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Study of electrical and dielectric behaviour of Mn-doped Copper Ferrite

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Abstract-The effect of Mn-substitution on the dielectric properties of $Cu_{1+x}Mn_xFe_{2-2x}O_4$ ferrites (x=0.0 to 0.6) were prepared by standard ceramic method. The ferrite samples were crystallized in the single phase spinel. The electrical conduction in ferrite is explained on the basis of the hopping mechanism. D. C. resistivity decreases with increase of temperature. Ferrite shows semiconducting behaviour. The activation energy of each sample is calculated from the plots of logρ versus $10^3/T$. The measurement of dielectric constant and dielectric loss showed increasing behaviour with increase of temperature while loss tangent decreases with increase in temperature. Seebeck coefficient (α) were measured as a function of temperature from room temperature up to 650°K. The measurement showed that on substitution of Mn^{4+} tend to convert Cu-ferrite from n-type to p-type semiconductor.

Keywords: Ferrites, X-ray diffraction, electrical resistivity, activation energy, thermoelectric power.

1. Introduction

Polycrystalline soft ferrites are magnetic semiconductors which cannot be replaced by any other magnetic material because ferrites are stable, relatively inexpensive, easily manufactured and have wide spread applications in electronics and communication industries due to their interesting electrical and magnetic properties [1]. Ferrite cores are used in electronic inductors, transformers and electromagnets where the high electrical resistance of the ferrite leads to very low eddy current losses. They are commonly seen as a lump in a computer cable, called a ferrite bead, which helps to prevent high frequency electrical noise from existing or entering the equipment. Ferrites powders are used in the coating of magnetic recording tapes such material is iron (III) oxide. Also ferrite particles are used in stealth aircraft and in the expensive absorption tiles lining the rooms used for electromagnetic compatibility measurements. Mn containing ferrites have various applications such as transformers [2], electromagnetic interference [3], asymmetric digital subscriber line [4] etc.

These properties of ferrites mainly depend upon chemical composition, method of preparation, sintering time and temperature [5]. By introducing small amount of foreign ion can change the electrical and magnetic properties of the ferrite [6-8]. Copper ferrites have attracted the attention of investigators, for its uniqueness condition. It shows remarkable effect in structural resistivity. The addition of tetravalent ions like Ti^{4+}, Ge^{4+}, Si^{4+} and Mn^{4+} influences the structural, magnetic and transition properties of the system [9]. Several studies have been reported on the addition of Mn^{4+} ions in copper ferrite and other ferrites [10-14]. However, no systematic studies of electrical properties of these materials have been reported. In the present work, a detailed investigation of the manganese doped copper ferrite with composition and temperature dependence of dielectric properties and thermoelectric power were carried out and results are presented in this paper.

2. Experimental details

Polycrystalline compositions of the series $Cu_{1+x}Mn_xFe_{2-2x}O_4$ (where x = 0.0, 0.1, 0.2, -----0.6) were prepared by standard ceramic method using analytical reagent oxides CuO, $MnO_2$and Fe_2O_3. These oxides were weighed in required mole proportions on a single pan balance and mixed thoroughly in stoichiometric proportions. This mixture was then ground in agate mortar for about two hours. All these compositions were presintered at 750°C for 12 hours in muffle furnace and cooled in the furnace slowly at the rate of 2°C/minute. The temperature of furnace was measured with the help of Platinum-Rhodium thermocouple. The presintering powder of each sample was again ground for minimum two hours. The powder was then palletized in a die of 10mm diameter by applying a hydraulic pressure of 5 tons per square inch for about 10 minutes. After removing the load pellet was taken out from the die. The pellets were finally sintered at 980°C for 24 hours and cooled in the furnace slowly at the rate of 2°C/minute.

The x-ray diffraction patterns of all samples were recorded using X-ray diffractometer (Philips Model PW 3710). Electrical measurements were carried out by means of a two probe method and ohmic contacts were made using silver paste. Thermoelectric power was measured using differential method.

