

Lead-free $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ piezoelectric ceramics fabricated by spark plasma sintering: Annealing effect on electrical properties

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Abstract Niobate ceramics such as NaNbO_3 and KNbO_3 have been studied as promising Pb-free piezoelectric ceramics, but their sintering densification is fairly difficult. In the present study, highly dense $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ ceramics with submicron grains were prepared using SPS, whose density was raised to 4.47 g/cm^3 (>99% of the theoretical density) at 920°C . Reasonably good ferroelectric and piezoelectric properties were obtained in the SPSed $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ ceramics after annealing in air. The effect of annealing time on the electrical properties was investigated to determine optimal processing condition. The piezoelectric parameter (d_{33}) of the $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ ceramics annealed properly reached 148 pC/N .

Keywords Lead-free piezoelectric ceramic · Spark plasma sintering · $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$

1 Introduction

Lead-free piezoelectric ceramics have received increasing attention from the viewpoint of environmental protection on the earth. Potassium niobate (KNbO_3) and sodium niobate (NaNbO_3) [1–9] have been studied as promising Pb-free

piezoelectric and ferroelectric ceramics. Jaeger and Egretton [2] fabricated highly dense $(\text{Na,K})\text{NbO}_3$ ceramics using hot pressing and reported that the hot-pressed $(\text{Na,K})\text{NbO}_3$ ceramics possessed high piezoelectric constants and Curie temperature. However, since then there have been just a few reports about piezoelectricity of $(\text{Na,K})\text{NbO}_3$ ceramics, probably because of their poor sintering ability and high volatility, in addition to lower piezoelectricity compared to $\text{Pb}(\text{Zr, Ti})\text{O}_3$ ceramics that have been widely used so far. Recently, $(\text{Na, K})\text{NbO}_3$ ceramics attracted special attention again because of the breakthrough made by Saito et al. [10], who obtained high d_{33} ($\sim 416 \text{ pC/N}$) in the textured $(\text{Na, K})\text{NbO}_3$ -based ceramics. Their work proved again the potential of the $(\text{Na, K})\text{NbO}_3$ ceramics as a promising candidate of lead-free piezoelectric ceramics. In addition, niobate ceramics are more environmentally friendly than other lead-free piezoelectric ceramics, such as $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, which are composed of toxic bismuth element.

As well known, it is difficult to fabricate high-density ceramics due to the high volatility of the sodium and potassium component during the sintering process. Recently, Spark Plasma Sintering (SPS) is increasingly used instead of conventional sintering method because of its advantages of rapid heating rate and short soaking time [8, 9]. In the present study, highly dense $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ ceramics were prepared using SPS. Although the SPSing temperature was as low as 920°C , reasonably good ferroelectric and piezoelectric properties were obtained in the resultant $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ ceramics with sub-micrometer grains. However, oxygen deficiency in crystal lattices was formed during SPS process, which was caused by the reduced atmosphere of SPS. Therefore, the annealing treatment afterward was important. The annealing condition related closely to final properties.

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2 Experimental procedure

Commercial sodium carbonate (Na_2CO_3 99.8%), potassium carbonate (K_2CO_3 99%) and niobium oxide (Nb_2O_5 , 99%) were used as raw materials. They were mixed according to a stoichiometric ratio with the nominal composition of $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$, followed by ball milling in an ethanol solution in a planetary ball mill using an Al_2O_3 jar ($\phi 75 \times 65\text{mm}$) and balls of 5–10 mm in diameter. After ball-milling for 4 h, the slurry was dried and calcinated at 750°C for 4 h to ensure the formation of a single perovskite phase. The synthesized niobate powders were charged into a SPS graphite die of 20 mm in diameter. After the SPS chamber was evacuated ($\sim 10^{-2}$ Pa), the temperature was raised to 920°C at a rate of $100^\circ\text{C}/\text{min}$ and kept for 5 min, under a constant pressure of 50 MPa along the Z-axis. The SPSed samples were annealed in air at 900°C for 1, 4 and 24 h, respectively.

