EFFECT OF SAMARIUM SUBSTITUTION ON THE TRUCTURAL AND DIELECTRIC PROPERTIES OF ZINC FERRITE

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Abstract

Samarium substituted Zinc ferrites, $ZnFe_{2-2x}Sm_{2x}O_4$ (x= 0.0000, 0.0125, 0.0250, 0.0375, 0.0500) have been synthesized by Conventional Ceramic Method. The structural properties have been investigated by the X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and dielectric measurements. The XRD analysis has confirmed the single cubic spinel phase of $ZnFe_{2-2x}Sm_{2x}O_4$with various compositions. The surface morphology has been observed from SEM micrographs. The average grain size has become smaller due to the substitution of Sm ion with larger ionic radius compared to that of Fe ion. FTIR analysis indicates the specific molecular vibrations at the spinel lattice in the wavelength range of 400 - 4000cm^{-1}. The dielectric constant was measured in the frequency range of 1kHz to 1MHz.

Keywords: Samarium, Conventional ceramic method, XRD, SEM, FTIR, Dielectric constant

Introduction

Ferrites are magnetic ceramics containing iron oxide as a major constituent in it. It is now some 70 years since ferrites debuted as an important new category of magnetic materials. Today ferrites are employed in a truly wide range of applications, and have contributed to the advances in electronics. In the area of new materials, ferrites with permeabilities up to 30,000 and power ferrites for frequencies upto 10 MHz have been made available commercially (Gopchandran KG et al., 1997). Even though, improvements and innovations continue to take place; many new applications, theories and preparation technologies are currently under development in field of ferrites.

Zinc ferrite is a good example of the direct relation between the nanoparticle structure, composition, and properties. When prepared as a bulk material, the zinc-iron oxide has a spinel structure AB_2O_4 with a tetrahedral A site occupied by Zn^{2+} ions and an octahedral B site by Fe^{3+}ions. Several methods including ceramic synthesis, co-precipitation method, tartrate precursor method, hydrothermal, combustion, auto-combustion, polymeric precursor route, solvothermal and sol-gel technique etc. have been used to fabricate the precursor (Safwat A M et al., 2011).

In this work, samarium substituted zinc ferrites ($ZnFe_{2-2x}Sm_{2x}O_4$) have been synthesized by Conventional Ceramic Method followed by the investigation of their structural, morphological vibrational analysis and dielectric measurement.

Experimental Procedure

Samarium substituted Zinc ferrites having the chemical formula $ZnFe_{2-2x}Sm_{2x}O_4$ (where x = 0.0000, 0.0125, 0.0250, 0.0375, 0.0500) have been synthesized by Conventional Ceramic Method. The starting materials are Zinc Oxide (ZnO), Ferric Oxide (Fe_2O_3), and Samarium Oxide (Sm_2O_3). Pure oxides have been mixed and ground into a very fine powder. The mixture

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has been pre-sintered at 900˚C for 5h in furnace with heating rate of 20℃/min and cooled down to room temperature. The powder has been again grounded and re-powdered about 15 min. The structural properties of the pre-sintered samples have been analyzed by X-ray diffraction (XRD) technique.

The pre-sintered samples have been prepared into pellets by using hydraulic press and final sintered for 5h at a temperature which is 100ºC higher than the pre-sintering temperature. After final sintering process, the phase formation and surface morphology of the synthesized samples have been carried out by X-ray diffraction (XRD)using Rigaku Multiflex X-ray Diffractometer with CuK_α radiation (λ=1.54056 Å) and Scanning Electron Microscope (SEM), respectively.

Fourier Transform Infrared (FTIR) spectra of $ZnFe_{2-2x}Sm_{2x}O_4$ samples have been recorded using (Perkin Elmer Spectrum IR version 10.6) in the range 4000-400 cm^{-1}. Dielectric measurements have been done by (GW INSTEK LCR-8110G) meter over a wide range of frequency from 20 Hz up to 20 MHz with drive voltage 1V at room temperature.

