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DC electrical resistivity and cation distribution in Zn^{2+} substituted copper ferrites

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ABSTRACT

Polycrystalline spinel ferrites with general formula $Zn_xCu_{1-x}Fe_2O_4$ (x=0, 0.2, 0.4, 0.6, 0.8 and 1.0) were prepared by oxalate co-precipitation method. On characterization by X –ray diffraction, they were found to be cubic spinels except x = 0, which is tetragonal in nature. Dc electrical resistivity suggests conductivity was due to hopping mechanism. The cation distribution of the system was investigated by employing Upadhyay and Baldha model wherein relative weighted magnetic interaction per formula unit is considered. The Curie temperature was calculated theoretically by employing this model as a function of distribution parameter. The cation distribution investigated reveals that the Cu^{2+} ion distributes partially among A and B –sites with maximum occupancy on A – site for x = 0.20.

Key words: Cation distribution, Copper ferrites, electrical resistivity.

INTRODUCTION

Structural, electrical and magnetic properties are important for applications of ferrites in various fields. They are found to be depending on the distribution of cation among A and B site [1]. Therefore the estimation of cation distribution in ferrite systems turns out to be important. Many workers reported the estimation of cation distribution in ferrite systems by employing the magnetization method [2, 3]. Using Gilleo method, Cation distribution in Cu-Zn ferrites system was reported by Kulkarni et al [4]. Gilleo method [5] assumes three magnetic ions per formula unit. It can be used to investigate the cation distribution; but for the ferrites like Cu-Zn, Cu-Cd, Co-Cd, Mg-Cd etc which consists two magnetic ions for formula. Upadhyay et al [6] modified the Gilleo model considering relative weighted magnetic interaction per formula unit. This modified model was used by Ladgaonkar et al [7] and Kolekar et al [8]. Vasambekar et al [9] further modified the Upadhyay model for trivalent substitution.

In this communication we are reporting results of estimation of cation distribution using modified Upadhyay model for Cu-Zn ferrite system prepared by oxalate precursor method.

MATERIALS AND METHODS

Polycrystalline spinel ferrites with general formula $Zn_xCu_{1-x}Fe_2O_4$ (x=0, 0.2, 0.4, 0.6, 0.8 and 1.0) were prepared by oxalate co-precipitation method using $CuSO_4$, $ZnSO_4$ and $FeSO_4$ (LOBA Chemi, INDIA). The materials required in

their atomic weight proportion were mixed with double distilled water. The pH of solution was maintained to be 1. The solution was warmed and excess amount of ammonium oxalate was added in order to complete the process of precipitation. The pH of precipitation was found to be 10. The reaction mechanism involved is given by,

$CuSo_4 + 2H_2O + C_2O_4^- \longrightarrow CuC_2O_4 2H_2O + SO_4^-$
$FeSO_4 + 2H_2O + C_2O_4^- \longrightarrow FeC_2O_4 2H_2O + SO_4^-$

This mixture was filtered through Whatman filter paper No. 41, using Buckner funnel. The filtrate was examined for presence of sulphur ions by $BaCl_2$ test. The washed and dried powder was presintered at 500 ^{0}C for 1 hour in a electrical furnace. The furnace temperature was measured by well-calibrated Chromel-Allumel thermocouple. Presintered powder was wet milled in agate morter using acetone base and was sintered 1000 ^{0}C for 2 hours. Pellets of 10 mm in diameter were formed by applying pressure of 7 tones/cm^2 using hydraulic up to 5 minutes. The pellets were finally sintered at 1000 ^{0} C for 2 hours for better compaction.

The powdered samples were characterized by X- ray diffraction method. The dc electrical resistivity measurement of palletized samples was carried out by two probe method in temperature range 300 ^{0} K- 850 ^{0} K. The cation distribution of the system was investigated by employing Upadhyay and Baldha model.

RESULTS AND DISCUSSION

A typical X-ray diffractogram is presented in Fig 1 From the X-ray diffraction study, it is seen that the completion of solid state reaction and the formed of spinel compounds. Typical X-ray diffractogram is presented in Figure 1. All the samples exhibit a cubic phase, except x = 0, which exhibits tetragonal character. The lattice constant calculated increases with Zn concentration and obeys Vegard' law.

The plots of log ρ Vs 1000/T obeys $\rho = \rho_0 \exp(-\Delta E/KT)$, Wilson relation and show change in the slopes at certain temperatures, which corresponds to the Curie temperature (Tc) in the respective samples. The samples with x= 0.8 and x= 1.0 show no such change in slope, which suggests that these samples exhibits paramagnetic in nature at room temperature. The resistivity decreases with increase in temperature. Such type of conductivity was attributed to the hopping of electrons on an equivalent octahedral sites between Fe $^{2+}$ and Fe^{3+} ions as $Fe^{2+} \rightarrow Fe^{3+} + e^-$. The values of Tc obtained from the plots are presented in table 1 and are used to determine cation distribution. From this table it is found that the Curie temperature decreases with increase in Zn^{2+} ion concentration. Zn^{2+} ion resides A site, this site preference reduces the A-B interaction [8] that is responsible for the decreases in Curie temperature.

