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# COMPLEX PERMEABILITY AND DIELECTRIC BEHAVIORS OF $EU^{3+}$ DOPED NI-ZN FERRITES

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## ABSTRACT

The present work is focused on the influence of substitutions rare earth europium ions ($Eu^{3+}$) in soft poly crystalline Ni-Zn ferrites. A series of ferrite samples of the compositions $Ni_{0.60}Zn_{0.35}Eu_{0.05}Fe_2O_4$, $Ni_{0.60}Zn_{0.30}Eu_{0.10}Fe_2O_4$ and $Ni_{0.60}Zn_{0.25}Eu_{0.15}Fe_2O_4$ were prepared by using double sintering solid state reaction technique. The pre-sintering and sintering were performed at temperature $1000^0$C for 3 hours and $1250^0$C respectively. The phase identification was carried out by using the X-ray diffraction (XRD). The XRD analysis revealed that undoped rare earth in sample shows formulation of cubic spinel structure with no extra peak but $Eu^{3+}$ doped samples show additional peaks other spinel structure and corresponding to a second orthoferrite phase. A slightly increase in bulk density has been found with increasing RE content. The average grain size increases significantly with increasing $Eu^{3+}$ content. The increase in density and grain growth of the samples may be attributed to the liquid phase at constant sintering temperature. Saturation magnetization, $M_s$ was observed and was found to increase with increasing, $Eu^{3+}$ contents. $Eu^{3+}$ substitution in the Ni-Zn ferrites leads to increase of $Fe^{3+}$ ions on the B-sites and consequently decreases $Fe^{3+}$ ions on A-sites which lead to the increase in saturation magnetizations. The change of $M_s$ with the augmentation of $Eu^{3+}$ substitution has been explained on the Neel's Collinear two sublattices magnetization model and Yafet-Kittels' non-collinear magnetization model. It is observed that addition of the rare earth europium ions ($Eu^{3+}$) in polycrystalline Ni-Zn rare earth ferrites play an important role in modification of structural and magnetization characteristics.

**Contribution/ Originality:** The paper's primary contribution is finding that this can be used as magnetic materials for transformer due to the stability of permeability for a high frequency range. Moreover, by studying the literature it is seen that it can be used as anode or cathode materials for Lithium Ion Batteries (LIB).

## 1. INTRODUCTION

The addition of small amount of rare earth ions to ferrite samples producing a change in their magnetic and electrical as well as structural properties depending upon the types and the amount of rare earth elements used. The rare earth substituted different ferrites are becoming the promising materials for different applications.

The development of high frequency ferrites was initiated by the work done by Snoek [1] who found that associated with excellent properties in the high frequency range. The spinel ferrites like Ni-Zn, Mg-Zn and Mg-Mn

ferrites are suitable for using in pulse transformers, inductances, reflection coils, antennas and modulators etc. Murty and Vishwanathan [2] due to their excellent electrical and magnetic properties at high frequency ranges. The most popular combinations are Ni-Zn [3] Ni-Cu-Zn [4-6] Mg-Zn [7] and Mg-Cu-Zn [8, 9] ferrites.

In high frequency application Ni-Zn ferrites became an important candidate to use due to their high electrical resistivity, high permeability, compositional stability and low eddy current losses [10, 11]. Many researchers reported the structural, magnetic and electrical properties of Ni-Zn ferrites of different combinations in bulk [12-18] forms.

In this work, the attempt was made to the complex permeability and dielectric properties of rare earth $Eu^{3+}$ substituted $Ni_{0.60}Zn_{0.40-x}Eu_xFe_2O_4$ (x =0.05 0.10 and x = 0.15) spinel ferrites and it was prepared by Standard Ceramic Method. These compositions could be used for technological applications.

Finally, we used powder particles as starting materials whose uniform microstructure exhibiting better magnetic and electrical transport properties. With the substitution of rare earth metals in the Ni-Zn ferrite system permeability and dielectric properties are improved. Thus this system can be used for good technological application in high frequency range. In our research in soft magnetic materials and in rare earth metal doped ferrites, Bangladesh may develop a profitable electronic industry.