Results and Discussion

Structural Analyses

The XRD spectra for the comparison on phase formation of the synthesized samples are shown in Figure 2. The XRD spectra show that all samples of $ZnFe_{2-2x}Sm_{2x}O_4$ where x = 0.0000, 0.0125, 0.0250, 0.0375, 0.0500) are successfully formed spinel phase cubic structures. The X-ray patterns of the ferrite display sharp and well-resolved diffraction peaks with good crystallinity. No additional peak of the second phase has been observed in the XRD patterns, showing that the ferrites have consisted of only spinel $ZnFe_2O_4$ phase. Therefore, it has been confirmed that Sm has totally entered into the lattice site of spinel ferrite. The diffraction peaks are indexed to be (220), (311), (222), (400), (331), (422), (511) and (440) of the crystal planes of spinel Zn ferrite respectively. The crystallite size has been estimated from the X-ray peak broadening of the (311) peak using Scherrer's equation. It is estimated to be about 34 nm without Sm substitution and the size has been decreased with increase in Sm substitution. It might be due to the decrease in crystallinity resulted from Sm substitution which slows down the crystallization process in ferrite. However, the lattice parameter is mostly constant and it is not affected by the Sm dopants. Table 1 shows variation of crystallite size for $ZnFe_{2-2x}Sm_{2x}O_4$ with composition of x.

The average crystallite size (D) of $ZnFe_{2-2x}Sm_{2x}O_4$ ferrite is calculated using Debye Scherrer's formula,

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

where, the constant K is taken to be 0·94, λ the wavelength of X-ray used which is CuK_α radiation (λ = 1.54 Å), β the full width at half maximum of the diffraction peak and θ is the diffraction angle.

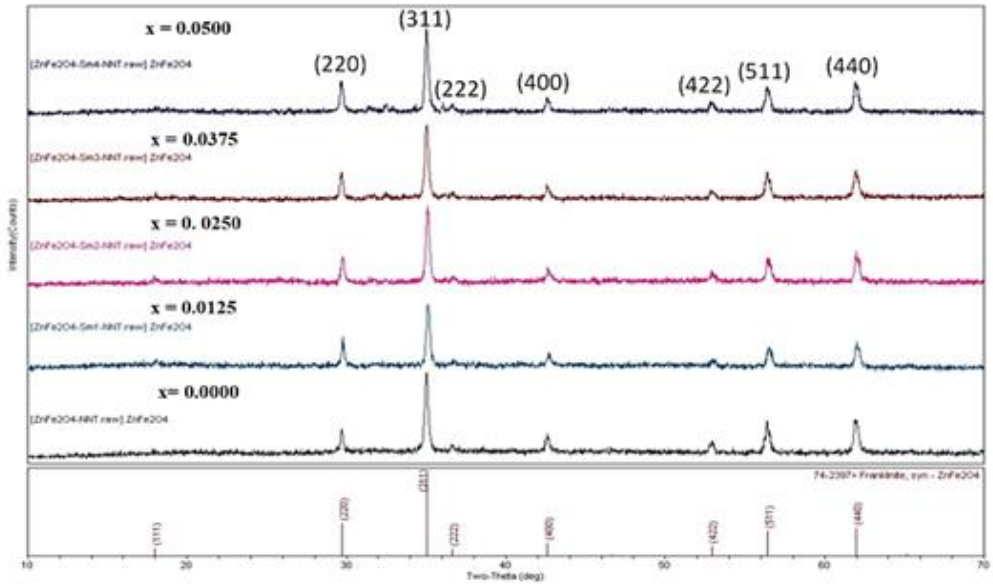

Figure 1 Comparison on phase formation of $ZnFe_{2-2x}Sm_{2x}O_4$ samples for (x=0.0000, 0.0125, 0.0250, 0.0375, 0.0500)

Table 1 Comparison on structural properties of $ZnFe_{2-2x}Sm_{2x}O_4$ sample

Composition (x)	Lattice parameter a (Å)	Crystallite size D(nm)
0.0000	8.4794	33.50
0.0125	8.4661	30.05
0.0250	8.4851	29.90
0.0375	8.4953	28.70
0.0500	8.4951	26.47

