Impact of Ca substitution on structural, optical, and the colossal permittivity dielectric properties of La1-xCaxNi0.5Ti0.5O3 (x = 0 and x = 0.2) nanomaterial’s for energy storage devices

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Research Article

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Posted Date: March 11th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1422917/v1

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Impact of Ca substitution on structural, optical, and the colossal permittivity dielectric properties of La$_{1-x}$Ca$_x$Ni$_{0.5}$Ti$_{0.5}$O$_3$ (x = 0 and x = 0.2) nanomaterial’s for energy storage devices

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Abstract:

Using the sol-gel method, we elaborated the La$_{1-x}$Ca$_x$Ni$_{0.5}$Ti$_{0.5}$O$_3$ (x=0.0 and x=0.2) nanopowders. These powders were sintered at 820°C. X-ray diffraction technique (DRX) and Fourier transform infrared spectroscopy (FTIR) verify the formation of a perovskite orthorhombic structure with the Pnma space group. The band gap energy was evaluated by UV–Vis spectroscopy for the compounds. Photoluminescence (PL) explains the process by which a substance absorbs photons and then re-emits photons. It is found that the imaginary part of the modulus ($M''$) are frequency-related, and display relaxation peaks that shift to higher frequencies with rising temperature. A non-Debye relaxation was confirmed in our samples. We have improved permittivity with the calcium substitution rate. We found giant
permittivity around $10^6$. The value of the giant dielectric constant decreases with rising frequency, demonstrates that there is dispersion in the range of low-frequency and exhibit Maxwell-Wagner interface polarization. We computed the activation energy from the dielectric constant and the modulus (M). The observed giant permittivity values specify that our materials may be appropriate for applications in energy storage devices and small-volume high-performance capacitors.

**Keywords:** Non-Debye relaxation; Giant dielectric permittivity; Sol-gel method; Energy storage; Optical behavior.

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1 **Introduction:**

Perovskite family AMO$_3$ (A: rare earth and M: transition metal) have been widely investigated because of their important physical properties in recent years. Among these important properties we can cite the optical, dielectric, electrical and magnetic properties.$^{1,2}$ This change is usually linked to various factors, like warming process $^3$, devices of magnetic or electric field $^4$, selection of the doping site $^7$ and synthesis route $^5$. In particular, the doping mechanism permits to collect all the characteristics of the various ionic components of the perovskite oxide$^6$.

In recent years, titanium-substituted LaNiO$_3$ is considered to be an acetone sensing compound, which has higher sensitivity, selectivity and stability likened with informed sensor samples. Through XPS analysis, the acetone sensing process of LaNi$_{1-x}$Ti$_x$O$_3$ will be examined along the structural changes$^7$. In addition, with a perovskite LaNi$_{0.5}$Ti$_{0.5}$O$_3$ they built
an amino acid electrochemical sensor based on a modified carbon paste electrode \(^8\). Also, they made composites with perovskite \(\text{LaNi}_{0.5}\text{Ti}_{0.5}\text{O}_3\) (LNT) for various applications among these composites can be mentioned: the \(\text{LaNi}_{0.5}\text{Ti}_{0.5}\text{O}_3 \quad \text{– NiFe}_2\text{O}_4\) composite was prepared using the sol-gel method and employed to construct a mediated glucose electrochemical chip \(^9\) and \(\text{LaNi}_{0.5}\text{Ti}_{0.5}\text{O}_3/\text{CoFe}_2\text{O}_4\) (LNT - CFO) composite were an excellent detection material for \(\text{H}_2\text{O}_2\) oxidation. LNT – CFO nanoparticles are thought to be a promising material for biosensors \(^{10}\).

Over the past few years, Giant-permittivity compounds \((\varepsilon'>10^4)\) were received rising regard owing to potential technological application like electrical energy storage devices, small-volume high-performance capacitors and, High-K gate dielectrics \(^{11,12}\). In fact, the size of the capacitor decreases as the dielectric constant raise. Capacitors premised on giant dielectric constant compounds can be utilized in devices with limited size to replace batteries.

Commonly, these compounds of permittivity known as «giant» or «colossal» are separated into two different categories \(^{13}\). The first appropriate categories are "intrinsic" giant dielectric constant compounds, which have improved dipole response, such as doped titanium samples \(^{14}\).

The second category is classified as "extrinsic" category, in which elevated effective permittivity is attained by increasing electrical conductivity or by establishing a composite material that carries a dielectric matrix with randomly or orderly distributed conductive charges \(^{15}\). Among the high permittivity extrinsic composites, we can cite Particular examples cover metal-laden ceramics specifically Mo-mullite \(^{16}\) and Ag-bismuth zinc niobate, \(^{17}\) metal-metal-loaded ferroelectrics like \(\text{BaTiO}_3\), \(^{18}\) metal-loaded glass, \(^{19}\) and metal \(^{20}\).

