Journal of Engineering Science 10(2), 2019, 79-84

JES
an international Journal

STUDY OF THE INFLUENCE OF LANTHANUM (La) SUBSTITUTION ON THE STRUCTURAL AND TRANSPORT PROPERTIES OF Cu-Zn FERRITE ($Cu_{0.15}Zn_{0.85}La_xFe_{2-x}O_4$) SYNTHESIZED BY SOLID STATE REACTION TECHNIQUE

Kamrun Nahar[1], Probal Roy[1]*, M. A. Hossain[1], S. D. Nath[1], M.N. I. Khan[2] and S. S. Sikder[1]

[1]*Khulna University of Engineering & Technology, Khulna – 9203, Bangladesh*
[2]*Materials Science Division, Bangladesh Atomic Energy Centre, Dhaka-1000, Bangladesh*

Received: 08 July 2019 Accepted: 12 November 2019

ABSTRACT

The effect of doping of rare earth material like Lanthanum (La) in various concentrations on polycrystalline Cu-Zn ferrite has drawn attention for their drastically variable nature. Expected $Cu_{0.15}Zn_{0.85}La_xFe_{2-x}O_4$ [x = 0.00, 0.02, 0.04, 0.06 and 0.08] were prepared by conventional solid state reaction method that was sintered at1150°C for 3 hours. The XRD patterns confirmed the formation of fcc type cubic spinel structure with a weak reflection peak that corresponded to the presence of secondary ortho-ferrite phase. The frequency dependent real part permeability of all the samples decreased at high frequency range. The quality factor showed the increasing tendency with the increase of frequency. The dielectric constant (both the real and imaginary part) indicated the trend of decreasing with the increase of frequency. The dielectric constant was studied on the basis of dielectric polarization and conduction theory. The temperature dependent DC resistivity presented the trend of increasing with the increase of both temperature and La content.

Keywords: *Synthesis; XRD; Permeability; Dielectric constant; Resistivity*

1. INTRODUCTION

In recent days, Polycrystalline ferrites have become a topic of engrossment due to their drastically applications in the field of research areas as well as in various applications. Their overwhelming electrical and magnetic properties make their applications widen in our practical life. Among them high resistivity, high permeability, low magnetic loss, thermodynamic stability, chemical stability, mechanical hardness, low cost etc are significant. These properties are responsible for the wide applications of polycrystalline ferrites for microwave devices, various transformers and electric generator storage devices (Gubbala *et al.*, 2004; Kulikowshi *et al.,* 1984). Their acceptable dielectric properties and good electrical conductivity are also providing their wide applications in radio wave and microwave frequency devices. Their electrical and transport properties provide a lot of information for which they are selected in various electronic and semiconducting devices (Shahida Akhter *et al.,* 2013).

In the last two decades, a remarkable development occurred in wireless technology as well as in the mass telecommunication technology. Internet accessible smart phones, high speed accessible local network etc are the suitable examples of that development. These system cores are based on the radiofrequency circuits (RF). These RF circuits include transmission and receiving parts that are important for signal amplification, modulation and filtering process. These transmissions and receiving blocks are the complex circuits that have a lot of capacitors and inductors. These inductors are now a day developed as multilayer chip inductors (MLCIs). These MLCIs are now developed by using various polycrystalline ferrite materials (Batoo *et al.,* 2012).

Basically, the variations of the properties of polycrystalline ferrites are responsible for their structural properties, Synthesis technique, chemical composition, types of impurity doping, sintering temperature etc. The super exchange interaction of Fe^{3+} in A-site (Tetrahedral) and B-site (Octahedral) are widely responsible for these outstanding electrical, magnetic and mechanical properties (Gupta *et al.*, 1968; Lange *et al*, 1989; Kigery *et al*., 1975; Ahmed *et al.*, 2003). Variation of any of these parameters can responsible for this super exchange interaction of Fe^{3+} ion in A-site and B-site. This is directly responsible for the remarkable changes in electrical, magnetic and mechanical properties of the specimens.