Surface Morphology

Surface morphology of Samarium substituted Zinc ferrite ($ZnFe_{2-2x}Sm_{2x}O_4$) has been examined by Scanning Electron Microscope (SEM). SEM images of $ZnFe_{2-2x}Sm_{2x}O_4$ final sintered at 1000°C are shown in Figure 2. The grains of Zinc ferrites are found to be uniform and it exhibits a homogenous grain distribution. However, with the substitution of Sm, smaller grains of Sm are formed on the surface of larger grains of $ZnFe_2O_4$. The number of smaller grains increased with increase in Sm concentration. Furthermore, it is found that pores are quite rare to visualize in the structure. The observation of homogeneous surfaces in SEM images well agrees with the single phase formation of spinel structures for all compositions of Sm dopants. The values of the grain size in $ZnFe_{2-2x}Sm_{2x}O_4$are shown in Table 2. The ionic radii of ions in the spinel ferrite are 0.964 Å for Sm, 0.74 Å for Zn and 0.645 Å for Fe. Therefore, it is worth to note that the grain formation has also been slow downed due to the substitution of Sm ion with larger ionic radius for Fe ion with smaller ionic radius resulting in smaller grains.

Table 2 Comparison on grain sizes of $ZnFe_{2-2x}Sm_{2x}O_4$

Composition (x)	Grain size (μm)
0.0000	1.28
0.0125	0.90
0.0250	0.80
0.0375	0.69
0.0500	0.53

