

SYNTHESIS AND MAGNETIC PROPERTIES OF Co-Zr SUBSTITUTED STRONTIUM NANO-HEXAFERRITE

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Abstract

M-type hexagonal ferrite series, $\text{SrCo}_x\text{Zr}_x\text{Fe}_{(12-2x)}\text{O}_{19}$ ($x = 0.2, 0.6, 1.0$), has been synthesized by microwave induced sol-gel auto combustion method. The X-ray diffraction pattern at room temperature shows that the prepared samples have a single phase and the effect of composition on the unit cell parameters, density and porosity had been studied. TEM study confirmed hexagonal structure of synthesized ferrite and particle size varies from 17-55 nm. Magnetic properties have been investigated as a function of substitution of Co and Zr ions at applied field of 15KOe. The substitution causes reduction in anisotropic field. Curie temperature increases with substitution due to strongness of superexchange interaction. The change in magnetic parameters results in possible use of substituted ferrite for recording media.

Keywords: microwave oven, Sol-gel auto combustion method, Anisotropy, Curie temperature.

1. Introduction

M-type hexagonal ferrites (barium or strontium) are known for their strong uniaxial magneto-crystalline anisotropy with easy magnetization along c-axis [1,2]. They are being used for magnetic recording applications due to good intrinsic properties [3,4]. These intrinsic magnetic properties, i.e. saturation magnetization and coercivity can be altered by cationic substitution of Fe^{3+} ions. However, it has been reported that substitution causes intrinsic coercivity to decrease effectively but at the expense of decrease in saturation magnetization, restricting the use of hexagonal ferrites for recording applications [5]. Thus efforts are being made to decrease coercive force and simultaneously increasing magnetization with substitution. The application of hexagonal ferrites in the area of magnetic recording demands proper control of homogeneity and morphology. In the literature, sufficient reports are available on variation of magnetic parameters of BaM ferrite with different substituents for example Co-Zr, Ni-Zr, Co-Ru, Co-Sn [6-9], etc. The present work involves magnetic studies of divalent Co^{2+} ions and tetravalent Zr^{4+} ions substituted Strontium ferrite synthesized by microwave induced sol-gel auto combustion method.

2. Experimental

The samples of M-type substituted hexaferrites with formula $\text{SrFe}_{12-2x}\text{Zr}_x\text{Co}_x\text{O}_{19}$ are synthesized for $x=0.2, 0.6, 1$. The reactive oxidants such as $\text{Sr}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{ZrO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ were dissolved into an unionized distilled water at the temperature of 90°C for 20-25 min. Citric acid is used as fuel which gives requisite energy to initiate exothermic reaction. The gel produced is then kept for an hour in the room temperature and then it is heated in the digitally controlled microwave oven of 2.54 GHz for 10-15 min, The gel get burnt and finally gets converted in homogeneous powder. The sample is then sintered by giving sporadic moderate heat treatments for further few minutes with further grinding.

The structural characteristics of the samples are studied by X-ray diffraction, TEM spectroscopy. The magnetic properties were measured by vibrating sample magnetometer (Lake Shore VSM 7307) at applied external field of 15 KOe. The phase structure was characterized using X-ray diffraction (Philips Expert Diffractometer) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) and microstructure was studied with TEM instrument. The Curie temperature was measured by gouy's method.

3. Results and discussion

3.1. XRD

X-ray diffraction pattern of samples (Fig. 1) show that magnetoplumbite structure has been formed.

