Structural Studies and Dielectric Dispersion of SrNiZn Mixed nano hexaferrites at low frequencies

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Abstract:

Y-type nano hexaferrites with generic formula $Sr_2Ni_{1-X}ZnCo_XFe_{12}O_{22}$ (x = 0, 0.1, 0.2, 0.3, 0.5) were synthesized by novel microwave assisted sol gel method. Structural characterizations of the prepared samples have been performed using X-ray powder diffraction pattern. The prepared samples are in single Y –type hexagonal phase with the space group $R\bar{3}m$ (no. 166). The lattice parameters, X-ray density, experimental density, and porosities of samples were measured from XRD data. It is observed that the lattice parameters "a" and "c" decreases with content of cobalt. The crystallite size is in the range 38- 72nm, shows nanosize of prepared samples. The ac electrical conductivity, dielectric constant and dielectric loss are measured in the range 100Hz to 0.2MHz. It was found that, the ac conductivity shows dispersion at high frequencies. This dispersion was explained on the basis of interfacial polarization that formed due to the inhomogeneous structure of ferrite material.

Keywords: Y-type nano hexaferrites, XRD, AC electrical conductivity, Dielectric constant,

1.Introduction

Nanometer-sized crystalline material continues to be of interested due their remarkably different properties compared with the bulk[1]. Ferrimagnetic nanocrystallites are of particular interest because they can exhibit a single magnetic domain. Y-type hexaferrites provide a useful combination of ferrimagnetic and insulating properties and well known for their use in magnetic –electric devices[2]. The Y-type hexaferrite is reported to have a higher cutoff frequency than spinel ferrites and can be synthesized by annealing at relatively lower temperature of 900 – 1100[o] C as compared with other hexaferrites[3]. Although the magnetic properties of hexaferrites are of immediate and common interest, numerous technological applications still require wider knowledge of their general physical properties. The ac conductivity of ferrites gives valuable information related to the localization of charge carriers at grain, grain boundaries, inter-granular tunneling of charge carriers across the grain boundary and dielectric polarization of magnetic ions [4,5].

In the present work, strontium based Y- type nanohexaferrites with generic formula $Sr_2Ni_{1-X}ZnCo_XFe_{12}O_{22}$ (where x = 0, 0.1, 0.2, 0.3, 0.5) were synthesized by novel microwave assisted sol- gel method. The objective of this work is to investigate the effect of the concentration of dopant on the structural and dielectrical properties of the synthesized materials.

2. Experimental Procedure

2.1 Synthesis Technique: The SrNiZn Y- type nano ferrite having generic formula $Sr_2Ni_{1-X}ZnCo_XFe_{12}O_{22}$ (where x = 0, 0.1, 0.2, 0.3, 0.4, 0.5) were prepared by novel microwave assisted sol gel method .The starting chemicals used were AR grade Strontium nitrate, Nickel nitrate, Zinc nitrate, Cobalt nitrate, Iron nitrate, and urea. Stoichiometric amount of all metal nitrates were put in a 500 ml borosil beaker containing 30 ml amount of triple filter distilled water to prepare a solution, to which urea was added. The solution was stirred for 30 minutes then heated with continuous stirring at about 90 ᵒC to obtained gel. The beaker containing gel was kept in a domestic microwave oven, and was irradiated with microwaves. Within 3 - 4 minutes of irradiation, dark brown fumes started coming out from the exhaust., immediately after that gel solution get fired and resulted into a foamy dark brown powder. The synthesized powder was grounded in a pestle mortar for about one hour, the powder then calcinated at 900 ᵒC for about six hour in furnace. The furnace is then cooled to the room temperature by a natural way. The calcinated powders were again grounded to get fine powder of nano hexaferrites.

For dielectric measurement, pallets were made by adding few drop of polyvinyl acetate as a binder to the prepared powder and using dye punch of 10 mm diameter and by applying a pressure of 6 tons. The binder was burnt off by heating pellets at 400ᵒC for 2 hours. The silver coating was applied on both sides of the pellet and cured for 10 minutes at 125 ᵒC to have good contact of silver with ferrite sample.

