

1.1 Introduction

Permanent magnets are important materials in modern life to empower the operation of various advanced instruments, motors and rotating machines. Permanent magnets (PM) facilitates the conversion of energy from one energy state to another energy state. The strength of PM is to retain a large magnetic flux within the material. It does occur even in the lack of an external field or fluctuations in external environments like demagnetizing field, temperature etc. The strength of PMs make it unique material which can be applied in an extensive range of applications like energy harvesting and conversion, power transport and generation, magnetic recording, microwave communications and sensor technologies etc. A list of summary in Table 1.1 shows the common applications of permanent magnets which illustrate their ubiquitous worldwide manifestation [Skomski and Coey (1999)]. The classification that defines the dominant role of the permanent magnets within a given sets of applications are stated below [Lewis and Villacorta (2013)]:

- Transformation of energy from electrical to mechanical energy (motors, loudspeakers, relays, MEMS, actuators, etc.)
- Transformation of energy from mechanical to electrical energy (alternators, generators)
- Application of magnetic repulsion or attraction to do mechanical work (bearing or coupling devices, separators and torque drives).
- Control and guide electric charges, ion or electron beams and plasmas (cathode ray tubes, magnetrons, klystrons and synchrotron insertion devices).
- Data storage (magnetic recording head).

The leading commercial permanent magnets are NdFeB, AlNiCo, SmCo and Ferrites from the last decades. Table 1.2 listed the permanent magnets and their properties with their market values as well.

Table 1.1 A collection of applications using advanced permanent magnets [Skomski and Coey (1999)].

Category	Applications
Computer and office automation	Hard disk drive and CD-ROM spindle motors, Voice coil motors and pick-up motors, Printer and fax motors
Consumer electronics	VCRs, Cameras and DVD players, Speakers, Microphones and headsets Cell phones
Appliances	Household appliance motors and air conditioners, Water pumps security systems
Factory automation	Magnetic couplings and bearings pumps, Motors, Servo motors and generators
Medical industry	MRI equipment, Surgical tools and medical implants
Automotive & transportation	Starter motors and brushless DC motors, Electric bicycles and hybrid/electric vehicles, Electric fuel pumps
Alternative Energy	Wind, Wave, Tidal power systems, Power generation systems, Energy storage systems
Military	Weapons systems, Precision-guided munitions vehicles, Watercraft, Avionics communications systems, Radar, Satellites

Table 1.2 Some permanent magnetic materials [Villacorta and Lewis (2014)].

Magnet material	Material characteristics			Market figures		
	B_r (kG)	iH_c (kOe)	$(BH)_{max}$ (MGOe)	Cost ratio	Weight %	Volume %
Ferrite	4.2	3.38	4.2	1	96	55
NdFeB	12.0	> 12.5	35.1	6	1	35
SmCo	9.0	15.1	18.8	11-16	0.5	8
AlNiCo	12.0	0.62	5.1	3	2.5	2

From the past studies, It is noticed that strong permanent magnets with better chemical and thermal stability are crucial to deal with the ongoing and upcoming

technological needs in the society. Recently, however, the proportion of rare earth (RE) specially NdFeB magnets has increased to reduce the power consumption and to increase the use of energy-saving equipment in order to cut CO₂ and other greenhouse gas emissions. RE elements like Nd, Pr, Sm, and Dy are important constituents in these magnets. The requirement of rare earth magnets are rapidly increased to follow up the demands of renewable energy and its efficiency.

1.1.1 Drawback of rare earth permanent magnet

Due to the instability in price and accessibility of rare earth materials leads to find the alternate materials and technology to overcome the crisis proportion. From the last few years, availability of rare earth materials and the selling prices of chief permanent magnet are accounted. It has been figured out that it is increased by more than four times within a year. Unfortunately, there is a performance void between the hard ferrites (<5 MGOe) with RE magnets (>30 MGOe). Alnico can be a better option if their costs are in between NdFeB magnets and ferrite. A long-term method is to produce non-RE magnets that can plug in this void between hard ferrite with RE magnets. Permanent magnet's R&D is concentrated on the two objectives: first, increasing the magnetic output and second is to reduce the product cost by using easily available materials. As primary component, it's highly suggested to choose more common materials. Truly rare earth elements would be avoided but minor rare earth materials can be acceptable but only in very lesser percentage.