A remarkable of polycrystalline ferrite is Cu-Zn ferrite which has drawn attention due to their physical and chemical stability, ferromagnetic attitude, reasonable saturation magnetization and for their applications. It is found that, smallest substitution of Fe^{3+} ion by various materials especially rare earth materials improve the structural, magnetic and transport properties of the materials remarkably (Chen *et al.*, 2000). Thus, the doped materials will be possible to obtain an affable position in industrial and experimental applications.

*Corresponding Author: probalroy@phy.kuet.ac.bd
https://www2.kuet.ac.bd/JES/

ISSN 2075-4914 (print); ISSN 2706-6835 (online)

The aim of this research is to discuss the synthesis of La doped Cu-Zn ferrite with composition $Cu_{0.15}Zn_{0.85}La_xFe_{2-x}O_4$ [x = 0.00, 0.02, 0.04, 0.06 and 0.08] and to study the La doping effect on the structural properties, frequency tuned permeability and dielectric constant of the samples.

2. EXPERIMENTAL

To prepare $Cu_{0.15}Zn_{0.85}La_xFe_{2-x}O_4$ [x = 0.00, 0.02, 0.04, 0.06 and 0.08] samples, Conventional solid-state reaction method was followed where the reactant metallic oxide powdered materials are required to be taken for reaction. Solid state reaction method is basically occurring when the reactant has regular crystal lattices and also has the restricted kinetic motion (Nelson *et al*, 1985). In this method, appropriate amount of powder samples is required for grinding, hand milling, calcination and sintering sequentially.

In this study, analytical grade powder of CuO, La_2O_3, ZnO and Fe_2O_3 were mixed for hand milling operation for 6 hours in a ceramic mortar. Basically, solid oxides never use to react together at room temperature maintaining normal time scale. To form reaction as well as to form crystalline phase, it's mandatory to provide heat treatment. To form crystalline phase, the calcination for all the samples were done at 800°C for 3 hours so that reaction can take place. The calcined samples were then crashed to prepare tablet and ring-shaped samples by using hydraulic press to apply uniaxial pressure. Then the sintering was done at 1150°C for 3 hours. After sintering, the structural phenomena of the specimens were carried out by X-ray diffraction pattern for both as-dried samples and for La doped samples using Philips X'pert Pro powder X-ray diffractometer (PW 3040). The transport properties were observed by using Wayne Kerr Precision Impedance analyzer (6500B) in the solid state physics laboratory of KUET.

3. RESULTS AND DISCUSSIONS

3.1 Structural Analysis

The structural view of La dope on the composition $Cu_{0.15}Zn_{0.85}La_xFe_{2-x}O_4$ [x = 0.00, 0.02, 0.04, 0.06 and 0.08] are expressed in the XRD pattern that are presented in Fig 1. The X-ray powder diffraction was done by Cu-K_α (λ = 1.54Å) radiation. The result is found from the X-ray diffraction pattern for all samples of Cu-Zn ferrite with the (hkl) values corresponding to the diffraction peaks of different phase on (111), (220), (311), (222), (400), (422), (333) and (440) which are either even or odd that confirms the evolution of fcc type spinel structure (Shil *et al.*, 2013; Sharmin Akhter *et al.*, 2019; Vucinic-Vasic *et al.*, 2013). Moreover, for the samples of x = 0.02, 0.04, 0.06 and 0.08 respectively, a weak reflection peak can be seen. This peak is identified as the weak reflection peak of the $LaFeO_3$ phase.