2.2**Sample Characterizations:** The structure was determined through the X-ray diffraction analysis. XRD patterns were taken using Cu Kα (λ = 1.5406 Å) radiation at room temperature. The average crystallite size, lattice parameters, bulk density, X-ray density and porosity were calculated using simple formulae [6]. The dielectric measurements were carried out at room temperature in the frequency range 100 Hz – 0.2MHz using LCR-bridge (Model Hemeg- 8118).

3. Results and Discussions:

3.1 Structural Properties: The X-ray diffraction patterns of $Sr_2Ni_{1-X}ZnCo_XFe_{12}O_{22}$ (X= 0.0, 0.1, 0.2, 0.3, 0.5) Y- type hexaferrites samples obtained at room temperature along with a standard pattern are shown in Fig 1. All the XRD reflection peaks are indexed by applying a hexagonal crystal system. It is observed that most of the peaks of prepared sample are matched with standard pattern, reveals that they are Y–type hexagonal ferrite with the space group $R\bar{3}m (no. 166)$.

The variation of lattice parameter a, c, with substitution of cobalt is depicted in Fig.2. It is observed that the lattice parameters 'a' and 'c' decrease with content of Co from 5.878 Å to 5.8743 Å and from 43.08 Å to 42.73 Å respectively.. This variation in lattice parameters with substitution indicates that substitutions are achieved on crystallographic sites. The decrease in the lattice parameters is attributed to the small cobalt ion radius of 0.65 Å, as compared to the nickel ion radius of 0.70 Å. Since the ionic radius of Co^{+2} is less than that of Ni^{2+}, the decrease in lattice parameters with Co^{+2} substitution is expected[7]. The unit cell parameters are in good agreement with the published values earlier[8,9].

The variation of experimental density D (Bulk density), X-ray density Dx (Theoretical density) and porosity P as a function as cobalt content is shown in Fig 3.It was found that the Dx values are nearly
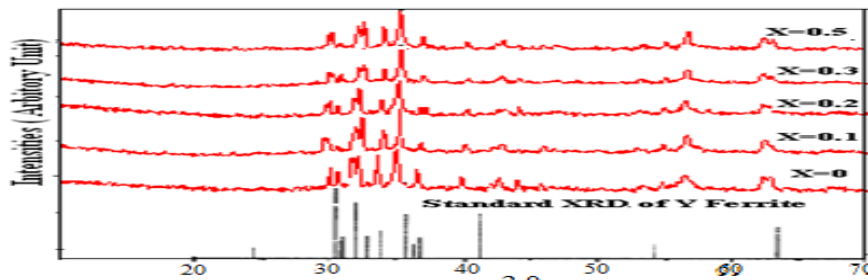

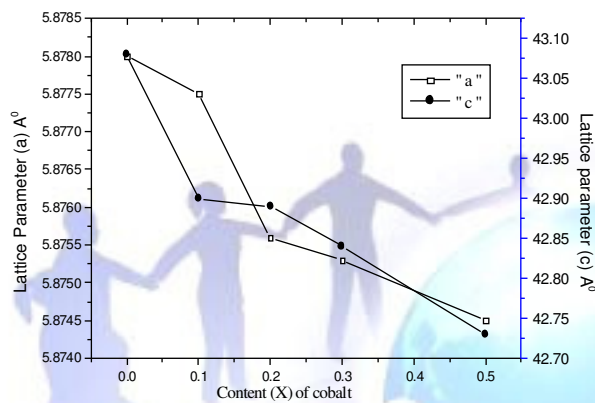Fig.1 XRD spectra of $Sr_2 Ni_{1-X} ZnCo_X Fe_{12} O_{22}$

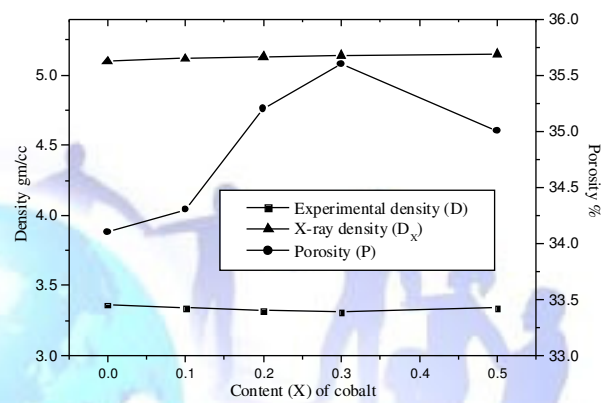Fig.2 Variation of lattice parameter with cobalt content

