### **2.1 Introduction**

In this chapter, an effort is made to provide the brief description about the synthesis of nano strontium hexaferrite (SrM) magnetic particles, and the influence of different nonrare earth and rare earth elements substitution on the electro-magnetic properties of strontium hexaferrite.

Magnetic nanoparticles (MNP) have been extensively investigated by many researchers. They have an extensive range of applications, including magnetic resonance imaging, information recording, magnetic visualization, permanent magnets (like rotating machine, transducer) and optical filter etc. [Vedernikova (2015)]. Owing to its unique applications, the researchers are highly focused to provide a number of synthetic ways to produce MNPs of different sizes, compositions and morphology. Though, the successful application of MNP is dependent on the particles stability under different conditions. The implication of size for controlling the electro-magnetic properties is obvious, because the assets of the magnetic nano particles are reliant on their morphology, and dimension. Thus, the synthesis of MNPs with their exposed surfaces and controlled size are of core importance.

# 2.2 Synthesis of hexaferrites

Strontium hexaferrite (SrM) are synthesized by various synthesis processes like solid state or ceramic method, co-precipitate, sol-gel process, and sol-gel auto combustion method etc.

Researchers have reported synthesis of strontium hexaferrite (SrM) by solid state method [Haberey and Kackel (1976), Sozeri *et al.* (2012), Talal *et al.* (2012), Kostishyn *et al.* (2015), Kostishyn *et al.* (2016), Gonzalez *et al.* (2016)]. In solid state method, reaction has

been carried out between  $SrCO_3$  and  $Fe_2O_3$  at high temperature. Beretka and Brown (1971) thoroughly have investigated the effect of different weight ratio of SrCO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> and the synthesis temperature. They have reported that 1:6 weight ratio is the most suitable for synthesis of pure SrM. Still temperature plays a major role to synthesis of the pure SrM phase. Beretka and Brown (1971) & Haberey and Kackel (1976) have reported the coexistence of  $SrFe_2O_4$  and  $Sr_2Fe_2O_5$  phases at low temperature but at higher temperature these two phases react with excess Fe<sub>2</sub>O<sub>3</sub> to form SrM. There is an ambiguity on the precise synthesis temperature range to form pure SrM. Many researchers have reported the existence of Fe<sub>2</sub>O<sub>3</sub> phase along with SrM phase. Sozeri et al. (2012) have reported the formation of 80% SrM along with Fe<sub>2</sub>O<sub>3</sub> phase at 1050 °C temperature. Presence of secondary phase degrades the magnetic properties of SrM. It makes the negative point for solid state method to synthesize the pure SrM compound. Valenzuela (1994) also have done the comparative study and claimed that solid state route is a time taking process. It requires a high calcination temperature and has to control many parameters to maintain the homogeneity [Valenzuela (1994)]. Chemical synthesis routes may get over the restrictions of this method.

Co-precipitation method has been broadly investigated by many researchers for formation of SrM [Kulkarni *et al.* (1989), Yamamoto *et al.* (1997), Hessien *et al.* (2008), Lu *et al.* (2011), Rashad and Ibrahim (2012), Davoodi and Hashemi (2012), Liu *et al.* (2014)]. For synthesis of SrM, this method is a kind of non-stoichiometry iron deficient route [Hessien *et al.* (2008)]. High solubility of  $Sr(OH)_2$  in NaOH makes complication to maintain the stoichiometry composition. To resolve this issue, extra strontium is needed in the preliminary composition [Fang *et al.* (2000)]. Further, many researchers have observed that it is very challenging to maintain the homogeneity in chemical composition, size and shape of the particles [Guo *et al.* (1997), Itoh *et al.* (2003), Kim *et al.* (2004), Liu *et al.* (2013), Liu *et al.* (2014)]. For resolving this issue, Rashad and Ibrahim (2012) have reported that high calcination temperature is needed, but it further promotes some difficulties like agglomeration and coarser particle size formation. Co-precipitation method is highly pH sensitive method and is not preferable for complex system of more than two metal ions [Giri *et al.* (2004), Hessien *et al.* (2008)].

Investigators have also reported the sol-gel method to synthesis the strontium hexaferrite [Lee *et al.* (2003), Ghasemi *et al.* (2008), Masoudpanah and Ebrahimi (2012), Nga *et al.* (2014), Das *et al.* (2015)]. Cerda *et al.* (2003) & Wong *et al.* (2014) have reported that the sol gel method requires high calcination temperature to synthesize SrM without any secondary phase formation. This method needs expensive alkoxide precursors and stringent processing [Giri *et al.* (2004)]. It produces highly agglomerated and partially sintered particles as well [Sapoletova *et al.* (2015)]. Thus, this method further requires milling procedure to make it suitable. Further milling process becomes the part for creating some structural defects, resulting deteriorate in magnetic property [Sapoletova *et al.* (2015)]. For avoiding further milling process, researchers have discovered the sol-gel auto combustion process which is more appropriate [Panchal and Jotania (2012)].

