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Sintering behavior, dielectric and piezoelectric properties of sodium potassium niobate-based ceramics prepared by single step and two-step sintering

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Abstract

In this work (1–x) $K_{0.48}Na_{0.48}Li_{0.04}Nb_{0.96}Ta_{0.04}O_3$–$x$$SrTiO_3$ ($0.0 \leq x \leq 0.10$) ceramics were fabricated via single step sintering (SSS) as well as two-step sintering (TSS) methods. Investigation of the sintering behavior of ceramics revealed that TSS could reduce sintering temperature effectively and it enhances densification. The relative densities of TSSed ceramics were about 3% higher than SSSed ones. Coexistence of orthorhombic and tetragonal symmetries in ceramic containing 1% $SrTiO_3$, resulted in maximum piezoelectric constant compared to others. Higher density and lower alkali elements loss in TSSed ceramics improved dielectric and piezoelectric properties compared to SSSed ceramics. Piezoelectric constant of the 0.99KNNLT–0.01ST ceramic sintered via SSS and TSS was measured at 208 and 278 pC/N, respectively.

Keywords: A. Sintering; C. Dielectric properties; Piezoelectricity; Piezoceramics

1. Introduction

Sodium potassium niobate (KNN)-based piezoceramics because of there high Curie temperature and relatively good piezoelectric properties, are considered as suitable candidates for replacement of lead-based piezoceramics, whose applications have been restricted due to lead toxicity [1]. This consideration was intensified especially after the work of Saito et al. [2] which reported comparable piezoelectric properties of KNN-based ceramics with lead-based ones. Unfortunately low sinterability of KNN-based ceramics and difficulty of their fabrication with high density via conventional sintering method under atmospheric pressure [3] have restricted their mass production and applications. Insufficient density of KNN-based ceramics, possibility of compositional deviation of sintered ceramic from stoichiometry composition and formation of secondary phases due to volatilization of alkali elements during sintering [4,5] are all results of low sinterability of KNN-based compounds and result in decline of piezoelectric properties of sintered ceramic.

So far many research works have been carried out to improve sintering behavior of KNN-based compounds via doping [6,7,8], modification [2,9,10] and using sintering aids [11,12]. Considerable improvements in piezoelectric properties of fabricated ceramics have been observed. Some investigators were able to fabricate dense ceramics with better properties using other sintering methods such as hot pressing [13] and spark plasma sintering [14], instead of conventional methods. However the complexity and expensiveness of these methods restrict their industrial applications. Therefore using a relatively simple and effective method to improve sintering behavior and piezoelectric properties of KNN-based compounds besides doping and modification of composition seems essential. One of the sintering methods which is capable of fabricating dense structure as well as fine microstructure is

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two-step sintering (TSS). This novel method was introduced in 2000 by Chen and Wang [15] and it has been used to sinter different compounds such as Al_2O_3 [16], ZrO_2 [17] and Y_2O_3 [18]. In first step of TSS, the sample is kept at a higher temperature (T_1) for a short time to reach a critical density and then rapidly cooled down to lower temperature (T_2) and is soaked for relatively prolonged time for densification without grain growth. Due to TSS, the potential to decrease the required sintering temperature effectively using this method for sintering compounds containing volatile elements, eliminates or at least decreases loss of volatile elements and enhances densification. So far, the use of TSS for sintering KNN-based compounds has not been studied so much. Therefore, in this work, sintering of $K_{0.48}Na_{0.48}Li_{0.04}Nb_{0.96}Ta_{0.04}O_3$ (KNNLT) modified with different amounts of $SrTiO_3$ (ST) via TSS was investigated. Moreover the conventional method (single step sintering) was also used. Sintering behavior, dielectric and piezoelectric properties of ceramics produced by two different sintering procedures were studied and compared.

