BARIUM (BA^{2+}) DOPED CU-ZN FERRITE: ELUCIDATION OF STRUCTURAL AND DIELECTRIC PROPERTIES

Vishal Tandon[1], M. Saleem[1,2], Netram Kaurav[1] and RC Dixit[1]

[1]Department of Physics, Govt. Autonomous Holkar Science College, Indore, 452001, India,

[2]School of Physics, Devi Ahilya Vishwavidhyalya, Indore, 452001, India.

Abstract: This study comprises of discussion on the synthesis and characterization of the Cu-Zn ferrites of the type $Cu_{0.5-x}Ba_xZn_{0.5}Fe_2O_4$ [x = 0.0, 0.05, 0.1]. The samples were synthesized by solid state reaction route. All the prepared materials were characterized by X-Ray diffraction and Raman spectroscopy technique to confirm the structure, phase and lattice formation. The samples were further studied for dielectric properties where dielectric constant and loss values studied. The analysis of XRD data conveyed that all the prepared samples have acquired cubic structure and exhibit *Fd*3*m* space group. The diffractograms are same in appearance and there is no new reflection visible within the limits of experimentation. This reveals the sample are mono-phase in nature where host site is effectively occupied by the guest ions. The lattice structure formation was witnessed via Raman spectral analysis with signature modes displayed by all the samples. The dielectric studies reveal the samples to be exhibiting low dielectric constant with low decreasing rate with respect to the field. Furthermore, the samples have low loss values which increase their ability for advanced technological applications.

Keywords: Ferrites, Solid state reaction, structure, dielectric properties.

Introduction:

Ferrites with formula of MFe_2O_4 (M: a divalent metal ion), usually called the spinel ferrites have wide technological applications. A peculiar improvement of spinel ferrites has been well realized in the field of electronics and communication for recent years. Spinel type of $M^{2+}M_2^{3+}O_4$ structure has attracted much attention due to its chemical stability and various potential applications. The various other applications of the ferrites include multilayer chip inductor, ferro-fluids,-speedy recording disks and sensor for humidity. In the nano-form, these ferrites have found applications in inter-body drug delivery, bio-separation, and magnetic refrigeration systems. Among spinel ferrites, zinc ferrites are used in gas sensing, catalytic application, photo-catalyst, and absorbent materials [1-6].

$CuFe_2O_4$ is a p-type semiconductor metal oxide. Its band gap (~ 1.4 eV) is ideal for solar photocatalytic applications like solar water splitting [7]. Many research groups have explored the vital use of these kinds of ferrites in numerous advanced techniques due to their unique physical, chemical and biocompatible properties. The indispensability of this ferrite for advanced technology is attributed to its high

electrical resistivity, high permeability, negligible eddy current losses, magneto-resistive and magneto-optical properties

As the physical properties highly rely on the preparation and processing methods, several routes have been reported in recent years for the synthesis of ferrite materials including co-precipitation, combustion method, hydrothermal/solvo-thermal method, microwave synthesis, sol–gel technique, hot injection thermolysis, microemulsion/reverse microemulsion process, conventional and SPS method, mechano-chemical (solid state route) alloying and complex-metric method out of which solid state route has been selected for the current study. The choice of method was based on the ease and control over the reaction though it consumes time and energy. This method yields according to the precipitation in the form of single phase and noiseless spectra. In addition to this, the improved microstructure via this method influences the dielectric and magnetic properties to a great extent [8-12].

In this study, we report the synthesis of $Cu_{0.5-x}Ba_xZn_{0.5}Fe_2O_4$ [x = 0.0, 0.05, 0.1] ferrites. The use of alkaline earth metal was experienced to study the effect on the structural and dielectric properties which is uniqueness of the report. Fortunately, the large ionic radii of Ba^{2+} ions have occupied the A- site of the 2-3 ferrite effectively revealed by the X-ray diffraction data. Further, the ferrites under study have displayed intriguing dielectric properties.

