Improve dielectric properties of Lamellar Calcium Niobate ceramics by spark plasma sintering

Xinxin Liu¹,2 Xiong Xie¹,3 Yunling Zhai¹,2 Liang Wang¹,2*

¹Chongqing Key Laboratory of Multi-Scale Manufacturing Technology, Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing, 400714, P.R. China
²University of Chinese Academy of Sciences, Beijing, 100049, P.R. China
³State Key Laboratory of Mechanical Transmission, College of Materials science and engineering, Chongqing University, Chongqing, 400044, P.R. China

*Corresponding author’s e-mail: wangliang@cigit.ac.cn

Abstract. The structure and dielectric properties of HCa₂Nb₃O₁₀·1.5H₂O (HCNO) and its exfoliated products (e-HCNO) ceramics were investigated. Where two-dimensional e-HCNO sheets were obtained by ion-exchange and exfoliating consequently. Spark plasma sintering (SPS) was introduced for products processing. After which, the dielectric constant of e-HCNO is 1300 and the loss is 0.002 at 2 MHz. Compared to ordinary solid phase sintering, the dielectric constant of ceramics was found to be directly improved by the SPS processing.

1. Introduction

Energy storage and conversion have always been a long-lasting technology focus, especially, for the production, storage and full use of electrical energy. Capacitors, as an indispensable item for power distribution and storage, have been widely used in electronic industry, high voltage field, communication field, new energy-powered vehicles and so on [1]. To satisfy the growing demand of the electronics industry, multilayer ceramic capacitors (MLCC) composed of a plurality of dielectric and electrode inner layers are being actively sought. However, the dielectric properties of conventional titanium oxides are continuously reduced when the thickness is reduced to less than 1 μm, which makes it not fit for downsized MLCC. Therefore, thin film materials with excellent dielectric properties and constant thickness are keys for triggering progress. Niobate materials such as KCa₂Nb₃O₁₀ and KSr₂Nb₃O₁₀, are belonging to the Dion-Jacobson family [2], the film combined niobate nanosheets that exfoliated from their parent bulk phase through Van der Waals force [3] exhibits a high dielectric constant even at a thickness of less than 100 nm. The dielectric films made from titanate and niobate nanosheets were also investigated by Sasaki and co-workers [4]. While HCNO (synthesized from KCNO by ion exchange) sintered by furnace exhibits an almost constant εr (~23.5) and dielectric loss (tanθ = 0.009) in a wide frequency range [5]. This phenomenon can be explained by the constant dielectric properties of films made from Ca₂Nb₃O₁₀ nanosheets [6]. Moreover, the crystal structure of exfoliated nanosheets is usually well-defined and almost free of defects such as oxygen vacancies [7].

Sintering is the most critical procedure to the final quality of ceramics. In addition to conventional sintering (CS), hot pressing (HP), two-step sintering (TSS), and spark plasma sintering (SPS) are used...
to synthesize ceramic materials. Among them, SPS is widely used due to its fast heating rate and short sintering time, which is beneficial to gain uniform and dense ceramics with good performance [8]. However, the dielectric properties of SPS sintered HCNO ceramics are rarely systematically studied or reported so far.

Here, we synthesized HCNO and e-HCNO nanosheets by combining with methods of ion-exchange, liquid phase stripping and SPS sintering. Their synthesis conditions were explored and samples were characterized using XRD, EDS and XPS. And the dielectric properties of HCNO and e-HCNO nanosheets obtained by liquid phase stripping were systematically studied.

2. Experimental

K$_2$CO$_3$, CaCO$_3$, and Nb$_2$O$_5$ were mixed at a molar ratio of 1.1: 4: 3 and ground for 30 min. Then, the ground mixture was placed in a Muffle furnace and calcined at 1,200 °C for 12 h in air. White KCa$_2$Nb$_3$O$_{10}$ (KCNO) powder was obtained after cooling down the mixture to room temperature. The identification of KCNO powder was performed using XRD and XPS analysis. Then, HCa$_2$Nb$_3$O$_{10}$·1.5H$_2$O(HCNO) was obtained by ion-exchange, 0.4 g of KCNO powder and 40 mL of nitric acid (1 mol/L) were put in a sealed beaker, the suspension was then stirred at 250-300 rpm with a magnetic stirrer for 72 hours. Next, the suspension was filtered and rinsed with water to completely remove the scrap. The residue was dried at 30 °C overnight (~12 h), and was confirmed as HCNO by XRD analysis. Then, for powder stripping, TBAOH/H$^+$ (H$^+$ refers to the protons of HCNO powder, i.e. [H$^+$] = [HCNO]) suspension was made by mixing HCNO powders (0.1 g) with 25 mL TBAOH solution (7.3 mmol/L). Both stripped and unstripped HCNO powders were placed in a graphite mold and sintered at 800 °C for 5 minutes in a vacuum of 7 Pa (SPS 625). After sintered, samples were annealed for 3 hours. The exfoliated powder was especially sintered at 850 °C for comparison.