3. Results and discussion

3.1 X-ray diffraction

X-ray diffraction pattern of all powdered compositions, suggest formation of single-phase spinel ferrite showing well known defined peaks [15]. The typical X-ray pattern of the series $Cu_{1+x}Mn_xFe_{2-2x}O_4$ for x=0.1 and 0.2 are as shown in Fig.1. The values of lattice parameter determined from X-ray data with an accuracy of ±0.002 $\mathring{A}$ for all compositions are represented in Table 1. From table, it is observed that lattice constant 'a' for given system decreases linearly from 8.398 t0 8.316 $\mathring{A}$ with increase of composition 'x'. This decrease in lattice constant 'a' with 'x' is due to replacement of $2Fe^{3+}$ (0.64 $\mathring{A}$) ion by Cu^{2+} (0.72 $\mathring{A}$) and Mn^{4+} (0.52 $\mathring{A}$) ions i. e.

$$2Fe^{3+} \rightarrow Cu^{2+} + Mn^{4+}$$

Regarding that ionic radius of $2Fe^{3+}$ ions are larger than that of Cu^{2+} and Mn^{4+} ions. So that increase of Mn^{4+} concentration leads to decrease of lattice parameter, obeying Vegard's laws [16]. Similar result is reported by Feng et al [17].

The X- ray density (d_x) of all compositions were calculated using the relation,

$$d_X = \frac{ZM}{NV}$$

where Z is number of molecules per unit cell (Z=8), M is molecular weight,

N is Avogadro's number (6.023×10^{23}) and V is volume of unit cell {$V=a^3$ for cubic}.

The values of X-ray density are listed in table 1. From table, it is observed that X-ray density (d_x) increases with increase of Mn^{4+}content. The increase in X-ray density is attributed to decrease in lattice constant 'a' with 'x' and increase in molecular weight of compositions.

The percentage porosity was calculated using the relation,

$$P = (1 - \frac{d}{d_X}) \times 100\%$$

Where d is bulk density and d_x is X-ray density.

It is tabulated in table 1. From table, it is observed percentage porosity decreases up to x=0.3 then it increases at x=0.4 after that it decreases continuously.

3.2 Electrical Resistivity

The variation of d. c. resistivity as a function of reciprocal of temperature is shown in Fig.2. From figure it is observed that the resistivity decreases with increase in temperature for all samples. The ferrites show semiconducting behaviour. The resistivity in ferrites obeys the relation,

$$\rho = \rho_0 \exp(\frac{E_g}{KT})$$

where E_g represent activation energy, K is Boltzmann constant, ρ_0 is temperature dependent factor and T is absolute temperature.

All the curves are almost linear at low temperature then a gradual change of slope occurs and finally the curves exhibit once again a linear behaviour at high temperature in all cases. This decrease in resistivity may be attributed to fact that in case of Mn-doped copper ferrite octahedral sites are occupied by Cu^{2+}, Fe^{3+} and Mn^{4+} ions [11]. The conduction mechanism in ferrite is considered as electron hopping between Fe^{2+} and Fe^{3+} in B-site [18]. Obviously the more Fe^{2+} ions content higher the conduction and consequently a decrease in the resistivity. Similar result of hopping conduction will be reported by Yue et al [11] in Mn-doped Ni-Cu-Zn ferrite.

