Effect of Magnesium Substitution on the Structural and Magnetic properties of M-type Strontium Hexaferrite

Bilal Hamid Bhat
Solid State Research Lab. Department of Physics, University of Kashmir, Srinagar-19006, J&K, India
Email: hamid.bilal767@gmail.com

Abstract

A systematic investigation on the structure and magnetic properties of strontium hexaferrites doped Mg was performed. All ferrite samples were prepared by the citrate-precursor method and characterized with a combination of X-ray diffraction, FTIR, and Vibrating sample magnetometer. XRD analysis confirms the magnetoplumbite structure with space group p63/mmc. Average grain size has been seen increasing with Mg substitution. The presence of peaks near 500-600 cm\(^{-1}\) in Fourier transform infrared spectroscopy spectra indicates the formation of M-type hexaferrites. An increase in coercivity and magnetization were observed for all the samples. Large value of coercivity suggests that these materials are useful in longitudinal recording media.

Keywords: Magnetization, XRD, FTIR.

DOI: http://dx.doi.org/10.26705.xxx.xxx.xxxx

Received : 06/12/2017 Published online : 13/12/2017

1. Introduction

The hexaferrite with M-type structure have been the interest of continuous research due to their various remarkable properties.[1-2] and industrial applications such as computer memory chip, high density recording media, transformer, microwave devices, plastic and permanent magnets[3-4] from last few decades. To date, several experiments have been carried out to examine the influence of various dopants on modifying the structural and magnetic properties of strontium hexaferrites to make them desirable for different applications [5-6]. Strontium hexaferrites have been synthesized by different techniques like hydrothermal process [7], the self-propagating high-temperature synthesis [8], the microwave-assisted calcinations route [9], and the citrate precursor [10]. Among these, the Sol-Gel method is well-known as a simple and low cost route for the preparation of hexaferrite nanoparticles [11]. Alam. et al [12] studied Magnetic and microwave absorption properties of BaMg\(_{0.2}\)Mn\(_{0.2}\)Co\(_{1.2}\)Fe\(_{12.4}\)O\(_{19}\) hexaferrite nanoparticles.

The present study presents the effect of Magnesium substitution on the structural and magnetic properties of strontium hexaferrites. In this context, novel strontium hexaferrite with nominal composition Sr\(_{1-x}\)Mg\(_x\)Fe\(_{12}\)O\(_{19}\) (x = 0.0, 0.1, 0.3, 0.4) were synthesized by Sol-gel method.

2. Experimental Details

Sr\(_{1-x}\)Mg\(_x\)Fe\(_{12}\)O\(_{19}\) (x = 0.0, 0.1, 0.3, 0.4) have been prepared by citrate-precursor method using analytical grade chemicals namely ferric nitrate nona-hydrate, strontium nitrate anhydrous, magnesium nitrate hexa-hydrate, citric acid anhydrous. Metal salts and citric acid were dissolved in a triply deionised water separately and then mixed together at room temperature with continuously constant stirring. Citric acid anhydrous acts as a fuel. The pH of the solution was adjusted at 6.5 by using ammonia (25%). The obtained solution was heated at 90°C till a gel solution was obtained. The so obtained gel was heated till combustion, ultimately leaving only loose ashes. These ashes were grinded by a motor pestle arrangement for about 30 min. The whole powder was then heated at 500°C
to remove the organic moiety. Finally the powder was calcinated at 950 °C for 3 h.

The phase of the synthesised samples were determined by the D8 Advance Bruker X-ray diffractometer with CuKα (\(\lambda = 1.5406 \ \text{Å}\)) radiation. Attached functional groups with samples have been analysed with Fourier transform infrared spectra [FT-IR interferometer IR prestige-21 FT-IR (model-8400S)] in the range of 400–4000 cm\(^{-1}\). Magnetization measurements of samples, major hysteresis loops, were obtained using a vibrating sample magnetometer (MicroSense EZ9 VSM) with maximum field strength of 20 kOe.

