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Structural, electrical and magnetic study in nanocrystallite $\text{La}_2\text{CuMnO}_6$ ceramics

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Abstract

Structural, dielectric and magnetic properties of nano-size polycrystalline, $\text{La}_2\text{CuMnO}_6$ (LCM) samples were studied in the temperature range 80 K to 300 K. Orthorhombic single phase with space group '*Pnma*' was confirmed by Rietveld refinement of XRD peaks. The small-polaron driven dielectric dispersion showed relaxation peaks in the vicinity of low-temperatures. The X-ray absorption spectroscopy (XAS) confirmed the charge states of Cu (2+) and Mn (4+) ions. DC-resistivity analysis supported the thermally activated conduction for high temperature and the variable range hopping (VRH) mechanism of conduction at low-temperature. The deviation of super-exchange angles between B-site cations from an ideal 180° value produced non-collinearity in the antiferromagnetic response of this ceramic and was confirmed canted antiferromagnetic behaviour. Positive Curie temperature along with finite coercivity indicated that the super-exchange interaction between Cu^{2+} and Mn^{4+} ions influenced the magnetic behaviour of this ceramics and showed a heterogenous magnetic response.

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1. Introduction

The double perovskite materials of the form $A_2B'B''O_6$, coupled with any pair of transition metals at B-site, provide a large number of choices to explore a variety of multifunctional materials. Both B-site ions can be alternately arranged along the three crystalline axis, as found in the NaCl-type of arrangement. This ordering controls the fundamental properties of materials, like; magnetic, dielectric, vibrational and ionic conductivity, particularly in manganese-based double perovskite compounds. These compounds have been studied extensively; because of the wide variation in their physical properties like charge spin dependent magnetoelectric, magnetoresistance and multiferroicity. The presence of electro-magnetic coupling makes these compounds compatible with modern electronic devices. In these compounds, the presence of small conductivity, near and above room temperature, offered a new class of dielectric materials, known as leaky dielectric materials, used for microelectronic applications [1-6].

The double perovskites compounds of the form $La_2B'MnO_6$ ($B' = Ni, Co$, or other transition elements) attracted lots of attention in the last decade due to their multifunctional properties [7-10]. The proper choice of *3d*-elements as B-site cations, provides peculiar magnetic and electrical properties due to their complex nature of charge states [11]. The discovery of magneto-dielectrics in La_2NiMnO_6 , accelerated the current pace of research activities [12], Lin et al. showed a relaxor-like dielectric behaviour occurred in La_2NiMnO_6 [13] and La_2CoMnO_6 [14]. In addition, ferroelectric and diffused ferroelectric properties were reported for different compositions of double perovskites [15-20]. Due to this substantial and promising dielectric response at high frequencies, double perovskites have been extensively studied [21-24]. Mir. et. al. studied the halfmetallicity properties of La_2CuMnO_6 and reported that La-O bond is ionic in nature, whereas Cu-O and Mn-O are covalent [23]. It was also reported that the Mn-*d* states along with notable contribution of Cu-*d* states are combinedly responsible for magnetic response in La_2CuMnO_6 ceramics [24]. Exploring the temperature dependent electrical and magnetic properties of such ceramics, will be very interesting for the fundamental physics as well as for the possible electronic device application point of view.

In our previous study, structural, morphological and high temperature dielectric properties of La_2CuMnO_6 (LCM) were reported [25]. The dielectric response of micro-structured LCM crystals showed Maxwell-Wagner dielectric relaxation and non-Debye

dielectric relaxation. Correlated Barrier Hopping (CBH) dependent conduction was observed in the micro-structured LCM crystals. However, the study was somewhat limited for micro size-grains and up to high-temperature electrical properties only. Therefore, investigation of below room temperature electrical and magnetic properties of this ceramic, will be fascinating.

In this work, a systematic study on the structural, electric and magnetic characteristics of nanostructured LCM ceramics and the effect of the nano-sized grains on the physical properties of this LCM ceramics were presented. An attempt to investigate the origin of non-collinearity in magnetic behaviour and to co-relate the low temperature dielectric anomalies with magnetic anomalies were made.