## 2. MATERIALS AND METHODS

The initiating materials for the preparation of the studied composition of Ni-Zn ferrites were in the form of powder oxides [$Fe_2O_3$, NiO, ZnO and $Eu_2O_3$,] of In Framat Advance Materials USA. The purity of our materials is up to 99.9%. The reagent oxide powders where weighted precisely according to their molecular weight. In the present research several compositions of RE (Eu) substituted ferrites are synthesized, characterized and investigated. The ferrites under investigation are:

(i) $Ni_{0.60}Zn_{0.35}Eu_{0.05}Fe_2O_4$

(ii) $Ni_{0.60}Zn_{0.30}Eu_{0.10}Fe_2O_4$ and

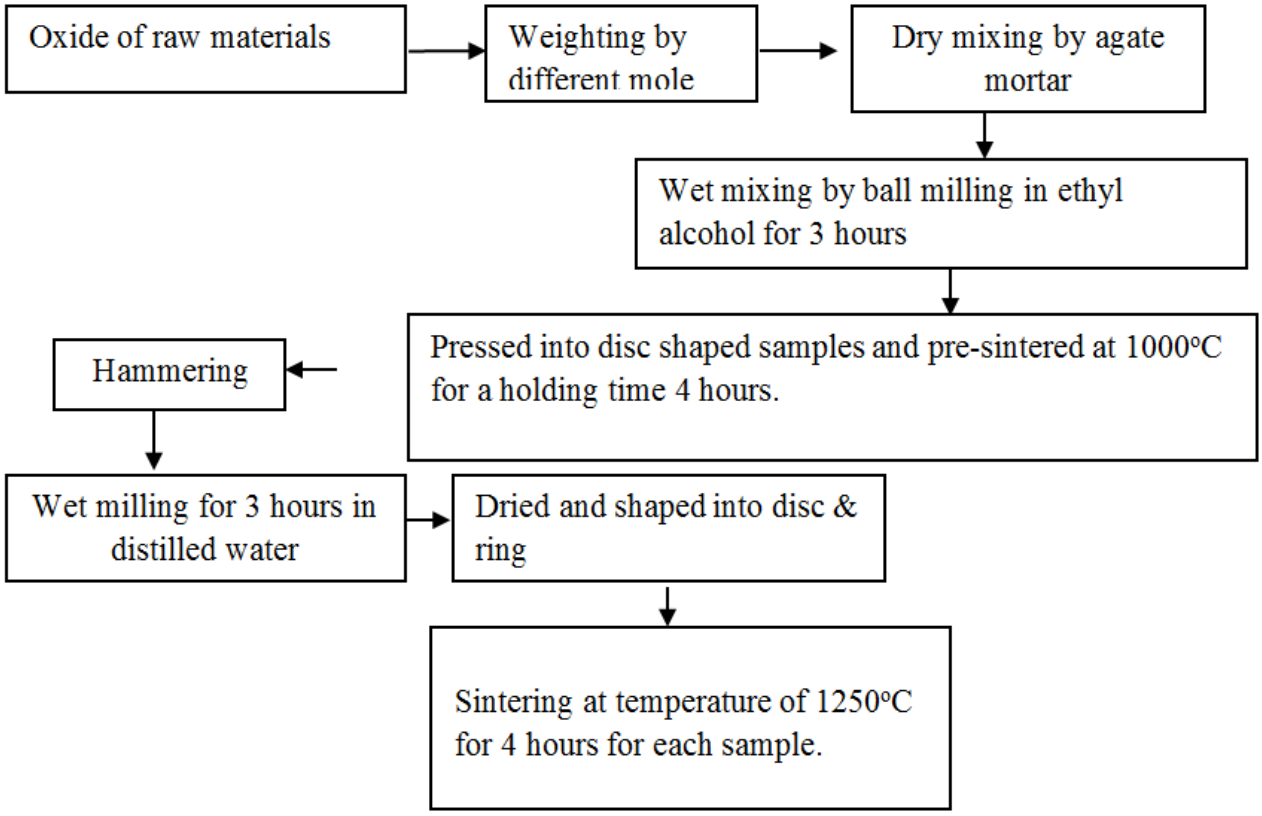
(iii) $Ni_{0.60}Zn_{0.25}Eu_{0.15}Fe_2O_4$

