

INFLUENCE OF Mo^{6+} ON THERMO ELECTRIC POWER PROPERTIES OF COPPER FERRITE

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ABSTRACT

Two series of copper ferrites with the substitution of Molybdenum having the chemical compositional formulae $\text{Cu}_{1.0-3y}\text{Fe}_{2.0-2x}\text{Mo}_{x+y}\text{O}_{4.0}$ have been prepared. Substitution of Mo^{6+} at the expense of Fe^{3+} varying 'x' or changing Cu^{2+} with 'y' terming them F and C series materials respectively is carried out. Investigations are performed to understand the impact of Mo^{6+} on the thermal properties of copper ferrite. Thermoelectric power (Q), carrier concentration (n) and mobility (μ) as a function of substituent concentration (x or y) and temperature (T) are evaluated. The 'Q' is found to decrease for 'F' series materials while it increases for 'C' materials in the range $x=0.04$ to 0.08 , but it increased for both the series materials at higher concentration of Mo^{6+} . All the curves of plots 'Q' Vs 'T' show four regions due to change in their slope having three break temperatures which are designated as T_1 , T_2 and T_3 except for $y=0.10$ and 0.20 of C-series ferrites. The T_3 values are close to the materials Curie temperature values. The evaluated charge carriers' values are on the order of 10^{22} per cm^3 . The observed drift mobility (μ_d) found to have of the order 10^{-8} for lower values of Mo^{6+} while for its higher values has of the order 10^{-7} . Obtained results are interpreted on the basis of different possible mechanisms.

KEYWORDS: Copper Ferrite, Concentration, Molybdenum, Mobility, Thermo Electric-Power

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 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 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 favorable properties [4, 5] for different applications. Part of the Cu^{2+} ions can be frozen in tetrahedral sites when the ferrites were quenched in air from above 400°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 behavior shows impact on thermal properties of the materials.

In literature, though there are some studies on thermo electric power of copper ferrites [7-9] by substitution of divalent (2+) and tetravalent (4+) cations, no studies with the substitution of high valence cations namely 6+ are available. By substitution [7] of two non-magnetic ions like Zn or Cd in copper ferrite, investigations were carried out and observed n-type conduction from room temperature to 750 K i.e. in the complete range of study. Contrary to this, Patil et al. [8] reported p-type conduction in copper ferrite up to certain temperature beyond which it converted into n-type conduction

due to substitution of Ti^{4+} . But, Davidovich et al. [9] observed predominant hole conductivity between the chemical compositions of the $CuFe_2O_4$ and $Cu_{0.75}Fe_{2.25}O_4$, where as electron conductivity between the compositions $Cu_{0.75}Fe_{2.25}O_4$ and $Cu_{0.5}Fe_{2.5}O_4$. Thermo-electric power measurement provides knowledge of conduction processes along with different mechanisms, charge carries, their concentration, Fermi energy, mobility etc that are responsible for the conduction. One can improve thermo electric functionality of a material by substituting or adding a foreign cation in the crystal lattice of ferrite materials. In light of the above studies, the present investigation by substituting high valence cation such as molybdenum (Mo^{6+}) in copper ferrites has been performed with an aim to know impact of substituted cation on thermo electric power of copper ferrite.

Samples Preparation and Experimental Details

Two series of Mo^{6+} substituted copper ferrites have been prepared having the chemical compositional formulae $Cu_{1.0-3y}Fe_{2.0-2x}Mo_{x+y}O_{4.0}$. Substitution of Mo^{6+} at the expense of Fe^{3+} varying 'x' or changing 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 $750^{\circ}C$ and sintered at $950^{\circ}C$ 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 $600^{\circ}C$ and later the furnace cooled in air atmosphere.

XRD spectra confirmed the single phase formation of the intended ferrites. Thermoelectric power studies were carried out from room temperature to beyond their Curie temperature with the experimental equipment manufactured and supplied by the Pushpa Scientifics, Hyderabad. It consists of a microvolt meter connected to a sample holder that placed in a small furnace which coupled with a dimmer start for increasing the temperature of the sample holder. In this, a probe which getting supply of heat was considered as hot junction, connected to the top or upper surface of the specimen. The bottom surface was considered as cold which relatively stay at lower temperature than upper one. Temperature indicator was used to record the both hot and cold junctions' temperature values. The specimens were in the pellets shape having 8 mm diameter and 3.5 mm thickness.

