IMPACT OF ZINC SUBSTITUTION ON STRUCTURAL AND OPTICAL BEHAVIOR OF MIXED FERRITES

Dilip Badwaik
Kamla Nehru Mahavidyalaya, Nagpur., India

ABSTRACT

A series of zinc substituted mixed cadmium magnesium nano sized ferrites with composition $Cd_{(0.5)}Mg_{(0.5-x)}Zn_{(x)}Fe_{(1.5)}$ (CoTi) $_{(0.25)}O_4$ (X = 0, 0.1, 0.2, 0.3, 0.5) were synthesized by sol gel auto combustion route. The structural and crystal phase of the nanocrystalline powders were characterized by X-ray powder diffraction pattern, which shows formation of single cubic spinel phase. The lattice parameter, X-ray density (Dx), jumping length at tetrahedral and octahedral site of the samples are measured from XRD data. The lattice parameter demonstrated a slight variation with increasing Zn content. The crystallite size is in the range 62- 136 nm, shows nano sized of prepared samples. The FTIR spectroscopy is used to deduce the structural investigation and confirmation of ferrite.

Keywords: Nano ferrites, sol gel auto combustion, structural analysis, FTIR.

I. INTRODUCTION

Spinel ferrites are good dielectric materials because of their high resistivity and low loss behaviour and hence vast applications over a wide range of frequencies. The importance of the soft magnetic ferrites, in low frequency inductors, antenna rods and wide-band are well known and their uses in the fields have been continuously increasing for several decades. In nano region the properties of ferrites are strongly depends on the particle size. Due to large surface/volume ratio the properties of nanoferrites are different from their bulk counterparts [1.2]. The nano scale size of the well-known spinel ferrites has opened up the door for intensive research to utilize their properties for biomedical applications [3, 4].

Mixed spinel ferrites have been studied intensively over the last few years due to their potential applications. Spinel ferrites have the chemical formula MFe_2O_4 in which M can be any divalent metal cations. In spinel ferrite, oxygen forms face centre cubic (FCC) lattice with divalent cations at tetrahedral (A) and/or octahedral (B) sites. Numerous methods were reported in literature showing the possibilities of producing particle with size in the range of 2 - 100 nm. Among these methods are co-precipitation, hydrothermal and sol-gel Methods [5, 6], which were reported to be fast and producing high quality nanoparticles. Magnesium ferrite ($MgFe_2O_4$) has an inverse spinel structure with the preference of Mg^{2+} cations mainly on octahedral sites [7, 8], while Zinc ferrite ($ZnFe_2O_4$) has normal spinel structure, in which Zn^{2+} cations mainly occupy tetrahedral sites [7].

In this work, the aim is to synthesis nano-ferrites using sol gel auto combustion method and to investigate its structural and optical properties. Moreover, the effect of doping of Zinc (Zn) substituted cadmium magnesium ferrites was investigated. X-ray diffraction (XRD) was used to confirm the formation of single phase spinel structure and to determine the crystalline size. Fourier Transform Infrared Spectroscopy (FTIR) is used in order to explore the effect of Zn substitution on the optical properties of cadmium magnesium nano-ferrites.

I. EXPERIMENTAL DETAILS

A series of polycrystaline mixed cadmium magnesium nano ferrites substituted with Zn having composition $Cd_{(0.5)}Mg_{(0.5-x)}Zn_{(x)}Fe_{(1.5)}$ (CoTi) $_{(0.25)}O_4$ (X = 0, 0.1, 0.2,

0.3, 0.5) were synthesized by sol gel auto combustion method using stoichiometric proportion of 99.9% pure AR grade cadmium nitrate ($Cd(NO_3)_2$,$4H_2O$), zinc nitrate ($Zn(NO_3)_2$, H_2O), magnesium nitrate ($Mg(NO_3)_2$,$6H_2O$),ferric nitrate ($Fe(NO_3)_3$, $9H_2O$), cobalt nitrate ($Co(NO_3)_2$,$6H_2O$)and titanium tetrachloride ($TiCl4$) as starting materials. Urea is used as fuel to supply requisite energy to initiate exothermic reaction amongst oxidants. Starting materials and fuel were dissolved in minimum amount of double distilled water; stirred the solution for 1h at room temperature to obtained uniform solution. Continue the stirring of the mixed nitrate aqueous solution on a magnetic hot-plate stirrer maintaining the temperature 60 °C. During the evaporation stages, solution became viscous and later on formed a viscous brown gel. Increase the temperature slowly above 60 °C, a sticky gel began to bubble for few minutes in a beaker. Finally gel got ignited automatically and burned with a glowing flint. The product of this reaction is fluffy loose powder of brown coloured ash could be termed as $Cd_{(0.5)}Mg_{(0.5-x)}Zn_{(x)}Fe_{(1.5)}$ (CoTi) $_{(0.25)}O_4$ presintered ferrite. The fluffy brown ash grinded in pestle mortal for 1h, then calcinated at 900 °C for 6 hours. Grind the samples again for 1h to get nano ferrites ready for characterization.

