

## 9th International Conference on Materials for Advanced Technologies (ICMAT 2017)

### Enhancement Of Magnetic Properties Of Calcium Hexaferrites With Aluminium Substitution

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**Abstract:** Ferrites are large class of oxides with astonishing magnetic properties, which have been investigated and applied for the past 50 years. Their applications range from millimeter wave integrated circuitry to magnetic recording & microwave devices. These applications are based on very basic properties of ferrites; such as significant saturation magnetization, high electrical resistivity, low electrical losses, and good chemical stability. Ferrites can be obtained in different crystal systems by many methods, and the feasibility in preparation opens the means to tailor their properties for many applications. By reducing the scale to the Nanometric size, new and technologically interesting properties have been obtained. In the current study, Structural and Magnetic properties of Aluminium substituted calcium hexaferrites are reported. A series of Aluminium substituted Calcium hexaferrite samples, have been prepared by Solution combustion synthesis. XRD patterns confirmed the formation of Hexagonal phase with space group  $P6_3/mmc$ . Lattice parameter values decreased with  $Al^{3+}$  content. Magnetic properties such as saturation magnetization ( $M_s$ ), remanence ( $M_r$ ) and magneton number ( $n_B$ ) were found to decrease, while the coercivity ( $H_c$ ) and reduced remanence ( $M_r/M_s$ ) of the samples were found to increase with increasing  $Al^{3+}$  content. Results of VSM studies show the decrease in saturation magnetization with increase in Al concentration. However, the coercivity and Retentivity increased with Al concentration. The high values of retentivity and coercivity make these materials best for high-density recording media and permanent magnets. Our work suggests that, substitution can be used to alter magnetic property. This is the encroachment for selecting suitable materials for various technological applications.

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Selection and/or peer-review under responsibility of the scientific committee of Symposium 2017 ICMAT.

**Key words:** Nanomaterials, Hexaferrites, combustion, coersivity, retentivity.

### 1. Introductions

Ferrimagnetic materials are usually known as Ferrites. The magnetic behavior exhibited by these materials is called ferrimagnetism [1-4]. With the discovery of hexagonal ferrites [5], there has been an extensive study of ferrimagnetism of such compounds because of their applications in the field of material science as permanent magnets, microwave devices so on and so forth. Substituted hexaferrites belonging to the family of magnetoplumbite with general formula  $M(Fe_{12}O_{19})$  where M is usually barium, strontium, Calcium or Lead, are interesting and attracting researchers due to their specific magnetic behavior. The basic structure consists of 38 oxygen ions occupying the interstitial sites forming a close packed hexagonal structure. 24 ferric ions occupy five different locations in the unit cell in which 2a, 4f<sub>2</sub> and 12k are octahedral, 4f<sub>1</sub> 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 ferrite nanoparticles, various synthesis methods such as chemical co-precipitation [13], hydrothermal [14], sol-gel [15,16], Solution combustion Synthesis [17] etc. have been developed. In the present work, Calcium hexaferrites substituted with trivalent Al ions synthesized in solution combustion method. Their structural and magnetic properties are studied and reported.

### 2. Experimental

#### 2.1. Synthesis techniques

A series of M-type aluminum substituted Calcium hexaferrites with general formula  $CaAl_xFe_{12-x}O_{19}$  ( $x=0,1,2,3,4$ ) were prepared successfully by solution combustion synthesis to study the structural and magnetic properties. Samples were prepared with AR grade calcium nitrate  $Ca(NO_3)_2 \cdot 4H_2O$ , iron nitrate  $Fe(NO_3)_3 \cdot 9H_2O$ ,

aluminum nitrate  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and freshly prepared Oxalyl dihydrazide ODH ( $\text{C}_2\text{H}_6\text{N}_4\text{O}_2$ ) [18]. In Solution combustion method, stoichiometric amounts of metal nitrates act as an oxidizing agent and fuel (Oxalyl dihydrazide (ODH) [ $\text{C}_2\text{H}_6\text{N}_4\text{O}_2$ ]) acts as reducing agent with exothermic reaction. Metal nitrates along with ODH were dissolved completely in double distilled water to form an aqueous solution. Combustion process was performed in a muffle furnace and samples were calcined at  $900^\circ\text{C}$ . Prepared powders are loose, Foamy, pores, and highly friable.

## 2.2. Structural studies

Structural studies were carried out on powder X-ray diffractometer with step size of  $0.2^\circ$  in  $2^\circ$  range of  $20^\circ$  -  $80^\circ$  at RT. The PXRD pattern of Calcium hexaferrites substituted with Aluminum is shown in Figure 1. X-ray diffraction studies confirm the formation of hexaferrites with the space group  $\text{P6}_3/\text{mmc}$ . The intensity diffraction peaks of samples were found at (006), (107), (202), (109), (206), (214), (303), (332), (222), (224) etc. orientations as mentioned in the figure. And the highest intensity diffraction peaks of samples were found with (107) orientation. Structural values such as lattice parameters (a, c), particle size (D), Volume (V) and c/a ratios are calculated and given in table 1.