2. Experimental

LCM nano-sized polycrystalline samples were synthesized by the sol-gel reaction of stoichiometric quantities of highly pure reagents $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (by Loba chemicals), $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and citric acid (by Merck). These chemicals were mixed in distilled water and this solution was stirred for 10 hours at 80 °C under uniform heat on a magnetic stirrer to obtain a thick gel. The thick gel was kept in the oven at 180 °C for the next 10 hours and calcined it at 750 K for 6 hours. Several pellets prepared for various characterizations were sintered at 800 °C. Room temperature X-ray powder diffraction measurements were performed using Rigaku Ultima IV, Japan ($\text{Cu-K}\alpha$, $\lambda = 1.54 \text{ \AA}$) and Rietveld refinement of XRD data was performed by using FULLPROOF software. The JSM-5410 scanning electron microscope (equipped with Si (Li) X-ray detector) was used to study the surface morphology of the nanostructured LCM polycrystalline ceramics. The scanning electron images (SEIs) and backscattered electron images (BEIs) were taken at room temperature. The energy-dispersive spectrum (EDS) was recorded within the energy range of 0–10 keV. The transmission electron microscope (TEM) images were taken using JEM-100 CX II (with resolution 3 Å to 1.4 Å and accelerating voltage 20-100 kV in 20 kV steps). Soft X-ray absorption spectroscopy (XAS) at Mn, Cu L-edge were recorded at polarized light soft X-ray absorption beamline Indus-2 at RRCAT, Indore India. The sintered pellets' surface was polished and coated with high purity silver pest (Alfa Aesar) for electrical measurements. The temperature-dependent electric measurements were carried out using the Novo-Control GmbH set-up. Temperature-dependent DC-magnetization measurement was carried out using 7 Tesla SQUID-VSM (Quantum Design Inc., USA).

3. Results and Discussion

3.1 Structural Analysis

3.1.1 X-ray Diffraction Analysis

Room temperature X-ray diffraction (XRD) patterns of LCM are shown in Fig. 1 along with their Rietveld refinement patterns, where red-colored open circle curve represents the recorded XRD pattern, the black-colored solid-line curve represents the calculated patterns of XRD refinement data, the green vertical lines show Bragg's positions of XRD peaks and the blue-colored curve shows the difference between the observed and calculated XRD data. The Pseudo-Voigt function with '*Pnma*' space group (for orthorhombic phase) is used to fit XRD patterns. The linear interpolation method is used for background data fitting. The scale factor, half-width parameters and isotropic thermal parameters (B_{iso}) are kept varying throughout the refinement process.

The peak splitting in the vicinity of 32° , whose hkl indices are (002) and (121) and d -spacings are 2.7688 Å and 2.7570 Å, respectively, is an indication of the particular space group. Table 1 shows the results of XRD refinement, where the B_{iso} values of Cu/Mn and Oxygen atoms are higher than La-atoms, indicating that the displacements of B-O bonds significantly affect the physical properties of this ceramic [26-28].

Scherrer's equation has been used to measure the average crystalline size of LCM, as given below:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad \dots (1)$$

where D is average crystalline size, k is a constant (shape factor = 0.9), λ is the wavelength of the X-ray radiation used ($\lambda_{Cu} = 1.5406$ Å), β is the full width half maximum (FWHM) and θ is the respective angle. The observed average crystal size is 38 ± 2 nm.

It is well known that the nano-sized crystals influence the spontaneous orthorhombic lattice strain. Therefore, in order to observe this effect, spontaneous lattice strain was measured by using equation (2):

$$S = \frac{2(c-a)}{(c+a)} \quad \dots (2)$$

where a and c are the lattice parameters (for '*Pbnm*' space group c replaces by b) and ' S ' is the spontaneous lattice strain. The obtained spontaneous strain value (S) is 7.1×10^{-3} , which

is higher than micro-structured ceramics (6.7×10^{-3}). This small change in strain affects the bond angles between Mn-O-Mn, which in turn affects the physical properties of this ceramic.

3.1.2 Geometrical analysis

Fig.2 shows a schematic crystal structure of LCM, in which each $\text{Cu}^{2+}/\text{Mn}^{4+}$ -ion octahedra surrounded by six O^{2-} -ions (two O_1 and four O_2). The presence of Cu^{2+} -ions produces Jahn-Teller (JT) distortion in the lattice structure of this ceramic, which can be identified by observing orbital mixing coefficient c_1 and c_2 . These coefficients can also determine the orbital occupation. The results of crystal geometry analysis are shown in Table 2. The distortion parameter Δ of a polyhedron with an average B-O distance $\langle d \rangle$, is defined as $\Delta = \left(\frac{1}{N} \right) \sum_{n=1}^N \left\{ \frac{d_n - \langle d \rangle}{\langle d \rangle} \right\}^2$. The average tilt angle $\langle \varphi \rangle$ of BO_6 octahedra around the pseudo cubic [111] direction is obtained from the two super-exchange angle θ_1 and θ_2 . The local modes characterizing the JT-effect defined as $Q_2 = 2(l - s)/\sqrt{2}$ and $Q_3 = 2(2m - l - s)/\sqrt{6}$, where l , m and s stand for long, medium and short Mn-O distances. The orbital mixing coefficient c_1 and c_2 ($c_1^2 + c_2^2 = 1$) can be obtained from the relations: $\tan \varphi = Q_2/Q_3$ and $\tan \left(\frac{\varphi}{2} \right) = c_1/c_2$ [29]. As both super-exchange angles, Mn- O_1 -Mn and Mn- O_2 -Mn are deviated from 180° , which affect the possible magnetic interactions in the system (which will be discussed in the section 3.3). The observed value of distortion factor Δ is indicative of Jahn-Teller distortion in LCM. Owing to JT-distortion, $\text{Cu}(2+)$ ions in LCM produce vacant 3d-states, which may act as a hoping sites for charge carriers and improve the electrical characteristics of the LCM. Furthermore, this distortion leads to super-exchange interaction between Cu-O-Mn, which causes non-collinearity in the AFM response of LCM. The difference in the numerical values of orbital mixing coefficients c_1 and c_2 is indicative of the orbital disordering and also improves the short-range interactions, which affect the electrical and magnetic characteristics of LCM. In order to probe the effect of geometrical variations on crystal symmetry, we have observed the crystallographic structure of LCM by using geometrical parameters, following expressions of tolerance-factors are used [30]:

$$f = \frac{r_A + r_O}{\sqrt{2} (\langle r_B \rangle + r_O)} \quad \dots (3)$$

$$f_{obs} = \frac{d_{A-O}}{\sqrt{2} \langle d_{B-O} \rangle} \quad \dots (4)$$

where r_A , r_B and r_O represent the effective ionic radius of the A-site, B-site cations and oxygen atom, respectively. d_{A-O} represents the average atomic distance between A-site cations and the nearest oxygen atoms and d_{B-O} represents the average distance between B-site cations to the nearest oxygen atoms, respectively. ' f_{obs} ' stands for the observed tolerance factor that defines the experimental value obtained from the XRD experiment. After putting appropriate values of r_A , r_B , r_O , d_{A-O} , and d_{B-O} , the estimated tolerance factors are $f = 0.87$ and $f_{obs} = 0.91$, indicating that the symmetry of the compound is either monoclinic or orthorhombic [29-32].

The deviation of tolerance factor from the ideal rock-salt structure may also introduce lattice strain [33]; therefore, to estimate the average crystal size and strain parameters, the given size-strain expression (equation-5) is employed [34-38]:

$$\left(\frac{d_{hkl} \beta \cos\theta}{\lambda}\right)^2 = \frac{k\lambda}{D} \left(\frac{d_{hkl}^2 \beta \cos\theta}{\lambda^2}\right) + \left(\frac{\varepsilon}{2}\right)^2 \quad \dots (5)$$

where ' d_{hkl} ' represents the inter-planar spacing of particular planes and ' ε ' represents the average strain of the lattice. ' β ' represents FWHM of the corresponding peaks and ' D ' represents the average crystalline size. ' k ' is the Scherrer constant or shape constant ($k = 0.9$). Fig.3 shows the respective plot of equation (5). The estimated average size of the crystals is 45.3 ± 3 nm, consistent with the measured value using Sherrer's equation (1) (38 ± 2 nm). The evoked strain is estimated by extrapolating the fitting line and it is equal to 9.02×10^{-3} .

3.1.3 Morphological analysis (SEM and TEM analysis)

Figs. 4 (a) and (b) show scanning electron microscope (SEM) images of the cleaved LCM ceramic surface, where irregular shape of grains of different sizes are visible. Fig. 4 (c) shows the low contrast backscattered electron image (BEI), indicating uniform chemical composition distribution with lack of precipitates. The energy dispersive spectrum (EDS) is shown in Fig. 4 (d) recorded at different sites marked by orange-colored cross symbols (+) in Fig. 4 (c). The EDS of LCM shows sharp energy lines for all constituent elements of ceramics and confirming the uniform stoichiometry of this compound.

Fig. 5 (a) shows the HRTEM (high resolution transmission electron microscopy) image of the individual grain of LCM, where estimated inter-planar spacing values, $d = 1.948 \text{ \AA}$ and $1.203 \text{ \AA}$, are consistent with the d -spacing of the planes (040) and (243). The inset of Fig. 5 (a) shows the close view of a crystal (TEM image), indicating $53.6 \pm 2 \text{ nm}$ -sized crystal. This individual grain's measured size is larger than that of the average crystalline size, which was estimated using Scherrer's equation ($38 \pm 2 \text{ nm}$) and from the fitting of size-strain plot ($47.3 \pm 3 \text{ nm}$). We deduced from the high-resolution TEM that the grains consist of smaller crystallites with different orientations (Fig. 4 (a)). Fig. 5 (b) shows the selected area electron diffraction (SAED) patterns of LCM. Bright spots are indicative of the single-phase crystals. However, several sites display two bright spots due to the overlap of the HRTEM.

