Impedance Spectroscopy of Pb$_{0.8}$La$_{0.2}$Fe$_{0.1}$Cr$_{0.1}$Ti$_{0.8}$O$_3$

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Abstract. In this paper, we have focused on the structural and electrical properties of Pb$_{0.8}$La$_{0.2}$Fe$_{0.1}$Cr$_{0.1}$Ti$_{0.8}$O$_3$ ceramic through complex impedance spectroscopy method. It was synthesized by the conventional solid-state reaction technique. Detailed analysis of complex impedance and modulus plot was done, which proposed the semiconducting nature (NTCR) of the sample. Temperature dependant relaxation processes are going on inside the material, which is of non-Debye type.

Keywords
XRD, SEM, solid-state reaction, NTCR behaviour

1. Introduction

Amid various ferroelectric materials of different structural families (pyrochlore, tungsten bronze, perovskite etc.), materials having perovskite structure is of great interest due to their admirable functional properties. These ABO$_3$ based structures have a high dielectric constant, piezoelectricity, electrostrictive effects useful for device application like ceramic capacitor, transducer, microwave application, actuator etc. ‘[1, 2]’. Titanate ceramic materials (mainly lead titanate; PbTiO$_3$) have eye-catching room temperature application because of its high dielectric constant, good pyroelectric coefficient, large spontaneous polarization, low tangent loss and highest Curie temperature ‘[3-6]’.

However, the properties of lead titanate are affected by the incorporation of the isovalent ion into both A and B site. In order to get an actual picture of the material under study, it is very much necessary to modify the dielectric and electrical data in various kind of formalism and evaluate them. The electrical properties of the material are an outcome of the contribution from numerous component and process
(like charge transport, dielectric relaxation etc.) occurring inside it. The charge transport occurs through various manners like charge displacement, dipole orientation and space charge formalism.

When an electric field is applied, dielectric relaxation takes place inside the sample, which is influenced by the number of polarization caused due to the transport of charges. Complex impedance spectroscopy (CIS) study is an eminent and suitable non-destructive method for characterization of the electrical process going on inside a sample [7]. In this paper, we have reported our results based on the study of the various parameter (impedance, modulus etc.) related to electrical properties.

2. Experimental

2.1. Synthesis

High purity (CDH, ≥ 99.9%) Lead monoxide (PbO), lanthanum oxide (La₂O₃), ferric oxide (Fe₂O₃), chromium oxide (Cr₂O₃) and titanium dioxide (TiO₂) are used as precursors for the synthesis of Pb₀.₈La₀.₂Fe₀.₁Cr₀.₁Ti₀.₈O₃ (PLFCTO) using mixed oxide method. The required amount of precursor is weighed carefully and an additional amount (2 mole %) of PbO was added to indemnify the loss of lead during sintering. The ingredients are mixed properly through dry grinding for 2.30 hours followed by wet grinding for 2 hours (methanol is used as a wet medium) using an agate mortar and pestle. The mixed powder was kept in a closed alumina crucible and subjected to calcination at 850°C for 5 hours. Polyvinyl alcohol (PVA) was added to the calcined powder, which acts as a binder for the reduction of brittleness and burns out during sintering. Then in a hydraulic press, the fine calcined powder was cold-pressed to form pellets having dimensions of 12 mm in diameter and 1-2 mm in thickness by applying 5*10⁶ Pa pressure. The pellets were sintered at 900°C for 4 hours.

2.2. Characterisation

For characterisation, various instruments were used. The phase formation and quality of the sample was examined with an X-ray diffractometer (ULTIMA IV model-Rigaku, Japan). The CuKα radiation (λ=1.5405Å) was used for the recording of data in an extensive range of Bragg’s angle 2θ (20° ≤ θ ≤ 80°) and scanning rate of 3° per minute. For the study of microstructure and texture of the sample, images were taken at different magnification by scanning electron microscope (HITACHI, SV3500). To obtain the electrical parameters, the pellets were polished by an emery paper, electrode with conductive silver paint and then readings are taken using impedance analyser (HIOKI, IM3570).

3. Results and Discussion

3.1 Structural and microstructural analysis

The XRD pattern is displayed in ‘Figure 1’. It possesses orthorhombic crystal structure (a = 5.5630Å, b = 7.8520Å, c = 5.5540Å, α = β = γ = 90°) with volume = 242.60 Å³ and space group pnma, which is obtained by analysing the pattern in XPert high score software (ICDS no: 98-011-6780).
Figure 1. XRD pattern and SEM (inset) of PLFCTO.