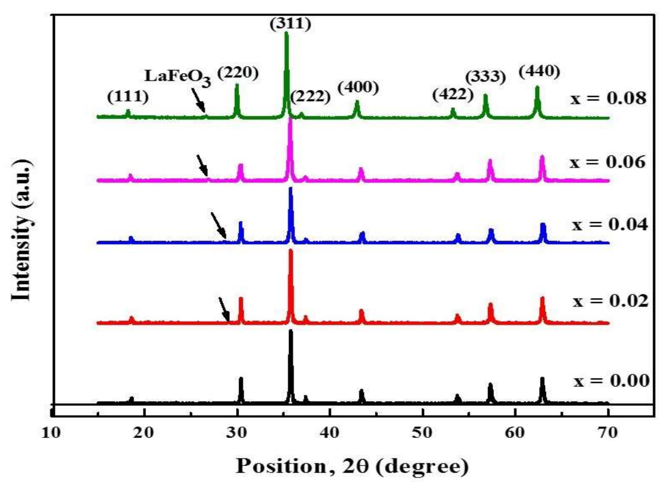

Figure 1: XRD patterns for the $Cu_{0.15}Zn_{0.85}La_xFe_{2-x}O_4$, [x = 0.00, 0.02, 0.04, 0.06 and 0.08] sintered at 1150°C for holding time of 3 hours.

Various structural parameters such as Lattice parameter (a), X-ray density (ρ_x), bulk density (ρ_B), and porosity (P) are also studied. The lattice parameter "a" for all the specimens were calculated by following formula (Roy *et al.*, 2018),

$$a = d_{hkl} \times \sqrt{h^2 + k^2 + l^2} \quad (1)$$

The calculated values of the above mentioned parameters of the samples are presented in Table 1. It has been seen here that, with the increasing La content, Lattice parameter has a trend of decreasing initially and then increases. The Bulk density and X-ray density have the tendency of remaining almost same for all samples. The porosity presents the increasing phenomenon with the increasing La content. It can be observed that, the values of bulk density are lower than the values of X-ray density. The existence of pores that may be formed during the time of synthesis and sintering process are probably responsible for that observation. The Bulk density and X-ray density were found by using the following formulas

$$d_B = \frac{m}{V} = \frac{m}{\pi r^2 h} \quad (2)$$

and $$d_x = \frac{8M}{na^3} \quad gm/cm^3 \quad (3)$$

Table 1: Data of the lattice parameter (a), X-ray density (ρ_x), bulk density (ρ_B), porosity (P %) of $Cu_{0.15}Zn_{0.85}La_xFe_{2-x}O_4$, [x=0.00, 0.02, 0.04, 0.06 and 0.08] ferrites sintered at 1150°C for 3 hours

Compositions	'a' in (Å)	Bulk density ρ_B (gm/cm^3)	X-ray density ρ_x (gm/cm^3)	Porosity P (%)
$Cu_{0.15}Zn_{0.85}Fe_2O_4$	8.266	4.99	5.55	9.92
$Cu_{0.15}Zn_{0.85}La_{0.02}Fe_{1.98}O_4$	8.258	4.91	5.58	11.87
$Cu_{0.15}Zn_{0.85}La_{0.04}Fe_{1.96}O_4$	8.257	4.88	5.7	14.33
$Cu_{0.15}Zn_{0.85}La_{0.06}Fe_{1.94}O_4$	8.275	4.88	5.69	14.18
$Cu_{0.15}Zn_{0.85}La_{0.08}Fe_{1.92}O_4$	8.360	4.88	5.65	13.58

