

Effect of Li⁺ ion occupancy on microstructure and dielectric characteristics in K_{Sr}2Nb₅O₁₅ tungsten bronze ceramics



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ARTICLE INFO

Article history:

Received 28 January 2016

Received in revised form 20 April 2016

Accepted 12 May 2016

Available online 18 May 2016

Keywords:

K_{Sr}2Nb₅O₁₅

Ferroelectric ceramics

Microstructure

Dielectric property

ABSTRACT

Li-doped K_{Sr}2Nb₅O₁₅ (KSN) tungsten bronze ceramics were prepared by the conventional solid-state method. Fine KSN crystalline fabricated by a two-step molten salt synthesis were used as raw material. The effects of Li₂CO₃ content on microstructure and dielectric properties of the ceramics were investigated. It was found that a small addition of Li₂CO₃ was effective in inhibiting the abnormal grain growth and crack formation. Investigations of the microstructure indicated that grain size transformed from normal to bimodal distribution when Li₂CO₃ content was increased. For the case of 8 mol%, a unique keyboard structure was observed in coarse grains. Dielectric spectra of all compositions displayed temperature-stable high dielectric constant. A broad low temperature relaxor-like dielectric anomaly was observed in addition to the high temperature maximum around 70°C. It was interesting to note that the high temperature peak gradually became significant with the increase of Li₂CO₃ content.

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1. Introduction

K_{Sr}2Nb₅O₁₅ (KSN) is a ferroelectric material with electrical properties that are comparable with Sr_{1-x}Ba_xNb₂O₆ (SBN) solid solutions [1]. KSN has the tetragonal tungsten bronze (TTB) structure in space group P4bm at room temperature [2,3]. The tungsten bronze structure has a tetragonal unit cell with a general formula of (A1)₄(A2)₂C₄(B1)₂(B2)₈O₃₀, typified by oxygen octahedra sharing their corners in a complex way to yield three types of openings: A1, A2 and C (as shown in Fig. 1) [4]. Although the terms “filled” and/or “unfilled” TTB structure are often applied in the literature, the small C site is empty and the term filled refers to the situation in which A1 and A2 are occupied. Only small cations like Li are found in the C site [4,5]. In KSN, each square A1 is occupied by Sr²⁺ and each pentagonal A2 site is statistically occupied by equal quantities of K⁺ and Sr²⁺, whereas the C sites are empty [2].

The specific manifestation of the dielectric properties, and the interrelationship of the ferroelectric and ferroelastic properties make the TTB family very interesting for experimental and theoretical studies [6–12]. In addition, because of the substantial anisotropy of piezoelectric properties [13] and easy preparation of needlelike microcrystalline [14], the textured KSN ceramics will be used in technology as material for piezoelectric application. Highly [001] textured KSN ceramics had been obtained by various methods. Kimura et al. [15] fabricated texture degree of 86% (measured by the Lotgering factor) by hot pressing technique. Tanaka et al. [16] reported

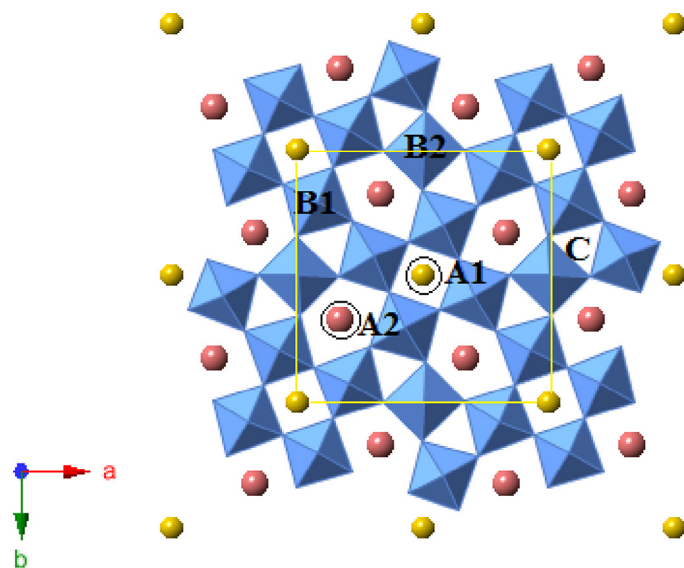


Fig. 1. Schematic representation of the structural skeleton of the TTB-type structure projected on the *ab* plane. Square, pentagonal, and triangular tunnels available for cation inclusion are labeled as A1, A2 and C, correspondingly. The unit cell of the basic tetragonal structure has been outlined with line.