3. Results and Discussions

3.1 XRD ANALYSIS

The X-Ray diffraction patterns of \(\text{Sr}_{1-x}\text{Mg}_x\text{La}_x\text{Fe}_{12-x}\text{O}_{19}\) demonstrate that all the samples of the series have magnetoplumbite structure space group p63/mmc (PDF No. 41#1373) and only a small trace of \(\text{Fe}_2\text{O}_3\) was detected. The presence of \(\text{Fe}_2\text{O}_3\) is related to an incomplete calcinations reaction [13]. Various lattice parameters are listed in Table 1. From table 1 lattice constant \(a, c\) and volume cell agree with the reported literature. A small change in the lattice parameters were observed by the substitution of Mg dopants. The volume cell was calculated by using the following relation [14];

\[
V_{\text{cell}} = 0.8666a^2c
\]

Where \(V_{\text{cell}}\) is the volume of the unit cell and 'a' and 'c' are the lattice constant.

\[
\rho = \frac{2M}{N_A V}
\]

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

Where \(\lambda\) is the X-ray wavelength, \(\beta\) is the half peak width, \(K = 0.96\), the constant, \(Z\) the number of formula units in a unit cell, \(M\) the molecular mass of the sample and \(N_A\) Avogadro’s number. The values of X-ray density and crystallite size are listed in table 1. It is observed that the average grain size is in between 6nm to 25nm which is smaller than that reported earlier i.e. 14-30nm for the M-type hexaferrites [15]. The value of X-ray density shows slight variation with increase in concentration of the doped ion, Mg. Also the average grain size D increases with Mg concentration.

3.2 Fourier transform infrared spectroscopy (FTIR) Analysis:

The FT-IR spectra for the un-annealed \(\text{Sr}_{1-x}\text{Mg}_x\text{Fe}_{12}\text{O}_{19}\) (\(x = 0.0, 0.1, 0.3, 0.4\)) hexaferrite powders are depicted in Fig. 2. FTIR provides the information regarding attached molecular bands or presence of functional groups, which are remains of chemicals use in the synthesis process. The band near 500–600 cm\(^{-1}\) attribute to the vibration of the ferric crystallographic site (octahedral and tetrahedral) [16]. The band appearing around 2000cm\(^{-1}\)-2500cm\(^{-1}\) is related to antisymmetric stretching of carbon dioxide in the atmosphere. One can notice a gradual red shift of both bands with the increase of dopants content.

![Fig 1. XRD pattern of \(\text{Sr}_{1-x}\text{Mg}_x\text{Fe}_{12}\text{O}_{19}\) (\(x = 0.0, 0.1, 0.3, 0.4\)) at room temperature.](image)

![Fig 2. FTIR spectrum of \(\text{Sr}_{1-x}\text{Mg}_x\text{Fe}_{12}\text{O}_{19}\) (\(x = 0.0, 0.1, 0.3, 0.4\)) at room temperature.](image)
Table 1. Table showing various parameters of $\text{Sr}_{1-x}\text{Mg}_x\text{Fe}_{12}\text{O}_{19}$ ($x = 0.0, 0.1, 0.3, 0.4$).

| Variation X=0.0 to 0.4 | Average Grain Size $D$ (nm) | Lattice Constant | $V_{\text{CELL}} = 0.866a^2c$ Å$^3$ | $X_{\text{Ray}}$ Density $g/cm^3$ | $M_r$ | coercivity | $M_s$ |
|------------------------|-----------------------------|-----------------|-------------------------------|---------------------------------|------|------------|------|
|                        |                             |                 |                               |                                 |      |            |      |
| 0.0 before heating      | 10.55nm                     | 5.88            | 23.02                         | 686.29                          | 5.11 | *          | *    |
| 0.0 heated             | 12.57nm                     | 5.88            | 23.02                         | 685.25                          | 5.11 | *          | *    |
| 0.1                    | 13.37nm                     | 5.86            | 22.96                         | 681.25                          | 5.17 | 11         | 2300  |
| 0.2                    | 23.17nm                     | 5.87            | 23.00                         | 688.46                          | 5.12 | *          | *    |
| 0.3                    | 24.98nm                     | 5.86            | 22.99                         | 684.88                          | 5.17 | 14         | 4496  |
| 0.4                    | 17.73nm                     | 5.86            | 22.95                         | 683.29                          | 5.19 | *          | *    |

This shift is related to the substitution of Mg$^{2+}$ cations that affects the distribution of Fe$^{3+}$ in the lattice. The peak in the area between 1100–1600 cm$^{-1}$ is related to (metal–oxygen–metal) band vibration such as Fe–O–Fe [17].

3.3 Magnetic Measurements:

Fig.3. shows magnetic hysteresis loops for 0.1 and 0.3 Mg doped SrFe$_{12}$O$_{19}$ at 300 K. The prepared materials show the behaviour of a hard magnetic material with high coercivity and magnetization. Various magnetic parameters of all samples are listed in table. It is evident from the table that saturation magnetization, coercivity and $M_r$ increase with the substitution of Mg.