The bulk density of the SPSed samples was measured by the Archimedes method. The crystal structure was determined using X-ray powder diffraction (XRPD) with a $\text{Cu K}\alpha$ filter with a Ni foil (Rigaku; RAD-B system). The sintered microstructure was observed using a scanning electron microscopy (SEM) and a transmission electron microscopy (TEM).

For measurement of the dielectric and piezoelectric properties, silver paste electrodes were formed at the two surfaces of disk-shaped specimens, which were fired at 650°C for 30 min. The dielectric properties were measured in the temperature range from 200 to 550°C , using an

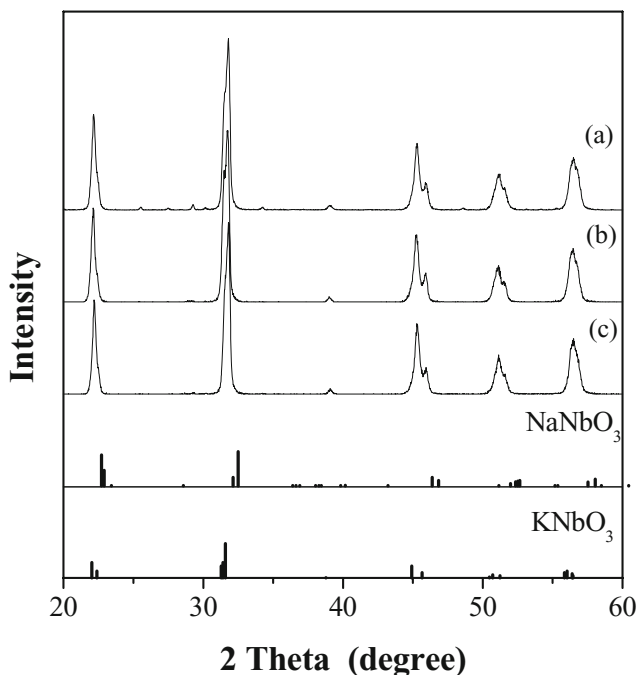


Fig. 1 XRD patterns of the $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ ceramics that were annealed at 920°C for (a) 1 h, (b) 4 h, (c) 24 h

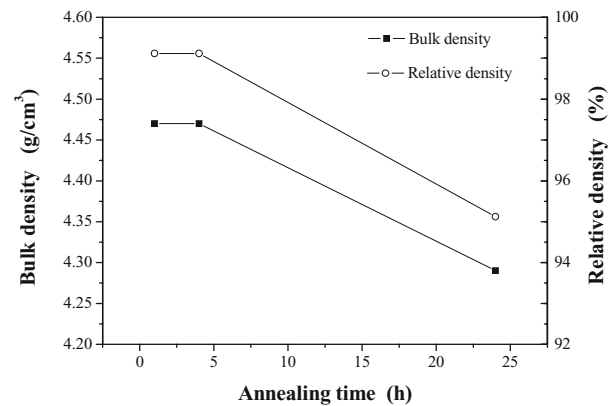


Fig. 2 The density of the SPSed samples as a function of annealing time

Agilent 4294A precision impedance analyzer. The ferroelectric hysteresis loops were measured at room temperature by using a ferroelectric tester (RT6000HVA, Radiant Technologies Inc.) at 100 Hz. The piezoelectric properties were measured using a quasi-static piezoelectric constant testing meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Science), for the samples that were poled under $30\text{ kV}/\text{cm}$ bias at 130°C in a silicone oil bath for 10 min.

