Indexing the structural parameters and investigating the magnetic properties of lanthanum doped strontium hexaferrites

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Abstract. Sr$_{1-x}$La$_x$Fe$_{12}$O$_{19}$ ($x=0, 0.1, 0.15, 0.2$) nano-crystallites were synthesized using a sol-gel based combustion technique. Sintering of the samples at 800 ºC helped to develop the stable hexagonal phase. Data received from the X-ray diffraction was used to confirm and determine the crystal structure of the samples by manipulating the lattice parameters, volume of the unit cell, crystallite size, X-ray density and porosity of the samples. Room temperature magnetic measurements were performed using a vibrating sample magnetometer with an applied field of ± 10 kOe. The magnetic hysteresis loops reveal that lanthanum doping at Sr-sites has enhanced the coercivity of the samples in the series with some compromise on magnetization while remanence remains almost constant, enabling the lanthanum doped samples appropriate for hard magnetic applications.

1. Introduction
Strontium hexaferrites are important magnetic materials due to their significant applications in diversity of fields. Owing to their easy, low cost manufacturing and excellent chemical stability, these materials are being synthesized by various methods [1]. In addition to co-precipitation, microemulsion [2] and conventional ceramic methods [3], these ferrites are also being synthesized by sol-gel method [4]. The dynamic properties of these ferrites can be tuned according to the requirement with the assistance of conventional doping process. Doping of some appropriate element in a particular proportion can play a vital role in altering the astonishing properties of the materials. For example, doping of La in SrFe$_{12}$O$_{19}$ lowers its coercivity and remanence due to which general behavior of these ferrites is changed [1]. Crystal structure of the material controls its various properties [5]. Ferrites are classified with respect to their properties as well as crystal structure. Different types of ferrites like spinel, garnet and hexaferrites have different structures, varying from very easy to most complex [6]. Many scientists preceded their research work on investigation of crystal structure of SrFe$_{12}$O$_{19}$ and reported their detailed results. For instance, Lechevallier et al. [7] figured out the magnetic and structural properties of hexagonal ferrites Sr$_{1-x}$Sm$_x$Fe$_{12}$O$_{19}$. The scientists have determined that the crystal structure of SrFe$_{12}$O$_{19}$ is hexagonal. Choit et al. [8] carried out experiment to synthesize La-Co doped Sr-ferrite (La-Co)$_x$Sr$_{1-x}$Fe$_{12}$O$_{19}$ by sol-gel method in order to investigate its magnetic and structural properties. Researchers concluded that crystal phase of (La-Co)$_x$Sr$_{1-x}$Fe$_{12}$O$_{19}$ is single M-type hexagonal phase. To investigate the material properties, it is necessary to know about its structure. Without attaining the knowledge of crystal structure of the materials, it becomes very hard...
to investigate its properties [5]. In the present paper, X-ray diffraction analysis of the compositions \( \text{Sr}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19} \) (\( x = 0, 0.1, 0.15, 0.2 \)) has been discussed in details. A complete procedure of indexing and calculating various related structural parameters are explained in a simple way. This knowledge will provide a way to make a precise analysis of diffraction patterns of other materials.

2. Experimental

Sol-gel auto-combustion technique was used for the preparation of various compositions of La doped \( \text{SrFe}_{12}\text{O}_{19} \). To prepare the series of samples with general formula, \( \text{Sr}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19} \) (\( x = 0, 0.1, 0.15, 0.2 \)), stoichiometric amounts of analytical grade reagents, i.e., strontium nitrate (99%), iron (III) nitrate (98%), lanthanum (III) nitrate (99%) and citric acid (99.5%) were weighed with the help of a precise digital balance. These metal nitrates and citric acid (used as a fuel) were dissolved in de-ionized water separately, and then mixed to make a total volume of 50 ml. pH-meter measured the pH of the solution as 2.5. The magnetic capsule (stirrer) was put in the solution and beaker was placed on a hot plate. The setup was housed in an ESCO fume hood. Stirring of solution was started and temperature of the hotplate was increased gradually up to 150 \( ^\circ \text{C} \). The solution was heated and stirred for about 45 minutes, till the gel was formed. As the gel was formed, the temperature of the sample was further increased up to 250 \( ^\circ \text{C} \). The gel was heated at this temperature for about 30 minutes when its combustion was started. It was allowed to combust normally. The sample took about 30 minutes for its complete combustion. During this interval, various gases were evolved from the beaker. The end product was a homogenous dry powder.

