Dominating the Structural, Microstructural and Magnetic Features of Li^+ Substituted Strontium Hexaferrite ($\text{Sr}_{1-x}\text{Li}_{2x}\text{Fe}_{12}\text{O}_{19}$)

Mahmoud Hessien (✉ hessienmahmoud@yahoo.com)

Taif University, Faculty of Science <https://orcid.org/0000-0003-2607-0050>

Nader El-Bagoury

CMRDI: Central Metallurgical Research and Development Institute

M. H. H. Mahmoud

Taif University

M. Alsawat

Taif University

Abdullah ALanazi

Taif University

M. M. Rashad

CMRDI: Central Metallurgical Research and Development Institute

Research Article

Keywords: M-type hexaferrite, Lithium ion, Synthesis, Powders, Characterization, Magnetic properties

Posted Date: March 18th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-299544/v1>

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Abstract

Lithium ion substituted hexagonal strontium ferrite ($\text{Sr}_{1-x}\text{Li}_x\text{Fe}_{12}\text{O}_{19}$, where $x=0.1, 0.2$, and 0.3) powders have been felicitously fabricated using tartrate precursor scheme. The impact of the Li^+ content, as well as the annealing temperature on the phase evolution, microstructure and magnetic performance, was commanded by X-ray diffraction profile (XRD), scanning electron microscopy (SEM), and vibrating sample magnetometer (VSM). Single phase hexagonal ferrite was consummated at a Li^+ ratio of 0.2 and different annealing temperatures, from 1000 to 1200°C for 2h . An impurity $\alpha\text{-Fe}_2\text{O}_3$ phase was noted at a high Li^+ concentration of 0.4 and 0.6 at all temperatures. The crystallo-aspects characteristics were altered with Li^+ content and annealing temperature. The microstructure of pure hexagonal ferrite sample visualized platelet like structure. A fine spherical shape displayed with platelet shape by enhancing the Li^+ content up to 0.4 and 0.6 . EDX analysis emphasized Fe, Sr, O, and Li atoms spread between the plate and spherical shapes. Good saturation magnetization ($M_s=60.88\text{ emu/g}$) was realized for Li^+ content of 0.2 as the results of increasing the thickness of the nanoplatelet structure.

1. Introduction

Hexaferrites (M, W, X, U, Y, Z types) have a significant request in daily life during the last decades. Among them, Strontium-based M-type hexaferrite ($\text{MFe}_{12}\text{O}_{19}$) is a paramount demand for different industrial, military, and home equipment applications [1–2]. In this context, $\text{SrFe}_{12}\text{O}_{19}$ emerges exemplary features involving relatively large saturation magnetization, high coercive force, outstanding Curie temperature, pronounced magneto-crystalline anisotropy, excellent chemical and thermal stability, high dielectric constant, low conductive losses, corrosion resistance, non-toxicity, and simple accessibility [3–6]. Due to such superior properties, $\text{SrFe}_{12}\text{O}_{19}$ is a multidisciplinary technological component indispensable for refrigerator magnets, permanent magnets, recording media, automotive industries, microwave devices, sensors, biomedicine, photocatalyst, magneto-optics devices, magnetic fluids, sound devices, electric motors, generators, etc. [4–10]. Consequently, enhancing the magnetic feature of strontium hexaferrite has been a theme of comprehensive examination work. Nevertheless, the substitution of Fe^{3+} or Sr^{2+} sites is an efficacious route to monitor the magnetic properties of strontium hexaferrite. Many previous published works are focused on the manipulation of rare earth elements [4–7], Bi^{3+} [9], Mn^{3+} [10], Co^{3+} [11], Cr^{3+} [12] or combined of divalent or trivalent ions with rare earth elements [13–16]. However, the manipulation of Li^+ substitution at Sr^{2+} ion sites on the structural and magnetic properties of M-type strontium ferrite is not mentioned in the literature. Therefore, in this report, the impact of Li^+ ion substitution at the Sr^{2+} ion sites on the structural, microstructure, and magnetic properties manufactured based on tartaric acid precursor approach at different temperatures from 1000 to 1200°C was considered in details.

