

CHAPTER VI

CONCLUSIONS AND SUGGESTIONS

6.1 Li and Ti co-doped NiO system

In conclusion, $\text{Li}_x\text{Ti}_y\text{Ni}_{1-x-y}\text{O}$ ceramics ($x = 0, 0.02, 0.05, 0.10$ and $y = 0, 0.02, 0.05, 0.10, 0.15$) were synthesized using powders prepared by a polymer pyrolysis method. The phase formation and crystal structure of the powders as well as ceramics were investigated by X-ray diffraction (XRD) technique. The microstructure and chemical compositions were studied by scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS), respectively. The electrical and dielectric properties were investigated as functions of frequency and temperature. The effects of surface layers and oxygen vacancies on the dielectric and electrical properties were investigated by polishing surfaces and annealing in Ar atmosphere, respectively.

For the XRD results, it was found that the Li and Ti doping concentrations had a remarkable influence on the phase formation of the $\text{Li}_x\text{Ti}_y\text{Ni}_{1-x-y}\text{O}$ ceramics. All of the powder and ceramic samples exhibited the main phase of NiO. In $\text{Li}_{0.05}\text{Ti}_y\text{Ni}_{0.95-y}\text{O}$ ceramic samples, the second phase of NiTiO_3 could be detected in the samples for y (Ti) = 0.05-0.15, but could not for $y = 0.02$. The peak intensity of the NiTiO_3 phase increased with increasing the Ti doping concentration. For $\text{Li}_x\text{Ti}_{0.05}\text{Ni}_{0.95-x}\text{O}$ ceramic samples, interestingly, the NiTiO_3 phase, which relates directly to the Ti doping concentration, was only observed in the XRD patterns of the samples for x (Li) = 0.02-0.05. It could not be detected for $x = 0.10$. Certainly, it was not detected in the $\text{Li}_{0.10}\text{Ti}_{0.02}\text{Ni}_{0.88}\text{O}$ ceramic as well. The Ti doping preferred to form the NiTiO_3 phase; in contrast, the Li doping preferred to substitute the Ni sites in the NiO crystal lattice, and also contributed to the substitution of the Ti doping ions into the Ni sites.

For the SEM-EDS results, the average grain size of the $\text{Li}_x\text{Ti}_y\text{Ni}_{1-x-y}\text{O}$ ceramics was found to increase with an increase in the sintering temperature from 1200 to 1280 °C. It was also demonstrated that the surface morphologies and microstructure depended strongly on the Li and Ti doping concentrations. The sub-micron grains of

NiTiO₃ introduced on the top surfaces of the Li_{0.05}Ti_yNi_{0.95-y}O samples with $y = 0.05-0.15$. The interesting result can be observed in the Li_xTi_{0.05}Ni_{0.95-x}O samples. The NiTiO₃ phase segregated largely along the grain boundaries of the Li_{0.02}Ti_{0.05}Ni_{0.93}O ($x = 0.02$) sample. When $x = 0.05$, the accumulated NiTiO₃ was homogeneously dispersed in to the grain regions and transformed to the sub-micron grains. Surprisingly, the sub-micron grains were totally erased by increasing $x = 0.10$ corresponding to the XRD result. The microstructural evolution could be ascribed based on the liquid-phase sintering.

