Effects of Fe, Ti, and V doping on the microstructure and electrical properties of grain and grain boundary of giant dielectric NiO-based ceramics

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We report the giant dielectric response and electrical properties of Li0.05B0.02Ni0.93O (B = Fe, Ti, and V) ceramics prepared by a polymer pyrolysis route. The giant dielectric response in these materials can be ascribed based on the Maxwell–Wagner polarization and thermally activated mechanisms. It is found that Fe, Ti, and V doping has a strong effect on the microstructure and the conduction of grains and grain boundaries of these NiO-based ceramic systems, which make large contribution to their dielectric properties. © 2009 American Institute of Physics. [DOI: 10.1063/1.3072356]

Generally, the relationship between the structure of materials and their properties is studied at two different levels of length scale: microscopic and microstructural levels. Thus, the inhomogeneities within macroscopically homogeneous materials and their properties is studied at two different levels of these inhomogeneities, respectively.1

In recent years, high permittivity Bi/Pb-free dielectric materials with good thermal stability particularly attracted ever-increasing attention for their practical applications in microelectronics such as capacitors and memory devices. High-permittivity A,B,Ni1−x−y−z−wO ceramic system (where A =Li, Na, and K and B = Ti, Al, Ta, and Si) is one of the most important high-permittivity materials that has been intensively researched in recent years.2–8 It is widely accepted that a high dielectric permittivity (ε′) of these materials is attributed to the Maxwell–Wagner (MW) polarization mechanism based on the existence of the inhomogeneities of grain, grain boundary (GB), and defects within the materials.9–11 Interestingly, the dielectric properties and related electrical response of these NiO-based systems can be tuned by changing the composition of the additives of A and B.12,13 which normally have the effects on the grain and GB properties, respectively. However, it has been reported that the Ti content in the Li,Ti,Ni1−x−y−z O system also has a strong effect on the transport properties inside the grain, which should be attributed to the fact that some part of Ti entered into the NiO crystal lattice. Moreover, it was found that the dielectric properties of NiO-based ceramics depended on the sintering temperature14 and the feature of microstructure.15

In this work, we studied the effects of the microstructure, grain, and GB modifications on the giant ε′ properties of the Li0.05B0.02Ni0.93O (B = Fe, Ti, and V) ceramics. The results suggested that Fe, Ti, and V dopings had great impact on the microstructure and the electrical transports of the grains and GBs, which are major contributions on the giant ε′ response in these materials.

Ni(NO3)2·6H2O, LiNO3, C14H28O6Ti, Fe(NO3)3·9H2O, C10H12O2V, (NH4)2S2O8, and acrylic acid were employed as starting raw materials. The polycrystalline Li0.05Ti0.02Ni0.93O (LTNO) ceramic sample was prepared by a polymer pyrolysis route. First, stoichiometric amounts of Ni(NO3)2·6H2O, C16H28O6Ti, and LiNO3 were dissolved in 10 g of acrylic acid aqueous solution (acrylic acid: H2O = 70:30 wt %) under constant stirring and heating at 100 °C. Second, a small amount (0.5 g) of 5% (NH4)2S2O8 aqueous solution as the initiator was added to the mixed acrylic acid solution to promote the polymerization. Then, the gel precursor was dried at 350 °C for 1 h. The dried gel was ground and later calcined at 700 °C for 5 h in air. The LTNO powder was pressed into pellet of 9.5 mm in diameter and ~1–2 mm in thickness by a uniaxial pressing method at 200 MPa. Finally, this pellet was sintered at 1280 °C for 4 h in air. The Li0.05V0.02Ni0.93O (LVNO) and Li0.05Fe0.02Ni0.93O (LFNO) samples were also prepared by the same method, but Fe(NO3)3·9H2O and C10H12O2V were used instead of C16H28O6Ti for the preparation of LVNO and LFNO, respectively.