In this work, $Cd_{(0.5)}Mg_{(0.5-x)}Zn_{(x)}Fe_{(1.5)}$ (CoTi) $_{(0.25)}O_4$ (X = 0, 0.1, 0.2, 0.3, 0.5) were synthesized by sol gel auto combustion method. X-ray diffraction (XRD) was used to investigate the structure of Zn substituted cadmium magnesium nano-ferrites and to determine the lattice parameters and the space group symmetry. The Fourier Transform Infrared (FTIR) spectra of the synthesized powders were recorded using FTIR spectrometer in the wave number range 4000 cm^{-1} to 400 cm^{-1} using KBr pellets to ratify the spinel structure of the samples.

II. RESULTS AND DISCUSSION

A. STRUCTURAL PROPERTIES

Fig. 1 shows the powder x-ray diffraction pattern of $Cd_{(0.5)}Mg_{(0.5-x)}Zn_{(x)}Fe_{(1.5)}$ (CoTi) $_{(0.25)}O_4$ nano ferrites where, (X= 0.0, 0.1, 0.2, 0.3, 0.5).The peak were indexed as (220), (311), (400), (422), (511) and (440) corresponding to 2θ values of 30º, 35º, 42.5º, 53º, 56.5º and 62º. From XRD patterns we confirmed that all prepared samples have single phase cubic spinel structure,as all observed peak matched well with the(JCPDS Card No.019-0629) .In addition , the patterns were also the same for all values of x , indicating that the crystal structure of Zn substituted CdMg nanoferrite samples remain the same as X = 0. The broadness of the peaks shows small crystallite size of particles. The unit cell dimensions are determined from the d-spacing of a most intense peak (3 1 1) by making use of the cubic formula for inter-planer spacing.

$$a = d \ (h^2 + k^2 + l^2)^{1/2}$$

Where,

a = Lattice constant;

d = Inter planer distance;

(h k l) is the miller indices of the crystal planes

The theoretical density (X-ray density) was calculated from XRD data using the following equations.

$$D_x = ZM/Na^3$$

Where,

Z= No. of molecules per unit cell (Z = 8)

M=Molecular weight of the sample.

N= Avogadro's number (N = 6.023*10^{23}),

a = Lattice constant.

The crystallite size has been calculated from most intense diffraction peak (3 1 1) by Debye Scherrer formula,

$$D = K\lambda/ \ \beta \ Cos\theta$$

Where,

D = Crystallite size,

λ = Wavelength of incident X-rays,

θ =Diffraction angle

β =Full-width at half-maximum (FWHM), and

K = Shape factor, about 0.9 for spherical shaped particles.

The crystallite size is found to scattered in the range 62 – 136 nm for different composition. It is noticed that the size of particle decrease with the increase of Zn concentration up to X = 0.2 then it increase.

The lattice parameter, X-ray density, crystallite size, cell volume, has been calculated from XRD data are furnished in the Table 1. The lattice parameter demonstrated a slight variation with increasing Zn content. This may be due to difference in the ionic radii of Mg^{+2} and Zn^{+2}. The value of lattice parameter calculated in the prepared sample is in agreement with earlier reported values [9]. It is observed that the value of X-ray density goes on increasing with content of Zn^{+2} ion is due to the fact that molecular weight of Zn ion(65.38 g/m) is more than Mg ion (24.3050g/m)..

Using the values of lattice constant "a" the distance between magnetic ions(ion jumping length) in tetrahedral A-site and octahedral B-site ie "L_A" and "L_B" respectively was calculated by using the following equation [10],

$$L_A = (\sqrt{3}/4)\,a$$
$$L_B = (\sqrt{2}/4)\,a$$

The calculated values of ion jump lengths (L_A and L_B) are given in Table 4.6. The behavior of ion jump lengths with Zinc concentration (x) is attributed to the variation of lattice constant with the Zn content (x).
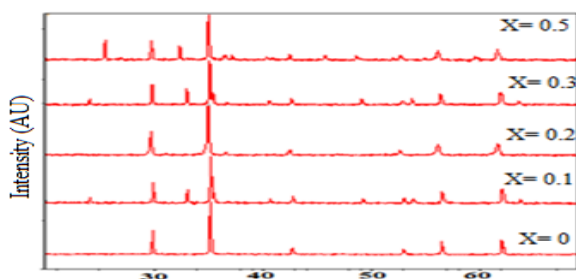