Sol-gel auto combustion synthesis route has been recommended as a suitable synthesis route to form pure phase of hexaferrites [Garcia *et al.* (2012)]. Panchal and Jotania (2012) have reported the synthesis of SrM by the sol-gel auto combustion process and have claimed the pure SrM formation at lower temperature as compare to other synthesis route. On the other hand, this method leads the consumption of inexpensive precursors which uses low external energy. Consequently, nano-sized, highly reactive and homogeneous powder is

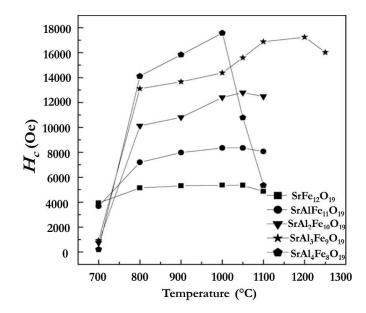
formed [Roy and Bera (2005), Ashiq *et al.* (2015)]. This method also allows the formation of narrowly sized hexaferrite particles that forms at relatively low calcination temperature along with worthy magnetic properties [Zhong *et al.* (1997a), Zhong *et al.* (1997b), Lee *et al.* (2003), Nga *et al.* (2014)]. Generally, metal nitrate salts are used as reactant and glycine, urea, hydrazine, alanine, carbo-hydrazide and citric acid are used as fuel in sol-gel auto combustion synthesis route. Citric acid is used generally as fuel because other fuels contain  $N_2$  and releases extra amount of pollutant  $N_2$  gas during combustion reaction.

### 2.3 Effect of non-rare earth ions substitution

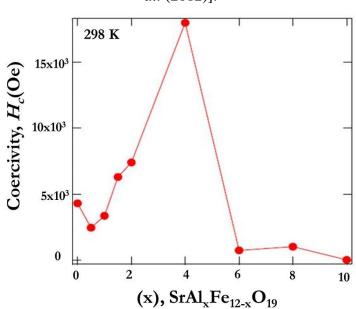
Researchers have been motivated to improve the electro-magnetic properties by the substitution of non-rare earth ions in SrM. Generally, non-rare earth ions like Al, Co, Cr, Sn, Ni, Zr etc. or their mixture are substituted at different sites in SrM. These substitutes take different sitting sites in the structure. Thus, they can change many properties as a result of modified cation distribution in the hexaferrite.

Al<sup>+3</sup> are used to modify the electro-magnetic properties in the hexaferrite. Wang *et al.* (2012) have prepared Al substituted SrM, i.e.,  $SrAl_xFe_{12-x}O_{19}$  and reported the effect of Al<sup>+3</sup> on magnetic properties. With Al<sup>+3</sup> substitution, saturation magnetization ( $M_s$ ) is found to decrease due to the preference of Al<sup>+3</sup> at spin up site of Fe ions. It may also be due to the magnetic Fe<sup>+3</sup> ions are being substituted by smaller ionic radii nonmagnetic Al<sup>+3</sup> ion. This decreases the lattice parameters through the fluctuation of the distance among magnetic ions. This fluctuation leads to suppress the super-exchange interactions and deteriorates the interaction between magnetic ions. However, it enhances the anisotropy of the system. Thus, coercivity ( $H_c$ ) has increased up to maximum value of 17570 Oe at x = 4.0, i.e., SrAl<sub>4</sub>Fe<sub>8</sub>O<sub>19</sub>. It is much larger value than the pure strontium hexaferrite (5356 Oe) and it is even larger

