Controlled and Enhanced Dielectric Properties of High-Titanium Containing $\text{Li}_x\text{Ti}_{0.1}\text{Ni}_{1-x}\text{O}$ via Chemical Composition-Tailoring

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Abstract

Tuning the dielectric properties via composition-tailoring is demonstrated for variable-lithium, constant-titanium co-doped nickel oxide ($\text{Li}_x\text{Ti}_{0.1}\text{Ni}_{1-x}\text{O}$; $x=0.05-0.30$; referred to LTNO).. The effect of variable Li-content on the structure and dielectric properties of LTNO is investigated. X-ray diffraction studies confirm the formation of a cubic NiO phase in LTNO for $x=0.05-0.30$. However, lattice parameter reduction was evident with increasing Li-content. Composition-driven giant dielectric constant (10^4-10^5) was observed for a higher lithium content ($x=0.15-0.30$) leading to realization of LTNO ceramics. The origin of the high dielectric constant observed in these low density LTNO ceramics is attributed to the Maxwell–Wagner polarization mechanism.

Keywords: Lithium-Nickel Oxide Ceramics; Chemical Composition; Giant Dielectric Constant; Electrical Properties

1. Introduction

Simple and multi-component oxide dielectrics play key role in a wide variety of current and emerging technologies [1-5]. While there has been a great deal of interest in the wide band gap oxide materials for electronics, electro-optics, opto-electronics and magneto-electronics, a special attention is drawn in recent years towards the materials with high and/or giant dielectric constant for their expected revolutionary applications in micro/nano-electronics industry [1-6]. Such materials will have enormous applications in electrical storage and electronic data processing devices. Specifically, dielectric ceramics are important for a wide variety of electrical components such as capacitors, memory devices, filters, resonators and communication systems.

Nickel-based, multi-component oxide ceramics have been the recent attention of researchers in view of their ability to tune the dielectric constant exceedingly higher than their counter part binary oxides [7-11]. Nickel oxide (NiO) is a transition-metal oxide, which is typically categorized as a Mott-Hubbard insulator with a very low electrical conductivity [$10^{-13} (\Omega\text{cm})^{-1}$] at room temperature [12]. NiO 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 [12,13]. Although intrinsic NiO exhibits poor or low dielectric constant at any given temperature, dielectric constant and electrical properties of NiO can be tuned by the introduction of Ni^{2+} vacancies and/or interstitial oxygen by selectively doping with monovalent impurities like Li^+ [7-12]. The other way of manipulating the dielectric properties is demonstrated for Ni-Fe based oxides by selectively doping them with rare-earth ions. For instance, the dielectric constant and electrical resistivity of Ni-ferrites was dramatically enhanced when doped with Sm or Ho, more specifically substituted for Fe site in the host spinel lattice [3,14]. In

the latter case, lattice distortion coupled with bond length increase and secondary phase (ortho-ferrite) formation due to rare-earth ion doping were the primary factors contributing to their enhanced dielectric properties [3]. However, while improved dielectric constant values are essential for efficient utilization in various electrical and electronic applications, methods such as rare-earth ion doping can increase the overall physical density of the ceramics which may not be useful for light weight, high-energy-density storage applications. On the other hand, high-level defect concentration is also not desirable for reliable and durable operation of the devices with such ceramics integrated as the key electrical/electronic components. In this context, the present work was performed on lithium (Li), titanium (Ti) co-doped NiO (Li-Ti-Ni-O or LNTO) ceramics to understand the effect of variable Li content on the structural and dielectric properties. The goal is not only to elucidate the fundamental science and mechanism of Li effect but also to realize, if possible, the LNTO ceramics with low physical mass density for selective aforementioned applications. As such, with pre-determined Ti content kept constant (10%), the amount of Li is varied in a wide range to obtain LNTO ceramics and studied their structural and dielectric properties. Interestingly, as presented and discussed in this letter, the results demonstrate that tuning the dielectric properties of LNTO ceramics with low mass density is possible through a chemical composition – dielectric property relationship.

