Conductivity relaxation and oxygen vacancies-related electron hopping mechanism in Pb$_{1-x}$La$_{x/2}$Sm$_{x/2}$Ti$_{1-x}$Fe$_x$O$_3$ solid solutions

Vandana Sharma$^a$, Randeep Kaur$^b$, Mandeep Singh$^b$, Rachna Selvamani$^b$, Surya M. Gupta$^b$, Vidya Sagar Tiwari$^b$, A. K. Karnal$^b$ and Anupinder Singh$^b$

$^a$Multifunctional Materials Laboratory, Physics Department, Guru Nanak Dev University, Amritsar, India; $^b$Ceramic Laboratory, Laser Materials Development and Devices Division, Raja Ramanna Centre for Advanced Technology, Indore, India

ABSTRACT
Polycrystalline samples of Pb$_{1-x}$La$_{x/2}$Sm$_{x/2}$Ti$_{1-x}$Fe$_x$O$_3$ (x = 0.20 and 0.30) have been prepared by solid state reaction route. The electrical properties of synthesized samples have been investigated using complex impedance spectroscopy as a function of frequency (100 Hz–1 MHz) within the temperature range of (448–573 K). The fitting of the Nyquist plots reveals that both grain and grain boundary contribute to relaxation and the grain boundaries are more resistive and capacitive than the grains. Modulus analysis shows that relaxation in both the samples is of non-Debye type and temperature independent. The Jonscher’s power law fit to the ac conductivity data confirms that the conduction in the prepared samples is due to the hopping of charge carriers. Long range conductivity type of relaxation is found in both the samples.

1. Introduction
Lead titanate-based solid solutions form a series of ferroelectric materials which are used in variety of electroceramic devices such as multilayer capacitors, generators and nonvolatile memories. The physical properties of these solid solutions are highly dependent on the compositional variation, nature of dopants and sintering conditions, etc. [1–3]. Various research groups have reported on the importance of doping in ABO$_3$ (PbTiO$_3$/PZT/BaTiO$_3$/SrTiO$_3$) systems for the fabrication of multifunctional devices [4–9]. It is well explained that the introduction of rare-earth ions like La$^{3+}$, Ce$^{3+}$ and Nd$^{3+}$ (donor ion) when added in right stoichiometry at A-site enhances the ferroelectric polarization, whereas the substitution by transition-metal ions like Fe$^{3+}$ and Mn$^{2+}$ (acceptor ion) at B-site not only induces magnetic character in them but also leads to the thermally activated conduction due to presence of oxygen vacancies [10]. It is observed that the substitution of rare-earth ions (La$^{3+}$/Sm$^{3+}$) at Pb and transition metal ion (Fe$^{3+}$) at Ti site helps in controlling leakage current and getting enhanced electrical properties [11]. The effect of electron migration between the substituent and constituent ions has been explained earlier [12]. In addition, oxygen vacancies’ segregation causes polarization fatigue due to domain pinning effect [13]. So, it becomes quite interesting to study such materials where charge transportation is carried by different mechanisms like space charge formulism, charge displacement and dipole relaxation [14]. To explore all these mechanisms, complex impedance spectroscopy (CIS) is the best technique to study these systems. Focusing on the area of interest, our literature review shows that most of the research papers have been reported on rare-earth-modified PZT ceramics [15–20]. However, no research has been carried out on the simultaneous substitution of lanthanum, samarium and iron in lead titanate ceramics. Therefore, we here report the detailed study on the impedance, modulus and conductivity behavior of the solid solutions of Pb$_{1-x}$La$_{x/2}$Sm$_{x/2}$Ti$_{1-x}$Fe$_x$O$_3$ with $x = 0.20$ and 0.30. However, dielectric properties of the same composition have been reported elsewhere [21].

Theory
CIS is very useful and nondestructive technique for studying electrical properties of polycrystalline materials with in a wide frequency range. This technique is beneficial in separating the contributions of electroactive regions, such as bulk grains and grain boundary effects [14]. In CIS, a small ac signal is applied as input. The output signal is generally complex having both resistive (real part) and reactive (imaginary) components. In CIS, the electrical behavior of material can be understood in terms of complex impedance ($Z^*$), complex electric modulus ($M^*$), complex dielectric constant ($\varepsilon^*$) and $\tan\delta$ which are related to each other via following relations:

CONTACT Anupinder Singh anupinders@gmail.com

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Complex permittivity, \( \varepsilon' = \varepsilon' - j \varepsilon'' \) and \( \tan \delta = \frac{\varepsilon''}{\varepsilon'} \)  \hspace{1cm} (1)

Complex impedance, \( Z''(\omega) = Z' - j Z'' \)
\[ = R_s - j \left( \frac{1}{\omega C_s} \right) \]  \hspace{1cm} (2)

Complex modulus, \( M''(\omega) = M' + j M'' = \omega C_0 Z \)  \hspace{1cm} (3)

where \((Z', M', \varepsilon')\) and \((Z'', M'', \varepsilon'')\) are the real and imaginary components of complex impedance, modulus and permittivity, respectively, \( j = \sqrt{-1} \) the imaginary factor, \( C_0 \) = vacuum capacitance [22]. The complex plots hence obtained appear in the form of succession of semicircles representing contribution due to grains (bulk), grain boundary and interfacial polarization. These semicircles are also the imprints of different types of relaxations phenomenon taking place in the system. The parametric equations of these semicircles are derived from Debye’s equations [23]. These semicircles pass through origin with center on x-axis implies Debye-type behavior, otherwise non-Debye-type behavior [24].

2. Experimental details

The conventional solid-state reaction route was followed for synthesizing solid solutions of \( \text{Pb}_{1-x} \text{La}_x \text{Sm}_{1/2} \text{Ti}_{1-x} \text{Fe}_x \text{O}_3 \) with \( x = 0.20 \) and \( x = 0.30 \) as been discussed elsewhere [21]. For the measurement of electrical properties, pallets were initially polished to obtain a smooth surface. The electrodes were then formed on the smooth surface by applying high conductivity silver paste. These pellets were then dried at 200°C for 5 h to remove moisture. The sample was mounted on the sample holder and then placed in a variable temperature furnace. The impedance and phase angle parameters were measured over a wide frequency range (100 Hz–1 MHz) in the (448–573 K) temperature range using HP 4194A impedance analyzer.

3. Results and discussion

3.1. Impedance analysis

Figure 1(a,b) shows the variation of \( Z' \) with frequency from 100 Hz to 1 MHz at different temperature from 448 to 573 K for \( x = 0.20 \) and \( x = 0.30 \) samples. It is clear from the plots that for both the samples, value of \( Z' \) (at all temperature) decreases continuously with increasing frequency up to \( 10^4 \) Hz and afterward, it almost becomes independent of frequency; also further, the value of \( Z' \) decreases with increase in temperature for a given frequency. The dispersion is higher for \( x = 0.20 \) sample. The decrease in value of \( Z' \) with increasing frequency may be attributed to release of space charge carriers and a consequent reduction in the barrier properties of the material [25]. It may be noted that the data sets for \( x = 0.20 \) sample are merged beyond frequencies >10^3 Hz, whereas for \( x = 0.30 \) sample, the data sets merge over whole of the frequency range.

The Figure 2(a,b) shows asymmetric peaks of \( Z'' \) as a function of frequency at different temperature for \( x = 0.20 \) and 0.30. It is clear from plots that \( Z'' \) consistently decreases and merges at high temperature. The nonexistence of peak maxima at lower temperature shows absence of relaxation phenomenon in the sample, which may be due to immobile charge carriers. However, peak maxima start arising with temperature and shift to the right with increase in frequency. The peak width of spectrum refers to the distribution of relaxation times [26]. The inset diagrams of both \( Z' \) and \( Z'' \) for both the sample show two clear broad peaks at all temperatures (except 448 K) which indicate the presence of relaxation in both samples.

Figure 3(a,b) shows the complex impedance spectrum (\( Z' \) vs \( Z'' \)) known as Nyquist plots or cole-cole plots at various temperatures (448–573K) over a wide frequency range. Two semicircular arcs have been observed for \( x = 0.20 \) at all temperatures, whereas slope type behavior is observed at starting temperatures for \( x = 0.30 \), but as the temperature increases, it takes

