Investigation of the Structure and Magnetic Properties of Co$^{+2}$ –Ti$^{+4}$ Substituted Barium Ferrite Powder Prepared by Sol – Gel Method.

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Abstract. In this research, Hexagonal barium ferrites and Co$^{+2}$-Ti$^{+4}$ substituted barium hex ferrite particles are prepared by the Sol-gel method. The starting materials were appropriate amount of barium nitrate (Ba(NO$_3$)$_2$), Iron nitrate (Fe(NO$_3$)$_3$) and citric acid (C$_6$H$_8$O$_7$•H$_2$O) were dissolved into distilled water. When water evaporated, the mixture became viscous and finally formed a very viscous brown dried gel. The sample was calcined at 950°C for 5 h at a rate of 150°C/h. to obtain a ferrite powder. The XRD method, using Cu$K_α$ radiation (wave length $λ=0.15405$ nm) was used for product identification and phase structure at room temperature. The surface morphology of the powder was examined by scanning electron microscope (SEM). The absorption vibrations of the prepared samples were performed by a Fourier transformed Infrared (FTIR) spectrometer from 4000 cm$^{-1}$ to 400 cm$^{-1}$. The magnetic properties for the prepared samples were obtained using a vibrating sample magnetometer.

1. Introduction
Barium Ferrite (Ba Fe$_{12}$O$_{19}$) one of the most important materials. The sol – gel technique has an attention as a promising technique for producing different materials. This technique have different advantages like low temperature processing. Sol – gel method makes it possible to obtain fine particles that is necessary for improvement useful properties in practical materials. So the Sol-gel process now made an important developments in materials technology [1]. Studying the magnetic properties of Barium Ferrite have recently been carried out in many of scientific researches, where, they have been recommended to use the Sol-gel technique for preparation of hexagonal Barium Ferrite [2]. Some types of magnetic materials, it have to some extent large saturation magnetization ($M_s$), and it have also high values of coercivity ($H_c$), magnetic anisotropy ($H_a$), Curie temperature, magnetization, magneto crystalline anisotropy and excellent chemical stability[3],[4].

The classical ceramic method for preparing barium ferrite requires high temperature solid-state reactions between the raw materials. The negatives of this conventional method can be represented by impurities and non-uniform particle size, which reduce the process of product development. For the purpose of overcoming these problems and constraints, and for the purpose of achieving the requirements of product development, different chemical methods like Sol-gel technique, microemulsion process, co-precipitation technique, glass crystallization and plasma spraying have been used for producing fine powder of hexa-Barium Ferrite with promising magnetic properties[5]. In this research, Hexagonal barium ferrites and Co$^{+2}$-Ti$^{+4}$ substituted barium hex ferrite particles are prepared by the Sol-gel method, the structural and magnetic properties were studied.
2. Experimental Procedure.
Hexagonal barium ferrites (BaO.6Fe₂O₃) and Co⁺²-Ti⁺⁴ substituted barium hex ferrite particles (BaCoₓFe₁₂₋₂ₓO₁₉) are prepared by the Sol-gel method, this method has the unique advantage for the low costs using simple equipment in large-scale high purity. The Sol-gel synthesis of hexagonal barium ferrite was adopted to be especially conspicuous in the process of converting Fe₂O₃ into barium ferrite. The starting materials were appropriate amount of barium nitrate (Ba(NO₃)₂), Iron nitrate (Fe(NO₃)₃) and citric acid (C₆H₈O₇. H₂O) were dissolved into distilled water. All the materials were supplied from Sigma Aldrich company. The mixture solution was evaporated to dryness by heating on a hot plate with continuous magnetic stirring at 80 °C. When water evaporated, the mixture became viscous and finally formed a very viscous brown dried gel. Then, the dried gel transferred to a furnace with the temperature 150 °C for 6 h to obtain a dried precursor. Then, the sample was calcined at 950 °C for 5 h at a rate of 150 °C/h. to obtain a ferrite powder.

The XRD method, using CuKα radiation (wave length λ=0.15405 nm) was used for product identification and phase structure at room temperature. The surface morphology of the powder was examined by scanning electron microscope (SEM). The absorption vibrations of the prepared samples were performed by a Fourier transformed Infrared (FTIR) spectrometer from 4000 cm⁻¹ to 400 cm⁻¹. The magnetic properties for the prepared samples were obtained using a vibrating sample magnetometer.

