Graphical Abstract

Chemical Composition-Tailored $\text{Li}_x\text{Ti}_{0.1}\text{Ni}_{1-x}\text{O}$ Ceramics with Enhanced Dielectric Properties

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Abstract

This paper reports on the synthesis of polycrystalline (Li,Ti)-doped NiO powders (i.e., $\text{Li}_x\text{Ti}_{0.1}\text{Ni}_{1-x}\text{O}$, abbreviated as LTNO) by the solid-state synthesis method. Note that, the doping concentration of Ti is kept constant ($x \sim 0.10$) in the stoichiometry, the difference in the material behavior of LTNO samples can only be attributed to the effect of Li. X-ray diffraction patterns confirmed a cubic rock-salt structured NiO-based phase with the presence of minor NiTiO_3 phase, were reported elsewhere [Venkata et. al., Chem. Phys. Lett., 649 (2016) 115–118.]. Dense microstructures were obtained using ultra high resolution scanning electron microscope. A high dielectric constant ($\epsilon \sim 10^4$) near room temperature at low-frequency was observed in LTNO ceramics. Weak temperature dependence of dielectric constant over the measured compositions ($x=0$ to 0.10) was observed in the LTNO ceramics. A giant dielectric constant of 10^4 – 10^5 at high temperatures (120 – 170°C) for certain LTNO compositions ($x=0.15$ to 0.3) was observed in the sintered ceramics. The origin of the high dielectric constant observed in these LTNO ceramics is attributed to the Maxwell–Wagner polarization mechanism and a thermally activated mechanism.

Key Words: LTNO, NiO, Cubic, Giant Dielectric constant, Maxwell–Wagner

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1. Introduction

High dielectric constant materials with weak temperature dependence or nearly temperature independent have been playing a significant role in microelectronics industry, since they have been used as important devices such as capacitors and memory devices, filters, resonators and communication systems. Nickel oxide (NiO) is a transition-metal oxide, Mott-Hubbard insulator with a very low electrical conductivity [$10^{-13} (\Omega\text{cm})^{-1}$] at room temperature, which crystallizes in a high-temperature rocksalt structure and exhibits anti-ferromagnetic behavior below 523 K, which has been widely studied and used in various applications, including smart windows, active optical fibers, electro-chromic materials for display panels and temperature sensors [1]. NiO is also used as negative electrode materials in Li-ion batteries [2, 3]. Non-stoichiometric NiO is a candidate material for p-type transparent conducting films with energy band gap from ~ 3.6 to 4.0 eV [4]. Non-ferroelectric NiO based materials show highest structural stability and do not decompose normally [5]. Electrical conductivity of NiO is dramatically increased by the introduction of Ni^{2+} vacancies and/or interstitial oxygen in NiO crystallites by doping with monovalent impurities like Li^+ [6, 7]. However pure NiO has shown low dielectric permittivity values both at room temperature and high temperatures.

Improved dielectric permittivities are essential for efficient utilization in various electrical and electronic applications. Recently lead-free body centered cubic perovskite like $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO), and non-perovskite $\text{Li}_x\text{Ti}_{0.1}\text{Ni}_{1-x}\text{O}$ (LTNO) with giant dielectric permittivity ($\epsilon \sim 10^4$ - 10^5 @ kHz region frequency) values are noticeable attention for various applications [8-10]. Giant dielectric permittivities were also observed for CCTO-LTNO composites at wide range of frequencies (100 kHz–1 MHz) [11]. The origin of the high permittivity in non-ferroelectric CCTO based materials could be attributed to space charge polarization and is not an intrinsic property associated with the crystal structure and in particular these materials were used in internal barrier layer capacitors due to the development of Schottky barriers at grain boundaries [8]. And this high permittivity CCTO ceramic material is electrically heterogeneous consisting of semiconducting grains and insulating grain boundaries [12]. And such a giant dielectric permittivity response in LTNO based ceramic is also attributed to barrier layer capacitor (BLC) mechanism [10]. High dielectric permittivity in these types of materials is generally related to Maxwell–Wagner polarization (interfacial polarization), which often arises in a material

consisting of grains which become semiconducting, while grain boundaries are insulating [13, 14, 15].

