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Densification of (Na,K)NbO$_3$ piezoelectric ceramics by two-step mixing process

Satoru Ishihara · Ken-ichi Kakimoto · Isao Kagomiya

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Abstract Lead-free Na$_{0.5}$K$_{0.5}$NbO$_3$ (NKN) piezoelectric ceramics were sintered with a new process, "two-step mixing process," in which a part of alkali source powders was initially preserved and mixed with the rest matrix powders after the calcinations step. As a result, the sintering of NKN ceramics was improved, and the sample sintered at 1082 °C with the initial preservation ratio (R_A) of 5% demonstrated the highest density of $\rho = 4.38$ g/cm^3 (97.1% of the theoretical density), compared with $\rho = 4.36$ g/cm^3 (96.7% of the theoretical density) for the non-preservation specimen ($R_A = 0\%$). The former sample showed the best piezoelectric constant of $d_{33} = 125$ pC/N and electromechanical coupling coefficient of $k_p = 0.42$, while the latter sample had $d_{33} = 116$ pC/N and $k_p = 0.37$. These results indicated that the two-step mixing process was effective for the sintering of lead-free NKN ceramics, despite no sintering additive and cold isostatic pressing were used.

Introduction

Pb(Zr,Ti)O$_3$ (PZT) family ceramics are the most popular industrial piezoelectric materials due to their excellent piezoelectric properties. However, the toxicity of lead oxide and its high vapor pressure during processing have led to a strong demand for the development of alternative lead-free piezoelectric materials, such as alkali niobate ceramics. Na$_{0.5}$K$_{0.5}$NbO$_3$ (NKN) is one of basic alkali niobate compositions and has a long history of the research since 1950s [1–4]. At present, further improvement in the piezoelectric property is strongly required for NKN-based alkali niobates to be applied for industry. Most of the NKN ceramics fabricated by pressure-less conventional sintering has showed relatively lower electrical performance due to the difficulty in the processing of dense ceramics. Successful results were only reported in the studies based on the pressure sintering such as hot-press (HP) and spark-plasma sintering (SPS) [3, 5–10]. In general, the pressure sintering technique is effective not only to densify the ceramics, but also to decrease their sintering temperatures; however, such pressure sintering techniques are not best suitable for industrial application due to their low mass productivity. Thus, a number of studies have been carried out to improve the densification and piezoelectric properties of NKN ceramics by the selection of good sintering additives [11–17]. However, it is generally accepted that only limited additives are able to increase both of the density and piezoelectric property, whereas the most of additives decrease piezoelectric property even if they are effective for the densification.

In this study, a new easy process in which a part of alkali source powders was initially preserved and mixed with the rest matrix powders after the calcinations step has been proposed in order to improve both of the density and

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S. Ishihara (✉) · K. Kakimoto · I. Kagomiya
Department of Materials Science and Engineering,
Graduate School of Engineering, Nagoya Institute of
Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan
e-mail: ishihara@etigo.nagaokaut.ac.jp

Present Address:
S. Ishihara
Extreme Energy–Density Research Institute, Nagaoka University
of Technology, 1603-1 Kamitomioka, Nagaoka,
Niigata 940-2188, Japan

piezoelectric properties of NKN ceramics fabricated by pressure-less sintering without using any additive element.

Experimental procedure

The new process was based on the conventional mixed-oxide route, except for an original way of the mixing step for alkali sources. The starting chemicals used in this study were Na_2CO_3, K_2CO_3, and Nb_2O_5 of 99.9% purity to prepare $Na_{0.5}K_{0.5}NbO_3$ (NKN) ceramics. A part of alkali source powders of Na_2CO_3 and K_2CO_3 was initially preserved and mixed with the rest matrix powders after the calcinations step. The preservation ratio in wt% of the alkali sources against the total amount of alkali sources was described as R_A. In this study, the samples with $R_A = 2$, 5, 7, or 10% were prepared in addition to the sample with $R_A = 0\%$ which corresponds to the ordinal weighing for the preparation of NKN ceramics. The weighed mixture was milled in polyethylene bottles with ZrO_2 balls for 12 h using acetone as a medium. After the calcination in air at 850 °C for 10 h, the calcined powders were mixed with the additional Na_2CO_3 and K_2CO_3 powders which was equal to the preservation amount (R_A) at the first mixing. The mixed powders were ball-milled again in acetone for 24 h and dried, then polyvinyl butyral (PVB) was added as a binder. These powders were subsequently granulated and pressed into disks of 12 mm in diameter under 98 MPa. These powder compacts were sintered in air at temperatures in the range between 1062 and 1098 °C for 2 h. At the calcination and sintering stages, the samples were set in closed alumina crucibles to control volatilization of Na and K.

