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Structural, morphological and magnetic properties of M-type strontium hexaferrite synthesized via sol-gel auto combustion technique

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Abstract:

Strontium hexaferrite nanoparticles with the composition $SrNi_xZr_xFe_{12-2x}O_{19}$ (where x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) have been successfully synthesized via sol-gel auto combustion technique. The structural characterizations were systematically investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The X-ray diffraction results showed that the crystallite size obtained is in the range of 36-47 nm. The lattice constant 'a' almost remains constant while 'c' increases as Ni-Zr concentration 'x' increases. The other parameters like cell volume, X-ray density, bulk density and porosity have also been calculated. Scanning electron microscopy (SEM) showed that most of the particles formed had hexagonal structure and energy dispersive spectroscopy (EDS) confirmed that the composition obtained is near stoichiometric. Magnetization measurements at room temperature were performed using vibrating sample magnetometer (VSM) technique. The values of saturation magnetization (Ms), remenanace magnetization (Mr) and magneton number (n_B) increases up to x = 0.8 and then decreases for higher substitution while coercivity (Hc) decreases continuously as Ni-Zr content increases.

Keywords: Strontium ferrite, Sol-Gel auto combustion, SEM, XRD, Magnetic properties.

INTRODUCTION

Among several families of ferrites, M-type hexaferrites are widely used in industry and technology due to their excellent saturation magnetization and magneto crystalline anisotropy [1]. Nano-crystalline strontium hexaferrite (SrFe₁₂O₁₉) powder is a promising material for use as microwave absorbers in the gigahertz (GHz) range due to its high saturation magnetization, high coercivity, high electrical resistivity and because of its low dielectric and magnetic losses in the microwave frequency band [2, 3].

The structural, morphological, and magnetic properties of $SrFe_{12}O_{19}$ are related to purity, size and morphology of precursor powder. Controlling the chemical composition, size, morphology and by modifying microstructure its properties can be improved [4]. Strontium hexaferrite nano particles have been widely investigated because of their

several recent applications. M-type hexaferrite have extensive applications in telecommunication, microwave devices and magnetic recording media due to their good chemical stability, corrosion resistance, combined electrical and magnetic properties [5, 6]. Magnetic properties of Sr hexaferrite are strongly influenced by composition and synthesis methods. Different methods have been used to prepare strontium ferrite including modified chemical co-precipitation [7], sol-gel [8], salt melt method [9], ball milling [10] and hydrothermal [11].

Several researchers have substituted various cations in place of Fe^{3+} ions [12-14]. To improve the structural, morphological and magnetic properties of strontium hexaferrite nanomaterials, tetravalent (Fe^{3+}) ions are substituted by divalent (Ni^{2+}) and tetravalent (Zr^{4+}) ions synthesized via sol-gel auto combustion technique in the present work .

MATERIALS AND METHODS:

Analytical Reagent (AR) grade strontium nitrate Sr(NO₃)₂, ferric nitrate Fe(NO₃)₃.9H₂O, Zirconium $ZrO(NO_3)_2.H_2O_1$ nitrate nickel nitrate Ni(NO₃)₂.6H₂O and citric acid C₆H₈O₇.H₂O as a fuel were used as starting materials. According to the composition of $SrNi_xZr_xFe_{12-2x}O_{19}$ (where x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0), all the nitrates were separately dissolved in minimum amount of deionized water and stirred on magnetic stirrer for ten minutes. All the solutions have been mixed together and stirred on a magnetic stirrer until the nitrates were completely dissolved. The metal nitrate to citric acid ratio was taken as 1:3. The solutions were made with continuous stirring on magnetic stirrer, drop by drop ammonia solution was added to adjust the pH value to 7. Then the solution was heated on hot plate at 80 °C with constant stirring until gel was formed. Instantaneously gel ignites with the formation of large amount of gas, resulting in to light weight voluminous powder. The resulting precursor powder was calcined at 950 °C for 9 hrs to obtain pure $SrNi_xZr_xFe_{12-2x}O_{19}$ hexaferrite powder.

CHARACTERIZATION TECHNIQUES

The prepared samples of SrNi_xZr_xFe_{12-2x}O₁₉ were characterized by X-ray diffraction (XRD) using Rigaku Miniflux-II in the 2θ range from 20^0 to 80^0 at room temperature using CuKa radiation (wavelength $\lambda = 1.5406$ Å). Scanning electron microscopy (SEM) using Scanning electron microscope (Model No. LEO 1430) equipped with Energy dispersive spectroscopy (EDS) were employed to analyze the morphology, chemical composition and microstructure of samples. Magnetization measurements at room temperature were performed vibrating sample using magnetometer (VSM) technique. Using M-H plots, the saturation magnetization (Ms), corecivity (Hc), remenanace magnetization (Mr), remenanace ratio (Mr/Ms) and magneton number (nB) were calculated.

