Chapter-5
Effect of quenching on the mixed ferrites of present study

5.1 INTRODUCTION

Ferrite microstructures are extremely sensitive to processing because the pre reaction and grinding of raw materials, forming technique employed, sintering time, and temperature and cooling conditions influence crystal composition and size and also the size and volume of pores[1-10]. Microstructure plays a strong role because fine grained ceramics can only reverse magnetization by rotation since domain walls are energetically unfavourable in fine grains. Also, the coercive fields increase with porosity because of internal demagnetizing fields.

Particularly high permeability materials are fired at high temperatures for long periods of time to develop high density, large grained ceramics. This process accentuates volatility and can produce a surface layer deficient in zinc oxide. The zinc poor ferrite surface layer will have a higher Curie temperature and lower permeability than the bulk, reducing the effective permeability. Zinc oxide volatility is a very severe problem in mixed zinc ferrites[11,12].

5.2 $\text{Ni}_{0.55}\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ SYSTEM

Ni-Zn-Cu mixed ferrites synthesized by sintering (Chapter-2) are explained to have a better compaction with a small amount of loose packing
using the XRD data. It is seen from Figure-5.1 that the curves of theoretical and experimental lattice constants of the sintered ferrite show a straight line behavior and an increasing trend with concentration. It is predictable that the larger Zn$^{2+}$ ion substitution for smaller Ni$^{2+}$ ions clearly reasons the increasing trend of lattice constant. Moreover the gap between the theoretical and experimental lattice constant curves is interpreted by 1. A sizable contribution of loose packing of the interstitial ions. 2. The distortions in the crystal field imparted by the Jahn-Teller effect due to the presence of Cu$^{2+}$ ions in the B site.

The proposed cation distribution of sintered Ni-Zn-Cu ferrite is:

$$\text{(Zn}^{2+}_{x\cdot y} \text{Fe}^{3+}_{1-x\cdot y})_A [\text{Ni}^{2+}_{0.5-x} \text{Zn}^{2+}_x \text{Cu}_{0.5} \text{Fe}^{3+}_{1+x\cdot y}]_B \text{O}^{2-}.$$ 

where $x = 0.1, 0.2, 0.3, 0.4$ and 0.5, $y = 25\%$ of $x$.

The observed and theoretical lattice constants of quenched Ni-Zn-Cu mixed ferrite system are shown in Figure-5.1 to enable a comparison with its sintered system. It is seen from figure the quenched ferrites show a remarkable shift in the observed lattice constant. The theoretical lattice constant of the quenched system needs to be calculated by a different proposal of distribution of cations. A suitable cation distribution for the quenched system is given as

$$\text{(Zn}^{2+}_{x\cdot y} \text{Fe}^{3+}_{1-x\cdot y})_A [\text{Ni}^{2+}_{0.5-x} \text{Zn}^{2+}_x \text{Cu}_{0.5} \text{Fe}^{3+}_{1+x\cdot y}]_B \text{O}^{2-}.$$ 

where $x = 0.1, 0.2, 0.3, 0.4$ and 0.5 and $y = 75\%$ of $x$.

It is clearly understood from Figure-5.1 that the quenched ferrites have lattice expansion due to Jahn-Teller effect of Cu$^{2+}$ ions as well as the effect of quenching. The difference between the slopes of the lattice constant curves of
Variation of lattice constant with concentration for the samples of Ni$_{44.3}$Zn$_{4.4}$Cu$_{5.6}$Fe$_2$O$_5$ system.

![Graph of lattice constant variation](image)

**Figure 5.1**

Variation of Curie temperature with concentration for the samples of Ni$_{44.3}$Zn$_{4.4}$Cu$_{5.6}$Fe$_2$O$_5$ system.

![Graph of Curie temperature variation](image)

**Figure 5.2**
quenching and sintering is attributed to the change of y in the formula from 25% to 75%. It is evident that the effect of quenching pins the highly volatile Zn$^{2+}$ ions in their interstitial sites. Conversely a serious volatilization of ZnO occurs because of high sintering temperature and long sintering times in the former case.

AC susceptibility measurements have provided experimental values of Curie temperature viz. Chapter-2 for sintered and quenched samples. A direct comparison of the results of Curie temperature for quenched and sintered samples is made possible from Figure-5.2. The substitution of Zn ion is supposed to reduce the transition temperature since they are non magnetic. Incidentally the distribution of the cations appears to provide a contrasting picture. Magnetic energy is a direct function of Curie temperature. Consequently the main mechanism for the reduction of $T_C$ is attributed as the reduction of crystal field due to Jahn-Teller splitting.