2. Experimental procedure

(1–x)KNNLT–xST ($0.0 \le x \le 0.10$) powders were synthesized by a conventional solid state reaction method using Na_2CO_3, K_2CO_3, Li_2CO_3, Nb_2O_5, Ta_2O_5, SrO and TiO_2 with more than 99% purity as raw materials. At first, these powders were dried in an oven at 100 °C for 24 h and then were weighed for each composition according to a stoichiometric formula. Each powder mixture was ball-milled for 24 h with zirconia balls using ethanol media. The dried slurries were calcined at 880 °C for 6 h. In order to increase the homogeneity of the composition, the calcination was carried out twice, separated by 24 h ball milling. Calcined powders were mixed with polyvinyl alcohol as a binder and then pressed into green disks with a diameter of 12 mm at 50 MPa. The green disks were sintered via TSS and single step sintering (SSS). Time and temperature conditions as well as heating and cooling rates in TSS and SSS procedures are compared in Fig. 1. For TSS, samples were sintered in the range 1060–1150 °C with a 10 °C interval. The densities of all sintered ceramics were measured by the Archimedes method and the temperature that yielded the maximum relative density for each composition was chosen as the optimum sintering temperature. The crystal structure of the samples was determined using an X-ray diffractometer (XRD, X'pert PRO MRD, Philips). The microstructure of ceramics was observed using a scanning electron microscope (FE-SEM, JEOL, JSM-65OFF, Japan). For electrical measurements, silver paste was applied on the lapped surfaces of the disks to serve as the electrodes. The temperature dependence of dielectric properties was measured using an impedance analyzer (HP 4192A) in a temperature range of 25–500 °C. Some samples were poled at 100 °C in silicon oil bath by applying an electric field of 3–4 kV/mm for 30 min. The piezoelectric constant d_{33} was measured using a piezo-d_{33} meter (ZJ-6B, China).

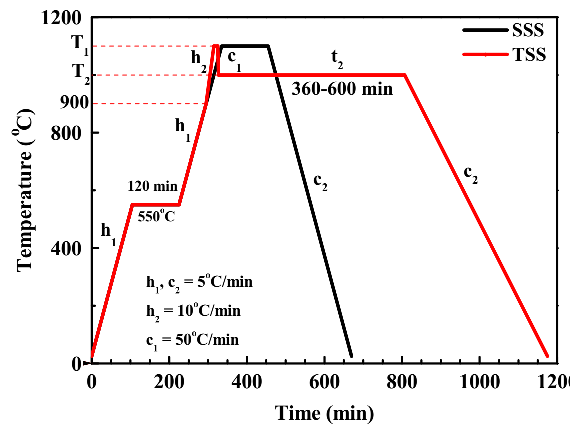

Fig. 1. Time–temperature profile of SSS and TSS.

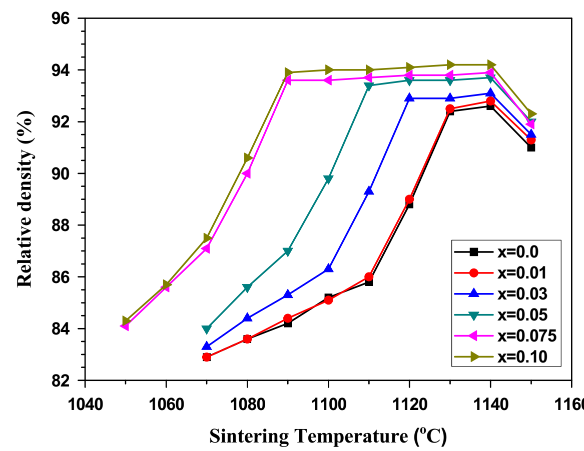

Fig. 2. The variation of relative density of SSSed KNNLT ceramics versus temperature.

3. Results and discussion

3.1. Densification

3.1.1. Single step sintered samples

Variation of relative density (RD) of SSS (1–x)KNNLT–xST ceramics for 2 h versus sintering temperature is shown in Fig. 2. As can be seen, for all compositions variation of RD follows a four-step trend. In the first step, density increases with a relatively slow rate while in the second step a sharp increase can be seen. Mechanism change, from solid state to partial liquid phase sintering [19,20], which enhances diffusion and mass transport is the probable reason for this observation. Increasing the temperature in the third step does not increase the density considerably due to domination of grain growth over densification. In this step, the driving force for sintering is consumed mainly for grain growth without having a considerable effect on densification of samples. At temperatures higher than 1140 °C a sharp drop in densities of all compositions occurs which is due to the loss of Na and K volatile elements resulting in reduction of the sample's mass. Appearance of such behavior during sintering of KNN-based compounds results in