

# INFLUENCE OF $\text{MO}^{6+}$ ON FTIR AND MÖSSBAUER SPECTROSCOPIC PROPERTIES OF COPPER FERRITE

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**Abstract:** To understand the impact of  $\text{Mo}^{6+}$  on some structural parameters of copper ferrites, it was substituted in the chemical compositional formulae  $\text{Cu}_{1.0-3y}\text{Fe}_{2.0-2x}\text{Mo}_{x+y}\text{O}_{4.0}$ . Spectra of FTIR and Mössbauer were recorded at room temperature. These are found to show three principal bands of absorption in the range of lower x or y values and started to show a shoulder or split at higher values of x and or y values in the FTIR studies. Based on the Mössbauer spectra, Magnetic hyperfine field, Isomer shift and Line width values are evaluated. Thus generalized chemical compositional formula has been proposed for cation distribution in the Mössbauer studies. The obtained results and evaluated values are interpreted on the basis of different possible mechanisms.

**Key words:** Copper ferrite, Concentration, Molybdenum, FTIR, Mössbauer

## I. INTRODUCTION

Copper ferrite is known to have its own identity and importance over all other spinel ferrites because of its existence in two crystallographic lattice structures namely tetragonal and cubic besides its phase transition at certain critical temperature and concentration of  $\text{Cu}^{2+}$  where as other spinel ferrites show only cubic structure. The temperature of the order – disorder transformation depends on the content of octahedral cupric ions and on the non stoichiometry [1]. Its spinel lattice is highly distorted ( $c/a \sim 1.06$ ) because of  $\text{Cu}^{2+}$  ion, as it is a Jahn-Teller(JT) ion arising from the octahedral cupric ions [2,3] and also shows the inability to have a cation/oxygen ratio higher than 3/4. However, on the other hand it found to show anomalous favourable properties [4, 5] for different applications. Part of the  $\text{Cu}^{2+}$  ions can be frozen in tetrahedral sites when the ferrites were quenched in air from above the  $400^\circ\text{C}$  [6]. The resulting ferrite material shows smaller tetragonal distortion since a great proportion of the cupric ions exist on tetrahedral sites. This sort of behaviour is assumed to show impact on the position and valence of the ions in the crystal structure and Infra-red spectra can give information about position and valence of the ions in crystal lattices. Mazen et al. [7] have observed two main absorption bands  $\nu_1, \nu_2$  for Cu-Ti ferrite at  $\nu_1 = (540 \pm 5) \text{ cm}^{-1}$  and  $\nu_2 = (385 \pm 5) \text{ cm}^{-1}$  reflecting these bands as common feature of ferrite. According to Waldron's classification [8], vibrations of unit cell of a cubic spinel can be constructed from the contributions of tetrahedral site (A-site) and octahedral site (B-site) atomic vibrations. So the absorption  $\nu_1$  and  $\nu_2$  arises by the stretching vibration of the tetrahedral metal oxygen band,  $\nu_2$  occurs due to octahedral metal-oxygen band. IR spectral study on Cu-Ti mixed ferrite by Elfaki et al. [9] revealed two-absorption bands at  $575 \text{ cm}^{-1}$  and  $400 \text{ cm}^{-1}$ . Cation distribution of a ferrite was proposed earlier from various studies viz. X-ray diffraction and Mössbauer effect [10]. Using magnetization [11] and Curie temperature [12] studies also distribution of cations was evaluated. Cervinka et al. [10] studied the distribution of copper ions by means of X-ray diffraction and saturation magnetization measurements in some Cu-Mn ferrites. The amounts of copper in octahedral

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position for the ferrites  $\text{Cu}_{0.5}\text{Fe}_{2.5}\text{O}_4$  and  $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$  were found to be  $0.28 \pm 0.02$  and  $0.47 \pm 0.03$  respectively. From the Curie temperature studies of  $\text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ , Sawant et al. [11] proposed the cation distribution in the form  $(\text{Zn}^{2+}_x\text{Fe}_{1-x}^{3+})_A (\text{Cu}_{1-x}^{2+}\text{Fe}_{1+x}^{3+})_B \text{O}_4$  and this formulae was found to valid for their system only up to 50% content of zinc. At room temperature, Barber [13] observed the presence of monovalent copper in 'A' sites and divalent Cu both in 'A' and 'B' sites. The tetrahedral  $\text{Cu}^{1+}$  ions showed remarkable negative shift of the core-levels in comparison with metallic copper (1.4-1.7 eV). Studies of Lenglet et al. [14] on  $\text{Cu}_{0.5}\text{Mn}_x\text{Fe}_{2.5-x}\text{O}_4$  ( $0 < x < 1.5$ ) indicated that copper and iron were in divalent and trivalent states respectively while manganese found to be in 2+ and 3+ oxidation states. In literature, though there are some studies of infra-red and Mössbauer spectroscopic studies on copper mixed ferrites, no studies relating to FTIR and  $\text{Mo}^{6+}$  substituted copper ferrites are available. The present investigation by substituting high valence cation such as molybdenum ( $\text{Mo}^{6+}$ ) in copper ferrites has been performed with an aim to know impact of substituted cation on FTIR and Mössbauer spectroscopic parameters of copper ferrite.

## II. SAMPLES PREPARATION

Two series of  $\text{Mo}^{6+}$  substituted copper ferrites have been prepared having the chemical compositional formulae  $\text{Cu}_{1.0-3y}\text{Fe}_{2.0-2x}\text{Mo}_{x+y}\text{O}_{4.0}$ . Substitution of  $\text{Mo}^{6+}$  at the expense of  $\text{Fe}^{3+}$  varying 'x' or changing  $\text{Cu}^{2+}$  with 'y' from 0.00 to 0.40 (x and or y is varied in steps of 0.02 from x or y=0.00 to x=0.08, beyond this, in steps of 0.10) terming them 'F' and 'C' series materials respectively. These materials were calcinated for four hours at  $750^\circ\text{C}$  and sintered at  $950^\circ\text{C}$  in muffle furnace. Samples were heated following heating rate 100 C/hr and cooling was also done at the rate of 100 C/hr until  $600^\circ\text{C}$  and later the furnace cooled in air atmosphere.

