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Structural, magnetic and microwave absorption properties of $SrFe_{12-2x}(Mn_{0.5}Cd_{0.5}Zr)_xO_{19}$ ferrite

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ABSTRACT

In this research, the M-type strontium hexaferrite nanoparticles, $SrFe_{12-2x}(Mn_{0.5}Cd_{0.5}Zr)_xO_{19}$, ($x = 0.0-1.6$), have been synthesized by the coprecipitation method. X-ray diffraction, a field emission scanning electron microscope, a vector network analyzer and a vibrating sample magnetometer were used to characterize their structures, electromagnetic and microwave absorption properties of samples. The results indicated the formation of hexaferrite structure for all samples. The sample with $x = 1.4$ showed a minimum reflection loss of −52 dB at 14.5 GHz with reflection loss less than −20 dB over the extended frequency range of 13.6–16.5 GHz. Finally $SrFe_{9.2}(Mn_{0.5}Cd_{0.5}Zr)_{1.4}O_{19}$ could be considered as a good candidate for thin microwave absorbers in the gigahertz range.

1. Introduction

Strontium hexaferrite exhibits relatively high values of electrical resistivity, magnetic anisotropy, and Curie temperature, and excellent chemical stability and corrosion resistivity [1,2]. With regard to the above mentioned properties, micron to submicron hexaferrite particles are good candidates for scientific and technological applications in the field of recording industry, telecommunication, magneto-optical devices and microwave systems [3–5]. The properties of strontium ferrite are largely dependent on the processing routes used for fabrication. The conventional way to synthesize strontium hexaferrite is firing of a mixture of $SrCO_3$ and Fe_2O_3 at high temperature (> 1200 °C). This method has disadvantages such as uncontrolled particle morphology, chemical inhomogeneity, and large particle and agglomerate sizes. The milling of the calcined strontium ferrite powders leads to entrance of impurities and lattice strain and, therefore, degrading of the magnetic properties [6]. As a consequence, a large number of low-temperature methods such as sol–gel [7], aerosol pyrolysis [8], glass crystallization [9], microemulsion [10], co-precipitation [11,12] and hydrothermal [13] techniques have been developed to control the particle size, shape and the properties of the materials. The chemical coprecipitation method is a low cost technique suitable for mass production as compared to other above mentioned methods. Strontium hexaferrite is a ferrimagnetic material, with a hexagonal structure belonging to the space group of P63/mmc and uniaxial magnetocrystalline anisotropy with easy axis parallel to the *c* axis of the hexagonal unit cell. Its crystal structure is built of alternate basic blocks S and R [14]. The S block contains two oxygen layers forming a spinel structure and R block is a three-oxygen layer block, with a hexagonal structure, containing the strontium ion. The 24 Fe^{3+} atoms are distributed over five sublattice sites: three octahedral sites (12k, 2a, and $4f_2$), one tetrahedral site ($4f_1$), and one bipyramidal site (2b). The Fe^{3+} ions with up-spin are distributed on the 2a, 12k and 2b sites, and ions with down-spin are located on the $4f_1$ and $4f_2$ sites. The substitution of cations at Fe or Sr sites is an effective method to vary the physical, magnetic and electrical properties of strontium hexaferrite. During the last two decades, various substituted strontium ferrites, in which Fe^{3+} cation was replaced by several tetravalent (Ti^{4+}, Sn^{4+}, Zr^{4+}, Ir^{4+}, and Ru^{4+}) and divalent (Co^{2+}, Mn^{2+}, Zn^{2+}, and Ni^{2+}) cations, have been extensively studied for modifying the dielectric and magnetic properties for the magnetic recording and high frequency applications [15–18]. It is noteworthy that the domain-wall-displacement, initial permeability, the coercive force, the effective linewidth, and the spinwave linewidth were identified to be grain-size dependent [19]. When particle size decreases to the nanometer scale, some new absorption mechanisms appear and the nanosized ferrite particles absorb more microwave energy. In this research, the nanoparticles of M-type strontium hexaferrite, $SrFe_{12-2x}(Mn_{0.5}Cd_{0.5}Zr)_xO_{19}$, have been synthesized by the coprecipitation method. To the best of our knowledge, this is the first report about nanocrystalline $SrFe_{12-2x}(Mn_{0.5}Cd_{0.5}Zr)_xO_{19}$. We discuss the structural, magnetic and microwave properties of these new components.

