

PHYSICAL APPEARANCE OF Cd-SUBSTITUTED COBALT FERRITE NANOPARTICLES

C.M. KALE*¹, M.K. BABREKAR¹, V.K. BAROTE², S.D. MORE³, S.J. SHUKLA³

^{*1}Department of Physics, Indraraj Art, Commerce, and Science College, Sillod, ²Department of Physics, Sant Dnyaneshwar Mahavidyalaya, Soegaon ³Research Center, Deogiri College, Aurangabad, (M.S.) India. Email: cmkale1973@gmail.com

Received: 25 January 2020, Revised and Accepted: 17 March 2020

ABSTRACT

Objective: Ferrites are an important class of magnetic materials and the most important property of ferrite is its high electrical resistivity, low eddy current, and dielectric losses. The nanostructured ultrafine samples of the ferrite series are prepared by using the Sol-Gel auto combustion method. The prepared samples were characterized by X-ray diffraction (XRD) and Scanning Electron Micrograph (SEM) techniques. X-ray analysis confirms the formation of a single-phase cubic spinel structure.

Materials and Methods: A series of polycrystalline nano ferrite having the chemical formula $Co_{1-x}Cd_xFe_2O_4$ (where, $x= 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$) were prepared by using Sol-Gel auto combustion method. The starting materials cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$), ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), Cadmium nitrate ($Cd(NO_3)_2 \cdot 9H_2O$), citric acid ($C_6H_8O_7 \cdot H_2O$) and ammonia (NH_3) solution were taken in 99.9% AR grade.

Results: In the $Co_{1-x}Cd_xFe_2O_4$ ferrite system, the lattice constant, hopping length (L_A and L_B) and A-site (A-O) and B-site (B-O) bond length of the samples has been increased due to the increase in cadmium content. The crystalline size of the samples lies in the range between 18nm to 33nm calculated by using Sherrer's formula

Conclusion: Nano-sized $Co_{1-x}Cd_xFe_2O_4$ system was synthesized by using the sol-gel technique.

Keywords: - Nano ferrite, X-ray diffraction, Sol-gel Auto combustion, SEM.

INTRODUCTION

During the last few decades, ferrites have been studied extensively because of their importance in the basis as well as in applied research [1]. The spinel ferrite having general formula MFe_2O_4 , (where; M = a divalent cation) is belongs to an important class of magnetic material because of their remarkable magnetic properties particularly in the radiofrequency region, high electrical resistivity, low eddy current and dielectric losses, high saturation magnetization, high Curie temperature, mechanical hardness and chemical stability [2]. The important magnetic and electrical properties of ferrite mainly depend on the methods of preparation, type and amount of dopant, cation distribution, etc. [3]. Based on the crystal structure, ferrites are grouped into three important classes, namely spinel ferrite, garnet and hexaferrite [4]. The crystal structure of spinel ferrite consists of two interstitial sites, tetrahedral (A) and octahedral [B] sites, in which cations are occupied.

The structural properties of ferrite materials can be changed by the substitution of various types of M^{2+} ions among divalent cations. The effects of high-density divalent metal ions on the structural, magnetic and electrical properties of ferrite were studied by many researchers [5, 6]. Few reports are available to show the effect of high-density cadmium cations substitution on the properties of cobalt ferrite [7].

This work aims to investigate the structural effect of cadmium substitution ions on the highly magnetic cobalt material with the chemical formula $Co_{1-x}Cd_xFe_2O_4$, where $0.0 \leq x \leq 0.5$ in the step of 0.1, were prepared by using Sol-Gel auto combustion method. The structural properties were investigated using X-ray diffractometry, SEM and other measurements.

EXPERIMENTAL

The ultrafine samples of the ferrite series $Co_{1-x}Cd_xFe_2O_4$ (where, $x= 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$) prepared by using Sol-Gel auto combustion method. The starting samples were taken in the form of high purity.

A. R. grade (>99%) nitrates as, Cobalt Nitrate ($Co(NO_3)_2 \cdot 6H_2O$), Cadmium Nitrate ($Cd(NO_3)_2 \cdot 9H_2O$), and ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$). The molar ratio of metal nitrates to citric acid was taken as 1:3. The metal nitrates were dissolved together in a minimum amount of double distilled water to get a clear solution. An aqueous solution of citric acid was mixed with metal nitrates solution, then ammonia solution was slowly added to adjust the pH at 7. The mixed solution was kept on to a hot plate and the solution is continuously stirred at 90°C. The steps of the formation of ultrafine samples of the ferrite series $Co_{1-x}Cd_xFe_2O_4$ as shown in the following photograph Fig.1.

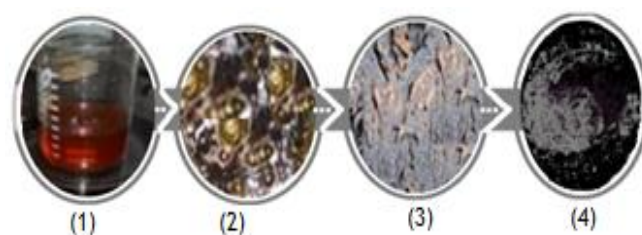


Fig.1: Steps of formation of ferrite sample by Sol-Gel auto combustion method.