than the Nd<sub>2</sub>Fe<sub>17</sub>B (15072 Oe) (Figure 2.1) [Wang et al. (2012)]. Further, Bukhtiyarova et al. (2009) have reported the effects of different cations on the hexaaluminates. The doping of transitional metals into the hexaaluminate, accelerates the crystallization process [Bukhtiyarova et al. (2009)]. Luo et al. (2012) have prepared successfully Al<sup>+3</sup> doped  $SrFe_{12}O_{19}$  and observed that  $M_s$  and remanence magnetization  $(M_r)$  decreases up to x = 0.4 while,  $H_c$  reaches its maximum value up to 18.1 kOe at x = 4.0, as shown in Figure 2.2. Decrease in  $M_s$  and  $M_r$  are explained by the decrease in super-exchange interaction among magnetic ions and by the magnetron numbers as well. The magnetron number, i.e.,  $\mu_B$  is related to  $M_s$  of the sample. Luo *et al.* (2012) further have added that non-magnetic Al<sup>+3</sup> substitution decrease the net  $\mu_{\rm B}$  of the system. That is responsible for decreasing the  $M_s$  and  $M_r$  of the system. The 321% of enhancement in  $H_c$  is credited to the magneto-crystalline anisotropy and grain size. In addition, if grain size is greater than the critical grain size of strontium hexaferrite than particles are in multi-domain structure, if less, than particles belong to mono-domain structure [Luo et al. (2012)]. It is observed that the average grain size of prepared Al substituted SrM is larger than the critical grain size which is 1µm [Stuijts et al. (1968)]. This indicates, the prepared samples are having the multi domain structure [Stuijts et al. (1968)]. However, within the multi domain structure, grain size decreases with composition and increases the numbers of grain boundaries in the system. It induces the hindrance in domain wall motion which is responsible for increasing the  $H_c$ . Since, maximum  $H_c$  is observed by Al substitution in SrM. Further, many works have been carried out by Haiyan He in 2010 and 2011 on SrAl<sub>4</sub>Fe<sub>8</sub>O<sub>19</sub> to investigate the magnetic property, variation in morphology and magneto-crystalline anisotropy properties [He (2010), He et al. (2011)].



**Figure 2.1** Curve of the  $H_c$  of SrAl<sub>x</sub>Fe<sub>12-x</sub>O<sub>19</sub> ( $0 \le x \le 4$ ) vs. annealing temperature [Wang *et al.* (2012)].



**Figure 2.2**  $H_c$  plot of SrFe<sub>12-x</sub>Al<sub>x</sub>O<sub>19</sub> samples with the function of Al<sup>+3</sup> content [Luo *et al.* (2012)].

Figure 2.3 shows the formation of uniform, hexagonal platelet like surface morphology of prepared SrM [He (2010)]. Ashiq *et al.* (2011) have stated the dielectric effect

of Al-Cr substituted SrM. They have reported the decrement in dielectric constant ( $\mathcal{E}$ ) with substitution. With the substitution, the substituted cations occupy the octahedral site of the Fe<sup>+3</sup> ion and reduces the Fe<sup>+3</sup> ions for conduction mechanism caused by electron hoping at octahedral site. Iqbal *et al.* (2008) also have described the increment in the resistivity ( $\rho$ ) with Al-Ga substitution, whereas, decreases the dielectric constant in SrM system.

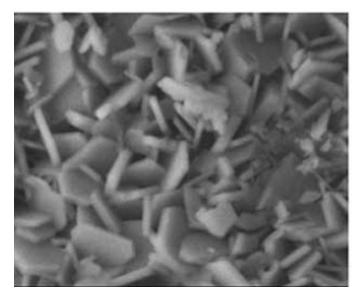
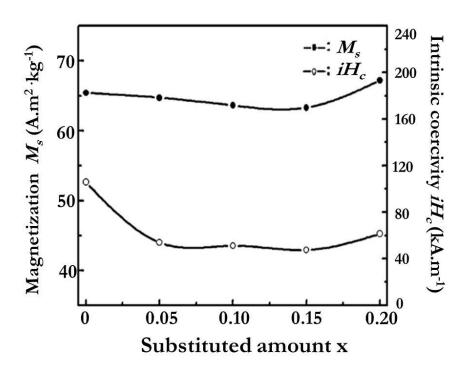


Figure 2.3 SEM image of SrAl<sub>4</sub>Fe<sub>8</sub>O<sub>19</sub> [He (2010)].

Cobalt is normally used in hexaferrite to enhance the densification as well as electromagnetic properties. Xie *et al.* (2012) have observed the effect of Co on SrM and found that the  $M_s$  is increased with substitution. Liu *et al.* (2012) have also reported that with increasing the Co content, the intrinsic  $H_c$  and  $M_s$  are modified (Figure 2.4). Further, Ebrahimi *et al.* (2012) have claimed about physical properties of Co doped SrM. Substitution of Co enhances the densification of the system and affects the electro-magnetic properties of synthesized sample. Ruikar *et al.* (2013) have synthesized the Co substituted SrM and found that the absorption band in Fourier-transform infrared spectroscopy (FTIR) has been shifted to higher frequencies which are attributed to stretching of Fe-O bonds. Shifting in higher frequencies and elongation of Fe-O bonds give the sign about the substitution of Co is being taken placed in the system. By the substitution of Co,  $M_s$  improves [Mal *et al.* (2012), Carroll *et al.* (2017)]. This is may be owing to the Co<sup>+2</sup> which replace the Fe<sup>+3</sup> from spin down site and improve the net magnetic moment of the system [Ruikar *et al.* (2013)]. They also have stated that higher concentration of Co<sup>+2</sup> in strontium hexaferrite enhances the charge carrier concentration and activation energy of hopping electrons [Ruikar *et al.* (2013)]. Joshi *et al.* (2017) have explored the effect of W<sup>+4</sup> on Co<sup>+2</sup> doped strontium hexaferrite. They have reported that the anisotropy field and  $M_s$  are increased, whereas,  $H_c$  is decreased with substitution and also claimed the enhancement in energy product  $(BH)_{max}$  of SrM.



