Crossover from meta-magnetic state to spin-glass behaviour upon Ti-substitution for Mn in CuMn$_2$O$_4$

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ABSTRACT

Tetragonal distorted spinel of CuMn$_{2-x}$Ti$_x$O$_4$ ($x = 0$, 0.25 and 0.50) was prepared by solid state reaction method followed by neutron diffraction, FTIR spectroscopy, dielectric spectroscopy and magnetic measurements. The confirmation regarding phase formation and identification of additional phase has been carried out by analysing the room temperature neutron diffraction. Besides, FTIR spectroscopy data have also assisted in ascertaining these results. Then, the magnetic susceptibility study of CuMn$_2$O$_4$ shows clearly the ferromagnetic order below 76 K associated with meta-magnetic state of CuMn$_2$O$_4$ which turns into spin-glass behaviour in CuMn$_{1.50}$Ti$_{0.50}$O$_4$. In addition, the room temperature M(H) of all the spinels are described by the Arrot’s plot for weak ferromagnetism. Further, the abrupt change in magnetic susceptibility due to Ti-substitution at room temperature is analysed by electrical property using complex dielectric spectroscopy measurements.

1 Introduction

The oxide spinel’s are often represented by the general formula AB$_2$O$_4$ which crystallizes as face-centred cubic (FCC) lattice with cubic-closed pack of oxide anions and thus possessing space group Fd$ar{3}$m (s.g. no. = 227). The spinels can further be divided into three types according to their cationic distributions amongst the tetrahedral and octahedral sites as \{A$_{1-2}$B$_{x}(B_{2-2}A_{1})$O$_4$\} which provides (a) normal spinel for \{x = 0\}, (b) inverse spinel for \{x = 1\} and (c) mixed spinel for \{0 < x < 1\}. Nowadays, spinel materials are becoming very important for condensed matter physics research group all across the world, due to their potential multifunctional properties and technological applications [1–4]. One such spinel compound is CuMn$_2$O$_4$, in which Manganese (Mn) and Copper (Cu) possess more than one oxidation state and their distributions amongst tetrahedral and octahedral sites depend strongly on the preparation conditions, due to which variation in physical properties has been reported [5–9]. As a consequence, it creates a centre of attention for the scientific community. So far, most of the results in CuMn$_2$O$_4$ are reported where tetragonal symmetry prevails. Further, it is anticipated that the coherence in degenerate energy levels of Cu and Mn result the change in cubic symmetry of CuMn$_2$O$_4$ to tetragonal symmetry.

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On the other hand, if the distortion at B-site corresponds to $c/a > 1$ compensate by opposite distortion at A-site corresponds to $c/a < 1$ then cubic symmetry of CuMn$_2$O$_4$ can be retained [12]. Besides the effect of site distribution on multivalent cations of Cu and Mn, a significant change in magnetic and dielectric properties has been reported by substituting foreign cations, irrespective of the crystal symmetry [7, 12–16].

As per the available literature on the title compound, most of the scientific groups have made an attempt to study CuMn$_2$O$_4$ by substituting foreign atoms (Ni and Zn) at tetrahedral site with copper, resulting considerable change in structure and electrical behaviour, whereas Cd-substitution at tetrahedral site shows BB-interaction leads to the reduction of ferromagnetic behaviour [12–15]. On the other hand, the octahedral site substitution by foreign atoms (Al and Cr) with manganese provides clustering of octahedral John–Teller ions leading to tetragonal distortion whereas Fe-substitution at octahedral site provides increase of catalytic activity [7, 16]. But, we could not found the study in the literature where the large ion has been substituted at octahedral site, thus, we have substituted Titanium (Ti) in Mn-site (octahedral site) to confirm the tetragonal distortion phase as size of the Ti lies in between Al and Cr. Due to disorder effect, magnetic behaviour is expected to be changed significantly. Here, in the present work, we have studied the room temperature neutron diffraction, FTIR spectroscopy, dielectric spectroscopy and temperature-dependent magnetization on CuMn$_{2-x}$Ti$_x$O$_4$. These studies enabled us to understand the change in magnetic and electrical behaviour associated with structural parameters. Here, the room temperature neutron diffraction data analysis assisted us in understanding the FTIR spectroscopy in terms of bond lengths and electrical properties in terms of grain and grain boundary through dielectric study. But, the temperature and field-dependent dc magnetization have analyzed to explain the magnetic behaviour of CuMn$_{2-x}$Ti$_x$O$_4$ in which we observed meta-magnetic state in CuMn$_2$O$_4$ quite similar to the result of earlier material [9]. However, here, we obtained spin-glass-like behaviour in CuMn$_{1.50}$Ti$_{0.50}$O$_4$ when different concentrations of Ti are substituted at Mn-site of CuMn$_2$O$_4$. Generally, dc magnetization provides a combination of characteristics and can’t identify conclusively a spin glass. Because, the possible spin-glass behaviour in a system is due to either magnetic frustration or magnetic reflection or spin disorder [17]. Magnetic frustration exhibits no steady state due to the competition between ferromagnetic and antiferromagnetic moments whereas magnetic reflection relates to canted spin that results a net magnetization which shows ferromagnetic and spin-glass behaviour simultaneously. But spin disorder-based spin freezing of cation ordering can be explained by either due to freeze of antiferromagnetic clusters forming cluster spin glass or due to segregation of antiferromagnetic clusters and spin-glass regions that reveals the coexistence of antiferromagnetic and spin-glass behaviours. Here, we suggest the spin glass-like behaviour in CuMn$_{1.50}$Ti$_{0.50}$O$_4$ by spin disorder-based spin freezing of cation ordering.

