

EFFECT OF Zr⁴⁺ DOPING ON CURIE TEMPERATURE, STRUCTURAL AND MAGNETIC PROPERTIES OF Mg-Cr NANO-FERRITE

N.N. SARKAR^{a1}, K.G. REWATKAR^b, V.M. NANOTI^c AND D.S. BHOWMICK^d

^{ab}Department of Physics, Dr. Ambedkar College Deekshabhoomi, Nagpur, Maharashtra, India

^cDepartment of Applied Physics, Priyadarshani Institute of Engineering and Technology, Nagpur, Maharashtra, India

^dDepartment of Physics, Jhulelal Institute of Technology, Nagpur, Maharashtra, India

ABSTRACT

Zr substituted magnesium ferrite nano-powders, Mg_(1+x)Zr_x(Fe Cr)_(1-x)O₄ (x = 0.2, 0.4, 0.6, 0.8) were successfully synthesized using sol-gel auto combustion method. X-ray diffraction patterns of the synthesized ferrites shows that the lattice parameter and the average crystallite size increase with the addition of Zr-ion substitution. Curie temperature (T_c) measurements exhibit increasing trend with zirconium content for all the compositions. Enhancement in Curie temperature is observed due to the double phase present in the crystal structure. The saturation magnetization (M_s) initially increases with Zr concentration.

KEYWORDS: XRD, Curie Temperature, Magnetic Moments, Ionic Radius

Magnetic nanoparticles of spinel ferrites are of immense interest in fundamental science, which are of great interest for their remarkable magnetic, optical, and electric properties (Gawali et. al., 2012). Distribution of cations and physical properties are tied together and it presents a well-defined understanding of magnetic properties of spinel ferrite nanoparticle (Shetty et al., 2017). Spinel ferrites are iso-structural with the mineral MgAl₂O₄ and have the general molecular formula (M²⁺) [Fe₂³⁺] O₄²⁻, here; M²⁺ and Fe³⁺ are the divalent and trivalent cations, respectively belonging to the space group Fd3m. The lattice consists of 32 divalent oxygen ions which are in direct contact with one another, forming a closed pack face centered cubic arrangement with 64 tetrahedral interstitial sites (A sites) and 32 octahedral interstitial sites (B sites) (Safi et.al., 2015). Out of these, eight tetrahedral (A sites) and 16 octahedral (B sites) sites are engaged by the divalent and trivalent cations. The cation distribution of normal spinel ferrites which can be represented by the general formula.



Where the amounts in brackets represent the average occupancy of A sites and B sites and i is the inversion parameter. Depending on cation distribution, a spinel can be normal, inverse, or partially inverse. Since the peculiar properties of ferrites are strictly related to the distribution of cations between octahedral and tetrahedral sites in the spinal structure, the control of cation distribution provides a means to tailor their properties (Darokar et. al., 2000). Cation distribution depends on the electronic configuration and valence of ions. In the present

investigation, Mg_(1-x)Zr_x(Fe Cr)_(1-x)O₄, with contains four different cations Mg²⁺, Cr³⁺, Fe³⁺ and Zr⁴⁺ For such complex system, several new magnetic states are predicted depending on the strength of the anisotropy related to exchange interactions (Oliva et.al., 2012). The parameter “x” varied from x = 0.2, 0.4, 0.6 and 0.8 aim of this present work is to variance magnetic property in accordance with cation distribution of crystal structures and to determine the Curie temperature of the Mg_(1-x)Zr_x (Fe Cr)_(1-x) O₄ compound.

MATERIALS AND METHODS

The nano sized Mg, Zr and Cr doped mixed ferrite prepared by using magnesium nitrate, ferric nitrate, Chromium nitrate, Zirconium Oxycynitrate and Urea in a certain molar ratio and then dissolved in distill water. Urea helps the homogenous distribution of the metal ions to get segregate from the solutions. The solution is later subjected to a continuous stirring for the duration of 4 hrs; under constant heating of 100 °C to condense it into a gel [Javed and Rukh, 2008 & Kannan et. al., 2017]. Later on this drying up process a brown colored dried gel is held. The gel is further put in microwave oven to fire, crushed the burnt sample in a mortar pastel to obtain the homogeneous nano sized powders. Further the powder is subjected to sintering in a furnace.

