamma (metastable).

2.1.1 Kappa Alumina

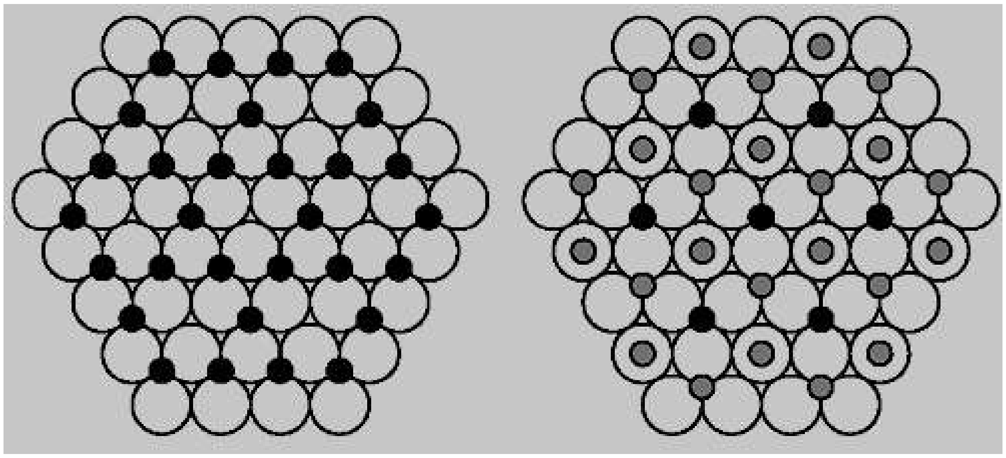
Kappa alumina has an orthorhombic crystal structure (Pna21) with close-packed planes of oxygen in an ABAC stacking sequence along the c-axis.1/4 of the Al ions occupy tetrahedral interstitial positions and 3/4 occupy octahedral positions. The tetrahedrally coordinated Al ions form zig zag lines along [100] in the structure as can be saw in Fig. 1.3 below left. There are also vacancy lines in the structure along [100] as can be seen in Fig. 1.3 (right).



Schematic drawing of the first two layers in the kappa alumina structure. Octahedral Al ions are black, tetrahedral are grey [1]

2.1.2 Gamma Alumina

Gamma alumina is cubic with space group Fd-3m and is base on an FCC . . . ABCABC stacking of oxygen.



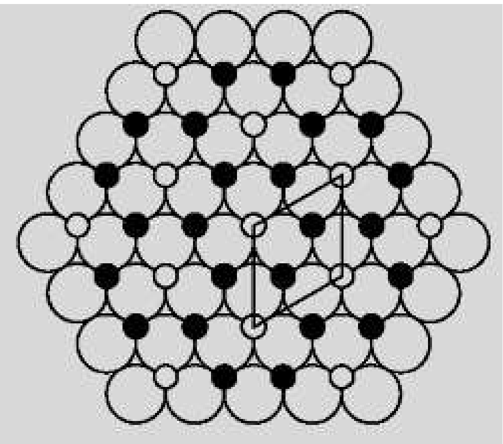
Schematic drawing of the first two layers in the gamma alumina structure [2]

The structure is often describing as a defect cubic spinal structure with vacancies on part of the cations positions. Each unit cell contains 32 oxygen and 64/3 aluminum ions to fulfil stoichiometry.

The aluminum ions occupy both octahedral and tetrahedral positions, but the relative partial occupancy in each position is still a matter of dispute.

2.1.3 Alpha Alumina

Alpha alumina is the only stable alumina phase at all temperatures. It has a trigonal structure (R-3c) and is usually describe as ABAB stacking of oxygen planes along the c-direction with Al ions in 2/3 of the octahedral interstitial positions.



Schematic drawing of the first layer in the alpha alumina structure [3]

3. Spinel

The magnesium aluminate spinel is the member of the larger spinel group of minerals. It has the formula $MgAl_2O_4$ in the cubic crystal system. Spinel compounds are the group of minerals that are oxides of Magnesium, Iron, Manganese or Aluminium. The term spinel is derived from spina (Latin, thorn) in reference to its pointed octahedral, crystal habit. Spinel minerals are widely distributed in the earth, in meteorites and in rock from moon. The spinel series is evolved from the classification: Spinel, Magnetite and Chromite. These are very hard, variously colored minerals, having usually octahedral crystals and occurring in ignition and carbonates rocks. Spinels are very attractive subjects for material research and engineering applications. Aluminous spinels are highly refractory, varying from translucent to transparent and from colorless to green, blue, brown and black.

Magnesium aluminate spinel offers a unique combination of high-temperature properties including a high melting point, excellent resistance against chemical attack, potentially high strength even at high temperatures and very good thermal characteristics.

3.1 Structure, Property and Phase Diagram

3.1.1 Spinel Structure

- Formulae – $(A^{2+})(B^{3+})_2O_4$ or AB_2O_4 or $AO.B_2O_3$
- FCC Packing of anions
- Partial occupancy of both tetrahedral and octahedral sites i.e.1/8th of tetrahedral and ½ of the octahedral sites are occupied.
- A spinel unit-cell is made up of eight FCC cells made by oxygen ions in the configuration 2×2×2, so it is a big structure consisting of 32 oxygen atoms, 8 A atoms and 16 B atoms.
- Depending on how cations occupy different interstices, spinel structure can be Normal or Inverse.

3.1.2 Normal Spinel

- Chemical formula: $(A^{2+})(B^{3+})O_4$
- Examples are many aluminates such as $MgAl_2O_4$, $FeAl_2O_4$, $CoAl_2O_4$ and a few ferrites such as $ZnFe_2O_4$ and $CdFe_2O_4$.
- In this structure, all the A^{2+} ions occupy the tetrahedral sites and all the B^{3+} ions occupy the octahedral sites.
- Apply bond strength rule to verify the stoichiometry
- Cations :- A^{2+} - $^{2}/_{4}$;B^{3+} - $^{3}/_{6}$Oxygen valence = $(^{2}/_{4}\text{x}1)+(^{3}/_{6}\text{x}3) = 2$

3.1.3 Inverse Spinel $B(AB)O_4$

- Chemical formula: $(A^{2+})(B^{3+})_2O_4$ but can be more conveniently written as $B(AB)O_4$.
- Most ferrite follow this structure such as Fe_3O_4 (or $FeO.Fe_2O_3$), $NiFe_2O_4$, $CoFe_2O_4$ etc.

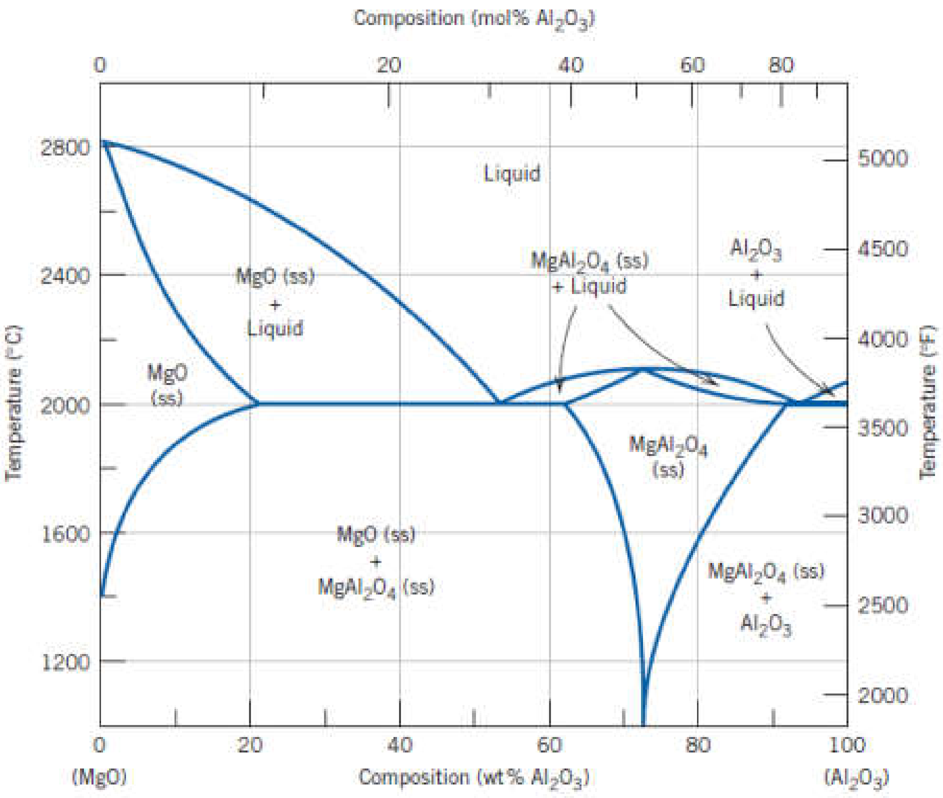
- In this structure, ½ of the B^{3+} ions occupy the tetrahedral sites and remaining ½ B^{3+} and all A^{2+} ions occupy the octahedral sites (now you can hopefully make sense of the formula in the previous line).

3.1.4 Physical property

Density (g/cm)	3.58
Thermal conductivity(W/mK)	5.9
Thermal expansion coefficient (dl/LK 10)	7.6

3.1.5 Spinel phase diagram

- Pure magnesia melts at 2800°C.
- Pure alumina melts at 2054°C.
- Magnesia can dissolve up to 2% alumina, the maximum solubility occurring at 2000°C. The name given to this solid solution of alumina in magnesia is "periclase."
- Magnesia has no solubility in alumina.
- "Spinel" is the name normally associated with the compound MgAl2O4, but it is also the name of a phase in the magnesia-alumina binary system with solubility ranging from 40% alumina (at 2000°C) to 84% alumina (at 1800°C). The spinel phase with a composition of 50% alumina melts congruently at 2200°C.
- At 2200°C, an 82% magnesia alloy is partially solidified, consisting of equal parts periclase and liquid.
- At 2000°C, a 68% magnesia alloy transforms on cooling from a liquid phase to two solid phases. One of the solid phases is periclase with 2% alumina content and the other is spinel with 40% alumina content.
- At 2000°C, a 73% alumina alloy is half liquid and half spinel. • At 1800°C, a 95% alumina alloy solidifies on cooling into two solid phases, one a spinel of 84% alumina, and the other, pure alumina.
- At 1000°C, a 75% magnesia alloy has equal parts periclase, with a composition of 100% magnesia, and spinel, with a composition 50% magnesia.
- At 1000°C, a 77% alumina alloy has equal parts alumina phase and spinel phase, the latter with a composition of 54% alumina.



MgO–Al_2O_3 phase diagram Reference

4. Statement of Problem:

It is known from literature study that alumina can act as refractory material for iron & steel industry. In this studies we will try to find out the low temperature process treatment for spinelization followed by characterization of mixture of magnesium oxide-aluminium oxide ($MgAl_2O_4$) prepared through solution combustion method. Details structural and morphological studies be undertaken to check if it shows refractoriness property at low temperature synthesis. This can save lot of energy which can be avoided by this rout magnesium-aluminate formation.

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CHAPTER II

LITERATURE REVIEW

1. $MgAl_2O_3$ Spinel as a refractory material:

Refractories play an important role in metallurgical, glassmaking and ceramic industries[1,2]. The main problems faced in steel ladle refractories are corrosion by steel slags, abrasion by liquid metal, thermal spalling, oxidation of carbon layer, deterioration of strength at high temperature and molten steel penetration[3-5].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 sinterability 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 [6-8]. In this study aluminium nitrate and magnesium nitrate with thiourea (as a fuel) were used as starting materials for preparation of magnesium-aluminium spinel ceramics.

The magnesium-aluminate with 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 [9-11]. Due to these properties, it is greatly desired as a refractory material[12]. Humidity sensor[13], catalyst or catalyst support and recently as an excellent transparent ceramic material for high temperature arc-enclosing envelopes and alkali-metal vapor discharge devices[14]. Nowadays this spinel has owned many applications in metallurgical, chemical, electro technical, catalysis, electronic and glass industries[15-16]. Over the last few decades various novel techniques have been applied for the synthesis of $MgAl_2O_4$ spinel including Sol-Gel[17], spray drying[18], freeze-drying[19], mechanical activation[20], organic gel-assisted citrate process[21]. 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[22-25]. 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[26,27]. 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[28-31].

Magnesium aluminate spinel, which is the only stable compound in the MgO-Al2O_3 system, has long been considered an important ceramic material. Many studies have reported its properties, applications and different processing methods [33]. 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 [34].

2. Different Types of Synthesis Method for spinel:

2.1. Sol-gel Method: **C. B. Mo** et al used Aluminum tri-sec-butoxide ($Al(OBu)_3$) as a precursor of alumina. The multi-wall carbon nanotubes fabricated by CVD using alumina supported catalyst have dimension of 15–30 nm in diameter, 10–50 μm in length, and the density of 1.6 g/cm^3. Alumina sol was synthesized by Yoldas' process, which consists of hydrolysis and peptization of aluminum hydroxide (AlOOH). The carbon nanotubes dispersed in form of suspension within ethanol were added to alumina sol during the gelation process. They controlled the volume fraction of CNTs as 0, 1.5, and 3.3%. Then they dried carbon nanotube/alumina gel at 350 0C for 6 h. The carbon nanotube/alumina composite powders were fabricated by calcinations of gel powder at 1250 0C for 1 h in vacuum of 10 Pa**[39]**.