![Figure 1](image-url)
the shape of depressed semicircular arcs with their centers below real axis. The depressed semicircles confirm the presence of non-Debye-type relaxation. The evolution of two type of semicircles in \( x = 0.20 \) shows the existence of grain and grain boundary effects. The impedance data simulated with equivalent R-CPE circuits model are given in the inset of Figure 3(a,b), for non-Debye-type system constant phase element (CPE) is introduced in the circuit instead of capacitance [27]. The intercepts of semicircular arcs on the real \( Z' \) axis gave the values of grain boundary (\( R_{gb} \)) and bulk resistances (\( R_b \)) which are tabulated in Table 1. In the complex impedance plots, the presence of peak is the characteristics of relaxation phenomenon (\( \omega_r = 2\pi f \) and \( \omega_r RC = \omega_r \tau \)) [28]; therefore,

\[
f_r = \frac{1}{2\pi RC} = \frac{1}{2\pi \tau}
\]

where \( \tau \) is relaxation time, \( R \) is resistance and \( C \) is capacitance, so the respective value of bulk capacitance (\( C_b \)) and grain boundary capacitance (\( C_{gb} \)) (given in Table 1) can be calculated using the above relation. It is clear from Table 1 that grain boundaries are more resistive and capacitive than grains in both the sample. The activation energies of grain (bulk) and grain boundary (given in Table 2) for the two compositions are evaluated by plotting ln (\( R_b \)) and ln (\( R_{gb} \)) against inverse of absolute temperature (1000/\( T \)) as shown in Figure 4(a,b). It has been reported that activation energy of oxygen vacancies lies between 0.3 and 1.0 eV [29]. The values of activation energies for grains (\( E_g \)) and grain boundaries (\( E_{gb} \)) are 0.70 and 0.43 eV for \( x = 0.20 \) and 0.49 and 0.68 eV for \( x = 0.30 \), respectively. This means that dielectric relaxations in our case is due to singly and doubly ionized oxygen vacancies (\( E_a \) for doubly ionized oxygen vacancies >0.6 eV and for singly ionized oxygen vacancies <0.6 eV). The parameter \( \beta \) is calculated after fitting for grain and grain boundary of two compositions as shown in Figure 5(a,b) and it is found that \( \beta < 1 \) in both the cases confirming non-Debye nature of grain and grain boundary for both compositions.

### 3.2. Modulus analysis

The complex modulus spectroscopy is a very useful characterization technique in order to differentiate the electrical dynamics of the polycrystalline material coming from grain (bulk) and grain boundaries regions. The impedance spectra give information of large resistances, whereas the study of modulus behavior emphasizes more on smaller capacitances of the material. The

![Figure 2. The frequency dependence imaginary part of impedance (Z″) at different temperature for (a) x = 0.20 and (b) 0.30.](image1)

![Figure 3. The fitted Nyquist (cole-cole) plots between Z’ and Z″ at different temperature for Pb_{1-x}La_xSm_{x/2}Ti_{1-x}Fe_{x}O_3 (a) x = 0.20 and (b) 0.30.](image2)
complex modulus ($M^*$) can be calculated using relation given below:

$$M^*(\omega) = \frac{1}{\varepsilon} = \frac{\varepsilon'(\omega)}{[\varepsilon'(\omega)]^2 - i \frac{\varepsilon''(\omega)}{[\varepsilon'(\omega)]^2}}$$  \hspace{1cm} (5)$$

$$M'(\omega) + i M'' = M_{\infty} \left[ 1 - \int_0^\infty \exp(i\omega t) \frac{d\varphi(t)}{dt} dt \right]$$  \hspace{1cm} (6)$$

where $M_{\infty} = \frac{1}{\varepsilon_{\infty}}$ is the limiting high-frequency real part of permittivity and function; $\varphi(t)$ is a relaxation function or Kohlrausch-Williams-Watts (KWW) function\[14\] given by

$$\psi(t) = \exp\left[-\left(\frac{t}{\tau_m}\right)^\beta\right] 0<\beta<1$$  \hspace{1cm} (7)$$

where $\tau_m$ and $\beta$ parameters are called as conductivity relaxation time and Kohlrausch stretched coefficient (symbolizes degree of non-Debye behavior). Bergman modified KWW function is given by \[30,31\]:

Table 1. The grain and grain boundary contribution evaluated after fitting of impedance data of Pb$_{1-x}$La$_{x/2}$Sm$_{x/2}$Ti$_{1-x}$Fe$_3$O$_{3}$ with $x = 0.20$ and $0.30$.

| Temp (K) | $R_g$ | $C_g$(nF) | $\beta_g$ | $R_{gb}$ | $C_{gb}$(nF) | $\beta_{gb}$ |
|----------|-------|-----------|-----------|----------|-----------|-----------|
| 448      | 97,584| 3.30      | 0.96      | 275,770  | 9.89      | 0.97      |
| 473      | 33,960| 1.77      | 0.97      | 121,400  | 19.56     | 0.89      |
| 498      | 16,048| 1.06      | 0.98      | 68,116   | 32.91     | 0.82      |
| 523      | 7131  | 0.80      | 0.99      | 45,295   | 96.9      | 0.69      |
| 548      | 2927  | 0.82      | 0.98      | 33,465   | 140.19    | 0.64      |
| 573      | 1967  | 0.92      | 0.96      | 22,482   | 255.4     | 0.60      |