The breaks in resistivity plots denote two regions of conductivity and the temperature corresponding to the break was found to be at Curie temperature (T_c) of the sample. The lower temperature region below T_c corresponds to the ordered ferrimagnetic region with low activation energy while the higher temperature region above T_c corresponds to a paramagnetic disordered region with comparatively high activation energy [19]. The activation energy for electric conduction E_g in the ferrimagnetic and paramagnetic regions were determined from slopes of these lines. The activation energy can be calculated by using relation [14],

$$E_g = 0.198 \times 10^{-3} \times \frac{d(\log \rho)}{d\left(\frac{1}{T}\right)}$$

Details of activation energy and Curie temperature of the series $Cu_{1+x}Mn_xFe_{2-2x}O_4$ is as shown in Table 2. The value of activation energy in the ferrimagnetic region is lower than that of paramagnetic region. The lower activation energy in the ferrimagnetic region is attributed to the magnetic spin disordering [20] due to decrease in the concentration of current carriers while the change in activation energy is attributed due to change in conduction mechanism [21]. From table 2, it is observed that the value of Curie temperature (T_c) decreases from 727°K to 615°K. Such decreases in T_c with increase of 'x' are associated with increase of Mn^{4+} and simultaneously decrease of Fe^{3+} ions in the B-sublattice. This leads to a decrease in A-B interaction which reduces the magnetization and consequently decreases in Curie temperature.

3.4 Dielectric study

The variation of dielectric constant (ε'), dielectric loss (ε") and loss tangent (tanδ) as a function of temperature at a fixed frequency 1 KHz is as shown in Fig. 3, 4 and 5 respectively. From figure 3 and 4 it is observed that both dielectric constant (ε') and dielectric loss (ε") increases gradually with an increasing temperature for all values of Mn^{4+} concentration. Fig.5 shows that tanδ decreases with increase of Mn^{4+} concentration.This behaviour of temperature dependence of ε', ε" and tanδ is very good agreement with well known ferrites [22]. The increase in the dielectric constant with temperature suggests that the effect of temperature is more pronounced on the interfacial than on dipolar polarization. The composition dependence of dielectric constant can be explained by using the assumptions that the mechanism of dielectric polarization is similar to that of conduction process. It has been concluded that the electron exchange between Fe^{2+} and Fe^{3+} results in the local displacement of charge in the direction of an electric field which is responsible for polarization in ferrites [23]. The magnitude of exchange depends on the concentration of $\frac{Fe^{3+}}{Fe^{2+}}$ ion pairs present on B-site. For the present ferrites, incorporation of Mn in B-site of ferrite may increase the concentration of $\frac{Fe^{3+}}{Fe^{2+}}$ ion pairs.

3.5. Thermoelectric Power

Thermoelectric power or the Seebeck coefficient (α) is due to the diffusion of electrons or holes which have more kinetic energy directed at hotter surface towards the colder surface and hence the emf is produced. It is given by relation as,

$$\alpha = \frac{dV_{12}}{dT}$$

Where dV_{12} represent emf across the junction 1 and 2 and dT represent the temperature difference in degree Kelvin across the sample.

The temperature variation of the Seebeck coefficient for the series $Cu_{1+x}Mn_xFe_{2-2x}O_4$ is shown in Fig.6. From figure it observed that the thermoelectric for base ferrite at x=0 is negative indicating that electrons are charge carriers. The conduction for electron hopping process for the n type composition will be

$$Fe^{2+} \Leftrightarrow Fe^{3+} + e^{-1}$$

For x>0, thermoelectric power at low temperature show p-type of conduction i.e. thermoelectric power is positive. Further increase in temperature conduction changes from p-type to n-type. For p-type compositions, Cu^{+} ions formed during the sintering process due to reduction of Cu^{2+} [24]. The existence of Cu^{+} ions tends to initiate hopping conduction with Cu^{2+} and a hole e^{+} is involved as follows,

$$Cu^{2+} \Leftrightarrow Cu^{+} + e^{+}$$

Since, the possibility of Cu^{+} formation increases with the increase of tetravalent ions Ge^{4+} then higher the value of 'x', higher the positivity of thermoelectric power α at room temperature. The transition temperature (T_s) at which thermoelectric power changes from positive to negative was evaluated for each value of cationic parameter 'x'. The variation of T_s against composition 'x' is as shown in table 2. From table it is observed that T_s continuously increases with increase of 'x'. The similar variation of the thermoelectric power with temperature was observed by several investigators in various ferrite systems [25].

