

Role of Mn-Zn Substitution on Structural and Electrical Properties of CuSr_2 - W Type Hexaferrite

A.K. Akant¹, C.L. Khobaragade², K.G. Rewatkar³

¹Department of Physics, Manoharbai Patel Institute Of Engineering and Technology, Gondia, INDIA

²Department of Physics, Govindrao Wanjari College of Engineering, Nagpur, INDIA

³Dr. Ambedkar College, Deeksha Bhoomi, Nagpur, INDIA

ABSTRACT

In the present investigation the samples with chemical composition $\text{CuSr}_2(\text{MnZn})_{x/2}\text{Fe}_{16-x}\text{O}_{27}$ ($x=0,1,2,3,4,5$) have been synthesized by chemical co-precipitation method. X-ray diffractometer and Scanning Electron Microscopy were used to study structure, lattice constants, particle size, x-ray density, bulk density, porosity and shape of ferrite powders. The prepared samples were found to have W-type hexagonal structure with the lattice parameters $a=(5.81 \text{ \AA} \text{ to } 5.83 \text{ \AA})$ and $c=(32.85 \text{ \AA} \text{ to } 33.17 \text{ \AA})$. The average particle size calculated from XRD analysis is found to be 57.03 nm. It was found that, we could obtain single phase W-type $\text{CuSr}_2\text{Fe}_{16}\text{O}_{27}$ nanocrystals at 1000°C . The conductivity, dielectric constant and loss tangent ($\tan \delta$) were measured as a function of frequency and temperature and composition. The dielectric constant and loss tangent decrease with frequency. The room temperature resistivity is found to be $2 \times 10^6 \Omega \text{ cm}$. Study of electrical properties shows that the compound under study is semiconducting.

Keywords----- XRD, VSM, Electrical Properties, Resistivity

and Me represents a divalent metal ion, has same crystal structure as that of M-type ferrite except the structural R blocks are separated by two S blocks. The unit cell is composed of sequence R S S R* S* S*, where * represents rotation through 180 degree [9-13]. The presence of divalent and trivalent cations makes the W-type ferrites interesting for different technical application, since their characteristics may be varied by substitution of both divalent and trivalent cations. W-type hexaferrites are widely used in high density magnetic recording media, overcoat-free, contact or semi-contact recording media and microwave tunable devices working at high frequency, above 70 GHz[14-17]. Method of synthesis plays an import role in controlling homogeneity, morphology and magnetic properties of hexagonal ferrites.

In the present work, a co-precipitation method was used to obtain homogeneous, ultra fine and reproducible $\text{CuSr}_2(\text{MnZn})_{x/2}\text{Fe}_{16-x}\text{O}_{27}$ [$B_1 - B_6$]hexaferrites particles. This method is suitable for preparing particles in the nano range.

I. INTRODUCTION

Hexagonal ferrites have been a topic of interest due to their high resistivity and low eddy current losses [1-8]. Due to their low eddy current losses, there exist no other materials with such wide ranging value to electronic applications in terms of power generation, conditioning, and conversion. There are six types of hexagonal ferrites, M-type ($\text{AFe}_{12}\text{O}_{19}$), W- type ($\text{AMe}_2\text{Fe}_{16}\text{O}_{27}$), Y -type ($\text{AMe}_2\text{Fe}_{12}\text{O}_{22}$), X -type ($\text{A}_2\text{Me}_2\text{Fe}_{28}\text{O}_{46}$), U - type ($\text{A}_4\text{Me}_2\text{Fe}_{36}\text{O}_{60}$) and Z-type ($\text{A}_2\text{Me}_2\text{Fe}_{24}\text{O}_{41}$). A W-type ferrite with chemical composition $\text{AMe}_2\text{Fe}_{16}\text{O}_{27}$, where A represents alkali earth metals, usually Ba, Sr, Ca, Pb etc

II. EXPERIMENTAL

$\text{CuSr}_2(\text{MnZn})_{x/2}\text{Fe}_{16-x}\text{O}_{27}$ hexaferrites particles were prepared by chemical co-precipitation method. A.R. Grade Calcium nitrate ($\text{Cu}(\text{NO}_3)_2$), Strontium nitrate ($\text{Sr}(\text{NO}_3)_2$), Manganese nitrate ($\text{Mn}(\text{NO}_3)_4$), Zinc nitrate ($\text{Zn}(\text{NO}_3)_2$) and Ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were used as starting materials. Stoichiometric amounts of Calcium nitrate, Strontium nitrate, Manganese nitrate, Zinc nitrate and Ferric nitrate were dissolved one by one in 100 ml of distilled water. Ammonia solution (25%) was added slowly to adjust pH of 7. The mixed solution was stirred for two hours by using magnetic stirrer and was kept for 24 hours for ageing. The Copper-Strontium hexaferrite precipitate was separated in a centrifuge machine. The

precipitate was washed in 1:1 mixture of methanol and acetone followed by 100% de-ionized water to remove impurity. The precipitate was dried at 100° C for about 24 hours and crushed and calcinated at 1000°C for 4 hours. Finally crushed for 5 hours to obtained $\text{CuSr}_2(\text{MnZn})_{x/2}\text{Fe}_{16-x}\text{O}_{27}$ hexaferrite particles.

