



Study of Structural and Magnetic Properties of Cobalt substituted Calcium Hexaferrites

CH. MAMATHA¹, SANKARARAO G² K. G REWATKAR³ B.
SREEDHAR⁴, M. KRISHNAIAH*, C. S. PRAKASH@

^{1&2}Department of physics MVJ College Of Engg, Channasandra, Bangalore. India
(mamathasree@yahoo.co.in)

³Department of Physics Dr. Ambedkar College, Deeksh Bhoomi, Nagpur, MS, India.

⁴Inorganic and Physical Chemistry Division, IICT, Hyderabad, India.

* Department of physics, Sri Venkateshwara University, Tirupati, India.

@ Department of physics, SJCT, Chikkaballapur, Karnataka, India.

ABSTRACT:

Off late, the need of new magnetic materials is distinct interest of researchers on the study of hexagonal ferrites, due to their demanding applications in emerging technologies. In the present work, Calcium hexaferrite nanoparticles substituted with Cobalt with general formula $\text{CaCo}_x\text{Fe}_{12-x}\text{O}_{19}$ ($0 \leq x \leq 4$) were successfully synthesized by solution combustion synthesis. Structural and magnetic properties are studied and reported. The structural properties are characterized by X-ray diffractometer and SEM. The XRD data of all the samples have confirmed the formation of single-phase M-type hexagonal ferrites with the space group of $P6_3/mmc$. Magnetic properties are studied with the help of vibrating sample magnetometer (VSM). Saturation magnetisation, remanent magnetisation, Coercive field are calculated and reported. Results of VSM studies show the increase in saturation magnetization with the substitution.

Keywords: hexaferrite, Combustion, Remanent magnetization and Coercive field.

1. INTRODUCTION

Hexagonal ferrites are a large family of ferrimagnetic materials. Among these, M-type hexaferrites are the most popular due to their large applications as permanent magnets. Substituted hexaferrites belong to M-Type with general formula $\text{MFe}_{12}\text{O}_{19}$ where M is usually barium, strontium, Calcium or Lead, are of the significant attractions for researchers because of their applications in the field of material science as permanent magnets, microwave devices so on and so forth (1-5). The basic structure is hexagonal with all 38 oxygen ions occupying the interstitial sites forming a close packed assembly. 24 ferric ions occupy five different locations in the unit cell such as 2a, 2b, 4f₁, 4f₂ and 12k, where 2a, 4f₂ and 12k are octahedral, 4f₁ is tetrahedral and 2b is bi-pyramidal sites. The magnetic nature of magnetoplumbites is determined by the substituted trivalent ions for ferric ions, which occupy different sites in the structure (6-10). The Fe⁺³ ions when replaced partially by other trivalent metal ions, the magnetic properties of the calcium ferrite under go changes [11,12]. To prepare Hexagonal ferrites,





various synthesis methods like chemical co-precipitation [13], hydrothermal [14], sol-gel [15,16], combustion [17] etc. have been developed. In the present work, Calcium hexaferrites substituted with trivalent Co ions synthesized by combustion method are studied and reported.

2. EXPERIMENTAL

2.1 Synthesis techniques: Calcium hexaferrites substituted with trivalent Co^{+3} ions with general formula $\text{CaCo}_x\text{Fe}_{12-x}\text{O}_{19}$ ($0 \leq x \leq 4$) have been synthesized successfully by solution combustion technique. Samples were prepared with AR grade calcium nitrate, iron nitrate and Cobalt nitrate. ODH ($\text{C}_2\text{H}_6\text{N}_4\text{O}_2$) was used as fuel. Samples were calcinated at 900°C for 3 hours and allowed to cool gradually.

2.2. Structural studies: The structural characterization of the samples was performed by PANalytical X'pert Pro diffractometer with Cu-K α radiation ($\lambda=1.5405\text{\AA}$) in the 2θ range of 10-80, in angular steps of 0.02° . The average particle size D , was determined from line broadening of (107) reflection using Scherrer formula given by

$$d = \frac{k\lambda}{\beta \cos \theta}$$

Where β is the angular line width at half maximum intensity and θ the Bragg angle for the that peak. Values of lattice constant 'a' and 'c' and unit cell volume 'V' were calculated by using following equations and are given in table 1. The morphology and size of the particles were studied using SEM (fig. 2.) The particle size of each sample was analysed from the SEM images with the help of Image J software and the values are found to be in comparable with calculated values.

2.3. Magnetic studies: The magnetic properties were studied using vibrating sample magnetometer at room temperature. Applying the field in the range of -20K - +20K, carried out measurements. Saturation magnetization, Coercive field and Remanent magnetization were calculated and reported (Table 2).