3.1.4 XAS analysis

XAS spectra were recorded at the Cu L-edge and Mn L-edge to investigate the charge state of Cu and Mn ions in LCM. Figs.6 (a) and (b) show the room temperature XAS spectrum of LCM along with the reference samples CuO (for Cu^{2+} state) and MnO_2 (for Mn^{4+} state). In Fig. 6 (a), of Cu-L edge, two broad features centered around 932 eV and 954 eV indicate the spin orbit split multiplets of L₃ and L₂ edges, respectively entirely consistent with the reference peaks of CuO, indicating 2+ valence state of Cu-ions in LCM. Similarly, for Mn ions, the peaks at 645 eV and 657 eV indicate L₃ and L₂ edges, respectively, consistent with the reference spectrum of MnO_2 , L₃, and L₂ edges. These features confirm the presence of the 4+ valence state of Mn-ions in LCM [39].

3.2 Electrical Characterization

3.2.1 Dielectric Analysis

Fig. 7 (a) shows the real part ϵ' of complex dielectric permittivity in the temperature range 80 K to 300 K and in the frequency range 3 kHz to 1 MHz. This plot shows two anomalies; (i) A steep-increasing behavior in the temperature range of 80 K to 120 K, indicating the orientation of local charge carriers or dipoles, which were not settle-down at low temperatures [40-42]. As the frequency increases, these anomalies are tending to higher temperatures, indicating dielectric-relaxation in this region. (ii) The plateau regions, with $\epsilon' \sim 500$, in the temperature range 120 K to 200 K, indicating saturation of polarization of the local charge carriers or dipoles, were available at low temperatures. In addition, the values

of dielectric dispersion decrease for higher field frequencies in the temperature range 200 K-250 K, which indicates the lack of polarization of the available dipoles in LCM [43-47]. Furthermore, the increase in dispersion values, reaching $\epsilon' \sim 10^3 - 10^4$, near room temperature, indicates that the accumulation of local charge carriers and thermally generated new charge carriers at grain boundaries improve the dielectric dispersion features of LCM.

The crystalline size of the ceramics and conducting nature of the grain boundaries also play a significant role in the complex dielectric permittivity measurement [45, 47-49]. As the crystalline size of this ceramic is nanometric, the contribution of individual grains and grain boundary surface layers becomes more significant, leading to such a high dielectric response of LCM ($\sim 10^4$). In our previous study [25], it was reported that the magnitude of dielectric permittivity of the order of $\sim 10^2$ for the micro-sized LCM.

Fig. 7 (b) shows the imaginary part of the dielectric permittivity ϵ'' as a function of temperature (80 K to 300 K) and at various field frequencies (3 kHz to 1 MHz). A sigmoidal increase in absorption data indicates the dominating nature of thermally generated charge carriers near room temperature. In addition, hopping of local charge carriers gives well-resolved relaxation peaks in the vicinity of low temperatures (85 K to 110 K) and in the frequency range (20 kHz to 1 MHz) as shown in Fig. 8 (a). These peaks indicated the occurrence of more than one type of relaxation process in this ceramic [45, 50-54]. The relaxation-peak frequency (f_{max}) was estimated by using equation (6):

$$\omega\tau = 1 \quad \dots (6)$$

where $\omega = 2\pi f_{max}$ and τ is the most probable relaxation time. The characteristic relaxation time τ_o can be determined by the modified Arrhenius equation given below:

$$\tau = \tau_o \exp\left(\frac{E_a}{k_B T}\right) \quad \dots (7)$$

where τ_o is the characteristic relaxation time at infinitely high temperature, E_a is the activation energy involved in dielectric relaxation, k_B is the Boltzmann constant and T is the temperature in Kelvin. The respective plot of equation (7), in the temperature range 85 K-110 K is shown in Fig. 8 (b).

The estimated activation energy values of E_a and the characteristic relaxation time τ_o , are 127 meV and 16 ps respectively, indicating that the relaxation process is driven by the nearest-neighbor-hopping (NNH) of small polarons [55-57].

3.2.2 Electric modulus analysis

We can elucidate the opacity resulting from grain/grain boundary effects during the analysis of the complex dielectric behavior of this sol-gel-derived nano-sized LCM ceramics by electric modulus analysis. The electric modulus plots were prepared using the following equations with the help of complex dielectric data [56]:

$$M^* = 1/\varepsilon^* = 1/(\varepsilon' + i\varepsilon'') = M' + iM'' \quad \dots (8)$$

where:

$$M' = \frac{\varepsilon'(f)}{\varepsilon'^2(f) + \varepsilon''^2(f)} \quad \text{and} \quad M'' = \frac{\varepsilon''(f)}{\varepsilon'^2(f) + \varepsilon''^2(f)}$$

Fig. 9 (a) shows the real part of modulus spectra M' as a function of frequency 'f' at various temperatures. Smaller values of M' in the lower region of frequency indicate that the electrode polarization has a small contribution to the dielectric behavior of LCM. Furthermore, an exponentially decaying nature of M' vs logf plot indicates the short-range mobility of charge carrier and the appearance of a conductive dielectric relaxation process. Saturation in high-frequency regions indicates that the thermally generated charge carriers have weak restoring-force against the applied field frequency, producing short-range mobility in the charge carriers.

