The Evaluation of Structural, Electrical and Magnetic Properties of Samarium substituted Spinel Ferrites

Muhammad Shakil Shah, Salma Aman, Naseeb Ahmad, Muhammad Bilal Tahir, Z. A. Alrowaili, M. S. Al-Buraihi, Hafiz Muhammad Tahir Farid, Rabia Yasmin Khosa, Enas E. Hussein, Ashraf Y. Elnaggar and Zeinom H. El-Baby

ABSTRACT
The spinel ferrites have been manufacturing long time because of their variety of applications in technological and industrial field. In the following study, the samarium doped spinel ferrites were under examination. The prepared compositions were denoted as; SrSm1–xFe2+xO4, x = 0, 0.025, 0.05, 0.075, 0.10. Sol–gel procedure was employed to make these samples. All the samples were investigated through the X-ray diffraction technique. The phase of prepared product was detected for the first three samples. However, the orthorhombic phase, that is, SmFeO3, was traced when samarium (Sm) composition reached 0.075 and above. The smaller width of the M–H loop confirmed the formation of soft ferrites. Saturation and remanence values were diminished with the substitution of samarium ions. But the anisotropy constant as well as coercivity values was enhanced with the samarium contents. Above mentioned features of spinel ferrites showed their possible usage in high-density recording applications.

1. Introduction
On behalf structural mechanism, the ferrite particles were separated into garnet, spinel and hexagonal. Out of these, spinel ferrites were excessively used due to their wide applications such as electronics, enlargement of magnetic resonance imaging, bioprocessing and power conditioning [1]. The spinel ferrites can function over microwave frequencies owing to their large resistivity and less eddy current consumptions [2]. General chemical formulation for the Nano sized spinel ferrites was transcribed as MFe2O4. Here, M denotes divalent metallic ions which may be Ni2+, Mg2+, Zn2+, Cu2+, Cd2+, Fe2+ and Sr2+ etc. [3,4]. The structure of spinel ferrite is face centred cubic “FCC” having 8 formula units in single unit cell. The arranged O2– ions among the lattice form the crystal structure of spinel ferrites. The spinel nanoparticles have a wider range of applications, such as microwave and switching appliances was determined by Hakeem et al. [5]. The features of these nanoparticles were modified when they were combined with rare-earth ions. In previously published reports, many authors tried to explore the rare earth substituted spinel ferrites, and they got fantastic features of resulted nanoparticles. Their structural and magnetic behaviour was modified with surprising features [6–8]. The effect of samarium ions doping in ferrites was revealed by many investigators [9–11].

Moreover, it was known that the interactions of Fe–Fe ions have a strong impact on the resistivity and ferromagnetic behaviour of ferromagnetic oxides. However, when the rare-earth (RE) ions were involved with ferromagnetic oxides, the interactions of the RE–Fe ions introduce 3d–4f coupling, which may cause the changing electrical and magnetic behaviour. Different rare-earth ions substitutions have different impacts upon the ferrite particles. When rare-earth ions are introduced into spinel ferrite, it undergoes structural distortion and strain, as well as significant changes in magnetic and electrical properties [12]. Rashad et al. [13] used the citrate precursor method to create samarium-substituted CoFe2O4 and discovered that adding Sm3+ ions decreased saturation magnetization and coercivity. According to Peng et al. [14], doping gadolinium with cobalt ferrite nanoparticles increased the...
crystallite size. According to Guo et al. [15], adding Sm$^{3+}$ to NiFe$_2$O$_4$ increases the lattice parameter while decreasing crystallite size. Tahar et al. [16] investigated the effects of strontium ferrite doped with samarium is required. The structural and magnetic properties of strontium ferrite nanoparticles synthesized using the sol–gel method are improved when Fe$^{3+}$ ions are replaced with Sm$^{3+}$ ions, as described in this paper.