The crystalline phases of the KCNO and HCNO powders were characterized by X-ray diffraction (XRD, Rigaku Dmax-2000 diffractometer) using Cu Kα radiation from 20°-80° (2-theta). The morphology and compositions of the products were characterized by scanning electron microscopy (SEM, JSM-7800F) with energy dispersive X-ray spectroscopy (EDS) and X-ray Photoelectron Spectroscopy (XPS, Thermo escalab 250Xi). The dielectric properties of sintered samples were measured by Agilent E4980A LCR meter in a wide frequency range of 20-2 MHz.

3. Results and discussion

The XRD patterns of the synthesized compound are shown in Fig. 1. The synthesized product were confirmed to be KCNO and HCNO as expected, and all the samples are in their single perovskite phases since no obvious impurity peaks was observed.

![Fig. 1 XRD patterns of the KCNO and HCNO ceramics, 2θ = 5°-70°](image-url)
We could evaluate the surface chemical composition and the oxidation state of individual element in the powders by XPS shown in Fig. 2 where the positions of peaks were corrected using the C 1s peak at 285 eV as a reference. The XPS survey spectra of KCNO in a wide energy range are shown in Fig. 2a.

Fig. 2b reveals the typical Nb 3d core level. The 3d peaks are split into two components, 3d_{3/2}, 3d_{5/2}, respectively, as a result of spin-orbit coupling with ratio of 2:3 \[^9\]. The peaks of Nb 3d centred at 206.8 eV and 209.5 eV can be assigned to 3d_{5/2} and 3d_{3/2} states respectively, since they are identical to the binding energy of Nb^{5+} in Nb_2O_5 \[^10\]. It indicates that niobium in prepared samples exists as Nb^{5+} ion. As can be seen from Fig. 2c, the characteristic peaks of Ca 2p located at about 346.4 eV and 349.9 eV, are assigned to the Ca 2p_{3/2} and Ca 2p_{1/2} binding energies, respectively. At the same time, The O 1s XPS spectrum of the KCNO sample is displayed in Fig. 2d. It can be deconvoluted to three components. The major peak of lower binding energy (529.4 eV) was ascribed to the lattice oxygen in Nb-O bond; while the minor peak located at 531.2 eV \[^11\] and 532.4 eV was assigned to the hydroxyl OH- group and absorbed oxygen in the surface, respectively \[^12\].

Fig. 3 shows the SEM images of synthetic (a) KCNO, (b) HCNO and post-stripped HCNO samples. In Fig (a) and (b), particles with a size of 2-8 μm are observed, and the images clearly show that the
compound exhibits a layered structure. The HCNO sample retained the morphology of its precursor (KCNO). However, compared with KCNO, the interval between the CNO layers in the HCNO remained unchanged, but the HCNO sample after peeling was significant distinction. To confirm whether all K ions were extracted and replaced during the ion exchange process, the XRD analysis was performed and shown in Fig. 1.

Fig. 4 Frequency dependence of dielectric constant and loss of (a) HCNO sintered at 800 °C (b) e-CNO sintered at 800 °C and (c) e-CNO sintered at 850 °C from 100 Hz to 2 MHz.

Fig. 4 shows the dielectric constant spectrum and dielectric loss spectrum of samples. From Fig. 4a, 4b, and 4c, the HCNO and e-HCNO samples sintered at 800 °C, and the e-HCNO samples at 850 °C, respectively, we can see that both the dielectric constant and loss of all samples decrease with increasing frequency. The dielectric properties of e-HCNO are superior to HCNO after 800 °C sintering, which may be caused by the decrease of H⁺ in the e-HCNO sample during stripping. Because the smaller H⁺ that intercalated between the CNO layers can cause a small interlayer distance. It was reported that the dielectric constant of films made of CNO nanosheets [6] keep constant, which could explain the behaviour of e-HCNO dielectric constant in a wide frequency range. Comparing with Fig. 4b and 4c, it is found that the dielectric constant of 800 °C is higher than that of 850 °C while the loss is lower.

4. Conclusion
In this paper, the dielectric properties of plasma spark sintered calcium niobate ceramics are studied. The HCNO precursor was synthesized by substituting K ions with H ions. And CNO nanosheets were obtained by removing a large amount of H⁺ between the HCNO perovskite layers by liquid phase exfoliating. The samples were analysed by XRD, SEM and EDS. It shows that there is almost no structural change in ion exchange, and both samples exhibit a layered perovskite structure. This layered structure could also be observed by SEM. The dielectric constant and loss factor are measured over a frequency range of 20-2M Hz. The e-HCNO sample obtained by liquid phase exfoliated, then sintering at 800 °C for 5 min, exhibits a higher relative dielectric constant (ε_r = 1300) and lower dielectric loss (tanθ = 0.002).

Acknowledgments
This work was supported by the National Natural Science Foundation of China (No.21875245) and the Program of Hundreds Talents of Chinese Academy of Science.

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