In this paper, we report the investigations of morphology, dielectric and impedance spectroscopic properties of pure NiO and Li (Li,Ti) doped NiO ($\text{Li}_x\text{Ti}_{0.1}\text{Ni}_{1-x}\text{O}$, $x=0.05-0.3$, abbreviated as LTNO) using, scanning electron microscopy (SEM), dielectric and impedance spectroscopy techniques. Samples are prepared by solid-state reaction method. Detailed analyses of dielectric and impedance data were carried out to infer the giant dielectric permittivity behavior of LTNO ceramic. A correlation between chemistry and dielectric properties is established and a heterogeneous proposed model is accounted for dielectric properties is reported elsewhere [16].

2. Experimental Procedure

In the preparation of LTNO powders, LiCO_3 , TiO_2 , NiO (99.7%; Alfa Aesar, USA) were used in synthesis. Stoichiometric amounts of $\text{Li}_x\text{Ti}_{0.1}\text{Ni}_{1-x}\text{O}$ ($x=0, 0.05, 0.10, 0.15, 0.2, 0.3$) were weighed and ground in ethanol for 1.5 h in agate mortar and pestle. Intimately mixed powders were calcined at 1250°C for 10 h for carbonate burn out. Phase identified powders were made into pellets by uniaxially pressing in a 13 mm die. The pellets were sintered at 1350°C for 6 h in air in a box furnace with heating and cooling rates of $10^\circ\text{C}/\text{min}$. Surface morphology, more specifically the grain analysis, is primarily obtained from scanning electron microscopy (SEM). Surface imaging was performed using a high-performance and ultra high resolution scanning electron microscope (Hitachi S-4800) at 15 kV and 4 A. Temperature dependent dielectric response of the sintered pellets was measured using a Hewlett–Packard 4284A impedance analyzer over the frequency ranges from 100 to 1 MHz and at an oscillation voltage of 1 V. The measurements were performed over a temperature range from 30 to 170°C using an inbuilt heating system.

3. Results and discussion

3.1. Structure and Morphology of NiO, LTNO ceramics

Detailed structural characterization and analysis of pure NiO and LTNO ceramics sintered in air at 1350°C for 6 h are reported elsewhere [16] using XRD technique. All the XRD patterns are in

analogous to cubic NiO with rock salt crystalline structure (JCPDS card No. 04-0835) and as well as in earlier reports [8,15,18]. In addition to pure NiO peaks, few minor peaks corresponding to NiTiO₃, Ni are also observed in the LTNO system with increasing Li content [16]. Fig. 1 shows the scanning electron microscopic (SEM) images of the NiO, LTNO ceramic samples. The average grain size of the pristine NiO (~ 10 µm) is smaller than that of LTNO ceramics (~15-20 µm). And there exists some pore or voids among the grains ensuing Ni²⁺ vacancies and/or interstitial oxygen in NiO, during synthesis at high temperature sintering for all the ceramics. As the Li content increased grain size is increased. Over all SEM images reveal the dense microstructure with clear grain and grain boundaries. It is also observed from that as the Li content increased from $x=0.05$ to $x=0.3$ in LTNO, clearly grain growth is clearly visible. Improved grain growth might be the reason for enhanced dielectric constant in this composition tailored high Li content LTNO ceramics.

3.2 Dielectric properties

Electrical studies provide insight into the localized electric charge carriers and which leads to understanding of electrical conduction mechanism and dielectric polarization. Using the measured capacitance values, the dielectric constant for all the parallel plate dielectric capacitors was calculated at the 10 kHz frequency at different temperatures (30°-170°C) using the following equation (1). The dielectric constant (ϵ) of a capacitor represents the ability of a material to store the charges during the dielectric polarization.

$$\epsilon = \frac{C \cdot d}{\epsilon_0 \cdot A} \quad (1)$$

Where ϵ is the dielectric constant of the material, C is the measured capacitance (pF) by the LCR meter, d is the thickness of the capacitor measured in centimeters (cm), ϵ_0 is the permittivity of the free space or vacuum (**8.854 x 10⁻¹² pF/m**), and A is the surface area of the electrode of the capacitor calculated in cm². Fig. 2 shows the temperature dependence of the dielectric constant ϵ (T) and the loss tangent $\tan \delta$ (T) of the NiO and LTNO at 10 kHz. Note that, because the doping concentration of Ti is kept constant, the difference in dielectric behavior of LTNO samples can only be attributed to the effect of Li. ϵ (T) is larger than 10⁴ above 60°C. The pure NiO and low