2. Synthesis of spinel ferrites and characterization

Sol–gel auto combustion scheme was implemented to prepare the samples. One hundred ml deionized water was taken in beakers, and all the raw materials (Sr(NO$_3$)$_2$, Fe(NO$_3$)$_2$) of analytical grades were put into the water. The measured quantity of 99.99% pure Sm$_2$O$_3$ was mixed with HNO$_3$ solution to get the Sm(NO$_3$)$_3$ and then combined with the prepared solution. Citric acid acts as a chelating agent. The homogeneity of all the products was obtained through the stirring of precursors at 80°C temperature. The pH value of products was set at seven through the continuous application of drops of ammonia. To get the viscous gel, the same process was continued for eight hours. The viscous gel was subjected to self-combustion for three hours under 370°C temperatures, and the gel was altered into fluffy type material. This fluffy material was crushed, milled into fine powder shape, and then kept in the furnace for sintering over high temperature of 700°C for up to five hours. The fine powder was changed into pellets through a hydraulic press. A high-quality hydraulic press (Paul Otto Weber) was selected to form the pellets along 0.18 cm thickness under the load of 30 kN. Around 3–5% of the polyvinyl alcohol (PVA) weight percentage was combined with pellets as the binder. The annealing treatment of pellets to avoid binder was completed by baking them at 250°C for one hour.

The product was then sintered at 950°C for seven hours. The detailed preparation process was displayed in a flow chart as Figure 1. X-ray diffraction study was done through X-ray diffractometer; Model: D-8 Bruker Axis. The diffraction analyse was completed within the 2$\theta$ range of 15–80°. Cu$\alpha$ was used as the radiation source. The vibrating sample magnetometer (VSM) is a device used to evaluate the magnetic behaviour of the sample. Coercivity, saturation magnetization and remanence were measured through VSM under room temperature conditions within the applied field (H) of 0–2 kOe. The hysteresis loop analyze gave the values of squareness ratio, Y–K angles, and anisotropy constant ($K_1$).

Figure 1. Processing steps of Sm-substituted spinel ferrites.
3. Results and discussions

3.1. Structural properties

The diffraction technique outcomes of samples are displayed in the Figure 2. The samples with less quantity of Sm ($x = 0.00, 0.025$ and $0.05$) possessed a cubic assembly. The peaks developed into wider and shorter form with increase of samarium content. This is due to the slow development process of crystallites and weak crystallization mechanism. Some traces of SmFeO$_3$ were detected for samples having samarium content greater than or equal to $0.075$. The peaks related to these traces were denoted by $\ast$ which are associated with $2\theta$ angles of $46.19^\circ$ and $32.11^\circ$. Standard JCPDS (joint committee for powder diffraction standard) cards: 82–1780 were used to index all the peaks with a standard value. The SmFeO$_3$ traces were appeared due to the presence of highly reactive Fe$^{3+}$ ions. These secondary traces were orthorhombic and possessed insulating nature [14]. Parameters such as bulk and X-ray density, lattice parameter, crystallite size were established through XRD patterns, and their values are listed in Table 1.

$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2}$$

In Equation (1), $h$, $k$, and $l$ are the miller indices, while $d_{hkl}$ is the path difference (spacing of the crystal layers). Using value of lattice constant in the set of Stanley’s relations, we can discover ionic radius for both A & B sites and bond lengths (A–O and B–O). In the set of this equation, “a” represents the lattice parameter; $r$ (O$^{2-}$) is the ionic radius of oxygen which is $1.35$ Å. Ideal value for “$\mu$” is $3/8$ for spinel ferrites [14].

$$r_A = \left(\mu - \frac{1}{4}\right) a\sqrt{3} - r$$

$$r_B = \left(\frac{5}{8} - \mu\right) a - r$$

$$A - O = \left(\mu - \frac{1}{4}\right) a\sqrt{3}$$

$$B - O = \left(\frac{5}{8} - \mu\right) a$$

$$L_A = a_o \frac{\sqrt{3}}{4}$$

$$L_B = a_o \frac{\sqrt{2}}{4}$$

Table 1 contains all the parameters which are found through a set of Standley’s equations. Figure 3 revealed that the lattice parameter linearly upsurges with the addition of samarium ion. This up-gradation in lattice constant is because of the greater ionic magnitude of samarium as compared to iron. Ionic radius of samarium and Fe ions is approximately $1.013$ and $0.64$ Å, respectively. Thus, the involvement of samarium ion disturbs the lattice parameter [14,15]. Lattice constant of the biphasic sample increased with the substitution of samarium ion. So, the secondary phase would not compress the lattice. Within the specified range of composition, that is, $0 \leq x \leq 0.10$ there were no limitations for samarium ion substitution. Other factors such as bond lengths, jump lengths, and ionic radii were enhanced with the rising of Sm substitution, which may happen due to two reasons: One is the bigger size of the dopant element, and the other is the division between A&B sites [16]. Numerical values of X-ray density and bulk density ($\rho_x, \rho_b$) were also enlarged with samarium replacement. These density values increased gradually due to the addition of more and more samarium content or the formation of smaller ferrite’s particles [17].