- Sol solution at continuous heating and stirring.
- Gel solution before ash.
- Ash of ferrite material.
- Fine sintered ferrite powder.

The obtained powder was then subjected to further heating treatment into a muffle furnace at relatively low-temperature 400°C for six hours. The final product is then ground and subjected to further study.

The powder X-ray diffraction (XRD) patterns were recorded at room temperature in the 2θ range of 20° to 80° and scanning rate 2 degrees per minute to confirm the formation of a single-phase cubic spinel structure. The particle size in the nanometer range was obtained by using the Scherrer formula. The particle size was also determined from SEM images by using the double line intercept method.

RESULTS AND DISCUSSION

X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) technique is very basic techniques, have been used extensively for the characterization of the structure of surfaces and interfaces and crystal structures. The techniques, however, work on the principle of Bragg diffraction law, i. e. $2d\sin\theta = n\lambda$. The following Fig. 2 shows the typical XRD pattern of, $\text{Co}_{0.8}\text{Cd}_{0.2}\text{Fe}_2\text{O}_4$ ferrite system.

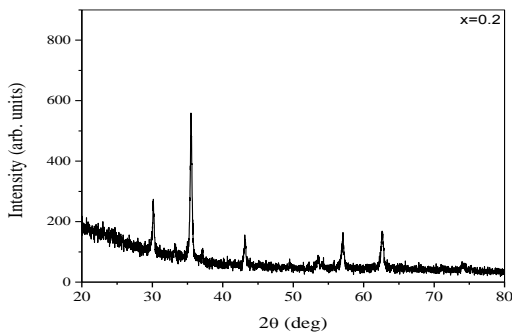


Fig. 2: XRD pattern of $\text{Co}_{0.8}\text{Cd}_{0.2}\text{Fe}_2\text{O}_4$ ferrite

Table 1: Lattice constant (a), Particle size (t), Hopping length (L_A , L_B), X-ray density (dx) of $\text{Co}_{1+x}\text{Cd}_x\text{Fe}_2\text{O}_4$ ferrite ($x = 0.0$ to 0.5) system

Cd content x	Lattice constant 'a' (Å)	Particle size 't'(nm)		Hopping length (Å)		X-ray density 'dx' gm/cm ³
		XRD	SEM	L _A	L _B	
0.0	8.3652	33.27	33	3.9966	2.9579	3.997
0.1	8.3662	29.36	30	4.0861	2.9583	4.086
0.2	8.3738	29.35	31	4.1659	2.961	4.166
0.3	8.3840	17.84	18	4.2402	2.9646	4.240
0.4	8.3951	27.72	26	4.3144	2.9685	4.314
0.5	8.3976	22.68	24	4.4006	2.9694	4.401

Scanning Electron Micrograph (SEM) analysis

The crystallite size determined from SEM (Scanning Electron Micrograph). The typical SEM images are given in the following Fig. 3, for sample, $x = 0.2$. The particle size obtained using the intersection method from SEM is varies between 18 nm to 33 nm and the obtained values are given in Table-1.

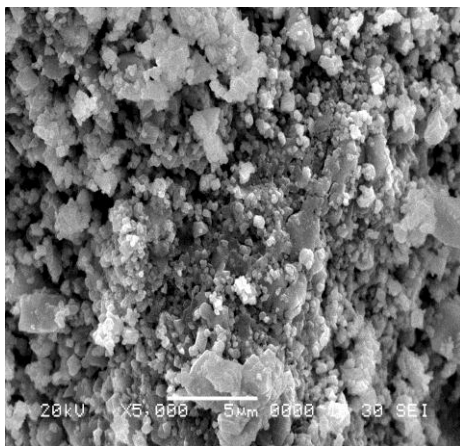


Fig.3: SEM image of $\text{Co}_{0.8}\text{Cd}_{0.2}\text{Fe}_2\text{O}_4$ ferrite

The XRD peak shows the sharp Bragg's peaks and there is no impurity peak observed. All the peaks are indexed by miller indices and it reveals that all the samples possess the single-phase cubic spinel structure. It is observed that the lattice parameter increases with an increase in Cd content 'x'. It is due to the replacement of smaller ionic radii atom Co^{2+} (0.82 A.U.) is replaced by larger ionic radii of Cd^{2+} (1.03 A.U.) [8].

Particle size and X-ray density

The other structural parameters like Particle size 't' and X-ray density 'dx' was calculated from the data obtained from X-ray diffraction patterns. The average crystallite size of the prepared samples was determined by Scherrer formula (stated below) using the highest intensity strongest peak of (311). The values of particle size obtained X-ray diffraction data are given in Table. The average sizes of the particles were found in the range 18nm to 33nm. The obtained results are close to the result obtained from SEM images.

The X-ray density (dx) of all the samples was calculated using the molecular weight and volume of the unit cell using the following relation.

$$dx = \frac{8M}{Na^3} \text{ gm/cm}^3$$

where M is molecular weight, N is Avogadro's number and a is the lattice constant.