5. Conclusion

In the study of manganese doped copper ferrite, the resistivity is found to be decreases with increase in temperature for all samples. The ferrites show semiconducting behaviour. The dielectric constant and dielectric loss factor increases with increasing temperature while dielectric loss tangent decreases with increase in temperature. This increase in dielectric constant with increase temperature is due to local displacement of electrons in the direction of electric field which determine the polarization process. Thermoelectric power indicates that both n-and p-type of charges are contributing for conduction.

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Table 1-Compositional Variation of lattice parameter (a), X-ray density and percentage porosity for the $Cu_{1+x}Mn_xFe_{2-2x}O_4$ system.

Composition (x)	Lattice Parameter (a) in $\overset{o}{A}$	X-ray density d_x in (gm/cm^3)	Porosity (P) in (%)
0.0	8.398	4.819	19.17
0.1	8.394	5.376	15.89
0.2	8.379	5.408	13.42
0.3	8.363	5.428	10.31
0.4	8.347	5.460	21.01
0.5	8.332	5.476	18.25
0.6	8.316	5.487	17.53

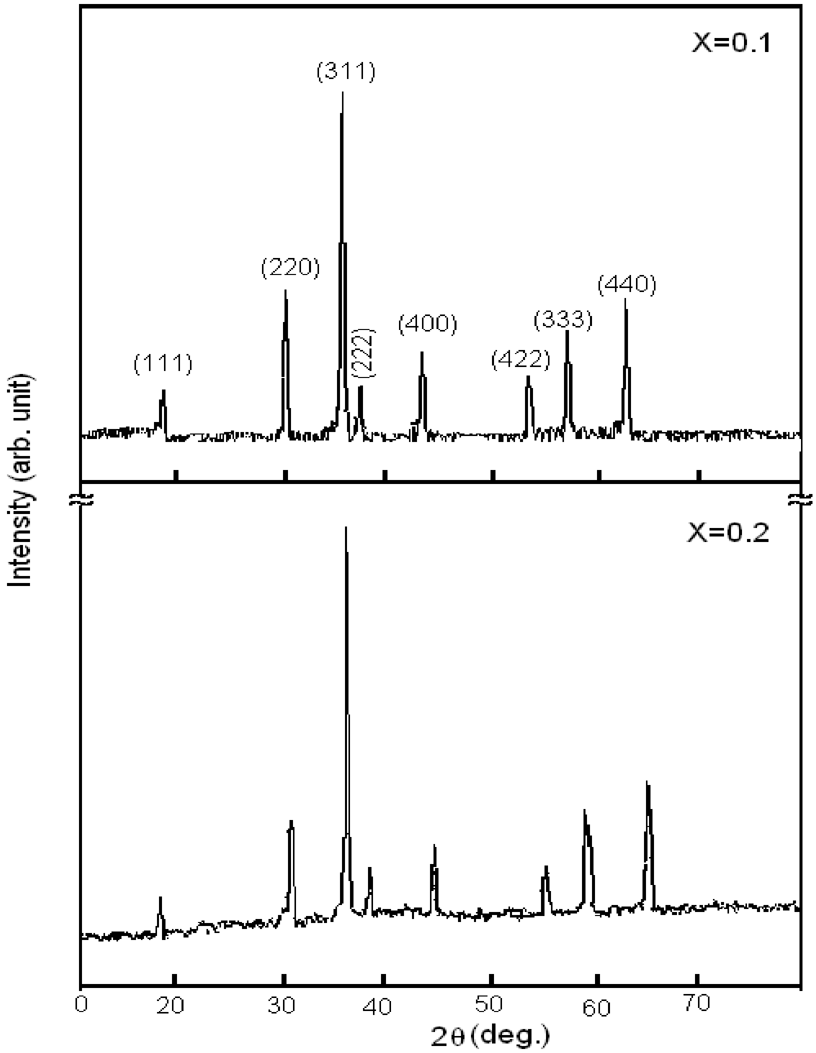

Fig.1- X-ray diffraction pattern of the $Cu_{1+x}Mn_xFe_{2-2x}O_4$ system for x=0.1and x=0.2