RESULTS AND DISCUSSIONS

The observed thermo-electric power (Q) for the Mo^{6+} substitution at the expense of Fe^{3+} (F-series) has improved initially i.e. at $x = 0.02$ relative to basic copper ferrite (x or $y = 0.00$) and it deteriorated for further 'x' values while for C-series ferrites it exhibits minimum at $y = 0.02$ and increases for further 'y' values. The substituted Mo^{6+} impact on copper ferrite F-series seems to show quite opposite behavior to C-series materials behavior up to $x = y = 0.08$ as shown in Fig. 1. It means the 'Q' found to decrease for F-series in the range $x = 0.04$ to 0.08 where as for C-series it increases in the range $y=0.04$ to 0.08 . At higher values of Mo^{6+} , both the series behavior seems to be similar having highest 'Q' at $x \leq 0.40$. For the basic ferrite; at $x = 0.02$ and 0.40 p-type conduction is observed while for all the other ferrite materials, n-type conduction is exhibited by them. The obtained 'Q' value of p-type conduction for the basic copper ferrite (x or $y = 0.00$) $28.1 \mu V/K$ has consistent with the earlier reported [10] value $24.9 \mu V/K$ of p-type conduction. The little discrepancy between these two values can be attributed to the material preparative conditions as it is sensitive to them. The observed p-type conduction can be understood with the p-type conduction that already reported elsewhere [11]. This may be ascribed to reduction of Cu^{2+} concentration changing into Cu^{1+} ions at elevated temperature during sintering process i.e. around $950^{\circ}C$ [12] and thus p-type conduction up to $x=0.02$ can be understood on these lines. It is known [13] that high valence cation(s) substitution localizes Fe^{2+} , consequently it decreases availability of Fe^{2+} / Fe^{3+} ratio to participate in conduction process. Therefore contribution to conduction due to hopping of these ions is expected to be small. Thus n-type conduction

can be attributed due to the mixed valence states of substituted molybdenum i.e. impurity levels in which loss of electrons take place (liberation of free electrons) resulting hot surface to become positively charged location where as cold junction turn as negatively charged surface leading to n-type conduction in the range $x = 0.04$ to 0.30 . Again at $x = 0.40$, presence of p-type conduction is probably due to significant role of copper ions. This is, as a result of large number of Cu ions migration to tetrahedral (A) sites from octahedral (B) sites and intersites cation exchange might contribute to the conduction process. In the case of C-series, as Mo⁶⁺ is substituted reducing Cu²⁺, copper role in 'A' sites become less probable and hence conduction till to $y = 0.20$ i.e. for all the c-specimens believed to be similar to the conduction processes that observed in the range $x = 0.04$ to 0.30 in 'F' series exhibiting n-type conduction.

To understand the variation of observed thermo electric power with increasing temperature (T), plots of thermo electric power (Q) Vs. temperature (T) have been drawn (for one of the series i.e. F-series is shown in Fig. 2 a & b). From these curves the following observations are drawn.

1. The thermal response of all these materials strongly dependent on temperature in the whole range of temperature studied.
2. All the curves show four regions due to change in their slope having three break temperatures except for $y=0.10$ and 0.20 of C-series ferrites. These are designated as T_1 , T_2 and T_3 and their values are shown in Tables 1 and 2 along with molybdenum concentration and experimentally observed Curie temperature for comparison purpose with T_3 .
3. For the basic ferrite and at $x=0.02$ and 0.40 the observed p-type conduction as mentioned above, found to decrease with temperature(T) and transform to n-type conduction at temperature approximately at 370 °K, which is consistent with the ' T_1 ' of values given in Table 1.
4. The T_1 values are in the range around 355 to 380 K for F-series and 335 to 380 K for C-series materials. For higher values of 'x' and 'y' the obtained T_1 seems to be higher relative to lower x' and 'y'.
5. The computed T_2 values are in the range approximately 400 to 560 K and 408 to 495 K for 'F' and 'C' series respectively. The T_3 values are close to the measured Curie temperature values.
6. Near Curie temperature i.e. around T_3 , all the materials that exhibiting n-type conduction and p-type material i.e. $x=0.40$, a cusp like minimum of 'Q' is observed while the basic and $x=0.02$ ferrites show almost constant value beyond T_3 .
7. Ferrite at $x=0.30$ (F-series), the observed thermal response is quite in opposite trend to the behavior of all the other ferrite materials
8. In the low temperature region at T_1 , an indication has been observed to develop a kink slowly increasing its size as a function of Mo⁶⁺ concentration for F-series up to $x=0.20$ and for C-series up to $y=0.08$. This behavior is more significant in C-series than F-series materials. For other values of x and y this sort of kink has not been observed.