Cation distribution

The formula for determination for Curie temperature as put forth by Upadhyay and Baldha [6] is,

$$T_c(x) = \frac{M^*(x=0)n(x)}{M^*(x)n(x=0)} T_c(x=0) \quad \text{.....(1)}$$

Where $M^*(x) = 2+(`1-x)\,\mu_M'/\mu_{Fe}$ .....(2)

T_c (x=0) is the Curie temperature of unsubstituted ferrite, μ_M' the magnetic moment of magnetic ion, μ_{Fe} the magnetic moment of Fe ion, x is the non magnetic ion concentration and n(x) is the number of relative weighted magnetic interaction per formula unit. The value of n(x) is given as,

$$n(x) = \frac{24}{\mu^2_{Fe}}[Z\delta\mu^2_M' + (\delta w + Z^2)\mu_M'\mu_{Fe} + WZ\mu^2_{Fe}] \quad \text{.....(3)}$$

Where,

$Z = 1-x-\delta$ ..... (4)

$w = 1=x+\delta$ ..... (5)

δ is the fraction of magnetic ion on A –site.

Above equation were used to calculate cation distribution and Curie temperature of the Cu-Zn ferrite system. The values of magnetic moments of Fe and Cu ions used are 5.0 and 1.1 respectively [8]. The T_c (x=0) value was taken from dc resistivity data.

Substituted Zn^{2+} resides A- site [7] and Cu^{2+} ions occupies both A –site and B- site [8], therefore, the formula used to proposed cation distribution is,

$$[Zn_x\ Cu_\delta\ Fe_{1-x-\delta}]^A\ [Cu_{1-x-\delta}\ Fe_{1+x+\delta}]^B O_4$$

Curie temperatures were calculated theoretically by varying distribution parameter δ from 0 to 1-x and plotted against δ. The exact value of δ is then obtained from these plots. The results are presented in table 1. From this table it is found that the values of Tc obtained from de resistivity measurements and calculated ones are good agreement; suggesting probably the correct cation distribution and the excellent fit of model to the system under investigation.

On inspection of table 1, it is found the copper ion distributed partially on A and B sites, showing maximum tetrahedral occupancy δ for the composition x= 0.20 and decreases for further values of x.

Table 1. Cation distribution and Curie temperature data of $Zn_xCu_{1-x}Fe_2O_4$ ferrite system

x	Cation distribution	T_c obtained from dc resistivity plots ^0K	T_c obtained theoretically from equation(1) ^0K
0.0	$[Zn_{0.000}\ Cu_{0.035}\ Fe_{0.650}]^A\ [Cu_{0.650}\ Fe_{1.350}]^B\ O_4$	667	664
0.2	$[Zn_{0.200}\ Cu_{0.330}\ Fe_{0.470}]^A\ [Cu_{0.470}\ Fe_{1.530}]^B O_4$	549	550
0.4	$[Zn_{0.400}\ Cu_{0.070}\ Fe_{0.530}]^A\ [Cu_{0.530}\ Fe_{1.470}]^B\ O_4$	500	499
0.6	$[Zn_{0.600}\ Cu_{0.002}\ Fe_{0.398}]^A\ [Cu_{0.398}\ Fe_{1.602}]^B O_4$	417	409
0.8	$[Zn_{0.800}\ Cu_{0.000}\ Fe_{0.200}]^A\ [Cu_{0.200}\ Fe_{1.800}]^B O_4$	--	--
1.0	$[Zn_{1.00}\ Cu_{0.000}\ Fe_{0.000}]^A\ [Cu_{0.000}\ Fe_{2.000}]^B\ O_4$	--	--

