



# Synthesis and Magnetic Characterization of Gallium-Cobalt Substituted Ca-Hexaferrites

C. L. Khobaragade\*, S. V. Soni@, A. K. Akant\$, C. Umare@, N. Waghdhare@, P. K. Gaidhane#, U. V. Rathod<sup>‡</sup>

\*Department of Applied Physics, Govindrao Wanjari College of Engg & Technology, Nagpur (MS), India.

@Department of Applied Physics, Yashwantrao Chavan College of Engineering, Nagpur (MS), India.

\$Department of Applied Physics, Manoharbai Patel Institute of Engg. & Technology, Gondia (MS), India.

# Department of Applied Chemistry, Govindrao Wanjari College of Engg & Technology, Nagpur (MS), India.

‡Department of Applied Physics, Dr. Ambedkar College of Engg. & Research Institute, Nagpur (MS), India.

E-Mail: [chanduparulk@gmail.com](mailto:chanduparulk@gmail.com)

## Abstract:

In the present investigation the samples with chemical composition  $\text{CaFe}_{11}\text{Ga}_x\text{Co}_{1-x}\text{O}_{19}$  with ( $x = 0.01$  to  $0.05$ ) were synthesized using perfect stoichiometric proportions of reacting oxides by standard ceramic technique. It shows hexagonal magnetoplumbite (M) structure having unit cell dimensions 'a' and 'c' which varies in the range between 5-6 Å and 21-23 Å with space group  $\text{P6}_3/\text{mmc}$  (No.194). The saturation magnetization ( $M_s$ ) decreases linearly from 27.39 to 26.72 emu/g with increasing doping content from 0.01 to 0.05. The coercivity and retentivity increases successively with increase in Ga-Co concentration by changing magnetic field at 80 kOe. Crystallographic studies were explained on the cation distribution consistent with Gorter spin model of parallel alignment.

**Keywords:** Hexaferrite, Saturation magnetization, Coercivity, Retentivity, Curie temperature.

## 1. Introduction:

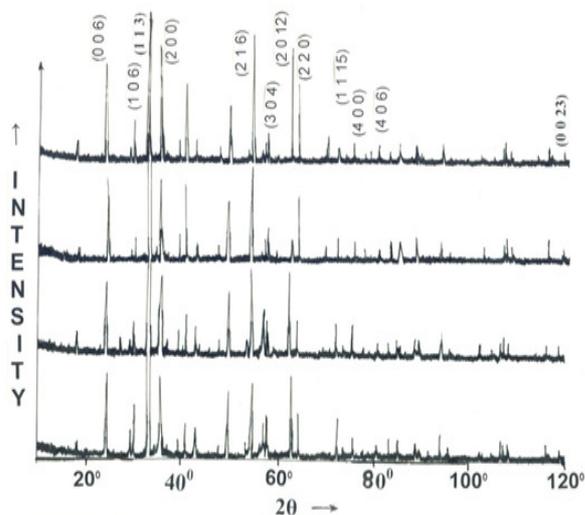
There have been numerous investigations on the hexagonal ferrites. The interest in this wide family is continuously growing due to their technological significance as permanent magnets, microwave device materials and perpendicular magnetic recording heads. These applications need different magnetic and electrical specifications and in this view, several attempts have been made to modify the properties of hexagonal ferrites using different materials processing routes including external doping [1, 2]. In CaM ferrites, three kinds of lattice sites  $2a(\text{S})$ ,  $4f_2(\text{R})$  and  $12\text{K}(\text{R/S})$ , trigonal bipyramidal  $2b(\text{R})$  and tetrahedral  $4f_1(\text{S})$  sites are fully occupied by  $\text{Fe}^{+3}$  ions. The  $\text{Fe}^{+3}$  ions when replaced partially by other trivalent metal ions or combination of tetra and divalent ions, the magnetic properties of the calcium ferrite will be altered [3, 4]. The magnetic behavior of the compound has been explained on the basis of the interactions between these ions occupying the five sites. Due to several possible site distributions, various comparative magnetic interactions can arise in the lattice and in turn all these decide the magnetic behaviour of the crystal.