The X-ray diffraction was studied using XPERT-PRO diffractometer. The lattice parameters (a and c), X-ray density, bulk density, porosity and particle size were calculated from the XRD analysis. The microstructure was studied using Scanning Electron Microscopy and Transmission electron microscopy.

III. RESULTS AND DISCUSSION

Structural characterization

The polycrystalline Mn-Zn doped $\text{CuSr}_2 - \text{W}$ type ferrites were studied by the X-ray powder diffraction method (Figure 1) and found to exhibit a hexagonal W-type symmetry. The lattice parameters were calculated from the relation

$$\frac{1}{d^2} = \frac{4(h^2+k^2+kh)}{3a^2} + \frac{l^2}{c^2}$$

The lattice parameters 'a' varies from 5.81 Å to 5.83 Å and 'c' varies from 32.85 Å to 33.17 Å. From structural parameters characterized by lattice constants 'a' and 'c' (Table 1), it becomes clear that lattice constant 'a' shows less variation and that of 'c' varies rapidly followed by slow variation with substitution. This is in agreement with the fact that all hexagonal ferrites exhibit constant lattice parameter 'a' and variable parameter 'c' [18].

The ionic radii of Mn (0.67 Å) and Zn (0.74 Å) are greater than that of iron (0.64 Å). Therefore the lattice constant 'c' should increase on substitution of Fe^{3+} by Mn-Zn. However the values of 'c' are found to decrease with the substitution. This may be due to change of the lattice distortion when Mn-Zn doping [19]. The particle size decreases with the substitution which may be attributed to suppression of Mn-Zn on the grain growth.

The X-ray density (d_x) was calculated from the relation,

$$d_x = \frac{2M}{N 0.866a^2c}$$

Where M is the molecular weight, N is Avogadro's number, "a" and "c" are lattice constants. The variation in X-ray density may be due to the difference in the molecular mass of doped samples (Mn – 55 amu and Zn – 65 amu) and undoped sample (Fe – 56 amu) [20].

The porosity (P) was calculated from the relation

$$P = 1 - \frac{d}{d_x}$$

Where d is bulk density and d_x is X-ray density.

The particle size (D) was calculated by using the relation

$$D = \frac{0.9\lambda}{b \cos \theta}$$

Where λ is the wavelength and b is FWHM.

The lattice parameters, unit cell volume, particle size, X-ray density, bulk density and porosity are shown in Table 1.

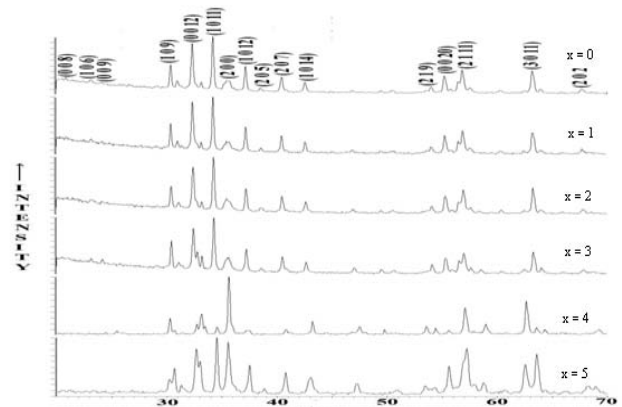


Fig 1. XRD of $\text{CuSr}_2(\text{MnZn})_{x/2}\text{Fe}_{16-x}\text{O}_{27}$

The morphology was studied by using TEM analysis. The TEM micrographs show that the particles are more or less hexagonal. The average particle size was found to be 54.3 nm which agrees nearly with that obtained from the XRD analysis. The crystallites are found to be agglomerated.