2.2. Magnesium aluminate gel precursor has been synthesized by rapid co precipitation technique at a relatively low temperature. This gel exhibits the evolution of spinel phase at significantly lower temperature than solid state sintering; however it is associated with secondary phase like corundum and periclase at higher temperature. The gel has been incorporated in different concentration 0.5-4.0 wt% to a high alumina based castable to fabricate in situ spinel-alumina monolithic refractory. Uncontrolled agglomeration and an enormous amount of -OH-, NH2 and C=O groups associated with the precursor gel indicates a serious apprehension about the performance of the castable. Nevertheless an optimum amount of 2.0 wt% of spinel gel renders a satisfactory role towards the physical properties of the castable. The microsilica content of the original batch should be reduced to eliminate the detrimental CaO-Al_2O_3-SiO_2 phase generated in the matrix[35].

2.3 It is known that the impurities present in raw materials can ultimately affect the quality of refractory products, the extent of their application area, and their lifespan [36]. The samples of raw amorphous magnesite were first crushed by a jaw crusher. The particle size was thereby reduced to nearly 2 mm. The pulverized powders were sieved by means of vibrating sieves and classified into different particle sizes. Then magnetic separation technique was applied to investigate the dressability of raw amorphous magnesite. The content of MgCO3 is 95% in the magnesium carbonate concentrate. The magnesium carbonate concentrate obtained was calcined at a temperature of 800°C with an exposure of 2 hours. A nanosized γ - Al_2O_3 powder was obtained by hydrothermal method (hydrothermal decomposition of aluminum hydroxide) [37]. The resulting caustic magnesia and seven volume percent of γ - Al_2O_3 nanopowders were mixed and milled in a ball mill during 30 min. Specimens of periclase-magnesium aluminate spinel ceramics were compacted to form a cylinder (diameter 21 mm, height 10 mm) by a bi directional axial compression without binder with the use of the hydraulic pelletizing press Herzog TP40/2d. Then obtained samples were sintered at 1500ºC with an exposure 2 hours at the maximum temperature. As a result samples of periclase-magnesium aluminate spinel ceramics were obtained. Phase composition of raw amorphous magnesite was determined by the X-ray phase analysis method (diffractometer Rigaku Ultima IV; Cu Kα – emission (radiation), Ni – filter). Examinations of the elemental composition were carried out by using electron ion microscope Quanta 200 3D and Nova NanoSEM (SEM). To determine the precise material ultimate composition of periclase-magnesium aluminate spinel ceramics, X-ray spectral analysis with the use of scanning electron microscope Quanta 200 3D was performed. The determination of nanosized γ - Al2O3 powder particle size was performed with the use of transmission electron microscope JEOL JEM 2100 (TEM). A volume helium pycnometer (AccuPyc II 1340, Micromerltics Ltd.) was used to measure the density of the periclase-magnesium aluminate spinel ceramics. Mean values and standard deviations were determined from five successive measurements. The temperature and sintering of the sample's behavior were determined by means of the high temperature dilatometer Netzsch L75H. The heating was performed at the temperatures ranging from 20 to 1550ºC at a rate of 2ºC/min. Microhardness of the ceramic samples was determined by an automatic microhardness tester DM-8B (Affri) by Vicker's test at a test load of 500 g. Indentation was carried out with the distance between the indents being 20 µm. On an average, 10 tests were used as an indicator of the sample hardness. The uni-axial compressive tests were carried out in air at ambient temperature by means of testing machine Instron 300LX.

2.4 Two series of batches for the hydrothermal synthesis of magnesia-alumina composites were pre-pared using magnesium hydroxide. 99% type C from Dead Sea Periclase (Israel) and aluminium hydroxide. 99%. SH I 00 from Sochalu (France). The reactants were weighed and mixed separately in water for 15 min at 333 K. Subsequently the two aqueous mixtures were fed into the laboratory reactor. The first batches. denoted spine) I. contained equimolar quantities of both hydroxides based on the oxides. i.e. forming $MgO\cdot Al_2O_3$. The second batches. denoted spine contained a double amount of aluminium hydroxide. i.e. forming $MgO\cdot 2Al_2O_3$. The pilot plant consists of two vessels connected to one another by means of a heat exchanger. One vessel is the reaction vessel. Its walls are heated electrically or with thermal oil (Santotherm 66). In the contents of the reaction vessel 50 kg water and 1 kg reactants is stirred continuously. The reaction time is 4 h. measured from the moment the vessel reached its pressure of 4 MPa at the corresponding saturated steam temperature of 523 K. After the reaction is completed, the products are transferred through the heat exchanger into the receiving vessel under controlled laminar conditions by creating a small difference in pressure between the two vessels. Damage of the product crystals is therefore avoided. The hydrothermally treated slurries thus obtained were fed into a laboratory spray dryer. The resulting powders are virtually dry, 0.6% was the highest recorded residual moisture content. Pellets and tablets were pressed uniaxially in a dye at a pressure of 13.5 MPa from approximately 2g of the powders harvested from the spray dryer. Green densities of about 55% of the theoretical were achieved without the use of any binder. The pellets were sintered under atmospheric conditions for two hours at 1873 K; both heating and cooling rates were 5 K/min. During sintering a weight loss of about 24% occurred, consistent with the formation of water from the decomposition of the hydroxide [38].

2.5 Analytical grade aluminum nitrate nonahydrate ($Al(NO_3)_3\cdot 9H_2O$), magnesium chloride hexahydrate ($MgCl_2.6H_2O$) and urea (CH_4N_2O) were purchased from Merck (99%) and were used without further purification. A solid mixture containing aluminum nitrate and Sol-Gel synthesized magnesium hydroxide with *n*(Al3+)/ *n*(Mg2+) = 1:2 and urea with *n*(urea)/*n*(metal) = 5:3 was taken in a pyrex glass dish and after complete mixing was irradiated with microwaves in a domestic microwave oven (National, 1000W, input range 210 230V-ac SOHZ, microwave frequency 2.45GHz)[40].

2.6 In this study, spinel ($MgAl_2O_4$) was produced by using alumina (Al_2O_3, Merck, Germany) and magnesia (MgO, technical purity), and aluminum titanate (Al_2TiO_5) was produced by using alumina (Al_2O_3, Merck, Germany) and titania (TiO_2, Merck, Germany) powders. Starting materials that we use are regarded as 99.9% percent pure. After the alumina and magnesia were weighed in terms of mole ratio (1:1) of spinel, with 1:1 molar ratio mixtures were dispersed in acetone and milled as wet with alumina balls of ϕ10 mm for 3 h. The materials containing Al_2O_3 and TiO_2 were prepared in the same way by wet ball milling. Al_2TiO_5 ceramics were synthesized by reaction sintering of an equimolar mixture of Al_2O_3 and TiO_2 powders. The powders were mixed homogenized by wet ball milling. The resulting mixtures were then sintered at 1550ºC for spinel ($MgAl_2O_4$) and 1600ºC for aluminum titanate (AT) in air for 2 h. Then, additions of AT in weight proportions of 0, 5, 10 wt% were made to the spinel + aluminum titanate (SAT) mixture (hereafter these mixtures are denoted SAT0 (100% spinel), SAT5 (95% spinel, 5% aluminum titanate) and SAT10 (90% spinel, 10% aluminum titanate), respectively). Each lot was again wet mixed according to the procedure. Then mixtures were pressed at 200 MPa into 30-30-5 mm^3 specimens. The compacts were sintered in air using a heating rate of 5ºC min^{-1}, soaked at 1700ºC. Bulk density, porosity and water absorption of the sintered samples were measured. Micro hardness (Shimadzu, HMV) was measured on the polished surface of the samples at room temperature. At least six individual tests with a peak load of 2000 g and a loading time of 20 s were performed for each set of composites. After sample sections were mechanically polished and then thermally etched at 1500ºC for 4 hours in air, the micro structural characterization of the sintered samples was carried out using scanning electron microscope. The morphological parameters of the various phases were characterized by using a semiautomatic image analyzer, Energy Dispersive X-ray spectroscopy (EDX) and the formed phases were analyzed by X-ray powder diffractometer (Rigaku, Dmax, IIIC) using Cu K-alpha radiation. The thermal behavior of the SAT composition was characterized by Differential Scanning Calorimetry (DSC) (Shimadzu, DSC-60). Thermal expansion coefficients were measured by using dilatometer (Anter, USA) [41]

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CHAPTER III
EXPERIMENTAL WORK

3.1 PREAMBLE

In this section the details experimental procedure for the study of Al_2O_3 synthesis and alumina and magnesium spinel synthesis has been discussed by solution combustion route. The amounts and ratio of the Al_2O_3, MgO and thiorea used for preparing the different batches in certain ratio were ascertained through the study of literature available on the subject. We will compare the characteristics of alumina and spinel in different treatment temperature. The raw material used in this work viz. aluminium nitrate, magnesium nitrate and thiorea were bought form the market of analytical grade.

3.2 MATERIAL PREPARATION

3.2.1 Preparation of alumina:

Aluminium nitrate ($Al(NO_3)_3.9H_2O$) and thiourea (CH_4N_2S) as a fuel were taken at the ratio of 1 : 1.5. The mixture was then mixed with very small amount of water. Water was used to mix the chemicals uniformly. Then the mixture was dried at 80ºC for 3-4 hours. After completing drying operation the mixture converted into fine powder. The powder was then divided into 3 equal parts. Each part was then carried out through a heat treatment for specific temperature for 2 hours. The treatment temperatures chosen for processing were 650ºc, 700ºc, 800ºc.

3.2.2 Preparation of spinel:

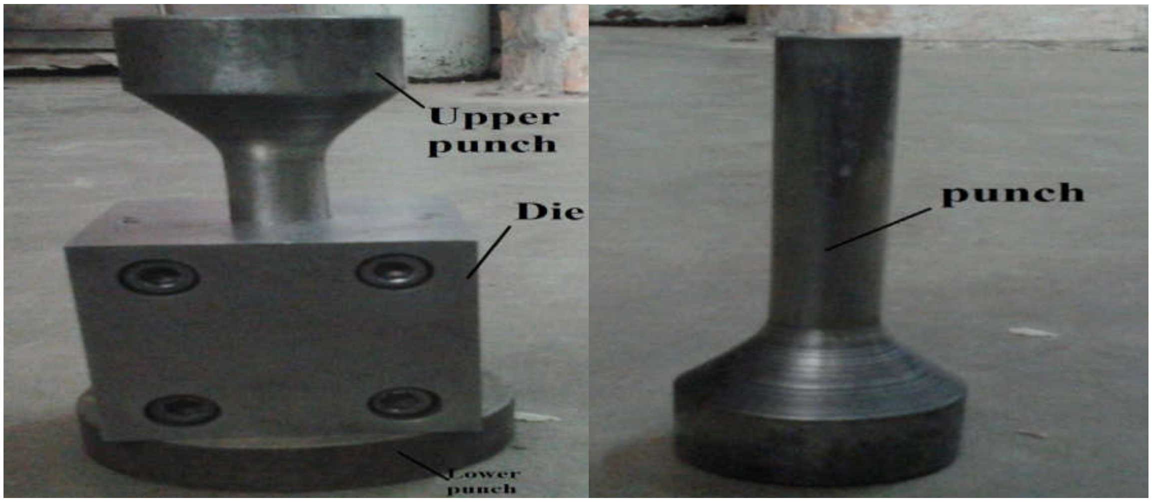
Aluminium nitrate, magnesium nitrate and thiourea were taken at the ratio of 1 : 1 : 1.5. The mixture was then mixed with very small amount of water. Water was used to mix the composition uniformly. Then the mixture was dried at 80ºc for 3-4 hours. After completing drying operation the mixture converted into fine powders. The powder was then divided into 3 equal parts. Each part was then carried out through a heat treatment for specific temperature for 2 hours. The selected temperatures chosen for processing were 650ºc, 700ºc and 800ºc.

Ceramic powder mixing bowl and mixing hammer

Drying machine

3.3 PRESSING/COMPACTION FOR MICRO HARDNESS TEST

The powder mixtures were poured into a 12mm diameter mould cavity in a die system consisting of two punches (a stationary lower punch/ base and a moveable upper punch) and the central block consisting of the cylindrical mould cavity. The entire die system was placed in a manually operated hydraulic pressing machine. Pressing was performed by applying an uniaxial pressure of 1500kg/cm^2. Cylindrical pellets of alumina and spinel of different heat treated powders were thus obtained.



Die and Punch System

Hydraulically controlled high-pressure pressing machine

3.4 CURING

The compacted samples were subjected to curing at 650^0C for about 1 hours. This was done in order to facilitate the following

- Elimination of residual water, volatile matters and phenols if present in sample.
- Development of sufficient strength and proper binding of the constituents so that tablets can be used as micro hardness test.