Li content LTNO ceramics have shown weak temperature dependent dielectric behavior over the measured temperature range (30 to 170°C). It was found that the value of the dielectric constant is significantly increased by Li substitution at the Ni-site in NiO. The interfacial space charge polarization is also called Maxwell–Wagner type polarization, increases with increasing temperature due to the increase in dc electrical conductivity; moreover, it decreases with increasing frequency due to the decrease in AC electrical conductivity (σ_{ac}) [20,21]. The space charge polarization effect is revealed as a rapid rise in the dielectric constant at high temperatures and at low frequencies [22]. Decrease in dielectric constant (ϵ) at lower temperatures is attributed to the freezing of electric dipoles through the relaxation process, and there exists decay in polarization with respect to the applied electric field. This typical behavior is due to the Maxwell–Wagner relaxation mechanism [5, 23] and as well thermally excited relaxation process rather than a thermally driven ferroelectric phase transition [9].

The ϵ (at 10 kHz) values at room temperature for the NiO and $\text{Li}_x\text{Ti}_{0.1}\text{Ni}_{1-x}\text{O}$ ($x=0.05-0.30$) samples are about 906, 8805, 8620, 34868, 18711 and 19866. Dielectric constant for NiO and LTNO compositions is nearly independent of temperature, as the Li content increases from $x=0.15$ to 0.30 there is an increase in dielectric constant with temperature. Dielectric constant attains a high value of $\epsilon \sim 10^3$ (NiO) and $\epsilon \sim 10^5$ for LTNO ($x=0.30$) at high temperatures, which is higher than the values earlier reported and as well which is higher than that of pure NiO of ~ 30 (at 1 kHz) [9,11,23]. However the dielectric anomaly in the present LTNO system is not due to a thermally driven phase transition, since there is no structural phase transition was observed from temperature dependent dielectric properties measurement [9].

The LTNO ceramics with ($x=0.3$) has shown the highest dielectric constant of the various LTNO samples studied. It is noteworthy that at high temperature the dielectric constant ($\epsilon \sim 119721$) much higher than that in pure NiO ceramic (~ 8757) at 10 kHz. A rapid increase of dielectric constant (ϵ) is observed as Li content increases from $x=0.15$ to $x=0.3$ in LTNO ceramics, being accompanied by the appearance of corresponding relaxation peaks in the $\tan \delta$. In general, the ratio between the dissipated and stored energy is referred to as the dissipation factor or loss tangent ($\tan \delta = \epsilon''/\epsilon'$). For initial Li dopant content ($x=0.05, 0.10$) in LTNO there is a decrease in $\tan \delta$ is observed and then it increased for higher content of Li. The $\tan \delta$ peak shifts to higher temperature as the Li content increased in LTNO ceramics. The increase in $\tan \delta$ at high

temperature may be attributed to the migration of excited electrical particles [23]. In our earlier paper [16], we report the dielectric dispersion using the modified Debye's model. The experimental data is in good agreement with the calculated data indicating the validity of modified Debye's function [16].

3.3 Impedance Spectroscopy

In order to clarify the observed behavior as mentioned above, we used impedance spectroscopy (IS) analysis to study the electrical behavior of LTNO ceramic. The variation of real (Z') and imaginary (Z'') parts of impedance with frequency at different temperatures are shown in Fig.3 for NiO and LTNO samples. **Z' values are high in the low frequency region (Fig.3) and decreases monotonically with increase in frequency up to 10 kHz and remains invariant at higher frequencies for all the compositions. There is no obvious reason for abnormal broadened hum like behavior in the low frequency region for $x = 0.20, 0.3$ compositions in LTNO (Fig.3 c, d).** Decreasing Z' with increasing temperature is attributed to negative temperature coefficient of resistance (NTCR) behavior usually observed in semiconductors [24-26]. And as well decreasing Z' with frequency may be due to an increase in ac conductivity with frequency. This is due to the increase in hopping of electrons between the localized ions. **Similar trend of impedance versus frequency plots were reported in the literature and is an indication of increasing conduction with temperature and frequency [i.e. (NTCR) behavior] [1, 25,26].**

