Effect of precursors on the structural, magnetic, dielectric, microwave and electromagnetic properties of Co–Zr doped nanocrystalline strontium hexaferrites synthesized via sol–gel method

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Abstract

In this study, we have presented a comparison of the structural, magnetic, dielectric, microwave and electromagnetic properties of four series of Co–Zr doped $\text{SrCo}_x\text{Zr}_x\text{Fe}_{(12-2x)}\text{O}_{19}$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0) synthesized by simple sol–gel method using ethylene glycol [series 1 (Chawla et al. in *J Magn Magn Mater* 378C:84–91, 2015)], citric acid [series 2 (Kaur et al. in *Ceram Int* 43(1):590–598, 2017)], tartaric acid [series 3 (Kaur et al. in *J Magn Magn Mater* 422:304–314, 2017)] and sucrose [series 4 (Kaur et al. in *Ceram Int* 42:14475–14489, 2016)] as precursors. Change of the precursor in sol–gel method has a great impact on the properties of final ferrite materials. The properties of these materials were studied by different characterization techniques viz. XRD, VSM, Mössbauer spectroscopy, impedance analyzer and VNA. The smallest particle size ranging from 21.83 to 33.68 nm was observed in series 4. A wide range of magnetic parameters were observed for the samples. The arrangement of dopant ions on different sites in the hexaferrite lattice is found to be dependant on the precursor used. The four series can be arranged in the order of increasing dielectric constant and losses as series 2 > series 1 > series 3 > series 4. Series 2 displays the maximum conductivity.

Keywords Strontium hexaferrites · Sol–gel · Citric acid · Tartaric acid · Sucrose · Magnetic properties · Dielectric properties · X-ray diffraction · Mössbauer

1 Introduction

M-type hexaferrites $\text{MFe}_{12}\text{O}_{19}$ ($\text{M} = \text{Ba}, \text{Sr}$ or Pb) account for over 90% of the total permanent magnetic materials manufactured globally. They have numerous applications in everyday life. For instance, they are used as permanent magnets in refrigerators and microwave ovens. Besides, they also find usage in telecommunication and magneto-optic recording, electromagnetic radiation suppression filters, microwave absorbers, transformers, inductors, duplexers, attenuators and circulators [1, 2].

These applications of hexaferrite materials depend on their magnetic parameters and electrical properties. Such properties are found to be sensitive to their compositional and preparatory techniques [3].

Sol–gel method is one of the most promising methods for preparing inorganic oxides. This method involves mixing of precursors in solution, which through hydrolysis and condensation reactions connect with each other so as to form a sol (solution of solid-dispersed phase in liquid-dispersion medium). Sol then undergoes gradual transformation into gel (solution of liquid-dispersed

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phase in solid-dispersion medium) by the addition of an organic coordinating agent or a fuel like ethylene glycol, citric acid, urea, oxalic acid and glycine, fructose, sucrose, tartaric acid, citric acid etc. [4, 5]. If only ethylene glycol is used as a complexing agent in the process, the method is called sol–gel method whereas when ethylene glycol is used along with some other fuel/precursor, the process is referred to as precursor sol–gel method. Fuel plays a major role in the formation of microstructure of polymeric intermediates by controlling the thermodynamic conditions of the combustion process, which helps to modify various properties.

During present investigations we have employed ethylene glycol alone/simple sol–gel (series 1 [6]) as well as along with closely related poly-hydroxyl carboxylic acids which serve the dual function of a complexing agent and a fuel. Three different low-cost acids-citric acid (series 2 [7]), tartaric acid (series 3 [8]) and sucrose–gluconic acid (series 4 [9])—with different carbon bulk—C₃, C₄ and C₁₂ respectively resulted in different combustion temperatures, different formation temperatures and hence in different properties of the final hexaferrites. Coupled substitution of divalent paramagnetic Co(II) and tetravalent diamagnetic Zr(IV) cations were applied because it allows the independent monitoring of saturation magnetization (M_s) and coercivity (H_c) for different applications.