The values of X-ray density obtained from the above equation and lattice constant (a), particle size (t), hopping length (L_A , L_B), listed in Table-1. It is observed that the X-ray density increases with the substitution of Cd^{2+} ions. The increase in X-ray density is inversely correlated with the substitution of cadmium ions in cobalt ferrite.

The small number of pores in SEM images reveals that the sintering is done satisfactorily for all the specimens. The effect of increasing cadmium content on the investigated samples is the enhancement of the grain growth as seen from the scanning electron micrographs [9]. Uniform grains are increased with increasing Cd^{2+} content x.

Hopping length

The hopping length L between magnetic ions (the distance between the ions) in the tetrahedral A-site and octahedral B-site be calculated by the equations are,

$$L_A = \frac{a\sqrt{3}}{4} \quad \text{and} \quad L_B = \frac{a\sqrt{2}}{4}$$

The estimated values of hopping length are given in Table-1 above. From Table-1, it is observed that the distance between the magnetic ions increases as the Cd content increases. This may be explained based on the difference in ionic radii of constituent ions Cd^{2+} and Co^{2+} .

Bond length

The bond length of tetrahedral (A) site ' d_A ' (the shortest distance between A-site cation and oxygen ion i.e A-O) and octahedral [B] site ' d_B ' (the shortest distance between B-site cation and oxygen ion i.e B-O), calculated by using the values of lattice constant 'a'

(A.U.) and oxygen positional parameter 'u', the values of tetrahedral and octahedral bond length (d_{Ax}) and (d_{Bx}), shared tetrahedral and octahedral edge can be calculated using the following relations.

$$d_{Ax} = a \sqrt{3} (u - 1/4)$$

$$d_{Bx} = a [3u^2 - (11/4)u + 43/64]^{1/2}$$

The values calculated from the above-mentioned expression are presented in Table-2.

Table2: The tetrahedral bond length (dAX) and octahedral bond length (d BX) of $Co_{1-x}Cd_xFe_2O_4$ ferrite system

Cd content	0.0	0.1	0.2	0.3	0.4	0.5
d_{Ax} (Å)	1.8980	1.8982	1.8999	1.9023	1.9048	1.9053
d_{Bx} (Å)	2.0095	2.0098	2.0116	2.0141	2.0167	2.0173

The **Table-2** indicates that the tetrahedral bond length d_{Ax} and octahedral bond length d_{Bx} decreases as Cd^{2+} content 'x' increases.

CONCLUSIONS

The Nano-crystalline cadmium substituted cobalt ferrite $Co_{1-x}Cd_xFe_2O_4$ (where, $x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$) system were synthesized successfully by using sol-gel auto combustion technique. The following are the conclusions are drawn in front of the present investigations.

$Co_{1-x}Cd_xFe_2O_4$ system was synthesized successfully by using the sol-gel auto combustion technique.

The X-ray powder diffraction pattern shows the formation of the cubic spinel structure of all the samples.

The crystallite size of the powders, calculated by the Sherrer method amounts to be between 17 - 33 nm.

The lattice constant increases with a decrease in cadmium content x.

The value of L_A and L_B varies concerning the lattice constant.

The values of tetrahedral and octahedral bond length (d_{Ax}) and (d_{Bx}) are good agreement with the previous report.

SEM study reveals that the grain size of all the samples is in the nanometer dimension.

ACKNOWLEDGMENT

The authors (CMK) is thankful to **Prof. K. M. Jadhav** Dr. B. A. M. U. Aurangabad, for their kind help and cooperation while fruitful discussion.

REFERENCES

1. Jan. Smith, H. Wijn, Ferrites, Philips Technical Library, Cleaver-Home Press Ltd., Netherland, 1959, pp. 299
2. V. B. Kawade, G. K. Bichile, K. M. Jadhav, *Mate. Lett.* 42(2000)33.
3. A.K.M. Akther Hossaina, S.T. Mahmuda, M. Sekib, T. Kawaib, H. Tabatab. *J. Magn. and Magn. Mate.* 312 (2007) 210.
4. Vinod N. Dhage, M. L. Mane, M. K. Babrekar, C. M. Kale, K. M. Jadhav. *J. Alloys Compd.* 509 (2011) 4394-4398
5. K. Kamala Bharathi, G. Markandeyulu, and C. V. Ramana. *J. Phys. Chem, C* 115 (2011) 554.
6. Muthafar F. Al-Hilli, Sean Li, Kassim S. Kassim. *J. Magn. Magn. Mate.* 324 (2012) 873.
7. Misbah-ul. Islam, K. A. Hushmi, M. U. Rana, Tabbas. *Solid State Com.*, 121 (2002) 51.
8. M. Siva Ram Prasad, B. B. V. S. V. Prasad, B. Rajesh, K. H. Rao, K. V. Ramesh, *J. Magn. Magn. Mater.* 323 (2011) 2115-2121
9. M. Raghassudha, D. Ravinder, P. Veerasomaiah, *Adv.in Mate.Phy. and Chem.* 3, (2013) 89-96