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Effect of Co substitution on absorption properties of $SrCo_xFe_{12-x}O_{19}$ hexagonal ferrites based nanocomposites in X-band

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ABSTRACT

Cobalt doped M-type strontium hexaferrite nanoparticles ($SrCo_xFe_{12-x}O_{19}$, x = 0.2–1.2) is synthesized and used as inclusions in Linear Low Density Polyethylene (LLDPE) matrix for developing nano-composites with 60 wt% of these nanoparticles. Absorption performance of the developed nano-composites is evaluated in the X-band. The thickness optimization is carried out for obtaining maximum reflection loss by using the transmission line model (TLM), with measured values of permittivity and permeability of the composite. The best reflection loss is observed experimentally for x = 0.8 with an absorber thickness of 3 mm for which a wide −10 dB bandwidth covering almost the entire X-band is obtained. The composites are light weight and not affected by exposure to water.

1. Introduction

Microwave absorbing materials are specialized kind of materials which are used to sufficiently reduce the electromagnetic interferences generated due to the increasing use of electronic equipments and systems. The electrical or magnetic properties of these materials can be tailored to achieve absorption (reflection loss) over broadband frequencies. Dielectric microwave absorbing materials manipulates complex permittivity and loss tangent to achieve good absorption performance, however, thickness of the absorber increases by many orders to get good attenuation [1–3].

Magnetic materials offer an effective way of alternating electromagnetic waves by way of better impedance matching at the interface of the absorber and also reducing its thickness. Absorbers are generally composites of different materials including ferrites and polymers. M-type ferrites and its doped versions have high saturation magnetization and crystalline anisotropy, which, when used as fillers in polymer composites form absorbers with low reflection loss [4–10].

The performance of the absorber is estimated by the equations derived from transmission line model (TLM) [11]. For a single layer absorber, the extent of absorption is generally assessed by reflection loss (*RL*) determined from the expression

$$RL(\mathrm{dB}) = 20\log\left|\frac{\sqrt{\mu_r/\varepsilon_r}\tanh[(j2\pi f/c)\sqrt{\mu_r/\varepsilon_r}\,t]-1}{\sqrt{\mu_r/\varepsilon_r}\tanh[(j2\pi f/c)\sqrt{\mu_r/\varepsilon_r}t]+1}\right| \quad (1)$$

where, t is the thickness of the absorbing layer, f is the incident microwave frequency and c is the velocity of light in the free space. ε_r ($\varepsilon_r = \varepsilon_r' - j\varepsilon_r''$), μ_r ($\mu_r = \mu_r' - j\mu_r''$) are the complex permittivity and complex permeability, respectively.

One of the conditions for effective absorption to occur is when the incident electromagnetic wave undergoes reflection at the air-absorber interface with a low reflection component. This can be achieved by designing the input impedance of microwave absorbing material to be close to that of free space. The input impedance, Z_{in} is found from the following equation

$$Z_{in}(\Omega) = Z_0\tanh\left[j\frac{2\pi ft}{c}\sqrt{\mu_r\varepsilon_r}\right] \quad (2)$$

where, Z_0 is the characteristic impedance of free space.

The em wave penetrating the microwave absorbing material attenuates exponentially as

$$\overline{E} = E_0 e^{-(\alpha+j\beta)y}\hat{a}_z \quad (3)$$

where α, the attenuation, is given as

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$$\alpha = \frac{\sqrt{2}\pi f}{c} \times \sqrt{\left(\mu_r''\varepsilon_r'' - \mu_r'\varepsilon_r'\right) + \sqrt{\left(\mu_r''\varepsilon_r'' - \mu_r'\varepsilon_r'\right)^2 + \left(\varepsilon_r'\mu_r'' + \varepsilon_r''\mu_r'\right)^2}} \quad (4)$$

From the above equations it can be seen that by carefully choosing the material properties viz. complex permittivity and complex permeability, good absorption can be obtained. Further optimum absorption can be achieved by considering the thickness of the absorbing layer, $t = \lambda_g/4$, to get destructive interference condition at the interface [12].

Doping of M-type hexaferrites with other metals improves its material properties viz. ε_r and μ_r [9,10,13] as required for good absorption. It is reported that relevant magnetic properties of strontium hexaferrite have slightly higher values than those of barium hexaferrite. Many studies have been conducted to modify the magnetic properties of strontium hexaferrite by substituting stoichiometrically either Sr^{2+} ion or Fe^{3+} ions with other metal ions [4,7,8,13–15]. Cobalt is a fast relaxer owing to its degenerate energy states which enhances the microwave properties [16,17]. Nanosized strontium ferrite doped with cobalt is synthesized and used as magnetic filler in LLDPE matrix. LLDPE has high percolation threshold [18,19] which allows higher quantity of filler to be included in the composite. The developed composites are tested for absorption in X-band.

2. Material synthesis and testing methods

Nano-sized $SrCo_xFe_{12-x}O_{19}$ (x = 0.2, 0.4, 0.6, 0.8, 1.0, 1.2) is prepared stoichiometrically using strontium nitrate (≥98%), cobalt nitrate hexahydrate (≥98%) and iron (III) nitrate nonahydrate (≥98%) dissolved in de-ionized water by co-precipitation technique. The solution is stirred continuously up to around 80 °C for an hour followed by dropwise addition of NaOH to control the size of the particles. Thereafter, oleic acid is added to prevent agglomeration. A brownish precipitate is formed, which is repeatedly washed with a distilled water and ethanol solution to remove traces of sodium and nitrate compounds. The mixed oxides of the starting materials are removed by calcinating the dried powder at a temperature of 1000 °C in a furnace.

