EFFECT OF PH ON PARTICLE SIZE OF COPPER SUBSTITUTED NICKEL FERRITE

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Abstract: In the present work we have discussed the effect of pH on particle size of mixed metal ferrite having compositional formula $Ni_{0.4}Cu_{0.6}Fe_2O_4$. The samples were synthesized via sol-gel auto combustion method at various pH and annealed at 800^0C. The samples were characterized using XRD and FTIR techniques which confirm the formation of nano ferrite with cubic spinel structure. The maximum crystallite size was observed for the ferrite sample synthesized at pH 7.

Keywords: Ni-Cu nanoferriets, auto-combustion, XRD, FTIR.

INTRODUCTION:

The metal oxide nanocomposite materials due to their easy mode of formation and multifunctional behaviour are attracting special attention of scientists. These nanoparticles exhibit electrical, optical and magnetic properties that are different from their bulk counterparts(Xu *et al*.2008). Metal oxides play a very important role in many areas of chemistry, physics, and material science (Fierro,2006; Henrich and Cox,1994).They have wide range of applications such as fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings against corrosion and as catalysts(Ertl *et al*.1997).Till now, there are still many potential applications of these materials under continuous investigation and new synthesis methods being developed(Joliwet, 2000). To exploit new applications metal oxide materials, spinel ferrite is one of the mean purposes of inorganic chemist.

Nickel ferrite ($NiFe_2O_4$) and Copper ferrite ($CuFe_2O_4$) are one of the most important spinel ferrites having inverse spinel structure. In the past, mixed spinel ferrites were prepared by conventional methods which have number of disadvantages such as high period heating. Now a day, numbers of physical and chemical techniques have been developed to prepare ferrite materials. The chemical techniques for the synthesis of nanostructured materials offer some advantages in comparison with the physical techniques in relation to simplicity, energy saving and product homogeneity. In the present work the Citrate-Gel auto combustion technique (Deganello *et al*.2009) has been used for the preparation of mixed nanocrystalline spinel ferrites with specific properties, such as controlled stoichiometry and narrow particle size distribution. The low cost, simplicity and short time of production and the purity and homogeneity of final product are some of its advantages.

MATERIALS AND METHODS :

AR grade iron nitrate nonahydrate $Fe(NO_3)_3.9H_2O$, Nickel nitrate hexahydrate $Ni(NO_3)_2.6H_2O$, Copper nitrate hexahydrate $Cu(NO_3)_2.6H_2O$, citric acid, liquor ammonia were purchased from SD fine-chem limited, with high purity of 99.99% and used without further purification.

Synthesis of Ferrite

To study the effect of pH of reaction mixture on particle size, the system $Ni_{1-x}Cu_xFe_2O_4$ with x = 0.4 is chosen. The ferrite samples for x = 0.4 are synthesized at various pH such as pH 3, 5, 7, 9, 11 and samples are annealed at 800^oC for two hours.

Ferrite Nanoparticles with compositional formula $Ni_{0.6}Cu_{0.4}Fe_2O_4$ were synthesized by sol gel auto-combustion method. The accurately weighed amount of metal ion precursors and citric acid in desired stoichiometric proportions were dissolved separately in minimum quantity of distilled water. Here citric acid and nitrate ions act as fuel and source of oxygen, respectively. The molar ratio of metal ion precursors to citric acid was kept 1:1. The individual solutions were then mixed together with constant stirring and the pH value of the solution was adjusted accordingly using aqueous ammonia solution (pH=3, 5, 7, 9 and 11). The solution was then stirred continuously and slowly heated on a hot plate magnetic stirrer at 80^oC till gel was formed which was ignited and burnt in a self-propagating combustion manner to obtain loose powder. The powder was finally annealed at 800^oC in a muffle furnace for 2 hours.

Characterization of $Ni_{0.6}Cu_{0.4}Fe_2O_4$ nanoparticles

Structural characterization of the prepared samples were carried out by X-ray diffraction studies using Bruker AXS, D8 Advance spectrophotometer with Cu-Kα radiation (λ=1.5418A^0) in a wide range of Bragg's angle (20-80^o) at room temperature. Infrared spectra of the powder samples were recorded using Fourier Transform Infra-Red Spectrophotometer (FTIR Nicolet, Avatar 370 model) by the KBr pellet method.