**Figure 2.4** The variation of saturation magnetization ( $M_s$ ) and intrinsic coercivity ( $iH_c$ ) as a function of Co content [Liu *et al.* (2012)].

Chromium substitution has also been explored by many researchers for improving the electro-magnetic properties in SrM. Jauhar *et al.* (2011) have examined the effect of Cr

substitution in SrM, i.e., SrCr<sub>x</sub>Fe<sub>12-x</sub>O<sub>19</sub>. Further, Asghar and Rehman (2012) have explored the Zn effect of Cr substituted SrM (SrCr<sub>x</sub>Zn<sub>x</sub>Fe<sub>12-2x</sub>O<sub>19</sub>). With substitution, the enhancement in  $H_c$  is observed due to decrease in grain size with the substitution. Huang et al. (2015) have explored the  $(BH)_{max}$  of Cr doped strontium hexaferrite through ramanence (Br) and intrinsic coercivity  $(iH_c)$  of the system. Behavior of Br is directly related to the magnetization ( $M_s$  and  $M_r$ ) and density. Replacing Fe<sup>+3</sup> (5µ<sub>B</sub>) by the Cr<sup>+3</sup> (3µ<sub>B</sub>), which has the lower magnetic moment than Fe<sup>+3</sup>, effects the net magnetization. The density, grain size and energy product is found to increase with the substitution. (BH)max, maximum energy product, is the maximum area of the second quadrant of B-H loop. It is influenced through the Br and  $iH_c$ values as illustrate in Figure 2.5. Since, improvement in density encourages the crystal growth of the system and decreases the porosity which reduces the shearing of domain pinning that is responsible for increment of Br. Meanwhile, intrinsic coercivity  $(iH_c)$ decreases due to increase in the grain size that reduces the hindrance of magnetic domain transfer in the prepared sample. Slimani *et al.* (2018) have investigated the Cr doped SrM;  $SrFe_{12-x}Cr_xO_{19}$ . They have observed that the anisotropy constant (k<sub>eff</sub>),  $M_s$  and  $H_c$  are increased at lower concentration of Cr in SrM. Ashig et al. (2011) have synthesized Al-Cr doped strontium hexaferrite (SrAl<sub>x</sub>Cr<sub>x</sub>Fe<sub>12-2x</sub>O<sub>19</sub>) and reported the modified magnetic properties. Asghar and Rehman (2012) have described the Cr-Zn effects on dielectric properties of SrM. Dielectric constant is decreased and resistivity is increased with the substitution.

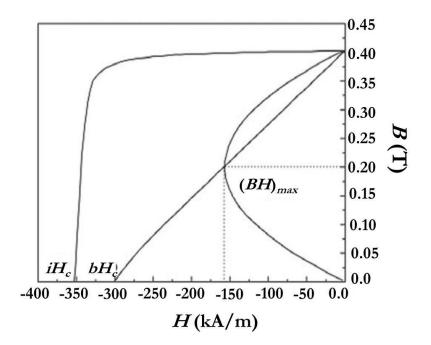


Figure 2.5 Typical demagnetizing loop of SrFe<sub>11.8</sub>Cr<sub>0.2</sub>O<sub>19</sub> ferrite [Huang et al. (2015)].