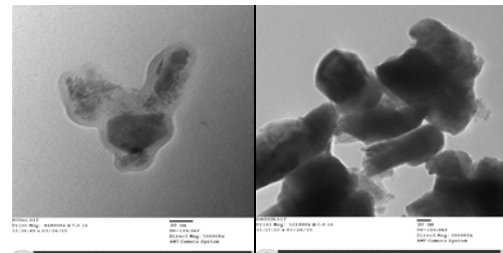


Fig 2 TEM images for $\text{CuSr}_2(\text{MnZn})_{0.5}\text{Fe}_{15}\text{O}_{27}$

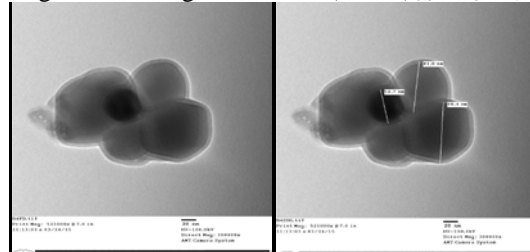


Fig 3 TEM images for $\text{CuSr}_2(\text{MnZn})_{1.0}\text{Fe}_{14}\text{O}_{27}$

Table 1.

Lattice parameters “a” &”c”, unit cell volume, particle size, X-ray density, bulk density and porosity

Sample	a (Å)	c (Å)	Volume(Å ³)	c/a	D (nm)	dx	d	P
B1	5.82	33.17	1121.92	5.70	74.32	5.35	3.08	0.42
B2	5.82	33.10	1121.64	5.69	65.80	5.36	3.04	0.43
B3	5.83	33.05	1124.95	5.66	53.32	5.36	3.19	0.41
B4	5.82	33.08	1119.92	5.69	51.89	5.40	3.09	0.43
B5	5.81	32.70	1102.02	5.63	56.61	5.50	3.09	0.44
B6	5.82	32.85	1113.36	5.64	40.25	5.46	3.07	0.44

Electrical Properties

The variation of conductivity with temperature is shown in figure 4. As expected the conductivity increases with temperature showing semiconductor behavior of the material. It can be seen that log σ increases linearly with that of temperature according to the Arrhenius equation $\sigma = \sigma_0 \exp\left(\frac{-E}{kT}\right)$, where E is the activation energy, k is Boltzmann’s constant and T is absolute temperature [8]. For each sample, there are two regions characterized by transition temperature and having different slopes. This is a magnetic transition from ferromagnetic to paramagnetic. The transition temperature is found to decrease with the MnZn concentration. The activation energy increases on passing through the transition temperature (Table 2). It may be due to valence exchange mechanism between Fe⁺³ and Fe⁺² [21].

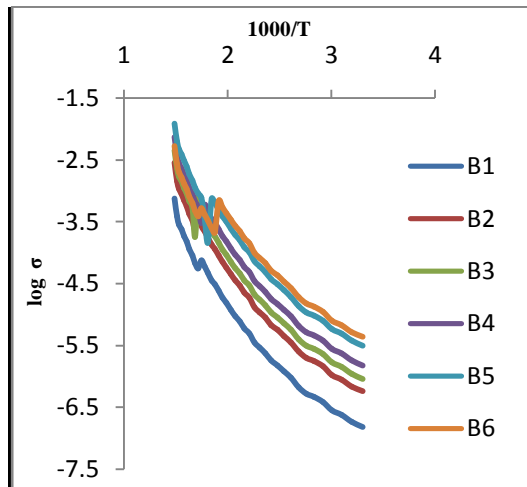


Fig 4. 1000/T V/S log σ

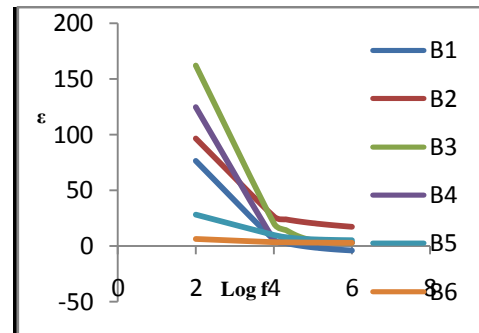


Fig 5 : Frequency dependence of dielectric constant

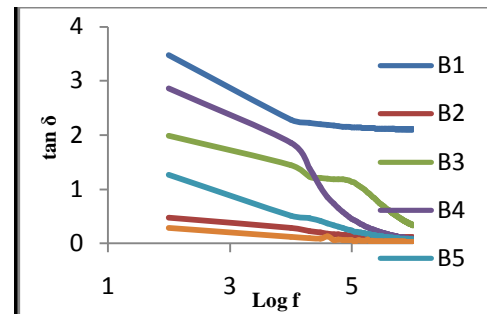


Fig 6 : Frequency dependence of loss tangent

Table 2

Activation Energy and Transition temperature

Code	Activation energy (eV)		Transition temperature (K)
	Ferri	Para	
B1	0.272	0.777	570.13
B2	0.314	0.807	583.09
B3	0.311	0.975	583.09
B4	0.298	0.800	563.06
B5	0.287	0.848	543.18
B6	0.276	0.536	523.01

The frequency dependence of dielectric constant is shown in figure 5. From the figure it is clear that the dielectric constant values are high at low frequencies that can be attributed to interfacial polarization that occur in heterogeneous structures. The dielectric constant decreases with the increasing frequency. Figure 6 shows variation of loss tangent ($\tan \delta$) with frequency. The loss tangent decreases with increasing frequency as expected [19].

