REVIEW OF RESEARCH

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Co^{2+} SUBSTITUTED NICUZN FERRITES FOR MLCI APPLICATIONS

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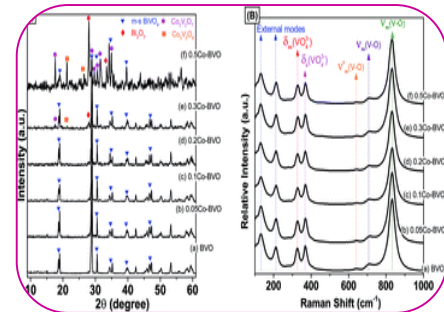
ABSTRACT

Co2+ is a fast relaxing ion which can enhance microwave properties. This work focuses on the synthesis and characterizations of $Ni_{0.25-x}Co_xCu_{0.30}Zn_{0.45}Fe_2O_4$ (x = 0.00, 0.05, 0.01, 0.15, 0.20 and 0.25) ferrites by auto combustion method using glycine as the chelating agent. From X-ray Diffraction (XRD) spectra, the structural parameters are analysed. The lattice parameter (a) decreases due to smaller ionic radius of Co2+ (0.072 nm) which replaces Ni2+ (0.078 nm). Bulk density and porosity measurements show that there are pores and lattice imperfections. FTIR spectra for the sintered samples showed two strong frequency bands $υ_1$ (712-719 cm^{-1}) and $υ_2$ (489 - 497 cm^{-1}) which are characteristic features of inverse spinel ferrites Low porosities indicate that the samples can be potential candidate for MLCI applications.

KEYWORDS: *microwave properties , potential candidate.*

1. INTRODUCTION

Magneto-dielectric material is one kind of dielectric material whose value of permeability can be varied on a large scale [1]. Magnetic nanoparticles of mixed spinel ferrites have been the subject of current interest because of their interesting optical, magnetic and electrical properties which are different from that of their counterparts [2]. However, in recent days, as surface mounting technology (SMT) advances, the electronic component technology has been in continuous pursuit of miniaturization, light weight, high density, high performance and multi functioning capacity. In the latest electronic industry, SMT is widely adopted instead of the insertion system of leaded components [3]. Also, as miniaturization and thick films are preferred for various high performance electronic components, compared to existing bulk types, a technology which has the same functions but also can improve properties is absolutely essential. Essentially as SMT advances, ferrite components are being converted into shapes of Multi Layer Chip (MLC) from the bulk and if ferrite chip components are to be manufactured then the development of an electric conducting material co-fired with the ferrite called printing technology has to be developed. At present NiCuZn ferrite is the suitable magnetic material because of its better magnetic properties at high frequencies compared with MnZn ferrite, as well as lower densification temperature compared with NiZn ferrites [4-5]. Properties of nano ferrites are very sensitive to the method of preparation and sintering conditions. Hence the use of suitable preparation technique is the key to obtain ferrites with required properties. Ferrite nanoparticles are usually prepared by various physical and chemical methods like mechanical alloying, high energy milling,

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plasma deposition method, inert gas condensation, hydrothermal reaction, citrate precursor technique, reverse micelle technique, sol gel technique and chemical coprecipitation [6-7] etc. Among the available chemical methods, sol gel method is an excellent technique to prepare ferrite nano particles with maximum purity and uniform grain size. Sol gel synthesis acts as a combination of chemical gelatin and combustion and it has the advantage of good stoichiometric control and production of ultrafine particles with a narrow size distribution. Hence we have synthesized the ferrite samples using auto combustion method with glycine as the chelating agent.

Cobalt ferrites are interesting due to their unusual optical, magnetic and electrical properties compared to their bulk counterparts. Co^{2+} is a fast relaxing ion which can enhance microwave properties. It is the anisotropic ion responsible for the magnetic response time. Their properties along with physical and chemical stability make them suitable for applications in magnetic recording, magnetic fluids and magnetic drug delivery.

Dimri et al. have reported complex permittivity and permeability of Co^{2+} substituted NiCuZn ferrites at radiofrequency and microwave frequencies in the system $(Ni_{0.2}Cu_{0.2}Zn_{0.6})_{1-x}Co_xFe_2O_4$ [8].