Davoodi and Hashemi (2011) have investigated the effect of Sn–Mg on strontium hexaferrites. With the substitution,  $M_s$  is increased while decrement in  $H_c$  is observed. Liyanage *et al.* (2013) have studied on Zn-Sn doped strontium hexaferrite, SrFe<sub>12-</sub> <sub>x</sub>(Zn<sub>0.5</sub>Sn<sub>0.5</sub>)<sub>x</sub>O<sub>19</sub>. With substitution, it is observed that  $M_s$  has drastically improved due to Sn<sup>+4</sup> and Zn<sup>+2</sup>, which prefers spin down site in SrM. Jamalian (2015) has investigated the Sn-Tb substituted SrM and noted that  $M_s$  and  $M_r$  have increased with falling in  $H_c$  with the substitutions. This behavior of magnetization ( $M_s$  and  $M_r$ ) is attributed to the non-magnetic ions (Sn<sup>+4</sup>-Tb<sup>+4</sup>), which are replacing Fe<sup>+3</sup> (5µ<sub>B</sub>) from the down spin sites. This improves the total magnetic moment of the system.  $H_c$  decreases due to decrease of magneto-crystalline anisotropy and increase in grain size [Jamalian (2015)]. Dixit *et al.* (2017) have investigated the effect of various ions substitution on SrM and reported that Sn, Bi, Sc and Sb improve the  $M_s$  whereas, Co, Al, P and Ti improve the anisotropy field of SrM. Ashiq *et al.* (2015) have investigated the Sn substituted SrM. They observed the curie temperature (Tc), i.e., transition state of ferrimagnetic to paramagnetic magnetic behavior, is increased with substitution. This is happened due to the spin canting phenomenon which is related to transition of collinear to non-collinear ordered spin [Ashiq *et al.* (2015)]. At lower frequency, maximum value of dielectric constant has been observed and decreases with the frequency [Murugan and Varma (2001), Prakash and Varma (2007), Sharma *et al.* (2008)]. This nature of dielectric constant has been elucidated by the Maxwell–Wagner [Wagner (1913), Thakur *et al.* (2015), Chanda *et al.* (2016)] model. According to the model, hexaferrites have a dielectric structure which is presumed to consist of two layers of conducting grains with a poor conducting grain boundary in between. The polarization is happened between the Fe<sup>+2</sup> and Fe<sup>+3</sup> through the conduction mechanism, which is known as hopping mechanism. With increasing the frequency, dielectric constant decreases due to the hopping of electrons, between Fe<sup>+2</sup> and Fe<sup>+3</sup>, which can not follow the external field.

Many more substitutions have been explored by many researchers. Likewise, Ni<sup>+2</sup> substitution [Iqbal *et al.* (2007), Kanagesan *et al.* (2014), Kuruva *et al.* (2015), Roohani *et al.* (2017)]. Iqbal *et al.* (2007) have explored the effect of  $Zr^{+4}$  and Ni<sup>+2</sup> on SrM. With substitution, magnetization increases by the enhancement in density and magnetic moment of the system. The coercivity is observed to decrease due to fall in magneto-crystalline anisotropy with substitution. Kanagesan *et al.* (2014), have reported that Ni<sup>+2</sup> substitution decreases the  $H_c$  and  $M_s$  in Sr hexaferrites. Kuruva *et al.* (2015) also have observed the decrement in Hc with Ni substitution. This decrease in  $H_c$  is happened due to Ni<sup>+2</sup> which encourages the grain coarsening of the system [Kuruva *et al.* (2015)]. Further, Mn-Co-Zr doped Sr hexaferrite have been explored by Ghasemi and Morisako (2008). Iqbal *et al.* 

(2009) have investigated the effect of Zr-Zn on SrM, i.e.,  $SrZr_xZn_xFe_{12-2x}O_{19}$ . The Curie temperature of the prepared sample decreases due to decrease  $Fe^{+3}$  ion which reduces the super-exchange interaction of the system. Whereas, dielectric constant increases with substitution. It can be described by the polarization mechanism analogous to the conduction manner.

#### 2.4 Effect of rare earth ions substitution

Researchers have observed that rare earth substitution in SrM improves its electromagnetic properties. They have observed that rare earth substitution remarkably modify the physical as well as magnetic properties. Many rare earth substitution like, La, Sm, Y, Gd, Er etc. or their mixture have been investigated by researchers in SrM.

Liu *et al.* (2002a) have reported the synthesis of La substituted SrM and observed that curie temperature is decreased with substitution. Initially,  $Fe^{+3}$  ions are aligned collinearly in SrM owing to super-exchange interaction. With substitution of La, valence of  $Fe^{+3}$  is started to change into  $Fe^{+2}$  which decrease the strength of interaction. The deviation in collinear arrangement is started and changed into non-collinear arrangement, i.e., known as spin canting structure. This spin canting structure decreases the curie temperature of the system with substitution due to decrease in the super-exchange interaction of Fe-O bond. Liu *et al.* (2002a) have further added that this interaction can be determined by the bond length and bond angle. This bond angle and bond length can be calculated by the structural parameters from the refinement technique. Anderson *et al.* (1963) have suggested that if the bond angle is near to 180°, then it shows the maximum interaction and near to 90°, it shows minimum interaction. In case of bond length, interaction comes to be insignificant over 3Å. Further, Li *et al.* (2011) have stated that La substitution leads to decrease the grain size and improves  $H_c$  with substitution in the synthesized sample. Thakur *et al.* (2013a) have stated that the La substituted SrM is having high coercivity (Figure 2.6a) along with high anisotropy constant. With substitution, resistivity (Figure 2.6b) increases whereas, dielectric constant decreases. This is attributed by the formation of smaller grain size with substitution. Nourbakhsh *et al.* (2014) have further explored the La-Co substituted SrM. They have claimed that the substituent helps to increase the intrinsic coercivity ( $iH_c$ ) and remanence (Br) of the system (Figure 2.7). Want *et al.* (2015) have reported the dielectric behavior of La substituted SrM. The dielectric behavior completely depends on the hopping mechanism between Fe<sup>+3</sup> and Fe<sup>+2</sup> ion and grain size parameters. Increasing in grain size enhances the system's dielectric constant [Vadla *et al.* (2018)]. Bigger grain relates to low resistivity because it requires small amount of energy to transfer the electrons between ions in the grains [Want *et al.* (2015)].

