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Normal sintering of (K, Na)NbO_3-based lead-free piezoelectric ceramics

Jing-Feng Li [a,*], Yuhua Zhen [a], Bo-Ping Zhang [b], Li-Min Zhang [b], Ke Wang [a]

[a] *State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China*

[b] *School of Material Science and Engineering, University of Science and Technology Beijing, Beijing 100083, PR China*

Abstract

Lead-free piezoelectric ceramics have received more attention due to the environmental protection of the earth. (K, Na)NbO_3-based ceramics are one of the most promising candidates. Normal sintering of un-doped and Li/Ta co-doped (K, Na)NbO_3 ceramics was investigated to clarify the optimal sintering condition for densification, microstructure and electrical properties. It was found that density increased greatly within a narrow temperature range but turned to decrease when the sintering temperature slightly exceeded the optimal one. Piezoelectric properties also showed similar relationship between the density and sintering temperature, but the highest piezoelectric strain coefficients were obtained at the temperatures lower than that for the highest density. The grain growth and property change as a function of sintering temperature were discussed on basis of the formation of liquid-phase and the composition deviation caused by the volatilization of alkali components during sintering.

Keywords: A. Sintering; C. Piezoelectric properties; D. Niobates

1. Introduction

Lead-free piezoelectric ceramics have received increasing attention from the viewpoint of environmental protection. Among various candidates for lead-free piezoelectric materials, ceramics based on potassium sodium niobate ($KNbO_3$–$NaNbO_3$, abbreviated as KNN) are the most promising, because of its outstanding piezoelectric and ferroelectric properties as well as its better environmental compatibility than other lead-free piezoelectric ceramics such as $Bi_{0.5}Na_{0.5}TiO_3$ and $Bi_4Ti_3O_{12}$, which are composed of bismuth, a toxic element. Although the studies on KNN ceramics can be traced back to 1950's [1], a recent paper in *Nature* by Saito et al. [2] again attracted worldwide attentions on this lead-free piezoelectric ceramics. Pressurized sintering, such as hot pressing (HP) [1], spark plasma sintering (SPS) [3–6], are often used to fabricate KNN ceramics because of the difficulty of densification resulting from the volatilization of alkali components. Recently, normal sintering processes are also successfully applied to the fabrication of dense KNN-based ceramics [7–10], and it was found that their densification behavior and sintered microstructure as well as electrical properties are very sensitive to the sintering temperature, whose optimal values vary depending on the doping elements to KNN matrix [7].

The normal sintering of pure KNN and Li/Ta co-doped (K, Na)NbO_3 ceramics was investigated in the present study to explore the optimal processing conditions for densification and piezoelectric properties. The present results showed that liquid-phase sintering contributes to the normal sintering densification of the KNN-based ceramics, which requires that the processing temperature exceeds the solidus line of the phase diagram; however, the highest piezoelectric coefficients were obtained at the temperatures lower than that for the highest density.

2. Experimental procedure

Commercial sodium carbonate (Na_2CO_3, 99.8%), potassium carbonate (K_2CO_3, 99%), lithium carbonate (Li_2CO_3, 99.5%), niobium oxide (Nb_2O_5, 99.5%), and tantalum oxide (Ta_2O_5, 99.9%) were used as raw materials. They were mixed by ball-milling in an ethanol solution according to the stoichiometric ratio with the nominal compositions of $K_{0.5}Na_{0.5}NbO_3$, $(Li_{0.04}K_{0.44}Na_{0.52})NbO_3$ and $(Li_{0.04}K_{0.44}Na_{0.52})(Nb_{0.85}Ta_{0.15})O_3$, which were abbreviated as KNN, LKNN and LKNNT, respectively. After ball-milling for 4 h, the mixed powders

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* Corresponding author. Tel.: +86 10 62784845; fax: +86 10 62771160.
E-mail address: Jingfeng@mail.tsinghua.edu.cn (J.-F. Li).

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were packed into an Al_2O_3 crucible and calcined at 800 °C for 5 h. The synthesized powders were then compacted into discs of 10 mm in diameter and 1.5 mm in thickness, then followed by cold-isostatic pressing (CIP) at 200 MPa. These green compacts were sintered at the temperatures shown later in air for 2 h using a special double-crucible method to suppress the volatilization of alkali components.