## 2 Experimental details

The CuMn$_{2-x}$Ti$_x$O$_4$ with $x = 0, 0.25, 0.5$ were prepared by mixing high purity ≥ 99.9% of CuO, TiO and MnO$_2$ ceramic oxides at appropriate molar proportion and calcinated at 900 °C for 50 h. Subsequently, the calcinated powder was grinded through an agate mortar pestle for homogenization by adding small amount of acetone as volatile substance. This is followed by making pellets through a hydraulic press and sintered at 950 °C for 72 h for densification.

To identify the phase purity of the above materials, the neutron diffraction and FTIR-spectra measurements were carried out at room temperature. The neutron diffraction (ND) measurement was done with neutron wavelength of 1.48 Å using multi position-sensitive detector (PSD) based focusing crystal diffractometer at the National Facility for Neutron Beam Research (NFFBR), Dhruva reactor, Mumbai (India) set up by UGC-DAE CSR Mumbai Centre [18]. Subsequently, FTIR-spectra measurements were done within the spectral range of 400–4000 cm$^{-1}$ using Germanium-coated KBr beam splitter and DLATGS detector at a resolution of 4 cm$^{-1}$. In addition, the magnetic and complex dielectric spectroscopy measurements were also presented on these materials. Here, the magnetic measurements were carried out in the temperature range 2 K to 300 K by employing M/s. Quantum Design USA make cryogen-free Helium Re-liquefier-based 9 T Physical Property Measurement System (PPMS) in vibrating sample magnetometer (VSM)
mode. Besides, the dielectric spectroscopy measurement was carried out at 300 K over the frequency range 60 Hz to 2 MHz for an oscillation voltage of 1.0 V with the help of precision LCR meter (Model E4980A, M/s. Keysight, USA).

3 Results and discussion

3.1 Crystal structure analysis

3.1.1 Neutron diffraction

The primarily analysed room temperature neutron diffraction (ND) patterns of CuMn$_{2-x}$Ti$_x$O$_4$ (X = 0, 0.25 and 0.50) were reported with few unfitted peaks due to lack of information on possible impurity phase [19]. We had then observed anomaly in room temperature magnetic and dielectric data, which emphasised the presence of additional phase thus we reanalysed ND data using Rietveld method by employing Fullprof suite programme. Indeed, all three materials were well fitted by distorted tetragonal symmetry of space group $I41/amd$ (s. g. number = 141) spinel phase with cell volume 286.522(6) Å$^3$ (with cell parameter $a = 5.871(3)$ Å, $c = 8.313(5)$ Å) along with traces of secondary phase Mn$_3$O$_4$ with same space group symmetry as that of parent material, i.e., $I41/amd$, but with relatively larger cell volume 310.547(4) Å$^3$ (with cell parameter $a = 5.741(7)$ Å and $c = 9.428(4)$ Å). This secondary phase has been a part of the parent system in most of the previous reports [9, 20, 21]. In order to emphasis for exhibiting the variation in the diffraction pattern, the slice of the diffraction data around maximum intensity peak is shown in Fig. 1. In our present analysis, the obtained parameters are slightly different, particularly for the derivatives, as compared to our earlier report [19]. Therefore, the detailed and augmented neutron diffraction data analysis is presented here in Tables 1 and 2. The goodness of the fitting parameters is also mentioned in Fig. 1. In our present analysis, bond lengths are obtained for Mn–O = 1.990 Å and 1.923 Å and Cu–O = 1.999 Å in CuMn$_2$O$_4$ associated with bond angle 97.52° and 82.48° for O–Mn–O and 111.05° for O–Cu–O, Mn–O(Ti–O) = 1.998 Å (1.998 Å) and 1.914 Å (1.914 Å) and Cu–O = 2.001 Å in CuMn$_{1.75}$Ti$_{0.25}$O$_4$ associated with bond angle 97.50° and 82.49° for O–Mn–O and 110.80° for O–Cu–O and Mn–O(Ti–O) = 2.011 Å (2.011 Å) and 1.914 Å (1.914 Å) and Cu–O = 2.009 Å in CuMn$_{1.50}$Ti$_{0.50}$O$_4$ associated with bond angle 97.49° and 82.50° for O–Mn–O and 110.61° for O–Cu–O.