2. Experimental

Lithium carbonate (LiCO_3 , 99%; Alfa Aesar, USA), titanium oxide (TiO_2 -99.99%-%; NOAH Tech., USA) and nickel oxide (NiO , 99.995%; NOAH Tech., USA) were used in the synthesis of LNTO ceramics. Synthesis of the LNTO ceramics has been carried out with Ti content kept constant at 10%, which is suitable for providing temperature stability. **Stoichiometric amounts of pure NiO and variable-lithium, constant-titanium were weighed and ground in**

ethanol for 1.5 h in agate mortar and pestle. The mixed powders were then immediately calcined at 1250 °C for 10 h for carbonate to burn out. Phase identified powders were made into pellets by uniaxially pressing in a 13 mm die with an applied pressure of 100 MPa. The pellets were then sintered at 1350 °C for 6 h in air in a box furnace with heating and cooling rates of 10°C/min. The LTNO ceramics (**both calcinated and sintered**) were characterized by X-ray diffraction (D8 Discovery X-ray diffractometer with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). The dielectric response of the sintered materials was measured using a Hewlett–Packard 4284A impedance gain phase analyzer over the frequency ranging 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

X-ray diffraction (XRD) patterns of LTNO ceramics are shown in Figure 1 as a function of variable Li composition. For comparison, the XRD pattern of NiO is also presented in Figure 1. All the main peaks observed are comparable to those of the powder XRD pattern of NiO as reported in JCPDS card No. 04-0835 as well as in references [8,15]. However, peak due to minor secondary phase corresponding to NiTiO₃ (indexed after JCPDS card No.04-0850) was observed in the LTNO with increasing Li content. In addition, evolution of small peak corresponding to metallic Ni is also noted as indicated in Fig. 1. **All the peaks corresponding to NiO, NiTiO₃ and Ni were marked with the symbols Δ , *, $\clubsuit$.** The most notable, significant change in the XRD patterns of LTNO ceramics compared to intrinsic NiO is the (200) peak shift towards higher angle side. Since the Ti content is kept constant, this peak shift must be reflecting the chemistry of Li content and associated changes in the host lattice of NiO.

The average crystallite size (D), calculated using the Scherer's formula, varies from 45.8 nm for intrinsic NiO to 59.4 nm for the highest value of x . The variation of D with x , the Li content, is shown in Fig. 2. The crystallite size initially decreased with progressive increase in Li content reaching a minimum of 33.4 nm at $x=0.15$, at which point increased trend prevails. Rapid increase in the crystallite size is noted with a further increase in the Li content beyond $x=0.20$. Increasing Li content to $x=0.3$ finally increased D value to 59.4 nm. The lattice parameter determined is 4.163 ± 0.001 Å, which is in close agreement to that of NiO (4.177 Å) as reported in the literature of the standard data (JCPDS card No. 04-0835). The lattice parameter is noted to experience a reduction with progressive increase in x values. Such reduction in the lattice parameter is possibly due to the complete substitution of Li^+ into Ni^{2+} , which is confirmed by shift of the most intense (200) XRD peak to the higher angles of 2θ . The observed peak shift and, hence, the lattice parameter reduction can be understood from the consideration of ionic radius difference for the Ni^{2+} ions (0.69 Å) compared to that of Li^+ (0.60 Å) [8]. The Li^+ ions substituting for slightly larger Ni^{2+} ions can result in the crystallographic distortions leading to reduction in the lattice parameter as well as unit cell volume. Such reduction was also noted in Li,Ti co-doped NiO [8, 11] and Li,Ta co-doped NiO ceramics [16]. However, a more direct comparison of our results and quantification with existing reports on Li-Ti-doped reports is not readily possible due to the fact that the Ti content in this case is relatively high compared to other works [7-11]. Using the XRD results, the density of the ceramics is calculated using the relation:

$$\rho = \frac{ZM}{NV} \quad [1]$$

where Z -number of formula units per unit cell (here $Z=4$ for NiO), M -molecular weight of compound, N - **Avogadro number**, and V -volume of crystalline unit cell as determined by XRD

($V=a^3 \text{ \AA}^3$). The density variation of LTNO ceramics with Li content is shown in Fig. 2. It can be seen that the mass density of the LTNO ceramics decreases continuously with progressive increase in Li content i.e., x values.