From Figure-5.3 the dependence of theoretical and experimental magnetic moments on the nature of the interstitial ions and the effect of quenching are correlatable. It is seen from Figure-5.3 that the observed and theoretical magnetic moments of sintered and quenched ferrites show a wide disagreement. With the increase of x the discrepancy of $n_B$ values suggests that a rising influence of canting of spins in both the cases. A comparison of magnetic moment data for quenched and sintered systems reveals that the values of magnetic moments are higher for sintered Ni-Zn-Cu mixed ferrites than that of the quenched ones. It is attributable to the clamping of more quantity of Zn$^{2+}$ ions in the A site during the
Variation of magnetic moment with concentration for the samples of Ni_{0.5-x}Zn_{x}Cu_{0.5}Fe_{2}O_{4} system.

![Graph showing variation of magnetic moment with concentration](Figure-5.3)

Variation of saturation magnetization with particle size for the samples of Ni_{0.5-x}Zn_{x}Cu_{0.5}Fe_{2}O_{4} system.

![Graph showing variation of saturation magnetization with particle size](Figure-6.4)
process of quenching. Similarly the observed saturation magnetization values are explained on the basis of the variation of A-B exchange interaction and a considerable spin canting in B site. The dependence of saturation magnetization on particle size for sintered and quenched systems is shown in Figure-5.4. The sintered ones bear a straight-line relation with particle size but with a a positive slope. On the other hand saturation magnetization and particle size for the quenched system show a horizontal straight-line behaviour. Behaviour of the former system is attributable to the discontinuous organisation of the particles. The later system explains a uniform and continuous chain of particle growth during quenching.

The measured values of activation energy versus concentration (Figure-2.12A) would be able to throw more light on the changes in the position of the energy bands due to incorporation of Zn$^{2+}$. This range of values is suggestive of hopping and the present system behaves like a semiconductor with intermittent energy levels in the localized d bands of neighboring Fe ions of B site. Based on these results we conclude that the Fe-3d electrons are important in the conduction process.

Conductivity measurements on the sintered and quenched systems are indicative of the presence of Ni$^{3+}$ and Fe$^{2+}$ ions in B site. A clear rising up of activation energy ($E_{ac}$) with concentration is observable from Figure-5.5 for quenched system. It is attributed to the widening of the band gap of 3d band of ions mainly in B site. Actually the increase of concentration alters the
Variation of grain boundary conductivity with particle size for the samples of $\text{Ni}_{0.6-x}\text{Zn}_{x}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$ system.

**Figure-6.6**

Variation of activation energy ($E_a$) with concentration for the samples of $\text{Ni}_{0.6-x}\text{Zn}_{x}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$ system.

**Figure-6.5**
composition of Ni and Zn. It is believed that Cu$^{2+}$ ion in B site is the cause of Jahn-Teller effect which makes the neighboring ions to go to the exited state[13].

The predominant conduction mechanism of Ni-Zn-Cu system of present investigation is explained to be due to the modifications of the nature of ions. Therefore the modified cation distributions of sintered ferrites is given as

$$(\text{Zn}^{2+}_{1-x-y} \text{Fe}^{3+}_{x+y})_A \left[ \text{Ni}^{2+}_{0.5-x} \text{Ni}^{3+}_x \text{Zn}^{2+}_y \text{Cu}_{0.5} \text{Fe}^{2+}_x \text{Fe}^{3+}_{1-x-y} \right]_B \text{O}^2-4.$$  

where $x = 0.1, 0.2, 0.3, 0.4$ and $0.5$, $y = 25 \%$ of $x$.

Similarly for quenched system the modified structure is

$$(\text{Zn}^{2+}_{x-y} \text{Fe}^{3+}_{1-x-y})_A \left[ \text{Ni}^{2+}_{0.5-x} \text{Ni}^{3+}_x \text{Zn}^{2+}_y \text{Cu}_{0.5} \text{Fe}^{2+}_x \text{Fe}^{3+}_{1-x-y} \right]_B \text{O}^2-4.$$  

where $x = 0.1, 0.2, 0.3, 0.4$ and $0.5$ and $y = 75 \%$ of $x$.

