Tailoring the magnetic properties of M-type strontium ferrite with synergistic effect of co-substitution and calcinations temperature

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**ABSTRACT**

SrFe₂O₅ samples were initially prepared using sol-gel auto-combustion method and calcined from 500 to 1100°C (for 6 h). XRD data established the phase formation temperature of SrM phase to be ≈1000°C. Thereafter, the effect of Zn²⁺-Zr⁴⁺ co-dopant on magnetic and structural properties of SrZnₓZr₁₋ₓFe₁₋₂ₓO₉ (x = 0.00–1.00) samples calcined between 900–1100°C was investigated. XRD data shows that the cell volume increases (from 690.45 Å³ (x = 0.00) to 705.72 Å³ (x = 1.00)) while crystallite size decreases (from 123.9 nm (x = 0.00) to 62.33 nm (x = 1.00)) calcined at 1000°C. The Rietveld refinement of XRD data confirms ə) x = 0.00 sample to be phase pure and b) the presence of ZnFe₂O₄ (x = 2.25) & SrZrO₂ (x = 2.93%) impurity phases in x = 1.00 sample, calcined at 1000°C. FESEM micrographs revealed that a) grain size decreases for x > 0.20 with ‘x’ at 900°C and b) increases from 122 nm at 900°C to 443 nm at 1100°C, for x = 0.00. Broading of Raman bands reveals generation of strain in the lattice with enhancement of Zn²⁺-Zr⁴⁺ concentration. The magnetic studies reveal that the coercivity monotonically decreases (from 5358 (x = 0.00) to 690 (x = 1.00) Oe at 1000°C) with enhancement of Zn²⁺-Zr⁴⁺ concentration. A maximum Mₘ value = 70.89 emu/g was observed in x = 0.20 sample at 1100°C. Mₘ value also decreases for x > 0.20 at each calcination temperature.

1. Introduction

Due to their remarkable magnetic properties, high electric resistivity, high thermal corrosion resistance and chemical stability [1], M-type hexaferrites (of Sr, Ba, Pb and Ca etc.) have drawn considerable attention since the last few decades. These nanomaterials find utility in applications such as loudspeaker magnets, transformers, radiofrequency coils, microwave, and electromagnetic shielding devices, memory cells, storage cum recording media, terrestrial and satellite communication, hyperthermia fluids, and water treatment [2–10]. Among the various types of hexaferrite (like W, X, M, Y, U, and Z type etc.), better magnetic properties are observed in hexagonal M-type ferrites having magnetoplumbite crystal structure as compared to their other counterparts [11]. A unit cell of M-type hexaferrite contains 64 ions (24Fe₃⁺, 28Ba²⁺ and 38O²⁻). The excellent magnetic properties of M-type hexaferrite's are due to the presence of 24 Fe₃⁺ ions. The 24 Fe₃⁺ ions are divided among five crystallographic sites having different symmetry viz. octahedral sites (12k, 2a & 4f2), tetrahedral site (4f1) and trigonal bi-pyramidal (2b). The Fe₃⁺ ions in some of these crystallographic sites (4f1 & 4f2) have their magnetic moments oriented opposite to Fe₃⁺ ions present at other site [9]. This results in a cancellation of magnetic moments which results in a reduction of their magnetic properties. By adequately substituting different types of cations at the M²⁺ or Fe³⁺ site, magnetic properties of M-type hexaferrite can be improved. Several authors have tried to tailor M-type hexaferrites properties by replacing Fe³⁺ by divalent cations such as Co, Cu, Ga, Ni [12–15], trivalent cations such as Al, Ce, La, Nd, Pr [16,17] and mixture of cations such as Co-Zr [18], Cu-V [19], Gd-Co [20], La-Co [21], Nd-Co [22], Zn-Mo [23], and Zn-Zr [24–29]. Very few studies have been reported on the alteration of SrM’s magnetic properties by co-substitution of Zn²⁺-Zr⁴⁺ cations [24–26]. Bhosale et al. [24] reported dielectric, structural, and morphological properties of SrZnₓZr₁₋ₓFe₁₋₂ₓO₉ (x = 0.00–1.00) nanoparticle samples synthesized using sol-gel auto combustion. They reported an improvement of both dielectric loss and dielectric constant with increasing concentration of Zn²⁺-Zr⁴⁺ dopants. Iqbal et al. [25] reported structural, magnetic and dielectric properties for SrZnₓZr₁₋ₓFe₁₋₂ₓO₉ (x = 0.00 to 0.80) samples synthesized by chemical co-