Flow chart for synthesis of Mg (1-x) Zrx (Cr Fe) (1-x) O₄ nanoferrites:

¹Corresponding author

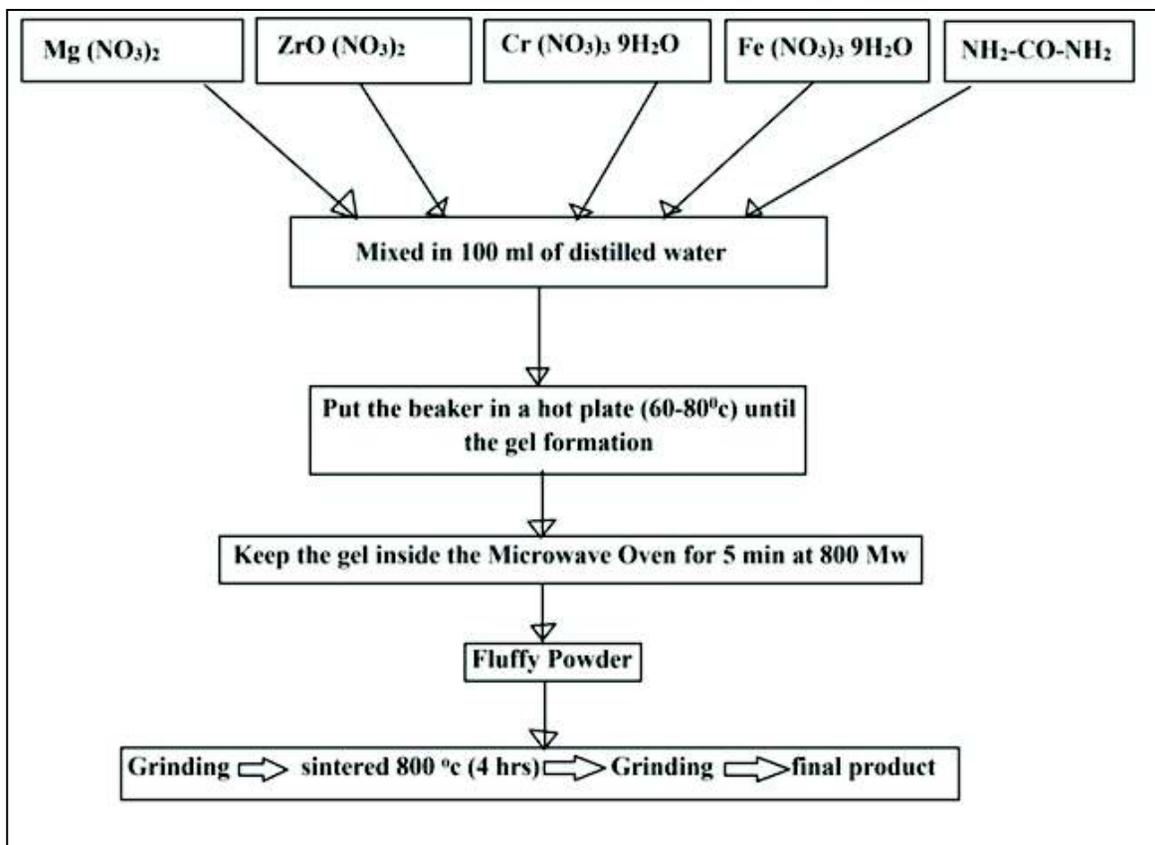


Figure 1: Flowchart of sample preparation

RESULTS AND DISCUSSION

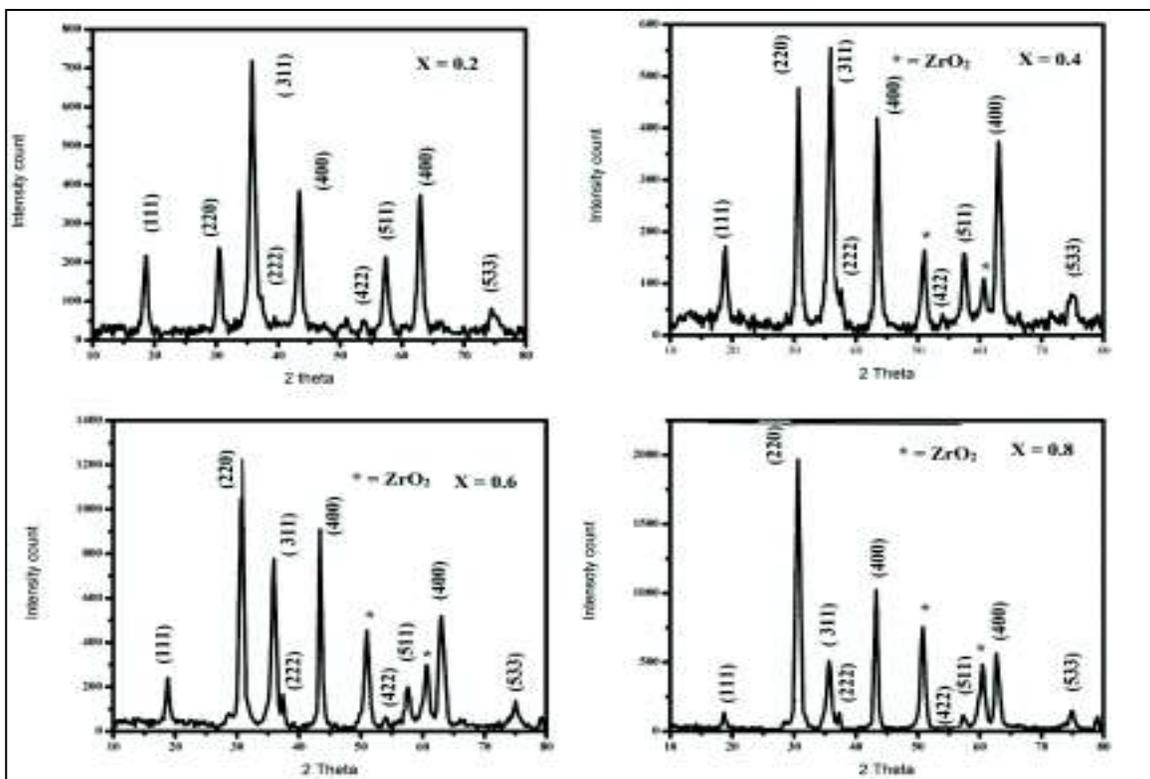
Structural Analysis Using XRD

Figure 2 shows the x-ray diffraction pattern of the Zr⁴⁺-substituted magnesium spinel ferrite, confirming the single-phase cubic spinel structure for $x=0.2$ and for other values of x shows the spinel structure with an extra phase of ZrO₂. An overall increase in lattice parameter (from $\sim 8.3341 \text{ \AA}$ for $x = 0.2$ to $\sim 8.4764 \text{ \AA}$ for $x = 0.8$), the lattice parameter can be calculated theoretically using the following equation (Abdallah and Moyo, 2014) (Han et al., 2012)

$$a_{th} = 8/(3\sqrt{3})[(R_A + R_B) + \sqrt{3}(R_A + R_O)] \quad (2)$$

Where 'R_O' is the radius of the oxygen ion (1.4Å), and 'R_A' and 'R_B' are the ionic radii of the tetrahedral (A site) and octahedral (B site) sites, respectively (Najafi Birgani et al., 2015). This increase in lattice constant is due to the increasing in substitution of Zr⁴⁺ ion having highest ionic radii 0.72 Å, from the X-ray diffraction data and using the Debye-scherrer formula we have calculated the

