Effect of Sintering Temperature on Structural and Dielectric Properties of $Li_{0.30}Cr_{0.02}Ni_{0.68}O$ Ceramic Doped With Kaolinite

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ABSTRACT

$Li_{0.30}Cr_{0.02}Ni_{0.68}O$ (LCNO) ceramics were prepared by sol–gel process and then doped with 1 %wt. kaolinite via solid state reaction. All doped samples were sintered at 1100-1300 °C. All sintered samples showed the single phase of cubic rock-salt NiO structure without extra phases. The microstructure of LCNO exhibited polyhedral grains with grain size of ~10-50 µm. With doping 1 %wt. kaolinite, the grain sizes were decreased to 0.5-5 µm. The grain sizes were increased with an increase of sintering temperatures. The grains were denser and larger as sintering temperature increased to 1300 °C. The dielectric properties of the 1% wt. kaolinite-doped LCNO ceramic were the highest dielectric constant (3.40×10^5) at 10 kHz and room temperature. Its loss tangent was 2.44 which was 2 times lower than that of the pure LCNO. The high dielectric constants can be explained by BLCs model.

Keywords: $Li_{0.30}Cr_{0.02}Ni_{0.68}O$, Kaolinite, Dielectric properties

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Introduction

Lead-free and non-ferroelectric materials with giant dielectric constant values ($\varepsilon_r \sim 10^4$-10^5) have been found in $CaCu_3Ti_4O_{12}$ (CCTO) [1-3] and (A,B)- doped NiO ceramics (where A = Li, Na, K ions and B = Ti, Cr, Al, V, Fe, Co, W, Pr, Zr, La ions) [4-12] for applications as capacitors and memory devices. The dielectric constants of these giant dielectric materials are also weakly dependent on temperature and frequency. The giant dielectric response in these materials is explained by the boundary layer capacitor (BLC) structures, corresponding to an electrically heterogeneous structure which consists of semiconducting grains and insulating grain boundaries [13]. However, loss tangents ($\tan\delta$) of these materials are very high, not suitable for capacitor applications. The reduction of $\tan\delta$ by adding the high-electrical resistivity dopants into dielectric materials has been studied such as MgO [13-14], ZrO_2 [15], $CaTiO_3$ [16] and SiO_2 [17] into CCTO, SiO_2 into $(Ba,Sr)TiO_3$ [18], Al_2O_3 into $Li_xCr_yNi_{1-x-y}O$ [5] and kaolinite into $BaTiO_3$ [19] in order to increase the electrical resistivity at grain boundary. For instance, Sun and coworkers [13] have studied the dielectric response in Mg-doped CCTO ceramics and found that the dielectric constant of the Mg (x=0.05) doped CCTO ($\varepsilon_r \sim 5.32\times10^4$) was a little higher than that of the pure CCTO ($\varepsilon_r \sim 2.00\times10^4$), relating to uniform microstructure with large grains of the doped CCTO. In addition, the loss tangent of the doped CCTO ($\tan\delta$=0.017) was lower than that of the pure CCTO ($\tan\delta$=0.041). Tang and coworkers have reported that the loss tangent decreased when SiO_2 was added into CCTO nanowires [17]. The loss tangent of the 40 % SiO_2/CCTO nanowires is 0.081, which is lower than that of the CCTO nanowires ($\tan\delta$=0.35). Khumpaitool and coworkers have synthesized Al_2O_3-doped $Li_{0.30}Cr_{0.02}Ni_{0.68}O$ (LCNO) by solid-state reaction via sol–gel process [5]. The 0.2 wt.% Al_2O_3/LCNO has the highest ε_r value (7.25×10^6) and the lowest $\tan\delta$ (2.37) at 1 kHz with stability of $\tan\delta$ over the measured frequency, which are better than those of the pure LCNO (ε_r =4.42×10^5; $\tan\delta$ =15.80). It is found that the $\tan\delta$ of the Al_2O_3-doped sample is nearly 7 times lower than that of the pure LCNO sample. Chen and coworkers have prepared $BaTiO_3$/kaolinite composites by conventional solid-state method [19]. XRD results showed that the new phase $BaAl_2Si_2O_8$ was formed as kaolinite added into $BaTiO_3$ and effect to decrease the $\tan\delta$.