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precipitation. They reported that the dielectric properties increased with the increase in Zn$^{2+}$-Zn$^{4+}$ dopant concentration. The highest magnetic saturation (M$_s$) value was reported at x = 0.40 beyond which the M$_s$ decreases whereas coercivity (H$_c$) continuously decreases with increasing dopant concentration [25]. Abdellahi et al. [26] reported structural, magnetic, and morphological studies of SrZn,Zr,Fe$_{12-2x}$O$_{19}$ (x = 0.00, 0.50–2.00) samples synthesized by mechanical milling for hyperthermia application. They observed highest value of M$_s$ at x = 1.00. However, studies reporting the effect of a) calcination temperature and b) co-substituent’s (Zn$^{2+}$-Zn$^{4+}$) on the structural & magnetic properties of SrM are still lacking. Further, the reported studies also lack the information regarding a) comprehensive structural (Raman studies and Rietveld refinement) and b) optimization of calcination temperature for different doping concentrations in SrZn,Zr,Fe$_{12-2x}$O$_{19}$.

Various methods such as ball milling method, citrate precursor method, co-precipitation method [11,30], hydrothermal method [31], Pechini method [32], micro emulsion method [33], solid-state method [34,35], solution-combustion method [11], and sol gel auto combustion method [32,36–38] have already been put to use for SrM synthesis (in pure and doped form). Literature survey shows that sol gel auto combustion has several benefits over other techniques [11,39–42]. These benefits include low cost, simplicity, lower phase formation temperature and better control over grain size.

In the present study, SrFe$_{12}$O$_{19}$ (SrM) samples were initially synthesized (using sol-gel auto-combustion method) and calcined from 500 to 1100°C, so as to establish the suitable calcination temperature for phase pure SrM synthesis. Thereafter, SrZn,Zr$_x$Fe$_{12-2x}$O$_{19}$ (x = 0.00–1.00) samples were prepared and subjected to calcination between 900 and 1100°C. The structural, micro-structural, and magnetic properties of these samples (at all stated calcination temperatures and compositions) were investigated using powder X-ray diffractometer (PXRD), Field Emission Scanning Electron Microscope (FESEM), Energy dispersive X-ray Analysis (EDX), Raman spectroscopy and Vibrating sample magnetometer (VSM) techniques. The study hence brings out optimum calcination temperature for obtaining a single SrM phase using chemical methods and reports the structural and magnetic properties of Zn$^{2+}$-Zn$^{4+}$ doped SrM samples in a wide range of compositions and at various calcination temperatures. The data suggest that the x = 0.2 samples display highest saturation magnetization at all calcination temperatures. The prepared samples exhibit tunable magnetic properties and may thus be suitable for applications in electromagnetic shielding/data storage devices and permanent magnets.

2. Materials and methods

Zn$^{2+}$-Zr$^{4+}$ co-substituted SrM were prepared by sol gel auto combustion technique by 1:1 metal nitrate to citric ratio (Fuel/chelating agent/reducing agent). Citric acid and nitrate salts of Strontium, Zinc, Zirconium and Iron were dissolved in deionized water. The solution of NH$_3$ was mixed (drop wise) using burette to bring pH of solution to 7. The resulting solution was heated between 80 and 100°C for 6–8 h under magnetic stirring. Dark brownish honey-like gel was obtained with the evaporation of excessive water. Highly porous and fluffy precursor material was obtained after heating the gel at 200–250°C for 1 h using hot air oven. The precursor material was ground into fine powder form with mortar pastel, and subsequently calcined at different calcination temperature (900–1100°C for 6 h at heating rate 100°C/h). For magnetic and Raman studies, the SrM powder was mixed with 2% PVA (binder material). Binder mixed SrM was then pressed into pellets by applying 10 ton pressure for 60 seconds. These pellets were further heated at 700°C for 3 h to remove PVA. Powder X-ray diffractometer (Miniflex-II from Rigaku (Japan) equipped with Cu-K$_\alpha$ anode) was employed to determine the structural characteristics, purity of phase, lattice parameters, and size of crystallite. The XRD data was collected at a scan speed 2°/min within a scanning range of 20–80°. EV-90 (from Microsense, USA) vibrating sample magnetometer was used for magnetic data recording. FESEM (Jeol, JSM-7100 (Japan)) was used to determine grain size and surface morphology. Raman (Renishaw (UK) using 514 nm source wavelength) spectra between 50 and 800 cm$^{-1}$, were collected to determine structural information and local strain in the crystal lattice.