particle size with increasing order as the value of x increases (Moharkar et. al., 2012). Because of the drastic change in the particle size, the surface to volume ratio has decreases, therefore it affect strongly on the physical properties of ferrite like Magnetic saturation, Curie temperature etc. (Rondinone et. al., 1999). From figure 2 it has been observed with progressive Zr⁴⁺ ion substitution in the magnesium ferrite has partially inversed spinel structure and is expected to affect its lattice parameter (Binu et. al., 2011). Zr⁴⁺ ions are known to occupy tetrahedral (A) sites due to their strong preference for tetrahedral coordination (Jamadar et. al., 2011). From the figure 2 it is observed that the maximum intensity peak of miller indices (311) is gradually decreases as the value of 'x' increases. It may be due to the large ionic radius of Zr⁴⁺ ion which can disturb the arrangement of atomic position in the cubic system, therefore the ratio of number of atoms from the (311) plane is reduce. Hence the intensity of (311) plane is decreases which is clearly seems from the figure 2 the phase of ZrO₂ increases with larger values of Zr⁴⁺ ions.

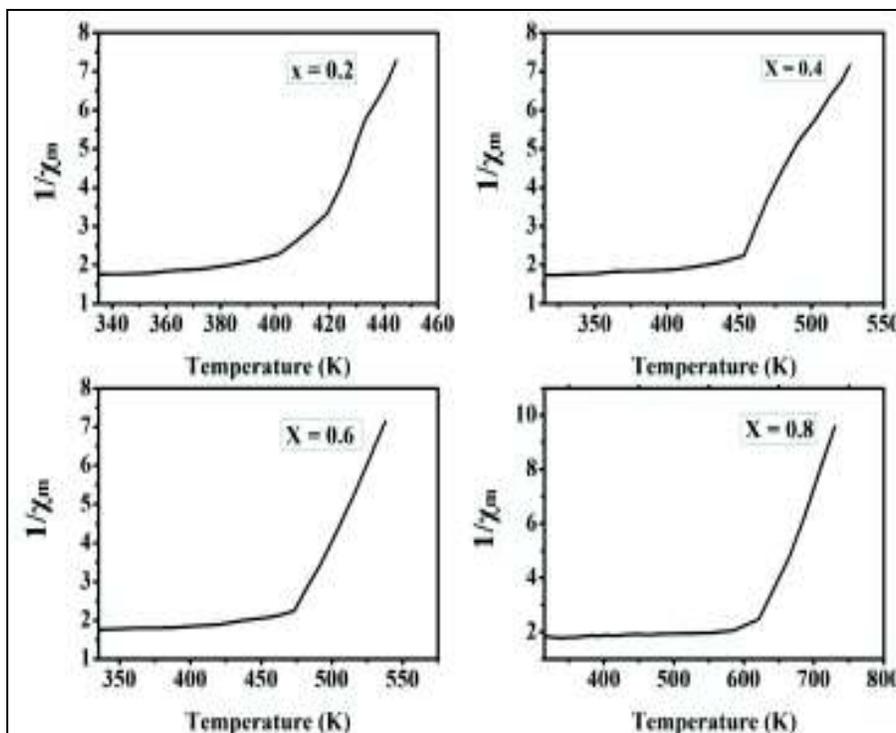
Figure 2: XRD of $Mg_{(1+x)}Zr_x(Fe Cr)_{1-x}O_4$ Table 1: Lattice parameter & Crystalline Size of $Mg_{(1+x)}Zr_x(Fe Cr)_{1-x}O_4$

Sr. No	Name of compound	Lattice parameter Theoretical (a_{th}) (Å)	Lattice parameter experimental (a_{exp}) (Å)	Crystalline size (nm)
1	$Mg_{1.2}Zr_{0.2}(Fe Cr)_{0.8}O_4$	8.5686	8.3341	15
2	$Mg_{1.4}Zr_{0.4}(Fe Cr)_{0.6}O_4$	8.6425	8.4122	20
3	$Mg_{1.6}Zr_{0.6}(Fe Cr)_{0.4}O_4$	8.7165	8.4601	35
4	$Mg_{1.8}Zr_{0.8}(Fe Cr)_{0.2}O_4$	8.8169	8.4764	43