Sujatha et al. have investigated the effect of Co^{2+} substitution of Mg^{2+} and Zn^{2+} on electromagnetic properties of NiCuZn ferrites [2].

Hemeda has reported the IR spectral studies of $Co_{0.6}Zn_{0.4}Mn_xFe_{2-x}O_4$ ferrites [9].

In this investigative work we have done the synthesis and characterizations of $Ni_{0.25-x}Co_xCu_{0.30}Zn_{0.45}Fe_2O_4$ (0.00 ≤ x ≤ 0.25) ferrites.

2 EXPERIMENTAL DETAILS
2.1 Synthesis of $Ni_{0.25-x}Co_xCu_{0.30}Zn_{0.45}Fe_2O_4$ ferrites

A series of ferrite samples with general formula $Ni_{0.25-x}Co_xCu_{0.30}Zn_{0.45}Fe_2O_4$ (x = 0.00, 0.05, 0.10, 0.15, 0.20 and 0.25 mol.) was synthesized by auto combustion method using glycine as the reducing agent. Stoichiometric ratios of AR grade $Ni(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$, $Cu(NO_3)_2.5H_2O$, $Zn(NO_3)_2.6H_2O$ and $Fe(NO_3)_2.9H_2O$ (99.9% pure Aldrich) were mixed with glycine (sd fine) in distilled water to prepare the precursor solution [10]. The solution when heated on an electric heater   formed   a gel and then ignited in a self propagating combustion to form a fluffy powder ash. The powder was then grinded and presintered at 650°C for   4h. Cylindrical disc shaped pellets of the ferrite samples were prepared by using a hydraulic press and applying pressure of 10 tons/m^2 for five minutes to the mixture of granulated fine powder and PVA binder. The pellets and torroids were finally sintered at 900°C for 2h and used for characterizations.

2.2 Characterizations

The crystallite phases of the sintered ferrites were identified by X-ray diffraction spectroscopy using CuK$_\alpha$ radiation with wavelength (λ = 1.5406 Å). The lattice parameter (a), X-ray density (d_x) and crystallite size (D) were calculated. The bulk densities (d_b) were evaluated by liquid immersion technique using xylene as the suspension medium. IR Perkin Elmer FTIR spectrometer was used to record IR spectra at room temperature over the range 400-1400 cm^{-1}. The ferrite samples for recording spectra were prepared in the form of pellets in KBr medium.

3 RESULTS AND DISCUSSIONS
3.1 X-Ray diffraction analysis

From Fig.1 single phase cubic spinel structure was confirmed which matches well with JCPDS card No. 08-0234 for each sample. The most intense peaks marked as (220), (311), (222), (400), (422) and (511) were used to calculate the lattice parameter (a)[11].
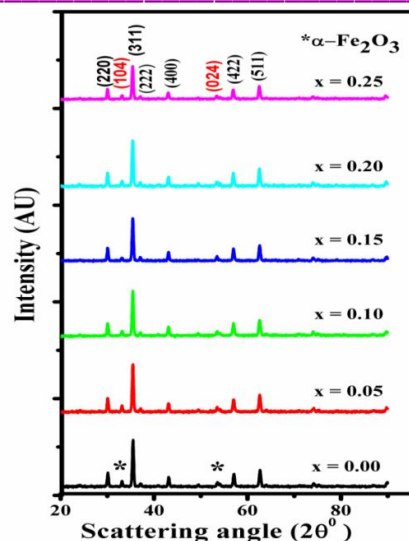
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Fig. 1 X-Ray Diffractograms of $Ni_{0.25-x}Co_xCu_{0.30}Zn_{0.45}Fe_2O_4$ ferrites.

It was observed from the X-ray patterns that small amount of traces of unreacted α-Fe_2O_3 (JCPDS card no. 33-0664) were also present. The ionic radius of Co^{2+} (0.72 Å) is slightly smaller than the ionic radius of Ni^{2+} (0.74 Å) which makes the lattice parameter (*a*) to decrease as depicted in Fig. 2 [12].

