



# Morphological and Magnetic Studies of Ir-Ni Substituted M-Type Strontium Nano-Hexaferrites Prepared By Sol-Gel Auto Combustion Technique

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## ABSTRACT:

M type  $\text{SrFe}_{12}\text{O}_{19}$  hexagonal ferrite powder with partial substitution  $x\text{Ir}^{+4} + x\text{Ni}^{+2}$  for  $2x\text{Fe}^{+3}$  have been prepared by Sol-gel auto-combustion process using urea as a fuel and nitrates and bromides as oxidants. The precursor was annealed at the temperature of 800°C. The effect of composition on the crystallography, particle morphology and magnetic properties of  $\text{SrO} \cdot (6-x)\text{Fe}_2\text{O}_3 \cdot x(\text{NiIr})\text{O}_3$ , ( $x= 0.02$  and  $0.04$ ) type hexagonal ferrite have been systematically investigated by an X-ray Diffractometer (**XRD**), Transmission Electron Microscopy (**TEM**) and Vibrating Sample Magnetometer (**VSM**). The obtained x-ray diffraction pattern of the samples showed magneto-plumbite phase for all the substituted compounds. Values of both 'a' and 'c' lattice parameters were found to increase with increasing concentration. TEM images of the sample demonstrate the formation of nanosize particles, which are found to decrease with substitution. Magnetic measurement showed that the coercivity ( $H_c$ ), saturation magnetisation ( $M_s$ ) and remanence ( $M_r$ ) tends to decrease with respect to Ir-Ni content.

**Key words** : Hexagonal ferrites; Sol-gel auto-combustion; crystallography; nanoparticles; magnetic properties etc.

## 1. Introduction:

Strontium hexaferrite  $\text{SrFe}_{12}\text{O}_{19}$  powders have been a subject of continuous interest and intensive study for several decades [1-2].  $\text{SrFe}_{12}\text{O}_{19}$  powders with a narrow size distribution are promising materials for industrial application due to their high coercivities and their moderate saturation magnetization [3-6]. Recently researchers on ferrites have been concentrated on nanoferrite material as the size of the particle is smaller than the critical size, the particle exists in single domain and domain wall resonance is avoided [7-8]. The nanosized particles can be produced by a large number of methods like co precipitation, citrate precursor, sol-gel, solid state method, hydrothermal synthesis, glass crystallization, etc. The magnetic properties of hexagonal ferrite depend on the intrinsic magnetic properties of M-type phase. An improvement of the intrinsic magnetic properties can be obtained by the partial substitution of Sr or Fe, or both. The improved magnetic properties with proper substitutions make hexaferrite an active ingredient in magnetic recording media [7-8]. Polycrystalline hexaferrites are also good dielectrics [9] and higher values of magnetic parameters makes them suitable for microwave applications [10] The present work investigates the preparation process of Ni-Ir substituted Strontium nano hexaferrites with improved sol-gel auto combustion process and their structural and magnetic properties.





## 2. Experimental :

**2.1 Synthesis:** The ferrites sample with composition  $\text{SrO} \cdot (6-x)\text{Fe}_2\text{O}_3 \cdot x(\text{NiIr})\text{O}_3$ , ( $x=0.02$  and  $0.04$ ) were synthesised by using sol-gel auto combustion method also called as self propagating synthesis to study the structural and magnetic properties. AR grade  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{IrBr}_4$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{CO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were weighed in appropriate stoichiometric proportions and dissolved in minimum amount of distilled water. The solution is then heated to transform into gel by intermediate heating of the solution. This reddish brown gel was placed in a microwave oven for auto-combustion which transform the gel into 'foamy blackish powder'. Then it is kept rotating but without any exposure of microwave to cool it and to get out all the fumes from it. The ash of the sample is then grinded in three cycles using pestle and mortar to make it more fine and ultrafine to produce nanohexaferrite. The polyvinyl alcohol solution (2-3 drops) has been mixed before they were pressed by hydraulic press into pellets using stainless steel die set under uniaxial appropriate pressure for 15min. The Poly Vinyl Acetate has been used as a binder. The pellets of the sample have been calcined at  $800^\circ\text{C}$  for about 4 hrs in the electric furnace to obtained M type strontium hexaferrites. The prepared samples are then stored in air tight containers by sealing them.