preparation of textured KSN ceramics using a rotating strong magnetic field. In recent papers, highly textured (98%) KSN ceramics using reactive templated grain growth (RTGG) were reported by Duran et al. [13,17]. Electric properties measurements indicated

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anisotropic properties that were close to single crystal values in the textured KSN ceramics. Mostly recently, we have reported randomly oriented KSN ceramics with doping 2 mol% Bi_2O_3 which were synthesized by using a conventional two-step sintering method with KSN seed [18]. Piezoelectric constant in the optimized composition was comparable to that of the KSN textured ceramics [13]. So, the study of new compounds in KSN ceramics is of great interest both from the viewpoint of further development of the physics of ferroelectricity and for environment-friendly applications. Much of the focus on recent TTB materials have been directed at A or B substitution [8,9]. It has been suggested that the electric behavior is dominated by the ionic radius difference between the ions on the A1 and A2 sites [8]. However, these uncommon phenomena, such as reentrant relaxor behavior, are still not well-understood. The low temperature dielectric properties in TTB structure have been tentatively attributed to the inherent randomness of the concerted rotation of oxygen octahedra or the structure (a vacancy and/or cationic disorder) [7–9]. In this sense, the C-site occupancy should be an additional parameter which may disturb the phase transition and dielectric properties although there are very limited numbers of studies reported in the literature [19].

In the present work, the effect of Li^+ ion occupancy on microstructure and dielectric characteristics in $\text{KSr}_2\text{Nb}_5\text{O}_{15}$ tungsten bronze ceramics have been investigated as a function of Li ion content.

2. Experimental procedures

To prepare $\text{KSr}_2\text{Nb}_5\text{O}_{15}$ (KSN) ceramics, KSN microcrystallite powder was fabricated by a molten salt synthesis (MSS) method. The two-step MSS methods combined with excess Nb_2O_5 was utilized to synthesize KSN particles. Details of the preparation of the particles were reported by our group in previous articles [14,20]. In the MSS method, the stoichiometric mixtures (SrCO_3 99%, Nb_2O_5 99.5%, KCl 99.5% and seed) were mixed by ball milling with zirconia balls as grinding media in ethanol for 24 h. The mixture was placed into an Al_2O_3 crucible. The crucible was covered with a flat Al_2O_3 lid to minimize KCl evaporation, and then heated to 1150°C at a rate of 5°C/min, held for 6 h and cooled to ambient temperature at a rate of 2°C/min. After heat treatment, the products were separated from the mass of solidified salt by washing several times in hot deionized water to ensure complete removal of the redundant KCl salt.

KSN microcrystallite powder was mixed by ball milling in ethanol for 24 h with an additional 0–8 mol% Li_2CO_3 (99%, $x = 0\text{--}0.08$). After drying, the mixture was granulated with PVA as a binder and then pressed into pellets ($\phi 12\text{mm} \times 1.3\text{ mm}$). The compacts were heated at 500°C for 1 h to burn out the binder and then sintered at 1350°C for 2 h and cooled in the furnace. The heating rate was 5°C/min. Silver paste was fired on both faces of the pellets at 780°C for 20 min as electrodes.

Bulk densities of the sintered discs were measured by using the Archimedes method. Theoretical density of KSN 5.002 g/cm³ [21] was used to calculate relative density of ceramics samples. Phases of the KSN powder crystals and ceramics were determined by XRD (Panalytical X'Pert PRO, Holland) using Cu K α radiation and a graphite monochromator. Microstructures of the polished and thermal-etched disks were examined by SEM (Quanta 600 FEG, America). The temperature dependence of the dielectric constant (ϵ) and dielectric loss ($\tan\delta$) were measured between –70°C and 125°C at 1 kHz, 10 kHz and 100 kHz with an LCR precision electric bridge (HP4284, Hewlett-Packard, Palo Alto, CA).