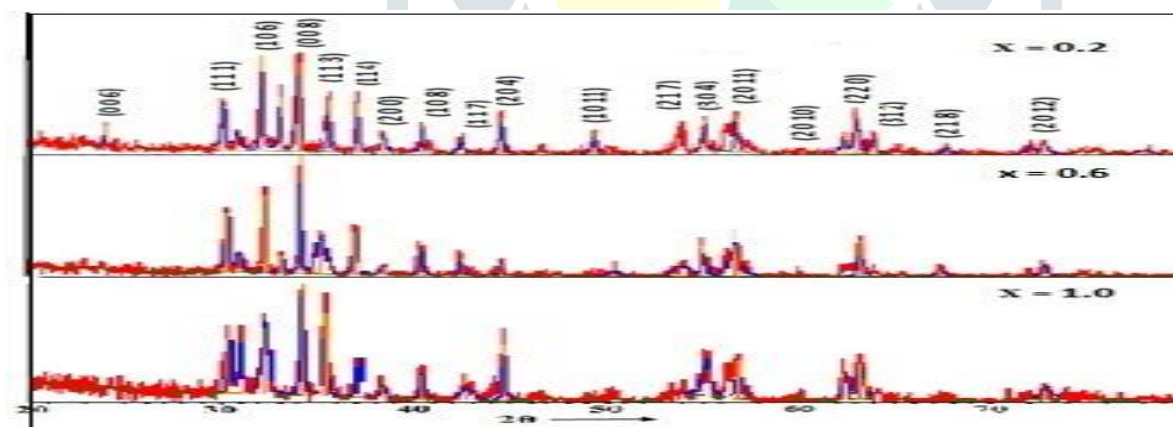


Fig1. X-ray diffraction of $\text{SrCo}_x\text{Zr}_x\text{Fe}_{(12-2x)}\text{O}_{19}$ ferrite (a) for $x=0.2$ (b) $x=0.6$ (c) $x=1$

The change in relative intensities may be related to occupation of crystallographic sites by substituted ions. From structural parameters characterized by lattice constants 'a' and 'c' (Table 1), it becomes clear that lattice constant 'a' shows less variation than lattice constant 'c' initially varies rapidly followed by slow variation with substitution. This is in agreement with the fact that all hexagonal ferrites exhibit constant lattice parameter 'a' and parameter 'c' [10]. It also indicates that change of easy magnetized c-axis is larger than a-axis with Co^{2+}

and Zr^{4+} ions substitution. This is attributed to large ionic radii of Zr^{4+} ion (0.72 \AA) and Co^{2+} ion (0.7 \AA) than Fe^{3+} ion (0.64 \AA) [7,11]

3.2. TEM

Fig 2 shows TEM micrograph of Co-Zr substituted Strontium ferrite. It is observed from TEM micrograph that the average particle size of Co-Zr substituted strontium ferrite is varying from 42 to 84 nm. TEM (Fig. 2) shows grains of different size attributing to large ionic radii of substituted Co^{2+} and Zr^{4+} ions in comparison to Fe^{3+} ions [7,11], thus grain size can be controlled with substitution.

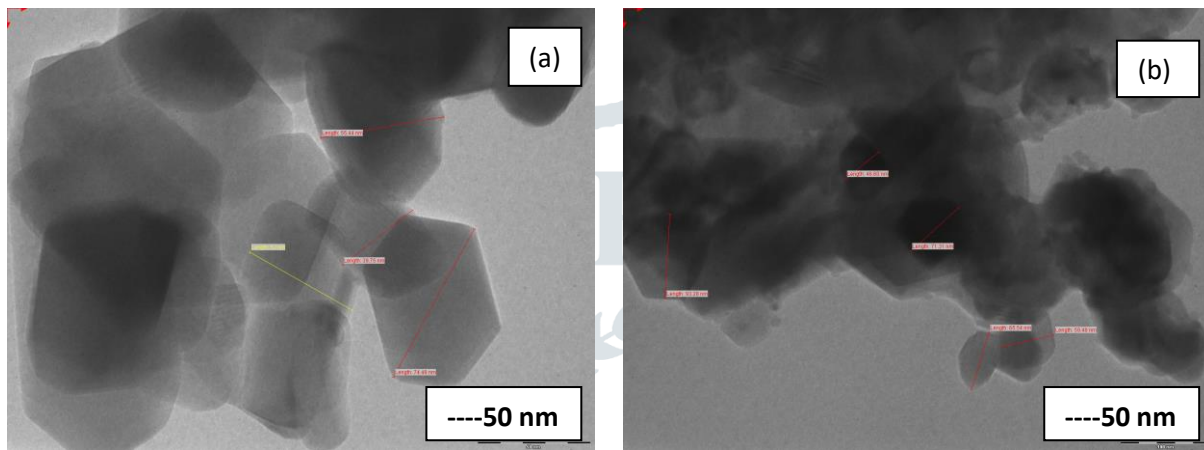


Fig2- TEM micrograph $SrCo_xZr_xFe_{(12-2x)}O_{19}$ (a) $x=0.2$ (b) $x=1$

Table 1 shows that cell volume variation (theoretical) corresponds to the change in bulk density (experimental). The reduction in calculated porosity matches with observed porosity diminution in microstructure (grain closeness).