RESULTS AND DISCUSSION A. Structural analysis

X-ray diffraction patterns for all the synthesized samples are shown in Fig. 1. X-ray diffraction analysis reveals that all the diffraction peaks seen in the XRD pattern well matches with the standard pattern of strontium hexaferrite. The analysis of XRD pattern revealed the formation of single phase M-type hexagonal structure.



Figure 1. X-Ray diffraction patterns of $SrNi_xZr_xFe_{12\cdot 2x}O_{19}$ (where x= 0.0, 0.2, 0.4, 0.6, 0.8, 1.0).

The values of all the structural parameters calculated using equations (given in our previous work) [15] are presented in the Table I. It is evident from Table I that the lattice constant 'a' almost remains constant while 'c' increases with increase in Ni-Zr content 'x'. This can be attributed to the fact that the ionic radii of Fe^{3+} ions (0.64Å) is smaller than that of substituted cations Ni^{2+} (0.69Å) and Zr^{4+} (0.80Å). Both the lattice constant 'a' and 'c' increases linearly obeying Vegard's law [16]. In the present case two Fe³⁺ ions are replaced by Ni²⁺ and Zr⁴⁺ ions. The behaviour of lattice constant of the present samples is analogous to Ni-Zr substituted Sr ferrite prepared by chemical coprecipitation method [17]. The unit cell volume (V) calculated is shown in Table I as a function of Ni-Zr content 'x'. It is observed that unit cell volume increases with increasing Ni-Zr content 'x', which

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is attributed to increase in lattice constant 'c' of the present samples.

It is also clear from Table I that the X-ray density (ρ_x) increases due to larger molar mass of substituted samples. The bulk density (ρ_m) also increases whereas porosity (P) decreases with Ni-Zr content 'x'. The crystallite size obtained from XRD data is in the range of 36-47 nm, indicating the nano crystalline nature of the present samples.

TABLE I

Crystallite size (D), lattice constants (a ,c), cell volume (V), X-ray density (ρ_x), bulk density (ρ_m) and porosity (P) of the series SrNi_xZr_xFe_{12-2x}O₁₉.

Parameters	x = 0.0	x = 0.2	x = 0.4	x = 0.6	x = 0.8	x = 1.0
Crystallite size (D) nm	44.76	41.46	47.41	46.03	41.91	36.46
Lattice constant (a) Å	5.870	5.876	5.880	5.885	5.890	5.895
Lattice constant (c) Å	23.06	23.10	23.13	23.17	23.21	23.26
Cell volume (v) Å ³	689.28	691.44	693.76	696.00	698.18	700.28
X-Ray density(ρ_{XRD}) g cm ⁻³	5.11	5.13	5.15	5.17	5.19	5.22
Bulk density $(\rho_m) \text{ g cm}^{-3}$	3.00	3.08	3.15	3.23	3.30	3.37
Porosity (P) %	0.41	0.38	0.37	0.37	0.36	0.36

B. Morphology

The typical images obtained by scanning electron microscopy (SEM) are as shown in Fig. 2. The results indicate that all the particles have a proper hexagonal shape. The average grain size calculated from SEM is found in the range of 40-90 nm. The results of energy dispersive spectroscopy (EDS) are in good agreement with its nominal composition and are shown in Fig. 3.





Figure 2. SEM images $SrNi_xZr_xFe_{12-2x}O_{19}$ at (a) x=0.0, (b) x=0.4, (c) x=1.0.



Figure 3. EDS patterns of $SrNi_xZr_xFe_{12-2x}O_{19}$ at (a) x=0.0, (b) x=0.4, (c) x=1.0.

C. Magnetic Aspects

The magnetic properties of all the samples were studied using vibrating sample magnetometer (VSM) technique. Magnetization (M) versus applied field (H) plots for all the samples exhibit ferromagnetic behavior. All the samples saturates well. The hysteresis loops for Ni^{2+} and Zr^{4+} substituted strontium hexaferrite samples are depicted in Fig. 4.

It is clear from Fig. 4 that, the saturation magnetization increases up to x = 0.8 and then decreases while the remanence magnetization increases up to x = 0.6 and then decreases with the increase in Ni-Zr content.



