DC-resistivity of Zn, Sb substituted Copper ferrite

R. DHANARAJU, M. KALYANARAJU*, K. SAMATHA
Department of physics, Andhra University, Visakhapatnam, India-530003

DC resistivity of $Cu_{1-x}Zn_xFe_2O_4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) and $Cu_{1-x}Sb_xFe_2O_4$ (x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5) are studied. Iron ion concentrations are also estimated to explain the observed variations in resistivity. Different types of conduction mechanisms have been noticed with these two substituents (Zn & Sb) having almost equal ionic radii.

(Received June 10, 2012; accepted October 30, 2012)

Keywords: $CuFe_2O_4$, Resistivity, Blocking mechanism, Hopping mechanism

1. Introduction

Ferrites find a wide variety of applications in the high frequency electromagnetic region of the spectra such as micro and radiowaves. At higher frequencies eddy current losses in ferrites plays a dominant role. Eddy current losses can be minimized by increasing the resistivity of the material as eddy current losses is inversely proportional to resistivity [1]. The electrical properties of ferrites are sensibly depends on extrinsic properties the composition of the ferrite, sintering temperature, Soaking time, method of processing and intrinsic properties like formation of grains, grain boundaries, liquid phases and other factors.

The resistivity of a ferrite material in general, depends upon the final chemical composition of the prepared ferrite due to sintering conditions, hopping mechanism and other conduction mechanisms. By the addition/substitution of cations to a ferrite produces changes in the resistivity (ρ). Further, the cation distribution among A and B sites, change electrical properties significantly. One has to consider Fe^{2+} ion concentration in order to discuss about eddy current losses in connection with electrical resistivity.

Copper ferrites and copper containing ferrites have been a focus of continued interest in the recent years. Copper–zinc ferrites are widely used in microwave devices due to their high resistivity and low dielectric loses. Being Cu is a sintering aid; it can provide the most desirable properties at relatively low sintering temperatures with the help of a few substituents. The substitution of Zn in the $Cu_{1-x}Zn_xFe_2O_4$ ferrites causes appreciable changes in its structural, electrical and magnetic properties. From the studies on exchange interactions in antimony substituted nickel-zinc ferrites [2] concluded that Sb^{5+} ion has octahedral preference compared to Ni^{2+} ions. Recently Gao et. al [3] supported the above observations while investigating Ni-Zn-Sb ferrite system. The aim of the work is to see the influence of Zn^{2+} and Sb^{5+} that have approximately same ionic radius (0.62Å) which is comparable to the ionic radius of ferric ion (0.64Å) on different conduction mechanisms. These cations have oxidizing properties and influence the resistivity of Cu-Zn ferrite. Thus the variation of resistivity as a function of substituent concentration (x), temperature and frequency was studied.

2. Experimental details

Two series of copper zinc & copper antimony ferrites have been prepared of basic composition.

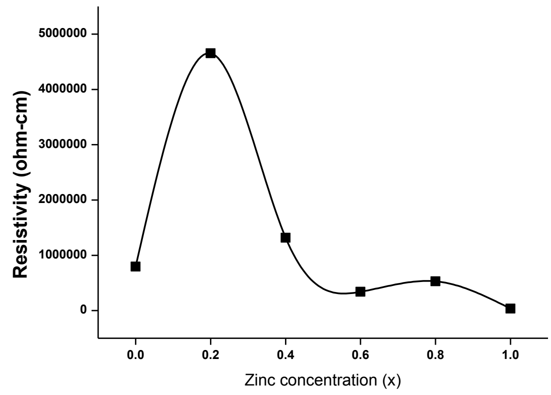
1) $Cu_{1-x}Zn_xFe_20_4$
2) $Cu_{1-x}Sb_xFe_20_4$

where, x varies from x = 0.0 – 1.0 in steps of 0.2 the solid state reactions are shown below.

