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Fabrication of textured $Sr_2Na_{0.9}K_{0.1}Nb_5O_{15}$ ceramics: Anisotropy in structures and electrical properties

Lingling Wei, Xiaokun Han, Zhaohu Li, Zupei Yang *

Key Laboratory for Macromolecular Science of Shaanxi Province, School of Chemistry and Materials Science, Shaanxi Normal University, Xi'an 710062, Shaanxi, PR China

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Abstract

Highly textured $Sr_2Na_{0.9}K_{0.1}Nb_5O_{15}$ (SKNN) ceramics were fabricated by reactive templated grain growth method using acicular $Sr_2KNb_5O_{15}$ (SKN) templates. CuO (1 wt.%) was used as sintering additive. SKN templates were aligned in matrix powders of $SrNb_2O_6$ and $NaNbO_3$ via tape casting and sintered at higher temperatures to obtain texture morphology. Through carefully controlling the processing conditions, a texture fraction of 86% was obtained. The structure evolution was explained by liquid-phase-assisted growth mechanism, in which the whole process was divided into 3 steps according to priority: phase formation stage, densification stage, and texture development stage. The textured ceramics exhibited anisotropic properties with the highest electrical properties obtained in *c*-axis direction: $\varepsilon_r = 2212$, $\varepsilon_m = 4869$, $P_r = 15.92\ \mu C\ cm^{-2}$ and $d_{33} = 82\ pC\ N^{-1}$, showing that reactive templated grain growth method is very effective to improve the physical properties of SKNN ceramics.

Keywords: Tape casting; Texture; Dielectric properties; Ferroclectric properties; Niobates

1. Introduction

The research on properties of lead-free ferroelectric ceramics and their applications is extremely important nowadays due to the environmental protection and the sustainable development all over the world.[1–3] As one member of the lead-free ferroelectric systems, tungsten bronze compounds have attracted considerable attention because of their superior electro-optic, piezoelectric, ferroelectric and pyroelectric properties. $Sr_2NaNb_5O_{15}$ (SNN), which has a filled tetragonal tungsten bronze structure with a chemical formula of $(A1)_4(A2)_2(C)_4(B)_{10}O_{30}$, is a ferroelectric solid solution between $SrNb_2O_6$ and $NaNbO_3$. In recent years, SNN-based ceramics have received increasing interests.[4–6] Most studies on SNN have mainly focused on the substitution of calcium or barium for strontium in A1 sites[7–9] or the substitution of potassium for sodium in A2 sites.[10] However, the reported electrical properties are not satisfactory. The inferior electrical properties in randomly oriented polycrystalline SNN-based ceramics are due to averaging of the limited numbers of polarization directions.As for the polycrystalline ceramics, the physical properties are mainly dependent on the composition, processing conditions and the microstructure. Through microstructure control to make the ceramic grains grow along the preferred orientation is an effective way to improve the physical properties. The ceramics with the crystal axis intentionally aligned are called textured ceramics.[11] It is well known that reactive templated grain growth (RTGG) technique is an effective and convenient method to obtain the textured ceramics,. The RTGG method allows the texture development by preferential growth of high oriented anisotropic template particles, which is driven by the difference in the surface free energy between the anisotropic template particles and the fine-grained matrix powders during heat treatment.[12–14] During RTGG process, some critical factors can affect the final texture: morphology and size of anisotropic template particles, homogenous and fine-grained matrix powders, uniform contact and an epitaxial match between the matrix and template, and a mechanism for boundary migration.[15–17]

According to JCPDS Cards # 34-0108 and # 34-0429, $Sr_2KNb_5O_{15}$ (SKN) has the same phase structure (tetragonal tungsten bronze structure) as SNN and the lattice parameter difference is less than 0.01 in both *a* and *c* directions at room

* Corresponding author. Tel.: +86 29 8531 0352; fax: +86 29 8530 7774.
E-mail address: yangzp@snnu.edu.cn (Z. Yang).

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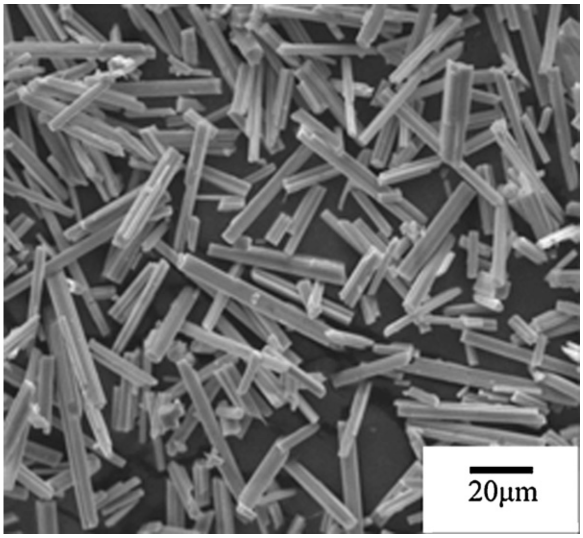

Fig. 1. Scanning electron microscopy micrograph of $Sr_2KNb_5O_{15}$ templates.

