

Study of Annealing Temperature on Prepared Iron oxide Nanoparticles by Sol-Gel Method

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ABSTRACT: Iron Oxide nanoparticles are synthesized by Sol-gel route from mixed two source materials [0.1] M ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and [0.2]M monohydrated citric acid ($\text{C}_6\text{H}_8\text{O}_7$) then annealed at different annealing temperature (150,300,500 and 700) °C. The structural, morphological and the optical properties are studied by XRD, SPM and UV-visible spectrum. It can be noticed from results XRD test that iron oxide has the multiple phases when prepared in this method, where it's found that the crystal structure of sample iron oxide nanoparticle at 150 °C is amorphous while the other samples are polycrystalline cubic (magnetite), hexagonal and Rhombohedral (hematite). The average size of nanoparticles in the range of (11.2, 29.48 and 46.2)nm at 300,500 and 700 °C respectively, increased annealing temperature of the gel led to increase the average size. The $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles strongly depend on the precursors composition, the pH solution and heated treatment. SPM results show that the morphology of samples at 500, 700 more homogeneous. It can be found from UV-visible analysis that energy gap about 2.6 eV at 700 °C, the band gap increasing with increasing temperature, also the absorption spectrum increasing at 700 °C more than other samples while low at 150 and 300, the spectrum near to visible region around 400 nm.

KEYWORDS: $\alpha\text{-Fe}_2\text{O}_3$ Nanoparticles, Iron Oxide, Structural Properties, Sol-Gel

I. INTRODUCTION

In the last few years, Metal oxide nanoparticles (NPs) became extensively investigated for fascinating functional materials, the nanoparticles of iron oxides is one of these transition metal oxides that evoked remarkable interest in all aspects as theoretical fields or the various potential applications in nanodevices. [1][2] The oxides of iron (Ferrous and ferric) is existed in seven crystalline phases, the most famous structures are: Magnetite (Fe_3O_4), the ferrimagnetic $\gamma\text{-Fe}_2\text{O}_3$ (Maghemite) and antiferromagnetic $\alpha\text{-Fe}_2\text{O}_3$ (Hematite) where hematite crystallizes in the trigonal system; while other phases are $\beta\text{-}$ and $\epsilon\text{-Fe}_2\text{O}_3$ are the less commonly that belong to their good properties such as optical, electrical and magnetic, [3,4] that extensively investigated by researchers in different specializations like chemists, Physicists and engineers. Iron oxides are used efficaciously in many Applications and in various fields; the nanoparticles of magnetite that can be used in cancer diagnosis and therapy whereas maghemite is widely used in magnetic recording systems and catalysis [5,6], while hematite is used as an anticorrosive agent, catalytic reactions, red pigments [7] printing ink [8], nano fillers [9] gas sensors [10,11] and dye sensitized solar cells [12] magnetic resonance imaging (MRI), also advantages of Fe_2O_3 nanoparticles have narrow band gap (about 2.2 eV), n-type semiconducting material, abundant, cheap non-toxic, thermally stable. [13] There several techniques are used to synthesis $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles such micro-emulsion technique [14], vapor-solid growth technique [15] forced hydrolysis [16]. In this work we use the sol-gel process to prepare iron oxides nanoparticles from ferric nitrate and mono hydrated citric acid, the structural and morphological and optical properties are studied by XRD, AFM and UV-Visible spectrum. where it takes better the conditions to prepare the nanoparticles of iron oxides which depended on the dilution solutions, concentrations of the citric acid solutions and time of the annealing temperature after synthesis.

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II. EXPERIMENTAL WORK

The nanoparticles of iron oxides (hematite and magnetite) is prepared via the sol gel route and to identify the parameters that affect on the nanosize of particles . The preparation for these nanosize particles by a slightly modified method for greater simplicity. The mixture consist of two solutions, the first one ,100 ml (0.1M) of iron nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (4.039g) was used as a precursor solution, and was gelyed by using 100 ml of mono hydrated citric acid($\text{C}_6\text{H}_8\text{O}_7$)solution (0.2M)of (3.842g)as ligand molecules, and singly distilled water as the solvent. The iron solution that gives the yellow solution added to the citric acid solution drop by drop with vigorous stirring that puts into magnetic stirrer at room temperature for 4 hours. Then this solution reached to a temperature of 80°C , while maintaining vigorous stirring until the gel was formed and the contained water was evaporated ,after that the gel put in autoclave in order to annealing at temperatures ranging from (150, 300, 500 and 700°C) for 1 hour then the sample mills and collects to purpose of study its properties as shown in Figure (1) , the samples appears different colors after the annealing as shown in Figure (2) depending on the annealing temperature ,also to study optical properties used HCl as solvent for samples . We used an X-ray diffractometer is recorded by SHIMADZU XRD-6000 (CuK α radiation $\lambda=0.154\text{nm}$) in 2θ range from(20° to 80°)for the verification of the crystal structure and for the average size of the particles for hematite. The surface studies or Microscope Atomic Force Microscopy studies for samples is investigated , the morphology of the hematite nanoparticles produced is studied using Scanning Probe Microscope (type AA3000) , supplied by Angstrom Advanced Inc. to determine the nanoparticles dimensions range of the prepared layer form the samples and their statistical distribution. UV-visible spectrum is studied by SP- 3000NANO spectra made in Japan In rage 200-1100