RESULT & DISCUSSION

Characterization of ferrite:

X-ray diffraction studies:

X-ray diffraction patterns corresponding to $Ni_{1-x}Cu_xFe_2O_4$ ferrite system (x = 0.4) at various pH 3, 5, 7, 9 and 11 are shown in Fig. 1 and corresponding analytical data for the most intense peak at (311) plane is shown in table 1. For all samples 2θ value for the most intense peak at (311) plane ranges from 35.41° to 35.53°, a characteristic of cubic spinel ferrite. The most intense peak at (311) was used to determine the average crystallite size of nanoparticles. The average crystallite size of the samples was determined by using the Debye-Scherer's formula(Kiug and Alexander,1954) given by,

$D_{hkl} = 0.9\lambda / \beta \cos\theta$

where, D_{hkl} = crystallite size, λ is wavelength of the X-ray radiation, β is the full width at half maximum (FWHM) of the most intense diffraction peak and θ is Bragg's angle.

The average crystallite size of the samples was found in the range 34.83nm to 63.05nm. It was found to increase from 35.42nm (pH 3) to 63.05nm (pH 7) and then decreases to 37.34nm (pH 11). The maximum crystallite size is observed for sample synthesized at pH 7, viz. 63.05nm. Further, from XRD pattern, it can be seen that peaks became sharper for sample synthesized at pH 7. It is also reported that the peaks become sharp and intense with increasing pH values, indicating an increase in crystallite size. As the pH increases, the diffraction maxima become sharper and more pronounced. This indicates that the crystallinity and the average crystallite size are increased as the pH increases. Due to the rapid combustion rate and high flame temperature with increasing pH, higher pH produces larger crystallite size and good crystallinity(Win *et al*.2015).

The lattice constant of each composition was calculated using Le Bail refinement method(Hui *et al*.2004).

$$a = d\sqrt{h^2 + k^2 + l^2}$$

where, a is lattice constant; d is inter planar spacing; (hkl) are Miller Indices.

The lattice parameters of the ferrite nanoparticles are found in the range 8.373Aº to 8.401Aº, which are close to the standard ferrite samples.

X-ray density is calculated using relation:

$$dx = \frac{8M}{N_A X a^3}$$

where M is molecular weight of the composition; N_A is Avagadro's number and a is lattice constant.

FTIR studies

FT-IR spectra of $Ni_{1-x}Cu_xFe_2O_4$ (x = 0.4) synthesized at various pH are shown in Fig 2 and corresponding analytical data is shown in table 2. The broad band around 3440 cm^{-1} can be assigned due to the δ(H-O-H) stretching vibrations of water from the surrounding absorbed by ferrite nanoparticles. The intense broad peaks around 1600cm^{-1} are because of the δ (H-O-H) in plane bending vibration. The intense peak around 580 cm^{-1} can be attributed to intrinsic Fe-O vibration of tetrahedral Fe^{3+} and another peak near 400 $cm^{-1}$to that of octahedral Fe^{2+} sites indicating the spinel structure of synthesized ferrite samples(Ahmed *et al*.2005).

CONCLUSION :

Copper substituted nickel ferrite with compositional formula $Ni_{0.6}Cu_{0.4}Fe_2O_4$ was synthesized successfully using sol gel auto combustion method of synthesis. The synthesis was carried out at various pH of reaction mixture such as pH 3, 5, 7, 9 and 11. Polycrystalline cubic spinel structure of the prepared nanoferrites was confirmed by X-ray diffraction analysis. The average crystallite size of ferrite samples was found in the range 34.83nm to 63.05nm. The maximum crystallite size was observed for sample synthesized at pH 7, viz. 63.05nm. FTIR studies also confirm the formation of spinel nanoferrite.

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Table-1:- Values of 2θ (degrees) and β (degrees) (FWHM), d–spacing (d), crystallite size, lattice parameter (a) of $Ni_{0.6}Cu_{0.4}Fe_2O_4$ synthesised at different pH.