3. Results and discussions

3.1. Structural studies

Figure 1a reveals that the X-ray diffractograms of SrZn$_x$Zr$_x$Fe$_{12-2x}$O$_{19}$ (x = 0.00) samples at different calcinations temperature. The figure clearly shows that magnetoplumbite phase starts appearing at temperature ≥800°C. However, secondary phase (α-Fe$_2$O$_3$) was noticed up to 950°C calculations temperature beyond that the samples would be phase pure and highly crystalline in nature. This shows that the minimum temperature of phase pure SrM formation is ≈1000°C. Figure 1b shows the X-ray diffractograms of SrZn$_x$Zr$_x$Fe$_{12-2x}$O$_{19}$ (x = 0.00–1.00) samples which were calcined at 1000°C. A comparison of the reported (ICSD 98–002-6353, structural data of SrFe$_{12}$O$_{19}$) and experimental peak positions shows that a) the absence of secondary phases such as α-Fe$_2$O$_3$ and SrFe$_2$O$_4$ and b) Zn$^{2+}$-Zr$^{4+}$ cations have successfully replaced the Fe$^{3+}$ ions in the SrM unit cell. Further, Figure 1c clearly reveals the
shifting of two highest intensity peaks (107 and 114) toward lower 2θ with increase in ‘x’. This shifting of peak position is indicative of lattice expansion which is due to higher atomic radii of Zn²⁺ (0.74 Å) and Zr⁴⁺ (0.80 Å) in comparison to Fe³⁺ (0.64 Å) [43].

The lattice parameters of (‘a’ & ‘c’) and cell volume of pure doped samples (having different compositions and calcined at different temperatures) are given in Table 1. It is clear from the table that the lattice parameter ‘a’ is varies between 5.8802 to 5.9148Å whereas ‘c’ varied in between 23.0574 to 23.2925Å with composition in samples calcined at 1000°C. The variation can be explained on the basis of higher atomic radii of Zn²⁺ and Zr⁴⁺ ions as compared to Fe³⁺ [25,26,29]. The c/a ratios for the M-type hexaferrites has been reported to be lower than 3.98 [43]. In all our samples (x = 0.00 to 1.00), this ratio varies between 3.92 and 3.94, thereby indicating that all the samples are M type hexagonal ferrites. Scherer’s formula was used for these samples to determine the crystallite size [20,44] and is also given in Table 1. The crystallites size a) monotonically decreases from 123.9 to 62.3 nm with composition (x = 0.00–1.00) samples calcined at 1000°C and b) monotonically increases from 106 to 136 nm as function of increase in calcination temperature from 900–1100°C for x = 0.00 sample. This increase in crystallite size with temperature is due to fusion of smaller crystallite to give rise to larger crystallite because of increase in thermal energy with temperature [21,45]. Though the comparison of experimental peak positions with reference data has shown the absence of impurity phases, however, the peak overlaps may limit the detection of small amount of impurity phases in this comparison method. The presence of small amounts of impurity phases could be easily known by inspecting the difference data in Rietveld analysis. This analysis (only of x = 0.00 and x = 1.00 calcined at 1000°C) was hence carried out to confirm the phase purity of stated samples. The initial parameters of the SrM phase were taken from ICSD 98–002-6353. The procedure for carrying out Rietveld refinement is same as reported elsewhere [29,46]. The Rietveld refined (along with experimental and difference data) is shown in Figure 2a, b. It is clear from
Table 1. Structural parameters of SrZn$_{x}$Zr$_{x}$Fe$_{12-2x}$O$_{19}$ (x = 0.00–1.00) samples.