Magnetic Field (Oe)

Figure 4. Hysteresis plots of SrNi_xZr_xFe_{12-2x}O₁₉ samples

This can be explained on the basis of the Ni²⁺ and Zr⁴⁺ ions occupying different sites in the Fe³⁺ sublattices based on the previous research reports [18, 19]. From this report, Zr^{4+} ions replace Fe^{3+} ions at the 2b site for small substitutions (x = 0.1) and at 4f1 for higher substitutions, while Ni²⁺ ions replace Fe^{3+} ions at the 4f2 site for x = 0.1, and at the 12k site for larger values of substitutions. When a nonmagnetic Zr^{4+} ion replaces a Fe³⁺ ion at the 4f1 site with spin down, then the total number of unpaired electrons with upward spin is increased, causing the saturation magnetization of the samples to increase. The Ni^{2+} ions replace Fe^{3+} at the 12k site with spin up and a magnetic moment of 2 μ B, which is also less than that of Fe^{3+} (5 µB), but the total magnetic moment increases by 2 µB due to replacement of ferric ions by a nonmagnetic Zr⁴⁺ ion at the 4f1 site. The decrease in saturation magnetization above x = 0.8 is due to the larger amount of nonmagnetic ions which are responsible for the weakening of exchange interactions [20].

The coercivity decreases with increasing Zr-Ni content, which is due to the decrease in the magneto-crystalline anisotropy. There are very few reported examples in which the saturation magnetization increases and at the same time the coercivity decreases with substitutions in M-type hexaferrites. Recording media require high enough coercivity above 600 Oe and saturation magnetization as high as possible [21,22].

The values of saturation magnetization (Ms), corecivity (Hc), remenanace magnetization (Mr), remenanace ratio (Mr/Ms) are listed in Table II. From Table II. it is clear that the magnetic properties were influenced by Zr⁴⁺ and Ni²⁺ substitution in the strontium hexaferrite. Our results on magnetic measurements are in good agreement with the substituted strontium hexaferrite [23-24]. Table II

Saturation magnetization (Ms), remenant magnetization (Mr), remenance ratio Mr/Ms, coercivity (Hc) and magneton number (nB) of $SrNi_xZr_xFe_{12-2x}O_{19}$.									
Parameters	x=0.0	x=0.2	x=0.4	x=0.6	x=0.8	x=1.0			
Ms (emu/g)	60.16	62.03	66.50	68.63	70.20	66.64			
Mr (emu/g)	35.33	36.23	36.82	37.75	31.76	25.80			
Mr/Ms	0.58	0.58	0.55	0.50	0.45	0.38			
Hc (Oe)	3001.4	2991.7	1719.3	1193.9	787	511.8			
nB (µB)	11.43	11.87	12.82	13.32	13.73	13.12			

The magnetic behaviour of hexaferrite material is largely governed by the distribution of iron ions on the crystallographic lattice sites. In the M-type hexaferrite, 12Fe³⁺ ions are distributed at five different sublattices: three octahedral (12k, 2a, $4f_2$), one tetrahedral $(4f_1)$ and one trigonal bipyramidal (2b). Out of $12Fe^{3+}$ ions four have spin in downward direction i.e. $2Fe^{3+}$ ions at $4f_1$, $2Fe^{3+}$ ions at $4f_2$ while other $8Fe^{3+}$ ions have spin in upward direction i.e. $6Fe^{3+}$ at 12k, 1Fe at 2a, $1Fe^{3+}$ at 2b. The four upward and four downward spins cancel each other and the net magnetic moment is only due to the remaining four iron ions having spin in upward direction. So the total magnetic moment 20µB is due to uncompensated spin of electron in the upward direction [25-27].

The magneton number nB (μ B) was obtained using the equation

$$n_B = \frac{Molecular \text{ weight } \times M_s}{5585}$$

where, Ms is the saturation magnetization.

The behaviour of magnetic moment is same as that of saturation magnetization. The values of magneton number nB (μ B) (Table II) increases up to x = 0.8 and then decreases with increase in Zr^{4+} and Ni²⁺ substitution due to the replacement of low magnetic moment of Zr^{4+} and Ni^{2+} as compared to Fe^{3+} . The behaviour of the magnetic moment of the sample is in good agreement with the saturation magnetization.

CONCLUSION

 Ni^{2+} and Zr^{4+} substituted $SrFe_{12}O_{19}$ have been successfully synthesized by Sol-Gel auto combustion method. The X-ray diffraction pattern reveals the formation of M-phase hexagonal structure for all substitution levels of Ni²⁺ and Zr⁴⁺ without any secondary phases. The average grain size obtained from Scanning electron microscopy was found in the range of 40-90 nm. Energy dispersive spectroscopy analysis confirmed that the synthesized samples were near stoichiometric. The values of saturation magnetization and remenance magnetization increases up to x = 0.8 and then decreases for higher substitution while coercivity decreases continuously as Ni-Zr content increases. The magneton number (μ B) increases up to x = 0.8 and then decreases with Ni^{2+} and Zr^{4+} substitution.

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