Fig.3 Variation of Dx, D and Porosity with cobalt content

same for all composition and close to 5.12 gm/cm³ which are in agreement with the published results[10]. The experimental density values were found to be in general less than that X-ray density which was expected due to the presence of unavoidable pores created during sintering process[11]. It is observed that the experimental density is slightly decreased with increase of Co content up to X=0.3 then increases, but the porosity shows opposite trend. This behavior may be attributed to the facts that introduction of Co ions in hexagonal ferrite may affect the grain size development during sintering and increase porosity.

The mean crystallite size determined from the line broadening of diffraction lines using Scherer formula is found to be in range of 38 nm to 72 nm

3.2 Frequency dependence: The frequency dependent ac conductivity (log σ_{ac}); dielectric constant (ε') and dielectric loss (tan δ) were measured in the range 100 Hz – 0.2 MHz at room temperature for all prepared samples. Fig. 4 depicts ac conductivity as a function of frequency (log ω) for all samples. In general the results show dispersion in ac conductivity with respect to frequency. For sample with X=0, conductivity increases with frequency. But for remaining samples, ac conductivity is almost frequency independent at relatively lower frequencies. However at relatively higher frequencies, conductivity begins to increase sharply. Comparing the threshold frequency at with the dispersion of conductivity with frequency appears for samples X = 0.1, 0.2, 0.3, 0.5.It is shown that the threshold frequency increases with increasing X i.e. with increasing Co content the conductivity becomes more frequency independent. The dispersion of ac conductivity was observed before for other ferrites[12,13]. The dispersion in the ac electrical

conductivity of polycrystalline ferrites is explained on the basis of interfacial polarization that formed due to the inhomogeneous structure of ferrite material. According to Maxwell and Wagner model and Koops phenomenological theory[14], the ferrite is imagined to act as a multilayer capacitor in which the ferrite samples are characterized by a microstructure consisting of conductive thick layers, grains (with conductivity σ_1; dielectric constant ε_1; and thickness d_1) separated by resistive thin layers, grain boundaries (with σ_2; ε_2; and d_2). The impedance of this multilayer capacitor can be represented as[15].

$$Z^{-1} = R^{-1} + J\omega c \qquad (1)$$

Where ω is the angular frequency ($\omega = 2\pi f$), R and c are the parallel equivalent resistance and capacitance of the material, respectively. According to Eq. (1), it is shown that above a certain frequency, the inverse impedance of the multilayer condenser and hence the ac conductivity of ferrite material rises with frequency.

The effect of frequency on the dielectric constant ε' is depicted in Fig. 5. It is shown that at relatively low frequencies the values of ε' is high and it decreases sharply with increasing frequency. The behavior of ε' with frequency can be explained on the basis of the assumption that the mechanism of
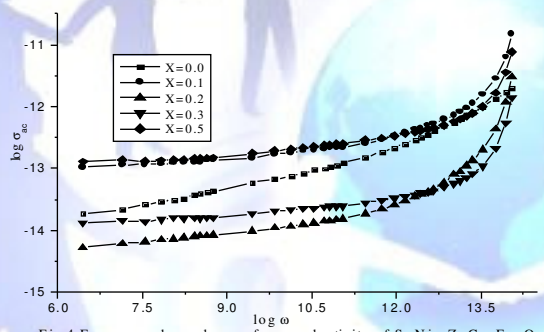

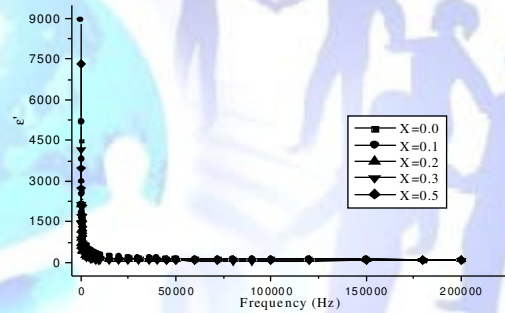Fig.4 Frequency dependence of ac conductivity of $Sr_2Ni_{1-x}ZnCo_xFe_{12}O_{22}$