Earlier in low temperature (T) region, Patil et al reported [8] the transformation of p-type conduction into n-type conduction for Ti⁴⁺ substituted copper ferrite and also for Zr⁴⁺ substituted copper ferrite [12] systems. Usually, the following two important conduction processes are to be considered in the low 'T' regions [14] for copper ferrites. These are





The presence of narrow 3d bands Cu^{2+} ($3d^9$) in these ferrites facilitates for formation of small polaron. The substituent molybdenum also has mixed valence states; therefore the observed low temperature p-type conduction can be attributed to small polaron through reaction 1 and mixed valence states. Formation of both type of centers namely Cu^{1+} and Fe^{2+} may result due to loss of oxygen during sintering [14] process. With the increase of 'x' or 'y', copper ions concentration is also expected to increase at tetrahedral sites as reported earlier [8]. Hence, present p-type conduction is attributed due to predominance of reaction 1 until T_1 . The substitution of high valence cation like Mo^{6+} might lead to create vacancies, voids, generate some free electrons for charge balance and localize iron ions obstructing hopping between Fe^{2+} and Fe^{3+} ions as mentioned above. Thus the observed n-type conduction in which electrons are majority carriers is ascribed to the impurity levels, defects and interstitials till to T_1 . The occurrence of copper ferrite phase transition at certain critical temperature and composition is a known fact [15] and hence change in the slope at T_1 is attributed to phase transition from tetragonal to cubic structure. On the other hand, for higher values of 'x' or 'y' where materials exhibited cubic structure, change of curve slope is understood due to impurity significance i.e. extrinsic to intrinsic conduction and T_1 is absence for C-series cubic structured materials. This sort of behavior might be due to mixed mechanisms of conduction. The observed conduction in the range T_1 to T_2 is believed to be intrinsic type. When the meta-stable CuFe_2O_4 heated, a temperature domain was noted where octahedral site Cu^{2+} ions increases in the range $473 \text{ K} < T < 548 \text{ K}$ with the conduction via inter site ions exchange [14] and this region might vary due to impact of the substituted Mo^{6+} . Therefore the observed conduction between T_2 and T_3 is believed to be because of the following reaction



This reaction gives n-type conduction. The transition at T_3 is attributed to the magnetic phase transformation from ferri to paramagnetic state where the ordering spins turn to random orientation. These values within the experimental limitations have consistence with the measured Curie temperature values given in Table 1 and 2 for 'F' and 'C' series materials.

The formation of cusp like minimum was already been reported earlier for Sn^{4+} substituted copper ferrite system [15]. This might be due to the filling up of oxygen vacancies by electrons reducing the mobile electrons at that temperature. The observed kink at low temperature region can be interpreted on the basis of lattice structure distortion as it appeared to all the tetragonal ferrites only. This is a considerable significant result in the present investigations. For the presence of kink one can say that materials turn to follow change in conduction mechanism with p-type behavior resulting decrease of n- type nature in this region i.e. between the temperatures T_1 to T_2 . In the earlier studies though the copper ferrite structural phase transformation from tetragonal to cubic was observed, presence of kink at this temperature has not been reported [8, 14]. The decrease of 'Q' in the certain region (T_1 to T_2 for tetragonal ferrites) can be understood by the references to an observation [16-17] where the conduction is assumed to be intrinsic in this region. In this region, hopping mechanism contribution to 'Q' becomes less significant due to decrease of its prominence in the intrinsic region. Then the thermoelectric power (Q) might occur probably due to mobility of holes lying far below the Fermi energy. Similar observation was made earlier for Nb and or Sn substituted Mn-Zn ferrites [17]. Hence the observed 'Q' can be understood on the same lines as reported earlier [18].

The observed thermal response of the $x=0.30$ (F-series), which is quite in opposite trend to the behavior of all the other ferrite materials probably due to thermally generated holes turning the material behavior towards p-type nature, compensating n-type conduction in which electrons are majority carriers. This indicates that the substituent (Mo^{6+}), at its

higher concentration seems to promote p-type behavior suppressing n-type conduction. Further this can be corroborated with the observed p-type conduction for the ferrite at x=0.40, which accelerated p-type behavior that exhibited by the ferrite at x=0.30 (F-series). This is believed to be due to Fe³⁺ ↔ Fe⁴⁺ and vacancies dominant role resulting conduction with hole type (p-type) over the n-type conduction.