## III. EXPERIMENTAL DETAILS

XRD spectra confirmed the single phase formation of the intended ferrites. The IR spectra were recorded on a Shimadzu FTIR 8001 spectrometer in the range  $450 - 4000\text{ cm}^{-1}$ . Mössbauer spectra were obtained at room temperature using  $\text{Co}^{57}$  source in rhodium matrix. The Wiffel Company (Germany) manufactured spectrometer was used in the present studies (IUC for DAE facilities, Indore, India).

## IV. RESULTS AND DISCUSSION

The obtained spectra of FTIR and Mössbauer studies have been analysed and interpreted the results as given below.

### A FTIR Studies

Using FTIR, spectra were recorded at room temperature for the present ferrite systems. Some of the typical spectra are shown in Fig.1 & 2 for 'F' and 'C' series respectively. The present mixed ferrites are found to show three principal bands of absorption in the range  $450 - 4000\text{ cm}^{-1}$ . Up to 0.02 concentration (x or y) of molybdenum ( $\text{Mo}^{6+}$ ) substitution in both the series of the materials, only one band at low frequency around  $582\text{ cm}^{-1}$  is exhibited clearly and for further concentrations (x or y) of  $\text{Mo}^{6+}$ , the same has been found at a frequency  $523\text{ cm}^{-1}$  in 'F' series  $526\text{ cm}^{-1}$  in 'C' series. The other two principal bands are resolved clearly at  $965\text{ cm}^{-1}$  and  $900\text{ cm}^{-1}$  for  $x \geq y \geq 0.06$ . From  $x=y=0.10$  onwards the absorption bands present at  $965\text{ cm}^{-1}$  and  $523\text{ cm}^{-1}$  in 'F' series  $526\text{ cm}^{-1}$  in 'C' series, began to show shoulder or split off at  $940\text{ cm}^{-1}$  and  $716\text{ cm}^{-1}$  respectively. On the other hand, for  $x \geq y \geq 0.2$  the band Presented at  $900\text{ cm}^{-1}$  also began to

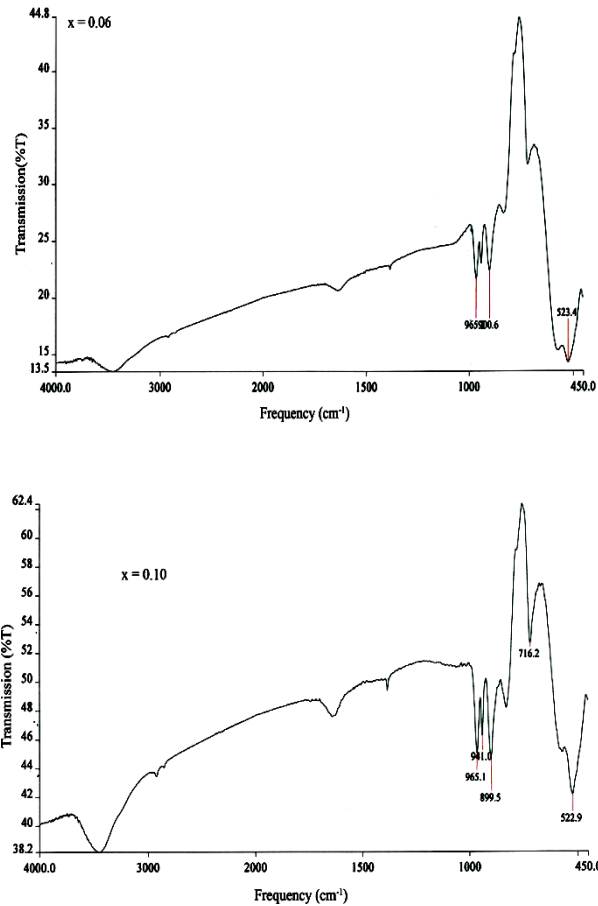


Fig.1. FTIR spectra of  $Cu_{1.0}Fe_{2-2x}Mo_xO_4$  system

exhibit shoulder at  $820\text{ cm}^{-1}$ . These values are given in Table 1 along with  $x$  or  $y$  values. The structure of a ferrite is similar to mineral spinel crystalline structure that exists usually in cubic form or some times in tetragonal form depending upon the ions participating in the concerned solid material. In general below  $1000\text{ cm}^{-1}$ , ferrites exhibit two principal absorption bands as their common feature. This behaviour was observed earlier in  $CaCl_2$  doped copper-zinc ferrite having  $\nu_1=600\text{ cm}^{-1}$  and  $\nu_2=400\text{ cm}^{-1}$ [15]. Similar sort of behaviour was observed in Zn substituted Li-Mg ferrites [16], Mg and Al co-substituted lithium ferrite [17] and Nd substituted Zn-Mg ferrite [18]. In the case of La substituted copper ferrite though two main bands were observed, at higher concentration of La substitution, two additional bands appeared. These were attributed to mixtures of  $CuFe_2O_4$  and  $La_2CuO_4$  [19]. Ravinder reported [20] the presence four bands in the range  $590 - 320\text{ cm}^{-1}$  in Li-Zn ferrites and the high frequency absorption band  $\nu_1$  assigned to tetrahedral,  $\nu_2$  and  $\nu_3$  were assigned to octahedral sites while low frequency last band  $\nu_4$  was interpreted due to lattice vibrations. For the  $Ni_{0.5+x}Zn_{0.5}Cu_xFe_{2-2x}O_4$  system Pradeep et al. [21] observed four bands and first two bands appeared at high frequency were ascribed to intrinsic lattice vibrations of E-symmetry, the third band was understood due to  $Cu^{2+} - O^{2-}$  complexes at 'B' sites and fourth band was attributed to vibrations of ions at 'A' sites. The studies of Ti/Nb substituted copper ferrites [22] also revealed two main bands. Besides these bands, the first band has a small split off band at  $600\text{ cm}^{-1}$  and a shoulder at  $795\text{ cm}^{-1}$  from 0.30 concentration onwards of substituent. The latter two bands were attributed to  $Fe^{2+}$  presence at 'B' sites and also their entry to 'A' sites based on Potakova et al [23] conclusions drawn on their observation of two bands around the  $\nu_1$  band. The presence of band at  $600\text{ cm}^{-1}$  was attributed to  $Fe^{2+}$  ions presence at 'A' sites [22]. The presence of bands takes place due to lattice vibrations of oxide ions against the cations.