The weight percentage of the oxide to be mixed for various samples was calculated by using formula:

$$\text{Weight \% of oxide} = \frac{M.wt \cdot of\ oxide \times required\ \ weight\ of\ the\ sample}{Sum\ of\ Mol.wt.of\ each\ oxide\ in\ a\ sample}$$

Different metal and rare earth metal oxides are mixed and calcined to get ferrite powders in Solid State Reaction Technique. However mechanical mixing of different oxides is hardly intimate and homogeneous and hence its results in composition fluctuation at every stage of processing that also persist after sintering [19]. Solid state process requires calcinations temperature more than $600^0$C for phase formation and sintering temperature more than $1000^0$C to achieve better densification. This high sintering temperature evaporation of Zn leads to the formation of chemically inhomogeneous material [20]. The ferrite is not completely defined by its chemistry and crystal structure but also requires knowledge and control of parameters of its microstructure such as grain size, porosity, intra and intergranular distribution.

The following block diagram in represents the method employed for the rare - earth ferrites:




## 3. RESULTS AND DISCUSSION

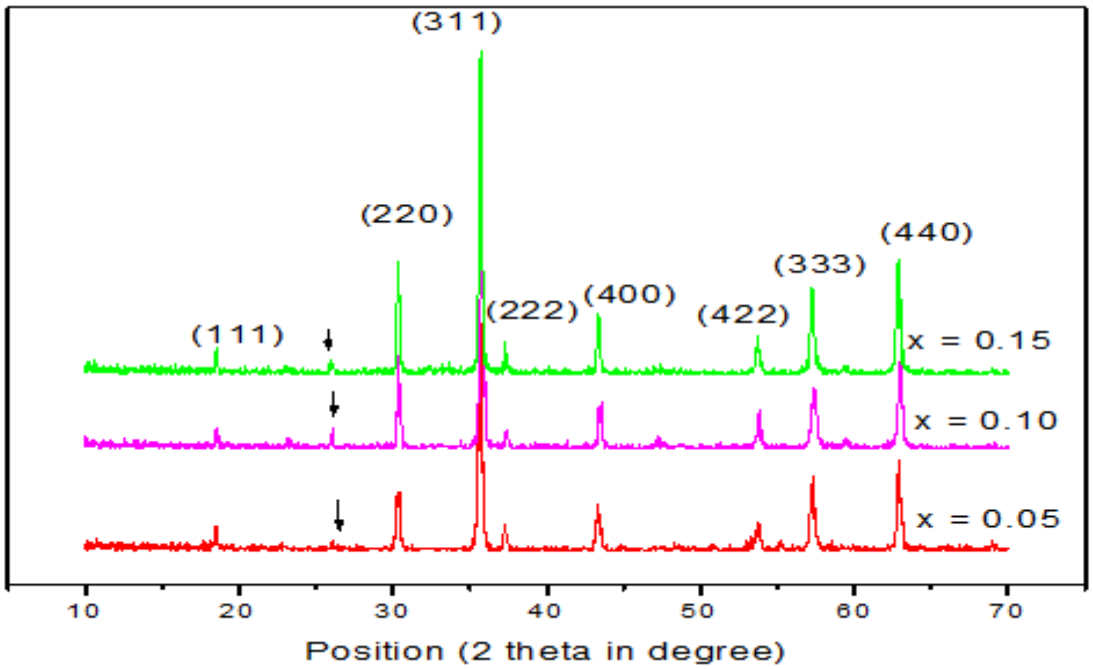



**Figure-1.** X-ray diffraction patterns of $Ni_{0.60}Zn_{0.40-x}Eu_xFe_2O_4$ [x = 0.05, 0.10 and 0.15] ferrites sintered at 1250°C/3hrs. PHILIPS X' Pert PRO X-ray diffractometer Atomic Energy Center Dhaka, Bangladesh

XRD patterns are demonstrated in the Figure-(b) for $Eu^{3+}$ doped samples of $Ni_{0.60}Zn_{0.40-x}Eu_xFe_2O_4$[x = 0.05, 0.10 and 0.15] ferrites sintered at 1250° C for 3 hrs. It is clearly noticed that with $Eu^{3+}$ doped samples additional peaks other than spinel structure and probably corresponding to a second phase of $EuFeO_3$ (Ortho ferrite) shown in Figure-1. Determination of exact phase could not be possible, since the number of extra peaks other than spinel is

not sufficient for accurate analysis. XRD analysis evidenced that the compounds containing $Eu^{3+}$ions are pluri-phasic. Rare earth is formed orthoferrite ($REFeO_3$) phase and the formation of these secondary phases in ferrite during sintering process was governed by the type and the amount of $RE^{3+}$[ $Eu^{3+}$] ions used.