**2.2 Characterization:** X-ray diffraction analysis was performed by XRD (Bruker Kappa Apex II D8 advance, Cu  $K\alpha$  radiation  $\lambda = 0.1540$  nm) to determine the phase, unit cell parameters and crystalline structure. The crystalline size for each composition are calculated from XRD line width using Scherer formula

$$D = k\lambda / h\cos\theta$$

where D is average size of the crystallites, k is Scherer constant (0.9),  $\lambda$  is wavelength of radiation ( $1.54056\text{\AA}$ ) and h is peak width of half height (FWHM). The particle size of the each sample was examined by Transmission Electron Microscopy (TEM-CM 200 at operating voltage of 20-200KV with the resolution of  $2.4\text{\AA}$ ). Moreover, magnetic properties and characters of the samples are examined by the study of hysteresis loops obtained by using Vibrating Sample Magnetometer.

## 3. Results and discussion:

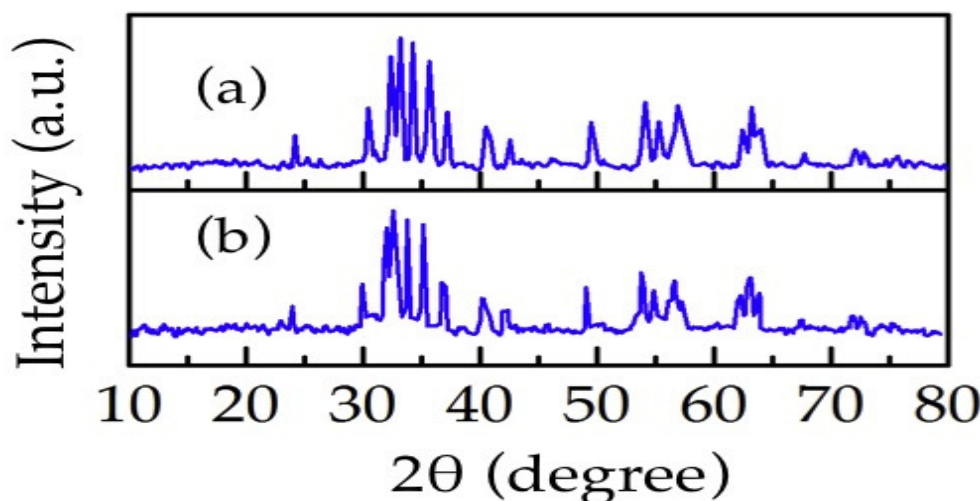
**3.1 Structural Analysis:** The XRD pattern of high purity Ir and Ni doped strontium ferrites with different doping concentration were depicted in figure 1. The intensity diffraction peaks of the samples were found at (0 0 6), (1 0 7), (1 1 4), (2 1 3), (2 0 0) which belong to magnetoplumbite strontium ferrite phase with space group  $P6_3/mmc$  and no intermediate phases were observed. This indicates that the substitution of  $\text{Fe}^{+3}$  by Ni-Ir in the M-type phase is complete. The broad XRD line indicates that the ferrite particles are in nano size. The crystalline size for  $\text{Sr}(\text{NiIr})_{.02}\text{Fe}_{11.96}\text{O}_{19}$  and  $\text{Sr}(\text{NiIr})_{.04}\text{Fe}_{11.92}\text{O}_{19}$  is  $39.18\text{nm}$  and  $20.61\text{nm}$  respectively, calculated from XRD line width using Scherer's formula. There is slight increase in the value of 'a' and 'c' with increase in dopant concentration shown in table 1 pertaining to the fact that the ionic radii of doping Ir ( $0.68\text{\AA}$ ) and Ni ( $0.69\text{\AA}$ ) is not same as that of  $\text{Fe}^{+3}$  ( $0.64\text{\AA}$ ) ion. As a result, the cell volume of strontium ferrite increases after being doped with  $\text{Ni}^{+2}$  and  $\text{Ir}^{+4}$  ions. The similar trend of lattice parameter and cell volume was reported by K.G.Rewatkar [17] in Cu-Ti substituted calcium ferrites.



