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Optical and functional properties of hydrothermally synthesized tetragonal Ba$_{0.4}$Cu$_{0.6-x}$La$_x$TiO$_3$ (x = 0.2–0.6) nanoparticles

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Abstract

Ba$_{0.4}$Cu$_{0.6-x}$La$_x$TiO$_3$ (x = 0.2, 0.4 & 0.6) (BCLT) nanoparticles were prepared by hydrothermal method. The x-ray diffraction (XRD) pattern established the existence of tetragonal phases. The nanospheres were observed in the surface morphology of present materials using the transmission electron microscopy (TEM). The optical properties were investigated to confirm the presence of metal oxide bonds as well as the optical band-gap energy of BCLT nanoparticles. The dielectric and impedance parameters were studied as a function of frequency and composition. The Cole-Cole plots were drawn to understand the microstructure and electrical conduction mechanism. In addition, the ferroelectric nature was carried out with the help of polarization versus electric field (P-E) loop tracer.

1. Introduction

It is a known fact that most of the ceramic titanate materials contain the cubic perovskite structure with a general chemical formula ABO$_3$, where 'A' atom is located at the corner position, 'B' atom occupies the body centre position and the oxygen atom prefers at the face centre position of the cubic unit cell [1–10]. In general, the barium titanate (BT) is a promising dielectric material exhibiting very attractive and tremendous applications caused due to the low particle size [11]. In addition, the barium titanate is extensively investigated by many researchers because of its excellent practical applications such as colossal magnetoresistance, ferroelectric, magnetoelectric and electro-optic effects [12]. Because of intrinsic capability of perovskite structure to host dopants in different size, the BaTiO$_3$ lattice can be accommodated with large number of distinct dopants. This behavior can lead to exhibit the semiconducting nature. However, it is produced by atmospheric reduction method by doping with trivalent elements (La, Y & Sb) at Ba-cationic sites [13]. The ferroelectric nature of barium titanate (BT) mainly depends on the pressure, temperature, time of sintering, grain size, defects and different types of doping agents. The modification of ferroelectric and dielectric properties is achieved by the substitution of dopants Ba or Ti with small concentrations [14]. In case of the nanoparticles synthesis, it gives more advanced results than the bulk synthesis. Many researchers prepared the BT bulk material and dielectric properties through various methods like hydrothermal, sol-gel, micro-emulsion, polymeric precursor, conventional sintering and micro wave heating [15–18]. In addition, the BT microspheres were formed via the hydrothermal method [13]. Besides, the barium copper titanate nanoparticles with cubic structure were prepared and investigated for structural, morphological and optical properties via the hydrothermal technique [14]. After completion of literature survey, it is concluded that there is no work on La-substituted barium copper titanate nanoparticles. Hence, the authors put efforts on the synthesis and characterization of BCLT nanoparticles via hydrothermal method.

2. Materials and methods

Ba$_{0.4}$Cu$_{0.6-x}$La$_x$TiO$_3$ (x = 0.2, 0.4, & 0.6) nanoparticles were synthesized via hydrothermal technique. The flow chart for the preparation of BCLT samples was depicted in figure 1. The starting raw materials of Ba(NO$_3$)$_2$·6H$_2$O...
(99.8% purity, Sigma-Aldrich), Cu(NO₃)₂·2H₂O (99.9 % purity, Sigma-Aldrich), LaN₂O₆·6H₂O (99.8 % purity, Sigma-Aldrich) and TiO₂ (99.9 % purity, Sigma-Aldrich) were weighed according to the stoichiometric ratio using a sensitive digital weighing machine. The copper nitrate and lanthanum nitrates were taken in a glass beaker and mixed with distilled water with 1:3 ratios. Then NaOH was added slowly to the resultant solution. As a result, we observed the pH varying from 9 to 12. Afterwards, the total solution was taken into a 300 ml teflon-lined steel autoclave. Furthermore, this solution was posted to a hot-air oven and reaction was made at 150 °C for 8 h. At the end of the experiment, the autoclave was slowly cooled to room temperature. The final Ba₀.₄Cu₀.₆−ₓLaₓTiO₃ nanoparticles were removed from the Teflon lined autoclave and washed with acetone and distilled water till the pH becomes equal to 7. In this process, the obtained fine powder was completely grinded and then heated for one hour.

