Synthesis And Characterization of Zinc and Magnesium Doped Ferric Oxide Nano Particles by Sol-Gel Method

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***Abstract*—Zinc and Magnesium doped Ferric Oxide nanoparticles were synthesized by Sol - gel assisted technique from the chlorides of Iron (III) and Zinc (II) and Magnesium (II). Initially 0.2 mol of Aqueous $FeCl_3$ was taken, added with acetic acid and continuously Stirred at 300 RPM. Later NaOH solution is added to the above prepared solution till it reaches $P^H = 7$. Then solution heated with magnetic heater at 80^0 C for one hour, observed gel like solution washed, filtered and dried. Given Molar Percentage of Zinc Chloride (0.005M, 0.01M, 0.015M) and Magnesium Chloride (0.005M, 0.01M, 0.015M) added for Doping to Iron Chloride at $P^H = 7$ of the solution and stirred for 10 minutes. The prepared solution is placed on magnetic stirrer with heater at 80^0 C for one hour, observed gel like solution washed, filtered and dried. The filtered and dried powder was then calcinated at 450^0 C for 1 hour. The synthesized nanoparticles were characterized for determining the structure of material by X-ray diffraction, size and morphology by Scanning Electron Microscopy, Band Gap by UV-VIS spectroscopy, Modes of Vibration by Raman Spectroscopy. SEM analysis results revealed that the formation of Iron Oxide as sponge like or porous shapes visible as cotton balls and every 200nm size particles are combination of two or more particles of less than 100nm and grouped as single one. The doaping of Zinc and Magnesium increased the reflective nature and changed the shape and size of particle as random rod like particle morphology. The change in morphology was observed with addition of Zinc and Magnesium dopant, heating environment with the Na^{+} and OH^{-} and Acetic acid are combinedly acts for a morphology change and self-assembling. UV-VIS spectroscopy shows the drastic increase in band gap due to doping of Zinc and Magnesium in Ferric Oxide matrix.**

***Index Terms*—UV, XRD, SEM, RAMAN**

I. INTRODUCTION

The word Nano science refers to the study, manipulation and engineering of matter, particles and structures on the nano meter scale (one millionth of a milli meter, the scale of atoms and molecules). The way of molecules and atoms assemble on the nano scale and they tailor the properties of nano-structures. Important properties of materials, such as the electrical, optical, thermal and mechanical properties, are determined by different advanced characterization techniques. Moreover, in nano meter size structures these properties are often different then on macro scale, because quantum mechanical effects become important.The word itself is a combination of Nano, from the Greek “Nanos” (or Latin “Nanus”), meaning “Dwarf”, and the word "Science" meaning knowledge. It is an interdisciplinary field that seeks to bring about mature Nanotechnology, focusing on the Nano scale intersection of fields such as physics, biology, engineering, chemistry, computer science etc.

II. SYNTHESIS METHOD

Sol-Gel Techniques:
In addition to techniques mentioned above, the sol-gel processing techniques have also been extensively used. Colloidal particles are much larger than normal molecules or nanoparticles. However, upon mixing with a liquid, colloids appear bulky whereas the nanosized molecules always look clear. It involves the evolution of networks through the formation of colloidal suspension (sol) and gelatin to form a network in continuous liquid phase (gel). The precursor for synthesizing these colloids consists of ions of metal alkoxides and aloxysilanes. The most

widely used are tetramethoxysilane (TMOS), and tetraethoxysilanes (TEOS) which form silica gels.[18] Alkoxides are immiscible in water. They are organo metallic precursors for silica, aluminum, titanium, zirconium and many others. Mutual solvent alcohol is used. The sol gel process involves initially a homogeneous solution of one or more selected alkoxides. These are organic precursors for silica, alumina, titania, zirconia, among others. A catalyst is used to start reaction and control pH. Sol-gel formation occurs in four stages. 1)Hydrolysis 2) Condensation 3) Growth of particles 4) Agglomeration of particles.