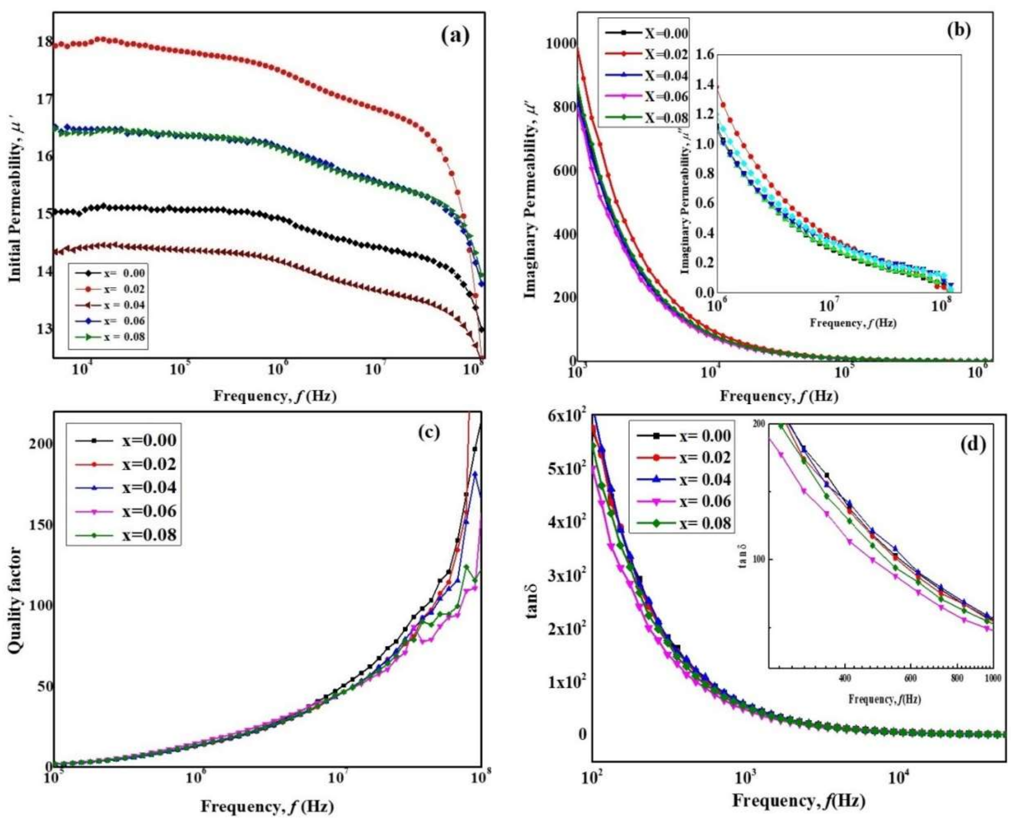

Figure 2: The frequency dependent (a) Real part of complex permeability, (b) Imaginary part of complex permeability, (c) Loss factor and (d) Quality factor of $Cu_{0.15}Zn_{0.85}La_xFe_{2-x}O_4$, [x = 0.00, 0.02, 0.04, 0.06 and 0.08].

3.2 Permeability Observation

The magnetic permeability under an oscillatory electric field can be represented by the following formula,

$$\mu = \mu' - i\mu'' \quad (4)$$

Where μ' and μ" stand for real part of complex permeability and imaginary part of complex permeability respectively (Torikul Islam *et al.*, 2014). Here, the real part of the frequency dependent permeability is tuned by some factors such as the reversibility of domain wall displacement, the category and the quantity of dopant ion, porosity etc. The permeability data was taken at room temperature maintaining wide range of frequency form 1 KHz to 120MHz. For the toroid shaped samples of $Cu_{0.15}Zn_{0.85}La_xFe_{2-x}O_4$ [where x = 0.00, 0.02, 0.04, 0.06 and 0.08] sintered at 1150ºC holding time 3hours various parameters of complex permeability including μ', μ" and Quality factor were determined as a function of applied frequency by using the Wayne Kerr Impedance analyzer. All these variations are shown in the Figure 2.

It is seen here that, the real portion of the complex permeability μ' is almost constant for a certain frequency range and then it starts to fall rapidly within a lower range of higher frequency. The hopping electron transfer between Fe^{2+} and Fe^{3+} is significantly responsible for the stability of μ' initially. With the increasing of frequency, the imaginary part, μ" slowly decreasing and reached a minimum frequency. At low frequency zone for all samples μ" remains initially high and then decreases with the increasing of frequency and remains almost constant. Thus, the mutual mismatching can be found on the effect of rare earth content of high frequency and high permeability.

