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Synthesis and characterization of cobalt substituted zinc nano-ferrites by conventional sol-gel auto-combustion method

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Abstract
Cobalt substituted zinc nano-ferrites ($CO_xZn_{1-x}Fe_2O_4$) for x=0, 0.1, 0.4, 0.7, 0.9 have been synthesized by sol-gel auto-combustion technique using suitable amount of nitrates in the presence of citric acid and ethylene glycol as a gelling agent. Initial solution was prepared at low temperature to attain final pH 7. The synthesized nano-powder was annealed at 600°C for 4 hours. X-Rays diffraction technique reveals the simple cubic spinel structure of nano-ferrites. This method is very simple, cost effective and used for processing at low temperature. Cobalt concentration has a significant effect on structural and dielectric properties such as dielectric constant (ε′), complex dielectric constant (ε′′) and tangent loss which shows a decreasing trend with increase of frequency while an increasing trend of all these properties were seen with Cobalt concentration.

1. Introduction
Ferrites are magnetic materials which consist of ferric ions and oxides, which shows ferromagnetic property due to high magnetic permeability, conduct magnetic flux well and high electrical resistivity [1-2]. The properties of ferrite depend on substitutions and doping of unlike cation, synthesis technique, sintering parameters like temperature, sintering density and time. Nano-structured iron-containing metal oxides have been the subject of exploration. Nano-structured materials exhibit interesting chemical and physical characteristics, significantly different from bulk materials due to large surface area and extremely small particle size [3].

Nano-ferrites are the compounds in powder as well as in ceramic form and formed by iron oxides. The characteristics of nano-sized structured getting our interest from certain years ago due to pore size, crystal shape distribution of particle size and phase purity of nano-powders [4-5]. These outstanding characteristics of nano-ferrites make them suitable for high frequency applications. Ferrite structures have found considerable interest due to greater heat and corrosion resistance as well as lower price. Nano-ferrites are the current subject of interest due to its many applications in research areas as well as in commercial areas. Substitutions of nano-ferrites with various metals are commonly used to enhance their magnetic and electrical properties. Cobalt substituted Zinc nano-ferrites are the technological important ferrites. Cobalt ferrite is the most important magnetic material that has remarkable chemical stability,

large magnetic anisotropy, and mechanical hardness. Synthesis techniques play an important role for nano-ferrites having certain characteristics such as distribution size, crystalline shape and homogeneity [6-7]. As an alternative to solid-state chemistry, a range of solution techniques have emerged, including co precipitation, hydrothermal processing, and sol–gel chemistry. Among these techniques, sol–gel chemistry offers some particular advantages, centered on the ability to produce a solid-state material from a chemically homogeneous precursor [8].
In the present research Sol-gel auto-combustion technique used for preparation of Cobalt substituted Zinc nano-ferrites. The obtained samples were used for structural and dielectric characteristics.

2. Material and Methods

Cobalt substituted Zinc nano-ferrites ($Co_xZn_{1-x}Fe_2O_4$) were prepared by conventional sol-gel auto-combustion method. The gel was prepared by using stoichiometric amount of nitrates; Iron(III) nitrate nano-hydrate ($Fe(NO_3)_3.9H_2O$), Cobalt(II) nitrate hexa-hydrate ($Co(NO_3)_2 .6H_2O$) and Zinc(II) nitrate hexa-hydrate ($Zn(NO)_3 .6H_2O$) as raw materials. For the preparation of samples required nitrates were dissolved into distilled water and continuously stirred at 90°C for 25-30 mins to get homogeneous solution. Citric acid anhydrous ($C_6H_8O_7$) dissolved in ethanol and the molar ratio of nitrates to citric acid was 1:1. The pH of the solution must be attaining neutral. The gelling agent ethylene glycol used by adding 18-19 drops to form gel and dried it at 210°C for 24 hours into the oven until its color changed into grayish black. Grind the dried gel to form nano-particles and annealed at 600°C in a muffle furnace for 4 hours. Finally the cobalt substituted zinc nano-ferrites ($CoxZn1_{-x}Fe_2O_4$) for x=0, 0.1, 0.4, 0.7, 0.9, 1 were prepared by the sol-gel auto-combustion technique.

3. Results and discussion

X-ray diffraction technique (XRD) is used to examine all kind of materials. The prepared samples $Co_xZn_{1-x}Fe_2O_4$ (x=0, 0.1, 0.4, 0.7, 0.9, 1) were characterized by XRD using source of Cu-Kα radiations with wavelength λ=1.54118A°. The obtained data confirm the single phase mixed spinel cubic structure of each sample as shown in Fig.1.

