Magneto-dielectricity in Li_{0.05}Ti_{0.02}Ni_{0.93}O at room temperature

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Abstract
We present direct evidence of room-temperature magneto-dielectricity in single-phase Li_{0.05}Ti_{0.02}Ni_{0.93}O with above-ambient antiferromagnetic ordering. Temperature-hysteresis in warming/cooling heat-flow thermograms evidences the discontinuous nature/first-order of the cubic-to-rhombohedral structural change which concurs the AFM transition. At T_N = 488 K, magnetization features a sharp slope-and-curvature break and dielectric constant shows a peak anomaly. We find genuine and positive room-temperature magneto-capacitance up to 9 Tesla, which is linear at low fields (MC ∝ H_{low}); the prefactor slope (dlnε'/dH_{low}) features a positive frequency coefficient and rises from O(10^{-3}/T) at 0.1 MHz to O(10^{-1}/T) at 4 MHz, giving dε'/dH as large as 120/T with prospects of enhanced functionality across the microwave range.

Introduction
Multiferroics with two or more coexistent ferroic orders are useful materials for the construction of four-state logic-storage devices. The coupling of electrical and magnetic orders is the key functionality of a magneto-electric (ME) multiferroic. With the ever-rising demands of modern storage devices, intensive research is focused on multiferroics; unfortunately the low energy-scale (temperature, frequency, and field-strength) for the linear coupling of these two orders renders very few MEs as serious device candidates [1]. In almost all known MEs this coupling is realized below room temperature, except in BiFeO_3 which features above-ambient magnetic and electrical orderings. BiFeO_3 is a very rare ME multiferroic, having both ferromagnetic and ferroelectric orders in its thin film form [2]. However, it has issues with reproducivity and stability of the results, and the presence of impurity phases [3]. The true room-temperature single-phase ME multiferroic is as elusive as the room-temperature superconductor! The well-known room-temperature multiferroic BiFeO_3 has major issues and challenges related to its high leakage current [4–6]. We present here the magneto-dielectric character above room temperature in a simple material, obtained in single phase without extraneous effort.

The coupling of electricity and magnetism has been known since the 19th century in the form of Maxwell equations. Multiferroic research started with the work of Landau and Lifshitz [7]; thereafter, many research articles investigated the nature of multiferroics, where the electrical order that couples to the magnetic one can be of several origins. For example, the ferroelectricity (FE) in BiFeO_3, BiMnO_3, and PbVO_3 is due to the lone-pair electrons [8] and in Pr_3Ca_2MnO_3 charge-ordering causes the same [9]. While in geometrically frustrated antiferromagnet YMnO_3, the tilting of Mn-O_5 polyhedra and buckling of Y-O planes is responsible for the FE [10], the latter also emerges in conjunction with the spiral magnetic phase, of mainly the cycloidal type [10] e.g. in TbMnO_3 [11]. A few years ago, an interesting letter was published on cupric oxide [12], wherein AFM-induced FE was determined to be the cause of multiferroicity. Here, we report witnessing magneto-dielectricity in a doubly doped derivative Li_{0.05}Ti_{0.02}Ni_{0.93}O (LTNO) of nickel oxide, with concuring above-ambient AFM and structural transitions, and contend its placement in the extremely scarce group of room-temperature magneto-dielectrics. The particulate mildly doped composition is not investigated for the first time here. In fact, the Li- and Ti-doped NiO system became famous after the discovery of the colossal dielectric constant (CDC) in these compounds [13]. It was known that pure NiO is anti-ferromagnetic with transition at T_N = 250 °C, which decreases on doping at the Ni-site. Also, the CDC was reported in the exact Li_{0.05}Ti_{0.02}Ni_{0.93}O composition [13] (below and far from T_N). Thus it is proven that dielectric measurability and the retention of its structure close to
the pure NiO (with established spin–lattice interaction) motivated its present dielectric and magnetization study across its AFM transition, which is closer to room temperature than the \( T_N \) of pure NiO. We indeed find strongly coupled electrical and magnetic degrees of freedom in LTNO at room temperature, even as the dielectric properties rapidly vary with changes in the Li-doping [13].