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2. Experimental procedure

2.1. Preparation of powders

$SrFe_{12-2x}(Mn_{0.5}Cd_{0.5}Zr)_xO_{19}$ hexaferrites with $x=0-1.6$ were synthesized by the chemical coprecipitation method. Desired amounts of $SrCl_2\cdot 4H_2O$ (Merck, $>99\%$), $FeCl_3\cdot 6\,H_2O$ (Merck, $>99\%$), $ZrOCl_2\cdot 8\,H_2O$ (Merck, 99%), $MnCl_2\cdot 4H_2O$ (Merck, $>99\%$) and $CdCl_2\cdot 4H_2O$ (Merck, $>99\%$) were mixed to yield a clear aqueous solution. The molar ratio of strontium was kept higher, i.e. 1.2, to maintain the stoichiometry of the product in these samples because the solubility of $SrCl_2$ is higher as compared to $FeCl_3$. The total weight of starting materials was 20 g. An aqueous solution of NaOH and Na_2CO_3 (5:1) was added to this mixed solution drop by drop using vigorous stirring at 70 °C. The pH value reached around 13 after completion of titration. The resultant homogeneous product of coprecipitation was stirred for about 3 h. And then, the precipitate was filtered off and washed a few times with deionized water at 100 °C, followed by washing with ethyl alcohol until no NaCl could be detected and the pH value was less than 8. The washed powders were dried at 80 °C and then calcined at 950 °C for 3 h. The heating rate of samples from room temperature to 600 °C with 6 °C min^{-1} and 3 °C min^{-1} to the final sintering temperature. The color of the powder was dark brown.

2.2. Preparation of composites

The composite samples were prepared by mixing strontium hexaferrite powders with acrylic resin powders with concentration of 70:30 by weight. The pressure of 5.5 MPa at 220 °C was used to shape the mixtures in the form of thin discs with diameter of 40 mm. Curing time was 20 min.

2.3. Physical measurements

The samples were characterized by X-ray Diffractometry (XRD) and Field Emission Scanning Electron Microscopy (FESEM). The magnetic properties were measured using a vibrating sample magnetometer (VSM). Microwave absorption properties were evaluated in Ku-band by using a vector network analyzer (VNA) system.

3. Results and discussion

3.1. Structural properties

XRD patterns of $SrFe_{12-2x}(Mn_{0.5}Cd_{0.5}Zr)_xO_{19}$ samples are shown in Fig. 1. The observed peaks match the standard pattern for strontium hexaferrite with no extra peaks as shown in Fig. 1 but with different intensities. We can see from XRD patterns, with increasing doping, that the relative intensities decrease and peaks begin to broaden, indicating a decrease in particle size, which agrees well with FESEM images. Crystallite size (*D*) was calculated by using the Scherrer formula [20]

$$D=\frac{k\lambda}{\beta\ \cos\ \theta}$$

where β is the broadening of diffraction lines at half of its maximum intensity, λ is the wavelength (1.540 Å), θ is the Bragg angle and k is the shape factor that is equal to 0.89 for the hexaferrites. Table 1 shows the lattice constants (*a* and *c*), cell volume (*V*) and crystallite sizes of samples, which were calculated from the XRD data [20]. The crystallite sizes are in the range of 49–67 nm. The values of lattice constants (*a* and *c*) and cell volume (*V*) increase by increasing the Zr–Mn–Cd content of the samples, which is due to large ionic radii of the doped ions Zr^{4+} (0.80 Å), Mn^{2+} (0.67 Å) and Cd^{2+} (0.97 Å) as compared to Fe^{3+} (0.64 Å).