$$D_m = \frac{M}{\pi r^2}$$

$$D = \frac{0.94A}{\beta\cos^2\theta}$$

Crystallite sizes of samples were measured via solving Debye Scherrer’s relation and the most intense peaks were (3 1 1) considered [18]. In this relation, $\theta$
Table 1. XRD parameters of Sm substituted ferrites.

| Composition  | $x = 0.00$ | $x = 0.025$ | $x = 0.05$ | $x = 0.075$ | $x = 0.10$ |
|--------------|------------|-------------|------------|-------------|------------|
| Lattice constant “a” [Å] | 8.27 | 8.31 | 8.34 | 8.38 | 8.42 |
| Volume [Å$^3$] | 565.69 | 573.86 | 580.09 | 588.48 | 597.31 |
| $D_s$ (gm/cm$^3$) | 5.36 | 5.4 | 5.43 | 5.46 | 5.52 |
| $D_i$ (gm/cm$^3$) | 4.28 | 4.31 | 4.33 | 4.35 | 4.37 |
| $r_A$ [Å] | 0.4405 | 0.4492 | 0.4557 | 0.4643 | 0.4734 |
| $r_B$ [Å] | 0.7175 | 0.7275 | 0.7350 | 0.7450 | 0.7554 |
| A–O [Å] | 1.7905 | 1.7991 | 1.8056 | 1.8143 | 1.8235 |
| B–O [Å] | 2.0675 | 2.0775 | 2.085 | 2.095 | 2.1055 |
| Jump length ($L_A$) [Å] | 3.5811 | 3.5984 | 3.6114 | 3.6287 | 3.6467 |
| Jump length ($L_B$) [Å] | 2.9239 | 2.9380 | 2.9487 | 2.9628 | 2.9775 |
| Crystallite size [nm] | 63 | 57 | 53 | 48 | 44 |

is used for Bragg’s angle, $\lambda$ is showing wavelength of X-rays and $\beta$ is full-width half maxima. As the concentration of Sm increases in the lattice, the grain growth is hampered. This is because of the segregation around the boundaries, which hinders its passing.

3.2. AC magnetic susceptibility

The magnetic behaviour of samples is explained on behalf of the spin coupling of three-dimensional electrons (Fe–Fe interactions) [19]. When a small quantity of rare-earth ions was involved in the samples, then RE–Fe interactions produced 3d–4f coupling, which regulates the magnetic behaviour. The knowledge about such interactions was usually received through the inspection of Curie temperature or magnetization [20]. Before finding the Curie temperature, one must know the value of the magnetic susceptibility of samples. The magnetic susceptibility was found using the mutual inductance technique within the 300–600-kelvin temperature range. In the process, the frequency was set at 20 Hz. The dimensionless constant quantity is called termed magnetic susceptibility. It shows the degree of magnetization within the presence of the external field. Graphical variation of magnetic susceptibility versus temperature is shown in Figure 4. The susceptibility is denoted by $\chi/\chi_{RT}$, and temperature is measured in kelvin. The susceptibility of pure and lightly doped samples ($x = 0.00, 0.025$) was noticed to be increased slowly with a rise of temperature up to 300 K. At some particular temperatures, the susceptibility reached to maximum peak value. The certain temperature is termed a Blocking temperature. However, when Sm$^{3+}$ ion content increased beyond 0.025, the susceptibility became zero suddenly.