The loss factor tanδ (= μ″/ μ′) which represent the losses in the material as well as indicates the inefficiency of materials magnetic system. The magnetic losses cleave up into three components. These are hysteresis losses, losses of eddy current and residual losses. This can be written by the following formula, $\tan\delta_m = \tan\delta_h + \tan\delta_e + \tan\delta_r$. Value of tanδ is less frequency dependent in the frequency range from ≥ 10MHz. Cu-Zn-La ferrites are found to show reasonably affable permeability at room temperature that cover wide range of stable frequency which can be used for MLCF application, such as embedded inductors or embedded capacitors. These mean that Cu-Zn-La ferrite materials exhibits suitability for high frequency applications with high permeability. The quality factor for all sample show the trend of increasing with the increase of frequency. Initially the Q-factor increases with very low value but at higher value of frequency, it presents the drastically increasing phenomenon.

3.3 Dielectric properties observation

The frequency dependent dielectric studies that include both real part dielectric study and imaginary part dielectric study are shown in figure 3. It can be seen that the dielectric constant falls constantly with the increase of frequency for all the specimen. With the addition of La, these ferrites have no prominent effect on the dielectric constant in the range of high frequency, but at low frequency range a radical decrease of dielectric constant can be found. The dielectric behavior for this sample can be described on the basis of the mechanism of polarization process in ferrites which is similar to that of conduction. The electron exchange process of $Fe^{2+} \leftrightarrow Fe^{3+} + e-$ is responsible for local displacement of electrons in the direction of an applied electric field, which creates polarization in ferrites (Zhenxing *et al.*, 2001). With increasing frequency, the imaginary portion of dielectric constant, ε" also decreases. At very high frequency the value of ε" becomes too small that it remains independent of applied frequency.

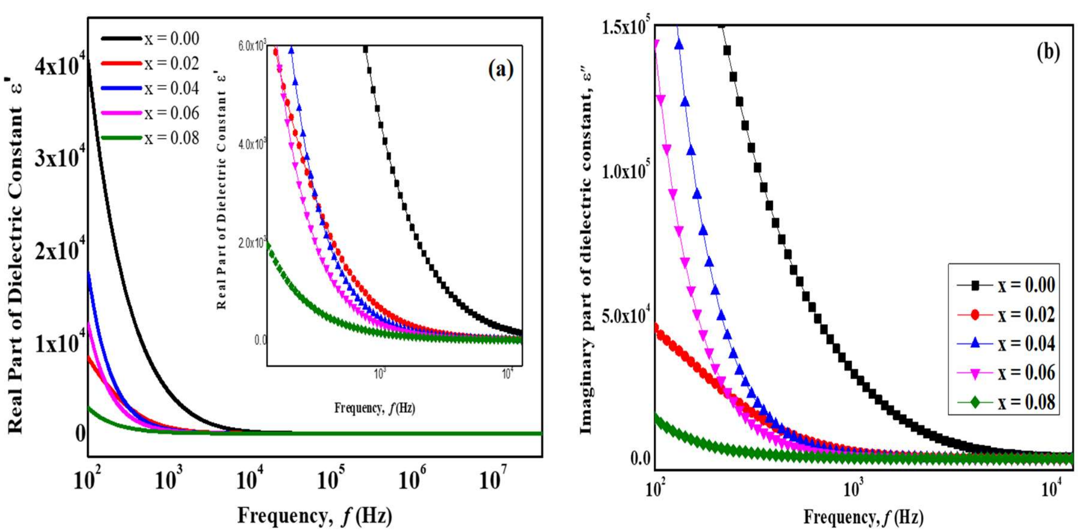

Figure 3: The frequency tuning (a) Real part, (b) Imaginary part of dielectric constant of $Cu_{0.15}Zn_{0.85}La_xFe_{2-x}O_4$, [x = 0.00, 0.02, 0.04, 0.06 and 0.08].

3.4 DC resistivity observation

The variation of DC resistivity as a function of La content in Cu-Zn ferrites is shown Figure 4. With increasing La content except for x = 0.00 sample the electrical DC resistivity increases from 9 MΩ-cm to 12MΩ-cm. This is because La is more resistive than Fe where the values of the resistivity of La and Fe are 61.5×10^{-8} Ω-m and 9.71×10^{-8} Ω-m respectively (Ghazanfar *et al.,* 2005). For individual samples, the resistivity with the increase of temperature is also shown in Figure 4(b). Here, with the increase of temperature, resistivity increases linearly.