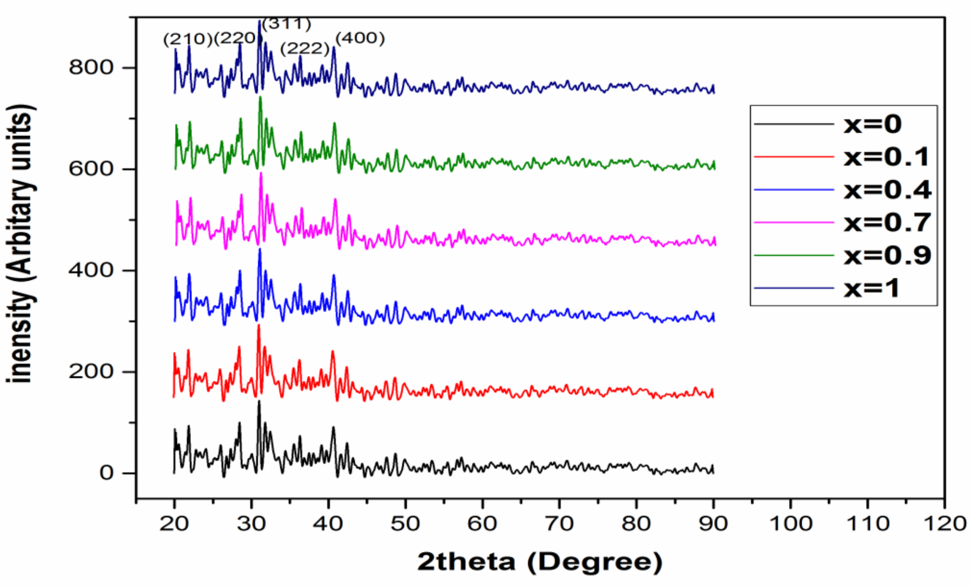

Figure 1: X-rays diffraction pattern of $Co_xZn_{1-x}Fe_2O_4$

3.1 Dielectric Study

Dielectric measurements were calculated by parallel plate capacitor and the dielectric constant and dielectric loss tangent of each sample were investigated by equations [9];

$$\varepsilon' = \frac{cd}{\varepsilon^{\circ} A} \ldots\ldots\ldots\ldots\ldots \text{(i)}$$

$$\varepsilon'' = \varepsilon' \tan\delta \ldots\ldots\ldots\ldots \text{(ii)}$$

Where "d" is spacing between capacitor plates, C is capacitance, ε° is free space permittivity, and "A" is the area of the sample between plates. The dielectric structure of ferrites consists of grains which are conductive and separated by the grain boundaries that are poor conductor. The real permittivity related to the electric field and describes how much energy store up in material by the response of electric field. The imaginary permittivity of the samples is the measure of dissipation of energy by the response to the AC field. The dielectric properties of $CO_xZn_{1-x}Fe_2O_4$ for x=0, 0.1, 0.4, 0.7, 0.9 and 1 were considered in different frequency ranges and investigate the effect of real and imaginary permittivity in response to different frequencies (logf) as shown in Fig.2 and Fig.3 respectively. Initially dielectric constant of all the samples increases with lowest value of frequencies but whenever frequency changes to higher value, gradually the value of dielectric constant shows decreasing trend and then constant. This may be due to the electronic exchange among cations that do not follow the higher frequencies of externally applied electric field. At different frequencies, real as well as imaginary permittivity with Co^{+2} concentrations was analyzed and it was found that the dielectric constant increases with increase in Co^{+2} concentrations.