CHARECTERISATION TECHNIQUES:

1. X-ray Powder Diffraction (XRD)
2. Scanning Electron Microscope (SEM)
3. UV-VIS SPECTROSCOPY
4. Raman Spectroscopy

III. MATERIALS

1.Ferric Chloride
2.Zinc Chloride
3.Magnesium Chloride
4.Acetic Acid
5.Sodium Hydroxide pellets
6.Double DistilledWater
7.Ethonol

Synthesis of Ferric Oxide nano particles by Sol-gel Technique

Sol gel synthesis method is used to control the crystalline size of the metal oxide. Firstly, using molarity formula, the weight of particular material is calculated. For 0.2M Ferric Chloride, it weighs 3.244gm for 100ml of water and 8M of NaOH weighs 32gm for 100ml of water. The chemical is taken accordingly to the calculations and 2ml of Acetic Acid is added to 0.2M of Ferric Chloride. The solution is stirred on magnetic stirrer until it is completely dissolved. NaoH solution is taken in to the burette and this solution is added drop by drop to the Ferric Chloride solution while stirring. The pH is occasionally checked when the pH reached 7 the process is stopped and heating at 80^0C for 1 hour and the gel formed is filtered using whatman filter paper and the filtered particles are washed for 7 times using distilled water and are dried at room temperature for 2 days. The dried particles are collected and are calcinated in muffle furnace for about 1 hr at 450^0C and are collected and stored. The same process is carried out for other 3 samples where the Ferric Chloride concentrations are 0.19M and 0.18M amd 0.17M with Zinc and Magnesium doping at 8M of NaOH concentration.

Synthesis of Zn and Mg doaped doped Ferric Oxide nano particles:

Three different doping concentrations Zinc and Magnesium are done. Firstly 0.19M of Ferric Chloride solution and 0.005M of Zinc Chloride solutions and 0.005M of Magnesium Chloride solution are prepared using 100ml water. These solutions are added and are stirred for 5 min to dissolute completely. 8M of NaOH solution is prepared using 100ml of water. This solution is taken in to the burette and is added drop by drop to the above combined solution. The pH is occasionally checked when the pH reached 7 the process is stopped and heating at 80^0C for 1 hour and the gel formed is filtered using whatman filter paper and the filtered particles are washed for 7 times using distilled water and are dried at room temperature for 2 days. The dried particles are collected and are calcinated in muffle furnace for about 1 hr at 450^0C and are collected and stored.

Simillarly this is carried out to $FeCl_2$ (0.19,0.18,0.17) M + $ZnCl_2$(0.005,0.01,0.015) M + $MgCl_2$(0.005,0.01,0.015) M respectively.