Finally, the prepared material was characterized using characterization techniques like X-ray diffractometer (Bruker XRD, CuKα, λ = 0.15406 nm), High Resolution Transmission Electron Microscope (HRTEM: Model Tecnai G20, FEI, USA), Field-emission Scanning Electron Microscope (Ultra 55, FE-SEM Carl Zeiss), FT-IR spectrophotometer (IR affinity-1, Shimadzu), UV-Visible spectrophotometer (JASCO, V-670 PC), LCR controller (HIOKI 3532-50, operating electric field frequency ranging from 42 Hz–5 MHz) and polarization versus electric field (P-E) loop tracer (Marine India Ltd) for the structural, morphological, optical, transport and ferroelectric properties respectively. In particular, we considered the samples in two forms such as fine powder and pellets. The fine powder was used to perform the characterizations like XRD, FE-SEM, HR-TEM, FTIR, and UV-Visible spectral analysis. Further, the pellets were prepared with dimensions of 0.14 cm thickness and 0.94 cm diameter in order to perform the dielectric and P-E loop measurements. For achieving the dielectric properties, the prepared pellets were coated with silver paste on upper and lower side. Herein, the silver paste can work as ohmic contact. Afterwards, the pellet was heated on the hot plate of the magnetic stirrer at 50 °C for 30 min. In next step, the sample was inserted between the brass electrodes (with 1.2 cm diameter) of the sample holder within the LCR measurement (with external ac power supply 1–10 mV). In the same fashion, in order to perform the P-E loop measurement the pellet (coated with silver paste) was connected parallel to 4 μF capacitor for compensation. The ferroelectric hysteresis loops of BCLT nanoparticles were carried out under an applied frequency of 600 Hz at an operating voltage of 600 V at room temperature.

3. Results and discussions

3.1. XRD Analysis

Figure 2 showed the x-ray diffraction pattern of BCLT nanoparticles. It was obvious that the x = 0.2 to 0.6 contents revealed the formation of single phase tetragonal structure. The Miller indices of these tetragonal
phases were indexed in the diffraction pattern. In addition, these reflection planes were in good consistent with the standard ICDD: 82–1269. All the peaks were of broad and high crystallinity in nature. However, the maximum intense peak was recorded at around $\sim 32.14^\circ$. Further, the average crystallite size ($D$) was calculated using the Debye Scherrer method $[19]$. The results listed in table 1 expressed that the $D$ value was noted to be changing from approximately 23 to 30 nm. Herein, the unsystematic trend of $D$ was attributed to the unsystematic manner of developed microstrain ($\varepsilon$) as a function of composition (see table 1). That is, the $D$ value of $x = 0.2$–0.4 was first increased from 27.42 to 23.13 while for $x = 0.6$, it was noted to be 29.87 nm. Thus, in overall, it showed unsystematic variation trend as function of $x$. This was attributed to the unsystematic variation trend of microstrain from 0.023 to 0.028 radian for $x = 0.2$–0.4 contents while $x = 0.6$ content showed 0.019 radian. In addition, the increasing manner of $D$ was achieved due to the decreasing trend of microstrain and vice versa. From this data, it was understood that there was a proportional relationship between average crystallite size and microstrain. This type of observation was also found in the literature $[20–26]$. The lattice constants were evaluated and presented in table 1. The results showed that the tetragonal lattice constants were increased from 4.200–4.320 Å ($a = b$) and 3.900–3.980 Å ($c$) respectively with increase of composition. It can be happened due to the cationic replacement by the effect of substituent in the perovskite structure. That means, the ionic radii of cations present in BCLT material were listed according to Shannon reports $[27]$ like this: $\text{Ba}^{2+}:1.35$ Å, $\text{Cu}^{2+}:0.73$ Å, & $\text{La}^{3+}:1.032$ Å, and $\text{Ti}^{4+}:0.670$ Å. From these reports, it was confirmed that the locations of larger ionic radii will have the probability to replace the Ti-cations of smaller ionic radii $[1]$. Thus, there may be a possibility for the enhancement of unit cell dimensions which in turn leads to the increase of

| Parameter | 0.2  | 0.4  | 0.6  |
|-----------|------|------|------|
| $L$ (Å)   | 4.200| 4.230| 4.320|
| $V$ (Å$^3$) | 68.796 | 70.68 | 74.28 |
| $D$ (nm)  | 27.24| 23.13| 29.87 |
| $d_h$ (g/c.c) | 5.04 | 5.21 | 5.37 |
| $d_0$ (g/c.c) | 4.71 | 4.92 | 5.04 |
| $P$       | 6.5  | 5.5  | 6.1  |
| Microstrain ($\varepsilon$) | 0.023 | 0.028 | 0.019 |
| W-H strain ($\varepsilon^*$) | 0.0039 | 0.0053 | 0.047 |
| $D'$ (nm) | 31.71| 26.42| 37.22 |
| $s$ (m$^2$/g) | 17.7  | 29.43 | 13.98 |