2 Experimental

2.1 Sample preparation

All the starting chemicals were of an analytical grade and used without further purification following the reaction:

The ratio Fe:Sr was kept ten. Initially, desired amount of ferric nitrate was converted to ferric hydroxide by the addition of ammonia. The precipitates of ferric hydroxide were then dissolved in aqueous solution of fuel (acid: total metal = 1.1:1). This was followed by the addition of strontium carbonate and aqueous solutions of cobalt nitrate and zirconium nitrate in stoichiometric amounts. Hydrogen peroxide (H₂O₂) was then added to remove any excess of SrCO₃ followed by the addition of ethylene glycol (10% by volume of the solution). Ammonia (NH₃) was added to neutralize the solution and ammonium nitrate was added as an oxidant. The resultant solution was then stirred

continuously for 3 h and heated slowly on a water bath in order to get black-colored gel which was then heated at 150 °C to obtain a porous polymeric powder. This powder was properly ground in agate mortar and pestle. The final sintering of powders was done at different temperatures (800 or 900 °C) depending upon the fuel used, in a proportional–integral–derivative (PID) controlled box furnace. Figure 1 shows the stepwise experimental procedure.

2.2 Characterization

The phase composition and purity of the hexaferrites was carried out by using a X-ray diffractometer Panalytical X'pert pro with Cu-Kα radiation ($\lambda = 1.5406 \text{ \AA}$) in 20°–80° angle range with 0.2°/s scan speed. Micro-sense Vibrating Sample Magnetometer (Model 10) was used to study the magnetic properties of the samples. Mössbauer spectra were recorded with a conventional spectrometer operated in constant acceleration mode in transmission geometry with ⁵⁷Co source in Rh matrix. LCR meter (Modelno.8714ET) was used to study the dielectric parameters whereas Agilent N5225A PNA series network analyzer was used for the measurement of complex permeability, complex permittivity and reflection loss in Ku-band (12.4–18 GHz). A detailed account of characterization and physical measurements of powdered ferrites has been mentioned in earlier publications [8, 9].

3 Results and discussion

3.1 X-ray diffraction analysis

As indicated by powder X-ray diffraction pattern (PXRD) shown in Fig. 2, both α -Fe₂O₃ (JCPDS card 33-0664) and

γ -Fe₂O₃ (JCPDS card 86-0550) phases are obtained as intermediate in the as-produced ferrite powders obtained by using series 4 whereas in series 1–3 only γ -Fe₂O₃ phase is obtained. This may be the reason for the higher formation temperature of strontium hexaferrite (JCPDS card 01-084-1531) in series 4 (900 °C) in comparison to series 1–3 (800 °C) since it is suggested in literature that barium ion is able to form an interstitial solid solution with γ -Fe₂O₃ to form a hexagonal phase directly [10, 11]. As is clear from Fig. 2, in series 1–3, almost all the peaks indicative of hexaferrite phase appear at 600 °C, however their intensity increases up to 800 °C. Whereas in series 4, at 600 °C, along

Fig. 1 Flowchart showing the stepwise experimental procedure

with the peaks corresponding to hexaferrite phase, some α - Fe_2O_3 impurity is observed. In this case, pure strontium hexaferrite phase is observed only at 900 °C.