Pot furnace

3.5 CHARACTERISATIONS /TESTS:

3.5.1. Differential Thermal& Thermo gravimetric Analyzer:

Differential Thermal & Thermo gravimetric Analysis is very important characterization tool for characterization. In DTA/DSC-TGA we can identify any phase change or any chemical/physical change in the system where enthalpy changes occurs are measured by controlling temperature at particular rate of heating or cooling. Diamond DT-TGA can also analyze 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-

DTA/DSC-TGA instrument

DTA/DSC-TGA analysis was carried out with:

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 of different batches (identification of phases):

X-ray diffraction machine

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

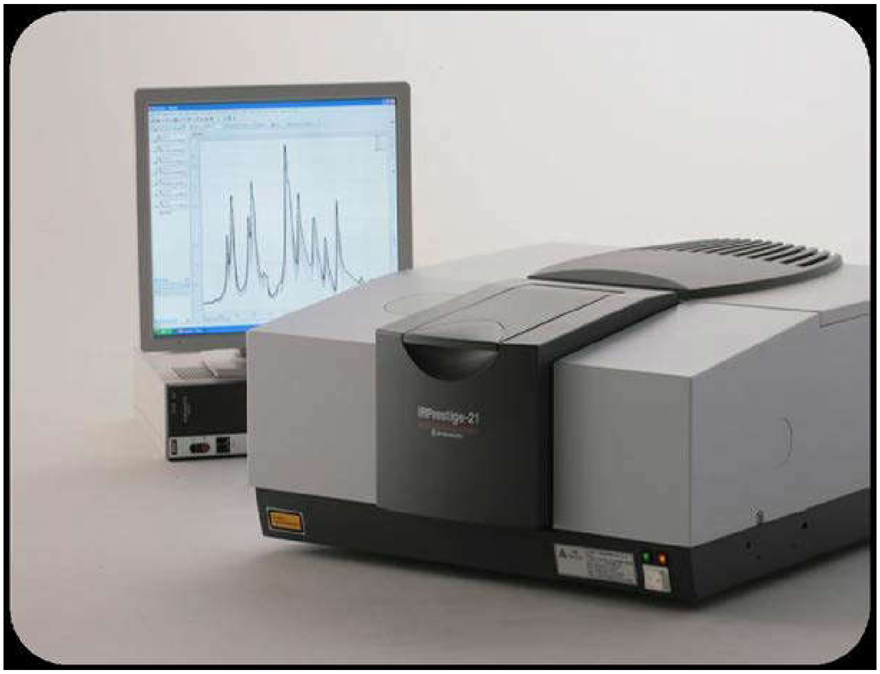
These settings were used throughout the entire XRD analysis. The XRD spectrum gives us the diffraction intensity Vs 2θ plot, where θ is the Bragg's angle in degrees. The XRD plot gives the d-values of the samples along with the values of flex width, 2θ and intensity of the respective peaks. The calculated d-values for the respective peaks in the XRD plot of $MgAl_2O_4$ (spinel), pure Al_2O_3, and were matched with the standard JCPDS data and all the phases corresponding to each of these peaks were identified.

3.5.3 Fourier Transform Infrared Spectroscopy (FTIR) spectroscopy of different batches:

In FTIR 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 sample.
- Determine the amount of the components in a 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.



Shimadzu IRPrestige-21 FTIR spectrometer

3.5.4 SEM analysis of different batches:

Scanning Electron Microscope

The microscopic study of the samples was performed under a SEM (Scanning Electron Microscope) which has a large depth of field, which allows a large amount of the sample to be in focus at one time and produces an image that is a good representation of the three-dimensional sample. SEM can provide us many topographical and elemental information like grain size, surface roughness, porosity, particle size distributions, material homogeneity etc. For the SEM we use directly alumina and $MgAl_2O_4$ (spinel) samples of heat treated in different temperatures. The main aim of doing SEM is to study the morphology and particle size distributions of the alumina and $MgAl_2O_4$ (spinel).

Theory:

Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathodoluminescence--CL), and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination). X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbital (shells) of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam. SEM analysis is considered to be "non-destructive"; that is, x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly.

Essential components of all SEMs include the following:

- Electron Source ("Gun")
- Electron Lenses
- Sample Stage
- Detectors for all signals of interest
- Display / Data output devices

Infrastructure Requirements:

- Power Supply
- Vacuum System
- Cooling system
- Vibration-free floor
- Room free of ambient magnetic and electric fields

CHAPTER-IV

RESULTS AND DISCUSSIONS

4.1 DSC/TGA Analysis of various compositions

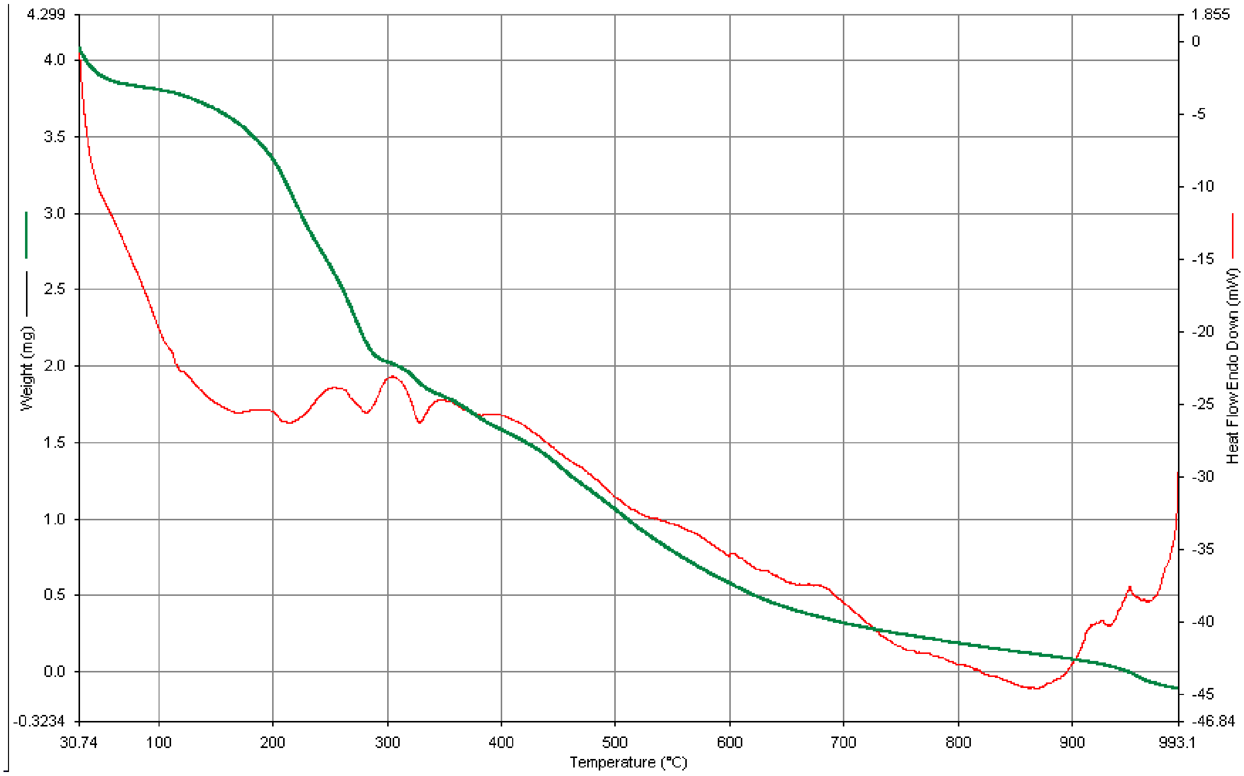


Fig 4.1 DSC/TGA of spinel with heating rate of 10ºC/min

Thermal analysis of precursors material of alumina and MgO has been studied at the heating rate of 10ºC/ min from room temperature to 1000ºC (Fig 1). TG (green colored) plot indicates a steady constant weight loss from room temperature to 1000ºC with three steps. Initial drop of weight is due to removal of moisture and physically held volatile content up to the 150ºC. 150ºC onwards there is a drastic drop of weight due to dissociation of chemically held moisture content. Form 350ºC onwards the change in weight has been observed almost at a constant rate nearly upto the 1000ºC. For DSC plot there are three drop of curve at 220ºC, 280ºC, 340ºC. All the drops are due to endothermic reaction. Release of chemically held moisture occurs in these regions. At 850ºC onwards crystallization of Al_2O_3 occurs which is indicated by exothermic trends. Hence a strong exothermic peak is observed at 1000^0 C.

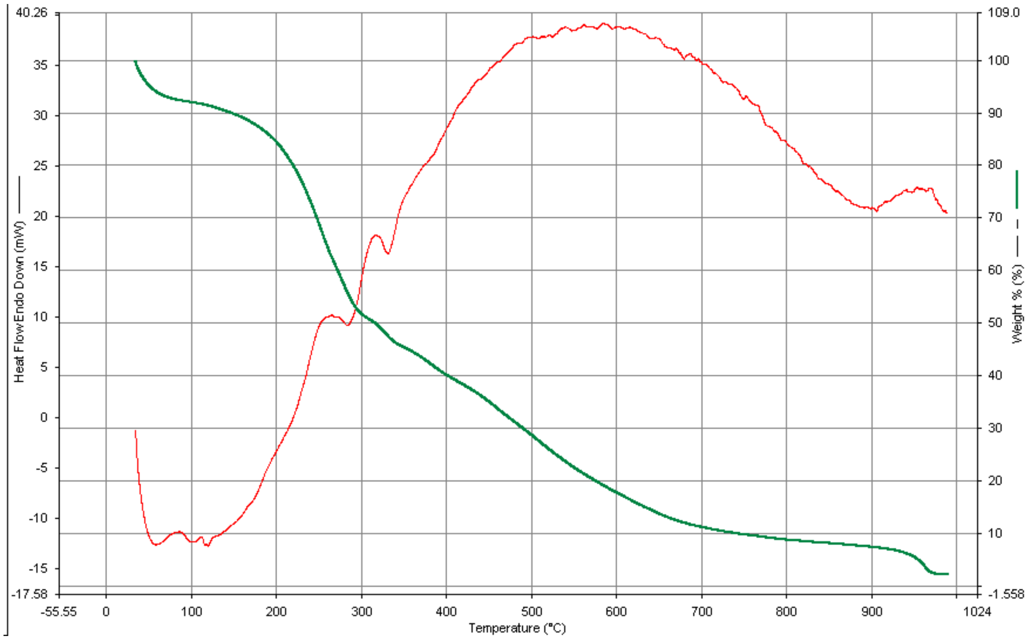


Fig 4.2 DSC/TGA of spinel with heating rate of 12.5°C/min

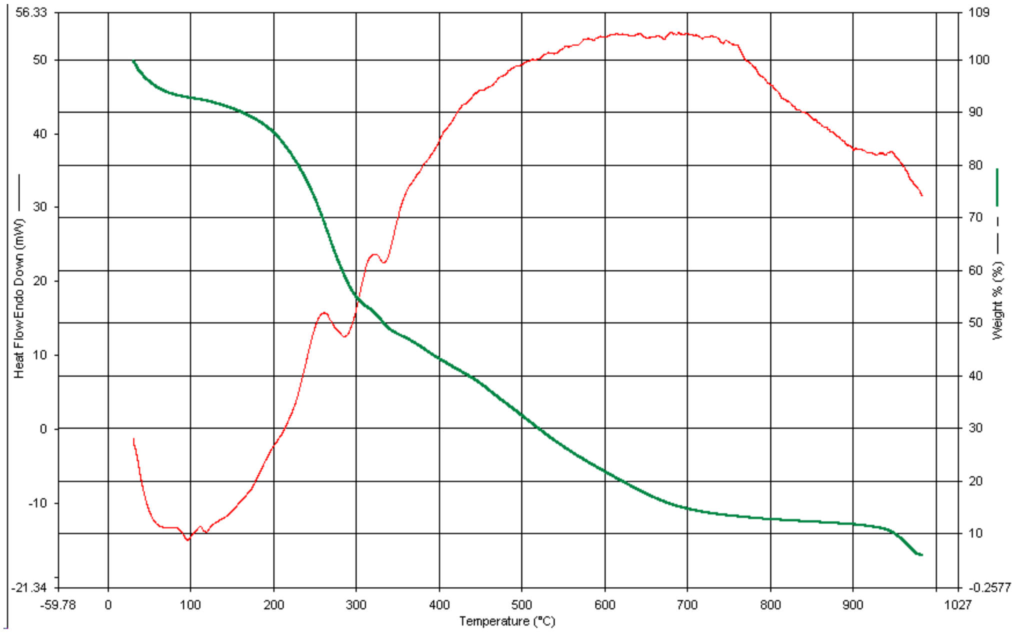


Fig 4.3 DSC/TGA of spinel with heating rate of 15°C/min

Figure 4.2 and 4.3 representing DSC/TGA plot of 12.5 and 15ºC/min showing some change in the behavior compare to 10ºC/min. Initial weight change upto 150ºC may be due to loss of volatile matter which is also reflected in DSC plot showing endothermic behavior. The change in endothermic nature is also observed in DSC plot at 300ºC and 340ºC due to loss of chemically held moisture. The exothermic nature is observed subsequently due to formation of crystallized phase of alumina at about 600ºC. Near about 800ºC almost constant weight is observed showing complete alumina formation during solution combustion process.

