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Effect of site preferences on structural and magnetic switching properties of CO–Zr doped strontium hexaferrite $SrCo_xZr_xFe_{(12-2x)}O_{19}$

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ABSTRACT

The aim of this work is to investigate the correlation between the distribution of cations over five crystallographic sublattices and magnetic properties of Sr-hexaferrites in the coupled substitution of magnetic Co^{2+} and non-magnetic Zr^{4+} for Fe^{3+}. During present work, we have synthesized a series of $SrCo_xZr_xFe_{(12-2x)}O_{19}$ ferrites ($x=0.0$, 0.2, 0.4, 0.6, 0.8 and 1.0) using sol–gel route at a much lower temperature of 800 °C. These compounds were characterized by TGA, FT-IR, XRD, EDS and TEM. XRD data reveal the formation of polycrystalline magnetoplubite structure for all the compounds of the series. The crystallite size of nanoparticles lies in the range of 30–55 nm. Mössbauer spectroscopy was employed to probe magnetic properties at microscopic level. Mössbauer analysis indicates that dopant ions largely prefer $12k$, $4f_1$ and $2b$ sites at $x=0.2$ and 0.4 levels whereas at higher concentrations substitution takes place at $12k$ and $4f_2$ sites. Magnetic measurements reveal that the values of coercivity (H_C) reduced from 6082 ($x=0$) to 1104 Oe ($x=1.0$) but the net magnetization of the samples is not correlated with dopant level. The saturation magnetization (M_S) values are in the range of 64.8–56.8 emu/g. Our results suggest that magnetization and magneto-crystalline anisotropy are closely related to the distribution of Co–Zr on the five sublattices of the crystal.

1. Introduction

Hexagonal ferrite is a class of magnetic material with great scientific and technological interest. Nowadays ferrites have found applications in every facet of modern life. They have been widely used for permanent magnets, magnetic recording media, and as microwave absorbers because of their high stability, excellent high-frequency response, large magneto-crystalline anisotropy and large magnetization [1,2]. Ferrites have played a key role in the advancement of microwave materials technology over the past five decades [3,4]. Recently there has been a renewed interest in the study of nano-ferrites because of their potential applications in nanoscience and technology [5]. Both structural and magnetic properties of ferrites can be modified by addition of small amount of dopants. Mixed metal nano-ferrites have superior properties than pure ferrite materials [6,7]. Nanoparticles with coercive field strength above 5000 Oe in the case of sol–gel derived Ba, Sr ferrites are convenient magnets, but the magnato-crystalline anisotropy is very large for recording media applications. Partial substitution of Fe^{3+} ions of the hexaferrite phase by metals like Co^{2+}, Mn^{2+}, Ni^{2+} and Ti^{4+} etc were attempted to modify various magnetic properties [8–10]. The substitution by non-magnetic ions is known to substantially reduce the ferrimagnetic resonance of Sr-hexaferrite [11,12]. The current challenge is to synthesize ferrites with well controlled shape and size, fine morphology, uniform composition and desired magnetic properties at lower sintering temperatures for their use in electronic material industry.

During present investigations, we have chosen the coupled substitution of magnetic Co^{2+} and non-magnetic Zr^{4+} cations for Fe^{3+} to vary the structural and macroscopic magnetic properties of $SrFe_{12}O_{19}$. We accomplished the synthesis of $SrCo_xZr_xFe_{(12-2x)}O_{19}$ ($x=0.0$, 0.2, 0.4, 0.6, 0.8 and 1.0) by the sol–gel method. Sol–gel auto-combustion method has aroused special interest because of the utilization of the heat released from the oxidation of the hydrocarbon species used in reaction to lower the formation temperature.

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2. Experimental

All the starting reagents were of an analytical grade and were used as received as per the following stoichiometric equation:

$$\mathrm{Sr(NO_3)_2} + x[\mathrm{Co(NO_3)_2{\cdot}6H_2O}] + x[\mathrm{ZrO(NO_3)_2{\cdot}6H_2O}] + (12-2x)[\mathrm{Fe(NO_3)_3{\cdot}9H_2O}] \overset{\text{ethylene glycol}}{\Longrightarrow} \mathrm{SrCo}_x\mathrm{Zr}_x\mathrm{Fe}_{(12-2x)}\mathrm{O}_{19}.$$

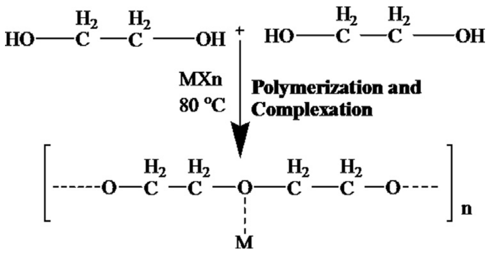
(x=0.0, 0.2, 0.4, 0.6, 0.8 and 1.0)

Desired metal nitrates in appropriate ratio were taken in minimum amount of distilled water followed by the addition of ethylene glycol (50% by volume of solution) and stirred until a homogeneous mixture was observed. The solution was heated on the water bath at 80–90 °C for the formation of gel. The gel so obtained was further heated at 150 °C for 2 h. Self combustion occurred and dry fluffy mass was obtained. The material was finely ground. The final sintering was done at 800 °C for 6 h in a PID controlled box furnace where the heating and cooling rates were maintained at 20 °C/min (Scheme 1).