3. Results and Discussion
The X-ray diffraction results of the prepared samples are shown in Fig. 1, which gives the pattern of such an investigation for the Co⁺²-Ti⁺⁴ substituted barium hex ferrite particles. The coprecipitated product directly crystallized to hex ferrites. It can be observed from fig. (1), sample (1) that the formation of BaFe₁₂O₁₉ were done at calcination temperature and the time (950°C/5 hr). On the other hand, beyond of BaFe₁₂O₁₉, other peaks can be attributed to hematite (α-Fe₂O₃). The formation of these phases other than BaFe₁₂O₁₉ can be related to the reactivity of the different phases formed during the coprecipitation, these results were consisted with [7]. Figure (1), sample (2), shows XRD profiles for Co⁺²-Ti⁺⁴ substituted barium hexaferrite particles heat treated at 950°C for 5 hr. The coprecipitated products directly crystallized to hexaferites by heat treatment, the results indicate that the behavior of crystallization of the sample was predominated by that of Barium hexaferrite. The result indicate that the doping element has been successfully substituted into the structure [4], [8].
3.1. Fourier Transform Infrared Studies (FT-IR).

FT-IR has been used to explain the interactions between atoms or ions in (BaO.6Fe₂O₃) and (BaTi₀.75Co₀.75Fe₁₀.5O₁₉). These interactions can give us the changes in the vibrational modes of the compound. The FT-IR transmittance spectra of (BaO.6Fe₂O₃) and (BaTi₀.75Co₀.75Fe₁₀.5O₁₉) material are shown in figure (2), recorded at room temperature in the range (4000 - 400) cm⁻¹, and presented in the tables (1-2). The results of infrared spectra showed that the Co-Ti substituted barium hex ferrite particles causing slight changes in the resulting spectrum of (BaO.6Fe₂O₃). It shows not clear some new absorption bands with slight changes in other absorption bands. These new bands in the spectrum may be associated with the development of defects resulting from the state of transport of the charges associated with the reaction between Barium Ferrite and substitution ions, the FTIR spectrum of materials shows broad band and strong bands are observed at (560, 570) cm⁻¹ which attributed to Ba-O and Fe-O stretching vibration for the hexagonal barium ferrite and (553-555, 593-602) cm⁻¹ which attributed to Ba-O and Fe-O stretching vibration for the Co-Ti substituted barium hex ferrite particles, the shift in the values of the position of stretching vibration can be attributed to Co⁺²-Ti⁺⁴ substituted Fe ions. The spectrum also show broad and strong bands at (700, 770) cm⁻¹ which attributed to (Ba-O-Ba) bending vibrations for (BaO.6Fe₂O₃) material, and only (770) cm⁻¹ which assigned to (Ba-O-Ba) bending vibrations for (BaTi₀.75Co₀.75Fe₁₀.5O₁₉) material. Furthermore, the FTIR spectrum of materials shows broad and strong bands are observed at (567) cm⁻¹ which assigned to specific vibration for Fe-Co bands, (523) cm⁻¹ which assigned to specific vibration for Ti-O band and (570) cm⁻¹ which is attributed to specific vibration for Ti-Co bands.

FTIR spectra shows slight shift in peak position as well as the change in shape and intensity, comparing between Hexagonal Barium ferrite and the Co-Ti substituted barium hex ferrite particles. This indicates that the substitution of Co⁺²-Ti⁺⁴ to Fe ions are responsible for all changes in the stretching and bending vibration, these results were consistent with [4].

Figure 2. FT-IR graph (a) Barium Ferrite and (b) Co⁺²-Ti⁺⁴ substituted Barium Ferrite.
Table 1. FT-IR Sites transmittance bands with their assignments for (BaO.6Fe₂O₃) materials.

| Wavenumber (cm⁻¹) | Assignment                                                                 |
|-------------------|-----------------------------------------------------------------------------|
| 560               | Specific vibrations of Fe-O and Ba-O bonds                                  |
| 570               | Specific vibrations of Fe-O and Ba-O bonds                                  |
| 700               | Ba-O-Ba bending vibrations                                                  |
| 770               | O₂Ba-O-BaO bending vibrations                                               |
| 930               | Ba–O stretching vibration of BaO₄units in tri-, tetra- and pentaborate groups |
| 1060              | Ba–O stretching vibration of trigonalBaO units in boroxol rings             |
| 1230              | Ba-O stretching vibrations of BaO units in meta-, pyro- and orto-borate groups. |