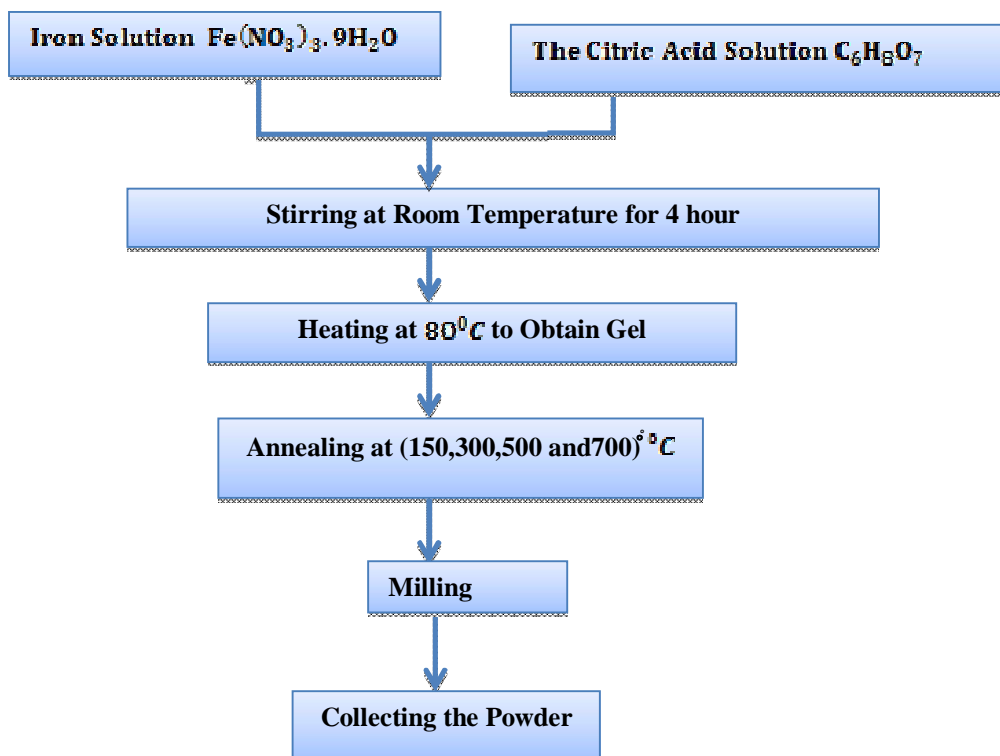


Figure. 1. Schematic of procedure to prepare iron oxide nanoparticles.

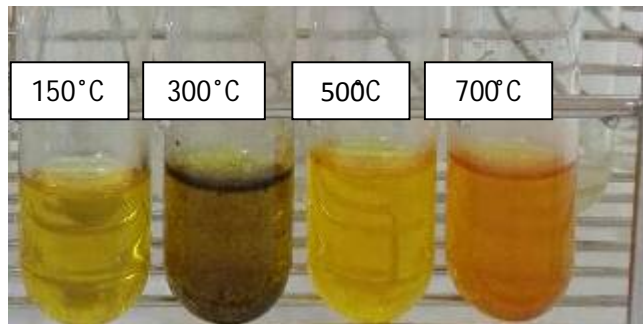


Figure. 2 . The color Samples of the iron oxide nanoparticles at different annealing temperature solvent in HCl.