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Table 1. The observed principle bands and their shoulders for the  $\text{Cu}_{1.0-3y}\text{Fe}_{2.0-2x}\text{Mo}_{x+y}\text{O}_{4.0}$  system

S. No	x	$\nu_1$	$\nu_2$	$\nu_3$
1	0.00	-	-	582.8
2 (x)	0.02	-	-	582.8
3	0.06	962.2	900.6	523.4
4	0.10	965.1 ↑ 941.0	899.5	522.9 ↑ 716.0
5	0.20	965.0 ↑ 945.0	900.0 ↑ 816.0	522.0 ↑ 716.0
6	0.30	964.7 ↑ 940.2	899.0 ↑ 823.0	523.7 ↑ 717.0
2 (y)	0.02	-	-	582.8
3	0.06	965.1	900.3	574.9
4	0.10	965.2 ↑ 940.0	900.0	526.9 ↑ 715.1
5	0.20	963.0 ↑ 940.0	900.0 ↑ 820.0	526.0 ↑ 715.0

According to Waldron [8], of the 42N normal vibrations, 8 discrete infrared bands only should occur. Each oxide ion is bonded to three octahedral ions and one tetrahedral ion. In the case of normal spinel, the three 'B' site bonds lie along the coordinate axes and provide an isotropic force field which would permit the oxide ion to oscillate in any direction with a constant frequency if the tetrahedral bonds are absent [8]. Therefore the absence of band at high frequency related to 'A' sites in the present materials up to  $x = y = 0.02$  can be understood on the lines mentioned above. But the tetrahedral bonds will show effect by increasing frequency for vibrations along the  $t - O$  axis. The observed low frequency band ( $\nu_3$ ) at  $580 \text{ cm}^{-1}$  can be attributed to the octahedral metal ions and oxygen complexes. The decrease of ' $\nu_3$ ' value from 580 to 523 or  $526 \text{ cm}^{-1}$  with increasing concentration of  $\text{Mo}^{6+}$ , might be due to modified distribution of cations that present in 'B' sites because of  $\text{Fe}^{3+}$  or  $\text{Cu}^{2+}$  ions replacement with substituted  $\text{Mo}^{6+}$  and or  $\text{Fe}^{3+}$  ions movement to 'A' sites besides existence of copper ions. The observed ' $\nu_3$ ' value deviate some extent with the reported value ( $450 \text{ cm}^{-1}$ ) of the basic ferrite; this may be due to variations in the preparative conditions since ferrites are highly sensitive to them. It is known [24] that molybdenum occupies 'A' sites at its lower concentration while at its higher concentration it enters into 'B' sites. This has been substantiated by the results obtained in the present studies of the materials. The obtained high frequency band ( $\nu_1$ ) at  $965 \text{ cm}^{-1}$  can be interpreted on the basis of tetrahedral molybdenum-oxygen stretching frequency as observed [25] earlier in the studies of molybdenum coordination compounds at  $1000 \text{ cm}^{-1}$ . The occurrence of shoulder to ' $\nu_1$ ' at  $940 \text{ cm}^{-1}$  probably due to molybdenum-oxygen interaction in 'B' sites indicating significance of  $\text{Mo}^{6+}$  in 'B' sites from  $x = y = 0.10$ . The band appeared at  $900 \text{ cm}^{-1}$  can be related to tetrahedral metal ions-oxygen complexes. Significantly from  $x=y=0.10$ , the presence of shoulder at  $716 \text{ cm}^{-1}$  to ' $\nu_3$ ' may be due to divalent metal ions and oxygen interaction and or with the influence of  $\text{Cu}^{2+}$  ions Jahn-Teller effect presence in octahedral sites as observed earlier [21]. A similar behaviour was observed earlier in Co-Zn ferrites too [26]. The presence of  $\text{Mo}^{6+}$  in 'B' sites replacing iron or copper ions and due to loss of oxygen occurrence during sintering process might create valence fluctuation of ions leading to formation of divalent iron ions, since existence of  $\text{Fe}^{2+}$  ions in 'B' sites is an established fact for ferrite materials. In inverse spinel structure, copper ions present in 'B' sites while iron present in both 'A' and 'B' sites [22, 24]. The decrease of ' $\nu_3$ ' value with the rise of 'x' or 'y' and the presence of shoulder to ' $\nu_2$ ' at  $820 \text{ cm}^{-1}$  from  $x = y = 0.20$  probably due to some sort of evidences for movement of metal ions such as iron and copper from 'B' to 'A' sites. This has been corroborated by the XRD studies

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in which materials have exhibited structural phase transition from tetragonal to cubic due to entry of copper ions into ‘A’ sites. It is known that 0.25 is the critical value of copper ions occupancy at ‘A’ sites causing crystal distortion [27]. Though  $Fe^{2+}$  ions strongly prefer to appear in octahedral sites, under some exceptional cases these ions exist in tetrahedral site too as stated by Waldron [8] on basis of his observation in  $MnFe_2O_4$  system and also by Potakova et al. [23]. Hence the observed shoulder to ‘ $\nu_2$ ’ at  $820\text{cm}^{-1}$  is believed to be because of tetrahedral divalent metal ions and oxygen complexes.

The difference in the position of two strong bands relating to  $Fe^{3+} - O^{2-}$  that occur in octahedral and tetrahedral sites can be attributed to the difference in  $Fe^{3+} - O^{2-}$  distance in ‘A’ and ‘B’ sites. The bond length of it in ‘A’ sites was found to be 0.189 mm, which is smaller than that of in ‘B’ sites (0.199mm) [28]. Hence it indicates that shorter bond length (tetrahedral) needs high frequency for initiation of normal mode vibration than that of longer bond length (octahedral).