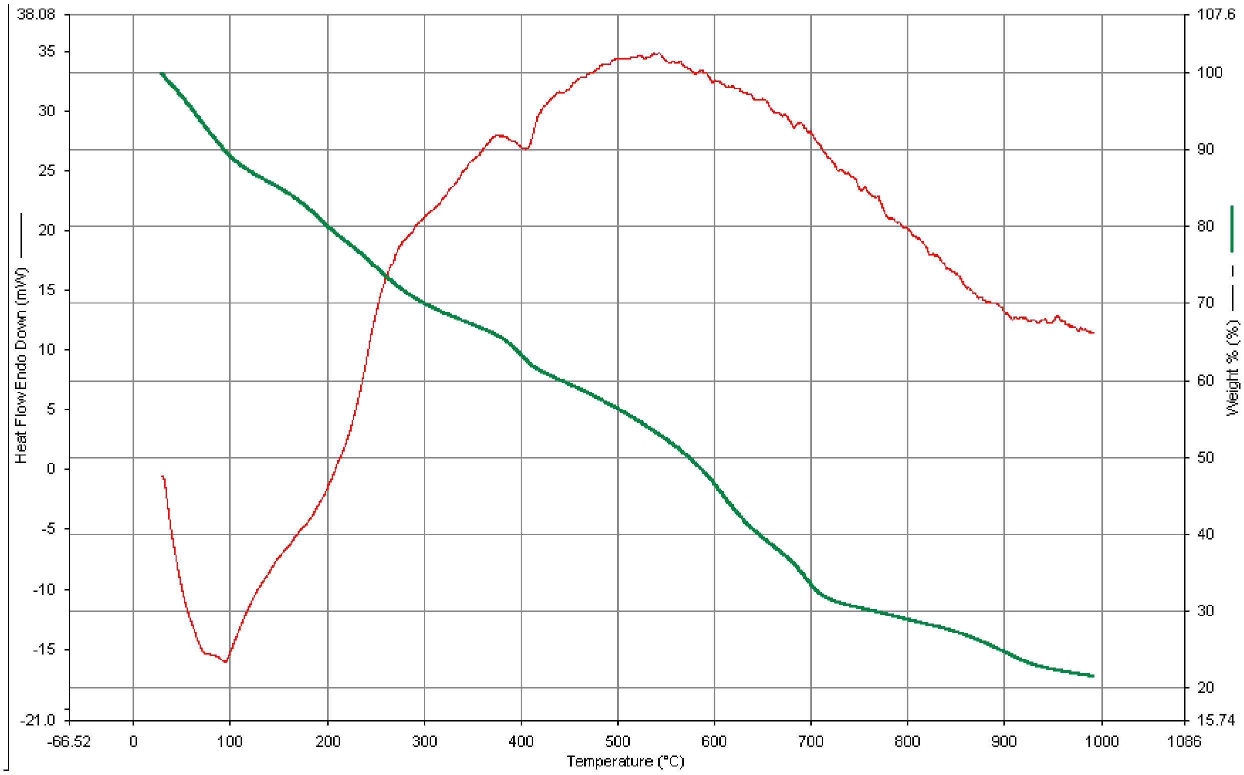


Fig 4.4 DSC/TGA of spinel with heating rate of 10ºC/min

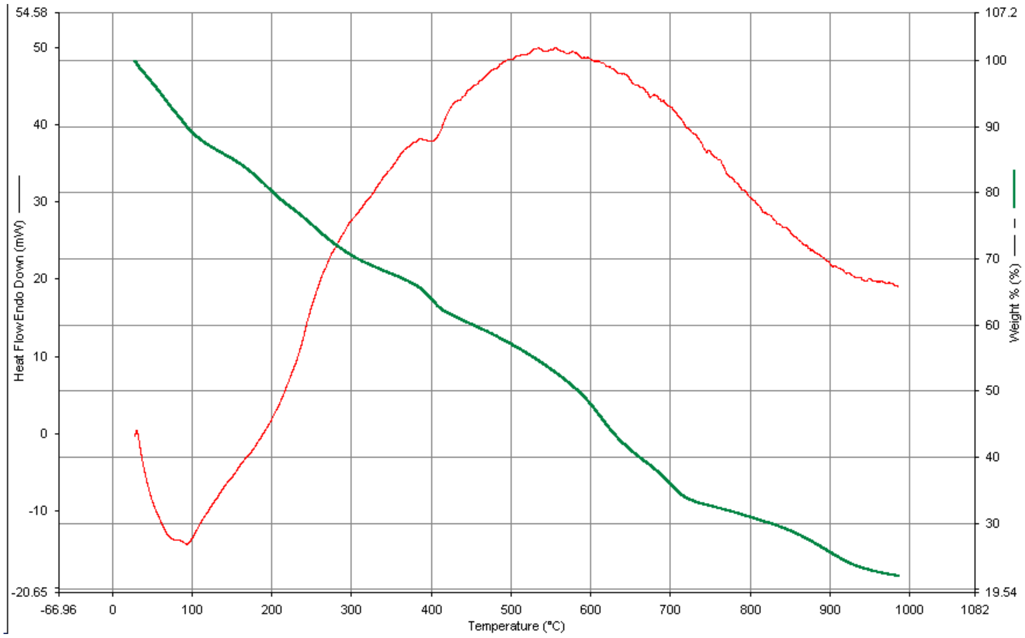


Fig 4.5 DSC/TGA of spinel with heating rate of 12.5ºC/min

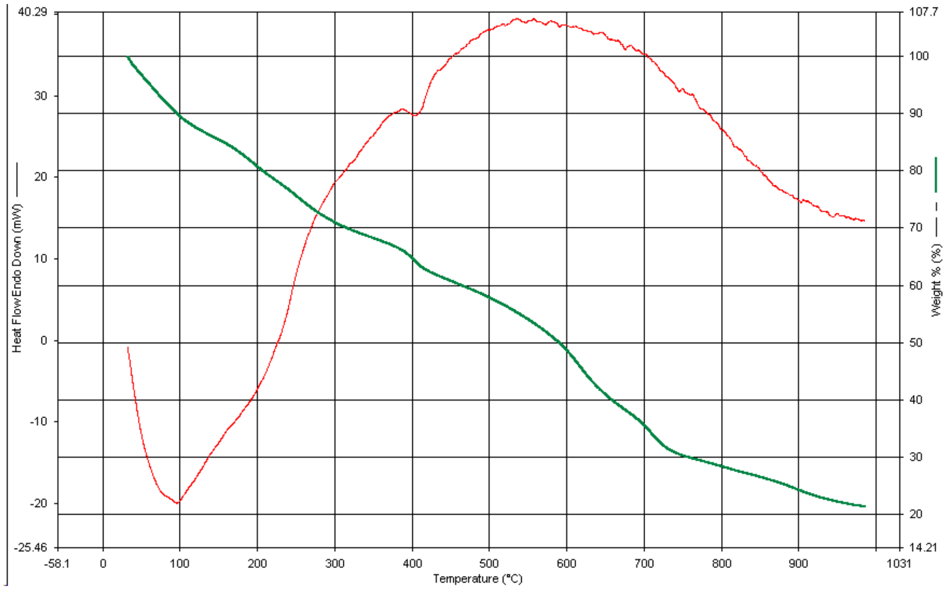


Fig 4.6 DSC/TGA of spinel with heating rate of 15ºC/min

Fig 4.4 to 4.6 shows the plot of DSC/TGA of spinel precursors with the variation of heating rate from 10, 12.5 and 15 ºC/min. An endothermic peak is observed initially with in 200ºC showing loss of volatile content. Another change in the DSC plot is observed around 400 ºC reflecting removal of chemically held moisture. The above observation also confirmed from TG curve showing constant steady state weight loss. The crustallisation of spinel formation is observed at around 550 ºC in all the heating rate conversion that is 10, 12.5 and 15 ºC/min. The completion of spinellisation is observed at about 950ºC.

4.2 XRD ANALYSIS OF SYNTHESIS OF ALUMINA

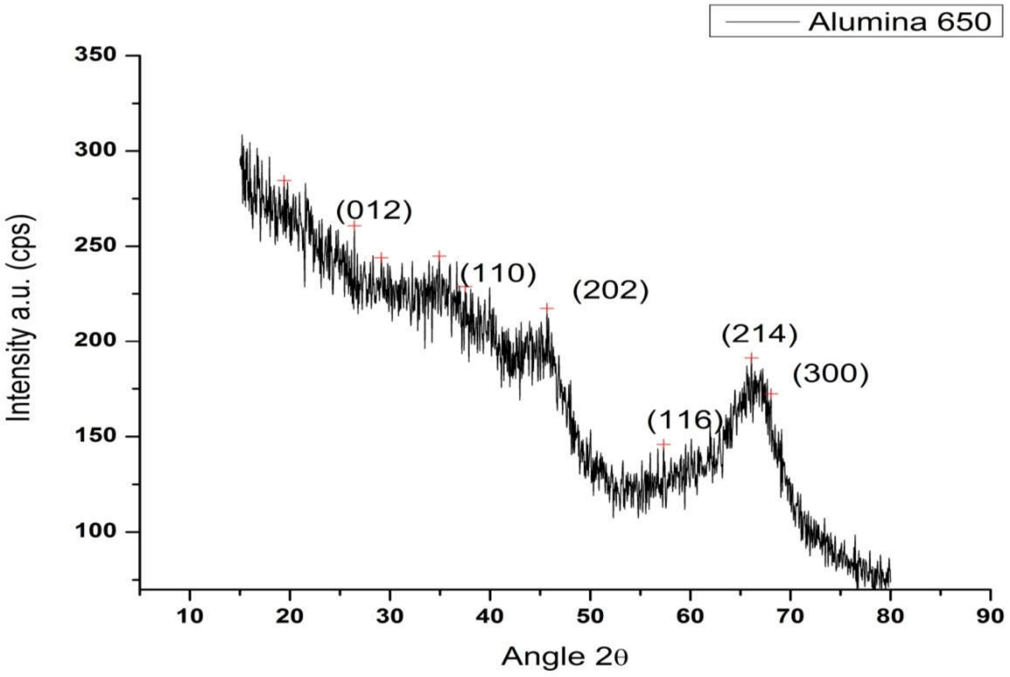


Fig 4.7 XRD of alumina heat treated at 650ºC

The planes corresponding to these peaks have been indexed with the help of the standard JCPDS library. Since no other distinct peaks are present in graph the material is phase pure Alumina. (The angle values are specified in degrees). From the nature of spectra it is clear that crystallization is just initiated in this condition at 650 ^{0}C.

Standard 2-theta value	Obtained2-theta value	Planes	Phase
25.566	25.052	012	Alpha and gamma powder(Al_2O_3)
37.762	36.767	110	Alpha and gamma powder(Al_2O_3)
46.160	46.010	202	Alpha and gamma powder(Al_2O_3)
57.476	56.762	116	Alpha and gamma powder(Al_2O_3)
66.491	67.239	214	Alpha and gamma powder(Al_2O_3)
68.181	67.800	300	Alpha and gamma powder(Al_2O_3)

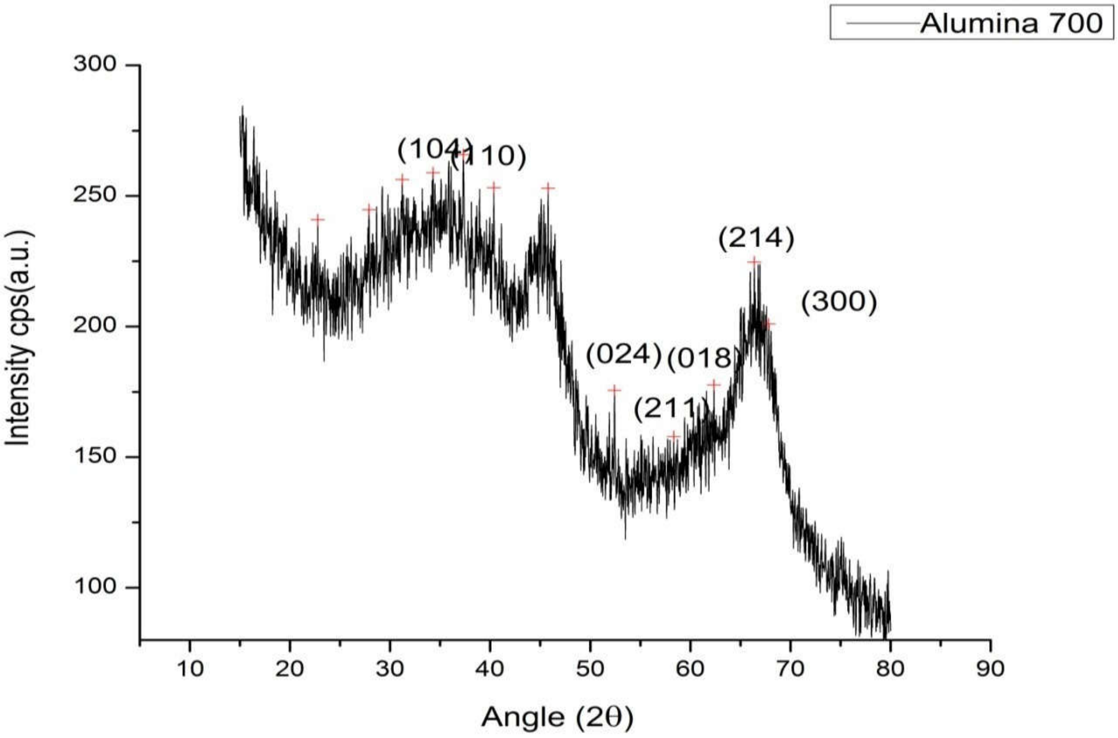


Fig 4.8 XRD of alumina heat treated at 700°C

Fig. 4.8 gives the planes corresponding to these peaks have been indexed with the help of the standard JCPDS library for heat treated at 700^0C. Since no other distinct peaks are present in graph the material is pure Alumina. (The angle values are specified in degrees). On comparing with Fig 4.7 the degree of crystallinity is enhanced at 700^0C.