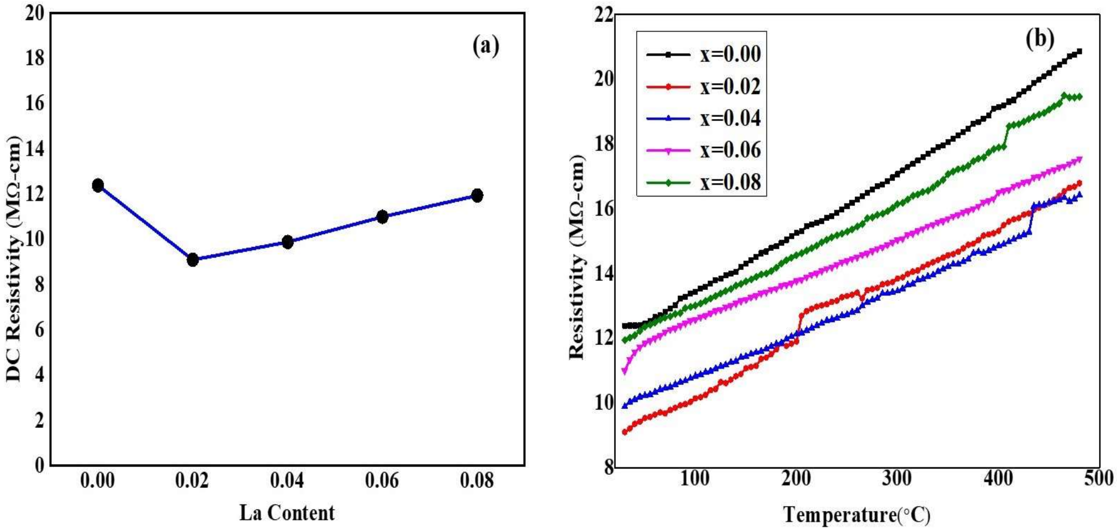

Figure 4: (a) Variation of DC resistivity with La content, (b) Temperature dependence DC resistivity of $Cu_{0.15}Zn_{0.85}La_xFe_{2-x}O_4$, [x=0.00, 0.02, 0.04, 0.06 and 0.08].

4. CONCLUSIONS

In this study, the effect of the substitution on the rare earth materials like Lanthanum (La) on Cu-Zn ferrite with various concentrations provides the following consequences:

i. The samples with formula $Cu_{0.15}Zn_{0.85}La_xFe_{2-x}O_4$, [x=0.00, 0.02, 0.04, 0.06 and 0.08] that was prepared by solid state reaction method forms the fcc type spinel crystal structure which was confirmed by X-ray diffraction pattern. Moreover, a weak reflection peak can be seen that establishes the formation of secondary orthoferrite phase.
ii. The frequency dependent permeability (Both real part and imaginary part) have the trend of decreasing monotonically with the increase of frequency.
iii. Dielectric constant as the function of frequency decreases with the increase of frequency. This is also same for the imaginary part of dielectric constant. These phenomena are delineated on the basis of dielectric polarization of materials.
iv. The temperature dependent DC resistivity exhibits the increasing phenomenon with the increase of temperature.

Finally, it can be said that, the substitution of La^{3+} content develops the properties of pure Cu-Zn ferrite in a remarkable sense which can be used widely in the context of various electrical and electronic industries.

ACKNOWLEDGEMENT

The authors are greatly acknowledging the Solid State Physics laboratory of KUET and Materials Science division, Bangladesh Atomic Energy Centre, Dhaka for laboratory assistance.

RFERENCES

Ahmed, M. A., Okasha N., and Salah L., 2003. Influence of yttrium ions on the magnetic properties of Ni-Zn ferrites, *J. Magn. Magn. Mater*, 264(2-3), 241-250.

