Investigating structural, magnetic and multiferroic properties of gadolinium substituted strontium hexaferrite (SrFe$_{12-x}$Gd$_x$O$_{19}$)

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Abstract. An economical and citrate precursor based sol-gel technique is employed for pure phase synthesis of Gd$^{3+}$ substituted M-type strontium hexaferrite (SrFe$_{12-x}$Gd$_x$O$_{19}$) for $x = (0.25 - 1.00)$. The XRD patterns reflected all prominent planes related to hexagonal symmetry ($P6_3/mmc$ space group). The crystallite size and induced strains is determined using Williamson-Hall plot. Lattice constants ($a$) and ($c$) shows minor increments with Gd$^{3+}$ concentration. Particle distributions in SEM micrograph agree with W-H plot analysis. FTIR analysis is in consistent with X-ray intensity results. The ‘Law of Approach’ to saturation is applied to estimate parameters such as, magnetization ($M_s$) of order 40.91 to 57.7 emu/g and retentivity ($M_r$) ranging from 26.3 to 32.5 emu/g. A remarkable increase in coercivity ($H_c$) is observed with increasing Gd$^{3+}$ composition, with a value of 2500 to 6310 Gauss. Moreover, incorporation of Gd$^{3+}$ in SrFe$_{12-x}$Gd$_x$O$_{19}$ lattice hinders electrical leakage profitably to yield remanent ($P_r$) and coercive polarization ($P_c$) of order 0.19 μC/cm$^2$ and 17 kV/cm respectively. Thus sol-gel method proves to be useful in synthesizing nanomaterials of enhanced physical properties along with it being cost effective. Therefore, we are reporting tuning of magnetic and multiferroic properties of SrFe$_{12}$O$_{19}$ due to crystal strain mediated by Gd$^{3+}$ doping at Fe$^{3+}$ site.

1. Introduction

M-type hexaferrites are included in a category of magnetic materials possessing exceptional properties like high coercivity ($H_c$), magneto anisotropy and high magnetization ($M_r$) [1]. Hexaferrites are effectively being used as dense recording media, permanent magnets, magneto optical instruments etc. [2, 3, and 4]. The reported $H_c$ and $M_r$ for hexagonal ferrites are 6700 Oe and 72 emu/g respectively. The ferromagnetic to paramagnetic transformation point is about 450 °C [5]. The strontium hexaferrite, (SrFe$_{12}$O$_{19}$) have hexagonal symmetry and included in $P6_3/mmc$ space group [6]. SrFe$_{12}$O$_{19}$ is ferromagnetic in nature. The unit cell of SrFe$_{12}$O$_{19}$ has S and R blocks arranged in a superimposed manner. Its crystal unit have the ordering as RSR*S*, in which S* and R* represents 180 degree rotated S and R blocks [7]. The physical property of SrFe$_{12}$O$_{19}$ is influenced by domains such as, Fe$^{3+}$ ions occupancy (teta or octahedral) in the crystal, element being doped and the synthesis method [8]. Researchers have worked up on enhancing physical characteristics of SrFe$_{12}$O$_{19}$ by substituting with cations such as Sm$^{3+}$, Mn$^{3+}$, Ce$^{3+}$, Al$^{3+}$, etc. [9-12]. We have preferred citrate based sol-gel method, as this technique is economical and has the benefit of homogeneous particle distribution in synthesized samples [13]. The variant ions replacement develops crystal strains in unit cells, which influences physical properties. Therefore, in this paper we have explored crystallographic changes in SrFe$_{12}$O$_{19}$ with varying
Gd$^{3+}$ compositions for refining structural, magnetic and multiferroic properties of SrFe$_{12}$O$_{19}$. The refined physical parameters suggest this material to be effective as highly dense recording media and for dielectric applications. To the best of our beliefs, there is limited literature reported on Gd$^{3+}$ substituted SrFe$_{12}$O$_{19}$ and discussions on its multiferroic properties along with magnetic property have not been addressed before.

