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Dependence of magnetic and structural properties of $Ni_{0.5}M_{0.5}Fe_2O_4$ (M=Co, Cu) nanoparticles synthesized by citrate precursor method on annealing temperature

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Abstract

$Ni_{0.5}M_{0.5}Fe_2O_4$ (M = Co, Cu) ferrite nanoparticles were synthesized using citrate precursor method. The citrate precursor was annealed at temperatures 400°C, 450°C, 500°C and 550°C. The annealed powders were characterized using X-ray diffractometer (XRD) and vibrating sample magnetometer (VSM). Observed XRD data was further analyzed using Rietveld analysis which showed that particles annealed at temperatures upto 450°C display cubic spinel structure while the particles formed at temperature higher than 450°C display a tetragonal spinel structure. Sharp changes were observed in particle size, lattice constant, magnetization and retentivity in the range 450-500°C temperature suggesting that nucleation/growth mechanism is different at temperatures above and below a critical temperature in this range.

Keywords: Ferrites, magnetic nanoparticles, citrate precursor, magnetization.

1. Introduction

Growth and study of spinel nanoferrites have been intensively pursued because of their special magnetic and electric properties (Ishino and Narumiya*.,* 1987; Sugimoto 1999). Magnetic ferrites such as Ni-ferrite ($NiFe_2O_4$) have a wide range of applications in areas such as biomedical, magnetic ferrofluids, microwave absorption, repulsive suspension for levitated railway systems, gas sensing capabilities, *etc.* (Ramankutty and Sugunam 2001; Reddy *et al.,* 1999). Also, Co ferrite has been used for magnetic and/or digital recording applications in audio as well as video tapes (Skomski, 2003; Baykal *et al.,* 2009). Apart from being strongly dependent on particle size, the magnetic properties of ferrite nanoparticles also get influenced by the method of synthesis and process parameters even though the common diagnostic tools such as XRD show similar crystalline structure (Sugimoto, 1999; Rajendran *et al.,* 2001). In recent years, the development of a number of synthetic procedures to produce ferrites at nanoscale has received considerable attention (Pal and Chakravorty 2003). The synthesis of ferrites using citrate precursor method has a distinct advantage over other chemical methods such as maximum reactivity, short time, low preparation temperature, homogenous distributions of ions and low cost (Verma *et al.,* 2000). It is based on wet chemical processes and one of the main controlling parameters is the annealing temperature at which the precursor powder is heated.

It is known that the magnetic properties depend on the site occupancies by the magnetic ions (Uen and Tseng 1982; Ma *et al.,* 2000; Albuquerque *et al.,* 2001). In bulk size Ni-ferrite, Ni^{2+} ions remain at octahedral sites. Also, it is observed that Co^{2+} ions have a strong preference for octahedral sites while Cu^{2+} ions prefer tetrahedral sites. As Cu^{2+} ions do not have magnetic moment, magnetic properties of the two systems will be different. It will be, therefore, interesting to see the effect of partial substitution of Co^{2+} and Cu^{2+} in $NiFe_2O_4$ on the structural and magnetic properties. Accordingly, the present work reports the effect of annealing temperature on the structural and magnetic properties of two Ni-based ferrites, namely $Ni_{0.5}Co_{0.5}Fe_2O_4$ and $Ni_{0.5}Cu_{0.5}Fe_2O_4$ prepared using citrate precursor method.

2. Experimental

Nitrates of all the three cations (Ni^{2+}, Co^{2+}/Cu^{2+} and Fe^{3+}) were taken in proper stoichiometric proportions as starting materials. Aqueous solutions of these salts were prepared separately by dissolving the salts in minimum amount of deionized water and stirring constantly. The solutions were then mixed together. Aqueous solution of citric acid was prepared in adequate quantity according to molar ratio (5% more compared to stoichiometric) and was added to the prepared salt solutions. It has been shown (Gajbhiye et al., 1995) that such precursor is sufficient for preparation of required ferrite. The mixture was heated at 60°C-80°C for two hours with continuous stirring for both the cases. The solutions were allowed to cool to room temperature and finally dried at 60-65°C in an oven until they turned into brown colored fluffy mass. The precursors were annealed at temperatures respectively 400°C, 450°C 500°C & 550°C for one hour each in a muffle furnace. During this process, the precursors thermally decomposed and gave ferrite powder. The structural characterization was carried out using an X-ray Diffractometer (Rikagu Miniflex, Japan) with Cu K_α radiation λ = 1.5405Å between the Bragg angles 20° to 80°. The *2θ vs.* intensity data obtained from this experiment were plotted with WinPLOTR program (Rosinel and Rodriguez-Carvajal 2001) and the angular positions of the peaks were obtained. The dimensions of the unit cell, *hkl* values and space group of $Ni_{0.5}Co_{0.5}Fe_2O_4$ and $Ni_{0.5}Cu_{0.5}Fe_2O_4$ nanoparticles were obtained using the TREOR program in the FullProf (Rodriguez-Carvajal 2000). The Bragg peaks were modeled with pseudo-Voigt function and the backgrounds were eliminated using linear interpolation technique. Rietveld analysis was done to confirm the structure indicated by matching of peak positions (Rodriguez-Carvajal 2000, McCusker *et al.,* 1999). Magnetization behavior was studied by Vibrating Sample Magnetometer (model PAR-155).

