Electrical responses in high permittivity dielectric (Li, Fe)-doped NiO ceramics

Prasit Thongbai,¹ Teerapon Yamwong,² and Santi Maensiri¹,a

¹Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand
²National Metals and Materials Technology Center (MTEC), Thailand Science Park, Pathumthani 12120, Thailand

(Received 1 March 2009; accepted 25 March 2009; published online 17 April 2009)

Electrical properties of giant-permittivity core/shell structured Li₀.₀₅Fe₀.₁₀Ni₀.₈₅O (LFNO) ceramics are studied as functions of frequency, temperature, and dc bias. Three electrical responses of depletion surface (DS), grain boundary (GB), and bulk grain are detected in the LFNO ceramics. The DS and GB effects can be separated by removing the surface samples, whereas the grain effect is extracted by applying dc bias. It is found that the interfacial polarizations at the DSs and GBs are suppressed by applied voltages. Our results suggest that the polarization relaxation in the LFNO ceramics is closely related to the electrical response inside the grains. © 2009 American Institute of Physics. [DOI: 10.1063/1.3120567]

It is generally believed that the presence of insulating layers in polycrystalline ceramics has remarkable effects on their electrical properties, and they are usually used to design ceramic properties for practical applications. The effects of insulating layers, e.g., depletion surfaces (DSs), grain boundaries (GBs), and internal domains within the bulk grain, on high dielectric properties of materials are often observed. For example, the existence of these three insulating layers in CaCu₃Ti₂O₁₂ (CCTO) ceramics have an influence on the giant dielectric permittivity (ε′) of the CCTO. ¹–³ The Maxwell–Wagner (MW) polarization (interfacial polarization) at these insulating layers has, therefore, been used to ascribe the giant ε′ response in this material. For (A,B)-doped NiO ceramics (A=Li, Na, K and B=Ti, Si, Al, Ta, V, Fe), ⁴–⁹ it is widely accepted that the giant ε′ response in these ceramics is associated with their heterogeneous microstructure, consisting of semiconducting grains (A-doped NiO) and insulating GBs (B-rich insulting boundaries). It is interesting that the dielectric properties and the related electrical response of these NiO-based systems can be modified by varying the composition via additions of A and B.⁴–⁹ Most recently, we found that the dielectric properties of (Li, Ti)-doped NiO ceramics system depended on both sintering temperature and grain size.¹⁰ The presence of oxygen vacancies and the existence of internal domains might be responsible for these observations. These results imply that both DS and bulk grain effects may have impacts on the electrical and dielectric properties of these NiO-based ceramics. However, the experimental results supported these are still missing.

In this paper, the effects of insulating layers on the electrical properties of high-permittivity Li₀.₀₅Fe₀.₁₀Ni₀.₈₅₋₀.₀₅O (LFNO) ceramics are investigated. The results reveal that the electrical responses in the DSs, GBs, and grains have significant effects on the electrical properties of the LFNO ceramics. The evident DS effect is proved by removing the sample surface layer, while the bulk grain effect is identified by applying dc bias. The close relationship between the relaxation mechanism and the electrical transport inside the grains is observed.

The polycrystalline Li₀.₀₅Fe₀.₀₅Ni₀.₉₅O and Li₀.₀₅Fe₀.₁₀Ni₀.₈₅O ceramic samples were prepared by a polymer pyrolysis method. Details about the sample preparation were given elsewhere.⁹ The sintered LFNO samples were characterized by x-ray diffraction (XRD) (Philips PW3040, The Netherlands), Field-emission scanning electron microscopy (FE-SEM) and energy-dispersive X-ray spectroscopy (EDS) (Hitachi S-4700, Japan). XRD patterns (not did show) confirmed a main phase of NiO in both samples. However, the second phase of NiFe₂O₄ could only be observed in the XRD pattern of the Li₀.₀₅Fe₀.₁₀Ni₀.₈₅O sample. The dielectric and electrical properties of both as samples (before polished) and polished samples were measured using a Hewlett-Packard 4194A impedance gain phase analyzer over a frequency ranging from 100 Hz to 10 MHz and an oscillation voltage of 1.0 V. The measurements were performed over a temperature ranging from −50 to 200 °C using an inbuilt cooling-heating system. Each measured temperature was kept constant with an accuracy of ±1 K. Silver paint was used as the electrodes. Throughout this paper, we assigned symbols of LFNO-1Be and LFNO-2Be for the as-sintered samples of Li₀.₀₅Fe₀.₀₅Ni₀.₉₀O and Li₀.₀₅Fe₀.₁₀Ni₀.₈₅O ceramics and LFNO-1Af and LFNO-2Af for the sintered samples with surface polishing of Li₀.₀₅Fe₀.₀₅Ni₀.₉₀O and Li₀.₀₅Fe₀.₁₀Ni₀.₈₅O ceramics.