| X    | Temperature (°C) | a (Å) (±0.0006) | c (Å) (±0.0038) | V (Å$^3$) (±0.30) | c/a | D(nm) (±0.5) |
|------|------------------|-----------------|-----------------|-------------------|-----|-------------|
| 0.00 | 900              | 5.8767          | 23.0555         | 688.9699          | 3.92| 106.6       |
|      | 950              | 5.8807          | 23.0538         | 690.4555          | 3.92| 113.4       |
| 0.20 | 1000             | 5.8802          | 23.0574         | 690.4566          | 3.92| 123.9       |
|      | 1050             | 5.8794          | 23.0575         | 690.2759          | 3.92| 132.0       |
|      | 1100             | 5.8783          | 23.0495         | 689.7580          | 3.93| 136.2       |
|      | 900              | 5.8862          | 23.0862         | 692.7172          | 3.93| 145.5       |
|      | 950              | 5.8862          | 23.0916         | 692.8791          | 3.92| 101.3       |
| 0.40 | 1000             | 5.8861          | 23.0934         | 692.9091          | 3.92| 110.7       |
|      | 1050             | 5.8846          | 23.0867         | 692.3586          | 3.92| 120.9       |
|      | 1100             | 5.8851          | 23.0941         | 692.3938          | 3.92| 126.0       |
|      | 900              | 5.8924          | 23.1363         | 695.6717          | 3.93| 103.3       |
|      | 950              | 5.8958          | 23.1562         | 697.0897          | 3.93| 89.4        |
| 0.60 | 1000             | 5.8856          | 23.1636         | 697.2761          | 3.94| 101.7       |
|      | 1050             | 5.8989          | 23.1842         | 698.6805          | 3.93| 109.3       |
|      | 1100             | 5.8953          | 23.1845         | 698.5314          | 3.93| 113.7       |
|      | 900              | 5.8969          | 23.1713         | 697.8105          | 3.93| 65.0        |
|      | 950              | 5.8995          | 23.1894         | 698.9696          | 3.93| 74.3        |
| 0.80 | 1000             | 5.9058          | 23.2269         | 701.5972          | 3.93| 87.0        |
|      | 1050             | 5.9059          | 23.2267         | 701.9098          | 3.93| 98.3        |
|      | 1100             | 5.9057          | 23.2416         | 702.0079          | 3.94| 106.7       |
|      | 900              | 5.9025          | 23.2023         | 700.0643          | 3.93| 57.0        |
|      | 950              | 5.9063          | 23.2358         | 701.9808          | 3.93| 62.4        |
| 1.00 | 1000             | 5.9116          | 23.2846         | 704.7126          | 3.94| 73.9        |
|      | 1050             | 5.9169          | 23.3180         | 706.9858          | 3.94| 87.5        |
|      | 1100             | 5.9155          | 23.3133         | 706.5154          | 3.94| 95.3        |
|      | 900              | 5.9089          | 23.2296         | 702.4029          | 3.93| 42.7        |
|      | 950              | 5.9078          | 23.2351         | 702.3198          | 3.93| 51.0        |
|      | 1000             | 5.9148          | 23.2925         | 705.7252          | 3.94| 62.3        |
|      | 1050             | 5.9153          | 23.3071         | 706.2819          | 3.94| 80.5        |
|      | 1100             | 5.9186          | 23.3382         | 708.2036          | 3.94| 89.8        |

the figure that the difference data in x = 0.00 is randomly distributed about zero reference line which explains a) the aptness of the fit and b) absence of impurity phases. The GoF value for this sample was obtained to be 1.1. However, the difference data in the x = 1.00 sample (Figure 3b) is not randomly distributed about zero reference line in the entire 2θ range. The discrepancies between the experimental and fitted data have been highlighted in Figure 2b. The GoF value for this sample (using single phase SrM fitting) was ≈1.69. The high GoF and mismatch between experimental and fitted data shows that in addition to majority SrM phase, some other minority phases are present. A detailed peak position matching revealed the possible presence of two more phases (ZnFe$_2$O$_4$ (ICSD 98–004-1482), SrZrO$_3$ (ICSD 98–004-7635)). Hence, a multiphase Rietveld refinement was also carried out for x = 1.00 sample. The data (refined using multiple phases) for x = 1.00 sample is shown in Figure 2c. The data clearly reveal that after incorporating additional minority phases, the difference data becomes almost randomly distributed about zero reference line. The GoF value also comes down to 1.16. This clearly establishes the presence of multiple phases in the x = 1.00 sample calcined at 1000°C. The fraction of SrM, ZnFe$_2$O$_4$ (Cubic) and SrZrO$_3$ (Cubic) phase from Rietveld refinement were obtained to be ≈94.82%, ≈2.25 and ≈2.93%, respectively. Thus, the data suggest the presence of ≈5.18% (in total) minority phases in x = 1.00 samples calcined at 1000°C. The important results obtained from Rietveld refinement on these two samples have been tabulated in Table 2.