## 2. Experimental Technique:

The synthesis of polycrystalline  $\text{CaFe}_{11}\text{Ga}_x\text{Co}_{1-x}\text{O}_{19}$  with ( $x = 0.01$  to  $0.05$ ) samples were done by high temperature solid state diffusion reactions of stoichiometric mixtures of AR grade  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CoO}$ ,  $\text{GaO}_4$  oxides. The synthesis was divided into two steps: (i) after calcinations at  $800^\circ\text{C}$  for 2 h in air, the mixture was grinded and dried, compressed into pellets, and (ii) finally subjected to a thermal treatment at  $1040^\circ\text{C}$  for 106 h with intermediate grinding and were quenched in air.



The XRD patterns were taken to identify the phases formed and to confirm the chemical reaction by using Phillips X-ray diffractometer using CuK $\alpha$ -radiation with Ni as a filter. The X-ray diffraction pattern (**Fig.1**) shows a single crystalline phase without traces of impurities.



**Fig.1:** XRD analysis of CaFe<sub>11</sub>Ga<sub>x</sub>Co<sub>1-x</sub>O<sub>19</sub> (x = 0.01 to 0.04) compounds

The patterns were indexed to hexagonal magnetoplumbite structure [5] belongs to the space group P6<sub>3</sub>/mmc (No.194).

The magnetic properties of polycrystalline sample have been measured by using a vibrating sample magnetometer in the applied field upto 80 kOe at room temperature. In order to prevent rotation of the powder grain, pressed samples were used. The transition temperature (T<sub>c</sub>) has been measured using a Gouy's balance.

### 3. Results and Discussion:

The lattice parameters 'a' and 'c' of CaFe<sub>11</sub>Ga<sub>x</sub>Co<sub>1-x</sub>O<sub>19</sub> with (x = 0.01 to 0.05) are listed in **Table-1**, which calculated from the X-ray data. It varies between 5-6 Å and 21-23 Å. All the reflections can be indexed applying a hexagonal crystal system, which confirms that the phase belongs to the magnetoplumbite crystal structure [6]. By isomorphism of the M compounds the space group is presumed to be D<sub>6h</sub><sup>4</sup> or P6<sub>3</sub>/mmc [7].

Sugg and Vincent [8] reported the saturation magnetization M<sub>s</sub> = 86 emu/g in the single crystals of the composition BaFe<sub>10.25</sub>Ir<sub>0.85</sub>Co<sub>0.85</sub>Bi<sub>0.05</sub>O<sub>19</sub>, was calculated by assuming magnetic moment of Fe<sup>3+</sup> to be 5μ<sub>B</sub> and Co<sup>2+</sup> to be 3.7μ<sub>B</sub>. The saturation magnetization of polycrystalline sample for x = 0.01 to 0.05 for CaFe<sub>11</sub>Ga<sub>x</sub>Co<sub>1-x</sub>O<sub>19</sub> compounds are 27.39 to 26.72 emu/g respectively; is smaller than M<sub>s</sub> = 86 emu/g value measured on the single crystals. The lower value observed on polycrystalline samples is probably due to stacking defects of R-S blocks along c-axis. As the reported compounds that are in powder form could have small domain invisible by X-ray, where rich calcium blocks (T or β-alumina like conduction blocks) have been substituted for R-blocks, which promotes weaker magnetization.

It is seen from the **Table-1** that the substitution of Ga<sup>4+</sup>-Co<sup>2+</sup> in CaFe<sub>11</sub>Ga<sub>x</sub>Co<sub>1-x</sub>O<sub>19</sub> results in a sharp decline trend in the saturation magnetization. This probably could be due to stacking defects in spinel blocks as is seen in Zn-substituted aluminium ferrites [9].



**Table-1:** Lattice parameter ('a', 'c'), saturation magnetization ( $M_s$ ), coercivity ( $H_c$ ), retentivity ( $Br$ ) and Curie temperature ( $T_c$ ) of  $CaFe_{11}Ga_xCo_{1-x}O_{19}$  ( $x = 0.01$  to  $0.05$ ) compounds.