3. Results and Discussion

3.1 Structural studies

X-ray diffraction patterns for Ni-Co ferrite and Ni-Cu ferrite samples annealed at 400°C, 450°C, 500°C and 550°C are shown in Figures 1 and 2 respectively. It can be seen that the peaks become sharper and their intensity increases with the rise of annealing temperature for both the compounds. The average crystallite size was determined from the broadening of the most intense peaks (311) using Debye Scherrer equation (Cullity 2001) and the values are shown in Figure 3. It is observed that the values of the average crystallite size increase with increase in annealing temperature for both the compounds and it is always lower in case of Ni-Cu in comparison with Ni-Co. Moreover, there appears a sudden jump in crystallite size as the annealing temperature increases from 400 to 450°C. This suggests that there is a critical temperature in the range 450-500°C and nucleation/growth mechanism is different at temperatures below and above this temperature**.**

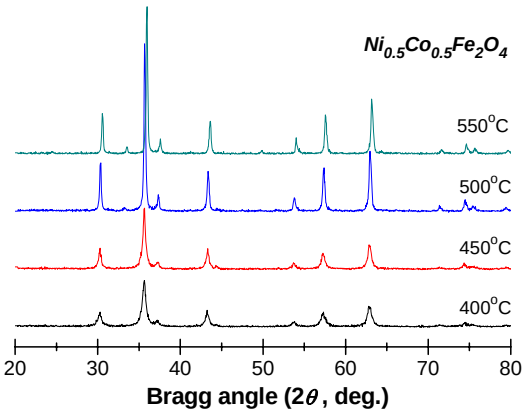

Figure 1. XRD pattern of $Ni_{0.5}Co_{0.5}Fe_2O_4$

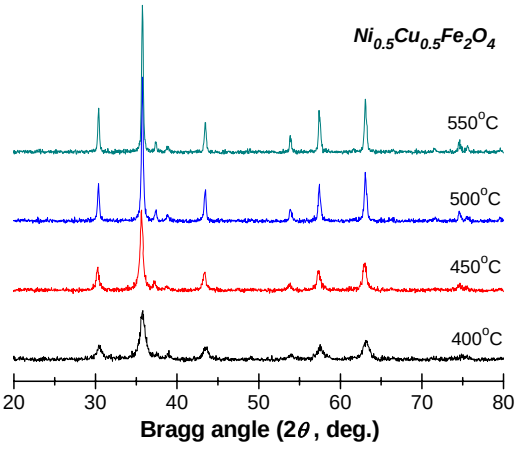

Figure 2. XRD pattern of $Ni_{0.5}Cu_{0.5}Fe_2O_4$

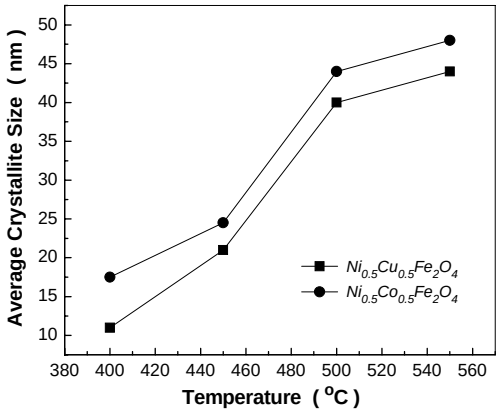

Figure 3. Crystallite size as a function of annealing temperature

For the Ni-Co ferrite samples synthesized below 500^0C, all the visible peaks are lying well above the background (Figure 1), and these can be identified with spinel cubic structure. Samples prepared at 500^0C and 550^0C show additional peaks (or splitting of peaks) of small intensity especially at 33.20^o and 33.50^o (2θ positions) indicating thereby change in cell structure at high temperature or formation of new phases through newer reactions.