X-ray diffraction (XRD) (Philips PW3040, The Netherlands) and scanning electron microscopy (SEM) (LEO 1450VP, UK) with energy dispersive x-ray spectrometer (EDS) were used to characterize the phase composition and microstructure of the NiO-based ceramics. XRD patterns (not presented) confirm a main phase of NiO in all samples with no diffraction peaks of possible impurity phases. The sintered ceramic samples were polished and electroded by silver paint on both sides of the disk-shaped samples. The dielectric and electrical responses of the samples were measured using a Hewlett Packard 4194A impedance gain phase analyzer over wide range of frequency (100 Hz–10 MHz) and temperature (from −60 to 150 °C) at the oscillation voltage of 1.0 V. Each measuring temperature was kept constant with an accuracy of ±1 °C.

Figures 1(a)–1(c) show surface morphologies of the LFNO, LTNO, and LVNO ceramic samples, indicating that Fe, Ti, and V dopings have a remarkable effect on their microstructures. The mean grain sizes of the LFNO, LTNO, and LVNO samples are 3.3 ± 0.9, 4.8 ± 2.0, and 46 ± 14 μm, respectively. The observed abnormal grain growth in the LVNO sample is attributed to a typical liquid phase of their microstructure, which usually contribute to form grain-to-grain bridges and to eliminate intergrain pores. The effect of
The overall dielectric behavior is similar to those observed in other NiO-based ceramics, which is in marked contrast to the well-known ferroelectric one resulting from the structure distortion due to the soft-mode condensation. Figure 2(a) demonstrates the frequency dependence of \(\varepsilon'\) and \(\tan\delta\) of the samples of LFNO, LTNO, and LVNO at room temperature, showing the giant \(\varepsilon'\) (10^4–10^5) response in all samples. The LTNO sample has the lowest \(\varepsilon'\) among these three samples over the measured frequency range, corresponding to the observed lowest value of \(\tan\delta\). The \(\varepsilon'\) of the LVNO sample is slightly higher than that of the LFNO sample, and interestingly its \(\tan\delta\) is lower than that of the LFNO sample at below and above frequency 10^4 Hz. The small step decrease in the LVNO sample at the frequency at about 10^4 Hz might be attributed to the heterogeneous relaxation such as defect-induced polarization. Figure 2(b) illustrates the temperature dependence of \(\varepsilon'\) of the LVNO sample at the selected frequencies. The temperature independence of \(\varepsilon'\) can be observed at frequency below 100 kHz. However, with increasing frequency, \(\varepsilon'\) drops dramatically to the low values at low temperatures, and such step decrease moves to the higher temperature range with increasing frequency. This is a suggestion of the thermally excited relaxation process. The overall dielectric behavior is similar to those observed in other NiO-based ceramics, which is in marked contrast to the well-known ferroelectric one resulting from the structure distortion due to the soft-mode condensation.

Figures 3(a) and 3(b) display the complex impedance plane plots of the LVNO and LTNO samples, respectively.
responses of grains in both samples shift out of the measured frequency range. However, we can assign the nonzero intercepts at low temperatures to the effects of the grains.\textsuperscript{15} Consequently, the core/shell model is appropriate for further analysis. According to the polaron theory, the temperature dependence of the conductivity ($\sigma$) is, with a temperature dependence prefactor, ascribed as:\textsuperscript{5,9}

$$\sigma = T^{-1} \exp(-E/k_B T),$$

(1)

where $E$ is the conduction activation energy and $k_B$ and $T$ are the Boltzmann constant and the absolute temperature, respectively. Generally, the GB effect on electric conductivity may originate from a GB potential barrier,\textsuperscript{9} which should be ascribed by the Fe-, Ti-, and V-rich boundaries for our NiO-based systems. Based on the RC model,\textsuperscript{13} the resistances of the grain and GB can be obtained at various measuring temperatures. According to the fitted curves using Eq. (1) for the LFNO, LVNO, and LTNO samples shown in Figs. 3(c) and 3(d), the conduction activation energies inside the grain ($E_g$) and at the GB ($E_{gb}$) can be estimated—the values of $E_g$ are 0.190, 0.216, and 0.293 eV, while the values of $E_{gb}$ are 0.240, 0.304, and 0.453 eV for the samples of LFNO, LVNO, and LTNO, respectively. These results indicate that the grain and GB of these materials have different characteristics of electrical transport.