3 Results and discussion

Figure 1 shows the XRD patterns of the $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ ceramics that were annealed at 920°C for 1 h (a), 4 h (b), 24 h (c). The diffraction peaks from the NaNbO_3 (JCPDS-ICDD file no.33-1270) and KNbO_3 (JCPDS-ICDD file no.32-0822) are also shown in the underside of the figure, using a vertical line for comparison. As shown in Fig. 1, all

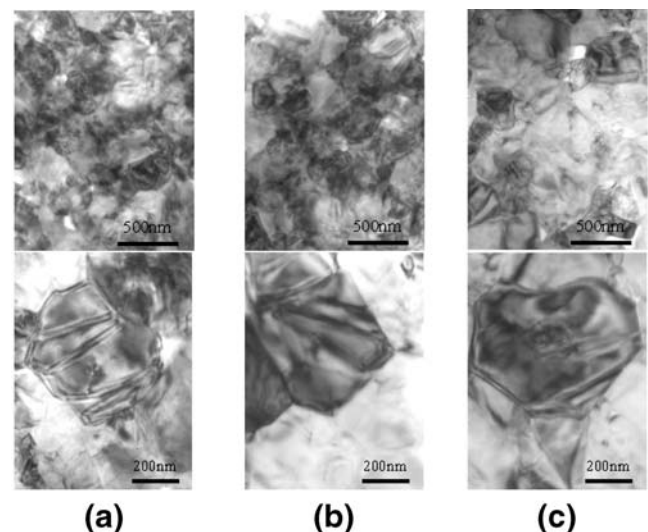


Fig. 3 TEM micrographs of the $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ ceramics annealed at 900°C for different time (a) 1 h, (b) 4 h, (c) 24 h

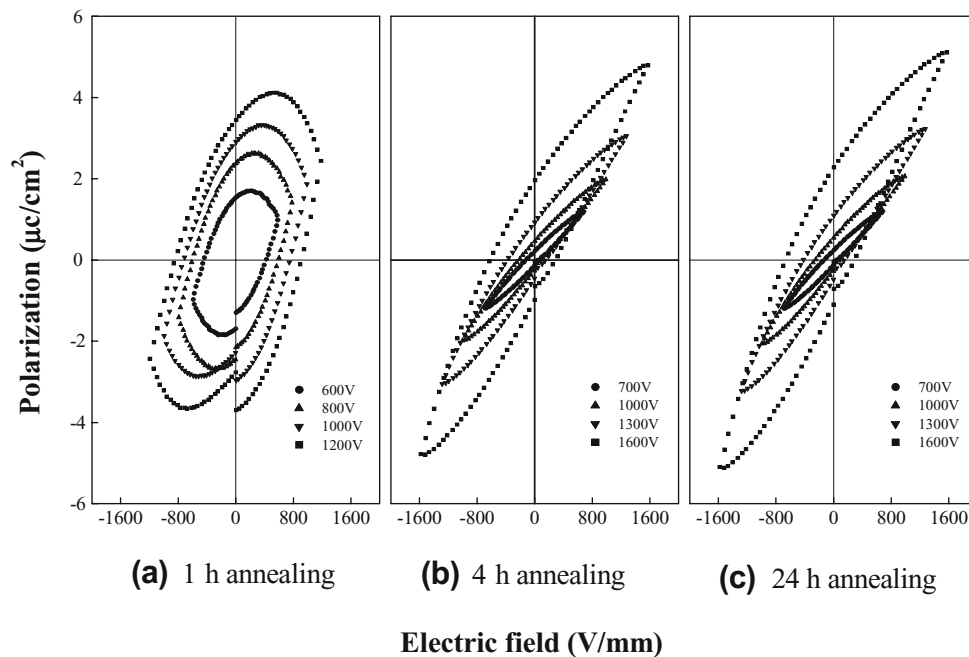


Fig. 4 *P*–*E* hysteresis loops of the $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ ceramics annealed at 900 °C for 1, 4 and 24 h, respectively

peaks of the $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ ceramic are consistent with those of NaNbO_3 and KNbO_3 , suggesting that single perovskite structure was formed. The little shift of peaks with increasing annealing time probably was caused by the volatilization of sodium and potassium component.

Figure 2 shows the change in sintered density of the SPSed sample as a function of annealing time. The

densities of specimens of 1 and 4 h annealing are the same, with the bulk density being 4.47 g/cm³ and the relative density reaching 99%. But the bulk density declined to 4.29 g/cm³ when the annealing time was extended to 24 h. Overtime annealing treatment caused high volatilization.