Table 1. Crystal data and refinement factors of $Ni_{0.5}Cu_{0.5}Fe_2O_4$ and $Ni_{0.5}Co_{0.5}Fe_2O_4$ nanoparticles obtained from X-ray powder diffraction data.

	$Ni_{0.5}Cu_{0.5}Fe_2O_4$		$Ni_{0.5}Co_{0.5}Fe_2O_4$	
Parameters*	**450°C**	**550°C**	**450°C**	**550°C**
Crystal System	Cubic	Tetragonal	Cubic	Tetragonal
Space group	*Pm*3*m*	*P*4/*mmm*	*Pm*3*m*	*P*4/*mmm*
a (Å)	8.3454	8.3316	8.3492	8.3185
c (Å)	--	6.2855	--	6.2056
V (Å^3)	581.2128	436.3076	582.0098	429.4135
R_p	42.8	32.9	24.0	22.0
R_{wp}	41.1	35.4	33.1	28.7
R_{exp}	39.7	35.7	31.3	26.8
R_B	2.65	0.0622	0.0829	0.147
R_F	2.64	0.130	0.122	0.466
χ^2	1.073	0.9805	1.117	1.144
d	1.4602	1.4924	1.5002	1.4839
Q_D	1.8052	1.8079	1.8103	1.8117
S	1.035	0.991	1.058	1.071

***Description of parameters**

R_p (profile factor) = $100[\Sigma|y_i\text{-}y_{ic}|/\Sigma|y_i|]$, where y_i is the observed intensity and y_{ic} is the calculated intensity at the ith step.

R_{wp} (weighted profile factor) = $100[\Sigma\omega_i|y_i\text{-}y_{ic}|^2/\Sigma\omega_i(y_i)^2]^{1/2}$, where $\omega_i = 1/\sigma_i^2$ and σ_i^2 is variance of the observation.

R_{exp} (expected weighted profile factor) = $100[(n\text{-}p)/\Sigma\omega_i(y_i)^2]^{1/2}$, where *n* and *p* are the number of profile points and refined parameters, respectively.

R_B (Bragg factor) = $100[\Sigma|I_{obs}-I_{calc}|/\Sigma|I_{obs}|]$, where I_{obs} is the observed integrated intensity and I_{calc} is the calculated integrated intensity.

R_F (crystallographic R_F factor) = $100[\Sigma|F_{obs}-F_{calc}|/\Sigma|F_{obs}|]$, where F is the structure factor, $F = \sqrt{(I/L)}$, where L is Lorentz polarization factor.

$\chi^2 = \Sigma\omega_i(y_i-y_{ic})^2$.

d (Durbin–Watson statistics) = $\Sigma\{[\omega_i(y_i-y_{ic})-\omega_{i-1}(y_{i-1}-y_{ic-1})]^2\}/\Sigma[\omega_i(y_i-y_{ic})]^2$.

Q_D = expected d.

S (goodness of fit) = (R_{wp}/R_{exp}).