3. Results and discussion

3.1. Synthesis of KSN crystalline

Prior to $\text{KSr}_2\text{Nb}_5\text{O}_{15}$ (KSN) ceramics preparing, KSN powder crystals were fabricated by a molten salt synthesis (MSS) method. The

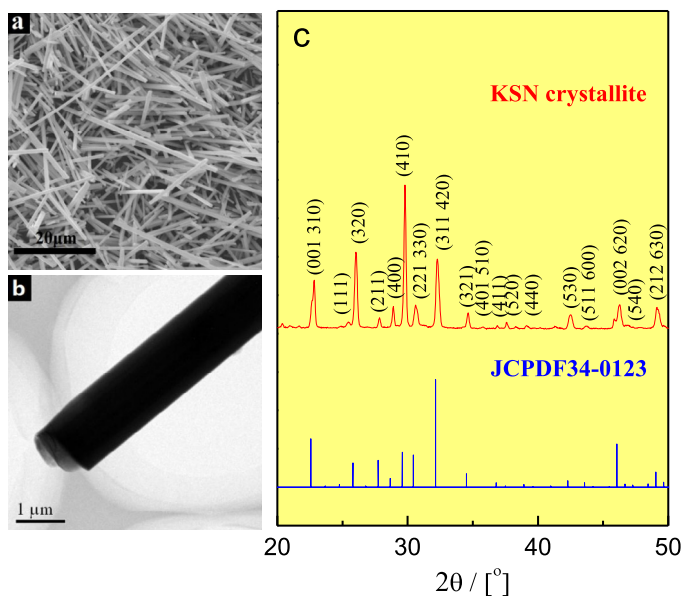


Fig. 2. Morphology and XRD pattern of the KSN crystallite synthesized by molten salt method.

anisometric KSN particles were synthesized by reacting KCl salt with oxides powder (SrCO_3 and Nb_2O_5), e.g. KCl– SrCO_3 – Nb_2O_5 system. KSN seed and excess Nb_2O_5 were added in the system. The addition of excess Nb_2O_5 and seed had a meaningful influence on the morphology and size (length and diameter) of the product particles. It was found that KSN crystalline growth process was similar to the mesocrystal growth mechanism [22], which does not proceed through ion-by-ion attachment but by a modular nano-building-block route. Alignment of $[\text{NbO}_{6/2}]$ octahedral building blocks on seed surface by sharing a common crystallographic orientation is the key feature for KSN particles growth [14].

In our study, we have investigated increasing the seed content up to 20 wt% and excess Nb_2O_5 up to 100 wt%. The results indicated that the aspect ratio of KSN particles increased and then decreased with increasing seed and excess Nb_2O_5 content. It was found that the diameter of KSN particles was minimum and uniform at seed content = 10 wt% and excess Nb_2O_5 = 60 wt% (Fig. 2). As shown in Fig. 2a and b, the KSN crystalline achieved an average length of 50 μm and diameter of 1.2 μm . As known to all, fine powder contributed to densification and grain growth of the sintered ceramics. Thus, KSN crystalline powder fabricated by the two-step MSS with 10 wt% seed content and excess 60 wt% Nb_2O_5 were used in the rest of the study.

The XRD pattern of KSN crystalline also was given in Fig. 2c. All the XRD diffraction peaks could be readily indexed to the tetragonal KSN phase. The diffraction lines shifted toward larger 2θ angle due to the $\text{K}^+/\text{Sr}^{2+}$ vacancies [23]. The most intense peak was (4 1 0), instead of (3 1 1)/(4 2 0), which indicated that most of the lateral surface of KSN particle were {4 1 0} planes. This had been confirmed by the HRTEM image in our previous work [14,24]. Fig. 3 shows EDS spectra of the KSN crystallite after ball milling. The morphology of particles exhibited a short needle. And it was further confirmed that the KSN crystalline ($\text{K} : \text{Sr} : \text{Nb} = 4.14:6.50:22.57 \approx 0.92:1.44:5$) was lacking $\text{Sr}^{2+}/\text{K}^+$ compared with the standard stoichiometric ratio of $\text{KSr}_2\text{Nb}_5\text{O}_{15}$ ($\text{K} : \text{Sr} : \text{Nb} = 1:2:5$).

3.2. Microstructure of KSN ceramics

To better understand densification and microstructure of the sintered samples with different Li_2CO_3 contents ($x = 0\text{--}0.08$), the

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