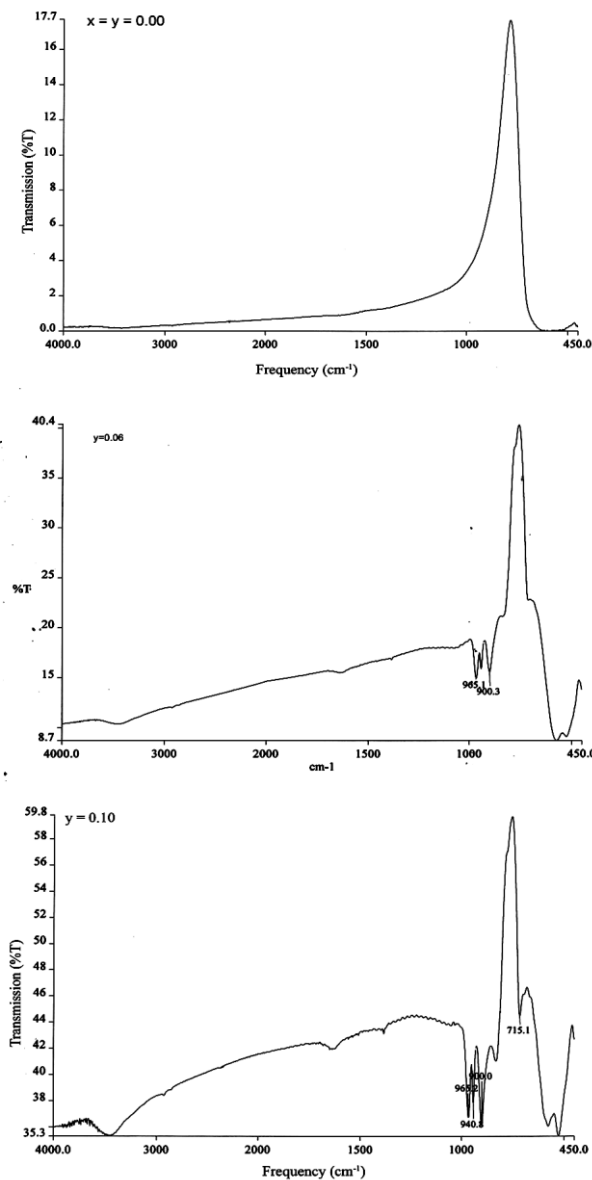


Fig. 2. FTIR spectra of  $Cu_{1-3y}Fe_{2.0}Mo_yO_4$  system

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The values of bond lengths have been computed and found the decrease of these values with 'x' and or 'y' indicating increased closer association of metal ions and oxygen due to substituted impurity. Hence increase of frequency value for normal mode vibration of these sites is expected, contrary to this, decrease of these values in the present studies is observed. This could be accounted by a substantial role of crystal field effect [29] that accounted by copper ions. No infrared studies on Cu-Mo-Fe system are available in literature and thus proper data is not existed for comparison of the obtained results. Around  $3445\text{ cm}^{-1}$  a band has been observed for both the series of ferrites from  $x = y = 0.06$  onwards, which may be related to the electronic transitions as studied earlier by Waldron [8] for Ni and Zn ferrites which exhibited at  $2700$  and  $2300\text{ cm}^{-1}$  respectively. However, according to him, these values are subject to considerable uncertainty, because the portion of scattering caused by the ferrite particles cannot be distinguished from absorption losses.

## B Mössbauer studies

In the present studies, typical Mössbauer spectra were recorded at room temperature for F and C series materials using Mössbauer spectrometer in the transmission geometry mode and shown them for one of the series in Fig.3

The present basic (un-substituted) copper ferrite is an inverse spinel having tetragonal crystalline structure. Most of the 'A' sites are filled up by ferric ions besides a small amount of copper participation too. Copper ions have strong preference to occupy octahedral sites, therefore in 'B' sites, copper and iron ions will present. Hence magnetic linkage from 'B' sites is expected to be more, relative to the magnetic linkage from 'A' sites. Thus the computed hyperfine field ( $h_f$ ) corresponding to higher value is related to 'B' site internal magnetic hyperfine field ( $h_{fA}$ ) and smaller is concerned to 'A' site internal magnetic hyperfine field ( $h_{fB}$ ). These values are given in Table 2 for 'F' and 'C' series ferrites. The basic copper ferrite obtained  $h_{fA}$  and  $h_{fB}$  values  $473.800$  and  $506.700$  kGs respectively show fair agreement with the reported values  $472$  and  $500$  kGs [30]. In magnetically ordered systems, magnetic field at the nucleus of Fe arises mainly from the Fermi contact interaction between the nucleus and the spin polarized magnetic field 's' electrons [31]. The average nuclear magnetic field for all the ions in a particular sub-lattice is proportional to the average magnetization of that sub-lattice. Such proportionality was clearly observed earlier in Ferro magnetic materials [32]. The evaluated magnetic hyperfine field values at tetrahedral (A) sites ( $h_{fA}$ ) and at octahedral (B) sites ( $h_{fB}$ ) are found to increase at  $x = y = 0.02$ , with the increase of 'x' or 'y' the ' $h_{fA}$ ' decreases at  $0.06$  and then stayed as invariant one, while the ' $h_{fB}$ ' also seems to be no change in its value except slight decrease at  $x=0.10$  in 'F' series. In the case of C-series materials ' $h_{fB}$ ' decreases up to  $y = 0.06$  but for further concentration at  $y = 0.10$  it found to increase. The observed variation of magnetic field in ferrimagnetic materials usually explained on the basis of Neel's two sub-lattices molecular field model [33] with distant neighbourhood exchange interactions. Each 'A' site ion in spinel structure has 12 'B' site neighbours in its immediate surrounding and each 'B' site ion has 6 'A' sites as its immediate neighbours. The exchange interaction  $\text{Fe}^{3+}(\text{A}) - \text{O}^{2-} - \text{Fe}^{3+}(\text{B})$  between iron ions is known to be the strongest where as A-A and B-B interactions such as  $\text{Fe}^{3+}(\text{A}) - \text{O}^{2-} - \text{Fe}^{3+}(\text{A})$  and  $\text{Fe}^{3+}(\text{B}) - \text{O}^{2-} - \text{Fe}^{3+}(\text{B})$  are relatively weak. Generally all other interactions namely  $\text{Fe}^{3+} - \text{O}^{2-} - \text{Cu}^{2+}$  and  $\text{Cu}^{2+} - \text{O}^{2-} - \text{Cu}^{2+}$  are considered to be weaker. Earlier the larger decrease of ' $h_{fB}$ ' than ' $h_{fA}$ ' was reported [33] due to the substitution of  $\text{Al}^{3+}$  by  $\text{Fe}^{3+}$  in the 'B' sites and it attributed to spin canting because of Jahn-Teller cation  $\text{Cu}^{2+}$  presence, which weaken the AB interactions and BB interactions compete AB. Contrary to this Kukarni et al. [34] observed the faster decrease of ' $h_{fA}$ ' than ' $h_{fB}$ ' with the substitution of  $\text{Al}^{3+}$  by  $\text{Fe}^{3+}$ . It was interpreted on the basis of increasing weak AB magnetic coupling due to non-magnetic ions substitution and also they observed the occupancy of  $\text{Al}^{3+}$  in both 'A' and 'B' sites along with the existence of canting angle. The increase of hyperfine magnetic field with the rise of Ni concentration and for lower concentration of Mn in the