The particle size obtained from Debye shearer’s formula ‘[8]’ \((x= 0.89\lambda/\beta\cos\theta, \lambda=1.5405\text{Å} \text{ and } \beta=\text{full width at half maximum})\) is 51.9nm. The SEM image (inset of Figure 1) shows uniformity in grain distribution having an average grain size of 2.7889µm.

3.2 Impedance study

This method is based on the analysis of ac signal as input perturbation and the successive calculation of impedance as a function of frequency. Using this method,

- We can correlate the electrical properties (conductivity, dielectric constant, loss tangent etc.) of the sample under study with its microstructure.
- Calculate and distinguish the influence of various components (grain, grain boundaries, interface etc.) to the complete electrical properties of the material in the frequency field.

The study of electrical properties is accomplished by using the relaxation frequency \( (\nu_{\text{max}}) \), which leads to a clear-cut result when compared with those found at a randomly selected fixed frequency. When plotted in a complex impedance plane plot, CIS gives us information having both resistive (real) and reactive (imaginary) part. In this method, the nature of the materials is represented in terms of complex permittivity \( (\varepsilon^*) \), complex impedance \( (Z^*) \), complex admittance \( (Y^*) \), complex electric modulus \( (M^*) \) and dielectric loss/dissipation factor. These are articulated as:

\[
\begin{align*}
\varepsilon^* &= \varepsilon' - j\varepsilon'' = -\frac{Z''}{\omega\varepsilon_0(Z'^2 + Z''^2)}, \\
\varepsilon'' &= -\frac{Z^*}{\omega\varepsilon_0(Z'^2 + Z''^2)} \quad (1) \\
z^* &= z' - jz'' \quad (2) \\
Y^* &= Y' - jY'' \quad (3) \\
M^* &= M' + jM'' \quad (4)
\end{align*}
\]
The interrelation between them are as follows:

\[ M^* = 1/\varepsilon^* = j\omega\varepsilon_0 Z^* \]  
\[ Z^* = 1/\varepsilon^* \]  
\[ \gamma^* = j\varepsilon_0\omega \varepsilon^* \]  
\[ \tan \delta = \varepsilon''/\varepsilon' = M^*/M^* = Z''/Z' \]

Here, \( \varepsilon_0 \) = geometrical capacitance, \( j = (-1)^{1/2} \), \( \omega \) = angular frequency (2πf)

Figure 2(a). \( Z' \) versus frequency plot of PLFCTO at multiple temperatures.

Figure 2(b). \( Z'' \) versus frequency plot of PLFCTO at various temperature.

The deviation of real part of impedance (i.e., \( Z' \)) as a function of frequency at some selected temperature region (300 – 450 °C) is displayed in ‘Figure 2(a)’. We can see that, the value of \( Z' \) drops down deliberately in the low frequency region depending upon temperature and spill down abruptly with rise in frequency. In addition, at high frequency (i.e., at frequency > 10 KHz) all the curve merge together which specifies that \( Z' \) becomes independent of both frequency and temperature in that region. It may entail the release of space charge and a consequent lowering of barrier properties in the material [9, 10]. It is clearly noticeable from the figure that the value of \( Z' \) reduces with increment in temperature. This confirms the NTCR (negative temperature coefficient resistance) behaviour of the sample. The fusion of curve at high frequency may lead to the enhancement in ac conductivity with temperature. This can be related to the influence of defects such as oxygen vacancies [11].
general, in perovskite ceramics the effect of oxygen vacancies is more at higher temperature. Because of this, ac conductivity increases with rise in temperature owing to the release of space charge and diminution of barrier properties in the material.

The fluctuation of imaginary part of impedance ($Z''$) with frequency (also known as impedance loss spectrum) at certain temperature range is depicted in ‘Figure 2(b)’. From the graph, we can predict that the values of $Z''$ first increase with rise in frequency reach to a maximal value at a peculiar frequency and then drop off. Eventually, the entire curve pattern coincides at high frequency. The frequency at which $Z''$ attains maximum value is entitled as relaxation frequency ($\omega_{\text{max}}$). Thus, the loss spectrum exhibit that

- Reduction in the height of peak with growth of temperature
- Substantial widening of peak with rise in temperature
- Asymmetrical pattern of peak
- Shifting of peak towards high frequency side