It is observed in the present investigation that Mg substituted strontium hexaferrite possess largest coercivity. It can be generalized that the increase of coercivity is attributed to enhancement in crystalline anisotropy field due to substitution of Mg. In other word, the substitution of Mg exerts intrinsic effects on the enhancement of coercive field. In the present study, the coercivity is more than $M_r/2$, thus the present material are hard magnets and are useful for high frequency applications [18].

4. Conclusions

The M-type hexaferrites $\text{Sr}_{1-x}\text{Mg}_x\text{Fe}_{12}\text{O}_{19}$ ($x = 0.0, 0.1, 0.3, 0.4$) hexaferrites were successfully synthesized employing citrate-precursor method. Phase formation was confirmed by X-ray diffraction. The XRD patterns exhibits that the prepared material were single phase of M-type hexagonal ferrite. The presence of peaks near 500–600 cm$^{-1}$ in Fourier transform infrared spectroscopy spectra indicates the formation of M-type hexaferrites. The incorporation of Mg cations increases the saturation magnetization and increase in coercivity. The good magnetic properties of the prepared materials may be useful for high density magnetic recording media and permanent magnets.

References

[1] H. Kojima, Fundamental properties of hexagonal ferrites with magnetoplumbite structure, in: E.P. Wohlfarth (Ed.), Ferromagnetic materials, North Holland, Amsterdam, 1982.
[2] R.A. McCurrie, Ferromagnetic Materials: Structure and Properties, Academic Press Limited, London (1994) 180–181
[3] S.A. Mazen, M.H. Abdallah, R.I. Nakhla, H.M. Zaki, F. Metawe, "X-
ray analysis and IR absorption spectra of Li–Ge ferrite”, Mater. Chem.
Phys. 34 (1) (1993) 35–40
[4] B. Bhat, Z. Habib, J. Sharma, B. Want, A. K. Srivastava,” Effect of
annealing temperature on different physical properties of
Sr0.5La0.5Mg0.5Fe11.5O19 hexaferrite” S A E A , 2(2) 128-133, (2017)
[5]Y. Liu, M. G. Drew, Y. Liu, “Preparation and magnetic properties of
barium ferrites substituted with manganese, cobalt, and tin”, J. Magn.
Magn. Mater. 323, 945-953(2011).
[6] M. J. Iqbal, M. N. Ashiq, P. H. Gomez, "Effect of doping of Zr–Zn
binary mixtures on structural, electrical and magnetic properties of Sr-
hexaferrite nanoparticles”, J Alloy Compd, 478, 736-740 (2009)
[7] M. Jean, V. Nachbaur, J. Bran, and J. Le Breton, "Synthesis and
characterization of SrFe2O19 powder obtained by hydrothermal process”
J. Alloy Compd, 496, 306 (2010)
[8] L. Qiao, L. You, J. Zheng, L. Jiang, and J. Sheng, "The magnetic
properties of strontium hexaferrites with La–Cu substitution prepared by
SNS method", J. Magn. Magn. Mater.318, 74 (2007)
[9] Z. Wang, L. Zhong, J. Lv, H. Qian, Y. Zheng, Y. Fang, M. Jin, and J.
Xu, J. Magn. Magn. Mater. 322, 2782 (2010)
[10].X. S. Liu, W. Zhong, S. Yang, Z. Yu, B. X. Gu, and Y. W. Du,
"Structure and Magnetic Properties of La1+–Substituted Strontium
Magn. Magn. Mater, 232, 259–263(2011),
[11] F. Song, X. Shen, J. Xiang, and H. Song: Formation and magnetic
properties of M-Sr ferrite hollow fibers via organic gel-precursor
transformation process. Mater. Chem. Phys. 120, 213 (2010).
[12] A. Baniasadi, A. Ghasemi, A. Nemati, M. A. Ghadikolaei, E.
Paimozd, Effect of Ti–Zn substitution on structural, magnetic and
microwave absorption characteristics of strontium hexaferrite, J.Alloy
Compd.583, 325–328 (2014)
[13] F. Ansari, A. Sobhani, M. S. Niasari, 'Facile synthesis, characterisation and magnetic property of CuFe12O19 nanostructures via a
sol–gel auto- combustion process”, J. Magn. Magn. Mater. 401,362–369
(2016)