The lattice parameter decreases with increasing Europium contents obeying Vagard's law. The bulk density is lower than the actual density of the sample. Bulk density is decreasing slowly with increasing $Eu^{3+}$. The porosity of the Ni-Zn-RE samples decreases with increasing $Eu^{3+}$ contents.

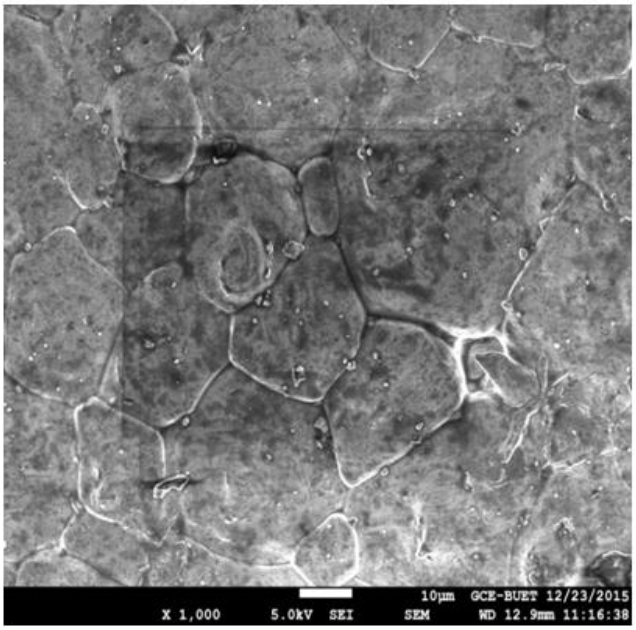



**Figure- 2(b):** x = 0.0

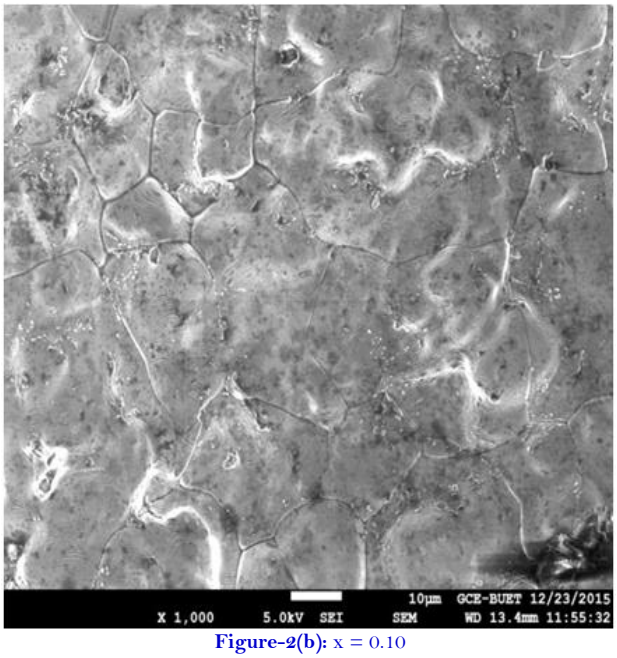



**Figure-2(b):** x = 0.10

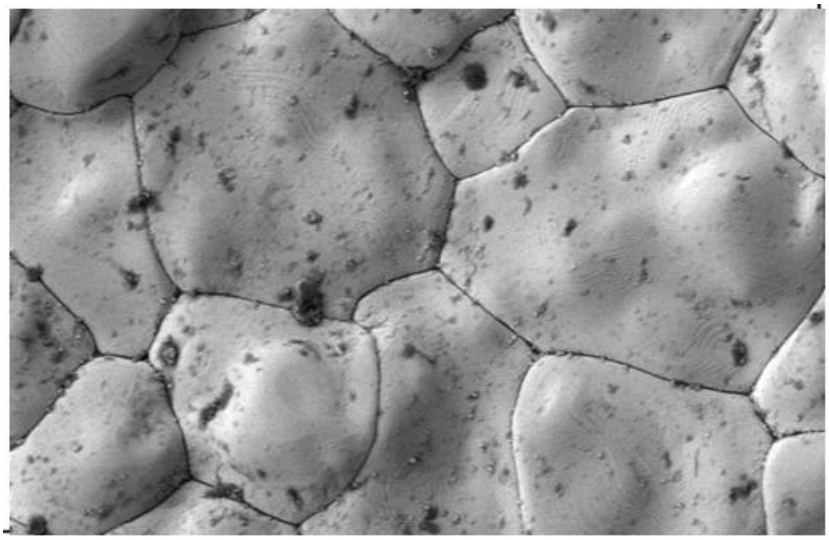


**Figure-2(b):** x = 0.15

**Figure-2 a,b and c).** Variation of SEM photographs with Eu content (x) of $Ni_{0.40}Zn_{0.40-x}Eu_xFe_2O_4$ ferrites whose x = 0.05, 0.10 and 0.15 sintered at 1250$^0$C/3 hrs. Scanning Electron microscope (SEM), Atomic Energy Center, Dhaka, Bangladesh.

Microstructure significantly affects the magnetic and electrical properties of ferrites. Figure - (a, b and c) shows the SEM microstructure of $Ni_{0.60}Zn_{0.40-x}Eu_xFe_2O_4$ferrites sintered at 1250$^0$C/3hrs. It is clear that the microstructure of Ni-Zn-Eu content in the samples. As the Eu content increases, the grain size increases gradually. It is also noticed from the microstructure that with increasing Eu-content grain grows bigger. This reflected in the

permeability also increase with Eu content. Since permeability is directly proportional to grain size D and $M_s$ which also increase with increasing $M_s$

$$\text{i.e. } \mu_i \propto \frac{M_s^2}{\sqrt{K_1}} D$$

The increase in grain size with Eu-content is clearly visible. Figure-(a, b and c) shows a biphasic microstructure constituted of a matrix of grains of a second phase ($EuFeO_3$). Energetically, small grains are less stable than large grains due to their higher specific surface areas. As a consequence, liquid phase layers would be dissolved in the liquid phase layers. It is observed that an increase in the amount of Eu (x = 0.15) content result in an increase in the coverage of the grains by the $EuFeO_3$ phase and this is beneficial to grain growth.