The calcined powders and sintered samples were characterized by X-ray diffractometer (XRD, Rigaku, D/Max-2500, Tokyo, Japan). The bulk density was measured by the Archimedes method. The microstructures of as-sintered samples were observed by a scanning electron microscope (SEM, S-450, HITACHI, Tokyo, Japan). For measuring electrical properties, disk-shaped samples with determined sizes were prepared and then coated with Ag paste on both surfaces and fired at 700 °C for 0.5 h. Then the samples were polarized along the thickness direction under a poling electric field of 3 kV/mm at 130 °C for 30 min in a bath of silicone oil. When the samples were aged for 24 h after poling, the piezoelectric coefficient d_{33} values were measured by a quaisistatic d_{33} meter (ZJ-3A, Institute of Acoustics, Beijing, China).

3. Results and discussion

The XRD analysis revealed that a single phase with perovskite structure was obtained in the calcined powders for the three compositions.

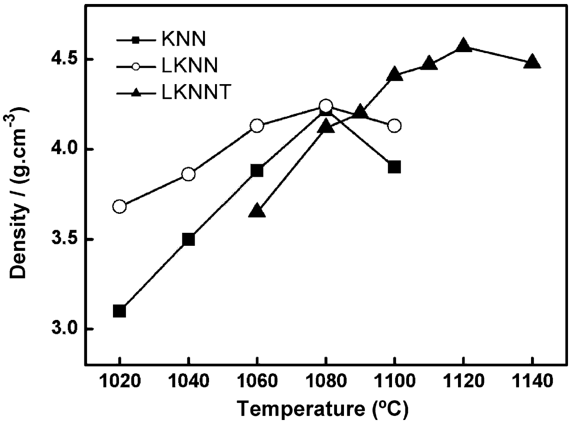

Fig. 1. Density change of KNN, LKNN and LKNNT samples as a function of sintering temperature.

Fig. 1 shows the change in the sintered densities of the KNN, LKNN and LKNNT samples as a function of sintering temperature. It was found that the change in density was very sensitive to the sintering temperature. Even though the sintering temperature was changed within a narrow range shown in Fig. 1, the resultant density changed significantly for all the compositions. The density increased rapidly and then decrease slowly after reaching a maximum. Ta doping apparently shifted the maximum sintering point to higher temperature, whereas the densification behavior was almost the same both for the

