



Synthesis and dielectric properties of strontium substituted calcium niobate ceramics



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ABSTRACT

Layered perovskite $\text{KCa}_{2(1-x)}\text{Sr}_{2x}\text{Nb}_3\text{O}_{10}$ ceramic ($x = 0, 0.2, 0.4, 0.6, 0.8$ and 1) materials were prepared by a conventional solid-state reaction method, and the effects of Sr substitution for Ca on the crystal structure and dielectric properties of the $\text{KCa}_{2(1-x)}\text{Sr}_{2x}\text{Nb}_3\text{O}_{10}$ system were investigated. Also, potassium ions were exchanged with proton ions to obtain $\text{HCa}_{2(1-x)}\text{Sr}_{2x}\text{Nb}_3\text{O}_{10}$. Then, X-ray diffraction, infra-red spectra, and energy dispersive detector analysis were carried out to verify immaculate substitution. Unlike alkali cations intercalated powder, the dielectric properties of $2\text{Ca}_{(1-x)}\text{Sr}_x\text{Nb}_2\text{O}_6\text{-Ca}_{2(1-x)}\text{Sr}_{2x}\text{Nb}_2\text{O}_7$ mixtures, which were obtained from $\text{HCa}_{2(1-x)}\text{Sr}_{2x}\text{Nb}_3\text{O}_{10}$ by sintering, showed high dielectric permittivity with increasing amounts of strontium, and remained unaffected by frequency change from 1 kHz to 1 MHz. Its compositional dependence behavior was analyzed through Raman spectral analysis. X-ray diffraction, differential thermal analysis, and thermogravimetry observation revealed the phase transition on sintering of $\text{HCa}_{2(1-x)}\text{Sr}_{2x}\text{Nb}_3\text{O}_{10}$.

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1. Introduction

Multilayer ceramic capacitors (MLCCs) for electronic devices have attracted a lot of attention because of their high capacitance density, and there is a strong demand for high-capacitance in small MLCCs to satisfy the requirements of miniaturized and multifunctional devices, such as wireless devices, mobile displays, and laptops [1]. To meet this demand, the ceramic materials of dielectric layers should have high dielectric permittivity with low dielectric loss, and the dielectric layers in MLCCs must be thinner than $0.5 \mu\text{m}$ and stacked in greater numbers for future applications. However, there are many limitations for downsizing. At present, the fabrication process of MLCCs involves tape casting of the dielectric layer, screen printing of the inner electrode on the dielectric layer, lamination, post-firing steps, and so on. However, the commercialized BaTiO_3 -based ceramics, Al_2O_3 , and HfO_2 , which are widely used as the dielectric film in MLCCs, yield a decreased dielectric constant when their thickness is thinner because of applied thermal stress during the firing step. Moreover, uniformly sized and spherical ceramic nano-powders are required for a

nano-sized layer dielectric film, but it is difficult to realize. Therefore, developing new dielectric materials, which retain a high dielectric constant regardless of decreased thickness, is urgently needed for the fabrication of advanced MLCCs.

Perovskite oxides have been widely investigated for various applications, such as transistors, gate insulators, and memory devices, because of their multifarious properties, such as ferroelectricity, photocatalytic activity and super conductivity. The layered perovskite oxides such as $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ and HLaNb_2O_6 , which is the Dion–Jacobson phase ($\text{M}[\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}]$), are especially considered to have enormous potential because of their property variability from changing ions between the perovskite layers through simple chemical ion-exchange processes [2]. For example, Osada et al. reported a $\text{Ca}_2\text{Nb}_3\text{O}_{10}$ (CNO) dielectric nanosheet which can be fabricated through a two-step cation exchange processes, and they reported its high dielectric permittivity ($\epsilon_r = \sim 200$) even with a 5 nm thickness [3]. A CNO colloidal nanosheet was obtained by exfoliation which included K^+ ions exchange to H^+ ions from $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ and then exfoliation by TBAOH intercalation from $\text{HCa}_2\text{Nb}_3\text{O}_{10}$. Likewise, various types of dielectric nanosheets, such as $\text{Sr}_2\text{Nb}_3\text{O}_{10}$ (SNO), Ti_2NbO_7 , and $\text{Ti}_{0.87}\text{O}_2$, have been reported [4,5]. These dielectric nanosheets demonstrated dielectric responses with thicknesses below 20 nm ; thus, these materials show boundless potential for use as next-generation dielectric alternatives.