3. RESULTS AND DISCUSSION

3.1 Structural analysis: X-ray diffraction spectrum for all the samples is shown in Figure 1. X-ray diffraction studies confirm the formation of



hexaferrites with the space group $P6_3/mmc$. There is a small shift in the peak position with the increase of substituting ion. This is due to the small ionic radius of Co^{+3} (0.61 \AA) compared to the ionic radius of Fe^{+3} (0.65 \AA). Structural parameters of the samples are given in table 1. There is a variation in the particle size with substitution. Volume of the cell also slightly decreases with the increase in substitution.

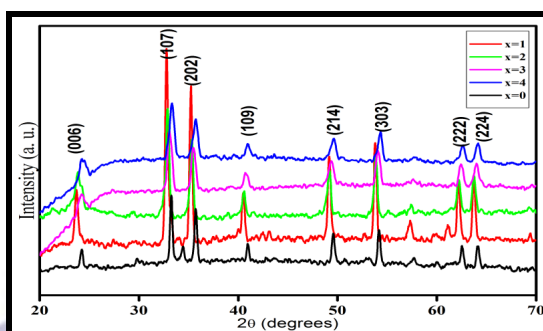


Figure. 1: XRD spectrum of $CaCo_xFe_{12-x}O_{19}$

Table 1: Structural parameters of $CaCo_xFe_{12-x}O_{19}$

| Sample $CaCo_xFe_{12-x}O_{19}$ | D (nm) | a(\AA) | c(\AA) | V(\AA^3) |
|-----------------------------------|-----------|-------------------|-------------------|---------------------|
| X=1 | 27 | 6.036 | 22.096 | 697.687 |
| X=2 | 13 | 6.044 | 21.979 | 695.932 |
| X=3 | 17 | 6.050 | 21.724 | 690.378 |
| X=4 | 24 | 6.055 | 21.629 | 686.237 |

3.2 Microstructural analysis: Figures 2 shows the SEM images of the samples. From the figure it is evident that particles are in Nano size and almost spherical in shape.

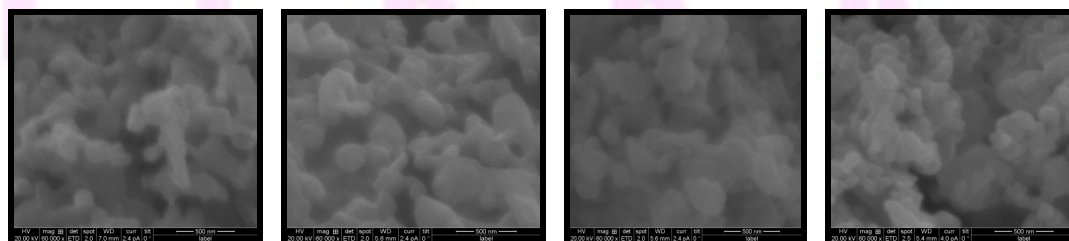


Figure 2: SEM Images of $CaCo_xFe_{12-x}O_{19}$ ($x=1,2,3,4$)

3.3 Magnetic studies : Figures 3 shows the magnetic hysteresis of Cobalt substituted calcium hexaferrites. Hysteresis increases with the substitution and maximum for $CaCo_3Fe_9O_{19}$. This may be due to the site preference of

Cobalt. Calculated values are shown in Table 2. From the squareness ratio it is confirmed that the samples are multi domain.

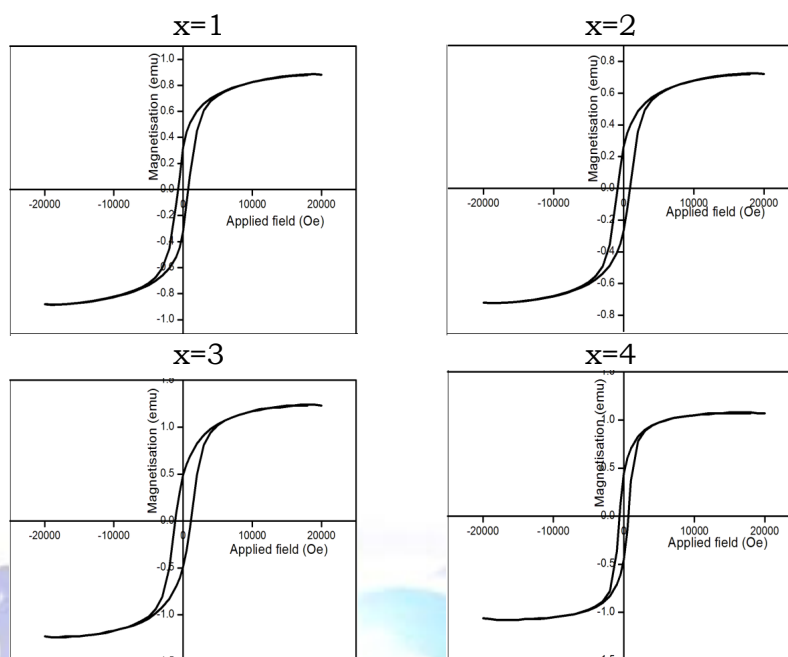


Figure 3: Hysteresis curve of $\text{CaCo}_x\text{Fe}_{12-x}\text{O}_{19}$ ($x=1,2,3,4$)