Curie Temperature Measurements Using Gouy's Balance

Figure 3 shows variation of Curie temperature with Zr^{4+} content for $Mg_{(1-x)}Zr_x(Cr Fe)_{(1-x)}O_4$ ferrites, from the figure 3 it is observed that the Curie temperature increase as the value of x increase from x= 0.2 ($T_c = 403$ K) to x= 0.8 ($T_c = 623$ K). The Curie temperature is depends on the strength of magnetic moments and its alignment in the direction of applied field (Monaji et al., 2017). In present research work the theoretical magnetic moment for the sample x = 0.2 is highest ($1.6 \mu_B$) and for x = 0.8 ($0.4 \mu_B$) as shown in table 2, but the Curie temperature gradually increases even if the magnetic moment decreases (Chougule, Kumbhar, Kolekar, & Bhosale, 2014). The

above said phenomenon is exactly contrast with the conventional theories because increase in Curie temperature is indication of enhancement in magnetic moment. In this case, this type of contradiction may be due to average distance between tetrahedral (A- site) and octahedral (B-site) as depicted in the table 2. Therefore, the average distance between the cation is gradually increasing as the strength of anti-parallel magnetic interaction simultaneously decreases (Monaji & Das, 2015). Hence the total magnetization depends on individual magnetic moment of each cation site. This phenomenon may happened due to the larger ionic radius of Zr^{4+} ions (0.72 \AA) than that of Fe^{3+} (0.69 \AA) (Kannan et. al., 2017). It is observed that the value of Curie temperature is analogous increases concentration.

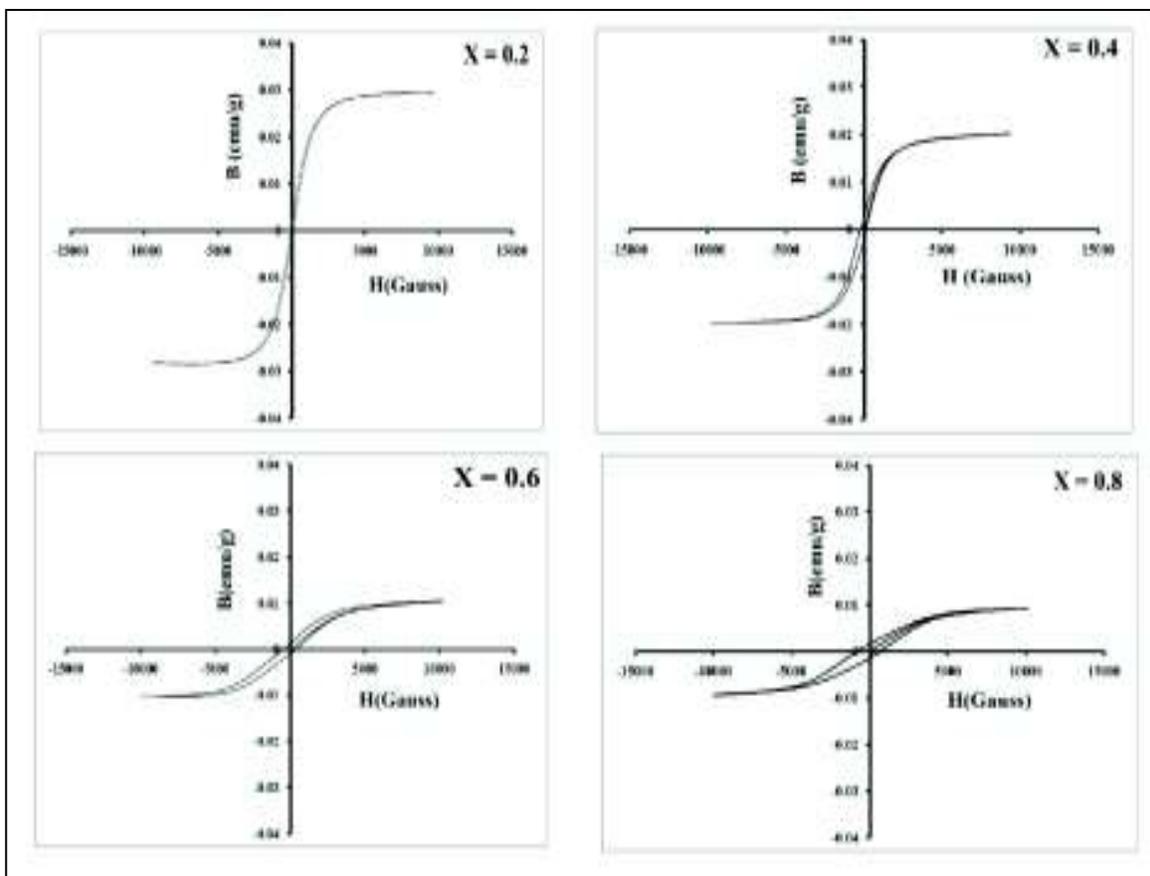
Figure 3: Curie temperature of $Mg_{(1+x)}Zr_x(Fe Cr)_{1-x}O_4$ Table 2: Cation distribution & Curie temperature of $Mg_{(1+x)}Zr_x(Fe Cr)_{1-x}O_4$