In the current work, our goal is to prepare the Ca -substituted nanomaterials with the sol gel method. We performed structural analysis to study effects on the lattice parameter and lattice
strain crystalline size, of nonmaterial. Also, we studied the optical behavior of the samples. In order to investigate the electrical properties of the compounds, we used the complex impedance spectroscopy. We used a broadband dielectric spectrometer (HP 4194) to check the dielectric properties of the samples in a range of temperature (233-313 K) and frequency (100 Hz-10^6 Hz).

2 Experimental procedures:

2.1 Nanoparticles preparation:

The La_{1-x}Ca_xNi_{0.5}Ti_{0.5}O_3 (x=0.0 et x=0.2) compounds are synthesized via sol-gel technique^21. To synthesize the samples, we utilized the following precursors: La (NO_3)_3 6H_2O, Calcium nitrate (Ca (NO_3)_2 4H_2O), Nickel nitrate ((Ni (NO_3)_2 6H_2O), titanium oxide TiO_2, ethylene glycol (C_2H_6O_2) and citric Acid (C_6H_8O_7). The quantities of precursors to prepare our samples are computed using the subsequent reaction equation:

(1-x)(La (NO_3)_3 6H_2O) + 0.5 (Ti O_2) +0.5 (Ni (NO_3)_2 6H_2O) + x (Ca (NO_3)_3 4H_2O) → La_{0.8} Ca_{0.2} Ni_{0.5}Ti_{0.5}O_3+δCO_2 + δ’ O_2

First of all, we blended the precursors in distilled water with a regular stirring at room temperature on a hot plate. After that, the citric acid and ethylene glycol were added to the solution blend which was stirred at 70 °C for 3 hours until they obtained a viscous gel. Then we heat the obtained mixture to 300 °C for 12 h until a black powder is produced. After that, we calcined the dried powder at 450 °C for 12 hours, and then squared it again. Employing a uniaxial pressure system, pellets with a diameter of about 12 mm and a thickness of about 1.6 mm were constructed. The pellets have been warming treated, first at 600°C for 24 hours, then the compounds under investigation was grounded and warmed up at 800°C several times for 23 hours. Again, we heated the ground powder to 820°C for 23 hours. We have determined the phase purity, homogeneity and lattice structure of the prepared powders.
2.2 Characterization of materials:

The structures of the compounds annealed at 820°C were characterized by XRD. The measurements were effected at 300 K utilizing a Bruker 8D Advance X-ray powder diffractometer in the range 15° to 110°, with CuKα1 radiation (λ = 1.5406 Å) and a step size of 0.02°. The morphology of the samples was analyzed by transmission electron microscopy (TEM). We performed the TEM images at a voltage of 200 KV, with a Tecnai G2 FEI microscope. Using the Shimadzu-8700 FTIR spectrometer we have obtained Fourier Transform Infrared Spectroscopy (FTIR) in the span of 450-4000 cm⁻¹. We used UV-3101PC scanning spectrophotometer to investigate the UV-visible spectra of the compounds at room temperature in the range of 200-1000 nm. Photoluminescence (PL) spectrum was carried at room temperature using iHR320 monochromator. For electrical measurements, the both parallel edges of the pellets are covered with silver paste as electrodes. The impedance measurement is connected to the computer by using impedance analyzer technology (HP 4194), the frequency range is 100-10⁶ Hz, and the temperature range is 233 K to 313K.

3 Results and discussions:

3.1 Study the Crystal structure:

3.1.1 X-ray diffraction investigation:

The X-ray diffraction diagrams of the investigated x=0.0 and x=0.2 compounds (Figure 1a and b) displays that the perovskite phase is a large principal phase 22, so our compounds are regarded as a single phase. We note that the samples admit a good crystallinity and prove the ability of the sol-gel elaboration technique to produce pure phases with an elevated crystallinity.

3.1.2 Refinement by the Rietveld technique:

Rietveld's refinements of XRD show that the investigated samples crystallize in an orthorhombic structure with the space group Pnma. The results of the refinement are
displayed in Figure 1a and b and the parameters of the structural are classified in Table 1. With the aim to validate the materials structures, Goldschmidt was specified a tolerance factor $t_G$, which uses geometric criteria to give information about the stability and deformation of the structure:

$$t_G = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} (1)$$

With $\langle r_A \rangle$ is the mean ionic radii of the perovskite site A, $\langle r_B \rangle$ is the mean ionic radii of the perovskite site B and $\langle r_O \rangle$ represents the mean ionic radii of the perovskite site O, whose values are provided by Shannon. We have computed the ionic radii of the ions occupying the positions A, B and O according to the following equation:

$$\langle r_A \rangle = 0.8 r_{La}^{3+} + 0.2 r_{Ca}^{2+}$$

$$\langle r_B \rangle = 0.5 r_{Ti}^{4+} + 0.5 r_{Ni}^{3+}$$

$$\langle r_O \rangle = r_{O2^-}$$

After a calculation, $t_G$ was found to be equal to 0.93 and 0.91 for $x=0.0$ and $x=0.2$ respectively.