Figure 3 shows TEM micrographs of the $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ ceramics annealed at 900 °C for different time, respectively.

Fig. 5 Temperature dependences of relative dielectric constant and loss of the $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ ceramics annealed at 900 °C for 1, 4 and 24 h, respectively

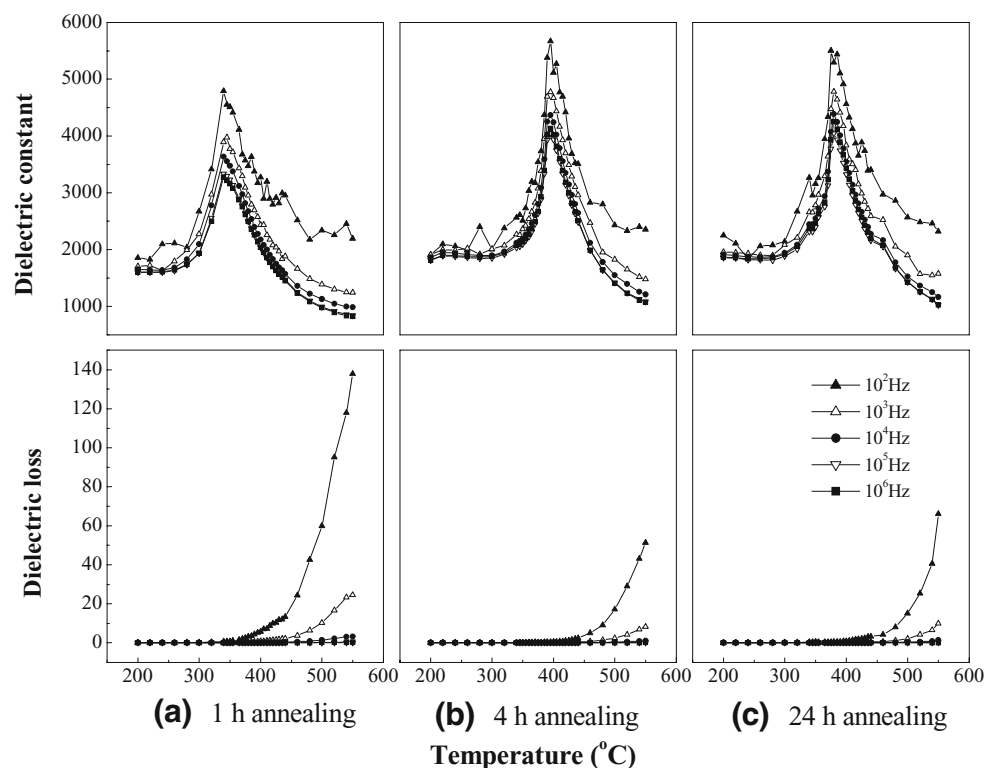


Table 1 Piezoelectric constants (d_{33}) and planar mode electromechanical coefficients (k_p) of $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ ceramics annealed at 900 °C for 1, 4 and 24 h, respectively.

Annealing time	1 h	4 h	24 h
d_{33} (pC/N)	148	148	150
k_p (%)	39.7	38.9	43.0

As clearly shown by the TEM micrograph, the grain sizes were in the range of 200–500 nm, and no apparent grain growth was observed even though the annealing time was increased. The annealing temperature may be too low to facilitate the grain growth.

Figure 4 shows the P – E hysteresis loops of the $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ ceramics annealed at 900 °C for 1, 4 and 24 h, respectively. The fat polarization hysteresis loop of the sample annealed for 1 h showed high current leakage at high voltage. The slim polarization hysteresis loops of the samples annealed for 4 and 24 h indicated better ferroelectric properties. The average coercive electric field (E_c) and remanent polarization (P_r) are 6 kV/cm and about 1 $\mu\text{C}/\text{cm}^2$, respectively. The low P_r may be attributed to fine grain size as shown in Fig. 4. For the SPSed samples, annealing in air was necessary to compensate for the oxygen deficiency caused during SPS, which was conducted under reduced atmosphere with graphite die and in vacuum. This is visible by the color difference before and after annealing. The present result suggested that annealing for >1 h was needed even though the color was the same for the samples with annealing time of 1 and 4 h.