Table 2: Magnetic parameters of $\text{CaCo}_x\text{Fe}_{12-x}\text{O}_{19}$

| Sample $\text{CaCo}_x\text{Fe}_{12-x}\text{O}_{19}$ | M_s (emu/g) | M_r (emu/g) | H_c (Oe) | M_r/M_s |
|--|------------------|------------------|---------------|-----------|
| X=1 | 26.3 | 0.95 | 732.51 | 0.363 |
| X=2 | 45.2 | 1.66 | 874.52 | 0.367 |
| X=3 | 62.8 | 2.47 | 1141.27 | 0.394 |
| X=4 | 64.6 | 2.68 | 634.14 | 0.415 |

4. CONCLUSIONS

A series of Cobalt substituted Calcium hexaferrite samples, $\text{CaCo}_x\text{Fe}_{12-x}\text{O}_{19}$ ($x = 0, 1, 2, 3, 4$) have been prepared using solution combustion technique. The X-ray diffraction patterns reveal the formation of hexagonal structure with space group $P63/mmc$, without any trace of secondary phases. A decrease in the lattice parameter 'c' with increasing Co^{3+} substitution is due difference in ionic radii of Co^{3+} ion (0.61 \AA) and Fe^{3+} ion (0.65 \AA). Increasing the amount of Cobalt affected the morphology of the particles. Agglomeration is increased with the increase of Cobalt content. From SEM it is confirmed



that the particles are Nano particles. It was found that replacement of Fe^{3+} with paramagnetic Co^{3+} leads to an increase in saturation magnetization, remanent magnetization and a significant increase in the coercive field. From the values of Squareness ratio it is clear that the particles are multi domain. Out of all four samples $\text{CaCo}_3\text{Fe}_9\text{O}_{19}$ shows good hysteresis and hard magnetic property.

5. REFERENCES

- [1] Lisjak D., Drofenik M. *J. Eur. Ceram. Soc.* **24**, 1841- 1845. (2004)
- [2] S. Singhal, A.N. Garg, K. Chandra, *J. Magn. Magn. Mater.* **285** 193 (2005)
- [3] Robert C. Pullar. *Progress in Materials Science* **57** 1191-1334 (2012)
- [4] Snoek, J.L., "New Developments in Ferromagnetic Materials", Elsevier Publishing Co., Inc., New York Amsterdam (1947).
- [5] V. Adelskold, *Arkiv Kemi Min. Geol* **1938**, 12/A/29, 1.
- [6] Kulkarni D.K. and Prakash C.S. *Bull Mater Sci.*, **17**, 35 (1994).
- [7] Prakash C.S. and Kulkarni D.K., *Ind J. Pure Appl Physics.* 32361
- [8] Prakash C.S., Nanoti V.M., Kulkarni D.K. And Rao G.M. *J. Magn. Magn. Mater.* 140-144 2089 (1995).
- [9] Prakash C.S., Nanoti V.M. and Kulkarni D.K. *Materials Letters* **24** 171 (1995).
- [10] Prakash C.S. and Kulkarni D.K. *International Journal of E-ISSN: Knowledge Engineering ISSN: 0976 5816 & 0976-5824, Volume 3, Issue 1, (2012).*
- [11] H. Kojima, K. Goto, in *Proceeding of Inter Conference on Ferrites, Center for Academic publication, Japan*, 198 p. 335.
- [12] P. Lubitz, C. Victoria, J. Schelleng, W.G. Maisch, *J. Magn. Mater.* 15145 (1980).
- [13] Ataei A. and Heshmati- Manesh S. *J. European Ceram. Soc.*, 21, 1951- 1955 (2001).
- [14] Wang J.F., Paton C.B., Ciossinger R., Harris I.R. *J. Alloys. Compd.*, 369, 170 177 (2004).
- [15] Jotania R.B., Khomane R.B., Chauhan C.C., Menon S.K., Kulkarni B.D. *J. Magn. Magn. Mater.* 310, 2477- 2479 (2002).
- [16] Junliang L., Yanwei Z., Cuijing C., Wei Z., Xiaowei Y. *J. European Ceram. Soc.*, 30, 993-997 (2010).
- [17] J. Huang, H. Zhuang, W. Li, *J. Magn. Magn. Mater.* 256 390 (2003).