Standard 2-theta value	Obtained2-theta value	Planes	Phase
35.137	35.030	104	Alpha and gamma powder(Al_2O_3)
37.762	36,532	110	Alpha and gamma powder(Al_2O_3)
52.530	51.102	024	Alpha and gamma powder(Al_2O_3)
59.717	58.919	211	Alpha and gamma powder(Al_2O_3)
61.277	59.905	018	Alpha and gamma powder(Al_2O_3)
66.491	65.032	214	Alpha and gamma powder(Al_2O_3)
68.181	68.211	300	Alpha and gamma powder(Al_2O_3)

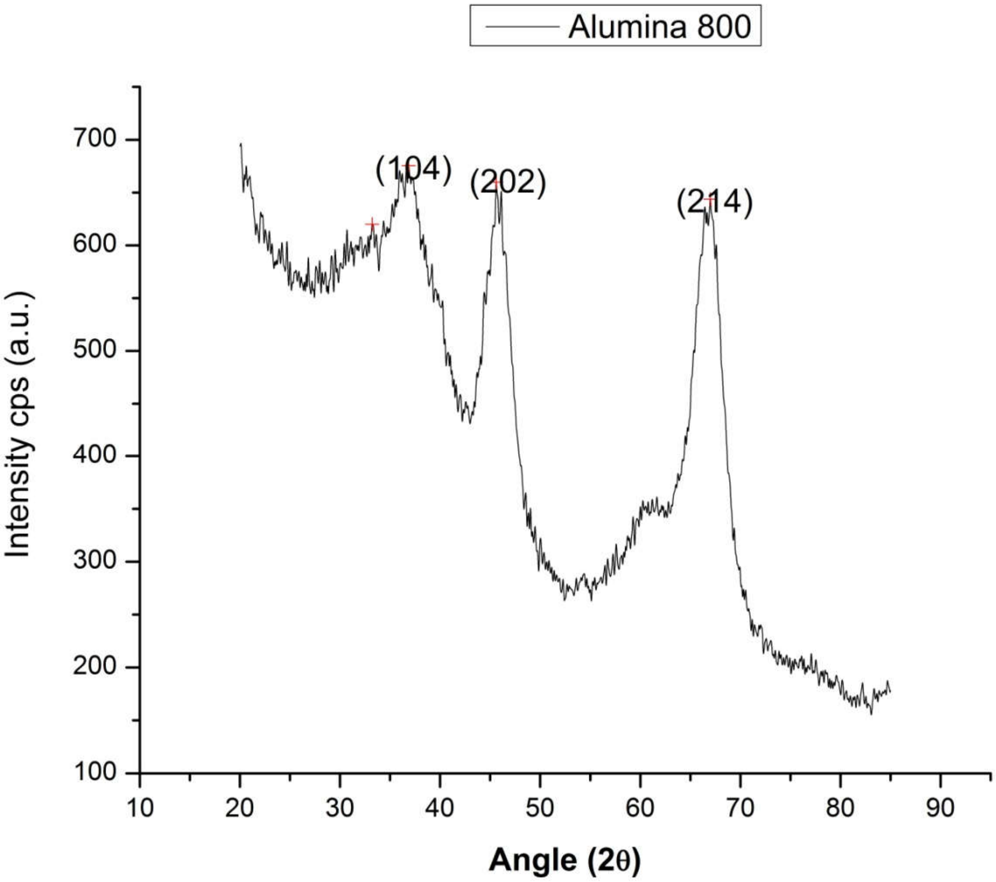


Fig 4.9 XRD of alumina heat treated at 800^{o}C

Fig 4.9 spectra gives the planes corresponding to these peaks have been indexed with the help of the standard JCPDS library for 800^{0}C treated sample. Since no other distinct peaks are present in the graph, the material is pure alumina. (The angle values are specified in degrees). Sharper prominent peak is observed for heat treating in this condition.

Standard 2-theta value	Obtained2-theta value	Planes	Phase
35.137	34.927	104	Alpha and gamma powder(Al_2O_3)
46.160	45.878	202	Alpha and gamma powder(Al_2O_3)
66.491	66.049	214	Alpha and gamma powder(Al_2O_3)

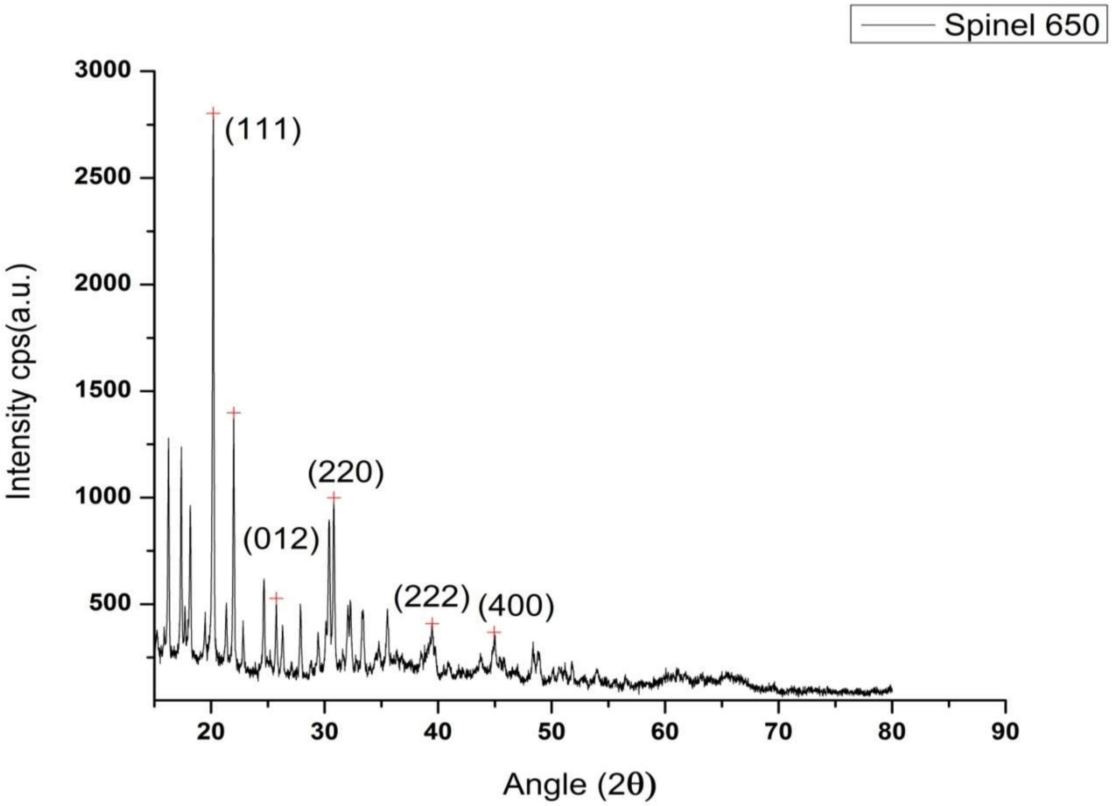


Fig 4.10 XRD of spinel heat treated at 650ºC

Fig 4.10 spectra show the planes corresponding to these peaks have been indexed with the help of the standard JCPDS library. The presence of peaks of $MgAl_2O_4$ is the sign of formation of spinel at 650ºC. (The angle values are specified in degrees).The result gives mixed phase formation of alumina and spinel with good crystallinity. Detail analysis is given below-

Standard 2-theta value	Obtained2-theta value	Planes	Phase
18.888	19.102	111	$MgAl_2O_4$ spinel
25.576	24.491	012	Alpha and gamma powder(Al_2O_3)
31.085	30.850	220	$MgAl_2O_4$ spinel
38.315	37.137	222	$MgAl_2O_4$ spinel
44.536	43.563	400	$MgAl_2O_4$ spinel

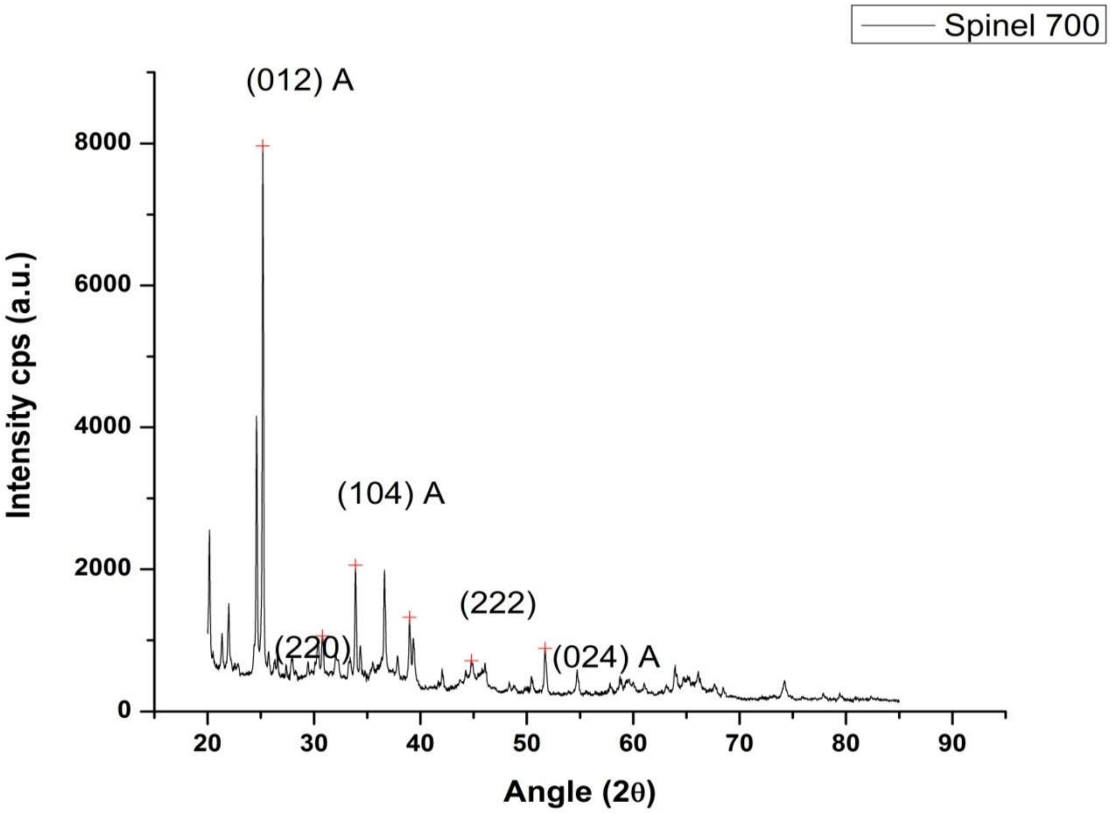


Fig 4.11 XRD of spinel heat treated at 700ºC

Fig 4.11 shows the XRD spectra for the planes corresponding to these peaks have been indexed with the help of the standard JCPDS library. The presence of peaks of $MgAl_2O_4$ is the sign of formation of spinel at 700ºC . (The angle values are specified in degrees).Here also mixed phase of alumina & spinel is identified. The list phases exist is given below-

Standard 2-theta value	Obtained2-theta value	Planes	Phase
25.576	25.450	012	Alpha and gamma (Al_2O_3)
31.085	30.065	220	$MgAl_2O_4$ spinel
35.137	34.370	104	Alpha and gamma (Al_2O_3)
38.315	37.305	222	$MgAl_2O_4$ spinel
52.530	51.530	024	Alpha and gamma (Al_2O_3)

