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Ceramics International 39 (2013) S611–S614

CERAMICS INTERNATIONAL

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Synthesis and dielectric properties of $HCa_2Nb_3O_{10}$ layered structure ceramics

Haena Yim[a], So-Yeon Yoo[a], Sahn Nahm[b], Seong-Ju Hwang[c], Seok-Jin Yoon[a], Ji-Won Choi[a,]*

[a]*Electronic Materials Research Center, Korea Institute of Science and Technology, Seoul 136-791, South Korea*
[b]*Departments of Materials Science and Engineering, Korea University, Seoul 136-701, South Korea*
[c]*Departments of Chemistry and Nano Sciences, Ehwa Womans University, Seoul 120-750, South Korea*

Abstract

We studied the structural and dielectric properties of $KCa_2Nb_3O_{10}$ (KCNO) and $HCa_2Nb_3O_{10}$ (HCNO) ceramics. HCNO ceramics were synthesized from KCNO powders with layered perovskite structure by chemical ion-exchange method at room temperature. After exchanging K^+ with H^+, the layered perovskite structure was retained in HCNO as well. Although the dielectric constant of KCNO altered with increase in frequency, HCNO showed a constant relative dielectric permittivity (ε_r) of around 23.5 and a low dielectric loss (tan δ) of 0.009 at a range of frequencies.

Keywords: C. Dielectric properties; D. Niobates; E. Capacitors

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1. Introduction

The demand for miniaturized and multifunctional electronic devices has been steadily increasing, and thinner capacitors with large capacities are much sought after. Downsizing multilayer ceramic capacitors (MLCCs), which consist of several dielectric and electrode inner layers, is being actively pursued to satisfy the growing needs of the electronics industry. Titanium oxides such as $BaTiO_3$ [1] and $(Ba_{1-x}Sr_x)TiO_3$ [2] are the commercial materials that are usually used as the dielectric layers in MLCCs. However, the dielectric properties of these materials continuously decrease because of thermal stress when their thickness is reduced below 1 μm, and hence, the conventional titanate materials are rendered unsuitable for use in downsized MLCCs. Thus, thin film materials with excellent dielectric properties that are invariant with thickness, which can be synthesized by simple processes, are key requirements to trigger progress in the fabrication of smaller MLCCs.

Many perovskite oxides that exhibit versatile properties like superconductivity [3], ferroelectricity [4], and photocatalytic activity [5], etc., have received much attention as promising materials for use in fabricating electronic devices. In addition, layered perovskite oxides are recognized as materials of immense potential, because ions between the perovskite layers can be exchanged with other ions. The ion exchange can result in novel intercalated materials showing unconventional properties, and thereby, new types of composite materials can be developed. For example, in $SrBi_2Ta_2O_9$ (which can be written as $(Bi_2O_2)^{2+}$ $(SrTa_2O_7)^{2-}$), the bismuth oxide plays an important role in minimizing the interlayer stress upon polarization, and extensive research with regard to changing and optimizing the bismuth content is in progress [6]. Likewise, niobate materials like $KCa_2Nb_3O_{10}$ and $KSr_2Nb_3O_{10}$, which belong to the Dion-Jacobson family [7], are considered as interesting dielectric materials due to their ability to be exfoliated into two-dimensional nanosheets by ion-exchange process. The thin films made of the oxide nanosheets obtained by chemical exfoliation do not require post-deposition annealing and exhibit high dielectric constants even at thicknesses lower than 100 nm. Research on dielectric thin films made of nanosheets of titanate and niobate oxides has been reported by

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*Corresponding author. Tel.: +82 2 958 5556; fax: +82 2 958 6720.
E-mail address: jwchoi@kist.re.kr (J.-W. Choi).

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http://dx.doi.org/10.1016/j.ceramint.2012.10.146

Sasaki and co-workers [8]. For instance, they reported the fabrication of multilayer dielectric thin films made of $Ca_2Nb_3O_{10}$ nanosheets from colloid solutions, synthesized by the exfoliation of $HCa_2Nb_3O_{10}$ (HCNO) obtained by subjecting $KCa_2Nb_3O_{10}$ (KCNO) to cation exchange. However, the dielectric properties of KCNO and HCNO bulk systems at a wide-range of frequencies have not been investigated.