Experimental Details

Synthesis

Polycrystalline ferrites of the formula $Cu_{0.5-x}Ba_xZn_{0.5}Fe_2O_4$ [x = 0.0, 0.05, 0.1] were prepared by high temperature solid state method. The stoichiometric amounts of starting materials CuO, ZnO, $BaCO_3$ and Fe_2O_3 were mixed in agate mortar for 5h using acetone for proper dispersion. The mixture was calcined at 950 ^oC for 5h. The materials were reground for 3h and double calcined at 1000 ^oC for 5h. The double calcined samples were pressed into the pellets at a pressure of 5 tons/inch and sintered sintered at 1100 ^oC. Finally, we silvered sintered pellets for smooth electrical contacts for dielectric measurements.

Experimentation

We performed X-ray diffraction (XRD) characterization on the synthesized Cu-Zn ferrite samples for phase formation and confirmation of structure. The experiment was performed on Bruker D8 advanced X-ray Diffractometer using Cu K_α radiation (λ=1.54060Å) at scanning rate of 0.02^o s^{-1} with angular range from 20^o <2θ< 80^o. Raman characterization was carried out using Micro Raman System from Jobin Yvon Horiba LABRAM-HR visible (400-1100 nm) with excitation source as Argon (488 nm). The samples were subjected to dielectric measurements exploiting the instrument of Model E4980A Precision LCR meter (2Hz-2MHz) from Keysight Technologies.

Results and Discussions

The bulk ferrites of the type $Cu_{0.5-x}Ba_xZn_{0.5}Fe_2O_4$ [x = 0.0, 0.05, 0.1] were effectively prepared by solid state reaction route. The synthesized were characterized for structural properties using XRD and Raman Characterizations. The XRD diffractogram of the synthesized ferrites is displayed in Figure 1. The X-ray diffraction data study conveys that all the samples under study are single phased, crystalline with large average particle size. The ferrites were observed to have crystallized into the cubic structure and have acquired Fd3m space group. The crystalline nature of the materials is evident from the sharp and intense reflections of the diffractogram. The large average crystallite size is obvious from the narrowness of the full-width at half maxima of all the reflections displayed by the XRD spectrum. The average crystallite size calculated using classical Scherer formula, $t = k\lambda/\beta\cos\theta$, where k= 0.9 and is called shape factor, λ is the wavelength of the X-rays [CuKα1, λ= 1.654Å], β is called the full-width at half maximum and θ is the Bragg diffraction angle. The particle size was found to be 41.916Å, 48.6Å and 45.74Å for $Cu_{0.5}Zn_{0.5}Fe_2O_4$, $Cu_{0.45}Ba_{0.05}Zn_{0.05}Fe_2O_4$, and $Cu_{0.45}Ba_{0.1}Zn_{0.5}Fe_2O_4$ respectively. The lattice parameters calculated were a = 8.385 Å, a = 8.392Å and a = 4.012 Å for $Cu_{0.5}Zn_{0.5}Fe_2O_4$, $Cu_{0.45}Ba_{0.05}Zn_{0.05}Fe_2O_4$, $Cu_{0.4}Ba_{0.1}Zn_{0.5}Fe_2O_4$ respectively. The slight variation in the lattice parameters are attributed to the difference in the ionic radii of the Cu^{2+} (0.73 Å) and Zn^{2+} (0.75 Å) and Ba^{2+} (1.34 Å).

Raman modes of $Cu_{0.5}Zn_{0.5}Fe_2O_4$ (CZFO) cubic structured materials are represented by $\Gamma = A_{1g} + E_g + 3T_{2g}$ [13]. In Figure 2, we displayed the room temperature Raman spectra of all samples in the frequency range 200 ~ 800 cm^{-1}. At ambient conditions, the three first-order Raman active modes viz. $A_{1g} + E_g + T_{2g}$, are observed where A_{1g} mode is due to symmetric stretching of oxygen atoms along Fe-O bonds, E_g mode is attributed to symmetric bending of oxygen with respect to iron ion and T_{2g} mode arises due to asymmetric stretching of Fe. The notations used for the representation of the Raman active modes of vibration using group theory such as notation A is used for represent one dimensional mode whereas E and T represent two and three dimensional Raman modes. In addition to this, the subscript g denotes the symmetry with respect to the center of inversion. The modes of vibration above 600 cm^{-1} observed in cubic spinel materials irrespective of ferrites generally correspond to the motion of oxygen with respect to A-site i.e. tetrahedral site of spinel ferrite materials. However, the modes of vibration in the lower frequency range represent the characteristics of B-site i.e. octahedral site of ferrites [13, 14]. The details of the Raman modes observed are tabulated in Table 1.