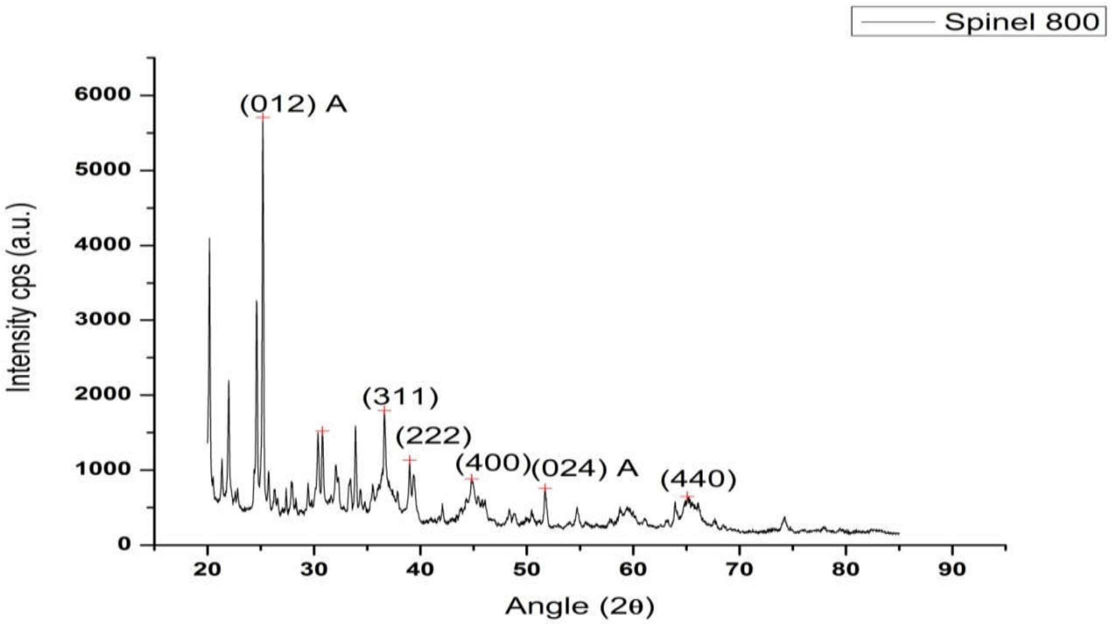


Fig 4.12 XRD of spinel heat treated at 800ºC

The planes corresponding to these peaks have been indexed with the help of the standard JCPDS library identified from fig 4.12 of XRD spectra. The presence of peaks of $MgAl_2O_4$ is the sign of formation of spinel at 800ºC. (The angle values are specified in degrees). Degree of crystallinity is enhanced at this temperature treatment. The detail analysis of phases is given below-

Standard 2-theta value	Obtained2-theta value	Planes	Phase
25.566	25.142	012	Alpha and gamma powder(Al_2O_3)
36.625	36.236	311	$MgAl_2O_4$ spinel
38.315	38.135	222	$MgAl_2O_4$ spinel
44.536	44.358	400	$MgAl_2O_4$ spinel
52.530	52.350	024	Alpha and gamma powder(Al_2O_3)
64.810	64.781	440	$MgAl_2O_4$ spinel

4.3 FTIR SPECTROSCOPY ANALYSIS OF DIFFERENT BATCHES

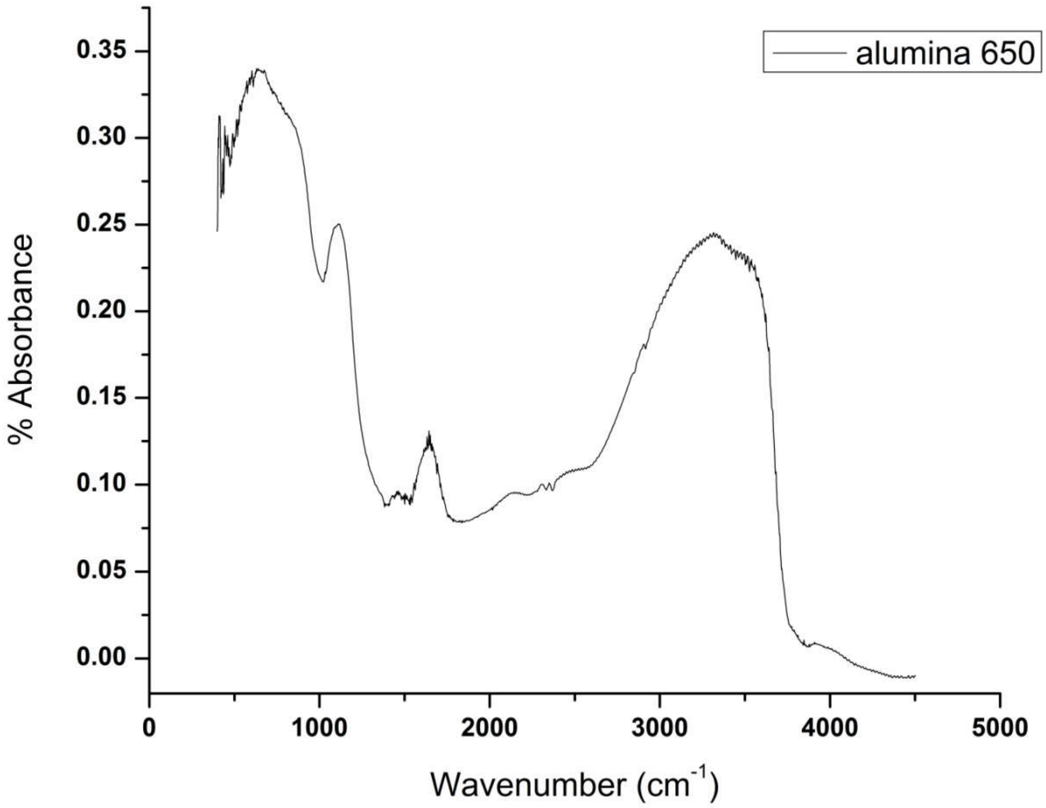


Fig 4.13 FTIR of alumina heat treated at 650°C

Wavenumber(cm^{-1})	Assignments
840	OH – deformation linked to Al^{+3}[1]
1124	Al-O streching-
3350	H – O – H stretching, absorbed[1]
3610	OH stretching, crystalline hydroxyl[1]

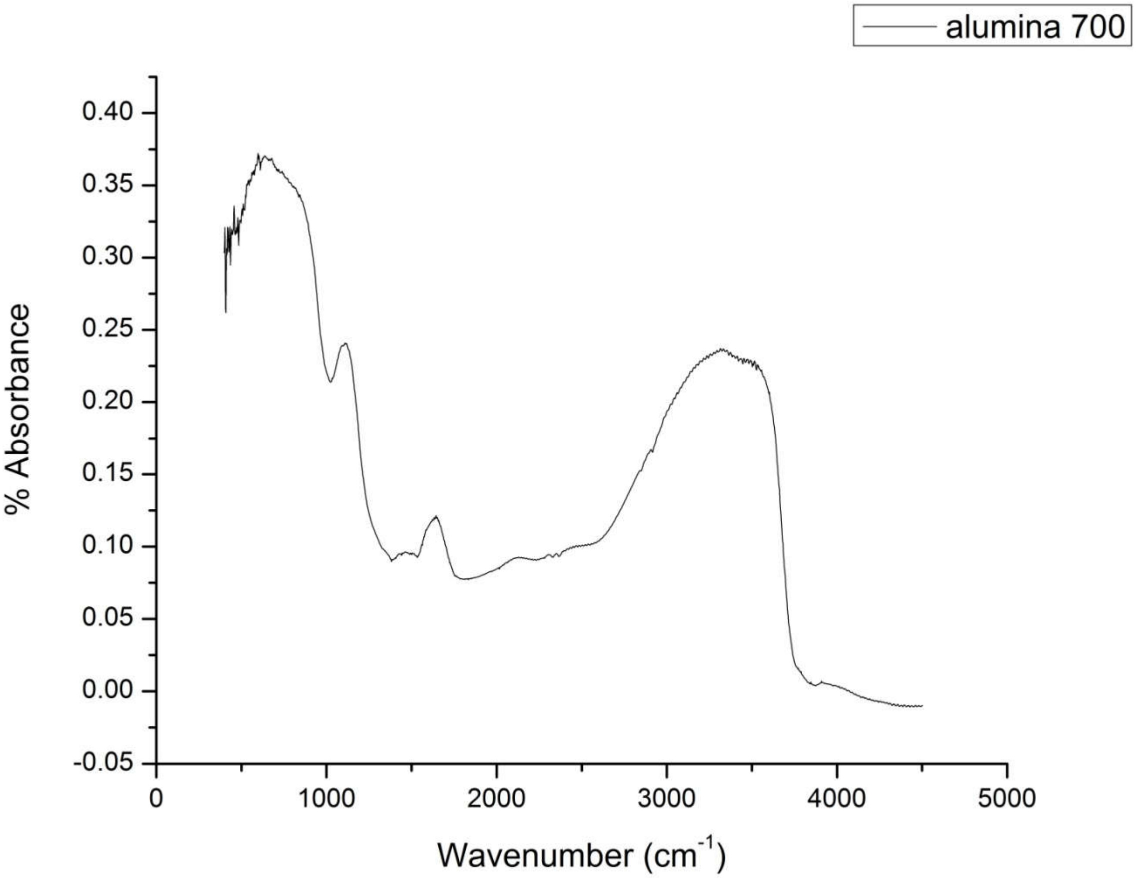


Fig 4.14 FTIR of alumina heat treated at 700ºC

Wavenumber(cm^{-1})	Assignment
812	**OH deformation linked to Al^{+3}[1]**
1125	**Al-O streching-**
1610	**H – O – H bending of water[1]**
3350	**H – O – H stretching, absorbed water[1]**
3610	**OH stretching, crystalline hydroxyl[1]**

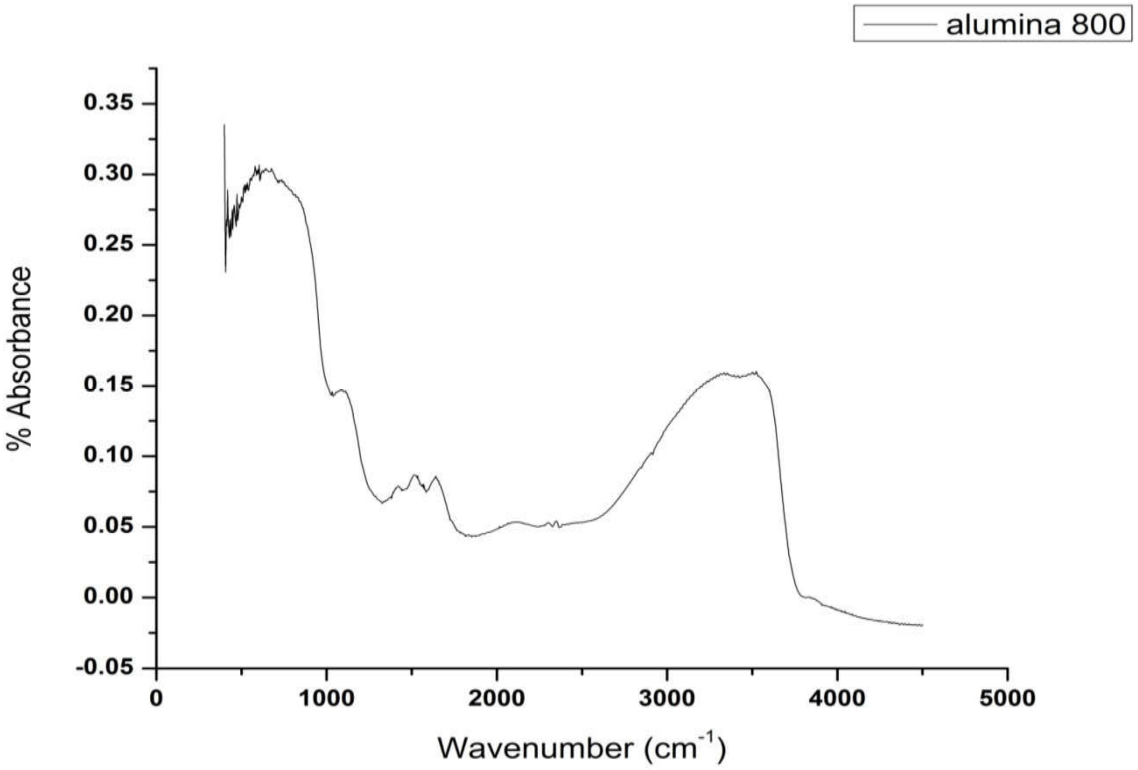


Fig 4.15 FTIR of alumina heat treated at 800ºC

Wavenumber(cm^{-1})	Assignment
630	**Al-O bond-**
1125	**Al-O streching-**
1520	**Aromatic nitrate[1]**
1625	**H – O – H bending of water[1]**
3320	**H – O – H stretching, absorbed water[1]**
3500	**OH stretching, crystalline hydroxyl[1]**

The figure 4.13 to 4.15 give the IR spectra value for alumina synthesized at 650,700 and 800 ^{0}C. The main bond available is mostly Al-O and OH stretching at various molecular vibrations. Not much variation could be observed in the above IR spectra but some contaminating constituents are observed which required further purifications before used as refractory material.