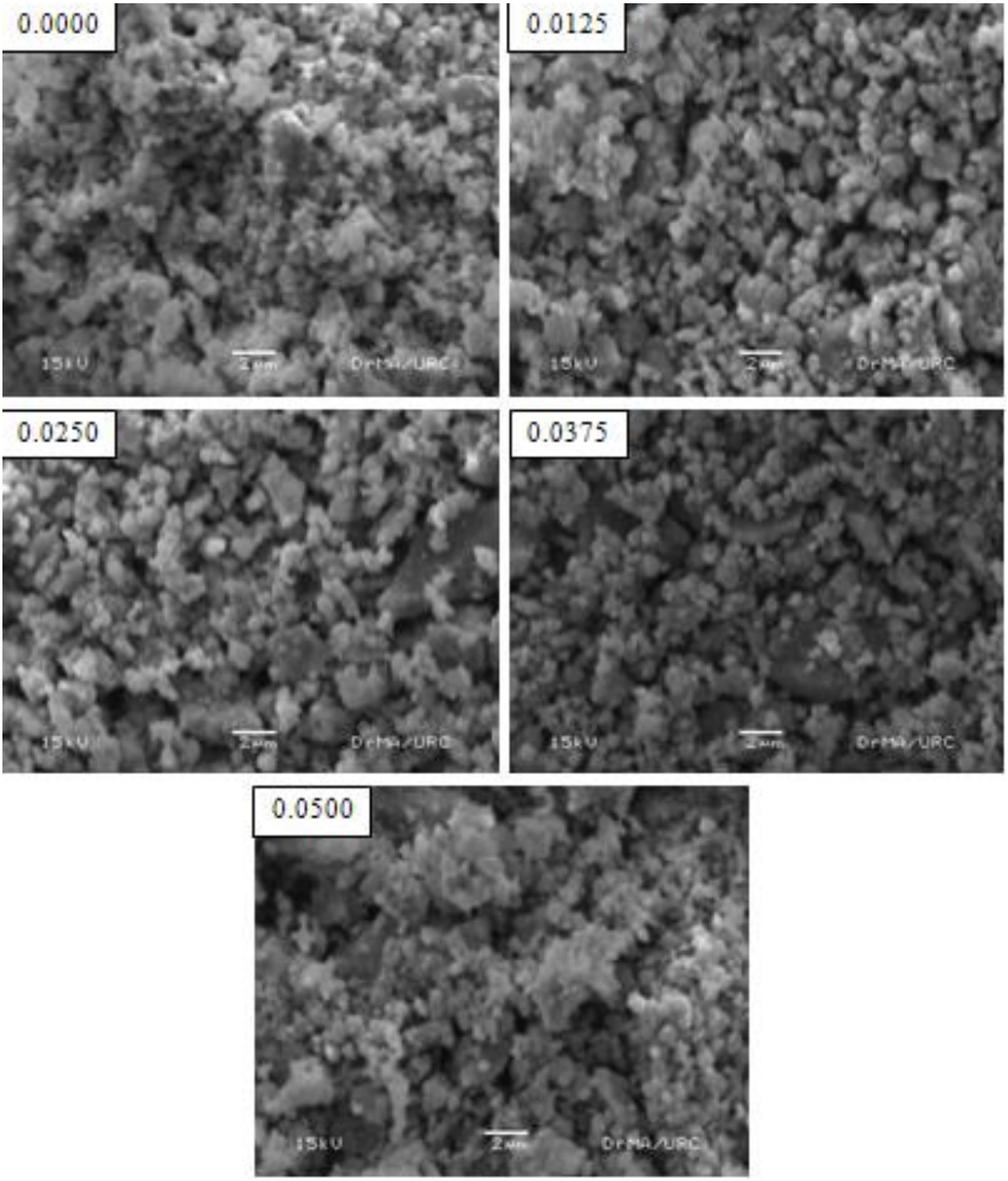

Figure 2 Variation of grains size in $ZnFe_{2-2x}Sm_{2x}O_4$ samples with Sm composition (x = 0.0000, 0.0125, 0.0250, 0.0375, 0.0500)

Fourier Transform Infrared Spectroscopic Analyses

In the wave number range of 4000–400 cm^{-1}, the infrared bands of solids are usually assigned to vibration of ions in the crystal lattice. Two main broad metal oxygen bands are seen in the IR spectra of all spinels, and ferrites in particular.

The highest band $\nu_1$is generally observed in the range 600–450 cm^{-1} corresponds to intrinsic stretching vibrations of the metal ions at the tetrahedral site. The lowest band $\nu_2$usually observed in the range 450–385cm^{-1}, is assigned to octahedral-metal stretching. FTIR spectra of the investigated $ZnFe_{2-2x}Sm_{2x}O_4$samples in the wave number range 900–450 cm^{-1} are shown in Figure 3. The prominent bands ν_1 present in all the samples. In order to see the ν_2 mode, the characterization has to be done in the range until 350 cm^{-1}. The vibrational frequencies of the IR bands are in agreement with the reported values in literature. Importantly, the value of $\nu_1$has shifted to lower frequency side with increasing samarium content. A slight broadening of the absorption band ν_1 is also noticed with increase in samarium concentration. This may be attributed to the substitution of Fe^{3+} ions by Sm^{3+} ions. It is known that increasing site radius reduces the fundamental frequency and therefore the central frequency should shift towards the lower frequency side.

Dielectric Measurements

The frequency dependence of the dielectric constant for all the samples has been studied at room temperature. The variation in dielectric constant (έ) with frequency range (1 kHz-1 MHz) at room temperature for the various $ZnFe_{2-2x}Sm_{2x}O_4$ samples with different Sm concentrations is shown in Figure 4. Comparison of dielectric constant for ferrite samples with different Sm concentration is shown in Table 3.

There is a fluctuation in έ values in the lower frequency range. However, the dielectric constant tends to be stable in the higher frequency range and importantly the dielectric constant has increased with increasing Sm content in Zinc ferrite. Theoretically the ferrite materials are applicable in the higher frequency region as the effect of microstructure especially grain boundaries can be eliminated in that region. It is worth to note that the large amount of rare earth Sm could make the ferrite to have larger value of dielectric constant. The observed variation in the dielectric constant with Sm concentration could be explained that the hoping of electrons in the spinel lattice may be enhanced by the octahedral site occupancy of Sm ions on the basis of local displacement of charge carriers in the presence of external electric field (Benny J et al., 1999 & **Chena H L et al., 2005).**