Sr. No.	pH	2θ (degrees)	β (degrees) (FWHW)	d-spacing (Å)	Crystallite size (nm)	Lattice Parameter in Å (a)	X–ray density (dx)	Volume of Unit Cell (V) $(Å)^3$
1.	3	35.43	0.411	2.5315	35.42	8.396	5.319	591.865
2.	5	35.41	0.317	2.53307	46.00	8.401	5.309	592.967
3.	7	35.53	0.231	2.52446	63.05	8.373	5.363	586.941
4.	9	35.43	0.418	2.53131	34.83	8.395	5.320	591.732
5.	11	35.53	0.390	2.52490	37.34	8.374	5.361	587.248

Fig. 1:- XRD spectrum of ferrite sample $Ni_{0.6}Cu_{0.4}Fe_2O_4$ at pH =3 to 11

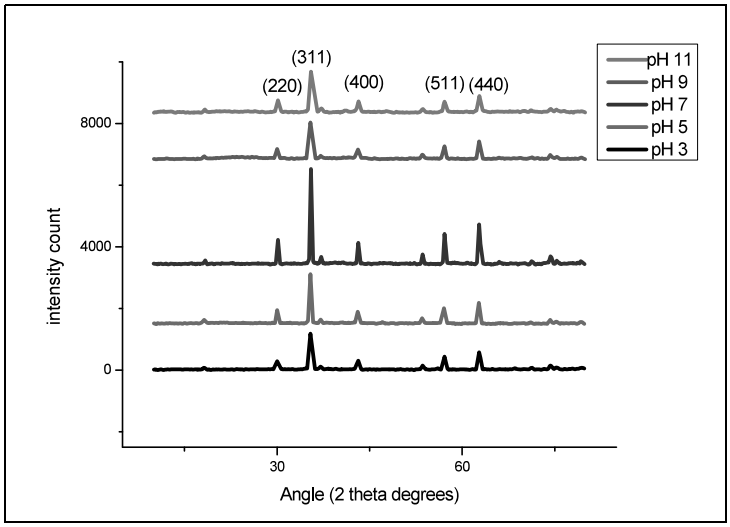
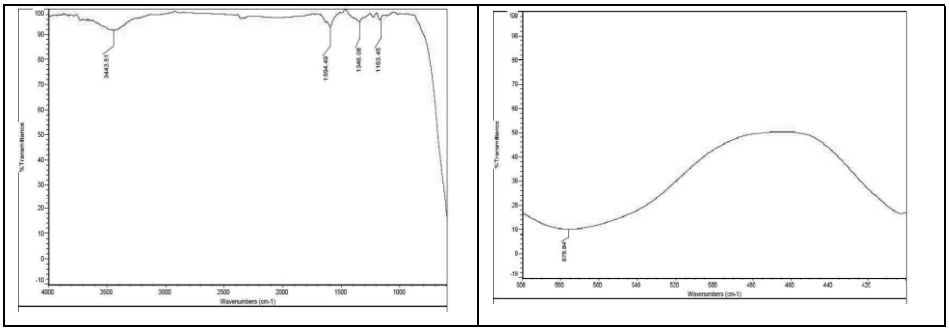


Table 4.2b: Infrared data of $Ni_{1-x}Cu_xFe_2O_4$ (x = 0.4) at various pH

Sr. No.	pH	υ (OH) stretching cm^{-1}	δ (H-O-H) bending cm^{-1}	υ_1 (M-O bond) cm^{-1}
1.	3	3443.51	1594.49	575.84
2.	5	3423.16	1607.26	572.64
3.	7	-	-	580.63
4.	9	3444.12	1632.30	574.60
5.	11	3425.06	1617.04	566.97

Fig. 2:- FTIR spectra of ferrite system $Ni_{0.6}Cu_{0.4}Fe_2O_4$ synthesized at pH 3, 5, 7, 9 &11