Table 2. Activation energy calculated from relaxation and conductance data.

| Composition | $E_a$ (Impedance) | $E_a$ (Modulus) | $E_a$ (Conductivity) |
|-------------|-------------------|-----------------|----------------------|
| $x = 0.20$  | 0.70              | 0.43            | 0.90                 |
| $x = 0.30$  | 0.49              | 0.68            | 0.62                 |

Figure 4. Arrhenius plots of resistances (grains and grain boundaries) at different temperature for Pb$_{1-x}$La$_{x/2}$Sm$_{x/2}$Ti$_{1-x}$Fe$_3$O$_{3}$ ($a$) $x = 0.20$ and ($b$) $0.30$.

Figure 5. Variation of $\beta$ (symbol of non-Debye-Debye behavior of system for grain and grain boundary) with temperature for ($a$) $x = 0.20$ and ($b$) $x = 0.30$.
\[ M'' = \frac{M''_{\text{max}}}{(1 - \beta) + \frac{\beta}{1+\beta} \left[ \partial \left( \frac{\omega_{\text{max}}}{\omega} \right) + \left( \frac{\omega}{\omega_{\text{max}}} \right)^\beta \right]} \] (8)

where \( M''_{\text{max}} \) is the maximum value of modulus \( M'' \), \( \omega_{\text{max}} \) is the maximum value angular frequency and \( \beta \) is the parameter which illustrates the Debye or non-Debye behavior (as discussed above).

The variation in real part of electric modulus (\( M' \)) as a function of frequency for \( x = 0.20 \) and 0.30 at selected temperatures is shown in Figure 6(a,b). At lower frequencies, \( M' \) tends to be very small (approximately zero) followed by continuous increasing asymptotic value with increase in frequency at all temperatures. This behavior may possibly be related to a lack of restoring force which governs the mobility of the charge carriers under the action of an induced electric field [32,33]. However, the small value in lower frequency region may be due to short range mobility of charge carriers which confirms the absence of electrode effect [19]. Higher constant value of \( M' \) (\( M'_\infty \)) at high frequencies for all the temperatures confirms the relaxation process occurring in the material.

Figure 7(a,b) shows variation in imaginary part of electric modulus (\( M'' \)) with frequency at different temperatures. The maximum value of \( M'' \) (\( M''_{\text{max}} \)) shifts to higher frequency side as the temperature increases depicting the relaxations are carried by thermally activated charge carriers. The peaks appearing in lower frequency region indicate that the mobile ions can move over long distances and those appearing in higher frequency region represent confinement of ions in potential well [34]. It is also observed that there is peak asymmetry in the plots of \( M'' \) vs frequency which indicates distribution of relaxation times with different time constants. This confirms the fact that relaxation is of non-Debye type. The experimental data of \( M'' \) vs Frequency plot is theoretically fitted with the KWW function given in Equation (8). Figure 7(a, b) shows that KWW function is well fitted for compositions \( x = 0.20 \) and 0.30. Figure 8 shows the variation in relaxation time \( \ln (\tau) \) (calculated from maximum frequency \( \omega_r \) of modulus spectrum obtained after fitting with KWW function) with inverse of absolute temperature (1000/T). The plot is linear and follows the Arrhenius relation, \( \tau = \tau_0 \exp \left( -\frac{E_a}{K_B T} \right) \), where \( \tau_0 \) is the pre-exponential factor, \( E_a \) is the activation energy, \( K_B \) is the Boltzmann constant and \( T \) is the absolute temperature [28]. From this plot, value of activation energy

![Figure 6](image-url). The frequency dependence real part of modulus (\( M' \)) at different temperature for (a) \( x = 0.20 \) and (b) 0.30.