Batoo, K. M., and Ansari M. S., 2012. Low temperature-fired Ni-Cu-Zn ferrite nanoparticles through auto combustion method for multilayer chip inductor applications, *Nanoscale Research Letters*, 7, 1-14.

Chen, N. S., Yang X. J., Liu E. S., and Huang J. L., 2000. Reducing gas-sensing properties of ferrite compounds MFe_2O_4 (M= Cu, Zn, Cd and Mg), Sensors and Actuators B: Chemical, 66(1-3), 178-180.

Ghazanfar, U., Siddiqi S. A., and Abbas G., 2005. Study of room temperature dc resistivity in comparison with activation energy and drift mobility of NiZn ferrites, *Materials Science and Engineering,* B, 118(1-3), 132-134.

Gubbala, S., Nathani H., Kozial K., and Misra R.D.K., 2004. Magnetic properties of nanocrystalline Ni-Zn, Zn-Mn and Ni-Mn ferrites synthesized by reverse micelle technique, *Physica B: Condensed Matter*, 348(1-4), 317-328.

Gupta, T. K., and Coble R. L., 1968. Sintering of ZnO: I, Densification and Grain Growth, *J. Am. Ceram. Soc*., 51, 521-525.

Kigery, W. D., Bowen H. K. and Uhlmann D. R., 1975. Introduction of Ceramics, New York, John Wiley and Sons.

Kulikowshi, J., 1984. Soft magnetic ferrites - Development or stagnation, *Journal of Magnetism and Magnetic Materials*, 41(1-3), 56-62.

Lange, F. F., 1989. Thermodynamics of densification: II, grain growth in porous compacts and relation to densification, *J. Am. Ceram. Soc*., 72, 735–741.

Nelson, J. D. and Riely D. P., 1945. An experimental investigation of extrapolation methods in the derivation of accurate unit-cell dimensions of crystals, *Proc. Phys. Soc.* London, 57, 160.

Roy, P., Hoque S. M., Liba S. I. and Shamima Choudhury, 2018. Investigation of various magnetic features of spinel type of cobalt ferrite ($CoFe_2O_4$) nanoparticles tuned by annealing temperature, *AIP Advances*, 8, 105124.

Shahida Akhter, Paul D. P., Hakim M. A., Saha D. K., Das H. N., Parveen A., and Anjuman B., 2013. Transport Properties of Polycrystalline Mixed Copper-Zinc Ferrites, *Materials Research*, 21(4), 1-6.

Sharmin Akhter, Roy P., Hossain M. A., Khan M. N. I. and Sikder S. S., 2019. Influence of Yttrium substitution on structural and transport properties of Ni-Zn ($Ni_{0.25}Zn_{0.75}Y_xFe_{2-x}O_4$) ferrite, *Journal of Engineering Science*, 10(1), 45-50.

Shil, S. K., Sinha R. C., Hakim M. A., and Sikder S. S., 2013. Influence of composition and Sintering temperature on complex permeability of spinel type Ni-Zn ferrite, *J. of Engineering Science*, 4, 119-125.

Torikul Islam M., Sikder S. S., Hakim M. A., Saroaut Noor and Saha D. K., 2014. Study on complex permeability of cobalt cadmium ferrites, *Journal of Engineering Science*, 5(1), 35-40.

Vucinic-Vasic, M., Bozin E. S., Bessais L., Stojanovic G., Kozmidis-Luburic U., Abeykoon M., and Antic B., 2013. Thermal evolution of cation distribution/crystallite size and their correlation with the magnetic state of Yb-substituted zinc ferrite nanoparticles, *The Journal of Physical Chemistry C*, 117(23), 12358-12365.

Zhenxing Yue, Zhou Ji, Longtu Li, Xiaolui Wang and Zhilun Gui, 2001. Effect of copper on the electromagnetic properties of Mg-Zn-Cu ferrites prepared by Sol-gel auto-combustion method, *Mater. Sci. Eng. B* 86(1), 64-69.