Giant Dielectric Permittivity Observed in Li and Ti Doped NiO

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(Received 2 July 2002; published 30 October 2002)

A giant low-frequency dielectric constant ($\varepsilon_o \sim 10^5$) near room temperature was observed in Li,Ti co-doped NiO ceramics. Unlike currently best-known high ε_o ferroelectric-related materials, the doped oxide is a nonperovskite, lead-free, and nonferroelectric material. It is suggested that the giant dielectric constant response of the doped NiO could be enhanced by a grain boundary-layer mechanism as found in boundary-layer capacitors. In addition, there is about a one-hundred-fold drop in the dielectric constant at low temperature. This anomaly is attributed to a thermally excited relaxation process rather than a thermally driven phase transition, as for that yielding ferroelectrics.

DOI: 10.1103/PhysRevLett.89.217601 PACS numbers: 77.22.Ch, 77.22.Gm, 77.84.Bw

High-permittivity dielectric materials have been playing a significant role in microelectronics, since they have been used as important devices such as capacitors and memory devices. Perovskites exhibit high dielectric constant values and are widely used in such technological applications. So far, there have been two kinds of high-permittivity perovskites with a static dielectric constant (ε_o) value above 1000. One is a ferroelectric oxide, e.g., Pb(Zr, Ti)O_3 (PZT) [1], that exhibits a dipole moment in the absence of an external electric field; another is a relaxor oxide, e.g., $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) [2], characterized by a ferroelectric response under high electric fields at lower temperature, but no macroscopic spontaneous polarization. However, both kinds of materials show the huge variation of their dielectric constants with temperature, which is undesirable for many applications [3]. For instance, capacitors need to have stably static dielectric constant values to operate properly under a variety of conditions; if the static dielectric constant ε_o has a strong temperature dependence, then the device will not be robust and may fail. On the other hand, most such perovskites contains lead. Lead-free materials with high dielectric constant values are increasingly attractive. Most recently, a lead-free perovskitelike oxide $CaCu_3Ti_4O_{12}$ (CCTO) [3,4] was reported to possess an extraordinarily high static dielectric constant at room temperature of $\varepsilon_o \approx 10^5$ which is comparable with those values for PZT or PMN, and its ε_o is only weakly temperature dependent between 100 and 380 K.

In this Letter we report a new type of high dielectric permittivity oxide in doped NiO which is nonperovskite, lead-free, and nonferroelectric. Of the transition-metal monoxides, NiO has received by far the greatest amount of attention, prompted by a remarkable range of motivations [5]. Despite a huge amount of investigations, a complete theory concerning the electrical transport mechanisms involved has not yet been evolved. NiO, having a very low electrical conductivity of less than 10^{-13} $(\Omega\,\mathrm{cm})^{-1}$ at room temperature, is a Mott-Hubbard insulator [6]. However, introduction of Ni^{2+} vacancies and/or doping with monovalent cations such as Li^+ can cause considerable increase in the conductivity [7,8]. The electrical transport is primarily associated with Ni^{2+} vacancies. Each Ni^{2+} vacancy in the lattice causes the transformation of two Ni^{2+} into two Ni^{3+} for meeting charge neutrality, and this transformation induces a local lattice distortion. The lowest possible energy state for this system consisting of one Ni^{2+} vacancy and two adjacent Ni^{3+} ions is that of quadrupole complex. At temperatures below 1000 K, the electrical transport is generally described with the correlated barrier hopping model of small-polaron hopping [6]. In this Letter, we report giant dielectric constant response in rocksalt-type Li and Ti co-doped NiO, simply expressed as $Li_{0.05}Ti_{0.02}Ni_{0.93}O$ (abbreviated as LTNO) in nominal composition. The observed dielectric behavior is quite similar to that observed recently in the perovskitelike oxide CCTO [3,4]. For example, the LTNO exhibits an extraordinarily high ε_o near room temperature of $\sim 10^5$, and also its ε_o shows weak temperature dependence over a wide temperature range. Both properties are very important for device implementation.

The LTNO specimens were prepared by the following procedure. A stoichiometric amount of $Ni(NO_3)_2 6H_2O$, $LiNO_3$ and citric acid were mixed and dissolved into an appropriate amount of distilled water to get the clear solution. Afterwards tetrabutyl titanate ($[CH_3(CH_2)_3O]_4Ti$) was added slowly, and then the solution was heated and stirred to form the gel. Dried gel was calcined at 800 °C for 1 h in air. Then the resultant ultrafine powder was pressed into pellets (10 mm in diameter), and the pellets were sintered at 1280 °C for 4 h. X-ray diffraction confirmed a single NiO-based phase with the absence of minor phases and revealed a rocksalt structure of NiO. A rhombohedral distortion of $\sim 0.1°$, as found in NiO single crystal [9], is too small to be observed in these measurements. A scanning electron micrograph (SEM) shows that the typical grain size in the specimens is several microns (see the inset of Fig. 1).