The modification of the cation distributions are in support of 75% of Zn in B site of quenched Ni-Zn-Cu system over the 25% of sintered system. It is inferred from Figure-5.6 that the grain boundary conductivity with respect to particle size can bring out the effect of quenching. The straight-line curve for quenched one show a higher amount of grain boundary conduction when compared to the sintered ones. It is suggestive of a less loss for the conduction as they contain a more probable amount of grains in the quenched ferrites.

5.3 Ni$_{0.5+x}$Zn$_x$Cu$_{0.5}$Fe$_{2.25}$O$_4$ SYSTEM

The Chapter-3 deals with Ni-Zn-Cu mixed ferrites obtained by sintering and reveals that the samples under study have a good amount of loose packing using the XRD data. It is seen from Figure-5.7 that the curves of theoretical and experimental lattice constants of the sintered ferrite show a straight line behavior.
and an increasing trend with concentration. Occurrence of crystal field distortions and Jahn-Teller effect are estimated as the cause mechanism of the gap between the theoretical and experimental lattice constants. It is also understood that the increasing trend of lattice constants with concentration is solely attributed to that part of Zn$^{2+}$ and Ni$^{2+}$ ions replacing Fe$^{3+}$ ions in the B site. Replacement of Fe$^{2+}$ ions by the doped Zn$^{2+}$ and Cu$^{2+}$ ions in the A sites contributes for the expansion of the lattice.

The proposed cation distribution of sintered Ni-Zn-Cu ferrite system of present study is:

$$(\text{Zn}^{2+}_{x-y} \text{Fe}^{3+}_{1-x+y-z} \text{Cu}^{2+}_{z})_A [\text{Ni}^{2+}_{0.5-x} \text{Zn}^{2+}_{y} \text{Cu}_{0.5-z} \text{Fe}^{3+}_{1+x-y+z}]_B \text{O}^{2-}_4.$$ 

Where $x = 0.1, 0.2, 0.3, 0.4$ and $0.5$, $y = 50\%$ of $x$ and $z = 50\%$ of $y$.

In the case of quenched system the observed lattice constants show a good agreement of the trend with the theoretical data obtained for an identical cation distribution of the former system. It is seen from Figure-5.7 that the quenched ferrites show a wide shift in the observed lattice constant. The curves of sintered and quenched systems illustrate expansion of the lattice for sintering when compared to the quenching. It is explained on the basis of the volatilability of Zn and Ni which can alter proportionately the quantity of Fe$^{2+}$ ions and Fe$^{3+}$ ions. It is wise to think that in the case of sintering a more probable formation of Fe$^{2+}$ ions contributes lattice expansions. Fundamentally the lattice expansion is initiated due to the presence of Cu$^{2+}$ ions in B sites which produces spin orbit coupling- Jahn-teller distortion. As $x$ increases Zn and Ni increase there by
Variation of lattice constant with concentration for the samples of \(Ni_{x+2}\) \(Zn\) \(Cu_{x}\) \(Fe_{2-2x}\) \(O_4\) system.

![Graph](image1)

Variation of Curie temperature with concentration for the samples of \(Ni_{x+2}\) \(Zn\) \(Cu_{x}\) \(Fe_{2-2x}\) \(O_4\) system.

![Graph](image2)
suppressing the Cu to remain in Cu2+ state consequently a reduction in Jahn-Teller splitting is effected by the enhancement of Ni ions in this present set of ferrites.

Experimental values of Curie temperature are estimated using AC susceptibility data (Chapter-3) for sintered and quenched samples. Figure-5.8 provides a direct comparison of the results of Curie temperature for quenched and sintered samples. The Zn ion substitution is supposed to reduce the transition temperature since they are non magnetic. The parameter Curie temperature is the sincere function total magnetic moment contribution of the spinel. The decrease of Curie temperature with concentration is explained to be due to the increase in the concentration of Zn2+ and Ni2+ ions whose relative magnetic moment at A and B sites amounts to a reduction in $T_C$. The values of Curie temperature show a consistent hike for quenching of the ferrites. It is indicative of an appreciable role for Jahn-Teller splitting in sintered ferrites, which is in agreement with the XRD results of the present study.

The dependence of theoretical and experimental magnetic moments on the nature of the interstitial ions and the effect of quenching are correlatable from Figure-5.9. It is seen from Figure-5.9 that the theoretical and observed magnetic moments of sintered and quenched ferrites show a wide disagreement. It is explained to be due to non-collinear spin alignment. Thus the observed moment variation has been explained on the basis of Yafet-Kittel angles existing on the B site spin instead of two sub lattice. Zn2+ ions going into B sites decrease the
Variation of Magnetic moment with concentration for the samples of Ni$_{0.6+x}$Zn$_x$Cu$_{0.6}$Fe$_{2-2x}$O$_4$ system.

