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The two-step sintering effect on the dielectric and piezoelectric properties of $(Na,K)NbO_3$-$BiScO_3$ lead-free ceramics

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ABSTRACT

In this paper, the two-step sintering process was employed to lower the sintering temperature and improve the dielectric and piezoelectric properties of $0.98(Na_{0.5}K_{0.5})NbO_3$–$0.02BiScO_3$ (0.98NKN-0.02BS) ceramics. By introducing the two-step sintering process for 0.98NKN-0.02BS ceramics, the volatilization of Na and K can be decreased. Dopants of Na and K have low-melting-point. By optimizing the dwelling time as 24 h in the two-step sintering process, the dielectric permittivity was enhanced up to 1287 at 1 kHz, while that of conventionally sintered ceramics is only 1201. By introducing the two-step sintering process, piezoelectric charge coefficient, piezoelectric voltage coefficient, electromechanical coupling factor were improved from 156 pC/N, 14.3 10^{-3} Vm/N, 39.9% to 168 pC/N, 14.7 10^{-3} Vm/N, 42.7%, respectively. We expect to enhance the dielectric and piezoelectric properties of $0.98Na_{0.5}K_{0.5}NbO_3$–$0.02BiScO_3$ lead-free piezoelectric ceramics by employing the two-step sintering process.

1. Introduction

Lead-free piezoelectric materials have been extensively researched to replace lead-based materials in electronic device applications. Among them, $(Na,K)NbO_3$ (NKN) ceramics are representative lead-free piezoelectric materials due to their high Curie temperature of 420 °C, and excellent piezoelectric coefficient of 80 pC/N [1]. Morphotropic phase boundary (MPB) of $(1-x)Na_{0.5}K_{0.5}NbO_3$-$xBiScO_3$ ceramic was reported at x=0.02 [2]. In general, it is reported that dielectric and piezoelectric properties can be improved near the MPB region [1,3].

The various processing technologies have been tested to enhance the dielectric and piezoelectric properties of ceramics such as spark plasma sintering [4], hot isostatic pressing [5], and cold isostatic pressing [6]. However, these processing technologies have high cost and require complicated processing system. Therefore, it is important to investigate alternative cheap processing technology to improve the dielectric and piezoelectric properties by modifying conventional processing technologies. It is believed that the two-step sintering process can avoid the evaporation of volatile components, such as Na and K in piezoelectric NKN ceramics, because this process can be performed near the temperature around the solidus and liquids line in the phase diagram [7]. Also, the two-step sintering process is a useful method to synthesis of ceramics. Moreover, this method has strong merits in improving bulk density, dielectric permittivity and piezoelectric coefficient as compared to those of conventionally sintered ceramics [8]. To apply two-step sintering process, the first step temperature is usually set as higher degree than that of second step to produce uniform microstructure and grain growth, which maintain an open network of pores at a higher density. And then the second step is held at lower temperature to enable full densification of the ceramics. Therefore, the fabricated ceramics have enhanced densification during the second step [9].

In this study, we expected that the $0.98Na_{0.5}K_{0.5}NbO_3$–$0.02BiScO_3$ ceramics would have improved dielectric and piezoelectric properties by introducing the two-step sintering process. In particular, we have intensively investigated the effects of dwelling time of the two-step sintering process on the $(1-x)Na_{0.5}K_{0.5}NbO_3$-$xBiScO_3$ ceramic properties.

2. Material and methods

The $0.98Na_{0.5}K_{0.5}NbO_3$–$0.02BiScO_3$ ceramics were prepared by employing a two-step sintering process. K_2CO_3 (99.0%), Na_2CO_3 (99.0%), Nb_2O_5 (99.9%), Bi_2O_3 (99.9%) and Sc_2O_3 (99.9%) were used as starting materials. The powders were dried in an oven at 120 °C for 12 h. According to the chemical formula, the powders were milled for 24 h with zirconia balls and dried, and then calcined at 900 °C for 2 h. The obtained powders were pressed with 1.0 metric ton into discs, using PVA as a binder. The discs were sintered by conventional

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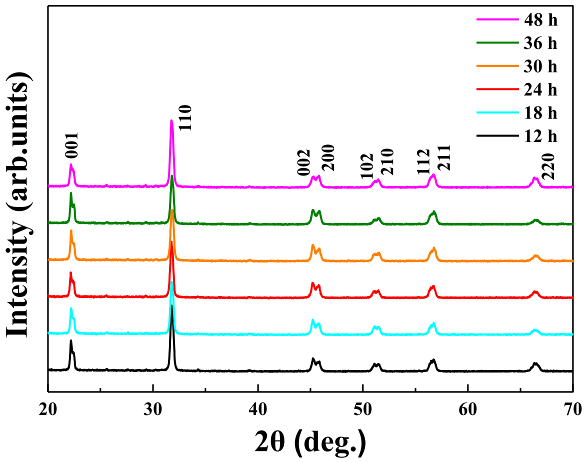

Fig. 1. The X-ray diffraction (XRD) patterns of the $0.98Na_{0.5}K_{0.5}NbO_3$–$0.02BiScO_3$ ceramics prepared by two-step sintering process with various dwelling times (12, 18, 24, 30, 36 and 48 h).

sintering and two-step sintering process. The conventional sintering process was employed at 1150 °C for 2 h for comparison with two step sintering process. Meanwhile, the two-step sintering process was preceded following several steps. First, the samples were heated at 600 °C for burn out PVA for 1 h with a heating rate of 5 °C/min. The samples were reheated from 600 °C to 1150 °C with a heating rate of 5 °C/min. It was kept at 1150 °C for 10 min, and then decreased to 1050 °C with a cooling rate of 5 °C/min. The temperature was fixed at 1050 °C with various dwelling times (12, 18, 24, 30, 36 and 48 h). The obtained samples were cut and polished, and silver paste was fired at 400 °C for 30 min. The samples were poled in 60 °C silicon oil by applying a DC electric field of 4.0 kV/mm for 30 min. To analyze the crystalline structure of the samples, X-ray diffraction (XRD) was performed. Field emission scanning electron microscopy (FE-SEM) was used to study the morphologies and microstructures of the samples.