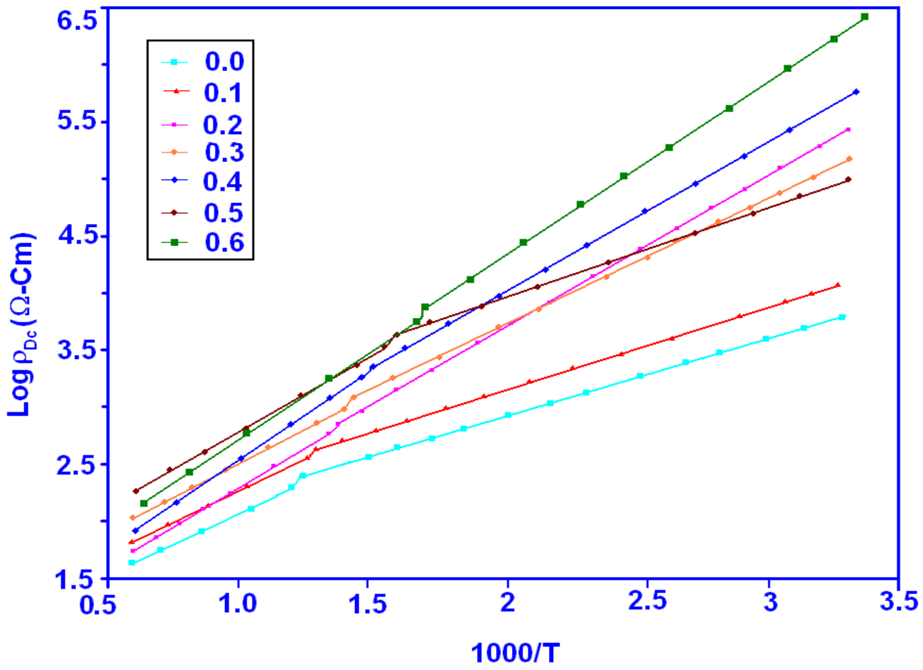

Fig.2- Variation of logρ vs. 1000/T for the $Cu_{1+x}Mn_xFe_{2-2x}O_4$ system

Table 2- Compositional variation of activation energy (E_g), Curie temperature and transition temperature for the $Cu_{1+x}Mn_xFe_{2-2x}O_4$ system.

Composition 'x'	Activation Energy (E_g)		Curie temp. (T_c) in (°K)	Transition temp. (T_s) in (°K)
	Ferri. Region (E_f) in ev	Para. Region (E_p) in ev		
0.0	0.347	0.580	727	------
0.1	0.396	0.713	714	350
0.2	0.262	0.951	701	360
0.3	0.474	0.633	691	365
0.4	0.449	0.474	660	375
0.5	0.396	0.322	648	385
0.6	0.237	0.311	615	390