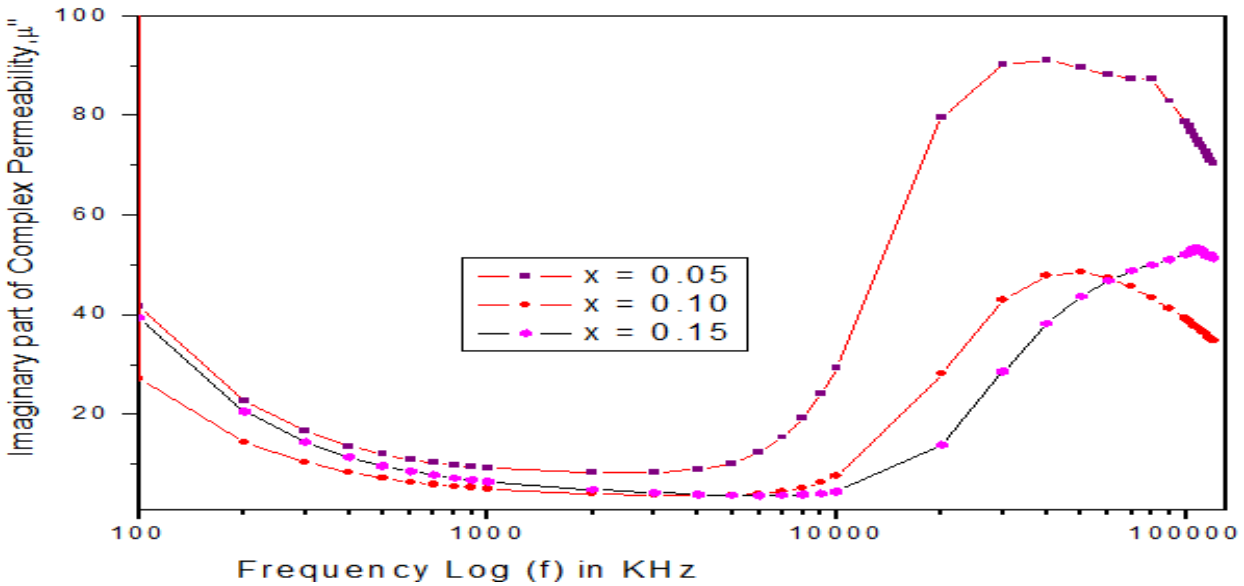



**Figure-3.** Complex imaginary permeability μ" with frequency of $Ni_{0.60}Zn_{0.40-x}Eu_xFe_2O_4$ [x = 0.05, 0.10, 0.15] ferrites sintered at 1250°C/3hrs. Impedance Analyzer Model-Hewlett-Packard 4192A, Atomic Energy Center, Dhaka, Bangladesh.

The complex permeability is given by $\mu = \mu' - i\mu''$, $\mu'$ is the real permeability (in phase) and $\mu''$ the imaginary permeability (90° out of phase). Complex permeability has been determined as a function of frequency, f up to 100 MHz at room temperature for all the samples of series [$Ni_{0.40}Zn_{0.40-x}RE_xFe_2O_4$ (RE = Eu and x= 0.05, 0.10 and 0.15] ferrites by using the conventional technique based on the determination of the complex impedance of circuit loaded with toroid shaped sample.

The imaginary part of μ" gradually increased with the frequency and attain a broad maximum at a certain frequency whose the real part of permeability rapidly decreased. The initial permeability μ' decreases with increasing rare earth content Eu, which is consistent with the decrease in density with Zn-content.

The initial permeability of the composition $Ni_{0.40}Zn_{0.40-x}Eu_xFe_2O_4$ [x = 0.05, 0.10 and 0.15] are stable within the range 20 to 40 MHz [17] the maximum frequency limit of the instrument. Figure 3 shows, the imaginary component μ" first rises slowly and then increases quite abruptly making a peak at a certain frequency where the real component μ' is falling sharply [17]. This feature is well known as the ferromagnetic resonance [21]. At high frequencies where the μ" parameters become more significant, the inductors show high impedance and become resistive and dissipate interfering signals rather than reflecting these to the source [22]. When frequency is low, permeability is high and when frequency is high permeability is low. Thus, an effective limit of product of frequency and permeability is established. So, that effect of rare earth content of high frequency and high permeability are mutually incompatible.

