

Structural and Magnetic Properties of Cerium Doped Cobalt Ferrite Nanoparticles

Grish Chandra¹, R.C. Srivastava² and K.Ashokan³,

¹Deptt. of Physics, D.S.B. Campus, Kumaun University, Nainital, Uttarakhand, India.

²G. B. Pant University of Ag. & Technology, Pantnagar 263145, Uttarakhand, India

³Inter University Accelerator Centre, Aruna Ali Asaf Marg, New Delhi 110067, India.

Abstract. A series of cerium doped cobalt ferrites were synthesized using the nitrate method. The effects of Fe³⁺ ions substitution by Ce³⁺ ions on structural and magnetic properties of cobalt ferrite nanoparticles were investigated. Crystallite size of the nanoparticles of cobalt ferrite depends directly on the thermal treatment and their compositions. Specific surface area varies from 108 to 28 m²/g as the crystallite size increases from 10nm to 40nm. X-ray density is found to be maximum for the lowest sintering temperature and it becomes almost constant above the sintering temperature of 500°C. Variation of lattice parameter is complex with sintering temperature. The value of saturation magnetization is increased gradually with crystallite size. The value of coercivity is decreased with sintering temperature and the remanence is first increased and then decreased. The value of the saturation magnetization for larger size particles of the pure cobalt is significantly higher (83.4 emu/g) than the bulk value (80 emu/g).

Keywords: Cobalt ferrite, Saturation Magnetization, Coercivity, Remanence, Hysteresis.

1. Introduction

Ferrites are magnetic ceramics of great importance in the production of electronic components as they have wide applications from microwave to radio frequency range [1-2]. Cobalt ferrite is a well known hard magnetic material with high coercivity and moderate magnetization. These properties along with their physical and chemical stability make them suitable for magnetic recording applications such as in audio and videotapes and in high density digital recording discs etc. Cobalt ferrite is ordinarily an almost inverse cubic spinel in which the degree of inversion is critically determined by the preparation conditions. It is having ferrimagnetic behavior with a Curie temperature of around 520°C [3]. The magnetic moment among lanthanide ions vary from 0 (such as La³⁺) to 10.5 μ_B (Dy³⁺). Moreover, lanthanide ions can be isotropic or anisotropic due to the variation in the f electron orbital contribution to the magnetic interactions. Therefore, the diverse properties of the Ln³⁺ (lanthanide) ions make them interesting candidates for doping CoFe₂O₄ nanoparticles to modulate the magnetic characteristics [4].

2. Experimental Details

A series of cerium doped cobalt ferrite (CoCe_xFe_{2-x}O₄ with x=0.00, 0.02 and 0.04) powder was synthesized by using nitrate route [5-6]. The stoichiometric amounts of Fe(NO₃)₃·9H₂O, Co(NO₃)₂·6H₂O and Ce(NO₃)₃·6H₂O were dissolved in distilled water. In the aqueous salt solution, citric acid solution was added with the cations to citric acid molar ratio of 1:3. The solution was heated at 80°C under constant magnetic stirring until the solution got converted into a viscous gel, and was allowed to cool at room temperature. The cooled gel was dried in a furnace at 100°C for overnight to form the precursor material. The precursor material was sintered at different temperatures ranging from 300 to 900°C for 2 hrs to get the nanoparticles of cobalt ferrite having different particle size.