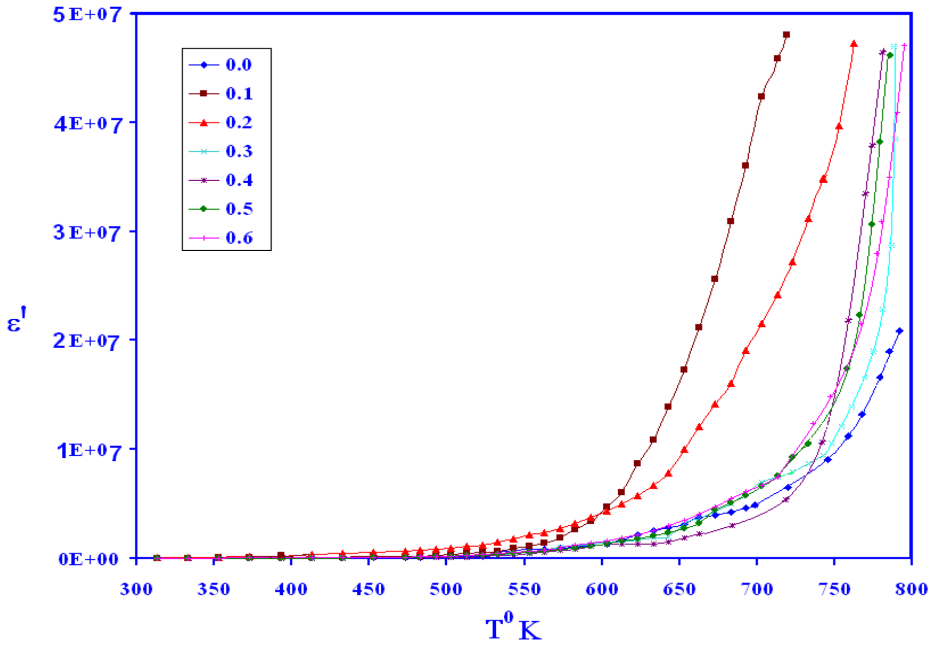

Fig.3- Variation of dielectric constant with temperature for the $Cu_{1+x}Mn_xFe_{2-2x}O_4$ system

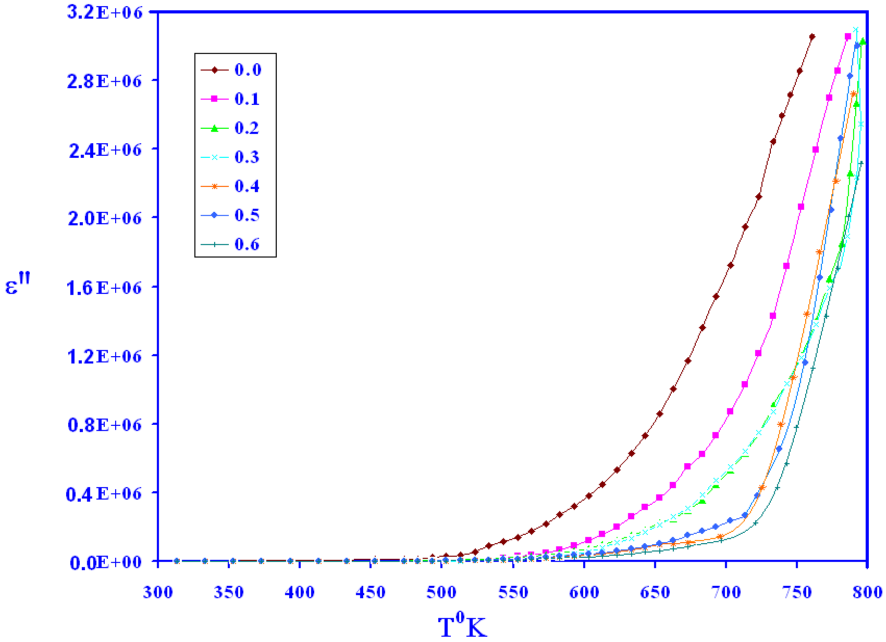

Fig.4-Variation of dielectric loss with temperature for the $Cu_{1+x}Mn_xFe_{2-2x}O_4$ system