The synthesized $Cu_{0.5-x}Ba_xZn_{0.5}Fe_2O_4$ [x = 0.0, 0.05, 0.1] spinel ferrites were examined for the dielectric properties in the frequency range of 1MHz-10MHz at room temperature. The spectra is displayed as dielectric constant as a function of logarithm of frequency in Figure 3. The dielectric constant was calculated using formula

$$\varepsilon = \frac{Ct}{A\varepsilon_0} \qquad (6)$$

Here, the symbols C, t, A and ε_0, represents the capacitance (in farad), thickness (in meters), cross-sectional area of the flat surface and constant of permittivity for free space ($\varepsilon_0 = 8.86 \times 10^{-12}$ F/m) of Cu–Zn ferrite

pellet, respectively and ε is the relative permittivity of the dielectric medium. The spinel Cu-Zn ferrites under observation can be seen to exhibit low dielectric constant. The dielectric constant is higher at low frequency range which gradually decreases in response to the increase in applied field and acquires field independent character at the higher field values. The low field higher dielectric constant is attributed to the piling up of the carriers at the grain boundaries and the decrease in the dielectric constant is based on the fact that higher field values provides sufficient momentum to the charge carriers to cross over the low conducting grain boundaries thereby the polarization acquired is destroyed that leads to the decrease in the dielectric constant values. The observed behaviour is attributed to the space charge polarization. The overall character is governed by the Koop's law and well explainable in the light of Wagner's theory [15, 16]. The general dielectric constant of the ferrites under study display low values which agrees the reported study elsewhere [17, 18]. The intriguing feature concerned to the dielectric constant of the current ferrite samples is that the higher order of dielectric constant value is retained for larger applied field with very low rate of decrease which makes them feasible for electric energy device applications.

Additionally, the dielectric loss value of the $Cu_{0.5-x}Ba_xZn_{0.5}Fe_2O_4$ [x = 0.0, 0.05, 0.1] spinel ferrites was investigated. The dielectric loss as a function of frequency is represented in the Figure 4**.** The dielectric loss tangent factor (tanδ) for Cu–Zn ferrite system was measured directly by the instrument used exploiting the inbuilt software, which is determinable in terms of real (ε′) and imaginary (ε″) parts of dielectric constant using the formula

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \text{ or } \tan\delta = \frac{1}{2\pi f \varepsilon_0 \varepsilon'}$$

The variation of dielectric loss tangent (tanδ) for the ferrite samples is due to the lag in polarization in relation to the applied *ac* electric field. It is obvious from the Figure 4 that dielectric loss initially decreases followed by well-behaved resonance peaks (shoulder like) with increase in frequency. The decrease in loss values occurs when the jumping frequency of charge carriers disobey the applied *ac* electric field beyond a certain critical frequency. The shoulder like behaviour called the resonance peak comes into the existence when jumping frequency of the localized charge carriers matches the frequency of the applied alternating current (*ac*) field [17-19]. Here, we observed the low loss value of the ferrites with enhanced resonance peaks and their shift toward higher frequency range with Ba doping. The collective behaviour in terms of constant and loss values are intriguing for electronic device applications.

Conclusions

In conclusion, we claim the successful synthesis of the $Cu_{0.5-x}Ba_xZn_{0.5}Fe_2O_4$ [x = 0.0, 0.05, 0.1] spinel ferrites via convenient high temperature solid state route. The samples on investigation of XRD data were found single phased cubic structured materials. The spinel formation was further verified via the Raman scattering technique through the fingerprint modes of vibration. The samples further reveal to be exhibiting low dielectric constant with exceptional low dielectric loss values. The rate of loss of dielectric with increasing field is very low and the resonance character displayed by the samples validate their technological feasibility.