The variation of dielectric constant of LTNO ceramics with Li content (x) is presented in Figure 3. The data shown are at different constant frequency values. It is evident from Fig. 3 that the Li content strongly influences the dielectric constant of the samples. The dielectric constant increases with increasing x values in LTNO ceramics. The increase in the dielectric constant with the inclusion of Li could be due to the fact that, with the inclusion of smaller size Li^+ ions for relatively larger Ni^{2+} ions, the NiO lattice is distorted giving rise to increase in the atomic polarizability subsequently the dielectric constant. In addition, grain boundaries with enriched Ti and formation of a small amount of the NiTiO_3 phase along with the presence of Ni embedded, charge accumulation enhances at the grain boundaries/interfaces in polycrystalline LTNO resulting the interfacial polarization, which contributes to the additional increase in dielectric constant with increasing Li content. In order to further understand the effect of Li content and its chemistry on the dielectric properties of LTNO ceramics, frequency dispersion of the dielectric constant for the ceramics was considered as a function of x values.

The frequency variation of the dielectric constant (ϵ') of LTNO are presented and compared with that of pure NiO in Figure 4. It can be seen that ϵ' decreases with increasing frequency. A decrease in ϵ' with increasing frequency is due to the fact the dipole lags behind the applied field at higher frequencies. The decrease of ϵ' with increasing frequency as observed for LTNO materials is a typical dielectric behavior seen in many of the traditional dielectrics with a high dielectric constant [2-4,11]. At room temperature, the values of ϵ' (at 100 Hz) in Li,Ti co-doped NiO compounds are exceedingly higher ($\sim 10^5$) than that of pure NiO (~ 900). Note that the

doping concentration of Ti (0.10) is kept constant in these LNTiO ceramics. Therefore, the difference in dielectric behavior of LTNO samples can only be attributed to the effect of variable Li-content upon balancing Ni in the ceramic.

In order to gain further insight into the dielectric properties of LTNO, attempts were made to further analyze the ϵ' -dispersion behavior. The experimental data can be theoretically calculated using the modified Debye's function that considers the possibility of more than one ion contributing to the relaxation [17]. Thus, the observed ϵ' -dispersion can be modeled using:

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

where ϵ' is the real part of dielectric constant, ϵ'_{∞} is the dielectric constant at higher frequency (1 MHz), ϵ'_0 is the dielectric constant at lowest possible frequency (100 Hz in our case), $\omega=2\pi f$ is the angular frequency with f is the applied frequency to the signal of 1 V, τ is the mean relaxation time, and α is the spreading factor of the actual relaxation times about the mean value. The spreading factor ' α ,' also referred as the Cole–Cole parameter, takes values between 0 and 1. For an ideal Debye relaxation with single relaxation time, $\alpha = 0$. If $\alpha > 0$, it implies that the relaxation has a distribution of relaxation times, leading to a broader peak shape than a Debye peak [11,17]. The pioneering work of Cole-Cole with the standard procedure [17] were adopted to fit the experimental data and to obtain the spreading factor ' α ' value for LTNO ceramics. However, we have considered the real part of dielectric constant instead of the complex part of dielectric constant and plotted the graph of $\ln(\epsilon'_0 - \epsilon' / \epsilon' - \epsilon'_{\infty})$ versus $\ln(\text{frequency})$ for all the compositions (Fig. 5). Such analysis was found to be quite useful to understand the dielectric constant dispersion behavior of Mn or Hf substituted CFO materials as reported elsewhere [18,19]. It can be seen in Fig. 5 that

the data obtained for NiO and LNTiO ceramics yield straight lines for various x values. Slope of the linear plot for each composition provides the value of $(1-\alpha)$ from which α is determined. The α determined for LNTiO ceramics in this work are in the range of 0.45-0.95, which are slightly higher for LNTiO ceramics reported in the literature [11]. However, these values closely agree with those reported for giant dielectric constant compounds $ACu_3Ti_4O_{12}$ (ACTO), where A was Ca, Bi, Y and La [20]. The reported values for these compounds were 0.80-0.96 [20]. The origin for the higher α values in this work could be the degree of heterogeneity in the materials due to higher content of Ti. On the other hand, the experimental data is in good agreement with the calculated data indicating the validity of modified Debye's function.