2. Experimental

2.1. Materials and procedure

Anhydrous iron (III) chloride; FeCl_3 (Sigma Aldrich), lithium chloride anhydrous; LiCl (Fluka), strontium chloride hexahydrate; $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ (RIEDEL-DE HAEN), and tartaric acid; $\text{C}_4\text{H}_6\text{O}_6$ (RIEDEL-DE HAEN) exploited in this work were employed without any further purification. In order to prepare the crystalline Li ion-substituted $\text{SrFe}_{12}\text{O}_{19}$ powders ($\text{Sr}_{1-x}\text{Li}_{2x}\text{Fe}_{12}\text{O}_{19}$ where $x = 0.1, 0.2$ and 0.3) as evinced in Fig. 1. The next steps were similar to the previously published elsewhere [4]. Table 1 represents the starting materials for tailoring of hexagonal ferrite at different Sr:Fe:Li molar ratios.

2.2. Physical properties

Crystal structure of the synthesized powders was identified by an X-ray diffractometer, model Bruker AXS (D8-ADVANCE) with $\text{Cu K}\alpha$ ($\lambda = 1.54056 \text{ \AA}$) radiation, operating at 40 kV and 10 mA. Crystallite size, lattice parameters, aspect ratio (a/c), and unit cell volume were estimated by equations invoked in work published by Hessian et al. [4]. Scanning electron microscopy (SEM) was recognized to demonstrate the change in microstructure through surface morphology and average particle size of the resultant ferrite. Magnetic particularities of the elaborated powders were defined using a vibrating sample magnetometer (VSM, 7410-LakeShore, USA) at room temperature in a maximum applied field of 20 kOe.

3. Results And Discussion

3.1. Phase development

Synthesis of Li^+ substituted strontium hexaferrite with the molar ratios 12:0.9:0.2 of Fe:Sr:Li at various temperatures from 1000 to 1200 °C for 2h indicated that all peaks were perfectly corresponded to a single well crystalline $\text{SrFe}_{12}\text{O}_{19}$ at annealing temperatures from 1100 to 1200°C without any other impurity species, as represented in Fig. 2. On the other hand, the change of the Fe:Sr:Li molar ratio to be 12:0.9:0.4 visualized the presence of diffraction peaks linked to $\alpha\text{-Fe}_2\text{O}_3$ as secondary impurity species as presented in Fig.3. Eventually, Fig.4 illustrates the impact of Li^+ ion with a ratio of 0.6 on the hexagonal phase evolution at Fe:Sr ratio of 12:0.8. The XRD diffraction analysis profiles evince $\alpha\text{-Fe}_2\text{O}_3$ phase is predestined with M-type phase at various temperatures. Applying Scherrer equation based on the main peak (107) of the XRD chart showed that the variation in the crystallite size, the lattice parameters, and unit cell volume may be related to the difference between the ionic radii of Li^+ (0.76 Å) Sr^{2+} (1.18 Å) and Fe^{3+} (0.64 Å) as recorded in Table 2.

3.2. Microstructure

Fig. 5 displays SEM images of clear hexagonal ferrites generated through tartaric acid approaches at different Li^+ concentrations. Fig.5 a, and b reveals the hexagonal platelet-like structure with well-defined hexagonal grains and prominent grain boundaries with the addition of 0.2 Li^+ . This defined microstructure further confirms the well crystalline $\text{SrFe}_{12}\text{O}_{19}$ phase. In contrast, further boost Li^+ ratio to

0.4 resulted in fine spherical particles pointed the formation of secondary iron oxide composed with the hexagonal platelet shape, as alluded in Fig.5 c and d. Consequently, wide size distributions were observed. Similar trends were also illustrated in Fig 5e-h with the increase of Li^+ ratios. Meanwhile, the $\alpha\text{-Fe}_2\text{O}_3$ spherical shape was also increased.

Qualitative elemental analyses through energy-dispersive X-ray interpretation (EDX) were detected on $\text{Sr}_{0.7}\text{Li}_{0.6}\text{Fe}_{12}\text{O}_{19}$ sample after heat treatment at 1100 °C to perceive allocation of each metal ion at the formation process. The EDX charts for Fe, Sr, O, and Li elements were presented in Fig. 6, and the spot analysis of $\text{Sr}_{0.8}\text{Li}_{0.6}\text{Fe}_{12}\text{O}_{19}$ annealed at 1100 °C is presented in Table 3. It is clearly that Fe, Sr, O, and Li elements were allocated between the plate- like structure (hexaferrite) and the small crystals, with larger concentration of Fe and Sr in the plate – like structure phase. Strontium was mostly presented in the plate- like structure, while lithium was mostly absent in the small crystals and in the plate – like structure. This may be attributed to the loss of Li^+ content at high temperature.