The size of the nanoparticles varies from 35.45 to 52.94 nm in series 1, 27.84–46.10 nm in series 2, 32.62–42.3 nm in series 3 and 21.83–33.68 nm in series 4, determined by taking the average particle size from the five most intense peaks (110), (107), (114), (203) and (220) observed from the PXRD data (Fig. 3). It is interesting to compare cell parameters of ferrites prepared by all these methods. The dimensional stability of magnetoplumbite structure of M-type hexaferrites is decided by the tolerance limit of ratio of lattice parameter c /lattice parameter a ($= 3.91$ for the ideal case to 3.97) as presented in Table 1 and Fig. 3. In strontium hexaferrite (SHF) samples prepared by series 1 the ideal magnetoplumbite structure is not realized even for a parent compound. On the other hand,

in case of series 2 and 4, the ideal structure is retained up to 0.2 level of substitutions whereas in case of series 3, up to 0.4 level of substitutions, the compound retained ideal structure. The maximum deviation is observed in series 2 whereas in case of series 4 the deviation from the ideal structure is minimum for all our compounds (up to $x = 1.0$). This commensurate well with the magnitude of cell expansion on substitutions. The cell expansion is 1.94%, 2.81%, 2.11% and 1.24% respectively for series 1–4 respectively.

3.2 Mössbauer spectroscopy study

In one formula unit of $\text{SrFe}_{12}\text{O}_{19}$, twelve Fe(III) are distributed over five different sub-lattice sites. Of these five sites, three sites are octahedral 12k and 2a (with upward spin of electrons) and $4f_2$ (with downward spin of electrons); one trigonal bipyramidal 2b (upward spin of electrons) and one

Fig. 2 PXRD of as-produced powders, at 600 °C and at formation temperature for $\text{SrCo}_x\text{Zr}_x\text{Fe}_{(12-2x)}\text{O}_{19}$ ($x=0.2$) prepared in **a** series 1, **b** series 2, **c** series 3, **d** series 4

tetrahedral $4f_1$ (downward spin of electrons) [12]. There are six Fe(III) in the $12k$ site, two Fe(III) each in $4f_1$ and $4f_2$ sites and one Fe(III) each in $2a$ and $2b$ sites. For uniformly distributed Fe(III) in these sites, statistically these sites should occupy 50:17:17:8:8 areas related to $12k$, $4f_1$, $4f_2$, $2a$ and $2b$ sub lattices, respectively [13, 14]. However, from Mössbauer spectroscopy for undoped and doped samples of the four series, it has been observed that the relative area occupied by Fe(III) decreases for some sub-lattice sites from their standard area values, thereby indicating the occupancy of dopant ions (Co(III) and Zr(IV)) in these sites. Furthermore, it has been observed that these dopant ions prefer different sites in different series. Room temperature Mössbauer spectra for compositions $x=0.0-1.0$ for Series 1 and 2 are shown in Fig. 4 [6, 7].

The analysis of Fe(III) habitation of different sites at different substitution levels has been made for series 1 [6] and series 2 [7]. It has been observed that for series 1 dopant ions occupy $12k$, $4f_1$ and $2b$ sites at $x=0.2$ and $12k$ site at 0.4 levels whereas for higher concentrations ($x=0.6-1.0$) substitution takes place at $12k$ and $4f_2$ sites [6]. However, in series 2, dopant ions are located on the $4f_1$ and $4f_2$ sites up to $x=0.4$, $12k$ and $2b$ site for $x=0.6$ and $12k$ site for $x=0.8-1.0$ [7]. This variation in relative area for the two series has been shown in Fig. 5.

3.3 Magnetic properties

Magnetic parameters viz M_s , H_C and remanent magnetization (M_r) have been found to be a function of the preparatory method. This is because the dopant ions rearrange in

Fig. 3 Comparison of **a** particle size, **b** ratio c/a for $\text{SrCo}_x\text{Zr}_x\text{Fe}_{(12-2x)}\text{O}_{19}$ ($x=0.0-1.0$) in the four series

Table 1 Cell volume, particle size and ratio c/a obtained for $\text{SrCo}_x\text{Zr}_x\text{Fe}_{(12-2x)}\text{O}_{19}$ ($x=0.0-1.0$) in the four series