After complete combustion of the sample, the temperature of the hotplate was decreased gradually. Within 10 minutes, the hotplate was switched off and the sample was cooled down in air at room temperature. Although, the material was already in powder form but it became very fine after grinding, using an Agate mortar and pestle. Fine powder was put in the sample bottle. All the compositions were prepared in the same way. The samples were sintered at 800 \( ^\circ \text{C} \) for two hours in a muffle furnace. The samples were pelletized using an Apex hydraulic press by applying a pressure of 4.5 ton. The prepared samples were analyzed for the crystal structure, using the diffraction pattern, obtained from X-ray diffraction (XRD). Magnetic properties were determined using a Lakeshore - 7404 vibrating sample magnetometer (VSM).

3. Results and Discussion

Data obtained from XRD for the first sample (\( x = 0 \)) has been plotted in figure 1. The first task is to determine the crystal structure of the sample using this data. It is very tough job to determine the crystal structure of some unknown material, than that of a known one. In a diffraction pattern, the pattern of diffracted lines tells about the crystal structure, the positions of lines have information about the unit cell and the positions of the atoms can be judged by the intensities of the lines [5]. From the XRD pattern shown in figure 1, it is expected that it is the diffraction pattern of hexagonal \( \text{SrFe}_{12}\text{O}_{19} \). The first step is to index this pattern that will tell about the crystal system, to which the material belongs to. For this, the values of \( \sin^2 \theta \) are calculated for all major diffraction lines, as tabulated in Table 1. These values provide a base to solve the pattern. If there are some diffraction lines due to impurities in material or due to other reasons, then it creates problems and needs extra skills to tackle with. A relation is developed by combing plane-spacing equation and Bragg’s law equation, which determines the Miller indices of some specific crystal system. For instance, for a cubic system, this expression can be written as [5].

\[
\sin^2 \theta / (h^2 + k^2 + l^2) = \sin^2 \theta / s = \mathcal{A}^2 / 4a^2
\] (1)
Here $\lambda^2/4a^2$ is a constant and $s = h^2 + k^2 + l^2$, which is determined by $\sin^2\theta$ values. For an unknown material, it has to be found that the values of $\sin 2\theta$ are integral multiple of which $hkl$ values? First, we check the $hkl$ values of a cubic system. If these do not satisfy, then we try for the other systems like tetragonal, hexagonal, etc. one by one. As the pattern under present study is expected to be of hexagonal crystal structure, hence it should obey the modified form of Eq. (1), given as [5].

$$\sin^2 \theta = A(h^2 + hk + k^2) + Cl^2$$

(2)

### Table 1. Diffraction lines and their corresponding angles taken from diffraction plot

| Line | $2\theta$ | $\theta$ | $\sin \theta$ | $\sin^2 \theta$ | $2\theta$ | $\theta$ |
|------|-----------|----------|----------------|-----------------|-----------|----------|
| 1    | 23.11     | 11.55    | 0.2002         | 0.0401          | 23.11     | 11.55    |
| 2    | 30.36     | 15.18    | 0.2618         | 0.0685          | 30.36     | 15.18    |
| 3    | 32.35     | 16.18    | 0.2786         | 0.0776          | 32.35     | 16.18    |
| 4    | 34.15     | 17.07    | 0.2935         | 0.0862          | 34.15     | 17.07    |
| 5    | 35.19     | 17.59    | 0.3022         | 0.0913          | 35.19     | 17.59    |
| 6    | 35.4      | 17.70    | 0.3040         | 0.0924          | 35.4      | 17.70    |
| 7    | 37.1      | 18.55    | 0.3181         | 0.1012          | 37.1      | 18.55    |
| 8    | 40.35     | 20.18    | 0.3449         | 0.1189          | 40.35     | 20.18    |
| 9    | 42.55     | 21.27    | 0.3627         | 0.1316          | 42.55     | 21.27    |