Fig.5 Frequency dependence of dielectric constant of $Sr_2Ni_{1-x}ZnCo_xFe_{12}O_{22}$

the polarization process in ferrites is similar to that of the conduction process[16]. Prakash and Baijal[17] suggested that, for nickel containing ferrite, Ni^{3+} ions can be formed during the sintering process due to reduction tendency of $Ni^{2+} \leftrightarrow Ni^{3+}$. It is known that, in the case of zinc containing ferrite a partial reduction of Fe^{3+} ions to Fe^{2+} ion can take place as a result of volatilization of zinc during the sintering process[17]. It was also suggested that, the presence of Ni^{2+} on the octahedral site fevours the following exchange interaction[18].

$$Ni^{2+} + Fe^{3+} \leftrightarrow Ni^{3+} + Fe^{2+} \qquad (2)$$

Thus the conduction mechanism for the samples under investigation can be explained with the aid of Verwey mechanism[19] and Heiks model[20], by two exchange interactions: electron hopping between Fe^{2+} and Fe^{3+} and hole transfer between Ni^{3+} and Ni^{2+} over the octahedral sites. The first exchange give rise to the displacement of the local charges in the direction of the external field leading to the main source of polarization in these ferrites, while the latter exchange gives rise to displacement of the holes in opposite direction of the external field leading to the second source of polarization in these ferrites. The decrease of the dielectric constant ε' with increasing frequency can be attributed to the fact that the electron exchange interaction between ferrous and ferric ions and hole exchange between Ni^{3+} and Ni^{2+}

cannot follow the frequency of the external alternating electric field beyond a certain frequency value[21]. The high values of the dielectric constant of these ferrites at relatively low frequencies) can be attributed to the inhomogeneous structure of these ferrites[14].

Fig.6 shows the dielectric loss tangent behavior as a function of frequency for all samples. The loss tangent is defined as the ratio of the loss or resistive current to the charging current in the sample. Also it is known that, there is a strong correlation between the conduction mechanism and the dielectric constant behavior (the polarization mechanism) in ferrites. From these two considerations we can see that the behavior of tan δ with frequency is showing the expected decrease of tan δ with increasing frequency. The decrease of tan δ with frequency could be accounted for using Koops's model.

In the low frequency region which corresponds to high resistivity (due to grain boundaries) more energy is required for electron exchange between Fe^{2+} and Fe^{3+} ions. Thus the energy loss is high. In the high frequency range which corresponds to low resistivity (due to the grains) a small energy is needed for electron transfer between Fe^{2+} and Fe^{3+} ions in the grains and hence the energy loss is small. The low loss values at higher frequencies show the potential applications of these materials in high frequency microwave devices[22].

3.3 Composition Dependence: The room temperature compositional dependence of the ac electrical conductivity (σ_{ac}), the dielectric constant (ε') and dielectric loss (tan δ) at 10kHz and 50kHz are illustrated in Fig. 7 to 9 respectively. It is shown that all the parameters decreases with increase in "X" until they reach a minimum value at X=0.2, after which they start to increase with further increase in cobalt content. It stated that, the electric conduction in the studied sample is related mainly to the hopping of charge carriers[23], which plays a major role in the electric conduction and dielectric polarization process in these ferrites by electron hopping between Fe^{2+} and Fe^{3+} ions and hole transfer between Ni^{2+} and Ni^{3+}. It is well known that Ni^{2+} ions prefer to occupy the octahedral (B- sites), while the iron ions are distributed between both A and B sites. The Co^{+2} ion generally preferred octahedral sites, but when particles size reduced to nano dimensions, there is change in cations distribution and Co^{2+} occupy both octahedral (B) and tetrahedral (A) sites[24]. Therefore the behaviour of σ_{ac}, ε' and tan δ with composition can be explained as follows: The substitution of Co^{+2} ions up to concentration X=0.2 reduces the Ni^{2+} content at B sites which will reduce the probability of hopping given by eqn. (2)

