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Piezoelectric properties of CuO-added $(Na_{0.5}K_{0.5})NbO_3$ ceramic multilayers

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Abstract

Multilayered ceramics (MLCs) laminated with 20 layers of CuO-added $(Na_{0.5}K_{0.5})NbO_3$ (CNKN) tape were well sintered at 960 °C with an average grain size of 5.0 μm. They exhibited good piezoelectric properties of $\varepsilon_{33}^T/\varepsilon_0 = 709$, $d_{33} = 114$ pC/N, $k_p = 0.34$ and $Q_m = 793$. The 80Ag/20Pd electrodes were well formed on the CNKN MLCs when they were co-fired at 960 °C for 2 h. A piezoelectric speaker fabricated using 6-layer CNKN MLCs exhibited an average sound pressure level (SPL) of 75 dB in the range between 300 and 20,000 Hz with a maximum SPL of 90 dB. This value is comparable with that of a loud stereo radio, indicating that the CNKN MLC is a good candidate material for piezoelectric speakers.

Keywords: Piezoelectric properties; Tape casting; Perovskite; Microstructure-final; Speaker

1. Introduction

$Pb(Zr,Ti)O_3$ (PZT)-based ceramics have outstanding dielectric and piezoelectric properties and are widely used for actuators, sensors, transformers and other piezoelectric devices.[1] However, the 60 wt% Pb content in these materials presents an environmental problem. Therefore, extensive investigations have been conducted to find lead-free piezoelectric materials for the replacement of PZT-based ceramics.[2–6] In particular, $(Na_{1-x}K_x)NbO_3$ (NKN) ceramics have attracted considerable attention because of their high piezoelectric properties and a high Curie temperature.[7–9] However, the sintering temperatures of NKN-based ceramics are generally high (≥1050 °C).[10–13] Therefore, for the application to multilayer devices, which are required to achieve a low driving force, as well as miniaturization and hybridization of the piezoelectric devices, the sintering temperature of NKN-based ceramics needs to be reduced to below 1000 °C. In particular, since Ag or 80Ag/20Pd is generally used as the electrode of the multilayer device, the NKN-based ceramics should be sintered at temperatures below1000 °C, which is the melting temperature of the 80Ag/20Pd electrode. The CuO-added and the CuO and ZnO co-doped NKN ceramics were reported to be sintered at 960 °C and 900 °C, respectively.[14,15] A V_2O_5 additive was also used to decrease the sintering temperature of the NKN ceramics to 900 °C. However, since the KVO_3 secondary phase, which was dissolved in the water, was formed, it was difficult to form the homogeneous NKN phase.[16] However, even though the displacement of the 0.95NKN–0.05$LiTaO_3$ multilayered ceramics (MLCs) was reported,[17] systematic investigations on the microstructure and the piezoelectric properties of the NKN-based multilayered ceramics and the properties of the NKN-based MLCs devices have not been reported. Therefore, in this work, NKN-based MLCs were fabricated under various process conditions and their microstructures and piezoelectric properties were systematically investigated. Moreover, the reaction between the NKN-based MLCs and the 80Ag/20Pd electrode was also studied. Finally, piezoelectric speakers were produced using the six-layers CuO-added NKN (CNKN) MLCs and their sound properties were evaluated.

2. Experimental procedures

Oxide compounds of K_2CO_3, Na_2CO_3, and Nb_2O_5 (all from High Purity Chemicals, >99%, Saitama, Japan) were mixed for

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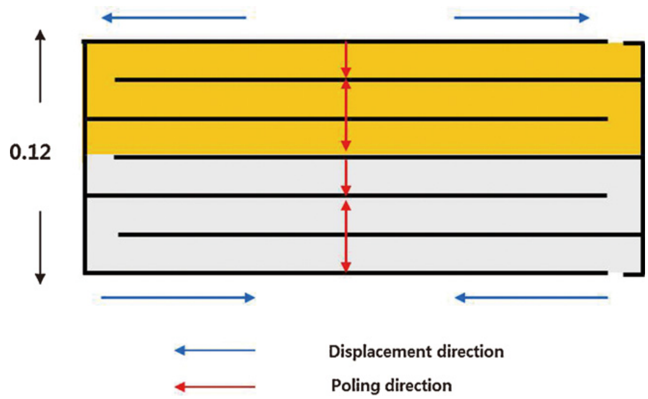

Fig. 1. Schematic diagram of the piezoelectric speaker consisting of six layers of CNKN tape.