IV. RESULTS AND DISCUSSION

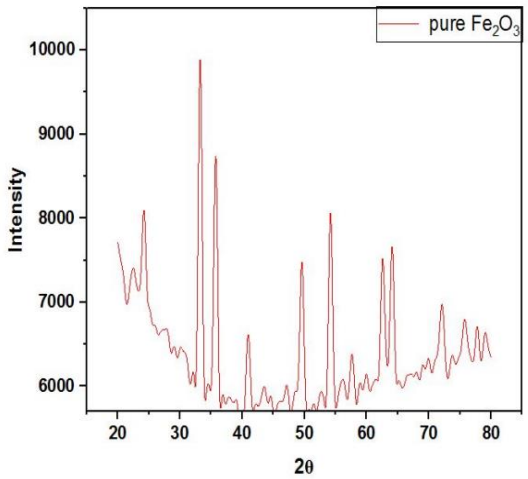

Fig SSSS: XRD analysis for Pure(0.2mol) Fe_2O_3

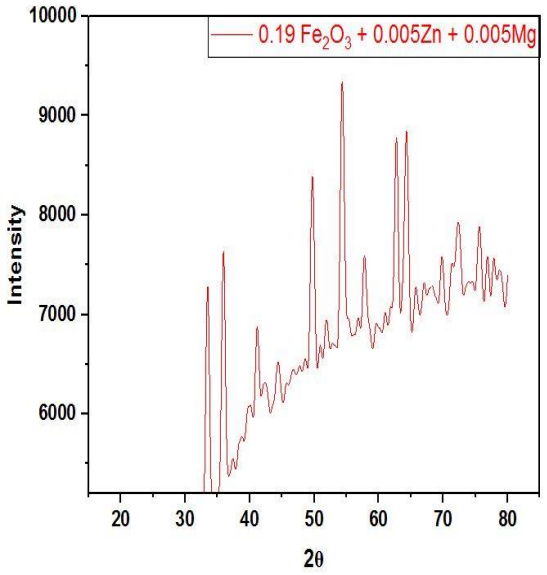

Fig: XRD analysis for 0.005mol Zn and 0.005 mol Mg doped with 0 .19 mol Fe_2O_3

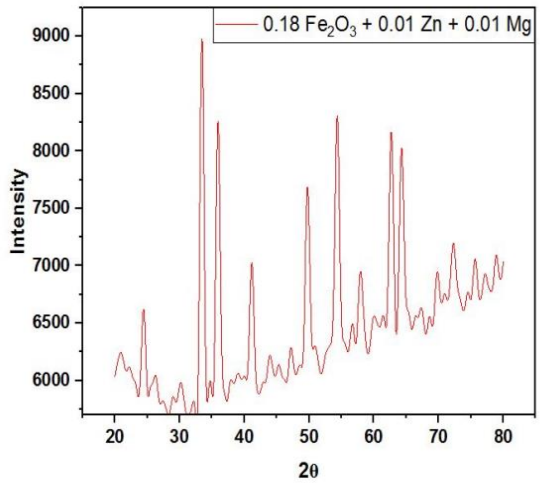

Fig: XRD analysis for 0.01mol Zn and 0.01mol Mg dopedwith 0 .18mol Fe_2O_3

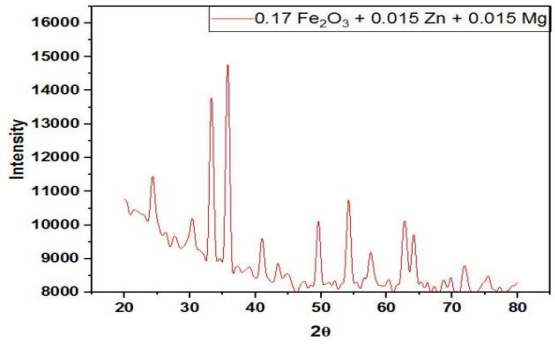

Fig 6.8: XRD analysis for 0.015mol Zn and 0.015mo Mg doped with 0 .17 molFe_2O_3

The crystalline size of pure Fe_2O_3 nano praticles of 0.2mol concentration ofFe_2O_3, is between 5nm-27nm and for 0.19 mol concentration of Fe_2O_3 the particle size is between 10nm to 27nm which shows as the concentration of Fe_2O_3 decreases the particle size decreased and from tabular column it is analysed that the strain and crystalline size are inversely proportional.

The crystalline size of Zn and Mg doped Fe_2O_3 nano particles is in the range of 17-55nm and for different doping concentration the crystalline size ranged from 14nm to 40nm. The observed diffraction peaks were well matched with the typical single crystalline phase of bulk Fe_2O_3..And all the XRD particles compared with JCPDS card no 39-1346 and it shows cubic and Tetragonal.The average Crystalline size observed as 24.2706nm.

V. UV-VISIBLE SPECTROSCOPY

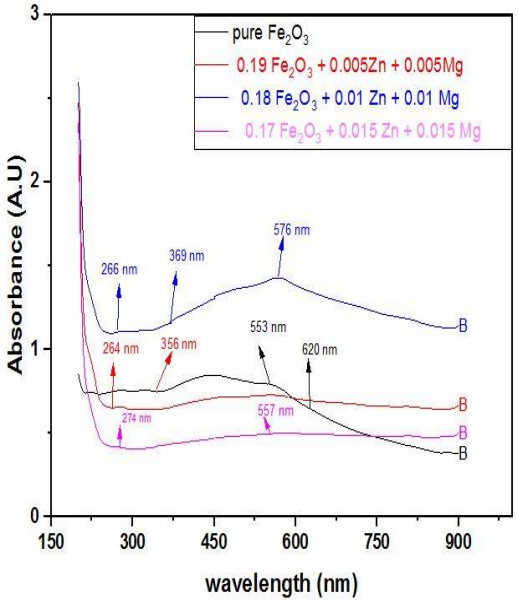

Fig: UV-VIS Absoption Spectra of Samples

Shows the plot between wave length (nm) and Absorbance (A.U) on X and Y axis respectively

UV-Visible spectrum is a technique to explore the optical properties of nano particles. The absorption spectra of pure and Zinc, Magnesium doped Ferrous oxide nanoparticles are investigated and optical properties are as shown in Fig.6.21. The absorbance of the nanoparticles is expected to depend on several

factors like band gap, oxygen deficiency, surface roughness and impurities of lattice center. The absorbance spectra exhibited absorbance at around 200-250 nm and Band gap is increased from 2.1eV to 5.0 eV. The absorption of different samples drastically changed as concentration of Zn, Mg in the Fe_2O_3 nanoparticles.