The bulk densities of the sintered samples were measured by the Archimedes method using distilled water as a medium. Their crystal structures were determined by X-ray powder diffraction (XRD, Rigaku; RAD-C system). The micrographs of the as-polished and thermally etched samples were obtained by a laser microscope (Model VK-9700II, Keyence). Thermo gravimetric differential analysis (TG-DTA) during sintering was carried out using model DTG-60, Shimadzu.

To investigate the electric properties, careful polishing and grinding steps were carried out for each pellet to obtain parallel surfaces, and silver pastes were fired at 750 °C on their major two surfaces as electrodes. For the piezoelectric measurement, the samples were immersed in silicone oil and electrically poled at 150 °C for 30 min under an applied electric field of 3 kV/mm. The electromechanical coupling factor k_p was determined using the resonance and antiresonance method based on IEEE standards using an impedance analyzer (4294A, Agilent Technologies Inc., Palo Alto, CA). The piezoelectric constant d_{33} was measured using a quasi-static d_{33} meter (ZJ-6B, Institute of Acoustics, Academia Sinica, Beijing, China).

Results and discussion

As a preliminary experiment to determine the sintering temperature of NKN ceramics ($R_A = 0\%$), the powder compacts were sintered at various sintering temperatures. The bulk densities of the sintered samples are shown as plots of open circle in Fig. 1. The bulk density of the sintered NKN samples ($R_A = 0\%$) increased with sintering temperature up to 1082 °C, then decreased at 1098 °C. The sample with $R_A = 5\%$ also showed a similar trend against sintering temperature, and the maximum bulk density was obtained at 1082 °C.

Figure 2 shows the variation in the density measured for the samples with different R_A. The results obtained at 1098 °C were also plotted for comparison. The bulk density of samples sintered at 1082 °C (open circle marks) increased with R_A, and then slightly decreased above $R_A = 5\%$. This fact suggests that the two-step mixing process is effective to improve sintering for NKN ceramics without any additive element. The maximum bulk density of the sintered samples which was fabricated under the condition of $R_A = 5\%$ was 4.38 g/cm^3. This value corresponds to 97.1% of the theoretical density for NKN ceramics, $\rho_{TD} = 4.51$ g/cm^3 [3]. The apparent specific density (closed circle marks) is compared with the each bulk density in Fig. 2. The apparent specific densities hardly changed when R_A was varied from 0 to 5%, and these were almost the same values as the bulk density measured for the sample with $R_A = 5\%$. At higher R_A than

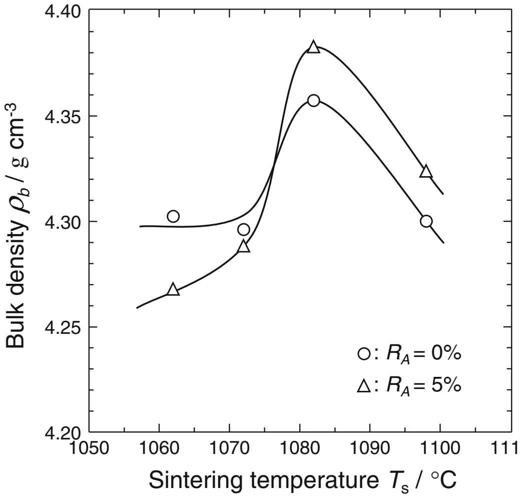


Fig. 1 Bulk density of the NKN and the $R_A = 5\%$ (the mixing ratio of the two-step mixing process) samples sintered at various temperatures