3.3. Coercivity (H_c), saturation magnetization (M_s)

Electro negativity relates to attraction of valence electrons and more electronegative ions tend to occupy octahedral site. This site is larger than tetrahedral site [7]. Electro negativity for Zr and Co atoms is 1.33 and 1.88, respectively. According to Ligand theory, ions site occupancy also depends on d-configuration and nature of other participating cation [12]. In other words, Co^{2+} ions prefer to occupy octahedral site with d^7 configuration and Zr^{4+} ions have no site preference owing to d^0 configuration. Also Zr^{4+} ions ($4p^6$ configuration) are less compressible than Co^{2+} ions ($3d^7$ configuration), therefore presumably occupy octahedral site. It has been reported that Co^{2+} ions have preferential occupancy of $4f_I-4f_{II}$ sites [13]. Zr^{4+} ions

show preference to occupy both tetrahedral, octahedral sites for lower substitution and octahedral sites for higher substitution [7], and Li et al. reported the occupancy of Co–Zr ions on 12k and 2b sites [6].

Table 1 Lattice constants *a* and *c*, X-ray density, bulk density, porosity and Curie temperature of $\text{SrCo}_x\text{Zr}_x\text{Fe}_{(12-2x)}\text{O}_{19}$ ferrite.

Substitution <i>x</i>	<i>a</i> (Å)	<i>c</i> (Å)	Cell volume <i>V</i> (Å) ³	B.D. (gm/cm ³)	Porosity (%)	Ms (emu/gm)	H _c (Oe)	T _c (K)
0.2	5.8088	22.083	645.280	2.611	52.6	25.619	4500	663
0.6	5.8505	22.1272	655.888	2.885	47.5	33.65	2742	713
1	5.8625	22.216	661.249	2.923	47.1	48.75	1500	753

In M-type hexagonal ferrite, Fe³⁺ ions occupy seven octahedral sites 12k and 2a, one trigonal site 2b with spins in one direction, two octahedral sites 4f₂ and two tetrahedral sites 4f₁ with spins in opposite direction. The variation of magnetic properties with substitution 'x' is shown in Fig.3.

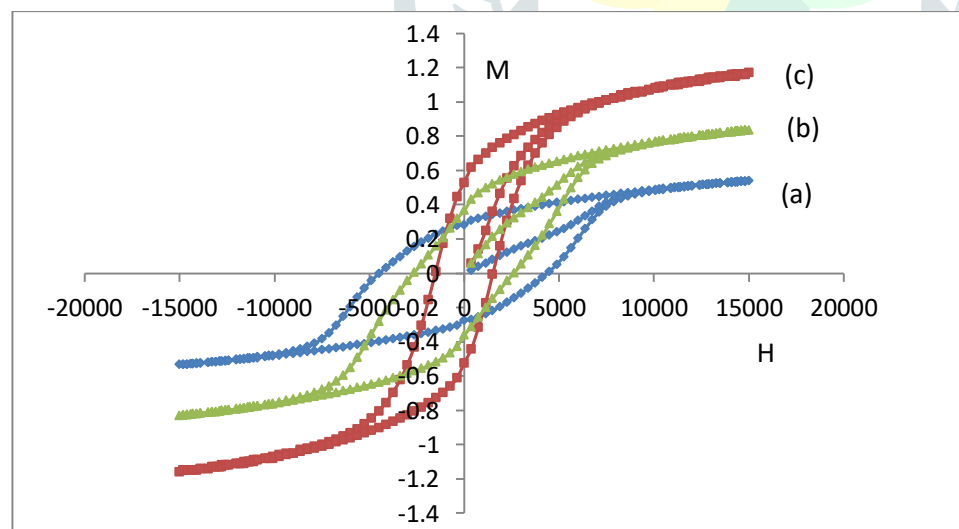


Fig.3. Hysteresis graphs of $\text{SrCo}_x\text{Zr}_x\text{Fe}_{(12-2x)}\text{O}_{19}$ ferrite (a) *x*=0.2 (b) *x*=0.6 (c) *x*=1 at room temperature.