Therefore, in this study, we attempted to assess the dielectric properties of KCNO and HCNO. HCNO was synthesized from KCNO by ion-exchange process. We will explain the synthesis conditions used to prepare both the ceramic compounds and discuss their characterization and dielectric properties.

2. Experiments

2.1. Preparation of the ceramic materials

To prepare the layered perovskite KCNO, K_2CO_3 ($\geq 99\%$, Aldrich), $CaCO_3$ ($\geq 99\%$, Aldrich), and Nb_2O_5 ($\geq 99.9\%$, Aldrich) were used as raw materials in stoichiometric proportion in a solid-state reaction. The raw materials were ball-milled in anhydrous ethyl alcohol ($\geq 99.99\%$, Aldrich) for 24 h and dried at 100 °C for 10 h. Subsequently, the mixture was ground and calcined at 1200 °C (heating rate of 2 °C/min was used) for 10 h in air. Then, the KCNO powders obtained (5 g) were added to 5 M HNO_3 solution (200 mL) and the mixture was stirred for 4 days at room temperature to synthesize HCNO. During the stirring process, K^+ ions in the niobates were substituted with H^+ ions. The products of the ion-exchange reaction were neutralized by repeated washing and were separated by centrifugation and dried in an oven at 50 °C overnight. The synthesized KCNO and HCNO powders were compressed into disc shaped pellets (of 12 mm in diameter and 0.5–1 mm in thickness) under a pressure of 100 kgf/cm^2. The KCNO and HCNO pellets were subsequently sintered in a furnace under air at 1250 °C and 1300 °C, respectively, for 2 h. Then, both sides of the sintered pellets were polished. The samples used to estimate the dielectric properties were prepared by applying screen-printed silver electrodes to both sides of the sintered pellets to ensure the formation of good electrical contacts. Then, these pellets were annealed at 600 °C for 10 min.

2.2. Characterization of the ceramics

X-ray diffraction (XRD) studies were carried out on the ceramic samples to identify the various phases present. The XRD patterns were obtained using a small-angle X-ray diffractometer (D/MAX-2500, Rigaku, US), which used Cu Kα radiation. The KCNO and HCNO powders were also characterized by infrared (IR) spectroscopy. The spectra were obtained using an FT-IR spectrometer (Nicolet iS10, Thermo scientific, US) in transmission mode from circular pellet samples, which were obtained by mixing KCNO or HCNO with KBr (FT-IR grade, Aldrich). The microstructure, particle size, and elementary composition of the powders were analyzed by environmental scanning electron microscopy (ESEM) and X-ray energy dispersive spectroscopy (EDS) (XL-30 FEG, FEI, US). The dielectric properties were characterized with an impedance analyzer (Agilent Technologies HP 4294 A, Santa Clara, CA), and the measurements were carried out in the frequency range 10^2–10^6 Hz.

3. Results and discussion

In the layered perovskite structure of the synthesized KCNO, a layer of intercalating K^+ ions was present after every three layers of CNO. These K^+ ions were easily exchanged with protons to form HCNO. The XRD patterns acquired from KCNO and HCNO are presented in Fig. 1, and all peak indexes shown agreed well with the previously reported patterns [9]. The inset in Fig. 1 shows that the main peak (at $2\theta = 6°$) in the pattern acquired from HCNO shifted slightly toward higher angles, indicating that the interlayer distance decreased due to the replacement of K^+ with the smaller H^+ ions.

The effects of exchanging K^+ with H^+ were also observed in the IR spectra. The typical spectra of HCNO and KCNO samples acquired over the range of 500–1000 cm^{-1} are shown in Fig. 2. The three peaks coincided with the asymmetric stretching vibrations of the O–Nb–O bonds. Among them, the peak at ~926 cm^{-1}, assigned to the $Nb–O_{terminal}$ vibrations, which appears as a single feature in the spectra of KCNO, was split into two peaks in the spectra of HCNO (obtained after the ion-exchange process). This could be attributed to the existence of H^+ and H_3O^+ ions in the interlayer [10].