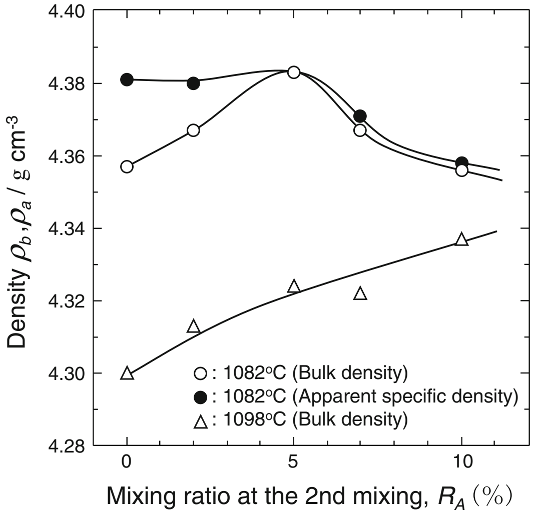
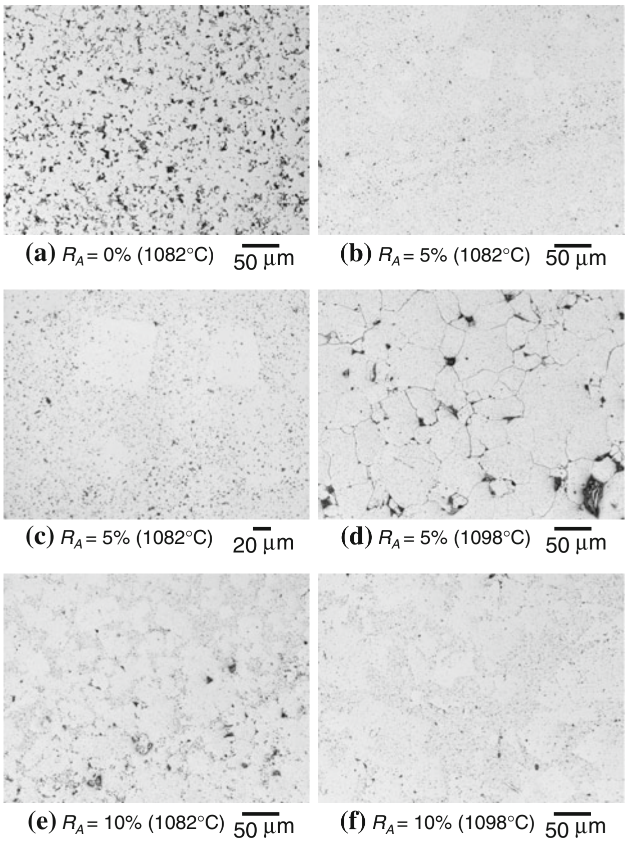


Fig. 2 Density of the sintered samples with various mixing ratio (R_A) of the two-step mixing process

5%, the apparent specific density almost equals to the each bulk density indicating almost no open porosity in the samples. On the other hand, the bulk density of the samples sintered at 1098 °C (plotted as triangle marks) was lower than the samples sintered at 1082 °C in any case where R_A was varied.

Figure 3 shows the as-polished cross-sectional microstructures of the sintered samples. The black or gray parts represent pores in these microstructures. The pore of the sample ($R_A = 5\%$) sintered at 1082 °C, as shown in Fig. 3b, c, shows much finer than that of the sample with $R_A = 0\%$ (Fig. 3a). Here, it should be noted that the pores of the sample with $R_A = 0\%$ may have been shown larger than actual pores, since ceramic particles of the sample are easily removed during the polishing. In contrast, the sintering at higher temperature of 1098 °C brought large pores (Fig. 3d). In the case of $R_A = 10\%$, however, pores are finer in size at the sintering temperature of 1098 °C (Fig. 3f) rather than 1082 °C (Fig. 3e). The XRD patterns of the samples sintered at 1082 °C are shown in Fig. 4. All of the patterns can be identified as an orthorhombic perovskite structure, and peak shifts are not recognized among the samples. These results imply that their chemical compositions are hardly affected even if their mixing procedures are different.


(a) R_A = 0% (1082°C) 50 µm **(b)** R_A = 5% (1082°C) 50 µm

(c) R_A = 5% (1082°C) 20 µm **(d)** R_A = 5% (1098°C) 50 µm

(e) R_A = 10% (1082°C) 50 µm **(f)** R_A = 10% (1098°C) 50 µm

Fig. 3 As-polished cross-sectional microstructures of the sintered samples with various mixing ratio (R_A) of the two-step mixing process, **a** $R_A = 0\%$ (NKN) sintered at 1082 °C. **b**, **c** $R_A = 5\%$ sintered at 1082 °C (**c** is enlarged section). **d** $R_A = 5\%$ sintered at 1098 °C. **e** $R_A = 10\%$ sintered at 1082 °C. **f** $R_A = 10\%$ sintered at 1098 °C

Figure 5 shows the thermally etched cross-sectional microstructures of the samples sintered at 1082 °C with various R_A. While the microstructure of the sample with $R_A = 0\%$ consists of relatively uniform grain-size distribution (Fig. 5a), the sample with $R_A = 5\%$ has bimodal structure which consists of some coarse rectangular grains having 30 µm and larger in size (Fig. 5b) and fine matrix grains with the average size of around 1 µm (Fig. 5c). The microstructure of the sample with $R_A = 10\%$ also shows a similar bimodal microstructure consisting of coarse grains and fine grains (Fig. 5d), but the number of coarse grains increases. The change in the grain-size distribution from uniform to bimodal is also reported in the samples that are sintered at increased sintering temperatures or sintered together with effective sintering additives [18, 19]. These structural changes are explained in terms of a reduction in the critical driving force for grain growth [18, 20, 21]. Based on this idea, structural change observed in this study also suggests that the degree of sintering was improved as a function of the R_A value.