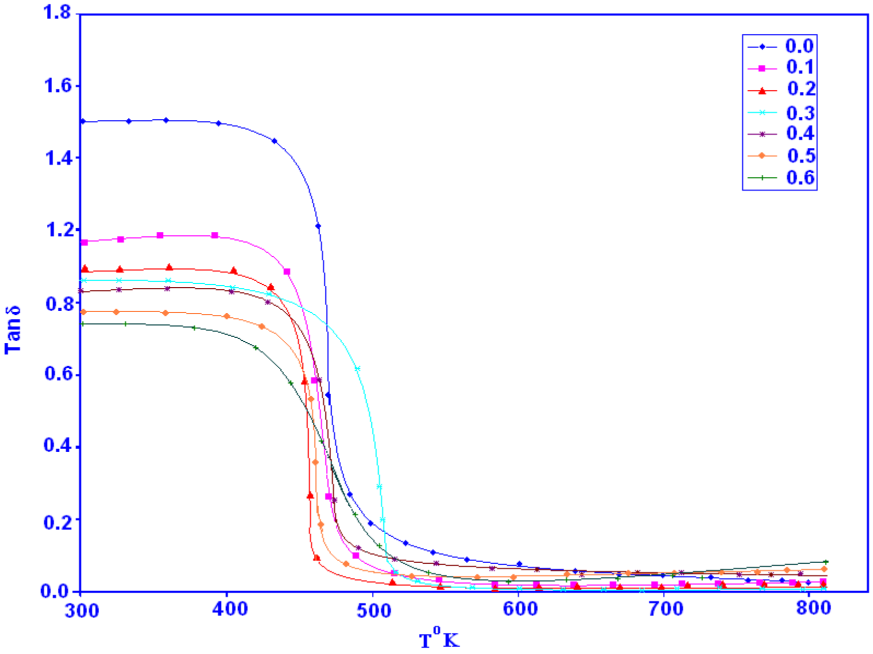

Fig.5-Variation of dielectric loss tangent with temperature for the $Cu_{1+x}Mn_xFe_{2-2x}O_4$ system

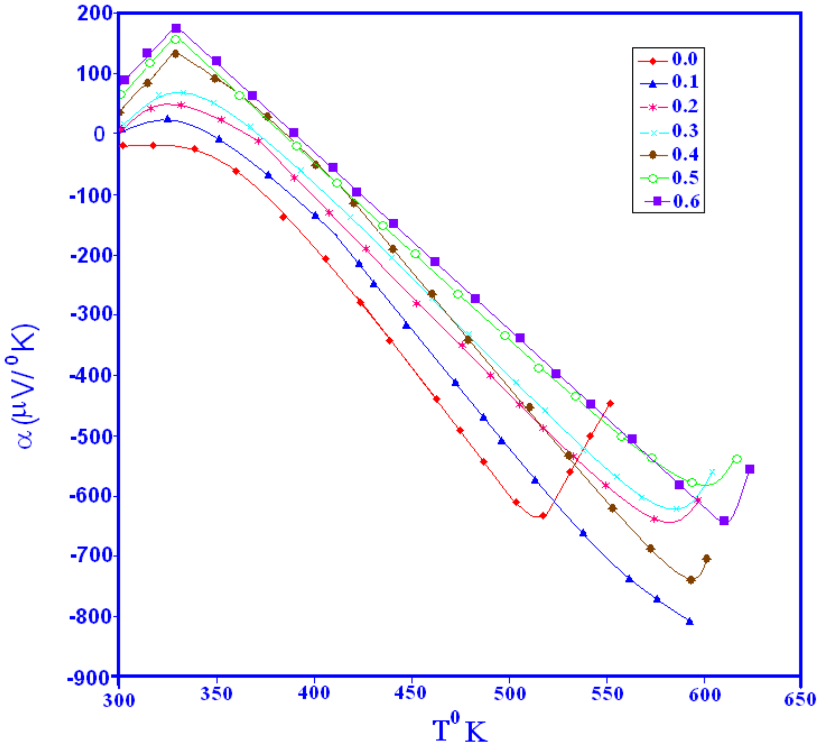

Fig.6-Variation of thermoelectric power with temperature for the $Cu_{1+x}Mn_xFe_{2-2x}O_4$ system