### Table 2. Values of $\sin^2 \theta$ and its multiple (by 1/3, 1/4, 1/7) to find out $hkl$

| Line | $\sin^2 \theta$ | $\sin^2 \theta/3$ | $\sin^2 \theta/4$ | $\sin^2 \theta/7$ | $hkl$ |
|------|-----------------|--------------------|--------------------|--------------------|-------|
| 1    | 0.0401          | 0.0133             | 0.0100             | 0.0057             |       |
| 2    | 0.0685          | 0.0225             | 0.0171             | 0.0098             |       |
| 3    | 0.0776          | 0.0259             | 0.0194             | 0.0111             |       |
| 4    | 0.0862          | 0.0287             | 0.0215             | 0.0123             |       |
| 5    | 0.0914          | 0.0305             | 0.0229             | 0.0131             | 200   |
| 6    | 0.0924          | 0.0308             | 0.0231             | 0.0132             |       |
| 7    | 0.1012          | 0.0337             | 0.0253             | 0.0144             |       |
| 8    | 0.1189          | 0.0396             | 0.0297             | 0.0169             |       |
| 9    | 0.1316          | 0.0439             | 0.0329             | 0.0188             |       |
In this relation, \( A = \frac{\lambda^2}{3a^2} \) and \( C = \frac{\lambda^2}{4c^2} \). The value of \( A \) can be obtained at \( hkl \) \((l = 0)\). Hence, the permissible values of \((h^2 + hk + k^2)\) are 1, 3, 4, 7, 9, etc. Now, divide the values of \( \sin^2 \theta \) tabulated in Table 1, by 1, 3, 4, 7, etc. to get \( hkl \) values for hexagonal system, as shown in Table 2. Lattice parameter ‘\( a \)’ is calculated for all values of \( \sin^2 \theta \). There is some order in particular values of ‘\( a \)’, being integral multiple of each other. Least value from them is the value of ‘\( a \)’ for 100 plane. Value \( a/2 \) is value of ‘\( a \)’ for 200 plane, and \( a/3 \) for 300 plane and so on. Generally, smallest repeating value in all columns is found and is considered to be ‘\( A \)’. Lattice parameter is calculated for this value and crystal structure is determined. But sometimes, ‘\( A \)’ cannot be found for 100 plane, hence lattice parameter ‘\( a \)’ is calculated at \( hkl \) for all \( \sin^2 \theta \) values, as has been proceeded in the present case. It is found that the diffraction line having \( \sin^2 \theta \) value of 0.0914, gives the most nearest value of ‘\( a \)’ for 200 plane. This repeating value was also found in the next column of Table 2, hence it was considered as ‘\( A \)’ value. ‘\( C \)’ was determined by the following relation [5].

\[
\sin^2 \theta - A(h^2 + hk + k^2) = Cl^2
\]  

(3)

The values of \( A, 3A, 4A, \) etc. were subtracted from corresponding \( \sin^2 \theta \) values to find the remainders 1, 4, 9, 16, etc., as shown in Table 3. The value of ‘\( C \)’ was found to be 0.0011. The corresponding value of \( \sin^2 \theta \) is combination of \( 2A \) and \( C \), hence \( hkl \) assigned to this value are 201. Such combinations \((A+C, 2A+2C, 3A+C, 3A+2C, \) etc.) of \( \sin^2 \theta \) values were found to assign \( hkl \) values to various diffraction lines. These \( hkl \) values are listed in the most right column of Table 3 and are shown in figure 2. These \( hkl \) values confirm that the diffraction pattern belongs to a hexagonal crystal structure. The lattice parameter ‘\( c \)’ was calculated with the help of Eq. (4) [5].