The imaginary part of impedance (Z'') exhibits an initial increase with frequency and temperature, attains a peak (Z''_{max}) value and then decreases with frequency at all measured temperature from (30°C to 170°C) (Fig.4). The other feature of this Z'' Vs. frequency spectrum at different temperatures is the position of relaxation frequency f_{max} (the frequency at which peak maxima occurs) shifts towards higher frequency region with the increase of temperature, the absolute value of Z'' decreases with temperature and at frequency above 100 kHz all the curves merge. **It is also observed that the magnitude of Z'' decreases considerably with a shift in the peak frequency towards the higher frequency side with increasing Li content in LTNO except for ($x = 0.3$). The non-existence of Z'' peak at temperatures and frequencies in pure**

NiO and LTNO ($x = 0.05$) ceramics is due to the absence of current dissipation in the material and for higher Li content in LTNO ($x = 0.1$ to 0.3) there exists a Z'' peak at ($Z''_{\max}$) at all temperatures is due to current dissipation in the material. The peak broadening and their shift towards higher frequency side indicate the presence of electrical relaxation phenomenon. And the absence of two peaks in spectrum called non-Debye type mechanism. A decrease in Z'' magnitude with frequency signifies the presence of polarization due to space charges, since their electrical behavior is frequency and temperature dependent [24]. In general impedance spectrum shows two distinct features: intra-grain (bulk) and inter-grain (grain boundary). From each Debye peak in the Z'' vs. frequency plot, capacitance (C) and resistance (R) values can be obtained using the following equations:

$$Z'' = R \frac{\omega R C}{1 + (\omega R C)^2} \quad (2)$$

Where, $\omega = 2\pi f$, R, and C are the angular frequency, resistance, and capacitance. At each Debye peak maximum $\omega_{\max}RC = 1$ holds good, where

$$Z'' = \frac{R}{2} \quad (3)$$

Temperature dependent resistance measurements were shown in Fig.5. The overall resistance values of the NiO, LTNO ceramics were less than 3 orders of magnitude. As the Li content increased in the LTNO ceramics, resistance of the samples decreased at all temperatures, which confirms the semiconducting NTCR behavior for these ceramics. As the Li content increased in LTNO ceramics, room temperature bulk resistance and capacitance values were decrease and increased respectively as shown in Fig.5 (inset). Temperature dependent bulk capacitance values for selected compositions were shown in Fig.5 (inset), as the temperature increases bulk capacitance values were invariant till 120°C and then it started increasing for these LTNO ceramics. Fig.5 (inset) also shows the composition dependent bulk resistance and bulk capacitance of samples. Bulk resistance decreased and bulk capacitance increased as the Li content increased in the LNTN ceramics. **From the Normalized imaginary impedance (data**

not presented here) observation, as the Li content increases in LTNO system, the peak frequency of ($Z''/Z''_{\max}$) shifts towards higher frequency side for most of the compositions. This shift reveals that presence of Li^+ in NiO triggers relaxation process. ($Z''/Z''_{\max}$) relaxation peaks at the low frequencies confirms the existence of the space-charge relaxation. The small grain response can be due to the presence of a high ionic conductivity phase along the grain. This is consistent with the high tangent loss observed in case of LTNO ceramic.

The Nyquist plots for respective NiO and LTNO ceramic samples measured at various temperatures in the frequency range from 100 Hz to 1 MHz, are shown in Fig.7. The impedance data (Z' Vs. Z'' curves) for the NiO and LTNO ceramics ($x=0.05$), up to certain temperature $\sim 120^\circ\text{C}$ do not take the shape of a semicircle arc in the Nyquist plots rather presents a straight line with large slope suggesting the insulating behavior. The Z' Vs. Z'' curves for all other LTNO ceramic samples ($x=0.05-0.3$) have shown a single semicircular arc. It can be seen from the impedance data (Z' Vs. Z'') semicircles become smaller with increasing temperature ($30^\circ-170^\circ\text{C}$). From the visual inspection of Nyquist plots for LTNO ceramics, given in Fig. 7, one can see that the complex plot is in the form of one depressed semicircle arc, starting from the origin, making an intercept on the real axis with a large radius at low temperatures. Appearance of this single semicircular arc suggests the presence of grain interior (bulk) property of the material [24-26]. **Impedance spectra were analyzed by an ideal equivalent parallel combination of bulk resistance (R_g) and bulk capacitance (C_g) which is shown in the Fig.7 (k,l) (as one example) for LTNO ($x=0.3$ at 80°C). The fitted bulk resistance (R_g) and bulk capacitance (C_g) values for equivalent circuit were 1.704 kOhm, 2.815E-8 F.** It is interesting to note that the observed and calculated complex impedance (Z' Vs. Z'') data matches fairly well. Semicircular arcs of LTNO ceramics have shown their centers lying off the real (Z') axis which is indicative of non-Debye type relaxation. For all the LTNO ceramic samples, the semicircle which appears at higher frequency side starts from origin of real part of the impedance. **The high frequency semicircular is due to the bulk (intra-grain) property and is attributed to space charge polarization and lower values of conductivity [24-26].**