The thermogravimetric and differential thermal analysis (TG-DTA) curves measured for the powder sources during sintering process are shown in Figs. 6 and 7. While the TG curve of the sample with $R_A = 0\%$ shows little weight loss at temperatures ranging from 670 to 940 °C, gradual weight losses occurs in the samples with R_A = 2–10% at the same temperature range. This weight loss suggests continued decomposition of the second Na_2CO_3 and K_2CO_3 powder sources. On the other hand, a large endothermic reaction is recognized at 1130 °C in the DTA

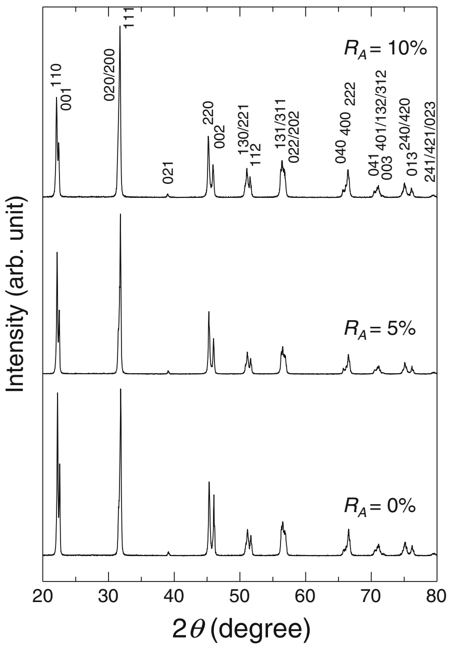


Fig. 4 X-ray diffraction patterns of the samples sintered at 1082 °C with various mixing ratio (R_A) of the two-step mixing process

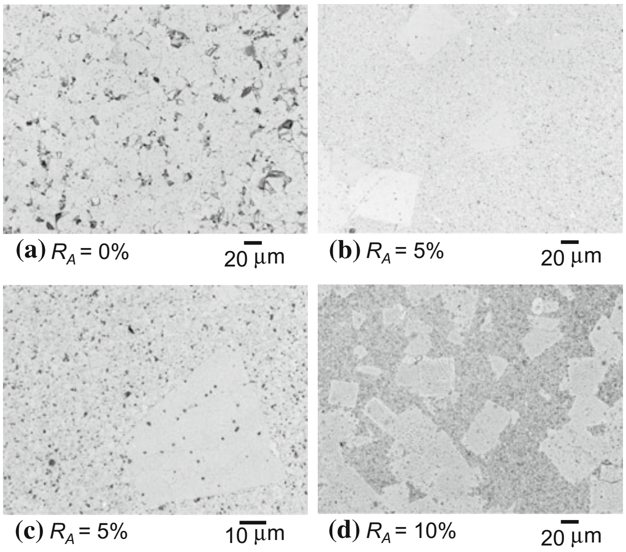


Fig. 5 Thermally etched cross-sectional microstructures of the samples sintered at 1082 °C with various mixing ratio (R_A) of the two-step mixing process: **a** $R_A = 0\%$ (NKN); **b**, **c** $R_A = 5\%$ (**c** is enlarged section); and **d** $R_A = 10\%$