24 h in a plastic jar with zirconia balls and then dried. The dried powders were calcined at 950 °C for 3 h. After re-milling with the CuO additive, the powders were dried and milled for 24 h with a polyvinyl alcohol solution (PVA, 20 wt% solution) to form a slurry, which was used to make thick films with a thickness of 40.0 μm. The thick films were produced by the doctor-blade method. The green sheets were cut into 25 mm × 25 mm pieces and an 80Ag/20Pd electrode was printed on the 40.0-μm thick CNKN green sheet using the screen-printing method. Six layers of sheets were laminated and the alternative internal electrodes were connected to the external electrode to synthesize piezoelectric speakers. The schematic diagram of the piezoelectric speaker is shown in Fig. 1. Moreover, 20 layers of CNKN green sheets were also laminated without an internal electrode for the analysis of the microstructure and the piezoelectric properties of the CNKN MLCs. The organic substances in the piezoelectric speakers and the 20 layers of MLCs were burned out at 500 °C for 10 h and they were subsequently sintered at various temperatures in the range 940–1000 °C. The microstructures and composition of the specimens were investigated by scanning electron microscopy (SEM: Hitachi S-4300, Osaka, Japan) and an energy dispersive X-ray (EDX: Horiba EMAX, Kyoto, Japan) spectroscope that was attached to the SEM. The densities of the sintered specimens were measured by a water-immersion method using the Archimedes principle. The specimens were poled in silicone oil at 120 °C by applying a DC field of 4.0 kV/mm for 60 min and the oil was then allowed to cool to room temperature while maintaining the applied voltage. The piezoelectric and dielectric properties of specimens were determined using a d_{33} meter (Micro-Epsilon Channel Product DT-3300, Raleigh, NC) and an impedance analyzer (Agilent Technologies HP 4294A, Santa Clara, CA) according to IEEE standards. The sound pressure level (SPL) of the piezoelectric speaker was measured using a sum of squares of regression (SSR) analyzer (Agilent Technologies AP240, Santa Clara, CA) at 5 V. The distance from the microphone was 10 cm. The sample was prepared to the KS CIEC 60268-5 standard.

3. Results and discussion

Fig. 2(a) and (b) shows SEM images of the fractured surface of the CNKN MLCs that were laminated with 20 layers