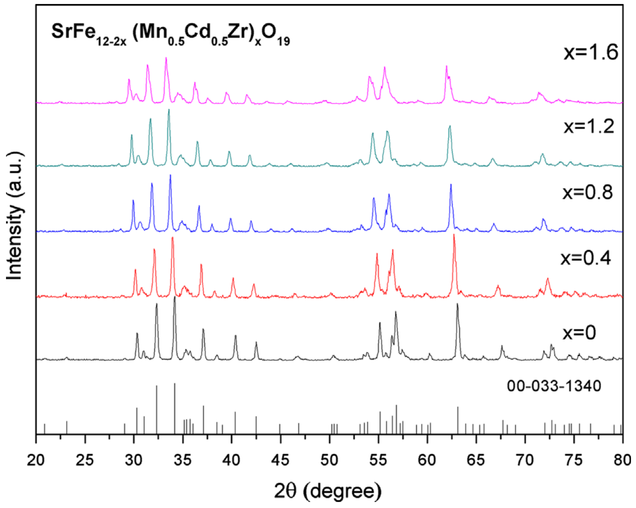

Fig. 1. XRD pattern for $SrFe_{12-2x}(Mn_{0.5}Cd_{0.5}Zr)_xO_{19}$ ferrite samples: (a) standard pattern (ICSD-00-033-1340), (b) $x=0$, (c) $x=0.4$, (d) $x=0.8$, (e) $x=1.2$, and (f) $x=1.6$.

Table 1
Lattice constants (*a* and *c*), cell volume (*V*) and crystallite size (*D*) for $SrFe_{12-2x}(Mn_{0.5}Cd_{0.5}Zr)_xO_{19}$ ferrite samples.

x	*a* (Å)	*c* (Å)	*V* (Å^3)	Crystallite size (nm)
0	5.86	22.96	683.25	56
0.2	5.87	23.03	687.68	67
0.4	5.89	23.11	694.78	63
0.6	5.91	23.20	702.23	54
0.8	5.92	23.26	706.43	51
1.2	5.95	23.41	718.21	49
1.6	5.98	23.58	730.74	55

Morphology and the shape of the samples are shown in Fig. 2. All samples have crystalline hexaferrite shape. Small deviation of crystalinity was observed at $x=1.6$. It is clear from Fig. 2 that particles become thinner and smaller as *x* increases.

3.2. Magnetic properties

Fig. 3 shows the hysteresis loops for $SrFe_{12-2x}(Mn_{0.5}Cd_{0.5}Zr)_xO_{19}$ samples. As mentioned above doping of strontium hexaferrite at small *x* does not significantly change the particle morphology but, as we can see from Fig. 3, has a significant effect on magnetic properties. Magnetic properties such as magnetic saturation (M_s), coercivity (H_c), and remanence (M_r) are obtained from hysteresis loops. Variation of M_s, M_r and H_c with doping concentration is shown in Fig. 4. It is clear that the value of saturation magnetization increases up to $x=0.2$ and then decreases slowly with increase in the amount of doping while the values of remanence and coercivity continuously reduce by increasing concentration of the dopant ions. It is known that out of 12 ferric ions, eight Fe^{3+} ions in 12k, 2a, 2b have spins in upward direction while four Fe^{3+} ions in $4f_1$ and $4f_2$ sites have spins in downward direction. Each Fe^{3+} has 5 μ_B magnetic moment. So strontium hexaferrite has a total moment of $((8-4)\times 5)=20\ \mu_B$ per formula unit. Cd ions replace iron ions at $4f_1$ sites while Zr ions for $x>0.1$ prefer $4f_1$ sites and for $x\leq 0.1$ occupy 2b sites [21]. The Zr^{4+} and Cd^{2+} are nonmagnetic ions while Mn^{2+} has the magnetic moment of 5 μ_B similar to the magnetic moment of Fe^{3+}. When these nonmagnetic ions, Zr^{4+} and Cd^{2+}, replace the Fe^{3+} from the site $4f_1$ with spins in downward direction the total magnetic moment increases, which causes