Cation Distribution of Cu^{2+} Substituted NiZn Ferrite.

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Abstract

Cation distribution of Cu^{2+} substituted NiZn ferrites having general formula $Ni_{0.5}Cu_{x/2}Zn_{(0.5-x/2)}Fe_2O_4$ (where x = 0.3,0.4,0.5,0.6) were investigated. From proposed cation distribution, it was found that Zn^{2+} occupied A and B site, which replaced Fe^{3+} ions. The distribution was confirmed by theoretical and experimental magnetic moment values as well as by theoretical and experimental lattice parameter values.

Keywords: Cation distribution; magnetic moment; lattice parameter.

Introduction

NiCuZn ferrites are commercially important because of their excellent magnetic and electrical properties[1]. Also, they are dominantly used in multilayer ferrites chip inductor (MLFCI), have better high frequency properties and low densification temperature[2-4]. The properties of NiCuZn ferrite depend mainly on the technique and conditions of preparation, which in turn affect the cation distribution over the tetrahedral A-site and the octahedral B-site. In present work, $Ni_{0.5}Cu_{x/2}Zn_{(0.5-x/2)}Fe_2O_4$ (where x = 0.3,0.4,0.5,0.6) were prepared at different chemical reaction temperature (100^0C, 125^0C, 150^0C) and were further sintered using microwave sintering method. The intension was to study the effect of composition and chemical reaction temperature on cation distribution of NiCuZn ferrite.

Material and Method

Synthesis – NiCuZn ferrite powders, having general formula $Ni_{0.5}Cu_{x/2}Zn_{(0.5-x/2)}Fe_2O_4$ (where x = 0.3, 0.4, 0.5, 0.6) have been prepared at three different chemical reaction temperature followed by sintering using microwave oven operating at maximum power output of 700 W, Godrej Microwave Oven, Model – GMS 17M07 WHGX. AR grade Nickel nitrate, ferric nitrate, zinc nitrate and copper nitrate were used as starting materials. The stoichometric proportions of nitrates were weighed and added in 100 ml of distilled water to produce an aqueous solution. The solution was kept in paraffin oil bath at three different chemical reaction temperature 100^0C, 125^0C, 150^0C with constant stirring using magnetic stirrer. The process was carried out for 3 h in which the nitrous fumes were released which could be seen directly. The solution was then obtained in the form of slurry which was transferred to the microwave oven. The

irradiation was given for 20 to 50 minutes at maximum power in the form of pulses and the release of nitrous fumes was allowed to escape. The irradiation process was stopped when nitrous fumes were evaporated completely. Soon the ferrite formed was taken out from the microwave oven and then was crushed in agate mortar.

Characterization – The XRD measurements were carried out using D8 Advance by M/s Bruker AXS, GmbH, Germany. EDAX measurements were carried out by the energy-dispersive X-ray spectrometer attached to FEG-SEM, model JSM-7600F.

Results and Discussion

Compositional Analysis – In order to confirm the chemical composition, EDAX (Energy Dispersive Analysis of X-rays) was carried out on all the samples and few are presented in Figure I, Figure II, Figure III and Figure IV. The obtained EDAX could quantify the Ni, Cu, Zn, Fe and O contents. The weight percentage (wt %) of different elements (Ni, Cu, Zn, Fe, O) calculated theoretically from the chemical composition $Ni_{0.5}Cu_{0.2}Zn_{0.3}Fe_2O_4$ (i.e. x = 0.4) prepared at chemical reaction temperature 100^0C and that obtained from EDAX analysis agrees with each other. The outcome of the calculations is summarized in Table I. The results of EDAX confirm the expected stoichiometry. No trace of any impurity (except for small amount of carbon) was found indicating the purity of the samples.

Table I – EDAX result for x = 0.4, Chemical reaction temp. = 100^0C

Element	EDAX (wt %)	Expected (wt %)
	x = 0.4	x = 0.4
Ni	9.40	12.061
Cu	6.34	5.221
Zn	8.42	8.057
Fe	42.82	48.361
O	25.43	26.296

Lattice Parameter

Lattice parameter of each of the samples was calculated from XRD data and listed in Table II. From the Table II, it is clear that lattice parameter slightly decreases with composition (x) for all the three chemical reaction temperatures (100^0C, 125^0C, 150^0C). Decrease in the lattice parameter was attributed to the replacement of larger Zn^{2+} (0.74 Å) ions by smaller Cu^{2+} (0.73 Å) ions[5]. Also the variation in lattice parameter was very small, due to small difference in ionic radius of Zn^{2+} and Cu^{2+} ions. With respect to chemical reaction temperature (Table II) it is clear that variation in lattice parameter showed same trend for the samples prepared at 125^0C and 150^0C, while samples prepared at 100^0C slightly differ. This can be attributed to chemical kinematics. Increasing chemical reaction temperature, increases reaction rates

because of the disproportionately large increase in the number of high energy collisions. Collisions only result in a reaction if the particles collide with enough energy to get the reaction started. This minimum energy required is called the activation energy for the reaction[6]. Values of lattice parameter given in literature, agrees well with the pure ferrites.