	Samples compositions (x)	Cell volume ($\text{\AA}^3$)	Particle size (nm)	c/a
Series 1 (Sol-gel method)	0.0	690.26	52.94	3.92
	0.2	692.39	43.30	3.92
	0.4	695.64	52.78	3.93
	0.6	697.95	35.45	3.94
	0.8	702.81	39.17	3.94
	1.0	703.65	38.05	3.94
Series 2 (Citrate precursor sol-gel method)	0.0	691.20	37.63	3.91
	0.2	691.87	37.68	3.91
	0.4	695.21	28.19	3.92
	0.6	698.41	27.84	3.93
	0.8	705.56	32.66	3.95
	1.0	710.64	46.10	3.96
Series 3 (Tartarate precursor sol-gel method)	0.0	691.20	34.05	3.91
	0.2	691.31	27.47	3.91
	0.4	692.90	36.82	3.91
	0.6	693.23	21.90	3.90
	0.8	695.59	30.16	3.90
	1.0	705.81	31.94	3.95
Series 4 (Sucrose precursor sol-gel method)	0.0	691.38	27.85	3.91
	0.2	691.37	30.78	3.91
	0.4	692.16	33.68	3.92
	0.6	697.76	21.98	3.93
	0.8	699.13	30.92	3.93
	1.0	699.96	21.83	3.92

the hexagonal structure. As a result, magnetic properties are also altered. Comparing the magnetic parameters of all the four series, maximum obtainable M_s is 64.84, 65.70,

61.07 and 64.84 emu/g for series 1, 2, 3 and 4 respectively with their H_C 2131.6, 4886.4, 3493.9 and 3735.3 Oe and M_r 32.84, 31.45, 32.71 and 33.26 emu/g. However, these

Fig. 4 Mössbauer spectra recorded at room temperature of Co–Zr doped strontium hexaferrites ($x=0.0$ – 1.0) for series 1 and 2 [6, 7]

parameters for the parent compounds are M_s 57.26, 64.29, 60.82 and 62.67 emu/g with their H_C 6082.0, 5446.3, 5484.4 and 5785.7 Oe and M_r 33.07, 34.53, 33.12 and 34.38 emu/g. Since among the four series, series 2 and 3 display the maximum and the minimum values of M_s , respectively, their hysteresis loops are shown in Fig. 6 [7, 8]. In these four series minimum M_s and H_C are obtained at 1.0 level of substitution with M_s 56.76, 53.19, 54.42 and 49.71 emu/g, H_C 1104.8, 2273.4, 1717.3 and 1796.5 Oe and M_r 24.01, 24.78, 26.81 and 22.32 emu/g. The magnetic parameters obtained for the four series are shown in Fig. 7.

3.4 Dielectric and electric properties in 20 Hz–120 MHz frequency range

Analyzing the variation of dielectric properties with respect to precursor used in synthesis process, it has been observed precursor also affects these properties. The compositions prepared using series 2 has the highest value of dielectric constant and loss [15] compared to the other series 1 [16], series 3 [15] and series 4 [9]. This could be due to the reason that in citric acid method, the phase

formation is completed at comparatively lower temperatures. Thus, comparatively larger grains are formed in citric acid method as a result of sintering. Large grains give rise to higher interfacial polarization and hence higher dielectric values. The method of preparation can be arranged in order of increasing dielectric constant and losses: series 2 > series 1 > series 3 > series 4. Series 2 has also shown the highest value of conductivity among all four. Such similarity in variation is obtained because both electrical conductivity and dielectric behavior depend on the same mechanism. The electronic exchange in these ferrites, which is origin of conductivity results in the local displacement of charges in the direction of the applied field, which determines the polarization of ferrites.