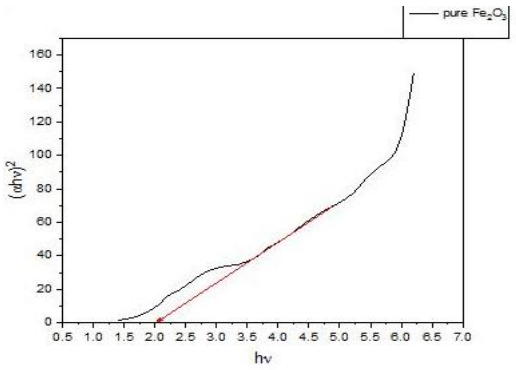

Fig: Tauc plot of pure Fe_2O_3 sample;
Band Gap=2.1eV

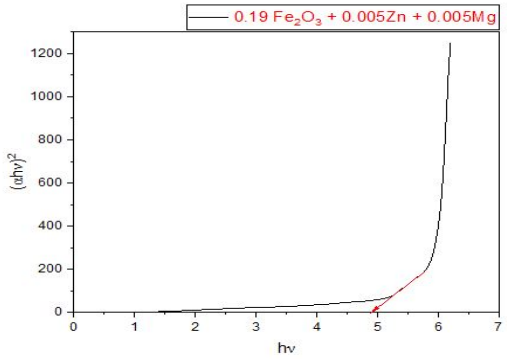

Fig: Tauc plot of 0.19mol Fe_2O_3+0.005mol Zn+0.005mol Mg sample
Band Gap=4.85eV

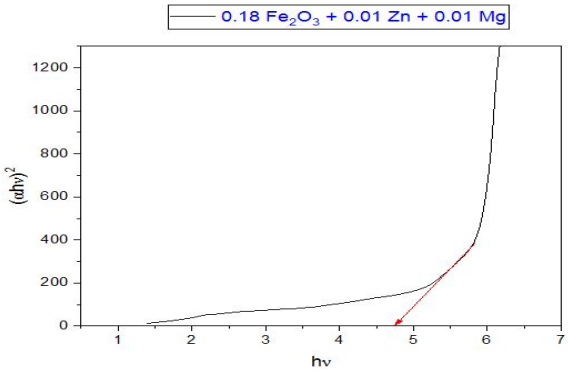

Fig: Tauc plot of 0.18mol Fe_2O_3 +0.005mol Zn+0.005mol Mg sample
Band Gap=4.75eV

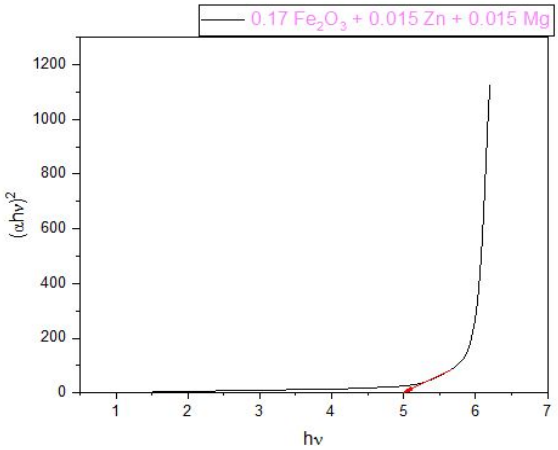

Fig: Tauc plot of 0.17 mol Fe_2O_3+0.005mol Zn+0.005mol Mg sample
Band Gap=5.05eV

The bandgap energy of pure Ferrous oxide and Zinc, Magnesium doped Ferrous oxide were calculated by using $(\alpha hv)^2$ vs hv Tauc plot graph, where α is the optical absorption coefficient from the obtained absorption data and hv is the energy of incident photon. The estimated bang gap energy measured by assuming a direct transition between valence and conduction bands from below expression.