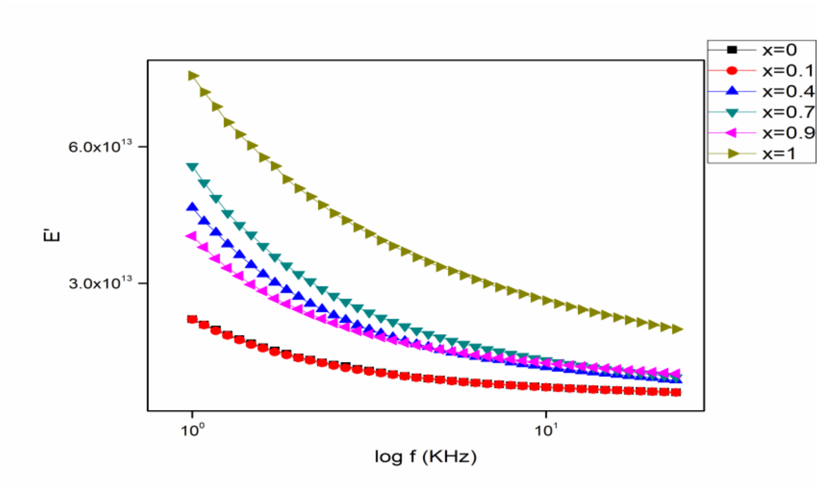

Figure 3: Real permittivity ε' with frequency

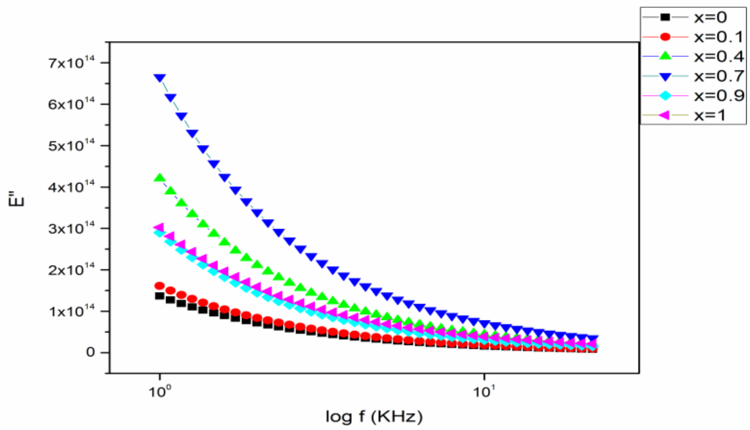

Figure 4: Imginary permittivity ε'' with frequency

As the frequency of the applied electric field increases, the electrons stuck up at grain boundaries that are non-conducting and lower the electron hopping between Fe^{+2} and Fe^{+3} ions, as a result of which the dielectric constant gradually decreases. The real and imaginary permitivity with Co concentration at different frequency ranges are shown in Fig.4 and Fig. 5 reveals an increasing behavior of Co concentration thats may be due to the configuration of Co^{+2} at octahedral sites which increases an electronic exchange between Co^{+2} and Co^{+3} and also due to the highest electronic polarization that may takes place between Co^{+2} and Co^{+3}.

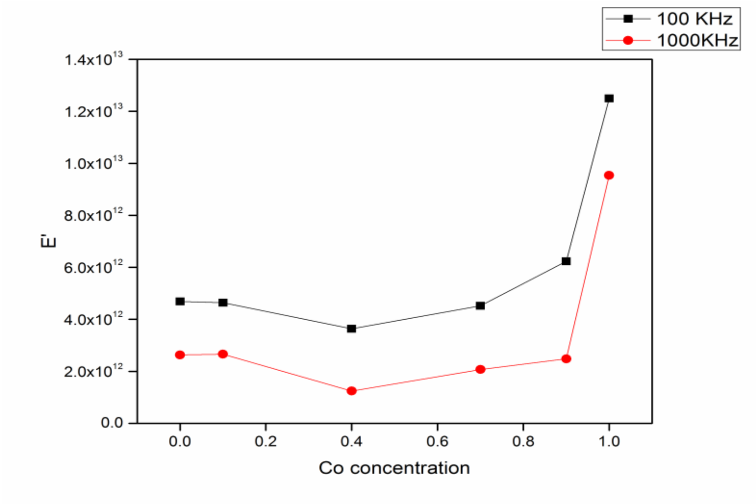

Figure 4: Real permittivity ε' with Co concentration

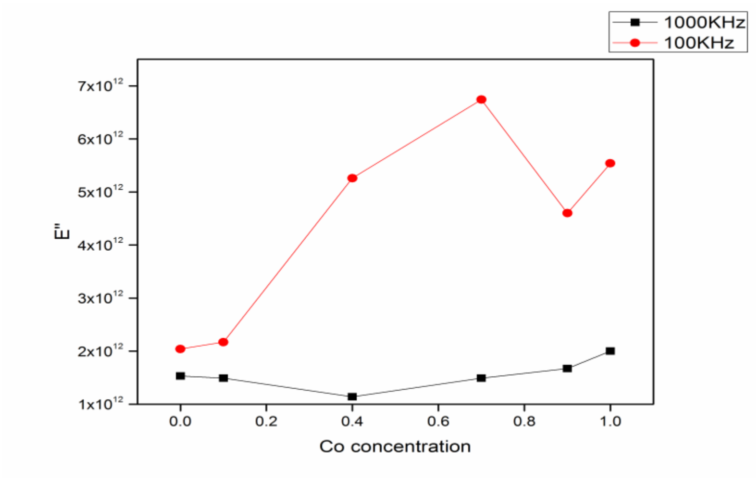

Figure 5: imginary permittivity ε'' with Co concentration

The dielectric loss tangent depends on the preparation technique and the composition of each sample because of the amount of nitrates; Fe^{+2} concentration and homogeneity etc. are all control the loss tangent. The tangent loss related to energy loss by the defects of dipoles, rotatory motion of diploes and the movement of grain boundaries by the reaction of external electric field. The maximum value of loss tangent looses huge amount of energy due to rotary motion of dipoles and the motion of domain wall, this manners only possible at low frequency (Fig. 6). But when frequency move to higher values, the movement of domain walls experience some resistance and change their location due to rotation. Rotation couldn't act in response to the electric field in result's the tiny amount of energy released at higher frequencies [10]. Ac conductivity calculated by the permittivity and loss tangent from equation;

$$\sigma = 2\pi f \varepsilon^{\circ} \varepsilon'' \ldots\ldots.. \text{(iii)}$$