3.5 Comparison of electromagnetic and absorption properties in 12.4–18 GHz frequency range (Ku-band)

Similar to MHz frequency range results, real part of permittivity is obtained to be highest in case of series 2 [7]. Spectra of imaginary part of permittivity show certain

Fig. 5 Variation in relative area (%) for **a** 12k, **b** 4f₁, **c** 4f₂, **d** 2a, **e** 2b sites for SrCo_xZr_xFe_(12-2x)O₁₉ (x=0.0–1.0) in series 1 and 2

peaks at particular frequencies, different for different compositions. The most intense dielectric peaks are obtained in case of series 2 followed by series 1 [16],

series 3 [17] and series 4 [18] respectively. Real part of permeability does not show significant variation with the synthesis method. With respect to doping amount,

Fig. 6 Hysteresis loops of $\text{SrCo}_x\text{Zr}_x\text{Fe}_{(12-2x)}\text{O}_{19}$ ($x=0.0-1.0$) for series 2 and 3 [7, 8]

Fig. 7 Comparison of **a** M_s , **b** M_r , **c** H_c as a function of Co–Zr doping in the four series

Fig. 8 Variation of Real part of permittivity (ϵ') and magnetic loss tangent ($\tan \delta_m$) with respect to frequency for $\text{SrCo}_x\text{Zr}_x\text{Fe}_{(12-2x)}\text{O}_{19}$ ($x=0.0$ – 1.0) series 2 and series 4 in Ku-band [7, 18]

the trend is justified on the basis of saturation magnetization. Imaginary part of permeability, signifying the magnetic loss shows increasing trend with the doping amount. Magnetic loss tangent peaks have higher values for series 2 than the other three series. Figure 8 shows the variation of real part of complex permittivity and magnetic loss tangent with respect to frequency for the prepared compositions in Ku-band for series 2 and 4 [7, 18]. With the variation of precursors in the synthesis method, the absorption properties are significantly changed. All the six compositions of series 1 and series 2 show great potential for microwave absorption

applications, whereas only three compositions of series 3 ($x=0.2$, 0.8 and 1.0) and three compositions of series 4 ($x=0.0$, 0.6 and 0.8) were reported to be useful for absorption applications in Ku band. Such difference in absorption behavior is due to difference in the dielectric and magnetic loss values. Comparing series 1 with series 2, it has been seen that reflection loss dip values and -10 dB absorption bandwidth is improved with the addition of citric acid in the synthesis process for series 2. Figure 9 shows the reflection loss curves of Co–Zr doped strontium hexaferrite ($x=0$ – 1.0) samples prepared in series 1 and 2 [7, 16].

Fig. 9 Variation of experimentally determined reflection loss curves (top panel) (down panel shows attenuation constant variation in first graph) with frequency for series 1 and 2 in Ku-band [7, 16]

4 Conclusion

The above comparison of structural, magnetic, dielectric, microwave and electromagnetic properties of four series of materials prepared by closely related methods prove their substantial different nature. Low sintering temperature of 800 °C is sufficient to form undoped and doped SHF in series 1, 2 and 3. Smallest particle size varying from 21.83 to 33.68 nm is observed in series 4 because of the severest combustion process in this case. The maximum deviation from ideal structure is observed in series 2 whereas in series 4 the deviation from the ideal structure is minimum for all our compounds (up to $x = 1.0$). Since the dopant ions rearrange in the hexagonal structure depending upon the precursor used, a range of magnetic parameters are obtained. The method of preparation can be arranged in order of increasing losses: series 2 > series 1 > series 3 > series 4. Dielectric analysis of the samples have revealed their usefulness in reduction of radar signatures and in dielectric resonators, filters, duplexers, antennas, attenuators, circulators and microwave devices. Magnetic loss tangent peaks have higher values for series 2 than the other three series. With the variation of precursor in the synthesis method, the absorption properties have significantly changed. Thus, our results show that the change of precursor in the sol-gel method has a great impact on the purity, homogeneity, formation temperature, structural, magnetic, dielectric and microwave absorption properties of the prepared hexaferrites which can be accordingly put to different uses in electronic industry.

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Compliance with ethical standards

Conflict of interest On behalf of all the authors, the corresponding author states that there is no conflict of interest.

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