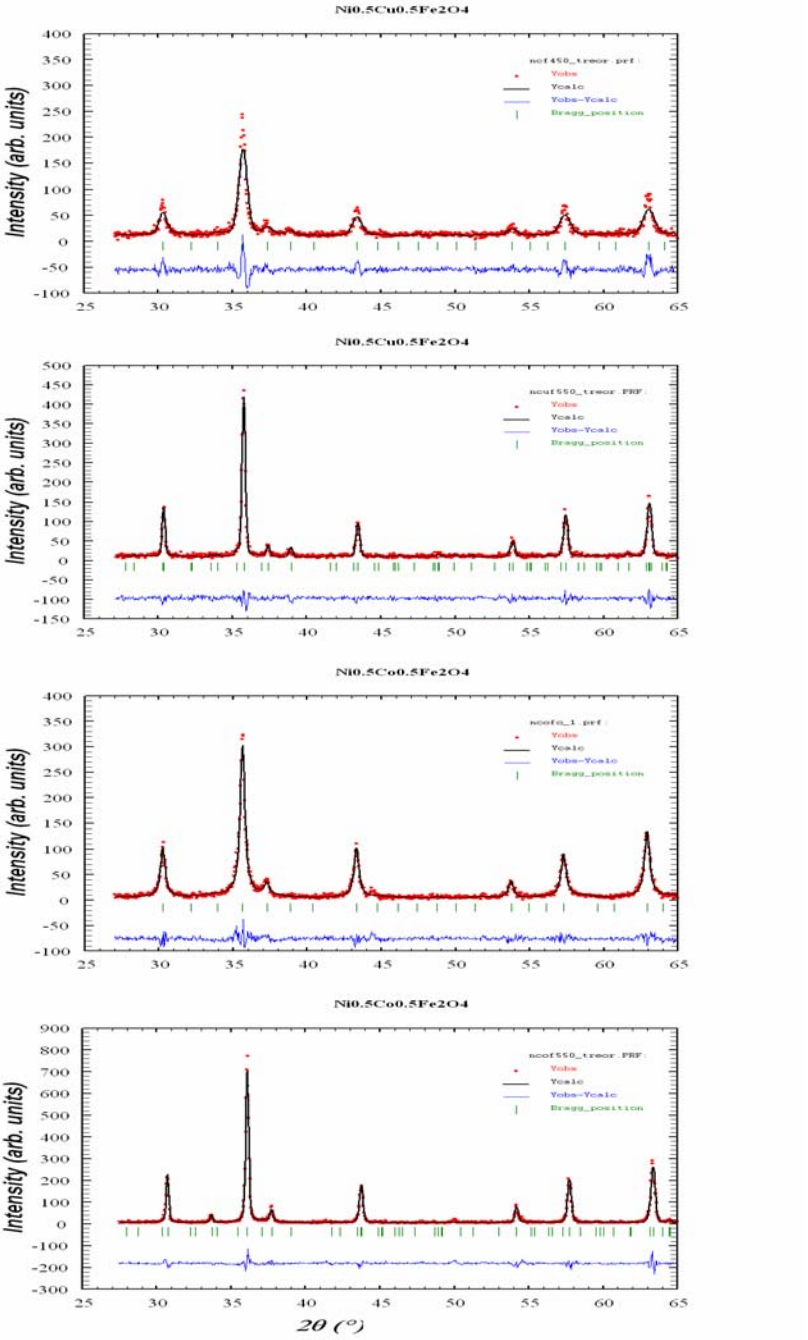

Figure 4. Rietveld refined patterns of $Ni_{0.5}Cu_{0.5}Fe_2O_4$ (a,b) and $Ni_{0.5}Co_{0.5}Fe_2O_4$ nanoparticles(c,d) annealed at 450°C and 550°C. Symbols represent the observed data points and the solid lines their Rietveld fit.

Rietveld refinements on the XRD data of Ni-Cu and Ni-Co were carried out. Figures 4a-d show the observed, calculated and difference XRD profiles, respectively, for Ni-Cu and Ni-Co samples annealed at 450°C and 550°C, after the final cycle of refinement. It can be seen that the profiles for observed and calculated values are matching very nicely. The value of χ^2 comes out to be ~1, which may be considered to be very good for estimations. The profile fitting procedure adopted was minimizing the χ^2 function (McKusker et al. 1999). The Rietveld analyses of XRD data indicate that both Ni-Cu and Ni-Co have a cubic unit cell structure upto 450°C and the structure becomes tetragonal upon further increase in temperature. Unit cell volume is smaller for both Ni-Cu and Ni-Co samples annealed at 550°C temperature showing greater compaction at this higher temperature. The crystal system and cell parameters for the samples annealed at 400°C are in very good agreement with the literature report (ICSD# 040040) for $NiFe_2O_4$. This clearly indicates that the partial replacement of Ni^{2+} ion by Cu^{2+} or Co^{2+} in the host $NiFe_2O_4$ compound does not change the basic crystal structure. The crystallographic data and refinement factors of Ni-Cu and Ni-Co, annealed at 450°C and 550°C, obtained from the XRD data, are depicted in Table 1.

3.2 Magnetization

M-H curves for the Ni-Cu ferrite samples are shown in Figure 5. Table 2 gives magnetization, coercivity and retentivity data for the samples. Copper substituted ferrites show a very small coercive field (Figure 5). This could be related to less number of magnetic ion A-B pairs in these samples as Cu^{2+} is nonmagnetic ion. Copper has stronger preference for tetrahedral sites and hence will inhibit Fe^{3+} ions to come to tetrahedral sites. Ni^{2+} has anyway strong preference for octahedral site. As a result the number of A-B magnetic ion pairs will be much less as compared to B-B pairs which provides only weak magnetic coupling. This might result in superparamagnetism, at least partially for the smaller particles in the sample, giving negligible coercive field and retentivity. This appears to be the case in the present samples. The saturation magnetization is likewise small.