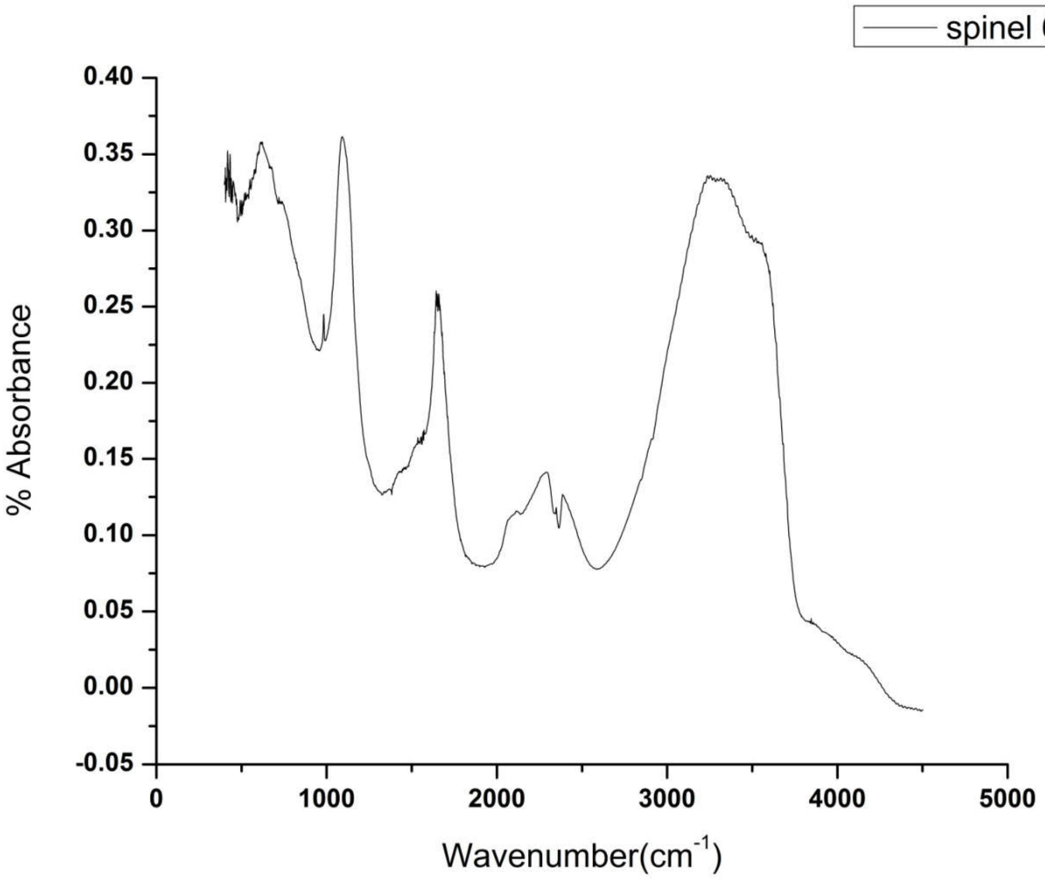


Fig 4.16 FTIR of spinel heat treated at 650°C

Wavenumber(cm^{-1})	Assignment
385	Assigned to the Mg-O stretching vibration in Mg$(OH)_2$[2,3]
562	Al-O streching-
1115	Al-Mg-O stretching bond vibration[2,3]
1625	Depends on the kind of sorbed ions[2,3]
2250	-
2375	-
3250	H_2O stretching bond can be formed[2,3]
3610	Attributed to the OH anti symmetric stretching vibration in the crystal structure of Mg$(OH)_2$[2,3]

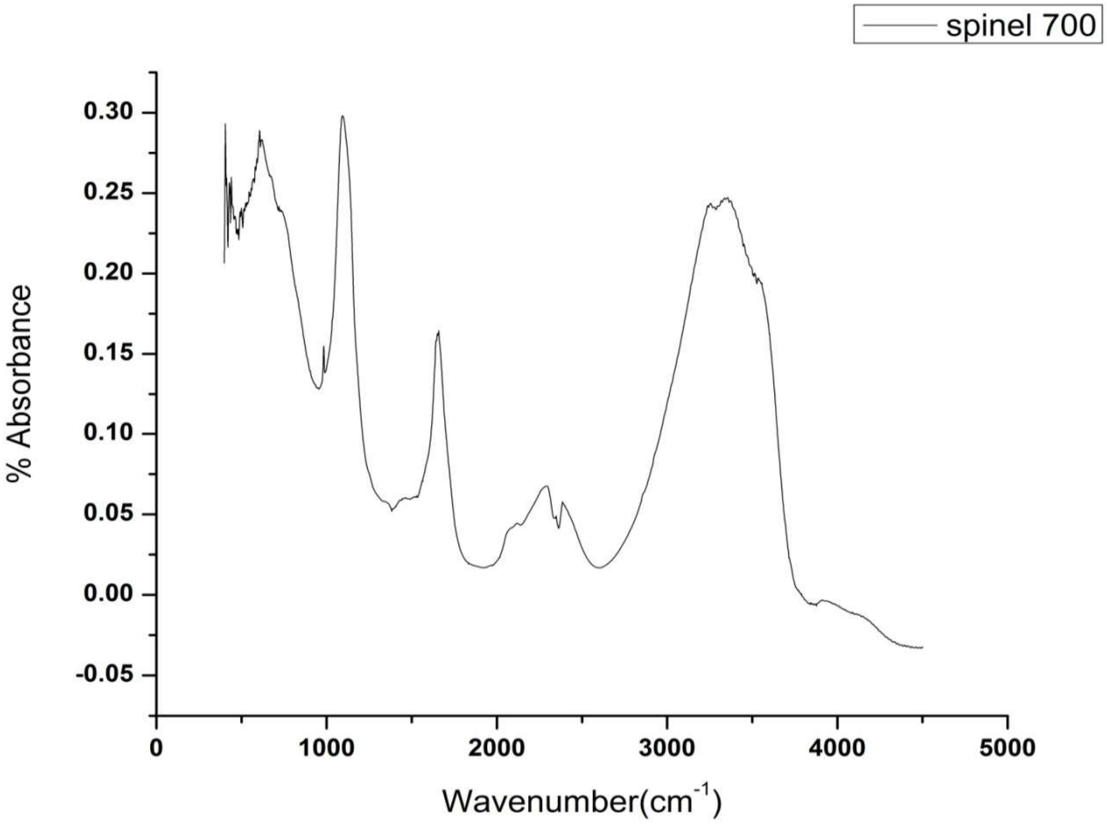


Fig 4.17 FTIR of spinel heat treated at 700ºC

Wavenumber(cm^{-1})	Assignment
385	**Assigned to the Mg-O stretching vibration in $Mg(OH)_2$[2,3]**
625	**Al-O streching-**
1110	**Al-Mg--O stretching bond vibration[2,3]**
1625	**Depends on the kind of sorbed ions[2,3]**
2221	**-**
2375	**-**
3250	**H_2O stretching bond can be formed[2,3]**
3610	**Attributed to the OH anti symmetric stretching vibration in the crystal structure of $Mg(OH)_2$[2,3]**

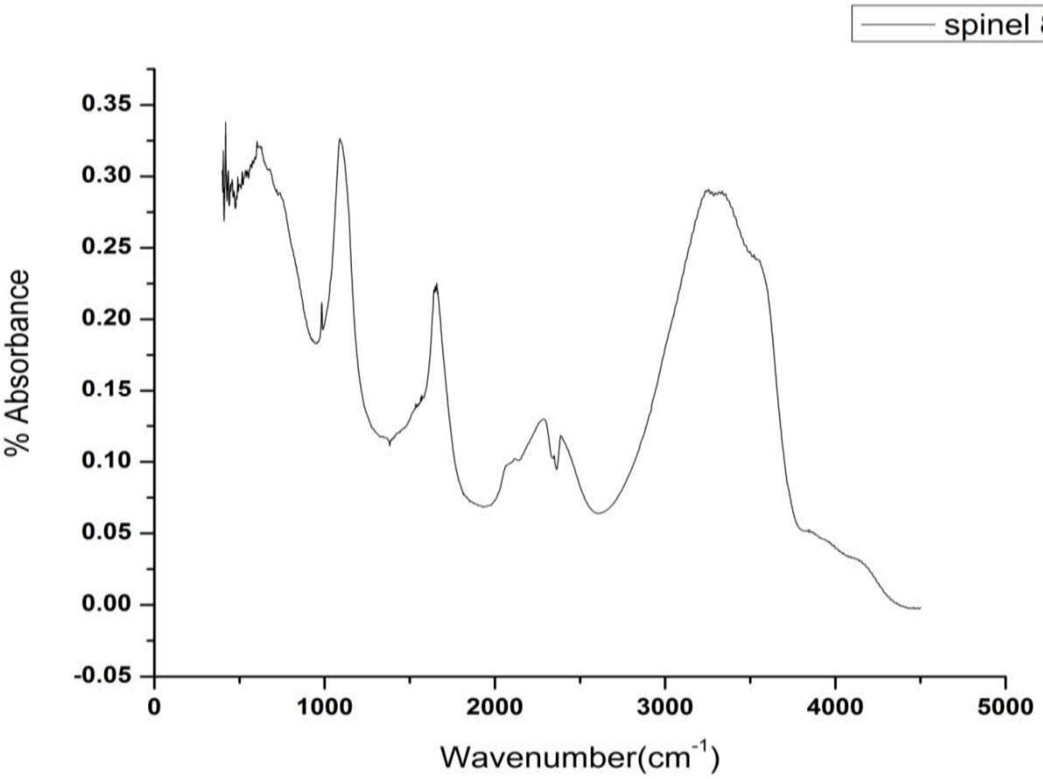


Fig 4.18 FTIR of spinel heat treated at 800ºC

Wavenumber(cm^{-1})	Assignment
385	Assigned to the Mg-O stretching vibration in $Mg(OH)_2$[2,3]
625	Al-O streching-
1110	Al-Mg--O stretching bond vibration[2,3]
1625	Depends on the kind of sorbed ions[2,3]
2221	-
2375	-
3250	H_2O stretching bond can be formed[2,3]
3610	Attributed to the OH anti symmetric stretching vibration in the crystal structure of $Mg(OH)_2$[2,3]

The figure 4.16 to 4.18 give the IR spectra value for alumina-magnesia synthesized at 650,700 and 800 ^{0}C. The main bond available is mostly Mg-O, Al-O, Al-Mg-O and OH stretching at various molecular vibrations. Four major peak is identified showing Al-Mg-O bonding causing spinalization. Not much variation could be observed in the above IR spectra but some contaminating constituents are observed which required further purifications before used as refractory material.