Objectives of the study

In this work, $Li_{0.30}Cr_{0.02}Ni_{0.68}O$ (LCNO) was prepared by sol–gel process and improvement of $\tan\delta$ of this material by adding the high-electrical resistivity dopant was considered. Kaolinite is clay that much interest because of its high electrical resistivity (1×10^3- 2.22×10^4 Ω•cm) and low cost. Therefore, kaolinite was chosen to dope into LCNO in order to reduce $\tan\delta$ while keeping high dielectric constant. Moreover, the effect of sintering temperature on structural and dielectric properties of kaolinite/ $Li_{0.30}Cr_{0.02}Ni_{0.68}O$ composite ceramics was also investigated.

Methodology

Research methodology of this study consists of three parts including the preparation of LCNO, the preparation of kaolinite-doped LCNO and characterization.

Preparation of LCNO

$LiNO_3$, $Cr(NO_3)_3 \cdot 9H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ were used as starting materials and ethylene glycol was used as cross linking agent. $LiNO_3$ and $Ni(NO_3)_2 \cdot 6H_2O$ were dissolved in deionized water to get a clear solution. $Cr(NO_3)_3 \cdot 9H_2O$ in stoichiometric proportion was then slowly added into the solution and refluxed for 2 h, followed by heating on a hot plate at 250 °C to get dried gel. The dried gel was calcined at 1000 °C for 3 h and then sintered at 1300 °C for 3 h to get oxide powder.

Preparation of kaolinite-doped LCNO

The LCNO sintered powder was ground and sieved using a 200 mesh sieve. The 1 wt% kaolinite powder was mixed with LCNO powder by using ZrO_2 ball milling for 6 h. The kaolinite-doped LCNO material was mixed with 3% Polyvinyl alcohol (PVA) as a binder and pressed into pellets of 11 mm in diameter and ~1-2 mm in thickness by hydraulic pressing method at 5 tons. The sintering temperatures for making kaolinite-doped LCNO materials were 1100, 1200 and 1300 ºC. The products were sintered for 2 h in a muffle furnace with a heating rate of 5 °C/min, and then coated with silver electrode.

Characterization

Phase composition of the sintered pellet samples was identified using an X-ray diffractometer (XRD, PANalytical, Empyrean) with Cu K_α radiation, a scan step of 0.02 from 10° to 80° (2θ). Microstructure of the sintered pellet samples was observed using scanning electron microscopy (SEM, LEO-1450VP). Capacitance and $\tan\delta$ measurements were performed using an impedance analyzer (HP4194A, Agilent) at frequency range from 100 Hz to 1 MHz and temperature range from -60 to 200 ºC.

Results and discussions

The XRD patterns of kaolinite-doped LCNO samples sintered at various temperatures are shown in Figure 1. All sintered samples show the single phase of cubic rock salt structures [JCPDS No. 47-1049] without extra phase, consistent with other works [5-6, 8]. When sintering temperature was increased from 1100 to 1200 °C, the peak intensity slightly increased due to the increase of crystallinity that is related to the increase of crystallite size. The crystallite size was calculated by the Scherrer equation using the full-width at half maximum height (FWHM) of three diffraction peaks as (111), (200) and (220). The crystallite size increases rapidly from 91 nm to 138 nm when the sintering temperature is changed from 1100 ºC to 1200 ºC. The lattice parameters are slightly changed with increasing sintering temperatures. That can be implied that no interdiffusion between LCNO and kaolinite phases occurs even at higher sintering temperature. Furthermore, the relative densities increase from 44.76% for the sample sintered at 1100 ºC to 56.64% for the sample sintered at higher sintering temperature. The crystallite size, lattice parameter, relative density and grain size of all sintered samples are summarized in Table 1.