III. RESULTS AND DISCUSSION

➤ STRUCTURE PROPERTIES

To study XRD patterns for all samples of iron oxides nanoparticles that prepared by sol-gel route at different annealing temperature (150,300,500and 700) °C , in Figure (3 - a ,b ,c and d) It can be observed the multiple phases of iron oxide crystals when annealed at variation temperature . It can be noticed that no diffraction peaks in sample of the iron oxide at 150 °C , as shown in figure (3- a) that is behaves as amorphous structure at low temperature due to the short -range order , while in Figure(3- b) it can be found that four peaks for samples annealing at 300 °C , it appears a cubic structure(magnetite type) , the intensity strongest peak correspond to reflection plane (311) at $2\theta=35.83^\circ$, so the other orientations are (220),(440)and (511) at 30.61° , 63.06° and 57.08° (JCPDS card No. 01-084-0307 where iron oxide in this temperature behaves transfer from amorphous to cubic crystal as magnetite(Fe_3O_4) depended on annealing temperature , long - range order and reaction conditions, in the high temperature at 500 and 700 °C the as-prepared samples of iron oxide nanoparticles in Figure.(3- c , d) the results showed that α - Fe_2O_3 nanoparticles at 500 °C have rhombohedral crystal system with a lattice constant of $a= 5.0258 \text{ \AA}$, $b=5.0248 \text{ \AA}$, $c=13.7489 \text{ \AA}$ (space group= $R-3c$) , these results in good agreement with[4][17].also, all diffractions peaks orientations in the (012), (104) , (110), (113), (024) , (116), (018) and (214)directions are in excellent agreement with JCPDS card number 86-0550. The strongest peak appears in (104) orientation at 500and 700 °C and the absence of any other peaks suggests that α - Fe_2O_3 nanoparticles give the high purity and the impurities disappeared . X-Ray diffraction data shows that α - Fe_2O_3 nanoparticles with a hematite-type structure are crystallized as polycrystalline in hexagonal crystal system with rhombohedral lattice structure at (500 and 700) °C [13]. It can be obviously the clear broadening in the peaks compare with bulk, the broaden affects with the crystallite size and the internal strains.[8] proved that the samples are formed the Nanocrystallines of iron oxide during preparation , also it can be noticed that the structure crystalline of the sample at 700 °C enhancement more than the other samples till more than 500 °C , that gives proof that the increasing annealing temperature enhances the nanostructure of samples , so it can be found that the crystalline size (D) for all samples from results of XRD by applying Scherre's equation(1) as written :[18]

$$D = 0.9 \lambda / \beta \cos \theta \dots\dots\dots(1)$$

Where D is the average crystallite size, λ (0.154nm) is wave length of X-rays , β is the full width at half maximum(FWHM) , and θ is the Bragg diffraction angle , all samples calculated D at the strongest peak .It is observed that the average crystallite size increased from 11nmto 46 nm as the processing temperature increased from 150– 700 °C , from above eq.(1) found that average crystallite size (D)of the nanoparticles iron oxide in range of (11.2 - 46.2)nm are listed in table (1) that appears the relation between different annealing temperature , structure , color and average of crystal size (D) of four samples in this work .

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Table (1)The relation between the structure,the color and average of crystal size of iron oxide nanoparticle at different annealing temperature .

| The Annealing temperature | Structure | Color | Average size of crystalline (D) |
|---|--------------|--------------------|---------------------------------|
| 150C | Amorphous | Grey | - |
| 300C (magnetite) Fe ₃ O ₄ | Cubic | Black | 11.2nm |
| 500C (hematite) Fe ₂ O ₃ | (hexagonal) | Red | 29.48nm |
| 700C(hematite) Fe ₂ O ₃ | Rhombohedral | dark reddish brown | 46.2nm |