The parent compound NiO is a Mott–Hubbard insulator, which becomes semiconducting when doped with Li and/or Ti. \( \text{Li}^{+}\text{Ti}^{4+} \) transforms \( \text{Ni}^{2+} \) into \( \text{Ni}^{3+} \) for exacting the charge-neutrality, creating locally distorted rhombohedra [13]. The motivation for synthesizing LTNO is to facilitate its dielectric characterization; inhibited in the pure polycrystalline NiO, due to its significant conductivity-enhancement at high temperatures [14]. Even with the single-crystal NiO, accurate high-\( T \) data are obtained only at very high frequencies [13]. The perturbatively doped LTNO specimen is supposed to have most of its other (lattice, vibrational, electronic etc.) attributes little different from the parent NiO, carrying over these features as mentioned below. In pure NiO, the appearance of the super-lattice peaks (reflections) in neutron (TEM) diffraction [15] confirms the structural change at \( T_N \), concurrent with the softening of the optical phonon mode [16]. The non-cubic character of transition-metal oxides in their magnetically ordered state reconciles with the signatures of high electronic polarizability in MnO and NiO [17]. A sharp transition observed [18] in the thermal conductivity of NiO at \( T_N \) has also confirmed a strong spin–lattice interaction in the system. Optical second harmonic generation (SHG) reported [19] in NiO just below \( T_N \) is traced to the allied polarization in the substantially wide magnetic domain walls, which suggests prospects for significant and ME-coupling. Weber et al. [20] established a strong magneto-elastic interaction in NiO, which governs the width and internal structure [21] of its Néel magnetic domain walls, specified by cycloidally rotating spin arrangement.

**Experimental**

\( \text{Li}_{0.05}\text{Ti}_{0.02}\text{Ni}_{0.93}\)O samples were synthesized through the sol-gel method. \( \text{Ni(NO}_3\text{)}_2\cdot 6\text{H}_2\text{O, LiNO}_3 \), and citric acid were mixed in stoichiometric amounts and dissolved into a sufficient amount of distilled water to get a clear solution. Thereafter, tetrabutyl titanate \( ([\text{CH}_3\text{(CH}_2\text{)}_3\text{O}]_4\text{Ti}) \) was added slowly, and the solution was heated and stirred to form the gel. Dried gel was then calcined at 800 °C for 1 h in air and finally sintered at 1100 °C for 12 h. Pellets of the sample were made for thermal, magnetic, and magneto-dielectric measurements. Room-temperature/high-temperature Synchrotron x-ray diffraction (SXRD) patterns were collected using a powder diffractometer on Indian Beamline BL-18B (Photon Factory, KEK, Japan), at x-ray wavelength of \( \lambda = 1.089\ \text{Å} \). Magnetization measurements were done on VSM-SQUID (Quantum Design) at 7 T fields. Magneto-dielectric data were collected with an Alpha-A high-performance frequency analyzer (NOVO-Control Technologies), using a 9 T superconducting-magnet Integra System (OXFORD Instruments). Heat flow and specific heat were obtained with differential scanning calorimeter MDSC-2910 (TA Instruments).

**Results and discussion**

\( \text{Li}_{0.05}\text{Ti}_{0.02}\text{Ni}_{0.93}\)O was synthesized in a single phase, having no extra Bragg-peaks in its XRD pattern within the detection sensitivity, as shown in figure 1 (inset); confirmed by the LeBail profile peak-fitting (Full-Prof software, profile matching with constant scale factor). At room temperature, \( \text{Li}_{0.05}\text{Ti}_{0.02}\text{Ni}_{0.95}\)O (LTNO) as a Li/Ti double-doped derivative has the same distorted rhombohedral structure as the pure NiO [15]. In figure 1 (main panel) we show the zoomed in the SXRD pattern of LTNO at 250 °C (fitted with cubic phase symmetry \( Fm\overline{3}m \); lattice parameters \( a = b = c = 4.1828 \) Å) and also at room temperature (fitted with the rhombohedral phase symmetry \( R\overline{3}m \); lattice parameter \( c = 2.9468 \) Å and rhombohedral angle \( \alpha = 60.056^\circ \)). The \( (222) \) reflection of the high-temperature cubic phase bifurcates below \( T_N = 488 \) K (523 K for pure NiO) [22] into two reflections (202 and 006), due to the rhombohedral distortion of the lattice across the transition. The \( R\overline{3}m \) structure may be represented as an angular distortion of the unit cell, with a concurrent displacement of the Ni sublattice, generating a contraction along a \( (111) \) axis of the original cubic lattice. The observed symmetry-reduction is attributed to the spin-induced internal strain, as discussed below. The rhombohedral structure in the type-II AFM state can be based on a mono–molecular unit cell, in which the angle \( \alpha \) is slightly larger than 60°. In the spin scheme used by Rooksby [22], below \( T_N \) the Ni spins in NiO are aligned in parallel arrangement on the \( [111] \) plane and those on the adjacent planes are coupled antiferromagnetically with each other [21]. The same spin scheme for the AFM ordering could be applied to the doped NiO (LTNO), also with concomitant magnetic and structural changes.