Using the Fermi energy values obtained due to observed thermo electric power (Q, Seebeck coefficient), values of charge carrier concentration (n) per unit volume of all the materials at different temperatures have been evaluated by following the theory that reported earlier [16]. These are on the order of 10²² per cm³. Here one must note a point that for computation of 'n', value of 'Q' is to be considered neglecting its sign as it reflects only respective type of carriers (negative sign indicates conduction due to electrons) responsible for conduction. Considering the variation of 'n' as a function of substituent concentration (x or y) for one of the series is depicted in Fig. 3 and the following results have been obtained.

- In F-series materials, initially decrease of 'n' is observed following reverse trend to the thermo electric power (Q) except at x=0.10.
- In the case of C-series ferrites, the 'n' value deteriorated initially and later found to increase with 'y'. An observation in these results reflects the follow of 'n' with the 'Q' trend as a function of substituent concentration (y).

For the case of low mobility semiconductors like ferrites containing extremely narrow bands or localized levels, value of 'n' was observed earlier on the order of 10²² per cm³ for several ferrites [17-19]. Therefore in the present studies the observed order of 'n' (10²² per Cm³) can be understood on the similar lines. The decrease of 'n' value at x=0.02 (which indicates role of electron carriers) shows the compliance with its observed p-type conduction (as shown in Fig 1) in which holes play dominant role. Similarly the reverse trend of 'n' in comparison with 'Q' as a function of 'x' reflects role of holes contribution for conduction. The observed same trend of 'n' and 'Q' with substituent concentration at y=0.02 and for higher values of 'y' which exhibit cubic lattice structure shows the significant role of electrons for conduction while for intermediate concentration of 'y' indicates the participation of hole type conduction too at considerable level besides 'n' type conduction. This can be corroborated with the variation of 'Q' as a function of temperature. The plots of temperature versus carrier concentration for one of the series i.e. 'F' series are drawn and shown in Fig. 4 (a & b). All these curves show linear relation between 'n' and temperature (T) increasing 'n' value with 'T' indicating generation of more number of electron charge carriers due to increased thermal energy because of raise in temperature. This can be understood with the earlier reported linear relationship between 'n' and 'T' for several spinel ferrite systems [19, 20].

With the relation given below, Drift mobility (μ_d) values are computed using the experimental results obtained in the studies of dc resistivity reported elsewhere [21] and thermoelectric power

$$\sigma = n e \mu_d \quad (4)$$

Where 'σ' is conductivity, 'n' is carrier concentration and 'e' is the charge of electron. The variation of mobility (μ_d) with the rise of temperature for 'F' series is depicted in the Fig. 5 (a & b). The observed drift mobility (μ_d) found to have on the order 10⁻⁸ for lower values of 'x' increasing its value up to x=0.06, there after it falls at intermediate concentrations, evaluated 'μ_d' has on the order 10⁻⁷ increasing its value for higher 'x' values of 'F' series materials. In the case of 'C' series materials, the 'μ_d' increases up to y=0.04 and for higher values of 'y' it decreases having on the order 10⁻⁸. The observed 'μ_d' as a function of temperature (T) shows it's non-dependence on 'T' up to certain critical temperature

(T_N) for both the series. This is around 500 and 445 K for 'F' and 'C' series materials respectively. Beyond ' T_N ', the ' μ_d ' increases showing on the order 10^{-7} .

The non-dependence of ' μ_d ' on temperature up to certain critical temperature (T_d) can be corroborated with the first transition temperature (T_1) values obtained in the resistivity studies reported elsewhere [21]. The values of ' T_d ' are coinciding with ' T_1 ' values, No change in mobility has been found causing invariance of conduction up to T_d . As mentioned above, no impact of charge carriers' mobility because of strong electronic bonds formed by the constituent ions of the ferrite materials is observed. Beyond ' T_d ' mobility contribution is significant where its value is increasing which contribute to conduction. The mobility of electron is higher relative to hole. Above the ' T_d ' temperature, electrons mobility is predominate over holes as thermally activated electrons are more in number than holes. In this region increase of the conduction or decrease of resistivity can be considered due to electrons hopping mechanism between Fe^{2+} and Fe^{3+} as reported earlier [7]. Below ' T_d ' probably holes might be more in number which exhibit low mobility. The increase of ' μ_d ' in 'F' series with 'x' indicates generation of more number of electrons relative to 'C' series in which ' μ_d ' decreases with the substituent concentration indicating dominant role of holes. This has compliance with the expected more number of vacancies in 'C' series than 'F' series ferrites as $3yCu^{2+}$ quantity of copper is substituted by yMo^{6+} in 'C' series whereas $2xFe^{3+}$ quantity is replaced by xMo^{6+} in 'F' series materials.