For the dielectric and electrical properties, all of the synthesized Li_xTi_yNi_{1-x-y}O ceramics exhibited the giant dielectric properties with $\epsilon' \sim 10^3-10^5$. However, the values of the loss tangent in the measuring frequency range for all the samples were found to be larger than 0.05, which are unsuitable for capacitor applications. It was found that the dielectric constant increased with increasing the grain size, which was due to the increase in the sintering temperature. Interestingly, two sets of thermally relaxations exhibited in the dielectric spectra of the samples that possessed the large accumulation of NiTiO₃ phase along the grain boundaries, i.e., Li_{0.05}Ti_{0.05}Ni_{0.90}O, Li_{0.05}Ti_{0.10}Ni_{0.85}O, Li_{0.05}Ti_{0.15}Ni_{0.80}O, and Li_{0.02}Ti_{0.05}Ni_{0.93}O samples. On the other way, just one dielectric relaxation exhibited in the samples that possessed the smooth grain and grain boundaries, i.e., Li_{0.05}Ti_{0.02}Ni_{0.93}O, Li_{0.10}Ti_{0.02}Ni_{0.88}O, and Li_{0.10}Ti_{0.05}Ni_{0.85}O samples. More interestingly, a low-frequency dielectric relaxation (LFR) was changed by polishing surface layers; whereas, a high-frequency relaxation (HFR) remained constant. By using the impedance spectroscopy, it was proved that the surface layers, which were covered with the NiTiO₃ sub-micron grains, behave as insulating layers. When the insulating surfaces were removed, the dielectric constant decreased due to the absent of polarization at this interface layers; while, the loss tangent increased due to the increase in the dc conduction on the surfaces. Both of the LFR and HFR could be ascribed by a Debye-like relaxation model, Cole-Cole model—the dielectric constant of the LFR and HFR could be well fitted by the Cole-Cole equation. However, the low-frequency loss tangent and dielectric loss could be well fitted by the Cole-Cole relaxation model combined with the dc conduction term.

For the effect of annealing on the giant dielectric properties, it was found that the oxygen vacancies had great influences on both of the LFR and HFR processes. For the samples that can exhibit the LFR, the low-frequency dielectric constant increased with annealing in Ar; whereas, the high-frequency dielectric constant was found to be decreased. While the low-frequency loss tangent of these ceramics decreased with the annealing in Ar. In contrast, the loss tangent of the $\text{Li}_{0.10}\text{Ti}_{0.02}\text{Ni}_{0.88}\text{O}$, and $\text{Li}_{0.10}\text{Ti}_{0.05}\text{Ni}_{0.85}\text{O}$ samples increased with annealing in Ar. By using the impedance spectroscopy, it was found that the resistance of all samples increased. Furthermore, it was found that the total resistance of the samples that can exhibit the LFR was found to increased; whereas, it decreased for the other two samples. According to the investigation of the surface and annealing effects, two suitably models of the microstructure were proposed for these two groups of the $\text{Li}_x\text{Ti}_y\text{Ni}_{1-x-y}\text{O}$ ceramic samples.

6.2 Li and Fe co-doped NiO system

In conclusion, $\text{Li}_{0.05}\text{Fe}_{0.05}\text{Ni}_{0.90}\text{O}$ and $\text{Li}_{0.05}\text{Fe}_{0.10}\text{Ni}_{0.85}\text{O}$ ceramics were synthesized using powders prepared by a polymer pyrolysis method. Surface morphologies and fractured surface were investigated by SEM-EDS techniques. The high dielectric permittivity LFNO ceramics were investigated as functions of frequency, temperature, and dc bias. The XRD and SEM-EDS results revealed that the second phase of NiFe_2O_4 accumulated along the grain boundaries. It was found that the dielectric constant decreased with the polishing surfaces; whereas, the dielectric relaxation behavior did not change. Three thermally activated electrical responses were observed at the surface layers, grain boundaries, and bulk grains. The effects of the surface and grain boundary 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 surface layers and grain boundaries could be suppressed by the applied voltage, but not for the bulk polarization.

6.3 Li and V co-doped NiO system

In conclusion, $\text{Li}_{0.05}\text{V}_{0.02}\text{Ni}_{0.93}\text{O}$, $\text{Li}_{0.05}\text{V}_{0.05}\text{Ni}_{0.90}\text{O}$ and $\text{Li}_{0.05}\text{V}_{0.10}\text{Ni}_{0.85}\text{O}$ ceramics were synthesized using powders prepared by a polymer pyrolysis method. The giant dielectric constant and related electrical properties of LVNO ceramics were characterized as functions of frequency and temperature. The EDS results revealed that the structure was rich in V dopant at the grain boundary, and contains an insulating $\text{Ni}_3\text{V}_2\text{O}_8$ phase. The concentration of V has a remarkable effect on the dielectric properties of the LVNO ceramics due to the difference in the values of the conduction activation energy of grains and the thickness of grain boundary. The values of dielectric constant of these three samples were found to be 6.2×10^4 , 3.5×10^4 , and 3.1×10^4 , respectively. The giant dielectric behavior of the (Li, V)-doped NiO ceramics could be explained based on the Maxwell–Wagner polarization (i.e. interfacial polarization) and thermally activated mechanisms.