curves of the samples with $R_A = 0–7\%$. This endothermic reaction is considered to have been caused by the formation of a liquid phase. The pseudo-binary phase diagram of the $KNbO_3–NaNbO_3$ system was reported by Jeffe et al. [22]. The melting point of $KNbO_3$ and $NaNbO_3$ compounds are at 1040 and 1420 °C, respectively. These compounds form a solid solution across the whole compositional range. For $Na_{0.5}K_{0.5}NbO_3$, the solidus and liquidus lines are at about 1140 and 1280 °C, respectively. In the case of the experimental data on the DTA curves of the samples with $R_A = 0–7\%$, the large endothermic reaction is recognized at 1130 °C which is almost same as the temperature of the above-mentioned solidus line. This fact is important to be noted, and suggests all of the sintered samples, even having different R_A in the range of 0–7%, kept compositions close to the nominal composition of $Na_{0.5}K_{0.5}NbO_3$. However, no endothermic reaction is recognized at the lower sintering temperatures of 1082 and 1098 °C; therefore, the main densification mechanism in the samples with $R_A = 5\%$ was not based on liquid sintering. The decomposition of sodium carbonate and potassium carbonate, and the diffusion of such sodium and potassium ions into Nb_2O_5 grains make progress continuously up to the sintering temperatures. While such phenomena caused the weight loss in the TG curves as seen in Fig. 6, they were not detected as large peaks in the DTA curves presented in Fig. 7. It is therefore considered that the decomposition of the carbonates must have made progress gradually, and the thermal change was too small to be detected.

Kosec and Kolar [23] reported that the relative density of $Na_{0.5}K_{0.5}NbO_3$, that were sintered by conventional technique, was increased from 94.5 to 97.1% of theoretical density by introducing 1% of Mg ion as an A-site dopant. They found that the density of $Na_{0.5}K_{0.5}NbO_3$ could be promoted by introducing A-site vacancies in the perovskite lattice, and this was also observed even in the samples in which their composition were “Nb-excess” compared with

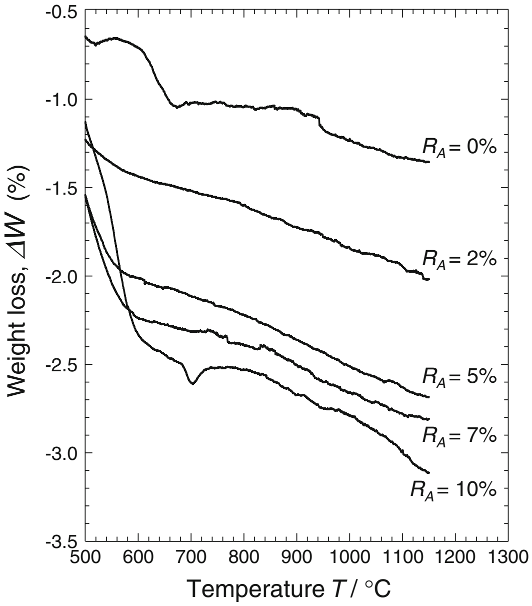


Fig. 6 Thermogravimetric analysis (TGA) curves of the calcined powders mixed with various mixing ratio (R_A) of the two-step mixing process

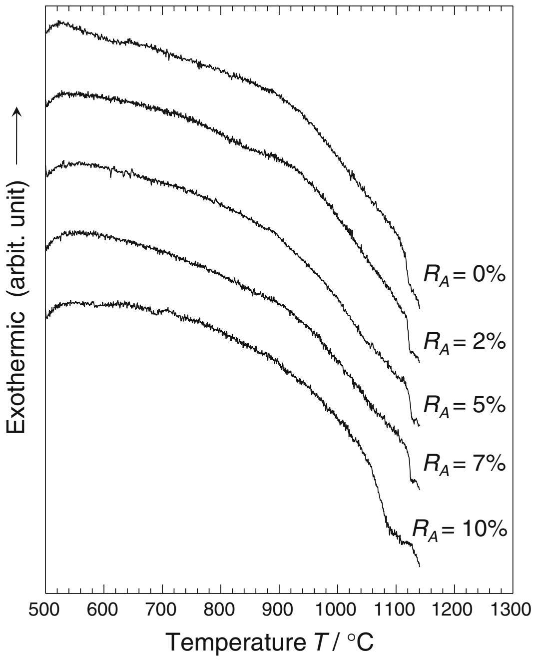


Fig. 7 Differential thermal analysis (DTA) curves of the calcined powders mixed with various mixing ratio (R_A) of the two-step mixing process

A-site alkali elements, and in another experiment where Ca and Sr dopants were used [16].

Similar to them, A-site vacancies must have formed in the calcined powders in this study, since a part of alkali source powders of Na_2CO_3 and K_2CO_3 initially preserved against the stoichiometric mixture ratio to Nb_2O_5 powder. As a result, the second alkali source powders could diffuse along the A-site vacancies during the next sintering step in order to contribute to densification of $Na_{0.5}K_{0.5}NbO_3$ ceramics and to decrease the critical driving force for grain growth. The reduction in the critical driving force brought the microstructure evolution consisting of a bimodal grain-size distribution. It should be therefore noted that the present “two-step mixing process” can introduce A-site vacancies in the perovskite lattice without using any additive element.