3. Results and Discussion

3.1. XRD study

Figure 1 shows representative XRD patterns of the cobalt ferrite sintered at 300 and 900°C and it confirms the formation of pure phase of $\text{CoCe}_x\text{Fe}_{2-x}\text{O}_4$ ($x=0.00, 0.02$ and 0.04) nanoparticles. The phase analysis was done with JCPDS card number 03-0864. The crystallite size was determined by using the Scherrer formula for strongest peak obtained from XRD patterns [7] as: $\langle D \rangle = \frac{K\lambda}{\beta \cos \theta}$, where λ is the wavelength of X-ray used, θ is the Bragg's angle, β is the full width at half maximum (FWHM) in radian and K is a constant approximately equal to 0.9. The average crystallite size for $\text{CoCe}_x\text{Fe}_{2-x}\text{O}_4$ samples increase from 10 ± 1 to 40 ± 1 nm for $x=0.00$, 12 ± 1 to 50 ± 1 nm for $x=0.02$ and 10 ± 1 to 57 ± 1 nm for $x=0.04$, as the sintering temperature increases from 300 to 900°C. These results are in good agreement with the values reported in the literature[8-9]. The lattice parameters were calculated with the help of the relation: $a = d_{hkl} \sqrt{h^2 + k^2 + l^2}$, where h,k,l are the Miller indices of the planes having interplaner spacing ' d_{hkl} '. The introduction of small amount of cerium ion gives a detectable change in the lattice constant. For pure cobalt ferrite lattice parameter was found to be $8.341 \pm 002 \text{ \AA}$ at the sintering temperature of 300°C. This value increases to $8.385 \pm 002 \text{ \AA}$ at the sintering temperature of 400°C and remains almost constant up to the sintering temperature of 900°C. In case of doped ferrites ($x=0.02$ and 0.04) also similar behavior of lattice parameter with the sintering temperature is obtained. Since the ionic radius of Ce^{+3} ion (1.02 \AA) is higher than that of Fe^{+3} ion (0.61 \AA), the replacement of iron ion by cerium ion leads to the increase of lattice parameter. Assuming all the particles to be of spherical shape, the value of specific surface area of nanoparticles was determined by using the relation [10-12] $S = 6000/D\rho \text{ m}^2/\text{g}$, where 6000 is the form factor for spherical particles, D is particle diameter and ρ is the x-ray density. It was found that specific surface area decreases almost linearly as the sintering temperature increases from 300 to 900°C. The value of specific surface area for pure cobalt ferrite varies from 108 to $28 \text{ m}^2/\text{g}$ while it varies from 112 to $22 \text{ m}^2/\text{g}$ for the Ce concentration of $x=0.02$ and 123 to $19 \text{ m}^2/\text{g}$ for $x=0.04$. These values are in good agreement with the values reported by other workers [12]. X-ray density ρ was calculated by using formula [13] $\rho = 8M / Na^3 \text{ g/cm}^3$, where M, N and a are the molecular weight, Avogadro's number and lattice parameter respectively. The factor 8 is due to the fact that there are eight molecules of cobalt ferrite per unit cell. The values of x-ray density for cobalt ferrite ($x=0.00$) decreases from 5.37 to 5.28 g/cm^3 , as the sintering temperature increases from 300 to 400°C. Above this temperature it remains almost constant at a value of 5.28 g/cm^3 . The value of x-ray density for the doped ferrites ($x=0.02$ and 0.04) show similar behavior with respect to the sintering temperature. The decrease in density may be due to increase in porosity in the system.

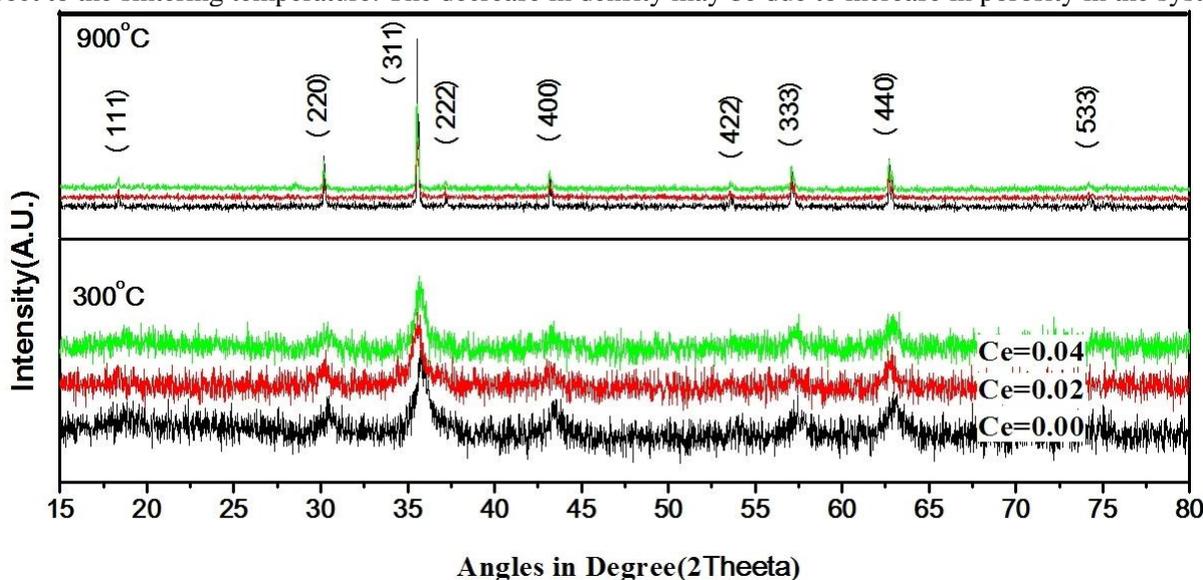


Fig. 1: XRD patterns of $\text{CoCe}_x\text{Fe}_{2-x}\text{O}_4$ ($x=0.00-0.04$) samples sintered at 300 and 900°C.