### 3.1.3 investigation the Debye Scherrer and the Williamson–Hall procedure:

Two methods were used, Debye-Scherrer and the Williamson–Hall procedure to specify the mean size of the crystallizers. The average crystalline size is yielded for both methods from the XRD peaks. We had given an explication of these both calculation methods. Firstly, the technique of Debye–Scherer, is given by:

$$D_{SC} = \frac{0.9 \times \lambda}{\beta \times \cos \theta} (2)$$

with, $\lambda$, $\theta$ and $\beta$ are respectively the used wavelength, the Bragg angle for the most intense peak and the half height width of this peak. Secondly, with the Williamson–Hall procedure,
the broadening of the X-ray line (b) is equivalent to the expansion resulted in the distortion of the crystal lattice ($\beta_{\text{Strain}}$) existing in the material \(^2\text{6}\) plus the contribution of the crystallite size ($\beta_{\text{Size}}$), and is given by the following formula:

$$\beta = \beta_{\text{Size}} + \beta_{\text{Strain}} \quad (3)$$

with, $\beta_{\text{Strain}} = 4\varepsilon \tan(\theta)$, where $\varepsilon$ is a coefficient linked to strain impact on the crystallites and $\beta_{\text{size}}$ is given by:

$$\beta_{\text{size}} = \frac{0.9\lambda}{D_{\text{WH}} \cos(\theta)}$$

By replacing $\beta_{\text{size}}$ and $\beta_{\text{strain}}$ by its values, equation 3 is equal to:

$$\beta = \beta_{\text{Size}} + \beta_{\text{Strain}} = \frac{0.9\lambda}{D_{\text{WH}} \cos(\theta)} + 4\varepsilon \tan(\theta) \quad (4)$$

As a result, the equation (2) is changed to: $\beta \cos(\theta) = \frac{0.9\lambda}{D_{\text{WH}}} + 4\varepsilon \sin(\theta)$. Then, we calculated the crystallite size ($D_{\text{WH}}$) and microstrain according to the plot of $\beta \cos(\theta) = f(4\varepsilon \sin(\theta))$ (*Figures 1c and d*) according to the intercept of the straight line when $x = 0$ and the slope of the linear adjustment data respectively. The values of the crystalline sizes $D_{\text{SC}}$, $D_{\text{WH}}$ and microstrain $\varepsilon$ are given in the table 1. It should be noted that since the Debye-Scherer procedure completely excludes the broadening effect caused by the micro-strain, the crystal size computed by the Debye-Scherer procedure is larger than the crystal size calculated by the Williams-Hall procedure.

3.1.4 Porosity:


Porosity is considered among the important parameters to fully characterize the dielectric behavior of materials. The porosity of the compounds is computed at employing the subsequent equation:

$$P(\%) = (1 - \frac{d_{\text{exp}}}{d_{\text{theor}}}) \times 100 \quad (5)$$

where, $d_{\text{theor}}$ is the theoretical X-ray density:

$$d_{\text{theor}} = \frac{Z \times M}{N_A \times V_P} \quad (6)$$

And $d_{\text{exp}}$ is the experimental density:

$$d_{\text{exp}} = \frac{m}{V} \quad (7)$$

where, $M$ represents the molecular mass, $N_A$ represents the Avogadro number, $V_P$ represents the volume determined from the XRD results, $m$ is the mass of the pellet and $V$ is the volume of the pellet.

The compactness $C$, of ceramics as a function of the theoretical and experimental density was computed by the following relationship:

$$C = \frac{d_{\text{exp}}}{d_{\text{theor}}} \quad (8)$$

The values of the theoretical X-ray density ($d_{\text{theor}}$), the experimental density ($d_{\text{exp}}$), the porosity ($p$) and the compactness $C$ are listed in the Table 2.

In hypothetical terms, all particles are spherical, and the specific surface area ($S$) is computed according to the relationship $S = 6000 / D_{\text{W-H}}d_{\text{exp}}$, where $D_{\text{W-H}}$ represents the
diameter of the particle in nm, and $d_{\exp}$ experimental density of the particle in g/cm$^3$. The parameter $S$ is highlighted in table 2.