Analysis of $M''(T, f)$ behavior gives more information about the mechanism of electrical transport and conductive relaxation under ambient conditions. Fig. 9 (b) shows M'' vs. logf plot at different temperatures. We discerned peaks in the spectrum, tending towards higher frequency with increasing temperatures, which indicates the thermally activated relaxation process. The condition of such maxima was already discussed in the dielectric absorption analysis section (See section 3.2.1).

The relaxation time-temperature-dependent plot is shown in Fig. 9 (c). The linear dependence of relaxation time with the reciprocal temperature allows us to apply Arrhenius law to fit experimental data using equation (7). The estimated activation energy is 107.2 meV, and the corresponding characteristic relaxation time is 5.02 ps. We deduce that the

phenomenon of charge transfer between the B-site ions is one of the reasons for the polaronic relaxation at low temperatures. However, the distribution of relaxation time, deduced from the broadness of the peaks in the spectra, indicates a distribution of small energy barriers. This effect could be verified by analyzing the stretch exponent value β of the Bergman approximation over the Kohlrausch-Williams-Watt (KWW) function. This approach enables us to fit the modulus data directly in the frequency domain; by using the following equation:

$$M''(f) = \frac{M''_{\max}}{1 - \beta + \frac{\beta}{1 + \beta} [\beta (\frac{f_{\max}}{f}) + (\frac{f_{\max}}{f})^\beta]} \quad \dots (9)$$

where $M''_{\max}$ is the peak value of the imaginary part of modulus and the $f_{\max}$ is the corresponding peak frequency, the corresponding plot at 80 K, is shown in Fig. 9 (d). We have chosen $\beta = 0.7$ to obtain the proper fitting of the curve, which indicates that the presence of non-Debye relaxation in the dielectric behaviour of this ceramic [56-61].

Fig. 9 (e) shows the Cole-Cole plot of modulus data in the coordinates of $M''(f)$ vs. $M'(f)$ at different temperatures. Fig. 9 (e) exhibits a deviation of the Cole-Cole plot from a perfect semicircle, indicating that the dielectric response has a non-Debye relaxation.. Fig. 9 (f) shows the normalized spectra of $M''(f, T)$ data i.e. $M''/M''_{\max}$ vs. $\log(f/f_{\max})$, where $M''_{\max}$ corresponds to the peak value of M'' and $f_{\max}$ corresponds to the frequency of the peak maximum of $M''(f, T)$. Fig. 9 (f), exhibits a complete overlap of all observed curves into a single master curve, indicating the relaxation time distribution is independent of temperature [60, 62].

3.2.3 Electrical conductivity analysis

Fig. 10 shows the variation of AC-conductivity as a function of temperature at various measuring frequencies (20 Hz to 1 MHz). The Koop's model explained that 'low-frequency conductivity influenced by grain boundary of the system and dispersion arises at higher frequencies is highly influenced by the conducting grains' [47]. In this LCM ceramics, nano-sized grains may serve as a hoping-sites for the charge carriers even at low temperature due to the presence of charge interaction between La-O, Mn-O and Cu-O at different energy states. These interfacial energy states act as conductivity centers, which are a function of frequency and temperature. The hoping of charge carriers between these conductivity centres causes relaxation peaks in the conductivity spectra of LCM, as shown

in inset (a) of Fig. 10, (in the temperature range 90 K to 140 K and in the frequency range 100 kHz to 1 MHz). The characteristics of these relaxation peaks are consistent with the dielectric absorption behavior of this LCM ceramics.

To study the conductivity behavior of LCM, we divided it into two parts; only the temperature dependent part and temperature and frequency dependent part of electrical conductivity. The first part of conductivity is related to the thermally drift of charge carriers and follows the Arrhenius relation:

$$\sigma_{dc}(T) = \sigma_0 e^{(-\frac{E_a}{k_B T})} \quad \dots (10)$$

where E_a is activation energy required for electrical conduction and σ_0 represents the pre-exponential factor. The plots of $\log \sigma$ vs. $1000/T$ for several applied frequencies are shown in the inset (Fig.b) of Fig. 10. The observed data points were fitted using equation (10) up to the reasonable linear limit for the lowest available frequencies. The average value of the estimated activation energy is 160 meV, which indicates the thermally generated small polaronic or electronic nature of electrical conduction [51, 56].

We propose that the hopping of charge carriers between trapping centers available at interfacial states present in this material is one of the strong reasons for relaxation peaks in the lower range of temperatures. The presence of Cu^{2+} -ions leads to the JT-distortion and breaks the degeneracy of $3d$ -orbital and produces vacant states, which function as additional hopping sites or trapping centers for charge carriers at low temperatures. The plot of peak relaxation times, $\tau_{\max}$ vs. reciprocal of the peak temperature, is shown in inset (Fig. b) of Fig.10. The estimated value of activation energy is 117 meV, which is consistent with the activation energy determined from M'' data (107.2 meV, see Fig. 9 (c)), suggesting that the phenomenon of electrical conduction dominated over dielectric relaxation, and both are driven by small polarons [63].

