

Structural and Magnetic Properties of Cd²⁺ Substituted Copper Ferrite Synthesized via Ceramic and Wet-chemical Route: A Comparative Study

S. V. Rajmane^{1*}, U. B. Dindore², S. V. Khirsagar³, K. M. Jadhav⁴
¹Physics Department, Jawahar ASC College, Anadur, Tuljapur, Osmanabad
²Physics Department, Adarsh College, Omurga, Osmanabad.
³Physics Department, K.S. K. College, Beed.
⁴Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad.

Abstract

Ferrite powders of Cu_{1-x}Cd_xFe₂O₄ (x = 0.0 - 0.6) have been prepared by using ceramic (C) and wet chemical co-precipitation method (W). The powders were characterized by room temperature X-ray diffraction technique and hysteresis techniques. Structural parameters like lattice parameter (a), X-ray density (d_x) and particle size (t) were calculated by using the most intense peak of XRD plots (311). The difference in particle size for different preparation techniques changes the structural and magnetic properties. Saturation magnetization (M_s), coercivity (H_c), remnant magnetization (M_r) and magneton number (n_B) were calculated.
Keywords: Ceramic method, wet-chemical method, particle size, saturation magnetization.

INTRODUCTION

Variety in technological and industrial applications attracts scientists from physics and chemistry to put their efforts for studying the ferrite materials at nanoscale dimension [1-4]. Reduced size of materials towards nano-scale than the bulk has unique and unlike properties in particular copper ferrite with spinel structure. The microstructure and the surface morphology of such fine powders have large implication in controlling the parameters required for any particular application which in turn depends on the method adopted for synthesis [5]. The structural and magnetic properties of ferrites depend upon chemical composition, methods of preparation and sintering temperature [11, 12]. Physical methods, such as conventional ceramic method has some limitations for the synthesis of ferrite powders at nano structure. But in chemical methods which includes chemical co-precipitation [6], sol-gel [7], oxalate precipitate method [5], hydrothermal [8], citrate method [9], and combustion method [10] overcomes the limitations of physical methods. In the present paper we have reported our results on Cu_{1-x}Cd_xFe₂O₄ (x = 0.0 - 0.6) prepared via ceramic and co-precipitation method.

EXPERIMENTAL:

Cu_{1-x}Cd_xFe₂O₄ (for x = 0.0 - 0.6) composition have been prepared by solid state reaction technique and co-precipitation technique. To obtain the samples by ceramic method, powders of Copper oxide (CuO) from Reidel (99.9%), cadmium oxide (CdO) from Loba Chemicals (99%) and ferric oxide (Fe₂O₃) from Reidel Chemical (99%) was taken as initial materials. Appropriate amount of required powders was mixed thoroughly and grinded for three to four hours in agate mortar pestle. These powders are pre sintered at 950 °C for 12 hours and reground for two hour. The pre-sintered powders are then pressed into disc shaped pellets and are finally sintered at 1150 °C for 24 hours and slowly cooled at room temperature as to obtain the final products. Cupric Sulphate (CuSO₄·5H₂O) of Qualigens (99.5%), Cadmium Sulphate (3CdSO₄·8H₂O) A.R. grade (99%) and Ferrous Sulphate (FeSO₄·7H₂O) of Qualigens (99%) are used to prepare the Cu_{1-x}Cd_xFe₂O₄ ferrite samples by using co-precipitation method. All the starting materials were mixed together by their weight proportion. A two molar (2M) Solution of NaOH was prepared as a precipitant. It has been suggested that the solubility product constant (K_{sp}) of all the constituents always exceeds when the starting solution is added in to the precipitant. Therefore, in order to achieve simultaneous precipitation NaOH and H₂O₂ was added to the mixture of sulphates (pH = 3). A suspension (pH = 11) containing dark intermediate precipitation was heated and kept at a temperature 60 °C, while oxygen gas was bubbled uniformly into the suspension to stirrer it and to promote the oxidation reaction until all the intermediate precipitant changed into the dark brownish precipitate of spinal ferrite. The samples were filtered, washed several times by distilled water and acetone and then dried. The samples were heated at 150 °C for 4 hours to remove the water content. The wet samples were finally annealed at 950 °C for 12 hours. The prepared samples were then characterized by XRD for the determination of structural parameters and room temperature hysteresis loop technique to study the magnetic properties.