The average crystallite size (*D*) of the ferrite nanoparticles was determined from XRD peak broadening of (311) plane using Scherrer formula. The values of *D* were observed to be in the range 24-53 nm and similar values are reported by   Hossain et al. [13]. X-ray density (d_{XRD}) was calculated for each ferrite sample [2]. The bulk density of each ferrite sample was determined by the principle of liquid immersion technique.
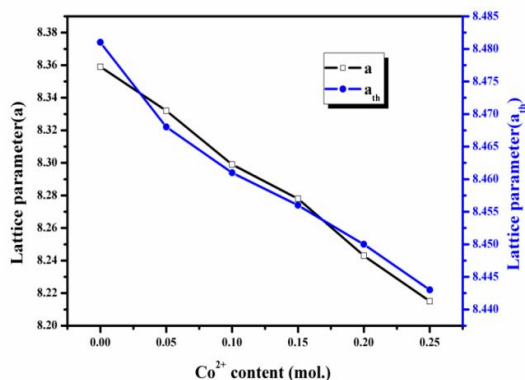

Fig. 2 Compositional variation of lattice parameter (a) and theoretical lattice parameter (a_{th}) of $Ni_{0.25-x}Co_xCu_{0.30}Zn_{0.45}Fe_2O_4$ ferrites.

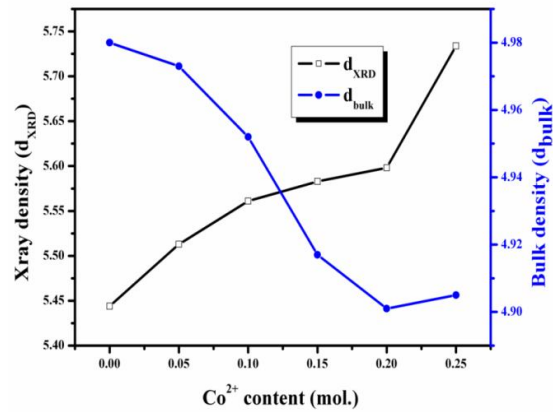Xylene was used as the suspension medium, based on Archimedes principle the values of d_{bulk} were estimated.

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Fig. 3 Compositional variation of X-ray density and bulk density of Ni$_{0.25x}$Co$_x$Cu$_{0.30}$Zn$_{0.45}$Fe$_2$O$_4$ ferrites.

The porosities (*P*) of the ferrite samples were also determined. X-ray density increased with Co^{2+} substitution as shown in Fig.3.
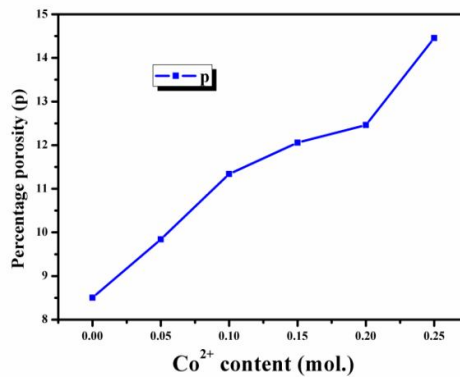

Fig. 4 Compositional variation of percentage porosity (P) of Ni$_{0.25-x}$Co$_x$Cu$_{0.30}$Zn$_{0.45}$Fe$_2$O$_4$ ferrites.

X-ray density varied between 5.444 gm/cm^3 and 5.734 gm/cm^3. This increase is attributed to the atomic weight and density of substituting (Co^{2+}) and substituted (Ni^{2+}) ions, atomic weight of Ni^{2+} (58.693 a.m.u.) is less than that of Co^{2+} (58.933 a.m.u.).

The density of Ni^{2+}(8.908 gm/cm^3) is slightly larger than density of Co^{2+} (8.90 gm/cm^3). The bulk density showed slight decrease because Co^{2+} ions enter inverse spinel structure as shown in Fig.3.The porosities are small and show increasing trend with content of Co^{2+} ions as shown in Fig. 4. This can be explained on the basis of anomalous densification and crystal imperfections which depend on stoichiometry, method of preparation and heat treatment conditions. Compositional data on molecular weight (M), lattice parameter (a), theoretical lattice parameter (a$_{th}$),tetrahedral site molecular weight (M$_A$),octahedral site molecular weight (M$_B$),tetrahedral bond length (L$_A$) and octahedral bond length (L$_B$) of Co^{2+} substituted NiCuZn ferrites is given in Table 1.

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Table 1. Compositional data on molecular weight (M), lattice parameter (a), theoretical lattice parameter (a$_{th}$),tetrahedral site molecular weight (M$_A$),octahedral site molecular weight (M$_B$),tetrahedral bond length (L$_A$) and octahedral bond length (L$_B$) of Co^{2+} substituted NiCuZn ferrites.