The power-law is employed to analyze the non-linear features of conductivity [64] as:

$$\sigma(\omega, T) = \sigma_0(T) \omega^n(T) \quad \dots (11)$$

where σ_0 is temperature-dependent pre-exponent of conductivity, n is the exponent parameter devoted to the deviation of the dielectric characteristics of this material from

Debye behavior and it also highlights the inter-ionic coupling strength. It has been mentioned in the literature that the polaronic-conductance mechanism includes locally degenerated charge carriers, electronic dipole moments and elastic energy [65, 66].

To study the effect of frequency on the conductivity behavior of LCM, we focused on the high frequency (> 50 kHz) data of this compound. Equation (11) is employed to fit the plots of $\log \sigma$ vs. $\log f$ (inset in Fig. 11) in the temperature range 120 K to 320 K. Fig. 11 shows the plot of exponent parameter n vs. T , obtained by the slope of the fitting of $\log \sigma$ vs. $\log f$ plots. The decreasing nature of n is followed by a saturation near 300 K, indicating that the conductivity characteristic of LCM is driven by the correlated barrier hopping mechanism associated with the overlapping of small-polaron tunneling mechanism. This characteristic influenced the dielectric behavior of this ceramic [34, 67-70].

3.2.4 DC resistivity analysis

To analyze the conductivity characteristic of LCM, more precisely, we studied its dc-resistivity, ρ , behavior across a wide range of temperatures. Resistivity ρ vs. temperature plot in the temperature range 80 K to 490 K is shown in Fig. 12. The resistivity value decreases with increasing temperature from 7.3×10^4 to $9.3 \times 10^{-3} \Omega \text{ m}$, supporting the negative coefficient of the temperature of resistivity. This temperature-dependent semi-conducting nature of resistivity characteristic of LCM suppresses the appearance of the relaxation-peaks in the high-temperature dielectric response of LCM [71-73]. To study the effect of temperature, we divided its dc-resistivity behavior into three-parts: (i) Conduction due to drift of the thermally active charge carriers at the temperature above 350 K, which supported thermally activated conduction (TAC) mechanism of the conduction (equation (12)), (ii) Conduction due to the presence of small polarons in the temperature range 190 K to 280 K, accompanied the nearest-neighbor hopping (NNH) mechanism (equation (13)) (iii) conduction due to the presence of available interfacial-sites (with distributed activation energy) at the temperature below 190 K, favoured the variable range hopping (VRH) mechanism of the conduction. We used the Mott-VRH model as proposed by Hunt (equation (14)) to study the VRH mechanism of conduction in the LCM [66, 74-76]:

$$\rho = \rho_0 e^{\left(\frac{E_{TAC}}{k_B T}\right)} \quad \dots (12)$$

$$\rho = \rho_0 e^{\left(\frac{E_{NNH}}{k_B T}\right)} \quad \dots (13)$$

$$\rho = \rho_0 e^{\left(\frac{T_0}{T}\right)^{\frac{1}{4}}} \quad \dots (14)$$

Here E_{TAC} and E_{NNH} are the activation energy related to TAC and NNH type of conduction and ρ_0 is the pre-exponent parameter. k_B is the Boltzmann constant, T is the absolute temperature. In equation (14), T_0 is the Mott-temperature related to the available density of state near Fermi energy $N(E_f)$ as:

$$T_0 = \frac{16\alpha^3}{k_B N(E_f)} \quad \dots (15)$$

where ' α ' is the tunneling probability [56].

The red-colored trace belongs to the region of the TAC mechanism and its corresponding Arrhenius fitting, by using equation (12) is shown in the inset (Fig. (a)) of Fig. 12. The observed activation energy $E_{TAC} = 185.5$ meV with $\rho_{TAC} = 1.4 \times 10^{-4}$ ($\Omega\cdot m$), which supported the short-range mobility of thermally generated charge carriers. In the temperature range, 190 K – 280 K, the nearest neighbor interstitial sites serve as hopping sites for charge carriers. Charge carriers can jump between these sites either by absorbing the phonons or by releasing the phonons. The activation energy required for such an NNH process could be estimated using equation (13), where E_{NNH} represents the required activation energy or potential fluctuation for defects level [77]. The estimated value of E_{NNH} is equal to 132.5 meV with $\rho_{NNH} = 9.8 \times 10^{-4}$ ($\Omega\cdot m$). We observed a non-linearity in the $\log \rho$ vs $1000/T$ plot as temperature goes below 190 K (see blue-colored incircle in the inset (Fig.(a)) of Fig. 12), indicates that the hopping of charge carriers is possible only at the most prominent sites available at low temperatures. The VRH mechanism of the conduction can be used to analyze such drifting of charge carriers. Hence, the resistivity at low-temperature was analyzed by using equation (14). On considering the three-dimensional hopping condition, we have chosen the exponential value '1/4', and the corresponding plot is shown in the inset (Fig.(b)) of Fig. 12. The estimated value of Mott temperature T_0 is 41.2×10^7 K and the corresponding value of available density of state near Fermi energy level is $N(E_f) = 2.75 \times 10^{25}$ eV⁻¹. Such density of defects may be generated due to the disordering (like; structural) and/or defects (like; antisite defects) present in ceramics, which influenced the conductivity and dielectric behavior of the ceramic [56, 68, 78, 79].