Acknowledgments:

Authors acknowledge UGC-DAE-CSR, as an institute for extending its facilities. Authors are thankful to Dr. M. Gupta for XRD measurements, Dr. V. G. Sathe for Raman characterizations, and Dr. Rajeev Rawat for Dielectric measurements. Authors extend special thanks to Satish Yadav, Layanatha Bhera at UGC-DAE-CSR and Dr. Netram Kaurav, Govt. Holkar Science College, Indore (M.P.) for laboratory facilities.

References

[1] T. Pannaparayil, R. Maranle, S. Komarneni, S.G. Sankar, *J. Appl. Phys*. **64** (1988) 5641.

[2] M. H. Sousa, F. A. Tourinhou, J. Phys. Chem. B **105** (2001) 1168-1175.

[3] D. E. Speliotis, J. Magn. Magn.Mater.**193** (1999) 29-51.

[4] P. C. Dorsey, P. Lubitz, D. B. Chrisey. J.S. Horwitz, J. Appl. Phys. **85** (1999) 6338-6354.

[5] O. H. Kwon, Y. Fukushima, M. Sugimoto, N. Hiratsuka, J. Phys. IV France **07** C1 (1997) 165-166.

[6] C.Y. Tsay, K.S. Liu, T.F. Lin, I.N. Lin, J. Magn. Magn.Mater. **209** (2000) 189-192.

[7] G. P. Joshi, N. S. Saxena, R. Mangal, A. Mishra, T. P. Sharma, Bull. Mater. Sci. **26** (2003) 387-389.

[8] M. A. Malana, R. B.Qureshi, M. N.Ashiq, Chemical Engineering Journal, **172** (2011) 721-727.

[9] T. F. Marinca, I. Chicinas, O. Isnard, J. Therm. Anal. Calorim., **110** (2012) 301–307.

[10] E. Moscardini, G. Furlani, F. Pagnanelli, F. Ferella, I. De Michelis, F. Vegliò, F. Beolchini, L. Toro, Chemical Engineering Transactions, **17** (2009) 281-286.

[11] J. Ortiz-Landeros, C. Gómez-Yáñez, R. López-Jureáz, I. Dávalos-Velasco, H. Pfeiffer, Journal of Advanced Ceramics **1(3)** (2012) 204-220.

[12] M. Salavati-Niasari, T. Mahmoudi, M. Sabet, S. M. Hosseinpour-Mashkani, F. Soofivand, F. Tavakoli, J. Clust. Sci., **23** (2012) 1003–1010.

[13] D. Varshney, K. Verma, A. Kumar, Journal of Molecular Structure, **1006** (2011) 447-452.

[14] M. Somani, and M. Saleem, AIP Conference Proceedings **1953** (2018) 030212.

[15] C. G. Koops, Phys Rev, **83** (1951) 121.

[16] K. W. Wagner, Ann Phys, **40** (1913) 817.

[17] M. Saleem, M. Padole, A. Mishra, (2019) Journal of Advanced Dielectrics, DOI:10.1142/S2010135X19500346.

[18] K. Alia, A. Bahadurb, A. Jabbarc, S. Iqbald, I. Ahmadc, M. I. Bashire Journal of Magnetism and Magnetic Materials **434** (2017) 30–36

[19] P. Reddy, T. Rao, J. Less, Common Met. **86** (1982) 255–261.

Figure Caption

Figure 1: X-ray diffraction spectra of $Cu_{0.5-x}Ba_xZn_{0.5}Fe_2O_4$ [x = 0.0, 0.05, 0.1] spinel ferrites.

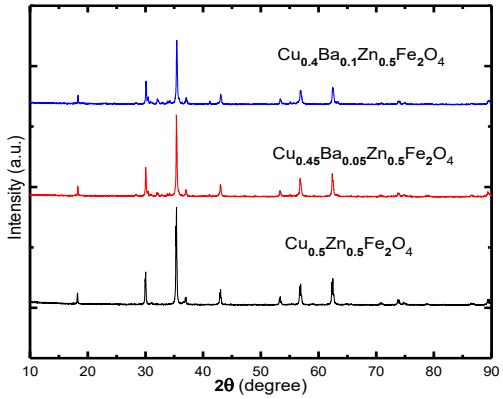

Figure 2: Raman Scattering plots for solid state $Cu_{0.5-x}Ba_xZn_{0.5}Fe_2O_4$ [x = 0.0, 0.05, 0.1] spinel ferrites.