In present work, the impurity phase of Mn$_3$O$_4$ is found to be around 15% in CuMn$_2$O$_4$ instead of two impurity phases of Mn$_3$O$_4$ and CuMnO$_2$ around 11% as per our earlier material [9]. However, the 15% impurity phase remains more or less constant with Ti-substitution concentration at $x = 0.25$. But with further Ti-substitution, the unreacted TiO$_2$ is observed at $x = 0.5$, though Mn$_3$O$_4$ phase appears to have decreased from around 15% to 8% and with additional phase of TiO$_2$ (~4–6%). Here we also noticed that overall cell volume increases, predominantly because of large Ti$^{4+}$ ion substitution. It is worth mentioning here that the goodness of fitting parameter improved upon considering the distortion in the material, i.e., Cu and Mn atoms were found on crossover the designated sites. This implies that
disorder has been intensified upon the Ti-substitution in the material, as Ti being in the $4^+$ valance state which likely to create Mn$^{3+}$ and Mn$^{4+}$ and correspondingly Cu$^{1+}$ and Cu$^{2+}$. The details of disorder for the series of material are described in Table 2. Further, the presence of TiO$_2$ as unreacted phase indicates the breaching of solubility limit in CuMn$_2$O$_4$. It is worth mentioning that the microscopic variation in the materials are observed as a consequence of Ti$^{4+}$ substitution, which are reflected in terms of the bond lengths and bond angle variation same as our earlier report and grain and grain boundaries by Z$'$ and Z$''$ [19, 22]. From Fig. 1, the variation in the maximum intense peak can be noticed that the two distinct peaks for CuMn$_2$O$_4$ merges into one upon Ti-substitution, which also signifies the reduction of Mn$_3$O$_4$ concentration ($\sim 15\%$ to $\sim 8\%$) as the left-hand side peak in the doublet is predominantly has a contribution from Mn$_3$O$_4$. Conversely, the formation of phase on CuMn$_{2-x}$Ti$_x$O$_4$ was also confirmed by room temperature FTIR spectroscopy analysis and the calculated bond length of FTIR spectroscopy are compared with the obtained bond length of Rietveld analysis.

### 3.1.2 FTIR spectroscopy

In order to verify the phase purity of CuMn$_{2-x}$Ti$_x$O$_4$, the room temperature FTIR-spectra were obtained within the spectral range of 400–4000 cm$^{-1}$ as shown in Fig. 2. A total of 20 scans were co-added at a resolution of 4 cm$^{-1}$ using Germanium-coated KBr beam splitter and DLATGS detector. However, the position of all the absorption bands except 633 cm$^{-1}$ and 973 cm$^{-1}$ looks like similar which implies the formation of same phase associated with the modification of bond lengths due to Ti-substitution in CuMn$_2$O$_4$. Because, the intensity of 973 cm$^{-1}$ decreases and 633 cm$^{-1}$ shifts towards the higher wave number side significantly upon Ti-substitution. Within the spectral range of 500–1000 cm$^{-1}$ which is commonly known as finger print region, CuMn$_2$O$_4$ shows four absorption bands at 510 cm$^{-1}$, 605 cm$^{-1}$, 633 cm$^{-1}$ and 973 cm$^{-1}$. However, the bond lengths of Mn–O = 2.078 Å and 2.017 Å, Cu–O = 2.132 Å and of CuMn$_2$O$_4$ are compared with the obtained bond length of Rietveld analysis.