3.2. Morphology and elemental analysis

SEM measurement provides us the lateral grain size which is the actual physical size of the grains\agglomerates in contrast to XRD data which provides the crystallite size (which is equal to the penetration depth of the X-rays from the top surface along the vertical direction up to which the grain scatters coherently). The FESEM micrographs of SrZn$_x$Zr$_x$Fe$_{12-2x}$O$_{19}$ (x = 0.00) samples calcined at 900°C, 1000°C and 1100°C are shown in Figure 3a-c while those of SrZn$_x$ Zr$_x$Fe$_{12-2x}$O$_{19}$ (x = 0.20–1.00) samples calcined at 900°C are shown in Figure 3d-h. The micrographs reveal that SrM material shows the presence of different shapes (polygonal shapes) of grains having non-uniform size. The grain sizes measured from FESEM data are given in Table 3. The table shows that the grain size increases with calcination temperature due to fusion of smaller grains into larger grains as already explained in many literature reports [21,45]. It is also observed from Table 3 that the grain size increases up to x = 0.20 and decreases with further substitution. This grain size increase at x = 0.20 may be due to an increase in magnetic interaction as well as the dipolar–dipolar interactions [27,31,47]. It is also reported in literature [32] studies that the grain size is increased due to increase in dipolar–dipolar interactions with the
incorporation of nonmagnetic dopants in two crystallographic spin down sites (4f1 and 4f2). These results are in good agreement with the magnetic studies data, which also show the highest value of $M_s$ at $x = 0.20$. The grain size monotonically decreases beyond $x = 0.20$. The reduction in size of grain might be due to the larger ionic size of both Zr$^{4+}$ and Zn$^{2+}$ which replace Fe$^{3+}$ ions. The huge difference in ionic size is likely to give rise to local strains that hinder growth of the grain as already reported [48]. In our case, both the Raman as well as XRD data confirmed straining in the SrM crystal structure. Further, reduction in size of grain may also be due to decrease in dipolar-dipolar interactions (beyond $x = 0.20$) with the incorporation of nonmagnetic dopants in crystallographic spin up locations (12 K, 2a, and 2b) [27]. Finally, the grain size as measured from FESEM data are larger than those calculated from XRD data. This could be due to the different principles of size measurements in these two techniques. Thus, because these techniques measure size along with different directions and in different ways results in different values of grain and crystallite size using different techniques.

The EDAX data for $x = 0.00$–1.00 samples (given in Table 3) clearly reveals that Sr, Fe, and O are present in all the samples. In addition, samples $x = 0.20$–1.00 also confirmed the existence of Zn and Zr. The weight percentage as well as atomic percentage of Zn$^{2+}$-Zr$^{4+}$ continuously increases while the Fe$^{3+}$ concentration continuously decreases with increasing dopant concentration as shown in Table 3.

### 3.3. Raman studies

Information on structural distortion, bond length, presence of secondary phases, local and dynamic symmetry of M type hexaferrites can be obtained from Raman spectroscopy. Figure 4a shows the Raman spectra of SrZn$_x$Zr$_{2-x}$Fe$_{12-2x}$O$_{19}$($x = 0.00$) sample calcined at different temperatures (850–1100°C). A comparison of these results with already literature reported [49] peak position reveals that the sample calcined at 850°C contains two additional peaks of $\alpha$-Fe$_2$O$_3$ secondary phase at 224 and 292 cm$^{-1}$ along with peaks corresponding to SrM phase at 83, 183, 314, 334, 411, 469, 523, 615 and 684 cm$^{-1}$. The presence of secondary phase is in agreement with XRD data which also shows small traces of $\alpha$-Fe$_2$O$_3$ secondary phase up to 950°C. The peaks of this secondary phase disappear when the calcination temperature raised to 900°C. This reveals the lower
sensitivity of Raman spectroscopy technique in detecting secondary phases as compared to powder X-ray diffraction technique. The intensity of the Raman peaks has been found to increase and width narrower with
3. Magnetic studies