The dielectric response of the specimens was measured using a HP 4192A gain phase analyzer over

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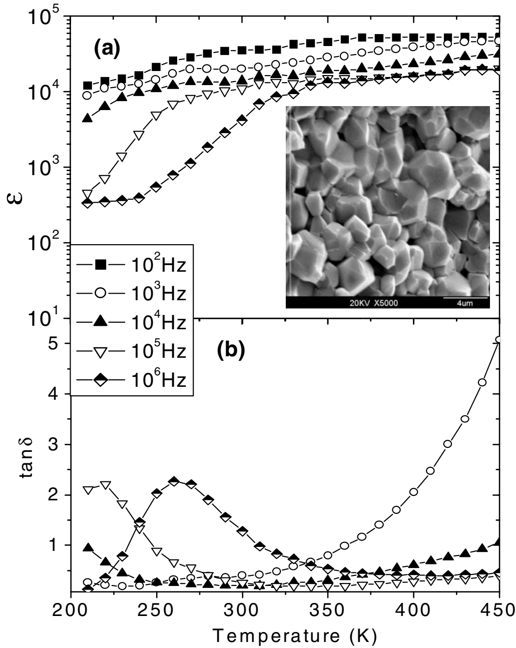

FIG. 1. The temperature dependence of (a) the dielectric constant ε and (b) the loss tangent $\tan\delta$ for the LTNO at various frequencies between 100 Hz and 1 MHz. The inset shows a typical scanning electron micrograph of the samples.

a frequency range from 100 Hz to 1 MHz and at an oscillation voltage of 1 V. These measurements were performed in the temperature range from -60 to 200 °C using an inbuilt cooling-heating system. Each measured temperature was kept constant with an accuracy of ± 1 °C.

Figure 1 shows the temperature dependence of the dielectric constant $\varepsilon(T)$ and the loss tangent $\tan\delta(T)$ of the doped oxide, at different frequencies between 100 Hz and 1 MHz. $\varepsilon(T)$ is larger than 10^4 at low frequency above 200 K, and the low-frequency dielectric constant is weakly temperature dependent over the measured temperature range. With decreasing temperature, however, there is an approximately one-hundred-fold drop in $\varepsilon(T)$ at a characteristic temperature which is strongly affected by the frequency, though this drop in $\varepsilon(T)$ below 10^4 Hz is not shown due to the limited temperature range of the measurement. Such an abnormal phenomenon is similar to that observed in the CCTO [3,4], which is in marked contrast to the well-known ferroelectric one resulting from structural distortion because of a soft-mode condensation. The anomaly in $\varepsilon(T)$ is not due to a thermally driven phase transition, since no structural phase transition was detected. Rather it suggests a thermally excited relaxation process as for the CCTO [3,4]. At low temperature, the electric dipoles freeze through the relaxation process, and there exists a decay in polarization with respect to the applied electric field, which is evidenced by the dramatic drop in $\varepsilon(T)$. Furthermore, the giant dielectric constant shows a temperature-independent behavior at high temperature, rather than a Curite-Weiss-like behavior. LTNO is neither a conventional ferroelectric nor a ferroelectric-based relaxor. These features were also observed in other specimens of $Li_xTi_yNi_{1-x-y}O$ with $x < 0.3$ and $y < 0.1$.

In Fig. 1(b), there is a broad peak in $\tan\delta(T)$ corresponding to the sharp drop in $\varepsilon(T)$ [Fig. 1(a)]. With decreasing frequency, the temperature at the dissipation peak shifts to a lower temperature range, which is also a hint of the thermally excited relaxation process. At high temperature, the increase in $\tan\delta(T)$ is mainly due to the dc conductivity contribution. As expected, the influence of the dc conductivity becomes apparent with increasing temperature and decreasing frequency.