### Table 1

| Compounds            | CuMn$_2$O$_4$ | CuMn$_{1.75}$Ti$_{0.25}$O$_4$ | CuMn$_{1.50}$Ti$_{0.50}$O$_4$ |
|----------------------|--------------|-------------------------------|-------------------------------|
| Lattice parameter (Å) | $a = 5.871$ (3) | $a = 5.894$ (6) | $a = 5.931$ (2) |
|                      | $c = 8.313$ (5) | $c = 8.284$ (4) | $c = 8.279$ (3) |
| Cell volume (Å$^3$)   | 286.522 (6)   | 287.438 (9)                  | 291.206 (5)                  |
| $\chi_0$ (emu/Oe.mole) | 0.0045       | 0.018                         | 0.0067                        |
| $T_N$ (K)             | 56           | 51                           | 25                            |
| $\theta_C$W (K)       | 75           | 70                           | 70                            |
| C(emuK/mole)          | 1.841        | 1.615                        | 1.757                         |
| $\mu_{eff}$($\mu_{B}$)/f.u. | 3.79         | 3.56                         | 3.71                          |

### Table 2

| Materials    | CuMn$_2$O$_4$ | CuMn$_{1.75}$Ti$_{0.25}$O$_4$ | CuMn$_{1.50}$Ti$_{0.50}$O$_4$ |
|--------------|--------------|-------------------------------|-------------------------------|
| Cu/Mn/Ti     | 0.92/0.08    | 0.84/0.13/0.03                | 0.90/0.07/0.03                |
| Mn/Cu/Ti     | 0.94/0.06    | 0.78/0.11/0.11                | 0.72/0.10/0.18                |

Fig. 2 Room temperature FTIR spectroscopy of CuMn$_{2-x}$Ti$_x$O$_4$ (Color figure online)
in CuMn$_2$O$_4$, Mn–O (Ti–O) = 2.090 Å (2.113 Å) and 1.895 Å (1.956 Å) and Cu–O = 2.124 Å in CuMn$_{1.75}$Ti$_{0.25}$O$_4$ and Mn–O (Ti–O) = 2.097 Å (2.120 Å) and 1.739 Å (1.759 Å) and Cu–O = 2.113 Å in CuMn$_{1.50}$Ti$_{0.50}$O$_4$ are calculated from three absorption bands that lies between 500 and 800 cm$^{-1}$ using $k = 24/r^3$ for Mn–O/Ti–O and $k = 19/r^3$ for Cu–O with $k = (2\pi fc)^2\mu$, where $\mu$ and $r$ are the reduced mass and average bond length between two atoms, respectively. These bond lengths are quite consistent with the bond lengths obtained from Rietveld analysis of neutron diffraction irrespective of the coordination in CuMn$_{2-x}$Ti$_x$O$_4$ [19].

### 3.2 Magnetic measurements

The zero-field cooled (ZFC) and field cooled (FC) magnetization measurements on CuMn$_{2-x}$Ti$_x$O$_4$ ($x = 0, 0.25$ and $0.50$) were carried out at 500 Oe measuring magnetic fields within the temperature range 2–300 K and depicted in Fig. 3. Here, the FC magnetization of CuMn$_2$O$_4$ prevails weakly temperature dependence from 300 K down to 80 K below which the magnetization rises rapidly may be due to spin-canting and becomes weakly temperature dependence below 24 K. However, the temperature dependence ZFC magnetization was found identical with FC magnetization above 56 K below which ZFC bifurcates from FC behaviour and attend a broad maximum around 24 K. Analogous to the result of our earlier material CuMn$_2$O$_4$, here, the bifurcation temperature for ZFC and FC is found at 56 K which is slightly higher than the previous value may be due to the phase pury and different cationic distributions [9]. Further, our magnetic behaviour on CuMn$_2$O$_4$ is quite similar with the reports of CuMn$_2$O$_4$ with the tetragonal symmetry and cubic symmetry [5, 9, 23].