Table II – Lattice parameter from XRD data, Ionic radii calculated from XRD data and cation distribution.

Chem. reaction temp.	Comp.	Lattice Parameter From XRD data	Ionic radius from XRD data A and B site		Ionic radius from cation distribution A and B site	
(^{o}C)	x	a_{expt} (Å)	r_A^I (Å)	r_B^{II}(Å)	r_A(Å)	r_B(Å)
100	0.3	8.3841	0.4152	0.6960	0.6402	0.6786
	0.4	8.4007	0.41872	0.7002	0.6437	0.6763
	0.5	8.3785	0.4139	0.6946	0.6422	0.6769
	0.6	8.3785	0.4139	0.6946	0.6411	0.6773
125	0.3	8.3924	0.4170	0.6981	0.6454	0.6756
	0.4	8.3841	0.4152	0.6960	0.6521	0.6714
	0.5	8.3841	0.4152	0.6960	0.6459	0.6748
	0.6	8.3785	0.4139	0.6946	0.6505	0.6718
150	0.3	8.3924	0.4170	0.6981	0.6445	0.6761
	0.4	8.3841	0.4152	0.6960	0.6453	0.6754
	0.5	8.3841	0.4152	0.6960	0.6424	0.6768
	0.6	8.3841	0.4152	0.6960	0.6436	0.6758

Estimation of Cation Distribution

Spinel ferrite with formula $MeFe_2O_4$ contains two types of sites – tetrahedral (A) site and octahedral (B) site. The distribution of the cations over these two sites can be expressed as[7] –

$$Me_\delta^{II} Fe_{1-\delta}^{III} \left[Me_{1-\delta}^{II} Fe_{1+\delta}^{III} \right] O_4 \quad \text{------ (1)}$$

where, the ions on tetrahedral (A) sites are given in front of the square brackets and the octahedral (B) site ions between the brackets. δ is a constant which can determine the cation distribution. For the system under investigation $Ni_{0.5}Cu_{x/2}Zn_{(0.5-x/2)}Fe_2O_4$, the cation distribution can be expressed as –

$$Zn_\delta Fe_{1.1-\delta} \left[Ni_{0.5} Zn_{\gamma-\delta} Cu_{x/2} Fe_{1.9-(0.5+\gamma-\delta+\frac{x}{2})} \right] \quad \text{------ (2)}$$

where, $\gamma = 0.5 - \dfrac{x}{2}$

Therefore the mean radius of the ion at the tetrahedral site is given by[8] –

$$r_A = \frac{1}{1.1} \left[\delta \, r_{zn} + (1.1 - \delta) \, r_{Fe} \right] \quad \text{------ (3)}$$

And the mean radius of the ion at octahedral site is given by[8] –

$$r_B = \frac{1}{1.9} \left[0.5 \, r_{Ni} + (\gamma - \delta) \, r_{Zn} + \frac{x}{2} r_{Cu} + (1.9 - (0.5 + \gamma - \delta + x/2)) \, r_{Fe} \right] \quad \text{------ (4)}$$

values of r_A and r_B are given in Table II. On the other hand, the mean radius of the ions at tetrahedral (A) and octahedral (B) sites can be calculated using lattice parameter (a) obtained from XRD data and oxygen parameter (u = 3/8 = 0.375) using equations[7] –