Table 2. FT-IR Sites transmittance bands with their assignments for (BaTi₀.75Co₀.75.Fe₁₂₋₂xO₃) materials.

| Wavenumber (cm⁻¹) | Assignment                                                                 |
|-------------------|-----------------------------------------------------------------------------|
| 553-555           | Specific vibrations of Ba-O bonds                                           |
| 593-602           | Specific vibrations of Fe-O bonds                                           |
| 567               | Specific vibrations Fe-Co bonds                                             |
| 523               | Specific vibrations Ti-O bonds                                              |
| 1416              | Specific vibrations Ti-O-Tibonds                                            |
| 570               | Specific vibrations Ti-Co bonds                                             |
| 770               | O₂Ba-O-BaO bending vibrations                                               |
| 930               | units in tri-, tetra- and penta- borate groups                              |
| 1015              | Ba–O stretching vibration of BaO₄                                           |
| 1054              | Ba–O stretching vibration of trigonalBaO units in boroxol rings             |
| 1200              | Ba-O stretching vibrations of BaO units in meta-, pyro- and orto-borate groups. |
| 1390              |                                                                              |

3.2. Scanning Electron Micrograph (SEM) results
The SEM test is used to characterize the morphology of particles, and to show the effect of substituted of Co and Ti on the morphology of the samples. The obtained SEM results of the prepared hex. barium ferrite (BaO.6Fe₂O₃) and Co-Ti substituted barium hex ferrite particles (BaTi₀.75Co₀.75.Fe₁₂₋₂xO₃) samples are shown in Figure (3), the particles of all the samples exhibit plate-like shape and they have different granular sizes with a clear agglomerate in several very large clusters. It is possible to note that the granularity within the sample seems to have grown, faster and be more uniform and homogeneous with the presence of Co-Ti substituted barium hex ferrite samples [7], [9], these results are shown in figure (3).
3.3. Magnetic properties

The magnetic hysteresis diagram of barium ferrite were obtained at ambient temperature using vibrating sample magnetometer. The results are shown in Figure (4- a , b) , the hysteresis curves of the prepared samples obtained from (BaO.6Fe_2O_3) and (BaTi_{0.75}Co_{0.75}Fe_{10.5}O_{19}), respectively. It is observed that the sample of Co-Ti substituted barium hex ferrite particles has a great effect in the magnetic properties of barium ferrite mainly in the saturation magnetization. The saturation magnetization M_s of the Co-Ti substituted barium hex ferrite (BaTi_{0.75}Co_{0.75}Fe_{10.5}O_{19}) reduces to 6 emu/gr while the M_s for the hexa barium ferrite (BaO.6Fe_2O_3) reaches to 25 emu/gr. On the other hand, the value of intrinsic coercivity increases to 1.5 Oe for Co-Ti substituted barium hex ferrite sample fig,(4-b).This result indicates that with Co-Ti substitution , a particle growth occurs , with consequent increasing of the intrinsic coercivity this result is inconsistent with the previously described in literature [7], [10]. The poor magnetic properties for Hexagonal Barium ferrite (BaO.6Fe_2O_3) as shown in fig. (4-a), can be attributed to the presence of nonferromagnetic α-Fe_2O_3 and antiferromagnetic BaFe_2O_4 and will lead to a greater decrease in the values of saturation magnetization and coercivity [5], [11], [12], [8]. The magnetic properties for the prepared samples are in good agreement with the results of structural properties (FTIR and XRD).

Figure 4. Hysteresis loop for (a) Barium Ferrite and (b) Co^{+2}-Ti^{+4} substituted Barium Ferrite.

Conclusion.

We concluded that the Sol-gel method enabled to prepare Barium Ferrite and Co^{2+}-Ti^{4+} substituted Barium Ferrite. The results show that the products calcined at 950°C for 5 h at a rate of 150 °C/h. to obtain a ferrite powder. The results of FT-IR indicates that the substitution of Co^{2+}–Ti^{4+} to Fe ions are responsible for all changes in the stretching and bending vibration. The particles of all the samples exhibit plate-like shape and they have different granular sizes with a clear agglomerate in several very large clusters The poor magnetic properties for Hexagonal Barium ferrite (BaO.6Fe_2O_3) can be attributed to the presence of non ferromagnetic α-Fe_2O_3 and antiferromagnetic BaFe_2O_4 and will lead to a greater decrease in the values of saturation magnetization and coercivity.
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