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# Studies on Anomalous Behaviour at Curie Point, $T_c$ of Some Classes of Mixed Ferrites

**M. Tofazzal Hossain,[a] Suravi Islam,[a] Mokbul Hossain Mondal[a] and A. H. Khan[b]**

*[a]BCSIR Laboratories, Dhaka and Department of Physics,*
*[b]Jahangirnagar University, Savar, Dhaka.*

## Abstract

A comparative studies on anomalous behaviour at Curie point between clay additives Mn-Zn ferrites and other mixed ferrites such as Mn-Zn, Ni-Zn, Mg-Mn and Ni-Mg have been carried out in this investigation. The changes in $T_c$ on compositions, additives and manufacturing processes of such soft mixed ferrites have been determined from the temperature dependent dc resistivity data and the log ρ vs. (1/1000T) graphs. It is observed that the Curie temperature is dependent on compositions, additives, manufacturing process and microstructure. Definite changes of Curie points of clay additives Mn-Zn ferrites with other ferrites were observed. Both the Mn-Zn ferrites and clay additives Mn-Zn ferrites showed some changes in their $T_c$ behavior. The $T_c$ value of Mn-Zn ferrites with clay additives decreases with increasing additives. In the case of clay substituted Mn-Zn ferrites the decrease of Curie point can be understood by a decrease of the number of $Fe^{3+}$ magnetic ions substituted by nonmagnetic $Al^{3+}$ ions on O sites of the system.

## Introduction

Curie temperature is the temperature when the energy of the thermal motion of the atoms is sufficient to overcome the interaction forces between the atomic moments. At this temperature a ferromagnetic substances changes over to paramagnetic substances. This temperature is also a measure of exchange forces in a ferromagnetics. Near Curie temperature, $T_c$, some of the intrinsic parameter such as the magnetization, the susceptibility, thermal and electrical conductivity are seen to behave differently than predicted by classical molecular field theory.

In general ferrite shows an increasing value of permeability with increasing temperature, until they approach their Curie points when the permeability falls sharply. This happens due to magnetic transition from the ferrimagnetic phase to the paramagnetic phase. The temperature variation of resistivity of magnetic materials shows similar irregularities at magnetic transition point. The magnetic transition point can often be clearly observed in the anomalous temperature variation of transport properties of magnetic material near $T_c$. The magnetic transition point $T_c$ of pure iron was studied by Lunchbury.[1] He studied temperature dependent electrical resistivity ρ and observed $T_c$ around $770^O$ C. The expected linear relationship between lnρ and 1/T has often been found for ferrite materials accompanied by a change in activation energy near the Curie temperature.

It has been observed that in mixed ferrites, where the divalent metal ions consist of some magnetic ions such as Ni, Co, Fe and some nonmagnetic ions such as Zn, Ca, Cu interesting phenomenon occurs. The diamagnetic $Zn^{2+}$ ions content of the mixed $Zn^{2+}$ ferrite has a marked effect on the Curie temperature. The Curie temperature decreases continuously as the Zinc content increased.[2] This was experimentally found out by Forestier in $Zn^{2+}$ ions substituted mixed ferrite.[3] On the other hand, the addition of diamagnetic $Zn^{2+}$ content increase the room temperature permeability of Mn ferrite from 250 to 1000 and Ni ferrite from 10 to 700. So, mixed ferrite of appropriate composition can yield convenient $T_c$ values for operating at high permeability.[4,5] The study of the variation of $T_c$ values with the content of a nonmagnetic substance like $Zn^{2+}$ ions is clearly of importance.

The aim of the present experiment is to investigate the value of $T_c$ of some mixed ferrites like Mn-Zn, Ni-Zn, Mg-Mn and Ni-Mg ferrites with varying the compositions, additives and manufacturing process and to observe the resulting change in their transition temperature, $T_c$. Besides, a comparative study of Curie points between Mn-Zn ferrites and clay additive Mn-Zn ferrites have been made in this investigation.