RESULTS AND DISCUSSION:

X-ray diffraction:

The powder X-ray diffraction (Philips, USA) of the prepared sample have been recorded to identify the crystalline phases present in the sample. When monochromatic beam of X-ray is incident on powder sample, it is reflected, the reflected rays interfere and interference is constructive only if the path difference between the interfacing rays is in

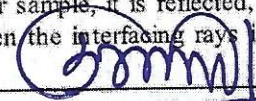

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Fig. 2. Hysteresis loop for (1-x) CuFe₂O₄ + (x) KNbO₃ ME composite

It is seen from hysteresis loop that the hysteresis loops of the composites shift towards the field axis with decreasing ferrite content. The hysteresis loops are used to obtain the values of saturation magnetization (M_s), remanent magnetization (M_r), and coercive field (H_c). The values of saturation magnetization (M_s), remanent magnetization (M_r) and coercive field (H_c) and magneton number (n_B) are given in Table 1. The saturation magnetization (M_s) decreases as ferrite content decreases. Using the values of saturation magnetization (M_s), the magneton number n_B (the saturation magnetization per formula unit in μ_B) was also calculated for all the composition.

The remanent magnetization (M_r) values obtained from M-H plots shows decreasing nature with increase in ferroelectric content. For $x = 1.0$ (pure ferroelectric), the M-H plot is not seen. The decrease in remanent magnetization (M_r) is due to increasing KNbO₃ content. It is evident from Table 1, that the coercivity of the composites decreases with KNbO₃ addition.

Table: 1. Saturation magnetization, Remnant magnetization, Coercive field and Remanence ratio for (1-x) CuFe₂O₄ +(x) KNbO₃ (x = 0.0-1.0)

Comp. 'x'	Saturation Magnetization M_s (emu/gm)	Remanent Magnetization M_r (emu/gm)	Coercive field H_c (Oe)	Remanence $R = (M_r / M_s)$
0.0	37.36	15.65	205.26	0.42
0.2	29.77	12.33	243.04	0.41
0.4	19.64	6.93	213.83	0.35
0.6	11.78	3.99	196.29	0.34
0.8	5.94	2.03	241.02	0.34

Conclusion:

The ME composites of (1-x) CuFe₂O₄+(x) KNbO₃ were prepared by solid state reaction method. Ferrite phase has a tetragonal structure and ferroelectric phase has a tetragonal perovskite structure was confirmed by XRD studies. The magnetic properties of above mentioned composites were investigated by using pulse field magnetic hysteresis loop tracer supplied by Magneta Company (Mumbai) at room temperature. The decrease in magnetic behaviour as observed from the values of M_s , M_r and H_c of composite under investigation is due to the reduction in the ferrite content of the composite.

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integral multiple of the wavelength of incident X-ray beam. The condition of constructive interference is given by Bragg's law,

$$2d \sin \theta = n\lambda \quad (1)$$

where, d is the inter-planer spacing, θ is glancing angle, λ is wavelength of incident radiation and n is an integer. The diffraction pattern were recorded in the 2θ range 20° to 80° with scanning rate of 2° per minute using Cu-K α radiation of wavelength 1.5418 Å. The unit cell dimensions are determined from the d -spacing of a line by making use of the cubic formula for inter planer spacing.

$$a = d (h^2 + k^2 + l^2)^{1/2} \quad (2)$$

where, a is the lattice constant, d is inter-planer spacing and $(h k l)$ is the miller indices.

Scherrer [5], shows that the mean diameter d of the crystalline composing a powder is related to the X-ray diffraction broadening (B) by the equation,

$$D = \frac{0.9\lambda}{B \cos \theta} \quad (3)$$

where, λ is the wavelength of incident radiation, B is the full width of half maxima, and θ is glancing angle for (311) peak.