Co^{2+} content (x)	0.00	0.05	0.10	0.15	0.20	0.25
Molecular weight (M) a.m.u.	238.844	238.856	238.868	238.880	238.892	238.904
Lattice parameter (a) Å	8.369	8.352	8.349	8.338	8.323	8.315
Theor. lattice parameter (a$_{th}$) Å	8.481	8.468	8.461	8.456	8.450	8.443
Tetrahedral mol. wt. (M$_A$) a.m.u.	86.266	83.063	80.840	78.659	76.454	74.251
Octahedral mol. wt. (M$_B$) a.m.u.	89.582	91.797	94.012	96.227	98.442	100.657
Tetrahedral bond length (L$_A$) Å	7.232	7.201	7.181	7.179	7.168	7.161
Octahedral bond length (L$_B$) Å	5.905	5.880	5.863	5.862	5.853	5.847

3.2 Fourier transform infra red (FTIR) analysis

FTIR spectra for the sintered samples showed two strong frequency bands υ_1 (712-719 cm^{-1}) and υ_2 (489 - 497 cm^{-1}) which are characteristic features of ferrites as shown in figure.5. The υ_1 band is assigned to vibrations of the bond between oxygen ion and the tetrahedral metal ion O-M$_{tetra}$ and the other band υ_2 arises due to vibrations of the bond between oxygen ion and the octahedral metal ion O-M$_{octa}$ [14]. The differences in band positions are observed in the spectra because of change in the bond length between Fe^{3+} - O^{2-} ions for tetrahedral and octahedral complexes. Both the bands were broad indicating inverse spinel structure in which the Fe^{3+} ions are distributed statistically at tetrahedral and octahedral sites based on stoichiometric composition.
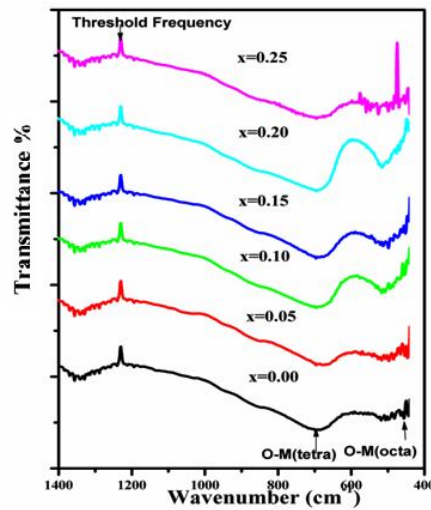

Fig. 5 FTIR spectra of Co^{2+} substituted NiCuZn ferrites.

The slight variation in band positions of υ_1 and υ_2 was affected by method of preparation, grain size and heat treatment conditions [15]. Waldron [14] has given the force constants for tetrahedral site (k$_t$) and octahedral site (k$_o$). Force constant is second order derivative of potential energy w.r.t. site radius (r$_A$ and r$_B$) and the other independent parameter are kept constant. The threshold energy (E$_{th}$) values were calculated

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from Planck's quantum theory   of radiation [14] where f is frequency of vibration, h is Planck's constant in eV-sec , h = 4.13×10^{-15} eV-sec, c is velocity of light and υ_{th} is threshold frequency in cm^{-1}. According to Waldron [14], the inflection point in graph of transmittance versus wave number (Fig.5) can be used to determine the threshold frequency υ_{th} for electronic transitions. The calculated E_{th} values decreased with content of Co^{2+}. It has been reported that the broadening of band is commonly observed when the system transfers from inverse spinel to normal spinel. Half band width (Γ_A) of tetrahedral sites showed decreasing nature with increase in Co^{2+} ions. The half band width (Γ_B) of octahedral sites could not be determined because band terminated below the experimental limits. The compositional variation   of tetrahedral frequency (υ_1),octahedral frequency (υ_2), threshold frequency (υ_{th}),threshold energy (E_{th}), tetrahedral force constant (k_t) and octahedral force constant (k_o) for ferrites is given in Table 2.