3.2. VSM study

Figure 2 shows few representative hysteresis loops for the samples sintered at 300 and 700°C. It is observed that the magnetization of the specimen do not saturate up to a field of 10 kOe. The saturation

magnetization was calculated by fitting the high field magnetization data using the relation [14]: $M = M_s(1 - a/H)$, where M_s is the saturation magnetisation, 'a' is the fitting parameter and H is applied external magnetic field. The specific magnetization measured at room temperature at high field strength varies almost linearly with $1/H$. The saturation magnetization is estimated from the intercept with the magnetization axis as $1/H$ approaches to zero. Figure 3(a) shows the variation of coercivity with sintering temperature. The coercivity of pure cobalt ferrite decreases from 1488 to 311 Oe as the sintering temperature increases from 300 to 900°C. For cerium doped cobalt ferrite ($x=0.02$ and 0.04) coercivity decreases from 1177 to 567 Oe and 1144 to 498 Oe respectively. The variation of coercivity may be explained on the basis of domain structure, critical diameter and the anisotropy of the crystal with the increase of sintering temperature, which ultimately controls the grain size of the specimens. In the single domain region as the grain size decreases the coercivity decreases because of thermal effects [10,13,15]. In the multi domain region the variation of coercivity with grain size can be expressed as $H_c = a + b/D$, where 'a' and 'b' are constants and 'D' is the diameter of the particle. Hence in the multi domain region the coercivity decreases as the particle size increases. The variation of remanence and saturation magnetization with different heat treatments are shown in figure 3(b) & (c).

The saturation magnetization of the samples increases almost monotonically with the increase of sintering temperature both for pure and doped cobalt ferrite. For $x=0.00$ (cobalt ferrite) it increases from 35.2 to 83.4 emu/g; for $x=0.02$ from 33.5 to 78.2 emu/g and for $x=0.04$ from 29.2 to 73.7 emu/g as the sintering temperature increases from 300 to 900°C. These values of M_s are larger than the values reported in the literature [16]. For smaller size of particles M_s value is low, this behavior may be attributed to the surface effects that arises due to the distortion of the magnetic moment at the nanocrystallite surface which could serve as a non-magnetic layer [17]. The effects are weaker as the size of the nanoparticle is larger.

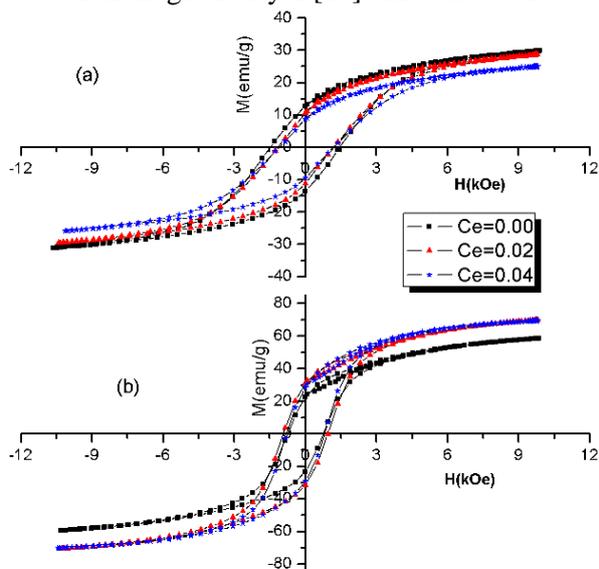


Fig. 2: M vs H loops for $\text{CoCe}_x\text{Fe}_{2-x}\text{O}_4$ ($x=0.00, 0.02$ and 0.04) samples sintered at (a) 300 and (b) 700°C.

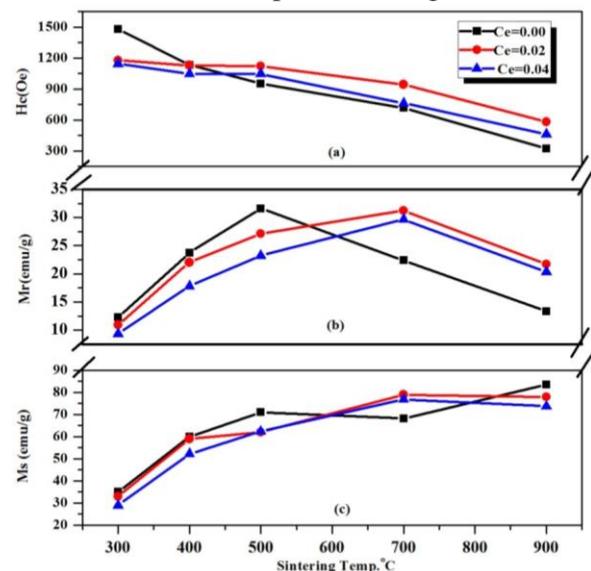


Fig. 3: Variation of (a) H_c , (b) M_r and (c) M_s with sintering temp. for $\text{CoCe}_x\text{Fe}_{2-x}\text{O}_4$ samples.