## 2.3 Magnetic studies:

To study the magnetic properties of synthesized samples, magnetic moment was recorded as a function of magnetizing field in the range of  $-20$  kG to  $+20$  kG at room temperature with the help of vibration sample magnetometer (VSM). Calculated Saturation magnetization ( $M_s$ ), Coercivity ( $H_c$ ) and Retentivity ( $M_r$ ) values are described in Table 2. Results of VSM studies show the decrease in saturation magnetization ( $M_s$ ) with the increase of Al concentration. Increase in magnetic properties such as coercivity ( $H_c$ ) and Retentivity ( $M_r$ ) confirmed the nature of hard ferrites.

## 3. Results and Discussions

### 3.1 Structural analysis

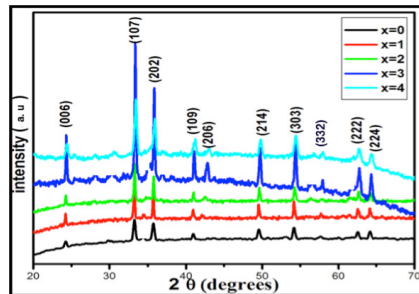


Figure 1: XRD spectrum of  $\text{CaAl}_x\text{Fe}_{12-x}\text{O}_{19}$

All peaks match perfectly with Bragg reflections of the Hexagonal structure with space group  $\text{P6}_3/\text{mmc}$  and matching with the PCPDF NO. 49-1586. A close examination of the PXRD pattern indicates slight variation in the parameters such as peak intensities, peak positions and peak width, with the increase in the Aluminum content due to the small ionic radius of  $\text{Al}^{3+}$  ion ( $0.54 \text{ \AA}$ ) than  $\text{Fe}^{3+}$  ( $0.65 \text{ \AA}$ ).

There are five positions of  $\text{Fe}^{3+}$  in the crystal lattice of magnetoplumbite, which are  $2a$ ,  $2b$ ,  $12k$ ,  $4f_1$  and  $4f_2$ . Out of these lattice sites,  $4f_1$  is tetrahedral site,  $2b$  is bi-pyramidal site and  $2a$ ,  $12k$  and  $4f_2$  are octahedral sites.  $\text{Al}^{3+}$  substitutions for  $\text{Fe}^{3+}$  causes the shrinkage of crystal lattice [19-22]. Consequently, the aberrance of the crystal lattice leads to the changes in the crystal lattice parameters a, c and variation in the radius of the crystal grains. This variation in crystallite size resulting in decrease in X-ray density and is responsible for the shift in X

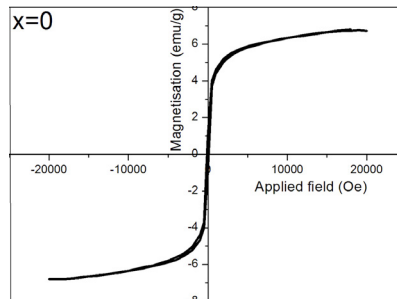
ray diffraction peaks. The  $c/a$  ratio lies in the expected range from 3.94 to 3.96 and exhibited the formation of M-type hexagonal structure [23]. The lattice parameters ratio  $c/a$  may be used to quantify the structure type and M-type hexaferrite structure might be assumed if the lattice parameters ratio is observed to be lower than 3.98.

Table: 1

Compound	D (nm)	a (Å)	c (Å)	V (Å <sup>3</sup> )	c/a
CaFe <sub>12</sub> O <sub>19</sub>	33	6.049	22.051	699.489	3.644
CaAlFe <sub>11</sub> O <sub>19</sub>	30	6.010	22.033	689.831	3.665
CaAl <sub>2</sub> Fe <sub>10</sub> O <sub>19</sub>	32	6.004	22.006	687.572	3.665
CaAl <sub>3</sub> Fe <sub>9</sub> O <sub>19</sub>	31	5.998	21.934	684.080	3.656
CaAl <sub>4</sub> Fe <sub>8</sub> O <sub>19</sub>	24	5.985	21.917	680.611	3.661

### 3.2 Magnetic properties

The magnetic measurements of Aluminum substituted calcium hexaferrites recorded at room temperature over a wide range of field -20 kOe to +20 kOe. Hysteresis of all samples is shown in Figures 2, 3 and 4. Figure 2 shows hysteresis of calcium ferrite without substitution. Figure 3 shows variation of hysteresis with Aluminum substitution and figure 4 shows the comparison. The shape of the curves indicates ferrimagnetic nature of samples. The area of the loop exhibits the nature of hard magnetic property. Observed increase in coercivity is because of the increase in magneto crystalline anisotropy. Magnetic properties such as saturation magnetization ( $M_s$ ), remanent magnetization ( $M_r$ ), Squareness ratio ( $M_r/M_s$ ), Coercive force ( $H_c$ ), and Magnetic moment per formula unit in Bohr magneton ( $n_B$ ) are reported in Table 2. Coercivity values increase with  $Al^{3+}$  substitutions. It is good enhancement than the earlier reported value of 21.13 Oe for  $CaFe_{10}Al_2O_{19}$  [24]. Out of all five samples, coercivity is observed to be more for  $CaFe_8Al_4O_{19}$ .