2. Experimental details

The purity grade SrFe$_{12-x}$GdxO$_{19}$ for x = (0.25 - 1.00) was prepared using an economical and chemical based sol-gel technique. The starting nitrates used as reactants were Sr (NO$_3$)$_2$, Gd (NO$_3$)$_3$, Fe (NO$_3$)$_3$ (99.9% purity). A definite amount of these reactants are mixed in DI water in individual beakers. All these solutions are then converted into the citric acid solution. Next, pH of this final solution is shifted to neutral by precisely adding ammonia. Thereafter, we put this mixed solution on hot plate set at 80 °C for (3-4) hours with vigorous stirring, till liquid becomes jelly type. This thick jelly like substance was put in hot air chamber at 120 °C for 1 hour for drying. It is observed that when temperature inside air chamber was increased to 250°C, gel starts swelling like a cake. We wait for 30 minute in this condition so as to allow total volumetric expansion of the jelly product. Then sample is allowed to cool and is collected in small containers after crushing down with mortar-pestle. A sufficient amount of each sample was annealed at 750 °C for 2 hours with a ramp rate of 2°C/min in microprocessor based furnace. The XRD patterns were recorded at a wavelength (λ=1.5406 Å) with the help of the X-ray diffractometer (Bruker). Magnetic hysteresis (M-H) curves were recorded at 300 kelvin using Vibrating Sample Magnetometer, Lakeshore (Model 7500) equipped with creating electromagnetic field of ±3.2 Tesla. The morphology of samples was checked with Scanning Electron Microscope (Carl Zeiss). The site occupancy of ions within unit cell was identified using FTIR (Perkin Elmer). The ferroelectric polarization patterns were obtained with Radiant Tech Precision 10 kV Multiferroic loop analyzer.

3. Results and discussion

3.1. X-ray diffraction analysis

As we can see in figure 1, XRD patterns justify pure phase synthesis of sample containing all crystal planes reported for hexagonal crystal structure (P6$_3$/mmc space group). Such intensity patterns have also been reported by research groups [14]. We can see in Fig. 1, that broadening of the prominent XRD peaks
decreases, with increment in Gd$^{3+}$ compositions, suggesting increment of particle size with dopants. It can be observed that the intensity of signature planes (107) and (114) increased with Gd$^{3+}$ compositions. Intensity peak near Bragg’s angle 2θ = 32.5, 35.3, planes (104) and (108) belongs to undesirable phases (α-Fe$_2$O$_3$). These intermediate phases were present in samples with higher Gd$^{3+}$ content (x = 0.75, 1.0). Further, heat treatment of samples at 750°C for 2 hrs do affect lattice parameter (a), (c), and so cell volume increases. The concern structural parameters are tabulated in table 1.

The increased lattice constants (a) and (c) alters the distance between Fe$^{3+}$ ions, causing enhanced ions interactions which further tunes magnetic parameters (sec 3.4). The Williamson-Hall plot is analyzed for finding out lattice strain values. In figure 2, βcosθ vs. 4 sinθ plot is lineally fitted for 0.25 moles doped strontium hexaferrite. Slope of the lineally fitted data (red line) directly quantifies value of lattice strain. For finding crystallite size, y-intercept value is equated to $k\lambda/D$, where D denotes crystal size. These results are included in table 1. We can notice a monotonic increment of strain with the increment of Gd$^{3+}$ ions in unit cell of SrFe$_{12}$O$_{19}$. The crystal strain of order 3.12×10$^{-3}$ is calculated (W-H plot) for SrFe$_{12}$O$_{19}$ substituted with 1 mole Gd$^{3+}$ions. The ionic radius of Gd$^{3+}$ ions (1.05 Å) being almost twice with respect to Fe$^{3+}$ (0.55 Å) ions can be the expected reason [15]. Prominent planes in the XRD patterns were analyzed to calculate lattice constants (a), (c) using equation (1). Planes selected for substitution in equation (1) are [107], [114], [203], [205] and [206].

$$\frac{1}{a^2} = \frac{4}{3} \left( \frac{h^2 + h k + k^2}{a^2} \right) + \frac{t^2}{c^2}$$

After getting lattice constants values, we calculate the lattice volume as

$$V = \frac{\sqrt{3}}{2} a^2 c$$

We can deduce from table 1, that the lattice constants (a), (c) and crystallite size increases with increment of Gd$^{3+}$ content in SrFe$_{12}$O$_{19}$, due to the increased crystal strains in samples [16].

| SrFe$_{12-x}$Gd$_x$O$_{19}$ | Crystallite size | Strain$^a$(10$^{-3}$) | a=b(Å) | c(Å) | cell volume(Å³) |
|---------------------------|----------------|----------------------|--------|------|----------------|
| X= 0.00                   | 44.1           | 1.01                 | 5.844  | 22.83| 675.238        |
| X= 0.25                   | 47.8           | 1.37                 | 5.857  | 22.98| 682.701        |
| X= 0.50                   | 52.2           | 1.59                 | 5.871  | 23.08| 688.954        |
| X= 0.75                   | 56.4           | 2.71                 | 5.878  | 23.13| 692.073        |

Figure 2. Williamson-Hall Plot for 0.25 mole Gd doped SrFe$_{12-x}$Gd$_x$O$_{19}$.
3.2 SEM analysis