Ethylene glycol is a weak complexing agent, generates a polymeric network and also acts as a fuel. The probable mechanism is given below:

3. Physical measurements

X-ray diffraction (XRD) patterns were obtained by using a diffractometer Panaltical X'pert pro with CuK_α-radiation (λ=1.5406 Å). Rietveld analysis has been done with models based on Kimura et al. of Sr-hexaferrite [13]. Thermo-gravimetric (TG) data were collected by using the apparatus TG-DTA (Model Q 600). FT-IR spectra of the samples were recorded on Varian Resolution Pro in the range 4000–400 cm^{-1} as KBr pellets. Low-pressure nitrogen-gas-sorption isotherm measurements were performed at 77 K on Micromeritics ASAP 2020 analyzer. SEM JSM-6100 (JOEL) with EDS attachment was used to investigate the composition of the Sr-hexaferrite samples. Hitachi (H-7500) 120 kV TEM equipped with a CCD camera was employed for recording surface morphology. The instrument had the resolution of 0.36 nm, and could magnify the sample up to 10^6 times. The Mössbauer spectra (MS) at room temperature were recorded with a conventional spectrometer operated in constant acceleration mode with Co^{57} source in Rh matrix of 50 mCi. MS were fitted using Win-Normos Fit program [14]. Hysteresis measurements of all the samples at room temperature in the field range of ±15 kOe were carried out by a vibrating sample magnetometer (Microsense Easy VSM software version 20130719-01).



Scheme 1. Proposed reactions involved in the synthesis of Sr-hexaferrite in the presence of ethylene glycol.

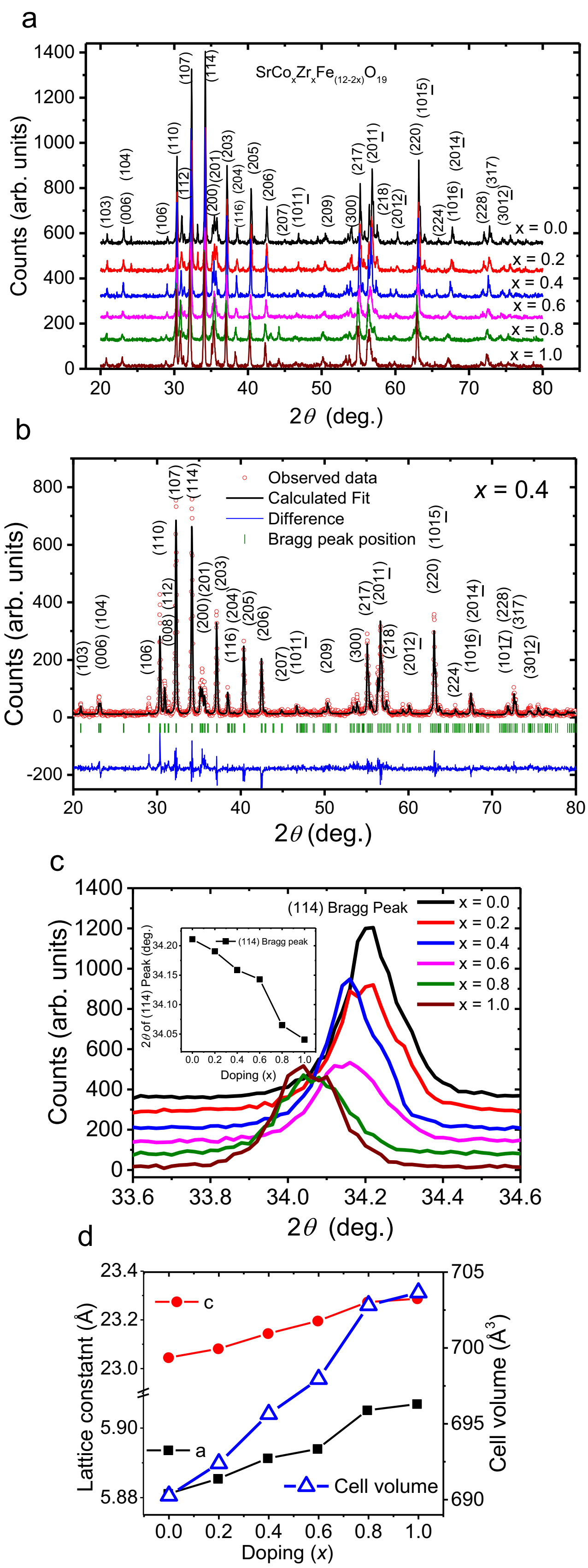


Fig. 1. (a) XRD patterns of M-type Sr-hexaferrite series (x=0.0, 0.2, 0.4, 0.6, 0.8, and 1.0). (b) The Rietveld refined XRD spectra of doped M-type Sr-hexaferrite (x=0.4) annealing at 800°C. (c) Enlarged view of the (114) Bragg peak. The inset of (c) shows the variation in 2θ of (114) Bragg peak position with substitution of Co–Zr in Sr-hexaferrites. (d) Variation of lattice parameters and cell volume with substitution of Co–Zr in Sr-hexaferrites.