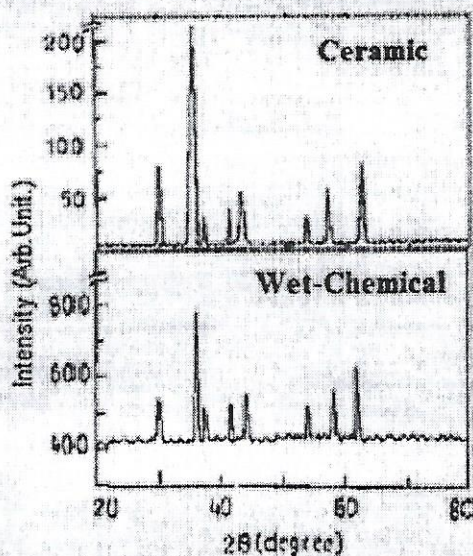


Fig. 1: Typical XRD patterns for $x = 0.0$ of W and C samples of $Cu_{1-x}Cd_xFe_2O_4$

Fig. 1 shows the typical X-ray diffraction peaks of the W and C samples for $x = 0.0$. The reflection intensity peaks (220), (311), (222), (400), (422), (333), (440) are observed for both C and W samples. The peak broadening is found slightly thick for W samples and the peak intensity is found slightly high for C samples. This difference in peak broadening and peak intensity is due to the fine particle nature of W samples and similar behaviour was reported earlier [5, 6]. For the sample $x = 0.0$, the structure is tetragonal and above $x \geq 0.1$ the structure of the samples become cubic spinel. The XRD data was used to determine structural parameter, like lattice constant (a), X-ray density (d_x), unit cell volume (V), and particle size (t). For $x = 0.0$ both ' a ' and ' c ' were calculated. The values of structural parameter for W and C samples are reported in Table 1. It is observed from Table 1 that the lattice constant of W sample is found higher than that of C sample. The synthesis method plays important role which changes the particle size of prepared materials. The fine particles make the difference in structural parameter of the bulk samples. The higher values of lattice constant for W samples cannot be explained only on the basis of degree of inversion. This can also be explain on the basis of different degrees of crystallinity of the W and C samples resulting from the difference in the temperature of crystallinity. The lower values of particle size are due to the difference of method of preparation and the heat treatment. The W samples are prepared at lower temperature, where as C samples were prepared at higher temperature.


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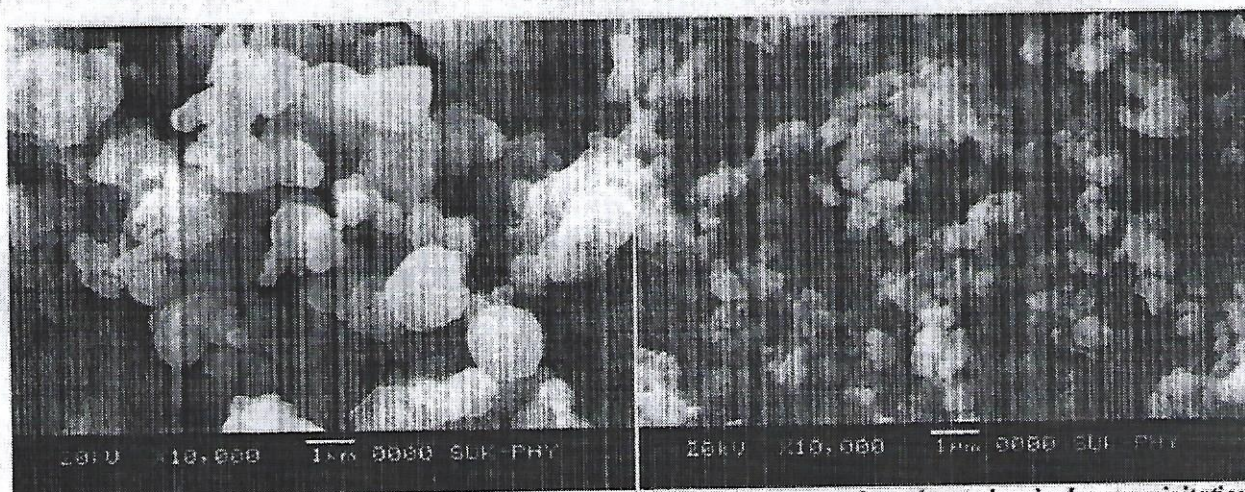


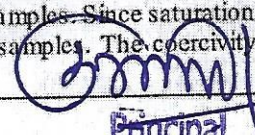
Fig.2: Scanning electron micrographs for $Cu_{1-x}Cd_xFe_2O_4$ prepared by ceramic and wet chemical co-precipitation technique.