The variation of ac conductivity were calculated using the relation, $\sigma_{ac} = [Z' * t]/A * [Z'^2 + Z''^2]$ [27]. The frequency dependent σ_{ac} at selected temperatures is shown in Fig. 7, where Z' , Z'' is real part and imaginary part of impedance, t is thickness and A is area of the ceramic pellet. It is well known from the frequency dependent ac conductivity measurements that in large polaron hopping, the ac conductivity decreases with frequency whereas in small polaron hopping it increases with frequency [24-26]. In the present case (NiO, LTNO ceramics); the plots for σ_{ac} measurements are moderately linear, indicating the conduction is due to small polarons. This linear increase in σ_{ac} relates to the electrical conduction by electron exchange between ($Ni^{+2} \leftrightarrow Ni^{+3}$) the Ni ions of with different valence (Ni^{+2} and Ni^{+3}) states. The observed ac conductivity behavior at wide range of frequencies (10^2 Hz to 10^6 Hz) at selected temperatures is attributed to the correlated barrier hopping model of small-polaron conduction electron hopping mechanism [9]. And this mechanism is a thermally activated relaxation process and obeys the Jonscher's universal power law [28,29], $\sigma(\omega) = \sigma_{dc} + A\omega^n$ where n is the frequency exponent with $0 < n < 1$ and A is the temperature dependent pre-exponential factor, σ_{dc} is the frequency independent dc electrical conductivity. The frequency dependent of ac conductivity at different temperatures is characterized by two plateau regions at one at lower frequency region till 10^4 Hz and frequency dispersion at high frequency region 1 MHz for all temperatures measured. The high frequency dispersion corresponds to the ac conductivity, whereas the low frequency plateau corresponds to the dc conductivity of the material. The value of σ_{dc} is found to increase with an increase of temperature, confirming semiconducting behaviour of the samples. The frequency at which the change in the slope takes in frequency dependent conductivity place is known as "hopping frequency (ω_p) and is shifted towards the higher frequency side on increasing the temperature [29]. The electrical conduction in NiO is due to the presence of Ni^{3+} ions and the electrical transport property is primarily associated with Ni^{2+} vacancies [9]. For charge neutrality, each Ni^{2+} vacancy in the lattice causes the transformation of two Ni^{2+} into two Ni^{3+} and this transformation induces a local lattice distortion [9]. These Ni^{3+} ions may be formed either by the appearance of nickel vacancies or by the incorporation of monovalent Li^+ atoms in NiO. Introduction of Li^+ into the NiO gives rise to acceptor centers Li^+-Ni^{3+} . At low temperatures, the Ni^{3+} holes formed are bound to a lithium ion, which has an effective negative charge and at higher temperatures these holes can detach from the Li^+-Ni^{3+} centers and move quasi-freely in the sample by exchange of electrons between Ni^{2+} and adjacent Ni^{3+} ions [4]. It was observed

from the frequency dependent electrical conductivity measurements that the addition of Li content to NiO leads to an increase in conductivity for all the LTNO compositions at different temperatures. This increase in conductivity (decrease in resistivity) with temperature indicates the NTCR (semiconducting) behavior of the ceramics [25, 26]. At each temperature the plot shows a frequency independent region (at low frequency) followed by a region above 10^4 Hz where σ_{ac} tends to increase with increasing frequency for LNT0 ($x=0.10, 0.15$) compositions. It is also observed from these measurements that as the Li content increased, electrical conductivities are also increased with frequencies at different temperatures, which is due to higher values of dielectric losses in these ceramic.