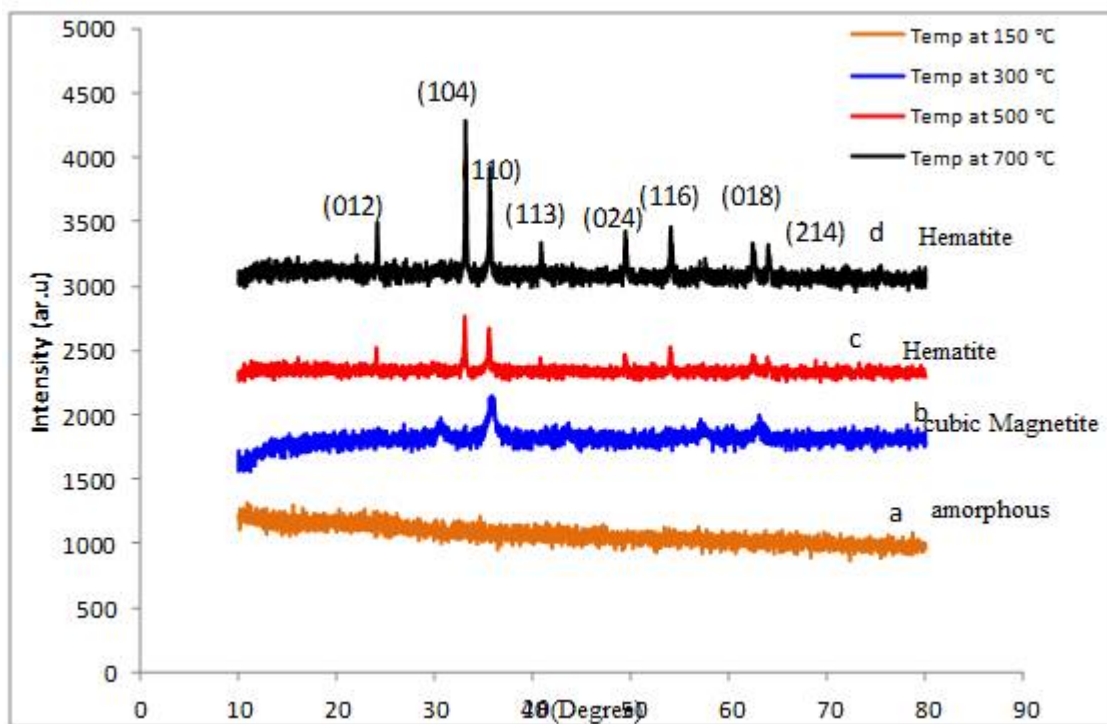


Figure .3 XRD patterns of iron oxide nanoparticles at different annealing temperatures.

➤ SCANNING PROBE MICROSCOPY

Scanning-Force Microscopy (SFM) is one type of scanning probe microscopy (SPM) a very-high-resolution , the resolution is demonstrated about (0.1 - 1 nm), its more than 1000 times better than the optical diffraction limit , all the samples of iron oxide nanoparticle is scanned by the SPM in Figure (4 a, b , c and d) shows that results of scanning images of the as prepared samples at variation temperature ,so it can be found that the average diameter sizes as shown in table (2)about (86.07- 92.65)nm and the average height around between (2-5.5)nm at different annealing temperature respectively ,where the size particles of iron oxide depended on the concentrations of the (citric acid) during the preparation also it can be appeared that the grain size in SPM are greater than XRD measurements due to the grain size consist of the crystals group (many small crystal) , the SPM is scanned at top surfaces of grains for samples ,while the diffraction in XRD test gives miller indices or (crystal planes) of crystals .