The surface analysis of samples is done with SEM, which is helpful in supporting crystallite size approximated using W-H plots. Therefore we have shown morphological images of SrFe$_{12}$O$_{19}$ for two decisive compositions, is shown in figure 3(a) and 3(b). The particles prefer to agglomerate with an objective to minimize its superficial area, with Gd$^{3+}$ content. The approximate particle size for SrFe$_{12-x}$Gd$_x$O$_{19}$ at compositions, $x = 0.0$ and $x = 1.00$ were 49.52 nm and 87.85 nm respectively. Particle size has been estimated with the help of ImageJ software by selecting numerous scanned areas and analyzing it one by one. As such related histograms are also shown as figure 3(a1) and 3(a2). The electron microscopy of samples were conducted at applied voltage of 20 EHT and samples were gold coated for 90 seconds by sputtering technique.

3.3 FTIR analysis

The FTIR transmission spectrums of SrFe$_{12-x}$Gd$_x$O$_{19}$ for ($x = 0.25$ - $1.00$) is shown in figure 4, with wavenumber (400 - 1000 cm$^{-1}$). For SrFe$_{12}$O$_{19}$, two absorbance infrared peaks are significant, one at 439 cm$^{-1}$ for occupancy at the octahedral sites in crystal and next one at 602 cm$^{-1}$ for tetrahedral occupied sites [17]. The wave number (418 - 438 cm$^{-1}$) quantifies octahedral bond dimension [18]. The frequency (585 -
601 cm⁻¹), reveals dimension of tetrahedral bond viz. (Fe/O), and (Sr/O) [19]. As the bond length of octahedral sites > tetrahedral site, we have higher vibrational frequency for tetrahedral sites.

![FTIR spectrum of SrFe₁₂₋ₓGdₓO₁₉](image)

**Figure 4.** FTIR spectrum of SrFe₁₂₋ₓGdₓO₁₉ for (x = 0.25- 1.00).

The bond length (r) is found using frequency (ν) and force constant (K). We firstly determine the effective mass (μ) which is expressed as [20]

\[
\mu = \frac{(M_o \times M_{Fe})}{(M_o + M_{Fe})}
\]

Where \( M_o \) and \( M_{Fe} \) = Mass of O and Fe atoms \hspace{1cm} (3)

Now the harmonic frequency equation is

\[
ν = \frac{\sqrt{K/μ}}{2\pi C}
\]

Where C is the speed of light. \hspace{1cm} (4)

Next, (K) and (r) are inter-related as

\[
K = \left( \frac{17}{Ar^3} \right)
\]

A minor shift in the transmittance peaks towards higher wave number with respect to Gd³⁺ composition (table 2) is noticed. The stretch in M-O bindings is the outcome of lattice strain created by bigger radius of Gd³⁺ ions (1.05Å). Such behavior is also mentioned by few researchers [21].

**Table 2.** Site occupancy details for SrFe₁₂₋ₓGdₓO₁₉.

| Site       | Samples | Wave number (cm⁻¹) | Force constant (N/m) | Bond dimension(A°) |
|------------|---------|--------------------|----------------------|--------------------|
| **Octahedral** | X = 1.0 | 437                | 174.97               | 2.21               |
| **Tetrahedral** | X = 1.0 | 601                | 246.88               | 1.89               |

**3.4 Magnetic Properties**
Moment versus magnetic field (MH) loops of SrFe$_{12-x}$Gd$_x$O$_{19}$ for $x = (0.25 - 1.00)$ is shown in Fig. 5. Magnetization curves confirm ferromagnetic property of all samples and shows high order of coercive field response. Hysteresis loops are observed to get saturated in the magnetic field of ±1.5 Tesla. We can notice from table 3 that $M_r$ and $M_s$ do not follow systematic pattern with varying Gd$^{3+}$ composition. The magnetization is highest for sample SrFe$_{11.75}$Gd$_{0.25}$O$_{19}$. The increase in magnetization is the outcome of increased hyperfine field, as we know that $M_s$ varies linearly with hyperfine field [22].

Further, $M_s$ is calculated applying the ‘The Law of approach’ to saturation. This law is effective in finding two important magnetic parameters, magnetization ($M_s$) and crystal anisotropy constant ($K_1$). The equation for “Law of approach” is [23].

$$M = M_s \left[1 - \left(\frac{A}{H}\right) - \left(\frac{B}{H^2}\right)\right] + \chi H$$  
Where A is const. and B is anisotropy.  