As previously reported,\textsuperscript{16} the different valence states of $A$ in the $A_{0.01}B_{0.01}Ni_{0.98}O$ ($A$=K$^+$, Mg$^{2+}$, and Y$^{3+}$) materials had a remarkable effect on the dielectric properties of NiO-based ceramics, which should be mainly attributed to the large variation in $E_g$ values. In the present work, the different observed values of $E_g$ and $E_{gb}$ of these three NiO-based ceramics imply that the Fe, Ti, and V doping have remarkable effects on both grain and GB conductivities. Such various $E_g$ values observed in the LTNO and LFNO samples may be caused by the substitution of some parts of Ti$^{4+}$ (0.68 Å) and Fe$^{3+}$ (0.64 Å) ions into the Ni$^{2+}$ (0.69 Å) ion sites in the NiO crystal lattice, which induces the different defects (i.e., Fe$_{90}^0$Ni$_{10}^0$ and Ti$_{90}^0$Ni$_{10}^0$) in the grain interiors.\textsuperscript{9,17} The different electrical properties of these two samples can suitably be referred to as the microscopic inhomogeneity effect. On the other hand, the V-doping is most likely to present only at GBs to form a second liquid phase, as clearly seen in Figs. 1(c) and 1(d). Subgrains usually develop inside larger grains and affect the mobility of charge carriers and the dielectric response at different frequencies.\textsuperscript{18} This would be responsible for the observed highest low-frequency $\varepsilon'$ of the LVNO ceramic among these three samples. These results indicate that the microstructural inhomogeneity has a strong effect on the electrical properties of the NiO-based ceramics. Additionally, the relaxation activation energies ($E_a$) of the LVNO (0.224 eV) and LTNO (0.287 eV) samples are almost the same as their $E_g$ values (data not shown). $E_a$ of the LFNO ceramic with the smallest $E_g$ cannot be obtained because its dielectric relaxation peak shifts out of the measured temperature range. Therefore, it is suggested that the observed lowest $\varepsilon'$ of the LTNO sample among these three samples and such disappeared relaxation peak of the LFNO sample are due to the fact that the polarization relaxation in these three samples has a close relation to the conductivity inside the grains. Therefore, it is reasonable to suggest that the Fe, Ti, and V dopants have significant effects on both the microstructure and the electrical transports inside the grain and at the GBs, which leads to the different dielectric responses in these NiO-based ceramics. These different ceramic properties can be ascribed to both microscopic and microstructural inhomogeneities, which should be due to the differences in the valence state and the melting point of the dopants, respectively.

We now turn to see the effects of Fe, Ti, and V doping on the GB conductivity in the NiO-based ceramics. Lin et al.\textsuperscript{17} reported the positive values of the Seebeck coefficient of Fe-doped NiO samples, indicating that holes are major carriers in these samples. In the case of the LFNO sample, we think that the different concentrations of the holes at the grains and GBs might be attributed to the effects of Li-doped NiO and Fe-doped NiO, respectively. This is responsible for the slight difference between $E_g$ and $E_{gb}$ in the LFNO sample. Thus, the different values of $E_{gb}$ in our NiO-based ceramic samples could be attributed to the difference in the intrinsic properties of the GBs, which are affected by the dopants.

In conclusion, the giant $\varepsilon'$ permittivity $Li_{0.05}B_{0.01}Ni_{0.98}O$ ($B$=Fe, Ti, and V) ceramics have been investigated. The giant $\varepsilon'$ response and related electrical properties of these materials are studied as functions of frequency and temperature. Our results reveal that Fe, Ti, and V dopings have great effects on both microstructure and electrical properties of the grains and GBs, resulting in the giant $\varepsilon'$ response in these materials. The giant $\varepsilon'$ behavior of these NiO-based ceramics can be explained based on the MW polarization and thermally activated mechanisms.

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