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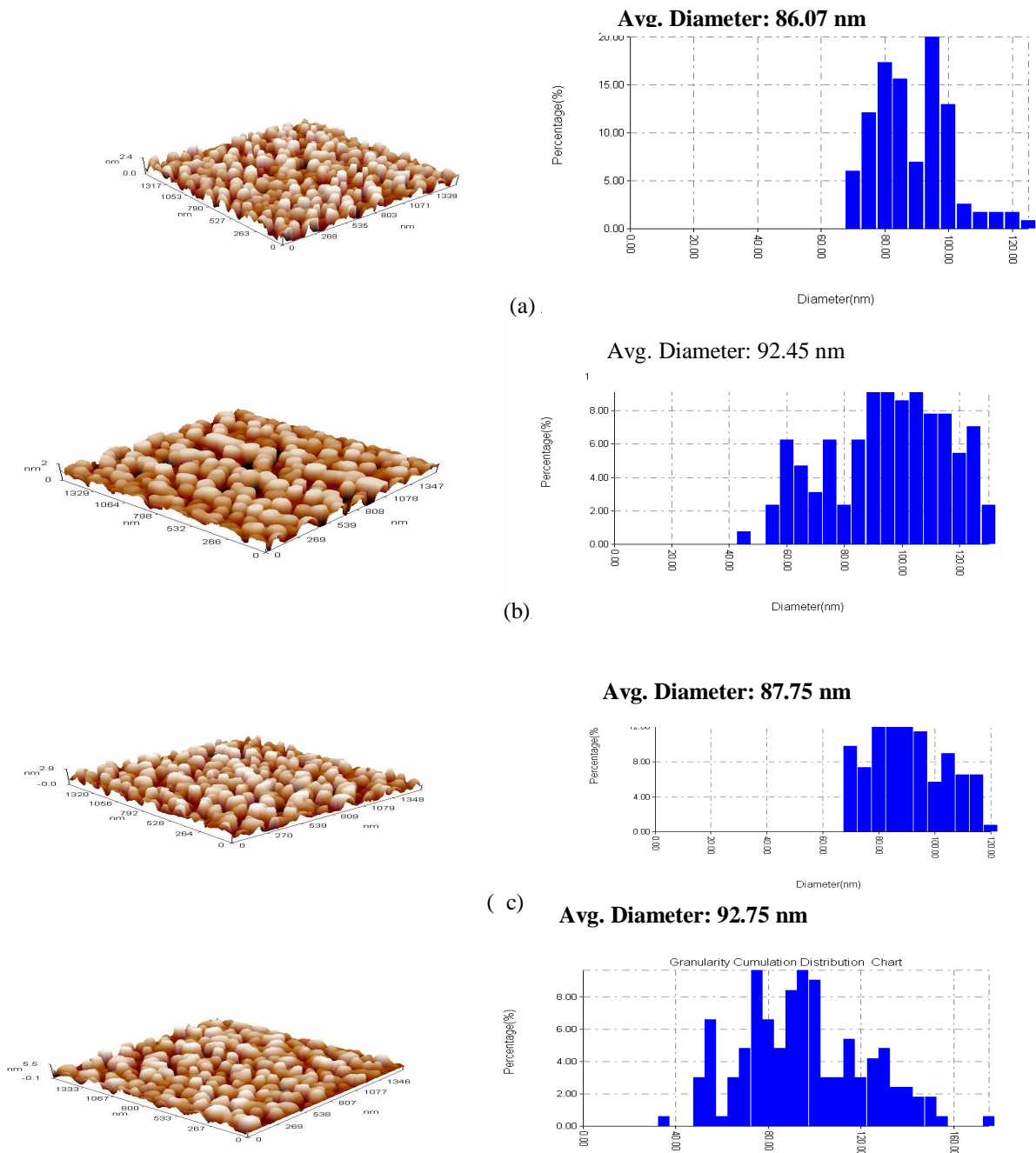


Figure (4) AFM of the iron oxide nanoparticles at different annealing temperature a - at 150 °C ,b-at300 °C c -500 °C , d-at 700 °C

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Table (2) Average diameter size of iron oxide nanoparticles at different temperature.

| The Annealing Temperature (°C) | Height of crystal (nm) | Average diameter size (nm) |
|--------------------------------|------------------------|----------------------------|
| 150 | 2.4 | 86.07 |
| 300 | 2 | 92.45 |
| 500 | 2.9 | 87.75 |
| 700 | 5.5 | 92.65 |

From SPM it is observed that the samples at (500 and 700)°C more homogenies and uniform especially at 700 this proved that at high annealing temperature the clearly improved to properties samples and more roughness from other sample. in the other hand ,the grains stable on the greatest area of the top surface , so the tip is the sensitive part of SPM moving vertically on surface of sample therefore the size represents the grain size that has the greatest area , while in XRD that rays incident oblique on sample to be on the small face of the grain.

➤ ABSORPTION SPECTRUM

The absorption spectra of iron oxide nanoparticles at variation temperature illustrates in figure (5) ,the electromagnetic wave incidents on substance and the excited electrons transits from the valence band (VB) to the conduction band(CB)where the transitions $n \rightarrow \sigma^*$, $n \rightarrow \pi$ and $n \rightarrow \pi^*$ are the possible electronic transitions between 350-950 nm .The optical absorbance of nanoparticles was investigated using Sp-3000nano optima (UV-Vis spectrophotometer) in the wavelength region of 200 to 1100 nm at room temperature as shown in Figure.5. shows the high absorption at visible region , the peak absorbance at around 400nm , generally the edges bands of absorption spectra is located at between (400-500) nm 486nm at 500°C 476nm at 700°C and 510nm 516nm and corresponding for the optical energies gaps of all samples (150,300,500 and 700)°C which recorded about(2.4 , 2.43, 2.55 and 2.6) eV respectively , it can be noticed that the increasing of energy gap of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles compared with bulk , these results similar to another optical absorption spectrum registered by [13] , the increasing of energies gaps gradually with increasing temperature also because the strong quantum confinement effect of the reduction particle size that due to the shift in the absorption spectrum of nanoparticles where its sizes become equal or smaller than Bohr radius of exciton [19] , The shift to the visible region illustrates that there increasing in the optical band gaps of all sample.