![Figure 7](image-url). The imaginary part of modulus \( M'' \) with frequency at different temperature \( \text{Pb}_{1-x}\text{La}_{x/2}\text{Sm}_{x/2}\text{Ti}_{1-x}\text{Fe}_x\text{O}_3 \) for (a) \( x = 0.20 \) and (b) 0.30.
is calculated given in Table 2. The value of activation energies obtained are 0.90 and 0.62 eV for \( x = 0.20 \) and 0.30 compositions and fall in the range of oxygen vacancies. The scaled master curve of normalized parameters \( M''/M''_{\text{max}} \) vs \( \ln \left( \omega/\omega_{\text{max}} \right) \) is shown in Figure 9(a,b). The region of peak shows the occurrence of transition from long range to short range mobility. From both the figures, it is clear that peaks of different temperature overlap in the same region of frequency indicating that relaxation process occurring in the material is independent of temperature.

It is well known that every physical parameter has characteristic peak at different frequency in its imaginary component because of different relaxation time constant. Also, the overlapping and separation of \( Z'' \) and \( M'' \) peaks are due to long range conductivity and localized relaxation processes respectively [35]. The normalized plots \( Z''/Z''_{\text{max}} \) and \( M''/M''_{\text{max}} \) vs \( \ln \left( \omega/\omega_{\text{max}} \right) \) for sample \( x = 0.20 \) and 0.30 have been shown in Figure 10(a,b). It is clear from both the plots that long range conductivity of free oxygen vacancies is responsible for the relaxation processes happening in both the samples.

### 3.3. Electrical conductivity study

The conductivity study is the prominent characterization to relate the electrical dynamics of system with microscopic movement of charge carriers. Oxygen vacancies are formed during heating treatment of materials, i.e. sintering; these oxygen vacancies are responsible for the creation of conducting electrons through ionization process as given in equations below:

\[
V_0 \rightarrow V_0' + e' \\
V_0' \rightarrow V_0'' + e'
\]

When temperature is increased, the created electrons become conduction electrons due to thermal activation energy. In addition to that, single (\( V''_{\text{pb}} \)) and double (\( V''''_{\text{pb}} \)) ionized vacancies of lead are also created when \( \text{La}^{3+} \) ion occupies site of \( \text{Pb}^{2+} \) ion in the
The lead vacancies cannot be activated at low temperature. They need activation energy of 2 eV for mobility, whereas the activation energies of singly ionized and doubly ionized oxygen vacancies fall in the range of 0.3–0.6 eV and 0.7–1.2 eV, respectively.

Figure 11(a,b) shows frequency dependent ac conductivity at different temperature (448–573 K) and is fitted with power law of conductivity. The analysis is done on the basis of universal power law of conductivity known as Jonscher’s power law [37].

\[
\sigma_{ac} = \sigma_{dc} + A\omega^n \tag{11}
\]
where \(\sigma_{dc}\) is frequency independent term, \(\omega\) is angular frequency, \(A = |N^2e^2/6k_BT(2\alpha)|\) is a constant measures of polarizability and \(n\) is measure of degree of interaction between mobile ions and lattice, whose value lies between 0 and 1. From the plots, it is clear that there are two specific regions: one is frequency-independent flat region (plateau region) at lower frequency which reflects dc conduction behavior of the system and another is frequency-dependent dispersive region at higher frequency. The significant frequency at which dispersion region starts originating from plateau region is known as hopping frequency (\(\omega_p\)).

The conductivity of the material can often be explained by the following relation [38]:

\[
\sigma(T) = \sigma_{ac}(T) + \sigma_{dc}(T) \tag{12}
\]

The first term in the relation (12) is frequency dependent given by: \(\sigma_{ac}(T) = A(T)\omega^n\); the parameters \(A\) and \(n\) have their usual meaning discussed above. Moreover, the variation of \(n\) with temperature which tells about the origin of conductivity can be explained by models (i) quantum mechanical tunneling model (QMT) and (ii) correlated barrier hopping (CBH) model [39,40]. If \(n\) is independent of temperature, then conduction can be explained by QMT model; if \(n\) decreases with temperature, then conduction is accompanied by CBH. If \(n\) increases with temperature, then it can be related with small polaron conduction mechanism [38]. If it decreases and is followed by increase with rise in temperature, then it is related to overlapping large polaron tunneling (OLPT) mechanism [41].