A clear signature of AFM ordering is observed in LTNO heat capacity (figure 2(a)). Heating/cooling hysteresis \( (T^+\rightarrow T^-) \sim 7 \) K (figure 2(a) inset) in the heat flow \( (W) \) confirms the kinetic (first-order) character of the concurrent structural transition, thus evidencing the coexistence of cubic and rhombohedral structural phases as reported, for example, in several composite multiferroics [23]. Figure 2(b) shows \( M(T) \) data of LTNO
and the AFM anomaly at the applied field of 7 T (also obtained at low fields); the nature of the transition (dip in the moment) resembles the anomaly associated with the AFM ordering in the CuO single crystals [12], concurrent with the latter’s FE ordering. The slope and curvature discontinuities at $T_N$ provide ample evidence
of Ni-spin ordering. Double doping with Li and Ti here quite suppresses the $T_N$ from 523 K (pure NiO) to 488 K ($\text{Li}_{0.05}\text{Ti}_{0.02}\text{Ni}_{0.93}$). Significant downshifting of $T_N$ vis-à-vis pure NiO is due both to the dilution of the magnetic ions as well as their site disorder. This alters the values of both $J_{nn}$ (nearest neighbor) and $J_{nnn}$ (next-nearest neighbor) exchange interactions, as in the case of Mg-doped NiO [24]. The AFM ground state is also confirmed by the reversible/single-valued $M$–$H$ curve (figure 2(b) inset).

Figure 3 shows the permittivity profile $\varepsilon'(\omega, T)$ of LTNO. It is well known that NiO is a charge-transfer insulator, becoming semi-conducting on the hole-doping, which creates Ni$^{+3}$ charge-states. The dielectric constant of LTNO ($\sim 10^3$) is quite high compared to that of the pure NiO ($\sim 5$ to $\sim 25$ at room temperature), both from theoretical estimates and measurements [16, 25], due to the difference in the density of Ni$^{+3}$ on doping [13]. Previously reported [13] measurements on LTNO were not recorded up to $T_N$, as the main focus was on the colossal dielectric constant (CDC) feature in the sub-$T_N$ regime. Here we present $\varepsilon'$ of LTNO up to 250 °C, collected over 1 Hz–10 MHz. Figure 3 (left main panel) depicts both (a) the Maxwell–Wagner (space charge) low-frequency (~100 Hz) conducting behavior (peak in $M''(\omega)$, $\varepsilon'' \sim \omega^{-1}$) due to electrical inhomogeneity and (b) the Debyeian (dipolar) high-frequency (~MHz) relaxational response of insulating background matrix. Combined (Maxwell–Wagner + Debyeian) fits (shown as solid lines) made onto the full-range spectra at 250 K above $T_N = 488$ K provide hugely different characteristic timescales (~0.1 s versus ~0.1 μs) for the two types of dielectric responses. The Cole–Cole plot ($\varepsilon''$ versus $\varepsilon'$, inset) clearly illustrates these well-resolved spectral regimes, precisely switching over at 20 kHz. At lower temperatures (especially at 300 K), this switching frequency reduces further. Therefore, we show in the right main panel the permittivity $\varepsilon'(T)$ at ~MHz frequencies, as reflecting entirely intrinsic dipolar characteristics. Small but clear peak anomalies seen here apparently resemble those reported [12] in CuO for its concurrent ferroelectric (FE) transition at $T_C = T_N$. The present dielectric anomaly coincides with the magnetic/structural transition temperature $T_N$ implying strong coupling of the three (lattice, dipole, and spin) degrees of freedom. The anisotropic change in $\varepsilon'(T_N)$ reported [26] for MnO and MnF$_2$ (undergoing the same isostructural transitions as LTNO here) may be a possibility in the present LTNO as well.