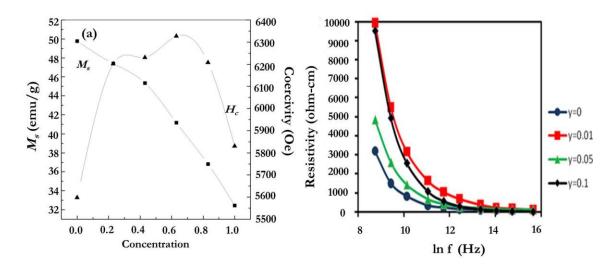


Figure 2.6 (a) Variation of magnetic properties of strontium hexaferrite with La<sup>+3</sup> [Thakur *et al.* (2013a)] and (b) Variance of electrical resistivity for Sm<sup>+3</sup> substituted strontium hexaferrite (x = 0.0–1.0) at room temperature [Hilli *et al.* (2012)].

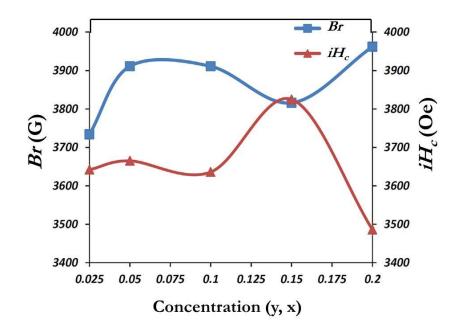


Figure 2.7 Variation of La and Co (x and y) on Br and  $iH_c$  [Want et al. (2015)].

Grossinger *et al.* (2003) have reported the effect of La, Sm and Nd in SrM and observed that Sm helps to increase in the intrinsic coercivity ( $iH_c$ ) without disturbing the other magnetic parameters like  $M_s$  and  $M_r$ . Increasing in intrinsic coercivity ( $iH_c$ ) is happened due to two main reasons. First is due to increase in magneto-crystalline anisotropy constant and second one, is due to doping of rare earth ions. Doping decreases the grain size which reduces the decoupling of grains and enhances the hindrance in the flow of magnetic spins. Therefore, Sm<sup>+3</sup> increase the  $iH_c$  by the 18% than other rare earth component (Figure 2.8) [Grossinger *et al.* (2003)]. Cui *et al.* (2014) have stated the Sm substituted SrM and reported that  $M_s$  is observed to increase with substitution. Wu *et al.* (2018) have prepared Sm-Cu substituted SrM. Ramanence (Br) is observed to increase up to a certain substitution and  $H_c$  is increased up to 6.8 kOe. Xie *et al.* (2018) have synthesized the Sm and Co substituted SrM. Asghar *et al.* (2018) have reported the Sm-Cr substituted SrM and stated the enhancement in  $M_s$  due to the occupancy site which increase the total magnetic moment of

the SrM. Luo *et al.* (2015) have synthesized Sm<sup>+3</sup> and Er<sup>+3</sup> substituted SrM. Sm<sup>+3</sup> increases the coercivity ( $H_c$ ) around 6.9 kOe. Buzinaro *et al.* (2016) have reported the synthesis of Sm substituted SrM and claimed that Sm<sup>+3</sup> substitution improves the  $H_c$  due to the improvement in magneto-crystalline anisotropy constant. Luo *et al.* (2015) have investigated the electrical behavior of Sm substituted SrM. With the substitution, it is found that the dielectric properties are improved. Singh *et al.* (2010) have investigated the dielectric behavior of rare earth doped SrM.

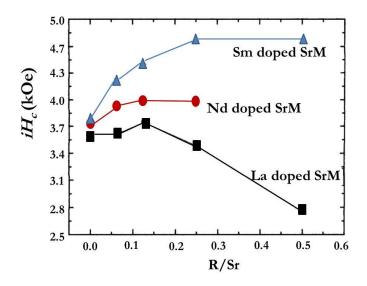
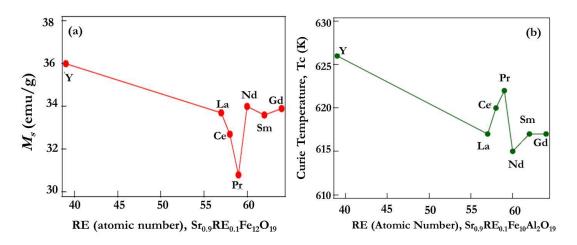


Figure 2.8 Variation of intrinsic coercivity ( $iH_c$ ) in R = La, Nd, and Sm substituted SrM with R/Sr ratios as the R-content [Grossinger *et al.* (2003)].