The second term in Equation (12) is called dc conductivity due to drifted charge carriers and followed by Arrehenius relation: \(\sigma_{dc} = \sigma_0 \exp(-E_a/k_BT)\). Figure 12 shows linear plot of \(\ln(\sigma_{dc})\) vs inverse of absolute temperature (1000/T). The activation energy evaluated from conductivity mechanism for both compositions is tabulated in Table 2. The obtained values of activation energies for \(x = 0.20\) and 0.30 composition are 0.45 and 0.54 eV which attributes to existence of singly ionized oxygen vacancy. According to A. Pelaiz-Barranco et al., dc conductivity is supposed to be happened according to the Equation (9) and (10) and electron created in this way may be captured by Ti\(^{4+}/\text{Fe}^{3+}\) and Ti\(^{3+}/\text{Fe}^{2+}\) sites and starts hopping in between these localized sites. This shows that conduction in the present sample is accompanied by long range hopping of electrons through oxygen vacancies in the prepared samples. After fitting with Jonscher’s power law, the obtained values of \(A, n\) and \(f_H\) (hopping frequency) are listed in Table 3 and variation of \(n\) with temperature is shown in Figure 13. We found that value of \(n\) increases...
with increase in temperature for both the compositions and also their values are less than 1 confirming non-Debye-type behavior of both the system [34,42]. The temperature-dependent plot of hopping frequency for both the sample is shown in Figure 14; it shows that hopping frequency increases with the increase in temperature in both the samples; however, carriers have high value of it at each temperature in case of \( x = 0.20 \) sample as compared to \( x = 0.30 \).

### Table 3. The parameters evaluated from ac conductivity of \( \text{Pb}_{1-x}\text{La}_{x/2}\text{Sm}_{x/2}\text{Ti}_{1-x}\text{Fe}_x\text{O}_3 \) with \( x = 0.20 \) and 0.30.

| Temp.(K) | \( \sigma_a (\text{scm}^{-1}) \) | \( A \) | \( n \) | \( f_n \) | \( \sigma_a (\text{scm}^{-1}) \) | \( A \) | \( n \) | \( f_n \) |
|---------|-------------------------------|--------|--------|--------|-------------------------------|--------|--------|--------|
| 448     | \( 3.764 \times 10^{-3} \)    | 2.85 \times 10^{-5} | 0.25 | 2015 | \( 7.407 \times 10^{-4} \)    | 3.46 \times 10^{-5} | 0.30 | 1000 |
| 473     | \( 2.668 \times 10^{-4} \)    | 4.66 \times 10^{-4} | 0.26 | 5988 | \( 1.060 \times 10^{-3} \)    | 3.67 \times 10^{-5} | 0.33 | 1487 |
| 498     | \( 4.703 \times 10^{-4} \)    | 5.62 \times 10^{-5} | 0.31 | 7962 | \( 2.296 \times 10^{-4} \)    | 3.49 \times 10^{-5} | 0.38 | 2022 |
| 523     | \( 7.701 \times 10^{-4} \)    | 4.83 \times 10^{-5} | 0.38 | 9459 | \( 4.965 \times 10^{-5} \)    | 3.09 \times 10^{-5} | 0.42 | 3454 |
| 548     | 0.0012                        | 3.03 \times 10^{-5} | 0.46 | 9918 | \( 8.965 \times 10^{-6} \)    | 2.88 \times 10^{-5} | 0.45 | 4409 |
| 573     | 0.0016                        | 2.68 \times 10^{-5} | 0.50 | 11,315 | \( 1.296 \times 10^{-6} \) | 2.65 \times 10^{-5} | 0.48 | 8612 |

#### 4. Conclusions

The polycrystalline ceramics \( \text{Pb}_{1-x}\text{La}_{x/2}\text{Sm}_{x/2}\text{Ti}_{1-x}\text{Fe}_x\text{O}_3 \) with composition \( x = 0.20 \) and 0.30 has been prepared by solidstate route. The electrical properties of both the sample have been studied with CIS. Impedance analysis shows electrical conduction is due to grains and grain boundaries, and their resistance decreases with increase in temperature showing negative temperature coefficient of resistance-type behavior in the system. Also grain boundaries are more resistive and capacitive as compared to grains in both the samples. Modulus spectra confirmed the presence of hopping mechanism and temperature-independent behavior of relaxation in both the samples. The ac conductivity analysis reveals the presence of small polaron conduction mechanism due to electrode polarization. The application of Jonscher’s power law on ac conductivity shows non-Debye-type behavior of both the materials. All the studied formalisms confirm non-Debye-type behavior of both the samples. The calculated activation energies show that presence of both singly and doubly ionized oxygen vacancies contributes toward the relaxation and conduction phenomena in the samples. Also the long range conductivity is responsible for all type of relaxations occurring in both the samples.

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#### Disclosure statement

No potential conflict of interest was reported by the authors.

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