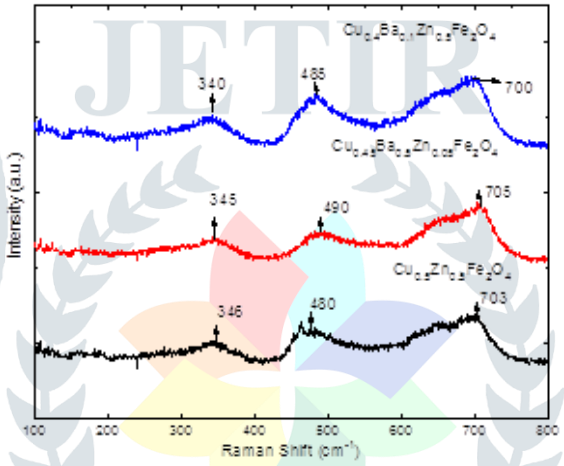

Figure 3: Dielectric constant of $Cu_{0.5-x}Ba_xZn_{0.5}Fe_2O_4$ [x = 0.0, 0.05, 0.1] spinel ferrites as a function of frequency at room temperature

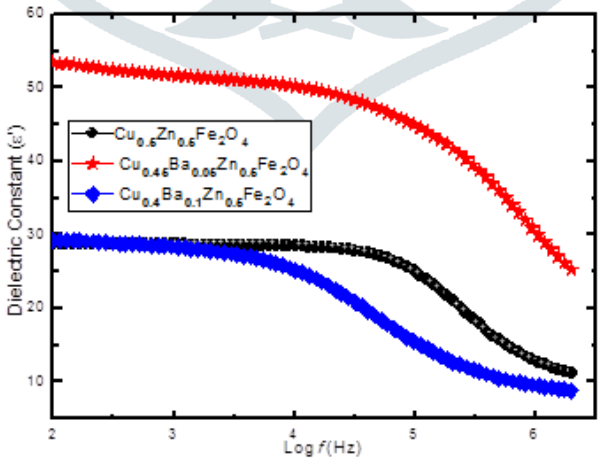

Figure 4: Dielectric loss as a function of $Cu_{0.5-x}Ba_xZn_{0.5}Fe_2O_4$ [x = 0.0, 0.05, 0.1] spinel ferrites

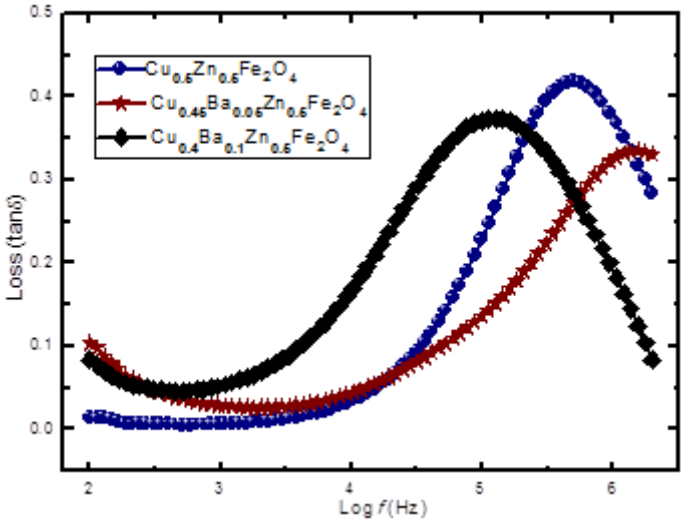

Table 1

Table 1: Raman Modes observed in $Cu_{0.5-x}Ba_xZn_{0.5}Fe_2O_4$ [x = 0.0, 0.05, 0.1] spinel ferrites

Name of Sample	Tetrahedral site modes (cm^{-1})	Octahedral site modes (cm^{-1})	
$Cu_{0.5}Zn_{0.5}Fe_2O_4$	700	346	485
$Cu_{0.45}Ba_{0.05}Zn_{0.5}Fe_2O_4$	705	345	490
$Cu_{0.4}Ba_{0.1}Zn_{0.5}Fe_2O_4$	703	340	480