The sudden drop of susceptibility value near the Curie temperature value was happened due to loss of magnetic nature, as exposed in Figure 4. The peak worth of susceptibility was attained for the first two samples showed that the ferrites contain multi-domain grains (MD grains) [21]. The samples with samarium concentration as $x = 0.05, 0.075, 0.10$ showed an exponential decrease in susceptibility value with temperature rise. The alteration in Curie temperature for samarium concentration was revealed in Figure 4. Value of Curie

temperature ($T_c$) is inversely related to samarium concentration. The value of $T_c$ is higher for lower samarium concentrations, and it is lower for more samarium concentrations. The main reason is the variety of angles Fe$^{3+}−O−Fe^{3+}$ and Fe$^{3+}−Fe^{3+}$ elementary interactions among the ferromagnetic substances [22]. The interactions of magnetic moments were decreased eventually. The pure samples have a very high Curie temperature value compared to RE doped samples [23–25]. The presence of magnetic moments collinearly within the ferric ions is due to the superexchange interactions. The superexchange interactions Fe$^{3+}−O−Fe^{3+}$ were responsible for partial and weaker disorders. A transition in valence state of Fe takes place after higher spin state towards lower spin state. For instance, a change was observed from 3d$^5$ (5 µB) to 3d$^6$ (4 µB) [26, 27]. These types of fluctuations introduce the scheme to go from collinear way to non-collinear fashion, which in turn causes to fall Curie temperature [28]. Moreover, the RE–Fe interactions over octahedral sites linked with Fe–Fe interactions may also be the reason for the lowering of Curie temperature value [29, 30].

3.3. Magnetic properties

The details of magnetization with respect to applied field (H) under room temperature conditions were given in Figure 5. The hysteresis loop was analysed to calculate saturation magnetization, remanance, coercivity,
Figure 5. M–H loops of Sm-substituted spinel ferrites.

etc. Variation of these magnetic parameters for samarium concentration is shown in Figure 6. The coercivity value remained small and hardly reached up to some hundred Oersted for all samples. This showed the samples were soft magnetic materials. Although the coercivity ($H_c$) value increased and magnetization values ($M_r$ & $M_s$) decreased with samarium ions. Three possible interactions may exist in the spinel ferrites, including A–A interactions, B–B interactions and A–B relations. The A–B interactions were prominent.

The flagging in the A–B interactions would be the cause of reducing magnetization [31]. The iron ions were present on both A and B sites, whereas the samarium ions existed over B sites. This is due to the greater ionic radius of samarium (1.013 Å) than iron (0.64 Å). Hence, samarium ion is a non-magnetic moment that induces less magnetic moment towards B site and high magnetic moment towards A sites. Thus, the introduction of samarium in the lattice has a very minor impact on the overall magnetization of the lattice. This may be another factor that is accountable for the lessening of magnetization. Shifting of Fe ions from octahedral to the tetrahedral site may also decrease saturation magnetization. The grain size increases the disorderliness of magnetic moments over the particle’s surface, which decreases saturation magnetization.

Consequently, the net magnetization lessened. Several reports with similar results of rare-earth-doped spinel ferrites were available [32,33]. The way of alteration of squareness ratio ($M_r/M_s$) for samarium amount in the lattice was labelled in Figure 6. It was observed that $M_r$ to $M_s$ ratio was uplifted by the addition of rare ions. The coercivity value is related to many aspects like particle size, porosity, domain length and surface morphology. The size of grains varied inversely for coercivity.

The movement of domain walls required a very little amount of energy as compared to domain rotation.

Figure 6. Magnetic properties Sm-substituted spinel ferrites.
This happens when the domain walls are magnetized or demagnetized. These results obey Brown’s relation, which stated that the magnetization and coercivity were inversely linked [34,35]. Following relation was considered to find Anisotropy constant [36]. Figure 6 showed that the Anisotropy constant (k1) enhanced with respect to samarium addition. Variational performance of both k1 and Hc was noticed to be similar [37]. Normally, the 4f electrons of rare-earth ions gave rise to magnetic moments at room temperature. But the positions of magnetic moments did not remain in the same orientation. So, the rare-earth ions have very little contribution to magnetization due to their paramagnetic nature. In the case of spinel ferrites, the value of "nB" does not depend upon the magnetic moment of subsequent ions. Bohr magnetic constant was determined by using the following relation. Here, Ms, Pb and MW were saturation magnetization, density and molecular weight, respectively [38]. The variation between "nB" and samarium concentration was displayed in Figure 6. With the growth of samarium amount in the lattice, the nB decreased. As a result, the saturation magnetization would also be reduced. Yafet–Kittle angles were found by considering various values of Bohr magnetron and using the following formulation [39,40].