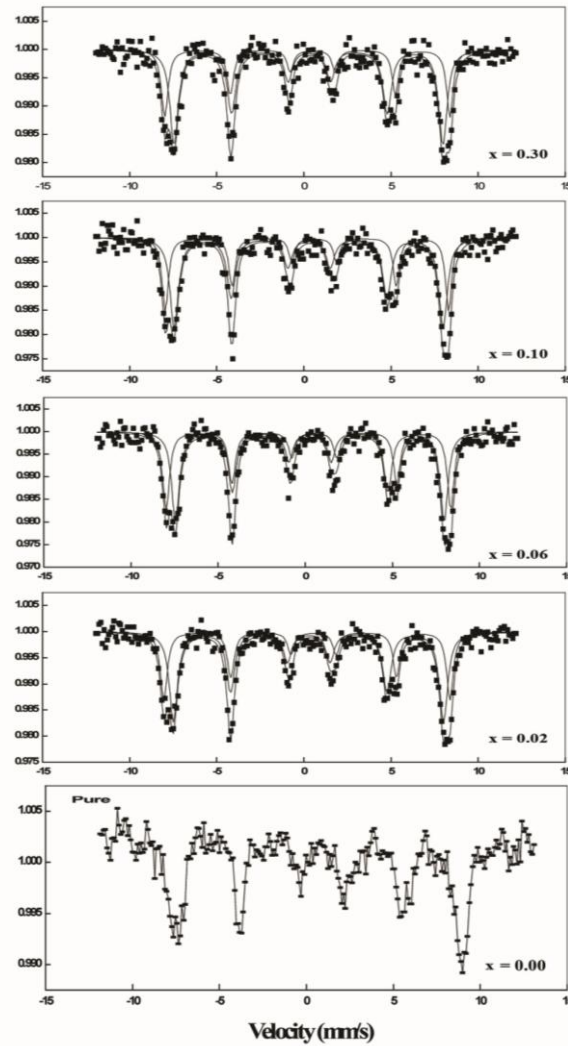


Fig. 3 Mössbauer spectra of  $\text{Cu}_{1.0}\text{Fe}_{2-2x}\text{Mo}_x\text{O}_4$  system

$\text{Cu}_{1-x}\text{M}_x\text{Fe}_2\text{O}_4$  (M= Ni/Mn) ferrite system was observed earlier [35] and it explained on the basis of super-transferred hyperfine (STH) field mechanism. The replacement of a non-magnetic ion by a magnetic ion at ‘A’ and ‘B’ sites will produce an increase of the STH contribution at both the sites.  $\text{Cu}^{2+}$  ions occupy both ‘A’ and ‘B’ sites displacing more and more  $\text{Fe}^{3+}$  ions from ‘B’ sites into ‘A’ sites. The observed decrease of field with the further rise of Mn concentration in the above mentioned ferrite system was attributed to the canting of spins [35]. In the present studies, with the increase of substituent ( $\text{Mo}^{6+}$ ) concentration, the observed hyperfine magnetic field rise in both ‘A’ and ‘B’ sites is substantiated by the observed increase of Curie temperature and magnetization for few specimens that obtained for both the series of ferrite systems. In earlier studies, at 0.10 concentration of  $\text{Mo}^{6+}$  in the  $\text{Mg}_{0.9}\text{Mn}_{0.4}\text{Mo}_{0.1}\text{Fe}_{1.6}\text{O}_4$  system the rise of hyperfine magnetic field relative to basic (un-substituted) ferrite in ‘A’ sites was reported and it [36] understood due to presence of  $\text{Mo}^{6+}$  in ‘A’ sites. The entry of  $\text{Mo}^{6+}$  into ‘A’ sites was confirmed by other investigators also [37]. Molybdenum possesses mixed valence states viz.  $\text{Mo}^{2+}$ ,  $\text{Mo}^{3+}$ ,  $\text{Mo}^{4+}$  and  $\text{Mo}^{6+}$ . Earlier studies of  $\text{Fe}_2\text{MoO}_4$  indicated that  $\text{Mo}^{4+}$  ion is not in low spin ( $S=0$ ) state and has two unpaired electrons which play a crucial role in overall magnetic behaviour of the compound [38]. Molybdenum that taken as  $\text{Mo}^{6+}$  in the present ferrite systems, makes strong