## Materials and Methods

In the present investigation, eight series of samples with various compositions and additives were prepared in our laboratory by using a ceramic method. The samples were classified into eight groups such as A, B, C, D, E, F and G. Group A-E are Mn-Zn ferrites with different compositions and sintering temperature, group F is Ni-Zn ferrites, group G is Mg-Mn ferrites and group H is Ni-Mg ferrites. The main emphasis of this study has been given on group E in which clay has been employed as an additive. More details about the preparation of the ferrite from oxides are given by Snelling and Ahsanullah.[4,5]

There are some methods available to determine Curie temperature, $T_c$. The Curie temperature is usually determined from magnetization or magnetic susceptibility data. The $T_c$ can also be determined by different techniques; which include specific heat, thermal expansion and electrical resistivity as a function of temperature. In our present experiment the Curie temperature measurement involved measuring the resistivity ρ, at varing temperature. The same method has been treated by M. A. Hossain, S. R. Swant and R. N. Patil and V. R. Kulkarni *et.al*.[6-9] To characterize the clay additive samples, the X-ray powder pattern were recorded on a Phillips X-ray diffractometer using Cu Kα radiation.

## Results and Discussion

### Structural Characterization

Figs. 1.1 to 1.3 show the X-ray diffraction patterns for clay additive Mn-Zn ferrites (group E samples). The patterns were analyzed by Phillips X-ray diffractometer and confirm formation of cubic system with space group Fd3m. The structural parameters are shown in Table I.

### Composition dependent Curie Temperature, $T_c$ values of Mn-Zn, Mg-Mn and Ni-Mg ferrites

To determine $T_c$ the temperature dependent dc resistivity data plotted as lnρ Vs (1000/T) have been used. In group A, the $Zn^{2+}$ ions content is constant and the weight % of the value of $Fe_2O_3$ and MnO are changed simultaneously. The values of $T_c$ on compositions of Mn-Zn ferrites (A-group) are shown in Fig. 2.1