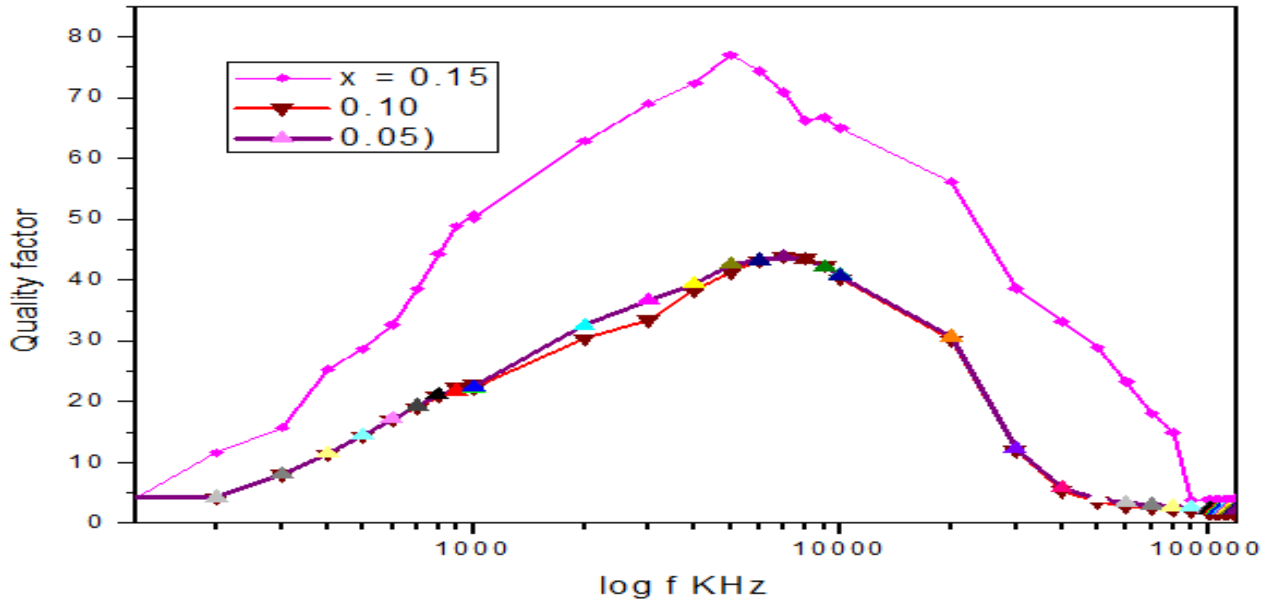



**Figure-4.** Variation of relative quality factor, as a function of frequency of $Ni_{0.60}Zn_{0.40-x}Eu_xFe_2O_4$ [X = 0.05, 0.10 0.15] ferrites sintered at 1250°C/3hrs. Impedance Analyzer Model-Hewlett-Packard 4192A, Atomic Energy Center, Dhaka, Bangladesh.

The frequency dependence of $Ni_{0.60}Zn_{0.40-x}RE_xFe_2O_4$ [RE = Eu] ferrites sintered at 1250°C/3hrs have been calculated from the relation Q = 1/ tanδ; where tanδ is the loss factor is used to measure the merit of the magnetic materials. Figures -5 shows the frequency dependence quality factors (Q-factors) of sample is $Ni_{0.60}Zn_{0.40-x}Eu_xFe_2O_4$(x = 0.05, 0.10 and 0.15) sintered at 1250°C for 3 hours respectively. Q-factor increases with an increase of frequency showing a peak and then decreases with further increase of frequencies. It is seen that Q-factor again deteriorates beyond 4MHz for Eu i.e. the loss tangent is minimum around 1 to 4MHz. The loss is due to the loss of domain wall motion with respect to the applied alternating magnetic field and is attributed to various domain defects which include non- uniform and non repetitive domain wall motion, domain wall bowing, and localized variation of flux density, nucleation and annihilation of domain walls.

The peak corresponding to maxima in Q-factor shifts to lower frequency range for Eu is significantly low. Sample with x = 0.15 possesses the maximum value of Q-factor for all the samples of Eu. The low frequency dispersions are associated with domain wall dynamics and high frequency to spin rotation.. This phenomenon is associated with the ferromagnetic resonance within the domains and at the resonance maximum energy is transferred from the applied magnetic field to the lattice resulting in the rapid decrease in Q-factor. Ni-Zn-Eu ferrites have been found to demonstrate reasonably good permeability at room temperature covering stable wide range of frequency indicating the possibilities for applications as high frequency up to several MHz induction and/or core materials. These mean that Ni-Zn-RE (Eu) ferrite materials are suitable for high frequency applications with high permeability.