Figure 2. X-Ray diffraction spectra of the BCLT nanoparticles.
lattice constants as a function of La-content. However, it showed the increase of tetragonal unit cell volume \(V = a^2c\) as listed in table 1. The results indicated that the \(V\) was increased from \(~69\) to \(74\,\text{Å}^3\). Furthermore, the X-ray density \(d_s\) and bulk density \(d_b\) were computed (table 1). It can be understood from the results that both the density parameters were found to be increasing with increase of La-content. That is, \(d_s\) and \(d_b\) were increased from \(5.04\) to \(5.37\,\text{g/cm}^3\), and \(4.71\) to \(5.04\,\text{g/cm}^3\) respectively with \(x\). In general, it can be occurred because of the enhancement of molecular weight with \(x\). The porosity \(P\) was observed to be altering between \(5.5\) to \(6.5\,\%\). Herein, the unsystematic trend of porosity indicated that the pore fraction was varied with composition during the hydrothermal reaction temperature. This established a fact that for the small value of pore fraction, we can expect the enhanced properties. Moreover, it was known that the specific surface area \(S\) can be a significant parameter reflecting the better improvement of distinct material properties. In the present study, the \(S\) value was noticed to be varying from \(~14\) to \(30\,\text{m}^2\,\text{g}^{-1}\). This revealed the unsystematic trend due to having the reciprocal relationship with crystallite size. Moreover, we can find alternatively the average microstrain \(\varepsilon'\) and average crystallite size \(D'\) of materials using the Williamson-Hall (W-H) plots (figure 3). In case of BCLT samples, the W-H plots were drawn between \(\beta\cos\theta\) versus \(4\sin\theta\) using linear fitting relation: \(y = 0.0039x + 0.0048\) (i.e. \(y = c + mx\) form), where the slope of straight line was associated to the microstrain \(\varepsilon'\), and the intercept value was related to the crystallite size \(D'\). The obtained values of \(\varepsilon'\) & \(D'\) were listed in table 1. It was obvious from the table 1 that both \(\varepsilon'\) & \(D'\) values were in consistent with the \(\varepsilon\) & \(D\) values obtained using Scherrer relations.

3.2. Surface morphology
The FESEM micrographs of BCLT nanoparticles were presented in figure 4. It was evident from the micrographs that all the samples revealed the well defined and small spherical grains. In addition, these were distributed homogeneously within the selected area of the sample. Particularly, few spots of present materials showed the grains which were accumulated closely. It may be acquired as a result of the high interactions existed among the nanosized grains. This kind of behavior was noted in the earlier reports [28–31]. Furthermore, the average grain size \(G\) was evaluated with the help of linear intercept method (LIM) [32–34]. These were noticed to be \(85\,\text{nm}\), \(53\,\text{nm}\) & \(52\,\text{nm}\) for \(x = 0.2, 0.4\) & \(0.6\) respectively. These results expressed a fact that the grain size was decreasing with increase of substituent content. It may be in general happened owing to the increase of microstrain during the reaction temperature as discussed in the literature [11]. Besides, the presence of nanoparticles was confirmed using the TEM micrographs as shown in figure 5. It can be obviously seen that there were large number of nanospheres like particles for \(x = 0.2\) to \(0.6\). Herein, the morphology showed the presence of some fiber type of elongated nanoparticles within the vicinity of nanospheres. Similar kinds of
observations were identified in the literature reported by Kumar et al [1, 11]. From the observations of present work and the literature [1, 11], it was concluded that the presence of ferroelectric cations such as Pb & Ba and La like rare earth cations can induce the morphology of samples. Thus, these cations were capable in obtaining the change of morphology. Moreover, weak agglomeration was detected among the nanoparticles. This may be generally incurred due to the interactions produced among the BCLT nanoparticles. Moreover, the particle size was found to be changing from 18 to 34 nm. The selected area electron diffraction (SAED) patterns of x = 0.4 & 0.6 materials were shown in figure 6. Both the SAEDs indicated the well defined rings with moderate intensity related to the tetragonal reflection planes. Figure 6 provided another supportive evidence for the diffraction pattern obtained using XRD spectra.