Compounds	a(Å)	c (Å)	$M_s$ (emu/g)	$H_c$ (Oe)	$Br$ (emu/g)	$T_c$ (K)
$CaFe_{11}Ga_{0.01}Co_{0.99}O_{19}$	5.7830	21.9609	27.39	1035	10.00	520
$CaFe_{11}Ga_{0.02}Co_{0.98}O_{19}$	5.8035	22.0248	27.32	1123	10.70	510
$CaFe_{11}Ga_{0.03}Co_{0.97}O_{19}$	5.7860	21.9595	27.28	1320	11.50	508
$CaFe_{11}Ga_{0.04}Co_{0.96}O_{19}$	5.7935	21.9803	26.93	1215	11.90	499
$CaFe_{11}Ga_{0.05}Co_{0.95}O_{19}$	5.8033	22.0069	26.72	1665	12.60	481

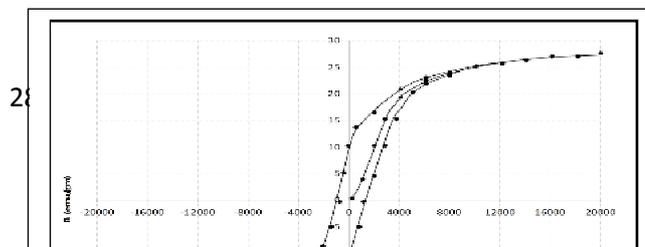
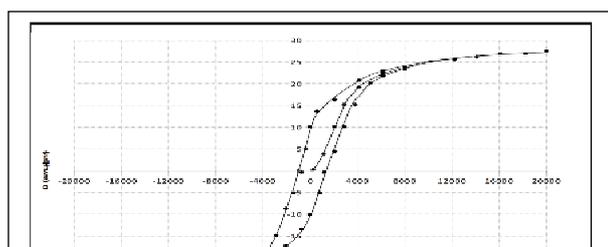
The formation of  $CaFe_{11}Ga_xCo_{1-x}O_{19}$  have been completed after 1040°C in 106 h heat treatment. It is interesting to notice that in method [10-13], there are no intermediate phases observed during the calcinations of the oxides. The greatest advantage of this method is that the calcinations time required to form the ferrites have been reduced to 1/25<sup>th</sup> of conventional high-temperature method. According to XRD examination during sintering at different stages,  $CaCO_3$  seen to decompose at 785°C on account of the fact that the bonding of  $CaO-Co_2$  weakened by the electron withdrawing oxygen's of  $FeO$  surrounding the  $Ca$ -ions and the reactive  $CaO$  species react instantaneously with  $Fe_2O_3$ ,  $GaO_4$ ,  $CoO$  to form crystalline  $CaM$  ferrite directly without the formation of intermediate phases.

The saturation magnetization measured at 80 kOe as a function of 'x' at room temperature. The magnetic moment of  $CaFe_{12}O_{19}$  results from 12  $Fe^{+3}$  ions, distributed on five lattice sites. The crystal structure of magnetoplumbite (M-type) compounds ( $P6_3/mmc$ ) can be described as the superposition of two structural blocks, namely the R-block with composition  $(CaFe_6O_{11})^{-2}$  and the S-block with composition  $(Fe_6O_8)^{+2}$ . The metallic cations are distributed within five different crystallographic sites with octahedral and tetrahedral environment. In **Table-2**, we have summarized the crystallographic characteristics of the five different sub-lattices together with the spin alignments corresponding to the collinear magnetic structure [14].