It is further interesting to note that the DTA curve of the sample with $R_A = 10\%$ indicates an endothermic reaction at about 1070 °C which is lower than its sintering temperature, as shown in Fig. 7. This may indicate that the alkaline constituents added at the second mixing step could not completely dissolve in the peroveskite lattice, and K-rich portions in the sample might melt to form small amount of a liquid phase. The liquid phase is also effective to decrease the open porosity, but the deviation from the stoichiometric composition might be the reasons why the lower density was measured in the samples with R_A above 5%.

The piezoelectric constant, d_{33}, and the electromechanical coupling coefficient, k_p, of the samples sintered at 1082 °C are shown in Figs. 8 and 9, respectively.

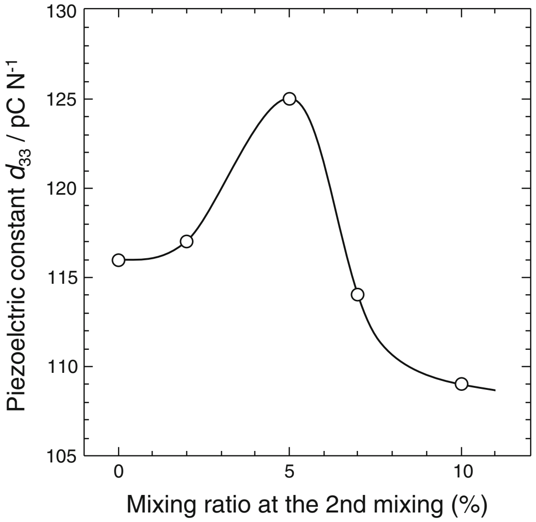


Fig. 8 Piezoelectric constant, d_{33}, of the samples sintered at 1082 °C with various mixing ratio (R_A) of the two-step mixing process

As similar to the measurement of the bulk density, both of the properties increased up to R_A of 5%, and then decreased. The best piezoelectric properties measured in this study were $d_{33} = 125$ pC/N and $k_p = 0.42$ at $R_A = 5\%$ at which the most dense sample was obtained. These values are quite high level in this field.

The improvement of the piezoelectric properties seems to have been caused mainly by the increase of the bulk density. In addition, a specific microstructure development, such as the mixture of fine matrix grains with the average size of around 1 μm and some coarse rectangular grains, is also possible to be connected in the enhancement of the piezoelectric properties for the sample with $R_A = 5\%$.

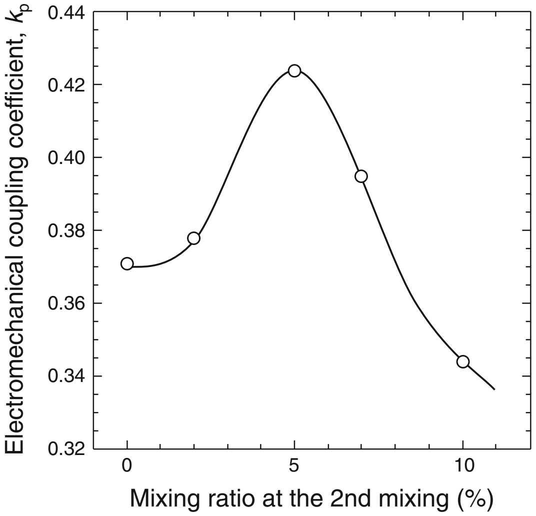


Fig. 9 Electromechanical coupling coefficient, k_p of the samples sintered at 1082 °C with various mixing ratio (R_A) of the two-step mixing process

Summary

The new sintering process, “two-step mixing process” has been developed to improve density and piezoelectric properties of lead-free NKN-based ceramics. A part (R_A) of alkali source powders of Na_2CO_3 and K_2CO_3 was initially preserved and mixed with the rest matrix powders after the calcinations step. As a result, the sintering of NKN ceramics was much improved, and the sample was prepared by $R_A = 5\%$ and sintered at 1082 °C demonstrated the highest density of $\rho = 4.38$ g/cm^3, which corresponds to 97.1% of the theoretical density. This sample also showed the best piezoelectric properties of $d_{33} = 125$ pC/N and $k_p = 0.42$. These results indicate that the two-step mixing process is effective for the densification of lead-free NKN ceramics, despite no sintering additive and cold isostatic pressing are used.

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