The average crystallite size of Cu-Cd series was determined by Scherrer formula and the data related to the strongest peak of (311) of the XRD pattern. The average sizes of the particles ranges from 25 to 27 nm for W samples and 177 - 287Å for C samples. The values of particle size obtained from Scherer formula are given in Table 1. The crystallite size was also determined from SEM (Scanning Electron Micrograph). The SEM images are given in Fig. 2 for typical samples. The particle size obtained from SEM data is given in Table 1.

Table 1: Lattice constant (a), X-ray density (d_x), bulk density (d), particle size (t) and average grain size for $Cu_{1-x}Cd_xFe_2O_4$

Parameter	Preparation method	Composition -x							
		0.0	0.1	0.2	0.3	0.4	0.5	0.6	
Lattice constant a	C	a=8.39, c=8.83	8.42	8.45	8.48	8.51	8.55	8.59	
	W	a=8.41, c=8.88	8.43	8.46	8.5	8.53	8.57	8.6	
X ray Density	C	5.381	5.432	5.482	5.531	5.578	5.604	5.628	
	W	5.342	5.413	5.463	5.492	5.539	5.564	5.608	
Particle Size	XRD	C(Å)	177	270	280	273	286	287	283
		W (nm)	26	25	26	27	26	25	26
	SEM	C(Å)	210	--	250	--	300	--	290
		W (nm)	24	--	27	--	26	--	25

Magnetic hysteresis loops for all samples of the series $Cu_{1-x}Cd_xFe_2O_4$ were recorded at room temperature. Magnetization loops for the W samples with $x = 0.0 - 0.6$ are given in Fig. 2. Using hysteresis loops, the values of saturation magnetization (M_s), coercivity (H_c) and remanence magnetization (M_r) are obtained. The values of magnetic parameters obtained from hysteresis loop are given in Table 2. The magneton number (n_B) calculated from observed values of saturation magnetization is listed in Table 2. It can be seen from Table 2, the higher value of saturation magnetization for W samples compare to the C samples is attributed to the stronger co-valiancy effect effects arising from smaller cationic sites dimension. Further, according to spin alignment the net magnetic moment of W sample is expected to be low because of the higher degree of inversion, compare to the C samples. Since saturation magnetization M_s is high for W samples, the magneton number n_B is also low camper to C samples. The coercivity values for W


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samples are found to be large for W samples compare to C samples. This can be attributed to the fact that the particle size of the C samples is very low compare to W samples.

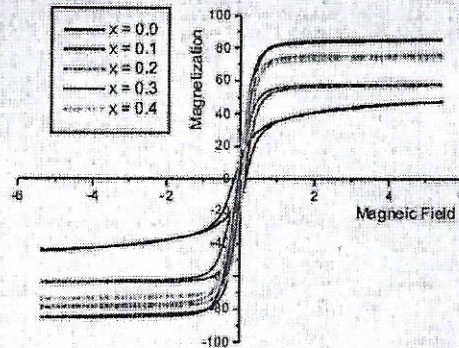


Fig.3: Hysteresis loops for the samples

Table 2 : Magnetization parameters for $Cu_{1-x}Cd_xFe_2O_4$ for (C) and (W) Sample.

Parameter	Preparative method	Composition -x						
		0.0	0.1	0.2	0.3	0.4	0.5	0.6
M_s (emu/gm)	C	27.09	41.54	45.93	49.54	49.68	44.63	19.28
	W	47.55	85.11	76.00	85.51	74.31	65.94	21.07
M_r (emu/gm)	C	7.19	3.85	4.39	6.53	6.95	7.07	5.66
	W	14.88	1.87	4.2	1.08	7.91	0.83	0.04
H_c (Oe)	C(Å)	245.13	56.82	63.31	76.3	79.55	133.12	97.40
	W (nm)	158.11	9.52	18.32	33.95	23.43	18.38	28.38

CONCLUSIONS

The samples of the series $Cu_{1-x}Cd_xFe_2O_4$ were successfully prepared by using ceramic and wet chemical co-precipitation method. XRD data confirms the cubic spinel structure of the samples. Addition of Cd in copper ferrite decreases the net magnetization and also the coercive force. The sintering temperature changes the particle size which affect on the structural and magnetic properties of copper ferrite.

ACKNOWLEDGEMENT:

Author SVR is thankful to Prof. Dr. K. M. Jadhav (Dept. of Physics, Dr. B.A.M.U. Aurangabad) for fruitful discussions and extending experimental facilities.

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