Table 2 Values of Magnetic parameters

Annealing Temp(°C)	Magnetization (emu/g)	Coercivity (Oe)	Retentivity (emu/g)	M_r/M_s	Magnetization (emu/g)	Coersivity (Oe)	Retentivity (emu/g)	M_r/M_s
	Ni-Co				Ni-Cu			
400°C	46.8	612	15.60	0.33	25.9	38	1.10	0.04
450°C	47.7	724	17.51	0.36	30.0	97	4.25	0.14
500°C	49.6	612	24.10	0.48	34.3	138	8.81	0.24
550°C	50.8	845	24.20	0.47	35.1	135	9.76	0.28

M-H curves for Ni-Co ferrites are given in Figure-6. Cobalt substituted ferrites show well developed hysteresis loops with large coercive field. This shows strong magnetic coupling as expected since all the three cations are magnetic and one will have larger number of A-B magnetic ion pairs. The saturation magnetization increases slowly with increase in annealing temperature. However, the retentivity sharply changes as the annealing temperature increases from 450°C to 500°C, a trend that has also been seen in particle size (Figure-3).

The M-H curves show that magnetization is not completely saturated till the field of 10 kOe used in these experiments. This could be due to the small size of the particles. The average crystallite size varies from 10-45 nm (Figure-3) in our case. There will be a size distribution allowing smaller particles to exist even when the average size is large. For such particles, the magnetic moments will fluctuate due to thermal energy reducing the overall magnetization. As the applied field increases, the fluctuations gradually reduce showing slight increase even at high fields.

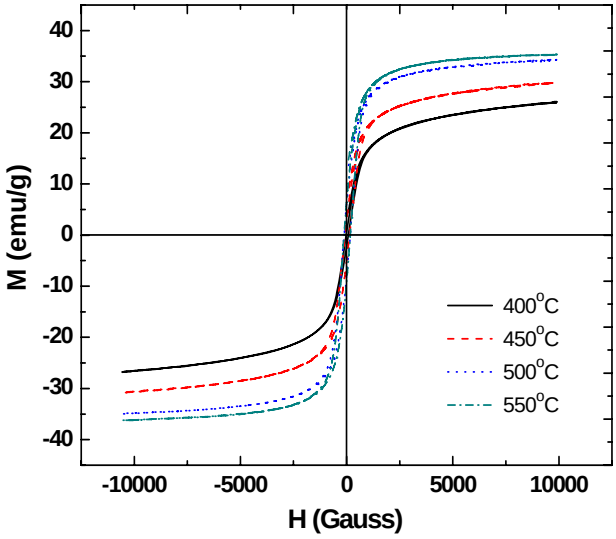

Fig. 5. Magnetization plots of $Ni_{0.5}Cu_{0.5}Fe_2O_4$ nanoparticles annealed at different temperatures.

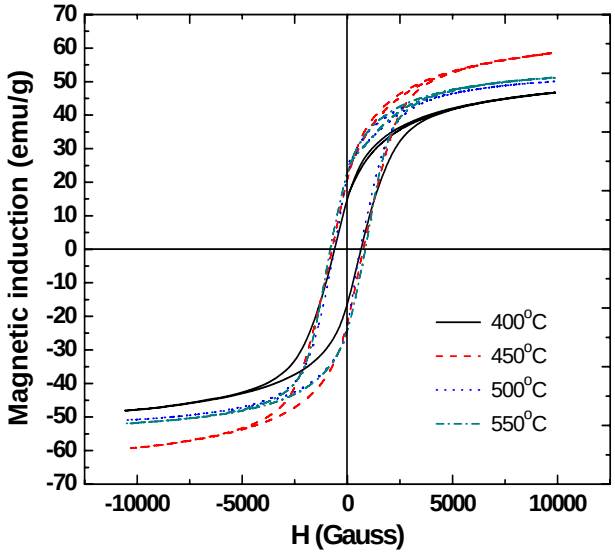

Fig. 6. Magnetization plots of $Ni_{0.5}Co_{0.5}Fe_2O_4$ nanoparticles annealed at different temperatures.

4. Conclusion

1. The properties of nanosize ferrite samples crucially depend on the synthesis temperature. In citrate precursor method, 450°C seems to be a critical temperature for growth of Ni-Co and Ni-Cu ferrites in pure phase. The growth of particles becomes much faster beyond this temperature.
2. Crystalline structure changes from cubic spinel to tetragonal spinel as 450°C temperature is crossed.
3. The particle size, lattice constant and also magnetization parameters show sharp changes at 450°C. This suggests that nucleation/growth/reaction mechanism is different below 450°C from that above it.

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Biographical notes

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