**Table-2:** Structural and magnetic characterization of magnetic sub-lattice in magnetoplumbite structure.

Sub-lattice	Co-ordination	Block	No. of ions/FU	Spin direction
2a	Octahedral	S	1	Up
2b	Pseudo-tetrahedral	R	1	Up
4f <sub>1</sub>	Tetrahedral	S	2	Down
4f <sub>2</sub>	Octahedral	R	2	Down
12K	Octahedral	S-R	6	Up

Successive decrease in the values of saturation magnetization due to the substitution of Ga-Co in the spinel blocks of the M-structure occupying the octahedral sites (12k). Coercivity ( $H_c$ ) and retentivity ( $Br$ ) carried out from the VSM (**Fig.2a, 2b, 2c, 2d & 2e**) for various compounds, illuminated in **Table-1**. The coercivity and retentivity increases continuously with the increase of Ga-Co concentration for increasing magnetic field at room temperature (300K).



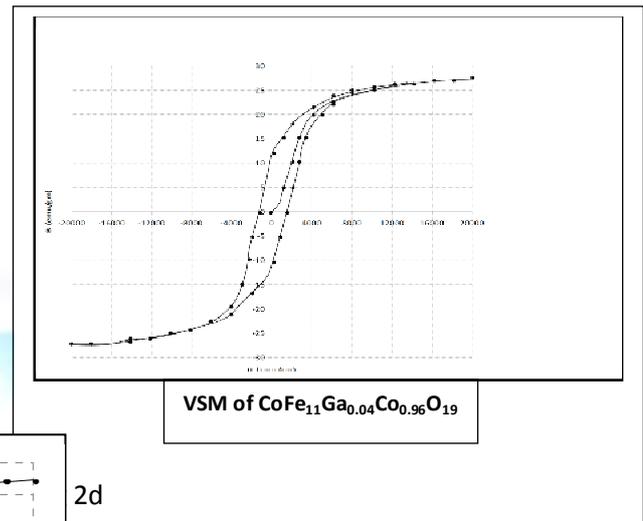
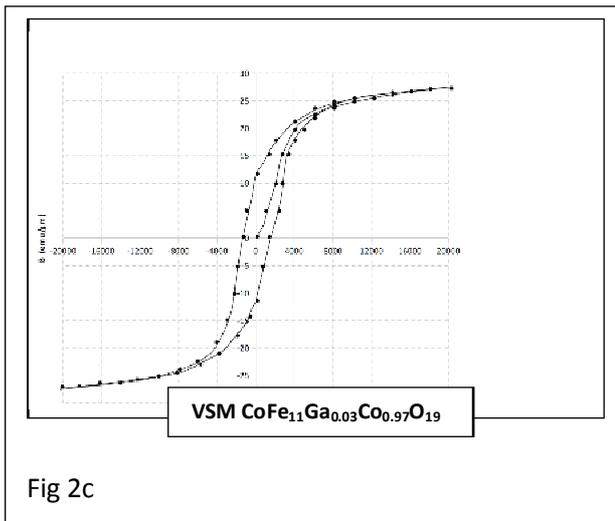
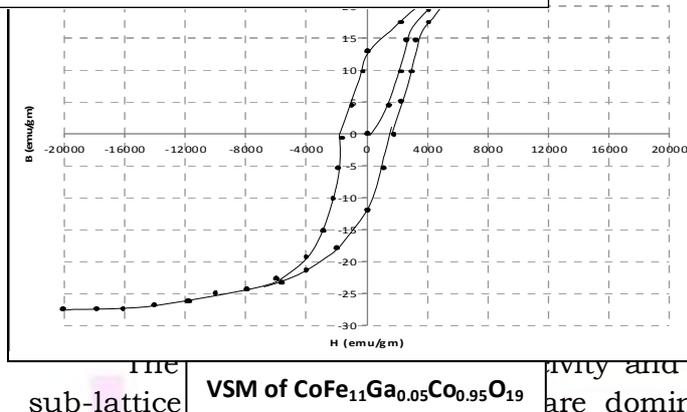


Fig 2c

2d



The sub-lattice activity and retentivity demonstrate that some inter are dominant. It can be seen that the spin co-linearity appears mostly in the spin up sub-lattice; especially the 12K sub-lattice has degree of frustration being in this way strongly affected by increase of 12K-4f<sub>IV</sub> interaction. A mean field analysis of the exchange interaction in BaM hexaferrites has been carried out [15]. The results shows that the Fe (12K) sublattice making a link among R and S structural block is subjected to very strong competitive exchange interactions. So, when the Fe<sup>+3</sup> ions in the 12K sub-lattice are substituted by ferromagnetic (Co<sup>+2</sup>) ions, strongness of the superexchange interaction between magnetic ions results in a fairly inclined ferrimagnetisms.