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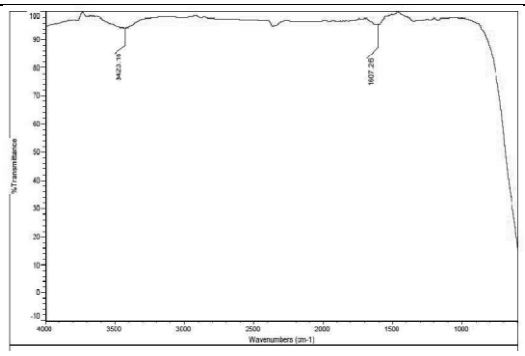	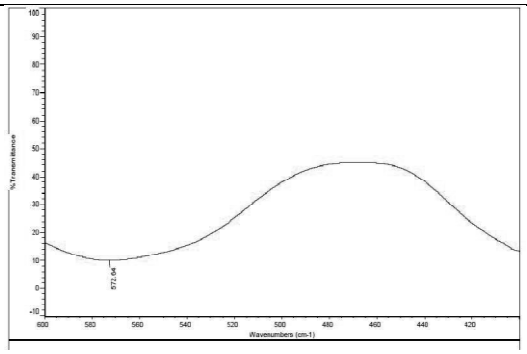
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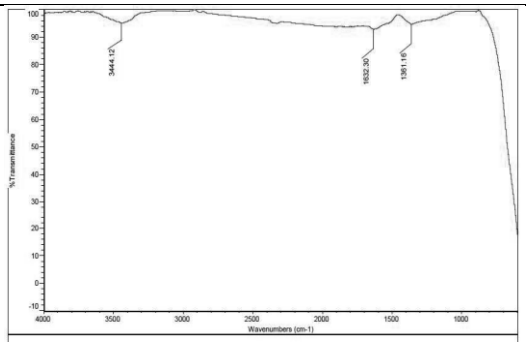	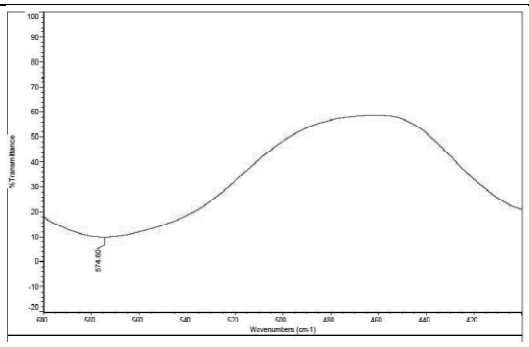
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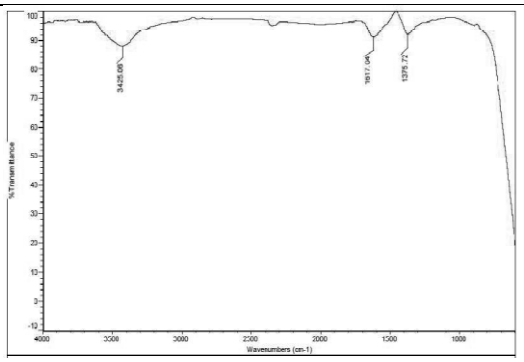	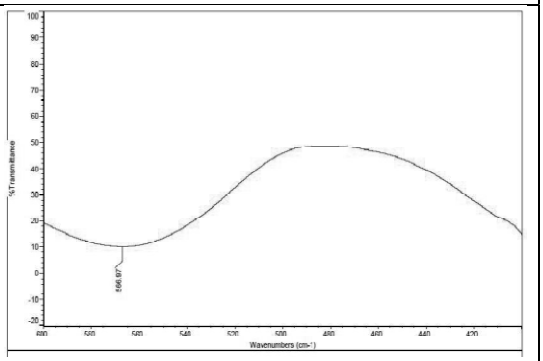
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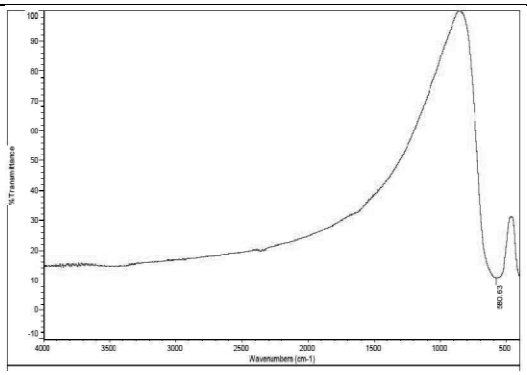 pH = 7	