The widening of peak with the growth in temperature indicates the occurrence of temperature dependant electrical relaxation process in the material. The relaxation is due to electron / immobile species at low temperature and defect at high temperature. In case of a dielectric material, the defect relaxation ‘[12]’ is predominant due to low dielectric ratio ($k$) ($k = \varepsilon_s/\varepsilon_\infty$). The asymmetry broadening of peak give an idea about the spread of relaxation time. The peak heights in the loss spectrum are strongly related to bulk resistance ($R_b$). It can be calculated by the equation $Z''=R_b\frac{\omega\tau}{1+\omega^2\tau^2}$. The shifting of peak towards high frequency causes the reduction of resistance of bulk material. Also, the dispersion of loss spectrum in the low-frequency region and their merging at high frequency suggest the disappearance of space charge polarisation at high frequency. The peak maxima of the impedance plot decreases and the frequency for maximum shift towards higher value with rise in temperature. It can be related to the existence of the distributed elements in the sample electrode system ‘[13, 14]’.
The Cole-Cole plots (i.e., the temperature dependent complex impedance spectrum between $Z'$ vs $Z''$) are depicted in ‘Figure 3’. At low temperature (25°C-200°C), the graph between $Z'$ and $Z''$ (‘Figure 3(a)’) are straight lines with large slope. The formation of semi-circular arcs at higher temperatures (> 200°C) is influenced by the strength of the relaxation and the frequency range that are available experimentally [15]. The radius of curvature of the semi-circular arc decreases with rising in temperature. It suggests the increase in conductivity with temperature and NTCR (Negative temperature coefficient resistance) behaviour of the sample. A perfect semi-circular arc with centre exactly on the abscissa (i.e., $Z'$ axis here) represents Debye-type relaxation. In this case, the impedance spectrum contains depressed semi-circular arc with centre below real $Z$-axis. This shows the poly dispersive non-Debye type of relaxation mechanism in the material. It also reveals that, the relaxation time here is distributed rather than having a single relaxation time [16, 17]. We can have a better interpretation and analysis of the experimental data if we have a model equivalent circuit, which provides realistic representation of the electrical properties. So, we have fitted the experimental data using the commercially available Zsimp win software to get an equivalent circuit (‘Figure 3(b)’).

According to the explanation of A.K Johnscher in “universal dielectric response”, the equivalent circuit in real dielectric material comprises of the Debye model type simple RC circuit. But in our sample, we may or may not get a real dielectric material. Further, in this system, the Nyquist plot is compared with an equivalent circuit of R(CR)(QR) type. This may be due to the simultaneous occurrence of the relaxation of dipole and charge carriers, i.e.

i. The conductivity relaxation, which involves the long-range migration of charge carriers.

ii. The dielectric relaxation owing to the permanent dipole orientation or other motions.

Here long-range movement of mobile charge carrier did not take place.

This interpretation can be considered as very good due to excellent matching between the experimental and simulated data. Here the deviation from ideal RC behaviour (non-Debye type behaviour) is modelled with a Q element, which is used to represent the constant phase element (CPE). Q is a very general element used for “imperfect capacitor”. CPE normally exhibit an 80-90° phase shift. CPE behaviour can be considered evidence of frequency dispersion. Its origin can be due to the dispersion of the resistance, capacitance or both. Further, this dispersion is due to different diffusing species and electrode materials. The nature of Nyquist plots implies the combined effect of grain and grain boundary. The details of fitted data are listed below in a tabular form (“Table 1”).

| Different parameters | Different temperature( in °C) |
|----------------------|-----------------------------|
|                     | 325 | 350 | 375 | 400 | 425 |
| $R_1$               | 4.375E+001 | 4.124E+001 | 3.678E+001 | 3.110E+001 | 2.698E+001 |
| $R_2$               | 1.982E+003 | 9.581E+002 | 4.885E+002 | 2.796E+002 | 1.643E+002 |
| $R_3$               | 8.600E+001 | 7.555E+001 | 7.410E+001 | 7.400E+001 | 7.575E+001 |
| C                   | 3.153E-009 | 3.765E-009 | 5.104E-009 | 6.830E-009 | 8.704E-009 |
| CPE                 | 1.080E-007 | 8.238E-008 | 5.652E-008 | 5.932E-008 | 1.009E-007 |
| Frequency power(n)  | 8.095E-001 | 8.229E-001 | 8.411E-001 | 8.287E-001 | 7.826E-001 |
| Chi square          | 7.613e-05 | 2.815e-05 | 8.645e-06 | 4.735e-06 | 1.783e-05 |
3.3 Modulus Study