CONCLUSIONS

1. The obtained thermo-electric power 'Q' (Seebeck coefficient) is found to decrease for F-series in the range $x=0.04$ to 0.08 while it increases in the same range for C-series ($y=0.04$ to 0.08).
2. For the basic ferrite; at $x = 0.02$ and 0.40 p-type conduction is observed while for all the other ferrite materials n-type conduction is exhibited.
3. All the curves show four regions due to change in their slope having three break temperatures which are designated as T_1 , T_2 and T_3 except for $y=0.10$ and 0.20 of C-series ferrites.
4. At T_1 , start of giving an indication to develop a kink slowly led to exhibit this as a kink in complete manner with increasing Mo^{6+} concentration for F-series up to $x=0.20$ and for C-series up to $y=0.08$ is observed. This is more significant in C-series than F-series. For other values of F and C-series materials, this kink has been disappeared.
5. The evaluated charge carriers' values are on the order of 10^{22} per Cm^3 .
6. The observed drift mobility (μ_d) found to have of the order 10^{-8} for lower values of Mo^{6+} while for its higher values has of the order 10^{-7} .

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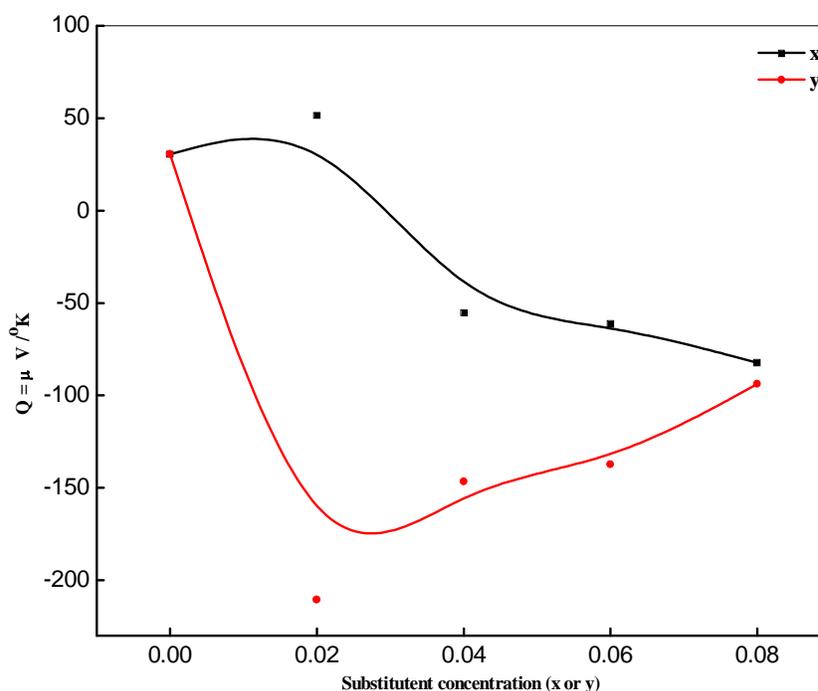


Fig. 1 Variation of thermo-electric power (Q) with molybdenum concentration

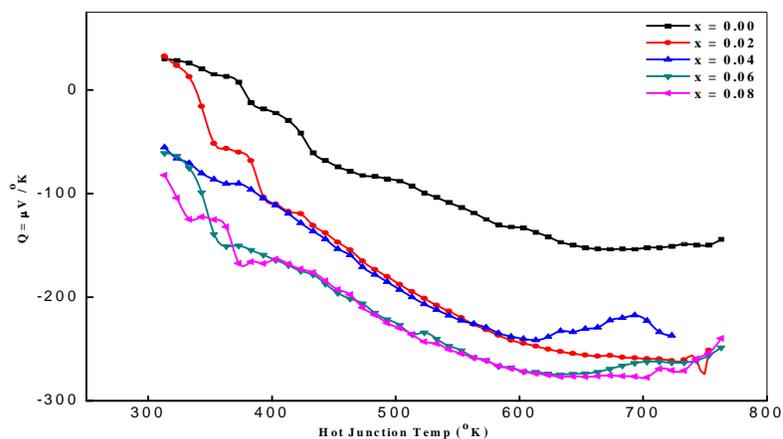


Fig.2(a) Variation of thermo electric power (Q) with increasing temperature for x = 0.00 to 0.08 (F-series)