6.4 Effects of various valent states of doping ions on the microstructure and electrical properties giant dielectric NiO-based ceramics

In conclusion, three NiO-based ceramic samples, i.e., $\text{Li}_{0.05}\text{V}_{0.02}\text{Ni}_{0.93}\text{O}$, $\text{Li}_{0.05}\text{Ti}_{0.02}\text{Ni}_{0.93}\text{O}$, $\text{Li}_{0.05}\text{Fe}_{0.02}\text{Ni}_{0.93}\text{O}$, were synthesized using powders prepared by a polymer pyrolysis method. The giant dielectric response and related electrical properties of these materials were studied as functions of frequency and temperature. The results revealed that Fe^{3+} , Ti^{4+} , and V^{5+} doping ions had great effects on both microstructure and electrical properties of the grains and grain boundaries, resulting in the giant dielectric response in these materials. The giant dielectric behavior of these NiO-based ceramics could be explained based on the MW polarization and thermally activated mechanisms. The larger dielectric constants of the $\text{Li}_{0.05}\text{V}_{0.02}\text{Ni}_{0.93}\text{O}$ and $\text{Li}_{0.05}\text{Fe}_{0.02}\text{Ni}_{0.93}\text{O}$ ceramics than that of the $\text{Li}_{0.05}\text{Ti}_{0.02}\text{Ni}_{0.93}\text{O}$ ceramic was attributed to the effects of microstructure and the electric transport inside the grains, respectively.

6.5 Dielectric and electrical properties of NiO-based ceramic systems prepared by a direct thermal decomposition method.

6.5.1 Li and Ti co-doped NiO ceramics: Effect of sintering temperature on dielectric properties

In conclusion, $\text{Li}_{0.05}\text{Ti}_{0.02}\text{Ni}_{0.93}\text{O}$ ceramics sintered at 1200 and 1280 °C were synthesized using powders prepared by a direct thermal decomposition method. The grain size was found to be increased by increasing the sintering temperature. The complex impedance spectroscopy indicated that the electrically heterogeneous structures may exist in the LTNO ceramics consisting of semiconducting grain and insulating grain boundary. The dielectric constant of the $\text{Li}_{0.05}\text{Ti}_{0.02}\text{Ni}_{0.93}\text{O}$ ceramics increased with the increase in grain size, and the dielectric response could be well explained by the Maxwell-Wagner polarization relaxation model. The experimental results indicated that the polarization relaxation has a close relation to the conductivity inside the grain. It was revealed that the relaxation activation energy and related grain conduction activation energy and grain boundary activation energy decreased with the increase in grain size. It could be proposed that the different microstructures lead to the chemical change (e.g., oxygen vacancies) inside the grains and at the grain boundaries.

6.5.2 Li and Al co-doped NiO ceramics

In conclusion, $\text{Li}_{0.05}\text{Al}_y\text{Ni}_{0.95-y}\text{O}$ ($y = 0.04, 0.06, 0.10$) ceramics were synthesized using powders prepared by a direct thermal decomposition method. The microstructure and phase formation of the prepared $\text{Li}_{0.05}\text{Al}_y\text{Ni}_{0.95-y}\text{O}$ powders and ceramics were characterized by XRD and FE-SEM. The phase formation of NiO-based ceramics and the grain growth mechanism were suppressed by the Al-dopant. It was demonstrated that the high dielectric constant of the $\text{Li}_{0.05}\text{Al}_y\text{Ni}_{0.95-y}\text{O}$ ceramics decreased with increasing the Al-dopant content. Giant dielectric response in such ceramics was attributed to the appearance of electrically heterogeneous structure, responsible for the observed high dielectric constant in the $\text{Li}_{0.05}\text{Al}_y\text{Ni}_{0.95-y}\text{O}$ samples. The results also showed that the Al-dopant has a strong effect on electrical transport in the grain interiors.