One can determine the high resistance of material from complex impedance plot. But, the complex modulus plot emphasizes the determination of low capacitance. The interpretation and analysis of the experimental data could be more accurately depicted; if the impedance data were plotted again using modulus formalism. The study of complex modulus spectroscopy provides a detailed idea of electrical transport phenomena and various parameters like carrier ion/hopping rate, conductivity, relaxation time, bulk property etc. with minimum capacitance occurring in the dielectric material under study. The modulus spectroscopy plots help us for the separation of a spectral component of those materials that have similar resistance but different capacitance. Another useful property of modulus formula is that here electrode effect is suppressed. Keeping above points in mind, complex modulus spectroscopy is preferred to be studied. The value of electrical modulus \( M^* \) can be estimated from the following relation \([18]\)

\[
M^*(\omega) = \frac{1}{\varepsilon^*} \left( \frac{\varepsilon'(\omega)}{\varepsilon^*(\omega)} - i \frac{\varepsilon(\omega)}{\varepsilon^*(\omega)} \right) \tag{9}
\]

\[
\Rightarrow M^*(\omega) = M'_*(\omega) + iM''(\omega)
\]

\[
\Rightarrow M^*(\omega) = M'_* \left[ 1 - \int_0^\infty e^{-i\omega t} \frac{\Delta e}{\Delta t} dt \right]
\]

**Figure 4 (a).** \( M' \) versus frequency plot of PLFCTO at different temperature

**Figure 4 (b).** \( M'' \) versus frequency plot of PLFCTO at different temperature.
‘Figure 4(a)’ illustrates the variation of real part of modulus (i.e., $M'$) as a function of frequency at different temperature. We can see from the graph that the values of $M'$ are negligibly small (almost zero) at lower frequencies. With increased frequency, $M'$ show a continuous dispersion. It can be related to the conduction phenomena occurring due to the short-range mobility of charge carriers ‘[19]’. Moreover, $M'$ reaches a constant value at higher frequency region. This suggests that under the influence of an electric field, there is a dearth of restoring force for the movement of charge carriers ‘[20]’. This confirms the diminishment of the electrode effect. The variation of the imaginary part of modulus ($M''$) with frequency (inset of ‘Figure 4(b)’) displays the existence of peak in the low-temperature region. From the graph, it can be seen that $M''$ increases with rise in temperature up to a certain range (i.e., maximum peak value) and then decreases. It a well-known fact that peaks in the imaginary part of modulus are the region where long distance transfer of carrier occurs. Generally, the carriers are restricted to potential wells and move short distance, at frequency above the peak maximum ‘[21]’.So, the range of frequency, within which the peak occurs indicates the transition from long range to short range mobility. Also, the nature of the curve indicates the occurrence of thermally activated process in the material. The peak maxima ($M''_{\text{max}}$) in the graph are shifting towards higher frequency with the rise in temperature. This asymmetric peak broadening specifies the spread of relaxation time with different time constants. Hence, the relaxation occurring here is non-Debye type. This phenomenon is called hopping mechanism and ratifies $M''$ is temperature dependent. At high temperature - high frequency region (‘Figure 4(b)’) $M''$ approaches $M''_{\infty}$. This behaviour depicts the charge ion mobility from short range to long range and the impact of grain boundary capacitance. As frequency increases, all the curves conflate into a single line. This can be attributed to the existence of a long-range conductivity process.

![Figure 4(a) showing variation of $M'$ with frequency at different temperatures](image)

‘Figure 5’ depicts the graph of $M'$ versus $M''$ at a selected temperature. It shows asymmetric and depressed semi-circular arc. The centre of the arcs lies off the $M'$ axis. This confirms non-Debye type...
relaxation process and is evocative for temperature dependent hopping type mechanism for transport of charges in the material under study [21]. From the graph, we can observe noticeable variation in the spectrum pattern with the growth of temperature. This signifies a possible change in the value of capacitance as a function of temperature [11]. In this figure, we find a skewing of the spectra occurs at an elevated temperature and higher frequencies. This indicates that definitely, some complicated electrical microstructure other than the bulk effect is influencing the electrical behaviour in the samples.

4. Conclusions
To put a perspective on the result obtained, the aforementioned processes can be summarized in a nutshell. The ceramic is synthesized by mixed oxide method and the crystal structure is found to be orthorhombic from XRD pattern. Detailed study of structural and electrical properties was carried out by using complex impedance spectroscopy method. The complex impedance and modulus plots give a detailed idea of the occurrence of temperature dependent non-Debye-type relaxation process and NTCR behaviour of the sample.

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