As $\chi H$ is applicable in elevated temperature domains and $A/H$ is negligible in current criterion, we get
The y-axis intercept in moment versus \((1/H^2)\) plot (Fig. 6), gives \(M_s\). The coercivity value is maximum for \(\text{SrFe}_{12}\text{O}_{19}\) doped with 0.75 mole Gd\(^{3+}\), owing to the amplified exchange interactions of Fe-O-Fe ions [24]. The higher coercivity of order 6310 Oe signifies prepared sample’s effectiveness as dense recording medium. The \((M_r / M_s)\) was greater than 0.5 for pure as well as doped samples (table 3), which justifies that \(\text{SrFe}_{12-x}\text{Gd}_x\text{O}_{19}\) will also be effective as permanent magnet [25].

### Table 3. Magnetic parameters details of \(\text{SrFe}_{12-x}\text{Gd}_x\text{O}_{19}\) for \((x = 0.25-1.00)\).  

| \(\text{SrFe}_{12-x}\text{Gd}_x\text{O}_{19}\) | Magnetization \((M_s)\) \((\text{emu/g})\) | Retentivity \((M_r)\) \((\text{emu/g})\) | Squareness ratio | Coercivity \((H_c)\) \((\text{Oe})\) |
|-------------------------------------|------------------------------------------|------------------------------------------|-----------------|----------------|
| \(x = 0.0\)                        | 40.91                                    | 29.8                                     | 0.728           | 2500           |
| \(x = 0.25\)                       | 57.70                                    | 31.9                                     | 0.552           | 6099           |
| \(x = 0.50\)                       | 53.34                                    | 32.5                                     | 0.609           | 6195           |
| \(x = 0.75\)                       | 54.48                                    | 28.2                                     | 0.517           | 6310           |
| \(x = 1.00\)                       | 42.74                                    | 26.3                                     | 0.615           | 5912           |

### 3.5 Multiferroic Properties

For multiferroic testing’s, few amount of samples (of each batch) has been given capacitor form by compressing them to disc shaped pellets of radius 6 mm and 2.5 mm thickness using hydraulic palletizer. Then these pallets were calcined at 700°C for 4 hrs to remove organic and moisture contents completely. Further, both sides of pallets were coated with silver paste to make it behave like a conducting electrode. Next, P-E loops of \(\text{SrFe}_{12-x}\text{Gd}_x\text{O}_{19}\) for \((x = 0.25-1.00)\) was recorded at 300 Kelvin, figure 7. As we can see, the P-E loop of \(\text{SrFe}_{12-x}\text{Gd}_x\text{O}_{19}\) for \(x = 1.0\) is obtained as full convex nature, suggesting the samples have electrical leakage. With increased Gd\(^{3+}\) ions in strontium hexaferrite lattice, ferroelectric loop becomes typical, signifying reduction in electrical leakage. It is interesting to observe that Gd\(^{3+}\) substitution in \(\text{SrFe}_{12-x}\text{Gd}_x\text{O}_{19}\) crystal geometry has considerably enhanced electrical polarization by
inhibition of electrical leakages. The incorporation of Gd\(^{3+}\) in SrFe\(_{12-x}\)Gd\(_x\)O\(_{19}\) lattice promotes phase purity in samples with remanent (P\(_r\)) and coercive polarization (P\(_c\)) of order 0.19 \(\mu\)C/cm\(^2\) and 17 kV/cm respectively.

4. Conclusions
Sol-gel technique is employed to synthesize monodispersed samples of strontium hexaferrite SrFe\(_{12-x}\)Gd\(_x\)O\(_{19}\) for x = (0.25 - 1.00). All prepared samples have hexagonal symmetry referred to \(P63/m\)mc space group. A monotonous increase in the lattice constants (a) and (c) was observed with increasing Gd\(^{3+}\) composition in strontium crystals. The particle size and crystal strain in samples amplified with an increasing Gd\(^{3+}\) content in lattice.

FTIR spectrum confirms tetrahedral and octahedral site occupancy. Magnetization value of about 57.70 emu/g is reflected for SrFe\(_{12}\)O\(_{19}\) doped with 0.25 mole Gd\(^{3+}\) ions. The coercive field of order 6310 Gauss is recorded for SrFe\(_{12}\)O\(_{19}\) doped with 0.75 mole Gd. Also, occupancy of Gd\(^{3+}\) ions in SrFe\(_{12-x}\)Gd\(_x\)O\(_{19}\) crystals successfully enhanced electrical polarization by prohibiting electrical leakages. These tuned physical properties of SrFe\(_{12}\)O\(_{19}\), due to lattice strain mediated by Gd\(^{3+}\) substitution suggests its futuristic technological applications. This study can be further extended to understand rare earth element’s doping at strontium site, by manipulating crystalline anisotropy for improving various materials’ properties.

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