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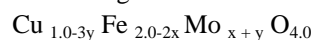
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bonds with neighbouring ions and during this process, generation of few  $\text{Mo}^{6+}$  ions might take place for maintaining charge balance. In the present studies  $\text{Mo}^{6+}$  is believed to occupy 'A' sites reducing number of Fe ions in the 'F' series which results rearrangement of  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  ions in both tetrahedral (A) and octahedral (B) sites. Consequently, environment around  $\text{Fe}^{3+}$  nuclei in both the sub-lattices changes and hence the increase of hyperfine magnetic field is probably due to enhanced contribution of super-transferred hyperfine (STH) field as reported earlier [36]. For further increase of  $\text{Mo}^{6+}$ , the decrease of hyperfine field values at tetrahedral (A) ( $h_{fA}$ ) and octahedral (B) sites ( $h_{fB}$ ) can be ascribed to spin canting that occurs in copper ferrite [30, 34]. However, from 0.06 concentration of  $\text{Mo}^{6+}$  onwards, the apparent invariance of magnetic field in 'A' sub-lattices for the both series of ferrites could be understood in terms of no change in the environment around 'A' sites  $\text{Fe}^{3+}$  nuclei expecting  $\text{Mo}^{6+}$  going into 'B' sites where change in the environment around 'B' sites  $\text{Fe}^{3+}$  nuclei might takes place substantiating the observed decrease of magnetic field. The observed lower values of ' $h_{fA}$ ' relative to ' $h_{fB}$ ' is understood on the basis of more covalent nature of the  $\text{Fe}^{3+} - \text{O}^{2-}$  bonds at the tetrahedral site compared to those at the octahedral site [30]. In general, quadrupole splitting (QS) arises due to non-cubic symmetry of  $\text{Fe}^{3+}$  at 'B' sites. For the present studies, of all the specimens the observed 'QS' is absent within the experimental errors as reported [34] earlier for Ni / Mn substituted copper ferrite. Probably this may be due to chemical disorder in the materials which apparently masks the shifts in the hyper fine field produced by the quadrupole interaction.

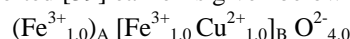
Table 2. Hyperfine field variation of  $\text{Mo}^{6+}$  substituted Copper Ferrites

S.No	(x or y)	Hyperfine Field (Gauss)		
		$h_{fA}$	$h_{fB}$	$\delta_H$
1	0.00	473.800	506.700	32.90
2	0.02 (x)	480.069	508.667	28.60
3	0.06	477.253	506.173	28.92
4	0.10	477.914	503.751	25.84
5	0.30	477.724	506.922	29.20
6	0.02 (y)	479.580	507.508	27.93
7	0.06	479.270	509.600	30.33
8	0.10	478.740	504.760	26.02

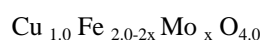
Based on the obtained magnetization, Curie temperature and other experimental results in association with the Mössbauer studies, the cation distribution for both the series has been proposed. The chemical compositional formula of the present copper ferrite with the substitution of  $\text{Mo}^{6+}$  is given below



If 'x' and 'y' values are zero, then the composition of the basic ferrite is (Un-substituted)  $\text{Cu}_{1.0}\text{Fe}_{2.0}\text{O}_{4.0}$ . Tetragonal crystalline structure has been observed for the present basic system, which is an inverse spinel. Therefore cation distribution of this chemical composition as reported [39] earlier is given below



For the 'F' series ferrite system, 'y' is equal to zero and 'x' is variable in the chemical composition, thus the chemical formula can be written as



For the above composition, the generalized formula of the cation distribution is given below ignoring vacancies concentration



In the 'F' series, substituted  $\text{Mo}^{6+}$  impact on cation distribution of all these materials has been presented in Table 3 along with the possible concentration of vacancies ( $\square$ ) in 'B' sites only, off course these have possibility to occur in both the sites. As molybdenum substitution is made due to iron, initially  $\text{Mo}^{6+}$  seems to exist in tetrahedral sites



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replacing Fe<sup>3+</sup> ions at x=0.02, but at x= 0.04 it occupies ‘A’ sites along with small amount of Cu<sup>2+</sup> that comes from octahedral (B) to tetrahedral sites increasing its concentration in steps of q=0.02 till to x=0.06. Further, the distribution in tetrahedral (A) sites seems to be invariant up to x=0.10 having compliance with the observed no change in the magnetic field value of tetrahedral sub-lattice that given in Table 3 for the materials that exhibited tetragonal crystallographic structure. For higher values of Mo<sup>6+</sup> i.e. from x=0.20 onwards it found to substitute ‘B’ site iron ions pushing large number of ‘B’ site Cu<sup>2+</sup> ions into ‘A’ sites increasing its content having value 0.10 as a function of ‘x’ while same quantity of Fe<sup>3+</sup> ions reduction is occurred with ‘x’ when these materials changed to crystallographic cubic structure from tetragonal structural phase. As the charge of molybdenum is 6+ and iron is 3+, for maintaining charge balance of the composition, iron has been reduced the two times of Mo quantity that substituted in ‘F’ series hence vacancies are formed and these are also shown in the cation distribution. The observed significant change in the

Table 3. The proposed cation distribution for the ferrite system Cu<sub>1.0</sub> Fe<sub>2.0-2x</sub> Mo<sub>x</sub> O<sub>4.0</sub>