According to Mostovoy, the cycloidal spiral spin structure in the Néel domain walls can produce an electric polarization locally, describable by the inverse Dzyaloshinskii–Moriya (ID–M) spin–orbit interaction [27]. Due to the magneto–strictive effect, uncommonly wide (150 nm) Néel walls materialize in the pure NiO [20] upon crystal twinning below $T_N$. We contend that the same character of the Néel walls is carried over to our scarcely doped L$\text{i}_{0.05}\text{Ti}_{0.02}\text{Ni}_{0.93}$O. The schematic at the top of figure 3(b) illustrates the Néel domain-wall configuration,
which can generate local polarization via the ID–M mechanism. Magnetically induced anisotropy is also predicted in the NiO crystal, thus presenting good prospects to obtain the expected DW-pinned polarization in the single-crystal doped-specimens. The MnO of this family exhibits anisotropy in the static dielectric constant [26], and orientation-dependent polarization is found in the CuO single crystals [12].

We have directly investigated the room temperature magneto-dielectricity in LTNO by its permittivity measurements under magnetic fields up to 9 T. Figure 4(a) left panel shows the dielectric constant versus frequency at three different field values over 100 kHz to 4 MHz (intrinsic response) range. High-frequency permittivity ε′(H) shown in the upper inset of figure 4(a) (left panel) features distinct ‘linear’ regimes, at low and high fields. The normalized low-field linearity prefactor (d ln ε′/dH)_{H \to 0} over the high spectral range (shown in the lower inset) features a positive (technologically desirable) frequency coefficient, with large 20 dB dynamic range. At the same key frequencies, figure 4(b) right panel shows the magneto-capacitance MC(H), evaluated as

\[
MC = [\varepsilon'(H)/\varepsilon'(0) - 1] \times 100.
\]

The parallel (\omega H, log-log plot) low-field behavior of MC(H) sustained over two decades of frequencies signifies a robust spectral integrity of the linear magneto-dielectric effect. Observed change in the dielectric constant on applying the magnetic field is almost +40% at the highest measurable frequency, greater in magnitude than that reported in the other famous room-temperature multiferroics [28, 29], viz., LuFe₂O₄ (−25%) and BiFeO₃ (±1%). Consistent with the two asymptotic linear behaviors evident in ε′(H, 4 MHz) (left panel, upper inset, as also obtained at all the relevant frequencies), MC(H) also marks distinct low-/high-field regimes. The \textit{positive} MC obtained in LTNO may be explained by the domain-aligning effect of the field (similar [21] to that in pure NiO), which tends to abet the cycloidal rotation of the spins in the domain walls. The local polarization (P) pinned to the Néel walls [20] and proportional to the spiral spin-rotation [27] ([S₁ × S₂]) would thus reduce under the applied field, and thereby enhance the polarizability and increase the (ac) permittivity.

The opposite effect of the magnetic field on permittivity (negative magneto-capacitance) [28] is illustrated by the charge-ordered multiferroic LuFe₂O₄. Since pure NiO can be easily grown as thin film [30], so the moderately doped LTNO with minutely different structural parameters ought to be feasible for thin film fabrication as well. This raises the desired prospects of, e.g., Tₜₒ to get even closer to the room temperature (weakening of the exchange interaction), enhanced magneto-dielectric coupling in fewer dimensions (higher magneto-anisotropy and more co-planar AFM domains, simulating the H-field effect), and reduction of the leakage-current (as witnessed, e.g., in the case of BiFeO₃ films [2, 31, 32]). Compared to BiFeO₃ and LuFe₂O₄...
though, the positive-definite magneto-dielectricity along with its large positive frequency coefficient (enhanced functionality at microwave range) renders LTNO a technologically more promising candidate as a novel device material.

Conclusions

In conclusion, we provide clear evidence of above-room-temperature magneto-dielectricity in Li$_{0.05}$Ti$_{0.02}$Ni$_{0.93}$O. Magnetization and high-frequency dielectric results confirm simultaneous bulk AFM ordering and an unconventional electrical organization at above-ambient temperatures. We determined a spectrally robust positive and field-linear magneto-dielectric effect, shooting up by orders of magnitude over the investigated frequency bandwidth. Our findings present LTNO as a peculiar room-temperature magneto-dielectric, which is easily synthesized in the single phase.

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