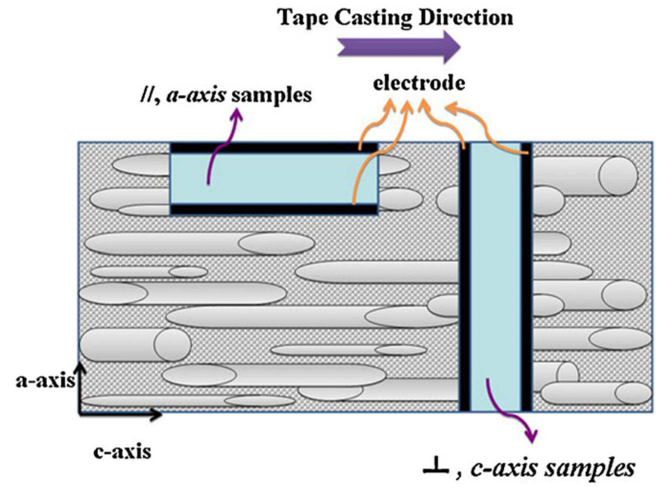

Fig. 2. Schematic depiction of the sectioning and electroding of samples from textured SKNN ceramics.

temperature. So SKN is selected as template to prepare SNN-based textured ceramics by RTGG method. In our previous work, the well-developed acicular SKN templates without any impurity were successfully prepared by using $SrNb_2O_6$–Nb_2O_5–KCl system via molten salt synthesis method.[18] Furthermore, effect of the acicular SKN seeds on the phase formation, densification and microstructure development in randomly oriented polycrystalline SNN ceramics during reactive sintering were also studied.[19]

In this work, RTGG method was employed to fabricate texture $Sr_2Na_{0.9}K_{0.1}Nb_5O_{15}$ (SKNN) ceramics using acicular SKN templates and reactive matrix powders of $SrNb_2O_6$ and $NaNbO_3$. A small amount of CuO was added to aid in densification and texture development. Phase formation, texture and microstructure development, densification behavior and electrical properties as a function of processing parameters such as sintering temperature and holding time were investigated in detail.

2. Experimental procedure

2.1. Sample preparation

The reactive matrix powders of $SrNb_2O_6$, $NaNbO_3$ and acicular $Sr_2KNb_5O_{15}$ (SKN) templates were used to fabricate textured $Sr_2Na_{0.9}K_{0.1}Nb_5O_{15}$ (SKNN) ceramics by tape casting and reactive sintering. $SrNb_2O_6$ was prepared by ball-milling $SrCO_3$ (99%) and Nb_2O_5 (99.5%) for 12 h in ethanol using zirconia balls. The mixed powders were dried and then calcined at 1100 °C for 4 h. Using the same procedure, $NaNbO_3$ was prepared by the solid state reaction between Na_2CO_3 (99.8%) and Nb_2O_5 at 800 °C for 3 h. X-ray diffraction (XRD, D/max-2200, Rigaku, Tokyo, Japan) results show that both $SrNb_2O_6$ and $NaNbO_3$ are single phase. The acicular SKN templates were prepared by reacting 60 wt.% KCl (99.5%) salt with 40 wt.% $SrNb_2O_6$ and Nb_2O_5 according to our previous work.[18] As shown in Fig. 1, the obtained pure acicular SKN templates have dimensions of 5–30 μm length and 2–4 μm diameter.

The ethanol-based slurry containing 10.16 wt.% SKN templates, $SrNb_2O_6$ and $NaNbO_3$ weighted with the weight ratio of 4.51, 1 wt.% CuO additive, solvents, binder and plasticizer were prepared. The solvents were ethanol and toluene. The binder and plasticizer were polyvinyl alcohol (PVA) and glycerin, respectively. The weight ratio of powders, solvents, binder and plasticizer was 1.00:0.10:0.27. Then the slurry was degassed under vacuum and tape cast to align the templates along the casting direction. The sheets were cut and laminated to form green compacts. The binder and plasticizer were burned out at 500 °C for 2 h. Then the samples were sintered at 900–1400 °C for 4–8 h.

2.2. Characterization

The crystalline phases and the degree of orientation were evaluated by X-ray diffraction (XRD, D/max-2200, Rigaku, Tokyo, Japan) with Cu$k\alpha$ radiation (step: 0.02°) on the surface which is perpendicular (⊥) to the casting direction. The degree of orientation was evaluated from the diffraction lines in the range of $2\theta = 20$–$50°$ by the Lotgering factor (texture fraction f). $f = 1$ and 0 indicate that the samples are completely textured or random, respectively. The microstructure was observed by scanning electron microscopy (SEM, Model Quanta 200, FEI Company, Eindhoven, the Netherlands) on the surface parallel (//) to the casting direction. The measured densities of sintered ceramics were determined by using Archimedes method with distilled water.

As shown in Fig. 2, silver electrodes were formed on both surfaces parallel to the tape-casting direction (//, *a*-axis samples) and perpendicular to the tape-casting direction (⊥, *c*-axis samples). Then the electrical properties in different directions of the sintered textured ceramics were measured after being fired silver at 850 °C for 30 min. Dielectric properties of the ceramics were investigated by measuring the capacitance C using an LCR meter (Agilent E4980A, Santa Clara, CA) at room temperature. The temperature dependence of dielectric constant