3.2 Morphological behavior:

The figure 2a and c display the TEM images of the developed $x=0.0$ and $x=0.2$ samples. These images display an almost uniform distribution, which proves that the sol-gel technique is an excellent technique for preparing homogeneous and dense compounds. We used image-J software exhibit in Figure 2b and d to carry out particle size measurement on TEM images. We noticed that the mean particle size rises with the substitution of calcium. Using a Lorentzian adjustment particle size distribution, the particle sizes ($D_{\text{TEM}}$) are about 45 nm and 62 nm for the $x=0.0$ and $x=0.2$ compounds, respectively. It is obvious that the $D_{\text{TEM}}$ values give an average value higher than the mean value specified from the XRD and higher than the mean value determined by the Halder-Wagner procedure. This difference is explained by the composition of each grain with several crystallites.

3.3 Optical behavior:

3.3.1 FTIR analysis:

Fourier Transform Infrared Spectroscopy information on the nature of chemical bonds and may be used for the identification of compounds. The FTIR spectra of the $x=0.0$ and $x=0.2$ compounds are presented in the figure 3 at temperature 300K. The absorption band in the span of 450–4000 cm$^{-1}$ was recorded. The FTIR spectrum is a procedure used to specify the existence of frequency bands because of ion vibrations in the structure. The bands are acquired at 544, 841 and 2358 cm$^{-1}$ for $x=0.0$ and 492, 673, and 2343 cm$^{-1}$ for $x=0.2$. The peaks near 2358 and 2343 cm$^{-1}$ in $x=0.0$ and $x=0.2$ compounds respectively specify the stretching vibration of OH group and the bending vibration of the adsorbed molecule water$^{27}$. The metal oxide band around 400-600 cm$^{-1}$ confirms the establishment of an
orthorhombic perovskite crystal, which is coherent with ancient investigations in the literature\textsuperscript{29}. The absorption bands of about 492 cm\textsuperscript{-1} for x=0.0 and 544 cm\textsuperscript{-1} for x=0.2 samples are believed to be owing to the existence of interconnected TiO\textsubscript{6} octahedra, and M–O is the stretching vibration \textsuperscript{30}, where M represents the position cation B (Ni, Ti). Furthermore, the peaks recorded by x=0.0 and x=0.2 samples at 841 and 673 cm\textsuperscript{-1} respectively are related to the sub-nitrate NO\textsubscript{3}\textsuperscript{-}molecule \textsuperscript{31}, which also confirms that the compounds have been successfully elaborated by this sol-gel method.

3.3.2 UV–Visible absorption investigation:

The absorption spectra of the compounds are exhibited in the figure 4a and c in a wavelength span prolonged from the ultraviolet (UV) to visible (VIS), or wavelengths in the span of 190 to 1000 nm. The spectra display that it has a maximum absorption band in the ultraviolet region. The recorded intense band of about 272nm gives the gap of the materials. The absorption may be owing to the photoexcitation of electrons from the valence band to the conduction band (the ligand-metal (p-d) type charge transition O\textsubscript{2p} $\rightarrow$ Ni\textsubscript{3d}). The optical band gap (E\textsubscript{g}) is the primary characteristics of the compounds and as possible excellent participants for optoelectronic devices. The energy of the optical interval (E\textsubscript{g}) samples is determined using the Tauc’s equation where E\textsubscript{g} is related to the absorption coefficient $\alpha$ by the next relation\textsuperscript{32}:

$$(\alpha h \nu)^n = A(h \nu - E_g) \quad (9)$$

where $\alpha$, $h \nu$, $A$, $E_g$ and $n$ are the absorption coefficient, the energy of the incident radiation formulated in eV, the constant reflection of the amorphous solid structure's disorder degree, the gap energy and the exponent described the type of optical transition, respectively. According to the nature of the electronic transition, the value of the exponent n can be 1/2
(indirect transition allowed), 3/2 (indirect transition forbidden), 2 (direct transition allowed) and 3 (direct transition forbidden) responsible for absorption.

We traced the graph of \((\alpha h \nu)^2\) vs. \(h \nu\) for \(x=0.0\) and \(x=0.2\) samples in the figures 4b and 4d. From the intersection of the linear part with the energy axis, we calculated the gap energy. The gap energy values for the \(x=0.0\) and \(x=0.2\) samples are equal to 2.30 and 2.51 eV respectively. Moreover, since the value of the optical band gap energy is bigger than the theoretical value of the energy required for water splitting \((\lambda> 1.23\text{ eV})\), this compound is a promising candidate for solar photocatalytic activity.

### 3.3.3 Photoluminescence:

Photoluminescence is a powerful optical technique for characterizing semiconductor materials and insulator. Its principle of operation is simple: the electrons of the studied samples are excited by radiation (usually monochromatic) and the emitted light is detected and analyzed. The photoluminescence (PL) indicated a non-destructive and sensitive experiment used to study semiconductor compounds in photocatalysis and the photochemistry and photophysics of dielectric.