Fig. 3 shows the SEM images of the synthesized (a) KCNO and (b) HCNO powders. In both samples, grains 2–8 μm in size were observed, and the images clearly revealed that the compounds exhibited a layered structure. The HCNO sample retained the morphology of its precursor (KCNO). However, despite containing H^+ ions (which are smaller than K^+ ions) in the intercalating layer, the intervals between the CNO layers in HCNO were maintained in comparison to that in KCNO.

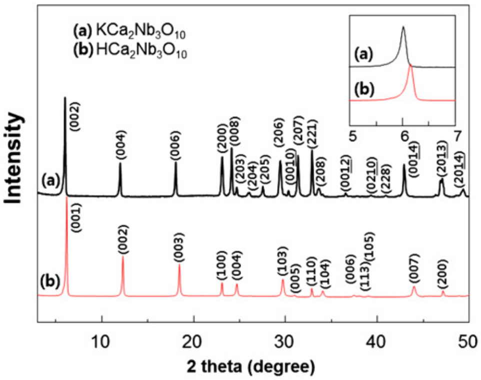

Fig. 1. XRD patterns acquired from: (a) KCNO and (b) HCNO samples. The inset shows the patterns in the low-angle regions.

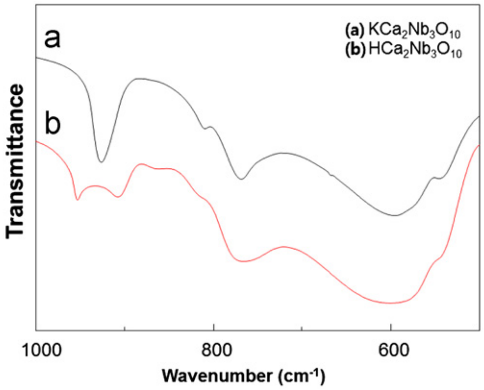

Fig. 2. IR spectra acquired from: (a) KCNO and (b) HCNO powders.

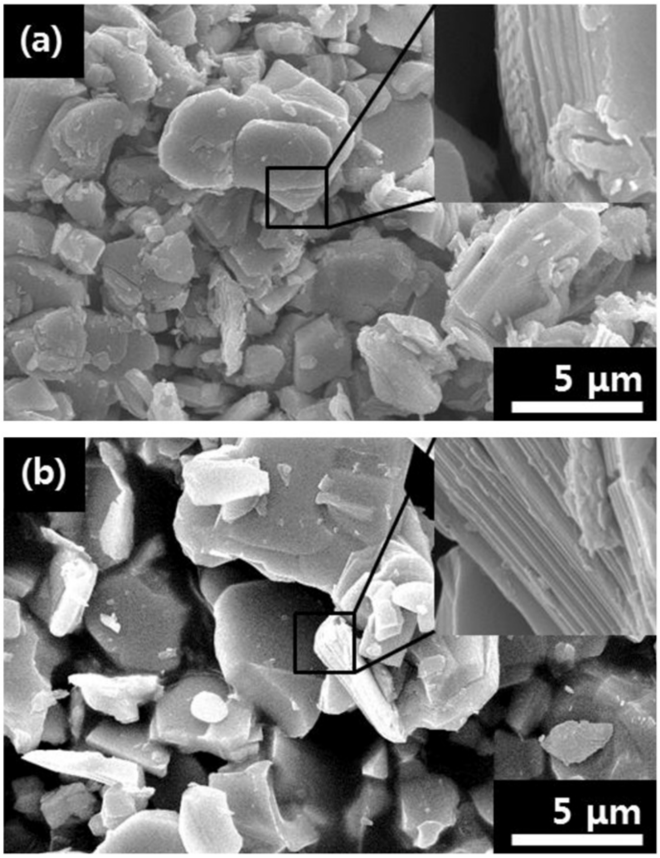

Fig. 3. SEM images of: (a) KCNO and (b) HCNO powders.