They have stated that at lower concentration, dielectric properties are increased whereas, at higher concentration it is decreased along with increasing the resistivity of the system [Singh *et al.* (2010), Lo *et al.* (2014)]. These are attributed by the formation of insulating secondary phase formation.

Rai *et al.* (2013a) have investigated the effect of different rare earth ions (RE) substitution on  $SrAl_2Fe_{10}O_{19}$  and explored the effect of RE; Y, Ce, La, Nd, Pr, Gd and Sm on

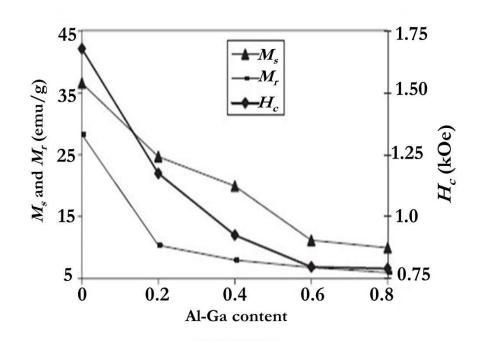
structural and magnetic property. Among them,  $Y^{+3}$  ion helps to improve the saturation magnetization ( $M_s$ ) (Figure 2.9a), the Curie temperature (Tc) (Figure 2.9b) and the coercivity by 20% due to enhancement in magneto-crystalline anisotropy constant ( $k_{eff}$ ) of the system [Rai *et al.* (2013a)]. Topkaya *et al.* (2016) have reported the  $Y^{+3}$  effects and observed that  $M_s$ is increased due to  $Y^{+3}$  substitutions which occupy at spin down site and increase the total magnetic moment of the system. Rehman *et al.* (2017) have synthesized the  $Sr_{0.7}Y_sLa_{0.3-}$  $_xFe_{12-y}Co_yO_{19}$  ferrite and reported that the  $Y^{+3}$  helps to improve the  $M_s$  by increasing the super exchange interaction at 2b and 12k sites. It also increases the magneto-crystalline anisotropy constant ( $k_{eff}$ ) of the system resultant,  $H_c$  increases. Bakis *et al.* (2016) have investigated the effect of  $Y^{+3}$  doping on dielectric properties. With the substitution, dielectric constant is decreased. This diminish in dielectric constant is due to the substituent which decreases the Fe<sup>+3</sup> ions from the charge transfer mechanism between Fe<sup>+3</sup> and Fe<sup>+2</sup> ions.



**Figure 2.9** (a) Variance of saturation magnetization ( $M_s$ ) and (b) Variation of Tc on rareearth ion substitution in Sr<sub>0.9</sub>RE<sub>0.1</sub>Fe<sub>10</sub>Al<sub>2</sub>O<sub>19</sub> [Rai *et al.* (2013a)].

Many other rare earth substitutions have been explored like, Iqbal *et al.* (2008) have synthesized the Al-Ga substituted SrM, i.e.,  $SrAl_xGa_xFe_{12-2x}O_{19}$  and have reported the

magnetic characterization like  $M_s$ ,  $M_r$  and  $H_c$  of the system (Figure 2.10). Rezlescu *et al.* (2008) have reported the synthesis of La, Gd and Er doped strontium hexaferrite and found that rare earth reduces the grain growth of the system by generating internal stress. Further, Doroftei *et al.* (2008) have studied on Gd substituted SrM. They have stated that with rare earth substitution, lattice parameter increase up to a certain limit due to the limited solubility of Gd in SrM. Litsardakis *et al.* (2007) have also reported that the outcome of Gd substituted SrM. They observed that Gd substitution influences their structural as well as magnetic properties of the matrix.



**Figure 2.10** Saturation magnetization ( $M_s$ ), remanence ( $M_r$ ) and coercivity ( $H_c$ ) as a function of Al–Ga content [Iqbal *et al.* (2008)].

## 2.5 Summary of literature review

The inclusive literature review tells that the synthesis of nano-crystalline Sr hexaferrite powder can be done by sol-gel auto combustion process, which has been attempted by many researchers. The electro-magnetic properties such as Br,  $H_c$ , Tc, dielectric

constant and resistivity are dependent on the densification, grain size and their distribution in the synthesized materials. Substitution of different cations in SrM has become the attractive approaches for investigators to enhance their properties and to increase their field of applications. Among all, non rare-earth substitutions like Al, Co, Cr and Sn shows significant improvement in the electro-magnetic properties of SrM.