Figure 5a shows magnetization (M) vs. applied magnetic field (H) plots of SrZn$_2$Zr$_4$Fe$_{12-2x}$O$_{19}$ (x = 0.00) samples calcined between 900–1100°C while Figure 5b shows M-H loops of SrZn$_2$Zr$_4$Fe$_{12-2x}$O$_{19}$ (x = 0.00 to 1.00) samples calcined at 1000°C. Figure 5a-b both clearly shows that all the samples have non-saturating hysteresis loops depicting strong magnetic order. The law of saturation (plot of M vs. H$^2$ and fitting a straight line to this data) was applied to M vs. H data in the 8 kOe to 12 kOe range to get M$_S$ [12,53,54]. The straight line fit and hence intercept for a typical (x = 0.20) sample is shown in Figure 5c. Table 4 lists the values of M$_S$ along with other magnetic parameters (derived from M-H loops) for both kinds of samples. It is clear from Table 4 that the value of M$_S$ increases from ≈64.11 emu/g to ≈69.5 emu/g (a change of 8.6%) and M$_S$ increases from ≈34.10 emu/g to ≈39.05 emu/g (a change of 14.5%) as x varies from 0.00 to 0.20 at 1000°C temperature. Both of these parameters decrease beyond x = 0.20. Similar trend was also noticed at calcination temperatures varying from 900°C – 1100°C. The M$_S$ value for SrM single crystal is reported to be ≈74.3 emu/g and the theoretical value for pure SrM is 76 emu/g. These values are higher than our results which may be due to difference in our experimental conditions such as pH, fuel ratio, calcination temperature, etc [55]. The combined effect of three factors a) down spin site preference by substituting non-magnetic ions (Zn$^{2+}$ and Zr$^{4+}$) at low dopant concentration [26], b) reduction of superexchange interaction and enhancements of canted spin with composition [25] and c) local straining due to the ionic size difference between Fe$^{3+}$ and substituting cations can be used to explain the variation of M$_S$.
Figure 4. Raman spectra of a) SrZn$_x$Zr$_{1-x}$Fe$_{12-2x}$O$_{19}$ (x = 0.00 sample) calcined between 850–1100°C and b) SrZn$_x$Zr$_{1-x}$Fe$_{12-2x}$O$_{19}$ (x = 0.00–1.00 samples) calcined at 1000°C and c) zoomed view about a single peak (684 cm$^{-1}$) of SrZn$_x$Zr$_{1-x}$Fe$_{12-2x}$O$_{19}$ (x = 0.00–1.00 samples) calcined at 1000°C.