$\alpha hv = K(hv-Eg)^{1\backslash 2}$ where K is a constant. The obtained energy band gap of pure Ferrous oxide and Zinc, Magnesium doped Ferrous oxide as shown in above figures and the value of pure Ferrous oxide 2.00eV. Due to doping of Zn^{2+} and Mg^{2+} ions to Fe_2O_3 the energy band gap is increased drastically. The calculated band gap energies Zinc, Magnesium doped Ferrous oxide was observed in 4.85eV, 4.75eV and 5.0eV respectively.

VI. RAMAN SPECTROSCOPY

Raman spectroscopy is used to find chemical structure,Vibrational Modes,Crystabillity and identify the materials. Firstly, prepare the sample and take it in a transparent zip lock cover so that while taking the readings the equipment will not touch the material directly. After opening the software initially subtract the dark then select the specifics like laser intensity, time of reading in ms etc., after selecting place the laser gun on the material containing cover and hold it until the time specified is completed, then the Raman shift can be observed.

For pure Fe_2O_3 nano particles the raman shift is

observed at 469cm^{-1} ,235 cm^{-1} which showed the presence of Iron Oxide nano particles and for doped nano particles the main peaks at 1077cm^{-1} ,440cm^{-1}, 285cm^{-1} showed the presence of zinc oxide, magnesium oxide along with Ferrous oxide which showed that doping is done.

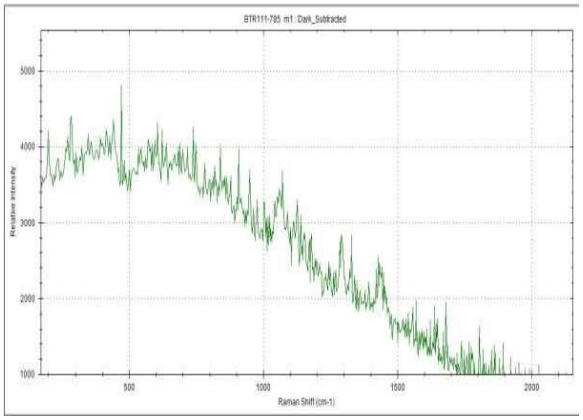

Fig: Raman shifts of Pure Fe_2O_3 nano particles

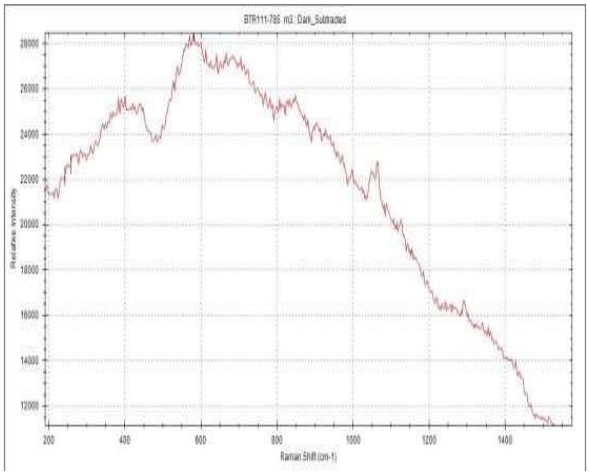

Fig: Raman shifts of 0.005 mol Zn and 0.005 mol Mg doped with 0.19mol Fe_2O_3 nanoparticles

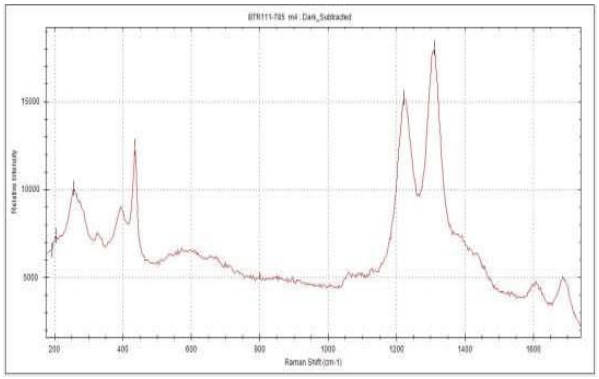

Fig: Raman shifts of 0.01 mol Zn and 0.01 mol Mg doped with 0.18 mol Fe_2O_3 nanoparticles