Upon Ti-substitution, the ZFC and FC magnetic behaviours are significantly altered particularly below 80 K as can be seen in Fig. 3. Therefore, the magnetic analysis is explained in two parts below 80 K and above 80 K. Below 80 K, the CuMn$_{1.75}$Ti$_{0.25}$O$_4$ shows very similar in behaviour with CuMn$_2$O$_4$ except the ZFC and FC bifurcation temperature which is shifted marginally towards lower temperature. But, most interestingly, the bifurcation temperature for ZFC and FC in CuMn$_{1.50}$Ti$_{0.50}$O$_4$ is shifted to 24 K which is associated with a sharp cusp in ZFC magnetization. This type of behaviour such as sharp cusp in ZFC and completely flattened in FC below the temperature of sharp cusp in ZFC are frequently obtained only in those materials where spin-glass state exist [17, 24, 25]. But above 80 K, the temperature variation of inverse susceptibility provides parabolic behaviour for all the materials as shown in inset Fig. 3 implies the existence of ferri-magnetic due to the anti-parallel ordering of nearest neighbour magnetic moments with unequal magnitude.

At room temperature, the inverse susceptibility of derivatives decreases irregularly with increasing Ti-concentration in such a way that CuMn$_{1.75}$Ti$_{0.25}$O$_4$ decreases by a factor of approximately half and CuMn$_{1.50}$Ti$_{0.50}$O$_4$ decreases marginally as compared to CuMn$_2$O$_4$. The marginal decrease of inverse susceptibility in CuMn$_{1.50}$Ti$_{0.50}$O$_4$ is expected to be due to the compensation of paramagnetic behaviour with diamagnetic behaviour of impurity phase TiO$_2$ [26]. Further, the possible causes behind it can be explained more elaborately using M(H) data in the next paragraph of this sub-section. In general, the ideal Curie–Weiss behaviour in the paramagnetic region denotes the non-interacting spins. Therefore, we have fitted the high temperature susceptibility (75–300 K for CuMn$_2$O$_4$ and CuMn$_{1.50}$Ti$_{0.50}$O$_4$ and 75–175 K for CuMn$_{1.75}$Ti$_{0.25}$O$_4$) by Curie–Weiss law \( \chi(T) - \chi_0 = C/(T - \theta) \) as can be seen in inset Fig. 4 to obtain the effective magnetic moments ($\mu_{\text{eff}}$), Curie–Weiss temperature ($\theta$), van-vleck paramagnetism ($\chi_0$) and depicted in Table 1.

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Fig. 3 Temperature-dependent magnetization of CuMn$_{2-x}$Ti$_x$O$_4$. Inset figure shows temperature-dependent inverse susceptibility of CuMn$_{2-x}$Ti$_x$O$_4$ indicating the ferrimagnetic state (Color figure online)
notice from Table 1 that $\mu_0 = 2.82\sqrt{C}$ decreases in CuMn$_2$O$_4$ upon Ti-substitution is ascribed with distributions of magnetic ions. Further, the frustrated parameters $f = |\theta|/T_N$ are calculated $\sim 1.33$, $1.37$ and $2.8$ for CuMn$_2$O$_4$, CuMn$_{1.75}$Ti$_{0.25}$O$_4$ and CuMn$_{1.50}$-Ti$_{0.50}$O$_4$ respectively due to the spin disorder in the materials.

Subsequently, we have derived a normalised susceptibility equation using the Curie constant ($C$) and Curie–Weiss temperature ($\theta$) as follows:

$$\frac{C}{\chi|\theta|} = \text{sign}(\theta) + \frac{T}{|\theta|}$$

This equation provides the magnetic interactions of the material which evolves with compositions. As can be seen from Fig. 4, the $C/\chi|\theta|$ vs. $T/|\theta|$ provides the occurrence of short-range interactions in all the materials because, depending on the ratio of magnetic ordering temperature to Curie–Weiss temperature, the deviation in Curie–Weiss behaviour corresponds to either short-range ($T/|\theta| \geq 1$) interaction or long-range ($T/|\theta| < 1$) interaction. In addition, all are showing downward deviation implying uncompensated interactions because upward deviation will give compensated interactions.