The frequency dependence of $\varepsilon(T)$ can be used to further constrain possible mechanisms. Figure 2(a) shows the frequency dependence of ε which can be well described by a Debye model. The frequency dependence of $\tan\delta$ shown in Fig. 2(b) demonstrates that the dissipation peak, in correspondence to a characteristic relaxation, shifts to higher frequency with increasing temperature. By fitting the data to the Debye model, we obtain the dielectric relaxation time τ. An Arrhenius plot of the relaxation rate, obtained from the dissipation and permittivity curves, as a function of inverse temperature is shown in the inset of Fig. 2. The rapid decrease in τ with

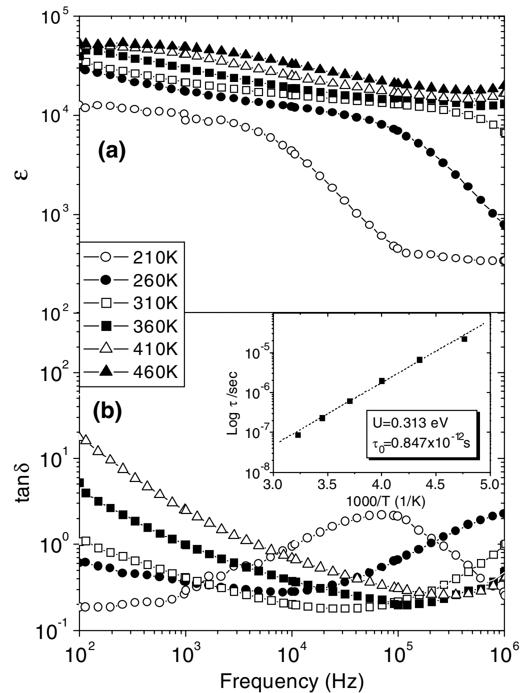

FIG. 2. The temperature dependence of (a) the dielectric constant ε and (b) the loss tangent $\tan\delta$ for the LTNO at several fixed temperatures. The log of the relaxation time τ versus $1/T$ plotted in the inset shows an activated behavior $\tau = \tau_o \exp(U/k_BT)$, and a linear regression of the data (see the dashed line) yields $U = 0.313$ eV and $\tau_o = 8.47 \times 10^{-13}$ s.

increasing temperature is suggestive of an increasing dipole density and a faster polarization process. The dielectric relaxation time τ can be expressed as

$$\tau = \tau_o \exp(U/k_B T), \quad (1)$$

where U denotes the activation energy required for the relaxation and τ_o is a preexponential factor. A linear regression of $\log\tau$ versus $1/T$ describes the data quite well, as indicated by the dashed line, and yields $U = 0.313$ eV and $\tau_o = 8.47 \times 10^{-13}$ s. This U value is nearly the same as $E_a = 0.309$ eV, i.e., the activation energy of the conductivity in the grain interiors of the LTNO ceramic specimens, obtained from the Arrhenius plots (not presented here) of the conductivity in the grain interiors [10], which indicates that such strong thermal activation of the polarization relaxation process has a close relation with the conductivity in the grain interiors.

Now let us turn to the giant dielectric constant of the LTNO. $\varepsilon_o \sim 10^5$ observed is one of the highest values reported for ceramic capacitors at present and can be comparable with the values for ferroelectric and relaxor compounds near their Curie temperatures [1,2]. As already discussed above, however, the abnormal temperature dependence of $\varepsilon(T)$ [see Fig. 1(a)] suggests that the polarization mechanism in the LTNO cannot be attributed to ferroelectric behavior. Alternatively, the huge ε_o observed in the LTNO could be caused by its microstructure because of the creation of an effective circuit of parallel capacitors [11], as found in boundary-layer capacitors (BLC) [12]. BLC, such as $(Ba, Sr)TiO_3$ ceramics, is one of the most efficient geometries for attaining high-density charge storage, whose static dielectric constant ε_o can reach as high as $\sim 10^5$. However, the strong dependence on temperature and frequency of ε for the BLC makes them unusable for most applications [13].

In the LTNO specimens, each Li^+ doped causes the transformation of one Ni^{2+} adjacent to the Li^+ into Ni^{3+} for meeting charge neutrality, and thus the concentration of Li^+ is equal to that of Ni^{3+} theoretically. Although Li^+ is hard to be detected, the concentration ratio of Ni^{3+} to Ni^{2+} can be confirmed by x-ray photoelectron (XPS) analysis. According to Fig. 3, the Ni $2P_{3/2}$ peak, corresponding to the valence band of Ni ions, can be divided into the contributions from Ni^{2+} and Ni^{3+}, and accordingly it can be estimated that the concentration ratio of Ni^{3+} to Ni^{2+} is close to the nominal ratio of Li^+ to Ni^{2+} in the specimens. On the other hand, according to the element distribution analysis on the fractured surface of the specimens, Ti dopant is rich on the grain boundaries but indigent within the grains. Thus the interiors of the grains are semiconducting (i.e., Li-doped NiO), while the shells of the grains are Ti-rich insulating boundaries, which creates an effective circuit of parallel capacitors.