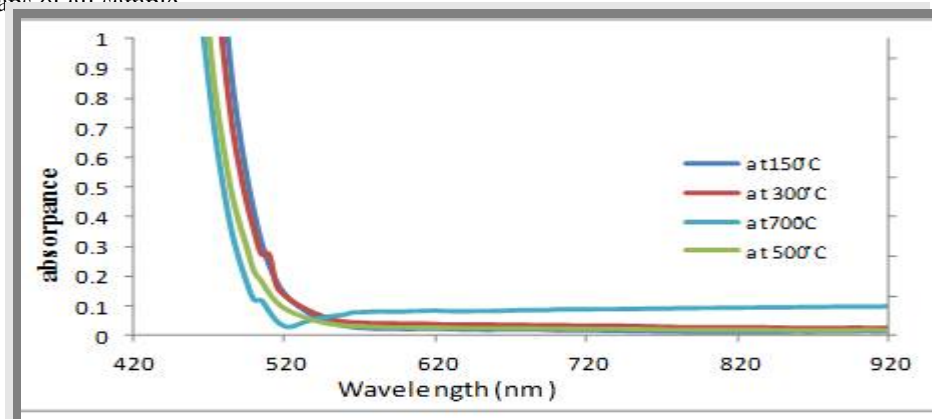


Figure 5 .Absorption spectrum for the nanoparticles of iron oxide at variation temperature .

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with applying the Tauc equation (2) to evaluate the optical energies gaps for these samples [20]as following :

$$(\alpha h\nu) = C(h\nu - E_g)^{1/2} \dots\dots\dots(2)$$

Where, $h\nu$ is photon energy (eV), C is constant, α is absorption coefficient(cm^{-1}), the average band gap energy is (E_g) and n is depending on the transition type if allowed or non- allowed . the Figure .6 shows the Tauc plot between the linear extrapolation of $(\alpha h\nu)^2$ versus to photon energy($h\nu$) of the iron oxide nanoparticles for all samples where the direct allowed transition of the nanoparticles iron oxide . The average energies gaps have found from the Tauc plot around (2.4,2.43, 2.55and2.6) eV at different annealing temperature respectively which are larger than the energy gaps of bulk for iron oxide the reason belong to the strong quantum confinement effect and re-arrangement the electronic states near to the Fermi level [21,22].

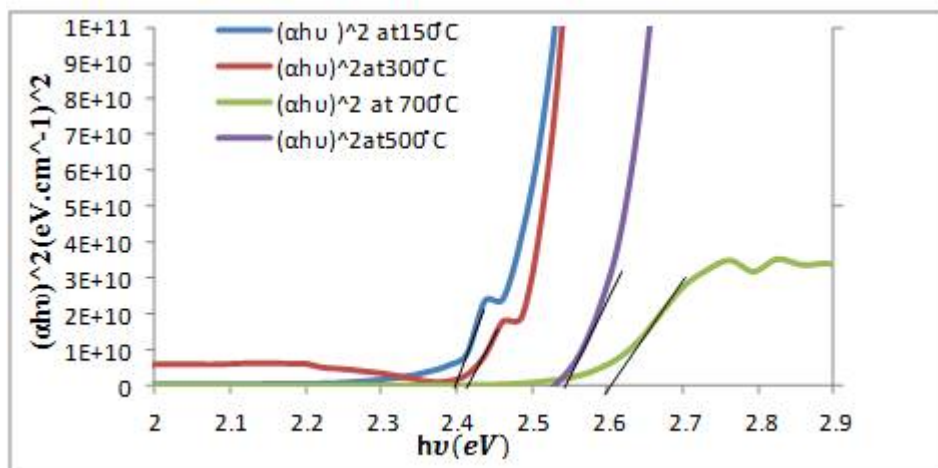


Figure . 6. the graph shows the relation between the photon energy ($h\nu$) and $(\alpha h\nu)^2$ for the nanoparticle of iron oxide at different temperature.

VI. CONCLUSION

The iron oxide nanoparticles is prepared successfully via sol- gel route, this method has several advantages as low cost, simple equipment and easy operation . it can be observed that there multiple phases of iron oxide nanoparticles as prepared in this method from analyses of XRD patterns and phase transfer to α - Fe_2O_3 nanoparticles at high annealing at(500,700 °C) with polycrystalline is hexagonal structure ,so all properties such as structural ,morphological and optical are improved at 500 and 700C , also obtains the high absorption in visible region at same temperature and low at 150 , the optical energy gap of nanoparticles is 2.6 at 700C increasing with respect to the bulk of iron oxide while the other energies gaps of other samples are smaller than annealing at700 °C .

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