The Effect of pH on Partial Size of Ferrimagnetic Powders Prepared by Auto Combustion Method

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Received on: 28/6/2015 & Accepted on: 20/1/2015

ABSTRACT
During the preparation of this research ferrites - copper powder chemical auto-combustion method has been studying the effect of changing (pH=3, 5, 7, 9, 11) coefficient on the particle size of the powder, used Debye-Scherrer Formula, to calculate the particle size by use of the highest peak (311) in X-ray diffraction (XRD) were obtained particle size ranges (11.5-13.75) nm, and also has been compared to the values obtained in drawing curves that represent change the lattice constant, particle size and density as a function of the (pH), and used Infrared spectroscopy (FTIR) to determine the internal structure of models, and also has been studying the microscopic structure took photos by electron scan microscopy (SEM) where indicated formation of high porosity homogeneous this change in the acidity coefficient(pH) led to change particle size and therefore a change in the properties of structural and physical.  
Keywords: Ferrtis, Auto-Combustion, Spinal. Particle size, pH.

INTRODUCTION
Spinell ferrites have the general formula of DFe₂O₄ (where D²⁺: Fe, Co, Ni, Zn, etc.) [1], and unit cell contains 32 oxygen atoms in cubic close packing with 8 tetrahedral and 16 octahedral occupied sites. By changing type of the divalent caution [2], depending on how these cations are distributed in the intersites, cubic spinel structures can be of two types: Normal spinel and Inverse spinel. Cu-ferrite has inverse spinel structure with almost all Cu²⁺ ions occupying octahedral sub lattice, whereas Fe³⁺ ions divide equally between the tetrahedral and octahedral sub lattices it is conceivable to take out significantly different physical and magnetic properties in these ferrites, [3-13] make it technologically significant group of materials due to their enhanced optical, magnetic, and electrical properties. These properties make them very important for a variety of medical or industrial applications [4]. Magnetic and electric properties of ferrites are having fundamental and technological and potential applications. Potential applications such as: high density information storage in computers; Ferro fluid technology, magneto-caloric refrigeration, magnetic resonance imaging (MRI) enhancement, magnetic guided drug delivery, microwave devices and magnetic recording media and magnetic sensors [14]. Ferrites powder prepared with deferent methods one of this methods auto computation way, which is chemical method depending on same parameters such as temperature of preparing or sintering and pH of solution [5]. Auto computation method is an auspicious method for the synthesis of fine Nano sized spinel oxides. The process is environmentally benign and versatile, since it does not involve any organic solvents [6, 7]. Auto computation method has been widely investigated for the synthesis of metal oxides as powders, nanoparticles and single crystals [9, 10, and 11]. Observed, that pH of reaction in the auto...
computation method plays a deterministic role in obtaining smaller sized particles [12]. The intent of this treat survey the influence of change of ph on particle size, where CuFe₂O₄ powder prepared in deferent ph =3, 5, 7, 9, 11 using auto combustion method, and this particles are to characterize with X-ray diffraction and Scanning Electron microscopy (SEM). However, in this survey, the effect of pH values of solutions was scrutinized to particle sizes and cristallinity.

Experimental Section

Synthesized by auto combustion method of Cu ferrites with a generic formula CuFe₂O₄, prepared with deferent (pH =3, 5, 7, 9, 11) were analytical grade with purity ≥99% of All the chemicals were used. In a typical procedure, cupric nitrate hydrate Cu(NO₃)₂·6H₂O, ferric nitrate monohydrate Fe(NO₃)₃·9H₂O were used as outset materials. The mixture was added to a citric acid solution (C₆H₈O₇·H₂O) 2M, in molar ratio citric (acid: nitrates) of 3:1. Mixed solutions of these materials were prepared in deionized water with vigorous stirring until the solution being a gal (2hour). A specific volume of ammonia NH₄OH was added to the above mixed solution. After, the solution of NH₄OH was added until pH values, reached (3, 5, 7, 9, 11) respectively. The intrinsic factor on which the final composition of the result depends was pH of solution, which can be varied to get the desired final product. The final powder specimens obtained were calcinations at 500°C for 2 hr. This method involves exothermic and self-sustaining thermally-induced anionic redox reaction of xerogel, which is obtained from aqueous solution containing desired metal salts (oxidizer) and organic complexant (reductant) [15-21]. Proportions between complexant and salts are usually calculated according to the valences of the reacting elements in order to supply the relation of oxidizer/reductant equal to (1) [16-22]. The nitrate salts are favored as precursors, because they serve as water-soluble low temperature NO–³ oxidant source for synthesis [17]. Metal nitrates possess hygroscopicity; consequently, they easily absorb moisture and become slurry. This variety of the sol–gel auto-combustion is called flash-combustion method xerogel during combustion is surely due to the heat generated from the exothermic reaction. Flame temperature during combustion could vary from 600°C to 1350°C. Decomposition of NH₄NO₃ produced O₂, thus accelerating the combustion process. Higher pH values of mixed solutions are expected for the synthesis of ferrite compounds [18-20].The chemical equation of that reaction can be presented in Eq.(1) as show :