According to the simple series-layer model for the BLC, the dielectric constant of the ceramic specimens

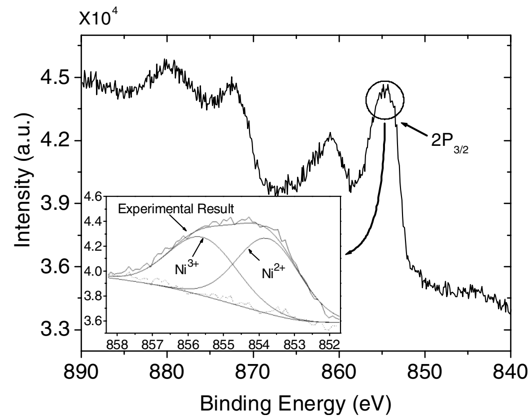

FIG. 3. XPS spectra of the Ni ion in the LTNO samples. The inset shows that the Ni $2P_{3/2}$ peak around 855 eV contains the contributions from the Ni^{2+} ion and the Ni^{3+} ion.

can be simply expressed as

$$\varepsilon \approx \varepsilon_b d/t, \quad (2)$$

where d (about 2–5 μm; see the SEM image in the inset of Fig. 1) is the grain size, t (about a few nanometers) is the boundary-layer thickness, and ε_b is the dielectric constant of the boundary layer and is roughly 10–50 estimated from measured ε. From this point of view, the dielectric constant ε of the bulk ceramics deceases with increasing t (by increasing Ti concentration). The inset in Fig. 4 shows such a decrease in the dielectric constant with the Ti concentration. On the other hand, the Li content has a remarkable effect on the dielectric constant of the LTNO specimens, as shown in Fig. 4. In the grain interiors, the carrier concentration raises with increasing Li concentration, and more charges accumulate at the two sides of the boundary layers, which is responsible for the higher dielectric constant of the specimens.

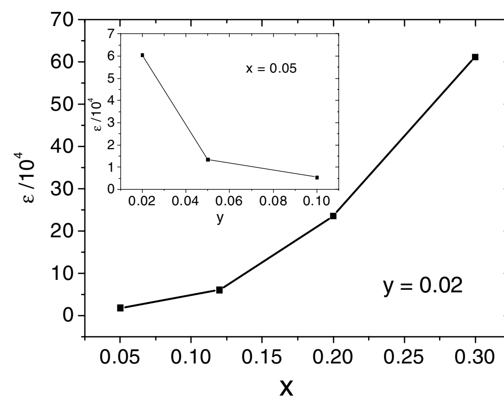

FIG. 4. The dependence of the dielectric constant at room temperature and 1000 Hz on the concentration of Li and Ti (see the inset) doped in $Li_xTi_yNi_{1-x-y}O$ ceramics.

The temperature dependence of the dielectric response was found to be influenced by the concentration of Li and Ti dopants, too. Although the temperature dependence of the dielectric response for other specimens of $Li_xTi_yNi_{1-x-y}O$ with $x < 0.3$ and $y < 0.1$ is similar to that shown in Fig. 1 for the LTNO, the temperature at the loss peak at a fixed frequency shifts to a low temperature range with increasing Li concentration or with decreasing Ti concentration. From this point of view, one can obtain the LTNO materials for the X7R EIA specification [14] with $\varepsilon_o > 10^4$ by adjusting the concentration of Li and Ti doped in NiO.

In conclusion, the Li, Ti co-doped NiO ceramics have been found to exhibit a giant low-frequency dielectric constant, $\varepsilon_o \sim 10^4$–10^5 which is temperature independent above 200 K, and an abnormal drop of approximately one-hundred-fold in the dielectric constant at low temperature. The origin of the large polarization is due mainly to its microstructure. The anomaly at low temperature is attributed to a relaxation process, corresponding to thermally excited conduction in the grain interiors. Our results have shown that the concentration of Li and Ti dopants has a remarkable effect on the dielectric properties of the LTNO ceramics. One can obtain the LTNO materials meeting the X7R EIA specification with $\varepsilon_o > 10^4$ by varying the concentration of Li and Ti doped. The giant dielectric constant and good thermal stability potentially make the oxide ceramics particularly attractive for practical applications.

This work was supported by the Ministry of Sciences and Technology of China (Grant No. G2002067103) and the NSF of China.

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