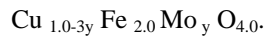
S.No.	x or y	Cation distribution
1	0.00	(Fe <sup>3+</sup> <sub>1.0</sub> ) <sub>A</sub> [Fe <sup>3+</sup> <sub>1.0</sub> Cu <sup>2+</sup> <sub>1.0</sub> ] <sub>B</sub> O <sup>2-</sup> <sub>4</sub>
2	0.02 x	(Mo <sup>6+</sup> <sub>0.02</sub> Fe <sup>3+</sup> <sub>0.98</sub> ) <sub>A</sub> [Fe <sup>3+</sup> <sub>0.98</sub> Mo <sup>6+</sup> <sub>0.0</sub> Cu <sup>2+</sup> <sub>1.00</sub> ] <sub>B</sub> O <sup>2-</sup> <sub>4</sub>
3	0.04	(Cu <sup>2+</sup> <sub>0.02</sub> Mo <sup>6+</sup> <sub>0.04</sub> Fe <sup>3+</sup> <sub>0.94</sub> ) <sub>A</sub> [Fe <sup>3+</sup> <sub>0.98</sub> Mo <sup>6+</sup> <sub>0.0</sub> Cu <sup>2+</sup> <sub>0.98</sub> ] <sub>B</sub> O <sup>2-</sup> <sub>4</sub>
4	0.06	(Cu <sup>2+</sup> <sub>0.04</sub> Mo <sup>6+</sup> <sub>0.04</sub> Fe <sup>3+</sup> <sub>0.92</sub> ) <sub>A</sub> [Fe <sup>3+</sup> <sub>0.96</sub> Mo <sup>6+</sup> <sub>0.02</sub> Cu <sup>2+</sup> <sub>0.96</sub> ] <sub>B</sub> O <sup>2-</sup> <sub>4</sub>
5	0.08	(Cu <sup>2+</sup> <sub>0.04</sub> Mo <sup>6+</sup> <sub>0.04</sub> Fe <sup>3+</sup> <sub>0.92</sub> ) <sub>A</sub> [Fe <sup>3+</sup> <sub>0.92</sub> Mo <sup>6+</sup> <sub>0.04</sub> Cu <sup>2+</sup> <sub>0.96</sub> ] <sub>B</sub> O <sup>2-</sup> <sub>4</sub>
6	0.10	(Cu <sup>2+</sup> <sub>0.04</sub> Mo <sup>6+</sup> <sub>0.04</sub> Fe <sup>3+</sup> <sub>0.92</sub> ) <sub>A</sub> [Fe <sup>3+</sup> <sub>0.88</sub> Mo <sup>6+</sup> <sub>0.06</sub> Cu <sup>2+</sup> <sub>0.96</sub> ] <sub>B</sub> O <sup>2-</sup> <sub>4</sub>
7	0.20	(Cu <sup>2+</sup> <sub>0.14</sub> Mo <sup>6+</sup> <sub>0.04</sub> Fe <sup>3+</sup> <sub>0.82</sub> ) <sub>A</sub> [Fe <sup>3+</sup> <sub>0.78</sub> Mo <sup>6+</sup> <sub>0.16</sub> Cu <sup>2+</sup> <sub>0.86</sub> ] <sub>B</sub> O <sup>2-</sup> <sub>4</sub>
8	0.30	(Cu <sup>2+</sup> <sub>0.24</sub> Mo <sup>6+</sup> <sub>0.04</sub> Fe <sup>3+</sup> <sub>0.72</sub> ) <sub>A</sub> [Fe <sup>3+</sup> <sub>0.68</sub> Mo <sup>6+</sup> <sub>0.26</sub> Cu <sup>2+</sup> <sub>0.76</sub> ] <sub>B</sub> O <sup>2-</sup> <sub>4</sub>
9	0.40	(Cu <sup>2+</sup> <sub>0.34</sub> Mo <sup>6+</sup> <sub>0.04</sub> Fe <sup>3+</sup> <sub>0.62</sub> ) <sub>A</sub> [Fe <sup>3+</sup> <sub>0.58</sub> Mo <sup>6+</sup> <sub>0.36</sub> Cu <sup>2+</sup> <sub>0.66</sub> ] <sub>B</sub> O <sup>2-</sup> <sub>4</sub>
10	0.02 y	(Fe <sup>3+</sup> <sub>1.00</sub> ) <sub>A</sub> [Fe <sup>3+</sup> <sub>1.00</sub> Mo <sup>6+</sup> <sub>0.02</sub> Cu <sup>2+</sup> <sub>0.94</sub> ] <sub>B</sub> O <sup>2-</sup> <sub>4</sub>
11	0.04	(Fe <sup>3+</sup> <sub>1.00</sub> ) <sub>A</sub> [Fe <sup>3+</sup> <sub>1.00</sub> Mo <sup>6+</sup> <sub>0.04</sub> Cu <sup>2+</sup> <sub>0.88</sub> ] <sub>B</sub> O <sup>2-</sup> <sub>4</sub>
12	0.06	(Fe <sup>3+</sup> <sub>1.00</sub> ) <sub>A</sub> [Fe <sup>3+</sup> <sub>1.00</sub> Mo <sup>6+</sup> <sub>0.06</sub> Cu <sup>2+</sup> <sub>0.82</sub> ] <sub>B</sub> O <sup>2-</sup> <sub>4</sub>
13	0.08	(Cu <sup>2+</sup> <sub>0.04</sub> Fe <sup>3+</sup> <sub>0.96</sub> ) <sub>A</sub> [Fe <sup>3+</sup> <sub>1.04</sub> Mo <sup>6+</sup> <sub>0.08</sub> Cu <sup>2+</sup> <sub>0.72</sub> ] <sub>B</sub> O <sup>2-</sup> <sub>4</sub>
14	0.10	(Cu <sup>2+</sup> <sub>0.08</sub> Fe <sup>3+</sup> <sub>0.92</sub> ) <sub>A</sub> [Fe <sup>3+</sup> <sub>1.08</sub> Mo <sup>6+</sup> <sub>0.10</sub> Cu <sup>2+</sup> <sub>0.62</sub> ] <sub>B</sub> O <sup>2-</sup> <sub>4</sub>
15	0.20	(Cu <sup>2+</sup> <sub>0.12</sub> Fe <sup>3+</sup> <sub>0.88</sub> ) <sub>A</sub> [Fe <sup>3+</sup> <sub>1.12</sub> Mo <sup>6+</sup> <sub>0.20</sub> Cu <sup>2+</sup> <sub>0.28</sub> ] <sub>B</sub> O <sup>2-</sup> <sub>4</sub>

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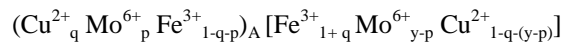
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cations distribution over ‘A’ and ‘B’ sites can be accounted due to crystalline structure change from tetragonal to cubic. In the case of ‘C’ series ferrite system, ‘x’ is equal to zero and ‘y’ is variable in the chemical composition, thus the chemical formula being.



For the above composition the generalized formula of the cation distribution is



As the  $\text{Mo}^{6+}$  substitution at the expense of  $\text{Cu}^{2+}$  is carried out in ‘C’ series,  $\text{Mo}^{6+}$  is expected to enter into ‘B’ sites. The proposed cation distribution of all these materials been presented besides vacancies concentration ( $\square$ ) too in the Table 4. Due to inversion nature of present basic (un-substituted) copper ferrite,  $\text{Cu}^{2+}$  ions present in ‘B’ sites, since  $\text{Mo}^{6+}$  has been substituted diluting  $\text{Cu}^{2+}$  in ‘C’ series, it seems to occupy ‘B’ sites unlike F-series ferrites. Therefore cation distribution in ‘A’ sub lattice does not affect until  $y = 0.06$  which exhibited tetragonal structure. From  $y = 0.08$  onwards  $\text{Mo}^{6+}$  seems to push some of the  $\text{Cu}^{2+}$  ions from ‘B’ to ‘A’ sites with a quantity of 0.04 for each successive rise of ‘y’ value, consequently the decreased iron ions at ‘A’ sites has been compensated in ‘B’ sites. Since the charge of molybdenum is 6+ and copper is 2+, to maintain charge balance, copper has been reduced three times of the Mo quantity for  $\text{Mo}^{6+}$  substitution and hence vacancies more than those formed in F-series materials have been expected to form and thus these are also shown in the cation distribution. These have shown their impact on electrical and thermal properties too.