\[
\text{Cu(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}+2\text{Fe(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}+3\text{C}_6\text{H}_8\text{O}_7+9\text{H}_2\text{O} \rightarrow \text{CuFe}_2\text{O}_4+4\text{N}_2+6\text{CO}_2+24\text{H}_2\text{O}+8\text{O}_2
\]

\[\text{(1)}\]

Results and Discussions:

XRD Patterns:

The XRD model of CuFe₂O₄ (pH=3, 5, 7, 11) samples shows in Fig.(1) Sharp and well defined peak are obtained for all samples, XRD patterns consistence of extra peak of CuO and Fe₂O₃, which can evasive by sintering of samples in high temperature to get pure CuFe₂O₄. XRD patterns show that all peaks indexed to pure cubic phase, where (220), (311), (400), (422), (511), and (440) be a symbol for the main crystal phase in CuFe₂O₄ spinel ferrite. Formation of single phase spinel ferrites structure clearly denote, by X-ray diffract gram. Where used the Eq.(2) for a cubic system for most intensity peak (311) to collected the lattice parameter (a);

\[a^2=(h^2+k^2+l^2)d^2\]  \[\text{...(2)}\]

h,k,l= miler index, d= the inter planer spacing.

Average grain size (D) and X-ray density (\(\rho x\)) are listed in Table(1). The XRD patterns were compared for deferent amount of pH value. As seen from Fig.(2), Average particle size (Dₓ) was calculated by using Debye-Scherrer Formula, from Eq.(3)

\[D_x=0.9\lambda/ (\beta \cos \theta)\]  \[\text{...(3)}\]
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\( \lambda \) = wave length of X-ray, \( \beta \) = broadening of the diffraction peak, \( \theta \) = diffraction angle, the calculated crystallite size from the broadening of the (311) XRD peak. And Eq. (4) used to calculate X-ray density (\( \rho_x \)):

\[
\rho_x = \frac{8 \cdot M_w}{N_a \cdot a^3}
\]  

(4)

\( M_w \) = molecule Wight, \( N_a \) = Avogadro's number, \( a \) = lattice constant, the value of \( D_x \) varies from (13.53 nm) of \( \text{pH}=3 \) to (11.72 nm) \( \text{pH}=11 \) which denotes an increase of average grain size with increasing pH value, that was attributed to higher combustion temperature because of increase in (NH\(_4\)OH) amount, which is as a fuel in the chemical reaction. Show in Fig. (3) increased in lattice constant, any change in the lattice constant lead to a change in density according to mathematics equation Eq. (4), where the relationship is inversely proportional with lattice constant and the density, that was obtained practically as show in Fig. (4).

Table (1): present value of lattice constant, XRD density, particle size of samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Lattice constant(A(^0))</th>
<th>XRD density (g/cm(^3))</th>
<th>Particle size(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{pH}=3 )</td>
<td>8.318</td>
<td>5.515</td>
<td>13.537</td>
</tr>
<tr>
<td>( \text{pH}=5 )</td>
<td>8.309</td>
<td>5.533</td>
<td>9.263</td>
</tr>
<tr>
<td>( \text{pH}=7 )</td>
<td>8.312</td>
<td>5.528</td>
<td>12.223</td>
</tr>
<tr>
<td>( \text{pH}=9 )</td>
<td>8.317</td>
<td>5.517</td>
<td>13.059</td>
</tr>
<tr>
<td>( \text{pH}=11 )</td>
<td>8.327</td>
<td>5.499</td>
<td>11.721</td>
</tr>
</tbody>
</table>

Figure (1): XRD patrons of samples with deferent pH, show that all peaks indexed to pure cubic phase, with extra peak denote by (*) of CuO, and Fe\(_2\)O\(_3\).
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Figure (2): Plot of average grain size of samples as a factor of pH denotes an increase of average grain size with increasing pH value.