Fig. 1 XRD spectra of $Cd_{0.5}Mg_{0.5-X}Zn_X Fe_{1.5} (TiCo)_{0.25}O_4$

Table 1. Crystallite size, Lattice constant, volume of the unit cell, X-ray density (Dx) and hoping length (L_A, L_B) of $Cd_{(0.5)}Mg_{(0.5-x)}Zn_{(x)}Fe_{(1.5)}(CoTi)_{(0.25)}O_4$

Sr. No.	X	Crystallite size 't' (nm)	Lattice constant 'a'(A°)	Cell Volume (A°)³	X-ray Density (gm/cm³)	L_A (A°)	L_B (A°)
1	0	136	8.4668	606.9727	5.3145	3.666	2.993
2	0.1	124	8.4409	601.3808	5.4547	3.655	2.984
3	0.2	62	8.4816	610.1572	5.4656	3.672	2.998
4	0.3	124	8.4532	604.0489	5.6112	3.660	2.988
5	0.5	99	8.4626	606.0655	5.7726	3.664	2.991

B. FTIR RESULTS

The FTIR spectroscopic technique is a very important tool to deduce the structural features and redistribution of cations between tetrahedral and octahedral site [11] of spinel structure of ferrite nanoparticles. The FTIR absorption spectra of the samples $Cd_{(0.5)}Mg_{(0.5-x)}Zn_{(x)}Fe_{(1.5)}(CoTi)_{(0.25)}O_4$ were recorded in the range of 400 cm^{-1} and 4000 cm^{-1} are shown in Fig. 2. The spectra shows two strong characteristics broad absorption bands, one for tetrahedral position around 600cm^{-1} (υ_1) and other for octahedral position around 400cm^{-1} (υ_2) and may be caused by metal oxide mode of vibrations in the tetrahedral site and is higher than that of octahedral site [12, 13] and according to Waldron which confirms the formation of single phase cubic spinel structure of ferrites. Since the tetrahedral site dimensions are less as compared to octahedral, the band frequency of 'υ_1' is higher than the 'υ_2'absorption band[14]. Further the spectrum shows absorption bands at 1627.92cm^{-1} corresponding to No_3^{-1} ions, and also due to the presence of carboxyl group (COO^{-1}). The broad band that appears at 3434.89cm^{-1} attributed to hydrogen bonded O – H stretching vibration [15].The difference in intensity of 'υ_1'and 'υ_2'absorption band is also due to the changes in bond length of Fe^{3+}- O^{-2} at tetrahedral A- site and octahedral B- site [16,17].

The position of absorption band 'υ_1'and 'υ_2' are enumerated in Table 2. The vibration frequency depends on cation mass, cation distance and bending force. From Table 2 it is noted that there is shifting of band position 600 cm^{-1} 'υ_1' towards lower wavelength region is due to increase of Zn^{+2} ion in ferrite and preferably occupies the tetrahedral site. Cd^{2+} ion also prefer tetrahedral site (A- site). However Mg^{2+} ion occupy the (B-site), but Fe^{3+} ion occupy both tetrahedral and octahedral site . Substitution of Zn^{2+}ion in the system decrease the amount of Mg^{2+} at octahedral site ,this leads to moving of Fe^{3+}ion from tetrahedral site to octahedral site. Thus there is increase in amount of Fe^{3+} ion in the octahedral B- site. This leads to shifting of band position (400cm^{-1}) υ_2 towards lower wavelength. The cation distribution of ferrite are represented as follows

$$(Fe_{1-x}\,Cd_{0.5}\,Zn_x)\,[Mg_{0.5-x}\,Fe_{1+x}]^3O_4{}^{2-}$$

The force constant for tetrahedral site (K_t) and octahedral site (K_0) were calculated by employing the method suggested by Waldron [18] and according to them the force constant (K_t) and (K_0) are given as

$$K_t = 7.62 * M_1 * \upsilon_1{}^2 * 10^{-7} \ N/m$$

$$K_0 = 10.62 * M_2/2 * \upsilon_2{}^2 * 10^{-7} \ N/m$$

Where,
M_1 and M_2 are respectively the molecular weight of cation at A and B- site. The calculated values of (K_t) and (K_0) are listed in Table 2. The octahedral force constant decrease as Zn^{2+} ion content increase in the ferrite system. The addition of Zn^{2+} ion content in tetrahedral site successively transfer Fe^{3+} ion form tetrahedral to octahedral site and which is responsible for the decrease of the octahedral force constant. In other word due to addition of Zn^{2+} ion the charge imbalance in the system takes place and hence the oxygen ions are likely to move away from Fe^{3+} ion which in turn decreases the octahedral force constant [19].
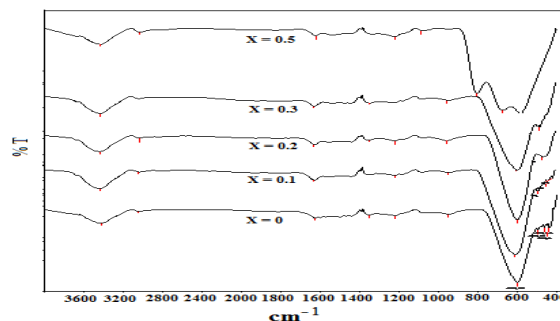