4.4 SEM analysis of Alumina & Spinel :

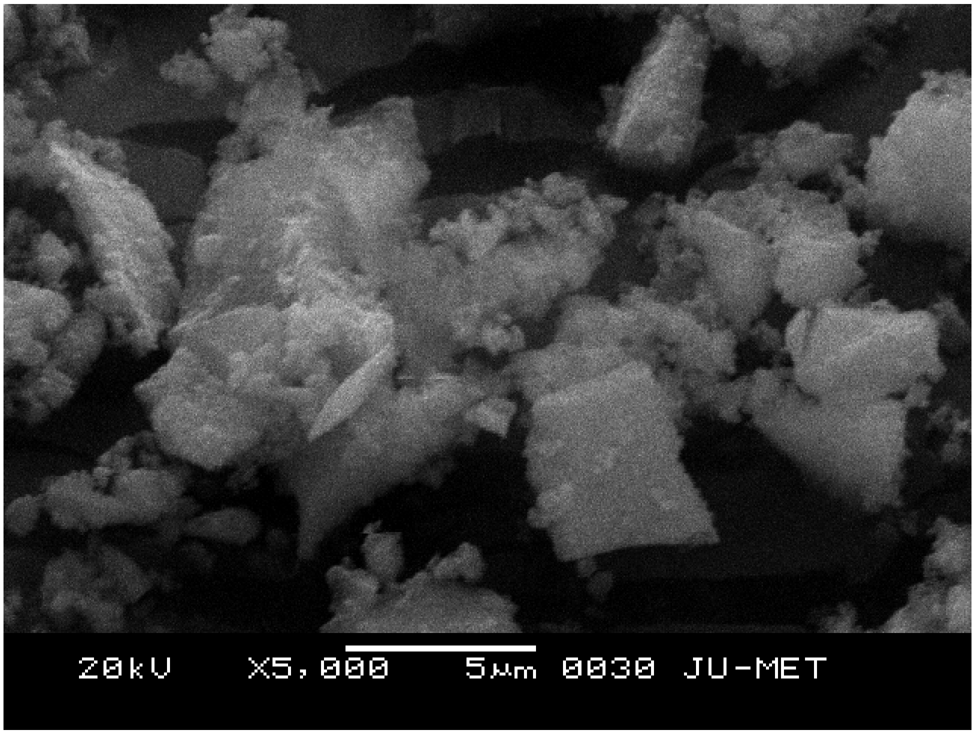


Fig 4.19 Alumina sample heat treated at 650ºC

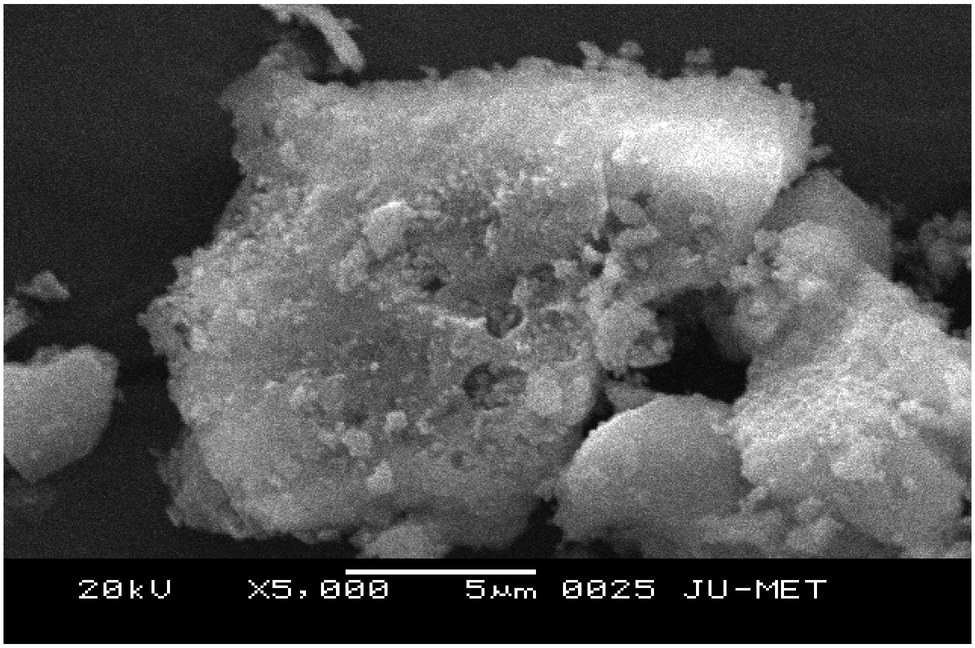


Fig 4.20 Alumina sample heat treated at 700ºC

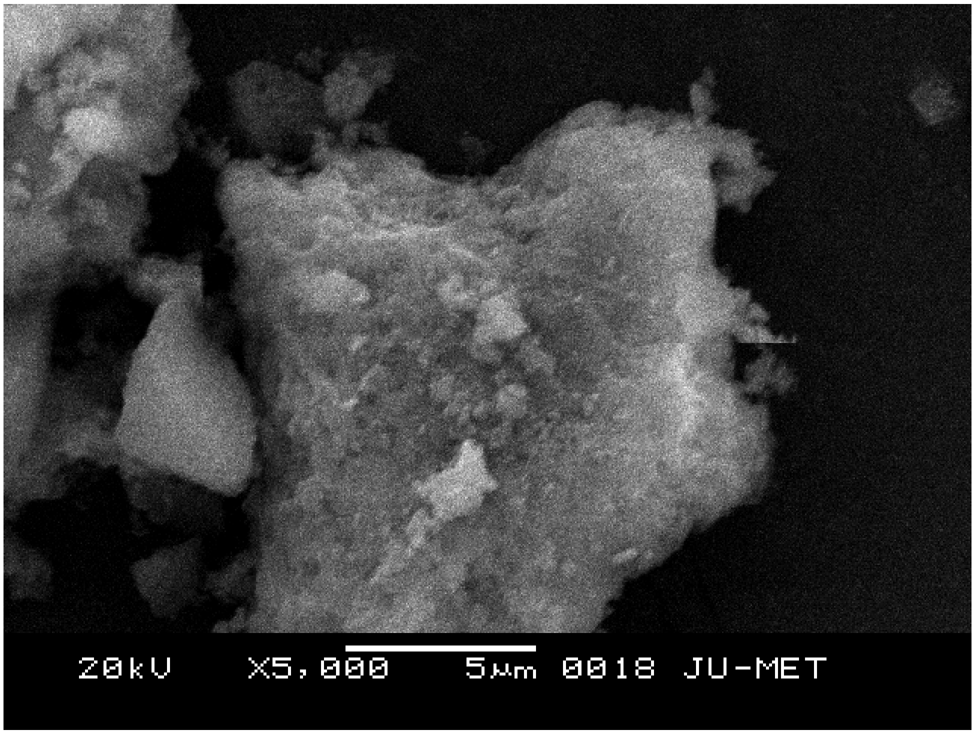


Fig 4.21 Alumina sample heat treated at 800ºC

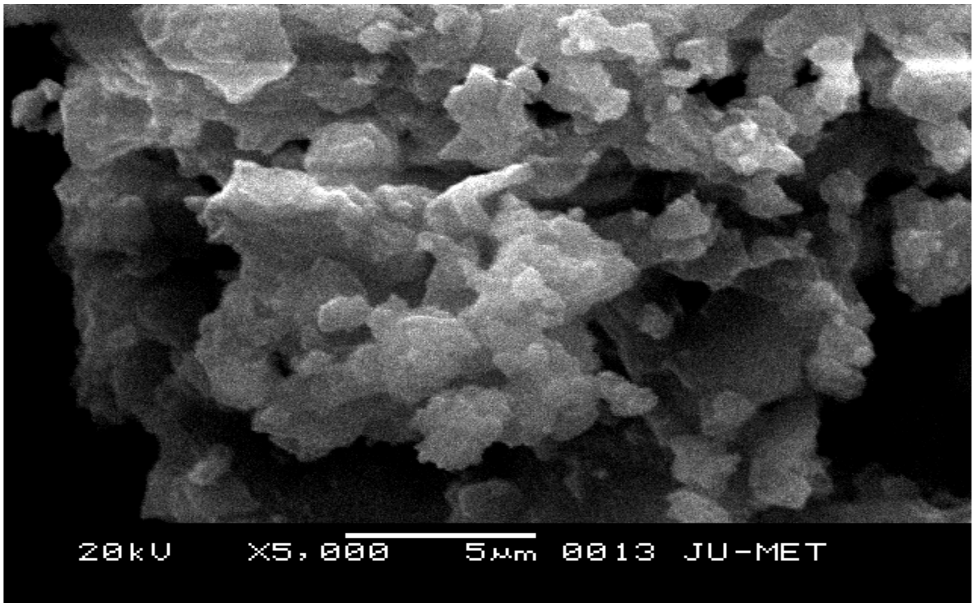


Fig 4.22 Spinel sample heat treated at 650ºC

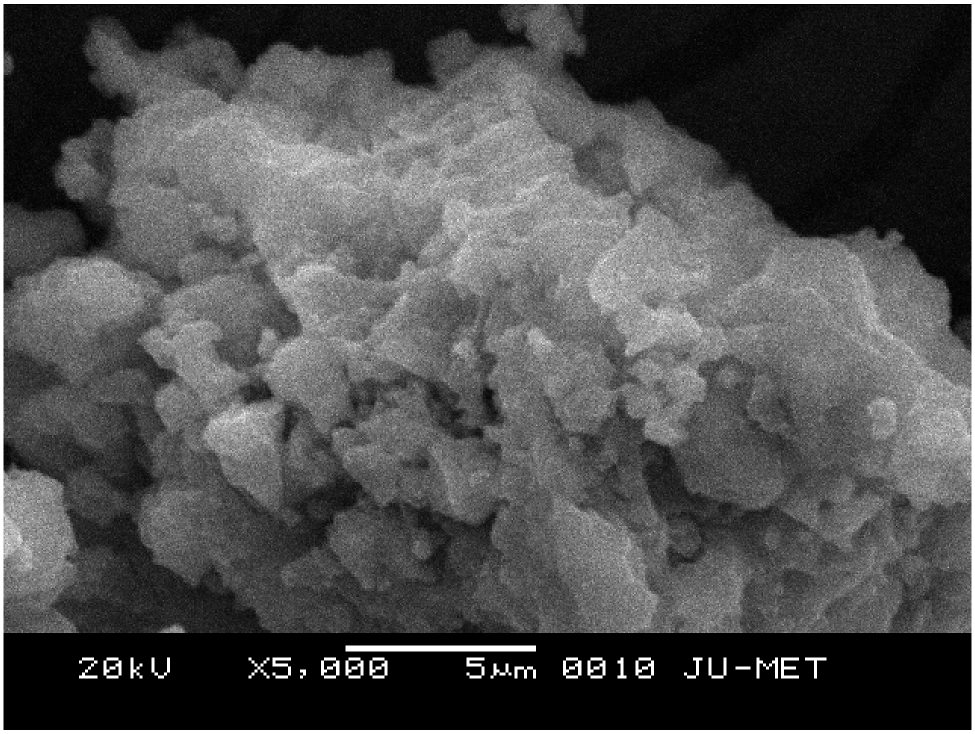


Fig 4. 23 Spinel sample heat treated at 700ºC

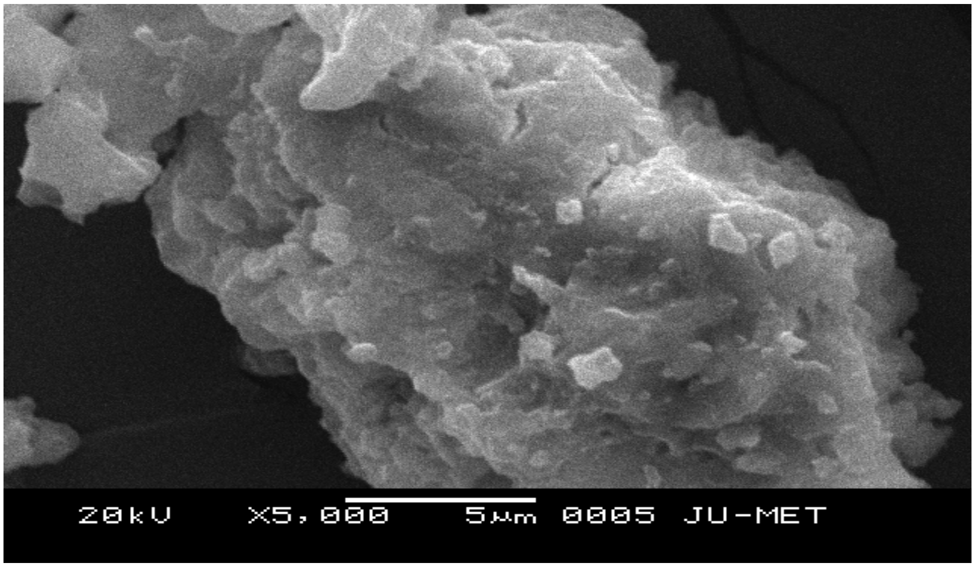


Fig 4.24 Spinel sample heat treated at 800ºC

Figure 4.19 to 4.24 give the scanning electron micrograph of synthesized alumina and spinel formed at various temperature treatments. All the micrograph revealed granulated agglomerated mass dispersed in various zone. Alumina particle shows much finer agglomerated figure 4.19-4.21.The spinel formation shows layered overlapping structure due solid state bonding of alumina and magnesia quite distinct in figure 4.22 to 4.24. The particle seems to be micron meter level on spinelization.

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E-Mail: Vaskar_R@Rediffmail.Com Received June 10, 2010; Revised July 27, 2010; Accepted August 9, 2010 J. Mod. Phys., 2010, 1, 206-210

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Z. Hubickia, E. Ziebac;¤, G. Wojcika And J. Ryczkowskib Adepartment Of Inorganic Chemistry, Bdepartment Of Chemical Technology University Of Maria Curie-Skłodowska, Pl. M. Curie-Skłodowskiej 3, 20-031 Lublin, Poland Cscanning Electron Microscopy Laboratory, John Paul Ii Catholic University Of Lublin Faculty Of Mathematical And Natural Sciences, Al. Racławickie 14, 20-950 Lublin, Poland Vol. 116 (2009)

3. Preparation And Characterization Of Mgo Nanoflakes By Wet Precipitation Method
Mageshwari K., And Sathyamoorthy R. * Pg & Research Department Of Physics, Kongunadu Arts And Science College, Coimbatore, Confluence 2012 Conference proceedings

CHAPTER - V

CONCLUSION

Studies have been conducted on the synthesis of the Alumina & Magnesia-Alumina spinel formation at different heating temperature. The homogeneous Alumina & Magnesia-Alumina dispersion for solid-solution conversion is fabricated by solution combustion route prior to heat treatment. Also the synthesis of phase pure Alumina & Magnesia-Alumina spinel with enhanced structural change is successfully synthesized by Molecular level mixing process and followed by Sintering. Various conclusions that can be drawn from these investigations are –

- From DTA/TGA data clear crystallization of alumina and spinel formation have been identified.
- From XRD data it was found that all the phases of the alumina are pure predominantly of alpha- gamma phase formation.
- XRD data also showed that there was a peak shift occurred between the pure alumina and the Magnesia-alumina nanocomposites due to the difference of heating temperature.
- As the wt% of Magnesium oxide or magnesium hydroxide increased in the samples, the shift of the peaks become more prominent.
- FTIR data showed that the spinel were very much stable with the increasing temperature treatment at 800^0 C.
- The variation of heating temperature in the alumina matrix plays an important role in the change of the characteristics, crystallization and morphology of the particle.
- From the SEM, we observed the granular formation of alumina with agglomerated product while layered structure of spinel formation clearly visible for solid-solid interaction.