![Graph showing variation of magnetic moment with concentration](image1)

Figure 5.9

Variation of saturation magnetization with particle size for the samples of Ni$_{0.6+x}$Zn$_x$Cu$_{0.6}$Fe$_{2-2x}$O$_4$ system.

![Graph showing variation of saturation magnetization with particle size](image2)

Figure 5.10
magnetic moment of the B sub lattice and also modify the A-B exchange interactions of A and B sites. Hence, the net magnetic moment decreases. A comparison of magnetic moment data for quenched and sintered systems reveals that the values of magnetic moments are higher for sintered Ni-Zn-Cu mixed ferrites than that of the quenched ones up to \( x = 0.3 \), after that the magnetic moment of quenched samples shoots to a higher value than that of sintered ones. So this cross over point \( (x=0.3) \) is termed as neutral point at which the sample has less sensitive for the heat treatment process. It is explained that the sample \( (x=0.3) \) is thermally stable. It may be accounted by the knowledge of A-B exchange interaction which is measurable using Mossbauer data.

The dependence of saturation magnetization on particle size for sintered and quenched systems is shown in Figure-5.10. The sintered ones bear a straight-line relation with particle size but with a positive slope. On the other hand saturation magnetization and particle size for the quenched system show a horizontal straight-line behaviour. Behaviour of the former system is attributable to the discontinuous organisation of the particles. The later system explains a uniform and continuous chain of particle growth during quenching.

The measured values of activation energy versus concentration (Figure-5.11A) would be able to throw more light on the changes in the position of the energy bands due to incorporation of Zn\(^{2+}\). This range of values is suggestive of hopping and the present system behaves like a semiconductor.
Variation of activation energy (ac) with concentration for the samples of $\text{Ni}_{0.8+x} \text{Zn}_{x} \text{Cu}_{0.8} \text{Fe}_{3-2x} \text{O}_4$ system.

**Figure 5.11**

Variation of grain boundary conductivity with concentration for the samples of $\text{Ni}_{0.8+x} \text{Zn}_{x} \text{Cu}_{0.8} \text{Fe}_{3-2x} \text{O}_4$ system.

**Figure 5.12**
Conductivity measurement is indicative of the presence of Ni\textsuperscript{3+} and Fe\textsuperscript{2+} ions in B site. The rising up of activation energy (\(E_a\)) with concentration is attributed to the widening of the band gap of 3d band of ions mainly in B site. The increase of concentration alters the composition of Ni and Zn. Generally Cu\textsuperscript{2+} ion in B site is the cause of Jahn-Teller effect which makes the neighboring ions to go to the exited state. It is also noticed that the effect of quenching tends to broaden the gap of energy levels of 3d bands with respect to concentration. It is suggestive of retaining of more quantity of Zn ions in the ferrites due to quenching. Widening of the band gap of 3d bands with \(x\) is correlatable to the relative strength of Jahn-Teller splitting and crystal field in the octahedral site of spinel ferrite.

The proposed cation distribution of both sintered and quenched Ni-Zn-Cu ferrite system of present study is:

\[(\text{Zn}_{x-y}^{2+} \text{Fe}_{x+y-z}^{3+} \text{Cu}_{z}^{2+})_A [\text{Ni}_{0.5-x}^{2+} \text{Fe}_{0.5-x}^{2+} \text{Zn}_{y}^{2+} \text{Cu}_{z}^{2+} \text{Fe}_{1+y+z}^{3+}]_B \text{O}_{4}^{2-}\]

Where \(x = 0.1, 0.2, 0.3, 0.4\) and \(0.5\), \(y = 50\%\) of \(x\) and \(z = 50\%\) of \(y\).

It is inferred from Figure-5.12 that the grain boundary conductivity with respect to particle size can bring out the effect of quenching. The straight-line curve for quenched one show a higher amount of grain boundary conduction when compared to the sintered ones. It is suggestive of a less loss for the conduction as there are a closed chain of grains in the quenched ferrites.
5.4 $\text{Mg}_{0.9}\text{Co}_{0.1}\text{Cr}_{2\text{z}}\text{Fe}_{2\text{z}}\text{O}_{4}$ FERRITE SYSTEM

$\text{Cr}^{3+}$ ions have been employed to improve the properties of Mg-Co ferrites, particularly to increase its resistivity and to decrease its losses. Foreign atoms can be produce changes in ferrite properties by (1) increasing the electrical resistively of the grain boundary, (2) enhancing densification of the compact, or (3) controlling grain growth.