$$r_A^I = a \sqrt{3} (u - 0.25) - R_o \quad \text{------ (5)}$$

$$r_B^{II} = a \left(\frac{5}{8} - u \right) - R_o \quad \text{------ (6)}$$

where, 'R_o' is the radius of the oxygen ion (1.32 Å), values of r_A^I and r_B^{II} are given in Table II.
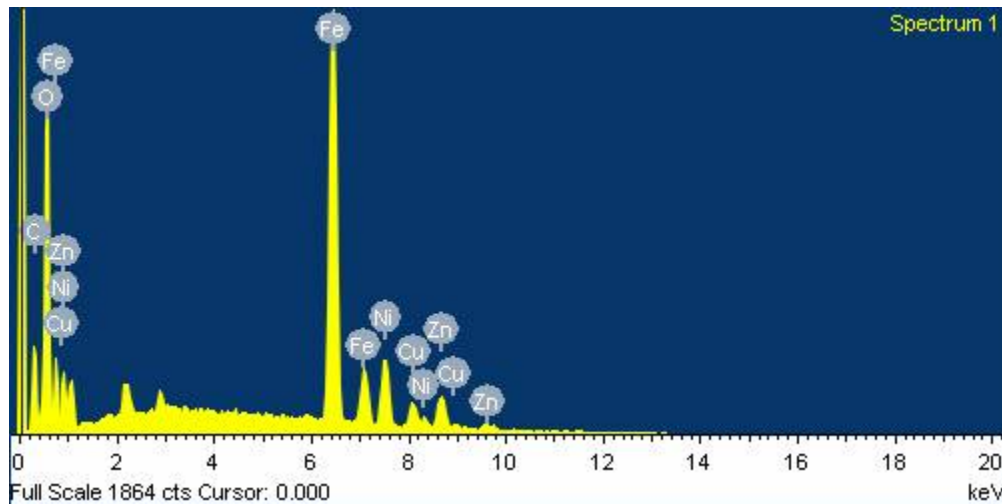

Figure I. EDAX - x = 0.3, Chemical reaction temp. = 100^{0}C

Comparing the values of ionic radius of tetrahedral (A) site and octahedral (B) site calculated using cation distribution (r_A, r_B) and using equation 5 & 6 (r_A^I, r_B^{II}) it is found that r_A^I is less than r_A and r_B^{II} is greater than r_B. This can be attributed to the deviation in the oxygen parameter 'u' from the value 3/8 (i.e. 0.375). If u > 3/8 (here, u = 0.385), which for most ferrites is the case, the oxygen ions are displaced in such a way that in AB interaction the distance between the A and O ion is increased and that

between the B and O ion is decreased. Which make the tetrahedral site larger and the octahedral sites are reduced in size so that the sizes of the two interstitial sites become more equal[7] (i.e. r_A, r_B in Table II).
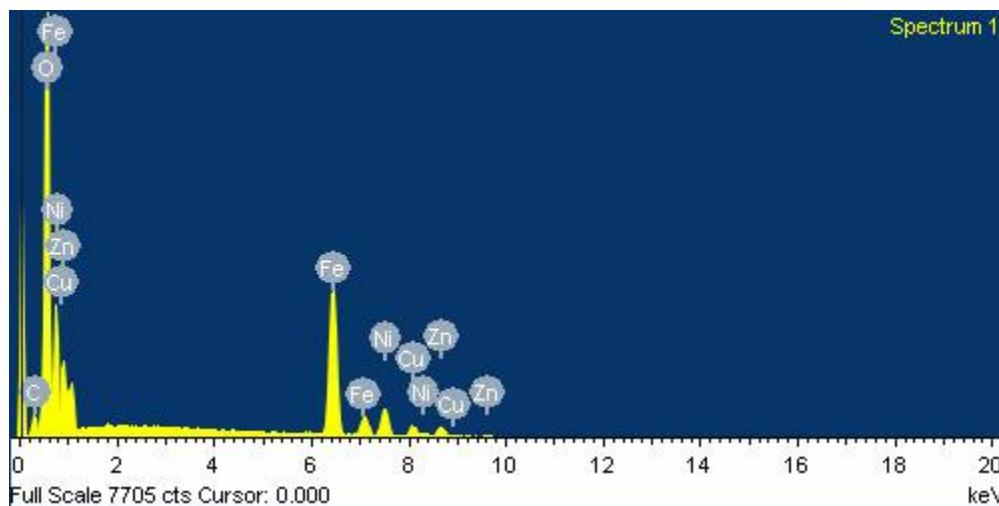