Table 1.3 summaries the properties of RE and non-RE magnets in 2016 and estimated for 2022. The table has \$/kG/kg/kOe to signify the cost property ratio, i.e., the magnet cost (\$/kg) divide by the remanent magnetization (kG) and by coercivity (kOe). For some non-RE magnets, it desires to propose a better \$/kG/kg/kOe rate than that of ferrites and NdFeB

magnets. It seems that ferrites magnets possess the modest magnetic properties and moderate remanent magnetization (Br), coercivity (iH_c) nonetheless excellent market values.

Table 1.3: Comparison between the RE and non-RE magnet motors and their properties in 2016 and 2022 [Cui *et al.* (2018)].

Motor magnets	$(BH)_{max}$ (MGOe)		iH_c (kOe)		Br (kG)		Price (\$/kg)		\$/kg/kG/kOe	
	2016	2022	2016	2022	2016	2022	2016	2022	2016	2022
NdFeBDy(NH42SH)	40-42	42	20	20	13-13.3	13	\$60	\$120	\$0.23	\$0.46
Sm-Co (SC-3215)	31-32	34	15	15	11.2-11.8	12	\$128	\$210	\$0.78	\$1.17
AlNiCo-9	9	11	1.4	2	10.5	10.5	\$71	\$80	\$4.83	\$3.81
Ferrite (Sr-8B)	3.8	3.8	3	3	4	4	\$4	\$4	\$0.33	\$0.33

The ferrite industry made an entry into India in the early sixties and at present there are approximate 2-4 companies for permanent magnet all over India. The major technology gap between India and the world arises largely out of the scale of operations. Nearly, all ferrite magnets are nowadays made using strontium due to the environmental and safety concerns associated with both lead and barium based hexaferrites. In the initial seventies, significant improvement is noticed in the composition. It's followed up to mid-nineties, optimized the composition and the processing parameters of Sr-ferrites. This optimizing parameter shows the improvement in magnetic performance as well as the decrement in the costs.

1.2 M-type hexaferrite

Sr-hexaferrite (SrM) shows excellent characteristics owing to its superior chemical stability, high Curie temperature, relatively large magnetization, and large microwave magnetic loss [Ashiq *et al.* (2011)]. However, low energy product $(BH)_{max}$ and low coercivity (H_c) compare to RE magnets, limits the application of Sr-hexaferrites. Many companies

produce only M-type Sr ferrite with low $(BH)_{max}$, which fail to meet the demand of the market. Henceforth, need to modify the electro-magnetic properties of SrM for increasing their applicability.

SrM is categorized by their chemical formula, i.e., $AFe_{12}O_{19}$ where, A is Sr and their crystal structure is Magnetoplumbite or ‘M’ structure. Three types of M-type hexaferrites are present in the nature such as $SrFe_{12}O_{19}$ (SrM - $SrO \cdot 6Fe_2O_3$), $BaFe_{12}O_{19}$ (BaM- $BaO \cdot 6Fe_2O_3$) and $PbFe_{12}O_{19}$ (PbM - $PbO \cdot 6Fe_2O_3$) [Kojima (1982)]. Among these hexaferrites, strontium hexaferrites have appealed much attention to the researchers due to its high coercivity (iH_c), high anisotropy field (H_a) and moderate saturation magnetization (M_s) as listed in Table 1.4.

Table 1.4 Comparison of magnetic properties among M-type hexaferrites [Pullar (2012)].