Various composition in the system  $SrAl_4Fe_8O_{19}$  have been investigated. Wang *et al.* (2012) have reported the Al substitution in SrM and found that at x = 4 ( $SrAl_4Fe_8O_{19}$ ) shows the maximum coercivity around 17.5 kOe. This optimum Al content is used by various other researchers for Sr hexa-ferrites. He (2010) has worked on  $SrAl_4Fe_8O_{19}$  ferrite to investigate their magnetic and anisotropy property. He *et al.* (2011) have also done further study about the magnetic properties of  $SrAl_4Fe_8O_{19}$  ferrite with various synthesis methods. This optimum composition can be applied for further exploring with other aspects like cation distribution and increasing their application fields with improved electro-magnetic properties.

Different varieties of electro-magnetic properties have been explored in Co substituted SrM. Xie *et al.* (2012) have reported the increasing in  $M_s$  whereas, Liu *et al.* (2012) have stated the modified  $iH_c$  and magnetization with Co substitution. Optimization of Co substitution with related to Fe and Al could be desirable for improved electro-magnetic properties.

The  $H_c$  is dependent on the k<sub>eff</sub>, grain size and their distribution. It has been claimed that Cr improves  $H_c$  in SrM due to enhance in anisotropy constant [Slimani *et al.* (2018)]. Whereas, many researchers have also observed that the Sn increases the magnetization of SrM [Jamalian (2015)]. These suggest that, the Cr and Sn substitution may improve the electro-magnetic properties in Sr hexaferrites. Effect of rare earth substitution on SrM has been investigated by many researchers [Liu *et al.* (2002a), Grossinger *et al.* (2003), Singh *et al.* (2010), Li *et al.* (2011), Thakur *et al.* (2013a), Rai *et al.* (2013a), Topkaya *et al.* (2016), Wu *et al.* (2018)]. Among all these rare earth substitutions, Y, La, and Sm shows remarkable improvement in magnetic properties which gives the option for exploring the hard magnetic properties of SrAl<sub>4</sub>Fe<sub>8</sub>O<sub>19</sub>.

Y substitution shows the increment in Curie temperature along with  $H_c$  of SrM [Rai *et al.* (2013a)]. Similarly, this substitution could enhance the electro-magnetic properties in SrAl<sub>4</sub>Fe<sub>8</sub>O<sub>19</sub>.

The investigation has shown that La remarkably improves the magnetization and intrinsic coercivity of the SrM [Liu *et al.* (2002a)]. Whereas, Grossinger *et al.* (2003) have reported the improvement in  $H_c$  by 18% due to Sm substitution. Hence, further research is desirable on the combined (La & Sm) substitution effect in SrAl<sub>4</sub>Fe<sub>8</sub>O<sub>19</sub> to improve the electro-magnetic properties.

From literature reviews, it is also found that the study about structural aspects like, bond length and bond angle which affects the magnetic properties and anisotropy, have not explored properly. The structural refinement and different cationic effects on  $SrAl_4Fe_8O_{19}$ have not been investigated yet. Thus, it gives the possibility for exploring different cationic effects on this composition and enhancing the application fields of  $SrAl_4Fe_8O_{19}$ .

# 2.6 Objectives of the work

The objective of the present work is to synthesize and characterize substituted  $SrAl_4Fe_8O_{19}$  magnetic materials with improved electro-magnetic properties. That can be fitted for rotating machine applications. The investigation comprises of the following stages: (a) the Al concentration of strontium hexaferrite will be fixed at  $SrAl_4Fe_8O_{19}$  composition and (b) The strontium hexaferrite materials will be synthesized by the sol-gel auto combustion process. The influence of synthesis process and substitutions on the electromagnetic properties of the strontium hexaferrite will be studied by the following objectives:

a) Optimization of the synthesis process in  $SrAl_4Fe_8O_{19}$  hexaferrite synthesis.

- b) Study the effect of  $Co^{+2}$  substitution for  $Fe^{+3}$  on electro-magnetic properties of the optimized  $SrAl_4Fe_8O_{19}$  hexaferrite.
- c) Analyze the effect of Cr<sup>+3</sup> and Sn<sup>+4</sup> substitutions for Fe<sup>+3</sup> on electro-magnetic properties of the optimized SrAl<sub>4</sub>Fe<sub>8</sub>O<sub>19</sub> hexaferrite.
- d) Study the influence of  $Y^{+3}$  substitutions for  $Fe^{+3}$  on electro-magnetic properties of the optimized  $SrAl_4Fe_8O_{19}$  hexaferrite.
- e) Study the effect of  $La^{+3}$  and  $Sm^{+3}$  substitutions for  $Fe^{+3}$  on electro-magnetic properties of the optimized  $SrAl_4Fe_8O_{19}$  hexaferrite.