\[
c = \frac{\lambda^2}{4C^2}
\]  

(4)

| Line | \( \sin^2 \theta \) | \( \frac{\sin^2 \theta - A}{A} \) | 006 | \( hkl \) | Line |
|------|-----------------|-----------------|-----|--------|------|
| 1    | 0.0401          |                 |     |        | 1    |
| 2    | 0.0685          |                 | 110 |        | 2    |
| 3    | 0.0776          |                 | 107 |        | 3    |
| 4    | 0.0862          |                 | 114 |        | 4    |
| 5    | 0.0914          | 0.0000          | 200 |        | 5    |
| 6    | 0.0924          | 0.0011          | 201 |        | 6    |
| 7    | 0.1012          | 0.0098          | 203 |        | 7    |
| 8    | 0.1189          | 0.0275          | 205 |        | 8    |
| 9    | 0.1316          | 0.0402          | 206 |        | 9    |
The same procedure was repeated for indexing the patterns of all the compositions as shown in figure 3 and their lattice parameters were determined in the same way. These values are listed in Table 4. The results show that the lattice parameters ‘a’ and ‘c’ are increased with increase in La concentration, as shown in figure 4. These changes may be due to larger ionic radius of La$^{3+}$ (117.2 pm) than that of Sr$^{2+}$ (112 pm) [9].

The c/a ratio was also calculated for all the samples. The volume of the unit cell was calculated by the relation [10].
Unit cell volumes of all the samples are also given in Table 4. Due to increasing trend of lattice parameters ‘a’ and ‘c’, the volume of the unit cell is also increased with increasing La contents, as reported previously [9]. The crystallite size was measured for peak (114) using Scherrer’s formula, given as [5].

\[ D = k\lambda / \beta \cos \theta \]  \hspace{1cm} (6)

Here, ‘D’ is crystallite size, ‘\(\lambda\)’ is wavelength of incident X-ray, ‘\(\beta\)’ represents full width half maximum (FWHM) in radians, and ‘\(\theta\)’ is Bragg’s angle. ‘k’ is a shape factor, having a value of 0.94 in the recent case. Crystallite size calculated for various compositions is given in Table 4. It is clear that crystallite size is increased with increase in doping ratio, which might be due to larger ionic size of La\(^{3+}\) [9]. Although, there was no distinct peak of lanthanum in diffraction patterns of La-doped compositions, but the increase in lattice parameters, unit cell volume and the crystallite size proves the presence of Lanthanum. The bulk density of the material was calculated [10].

\[ \rho_b = m / \pi r^2 h \]  \hspace{1cm} (7)

In this relation, ‘m’ is mass, ‘r’ is radius of the pellet in disk form and ‘h’ is height or thickness of the sample. Bulk density for all the materials has been calculated and it is observed that its value is increased with increase of lanthanum concentration which is according to the previous results [9]. The X-ray density was determined with the help of following expression [10].

\[ \rho_x = 2M / N_A V \]  \hspace{1cm} (8)

Where ‘M’ is molecular weight of the relevant composition and it is multiplied by ‘2’ because one unit cell contains two molecules of the material. ‘\(N_A\)’ is Avogadro’s number and ‘\(V\)’ is volume of the unit cell, determined by Eq. 1.5. The calculated values of X-ray density are tabulated in Table 4. Now, porosity of the material can easily be determined by the equation [10].
The porosity of the material decreases with the increasing concentration of La as reported previously [8]. The calculated values of porosity for all the samples are given in Table 4.

\[ P = 1 - \frac{\rho_b}{\rho_x} \]  
\( \text{(9)} \)