Hexaferrites	M_s (emu/gm)	iH_c (Oe)	H_a (Oe)
$BaFe_{12}O_{19}$	70	3187	17000
$SrFe_{12}O_{19}$	54	3593	20000
$PbFe_{12}O_{19}$	54	5001	13500

1.2.1 Crystal structure and cation distribution of strontium hexaferrite

Strontium hexaferrite has a similar structure with the natural occurring mineral ‘magnetoplumbite, of $P63/mmc$ space group [Lishun *et al.* (2008)]. Figure 1.1 shows the unit cell of strontium hexaferrite. A unit cell of strontium hexaferrite comprises two formula units. In which, one formula unit contains five oxygen layers and such two formula unit forms one unit cell. As of these five oxygen layers, one oxygen ion is replaced by Sr^{+2} ion due to similar ionic radii and acts as mirror plane. All these planes are perpendicular to c -axis of the hexagonal structure. However, it is said that every unit cell encloses 10 formula units which is formed by four blocks in sequence. Four blocks are S, R, S^* and R^* , where, S^* and R^* are 180° rotational symmetry with S and R blocks respectively. S and S^* blocks are

consisting two oxygen layers while, R and R* blocks are having three oxygen layers in which one oxygen ion of middle layer is replaced by Sr^{+2} ion [Hosseini and Naghibolashraphy (2008)]. Each block contains 5 interstitial sites of Fe^{+3} ions, i.e., one tetrahedral ($4f_i$) site, one trigonal bi-pyramidal ($2b$) site and 3 octahedral ($2a$, $12k$ and $4f_2$) sites. Strontium hexaferrite is having magnetism due to the ferric ions and each ferric ion has $5\mu_B$ magnetic moment.

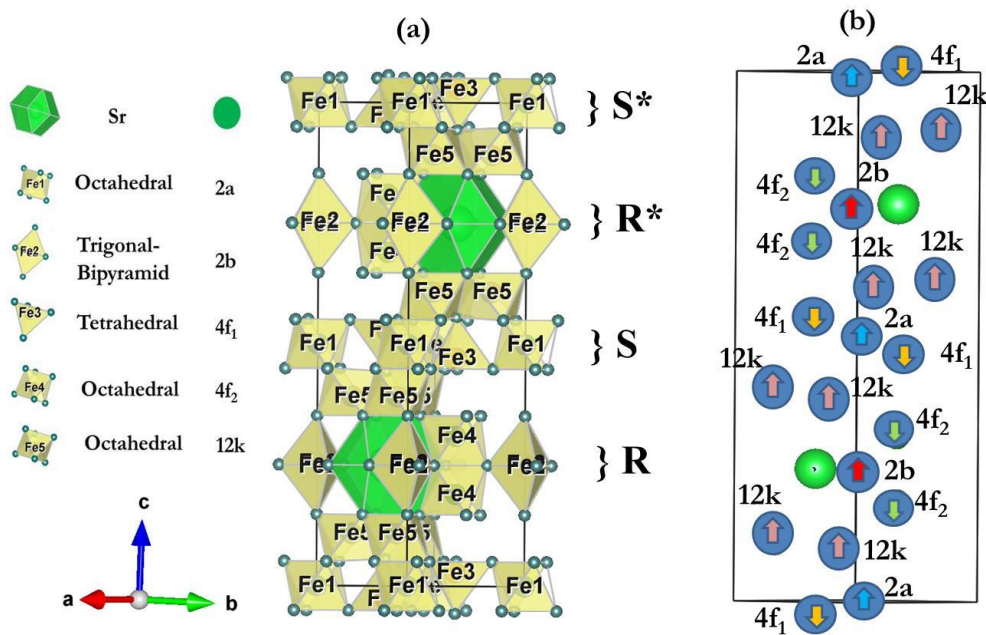


Fig. 1.1 (a) crystal structure of strontium hexaferrite ($\text{SrFe}_{12}\text{O}_{19}$), the green spheres symbolize the strontium atoms and the small grey spheres denote the oxygen atoms. The golden polyhedron represents the Fe^{+3} ions in different sites in the crystal. (b) Representation of the spin configuration of the Fe^{+3} ions in $\text{SrFe}_{12}\text{O}_{19}$.