3.3. Spectroscopic properties
The FTIR spectra of BCLT nanoparticles (of ABO3 perovskite form) were recorded over the frequency range of 400 to 4000 cm⁻¹ (see figure 7). It was obvious from figure 7 that the A and B-site frequencies were indicated as υB and υA. The frequency of A-site was noticed to be decreasing from 694.63 to 678.45 cm⁻¹ while the B-site frequency was observed to be increasing from 511.49 to 519.16 cm⁻¹. Thus, the A and B-site formation in turn suggested the formation of ABO3 perovskite structure of BCLT samples. These two sites in general will indicate the Ba–O, Cu–O, La-O and Ti-O metal oxide absorption bands. Further few absorption bands were noted at around 998.41, 1386.76, 1489.3, 1656.30, 2857.32, 2928.87, and 3429.72 cm⁻¹. Herein, the first three frequencies were associated to the bending vibrations of oxygen and hydrogen. These were acquired due to the OH-absorbed the BCLT ceramic nanoparticles [1]. In the same way, the frequencies of 2857.32, and 2928.87 cm⁻¹ were correlated to the intra-molecular stretching modes which were attributed to the various proportions of hydrogen bonding within the BCLT perovskite structure [11]. On the other hand, the frequencies
Figure 5. HRTEM pictures of BCLT nanoparticles.

Figure 6. SAED pattern of BCLT nanoparticles.
of 1656.30 and 3429.72 cm$^{-1}$ were interlinked sequentially to the O-H stretching vibrations as well as bending vibrations of water molecules absorbed by the BCLT nanomaterials [1].

In order to determine the optical band-gap ($E_g$) of BCLT nanoparticles, the $(\alpha h\nu)^n$ versus $h\nu$ plots (where $'\alpha'$ is absorptivity, and $'h\nu'$ is the photon energy) were drawn by considering $n = 2$. Since $n = 2$ is allowed for direct transition of charge carriers between the two energy bands [1, 11]. Hence the $(\alpha h\nu)^n$ versus $h\nu$ can be simply converted into the $(\alpha h\nu)^2$ versus $h\nu$ (as depicted in figure 8). It can be obviously seen from $(\alpha h\nu)^2$ versus $h\nu$ plots that the $E_g$ value was gradually increasing from 1.814 to 2.166 eV as a function of 'x'. The $E_g$ value was determined by extrapolating the linear portion of the plots (figure 8) towards the photon energy axis wherein, exactly, the absorptivity is identical to zero [1, 11]. From the results, we can understand that the increasing La-content predominantly induced in increasing the $E_g$ value.
3.4. Dielectric and impedance spectroscopic properties

The dielectric behavior of the BCLT nanoparticles was elucidated by means of studying various parameters like dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$), ac-electrical conductivity ($\sigma_{ac}$), and complex dielectric modulus ($M^{*}$). The variation of $\varepsilon'$ and $\varepsilon''$ was discussed as a function of frequency ($f$) from 100 Hz to 5 MHz as depicted in figure 9. In figure 9(a), we noticed that the high $\varepsilon'$ values were recorded at low frequencies whereas the low $\varepsilon'$ values were observed at high frequencies. The similar trend was identified in $\varepsilon''$ versus $f$ plots (figure 9(b)). This trend can be illustrated with the help of Koop’s theory which is also termed as double layer theory as described in the literature [35]. In view of double layer theory, a polycrystalline material consists of two layers such as grain and grain boundary. Within these two segments, the grain boundaries are more resistive than that of grains. Theoretically, it can be described as follows. That is, at low input electric field frequencies, all the charge carriers will be activated as well and further they will be drifted towards the grain boundary interface. Thus, it can lead to accumulation of larger number of charge carriers at the grain boundary interface. Subsequently, it can reinforce the formation of huge amount of Maxwell-Wagner’s interfacial or space charge polarization [36]. Therefore, the high $\varepsilon'$ as well as $\varepsilon''$ values can be obtained at small $f$-values. Nevertheless, at high frequencies the efficiency of space charge polarization will be reduced predominantly. Hence, the corresponding $\varepsilon'$ and $\varepsilon''$ values can be diminished at high frequencies. It was very much clear from figure 9. The similar trend was reported by the previous scientists in the literature [37–46]. In addition, the frequency dependence of $\varepsilon'$ as well as $\varepsilon''$ plots revealed the non-Debye type relaxations over the frequency range from 4 to 5 MHz. It can be normally happened due to the matching of applied electric field frequency with the oscillating electric dipole frequency [11]. As far as the numerical values of $\varepsilon'$ and $\varepsilon''$ are concerned, $\varepsilon'$ was about 73.84 while $\varepsilon''$ was $\sim -9.275$ at 20 kHz. Likewise, the $\varepsilon'$ was recorded as $\sim 2.19$ while $\varepsilon''$ was found to be $\sim 0.698$ at 5 MHz for $x = 0.6$. Indeed, these two evidences proved the BCLT nanomaterials obeying the double layer model.