Fig. 2 FTIR spectra of $Cd_{0.5}\,Mg_{0.5-x}\,Zn_x\,Fe_{1.5}\,(TiCo)_{0.25}O_4$

Sr. No	Content	υ_1	υ_2	K_t* 10^5 Dyne/cm	K_o* 10^5 Dyne/cm
1	X = 0	601.5	492.85	3.340	2.242
2	X = 0.1	605.52	491.88	3.385	2.233
3	X = 0.2	592.43	464.83	3.240	1.994
4	X = 0.3	596.57	478.83	3.285	2.116
5	X = 0.5	581.53	---	3.1220	---

Table 2. Data on the position of FTIR absorption bands (υ_1, υ_2) and force constants (K_t, K_o)

IV. CONCLUSION

Spinel ferrite having generic formula $Cd_{(0.5)}Mg_{(0.5-x)}\,Zn_{(x)}\,Fe_{(1.5)}(CoTi)_{(0.25)}O_4$ were successfully prepared by Sol-Gel auto combustion route. Particle size is in the range 62nm to 136nm. The slight variation in lattice constant may be due to slight difference in the ionic radii of compound. In observed that size of particle decrease with the increase of Zn concentration up to X = 0.2 then it increase. The x-ray density increase with increasing concentration of Zn is due to molecular weight of substituted Zn ion(65.38 g/m) is more than the molecular weight of Mg ion (24.3050 g/m) .The strong characteristics absorption band observe at 600 cm^{-1} for tetrahedral position and 400 cm^{-1} for octahedral position confirmed the formation of single phase cubic structure of spinel ferrites. From FTIR result it is clear that with Zn ion doping, the absorption band υ_2

shifts to the lower frequency side and v_1 shifts to the higher frequency side which indicates that the occupancy of Zn ions at octahedral site (B-site).

V. REFERENCES

[1] S. Roy, I. Dubenko, D.D. Edorh, N. Ali, J. Appl. Phys. 96 (2004) 1202–1208.

[2] J. Jacob, M. Abdul Khadar, J. Magn. Magn. Mater. 322 (2010) 614–621.

[3] Kumara, C.S.S.R. and Mohammad, F. Advanced Drug Delivery Reviews, 63,(2011) 789-808.

[4] Sharifi, I., Shokrollahi, H. and Amiri, S. Journal of Magnetism and Magnetic Materials, 324, (2012) 903-915.

[5] Chen, Y., Ruan, M., Jiang, Y.F., Cheng, S.G. and Li, W. Journal of Alloys and Compounds, 493, (2010) L36-L38.

[6] Liu, Q., Sun, J.H., Long, H.R., Sun, X.Q., Zhong, X.J. and Xu, Z. Materials Chemistry and Physics, 108, (2008) 269-273.

[7] Rahman, S., Nadeem, K., Anis-ur-Rehman, M., Mumtaz, M., Naeem, S. and Letofsky-Papst, I. Ceramics International,39, (2013) 5235-5239.

[8] Pradeep, A., Priyadharsini, P. and Chandrasekaran, G.. Journal of Magnetism and Magnetic Materials, 320, (2008) 2774-2779.

[9] P. B. Belavi, G. N. Chavan, L. R.. Naik,R. Somashekar,R. K. Kotnala.material chemistry and physics 132,(2012)138-144.

[10] Mamilla Lakshmi, K.Vijaya Kumar, K. Thyagarjan Advances in nanoparticles 5,(2016) 103-113.

[11] Heibd ,Z.K, Iman , N.G Mohamed, M.B.J. Mol. struct,1095, (2015) 61-68.

[12] M. A Amer physics stat. sol. (b) 237, No2, (2003) 459.

[13] S.C Watawe , S. Keluskar, Gonbare, R. Tangsali Thin solid films 505, (2006) 168.

[14] Gadkari A, Shinde T ,Vasambekar P..Journal of Alloys and compounds. 509(3), (2011) 966-72.

[15] Torkian S , Ghasemi A ,Shoja Razavari R,Tavoosi M. Journal of superconductivity and Novel magnetism.,29(6), (2016) 1627-40.

[16] Patil R, Delekar S, Mane D, Hankare P.Results in physics.3,(2013)129-33.

[17] Sairsath SE, Toksha B.G,Kadam R.H,Patange S.M,Mane D.R.Jangam G.S,et.al. Journal of physics and chemistry of solids.71(2), (2010)1669-75.

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

[19] W.D. Kingery, H.K.Bowen , O.R. Uhlmann , Intrduction to ceramics, Wiley, New York, 1975,P. 904