The hexaferrite structure covers 64 ions in each unit cell. These ions are distributed over 11 different sites [Liu *et al.* (2009)]. The unit cell encloses 38 oxygen ions, $2M$ ($M = \text{Sr}^{+2}$) ions and 24 iron ions. The 24 iron ions are allocated over five different interstitial sites like 3 octahedral sites viz $2a$, $12k$ with spin up and $4f_2$ with spin down, one tetrahedral site $4f_1$

with spin down and one trigonal bipyramidal site $2b$ with spin up state [Iqbal and Ashiq (2008)]. The oxygen ions reside over $4e$, $4f$, $6h$, and $12k$ sites [Lanje and Kulkarni (2001)]. The M ions are sited at $2d$ sites [Kim *et al.* (2000)]. Arrangement of 12 Fe^{+3} spins, as shown in Table 1.5, are positioned in different R (hexagonal) and S (spinel) blocks. Among them, 6 Fe^{+3} present in $12k$ site with spin up, 2 ions of $4f_1$ and $4f_2$ present with spin down arrangement and 1 ion in $2b$ and $2a$ site with spin up. Conclusively, 8 Fe^{+3} ions present in an upward direction and 4 ions present with downward direction. 4 Fe^{+3} ions upward spins are cancelled with downward spins. Eventually 4 Fe^{+3} ions are left per formula unit with upward spins. Each Fe^{+3} ions have five unpaired electrons of 3d orbital which is contributing $5\mu_B$ magnetic moment. According to spin orientation (Table 1.5) the total magnetic moment per formula unit as shown:

$$5\mu_B \times (1[2a] + 1[2b] - 2[4f_1] - 2[4f_2] + 6[12k]) = 20 \mu_B \quad (1.1)$$

Table 1.5 The distribution of Fe^{+3} spin in the sub-lattice [Iqbal and Ashiq (2007)].

Site	Co-ordination	No. of Fe^{+3} ions	Spins	Block
$12k$	Octahedral	6	Up	R-S
$2a$	Octahedral	1	Up	S
$4f_1$	Tetrahedral	2	Down	S
$4f_2$	Octahedral	2	Down	R
$2b$	Trigonal bipyramidal	1	Up	R

1.2.2 Properties of strontium hexaferrites

The strontium hexaferrite is an interesting material due to its unique magnetic, electrical and dielectric properties. Since last few years, various researchers are attracted towards strontium hexaferrites due to relatively high saturation magnetization with high magneto-crystalline anisotropy, low dielectric losses and electrical resistivity [Iqbal and

Ashiq (2007)]. Its magnetic properties are well explained by magnetic ordering of ferric ions and their strong exchange interaction [Iqbal *et al.* (2008)]. In the SrM, Fe⁺³ ions are distributed in five different sites, which are coupled magnetically by super-exchange interaction from O⁻² ions [Zi *et al.* (2018)]. These interactions can be compared analytically by structural aspects such as bond lengths and bond angles between the magnetic ions.

The magnetic property in the Sr-hexaferrite materials is due to the total magnetic moment of atoms or ions. SrM has 20 μ_B net magnetic moments. SrM is permanent magnet which possess the wider hysteresis loop with magneto-crystalline anisotropy constant (k_{eff}) $\sim 3.57 \times 10^6 \text{ erg cm}^{-3}$, critical diameter (D_C) $\sim 0.58 \mu\text{m}$, Curie temperature (T_C) $\sim 477 \text{ (}^\circ\text{C)}$ and coercivity (iH_c) $\sim 2.47 \text{ kOe}$ [Pullar (2012), Cui *et al.* (2018)]. It shows semiconducting nature, i.e., resistivity reduces with temperature. In the beginning, resistivity increases with temperature up to a fixed temperature (metallic nature). That certain temperature is called transition temperature (T_{M-S}). After the T_{M-S} , it starts decreasing with the temperature, that is called semiconducting nature. Pure strontium hexaferrites have $T_{M-S} \sim 318 \text{ K}$ [Ashiq *et al.* (2015)]. The electrical property of Sr-hexaferrite depends on many factors such as annealing temperature, synthesis route, type or amount of substituted constituents etc. [Wang and Zhang (2009)]. Strontium hexaferrite has higher electrical resistivity around 10^7 to 10^{11} ohm-cm [Goldman (2006), Ashiq *et al.* (2017)] than, the metals because of their structure sensitive belongings. SrM shows dielectric behavior also. It is observed that the dielectric constant of SrM decreases with frequency. This is a regular behavior of dielectric performance which is stated by many researchers in Sr ferrites [Smit and Wijn (1954), Want *et al.* (2015)]. This entire fact can be explained on the basis of Koops theory [Koops (1951)]. The dielectric constant of SrM is 19 has been observed at 1 MHz [Katoch *et al.* (2013)].