The isothermal hysteresis behaviour at 3 K and 300 K are already reported elsewhere, and here we have reported the detailed analysis of the temperature dependence magnetic behaviour [19]. In isothermal hysteresis, the possibility of kink around the origin in CuMn$_{1.75}$Ti$_{0.25}$O$_4$ at 300 K as shown in inset Fig. 5 and washing out of step-like behaviour due to weak ferromagnetic in meta-magnetic state upon Ti-substitution in CuMn$_2$O$_4$ at 3 K as shown in Fig. 5 were not explained in details. Therefore, here, we have given emphasis to correlate $M(H)$ with $M(T)$ behaviour to explain the effect of Ti-substitution at 3 K and 300 K. At 300 K, the kink in CuMn$_{1.75}$Ti$_{0.25}$O$_4$ around the origin of $M(H)$ can be explained using $M^2$ vs. $H/M$ plot which is commonly known as Arrott plot in the Stoner-Wohlfarth model of itinerant electron magnetism because, Arrott plot is an alternative method to investigate the weak ferromagnetic for a material. Inset Fig. 6 clearly shows the variation of $M^2$ vs. $H/M$ with shifting of $M^2(H/M)$ towards left in CuMn$_{1.75}$Ti$_{0.25}$O$_4$ and towards right in CuMn$_{1.50}$-Ti$_{0.50}$O$_4$ associated with curvatures in $M^2(H/M)$ curve as compared to CuMn$_2$O$_4$ which provides a vertical straight line. Generally, the straight line behaviour in $M^2$ vs. $H/M$ corresponds to homogeneous system without localized moments of spin and curvature corresponds to inhomogeneous system with localized moments. Further, if the tangent of the curve intercepts at positive $M^2$-axis implies weak ferromagnetic whereas magnetic phase transition occurs when the tangent intercepts at origin. As all the materials contain van-vleck paramagnetism, the $M^2(H/M)$ curves can’t be understood easily in the present form. Therefore, Arrott plot is re-plotted as $(M - M_0)^2$ vs. $H/(M - M_0)$ after subtracting the
magnetization due to van-vleck contribution \( (M_0) \) and shown in Fig. 6. It reveals that all the materials belong to system of inhomogeneous and weak ferromagnetic due to the localized moments which increases upon Ti-substitution for Mn in CuMn\(_2\)O\(_4\). However, the curve of CuMn\(_{1.75}\)Ti\(_{0.25}\)O\(_4\) intercepts the \((M - M_0)^2\)–axis at positive value significantly larger than CuMn\(_2\)O\(_4\) implying that the weak ferromagnetic ordering due to localized moment increases. However, the curve of CuMn\(_{1.50}\)Ti\(_{0.50}\)O\(_4\) intercepts \((M - M_0)^2\)–axis at positive value very close to CuMn\(_2\)O\(_4\) due to the additional diamagnetic behaviour of impurity phase TiO\(_2\) [26]. Here, the room temperature paramagnetic behaviour is explained by weak ferromagnetic associate with localized moments of itinerant electrons because, the magnetic exchange field causes the ferrimagnetic is negligible due to randomly oriented atomic magnetic moments. When temperature decreases, the atomic magnetic moments are gradually oriented in a particular order and its effect is observed clearly below Curie temperature. Therefore, based on frustrated parameters, the occurrence of spin glass-like behaviour in CuMn\(_{1.50}\)Ti\(_{0.50}\)O\(_4\) is expected to be due to the spin disorder based on spin freezing of cation below 24 K irrespective of the increased weak ferromagnetic due to localized moments. As a consequence, the magnetic field-induced hysteresis loops at I and III-quadrant washes out at 3 K in CuMn\(_{1.50}\)Ti\(_{0.50}\)O\(_4\).

In the above, the significant change in magnetization by Ti-substitution for Mn in CuMn\(_2\)O\(_4\) is explained using Curie–weiss law and Arrott plot which suggests the materials are transforming into inhomogeneous system upon Ti doping. Further, the room temperature susceptibility explained by Wohlfarth model of itinerant electron magnetism via Arrott plot suggests the weak ferromagnetic due to localized moments of itinerant electrons. So, in order to have a look in to the inconsistent change in magnetization at room temperature, the room temperature dielectric spectroscopy measurement is discussed in the next section. Because, the room temperature dielectric spectroscopy can confirm the disorder in the system that can give rise to localized states of electrons via which hopping conduction takes place.