A simple model can be formulated to explain the effect of variable Li content and composition-induced effects on the dielectric properties of $Li_xTi_{0.1}Ni_{1-x}O$ materials. Evident from the results and analysis, it is clear that the dielectric response depends on the Li content and, hence, the chemistry in addition to microstructure of $Li_xTi_{0.1}Ni_{1-x}O$ ceramics. Earlier we demonstrated and reported the realization of very high dielectric constants in rare-earth (RE) ion doped Ni ferrites [3,14]. Enhanced dielectric constant with inclusion of RE^{3+} ion in Ni ferrite lattice is attributed to the lattice distortion and increase in Fe (R) – O bond lengths giving rise to increase in the atomic polarizability [3,14]. In addition, formation of small amounts of the respective $REFeO_3$ phases at the grain boundaries leads to the accumulation of charges at the grain boundaries resulting the interfacial polarization, which contributes to the additional increase in ϵ' . However, in the present case, the sample heterogeneity accounts for the major portion of the observed increase in the dielectric constant of $Li_xTi_{0.1}Ni_{1-x}O$ ceramics as noted in $Li_xTi_{0.1}Ni_{1-x}O$ frequency dependent dielectric measurements. We believe that the heterogeneity in $Li_xTi_{0.1}Ni_{1-x}O$ is derived primarily the core-shell type of microstructure, where the semiconducting grains are surrounded by the

insulating grain boundaries, which act as barriers for charge transport. At room temperature, intrinsic NiO is a Mott–Hubbard insulator [12]. **Incorporation of monovalent Li⁺ ions for Ni²⁺ can dramatically increase the conductivity of NiO and, thus, NiO becomes semiconducting due to these defects [11].** Perhaps, with excessive Li content, the pronounced effect is the higher degree of such heterogeneity, where the semiconducting grains surrounded by the insulating boundaries giving rise to Maxwell-Wagner type interfacial polarization effects. It has been demonstrated, in the literature, that the Ti is rich on the grain boundaries but indigent within the grains in Li,Ti co-doped NiO ceramics [7,10,11]. Therefore, the increasing Li content and Ni contribute to the semiconducting type LTNO grain interiors whereas the exterior boundaries contain Ti-rich insulating boundaries. **The observed dielectric properties of LTNO ceramics, therefore, can be attributed to the interfacial effects and microstructure, which can be considered as an effective circuit of parallel capacitors with extremely small plate separation leading to well-known Maxwell-Wagner polarization.** Furthermore, dielectric dispersion observed in LTNO and validity of the Debye’s modified function (Fig. 5) seems to be unique to the materials, where the dopant ions introduce structural distortion and interfacial effects giving rise to Maxwell-Wagner type mechanism. A direct evidence for such mechanism operative in LTNO ceramics was provided by the temperature dependent measurements (not shown), where the space charge polarization effect is revealed as a rapid rise in the dielectric constant at high temperatures and at low frequencies.

Summarizing the results, Li_xTi_{0.1}Ni_{1-x}O ceramics were fabricated with variable Li content and studied their structure and dielectric properties. Increasing Li content strongly influences the microstructure and dielectric properties of the Li_xTi_{0.1}Ni_{1-x}O ceramics. **High dielectric constant in these ceramics is attributed to the interfacial effects and microstructure, which contribute**

to the interfacial charge polarization or the so called Maxwell-Wagner type polarization. The frequency dependent dielectric constant dispersion in $\text{Li}_x\text{Ti}_{0.1}\text{Ni}_{1-x}\text{O}$ ceramics fits to the modified Debye's function.

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Figure Captions

FIG. 1. XRD patterns of the LTNO ceramics. For comparison, XRD pattern of NiO is also presented. The NiO (200) peak shift is evident with increasing Li content in the LTNO ceramics.

FIG. 2. Variation of density and crystallite size with lithium content (x) in LTNO ceramics. The data was calculated using XRD results (see, text).

FIG. 3. Dielectric constant variation with Li content (x) in LNTNO ceramics. Dielectric constant increase with Li content is evident.

FIG. 4. Dielectric constant dispersion of LTNO ceramics with variable Li content. The data shown are at selected frequency intervals while full data set is shown in Fig. 5.

FIG. 5. $\ln(\epsilon'_0 - \epsilon' / \epsilon' - \epsilon'_\infty)$ with $\ln(\text{frequency})$ for LNTNO at room temperature. The data fits to Cole-Cole model (see, text). The spread factor (α) values were determined from the slopes of the linear plots.

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Intensity (arb.unit)

Figure 2

Figure 3

Figure 4

Figure 5