Cobalt $\text{Co}^{2+}$ ions produce unique and often useful changes in the properties of spinels and other magnetic oxide compounds. Divalent cobalt readily substitutes in octahedral sites, but the trivalent state is rarely observed. Cobalt ferrite has a theoretical moment of 3 Bohr magnetons, influenced to some degree by heat treatment[14-16]. Divalent cobalt has much more spin orbit coupling than the other 3d transition metal ions, resulting in very high magnetocrystalline anisotropy and magnetostriction constants. This strong binding of the magnetization vector to the crystal axis produces very low permeabilities and very high coercive forces.

Substitution of cobalt into another spinel such as nickel, manganese or ferrous (magnetite) ferrite can compensate for their negative anisotropy and produce a net low anisotropy, fulfilling one condition for high permeability. Usually the permeability will go through a slight peak at this compensation composition, providing higher permeabilities for high frequency ferrites.
Figure-5.13 is the outcome of the analysis of XRD data of sintered and quenched ferrites. It is seen from the Figure-5.13 that the observed lattice constants of quenched ferrites show considerable change from the observed ones of their counter parts. However theoretical computing of lattice constants using a single proposal of distribution of cations suits well with observed data.

It is seen that the variation of experimental and theoretical lattice constants is a linear one with minor discrepancy. The minor discrepancy in the variation of lattice constants (a) with x can be explained on the basis of degree of inversion of cations i.e. the structure changes from inverse to a certain degree of normal one. Therefore the occurrence of loose packing and redistribution of ions in A and B sites are estimated as the cause mechanisms for the gap between the theoretical and experimental lattice constants curves (Figure-5.13).

The proposed cation distribution for the mixed Mg-Co-Cr ferrites is:

\[(\text{Mg}^{2+}_{0.1+y} \text{Fe}^{3+}_{0.9-y})_A [\text{Mg}^{2+}_{0.8-y} \text{Co}^{2+}_{0.1} \text{Cr}_{2x} \text{Fe}^{3+}_{1.1-2x+y}]_B \text{O}^{2-}_4.\]

where \(x = 0.0, 0.1, 0.2, 0.3, 0.4 \text{ and } 0.5 \) and \(y = 10\% \text{ of } x.\)

The observed parallelism between quenched ferrites and theoretical data of lattice constants is attributed to the correctness of fit. It assures a good deal of presence of \(\text{Co}^{2+}\) ions in the B sites of spinel system, although they are highly volatile. It is seen from Figure-5.13 that for \(x = 0\) i.e., \(\text{Cr} = 0\) the quenched and sintered ferrites have one and the same set of lattice constants. For \(x > 0\) a discrepancy builds up. It is indicative of a considerable role of \(\text{Cr}\) and that should be a relative expansion of lattice due to Jahn-Teller effect of \(\text{Cr}.\) Further
Variation of lattice constant with concentration for the $\text{Mg}_{0.9} \text{Co}_{0.1} \text{Cr}_{2x} \text{Fe}_{2-2x} \text{O}_4$ system.

Variation of Curie temperature with concentration for the samples of $\text{Mg}_{0.9} \text{Co}_{0.1} \text{Cr}_{2x} \text{Fe}_{2-2x} \text{O}_4$ system.
it is inferred from Figure-5.13 that quenching appreciably suppresses the predominance of the Jahn-Teller effect of Cr.

In curves of $\chi_T / \chi_{RT}$ versus temperature presented in Chapter-4 Figure-4.3A for sintered ferrites of Mg-Co-Cr a cusp is observed up to $x=0.2$ and for $x > 0.2$ it disappears. The curves with cusp are indicative of single domain (S.D) with respective super paramagnetic (S.P) domain. The absence of cusp for the sample is due to the disappearance of super paramagnetic phases. A close look at Figure-4.3B for quenched ferrites shows the presence of cusp for all $x$ values. Therefore it explains the super paramagnetic and single domain phases in all the quenched ferrite samples. Super paramagnetic phases are formed by Co$^{2+}$ ions in B site. In other words higher the quantity of Co$^{2+}$ more the probability of formation of super paramagnetic phases.