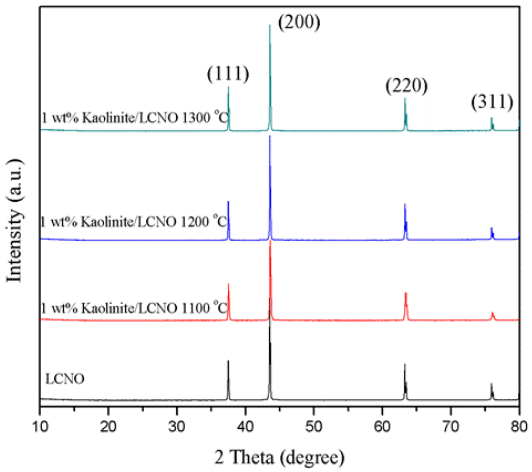

Figure 1 XRD patterns of the pure LCNO and kaolinite-doped LCNO samples sintered at various temperatures

Table 1 Summary of lattice parameter, crystallite size, relative density, grain size and dielectric properties of the pure LCNO and kaolinite-doped LCNO samples sintered at various temperatures

Samples	Lattice parameter *a* (Å)	Crystallite size [a] (nm)	Relative density [b] (%)	Grain size (μm)	ε_r at 10 kHz	tanδ at 10 kHz
LCNO	3.318	91.5	56.58	10-50	3.13×10^4	4.14
1wt.% Kaolinite/LCNO-1100	3.319	91.0	44.76	0.5-5	3.40×10^5	2.44
1wt.% Kaolinite/LCNO-1200	3.320	138.0	53.52	1-5	1.22×10^4	1.42
1wt.% Kaolinite/LCNO-1300	3.319	138.0	56.64	5-20	1.11×10^4	1.48

a Calculated by Scherrer equation

b Determined by using Archimedes method

Figure 2 shows the SEM images of surfaces (left hand images) and fracture surfaces (right hand images) of pure LCNO and kaolinite-doped LCNO with various sintering temperatures (1100 ºC, 1200 ºC and 1300 ºC). The pure LCNO reveals polyhedral grains with grain sizes of 10 to 50 μm. With 1 wt% kaolinite doping, uniformly small spherical grains appear (grain sizes ~ 0.5 to 5 μm). After that, as the sintering temperature is increased, the grain sizes increase, because of the agglomeration of small grains at higher sintering temperature. Grain size decreases with kaolinite doping because kaolinite particles could prevent the ion diffusion of LCNO phase and inhibit the grain growth of LCNO, corresponding with other work [18].

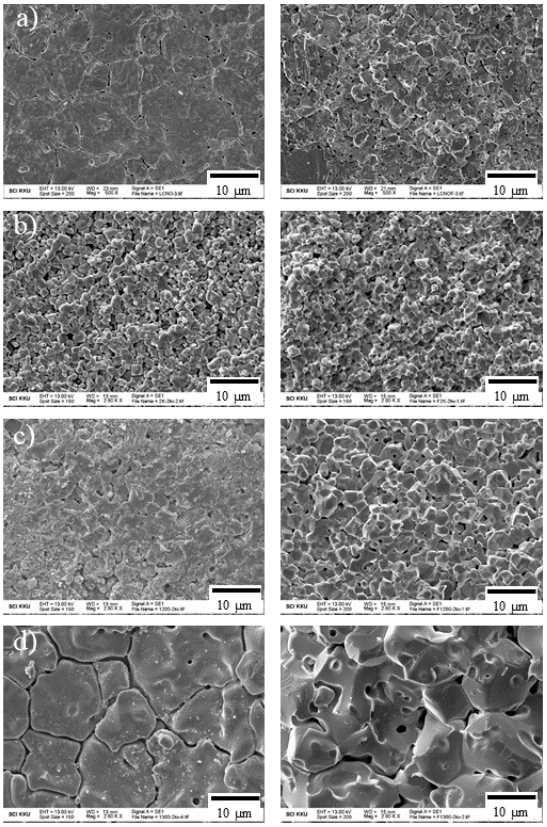

Figure 2 SEM images of surfaces (left hand images) and fracture surfaces (right hand images) of (a) the pure LCNO and the kaolinite-doped LCNO samples sintered at (b) 1100 ºC (c) 1200 ºC and (d) 1300 ºC