Furthermore, the PL also provides the following information: lattice defects, grain boundaries and surface oxygen gaps, as well as the isolation and recombination of the photo generated by the load carrier. The figure 5 presents the ambient temperature PL spectra of the \(x=0.0\) and \(x=0.2\) samples. The PL emission spectra were recorded with an excitation in the wavelength interval of 300 to 900 nm. We recorded green emission peaks close to 544 nm and 498 nm for compounds \(x=0.0\) and \(x=0.2\) respectively. In addition, it is seen that when calcium is inserted into the compound \(x=0.0\) the intensity of the PL response decreases. This can be clarified by the decrease in defects in the sample. In the case of the insertion of calcium, the peak at which the maximum emission occurs, shift to a zone of smaller wavelength (higher energy positions), and this effect may be related to the rise in the energy of the gap band. The
insert in the figure 5 exhibit the change in intensity versus (hv). The spectra show predominance luminescence peaks at 2.29 and 2.49 eV for x = 0.0 and x = 0.2, respectively. These values are a good accord with the prohibited bands mentioned by the UV-Visible absorption results.

3.5 Dielectric relaxation study:

3.5.1 Evaluation of the complex modulus:

In order to comprehend the relaxation mechanism and to make the difference between contributions through the investigated nanomaterial, the modulus is evaluated. The electrical characteristic of the sample can be mentioned employing the complex electric modulus $M^*$ is expressed as:

$$M^* = M' + iM'' = \frac{\varepsilon'^2}{\varepsilon'^2 + \varepsilon''^2} + i\frac{\varepsilon''^2}{\varepsilon'^2 + \varepsilon''^2}$$  \hspace{1cm} (12)

Where, $M'$ is the real parts and $M''$ is the imaginary parts. The figure 6a and b display the spectra of the values of $M'$ at various temperatures for the x=0.0 and x=0.2 samples. At bass frequency, it is observed that the value of $M'$ is low (close to zero) for all temperatures. This is due to the absence of electrode processes and long-distance movement of load carriers in the samples. Whereas when the frequency raises the values of $M'$ exhibit a dispersio towards $M_{\infty}$. Nevertheless, this pursued dispersion specifies that the electrical conduction in the samples may be caused by the displacement of the load carrier in a short region, where $M$ will not be modified by frequency. The figure 6c and d exhibit the frequency and temperature dependence of the $M''$, over the 233-313 K temperature range of the x=0.0 and x=0.2 compounds. It gives non-symmetric loss spectrum at all frequency range. It is noticed that the spectrum of $M''$ has a unique electrical relaxation, peak at all temperatures, which is related to the grain impact. The peaks at low frequencies display that load carriers can shift a
long distance, whereas the behavior at high frequencies signifies that load carriers are trapped in potential wells\(^{36}\). Obviously, as the temperature increases, the relaxation peak of our samples move to the high-frequency region, this explains the relation between the movements of the mobile ion load. Furthermore, the asymmetric peaks of \(M''\) specify that the conductive comportment is attributed to the non-Debye type\(^{37}\). In order to more differentiate the various contributions to the \(M''\), the experimental data have been fitted to the Bergman suggested Kohlrausch, Williams and Watts (KWW) formulation\(^{38}\):

\[
M'' = \frac{M_{\text{max}}''}{[1 - \beta(\beta l/(1 + \beta))(\beta(f_{\text{max}} / f) + (f / f_{\text{max}})^{\beta})]} \tag{13}
\]

In this equations, \(M_{\text{max}}''\), \(f_{\text{max}}\), \(\beta\) are the peak maximum value, frequency and stretch factor (0 <\(\beta\) <1), respectively, which explains that the relaxation is dielectric Debye or non-Debye characteristics\(^{39}\). In table 3, we have listed Adjustment parameters for \(M''\) (f) data employing Eq. (13). The results achieved by the fitted curve show that the \(\beta\) value is less than 1, which explains the non-Debye nature of our samples. In order to compute the activation energy, the change of \(\ln (f_{\text{max}})\) and the corresponding frequency of the maximum \(Z''\) are plotted according to Arrhenius' law:

\[
f_{\text{max}} = f_0 e^{-\frac{E_a}{k_B T}} \tag{11}
\]

Where, \(f_0\) is the pre-exponential term, \(E_a\) is the activation energy, and \(k_B\) is the Boltzmann constant. The changes of \(\ln (f_{\text{max}})\) versus 1000/T are plotted in Figure 6e and f to compute the activation energy provided by the \(x=0.0\) and \(x=0.2\) compounds. Based on Arrhenius' law (eq (13)), the fitting result and the \(E_a\) are given, which proves that for \(x=0.0\) there is one region the \(E_a\) is 0.213 eV, on the other hand, for \(x=0.2\) there are two regions: (R-I), the \(E_a\) is 0.533 eV and (R-II) the \(E_a\) is 0.180 eV.
3.6 Dielectric study:

3.6.1 Dielectric permittivity investigation:

For the purpose of determining the conduction phenomena, the dielectric analysis is carried out. It explains the provenance of the electrical, dielectric and relaxation losses. With the complex impedance \((Z', Z'')\), we obtained the complex permittivity \(\varepsilon^* (\omega)\) which can be described by:

\[
\varepsilon^* = \frac{1}{j\epsilon_0 Z''} = \varepsilon' + j\varepsilon'' = \frac{Z'}{\omega \epsilon_0 (Z''^2 + Z'^2)} + j \frac{Z'}{\omega \epsilon_0 (Z''^2 + Z'^2)}
\] (14)

With, \(\epsilon_0\) is the geometrical capacity. \(\varepsilon'\) and \(\varepsilon''\) are the real and imaginary parts of the dielectric constant, which correspond to the energy storage and energy loss in the compound, respectively. The Figures 7a and c show the change in dielectric constant versus frequency at various temperatures ranging from 233 K to 313 K for the \(x=0.0\) and \(x=0.2\) samples. Indeed, it is seen a giant permittivity of the order \(10^6\) for the compound substituted by the calcium. So, we have improved the dielectric constant with the substitution of calcium for the LNTO compound from \(10^3\) to \(10^6\). The behavior of the dielectric constant can be separated with the frequency. For the lowly frequency region below \(10^3\) Hz, the real part of the permittivity rises with temperature, which can be clarified by the high mobility of load carriers and the rise in polarization. It is reminded that the Maxwell-Wagner double-layer pattern is known for its inhomogeneous structures and corresponds to this observation. One considers that the samples consist of both layers, in which the grains admit elevated electrical conductivity, while the boundary grains have low electrical conductivity. The grain boundaries admitting a high resistivity at low frequencies this is explained by the gathering of electrons and the generation of polarization at the boundary. This phenomenon verifies the dielectric behavior of the nanomaterial’s in the low frequency zone. While in the high-frequency zone, \(\varepsilon'\) decreases, then it remains constant and is due to the orientation of the electric dipoles in the...
direction of the applied field. Thus, the polarization mechanism is reduced because dipoles cannot pursue the direction of the applied field\textsuperscript{43}. Therefore; the reorientational movement of the load carriers decreases the values of the real part of the dielectric constant. This phenomenon is identical to the one recorded for other amorphous semiconductors\textsuperscript{44}. The variation in the imaginary permittivity is presented in the figure 7b and d versus the frequencies and at diverse temperatures. At low frequencies, the obtained values are elevated. This explains the existence of all polarization mechanism (i.e. interfacial, dipolar, atomic, and electronic) in the x=0.0 and x=0.2 compounds. Whereas, at elevated frequencies, the electric dipole can no longer vibrate with the external alternating electric field, the dielectric loss is reduced\textsuperscript{45}. In contrast, as previously cited \textsuperscript{46}, there is no maximum point in the imaginary permittivity plot, which indicates that the polarization is controlled by a jump mechanism. The changed Debye equation is employed to simulate the frequency dependence of the dielectric constant for the x=0.0 and x=0.2 samples, which are presented in the Figures 7a and c as solid lines for chosen temperatures. The changed Debye equation is specified by\textsuperscript{47}:

\[
\varepsilon' = \varepsilon'_{\infty} + \frac{\varepsilon'_0 + \varepsilon'_\infty}{1 + (\omega \tau)^{2(1-\alpha)}}
\]  

(15)

where, \(\tau\), \(\varepsilon'_0\), \(\varepsilon'_\infty\), \(\omega\) are respectively the relaxation time, the dielectric constants in the low frequency limit, the dielectric constants in the elevated frequency limit and the angular frequency. The exponential parameters are regrouping in the table 4, varying between 0 and 1. In table 4, we classed the spreading factor (\(\alpha\)) and relaxation time (\(\tau\)) at the selected temperatures for x=0.0 and x=0.2 samples. The value of \(\tau\) resolute according to the changed Debye relaxation formula is suitable for the dispersion of \(\varepsilon'\) with frequency. The curve \(\ln (\tau)\) versus 1000/T (K\textsuperscript{-1}) is exhibited in the figure 7e and f. It follows the Arrhenius law\textsuperscript{48}.
\[
\tau = \tau_o \exp\left(\frac{E_a}{k_B T}\right) \quad (16)
\]

Where, \(\tau_o\), \(E_a\), \(T\), \(k_B\) are respectively the relaxation time at infinite temperature, activation energy, measurement temperature and Boltzmann constant. The activation energy of LCNTO is 0.543 eV. As well the corresponding relaxation time at infinite temperature \((\tau_o)\) is of the order \(1.98 \times 10^{-7} \) s.