IV. CONCLUSIONS

Nanocrystalline $\text{CuSr}_2\text{Fe}_{16}\text{O}_{27}$ hexaferrite powders were synthesized successfully by Co-precipitation method. The single domain particles of W-type hexaferrite were obtained at 1000°C . The X-ray diffraction patterns confirm that W-hexagonal phase is dominant. However, in some samples, few extra peaks corresponding to M – type were also observed. The particle size varies from 40.25 nm to 74.32 nm. The electrical conductivity increases with temperature indicating semiconducting behavior of material. The dielectric constant and loss tangent decreases with frequency of applied electric field. The high values of dielectric constant at low frequencies are due to the interfacial polarization ensuring that the samples can be considered as formed of well conducting grains and poorly conducting grain boundaries in agreement with Maxwell-Wigner theory with Koop's model.

REFERENCES

- [1] Mukhtar Ahmad, Ihasn Ali, M.U.Islam, *Ceramics International*, 38(2012) 1267-1273
- [2] B. Vishwanatha, V.R.K. Murthy, *Ferrite Materials; Science and Technology*, Narosa publishing house, New Delhi, U.P. 1990, pp. 429.
- [3] E.C. Snelling, *Soft Ferrites/Properties and Application*; second ed. Butter worths, London, 1988, pp.1.
- [4] J. Smith, H.P.J. Wijn, *Ferrites*, Philips Technical Library, Eindhoven, 1959, pp. 195.
- [5] A. Morisako, M. Matsumoto, M. Naoe, *IEEE Trans. Magn. M.* 3024 (1988)24.
- [6] T. L. Hylton, M. A. Parker, M. Ullah, K. R. Coffey, R. Umphress, J. K. Haward, *J. Appl. Phys.*75(1994)5960.
- [7] T.P. Niesen, M.R. de Guire, *J. Electroceram. M.* 169 (2001)6.
- [8] M. EL-SAADAWY *Journal of Materials Science and Engineering with Advanced Technology* Volume 5, Number 2, 2012, Pages 135-151
- [9] Mukhtar Ahmad, R. Grossing, Ihsan Ali, Ishtiaq Ahmad, M.U. Rana, *Journal of Alloys and Compounds* 577 (2013) 382–388
- [10] Gagan Kumar, Meenakshi Kanthwal, B.S. Chauhan, M Singh, *Indian Journal of Pure and Applied Physics*, Vol 44, Dec 2006, 930-934
- [11] K.J. Standley, *Oxide Magnetic Materials* (Clarendon Press, Oxford, 1962),p.36.
- [12] D.El Kony, S.A. Saafan, A.M. Abo El Ata. *Egypt. J. Sol.*, Vol. (23), No. (1), (2000)13.P.
- [13] R. Arjunwadkar, M. Y. Salunkhe, and C. M. Dudhe *Hindawi Publishing Corporation Journal of Solid State Physics* Volume 2013, Article ID 471472, 6 pages
- [14] M.U. Rana, M.U. Islam, Uzma Qadri, *Journal of Research (Science)*, Bahauddin Zakariya University, Multan, Pakistan. Vol.17, No.4, October 2006, pp. 219-224
- [15] R. Muller, *Journal of Magnetism and Magnetic Materials*,101(1991)230-232
- [16] C. Surig, K.A. Hempel, R. Muller, P. Gornert, *Journal of Magnetism and Magnetic Materials*, 150(1995)270-276
- [17] M.A. Ahmeda, N. Okasha, R.M. Kershi, *Materials Chemistry and Physics* 113 (2009) 196–201
- [18] H. Kojima, in: E.P. Wohlfarth (Ed.), (1982). *Ferromagnetic Materials*, vol. 3, North-Holland, Amsterdam, 305 pp.
- [19] Y. Wu et. al., *Journal of Magnetism and Magnetic Materials* 324(2012) 616-621
- [20] Imran Khan, Imran Sadiq, Muhammad Naeem Ashiq, Mazhar-Ud-Din Rana, *Journal of Alloys and Compounds* 509(2011)8042-8046
- [21] Heneda K., Kojima H., *Physica Status Solidi (A)*. 1971,6 , 256p