The ac-electrical conductivity ($\sigma_{ac}$) was calculated using a relation: $\sigma_{ac} = 6.28 \varepsilon_{o} \varepsilon'' f$, where $\varepsilon_{o}$ is the permittivity of free space, and other symbols have their usual meaning [1]. The frequency dependence of $\sigma_{ac}$ as a function of $x$ was depicted in figure 10. It was observed that the $\sigma_{ac}$ values were noted to be large in magnitude for $x = 0.2$ to 0.6 at 100 Hz. This can be attributed to a fact that the charge carriers will be activated quickly for the input field frequency and therefore, the electric dipoles begin to oscillate. During this action, the thermal energy can be developed as well. Thus, the thermal activation of charges comes into an existence. This will in turn lead to hopping of charge carriers between two cations like Cu$^{1+}$ ↔ Cu$^{1+}$ and Ti$^{4+}$ ↔ Ti$^{3+}$. But, for the higher frequencies, the $\sigma_{ac}$ was decreased to $2 \times 10^{-5}$ S cm$^{-1}$. This was attributed to the contribution of hole conduction mechanism due to the trapped holes on Ba-O bonds. For further increase of frequency, the $\sigma_{ac}$ was identified to be increasing slowly up to 3 MHz for all La-contents. Interestingly, between 3 to 5 MHz, an abrupt increasing trend of electrical conductivity was observed consisting of prominent relaxations curves. It was also clear that for $x = 0.2$ & 0.4 contents, the relaxations were established at $f = 4.5$ MHz whereas the $x = 0.6$ content revealed the relaxation frequency at 4 MHz. From this result, we can understand that the higher La-contents can influence the relaxation behavior of BCLT samples. During the relaxation process, the hopping rate of charge carriers becomes predominant owing to the resonance behavior. Hence, the maximum value of electrical conductivity can be noted at relaxation frequency. Furthermore, the power law fit was performed to log $\sigma_{ac}$ - log $\omega$ plots as depicted in figure 16 (see supporting information section). In fact these plots can provide the dc-conductivity regions. It was a familiar fact that the ac-electrical conductivity is a combination of temperature dependent ($\sigma_{ac}$ (T)) and frequency dependent ($\sigma_{ac}$ (f)) terms. It can be mentioned mathematically as:

$\sigma_{ac} = \sigma_{ac}(T) + \sigma_{ac}(f)$
obtained for x portion of the log Fr at resonance behavior was observed in case of M grain boundary interface which create the production of high space charge polarization. The similar kind of La-content. In fact, these resonance frequencies were formed due to the accumulation of charge carriers at the range mobility of charge carriers. It was occurred in case of M predominant at low frequencies. However, the region-I can be treated as the long range polarization region. As a dependence of M hopping conduction mechanism over the frequency range of region-II. In addition, the temperature happened as a result of the short range mobility of charge carriers. Usually, we can observe the short range polarization region. This was formed at above the relaxation point. The grain size, defects, strain, and temperature can be responsible for the fluctuated like nature.

The complex dielectric modulus (M*) is written as M" = M' + jM", whereas M' = (ε'/ε'' + jε''') and M" = (ε''/ε'''' + jε''''') [11]. The dielectric modulus analysis can offer the evidence for the space charge polarization effect and electrical conduction mechanism. The real and imaginary parts of dielectric modulus (M' & M" respectively) were elucidated at length for BCLT nanoparticles as depicted in figure 11(a) and (b). It was obvious from figure 11(a) that the whole plot (M'—f) was bifurcated into two portions due to the resonance frequencies (Fᵣ). That is, the region below the resonance frequency (region-I) and the region above the resonance frequency (region-II). For x = 0.6 content (M'—f plot), the Fᵣ was noted to be 1.6 MHz while for x = 0.2 & 0.4 contents, the Fᵣ was about 2 MHz. This suggested a fact that the resonance frequency was decreased with increase of La-content. In fact, these resonance frequencies were formed due to the accumulation of charge carriers at the grain boundary interface which create the production of high space charge polarization. The similar kind of resonance behavior was observed in case of M"—f plots of x = 0.2—0.6. Herein, the x = 0.2 & 0.4 contents exhibited the same Fᵣ (2 MHz) values as in case of M'—f plots. But, interestingly, the x = 0.6 content expressed Fᵣ at ∼0.8 MHz. This indicated a fact that the space charges were activated and further accumulated at the interface on applying even small input field frequency about 0.8 MHz. In addition, in the region-I (at 100 Hz—10 kHz), the M' values were noted to be almost zero. It suggested a fact that the electrode polarization was predominant at low frequencies. However, the region-I can be treated as the long range polarization region. As a result, the long range hopping conduction takes place in region-I. It was usually formed as a result of the long range mobility of charge carriers. It was occurred in case of M'—f plots. On the other hand, the x = 0.6 content was differed from the rest two compositions in case of M"—f plots. That is, the small resonance frequency was obtained for x = 0.6 while high resonance frequencies were noted for x = 0.2 & 0.4 contents. Indeed, the small resonance frequency can be produced due to a type of ion which may move long distances. In the same fashion, the high resonance frequencies were noticed due to presence of ions which can confine to only potential well. The similar trend was identified in the literature [11]. Moreover, the region-II was called as short range polarization region. This was formed at above the relaxation/resonance frequencies for x = 0.2—0.6. This was happened as a result of the short range mobility of charge carriers. Usually, we can observe the short range hopping conduction mechanism over the frequency range of region-II. In addition, the temperature dependence of M' and M" with log f was discussed as shown in figures 11(c) and (d) (see supporting information section). It was observed that the M'—log f and M"—log f plots of x = 0.2 and 0.4 contents showed a constant trend till log f = 5 for all the temperatures (from 40⁰C—100⁰C). Beyond log f = 5, there was an abrupt increasing manner till the relaxation frequency. For all the temperatures, it was seen that the variation of relaxation frequency was almost constant. That is, for x = 0.2 content, real and imaginary parts of dielectric modulus plots showed the log Fᵣ value ∼6.3. On the other hand, the x = 0.4 content revealed the constant trend till log f = 3. Above this frequency, we noticed a gradual increasing behavior of M' and M" values till the relaxation point. The grain size, defects, strain, and temperature can be responsible for the fluctuated like nature.