In general, Isomer shift (IS) values indicate iron ions valence state as 3+ and 2+ due to two sextets corresponding to ‘A’ and ‘B’ sites. The values of IS obtained for the two series of ferrite systems in the present studies are given in Table 4. Usually, in spinel

Table 4. Isomer shift variation of  $\text{Mo}^{6+}$  substituted Copper Ferrites

S. No	(x or y)	IS <sub>A</sub>	IS <sub>B</sub>	ΔIS
1	0.00	0.280	0.385	0.105
2(x)	0.02	0.271	0.365	0.094
3	0.06	0.270	0.352	0.082
4	0.10	0.286	0.383	0.097
5	0.30	0.290	0.353	0.063
6 (y)	0.02	0.278	0.373	0.095
7	0.06	0.276	0.355	0.079
8	0.10	0.262	0.376	0.114

ferrites ionic bond length of  $\text{Fe}^{3+}-\text{O}^{2-}$  at octahedral sites are larger than tetrahedral sites. Therefore Isomer shift values of ‘B’ sites are expected to be higher than ‘A’ sites. Thus the covalence is larger at ‘A’ sites relative to ‘B’ sites. In octahedral sites due to smaller covalence larger Isomer shift values arose [40]. The observed values of IS are found to show small decrease than the basic ferrite IS value. On the other hand, small increase of IS values at higher values of ‘x’ in F-series ferrite system is exhibited. The observed variation in the lattice constant of the present materials also substantiates the modified distance or gap between Mössbauer nucleus and s-electron resulting change in isomer shift values due to substitution of non-magnetic  $\text{Mo}^{6+}$  ions. The difference in Isomer shift values due to ‘A’ and ‘B’ sites believed to be due to slight  $\text{sp}^{3+}$  covalence present at ‘A’ sites ions [41]

#### 2.2.4. Line width.

The observed variation of FWHM values with increasing concentration of substituent ( $\text{Mo}^{6+}$ ) seems almost absent with very little increase which could be attributed to the experimental errors. However these values of ‘A’ sites are smaller relative to ‘B’ sites. This broadening of resonance line due to  $\text{Fe}^{3+}$  at ‘B’ sites can be ascribed to small amount of  $\text{Fe}^{2+}$

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ions presence at 'B' sites. Variation in the concentration of  $\text{Mo}^{6+}$  makes changes in the environment at  $\text{Fe}^{3+}$  ions leading to change in magnetic interaction, consequently it shows little broadening of Zeeman lines. This also might slightly affect Isomer shifts displacing sextets with respect to one another causing general broadening of the lines. The instrumental broadening which had been estimated is very small and it would also contribute to line broadening.

## V. CONCLUSIONS

1. The present mixed ferrites are found to have three principal bands of absorption in the range  $450 - 4000 \text{ cm}^{-1}$ . Up to 0.02 concentration (x or y) of molybdenum ( $\text{Mo}^{6+}$ ) substitution in both the series of the materials, only one band at low frequency around  $582 \text{ cm}^{-1}$  is exhibited clearly and for further concentrations (x or y) of  $\text{Mo}^{6+}$ , the same has been found at frequency  $523 \text{ cm}^{-1}$  in 'F' series,  $526 \text{ cm}^{-1}$  in 'C' series. The other two principal bands are resolved clearly at  $965 \text{ cm}^{-1}$  and  $900 \text{ cm}^{-1}$  for  $x \geq y \geq 0.06$ .
2. From  $x=y=0.10$  onwards the absorption bands present at  $965 \text{ cm}^{-1}$  and  $523 \text{ cm}^{-1}$  in 'F' series and or  $526 \text{ cm}^{-1}$  in 'C' series began to show shoulder or split off at  $940 \text{ cm}^{-1}$  and  $716 \text{ cm}^{-1}$  respectively. On the other hand, for  $x \geq y \geq 0.20$ , the band presented at  $900 \text{ cm}^{-1}$  also began to exhibit shoulder at  $820 \text{ cm}^{-1}$ . The presence of bands takes place due to lattice vibrations of oxide ions against the cations.
3. The evaluated magnetic hyperfine field values at tetrahedral (A) sites ( $h_{fA}$ ) and at octahedral (B) sites ( $h_{fB}$ ) are found to increase at  $x=y=0.02$ , with the increase of 'x' or 'y' the ' $h_{fA}$ ' decreases at 0.06 and then stayed as invariant one, while the ' $h_{fB}$ ' also seems to be no change in its value except slight decrease at  $x=0.10$  in 'F' series. In the case of C-series materials ' $h_{fB}$ ' increases up to  $y=0.06$  but at  $y=0.10$  it found to deteriorate.
4. For the present 'F' series ferrites the generalized chemical compositional formula of the proposed cation distribution is  $(\text{Cu}^{2+}_q \text{Mo}^{6+}_{x-p} \text{Fe}^{3+}_{1-q-(x-p)})_A [\text{Fe}^{3+}_{1+q-p} \text{Mo}^{6+}_p \text{Cu}^{2+}_{1-q}]_B \text{O}^{2-}_4$  and for 'C' series it is  $(\text{Cu}^{2+}_q \text{Mo}^{6+}_p \text{Fe}^{3+}_{1-q-p})_A [\text{Fe}^{3+}_{1+q} \text{Mo}^{6+}_{y-p} \text{Cu}^{2+}_{1-q-(y-p)}]_B \text{O}^{2-}_4$
5. The observed values of Isomer Shift (IS) are found to show small decrease than the basic ferrite IS value. On the other hand, small increase of IS values at higher values for 'x' in F-series ferrite system is exhibited.
6. The observed variation of FWHM values with increasing concentration of substituent ( $\text{Mo}^{+6}$ ) seems to be almost absent with very little increase which could be attributed to the instrumental uncertainty.

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