Highly pure analytical reagent grade Cu_2O, Fe_20_3 and Sb_20_5 chemicals were used. The oxides were taken in correct proportions, crushed and mixed thoroughly for 5 hours in methanol using agate mortar and pestle. The mixture was calcinated for 12 hours at 900^0C in muffle furnace and then it was allowed to cool in the furnace. Binder was added to the compound formed after crushing it for 2 hours. The material was granulated through sieves and the granules were palletized. The pellets and toroids were finally sintered at 1150^0C in Nabertherm Furnace with Eurotherm controller. Material was heated to 600^oC in an hour following heating rate with 100^0C/hr Until C and kept for 2 hours. Then it was cooled at the rate of 100^0C /hr and later the furnace was allowed to normal cooling in air atmosphere. D.C. resistivity of the ferrite materials in the bulk form was measured. A conductivity cell was used to study the variation of electrical resistivity/conductivity with temperature. The sample in the shape of pellet is freshly ground and coated with silver paste to ensure good ohmic contact in between the two electrodes of the cell, which could be pressed with spring. Iron ion concentrations can be determined using Atomic Absorption Spectroscopy (AAS).

3. Results and discussion

Variation of DC Resistivity at room temperature as a function of Zinc, Antimony concentration in Cu_{1-x} Zn_x Fe_20_4 and Cu_{1-x} Sb_x Fe_20_4 is presented in Figs. 1 and 2.



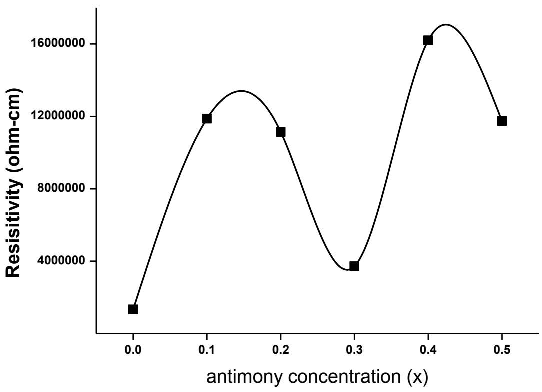


Fig. 1 and 2. DC resistivity of Cu-Zn and Cu-Sb ferrite systems.

The resistivity (ρ) of the zinc substituted Cu ferrite increases up to x = 0.2 and then decreases till x = 0.4 and seems to be remain constant further. In case of antimony substituted Cu-ferrites, the DC resistivity first increases up to x = 0.1and then decreases up to x = 0.3 followed by and increase for higher concentrations. In ferrites, Fe^{+2} and Fe^{3+} concentrations play a major role in deciding the conduction phenomenon. Thus, estimation of Fe^{2+} and Fe^{3+} ions concentrations has been carried out through chemical estimation and were given in Table 1.

Table 1. Ferrous and Ferric content (%) with substituent concentration.

Substituent concentration	**Zinc**		**Antimony**	
	Fe^{2+}	**Fe^{3+}**	**Fe^{2+}**	**Fe^{3+}**
0.00	0.446	53.700	0.446	53.700
0.10	1.004	34.840	1.116	30.230
0.20	1.620	21.110	0.446	25.264
0.30	2.680	12.310	1.004	23.744
0.40	2.568	11.780	0.670	19.675
0.50	2.345	6.348	0.558	16.074

At high temperatures i.e. during sintering process, formation of Fe^{2+} ions due to local charge neutrality conditions happens at A and B sites in the spinel lattice [4]. The observed increase of ferrous oxygen loss act as donor centers [5]. However, as the Fe^{3+} ions concentration decreases with 'x', consequently Fe^{2+} is expected to decrease along with other effects which influence the concentrations of ferrous and ferric ions. The electrons hop among these Fe^{2+} and Fe^{3+} ions to bring out conduction. The gradual decrease of electron hopping among the Fe^{2+} and Fe^{3+} ions has been noticed. An unusual increase in DC resistivity at x = 0.2 is because of formation of stable pairs of Fe^{2+} - Zn^{3+} ions. Beyond x = 0.2 though concentration of zinc increases systematically, a gradual decrease in iron concentration leads to decreasing stable pairs of Fe^{2+} - Zn^{3+} ions. Similar result is studied by Bhise et. al. in manganese substituted Cu-Zn ferrite [6] and it was reported that the resistivity increased with increase of Zn concentration till 0.5. This increase was explained due to hindering of Verwey hopping mechanism between Fe^{3+} and Fe^{2+} ions which resulted in the formation of Fe^{2+} - Zn^{3+} ions. Beyond x = 0.5 resistivity decreased. It was explained by formation of Zn^{3+} clusters, which lowered the concentration of stable pairs of Fe^{2+} - Zn^{3+} bonds. The substituted high valence cations localize the Fe^{2+} ions obstructing to the conduction mechanism [7].