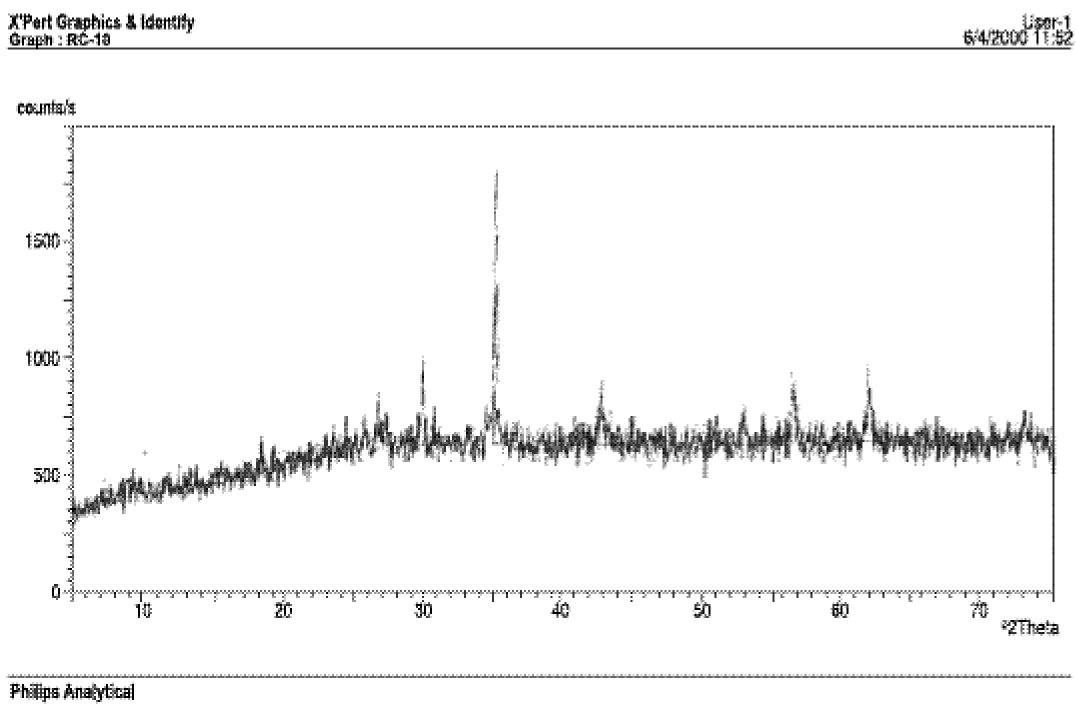


**Fig. 1.1. X-ray diffraction patterns for Rc**

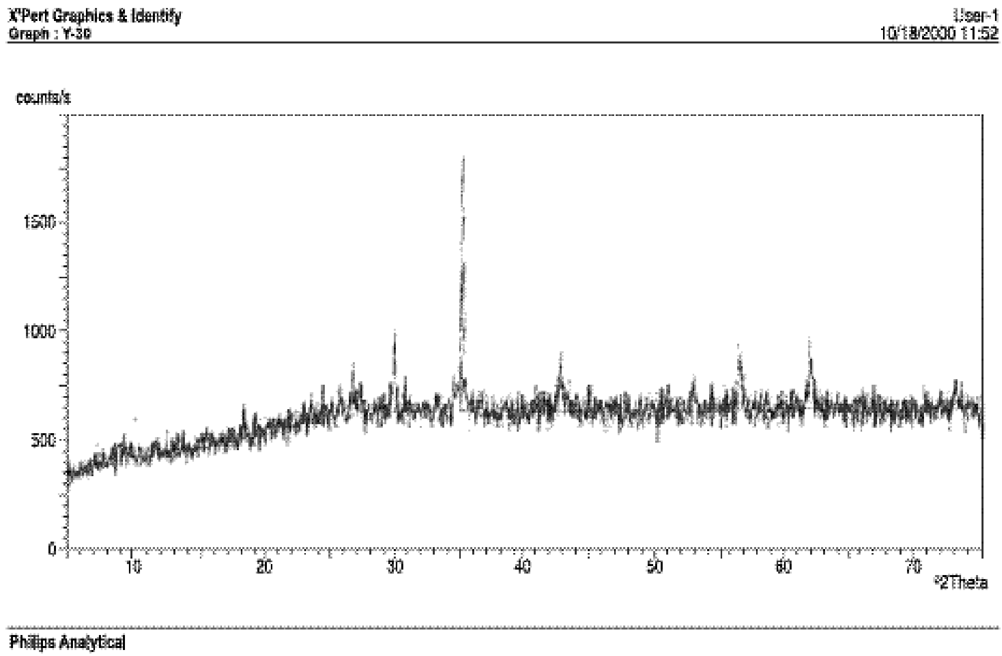


**Fig. 1.2. X-ray diffraction patterns for Bc**

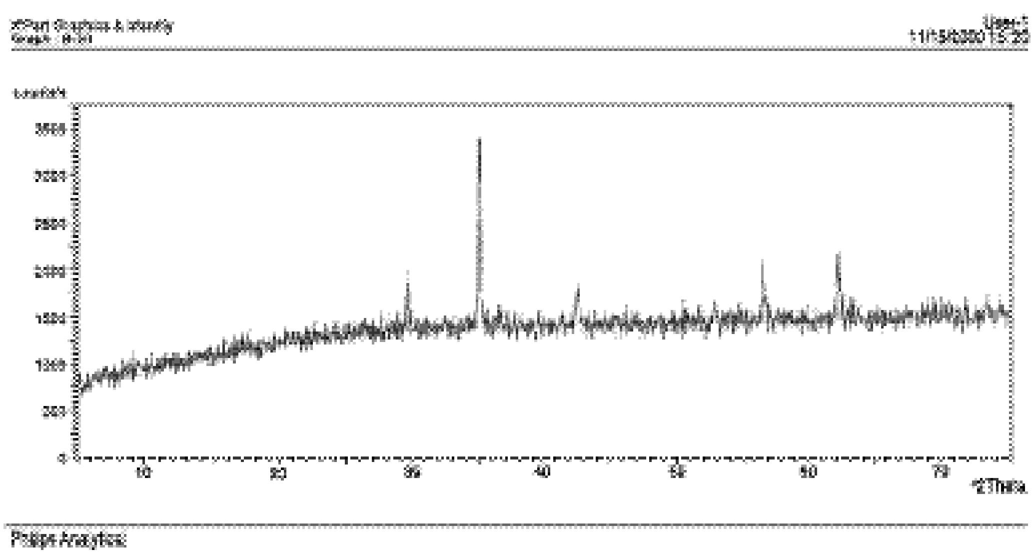

**Fig. 1.3. X-ray diffraction pattern for Yc.**

**Table I. The crystal system, space group and values of lattice parameters, density, number of formula units of clay additive Mn-Zn ferrites.**

| Samples | Structure | Space group | Lattice parameter unit $A^O$ | Density unit gm/cc | No of formula unit with unit cell |
|---|---|---|---|---|---|
| E1 | Cubic | Fd 3m | 8.5136 | 5.010 | 8 |
| E2 | Cubic | Fd 3m | 8.4975 | 5.084 | 8 |
| E3 | Cubic | Fd 3m | 8.4794 | 5.162 | 8 |

It is seen from Fig. 2.1 that the Curie temperature increases with the increase of weight % of $Fe_2O_3$. It is also observed that the slight variation in the composition ratio of $Fe_2O_3$ and MnO have a remarkable effect on Tc. It is also well known that the $T_c$ values are dependent on the exchange interaction of magnetic ions of ferrites between octahedral and tetrahedral sites. In the present study, the increase of $T_c$ values in the case of iron rich Mn-Zn ferrites is due to the increase of exchange interaction of AB or BB between octahedral and tetrahedral sites.

