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Structural, magnetic and microwave absorption behavior of Co-Zr substituted strontium hexaferrites prepared using tartaric acid fuel for electromagnetic interference suppression

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ABSTRACT

Strontium hexaferrites, doped with varying Co-Zr content (x) have been synthesized by sol-gel auto-combustion route using tartaric acid as fuel at 800 °C. X-ray diffraction and Fourier transform Infra-red have been carried out to confirm the phase formation, particle size (average 21.9–36.8 nm) and the bond formation respectively. Magnetic properties are scrutinized using vibrating sample magnetometer. Techniques like scanning electron microscopy, transmission electron microscopy and energy dispersive scattering have been employed to explore the surface morphology, particle size and composition of the nano-powders. Electromagnetic characterization of the prepared ferrites has been done using Vector Network Anlyzer in 12.4–18 GHz frequency range. The effect of calcination temperature (500–1000 °C) on the structure, morphology and magnetic properties has also been studied for $x=0.2$ and 800 °C has been found to be the most suitable temperature with the best magnetic properties. Increase in doping has resulted in resonance peaks in dielectric and magnetic loss spectra, leading to microwave absorption peaks. Ferrites with $x=0.2$, 0.8 and 1.0 have appropriate reflection loss less than −10 dB and bandwidth in Ku-band, hence can be used as effective absorbers in suppression of electromagnetic interference (EMI). The governance of impedance matching in deciding the absorption properties has been proved by using input impedance calculations.

1. Introduction

Strontium hexaferrites (SHF) have been an intriguing area of interest for researchers all over the world since past few decades due to a wide range of applications in permanent magnets, electronics, magneto-optical devices, gyromagnetic devices, medical devices, data storage materials, telecommunication, transport radars, computer memory chips, antennas, radio frequency coils etc. [1–3]. Efforts are being made ever since to mould these hexaferrites in order to obtain better properties desired for a particular field or area since different areas require different properties. For instance materials, with coercive field (H_C) greater than half of remanence ($M_r/2$) are useful for high frequency applications, while materials with $H_C < (M_r/2)$ are useful for information storage [4]. Structural and magnetic properties of hexagonal ferrites strongly depend on the synthesis technique as well as the synthesis conditions. Different methods of preparation [5–9], different synthesis environment [10,11] or different substitutions in the base hexaferrite [12–15] have been attempted to improve the magnetic and electromagnetic properties of SHF, hence making them suitable for different applications. Out of different methods of preparation, sol-gel method has aroused great interest because of the attainment of homogenous nanoparticles at comparatively lower temperatures. Focusing on the application area of these ferrites, these hexaferrites are becoming a major solution to overcome the problem of electromagnetic (EM) pollution these days. Ever increasing requirement of exploiting EM waves for wireless communication has driven the material research towards the fabrication of microwave absorbing materials (MAMs) [16]. For suppression of spurious EM waves by the material, two conditions must be satisfied: First, the wave must enter the material with-out front-end reflection and second, inside the material, the wave must get attenuated rapidly to an acceptable level [17]. The first condition is called impedance matching for which input impedance (Z_i) of the wave must be as close as possible to the characteristic impedance of the wave (Z_O=377 Ω), where characteristic impedance is the ratio of amplitudes of voltage and current of EM wave travelling in the waveguide and input impedance is the ratio of transverse components of electric and magnetic fields applied. For second condition,

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the material must possess ferromagnetic resonance and high electromagnetic losses in the scanned frequency region [18]. The combined presence and effectiveness of these two conditions result in a dip in reflection loss spectra.

In order to synthesize microwave absorbing materials for gigahertz frequency range, we have employed the sol-gel auto-combustion route using tartaric acid as fuel. Use of citric acid as fuel has been extensively studied in the previous time [10–12,19–24]. But the usage of tartaric acid as fuel in sol-gel auto-combustion method is very much restrained. Microstructural, magnetic and electrical properties of hexaferrites are considered as important parameters in deciding the significance of these materials for their technological consideration, out of which magnetic behavior is considered as the most important parameter. These properties have been found to be sensitive to their compositional and preparatory techniques. In sol-gel route, fuels used have been found to have a great impact on the various properties of hexaferrites because of their different combustion temperatures. Due to their different carbon bulk, structure, ligand strength and combustion temperatures, gluconic acid (generated *in situ* from sucrose) [25] and tartaric acid fuels are expected to result in different microstructural and magnetic properties of the samples.

The structural and magnetic properties of undoped SHF synthesized using tartaric acid fuel have been already reported by the author [26]. Hereby, the bi-substituted (Cobalt-Zirconium) strontium hexaferrites, prepared using tartaric acid, are reported. To the best of author's knowledge, doped SHF has not been prepared under these conditions before. The aim of the present work is to synthesize nano-crystalline homogenous SHF with better magnetic and electromagnetic properties in order to make them suitable for suppression of electromagnetic interference (EMI). The secondary aim of the author is to find out the best calcination temperature for tartaric acid fuel. Under microwave analysis section, the experimental results of reflection loss are successfully correlated with the theoretical calculations of input impedance of the EM wave. This proves that the reflection loss curves are governed by the impedance matching condition.