3.3. Magnetic properties

Figs 7, 8, and 9 specify the variation in the magnetic properties of Li^+ ion substituted $\text{SrFe}_{12}\text{O}_{19}$ powders at different annealing temperatures (1000, 1100, and 1200°C). Magnetic parameters such as saturation magnetization (M_s), coercive force (H_c), remanence magnetization, and squareness ratio (M_R/M_s) are shown in Table 4. The saturation magnetization improved with increasing the annealing temperature from 1000 to 1100°C, then diminished with further increasing the temperature up to 1200°C. Highest saturation magnetization ($M_s=60.88$ emu/g) was acquired at 1100°C for $\text{Sr}_{0.9}\text{Li}_{0.2}\text{Fe}_{12}\text{O}_{19}$ sample. Li et al emphasized that the magnetic moment of hexagonal strontium ferrite platelet was found to enhance as the thickness of nanoplatelet increased based on magnetic force microscopy (MFM) with nanoscale spatial resolution [] as profited in Fig. 5a, and b. However, the decrease in the saturation magnetization with increasing the Li^+ concentration at 1100°C could be correspond to the mass ratio of $\text{SrFe}_{12}\text{O}_{19}$ and $\alpha\text{-Fe}_2\text{O}_3$.

On the other hand, the coercive force of the formed Li^+ substituted SrM ferrites was extremely minified to lower than 1.5 KOe. Typically, H_c is rebated by both the intrinsic and extrinsic properties, such as the crystal structure, magnetic anisotropy, chemical content, composition, crystalline structure, average crystallite size, morphology, stress, lattice defects, and so on [18,19]. Based on XRD patterns and SEM specimens, it can be concluded that H_c was much dependent on the crystallinity, the average particle size and $\alpha\text{-Fe}_2\text{O}_3$ content. In this regard, the high H_c value was related to the high average particle size and $\alpha\text{-Fe}_2\text{O}_3$ content as well as magneto crystalline anisotropy. The variation on the M_s and H_c values at different temperatures was evinced in Fig. 10. The squareness ratios M_R/M_s of the hexagonal samples were low as the results of low crystallinity, formation of $\alpha\text{-Fe}_2\text{O}_3$ phase, and the hexagonal ferrite was in multi-magnetic domains.

4. Conclusions

A series of Li^+ ion substituted strontium hexaferrite at different Li^+ concentrations, and annealing temperatures was purposefully tailored based on the tartaric acid precursor pathway. Based on structural properties, a single phase of hexagonal strontium ferrite was affirmed without impurity phase of $\text{Sr}_{0.9}\text{Li}_{0.2}\text{Fe}_{12}\text{O}_{19}$ powders at Fe: Sr: Li ratio of 12:1:0.2 at different annealing temperatures from 1000 to 1200°C. Increasing the Li^+ concentration substituted Sr-M ferrite was found to develop the formation of $\alpha\text{-Fe}_2\text{O}_3$ as impurity phase. The lattice parameters, aspect ratio (a/c), and unit cell volumes of formed hexaferrite powders were varied with Li^+ content and annealing temperature. The SEM investigation showed that hexagonal powders at Fe: Sr: Li molar ratio 12:1:0.2 presented platelet-like structure at annealing temperature 1100 °C. However, wide particle distributions of platelet and spherical shapes were distinguished with rising Li^+ molar ratio. EDX analysis revealed that Fe, Sr, O, and Li elements were spread between the platelet structure (hexaferrite) and the small spherical crystals, with a larger concentration of Fe and Sr in the plate-like structure phase. Highest saturation magnetization ($M_s=60.88$ emu/g) was attained for $\text{Sr}_{0.9}\text{Li}_{0.2}\text{Fe}_{12}\text{O}_{19}$ sample at 1100°C. Various coercivities (443–1474 Oe) can be accomplished at different synthesis conditions.

Declarations

Due to technical limitations Declarations section is not available for this version.