The analysis of results of magnetic susceptibility curves of quenched and sintered ferrites suggest that the liberation of Co$^{2+}$ ions is restricted in quenched ferrites.

Basically $T_c$ of ferrites stems from the nature of magnetic ions in A and B sites Figure-5.14 shows a sharp of $T_c$ values with respect to $x$ for both the heating schedules of ferrites. The decrease of Curie temperature with concentration is explained to be due to the replacement of Fe$^{3+}$ ions (5.92$\mu_B$) by Cr$^{3+}$ (3.87$\mu_B$) ions as concentration increases. Substitution of Cr$^{3+}$ for Fe$^{3+}$ affects Fe$^{3+}$-O$^{2-}$-Fe$^{3+}$ superexchange linkages, which results in the fall of $T_C$ as $x$ increases. When Cr concentration is greater than 0.8, a sudden rise of $T_C$ is observed. It attributes to a
turning point in the magnetic structure of Cr bearing ferrites for \( x \geq 0.5 \) i.e. the material becomes more a chromate than a ferrite. X-ray studies of our work have indicated the transfer from inverse to normal structure, which is in support of the present explanation.

The observed moments for sintered, quenched and computed moment values for Mg-Co-Cr ferrites is shown in Figure-5.15. Theoretical predictions matches well with the observed set of data of moments. Fall of magnetic moment values with concentration of ferrites is interpreted as the weakening of A-B exchange when Cr\(^{3+}\) content increases. It is explained from Figure-5.15 that the net magnetization decreases. However for \( x = 0.5 \) the theoretical and experimental magnetic moments tend to become zero. It is also seen that the gap between the moment curves show a gradual widening as \( x \) increases. It is attributed to the fact that when Cr concentration increases the crystal field develops a distortion due to Jahn-Teller splitting of Cr\(^{3+}\) energy levels in 3d band. However concentration of Cr=0.4 shows a turning point which is independent of the process of heating.

Figure-5.16 shows the variation of saturation magnetization with the particle size. A non uniform growth of particles explains the change in the values of saturation magnetization of sintered and quenched materials. However quenched once are found to have a more non uniform growth of particles than sintered ones.
Variation of magnetic moment with concentration for the samples of \( \text{Mg}_{x}\text{Co}_{y}\text{Cr}_{z}\text{Fe}_{w}\text{O}_{4} \) system.

![Graph of magnetic moment vs. concentration](image)

**Figure-5.16**

Variation of saturation magnetization with particle size for the samples of \( \text{Mg}_{x}\text{Co}_{y}\text{Cr}_{z}\text{Fe}_{w}\text{O}_{4} \) system.

![Graph of magnetization vs. particle size](image)

**Figure-5.16**
Variation of Activation energy (ac) with concentration for the samples of Mg$_{0.5}$Co$_{0.1}$Cr$_{2x}$Fe$_{2-2x}$O$_4$ system.

at 10 kHz

![Activation energy vs Concentration graph](image)

Variation of Grain boundary conductivity with concentration for the samples of Mg$_{0.5}$Co$_{0.1}$Cr$_{2x}$Fe$_{2-2x}$O$_4$ system.

![Grain boundary conductivity vs Concentration graph](image)
The a.c conductivity analysis presented in Chapter 4 for sintered and quenched Mg-Co-Cr ferrites has established that the hopping of charges in between the energy levels of the 3d bands and instantaneous excitation of $\text{Co}^{2+} \rightarrow \text{Co}^{3+}$ and $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ are the causes of electrical conduction. The variation of activation energy with concentration of Cr, for sintered and quenched ferrites is shown in the form of least square fit line as in Figure-5.17. It is evident from Figure-5.17 that there is a substantial widening of gap between the localized d bands when Cr concentration increases. The effect of quenching is capable of tailoring the band gap of localized 3d bands of B site ions.

The outcome of results help to modify the cation distribution of Mg-Co-Cr system as follows.

$$(\text{Mg}^{2+}_{0.1+y} \text{Fe}^{3+}_{0.9-y})_A [\text{Mg}^{2+}_{0.8-y} \text{Co}^{2+}_{0.1} \text{Co}^{3+} \text{Cr}_x \text{Fe}^{2+} \text{Fe}^{3+}_{1.1-2x+y}]_B \text{O}^{2-}_4.$$ where $x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5 and $y = 10\%$ of $x$. 

183
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