3.3 DC magnetic field analysis

The dc-magnetic behavior provides charge exchange interaction between B-sites ions and Oxygen-ions. Fig. 13 (a) shows the Zero-Field Cooled (ZFC) and Field Cooled (FC) magnetization measurement at 100 Oe of LCM ceramics. It is evident from the magnetization behavior that the ZFC and FC cycles show a maximum at 18 K, below which the ZFC curve shows a sharp drop and FC curve gradually decreases down to 9 K (as shown in the inset of Fig. 13 (a)). These observations suggest that below 18 K, this compound has anti-ferromagnetic behavior. Moreover, a strong magnetic-irreversibility is observed in the M-T behavior of LCM, temperature above 18 K, indicating some additional magnetic coupling between B-site ions other than $\text{Mn}^{4+}\text{-O}^{2-}\text{-Mn}^{4+}$ networks. To probe the cause of such irreversibility, we have analyzed inverse susceptibility data with respect to temperature. Fig. 13 (b) shows the temperature-dependent inverse magnetic susceptibility plot fitted by Curie-Weiss (C-W) equation as; $1/\chi = (T-T_C)/C$, where T_C is the Curie temperature and C is the Curie constant. Deviation of the fitting near 100 K and positive value of Curie temperature (T_C) indicate the presence of short-range magnetic correlation and the existence of some ferromagnetic (FM) kind of interaction in this ceramic. By fitting, the estimated value of the effective-magnetic moment is $5.84\mu_B$ per ion, which is higher than the magnetic moment arise due to Mn^{4+} ions; $4.0\mu_B$. It confirms that not only Mn^{4+} ions are responsible for magnetic ordering, but also Cu^{2+} ions play a significant role in deciding the magnetic ordering of this material [80-85]. On the other hand, the presence of Cu (2+) ions produces John Teller-distortion (JT) in this polycrystalline ceramics, which provides vacant 3d-shells, strengthening the interaction between $\text{Cu}^{2+}\text{-O}^{2-}\text{-Mn}^{4+}$ ions, which is ferromagnetic in nature. Beside this observation, we have discussed in the section: 3.1.1 that the bond angles of Mn-O₁-Mn and Mn-O₂-Mn are not equal to 180°, which is one of the essential conditions for being a ceramic perfect antiferromagnetic. Also, the angle between O₁-Mn-O₂ is not exactly 90°. So, LCM was neither hold a complete ferromagnetic nature or antiferromagnetic nature. Therefore, LCM have canted antiferromagnetic behaviour.

Fig. 14 (a) shows the magnetization vs. magnetic field (M-H) loops at different temperatures for LCM. The non-linear nature of the M-H hysteresis loop at 25 K and 40 K confirms the existence of short-range magnetic correlation, which was reflected in the inverse magnetic-susceptibility behavior of this ceramic (χ^{-1} vs T plot). The M-H plots become straight as temperature goes above 100 K as expected for the materials paramagnetic state. Interestingly, at 5 K, the M-H hysteresis loop showed a coercivity of 700 Oe, but for a collinear-antiferromagnetic system, one would expect a linear hysteresis

behavior without any coercivity. Therefore, it appears that the present system has a non-collinear antiferromagnetic structure or canted antiferromagnetic structure. The positive value of the Curie temperature (31.4 K) supported this assumption as well. Moreover, at a lower temperature (below ~100 K), the magnetic moment was still unsaturated, even at 7 Tesla of the applied magnetic field and this feature again indicated the canted-antiferromagnetic nature of the sample. However, neutron diffraction study would be a promising approach to get a better idea of the magnetic structure, exchange interactions, and charge-states of such ceramics constituents. Overall, we can say that the magnetic response of LCM is canted-antiferromagnetic because of the super-exchange interaction between $\text{Cu}^{2+}\text{-O}^{2-}\text{-Mn}^{4+}$, a similar nature was observed by Blasse [86].