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However, the dielectric properties of layered perovskite bulk materials have been rarely investigated so far. The dielectric properties of bulk $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ and $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ have been reported [6,7]. The $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ ceramic materials showed the dielectric permittivity of 46 and the dielectric loss (D) of 0.009 at 100 kHz when it was sintered at 1375 °C. Also, in the case of $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ ceramic materials, the dielectric permittivity and dielectric loss were ~ 30 and ~ 0.5 at 100 kHz, respectively, when it was sintered at 800 °C. This reported dielectric permittivity is insufficient for application in dielectric devices, and the dielectric loss of $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ is too high for use in dielectric devices. To achieve high dielectric permittivity, substitution by more polarizable ions has been typically researched because of the very strong interrelation between ionic polarizability and dielectric permittivity [8].

Therefore, this paper focuses on the substitution of Sr^{2+} ions by Ca^{2+} ions which have greater polarizability. We report the dielectric properties in a layered perovskite $\text{KCa}_{2(1-x)}\text{Sr}_{2x}\text{Nb}_3\text{O}_{10}$ and $\text{HCa}_{2(1-x)}\text{Sr}_{2x}\text{Nb}_3\text{O}_{10}$ ceramic solid solution system, which incorporates starting materials of CNO and SNO dielectric nanosheet compositions, in the range of $x = 0-1$ aimed to investigate the influence of the compositional ratio of Ca/Sr. For this purpose, the structural and dielectric properties of the ceramic materials have been studied, and we achieved very good dielectric properties, that is, the dielectric permittivity of over 500 and the dielectric loss below 0.09 at 100 kHz.

2. Materials and methods

The layered perovskite, $\text{KCa}_{2(1-x)}\text{Sr}_{2x}\text{Nb}_3\text{O}_{10}$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$) was prepared through a solid-state reaction by using K_2CO_3 ($\geq 99\%$, Aldrich, USA), CaCO_3 ($\geq 99\%$, Aldrich, USA), Nb_2O_5 ($\geq 99.9\%$, Aldrich, USA), and SrCO_3 ($\geq 99.9\%$, High Purity Chemistry, Korea) in stoichiometric proportions as raw materials. The raw materials were ball-milled in anhydrous ethyl alcohol ($\geq 99.99\%$, Aldrich) for 20 h and dried at 100 °C for 10 h. Afterwards the mixture was ground and calcined at 1200 °C for 10 h in air. Then, the layered perovskite $\text{KCa}_{2(1-x)}\text{Sr}_{2x}\text{Nb}_3\text{O}_{10}$ powders were synthesized (Fig. 1(a)), and the obtained powders (5 g) were continuously stirred in 5–7 M HNO_3 solution (200 ml) using a mechanical stirrer for 4 days at room temperature to get $\text{HCa}_{2(1-x)}\text{Sr}_{2x}\text{Nb}_3\text{O}_{10}$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$). Through this process, the K^+ ions in those modified niobates were substituted by H^+ ions. Fig. 1(b) shows schematic illustrations of the crystal structure, and it shows that $\text{HCa}_{2(1-x)}\text{Sr}_{2x}\text{Nb}_3\text{O}_{10}$ consists of perovskite layers of $\text{Ca}_{2(1-x)}\text{Sr}_{2x}\text{Nb}_3\text{O}_{10}$ and intercalated H^+ ions. After replacement of the H^+ ions, the products were washed several times to neutralize them and were dried at 50 °C in an oven overnight. The synthesized $\text{KCa}_{2(1-x)}\text{Sr}_{2x}\text{Nb}_3\text{O}_{10}$ and $\text{HCa}_{2(1-x)}\text{Sr}_{2x}\text{Nb}_3\text{O}_{10}$ powders were compressed into disc shaped pellets of 12 mm in diameter under a pressure of 100 kg f/cm², and these pellets were polished to form disk with 0.5–1 mm thickness. Then, the pellets were sintered at 1250 °C for 2 h in a furnace under an air atmosphere. After that, the sintered pellets were polished on both side, and a silver electrode was screen printed on both sides and fired at 600 °C for 10 min to ensure good electrical contact for the estimation of dielectric properties.

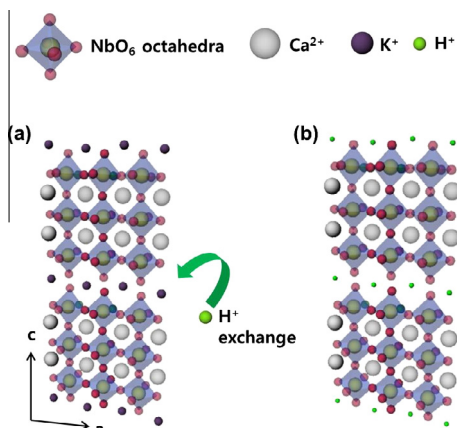


Fig. 1. Schematic diagram of $\text{KCa}_{2(1-x)}\text{Sr}_{2x}\text{Nb}_3\text{O}_{10}$ and $\text{HCa}_{2(1-x)}\text{Sr}_{2x}\text{Nb}_3\text{O}_{10}$.