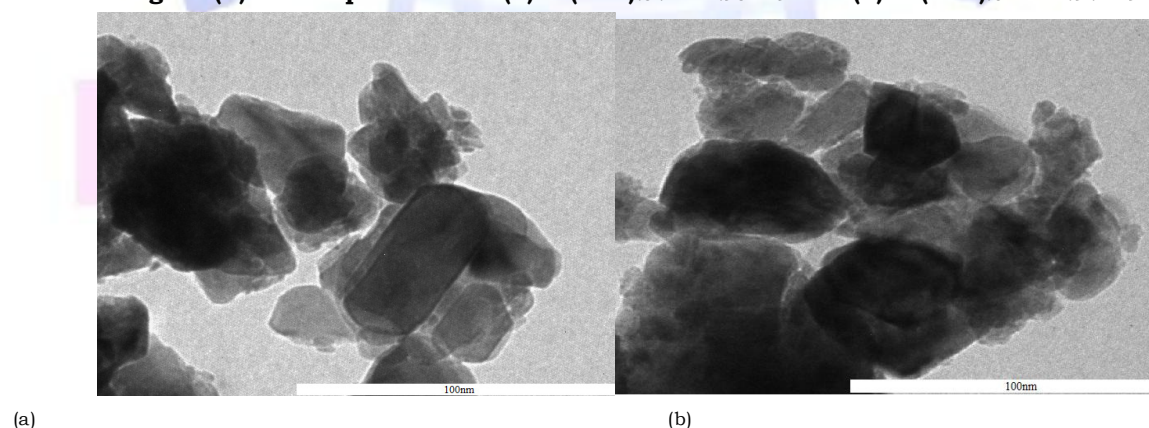
TEM photographs of the samples is shown in figure 2 confirm that the particles are in nano size and hexagonal shape. The reason why the small and perfect particles occur in can be explained by considering the high reaction temperature and fast cooling rate. The instantaneous high temperature benefits the substitution of Ni<sup>+2</sup> and Ir<sup>+4</sup> in the SrM lattice and the fast cooling after the synthesis restrains the grain growth and makes the particles hold their feature from the high temperature to the room temperature. The size of the particle is found to be reduced as the value of x increases from 0.02 to 0.04. It is reasonable to confirm that the doping of divalent and tetravalent ions does remain responsive to the particle size of the substituted hexaferrite [16].

**Table 1. Structural parameters of SrO.(6-x)Fe<sub>2</sub>O<sub>3</sub>x(NiIr)O<sub>3</sub>**

S.no.	Composition x	Particle Size (nm)	Lattice Constant (Å)		Volume (Å <sup>3</sup> )	ρ <sub>xray</sub> (gm/cm <sup>3</sup> )	ρ <sub>bulk</sub> (gm/cm <sup>3</sup> )	Porosity (%)
1	0.02	39.18	5.8133	22.074	646.01	5.47	2.92	46.48
2	0.04	20.61	5.8392	22.202	655.57	5.40	3.86	28.58



**Figure (1): XRD spectrum of (a) Sr(NiIr)<sub>0.02</sub>Fe<sub>11.96</sub>O<sub>19</sub> and (b) Sr(NiIr)<sub>0.04</sub>Fe<sub>11.92</sub>O<sub>19</sub>**



**Figure 2: TEM pictures of (a) Sr(NiIr)<sub>0.02</sub>Fe<sub>11.96</sub>O<sub>19</sub> and (b) Sr(NiIr)<sub>0.04</sub>Fe<sub>11.92</sub>O<sub>19</sub>**

**3.2 Magnetic Properties:** VSM of the sample shown in figure 3 depicting the magnetic behaviour of the sample in the presence of external magnetic field. Magnetisation curve for the sample shows a hysteresis indicating a hard magnetic property. It is seen that there is slight constriction in Figure 3(b) for the sample Sr(NiIr)<sub>0.04</sub>Fe<sub>11.92</sub>O<sub>19</sub> whereas no constriction is observed in fig 3(a) for the sample

$\text{Sr}(\text{NiIr})_{.02}\text{Fe}_{11.96}\text{O}_{19}$ . The appearance of constriction in the hysteresis loop can be explained from the viewpoint of aging effect. It was found that during the aging process, the migration of bivalent ions between tetrahedral (A-site) and octahedral (B-site) coordination induced a shrinking of the lattice, which is dominant after long time of aging. Due to the component-dependence of the constriction, both the content of ions and vacancies and the interaction between them may play a crucial role in the constricted effect [11]. Considering the migration of ions on A/B sites, which happens very quickly, it seems that the mechanism of this constriction is quite local and forms in a relatively short period of time.

The other magnetic parameters like coercivity ( $H_c$ ), saturation magnetisation ( $M_s$ ) and remanence ( $M_r$ ) tends to decrease with respect to Ir-Ni content as shown in Table 2. The usefulness of a particular magnetic material for a specific application depends on its relevant properties. One of these properties is the coercivity of M-type hexaferrites. High coercivity is the demand of a hard magnet while low coercivity is the need of soft magnet. The former is needed for energy storage applications. The later is needed for information storage media [16]. The origin of coercivity lies in the magnetic anisotropy, which is particularly uniaxial for the hexagonal close packing of the hexaferrites. The decrement in the value of coercivity ( $H_c$ ) indicates that the magnetic anisotropy decreases with increasing  $x$  [12] and their substitution is not in  $4f_2$  and  $2b$  sites because these sites contribute to large anisotropy field.