Fig.8 (a) shows the variation of ac conductivity (σ_{ac}) with temperature [$10^3/T$ (K)] at 1 kHz for NiO, LTNO ceramic e samples, in which the solid line is the fitted result obeying the Arrhenius law, (equation 4). In order to get more insight into the mechanisms responsible for conduction, we calculated the activation energy E_a (which is dependent on a thermally activated process) from the conductivity using the following relation:

$$\sigma_{ac} = \sigma_o \exp(-E_a/k_B T) \quad (4)$$

where k_B is the Boltzmann constant and σ_o is the pre-exponential factor. Calculated activation energies were 0.58 eV, 0.32 eV, 0.65 eV, 0.44 eV, 0.81 eV, 0.48 eV respectively for NiO, LTNO ceramics. Similar results were reported for LTNO based ceramic system [14,23]. This linear increase in σ_{ac} relates to the electrical conduction by electron exchange between ($Ni^{+2} \leftrightarrow Ni^{+3}$) the Ni ions of with different valence (Ni^{+2} and Ni^{+3}) states, the valence fluctuations may affect the activation energy values. As the temperature increased, electrical conductivity of NiO, LTNO ceramics increased. Finally, the smaller values of activation energy in case of ceramics samples imply an increased hopping process of charge carriers. The fitting of experimental data at 30° C, 170° C employing Jonscher's power law is shown in the Fig. 8(b,c), and fitting parameters were listed in table.1. **According to the 'universal dynamic response' (Jonscher's universal power law) for ionic conductors, the conductivity depends on frequency. And this mechanism is a thermally activated relaxation process and obeys the Jonscher's universal power law [28,29]. The main feature of this plot is the appearance of σ_{ac} in the low frequency ($< 10^4$**

Hz) region and σ_{ac} in the ($> 10^4$ Hz) high-frequency regions, and hence showing a change in slope at a particular frequency as shown in Fig.8(b,c) and Table.1. The frequency dependent ac conductivity behavior obeys the Jonscher's power law governed by the relation: $\sigma(\omega) = \sigma_{dc} + A\omega^n$ where n is the frequency exponent with $0 < n < 1$ and A is the temperature dependent pre-exponential factor, σ_{dc} is the frequency independent dc electrical conductivity [28,29].

Conclusion

In conclusion, we successfully prepared LNTO ($\text{Li}_x\text{Ti}_{0.1}\text{Ni}_{1-x}\text{O}$ with variable Li content) ceramics with giant dielectric constant for micro/nano-electronics industry applications using conventional solid state synthesis route. The high dielectric constant ($\sim 10^4$ – 10^5) and impedance spectra of NiO, LTNO ceramic were investigated as functions of both frequency, temperature. High dielectric constant in these ceramics is attributed to the interfacial space charge polarization (Maxwell–Wagner type polarization in agreement with Koops theory). Decrease in dielectric constant (ϵ) at lower temperatures is attributed and thermally excited relaxation process. The Nyquist plots with the semicircular arc lying with the centre below the real axis at higher temperatures. The complex impedance plots between real and imaginary impedance indicates that the polarization mechanism corresponds to the bulk semiconducting effect arising from the grains. The observed temperature dependent electrical conductivity behavior is correlated to barrier hopping model. This behavior obeys Jonscher's universal power law and is a thermally activated relaxation process. With increasing temperature, the value of σ_{dc} is found to increase, showing semiconducting behaviour. Impedance spectra revealed semicircular arcs for LTNO ceramic with their centers lying off the real impedance (Z') axis which is indicative of non-Debye type relaxation. NTCR behavior is also confirmed from temperature dependent resistance and impedance spectroscopy results.

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Figure Captions

Figure 1(a-f). High resolution SEM images of NiO, LTNO [Li_xTi_{0.1}Ni_{1-x}O ($x = 0.05, 0.10, 0.15, 0.20, 0.3$)] ceramics

Figure 2. (a) Variation of dielectric constant (ϵ) with temperature, (b) Variation of dielectric loss ($\tan \delta$) with temperature at 10 kHz frequency of NiO, LTNO [Li_xTi_{0.1}Ni_{1-x}O ($x = 0.05, 0.10, 0.15, 0.20, 0.3$)] ceramics.