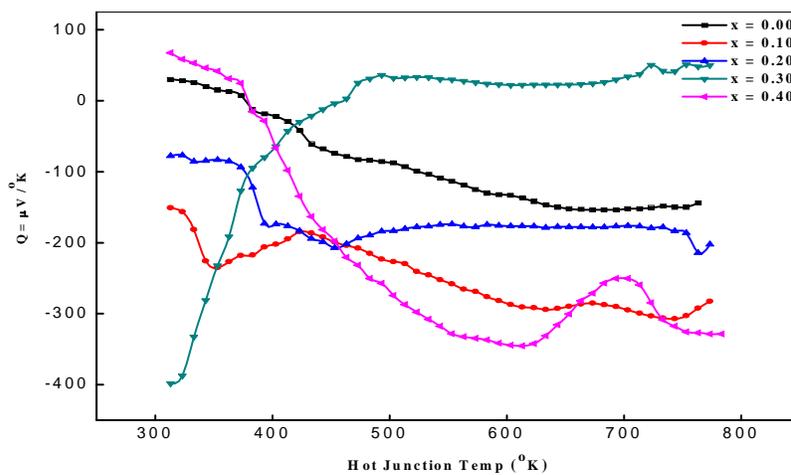


Fig.2(b) Variation of thermo electric power (Q) with increasing temperature for x = 0.00 to 0.40 (F-series)

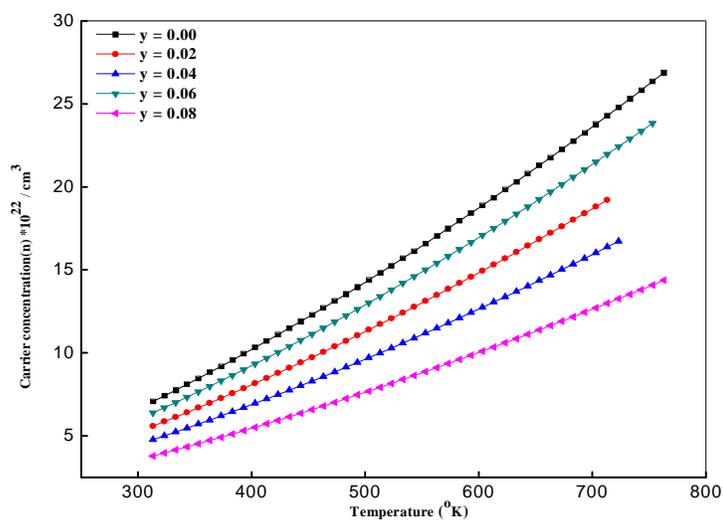


Fig.4(a) Variation of carrier concentration (n) as a function of temperature (T) for y = 0.00 to 0.08 (C-series)

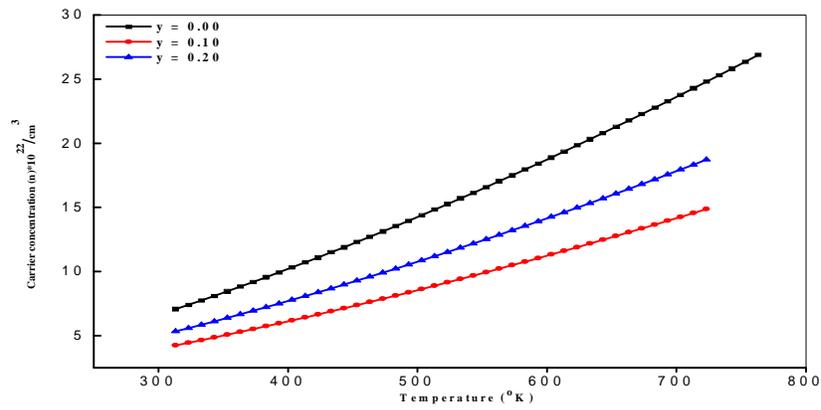


Fig. 4(b) Variation of carrier concentration (n) as a function of temperature (T) for y = 0.00 to 0.20 (C-series)