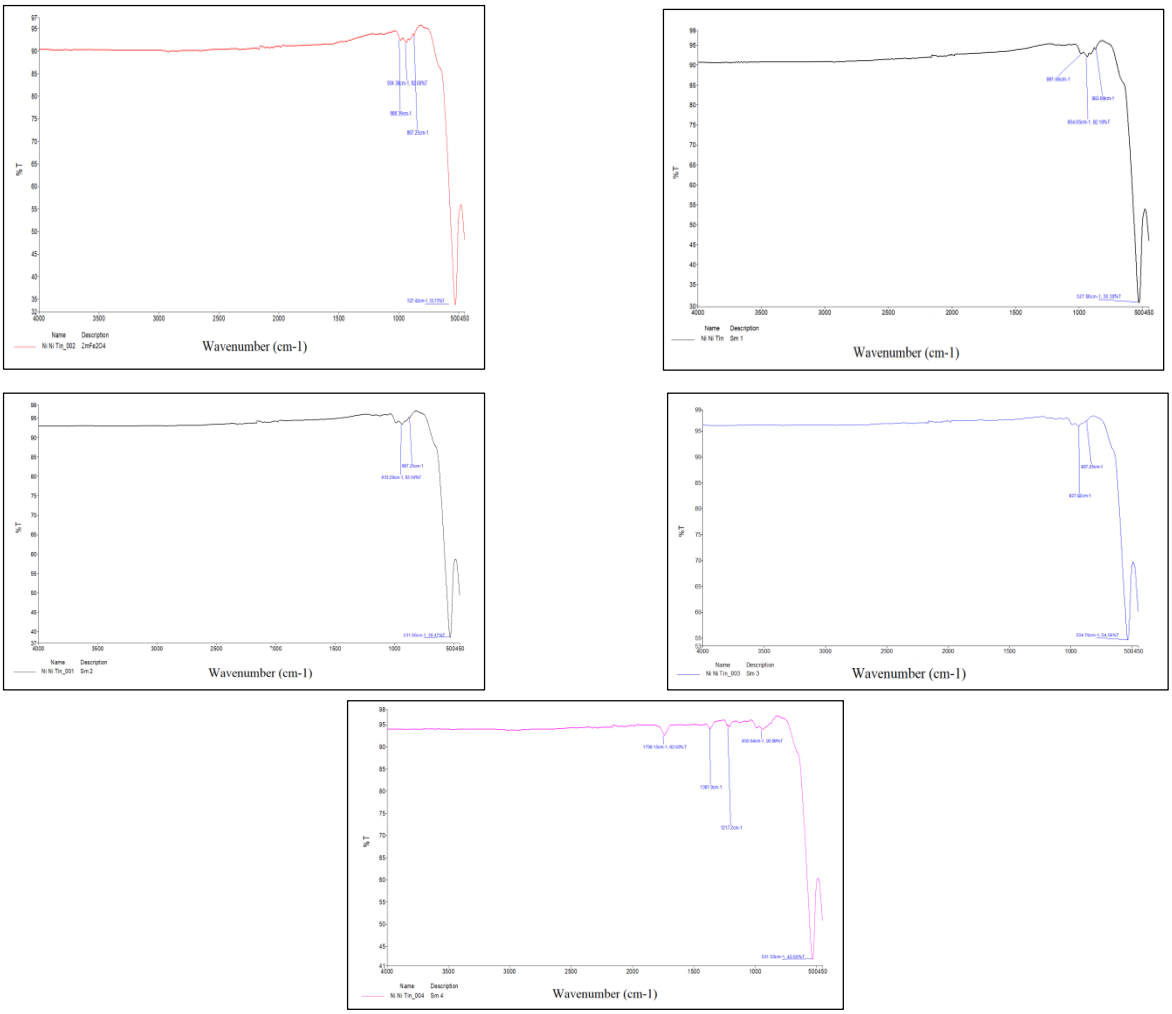

Figure 3 FTIR spectrum of $ZnFe_{2-2x}Sm_{2x}O_4$, (x = 0.0000, 0.0125, 0.0250, 0.0375, 0.0500)

Table 3 Comparison of dielectric constant for $ZnFe_{2-2x}Sm_{2x}O_4$ ferrite samples in the frequency range (1kHz - 1 MHz)

Frequency 10^3 (Hz)	**Dielectric Constant**				
	$ZnFe_{2-2x}Sm_{2x}O_4$				
	x = 0.0000	**x = 0.0125**	**x = 0.0250**	**x = 0.0375**	**x = 0.0500**
1.00E+00	7.7830	6.4417	7.3182	2.1324	3.5100
1.12E+02	0.4830	0.4973	0.4819	0.4459	0.4474
2.23E+02	0.4409	0.4735	0.4961	0.4991	0.5108
3.34E+02	0.4213	0.4538	0.4762	0.4749	0.4855
4.45E+02	0.3800	0.4155	0.4388	0.4357	0.4458
5.56E+02	0.3670	0.4020	0.4252	0.4204	0.4307
6.67E+02	0.3943	0.4310	0.4534	0.4485	0.4580
7.78E+02	0.4141	0.4514	0.4740	0.4689	0.4784
8.89E+02	0.4297	0.4673	0.4905	0.4851	0.4946
1.00E+03	0.4412	0.4800	0.5029	0.4976	0.5069