Figure 3. Variation of real impedance (Z') with frequency at different temperatures (30-170°C) of NiO, LTNO [Li_xTi_{0.1}Ni_{1-x}O ($x = 0.05, 0.10, 0.15, 0.20, 0.3$)] ceramics.

Figure 4. Variation of imaginary impedance (Z'') with frequency at different temperatures (30-170°C) of NiO,LTNO [Li_xTi_{0.1}Ni_{1-x}O ($x = 0.05, 0.10, 0.15, 0.20, 0.3$)] ceramics.

Figure 5. Bulk resistance and capacitance values (from imaginary impedance (Z'')) at different temperatures (30-170°C) of NiO, LTNO [Li_xTi_{0.1}Ni_{1-x}O ($x = 0.05, 0.10, 0.15, 0.20, 0.3$)] ceramics.

Figure 6. Nyquist plots (Z' Vs. Z'') at selected temperatures between (30-170°C) in the frequency range from 100 Hz to 1 MHz, of NiO, LTNO [Li_xTi_{0.1}Ni_{1-x}O ($x = 0.05, 0.10, 0.15, 0.20, 0.3$)]

ceramics (experimental and fitted data at 80°C for $x=0.3$).

Figure 7. Variation of ac conductivity as a function of frequency at selected temperatures

between (30-170°C) of NiO, LTNO [$\text{Li}_x\text{Ti}_{0.1}\text{Ni}_{1-x}\text{O}$ ($x = 0.05, 0.10, 0.15, 0.20, 0.3$)] ceramics.

Figure 8.(a)Temperature dependence of the ac conductivity (at 10 kHz), (b) frequency dependent ac conductivity at 30°C,(c) frequency dependent ac conductivity at 170°C of NiO, LTNO [$\text{Li}_x\text{Ti}_{0.1}\text{Ni}_{1-x}\text{O}$ ($x = 0.05, 0.10, 0.15, 0.20, 0.3$)] ceramics.

Table Captions

Table.1 Activation energy (E_a), σ_{dc} is the frequency dependent dc electrical conductivity at low frequency, A is the temperature dependent pre-exponential factor, n is the frequency exponent parameters obtained from fitting of the variation of ac conductivity as a function of frequency at selected temperatures between (30,170°C) of NiO, LTNO [$\text{Li}_x\text{Ti}_{0.1}\text{Ni}_{1-x}\text{O}$ ($x = 0.05, 0.10, 0.15, 0.20, 0.3$)] ceramics using the Jonscher's power law $\sigma(\omega) = \sigma_{dc} + A\omega^n$.

Table.1

Composition	σ_{dc} (30°C) low frequency region	σ (30°C) high frequency region	σ_{dc} (170°C) low frequency region	σ (170°C) high frequency region	A (30°C)	n(30°C)	A (170°C)	n(170°C)
NiO	1.21377E-6	1.51585E-8	8.79862E-6	3.14682E-7	1.29952 E-4	0.3602 5	0.0036 6	0.34166
Li _{0.05} Ti _{0.10} Ni _{0.85} O	4.42052E-7	8.23029E- 7/ 1.8482E- 6	1.25935E-6	6.71361E-7	9.80861 E-7	1.0493 8	1.0204 8E-6	0.96991
Li _{0.10} Ti _{0.10} Ni _{0.80} O	1.19955E-7	7.45419E-8	6.73962E-7	2.41007E-7	3.14735 E-7	0.8962 5	2.7644 7E-6	0.8237
Li _{0.15} Ti _{0.10} Ni _{0.75} O	8.06936E-6	1.56118E-6	2.40651E-5	1.03921E-5	0.00481	0.4329 4	1.3527 7E-5	0.98057
Li _{0.20} Ti _{0.10} Ni _{0.70} O	7.57315E-6	6.7437E-7	1.29394E-6	9.30531E-6	0.00312	0.4052 3	9.5774 E-4	0.66646
Li _{0.30} Ti _{0.10} Ni _{0.60} O	1.49953E-5	2.98341E-7	2.32353E-5	1.36034E-5	0.08062	0.1571 6	0.0010 3	0.68800

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6

Fig.7

Fig.8