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Tables

Table 1: Synthesis conditions of Li substituted strontium hexaferrite powders

Charge No	Conditions		Target
	Charges in mol (M)	Charges in gram (g)	
1	1.0 M $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ + 12 M FeCl_3 + 19 M $\text{C}_4\text{H}_6\text{O}_6$	$(\frac{266.62}{k})\text{g } \text{SrCl}_2 \cdot 6\text{H}_2\text{O} + (\frac{1946.52}{k})\text{g } \text{FeCl}_3 + (\frac{2851.65}{k})\text{g } \text{C}_4\text{H}_6\text{O}_6$	$\text{SrFe}_{12}\text{O}_{19}$
2	0.9 M $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ + 0.2 M LiCl + 12 M FeCl_3 + 19 M $\text{C}_4\text{H}_6\text{O}_6$	$(\frac{239.96}{k})\text{g } \text{SrCl}_2 \cdot 6\text{H}_2\text{O} + (\frac{8.478}{k})\text{g } \text{LiCl} + (\frac{1946.52}{k})\text{g } \text{FeCl}_3 + (\frac{2851.65}{k})\text{g } \text{C}_4\text{H}_6\text{O}_6$	$\text{Sr}_{0.9}\text{Li}_{0.2}\text{Fe}_{12}\text{O}_{19}$
3	0.8 M $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ + 0.4 M LiCl + 12 M FeCl_3 + 19 M $\text{C}_4\text{H}_6\text{O}_6$	$(\frac{213.3}{k})\text{g } \text{SrCl}_2 \cdot 6\text{H}_2\text{O} + (\frac{16.956}{k})\text{g } \text{LiCl} + (\frac{1946.52}{k})\text{g } \text{FeCl}_3 + (\frac{2851.65}{k})\text{g } \text{C}_4\text{H}_6\text{O}_6$	$\text{Sr}_{0.8}\text{Li}_{0.4}\text{Fe}_{12}\text{O}_{19}$
4	0.7 M $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ + 0.6 M LiCl + 12 M FeCl_3 + 19 M $\text{C}_4\text{H}_6\text{O}_6$	$(\frac{186.60}{k})\text{g } \text{SrCl}_2 \cdot 6\text{H}_2\text{O} + (\frac{25.434}{k})\text{g } \text{LiCl} + (\frac{1946.52}{k})\text{g } \text{FeCl}_3 + (\frac{2851.65}{k})\text{g } \text{C}_4\text{H}_6\text{O}_6$	$\text{Sr}_{0.7}\text{Li}_{0.6}\text{Fe}_{12}\text{O}_{19}$

k is an arbitrary scaling factor.

Table 2: Crystallite size, lattice parameters and unit cell volume on $\text{Sr}_{1-x}\text{Li}_{2x}\text{Fe}_{12}\text{O}_{19}$ nanopowder synthesized at various annealing temperatures from 1000 to 1200°C for 2h

Composition	Temperature, (°C)	Crystallite size, (nm)	Lattice constant			Unit cell volume, $V, (\text{\AA}^3)$
			$a, (\text{\AA})$	$c, (\text{\AA})$	a/c	
$\text{Sr}_{0.9}\text{Li}_{0.2}\text{Fe}_{12}\text{O}_{19}$	1000	146.3	5.6484	22.9593	3.914	683.91
	1100	146.8	5.86218	22.96048	3.9167	683.33
	1200	163.8	5.8755	23.0223	3.918	688.30
$\text{Sr}_{0.8}\text{Li}_{0.4}\text{Fe}_{12}\text{O}_{19}$	1000	165.7	5.86388	22.95656	3.9149	683.61
	1100	162.4	5.87158	23.00168	3.91746	686.75
	1200	152.5	5.87308	23.00352	3.916773	687.16
$\text{Sr}_{0.7}\text{Li}_{0.6}\text{Fe}_{12}\text{O}_{19}$	1000	146.9	5.86298	22.9624	3.91651	683.57
	1100	158.7	5.87208	22.98944	3.91504	686.50
	1200	170.2	5.87082	22.98272	3.91474	686.01

Table 3: Spot analysis range of constituent elements in the $\text{Sr}_{0.7}\text{Li}_{0.6}\text{Fe}_{12}\text{O}_{19}$ phase, wt-%