4. Conclusion

XRD patterns show the formation of pure crystalline phase of the cobalt ferrite by using the nitrate route. The crystallite size varies from 10 to 40 nm depending on the sintering temperature of the specimen. The specific surface area decreases with the increase of crystallite size for all the compositions. Vibrating sample magnetometer study shows the ferrimagnetic nature of the cobalt ferrite nanoparticles. Saturation magnetization increases from 35 to 84 emu/g as the sintering temperature varies from 300 to 900°C for pure cobalt ferrite.

5. Acknowledgements

The authors are thankful to the Director, IUC Indore centre for providing the experimental facilities. Special thanks are also due to Dr. Alok Banerjee, IUC Indore centre for taking keen interest in the magnetic measurements and useful suggestions.

6. References

- [1] Modern ferrite Technology, second edition, 2006 Springer Science Business Media, Inc.
- [2] Oxide Magn. Mat., K.J. Standley, Oxford Univ. Press 1962.
- [3] M. Rajendran, R. C. Pullar, A. K. Bhattacharya, D. Das, S. N. Chintalapudi, C. K. Majumdar, J. Magn. Magn. Mat. 232 (2001) 71– 83.
- [4] Myrtill L. Kahn and Z. John Zhang, App. Phy. Lett. Vol. 78, No. 23,4 June 2001.
- [5] J. P. Singh, R. S. Payal, R. C. Srivastava, H. M. Agrawal, Prem Chand, Amita Tripathi and R. P. Tripathi, J. Phys.: Conf. Ser. 217(2010) 012108.
- [6] Jae – Gwang Lee, Jae Yun Park, Chul Sung Kim, J. Mat. Sci.33(1998) 3965-3968.
- [7] B. D. Cullity-Introduction to X-ray diffraction (Addison-wesley, Newyork, 1972).
- [8] R.N. Panda, J.C.Shih, T.S.Chin, J. Magn. Magn. Mat. 257(2003)79-86.
- [9] S.H. Xaio, W.F.Jiang, L.Y.Li, X.J.Li, Mate. Chem. and Phy. 106(2007)82-87.
- [10] M. George, A.M.John.Swapna S. Nair, P.A.Roy, M.R.Anantharaman, J. Magn. Magn. Mat. 302 (2006) 190-195.
- [11] Wafaa Bayoumi, J. Mater Sci (2007)42:8254-8261.
- [12] Juliana B Silva, Walter de Brito, Nelcy D.S. Mohallem, Mat. Sci. and Engg. B 112(2004)182-187.
- [13] Sonal Singhal, S.K.Barthwal, Kailash Chandra, J. Magn. Magn. Mater. 306 (2006)233-240.
- [14] Richard J. Harrison, Andrew Putnis, American Mineralogist, Vol. 80, pages 213-221, 1995.
- [15] B. D. Cullity-Introduction to Magnetic Materials (Addison-wesley, Newyork, 1972).
- [16] Xiang-Hui Huang, Zhen-Hua chen, Scripta Materiala 54(2006)169-173.
- [17] Cheng-Chien Wang, I-Han Chen, Chun-Rong Lin, J. Magn. Magn. Mat., 304 (2006) e451-e453.



Dr. Grish Chandra was born on 01st May 1983 at District Almora, Uttarakhand. He passed his 10th from Inter College Machhor Talla Salt, Almora in 1999 and 12th from Government Inter College Bhatronjkan District Nainital in 2002. He received his B.Sc. degree from Govt. P.G. College, Ramnagar in 2005. Thereafter, he joined the college of Post Graduate Studies of G.B. Pant University of Agriculture and Technology in the year 2005 for the degree of Masters of Science in Physics. In August 2007, he joined Ph.D. degree programme in Physics at Department of Physics. The author was awarded by Rajeev Gandhi National Fellowship during Ph.D. programme. He Qualified the CSIR-NET, GATE and DRDO-SET exams and appointed as Assistant Professor at D.S.B. Campus Nainital in 2010.



Dr. R.C. Srivastava is working as Prof. & Head, Dept. of Physics, G.B. Pant University of Ag. & Technology, Pantnagar. He did his Ph.D. from I.I.T. Kanpur in 1990. He has teaching experience of about twenty five years at the U.G. & P.G. levels. His current area of research interest is magnetic nanomaterials, nanocomposites, thin films, swift heavy ion irradiation modification of materials etc. He has published about fifty research papers in peer reviewed national and international journals.



Dr. K. Asokan joined Inter-University Accelerator Centre in 1994 as scientist. He obtained PhD (Physics) from University of Rajasthan, Jaipur in the year 1992. As a part of post doctoral studies, he has visited Taiwan in 2000-01 and South Korea in 2008-9. He has over 150 research publications covering condensed matter physics and Materials Science. His major research interests are (i) ion beam interaction in materials and (ii) understanding the electronic structure of materials using Synchrotron Radiation based techniques mainly x-ray absorption spectroscopy.