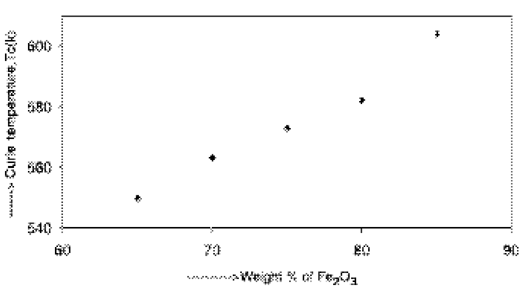


**Fig. 2.1. Composition dependent Tc in Mn-Zn Ferrites (Group A samples)**

In this study we have also investigated the composition dependent anomalous behaviour that is $T_c$ of Ni-Zn ferrites. In Ni-Zn ferrites the weight % of $Fe_2O_3$ remains constant and the ratio of the value of the ZnO and NiO are changed simultaneously. The Curie temperature of this system is shown in Fig. 2.2. It is seen from the figure that the Curie temperature decreases with the increase of ZnO or increases with increase of NiO. This type of behaviour has also been reported by Forestier in $Zn^{2+}$ ions substituted Ni-Zn ferrites.[3] As the ZnO in Ni-Zn ferrite increases exchange interaction of AB and BB between octahedral and tetrahedral sites decreases and thus decreases $T_c$. Reverse is in the case of NiO addition.

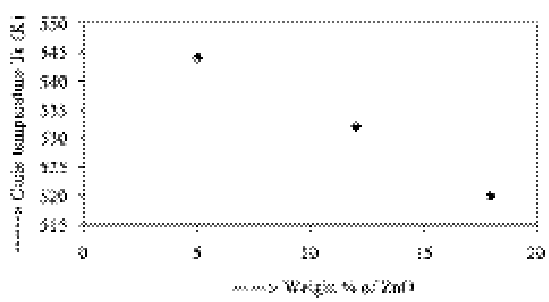


**Fig. 2.2. Composition dependent Tc in Ni-Zn ferrites**

In Mg-Mn and Ni-Mg we have seen that the Mg ions have remarkable effect on Curie temperature as in Figs. 2.3 and 2.4. It is seen from Fig. 2.3 that the Curie temperature

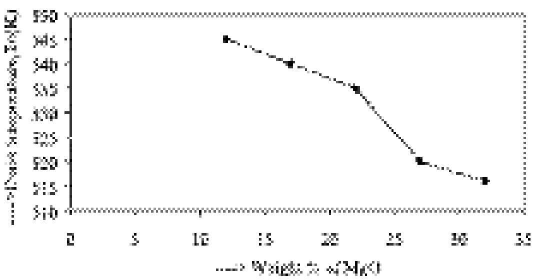

**Fig. 2.3. Composition dependent Tc in Mg-MnFerrites**

decreases with the increase of Mg ions. The decrease of Curie point with increase of Mg ions is due to the fact that Mg occupies O-sites, which weaken the AB interaction and hence decreases $T_c$. In case of Ni-Mg ferrite addition of NiO enhances AB and BB interaction resulting increased $T_c$ values which is evident in Fig. 2.4.