Sr No	Cation Distribution	Radius A-site (Å)	Radius B-site (Å)	Magnetic moment theoretical	Average distance between A and B (Å)	T _c (K)
1	(Zr _{0.2} Fe _{0.4})[Mg _{1.2} Cr _{0.8} Fe _{0.4}]	0.4	0.902	1.6 μB	0.651	403
2	(Zr _{0.4} Fe _{0.2})[Mg _{1.4} Cr _{0.6} Fe _{0.4}]	0.416	0.926	0.8 μB	0.671	453
3	(Zr _{0.6})[Mg _{1.6} Cr _{0.4} Fe _{0.4}]	0.432	0.950	0.8 μB	0.691	473
4	(Zr _{0.8})[Mg _{1.8} Cr _{0.2} Fe _{0.2}]	0.576	0.905	0.4 μB	0.740	623

Vibrating Sample Magnetometry (VSM)

Figure 4 shows field dependent magnetization curves (M-H) of Zr and Cr substituted Magnesium ferrites. Magnetization of all the compositions, at applied magnetic field of 1 KG.m, is observed to attain saturation at room temperature (Tahar et al., 2008). It is noted from the M-H curves that magnetization decreases with the increase in concentration of Zr⁴⁺ ions. The increasing coercivity is an indication of the change from superparamagnetic to ferromagnetic nature, which is verified experimentally (as shown in table 3). We know that the total magnetization in ferrites depend on the anti-parallel magnetic interaction between the magnetic moments of cations which are situated in tetrahedral (A- site) and octahedral (B- site) respectively (Li and Wang, 2009). Since, the overall magnetization comes from the difference between the

magnetization of the A and B sites respectively (Javed Iqbal and Rukh Siddiquah, 2008). The Zirconium ion occupied tetrahedral site therefore the magnetic moment of tetrahedral site is expected to decrease and the radius of A site cation increase which upsize the average distance between A and B site cations (Kumar and Kar, 2011). Therefore it augments the anti-parallel interaction between A and B site and hence magnetic moment gradually declines. On the basis of above explanation the magnetization step down with rise value of $x = 0.2$ to $x = 0.8$. From the XRD graph we have noticed that out of the four compositions only for $x=0.2$ composite is perfectly Single Cubic Crystal. While all other composition have an extra phase of ZrO₂, which is a key factor to reduce the magnetization of the given material, because ZrO₂ is perfectly non magnetic material.

Figure 4: BH curve studies of $Mg_{(1+x)}Zr_x(FeCr)_{1-x}O_4$ Table 3: Magnetization measurements of the compounds $Mg_{(1+x)}Zr_x(FeCr)_{1-x}O_4$