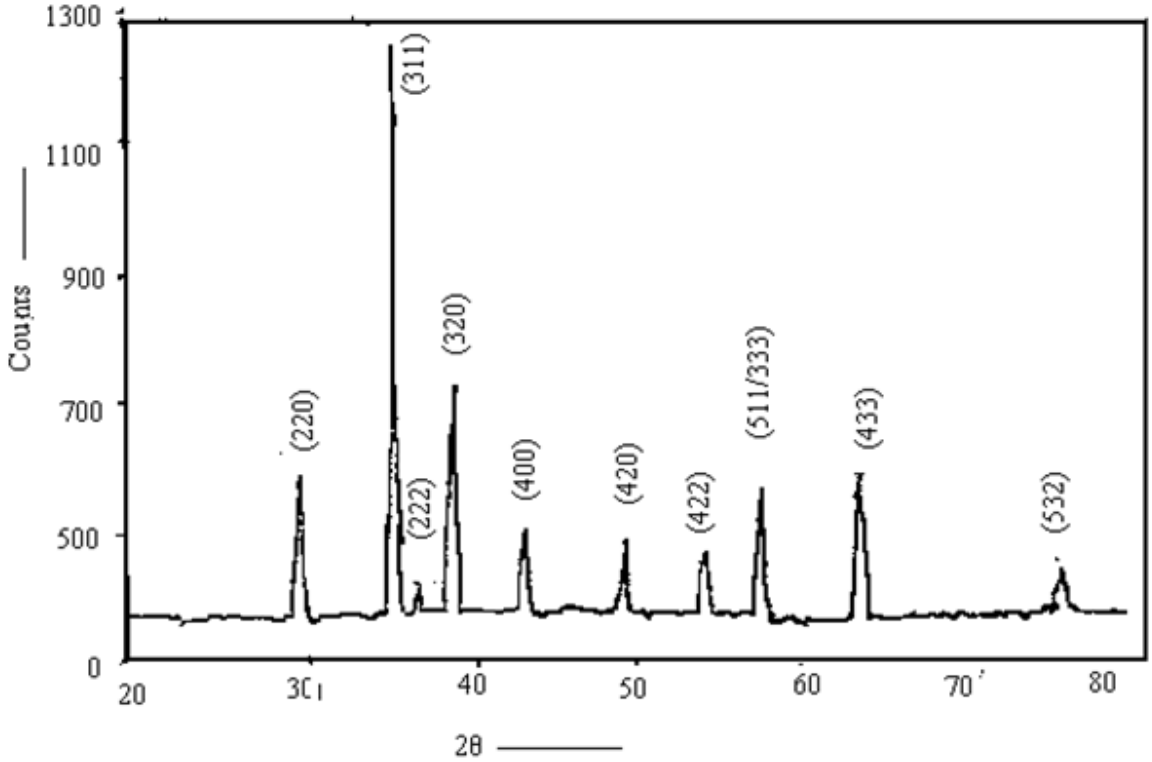

Fig.1. Typical X-ray diffractogram of $Zn_xCu_{1-x}Fe_2O_4$ ferrite system

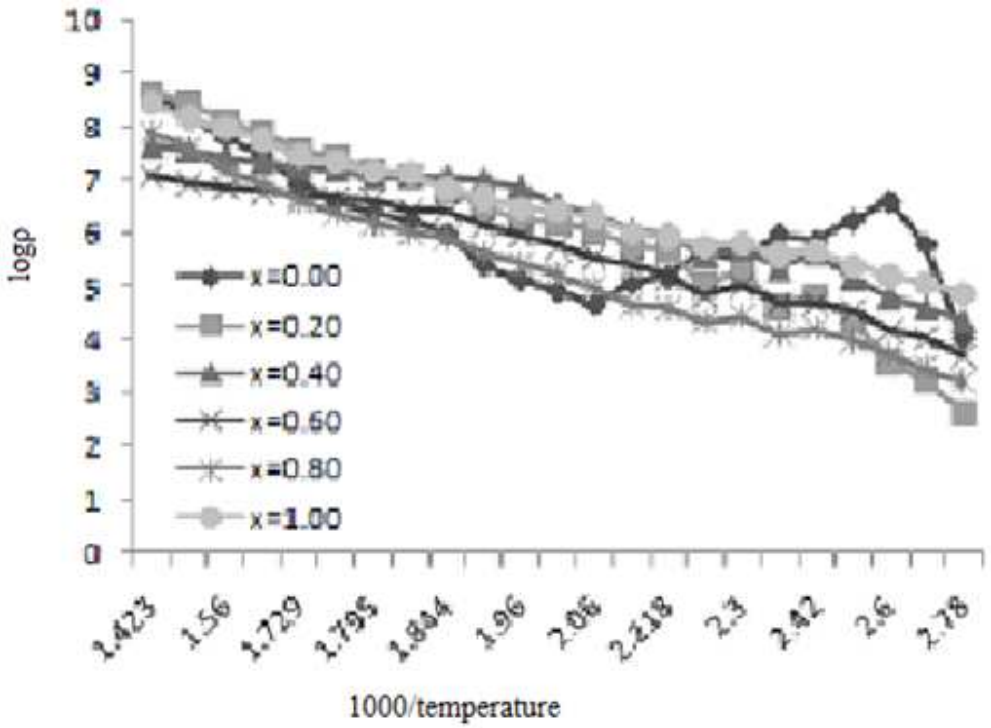

Fig.2. Typical Plot of logρ versus temperature of $Zn_xCu_{1-x}Fe_2O_4$ ferrite system

CONCLUSION

Preparation of ferrites by oxalate precipitation method is easiest method and gives good results of formation of ferrites than standard ceramic method. All the samples have cubic spinels except copper ferrite which exhibits in tetragonal character. Study of resistivity shows that resistivity decreases with increase in temperature. Ferrites change theie property from ferri-magnetism to para-magnetism at Curie temperature. Curies temperatures obtained from the graph is in good agreement with calculated values of Curie temperatures. Zinc ferrites exhibit para-magnetic in nature hence it will not show Curie temperature. The substituted Zn^{2+} ions occupy A site. The cation distribution obtained from the Upadhay model is in good agreement with the previously reported values.

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