The figures 8a and b illustrate the variation of the dielectric constant as a function of temperature at various frequencies for \(x=0.0\) and \(x=0.2\) samples. The dielectric constant is not coherent with rising temperature values. We noticed that in the temperature range \([233 \text{ K}-263\text{ K}]\) for \(x=0.0\) and \([233-273 \text{ K}]\) for \(x=0.2\), the dielectric constant display a speedy rise with the temperature rise. This increase is related to interfacial and bipolar polarizations\(^{49}\). The dielectric constant attainment a maximum value for the sample \(x=0.0\) of the order \(10^3\) at 263 K and for the sample \(x=0.2\) of the order \(10^6\) (permittivity of the giants) at 273 K. This temperature is called the dielectric transition temperature \(T_d\). While after the dielectric transition temperature \((T_d=263 \text{ K for the } x=0.0 \text{ sample and } T_d=273 \text{ K for the } x=0.2 \text{ sample})\), the dielectric constant begins to decrease. For our samples, the spontaneous polarization does not exist. Therefore, it verifies that this change is typical for polar dielectrics, in which the orientation of the dipole is contributed by the rise in temperature\(^{28}\). So, our materials may be appropriate for applications in energy storage devices and small-volume high-performance capacitors.

**Conclusion:**

To conclude, the \(\text{La}_{1-x}\text{Ca}_x\text{Ni}_{0.5}\text{Ti}_{0.5}\text{O}_3\) (\(x=0.0\) and \(x=0.2\)) perovskite materials was successfully elaborated by a sol-gel method and the resulting nanoparticles were annealed at temperature of 820°C. X-Ray diffractogramme showed that these compounds are pure and crystallizes in
the orthorhombic system with Pnma space group. The TEM images present a uniform
distribution of nanosize grains. FTIR results are coherent with the XRD analysis. The optical
band gap of about 2.30 eV for x=0.0 and 2.51 eV for x=0.2 Samples are related with the
semiconductor behavior. Photoluminescence (PL) clarifies the phenomenon of light emitted
by any category of matter after absorbing photons. The investigation of their dielectric
behaviors was performed versus the frequency and the temperature span of (10²-10⁶ Hz) and
(233–313 K). As the temperature rise, the relaxation and peak rise of the M'' spectra prove
Arrhenius's law. Furthermore, the relationships between the real and imaginary parts of the
dielectric constant were investigated versus of both the temperature and the frequency. The
value of the giant dielectric constant decreases with rising frequency, indicating that there is
dispersion in the low frequency region and showing Maxwell-Wagner interface polarization.
After attainment this region through the jump process, the accumulation of electrons at the
grain boundary can clarify this comportment. The investigated materials could be potential
candidates in technological applications like energy storage devices and small-volume high-
performance capacitors.

Conflict of interest:

The authors declare that they have no conflict of interest.

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**Tables Caption**

**Table 1:** Results of Rietveld refinements for La$_{1-x}$Ca$_x$Ni$_{0.5}$Ti$_{0.5}$O$_3$ (x=0.0 and x=0.2) powders.

**Table 2:** Calculated tolerance factor ($t_G$), X-ray density ($d_{exp}$), bulk density ($d_{theor}$), porosity (P) and the specific surface area (S) for the La$_{1-x}$Ca$_x$Ni$_{0.5}$Ti$_{0.5}$O$_3$ (x=0.0 and x=0.2) compounds.

**Table 3:** Theoretical parameters obtained from the fitted data of the imaginary part of the modulus as a function of frequency at various temperatures of La$_{1-x}$Ca$_x$Ni$_{0.5}$Ti$_{0.5}$O$_3$ (x=0.0 and x=0.2) compounds.

**Table 4:** Spreading factor ($\alpha$) and relaxation time ($\tau$) for La$_{1-x}$Ca$_x$Ni$_{0.5}$Ti$_{0.5}$O$_3$ (x=0.0 and x=0.2) compounds at selected temperatures.
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<td>Pnma</td>
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<td><strong>Cell parameters</strong></td>
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<tr>
<td>(a) (Å)</td>
<td>5.502(4)</td>
<td>5.5282</td>
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<tr>
<td>(b) (Å)</td>
<td>7.842(15)</td>
<td>7.8015</td>
</tr>
<tr>
<td>(c) (Å)</td>
<td>5.546(10)</td>
<td>5.522(8)</td>
</tr>
<tr>
<td>(V) (Å³)</td>
<td>239.378(0.053)</td>
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<td><strong>Atoms</strong></td>
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<td></td>
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<tr>
<td>((\text{La})/\text{(La/Ca)})</td>
<td></td>
<td></td>
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<tr>
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<td>4c</td>
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<tr>
<td>Symmetry of site</td>
<td>m</td>
<td>m</td>
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<tr>
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<td>1.064</td>
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<td>((\text{Ni/Ti}))</td>
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Table 2