Samples	Saturation Magnetization (Ms) (emu/g)	Retentivity (Mr) (emu/g)	Coercivity (Hc) (Gauss)	Bohr magnetron (μ_B)/molecule
$Mg_{1.2}Zr_{0.2}(FeCr)_{0.8}O_4$	29.7×10^{-3}	1.89×10^{-3}	20	1.0477×10^{-3}
$Mg_{1.4}Zr_{0.4}(FeCr)_{0.6}O_4$	20×10^{-3}	1.5×10^{-3}	190	0.4843×10^{-3}
$Mg_{1.6}Zr_{0.6}(FeCr)_{0.4}O_4$	11×10^{-3}	1.98×10^{-3}	310	0.2694×10^{-3}
$Mg_{1.8}Zr_{0.8}(FeCr)_{0.2}O_4$	8.6×10^{-3}	2×10^{-3}	669	0.2125×10^{-3}

CONCLUSION

The nanocrystalline, $Mg_{(1+x)}Zr_x(FeCr)_{1-x}O_4$ spinel ferrites of different composition (where $x = 0.2, 0.4, 0.6, 0.8$) were successfully synthesized by sol-gel auto combustion technique. The X-ray diffraction results showed the formation of single phase for $x=0.2$ concentration while it produces double phase spinel structure for higher concentration. The lattice constant gradually rises with of Zr^{4+} ion concentration. The Curie temperature was found to be higher for larger vale of 'x'. From the VSM study it is observed that the saturation magnetization (Ms) is maximum for $x = 0.2$ and minimum for $x = 0.8$. We have

noticed that, the magnetization in these ferrite varies due to ionic radii of substituted ions and the site preferences.

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REFERENCES

Abdallah H.M.I. and Moyo T., 2014. Superparamagnetic behavior of $MnxNi_{1-x}Fe_2O_4$ spinel nanoferrites. Journal of Magnetism and Magnetic Materials,