4. Conclusion

The LCM sample was prepared using the traditional sol-gel reaction method. The single-phase orthorhombic crystal structure (space group, '*Pnma*') was confirmed by XRD analysis and the charge states of Cu (2+) and Mn (4+) ions were confirmed by analysis of the XAS spectrum of LCM. The presence of divalent cation, Cu^{2+} at B-site, influenced the structural, electric and magnetic behavior of LCM. JT-distortion and degeneracy of 3d - shell, provided additional hopping sites for charge carriers and improved the VRH mechanism of conductance in the ceramic. It supported super-exchange interaction between $\text{Cu}^{2+}\text{-O}^{2-}\text{-Mn}^{4+}$ ions, one of the regions for the non-collinearity in the AFM response of LCM. The nano-sized grains strengthened the small-dipole moment at low temperature and enhanced the dielectric permittivity of this material. The value of stretched exponent parameter β confirmed the non-Debye relaxation and the observed relaxation time the dominant nature of small-polaron hopping in this material. The analysis of the ac-exponent parameter, n , confirmed the correlated barrier hopping mechanism associated with overlapping of small polaron tunneling mechanism of conductance. The interaction between copper (Cu^{2+}) and Manganese (Mn^{4+}) ions provided short-range hopping sites for charge carriers at low temperatures. The dc-resistivity response showed VRH mechanism at low temperature (below 180K) and TAC at high temperature (above 350K). Dc-magnetic measurement of this ceramic showed canted antiferromagnetic behavior and manifested a short-range magnetic correlation up to 100 K. The value of effective magnetic moment; $5.84 \mu_B$ favored the possibilities of spin-orbit coupling for magnetic behavior of LCM. The

positive value of Curie temperature (31 K) and finite value of coercivity also confirmed the canted-AFM interaction in LCM.

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Conflicts of interest

There are no conflicts of interest to declare.

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Figures

Figure 1

Rietveld refinement of the X-ray diffraction pattern carried out in the orthorhombic phase of La₂CuMnO₆ ceramics.

Figure 2

Crystal structures of $\text{La}_2\text{CuMnO}_6$ nano-ceramics. Pseudo-3D views are shown at different angles (a) a view looking along 'a'-axis of two adjacent layers of Cu/MnO_6 . (b) a view looking along 'b'-axis of two adjacent layers of Cu/MnO_6 .

Figure 3

Size – strain plot of La₂CuMnO₆ for analysing the average crystalline size.

Figure 4

(a) SEM image of LCM, (b) SEM image at higher magnification, (c) backscattered electron image (BEI) of the cleaved $\text{La}_2\text{CuMnO}_6$ ceramics, compositional analysis performed at several points are labeled by (+) and (d) EDS spectrum of the major phase.

Figure 5

TEM and HR-TEM images of $\text{La}_2\text{CuMnO}_6$ ceramics; (a) orange lines highlight the particular d-space and (b) blue incircles indicate the respective hkl plane.

Figure 6

XAS spectrum of La₂CuMnO₆ ceramics at particular states of (a) Cu²⁺ states and (b) Mn⁴⁺ states.

Figure 7

The variation of real part (a) and imaginary part (b) of dielectric permittivity with temperature of $\text{La}_2\text{CuMnO}_6$ at different frequencies ranging 3 kHz to 1 MHz.

Figure 8

(a) zoomed view of low-temperature peaks of dielectric absorption curve and (b) Arrhenius plot of the peak positions of the curves.

Figure 9

Electric modulus analysis diagrams of La₂CuMnO₆ nanocrystals. (a) M' vs $\log f$ at different temperatures, (b) M'' vs $\log f$ at different temperature, (c) $\log \tau$ vs $1000/T$ plot, (d) & (e) Cole-Cole plot of M'' vs M' at different temperature, (f) normalized scaling behaviour of imaginary part of modulus data.

Figure 10

Temperature variation of ac conductivity of La₂CuMnO₆ nanocrystals. (a) zoomed view of peak positions (b) Arrhenius fitting of respective peak positioned.

Figure 11

Stretched exponent parameter 'n' variation with temperature of ac conductivity of La₂CuMnO₆ ceramics estimated from $\log \sigma$ vs frequency plot.

Figure 12

Dc-resistivity variation with temperature of La₂CuMnO₆ nano-ceramics, (a) plot of log ρ vs inverse of T fitted by modified Arrhenius equations used for TAC and NNH mechanism of conductivity, (b) plot of $\ln \rho$ vs $T^{-1/4}$ fitted by Mott-VRH model.

Figure 13

(a) Magnetization vs temperature plots (zoomed view of M-T plot at peak position shown in the inset) and (b) inverse susceptibility versus temperature plot of $\text{La}_2\text{CuMnO}_6$ nano-ceramics.

Figure 14

(a) Magnetization versus magnetic field (M-H) diagrams at different temperatures, (b) zoomed view of M-H plot of La₂CuMnO₆ nano-ceramics at 5 K.

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