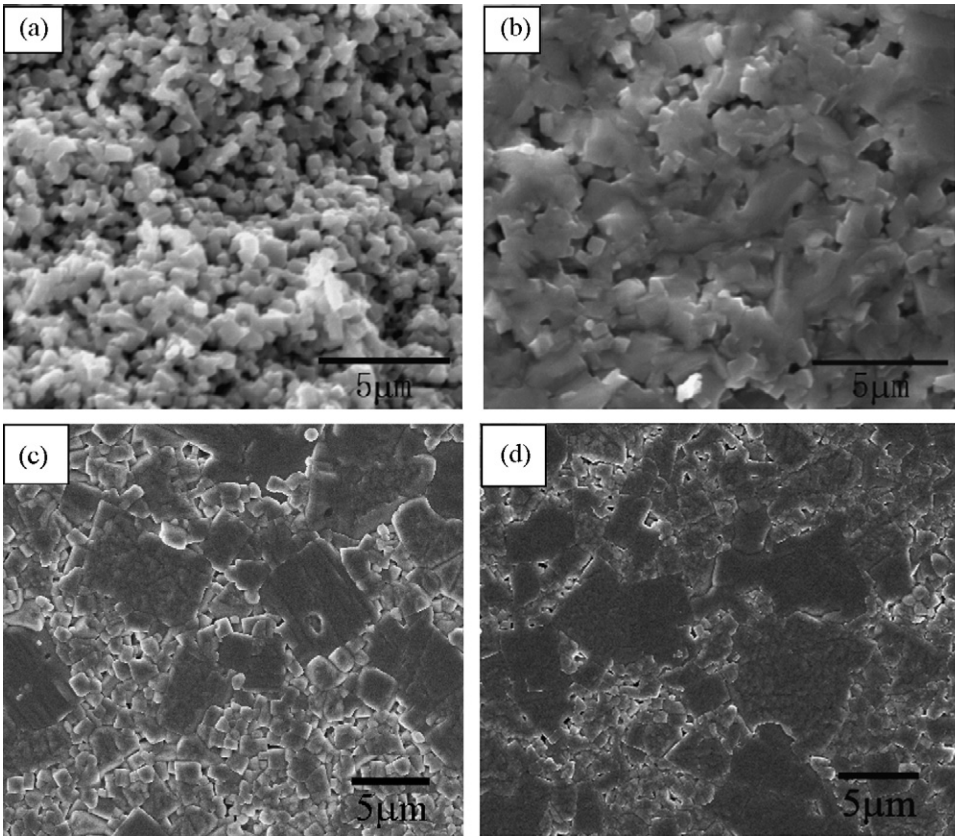

Fig. 2. SEM fracture surfaces of LKNNT samples sintered at (a) 1080 °C and (b) 1100 °C, thermal-etched surfaces of LKNNT samples sintered at (c) 1120 °C and (d) 1140 °C.

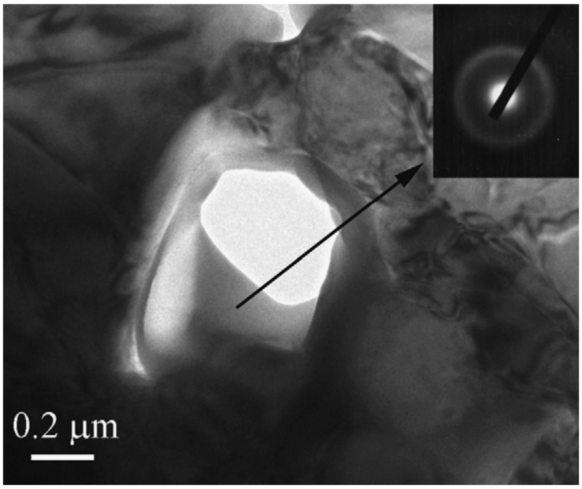

Fig. 3. A typical TEM micrographs of LKNNT ceramic samples sintered at 1120 °C, showing the existence of liquid-phase.

samples without and with Li doping. The highest density values obtained for the three compositions exceeded 95% of their theoretical densities.

The SEM observation experiments found that the microstructure of the sintered sample changed significantly with increasing sintering temperature. As shown in Fig. 2, grain growth was accelerated when the sintering was conducted at or a little above the peak temperature shown in Fig. 1. For the LKNNT ceramics, the grains were still within the submicron range even when sintered at 1080 °C. When the sintering temperature was raised to 1120 °C, there were some grains whose size exceeded 10 μm. The changes in density and microstructure showed that liquid-phase sintering occurred in the KNN-based ceramics. Actually, as shown in Fig. 3, amorphous phases at the grain boundaries were often observed in the KNN-based ceramics, which confirmed the formation of liquid-phase during sintering at enough high temperature.

The electrical properties of KNN, LKNN and LKNNT ceramics were evaluated as a function of sintering temperature. Fig. 4 shows the changes in piezoelectric coefficient d_{33} of the three compositions as a function of sintering temperature. It is interesting that similar tendencies were obtained for the relationship between d_{33} and sintering temperature as the case of sintered density. All the three compositions showed their peak d_{33} values at their corresponding sintering temperatures. However, it must be noted that the temperature where the maximum d_{33} value was obtained differed from the point where the peak density was achieved. For example, the highest density was obtained at 1120 °C for the LKNNT composition, whereas d_{33} of the resultant ceramics sample decreased apparently from the peak point if sintered at 1120 °C; the highest d_{33} value was obtained at the temperature which is about 20–30 °C lower than that where the highest density can be reached. In other words, the d_{33} values dropped apparently when sintered at the temperatures exceeding the points that correspond to the peak density shown in Fig. 1. On the other hand, the d_{33} values of the samples were relatively high, in spite of their low density when sintered at the temperatures below the point corresponding to the peak density. Fig. 5 shows the change in planar electromechanical coupling coefficient (k_p) as a function of sintering temperature, whose change was similar to the relationship between density and sintering temperature as shown in Fig. 1. Both Li-doping and Li/Ta co-doping markedly increased the electromechanical coupling coefficient of KNN ceramics. The LKNNT composition showed a relatively high and steady k_p constants of about 0.38–0.40 as the sintering temperature was increased from 1090 up to 1110 °C, and turned to an apparent drop happened when sintered above 1120 °C, which is consistent well with the rapid decrease in piezoelectric property shown in Fig. 4. For the LKNN system the k_p curve showed relatively small variations in the values between 0.35 and 0.38 with sintering temperature, but it still gave a similar tendency as that in piezoelectric property.