- 361**(Supplement C), 170–174. <https://doi.org/10.1016/j.jmmm.2014.02.077>.
- Binu P. Jacob, Kumar A., Pant R.P., Singh S. and Mohammed E.M., 2011. Influence of preparation method on structural and magnetic properties of nickel ferrite nanoparticles. *Bulletin of Materials Science*, **34**(7):1345–1350. <https://doi.org/10.1007/s11051-009-9833-5>.
- Chougule P.K., Kumbhar S.S., Kolekar Y.D. and Bhosale C.H., 2014. Enhancement in Curie temperature of nickel substituted Co-Mn ferrite. *Journal of Magnetism and Magnetic Materials*, **372**:181–186. <https://doi.org/10.1016/j.jmmm.2014.07.060>.
- Darokar S.S., Rewatkar K.G., Choukuse M.S. and Kulkarni D.K., 2000. Electrical properties of Li 0.5 Fe 0.5+ x Al 12-x O 19 ferrites. *Indian Journal of Physics. Part A*, **74**(2):155–157.
- Gawali S.R., Rewatkar K.G. and Nanoti V.M., 2012. Structural and electrical properties of M-type nanocrystalline aluminium substituted calcium hexaferrites. *Advances in Appl. Sci. Res*, **3**(5): 2672–2678.
- Han Q.J., Ji D.H., Tang G.D., Li Z.Z., Hou X., Qi W.H., Bian R.R., 2012. Estimating the cation distributions in the spinel ferrites Cu 0.5-xNi 0.5Zn xFe 2O 4 (0.0??x??0.5). *Journal of Magnetism and Magnetic Materials*, **324**(12): 1975–1981. <https://doi.org/10.1016/j.jmmm.2012.01.039>.
- Jamadar H.V., Shelar M.B., Bhandare M.R., Shaikh A.M. and Chougule B.K., 2011. Magnetic properties of nanocrystalline nickel zinc ferrites prepared by combustion synthesis. *International Journal of Self-Propagating High-Temperature Synthesis*, **20**(2):118–123. <https://doi.org/10.3103/S1061386211020087>.
- Javed Iqbal M. and Rukh Siddiquah M., 2008. Structural, electrical and magnetic properties of Zr-Mg cobalt ferrite. *Journal of Magnetism and Magnetic Materials*, **320**(6):845–850. <https://doi.org/10.1016/j.jmmm.2007.09.009>.
- Kannan Y.B., Saravanan R., Srinivasan N. and Ismail I., 2017. Sintering effect on structural, magnetic and optical properties of Ni_{0.5}Zn_{0.5}Fe₂O₄ ferrite nano particles. *Journal of Magnetism and Magnetic Materials*, **423**(Supplement C): 217–225. <https://doi.org/10.1016/j.jmmm.2016.09.038>.
- Kumar L. and Kar M., 2011. Influence of Al³⁺ concentration on the crystal structure and magnetic anisotropy of nanocrystalline spinel cobalt ferrite. *Journal of Magnetism and Magnetic Materials*, **323**(15):2042–2048. <https://doi.org/10.1016/j.jmmm.2011.03.010>.
- Li X. and Wang G., 2009. Low-temperature synthesis and growth of superparamagnetic Zn_{0.5}Ni_{0.5}Fe₂O₄ nanosized particles. *Journal of Magnetism and Magnetic Materials*, **321**(9):1276–1279. <https://doi.org/10.1016/j.jmmm.2008.11.006>.
- Moharkar P.R., Gawali S.R., Rewatkar K.G. and Nanoti V.M., 2012. Improvisation of structural, electrical and magnetic properties of nanocrystalline Ca 2 Y hexaferrite on Al-substitution. *Journal of Computer Applications (IJCA)*.
- Monaji V.R. and Das D., 2015. Influence of Zr doping on the structural, magnetic and magnetoelastic properties of cobalt-ferrites. *Journal of Alloys and Compounds*, **634**:99–103. <https://doi.org/10.1016/j.jallcom.2015.02.084>.
- Monaji V.R., Indla S., Rayaprol S., Sowmya S., Srinivas A. and Das D., 2017. Temperature dependent magnetic properties of Co_{1+x}TxFe_{2-2x}O₄ (T = Zr, Ti). *Journal of Alloys and Compounds*, **700**:92–97. <https://doi.org/10.1016/j.jallcom.2017.01.061>.
- Najafi Birgani A., Niyafar M. and Hasanpour A., 2015. Study of cation distribution of spinel zinc nanoferrite by X-ray. *Journal of Magnetism and Magnetic Materials*, **374**:179–181. <https://doi.org/10.1016/j.jmmm.2014.07.066>.
- Oliva M.I., Heredia A., Zandalazini C.I., Crivello M. and Corchero E., 2012. Magnetic behavior of Mg-Al-Zn-Fe mixed oxides from precursors layered double hydroxide. *Physica B: Condensed Matter*, **407**(16):3125–3127. <https://doi.org/10.1016/j.physb.2011.12.042>.
- Rondinone A.J., Samia A.C.S. and Zhang Z.J., 1999. Superparamagnetic relaxation and magnetic anisotropy energy distribution in CoFe₂O₄ spinel ferrite nanocrystallites. *The Journal of Physical*

- Chemistry B., **103**(33):6876–6880. <https://doi.org/10.1021/jp9912307>.
- Safi R., Ghasemi A., Shoja-Razavi R., Ghasemi E. and Sodaee T., 2015. Rietveld structure refinement, cations distribution and magnetic features of CoFe₂O₄ nanoparticles synthesized by co-precipitation, hydrothermal, and combustion methods. *Ceramics International*. <https://doi.org/10.1016/j.ceramint.2016.01.032>.
- Shetty K., Lokesh S.V., Rangappa D., Nagaswarupa H.P., Nagabhushana H., Anantharaju K.S. and Sharma S.C., 2017. Designing MgFe₂O₄ decorated on green mediated reduced graphene oxide sheets showing photocatalytic performance and luminescence property. *Physica B: Condensed Matter*, **507**:67–75. <https://doi.org/10.1016/j.physb.2016.11.021>.
- Tahar L. Ben, Artus M., Ammar S., Smiri L.S., Herbst F., Vaulay M.-J. and Fievet F., 2008. Magnetic properties of CoFe 1.9 RE 0.1 O 4 nanoparticles (RE= La, Ce, Nd, Sm, Eu, Gd, Tb, Ho) prepared in polyol. *Journal of Magnetism and Magnetic Materials*, **320**(23): 3242–3250.