Coercivity rapidly falls with substitution of Co²⁺ and Zr⁴⁺ ions at *x* =1. This fast reduction in anisotropy is primarily related to intrinsic effect associated with replacement of Fe³⁺ ions at 4f_{||} and 2b sites. These two sites contribute towards large anisotropic field [16]. Furthermore, microstructure shows more intergranular pores in sample *x*=0.2. These pores offer hindrance to the flow of applied field across the grains. The grain size

increment with substitution reduces intergranular pores. Therefore, ferrite can be demagnetized at low applied field, which decreases coercivity. This also confirms that porosity strongly affects coercivity [18]. However, M_s increases with the substitution attributing to the fact that the magnetic moments of both ions are not able to cancel out with spin-down moments of Fe^{3+} ions ($5\mu_B$) owing to weak magnetic moment of Co^{2+} ions ($3\mu_B$) and diamagnetic Zr^{4+} ions ($0\mu_B$). More specifically strong superexchange interaction ($FeA^{3+}-O-FeB^{3+}$) will not collapse with substitution of Zr^{4+} and Co^{2+} ions. This is confirmed from measured values of curie temperature varies from 663 k to 743 k with substitution.

4. Conclusions

The Co-Zr substituted Strontium ferrite has been synthesized using microwave induced sol-gel auto combustion method. The substitution of Zr^{4+} and Co^{2+} ions causes grain coarsening and more expansion of crystal lattice towards c -axis than a -axis. Coercivity decreases with substitution level, while enhancing saturation magnetization at the same time making it useful for recording media.

References

- [1] Y. Li, R. Liu, Z. Zhang, C. Xiong, Mater. Chem. Phys. 64 (2000) 256–259.
- [2] J.-H. Choy, Y.-S. Han, S.-W. Song, Mater. Lett. 19 (1994) 257–262.
- [3] D.E. Speliotis, IEEE Trans. Magn. 25 (1989) 4048–4050. [4] R.G. Simmons, IEEE Trans. Magn. 25 (1989) 4051–4053.
- [5] Q. Fang, H. Cheng, K. Huang, J. Wang, R. Li, Y. Jiao, J. Magn. Magn. Mater. 294 (2005) 281–286
- [6] Z.W. Li, L. Chen, C.K. Ong, J. Appl. Phys. 92 (2002) 3902–3907. [7] M.V. Rane, D. Bahadur, S.D. Kulkarni, S.K. Date, J. Magn. Magn. Mater. 195 (1999) L256–L260.
- [8] H.-S. Cho, S.-S. Kim, IEEE Trans. Magn. 35 (1999) 3151–3153.
- [9] D. Lisjak, M. Drofenik, J. Eur. Cer. Soc. 24 (2004) 1841–1845.
- [10] H. Kojima, in: E.P. Wohlfarth (Ed.), Ferromagnetic Materials, vol. 3, North-Holland, Amsterdam, 1982, 305 pp.
- [11] T.M. Meaz, C.B. Koch, Hyp. Interact. 156/157 (2004) 341–346.
- [12] M.V. Rane, D. Bahadur, A.K. Nigam, C.M. Shrivastva, D. Kulkarni, S.K. Date, J. Magn. Magn. Mater. 192 (1999) 288–296.
- [13] Z. Šimša, S. Lego, R. Gerber, E. Pollert, J. Magn. Magn. Mater. 140–144 (1995) 2103–2104.
- [14] U. Topal, H. Ozkan, H. Sozeri, J. Magn. Magn. Mater. 284 (2004) 416–422.

- [15] R. Grossinger, J. Magn. Magn. Mater. 28 (1982) 137–142.
- [16] G. Mendoza-Suárez, L.P. Rivas-Vázquez, J.C. Corral-Huacuz, A.F. Fuentes, J.I. Escalante-García, Physica B 339 (2003) 110–118.
- [17] J. Dho, E.K. Lee, J.Y. Park, N.H. Hur, J. Magn. Magn. Mater. 285 (2005) 164–168.
- [18] H.P.J. Wijn, E.W. Gorter, C.J. Esveldt, P. Geldermans, Philips Tech. Rev. 16 (1954) 49–58.
- [19] H.C. Fang, Z. Yang, C.K. Ong, Y. Li, C.S. Wang, J. Magn. Magn. Mater. 242–245 (2002) 430–433.
- [20] A. Ghasemi, A. Hossienpour, A. Morisako, A. Saatchi, M. Salehi, J. Magn. Magn. Mater. 302 (2006) 429–435.
- [21] Z. Yang, C.S. Wang, X.H. Li, H.X. Zeng, Mater. Sci. Eng. B 90 (2002) 142–145.
- [22] A. González-Angeles, G. Mendoza-Suárez, A. Grusková, J. Sláma, J. Lipka, M. Papánová, Mater. Lett. 59 (2005) 1815–1819.
- [23] X.Z. Zhou, A.H. Morrish, Z.W. Li, Y.K. Hong, IEEE Trans. Magn. 27 (1991) 4654–4656.