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<th>283K</th>
<th>293K</th>
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<th>313K</th>
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<td>0.86</td>
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<td>(f_{\text{max}}(\text{Hz}))</td>
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### Table 4

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<tr>
<td>(T)</td>
<td>(\alpha)</td>
<td>(\tau)</td>
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<td>313K</td>
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Figures

**Figure 1:** Refined X-ray diffraction patterns of Sol–Gel for the La$_{1-x}$Ca$_x$Ni$_{0.5}$Ti$_{0.5}$O$_3$ (x=0.0 (a) and x=0.2 (b)) samples: Solid black circle represents the observed pattern; Solid black circle corresponds to the observed pattern; continuous red line corresponds to the computed pattern and the blue line corresponds to the difference between the observed and computed patterns. Tick green markers represent the position of the allowed Bragg diffractions. Williamson–Hall plots of the La$_{1-x}$Ca$_x$Ni$_{0.5}$Ti$_{0.5}$O$_3$ (x=0.0 (c) and x=0.2 (d)) samples synthesized by the sol–gel methods.

**Figure 2:** (a),(c) TEM Micrographs and (b),(d) particle size distributions of La$_{1-x}$Ca$_x$Ni$_{0.5}$Ti$_{0.5}$O$_3$ (x=0.0 and x=0.2) samples.

**Figure 3:** FTIR spectra of perovskite of La$_{1-x}$Ca$_x$Ni$_{0.5}$Ti$_{0.5}$O$_3$ (x=0.0 and x=0.2) materials.

**Figure 4:** (a),(c) UV-visible absorption spectra and (b),(d) the Band-gap determination for La$_{1-x}$Ca$_x$Ni$_{0.5}$Ti$_{0.5}$O$_3$ (x=0.0 and x=0.2) materials.

**Figure 5:** PL spectra of La$_{1-x}$Ca$_x$Ni$_{0.5}$Ti$_{0.5}$O$_3$ (x=0.0 and x=0.2) materials.

**Figure 6:** (a),(b) Real part of electric modulus and (c),(d) Imaginary part of the electrical modulus plots as a function of frequency at different temperatures for La$_{1-x}$Ca$_x$Ni$_{0.5}$Ti$_{0.5}$O$_3$ (x=0.0 and x=0.2) compounds. (e),(f) Variation of ln($f_{max}$ (M’’)) as a function of 1000/T for La$_{1-x}$Ca$_x$Ni$_{0.5}$Ti$_{0.5}$O$_3$ (x=0.0 and x=0.2) compounds.

**Figure 7:** (a),(c) the dielectric constant $\varepsilon^\prime$ versus frequency plots of La$_{1-x}$Ca$_x$Ni$_{0.5}$Ti$_{0.5}$O$_3$ (x=0.0 and x=0.2) samples at the selected temperatures, which are modeled by the modified Debye model. (b),(d) The Variation of $\varepsilon''$ with frequency at several temperatures for La$_{1-x}$Ca$_x$Ni$_{0.5}$Ti$_{0.5}$O$_3$ (x=0.0 and x=0.2) compounds. (e),(f) The Arrhenius plots for relaxation time (s) versus temperature (1000/T) of La$_{1-x}$Ca$_x$Ni$_{0.5}$Ti$_{0.5}$O$_3$ (x=0.0 and x=0.2) samples.
Figure 1
Figure 2
Figure 3

The graph shows the transmission percentage as a function of wavenumber (cm$^{-1}$) for different compositions. Key wavenumbers are indicated with specific values:

- $2343 \text{ cm}^{-1}$
- $2358 \text{ cm}^{-1}$
- $673 \text{ cm}^{-1}$
- $492 \text{ cm}^{-1}$
- $841 \text{ cm}^{-1}$
- $544 \text{ cm}^{-1}$

For $x = 0.0$, the absorption spectra are shown with λ (nm) as the x-axis and absorption as the y-axis. The relationship $E_g = 2.30 \text{ eV}$ is highlighted in the inset graph.
Figure 4
Figure 5
Figure 6

(a) $x = 0.0$

- $E_{a1} = 0.213 \text{ eV}$
- $E_{a2} = 0.533 \text{ eV}$

(b) $x = 0.0$

- Dielectric constant $\varepsilon'$
- Frequency (Hz)
Figure 7
Figure 8