Figure 1 reveals the fractured surface of the Li₀.₀₅Fe₀.₁₀Ni₀.₈₅O ceramic sample, showing obvious structure consisting of grains and GBs. Interestingly, the EDS analysis, inset of Fig. 1, shows that the lower relative intensity of Fe is detected at the white core regions (points 2 and 5), but it is high at the hilly dark regions (points 1, 3, and 6). According to the XRD and EDS analyses, it is reasonable to suggest the existence of the core/shell structure in the LFNO ceramics, consisting of semiconducting core grains (e.g., Li-doped NiO)¹⁰ and Fe-rich insulating GBs (e.g., NiFe₂O₄). The existent core/shell structure in the NiO-based ceramics was also be observed in the (Li, Si)-, (Li, V)-, and (Li, Ti)-doped NiO ceramic systems.⁶,⁹,¹⁰ It is worth noting that the Fe-dopant is also rich on the outmost sample surfaces, as displayed in the inset (b).

¹Electronic addresses: sanmae@ku.ac.th and santimaensiri@gmail.com.
It is clearly seen from Fig. 2 that the DS has a significant influence on the high dielectric properties of the LFNO ceramics. As illustrated in Fig. 2, after the LFNO-1Be sample was polished evenly from both sides, the decrease in $\varepsilon'$ and the exponential increase in the loss tangent ($\tan \delta$) were observed in the polished-LFNO-1Be sample (LFNO-1Af sample). Under an applied electric field, some mobile charges in the inner part of the bulk LFNO ceramics may be blocked by the DS. Thus, the MW polarization is produced by the accumulated charges at the interface between the insulating DS layer and the inner part. After the DSs were removed, these accumulated charges are free and they become mobile charge carriers. Consequently, the polarization at the DS does not response, which causes decrease in the total polarization. On the other hand, the observed exponential increase in $\tan \delta$ is suitably attributed to the dc conductivity effect. It is interesting that the LFNO-1Af sample still exhibits the high $\varepsilon'$ response, implying that there may be other polarizations contributing to the dielectric responses in the LFNO-1Af sample.

Although the DSs were removed, the relaxation $\tan \delta$ peaks still appear and the activation energy for relaxation process ($E_a$) remains almost constant, i.e., $E_a=0.483\, eV$ (0.419 eV) and 0.468 eV (0.411 eV) for the LFNO-1Be (LFNO-2Be) and LFNO-1Af (LFNO-2Af) samples, respectively. Therefore, the $E_a$ values of the LFNO ceramics may actually be affected by the relaxation in the inner part of the LFNO ceramics. This is similar to that observed in the CCTO ceramic,\textsuperscript{3} which was clearly explained based on the different electrical conductivities between the DS and inner part due to the difference in oxygen concentration between them. This might be responsible for the formation of the insulating DS layer in the LFNO ceramics. Moreover, the DS effect may also be attributed to the fact that the shells of the grains are the NiFe$_2$O$_4$ phase, which is rich on the outmost surface layers of the LFNO ceramic samples [inset (b) of Fig. 1].

Figure 3(a) shows the impedance spectra of the as-sintered LFNO and polished-LFNO ceramic samples, proving the DS effect on their electrical properties. It is clear that after the DSs of the as-sintered samples were removed, the arcs of the polished-LFNO samples (LFNO-1Af and LFNO-2Af samples) at lower frequencies decreased, whereas the arcs at higher frequencies remained constant. These results strongly indicate that the enhanced arcs in the low frequency range contain two overlapped arcs, and thus the DS and GB effects are roughly separated. Consequently, it is reasonable to suggest that there are three sets of electrical responses in the LFNO ceramics, i.e., DS, GB, and bulk grain responses. Based on the above analysis, it is clearly proved from Fig. 3(b) that the interfacial polarizations of the DSs and GBs are suppressed by applying dc bias, whereas the bulk polarization is independent of the biases. This suppression of the interfacial polarization is similar to that observed in La$_0.7$Sr$_0.3$MnO$_3/BaTiO_3$ multilayers.\textsuperscript{12}