X-ray diffractometer (Rigaku Miniflex 200) with monochromatic CuKα radiation (λ = 1.54178 Å) is used to carry out X-ray diffraction analysis (XRD) over a 2θ angle from 20° to 70° to obtain inter-planar spacing and size of the filler inclusions. Transmission electron microscopy (TEM) of the powder sample are conducted to study the phase, structural morphology and size of the ferrite structure. TECNAI G2 20 S-TWIN transmission electron microscope (TEM; FEI Company, USA) operating at an accelerating voltage of 200 kV is used to carry out TEM analysis. A detailed study with varying wt% carried out by the current authors [20] on nanosized M-type strontium hexagonal ferrite ($SrFe_{12}O_{19}$) in LLDPE matrix showed that the best absorption performance and 90% absorption bandwidth is achieved for a wt% of 60%. In the present work, the composite specimens of 60 wt% are fabricated by mixing LLDPE powder and $SrCo_xFe_{12-x}O_{19}$ powder in situ. Composite pellets are made by die-moulding using hot-press technique. Scanning electron micrographs (SEM; JSM 6390LV, JEOL, Japan) of the $SrCo_x$-$Fe_{12-x}O_{19}$-LLDPE nanocomposite are taken at 10^{-11} A probe current and 20 kV accelerating voltage. Fourier transform infrared spectra (FTIR; IMPACT 410, NICOLET, USA) of the samples are obtained in a range between 550 cm^{-1} and 4000 cm^{-1}. The thermal stability of the nano-composites is investigated using Thermal Analyzer, (TGA-50, SHIMADZU). Water absorbance and density properties are also studied. Complex permittivity and permeability of the nano-composites are determined using Nicolson-Ross transmission/ reflection (TRL) technique [21].

The thickness of the single layer sheets of $SrCo_xFe_{12-x}O_{19}$-LLDPE nano-composites is optimized using Eqs. (1) and (2), to obtain a minimum reflection loss at an optimum thickness. Absorption measurement is carried out using waveguide method. A standard Agilent X-band waveguide WR-90X11644A is connected to one port of an Agilent Vector Network Analyzer (VNA) E8362C and calibrated to measure reflection loss (S_{11}) and the data is acquired via an interfaced computer. A fabricated sample of cross-section 10.38 mm × 22.94 mm, same as the inner dimension of the standard waveguide is mounted at the terminating end of the waveguide and shorted with a perfect electric conductor (PEC).

3. Results and discussions of characterizations

3.1. Structural morphology and physical properties

XRD pattern of the synthesized $SrCo_xFe_{12-x}O_{19}$ powder annealed at 1000 °C is shown in Fig. 1.

The diffraction peaks at 2θ values of 23.5°, 26.30°, 30.34°, 32.47°, 34.27°, 35.47°, 37.19°, 40.45°, 42.68°, 55.38°, 63.19°, 67.65° and corresponds to the strongest diffraction planes (1 0 6), (1 1 0), (0 0 8), (1 0 7), (1 1 4), (2 0 0), (2 0 3), (2 0 5), (2 0 6), (2 1 7), (2 2 0) and (2 0 1 4). These peaks correspond to hexagonal Sr-M type hexaferrite phase (JCPDS # 39-1346). No other phase is observed indicating that the structure is stable. The decrease of

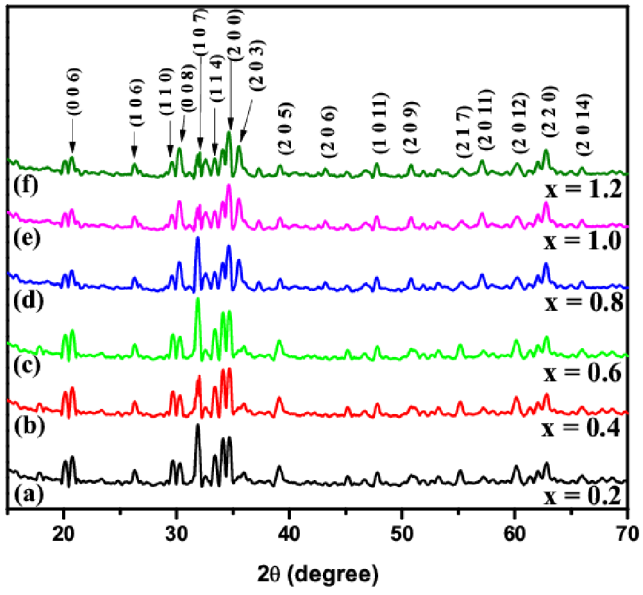

Fig. 1. XRD pattern.

Table 1
Crystalline size (D) and lattice parameter of $SrCo_xFe_{12-x}O_{19}$ (derived from XRD results).

Ferrite compositions	Average crystalline size (nm)	Lattice parameters (Å)	
		a	c
$SrCo_{0.2}Fe_{11.8}O_{19}$	24.39	5.83	23.01
$SrCo_{0.4}Fe_{11.6}O_{19}$	25.12	5.83	23.02
$SrCo_{0.6}Fe_{11.4}O_{19}$	27.78	5.87	23.03
$SrCo_{0.8}Fe_{11.2}O_{19}$	30.01	5.88	23.07
$SrCoFe_{11}O_{19}$	32.96	5.88	23.08
$SrCo_{1.2}Fe_{10.8}O_{19}$	33.07	5.87	23.08