The ac conductivity connected to conduction procedure in nano-ferrites, may occur between Co^{+2} to Co^{+3}. The conductivity of all the samples increases with increase in Co^{+2} concentration for the reason that Co^{+2} ions stoutly preferred to locate at the octahedral sites due to the fact Co^{+2} replaced the Fe^{+2} ions when substituted into ZnFeO [11] (Fig. 7).

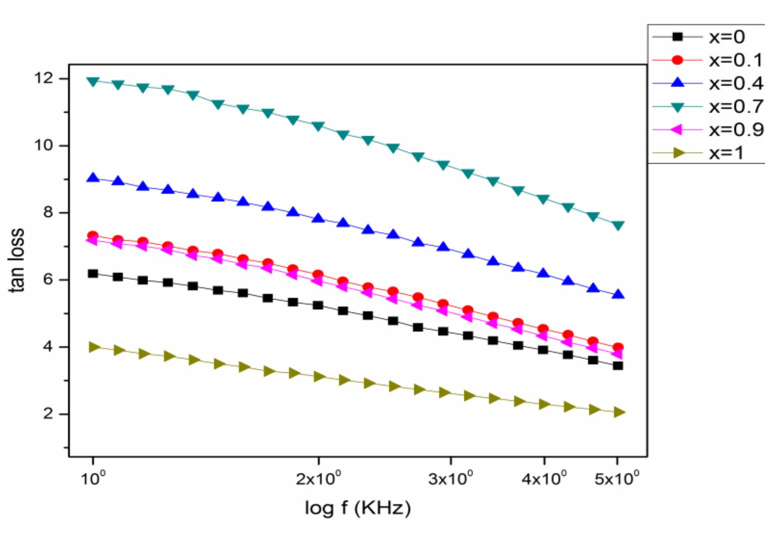

Figure 6: Variation of tangent loss with Freq.

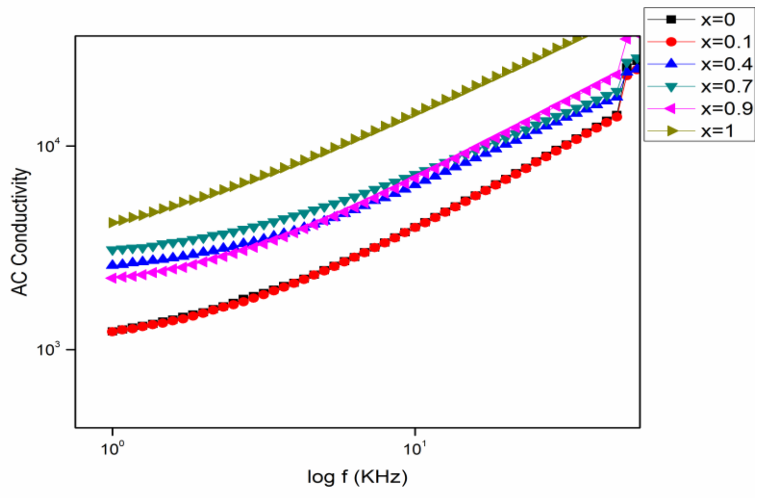

Figure 7: Variation of ac conductivity with Freq.

Conclusion

Sol-gel auto-combustion technique was utilized to prepare Cobalt substituted Zinc nano-ferrites, $CO_xZn_{1-x}Fe_2O_4$ (x=0, 0.1, 0.4, 0.7, 0.9, 1). The structural analysis was studied by XRD confirm the cubic spinel structure of $CoZnFe_2O_4$. The dielctric properties considered at room temperature in frequency range 1KHz-2MHz. Dielectric constant of each sample shows decreasing trend with incresing frequency while increase in Co^{+2} concentration increases ac conductivity. This trend may be due to maximum hopping of electrons from Fe^{+2} to Fe^{+3} which decreases the availability of Fe^{+2}. The dielectric loss depends upon the conduction losses and polarization in all samples. The tangent loss shows the decreasing tendency due to least amount of energy dissipation from the samples in the response of Co^{+2} substitution. Similarly the molecules in samples are in form of dipoles that tries to adjust themselves with action of electric field. When frequency increases, there is increase in ac conductivity.

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