$\sigma_{ac}(f,T) = \sigma_{dc}(T) + \sigma_{ac}(f)$ [11]. In the Figure 16, the frequency independent term is identified from the invariant portion of the log $\sigma_{ac}$—log $f$ plots. The calculated dc-electrical conductivity values were of $2.1 \times 10^{-5}$ (x = 0.2), $3.8 \times 10^{-3}$ (x = 0.4) & $3.2 \times 10^{-3}$ S cm⁻¹ (x = 0.6). This evidenced that the low dc-conductivity was recorded for x = 0.6 (high La-content). The rest of portions of x = 0.2—0.6 contents indicated frequency dependence trend.

The Figure 10. Frequency dependence of $\sigma_{ac}$ as a function of La-content at room temperature.

Figure 10. Frequency dependence of $\sigma_{ac}$ as a function of La-content at room temperature.
Figure 11. (a) $M'$—$f$ and (b) $M''$—$f$ plots of BCLT at room temperature.

in the dielectric modulus plots [47]. Moreover, the sharp increasing of dielectric modulus parameters was attributed to the increasing La-content in the resultant BCLT perovskite system. Apart from this, the $M'$ versus $M''$ plots were drawn to analyze the relaxation behavior as well as electrical conduction mechanism. It was depicted in figure 12(a). From figure 12(a), it was evidently noted that $x = 0.2 \& 0.4$ contents expressed the partial relaxations comprising of few distortions in the trajectory of plots. Whereas, $x = 0.6$ showed almost complete relaxation behavior due to its complete relaxation strength. However, the centers of the imagined semicircular were assumed to be below the $M'$-axis. Thus, the non-Debye relaxations were happened. The first arc indicated the occurrence of electrical conduction due to grain contribution instead of grain boundary. In figure 12(b) (see supporting information section), $M'$ versus $M''$ plots as a function of the temperature and content were shown. For $x = 0.2 \& 0.4$ contents, broad relaxation nature was diminished drastically with increase of temperature. Likewise, $x = 0.6$ showed the stepwise decreasing of relaxation with "T".