Magnetisation variation is related to distribution of substituent on five crystallographic sites i.e.  $12k-2a-2b$  (spin up) and  $4f_1-4f_2$  (spin down). The substitution of  $\text{Fe}^{+3}$  ions in spin up state reduces magnetisation and it increases with substitution on spin down state. Therefore the reason for the decrease in value of magnetisation as the  $\text{Ni}^{+2}$  and  $\text{Ir}^{+4}$  concentrations increased is their substitution in  $12k$  and  $2a$  sites of the lattice, in preference to the  $4f_2$  sites. Another reason for the decrease in the value of magnetization is may be due to lesser magnetic moment of  $\text{Ni}^{+2}$  ions ( $2.8-3.5 \mu\text{B}$ ) as compared to  $\text{Fe}^{+3}$  ions ( $5.7-6.0 \mu\text{B}$ ) [13]. In this, the magnetic moment of  $\text{Ir}^{+4}$  is assumed to be negligible as found in oxide and chloride [14-15]. The magnetic moment of both ions is not able to cancel out with spin down moments of  $\text{Fe}^{+3}$  ions, thereby decreasing  $M_s$  and  $M_r$ .

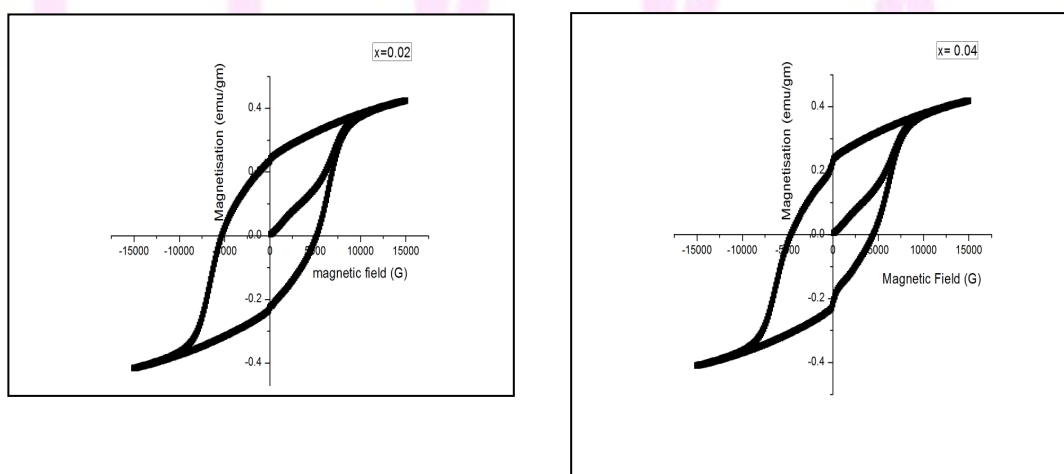


Figure 3 Hysteresis loop of (a)  $\text{Sr}(\text{NiIr})_{.02}\text{Fe}_{11.96}\text{O}_{19}$  and (b)  $\text{Sr}(\text{NiIr})_{.04}\text{Fe}_{11.92}\text{O}_{19}$



**Table 2. Magnetic parameters of SrO.(6-x)Fe<sub>2</sub>O<sub>3</sub>x(NiIr)O<sub>3</sub>**

S.no.	Composition x	Saturation magnetisation M <sub>s</sub> x 10 <sup>-2</sup> (emu/gm)	Remenent Magetisation M <sub>r</sub> x 10 <sup>-2</sup> (emu/gm)	Coercivity H <sub>c</sub> (G)
1	0.02	42.3	24.2	5380
2	0.04	41.7	23.7	4630

## 4. Conclusion:

Using Strontium Nitrate, Ferric Nitrate, Nickel Nitrate, Iridium Bromide and Urea as the starting materials, nano sized strontium hexaferrite powder have been synthesised successfully by the microwave induced combustion process. This method benefits forming better particle compared with traditional firing method. The x-ray diffraction studies confirm the formation of hexaferrites and the values of their lattice parameter support this confirmation. The size of the particle calculated by Scherer's formula comes out to be in nano range which is in close agreement with the TEM result. The coercivity decreases due to anisotropy field variation while magnetisation reduces due to replacement of Fe<sup>+3</sup> ions in spin up state.

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