1.3 Theme of the work

The theme of the present investigation is to enhance the magnetic properties, particularly coercivity and remnant magnetization in Sr-hexaferrite and make it useful for rotating machine applications. The challenge is that most of them do not exhibit high magnetization (M_s) and high coercivity (H_c) simultaneously. Improvement in remanence magnetization (Br) is tricky compared to improve in coercivity. High coercivity can be attained by either the high magneto-crystalline anisotropy, small particle/grain size, and shape anisotropy. High remanent magnetization involves high saturation magnetization and high degree of alignment of the grains along easy magnetic axis.

In this investigation, the Al content has been fixed, i.e., $\text{SrAl}_4\text{Fe}_8\text{O}_{19}$. Different compositions in the $\text{SrAl}_4\text{Fe}_8\text{O}_{19}$ systems are investigated. Further, the influence of synthesis process and cationic substitution on electro-magnetic properties in $\text{SrAl}_4\text{Fe}_8\text{O}_{19}$ hexaferrite have been investigated. The specific objectives of the study are as follows:

- a) Optimization of the synthesis process in $\text{SrAl}_4\text{Fe}_8\text{O}_{19}$ hexaferrite synthesis.
- b) Investigate the effect of Co^{+2} substitution for Fe^{+3} on electro-magnetic properties of the optimized $\text{SrAl}_4\text{Fe}_8\text{O}_{19}$ hexaferrite.
- c) Analyze the effect of Cr^{+3} and Sn^{+4} substitutions for Fe^{+3} on electro-magnetic properties of the optimized $\text{SrAl}_4\text{Fe}_8\text{O}_{19}$ hexaferrite.
- d) Study the influence of Y^{+3} substitutions for Fe^{+3} on electro-magnetic properties of the optimized $\text{SrAl}_4\text{Fe}_8\text{O}_{19}$ hexaferrite.
- e) Study the effect of La^{+3} and Sm^{+3} substitutions for Fe^{+3} on electro-magnetic properties of the optimized $\text{SrAl}_4\text{Fe}_8\text{O}_{19}$ hexaferrite.

1.4 Organization of the thesis

To meet the objectives mentioned above, the thesis is organized into five chapters:

Chapter-I gives a brief introduction about strontium hexaferrite and organization of the thesis.

Chapter-II Reviews the current state of the art of the subject. Efforts have been made to systematically categorize the available information in different sections systematically. This chapter includes the background information that supports to understand the aims and objectives of the present work, along with the reviews of recent reported investigations and results which can be compared.

Chapter-III provides a detailed description of the processing method employed for the preparation of strontium hexaferrite. Various characterization techniques have been applied to investigate the structural, magnetic and dielectric properties and explained briefly.

Chapter-IV explains the results and discussion and it has been divided into five sections (I-V). **Section I** explains the optimization of the synthesis process of $\text{SrAl}_4\text{Fe}_8\text{O}_{19}$, **Section II** describes the effect of Co substitution on the electro-magnetic properties of $\text{SrAl}_4\text{Co}_x\text{Fe}_{8-x}\text{O}_{19}$ ferrites. **Section III** narrates the effect of Cr-Sn substitution on electro-magnetic properties of $\text{SrAl}_4(\text{Cr}_{0.5}\text{Sn}_{0.5})_x\text{Fe}_{8-x}\text{O}_{19}$ ferrites. **Section IV** describes the effect of Y substitution on the electro-magnetic properties of $\text{SrAl}_4\text{Y}_x\text{Fe}_{8-x}\text{O}_{19}$ ferrites. **Section V** deals with the effect of La-Sm substitution on the electro-magnetic properties of $\text{SrAl}_4(\text{La}_{0.5}\text{Sm}_{0.5})_x\text{Fe}_{8-x}\text{O}_{19}$ ferrites. **Chapter-V** includes the conclusive remarks and the future scope of this work.

The entire list of references has been provided after the end of the chapter -V. Finally, a list of publications related to present work has been exhibited at the end.