The dielectric properties (ε_r and $\tan\delta$) of kaolinite-doped LCNO with various sintering temperatures as a function of frequency are shown in Figure 3. It was found that all samples show very high dielectric constants (~10^4-10^7). However, higher dielectric constants which are found at low frequency are observed for all samples, especially for the doped sample sintered at 1100 ºC. That is due to the space charge polarization which occurs at low frequency, as also reported in other works [2, 5-6]. The sample sintered at 1100 ºC exhibits the highest dielectric constant (ε_r ~ 10^5-10^7), relating to smaller spherical grains with more uniform and more dense grains when compared to others. The other sintering temperatures were agglomeration of small grains which ε_r is lower than sample sintered at 1100 ºC. For loss tangent, the doped sample sintered at 1100 ºC has the low loss tangent, which is rather stable over the measured frequency range, relating to the smaller, denser and more uniform grains when compared to the pure LCNO and other sintering temperatures. However, its $\tan\delta$ is a little higher than those of other doped samples. The dielectric properties measured at room temperature and various frequencies are summarized in Table 1.

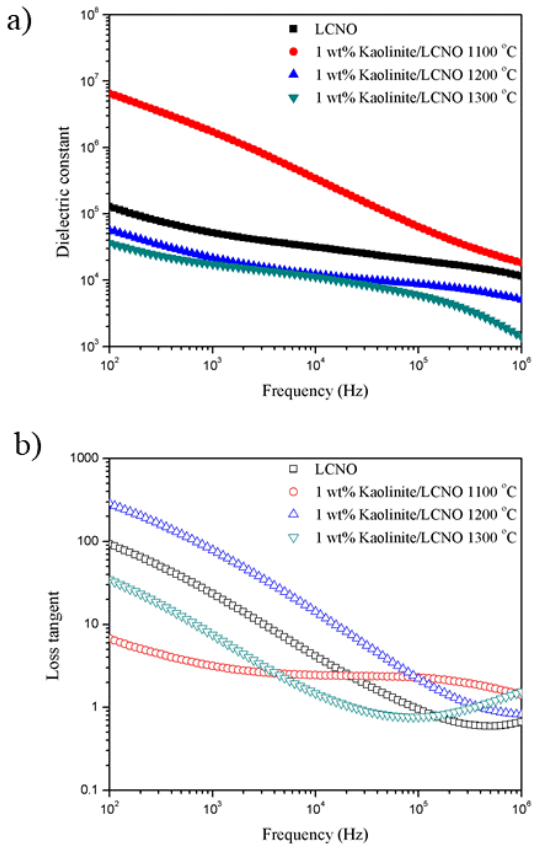

Figure 3 Frequency dependence of (a) dielectric constant and (b) loss tangent measured at room temperature of the pure LCNO and kaolinite-doped LCNO samples with various sintering temperatures

Figure 4 presents the temperature dependence of dielectric properties of kaolinite-doped LCNO with various sintering temperatures from 1100 to 1300 ºC. The ε_r of all samples, except the doped LCNO sintered at 1100 ºC, increase gradually with increasing temperature. Whereas, the weakly temperature dependent peak with the peak at ~70 ºC is observed for the doped samples sintered at 1100 ºC, which is in agreement with other reports [20-21]. Y. Pu et al. [21] reported that dielectric constant of the kaolinite-doped $CaCu_3Ti_4O_{12}$ (CCTO) was lower than that of the pure CCTO and the phase transition peak temperatures shifted to higher values with an increase of the kaolinite content. The loss tangents of doped samples, except the doped LCNO sintered at 1100 ºC, are nearly constant over temperature range from -60 ºC to 120 ºC and then increase with increasing temperature above 120 ºC, that is due to charge mobility at high temperature. The sample sintered at 1100 ºC exhibits the strong temperature dependence of the loss tangent with the peak at ~70 ºC, that could be implied the phase transition. The best dielectric properties are found for the doped sample sintered at 1100 ºC, its dielectric constant and loss tangent at 10 kHz, and room temperature are 3.40×10^5 and 2.44, respectively, which are better than those of the pure LCNO ($\varepsilon_r = 3.13\times10^4$, $\tan\delta = 4.14$ at 10 kHz). It is noted that kaolinite doping into LCNO can reduce the $\tan\delta$ by 2 times.