6.6 Dielectric and electrical properties of NiO-based ceramic systems prepared by a PVA method

6.6.1 Li and Fe co-doped NiO ceramics

The polycrystalline $\text{Li}_x\text{Fe}_y\text{Ni}_{1-x-y}\text{O}$ ceramic samples with different concentrations of Li and Fe, i.e., $\text{Fe}_{0.02}\text{Ni}_{0.98}\text{O}$, $\text{Li}_{0.02}\text{Fe}_{0.02}\text{Ni}_{0.96}\text{O}$, $\text{Li}_{0.05}\text{Fe}_{0.02}\text{Ni}_{0.93}\text{O}$, $\text{Li}_{0.10}\text{Fe}_{0.02}\text{Ni}_{0.88}\text{O}$, $\text{Li}_{0.05}\text{Fe}_{0.05}\text{Ni}_{0.90}\text{O}$, and $\text{Li}_{0.05}\text{Fe}_{0.10}\text{Ni}_{0.85}\text{O}$, were synthesized using powders prepared by a PVA method. The frequency and temperature dependences of the dielectric constant and loss tangent of the (Li, Fe)-doped NiO (LFNO) ceramics were studied. The variation of the Li and Fe concentrations had effects on the microstructure and electrical properties of these $\text{Li}_x\text{Fe}_y\text{Ni}_{1-x-y}\text{O}$ ceramics. It was suggested that the dielectric relaxation behavior and high dielectric response in this material system might be associated with both the hopping motions inside the grains and the Maxwell-Wagner polarization at the grain boundaries.

6.6.2 Li and Ti co-doped NiO ceramics

The high dielectric permittivity $\text{Li}_x\text{Ti}_{0.02}\text{Ni}_{0.98-x}\text{O}$ ($x = 0.05, 0.10, 0.20$) ceramics were successfully synthesized by a simple PVA sol-gel method. The XRD results showed the single phase of NiO. The temperature and frequency dependence of dielectric constant and dielectric loss were investigated. An excellent fit between the experimental and simulated data was obtained over a wide frequency and temperature using the modified Cole-Cole model with the consideration of the conductivity contribution. The high dielectric permittivity response could be ascribed to the Maxwell-Wagner polarization mechanism and defect-dipole polarization.

6.7 Comparison of giant dielectric properties of NiO-based and pure-CuO ceramics: Dielectric relaxation behavior

In conclusion, the high dielectric constant of $\sim 2.8\text{--}3.7 \times 10^4$ was observed in polycrystalline CuO ceramics fabricated from high purity (99.999%) CuO powder. The high dielectric response observed in the CuO ceramics could be described by the IBLC model. This work demonstrated that the giant dielectric constant was exhibited in the CuO ceramics without any dopants or impurities. The giant dielectric properties of CuO ceramics were similar to those observed in the NiO-based ceramics.

Moreover, it was also found that the Debye-type relaxation could exhibit in the CuO ceramics.

6.8 Suggestions

(1) According to the observed low-frequency relaxation (LFR), it is possible that the electrode effect may be related to the LFR (Li M et al., 2009a,b). Therefore, it is important to investigate the dielectric properties of the NiO-based ceramics as function of electrode materials such as gold sputtering, platinum sputtering, In-Ga sputtering.

(2) According to the annealing effect, the annealing in oxygen (O_2) atmosphere should also be conducted in the future works in order to obtain complete results.

(3) It was proposed that the annealing in Ar can introduce the insulating surface layers; therefore, the dielectric properties of polished-samples of the Ar-samples should be investigated further—this can be done by measuring the dielectric properties of the Ar-samples after they are polished to remove the induced insulating layer on the surfaces.