Figure II. EDAX - x = 0.4, Chemical reaction temp. = 150^{0}C
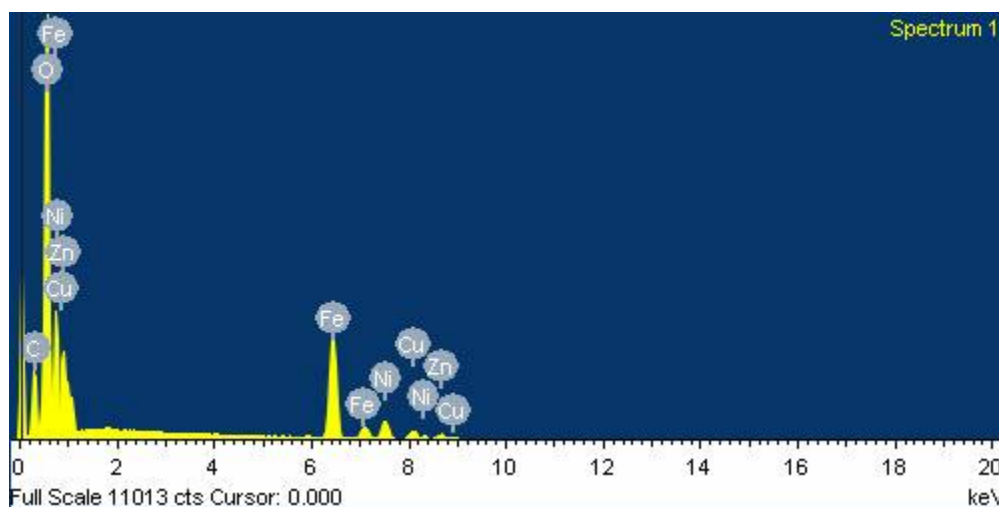

Figure III. EDAX - x = 0.5, Chemical reaction temp. = 1000C

Many researchers have reported that Zn^{2+} ions occupy A sites, while the tendency of Ni cations are in B sites. Fe and Cu cations can be distributed to both sites; however their preference is in B sites[7, 9]. Whereas in present proposed cation distribution shown in Table III, Zn^{2+} was found to occupy both tetrahedral as well as octahedral sites. This can be attributed to –

1) Rapid cooling of NiCuZn ferrite. When Zn ferrite is rapidly cooled from a high temperature, it becomes ferrimagnetic because not all the zinc ions occupy tetrahedral sites[7]. In present preparation

method, microwave sintered samples were soon taken out from the microwave oven after sintering process was finished.

2) Since the tetrahedral site is the smaller, one might expect that the smaller ions will prefer to occupy the tetrahedral sites. Trivalent ions are usually smaller than divalent ions and this tends to favor the inverse structure[7]. Ionic radius of Zn^{2+} is 0.74 Å and that of Fe^{3+} is 0.64 Å. A. Pradeep[10] and S.M. Attia[11] have reported occupancy of Zn^{2+} on both tetrahedral as well as octahedral sites.

Table III – Cation distribution, saturation magnetization, magnetic moment, lattice parameter experimental and theoretical.

Chem. reaction temp.	Comp.	Cations Distribution		Saturation Mag.	Magnetic moment (µB)		Lattice Parameter (Å)	
(°C)	x	A - site	B - site	M_s (emu/g)	Theo.	Expt.	Cation dist. a_{th}	XRD a_{expt}
100	0.3	$(Zn_{0.0024} Fe_{1.0976})$	$[Ni_{0.5} Zn_{0.3476} Cu_{0.15} Fe_{0.9024}]$	4.279	0.1860	0.1865	8.3474	8.3841
	0.4	$(Zn_{0.0407} Fe_{1.0593})$	$[Ni_{0.5} Zn_{0.2593} Cu_{0.2} Fe_{0.9407}]$	18.61	0.8105	0.8110	8.3467	8.4007
	0.5	$(Zn_{0.0247} Fe_{1.0753})$	$[Ni_{0.5} Zn_{0.2253} Cu_{0.25} Fe_{0.9247}]$	14.24	0.6205	0.6203	8.3460	8.3785
	0.6	$(Zn_{0.0122} Fe_{1.0878})$	$[Ni_{0.5} Zn_{0.1878} Cu_{0.3} Fe_{0.9122}]$	9.696	0.4220	0.4222	8.3453	8.3785
125	0.3	$(Zn_{0.0591} Fe_{1.0409})$	$[Ni_{0.5} Zn_{0.2909} Cu_{0.15} Fe_{0.9591}]$	23.77	1.0365	1.0362	8.3474	8.3924
	0.4	$(Zn_{0.133} Fe_{0.967})$	$[Ni_{0.5} Zn_{0.167} Cu_{0.2} Fe_{1.033}]$	50.37	2.1950	2.1950	8.3467	8.3841
	0.5	$(Zn_{0.0648} Fe_{1.03525})$	$[Ni_{0.5} Zn_{0.1853} Cu_{0.25} Fe_{0.96475}]$	28.04	1.2213	1.2214	8.3460	8.3841
	0.6	$(Zn_{0.116} Fe_{0.984})$	$[Ni_{0.5} Zn_{0.084} Cu_{0.3} Fe_{1.016}]$	33.65	1.4600	1.4652	8.3453	8.3785
150	0.3	$(Zn_{0.0494} Fe_{1.0506})$	$[Ni_{0.5} Zn_{0.3006} Cu_{0.15} Fe_{0.9494}]$	20.45	0.8910	0.8915	8.3474	8.3924
	0.4	$(Zn_{0.05775} Fe_{1.04225})$	$[Ni_{0.5} Zn_{0.2423} Cu_{0.2} Fe_{0.95775}]$	24.48	1.0663	1.0668	8.3467	8.3841
	0.5	$(Zn_{0.02635} Fe_{1.07365})$	$[Ni_{0.5} Zn_{0.2237} Cu_{0.25} Fe_{0.92635}]$	14.83	0.6453	0.6460	8.3460	8.3841
	0.6	$(Zn_{0.0391} Fe_{1.0609})$	$[Ni_{0.5} Zn_{0.1609} Cu_{0.3} Fe_{0.9391}]$	15.89	0.6910	0.6919	8.3453	8.3841