Moreover, the complex impedance ($Z'$) spectroscopy analysis was performed in order to understand the microstructure thereby elucidating the electrical conduction behavior of BCLT nanoparticles. According to this analysis, the complex impedance is given by $Z' = Z'_r - jZ'_i$, where $Z'_r$ & $Z'_i$ are the real and imaginary parts of the complex impedance parameters. Figure 13(a) and (b) showed the variation of $Z'_r$ & $Z''_r$ as a function of frequency. It was seen from figure 13(a) and (b) that the $Z'_r$ and $Z''_r$—$f$ plots revealed the high magnitudes of impedance parameters. This can be an indication for the grain boundary contribution in the microstructure towards achieving the high values of $Z'_r$ & $Z''_r$ at low frequencies. In other words, the electrode polarization was also responsible for this type of trend. It was also noted that the $x = 0.2 \& 0.4$ contents expressed the relaxation nature at low frequencies. This was an indication for long range polarization mechanism. It can be happened due to the presence of few ions which were in a position to move long distances [1]. The portion above the relaxation was generated as a result of short range polarization mechanism. Herein, the ions can cover only shorter distances. Furthermore, at high frequencies, the $Z'_r$ & $Z''_r$ parameters were observed to be very small in magnitude. This was established owing to the weakening behavior of space charge polarization. At this stage, the ac-electrical conductivity becomes high. This trend was acquired due the contribution of grain in electrical conduction mechanism. In the similar way, $x = 0.6$ showed less relaxation nature at low frequencies in $Z'_r$—$f$ and $Z''_r$—$f$ plots. However, a small relaxation was observed at 4.5 MHz in $Z'_r$—$f$ plot. It can be obtained because of accumulation of charges at the grain boundary interface. Figure 13(c) and (d) (see supporting information section) indicated the variation of $Z'_r$ and $Z''_r$ parameters with temperature and log $f$ function. We observed that in case of $Z'_r$—log $f$ plots, the $x = 0.2 \& 0.4$ contents showed a single relaxation around log $f = 5$ while $Z''_r$—log $f$ plots of the same contents revealed three consecutive relaxations at log $f = 3.3, 4.5$ and 6 respectively. Herein, the broad relaxation was found at log $f = 6$. In general, these relaxations were attributed to the confinement of charge carriers to the grain boundary interface. Moreover, at very high frequencies (at all temperatures), the sharp increase of $Z'_r$ and $Z''_r$ parameters was identified. This was occurred due to the electrode polarization effect. On the other hand, at $x = 0.6$ content, no relaxations were observed in the case of in $Z'_r$—log $f$ (figure 13(c)) and $Z''_r$—log $f$ (figure 13(d)) plots. The usual space charge polarization was found at low frequencies while it was decreased at high frequencies.

Besides, the Cole-Cole plots were drawn to understand the electrical conduction mechanism as a function of composition and temperature saying that whether it was happened through grain/grain boundary contribution.
Figure 12. (a) $M'$ versus $M''$ plots of BCLT at room temperature.

Figure 13. (a) $Z'$—f and (b) $Z''$—f plots of BCLT as a function of La-content at room temperature.
Obviously, it was seen from figure 14 that $x = 0.2 \& 0.4$ contents exhibited the complete single semicircular arcs with considerable distortions. The complete arc formation indicated that the present BCLT materials were of semiconducting in nature. Further, the noted distortions were seemed to be occurred owing to the grain size variations, defects, moisture effect, produced strain etc, as reported in the literature $^5$. It was also remembered
that the single arc was evolved due to the major contribution of grain rather than its boundary in the electrical conduction mechanism. Moreover, the complete relaxation strength of charge carriers was also a reason for this behavior. Clearly, it was seen that the grain or bulk resistance was found to be decreasing with increase of temperature from 40 to 100°C. Herein, the bulk resistance ($R_g$) was evaluated using a technique where exactly each of the single arc intersects with the $Z'$-axis. Thus, the obtained results manifested that the $R_g$ was found to be decreasing from 235 to 60 kΩ (for $x = 0.2$ content) with temperature from 40 to 100°C. In addition, the relaxation frequency of arcs was also decreased. This incurred that at low frequencies the grain boundaries were more active while the increase of temperature reinforced the charge carriers to break the grain boundary interface and further to make motion through grain. Therefore, it was confirmed that the majority of the electrical conduction in $x = 0.2$ content took place via the grains only. In addition, it was evident that the increase of temperature allowed increasing the electrical conductivity through conducting segments. If the centers of arcs were imagined, these were assumed to be below the real axis. Hence, it suggested that the non–Debye relaxations were predominantly observed in case of $x = 0.2$ [5]. At $40°C–60°C$ temperature range, the origin of arcs was almost identical while it was moved to larger distance at high temperatures. Thus, this manner indicated that the charge carriers were almost inactive at $40°C–60°C$ temperature range which can result low electrical conduction mechanism. But, the same charges were become more active beyond the $60°C$ temperature which led to acquire high electrical conductivity as well. Likewise, $x = 0.4$ content also revealed the similar trend by forming the single arcs like $x = 0.2$. It was observed that the bulk resistance was diminished from 185 to 47 kΩ as a function of temperature from 40 to 100°C. In comparison, this was seemed to be somewhat lesser than the bulk resistances of $x = 0.2$. Hence, it confirmed a fact that the electrical conductivity was increased with increase of La-content from $x = 0.2$ to 0.4. Specifically, at 40 and 50°C temperatures, low electrical conductivity was observed while the same was high at 50°C. This established a fact that $x = 0.4$ content showed significant electrical conductivity response even at low temperature ($>50°C$) rather than the $x = 0.2$ (60°C). Furthermore, the $x = 0.6$ content performed the partial formation single semicircular arc due to partial relaxation strength. This content showed almost insulating like nature from room temperature to 100°C. Hence, we can estimate that $x = 0.6$ content may reveal semiconducting nature at very high temperatures. As a whole, it was clear that $x = 0.2$ & 0.4 contents expressed the high electrical conductivity at high temperatures revealing the semiconducting behavior. Similarly, $x = 0.6$ content still required huge temperatures to perform semiconducting nature. Furthermore, the bulk resistance of $x = 0.2–0.6$ contents were calculated by considering the intersecting position of arcs at $Z'$-axis. Latter, the bulk conductivity ($\sigma_{dc} = \frac{t}{R_gA}$, where ‘t’ is thickness of pellet, ‘$R_g$’ is the bulk resistance, and ‘A’ is the area of cross section of pellet) was calculated for $x = 0.2–0.6$ contents at all temperatures. We found that the $\sigma_{dc}$ was increasing with temperature for all the samples (see table 2). This confirmed that the present perovskite system obeyed the Arrhenius law. Therefore, the Arrhenius plots were drawn (see figure 14)(b)) to find the activation energies. As a result, using the slope values of the $\ln \sigma_{dc}$ versus $1/T$ plots, we computed the activation energies. These values were noted as 0.017, 0.020, and 0.025 eV for $x = 0.2, 0.4$, and 0.6 contents respectively. This established a fact that the activation energy was increased from 0.017–0.025 eV with ‘x’. Normally, it can be happened owing to the decrease of conductivity with ‘x’.