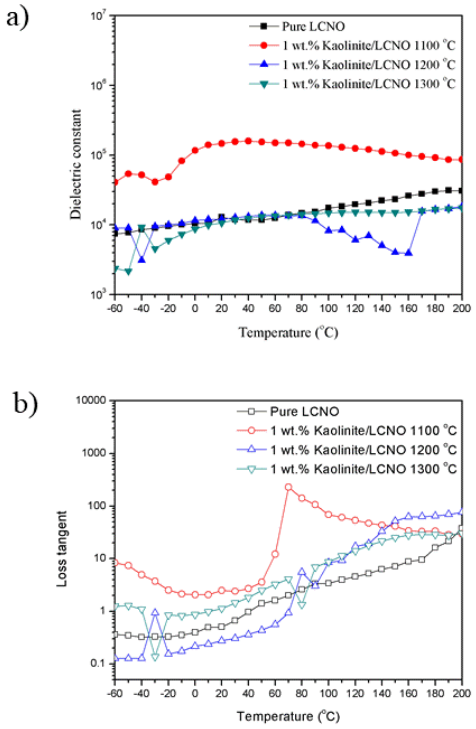

Figure 4 Temperature dependence of (a) dielectric constant and (b) loss tangent measured at 10 kHz of the pure LCNO and kaolinite-doped LCNO samples with various sintering temperatures

The Cole-Cole plots of pure LCNO and kaolinite-doped LCNO with various sintering temperatures are shown in Figure 5. The results indicate that the kaolinite doping and the increased sintering temperature cause the increase of electrical resistance at grain boundaries that could be observed from the magnitude of each semicircle on Z' axis. The large semicircular arcs show non-zero intercept as shown in the inset of Figure 5. Therefore, the electrical response is attributed to heterogeneous structure consisting of semiconducting grain of LCNO ceramic corresponding to other research [22]. J. Khemprasit et al. displayed the complex impedance spectroscopy of Cr-doped LCNO and found that a large semicircular arc with a non-zero intercept on the Z' axis at high frequency represented the contribution of semiconducting grains, while the low frequency arc represented the contribution of insulating grain boundaries.

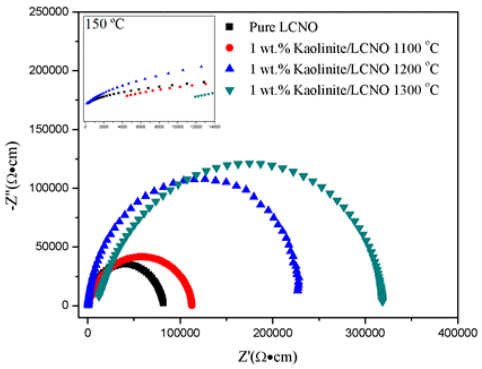

Figure 5 Complex impedance of the pure LCNO and kaolinite-doped LCNO samples with various sintering temperatures

Conclusions

The $Li_{0.30}Cr_{0.02}Ni_{0.68}O$ ceramics doped with kaolinite were successfully synthesized by solid state reaction via sol-gel process. All samples exhibited the single phase of the cubic rock-salt NiO structure without extra phase. The grain size of doped LCNO was smaller than that of the pure LCNO however when the sintering temperature was increased the grain size increased. All doped LCNO samples showed very high dielectric constants. The highest ε_r (3.40×10^5) and the low tanδ (2.44) at 10 kHz and room temperature were observed for the doped LCNO sintered at 1300 ºC that its tanδ is lower than the pure LCNO (tanδ = 4.14).

Acknowledgements

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