Figure 5 shows the temperature dependences of relative dielectric constant and loss of the $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ ceramics annealed for 1, 4 and 24 h at 900 °C. The relative dielectric permittivity increased rapidly from 300 °C and reached a peak at the temperature corresponding to Curie temperature (T_c). Accordingly, dielectric loss factor increased sharply as the temperature was increased closely to Curie temperature. However, the Curie temperature of the sample annealed for 1 h (340 °C) was lower than that of the other two samples annealed for 4 and 24 h, which were 395 and 380 °C, respectively; and the dielectric loss for the sample annealed for 1 h was the largest, as shown in Fig. 5. These results suggested that annealing for 1 h was not sufficient to eliminate the oxygen vacancy in the SPSed samples, so that the corresponding sample showed lower T_c and larger dielectric loss as compared to those samples annealed for 4 and 24 h.

Table 1 lists the piezoelectric constant (d_{33}) and planar mode electromechanical coefficient (k_p) of $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ ceramics annealed for 1, 4 and 24 h at 900 °C. Being

different from the above results, these two parameters did not change much while altering annealing time. The piezoelectric constants (d_{33}) were around 150 pC/N and planar mode electromechanical coefficients (k_p) were about 40%. This value is reasonably high for the KNbO_3 and NaNbO_3 system without other special dopants. In fact, according to the relationship between d_{33} and grain size for $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ -based ceramics [11], the d_{33} value can be further raised by properly increasing the grain size.

4 Conclusion

Sodium potassium niobate ceramics with the nominal composition of $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ were fabricated successfully using spark plasma sintering (SPS) at low temperatures (920 °C). By post-annealing treatment in air, the SPSed $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ ceramic sample shows typical ferroelectric and piezoelectric characteristics. The best annealing time, that is 4 h at 900 °C, was obtained after systemic comparisons. Although the fabricating conditions were not optimized at present, the resultant $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ ceramics show considerably high d_{33} of 148 pC/N.

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References

1. L. Egerton, D.M. Dillon, *J. Am. Ceram. Soc.* **42**, 438 (1959)
2. R.E. Jaeger, L. Egerton, *J. Am. Ceram. Soc.* **45**, 209 (1962)
3. B.T. Matthias, J. Remeika, *Phys. Verh.* **82**, 727 (1951)
4. T. Wada, K. Tsuji, T. Saito, Y. Matsuo, *Jpn. J. Appl. Phys.* **42**, 6110 (2003)
5. Y. Guo, K. Kakimoto, H. Ohsato, *Appl. Phys. Lett.* **85**, 4121 (2004).
6. R. Wang, R. Xie, T. Sekiya, Y. Shimojo, *Mater. Res. Bull.* **39**, 1709–1715 (2004)
7. M. Matsubara, K. Kikuta, S. Hirano, *J. Appl. Phys.* **97**, 114105 (2005)
8. B.-P. Zhang, L.-M. Zhang, J.-F. Li, H.-L. Zhang, S.-Z. Jin, *The Fifth Pacific Rim International Conference On Advanced Materials And Processing*, Pts 1-5 Materials Science Forum, 475–479 (2005)
9. J.-F. Li, K. Wang, B.-P. Zhang and L.-M. Zhang, *J. Am. Ceram. Soc.*, (2005) (accepted)
10. Y. Saito, H. Takao, I. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, M. Nakamura, *Nature* **432**, 84–87 (2004)
11. K. Takagi, S. Kikuchi, J.-F. Li, H. Okamura, R. Watanabe, A. Kawasaki, *J. Am. Ceram. Soc.*, **87**, 8 (2004)