In order to determine cation distribution, the values of magnetic moment were determined using saturation magnetization, given in Table III. For scientific interest theoretical calculation of magnetic moment of the ferrites was done by substituting the value of the respective ion in the Neel's formula[7] as per the proposed cation distribution given in Table III. A good agreement of the theoretical and observed magnetic moment values as seen in Table III supports the proposed cation distribution.

The cation distribution was also confirmed from the experimental and theoretical values of lattice parameter. It is known that there is a correlation between the ionic radii of both A and B sublattices and the lattice parameter. The lattice parameter can be calculated theoretically, using the following equation[12]

$$a_{th} = \frac{8\left[(r_A + R_o) + \sqrt{3}(r_B + R_o)\right]}{3\sqrt{3}} \text{--------- (7)}$$

where, R_o is the radius of the oxygen ion (1.32Å) and r_A and r_B are the ionic radii of the tetrahedral (A-site) and octahedral (B-site), respectively. Using the suggested cation distribution data, the mean ionic radii of tetrahedral A-site (r_A) and octahedral B –site (r_B) were calculated (Table II). Furthermore, the values of the theoretical lattice parameter a_{th} were calculated using equation 7. It is observed from Table III that both a_{exp} and a_{th} are almost same for respective composition (x), which once again confirms the agreeability of the suggested cation distribution.

The chemical reaction temperature again shows its effect on the cation distribution for same composition. This can be attributed to chemical kinematics and activation energy.

Table IV – Bond length of A-site d_{AL} and B-site d_{BL}, tetrahedral edge d_{AE}, shared and unshared octahedral edges, d_{BE} and d_{BEU}, and hopping length at A-site L_A and at B-site L_B for each sample.