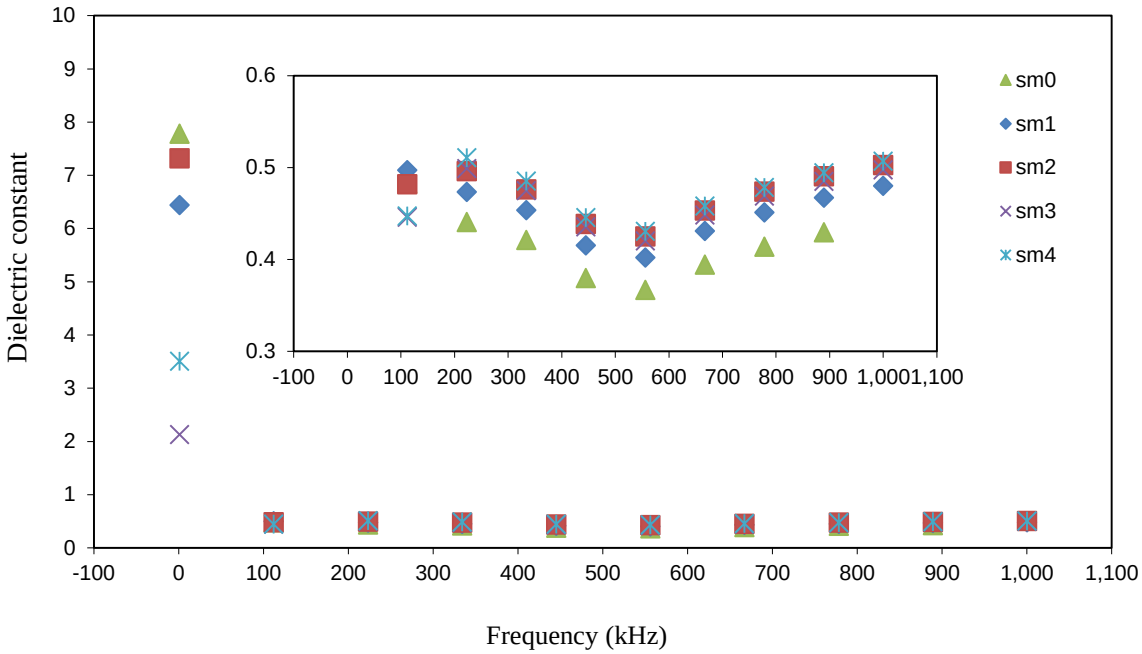

Figure 4 Frequency dependence of dielectric constant for $ZnFe_{2-2x}Sm_{2x}O_4$ ferrite nanoparticles (x = 0.0000, 0.0125, 0.0250, 0.0375, 0.0500) in the frequency range (1kHz-1MHz) (Inset : Frequency dependence of dielectric constant in small scale)

Conclusions

Samarium substituted Zinc ferrites ($ZnFe_{2-2x}Sm_{2x}O_4$) have been synthesized by Conventional Ceramic Method involving pre-sintering temperature at 900°C and final-sintering temperature of 1000°C. The structural, surface morphological and vibrational analyses of $ZnFe_{2-2x}Sm_{2x}O_4$ have been confirmed by XRD, SEM, FTIR. Dielectric measurements were performed in the range of 1 kHz-1 MHz. XRD analysis reveals that the samples are single phase inverse spinal cubic structure with crystallize sizes in the range of 26.47 nm to 33.5 nm which indicates the formation of nano-crystallize size. It is note to worth that the crystallize size has decreased with an increase in Sm doping. Sm dopants do not affect the lattice parameter in this process. Morphological analysis shows that the grain sizes are in the range of 0.53 µm to 1.28 µm. The grains are found to be homogeneously distributed on the surface and the grains become smaller with the substitution of Sm ions in $ZnFe_{2-2x}Sm_{2x}O_4$. The absorption bands are observed between the wave number 600-450 cm^{-1} due to the stretching vibrations in the tetrahedral metal oxygen bond. It is found that the dielectric constant of Sm substituted $ZnFe_{2-2x}Sm_{2x}O_4$ ferrite is higher than that of $ZnFe_2O_4$. It is concluded that small amount of Samarium substitution could affect on the Structural and dielectric properties of zinc ferrite.

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