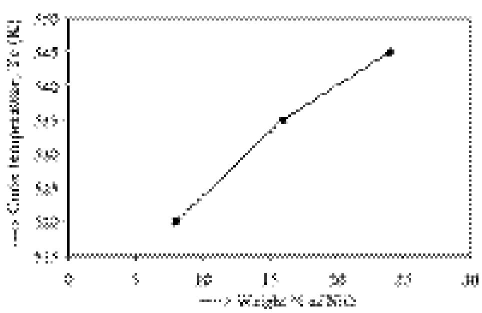

**Fig. 2.4. Composition dependent $T_c$ on Ni-Mg ferrite system**

**Effect of sintering temperature on Curie temperature, $T_c$**

The objective of the study of group C was to observe and gather a general knowledge about the $T_c$ values of Mn-Zn ferrites with different sintering temperature. This group of Mn-Zn ferrites was prepared by sintering at 1273 K, 1373 K, 1473 K and 1573 K Calculated values of Curie temperature, $T_c$ of Mn-Zn ferrites sintered at 1273 K, 1373 K, 1473 K and 1573 K are shown in Fig. 2.5 against sintering temperature. It is evident from Fig. 2.5 that the $T_c$ increases with increasing sintering temperature from 1000 to 1300$^{O}$ C. From the experimental findings it is observed that sintering temperature of the Mn-Zn ferrite samples bore some relations with their $T_c$. The $T_c$ of the experimental samples increases with the increase of the sintering temperature. Because at higher sintering temperature, the density and average grain of the magnetic ions of ferrites are increased. The magnetic ions of Mn-Zn ferrites not only increases magnetic moments but also increases the $T_c$ on sintering temperature.

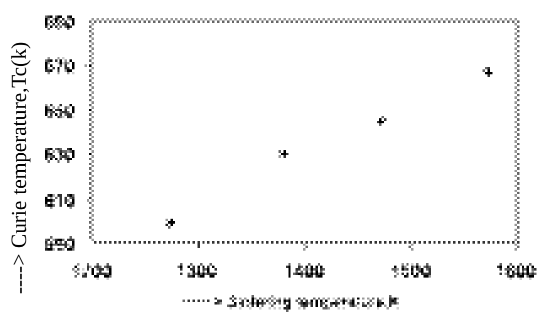


**Fig. 2.5. Variation of Tc on sintering temperature (Group C samples)**

**Effects of Zn-variables on Tc values in Mn-Zn ferrite**

The purpose of the study of group B samples was to observe the change in Curie temperature due to change of non magnetic $Zn^{2+}$ ion in Mn-Zn ferrite. In this investigation we have studied and have compared the $T_c$ of some mixed ferrites which containing $Zn^{2+}$ ions (sample no. $B_2$, $B_3$ and $B_4$) with other ferrite that does not contain $Zn^{2+}$ ions (sample no $B_1$).

It is observed that ferrite samples $B_1$ which does not contain $Zn^{2+}$ ions has higher Tc value than the other samples of this group. But if we gradually increase the $Zn^{2+}$ ions in mixed ferrite samples $B_2$ to $B_4$, $T_c$ value decreases. This result is in good agreement with the result of J. Roberts and Galleo.[2,10] This type of behavior was experimentally found out by Forester and Robert.[3,2] The decrease of Curie point is due to the tetrahedral site preference of the $Zn^{2+}$ ions. $Zn^{2+}$ ions always prefer A sites i.e. tetrahedral site. The exchange integral for A site i.e. $J_{AA}$ is almost negligible. So substitution of $Zn^{2+}$ ions only weaken the AB interaction effectively. If the number of substituted ions are not too high the overall ferrimagnetic arrangement is not destroyed even though some loosely bound spins may become canted or destroyed, at temperature $T< T_c$. For large substitution, the AB interaction became comparable to or even weaker than BB interaction. In this way the collinear ferrimagnetic arrangement often changes to canted one. Owing to this reduced A-B exchange interaction with increasing $Zn^{2+}$ ion content the Curie temperature will drop. So the study of the variation of $T_c$ values with the content of nonmagnetic substance like $Zn^{2+}$ ions is clearly important.

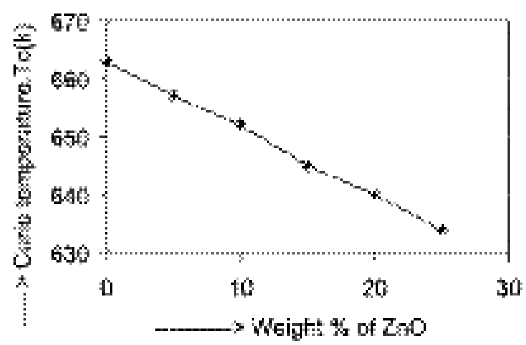


**Fig. 2.6. Composition dependent Tc in Mn-Zn ferrite (Group B samples)**

**Effects of replacement of ZnO by $Al_2O_3$, CdO and CaO**

We have already seen in group B that non magnetic material like $Zn^{2+}$ ions in mixed ferrites play an important role in relation to their $T_c$. It was found that with gradual increase of $Zn^{2+}$ content in mixed ferrites the Curie temperature decreases. Behavior of the substitution of non magnetic materials like Al, Cd, Ca, etc. in Mn-Zn ferrites have been also studied in the mixed ferrites (group D samples) to observe the similar effect. The calculated values of $T_c$ on substituted ions are shown in Fig. 2.7. From the experimental finding it was found that molecular weight of different samples bore some relations with