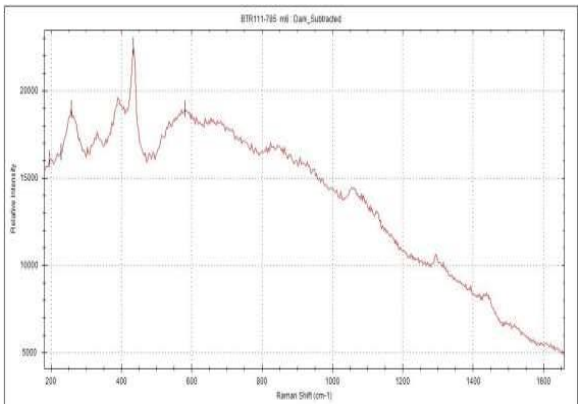

Fig: Raman shifts of 0.015 mol Zn and 0.015 mol Mg doped with 0.19mol Fe_2O_3 nanoparticles

SCANNING ELECTRON MICROSCOPE

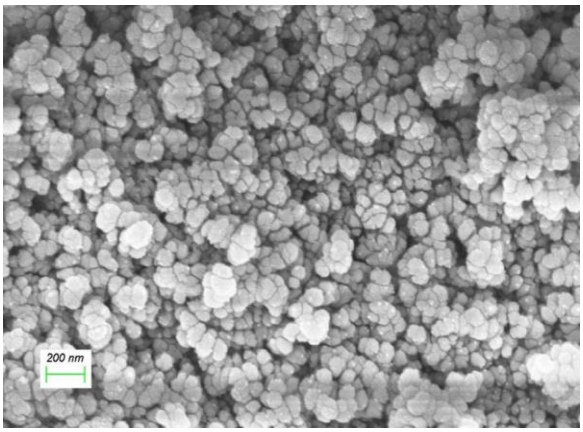

Fig: SEM images of pure Fe_2O_3 nano particles.

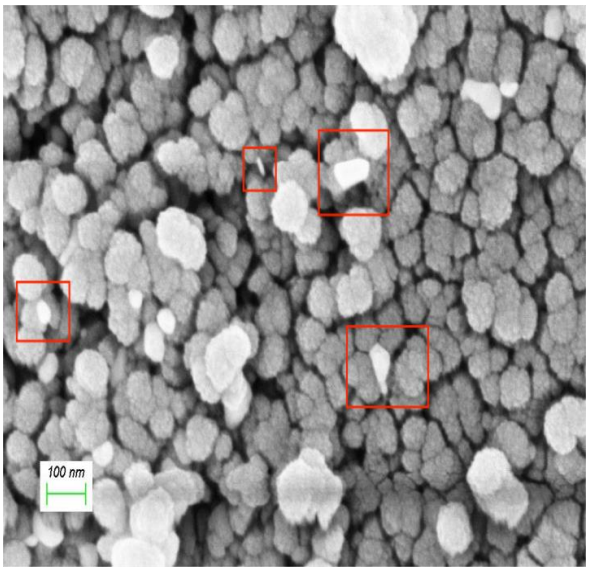

Fig: SEM images of 0.005 mol Zn, 0.005 mol Mg doped with 0.19mol Fe_2O_3 Nano particles

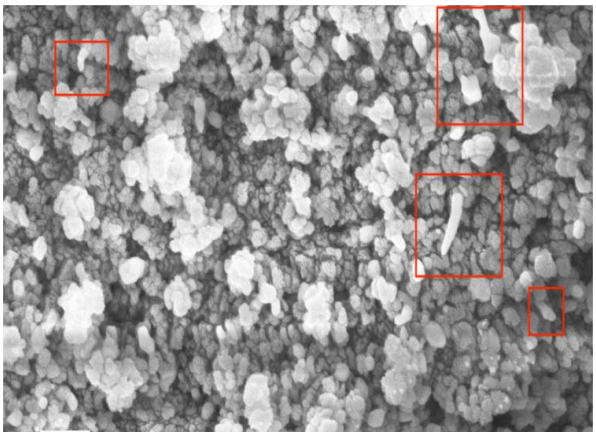

Fig: SEM images of 0.01 mol Zn, 0.01 mol Mg doped with 0.18mol Fe_2O_3 Nano particles