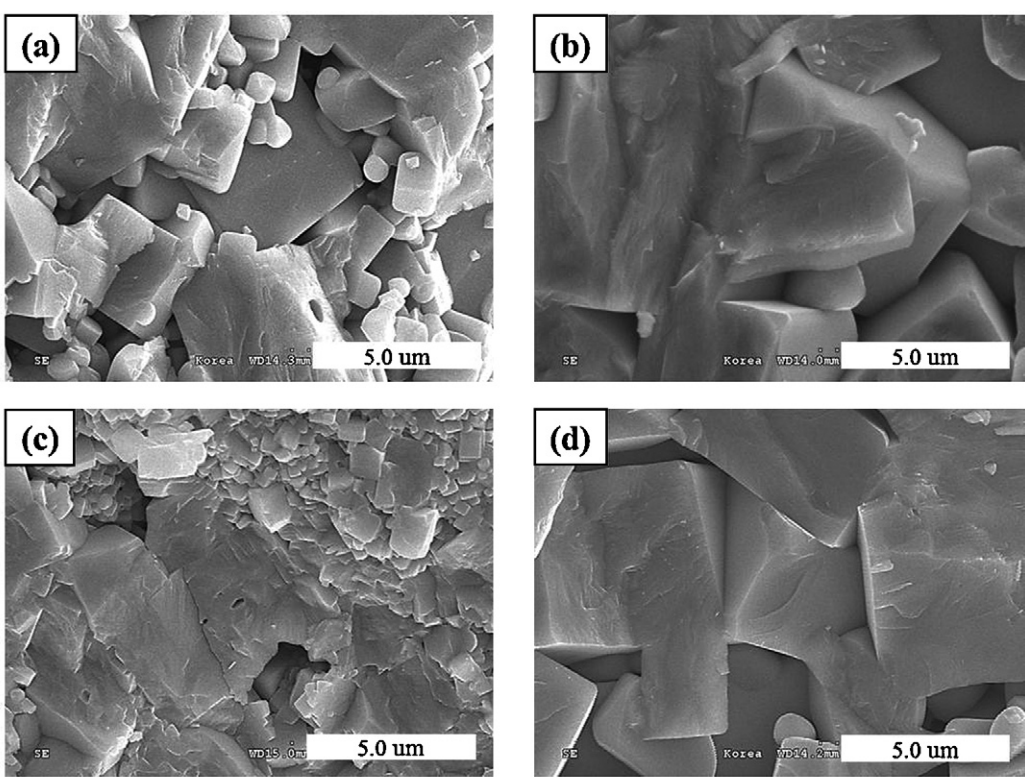

Fig. 2. SEM images of the fractured surface of the CNKN MLCs laminated with 20 layers of CNKN green tape without inner electrodes, sintered at various temperatures for various times: (a) 940 °C for 4 h, (b) 960 °C for 4 h, (c) 960 °C for 30 min, and (d) 960 °C for 2 h.

of CNKN green tape without inner electrodes and sintered at various temperatures for 4 h. For the MLC sintered at 940 °C, an inhomogeneous microstructure consisting of large and small grains was formed [see Fig. 2(a)], indicating the occurrence of incomplete grain growth. However, when the sintering temperature increased to 960 °C, a homogeneous and dense microstructure with large grains was developed, as shown in Fig. 2(b). SEM images of MLCs sintered at 960 °C for various times are shown in Fig. 2(c) and (d). An inhomogeneous microstructure was observed for the MLC sintered at 960 °C for 30 min, whereas a dense microstructure was developed for the MLC sintered for 2 h, indicating that the CNKN MLC needs to be sintered at 960 °C for more than 2 h for the formation of a homogeneous and dense microstructure. It is important to note that the size of the grains that developed in the MLC produced in this work was approximately 5.0 μm, which is much larger than that of the CNKN bulk ceramic (∼2.0 μm) sintered at 960 °C for 2 h.[14] Green tape is considered to have more pores than the green body of the bulk ceramics because organic materials were used to synthesize the green tape during the tape casting, whereas no organic materials were used to form the green body of the bulk ceramics. It is generally accepted that grain growth is expedited by the presence of pores.[18] Therefore, the larger grain size observed in the MLCs over bulk ceramics could be due to the presence of more pores in the green tape. The effect of the pores on the grain size of the tape was also explained in the previous work.[19]

The relative density, $\varepsilon_{33}^T/\varepsilon_0$, d_{33}, k_p, and Q_m values of the CNKN MLCs sintered at various temperatures are shown in Fig. 3. The relative density of the MLC sintered at 940 °C for 4 h was 94.1% of the theoretical density. This value increased with the increase of the sintering temperature and a high relative density, which was larger than 95.0% of the theoretical density, was obtained for MLCs sintered at temperatures ≥960 °C. Moreover, the MLC sintered at 960 °C for 2 h also exhibited a high relative density of 95.0% of the theoretical density, which is similar to that of the bulk CNKN ceramics with dense microstructures that were sintered under the same conditions.[14] The $\varepsilon_{33}^T/\varepsilon_0$ value of the MLCs sintered at 940 °C for 4 h was about 716 and it increased slightly with increasing sintering temperature. A maximum value of 778 was observed for the MLC sintered at 960 °C for 4 h. The MLC sintered at 960 °C for 2 h also exhibited a high $\varepsilon_{33}^T/\varepsilon_0$ value of 709. On the other hand, the bulk CNKN ceramic sintered at 960 °C for 2 h exhibited a small $\varepsilon_{33}^T/\varepsilon_0$ value of 229. Since the grain size of MLCs was much larger than that of the bulk ceramics, the large $\varepsilon_{33}^T/\varepsilon_0$ value observed in the MLCs could be explained by the increased grain size. The d_{33} value of all the MLCs ranged between 114 and 126 pC/N. This value is also larger than that of the bulk ceramics (∼90 pC/N) and it may be partially contributed by the larger grain size of the MLCs. The k_p value of the MLC sintered at 940 °C was low, approximately 0.28, probably due to the inhomogeneous microstructure and the low relative density. The k_p value increased with the sintering temperature to 0.36 for the specimen sintered at 960 °C for 4 h, which is comparable to that of the bulk ceramics (∼0.37).[14] In addition, the MLC sintered at 960 °C for 2 h also exhibited a large k_p value of 0.34. The Q_m value of the MLC sintered at 940 °C was low at about 285, probably due to the low density and inhomogeneous microstructure. The Q_m value increased with the sintering temperature and the MLC sintered at 960 °C for 2 h exhibited a high Q_m value of 793, which is comparable to that of CNKN bulk ceramics (∼844).[14] Therefore, the CNKN MLC sintered at 960 °C for 2 h, which exhibited a dense microstructure, had good piezoelectric properties of $\varepsilon_{33}^T/\varepsilon_0 = 709$, $d_{33} = 114$ pC/N, $k_p = 0.34$ and $Q_m = 793$.