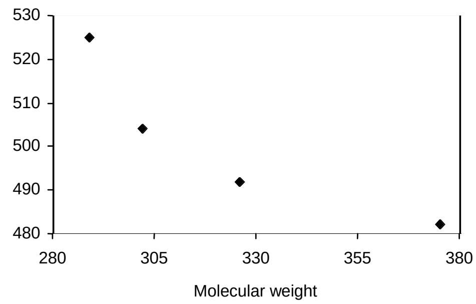


**Fig. 2.7. Variation of Tc on various substitute ions (Group D samples)**

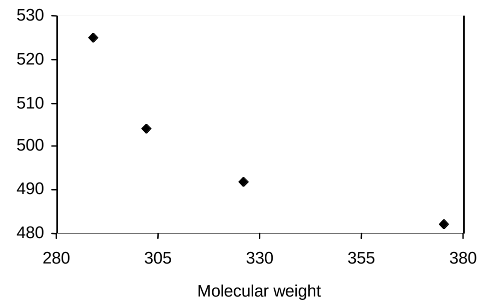


**Fig. 2.8. Variation of Tc on Fe content in various additives Mn-Zn ferrites.**

their Curie temperature. The Curie temperature decreases with the increase of molecular weight.

**Effects of clay additives in Mn-Zn ferrite on $T_c$**

In this investigation three types of clay additive Mn-Zn ferrites have been studied. These types of clay additives are denoted by Rc, Bc and Yc and found in Bijoypur and Savar region of Bangladesh. The main cations of clay material are Si, Al, Mn and Fe. The composition variations of $T_c$ values of clay adittives of ferrite are shown in Fig. 2.8. It is evident, as in Fig. 2.8, that sample $Y_c$ has the highest $T_c$ value.

The observed variation of $T_c$ values can be explained on the basis of AA, AB and BB interactions. In clay additive Mn-Zn ferrites, the cations are Fe, Mn and Si, which contribute to $T_c$ values. It is well known that the cation Fe is magnetic and occupy both the tetrahedral and octahedral sites. In the

**Table II. Composition variation of Tc values of clay additive ferrites**

| Sl. No | Composition of ferrites | Cations | Compound formula | Concentration % | Curie temperature $T_c$ (K) |
|---|---|---|---|---|---|
| 1. | Rc (Red clay substitute Mn-Zn ferrite) | Si<br>Mn<br>Fe | SiO<br>MnO<br>$Fe_2O_3$ | 25.79<br>20.50<br>33.70 | 561 |
| 2. | Bc (Black clay substitute Mn-Zn ferrite) | Si<br>Mn<br>Fe | SiO<br>MnO<br>$Fe_2O_3$ | 27.75<br>20.37<br>35.01 | 571 |
| 3. | Yc (Yellow clay substitute Mn-Zn ferrite) | Si<br>Mn<br>Fe | SiO<br>MnO<br>$Fe_2O_3$ | 31.80<br>18.38<br>44.50 | 577 |

present study the increase of $T_c$ value in the case of Fe rich clay additive Mn-Zn sample is due to the increase of exchange interaction of AB and BB between octahedral and tetrahedral sites.

## Conclusions

The Curie temperature $T_c$, of the various ferrites is strongly dependent on composition, sintering temperature and various additives. It is seen that the slight variation of the composition i.e ratio of major constituents have a remarkable effect on $T_c$.

It is also observed that the $T_c$ values depend on the exchange interaction of magnetic ions of ferrites between octahedral and tetrahedral sites and the observed variation may be explained on the basis of AA, BA or BB interactions of various cations and their site location between octahedral and tetrahedral sites.

It is evident that sintering temperature of the Mn-Zn ferrite sample bears some relations with their curie temperature. At higher sintering temperature the density and average grain of the magnetic ions of ferrites are increased and the magnetic moments are increased. This enhances the magnetic interaction and hence increases $T_c$ values.

In clay additive Mn-Zn ferrites, the cations are Fe, Mn and Si which contribute to $T_c$ values. It is well known that the cations Fe are magnetic and occupy both the tetrahedral and octahedral sites. In the present study the increase of $T_c$ value in case of Fe rich clay additive Mn-Zn sample is due to the increase of exchange interaction of AB and BB between octahedral and tetrahedral sites.

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