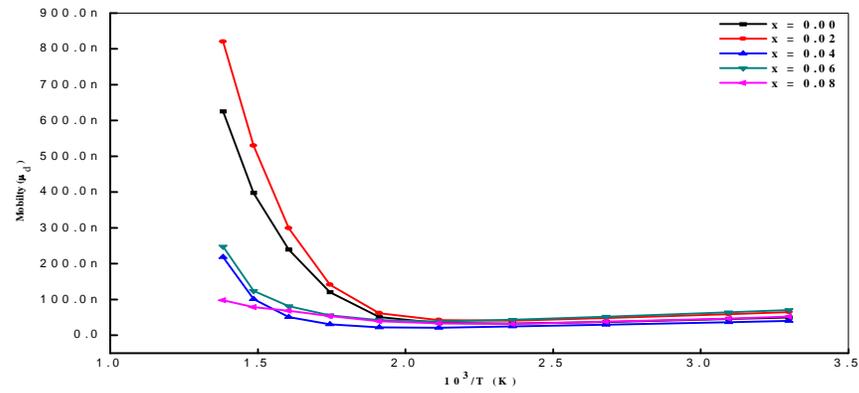


Fig.6(a) Variation of mobility with the increase of molybdenum concentration for x = 0.00 to 0.08 (F-series)

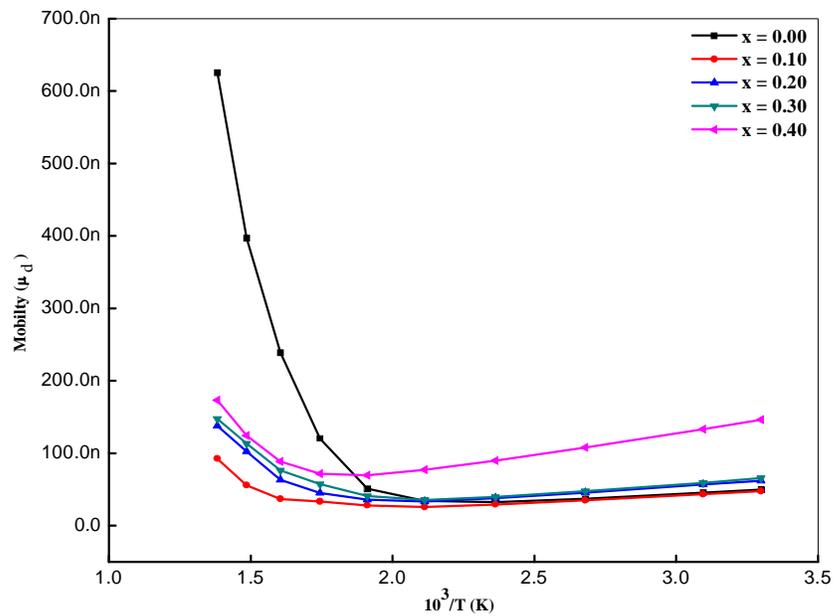


Fig: 6.(b) Variation of mobility with the increase of molybdenum concentration for x = 0.00 to 0.40 (F-series)

Table 1: Transition Temperatures along with Observed Curie Temperature as a Function of Molybdenum Concentration (x)

S.No	x (F-Series)	T ₁ (K)	T ₂ (K)	T ₃ (K)	T _C (K)
1	0	375	487	650	653
2	0.02	360	402	640	654
3	0.04	380	540	650	665
4	0.06	363	520	675	671
5	0.08	380	560	640	665
6	0.1	355	425	739	657
7	0.2	382	499	739	643
8	0.3	375	480	690	675
9	0.4	375	425	625	693

Table 2: Transition Temperatures Along with Observed Curie Temperature as a Function of Molybdenum Concentration (Y)

S.No	y (C-Series)	T ₁ (K)	T ₂ (K)	T ₃ (K)	T _C (K)
1	0	375	487	650	653
2	0.02	335	430	612	651
3	0.04	345	470	622	655
4	0.06	380	425	630	659
5	0.08	367	408	600	674
6	0.1	--	496	625	677
7	0.2	--	454	625	681