\[
\frac{n_B(\mu_B)}{\rho_B \times 5585} = \frac{M_s \times M_s}{n_B \times 5585}
\]

where nB represented magnetic moments, and samarium concentration was "x". The Y–K angles were enlarged with samarium substitution, as shown in Figure 6. It indicated that the triangular spin was favourable for B sites which produce flagging for A–B interactions. The spin canting effect was also responsible for the increase of Y–K angles. The canting angles were increased because of the diminution in grain size for samarium doping [41,42].

4. Conclusion

The samarium-substituted Nano-ferrites were synthesized through the Sol–gel auto combustion process. The cubic phase was confirmed for samples having lower samarium content (0.00, 0.025 and 0.05). However, the samples with high samarium concentrations (0.075 and 0.10) possessed SmFeO3 secondary phase. The morphological study tells about the non-uniform distribution of grains and partially occupied grains. The study revealed that the grain sizes reduced with the surge of samarium ions in the base product. Susceptibility indicates MD particles for the samarium concentration; x ≤ 0.025. But the domain changed from SD to SP if samarium concentration increased beyond this limit; x ≤ 0.05. The Curie temperature falls with the rise of samarium due to the dilution of A–B interactions. The graph showed that the susceptibility achieved some peak value at certain temperatures, which might be credited for grain size reduction. The magnetization values (Mr and Ms) were reduced with an increase in samarium content. The behaviour of coercivity and anisotropic constant (Hc and k1) was almost similar. All the mentioned features of prepared samples showed their suitability for large density magnetic recording media uses.

Data availability statement

Data sharing is not applicable to this article as no data sets were generated during the present study.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work was financially supported by the Taif University Researchers Supporting Project (TURSP-2020/32), Taif University, Taif, Saudi Arabia.