Table 4. Calculated values of lattice parameters ‘a’ and ‘c’, c/a ratio, volume of the cell (V), crystallite size (D), bulk density of the material (\(\rho_b\)), X-ray density (\(\rho_x\)), porosity (P), Magnetization (M), remanence (\(M_r\)), Coercivity (\(H_c\)) and ratio (\(M_r/M\))

| Parameter          | x = 0.00 | x = 0.1 | x = 0.15 | x = 0.2 |
|--------------------|----------|---------|----------|---------|
| a(Å)               | 5.8834   | 5.8854  | 5.8863   | 5.8872  |
| c(Å)               | 23.35    | 23.42   | 23.56    | 23.776  |
| c/a                | 3.9687   | 3.9793  | 4.0025   | 4.0385  |
| V(Å³)              | 699.941  | 702.516 | 706.933  | 713.63  |
| D(nm)              | 29.86    | 31.654  | 33.483   | 34.576  |
| \(\rho_b\)(g/cm³) | 3.19     | 3.71    | 4.51     | 3.72    |
| \(\rho_x\)(g/cm³) | 5.28     | 5.045   | 5.025    | 4.991   |
| Porosity(%)        | 39.5     | 26.4    | 10.2     | 25.4    |
| M (emu/g)          | 45.80    | 40.96   | 38.03    | 37.86   |
| \(M_r\)(emu/g)     | 22.55    | 21.20   | 22.82    | 22.032  |
| \(H_c\)(Oe)       | 2360     | 2093    | 3437     | 6547    |
| \(M_r/M\)          | 0.492    | 0.517   | 0.600    | 0.581   |

Room temperature magnetic measurements were performed in an applied magnetic field of ±10 kOe, as shown in figure 5. As obvious from the plotted magnetic hysteresis (M-H) loops, magnetization has not been completely saturated depicting that ±10 kOe as an applied field is not sufficient to saturate the samples in the present case. Anyhow, specific magnetic parameters of La\(_x\)Sr\(_{1-x}\)Fe\(_{12}\)O\(_{19}\) samples (x = 0, 0.1, 0.15, 0.2), such as value of magnetization (M) at ±10 kOe, coercivity (\(H_c\)), remanence (\(M_r\)) and ratio of remanence to magnetization (\(M_r/M\)) were determined and summarized in Table 4. The
value of $M$ was found to decrease from 45.8 emu/g at $x = 0$, to a value of 37.86 emu/g at $x = 0.2$. Hard ferrites usually display large coercive fields, and similar type of behavior has been observed in the present series with the values varying in the range of 2360-6547 Oe. The overall trend of $H_c$ was increasing with increasing La contents. It has been figured out previously that $H_c$ increases due to increase in magneto crystalline anisotropy constant [8]. On the other hand, $M_r$ does not vary significantly with the variation in ‘x’ and it almost remains constant. The $M_r$ obtained from the $M-H$ loops is observed as 22.03-22.82 emu/g. The observed trends are also in good agreement with previously reported results [11, 12]. The intrinsic magnetic properties, such as $M$, $H_c$ and anisotropy field depends on the atomic magnetism. The lanthanum addition to the strontium hexagonal ferrites induces major refinement in these properties. The La substitution might result in a decrease of the rectangularity of the demagnetizing curves [12]. Nevertheless, the subsequent tuning of the magnetic parameters results in exploiting these compositions for device applications where hard magnetic features are required.

4. Conclusion
La doped Sr-hexaferrites were successfully synthesized using sol-gel auto-ignition technique. A complete procedure has been adopted to determine the crystal structure from X-ray diffraction data. It was observed that lattice parameters and crystallite size increased with the increase of La content attributed to the larger ionic size of ‘La’ than that of ‘Sr’. This was due to the larger ionic size of La than that of Sr. Crystallite size had an increasing trend from 29.86 to 34.576 nm. Bulk density, X-ray density and porosity were also calculated for all compositions. The increase in bulk density and slight decrease in X-ray density reported with the increasing concentration of La which decreases the porosity of the material from 39.5 to 10.2. Saturation magnetization was observed to decrease and coercivity increased with the increase in concentration of La content. The increase in coercivity could mainly be attributed to the increase in magneto crystalline anisotropy constant.

5. References
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