X-ray diffraction (XRD) studies were carried out for phase identification. The XRD patterns were obtained using small-angle X-ray spectroscopy (D/MAX-2500, Rigaku, Japan) with $\text{Cu K}\alpha$ radiation. Also, the infrared (IR) spectra were measured from the KBr pellets in transmission mode using FT-IR spectrometry (Nicolet iS10, Thermo scientific, USA). The KBr circular pellets were prepared in an air atmosphere by compression from a mixture of KBr (FT-IR grade, Aldrich, USA) and powder of each composition. The microstructure and elementary composition of synthesized powders were observed by environmental scanning electron microscopy (ESEM) (XL-30 FEG, FEI, USA) and X-ray energy dispersive spectroscopy (EDS) (XL-30 FEG, FEI, USA). The dielectric measurements were acquired at a frequency range from 1 kHz to 1 MHz using an impedance analyzer (Agilent Technologies HP 4294A, Santa Clara, USA).

3. Results and discussion

As shown in Fig. 1, the HCSNO x powders are easily obtained by the exchange of intercalated K^+ ions for H^+ ions between every three layers of $\text{Ca}_{2(1-x)}\text{Sr}_{2x}\text{Nb}_3\text{O}_{10}$ from $\text{KCa}_{2(1-x)}\text{Sr}_{2x}\text{Nb}_3\text{O}_{10}$. The X-ray diffraction (XRD) patterns for the series of layered perovskite $\text{KCa}_{2(1-x)}\text{Sr}_{2x}\text{Nb}_3\text{O}_{10}$, which crystallize to a monoclinic unit cell with space group of $\text{P2}_1/\text{m}$ and has lattice parameters of $a = 0.77418$, $b = 0.77073$, and $c = 1.4859$ nm [9], are presented in

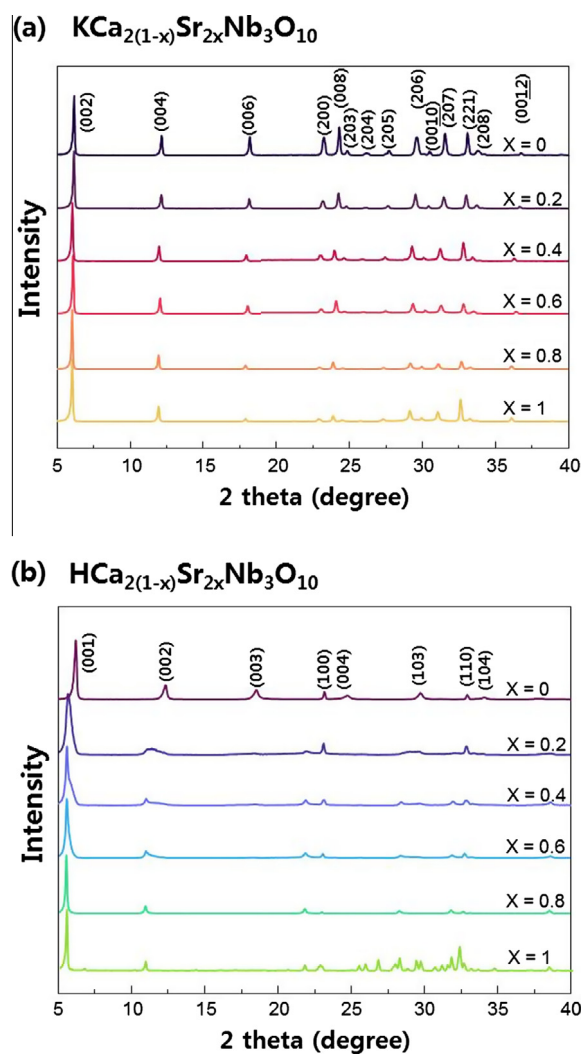


Fig. 2. X-ray diffraction patterns of niobate powders: (a) patterns from $\text{KCa}_{2(1-x)}\text{Sr}_{2x}\text{Nb}_3\text{O}_{10}$ correspond to the perovskite layered structure (JCPDS 97-015-7839, $\text{KCa}_2\text{Nb}_3\text{O}_{10}$); (b) patterns from $\text{HCa}_{2(1-x)}\text{Sr}_{2x}\text{Nb}_3\text{O}_{10}$ are also well matched (JCPDS 00-040-0884, $\text{HCa}_2\text{Nb}_3\text{O}_{10}$); (c) patterns from $[\text{H}]\text{Ca}_{2(1-x)}\text{Sr}_{2x}\text{Nb}_3\text{O}_{10}$, which was sintered for pelletizing, are indexed with two phases of $\text{Ca}_2\text{Nb}_2\text{O}_6$ (JCPDS 97-002-6010) and CaNb_2O_6 (JCPDS 97-001-5208).

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