References

[1] Abdellatif MH, El-Komy GM, Azab AA, et al. Crystal field distortion of La3+ ion-doped Mn-Cr ferrite. J Magn Magn Mater. 2018;447:15–20.
[2] Ramzan R, Taniq M, Ashiq MN, et al. Effect of yttrium ion on electrical and magnetic properties of barium based spinel ferrites. J Mater Res Technol. 2021;12:1104–1112.
[3] Hakeem A, Alshahrahi T, Muhammad G, et al. Magnetic, dielectric and structural properties of spinel ferrites synthesized by sol-gel method. J Mater Res Technol. 2021;11:158–169.
[4] Farid HMT, Ahmad I, Ali I, et al. Study of spinel ferrites with addition of small amount of metallic elements. J Electroceram. 2019;42:57–66.
[5] Hakeem A, Alshahrah T, Ali I, et al. Synthesis and characterization of composites for microwave devices. Chin J Phys. 2021;70:232–239.
[6] Shaban Munir IA, Laref A, Farid MT. Effect of Nd-substitution on hexagonal ferrites for memory devices. J Appl Phys A Mater Sci Process. 2020;126:722.
[7] Zhong XC, Guo XJ, Zou SY, et al. Improving soft magnetic properties of Mn-Zn ferrite by rare earth ions doping. AIP Adv. 2018;8(4):047807.
[8] Mahmoudi M, Kavanlouei M, Maleki-Ghaleh H. Effect of composition on structural and magnetic properties of nanocrystalline ferrite Li 0.5 Sm x Fe 2.5–x O 4. Powder Metallurgy Metal Ceram. 2015;54(1):31–39.
[9] Zelai T. Structural and magnetic properties of samarium-substituted spinel ferrites. J Magn Magn Mater. 2018;447:15–20.
[10] Priyadharsini P, Pradeep A, Rao PS, et al. Effect of samarium substitution on the structural and magnetic properties of nanocrystalline cobalt ferrite. Mater Chem Phys. 2009;116:207–213.
[11] Thankachan S, Jacob BP, Xavier S, et al. Effect of samarium substitution on structural and magnetic properties of magnesium ferrite nanoparticles. J Magn Magn Mater. 2013;348:140–145.
[12] Sileo EE, Jacobo SE. Gadolinium-nickel ferrites prepared from metal citrates precursors. Physica B. 2004;354(1–4):241–245.
[13] Rashad MM, Mohamed RM, El-Shall H. Magnetic properties of nanocrystalline Sm-substituted CoFe$_2$O$_4$ synthesized by citrate precursor method. J Mater Process Technol. 2008;198(1–3):139–146.
[14] Peng J, Hojamberdiev M, Xu Y, et al. Hydrothermal synthesis and magnetic properties of gadolinium-doped CoFe$_2$O$_4$ nanoparticles. J Magn Magn Mater. 2011;323(1):133–137.
[15] Guo L, Shen X, Meng X, et al. Effect of Sm$^{3+}$ ions doping on structure and magnetic properties of nanocrystalline NiFe$_2$O$_4$ fibers. J Alloys Compd. 2010;490(1–2):301–306.
[16] Tahar LB, Smiri LS, Artus M, et al. Characterization and magnetic properties of Sm- and Gd-substituted CoFe$_2$O$_4$ nanoparticles prepared by forced hydrolysis in polyol. Mater Res Bull. 2007;42(11):1888–1896.
[17] Ashiq MN, Iqbal MJ, Gul IH. J Magn Magn Mater. 2011;323:259–263.
[18] Iqbal MJ, Ashiq MN, Gomez PH, et al. J Magn Magn Mater 2008;320:881–886.
[19] Zhou J, Lv L, Chen XZ. J Ceram Process Res 2010;2(11):263–272.
[20] Shinde UB, Shirsath SE, Patange SM, et al. Ceram Int 2013;39:5227–5234.
[21] Ishaque M, Islam MU, Khan MA, et al. Physica B. 2010;405:1532–1540.
[22] Mohan GR, Ravinder D, Ramana Reddy AV, et al. Mater Lett 1999;40:39–45.
[23] Farid MT, Ahmad I, Murtaza G, et al. J Ovon Res. 2016;12(3):137–146.
[24] Farid HMT, Ahmad I, Ali I, et al. Structural and dielectric properties of copper-based spinel ferrites. Eur Phys J Plus. 2018;133(2):1–12.
[25] Peng Z, Fu X, Fu HGZ, et al. J Magn Magn Mater 2011;323:2513–2518.
[26] Gul IH, Maqsood A. J Alloys Compd. 2008;465:227–231.
[27] Farid HMT, Ahmad I, Bhatti KA, et al. Ceram Int. 2017;43:7253–7260.
[28] Ali I, Islam MU, Ashiq MN, et al. J Magn Magn Mater 2014;362:115–121.
[29] Ramana Reddy AV, Ranga Mohan G, Boyanov BS, et al. Mater Lett 1999;39:153–165.
[30] Vijaya Kumar K, Ravinder D. Int J Inorg Mater 2001;3:661–666.
[31] Kambale RC, Shaikh PA, Kambale SS, et al. J Alloys Compd. 2009;478:599–603.
[32] Rezlescu E, Rezlescu N, Pasnicu C, et al. Cryst Res Technol. 1996;31:343–352.
[33] Rezlescu N, Rezlescu E. Solid State Commun. 1993;88:139–141.
[34] Muthuselvam IP, Bhowmik RN. J Magn Magn Mater 2010;322:767–776.
[35] Costa ACFM, Tortella E, Morelli MR, et al. J Magn Magn Mater 2003;256:174–182.
[36] Roy PK, Bera J. J Magn Magn Mater 2008;320:1128–1132.
[37] Issa B, Obaidat IM, Albiss BA, et al. Int J Mol Sci 2013;14:21266–21305.
[38] Rana MU, Islam MU, Ahmad I, et al. J Magn Magn Mater 1998;187:242–246.
[39] Jadhav SA. J Magn Magn Mater 2001;224:167–172.
[40] Upadhyay RV, Rao SN, Kulkarni RG. Mater Lett 1985;3:273–277.
[41] Bhosale JL, Kulkarni SN, Sasmile RB, et al. Bull Mater Sci 1996;19:767–774.
[42] Upadhyay RV, Mehta RV, Prakash K, et al. J Magn Magn Mater 1999;201:129–132.