3.3 Dielectric spectroscopy measurements

3.3.1 Complex dielectrics and AC conductivity

The frequency dependence dielectric permittivity of CuMn\(_{2-x}\)Ti\(_x\)O\(_4\) was measured at 300 K and subsequently plotted the real part of dielectric permittivity \((\varepsilon')\) and its dielectric loss \((\tan \delta = \varepsilon''/\varepsilon')\) using semi-log scale in Fig. 7a and b, respectively. Figure 7a shows
clearly the exponential decrease in $\varepsilon'$ with increase in frequency of CuMn$_2$O$_4$ that implies the time-dependent relaxation. This is completely different compared to the result of our earlier material as expected due to the purity and different cationic distributions of present material [27]. Further, the very weak frequency dependence of $\varepsilon'$ in CuMn$_{1.75}$Ti$_{0.25}$O$_4$ and CuMn$_{1.50}$Ti$_{0.50}$O$_4$ suggests a phenomenon of nearly constant loss which results from the relaxation involving with the motion of highly localized charges rather than dominating hopping process [28]. Generally, the exponential decreasing behaviour in dielectric permittivity with frequency is explained by Koop’s theory for an inhomogeneous medium of two layers of the Maxwell–Wagner type in which, the grains and grain boundaries are the constituents [29, 30]. But, inset Fig. 7b shows that the dielectric loss ($\tan \delta$) of CuMn$_2$O$_4$ decreases exponentially below the frequency of 10 kHz above which continues as independent of frequency up to the higher limit quite similar with the result of our earlier material [26]. Upon substituting Ti for Mn in CuMn$_2$O$_4$, Fig. 7b shows the faster decrease in $\tan \delta$ as compared to pure one at low frequency as expected. However, the $\tan \delta$ value of CuMn$_{1.50}$Ti$_{0.50}$O$_4$ lies between CuMn$_2$O$_4$ and CuMn$_{1.75}$Ti$_{0.25}$O$_4$ below 10 kHz which may be due to the presence of impurity phase TiO$_2$ which increases the grain boundary effect and thus the low conducting phase of grain boundaries enhances the energy of electron to exchange.

In order to understand the conduction mechanism on these materials, the AC conductivities are obtained from real part of dielectric permittivity ($\varepsilon'$) and dielectric loss ($\tan \delta$) with respect to frequency [31] as given below:

$$\sigma_{AC} = 2\pi \varepsilon_0 \varepsilon' / \tan \delta$$

(2)

Here, $\varepsilon_0$ is the dielectric permittivity of free space and $f$ is the frequency of the applied field. Figure 8 shows clearly a linear variation in AC conductivity with frequency. Generally, the linear behaviour of AC conductivity with frequency in disordered materials behaves as $\sigma_{AC} \sim \omega^s$ which implies the hopping conduction. Here, $s$ is the exponent of frequency and defined as $s = 1 - (6k_B T/W_m)$ where $W_m$ is the maximum barrier height [32, 33]. Analogous to the result of our earlier material, the conductivity of CuMn$_2$O$_4$ decreases with decrease in frequency down to 10 kHz reveals that $s > 0$ implies $6k_B T < W_m$.

But below 10 kHz, conductivity of CuMn$_2$O$_4$ becomes almost independent of frequency. A similar type of frequency independent conductivities are obtained for CuMn$_{1.75}$Ti$_{0.25}$O$_4$ and CuMn$_{1.50}$Ti$_{0.50}$O$_4$ which provide $s \approx 0$ implies $6k_B T \approx W_m$ within the measurement region associated with increase of localized charge carriers. However, the frequency dependence conductivity of CuMn$_{1.50}$Ti$_{0.50}$O$_4$ lies between CuMn$_2$O$_4$ and CuMn$_{1.75}$Ti$_{0.25}$O$_4$ which may be due to the effect of TiO$_2$. But, the linear decreasing behaviour of $\sigma_{AC}$ within 0.1–1 kHz frequency range in CuMn$_{1.75}$Ti$_{0.25}$O$_4$ is related to relaxation of localized moments with increasing frequency. Further, the cause of increase in conductivity in CuMn$_{2-x}$Ti$_x$O$_4$ can be understood from impedance and electric modulus spectroscopy in the next sub-section.

### 3.3.2 Impedance and electric modulus

The room temperature frequency dependence of $Z'$ and $Z''$ for CuMn$_{2-x}$Ti$_x$O$_4$ are depicted using semi-log scale in Fig. 9a and b, respectively. In contrast to our impedance results of earlier CuMn$_2$O$_4$, the present material shows quite similar behaviour in $Z'$ and a broad peak at higher frequency side in $Z''$ instead of inflection point around 10 kHz [27]. Upon Ti-substitution, the magnitude of $Z'$ and $Z''$ reduces in such a way that CuMn$_{1.50}$Ti$_{0.50}$O$_4$ lies in between CuMn$_2$O$_4$ and CuMn$_{1.75}$Ti$_{0.25}$O$_4$. In the meanwhile, the peak position in $Z''$ shifts toward higher limit of frequency which implies that the relaxation depends strongly on chemical compositions. Here, the reduced
magnitude of $Z'$ is expected to be due to the decrease of immobile charges and their rapidly decreasing trend at higher frequency limit may be due to the increasing barrier effect. In order to distinguish the contribution of grain, grain boundary and electrode effects at room temperature, the complex impedances of CuMn$_{2-x}$Ti$_x$O$_4$ are analyzed by Nyquist plot ($Z''$ vs. $Z'$) as can be seen from Fig. 10. Within the range of measurement frequency, the Nyquist plot reveals the distinct effect of grain boundary associated with a single semi-circle at intermediate frequency range because higher frequency comprises with grain and lower frequency comprises with electrode effects. Here, the magnitude of the grain boundary effect can be noticed easily from the diameter of the semi-circle in Fig. 10. Further, all the semicircles are asymmetric in Nyquist plot which reveals the non-Debye type relaxation behaviour. Generally, the impedance in complex dielectric spectroscopy is due to only resistive components. Therefore, the contribution of capacitive reactance in CuMn$_{2-x}$Ti$_x$O$_4$ can be obtained by analysing electric modulus data as follows.