Figure 4 demonstrates the effect of dc bias on the frequency dependence of $\varepsilon'$ for the LFNO-1Af sample at room temperature. It is found that the $\varepsilon'$ values below $10^4$ Hz decrease with the increase of applied voltage, corresponding to the decrease in the capacitance of GBs,\textsuperscript{12,13} which is being accompanied by the decrease in $R_{GB}$ [inset of Fig. 3(b)]. These results suggest that, with increasing the applied voltage, the accumulated charge carriers are becoming more and more overcome the potential barrier at the GBs, implying that these accumulated charge carriers become mobile charges. Consequently, the intensity of the space charge polarization at this region is decreased by the increase in the applied voltage, while the conductivity increases due to the increase in the mobile charge. This is confirmed by the ob-

![Figure 1](image1.png)  
**FIG. 1.** (Color online) Fractured surface of the Li$_{0.05}$Fe$_{0.10}$Ni$_{0.85}$O sample. Inset (a) shows Ni (■) and Fe (▲) element profiles obtained from the EDS spectra at different points. Inset (b) is a SEM image of surface morphology.

![Figure 2](image2.png)  
**FIG. 2.** (Color online) Frequency dependence of (a) $\varepsilon'$ and (b) $\tan \delta$ for LFNO-1Be (symbols) and LFNO-1Af (solid lines) samples at various temperatures from $-40$ to $200\, ^\circ C$ with the step increase in temperature is $30\, ^\circ C$.

![Figure 3](image3.png)  
**FIG. 3.** (Color online) (a) Impedance spectra of LFNO samples before and after surface polishing at $20\, ^\circ C$. (b) Impedance spectra as a function of dc bias of LFNO-1Be. Inset shows impedance spectra of LFNO-1Af.

![Figure 4](image4.png)  
**FIG. 4.** Frequency dependence of $\varepsilon'$ for the LFNO-1Af sample at room temperature with the increase of applied voltage.
erved exponential increase in tan δ at the highest applied voltage, as shown in the inset of Fig. 4. When the applied voltage increases over 20 V, the dc bias is over limit balance (over 20 V) due to the large leakage current, which results from the large conductivity in the bulk ceramics.

Figure 5 displays the frequency dependence of the imaginary parts Z′′ of complex impedance at selected temperatures, in which Z′′ plots usually highlight phenomena characterized by the large resistance. Two thermally activated electrical responses are observed at lower and higher frequencies—both shift to higher frequency with increasing the temperature. To identify these electrical responses, the frequency dependence of Z′′ has been studied as a function of dc bias. As illustrated in the inset of Fig. 5, both the peak height and frequency of the Z′′ peak of the electrical response at the lower frequency are strongly dependent of the applied voltage, but not for the higher-frequency electrical response. As a result, the lower- and higher-frequency electrical responses are suitably identified to the GB and bulk effects, respectively. Moreover, it was found that the plots of (Z′′)max versus 1000/T follow the Arrhenius law, (does not present). The estimated activation energies of the LFNO-1A (LFNO-2A) were found to be 0.454 (0.408) and 0.444 (0.506) eV for the bulk grains and GBs, respectively. The two activation energies of the electrical responses in the LFNO-1A sample are similar to its relaxation activation energy. However, the activation energies of the grain electrical response in the LFNO-2A and its relaxation are almost the same in value, while its activation energy of the GB is larger than that of the relaxation activation energy. Therefore, it is appropriate to suggest that the relaxation mechanism in the LFNO ceramics has a close relation to the conductivity inside the grains. Lin et al. reported that the dc conduction activation energy of pure-NiO ceramics could be increased by doping with Fe ions, which was attributed to the effects of FeO2 defects and the nickel vacancies. This might be responsible for the observed large relaxation activation energy in the LFNO ceramics comparing to the other NiO-based ceramics systems. With the larger conduction activation energy, the dielectric relaxation of the LFNO ceramics are hardly activated by thermal. Thus, the polarization should fully be responded at higher temperatures. From these points of view, we think that the relaxation behavior of the NiO-based ceramics can be adjusted by varying the semiconductivity of grains. Note that the increase of GB conduction activation energy of the LFNO-2A sample might be associated with the accumulation of NiFe2O4 phase at the GB, as revealed in Fig. 1.

In conclusion, the high dielectric permittivity LFNO ceramics were investigated as functions of frequency, temperature, and dc bias. Three thermally activated electrical responses were observed at the DSs, GBs, and bulk grains. The effects of the DS and GB were separated by removing the surface samples, whereas the applied dc bias was used to identify the electrical response of the bulk grain. It was found that the interfacial polarizations of the DSs and GBs could be suppressed by the applied voltage, but not for the bulk polarization.

The authors would like to thank the Thai Microelectronics Center (TMEC) for FE-SEM facilities. P.T. would like to thank the Tgist for his Ph.D. scholarship. This work was financially supported by the Thailand Research Fund and The Commission on Higher Education, Thailand.