The main question about the above results is why the optimal sintering temperature for the electrical properties differed from that for the density? As shown above, the piezoelectric and dielectric properties changed with a similar tendency as the relationship between density and sintering temperature. However, the sintering temperatures where the highest d_{33} and ε_r were obtained, was not consistent with that where the highest density was reached. To answer this question, we must

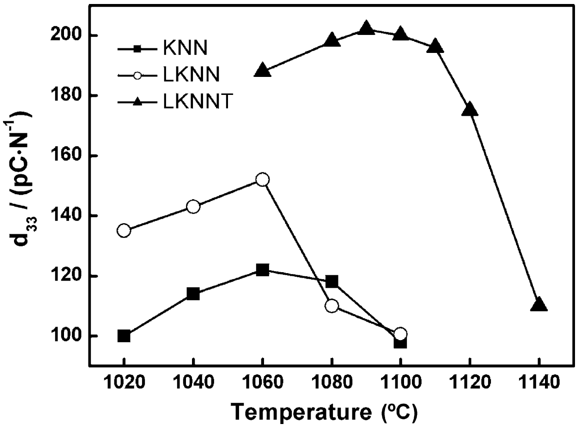

Fig. 4. Sintering temperature dependence of piezoelectric coefficient d_{33} of KNN, LKNN and LKNNT series.

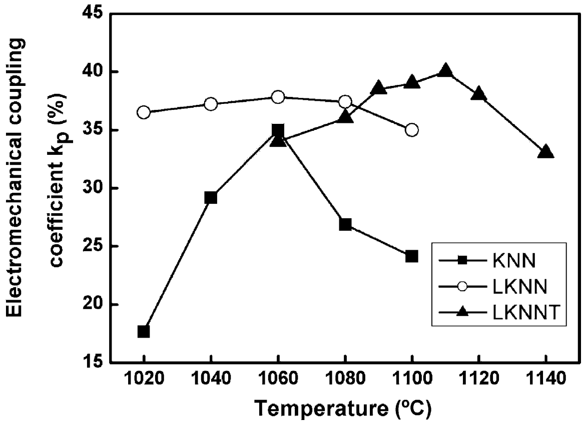

Fig. 5. Electromechanical coupling coefficient k_p as a function of sintering temperature.

take into account the volatilization of alkali components during the sintering, which occurred during the sintering of KNN-based ceramics and caused the composition deviation from the starting one. The volatilization may be accelerated when the liquid-phase appears, although which also enhances the densification at the same time. Our previous study [7] by energy dispersive X-ray spectroscopy analysis confirmed the volatilization, and it was found that Na volatized more seriously at high temperatures. Considering that the electric properties are sensitive to the composition change [6], and that the sample sintered to the highest density may not have the optimal composition, it is easy to understand why the highest piezoelectric and dielectric properties were obtained at somewhat lower sintering temperature than that for density. In addition, grain coarsening or abnormal grain growth was caused when the sintering temperature exceeded the peak point for the density, which may also not be favorable for the optimization of electrical properties.

4. Conclusions

Highly dense KNN-based ceramics can be fabricated by normal sintering in air, and liquid-phase sintering contributes to its densification. Density increases greatly within a narrow temperature range but turns to decrease when the sintering temperature slightly exceeded the optimal one. This is because the volatilization of alkali components and abnormal grain growth, which are accelerated by the appearance of liquid-phase during sintering. As a result of a balanced combination of density and composition as well as microstructure, the optimal sintering temperature for obtaining the highest piezoelectric properties are not consistent with that where the highest density was reached, and the piezoelectric coefficient d_{33} and electromechanical coupling coefficient k_p values decrease significantly when sintering temperature slightly exceeds the peak sintering temperature.

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