2. Experimental procedures

2.1. Sample synthesis

Tartaric acid was utilized as a fuel in the sol-gel method of preparation of Co-Zr doped SHF. The preparation of these hexaferrites was done in accordance with the following equation:

$$Sr(CO_3)_2 + xCo(NO_3)_2 + xZrO(NO_3)_2 + 12 - 2x[Fe(OH_3)_3] \xrightarrow[\textit{glycol, tartaricacid}]{\textit{ethylene}} SrCo_xZr_xFe_{(12-2x)}O_{19}$$

Firstly, ammonia was used to convert desired amount of ferric nitrate to ferric hydroxide [ferric hydroxide was used instead of ferric nitrate to avoid the additional steps of hydrolysis during the formation of ferrites]. The precipitates of ferric hydroxide were dissolved in aqueous solution of tartaric acid used as fuel (acid: total metal = 1.1:1). Subsequently strontium carbonate and aqueous solutions of cobalt nitrate and zirconium nitrate in stoichiometric amounts were added. Excess if any of $SrCO_3$ was removed by the drop wise addition of H_2O_2. This was followed by the addition of ethylene glycol (10% by volume of solution). The solution was then made neutral with NH_3. Amonium nitrate was added as an oxidant. The resultant solution was then stirred continuously and heated slowly in order to get black-coloured gel. The gel was then heated at 150 °C to obtain a porous polymeric powder which was then properly ground in agate mortar and pestle. The final sintering of powder $x=0.2$ was done at different temperatures (500–1000 °C) in order to find out the optimum sintering temperature. 800 °C was found to be the most favorable temperature with the finest magnetic properties. Hence, for all compositions from $x=0.0$–1.0, sintering of powders was done at 800 °C for 6 h. For the microwave measurements, the samples were shaped to fit exactly in the rectangular waveguide WR-62 (15.79 mm × 7.89 mm) after adding 5% polyvinyl alcohol as binder. Finally, the ferrite pellets were cured for 15 min.

2.2. Characterization of samples

The phase purity of the hexaferrites was carried out by using a diffractometer Panalytical X′pert pro with Cu-Kα radiation in angle range 20–80° with scan speed of 0.2 °/s. Varian Resolution Pro was employed for Fourier Transform Infra-Red (FT-IR) analysis in 400–4000 cm^{-1} range. Microsense Vibrating Sample Magnetometer (Model 10) and Carl Zeiss Supra 5S Scanning Electron Microscope; TECNAI 200 Kv Transmission Electron Microscope were used for magnetic and morphological measurements respectively. Agilent N5225A PNA series network analyzer was utilized for the measurement of complex permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$), complex permeability ($\mu_r = \mu' - j\mu''$) and reflection loss in Ku-band (12.4–18 GHz). The theoretical calculations of dielectric phase angle ($\tan\delta$) and input impedance (Z_{in}) were based on the following equations:

$$\tan\delta = \tan\delta_E + \tan\delta_M = \frac{\epsilon''}{\epsilon'} + \frac{\mu''}{\mu'} \quad (1)$$

$$Z_{in} = Z_O\sqrt{\frac{\mu_r}{\epsilon_r}}\, tanh\left[j\frac{2\pi fd\sqrt{\mu_r\epsilon_r}}{c}\right] \quad (2)$$

where, $\tan\delta_E$ and $\tan\delta_M$ are dielectric loss tangent and magnetic loss tangent respectively, Z_O is characteristic impedance (377 Ω), f is the frequency, d is the thickness of sample and c is the velocity of light in vacuum.

3. Results and discussion

The reaction procedure consists of the following three steps: (1) complexation of metal ions with tartaric acid in water; (2) polymerization of the formed chelates with ethylene glycol resulting in the formation of a stable tartarate-ethylene glycol-metal ion polymeric network (as shown in Fig. 1); and (3) the decomposition of the formed organic network to form a gel after evaporation on water bath. Here tartaric acid acts as a complexing agent and ethylene glycol apart from acting as a fuel forms a bridging network with tartaric acid through esterification. The polymerization reaction between tartaric acid-metal complexes and ethylene glycol inhibits cation segregation and achieves a homogenous precursor. Ethylene glycol favors the formation of polymeric porous intermediate which causes complete decomposition of organic derivatives yielding phase pure and organic free $SrZr_xCo_xFe_{(12-2x)}O_{19}$ at lower formation temperatures. In the present case the ratio FeSr = 10 has been used as it results in the formation of pure hexaferrite ($x=0.0$–1.0) with the absence of α-Fe_2O_3 [27,28].

3.1. Phase identification using XRD

XRD patterns of as-produced powder and powders calcined at 500 °C, 600 °C, 700 °C, 800 °C, 900 °C and 1000 °C for 2 h for