3. Results and discussion

Fig. 1 shows the XRD patterns obtained from the 0.98NKN-0.02BS ceramics from the two-step sintering process with various dwelling times. As shown in the figure, all specimens exhibit a single perovskite structure without any secondary phase. This means that $BiScO_3$ has diffused into the 0.98NKN-0.02BS ceramics and formed a solid solution. 0.98NKN-0.02BS ceramics were indicated to be a mixture of orthorhombic and rhombohedral phases. The position of (*002*)/(*200*) planes were moved to a lower angle by increasing the dwelling time of the two-step sintering process up to 24 h. The (*002*) peak positions of the 0.98NKN-0.02BS ceramics, sintered for 12, 18 and 24 h, were located in 45.23, 45.21 and 45.19°, respectively. However, as increasing the dwelling time above 24 h, the (*002*) peak positions were increased from 45.25 to 45.30°. This (*002*) peak positions imply that the lattice parameter of the 0.98NKN-0.02BS samples was increased with dwelling time up to 24 h, and then decreased.

Fig. 2 shows SEM top view images of the 0.98NKN-0.02BS ceramic surfaces, which were prepared by the two-step sintering process with different dwelling times. The average grain sizes of the 0.98NKN-0.02BS ceramics sintered for 12, 18, 24, 30, 36 and 48 h were approximately 4.23, 4.67, 4.98, 6.1, 8.82 and 11.48 μm, respectively. The grain size of the 0.98NKN-0.02BS ceramics gradually increased with increasing dwelling time in the two-step sintering process. It means that the first step of two-step sintering process could be related with the thermal effect of grain growth. Also, the average grain size of the ceramics can be increased by increasing the sintering temperature and dwelling time [10,11]. The grain size can be expressed by the following equation [12]:

$$\log G = \frac{1}{n}\log t + \frac{1}{n}\left(\log K_0 - 0.434\frac{Q}{RT}\right) \quad (1)$$

Here, G is the average grain size, n is the kinetic grain growth exponent, t is the sintering time, K_0 is the constant, Q is the apparent activation energy, R is the gas constant and T is the absolute temperature, respectively. As shown in the Eq. (1), the grain size was increased as increasing the dwelling time by large margin. Also, homogeneous and dense microstructure of 0.98NKN-0.02BS ceramics were observed for the two-step sintering. It means that the second step of the two-step sintering could be related to densification. Also, the two-step sintering can effectively eliminate porosity and prevent the evaporation of volatile components, such as sodium and potassium.

Fig. 3 shows the bulk density and relative density of 0.98NKN-0.02BS ceramics prepared by two-step sintering process with various dwelling times. As shown in the figure, the bulk density increased with increasing dwelling time up to 24 h, and then decreased. This result from the effect of the partial evaporation of sodium and potassium. It is known that the stoichiometric composition of NKN ceramics can be deviated during the sintering process with high sintering temperature and long dwelling time due to low melting point of 900 °C for sodium

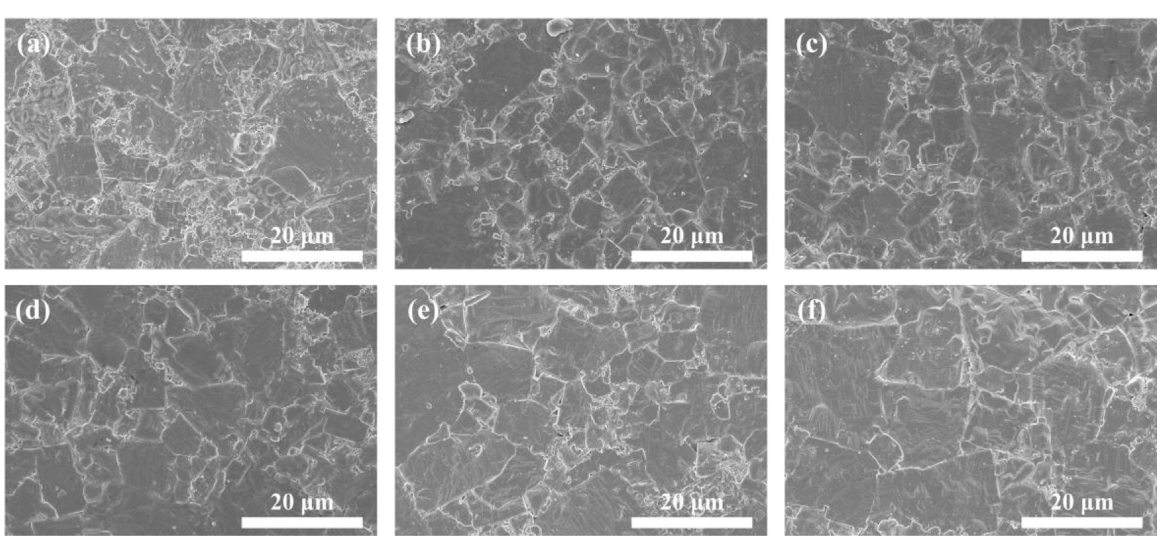

Fig. 2. SEM images of $0.98Na_{0.5}K_{0.5}NbO_3$–$0.02BiScO_3$ ceramics prepared by two-step sintering process with various dwelling times (a) 12 h, (b) 18 h, (c) 24 h, (d) 30 h, (e) 36 h and (f) 48 h.