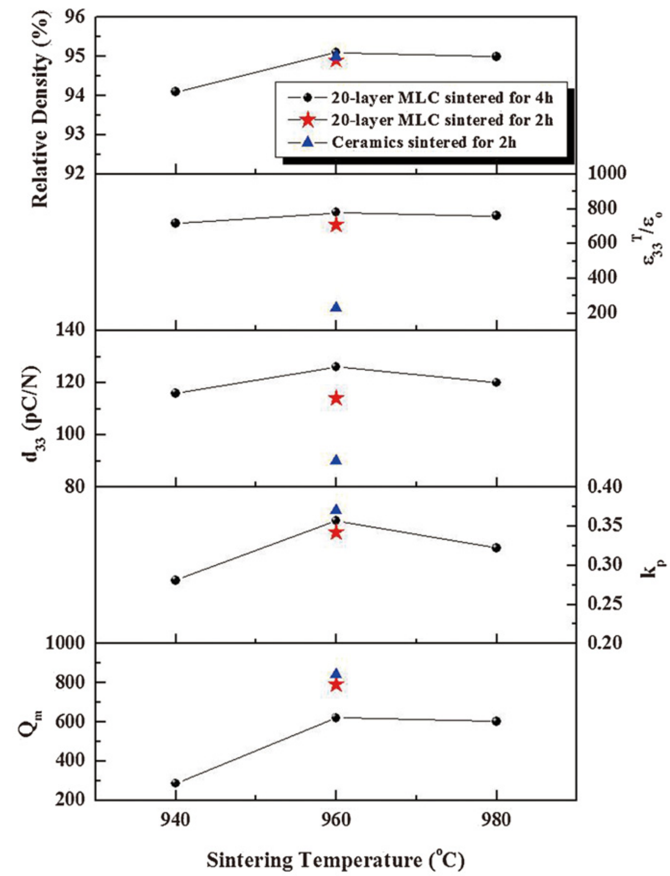

Fig. 3. Relative density, $\varepsilon_{33}^T/\varepsilon_0$, d_{33}, k_p, and Q_m values of the CNKN MLCs sintered at various temperatures for various times and the NKNC ceramics sintered at 960 °C for 2 h.

The 80Ag/20Pd electrodes were printed on the surface of the CNKN MLCs and sintered at various temperatures; their SEM images are shown in Fig. 4(a)–(d). For the specimen sintered at 940 °C for 4 h, the 80Ag/20Pd electrode was homogeneously formed on the surface of the MLC, as shown in Fig. 4(a), indicating that the shrinkage of the 80Ag/20Pd electrode was similar to that of the CNKN MLC sintered at 940 °C for 4 h. When the sintering temperature exceeded 940 °C with a sintering time of 4 h, some of the 80Ag/20Pd electrode disappeared and the MLC surface not covered by the electrode was exposed to the air, as shown in Fig. 4(b) and (c). According to previous works, the sintering temperatures of the pure Ag and 70Ag/30Pd electrodes were measured to be 800 °C and 830 °C, respectively.[20,21] Moreover, for the Ag electrode, obvious shrinkage behavior and partial coverage of the Ag electrode on the ceramic appear at 900 °C.[21] Therefore, it was considered that for the 80Ag/20Pd electrode, which was used in this work, the sintering