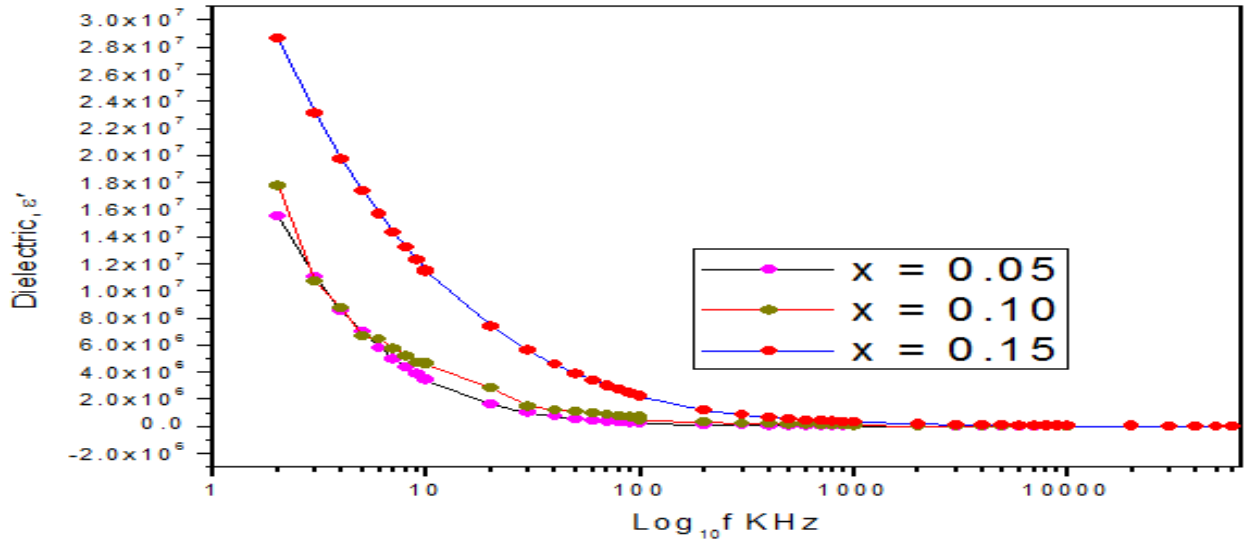



**Figure-5.** Dielectric constant as a function of frequency of the ferrite system of $Ni_{0.40}Zn_{0.40-x}Eu_xFe_2O_4$ [x= 0.05, 0.10 and 0.15] ferrites sintered at 1250°C/3hrs.

Figure -5 shows the variation of dielectric constant, ε' with frequency for different composition of $Ni_{0.60}Zn_{0.40-x}Eu_xFe_2O_4$ where x =0.05, 0.10, 0.15) ferrites sintered at 1250°C/3hrs for 1MHz to 100MHz at room temperature. It can be seen from the figure that the dielectric constant is found to decrease continuously with increasing frequency for all the specimens exhibiting a normal dielectric behavior of ferrites. The dielectric dispersion is rapid at lower frequency region and it remains almost independent at high frequency side. The incorporation of rare earth element Europium (Eu) into these ferrites has no pronounced effect on the dielectric constant in high frequency, but significantly decreases the dielectric constant in the low frequency range.

The dielectric behavior of ferrites may be explained on the basis of the mechanism of the dielectric polarization process and is similar to that of the conduction process. The electronic $Fe^{2+} \leftrightarrow Fe^{3+}$ gives the local displacement of electrons in the direction of applied electric field, which induces the polarization in ferrites [ ]. The magnitude of exchange depends on the concentration $Fe^{2+}/Fe^{3+}$ in pairs present on B-site for the present ferrite. All the samples have high value of ε/ in the order of $10^5$ at low frequencies. This could be explained using Koop's phenomenological theory [4.24] which was based on the Maxwell-Wagner model for the inhomogeneous double layer dielectric structure. The first layer is the fairly well conducting large ferrite grain which is separated by the second thin layer of the poorly conducting grain boundaries. The grain boundaries of the lower conductivity were found to be ferrite at lower frequencies while ferrite grains of high conductivity are effective at high frequency.

## 4. CONCLUSION

The XRD patterns confirmed the Ni-Zn ferrite sample is spinel cubic and the $Ni_{0.60}Zn_{0.40-x}RE_xFe_2O_4$ [RE= Eu and x =0.05, 0.10, 0.15] ferrites are pluriphasic (cubic and orthorhombic).Y doped Ni-Zn-Y ferrites are biphasic homogeneous microstructure constituted of dark ferrite matrix grains and small whitish grain at the grain junction. The initial permeability for Ni-Zn-Y ferrite remains constant up to 10-30MHz and the broad maximum also takes place at the frequency range 10-30 MHz.

The saturation magnetization increases with increasing the RE [Eu] by replacing the nonmagnetic Zn content in Ni-Zn-RE ferrites. RE substitution in the Ni-Zn-RE ferrites leads to increase of $Fe^{3+}$ ions on the B-sites and consequently decreases $Fe^{3+}$ ions on A-sites. Substitution rare earth in ferrites has been used as attractive approaches to enhance the electromagnetic properties.

Dielectric constant $\varepsilon'$ decreases with increasing frequency exhibiting normal dielectric behavior of Ni-Zn-RE [Y] ferrites. The dielectric dispersion is rapid at lower frequency region and remains almost independent at high frequency. The dielectric behavior of ferrites may be explained on the basis of the mechanism of the dielectric polarization process and is similar to that of the conduction process.

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