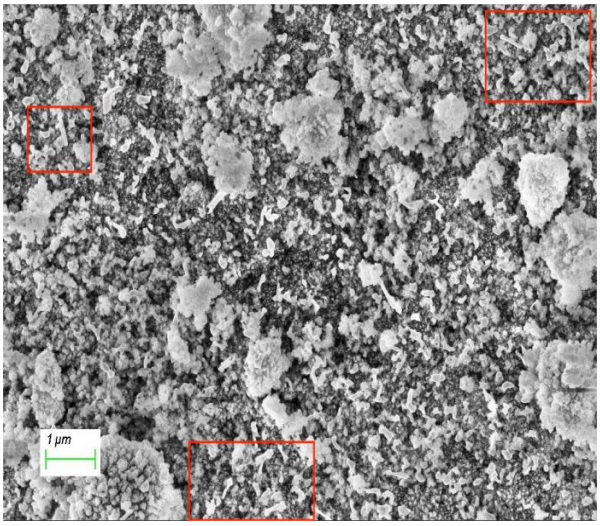

Fig: SEM images of 0.015 mol Zn, 0.015 mol Mg doped with 0.17 mol Fe_2O_3 Nano particles

VII. DISCUSSION

SEM technique provides the morphology of nano particles by scanning the surface with a focused beam of electrons, crystalline structure, and shape of materials of which the specimen is made and significantly less information regarding size distribution, true population, and its average. Characterization of particles using SEM requires conversion of the nano particle's solution into dry powder first, then the sample is mounted on a specimen holder. Thereafter, the sample is scanned with a focused fine beam of electrons. The back scattered emitted secondary electrons from the sample surface deliver the surface characteristics.

The size and shape morphology of Zinc, Magnesium doped Fe_2O_3 Nanoparticles were investigated using SEM.

In SEM images most of the nano particles showed agglomerated crystallinity of any particle is not specifically found. Well dispersed corrosive rock with porous like structures and patterns are observed with good reflectivity. Grouped patterns are clearly formed with small particles such as less than 100 nm.

The SEM images shown in red colour boxes is clearly reveals the transformation of Nanoparticles into rodlike structures and increasing the doping concentration increased rod like structures observed. The particles are quasi spherical and agglomerated and have cauliflower-like structures. It is clearly evident that particles appear in uniform and consistent shape with slightly constricted size distribution.

VIII. CONCLUSIONS

1)Zinc and Magnesium doped Ferrous oxide Nano particles ($xFe_2O_3 + yZn + yMg$ (x=0.2 mol, 0.19 mol, 0.18 mol, 0.17 mol and y= 0 mol, 0.005 mol, 0.01mol, 0.015 mol respectively) were successfully synthesized by Sol-gel method.

2)The XRD spectrum shows a good match with the standard JCPDS file for Fe_2O_3. (JCPDS NO. 39 – 1346). It confirms the phase γ Fe_2O_3 which is cubic and Tetragonl.

3)Specific amount of Zinc and Magnesium concentrations are increasing then strain is decreasing. and the properties of remaining are changed accoding to Zn, Mg concentration.

4)SEM analysis reviled that Fe_2O_3 and Zn, Mg doped Fe_2O_3 have sphrical in shape and flakes with rodlike structure observed at the percentage of 0.005, 0.01,0.015 mol doping concentrations. It shows small rod like structure, self-assemble nature of particles combination is observed at very low concentrations of doping is due to Zn, Mg. It confirms the spherical in shape along with some aggrigation of nanoparticles.

5)From UV visible spectroscopy characterization gives us energy band gap of pure Fe_2O_3 has 2.1eV, when Zn, Mg doped Ferrous oxide nano particles were had 4.75eV, 4.85eV, 5.00eV and is changed drastically and it accepts the blue shift conditions. The absorbance spectra exhibited absorbance at around 200-650 nm and increased band gap from 2.1 eV to 5.0 eV. The absorption of different samples

drastically changed as concentration of Zn, Mg in the Fe_2O_3 nanoparticles.

6) In Raman spectroscopy the main peaks of raman shift excisted at 235 cm-1 for pure Fe_2O_3 and 1077 cm-1, 440cm-1 for Zn, Mg doped Fe_2O_3 nano particles are clearly identified.

Future scope:

The Crystal structure of pure Fe_2O_3 nano particles shows the Gas sensor application.

Solar cell window material and Fuel cell coating for conversion of energies.

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