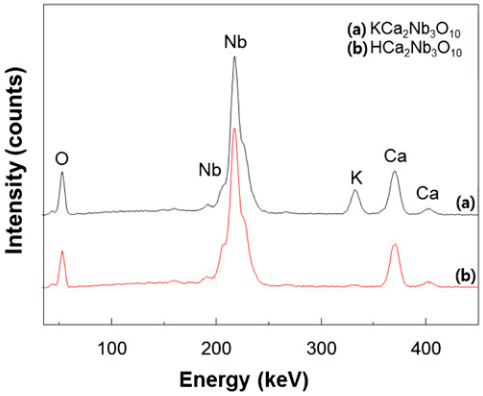

Fig. 4. Results of the EDS analysis of: (a) KCNO and (b) HCNO powders.

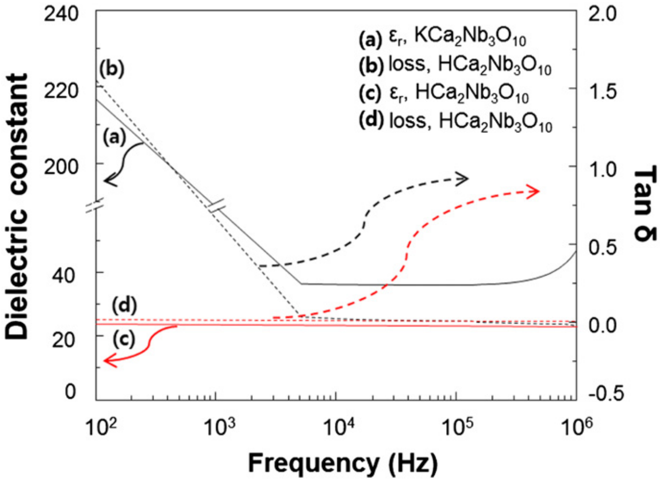

Fig. 5. ε_r and tan δ values shown by the KCNO and HCNO pellets at various frequencies.

The results of the EDS analysis, which was carried out to confirm if all the K^+ ions were extracted and replaced during the ion-exchange process, is presented in Fig. 4.

As shown in Fig. 4, peaks from K^+ were absent in the spectra of HCNO, indicating that K^+ ions were completely replaced by H^+ in the ion-exchange process during the synthesis of HCNO.

The dielectric properties of the sintered pellets were measured at a range of frequencies (10^2–10^6 Hz), and the variations in the relative dielectric permittivity (ε_r) values and loss factors (tan δ) with frequency are shown in Fig. 5. ε_r values of the KCNO pellets rapidly decreased with increasing frequency, which is the typical behavior reported [11]. In addition, tanδ values of the KCNO pellets began at unfavorably high values (of >1). However, HCNO (synthesized from KCNO by ion exchange) showed nearly constant ε_r values of $\sim$23.5 along with very low tan δ values of $\sim$0.009 over a wide range of frequencies.

This tendency of HCNO pellets to exhibit a constant ε_r value could be explained on the basis of the dielectric constant reported for films made of CNO nanosheets [11]. The relative dielectric permittivity was reported to be constant when all the K^+ ions between the CNO layers were extracted. Likewise, in our study, the absence of K^+ ions in the HCNO pellets resulted in the constant ε_r value.

4. Conclusions

KCNO-based ceramic materials were prepared by a solid-state reaction, and the K^+ ions were substituted with H^+ ions to synthesize HCNO ceramics. The structural properties of the samples were analyzed by XRD, IR spectroscopy, SEM, and EDS.

The analyses confirmed that all the K^+ ions were extracted well from the CNO layers during the ion-exchange process, and the H^+ ions replaced the K^+ ions. Moreover, the ion exchange resulted in hardly any structural changes, and both samples exhibited the layered perovskite structure. However, the main peak in the XRD profile shifted to higher angles in the case of HCNO samples, because the smaller H^+ ions that intercalated between the CNO layers reduced the interlayer distance. The layered structures of the samples were observed by SEM as well. The dielectric constants and loss factors were measured in the frequency range 10^2–10^6 Hz. The HCNO samples obtained by exchanging K^+ ions in KCNO with H^+ ions showed a constant relative dielectric permittivity ($\varepsilon_r = 23.5$) and low dielectric loss (tan $\delta = 0.009$).

Acknowledgements

This study was supported by the Core Technology of Materials Research and Development Program (no. 10041232) funded by the Ministry of Knowledge Economy, Republic of Korea.

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