In case of antimony substituted ferrites, antimony distributed into two valence states as Sb^{5+} and Sb^{3+} and exhibits valence fluctuation like valance $3Sb^{5+} \leftrightarrow 5Sb^{3+}$ and these ions indirectly influence exchange interactions among the iron ions. Sb^{3+} ions with Fe^{3+} ions form stable pairs as $Sb^{3+} \leftrightarrow Fe^{3+}$. On the other hand Sb^{5+} ions convert into pair like $Sb^{5+} \leftrightarrow Sb^{3+} + Fe^{2+}$ or $Fe^{3+} + Fe^{2+}$. Formation of all such pairs should have to decrease the resistivity in general. But the value of resistivity seems to be increasing with Sb substitution except at x = 0.3. Electrons tend to hop between the different ionic states of a single element i.e. Fe. But in this case though formation of ion pairs like $Sb^{3+} \leftrightarrow Fe^{3+}$and $Sb^{5+} \leftrightarrow Sb^{3+} + Fe^{2+}$ or $Fe^{3+} + Fe^{2+}$are occurring, being they are at equivalent ionic states they tend to block hopping of electrons among these pairs. Similar kind of formation of the ionic pairs is reported by some researchers [7-9]. Such a kind of blocking of ions in ferrite is also noticed by Srinivasa Rao et. al.[10]. The decrease in resistivity at x = 0.3 may due to less density of the sample (during sintering, formation of cracks has noticed in this sample particularly. It may be a reason for its decrease of resistivity).

4. Conclusions

Variation in DC resistivity of Cu-Zn and Cu-Sb ferrites is explained on the basis of electron hopping mechanism by determining the concentrations of Fe^{2+} and Fe^{3+} ions. The decrease in resistivity of Cu-Zn ferrites takes the formation of Fe^{2+} - Zn^{3+} ions where as another ion Sb having same radii that of Zn creates ion pairs which blocks the hopping mechanism.

References

[1] A. M. Kumar, M. C. Varma, G. S. V. R. K. Choudary, K. Srinivasa Rao, K. H. Rao, G. Gopala Krishna, J. Optoelectron. Adv. Mater. **12**(12), 2386 (2010).
[2] M. M. Rashad, M. H. Khan, K. S. Abdel Halim, J. Nanosci. & Nanotechnol. **6**, 26 (2006).
[3] F. Gao, D. L. Zhao, Z. M. Shen, Adv. Mater. Res. **105**,293 (2010).
[4] G. C. Jain, B. K. Das, R. B. Tripathi, R. Narayan, IEEE Trans on Mag. MAG B **18**(2), 776 (1982).
[5] A. M. Sankpal, S. R. Sawant, A. S. Vanigankar, Ind. J. Pure & Appl. Phys., **26**, 459 (1988).
[6] B. V. Bhise, M. G. Patil, M. B. Dongere, D. K. Sawant, P. A. Patil, Indian J. Pure & Appl. Phys., **30**, 385 (1992).
[7] C. B. Kolekar, P. N. Kamble, A. S. Vanigankar, J. Magn. and Magn. Mater., **138**, 211 (1994).
[8] A. D. P. Rao, B. Ramesh, P. R. M. Rao, S. B. Raju, Ind. J. Pure and applied Phys., **37**, 51 (1999).
[9] M. A. Ahmed, M. A. EI Hiti, M. K. EI Nimr, M. A. Amer J.Mags. & Mag. Mater., **152**, 391 (1996).
[10] K. S. Rao, A. M. Kumar, M. C. Varma, G. S. V. R. K. Choudary, K. H. Rao J. Alloys & Comp. **488**, L6 (2010).

*Corresponding author: kalyanrs09@gmail.com