Table 2. Compositional data on tetrahedral frequency (υ_1),octahedral frequency (υ_2), threshold frequency (υ_{th}), threshold energy (E_{th}), tetrahedral force constant (k_t), octahedral force constant (k_o) for Ni$_{0.25-x}$Co$_x$Cu$_{0.30}$Zn$_{0.45}$Fe$_2$O$_4$ ferrites.

Co^{2+} content(x)	0.00	0.05	0.10	0.15	0.20	0.25
Tetrahedral frequency (υ_1) x 10^{-2}m^{-1}	719	717	716	715	713	712
Octahedral frequency (υ_2) x 10^{-2}m^{-1}	496	495	494	492	490	489
Threshold frequency (υ_{th}) x 10^{-2}m^{-1}	1383	1382	1381	1381	1380	1378
Threshold energy (E_{th}) eV	0.1714	0.1712	0.1702	0.1700	0.1692	0.1690
k_t x10^{-3} N/m	3.36	2.26	3.16	3.07	3.05	2.87
k_o x10^{-3} N/m	0.84	1.19	1.22	1.23	1.27	1.31

4. CONCLUSIONS

The influence of Co^{2+} substitution on structural and morphological properties of Ni$_{0.25x}$Co$_x$Cu$_{0.30}$Zn$_{0.45}$Fe$_2$O$_4$ (0.00 ≤ x ≤ 0.25) inverse spinels was analysed. The synthesis used was autocombustion method employing glycine of high heat of combustion (-3.24 kcal/gm) as the reducing agent. XRD characterization confirmed single phase spinel structure for all the samples. The lattice parameter *(a)* decreased due to smaller ionic radius of Co^{2+} which replace the bigger Ni^{2+} ions. FTIR spectra exhibited two prominent bands υ_1 arising due to vibrations of tetrahedral complexes and υ_2 arising due to vibrations of octahedral complexes which is the common feature of inverse spinel ferrites. Energy threshold values (E_{th}) decreased because of lower atomic weight of Co^{2+}. Porosities were quite small, hence the low temperature sintered NiCuZn ferrities with Co^{2+} substitution are suitable candidates for MLCI applications.

REFERENCES
[1] E. C. Snelling, Ferrites, Properties & applications, 2nd edition (Butterworths,London) pp.1.
[2]C. Sujatha, K. Venugopal Reddy, K. Sowri Babu, A. Ramachandra Reddy, M. Buchi Suresh, K. H. Rao, J. of Phys. and chem. of solids,74 (2013) 917-923.
[3] M. Fujimoto, J. Am. Ceram. Soc.,77 (1994)2873.
[4] W.C. Kim, S.J. Kim, S.W. Lee, C.S. Kim, J. Magn. Magn. Mater. 1418 (2001) 226- 230.
[5]H.E. Zhang, B.E. Zhang, G.F. Wang, X.H. Dong,Y.Gao,J.Magn.Magn.Mater.312(2007) 126-130.
[6]M.C. Dimri, A. Verma, S.C. Kashyap, D.C. Dube, O.P. Thakur, Chandraprakash, Mater. sci. Engineering B133 (2006)42-48.
[7]S.A. Ghodake, U.R. Ghodake, S.R. Sawant, S.S. Suryavanshi, P.P. bakare, J. of Mater.305 (2006)110-119.
[8] M.C. Dimri, S.C. Kashyap, D.C. Dube, S.K. Mohanta, J. of Electroceramics,16 (4)(2000)   331-335.

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[9] O.M. Hemeda, J. of Magn. Magn.Mater.281(2004)36-41.

[10]M.S. Khandekar, R.C. Kamble, S .S. Latthe, J.Y. Patil, P.A. Shaikh, N. Hur, S.S. Suryavanshi, Mater. Letters 65 (2011)2972-2974.

[11] B.D.Cullity, Elements of X-Ray Diffration, Addison Wesley Pub.Co.INC,1956,p421.

[12] S.C. Watawe, B.D. Sutar, B.D. Sarwade, B.K. Chougule, International J.of Inorg. Mater .3(2001)819-823.

[13] A.K.M. Akther Hossain,M.L.Rahman, J.ofMagn.Magn.Mater.323(2011)1954-1962.

[14] R.D.Waldron,Phys.Rev. 99(1955)1727.

[15] B. K. Labde, C. Sable, N.R. Shamkwar, Mater. Lettrs. 57(2003)1651-1655.

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