Figure (3): Plot of lattice constant as a factor of pH, for powders at 500°C

Figure (4): Plot of XRD density as a factor of pH, for powders at 500°C.

Microstructure
The SEM images showed uniformity and homogeneity of the synthesized CuFe$_2$O$_4$ particles, the present powder as flicks and clear that powder has high porosity is correspond with XRD density where the density is decrease when porosity is increased. The scanning electron micrograph for CuFe$_2$O$_4$ shows they are dense and distributed regularly within the whole area as show in Fig.(4). In addition to this, these smaller crystallites are so closely arranged together, a clear boundary between neighboring particles can also be observed.
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Figure (4,a,b,c,d,e): SEM images of CuFe$_2$O$_4$ samples after calcination 500°C present porosity and boundary between neighboring particles can also be observed.

FTIR Measurement
At room temperature using FTIR, spectra were registered for the copper ferrites samples were recorded in the range of (2000-500) cm$^{-1}$ and are show in Fig.(9) for the (pH=3, 5, 7, 9, 11) respectively. Ferrite's structure was similar to mineral spinel crystalline structure that occurs usually in cubic form or sometimes in tetragonal form depending upon the ions participating in the solicitous solid material. The FTIR spectra of as-prepared samples in general below 1000 cm$^{-1}$, as show in Fig.(9) set the formation of spinel structure. Two main absorption band $V_1$ and $V_2$ as common feature of FTIR spectra show all spinel assembly, in identity to Waldron [8]. The ferrites can be considered as continuously bonded crystals, via ionic, covalent or Vander walls forces, to the nearest neighbor. Two different sub-lattice in ferrite metal ion are located in, namely tetrahedral (A sites) and octahedral (B sites) according to geometrical configuration of oxygen nearest neighbor, the band $V_1$ around 576 cm$^{-1}$ was attributed to stretching vibration of tetrahedral complexes and the band $V_2$ around 400 cm$^{-1}$ to the octahedral complexes. The values of absorption band frequency of samples with different pH, are given in Table(2). It can be seen that the high frequency band $V_1$ has value (576.72 cm$^{-1}$) for pH=3 samples. Such as copper ferrites that $V_1$ is due to (Fe$^{3+}$-O$^{2-}$) complex present at A sites and $V_2$ band due to vibration of octahedral metal complexes. The cu$^{2+}$ ions occupy mainly the octahedral sites and same fraction goes in to tetrahedral sites according to these shoulders, where found the cu-ferret is invers spinel ferrites, also found any change in partial size leads to shifting in spectrum as in Table (2).

Table (2): present value of $V_1$ due to (Fe$^{3+}$-O$^{2-}$) complex at A sites and $V_2$ band due to vibration of octahedral metal complexes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_1(\text{cm}^{-1})$</th>
<th>$V_2(\text{cm}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH=3</td>
<td>576.72</td>
<td>447.49</td>
</tr>
<tr>
<td>pH=5</td>
<td>555.14</td>
<td>414.70</td>
</tr>
<tr>
<td>pH=7</td>
<td>557.43</td>
<td>405.05</td>
</tr>
<tr>
<td>pH=9</td>
<td>549.71</td>
<td>324.34</td>
</tr>
<tr>
<td>pH=11</td>
<td>567.00</td>
<td>420.48</td>
</tr>
</tbody>
</table>
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(a) pH=3  
(b) pH=5  
(c) pH=7
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CONCLUSION
Cupper ferrite CuFe$_2$O$_4$ powders with nanocrystalline sizes were produced by a combination of sol-gel auto combustion of ammonia, as the fuel (the molar ratio of metal nitrates to fuel was 1: 3). The pH values were changed from 3 to 11. With an increase in the pH value, the combustion rate is increased significantly. All the samples are single phase ferrites (CuFe$_2$O$_4$) with cubic spinel structures. The synthesized powders had a particle size distribution in the range of (11.5-13.75) nm. The XRD results show that crystallite percent of CuFe$_2$O$_4$ phase grows with an increase in the pH from 5 to 7 and then it decreases. FTIR spectra results indicate that band peaking at about 570 cm$^{-1}$, where found the cu-ferret is invers spinel ferrites, also found any change in partial size leads to shafting in spectrum.

Figure (9a,b,c,d,e): FTIR patron of samples with different pH show that formation of spinel structure with two main absorption band $V_1$ and $V_2$ as common feature of FTIR in the rang of (2000-500) cm$^{-1}$
REFERENCES