Figure 11a and b show the frequency dependence of $M'$ and $M''$ respectively in semi-log scale for CuMn$_{2-x}$Ti$_x$O$_4$ at room temperature. In contrast to the room temperature electric modulus data of our earlier CuMn$_2$O$_4$, here, we obtained drastic change in $M'$ and $M''$ due to the purity and cationic distributions of the present material. However, both the figures show similar type of frequency dependence with very weak dependence of frequency below 10 kHz above which they exponentially increase which implies that the relaxation process is dominated by short-range mobility of localized charge carriers for all the materials. In addition, we have also plotted $M''$ vs. $M'$ for all the materials at room temperature as shown in Fig. 12 in which CuMn$_2$O$_4$ shows two
semitances one at lower frequency range associated with grain boundary effect and other at higher frequency range associated with grain effect quite similar to the result of our earlier material [27]. But, only one semicircle is obtained in the derivatives with increase in size within the measurement frequency range due to the increasing effect of capacitive grain boundary.

4 Conclusions

In the present work, we have reported the magnetization and dielectric spectroscopy measurements on tetragonal symmetry of polycrystalline CuMn$_{2-x}$Ti$_x$O$_4$ ($x = 0, 0.25, 0.50$). The formation of phase is also confirmed by FTIR spectroscopy. Further, the presence of little amount of TiO$_2$ as unreacted phase in CuMn$_{1.50}$Ti$_{0.50}$O$_4$ has influence on magnetic and dielectric behaviour. However, the effective magnetic moment ‘$\mu_{\text{eff}}$’ in CuMn$_2$O$_4$ is obtained less compared to our earlier material of CuMn$_2$O$_4$ may be due to the alteration in the cationic distribution of magnetic ions. These are also responsible for the decrease of $\mu_{\text{eff}}$ in CuMn$_{2-x}$Ti$_x$O$_4$ as expected. Here, the $\mu_{\text{eff}}$ of CuMn$_{1.50}$Ti$_{0.50}$O$_4$ is marginally reduced as compared to CuMn$_2$O$_4$ but significantly large as compared to CuMn$_{1.75}$Ti$_{0.25}$O$_4$ is expected to be due to the presence of unreacted TiO$_2$ phase. Further in the Arrott’s plot, the TiO$_2$ phase significantly reduces the room temperature with weak ferromagnetism due to localized moments in CuMn$_{1.50}$Ti$_{0.50}$O$_4$ as compared to CuMn$_{1.75}$Ti$_{0.25}$O$_4$ and thus very close to CuMn$_2$O$_4$. Interestingly, the magnetic field-induced hysteresis loop of CuMn$_2$O$_4$ gradually washes out upon Ti-substitution at 3 K and anti-ferromagnetic order freezes below 24 K in CuMn$_{1.50}$Ti$_{0.50}$O$_4$ in such a way that it reveals the spin-glass state. Here, freeze of anti-ferromagnetic ordering in a spin-glass state is expected to be due to spin disorder-based spin freezing of cations. In addition, the room temperature complex dielectric, impedance and electric modulus reveal the electronic conduction in CuMn$_2$O$_4$ by short-range mobility of localized charge carriers which increases upon substituting Ti for Mn in CuMn$_2$O$_4$. But, here, the dielectric spectroscopy data of CuMn$_{1.50}$Ti$_{0.50}$O$_4$ is very close to CuMn$_2$O$_4$ due to increasing grain boundary effect of TiO$_2$ as unreacted phase.

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Author contributions

All the authors contributed equally to this paper.

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