| Chem. reaction temp.	Comp.	d_{AL}	d_{BL}	d_{AE}	d_{BE}	d_{BEU}	L_A	L_B
(^{0}C)	x	(Å)	(Å)	(Å)	(Å)	(Å)	(Å)	(Å)
100	0.3	1.960147	2.015386	3.200907	2.726699	2.968541	3.629902	2.963803
	0.4	1.963351	2.01868	3.206138	2.731155	2.973392	3.635834	2.968646
	0.5	1.958534	2.013727	3.198272	2.724454	2.966098	3.626914	2.961363
	0.6	1.958534	2.013727	3.198272	2.724454	2.966098	3.626914	2.961363
125	0.3	1.962366	2.017667	3.204531	2.729785	2.971902	3.634011	2.967158
	0.4	1.960425	2.015672	3.201361	2.727086	2.968962	3.630417	2.964223
	0.5	1.960425	2.015672	3.201361	2.727086	2.968962	3.630417	2.964223
	0.6	1.959109	2.014318	3.199212	2.725254	2.966969	3.62798	2.962233
150	0.3	1.962366	2.017667	3.204531	2.729785	2.971902	3.634011	2.967158
	0.4	1.960425	2.015672	3.201361	2.727086	2.968962	3.630417	2.964223
	0.5	1.960425	2.015672	3.201361	2.727086	2.968962	3.630417	2.964223
	0.6	1.960425	2.015672	3.201361	2.727086	2.968962	3.630417	2.964223
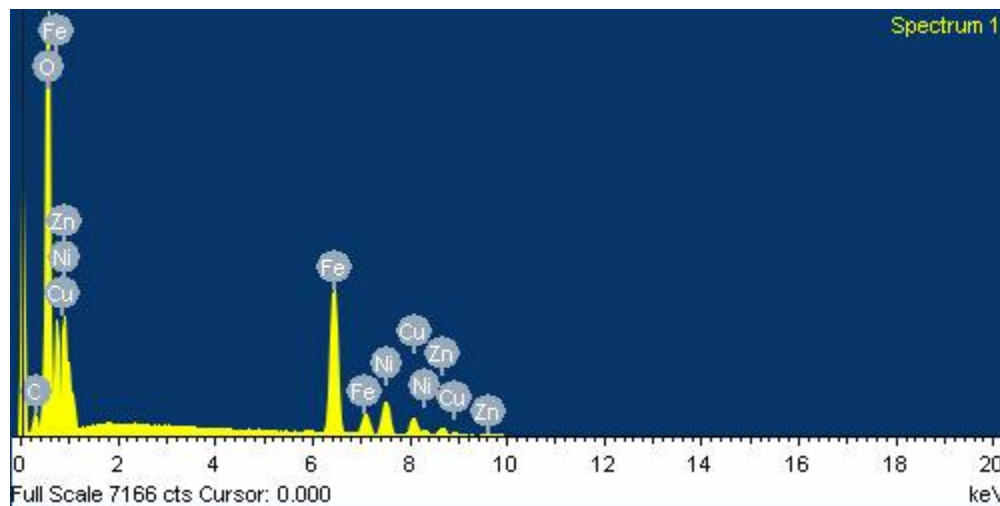
Figure IV. EDAX - x = 0.6, Chemical reaction temp. = 150^0C

Interionic Distances

The interionic distances i.e. cation – anion distances at A-site, d_{AL}, and B-site, d_{BL}, together with the distance of closest anion – anion approach, tetrahedral edge, d_{AE}, and shared and unshared octahedral edges, d_{BE}, d_{BEU} are calculated using following equations[13] –

$$d_{AL} = a\sqrt{3}(u - 0.25) \qquad \text{------ (8)}$$

$$d_{BL} = a\left(3u^2 - \frac{11}{4}u + \frac{43}{64}\right)^{1/2} \qquad \text{------ (9)}$$

$$d_{AE} = a\sqrt{2}(2u - 0.5) \qquad \text{------ (10)}$$

$$d_{BE} = a\sqrt{2}(1 - 2u) \qquad \text{------ (11)}$$

$$d_{BEU} = a\left(4u^2 - 3u + \frac{111}{16}\right)^{1/2} \qquad \text{------ (12)}$$

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The obtained values are listed in Table III. It is clear that the values of d_{AL}, d_{BL}, d_{AE}, d_{BE} and d_{BEU} decreases with increasing Cu^{2+} (ionic size 0.72 Å) and decreasing Zn^{2+} (ionic size 0.74 Å) ion content. This variation may be attributed to the substitution process and the cation distribution   (Table III).

The distance L_A and L_B between the magnetic ions at A-site and B-site respectively were obtained using equation[14] –

$$L_A = a\sqrt{3}/4 \text{ ------ (13)}$$

$$L_B = a\sqrt{2}/4 \text{ ------ (14)}$$

The obtained values of L_A and L_B are listed in Table IV. It was clear that L_A and L_B reflect the same behavior as that of lattice parameter 'a', where they decrease with increasing Cu^{2+} content. This may be due to the contraction of unit cell arising from the substitution of relatively smaller Cu^{2+} ions instead of Zn^{2+} ions.

Conclusion

i) EDAX characterization showed the purity and surety of the chemical composition.

ii) Chemical reaction temperature should be taken under consideration while formation of ferrites as it affects lattice parameter and cation distribution.

iii) The estimated cation distribution showed that Zn^{2+} occupy A and B site replacing Fe^{3+} ions whereas Ni^{2+} and Cu^{2+} occupy B site.

iv) Hopping length at A site L_A and at B site L_B decreases with increasing Cu^{2+} and decreasing Zn^{2+} content.

v) Bond length of A site d_{AL} and B-site d_{BL}, the tetrahedral edge d_{AE}, the shared and unshared octahedral edges, d_{BE} and d_{BEU} decreases with increasing Cu^{2+} and decreasing Zn^{2+} content.

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