Figure 2: Hysteresis of CaFe<sub>12</sub>O<sub>19</sub>

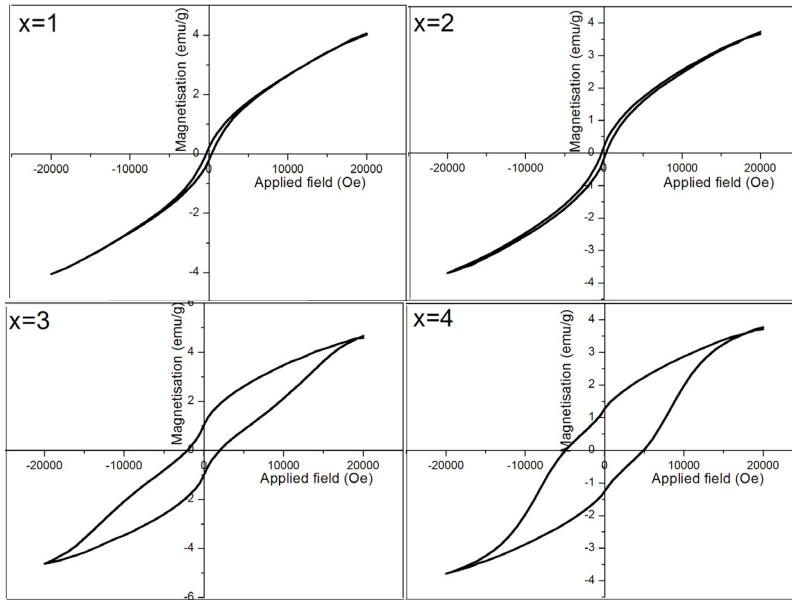


Figure 3: Variation of Hysteresis with Aluminum substitution  $CaFe_{12-x}Al_xO_{19}$  ( $x = 1,2,3,4$ )

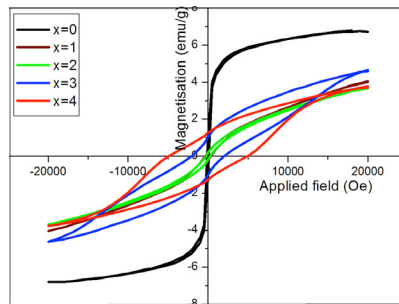


Figure 4: Hysteresis comparison of  $CaFe_{12-x}Al_xO_{19}$  ( $x = 0,1,2,3,4$ )

Values of  $M_r$ ,  $M_s$  and coercivity ( $H_c$ ) advocate the existence of three types of domain states, viz. single domain (SD), multi domain (MD) and superparamagnetic [25-27]. Magnetocrystalline anisotropy and exchange interactions can be roughly studied with the help of squareness ratio. It has been reported that the squareness ratio, which is the ratio of remanent magnetization  $M_r$  to saturation magnetization  $M_s$  at or above 0.5 indicates the material in single magnetic domain and below 0.5 can be attributed to the formation of multi domain structure. From the calculated values it is evident that all samples have multi domain structure. In general for ferrites the value of SQR if exists below 0.5 it is good for recording medium [28].

Table: 2

Compound	$M_s$ (emu/g)	$M_r$ (emu/g)	$M_r/M_s$	$H_c$ (Oe)	Bohr Magneton ( $n_B$ )
CaFe <sub>12</sub> O <sub>19</sub>	6.80	0.97	0.14	103.45	1.235
CaAlFe <sub>11</sub> O <sub>19</sub>	4.05	0.21	0.05	344.42	0.714
CaAl <sub>2</sub> Fe <sub>10</sub> O <sub>19</sub>	3.72	0.18	0.05	276.66	0.636
CaAl <sub>3</sub> Fe <sub>9</sub> O <sub>19</sub>	4.65	1.02	0.22	2031.69	0.772
CaAl <sub>4</sub> Fe <sub>8</sub> O <sub>19</sub>	3.77	1.26	0.33	4936.46	0.606

#### 4. Conclusion

Series of Al substituted CaFe<sub>12-x</sub>Al<sub>x</sub>O<sub>19</sub> ( $0 \leq x \leq 4$ ) Calcium hexaferrites have been prepared by solution combustion technique. Role of Al<sup>3+</sup> ions in place of Fe<sup>3+</sup> in M-type Calcium hexaferrites are studied. X-ray diffraction patterns reveal the formation of hexagonal structure with space group P6<sub>3</sub>/mmc for all level of Al<sup>3+</sup> substitutions without any trace of secondary phases. Decrease in the lattice parameters with increasing Al<sup>3+</sup> doping level is due to difference in ionic radii of Al<sup>3+</sup> ion (0.535Å) and Fe<sup>3+</sup> ion (0.645Å). It was found that replacement of Fe<sup>3+</sup> with paramagnetic Al<sup>3+</sup> leads to a decrease in saturation magnetization and to a significant increase in the coercive field. From the values of Squareness ratio it is clear that the particles are multi domain. From these studies it is evident that calcium ferrites can be used as alternating materials for magnetic storage devices.

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