Element	Sr		Fe		O		Li	
	Mass%	Atom%	Mass%	Atom%	Mass%	Atom%	Mass%	Atom%
EDX1-P1	5.69	2.94	84.07	68.10	10.25	28.97	0	0
EDX2-P1	8.13	3.04	62.36	36.57	29.51	60.40	0	0
EDX3-P2	2.47	1.29	88.51	72.80	9.02	25.91	0	0
EDX4-P2	2.29	0.79	63.67	34.61	34.05	64.60	0	0

Table 4: Effect of $\text{Fe}^{3+}/\text{Sr}^{2+}$ mole ratio, La^{3+} ion substitution and annealing temperature on the magnetic properties of the synthesized strontium hexaferrite.

Composition	Temperature, (°C)	Magnetic Properties			
		<i>Saturation magnetization</i>	<i>Retentivity</i>	<i>Coercivity</i>	M_r/M_s
		M_s (emu/g)	M_r (emu/g)	H_c (Oe)	
$\text{Sr}_{0.9}\text{Li}_{0.2}\text{Fe}_{12}\text{O}_{19}$	1000	55.41	9.18	443.9	0.166
	1100	60.88	9.34	509.74	0.153
	1200	57.55	21.99	1474.7	0.382
$\text{Sr}_{0.8}\text{Li}_{0.4}\text{Fe}_{12}\text{O}_{19}$	1000	51.69	9.18	497.58	0.178
	1100	55.44	9.51	562.83	0.172
	1200	53.02	16.78	1268.1	0.316
$\text{Sr}_{0.7}\text{Li}_{0.6}\text{Fe}_{12}\text{O}_{19}$	1000	47.53	7.74	477.29	0.163
	1100	49.05	8.144	541.25	0.166
	1200	45.60	14.59	1131.40	0.320

Figures

Figure 1

Flow-sheet diagram for synthesis $\text{Sr}_{1-x}\text{Li}_{2x}\text{Fe}_{12}\text{O}_{19}$ using tartrate precursor strategy

Figure 2

XRD patterns of $\text{Sr}_{0.9}\text{Li}_{0.2}\text{Fe}_{12}\text{O}_{19}$ synthesized from strontium – lithium – iron tartrate precursor treated at different temperatures (1000 -1200°C) for 2 h.

Figure 3

XRD patterns of $\text{Sr}_{0.8}\text{Li}_{0.4}\text{Fe}_{12}\text{O}_{19}$ synthesized from strontium – lithium – iron tartrate precursor treated at different temperatures (1000 -1200oC) for 2 h.

Figure 4

XRD patterns of $\text{Sr}_{0.7}\text{Li}_{0.6}\text{Fe}_{12}\text{O}_{19}$ from strontium – lithium -iron-tartrate precursor treated at different temperatures (1000 -1200oC) for 2 h.

Figure 5

SEM micrographs of $\text{Sr}_{1-x}\text{Li}_2\text{xFe}_{12}\text{O}_{19}$ nanopowders at various temperatures; (a,b) $x=1$ & 1100°C, (c,b) $x=0.2$ & 1100°C, (e,f) $x=0.3$ & 1100°C, (g,h) $x=0.3$ & 1200°C

Figure 6

SEM mappings of $\text{Sr}_{0.7}\text{Li}_{0.6}\text{Fe}_{12}\text{O}_{19}$ obtained at 1100°C for the distribution of (a) real image, (b) strontium, (c) iron, (d) oxygen, (e) lithium and (f) the associated EDX spectra

Figure 7

Effect of calcination temperature on the hysteresis loop of $\text{Sr}_{0.9}\text{Li}_{0.2}\text{Fe}_{12}\text{O}_{19}$.

Figure 8

Effect of calcination temperature on the hysteresis loop of $\text{Sr}_{0.8}\text{Li}_{0.4}\text{Fe}_{12}\text{O}_{19}$

Figure 9

Effect of calcination temperature on the hysteresis loop of $\text{Sr}_{0.7}\text{Li}_{0.6}\text{Fe}_{12}\text{O}_{19}$

Figure 10

Variation of Saturation magnetization (M_s) and Coercivity (H_c) as function of Li^+ ion ratio and annealing temperature