Therefore conductivity decreases up to X=0.2. However beyond X=0.2 Co^{2+} ions may occupy tetrahedral sites, which will force some of the iron ions to migrate from A-sites to B-sites to substitute the decrease in B-sites population[25]. Therefore the number of Fe^{2+} and Ni^{3+} will increase accordingly to eqn.(2). So, the hopping conduction by the electron transfer between Fe^{2+} and Fe^{3+} and holes transfer between Co^{2+} and Co^{3+} will increase. Consequently the electrical conductivity σ_{ac} increases. The behaviour of ε' and tanδ can be explained on the basis of the assumption that the mechanism of dielectric polarization is similar to that of electrical conduction hence it is expected that behavior of ε' and tanδ is similar to that of σ_{ac}.
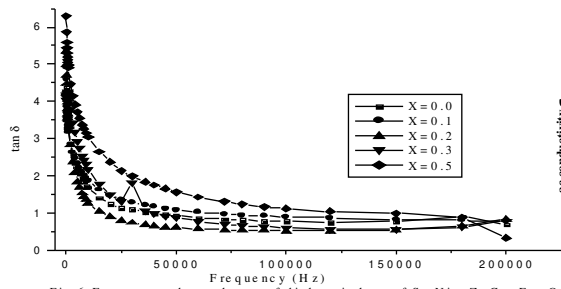
Fig.6 Frequency dependence of dielectric loss of $Sr_2Ni_{1-x}ZnCo_xFe_{12}O_{22}$

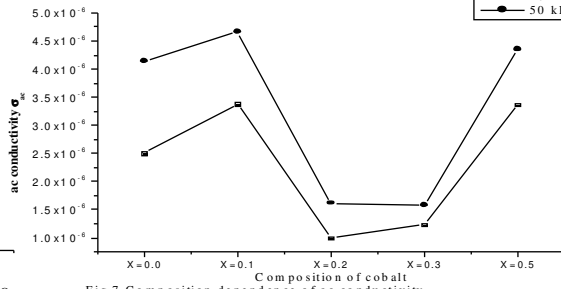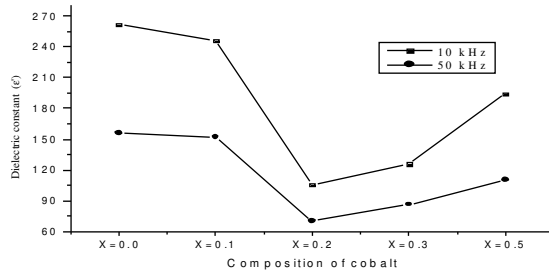Fig.7 Composition dependence of ac conductivity

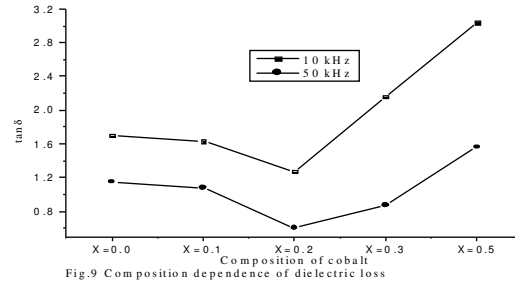Fig.8 Composition dependence of dielectric constant

Fig.9 Composition dependence of dielectric loss

4. Conclusions:

The X-ray diffraction patterns of $Sr_2Ni_{1-x}ZnCo_xFe_{12}O_{22}$ (X= 0.0, 0.1, 0.2, 0.3, 0.5) Y- type hexaferrites samples confirm the formation of Y- type hexaferrites. It is observed that the lattice parameters 'a' and 'c' decrease with substitution of Cobalt. This is attributed to the small radius of cobalt ion (0.65 Å), as compared to the nickel ion radius (0.70 Å). The crystallite size is in the range 38- 72 nm. The dispersion of ac electrical conductivity was observed at higher frequencies. This dispersion was explained on the basis of the double layer Koop's model. The values of the dielectric constant at relatively low frequencies were high and were due to the existence of interfacial polarization arising due to inhomogeneous structure of ferrite material.

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