In case of M-structure predominant superexchange interaction is due to 1-oxygen-2 ions in which appertaining angle  $\phi$  is large (approximately 140°), whereas the other interactions, the 2-oxygen-3 interactions which attempt to align the magnetic moments of these ions antiparallel, is smaller because the appertaining angle is unfavorable (appximately 80°). The orientations of the magnetic moments of the ferric ions in the crystals are generally aligned along the c-axis in antiparallel with each





other. This alignment occurs due to the superexchange interaction through oxygen ions which is responsible for spin alignment [16-17]. The coercivity and retentivity values may differ slightly because they also depend on the grain size [18].

#### 4. Conclusions:

XRD analysis shows a single crystalline phase without traces of impurities. The patterns were indexed to hexagonal magnetoplumbite structure. Successive decrease in the values of saturation magnetization due to the substitution of Ga-Co in the spinel blocks of the M-structure occupying the octahedral sites (12k). The coercivity and retentivity increases continuously with the increase of Ga-Co concentration for increasing magnetic field at room temperature (300K). The strong increase in coercivity and retentivity demonstrate that some inter sub-lattice exchange interactions are dominant. Due to this the ferrimagnetic nature of these compounds increases with the increase of Ga-Co concentration in this series of compounds.

#### References:

- [1] Collomb A., Obradors X., Isalgue A., Jobbert J. C., Adv. Ceram 15 (1985) 225.
- [2] Darokar S.S., Rewatkar K.G., Kulkarni D.K., Mater. Chem. Phys. 56 (1998) 84.
- [3] Kojima H., Goto K., in: Proceeding of Inter. Conference on ferrites. Center for Academic publication, Japan, 1980, p. 335.
- [4] Lubitz P., Victoria C., Schelleng J., Maisch W. G., J. Magn. Mater. 15 (1980) 1459.
- [5] De Roy M.E., Besse J.P., Chevalier R. and Gasperin M.G., J. Solid state chem. 67 (1987) 185.
- [6] Sharrock M.P., IEEE Trans. Magn. MAG-25 (1989) 4374.
- [7] Kojima H., in Ferromagnetic materials (Amsterdam: North Holland) Vol.3 (1982).
- [8] Sugg B., Vincent K., J. Magn. Mater. 139 (1995) 364.
- [9] Sankpal A.M., Suryawanshi S.S., Kaktkar S.V., Tengshe G.G., Patil R.S., Chaudhari N.D., Sawant S.R., J. Magn. Mater. 186 (1998) 349.
- [10] Heneda K., Miyakama C., Kojima H., J. Am. Ceram. Soc. 57 (8) (1974) 354.
- [11] Satyanarayana R., Murthy S.R., Rao T.S., Rao S.M.D., J. Loss Common Met. 90 (1983) 243.
- [12] Lipka V.J., Grustona A., Orlicky O., Sotek J., Milglirini M., Grove R., Huci M., Toth I., Hyperfine interaction 59 (1990) 381.
- [13] Rewatkar K.G., Darokar S.S., Ghyar P.B., Giriya M.N., Tabhane V.A., in: Processing of DAE-SSPS conference, Guru Ghasidas University Bilaspur, India, (2000).
- [14] Gorter E.W., IEEE Trans. Man. 104 B (1957) 255.
- [15] Isalgue A., Labarta A., Tejada J. and Obradore X., Appl. Phys. A-39 (1986) 221.
- [16] Neel L., "Magnetic properties of Ferrites; Ferrimagnetisms and Antiferromagnetism" (In Fr.) Ann. Phys. (Paris) 3, (1948) 137-98.
- [17] Anderson P.W., Phys. Rev. 79 (1950) 350.
- [18] Vander Zang et al (1994).