| $T$ (°C) | $0.2$ | $0.4$ | $0.6$ |
|----------|-------|-------|-------|
| 40       | $8.95 \times 10^{-7}$ | $1.21 \times 10^{-6}$ | $6.15 \times 10^{-9}$ |
| 50       | $1.13 \times 10^{-6}$ | $1.52 \times 10^{-6}$ | $9.56 \times 10^{-9}$ |
| 60       | $1.46 \times 10^{-6}$ | $2.29 \times 10^{-6}$ | $1.44 \times 10^{-8}$ |
| 70       | $1.78 \times 10^{-6}$ | $2.82 \times 10^{-6}$ | $2.09 \times 10^{-8}$ |
| 80       | $2.13 \times 10^{-6}$ | $3.26 \times 10^{-6}$ | $2.44 \times 10^{-8}$ |
| 90       | $2.52 \times 10^{-6}$ | $3.85 \times 10^{-6}$ | $2.93 \times 10^{-8}$ |
| 100      | $2.93 \times 10^{-6}$ | $4.94 \times 10^{-6}$ | $3.77 \times 10^{-8}$ |

3.5. Ferroelectric behavior

The ferroelectric behavior of the BCLT nanoparticles is investigated using the polarization electric loop (P-E loop) tracer by plotting graphs between electric field and polarization. The figure 15 shows the P-E loops of the BCLT pellets and they are exactly in banana shape as suggested by Scott [48]. It may be acquired as a result of the high lossy material. In other words, it may normally create the leakage current which could be occurred owing to the formed oxygen vacancies on the top surface of the grains, instead of polarization [48–50]. Moreover, the 108° ferroelectric domains were almost absent in case of $x = 0.2–0.6$ contents. Hence, the low values of saturation

Table 2. Temperature and composition dependence of bulk conductivity of BCLT nanoparticles.
polarization and retentivity were noted revealing the banana shaped P-E loops. As a whole, it is confirmed from the P-E loop analysis that within the BCLT nanomaterials, the ferroelectric nature is suppressed upon La-substitution.

4. Conclusions

The barium copper lanthanum titanate (BCLT) nanoparticles were synthesized via hydrothermal method. The average crystallite size (D) of BCLT nanoparticles is found to be varying between 23 to 30 nm. The morphological studies showed the nanospheres like particles using the TEM. FTIR study confirmed the presence of metal oxide bonds while the UV-Visible spectral studies revealed that the Eg was increasing from 1.814 to 2.166 eV as a function of x. The microstructure and electrical conduction mechanisms were deeply analyzed using impedance spectroscopy properties. The results pointed out that the x = 0.2 & 0.4 contents showed almost semiconducting nature even at low temperatures (60 °C − 100 °C) while x = 0.6 exhibited almost insulating nature over the above mentioned range. The ferroelectric behavior of present materials revealed the ‘banana’ shape P-E loop because of the formed oxygen vacancies on the top surface of the grains, instead of polarization.

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Conflicts of interest

The authors declare that we have no conflicts of interest.

Data availability statement

The data will be made available immediately based on the request.

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