With composition [43], it is well established that out of a total of 12 Fe$^{3+}$ ions in the SrM lattice, 8 (at 12k, 2a, and 2b sites) are in spin up configuration and 4 (at 4f1 and 4f2 sites) are in down spin configuration. This result in the cancellation of magnetic moments of 4 up spin and 4 down spins Fe$^{3+}$ ions. Now, at lower substitution level (upto x = 0.20) Zn$^{2+}$ ions preferably occupy 4f1 spin down site [56] whereas Zr$^{4+}$ occupies 2b site for x < 0.10 and 4f1 spin down site for x > 0.10 [57,58]. The preferable occupancy of downward spin sites by Zn$^{2+}$-Zr$^{4+}$ results in an enhancement in $M_r$ & $M_p$. Further, it is reported that the presence of large quantities of nonmagnetic Zn$^{2+}$ & Zr$^{4+}$ dopants (beyond x = 0.20) contributes to a) reduction of superexchange interactions between tetrahedral and octahedral sites (4f1-2a and 4f1-12k) and b) loss of magnetic collinearity resulting in canted spin structure [25,26]. This results in a decrease in the values of $M_r$ and $M_p$ beyond x = 0.20. A weakening of superexchange interaction has been reported in case of BaZn$_x$Zr$_{1-x}$Fe$_{12-2x}$O$_{19}$ by the measurement of magnetization vs. temperature data [29]. The decrease in $T_c$ from 711.9 K in x = 0.00 sample to 522.8 K in x = 0.80 sample confirmed the weakening of superexchange interactions. For comparison, Iqbal et al. [25] reported an enhancement in $M_r$ value up to x = 0.40 sample in Zn$^{2+}$-Zr$^{4+}$ doped SrM samples. The variation of $M_r$ and $M_p$ as a function of composition (at 1000°C) has also been graphically depicted in Figure 5d. The plots of $H_c$ vs. “x” and calcination temperature for SrZn$_x$Zr$_{1-x}$Fe$_{12-2x}$O$_{19}$ (x = 0.00–1.00) samples is shown in Figure 6. The figure clearly reveals that $H_c$ decreases with an increase in the value of “x”. The variation of $H_c$ can be explained by a) change in K (magnetocrystalline anisotropy constant), b) change in grain size, and c) presence of secondary phases. A reduction of K as a function of composition is likely to be the most prominent cause. The magnetocrystalline anisotropy constant (K) was calculated using the relationship $K = -\frac{H_{cl}H_{cm}}{M_s}$, where $\mu_0 = 1$ (in CGS units) is magnetic permeability of free space and other symbols have their usual
The simultaneous plot of $H_c$ and $K$ with “$x$” is shown in Figure 7. The plot clearly reveals that the both $H_c$ and $K$ follow the same trend with composition. This implies that the variation of $H_c$ with composition in our samples is directly linked to a decrease in the value of magnetocrystalline anisotropy constant. The decrease in the value of $K$ with doping can be explained as follows. It is well established that the 2b, 4f2 and 12 K sites are the main contributors to magnetocrystalline anisotropy in case of M type hexaferrites. Substitution of Fe3+ ions at 2b site with nonmagnetic Zn2+ and Zr4+ cations results in decreased magnetic interaction and hence decrease in the value of magnetocrystalline anisotropy. In view of one-to-one correspondence between $H_c$ and magnetocrystalline anisotropy constant as a function of composition, the impact of other factors on $H_c$ (as stated above) seems to be practically insignificant. However, the impact of these parameters could be significant for explaining the variation of $H_c$ with calcination temperature. The variation of $H_c$ with calcination temperature can hence be explained in terms of a competition between the effect of grain size and presence of secondary phase ($\alpha$-Fe2O3). As temperature increases from 900 to 1000°C, coercivity as well as grain size increases where as the concentration of $\alpha$-Fe2O3 decreases. The reduction in secondary phase ($\alpha$-Fe2O3) appears to have a more significant impact on the enhancement of coercivity upto 1000°C [59]. The value of coercivity
decreases between 1000 and 1100°C. However between 1000 and 1100°C calcination temperatures, the grain growth is a major factor that is responsible for reduction in coercivity. These results indicate that the increase in coercivity with increasing calcination temperature may be due to elimination of secondary phase up to 1000°C and beyond that decrease in coercivity is controlled by grain morphology (enhancement in grain size). The squareness ratio (SR) is $\geq 0.5$ is indicative of a ferrite material being single domain and therefore more anisotropic and magnetically hard. As can be seen in Table 4, the $x = 0.20$ sample has a maximum squareness ratio (0.56) as compared to other samples. For $x > 0.40$ samples, the squareness ratio is $< 0.5$, which means that the grains in these samples are randomly oriented and are multi domain in nature [43].

4. Conclusion

$Zn^{2+}$-$Zr^{4+}$ doped strontium hexaferrite ($SrZn_xZr_xFe_{12-2x}O_{19}$) samples were synthesized successfully by sol-gel auto combustion method. A comparison of the XRD,
Raman, and magnetic data (Hc as a function of calcination temperature), we conclude that the optimum calcination temperature of these samples to be 1000°C. The Rietveld refinement of the XRD data confirms a) the phase purity of x = 0.00 sample calcined at 1000°C and b) presence of two secondary phases (ZnFe2O4 ≈ 2.25 and SrZrO3 ≈ 2.93%) in x = 1.00 sample calcined at same temperature. The crystallite size decreases from 123.9 nm (in x = 0.00) to 62.3 nm (in x = 1.00) samples calcined at 1000°C. FESEM confirmed that grain size decreases from 156 nm (x = 0.20) to 80 nm (x = 1.00) in samples calcined at 900°C. EDX data confirm the stoichiometric of corresponding SrZn2Zrx Fe12-2xO19 (x = 0.00–1.00) samples. Raman data shows a) an enhancement in peak intensity and sharpness with increase in calcination temperature up to 1000°C and b) a widening of Raman bands with increasing dopant ion concentration (at 1000°C). The broadening of Raman bands with composition was explained in terms of strain induced by Zr4+Zr2+ dopants. The highest saturation magnetization was observed for x = 0.20 (at all temperatures) and was explained due to substitution of Fe3+ ions by non-magnetic Zn3+ & Zr4+ at 4f1 (spin down) crystallographic sites. The coercivity continuously decreases from 5358 (x = 0.00) Oe to 690 (x = 1.00) Oe at 1000°C. The reduction in the value of coercivity has been attributed to be due to a reduction in magnetocrystalline anisotropy.

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Disclosure statement

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

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