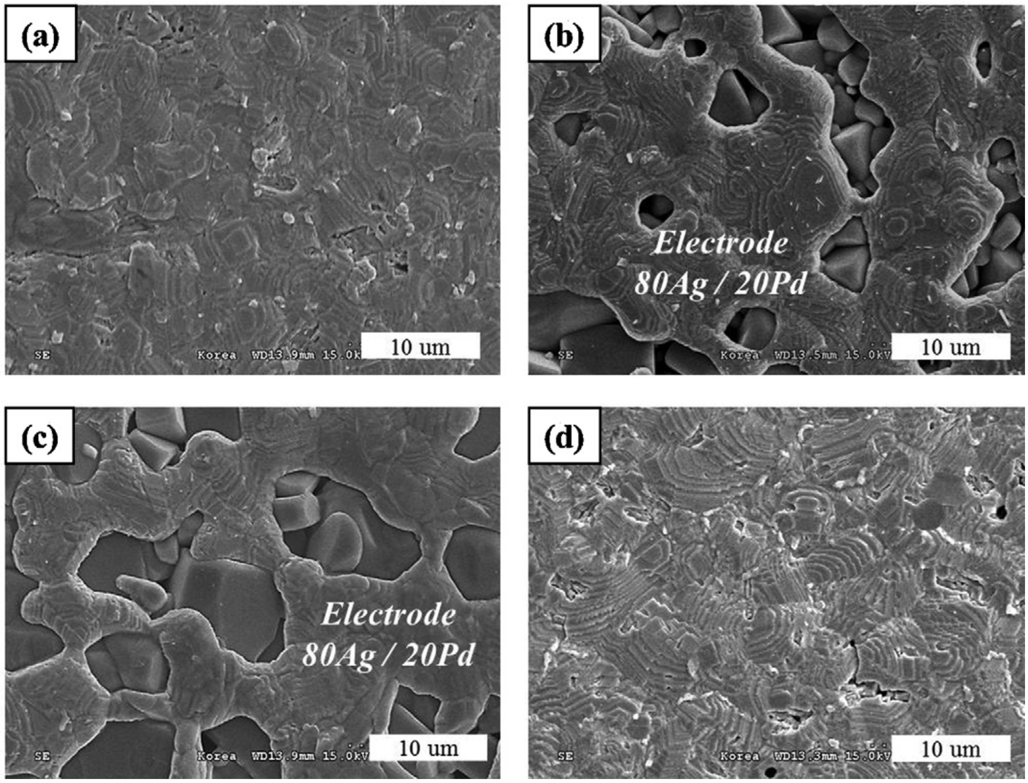

Fig. 4. Surface SEM images of CNKN MLCs with 80Ag/20Pd electrodes, which were sintered at various temperatures for various times:(a) 940 °C for 4 h, (b) 960 °C for 4 h, (c) 980 °C for 4 h, and (d) 960 °C for 2 h.

temperature is close to 820 °C and significant shrinkage with partial coverage of this electrode might occur near 950 °C. Therefore, it is considered that the partial coverage of this electrode, which was observed for the specimens sintered at temperatures above 940 °C for 4 h, occurred due to the greater shrinkage of the electrode. However, it is also possible that the partial coverage of the electrode could be due to the de-wetting of the electrode. On the other hand, for the specimen sintered at 960 °C for 2 h, the 80Ag/20Pd electrode completely covered the surface of the MLC [see Fig. 4(d)]. Therefore, the shrinkage of the 80Ag/20Pd electrode is influenced by the sintering time as well as the sintering temperature. Fig. 5(a) and (b) shows the cross-sectional SEM images of the MLCs sintered at 960 °C for 2 and 4 h, respectively, and the inner electrode of the MLCs is shown in these figures. For the specimen sintered for 2 h, the 80Ag/20Pd electrode was well formed without disconnects; the enlarged image also illustrates the good development of the electrode in this case. On the other hand, for the specimen sintered at 960 °C for 4 h, some part of the electrode was disconnected, as indicated by the arrowheads in Fig. 5(b). Therefore, for the formation of a homogeneous and continuous 80Ag/20Pd electrode, the CNKN MLCs should be sintered at 960 °C for 2 h.

EDX analysis was also conducted on the MLC sintered at 960 °C for 2 h, as shown in Fig. 6(a). The interface between the 80Ag/20Pd electrode and the CNKN tape was well developed and diffusion of Ag or Pd atoms into the CNKN tape was not detected. Furthermore, the XRD pattern of this specimen, shown in Fig. 6(b), did not show any peaks for secondary phases related

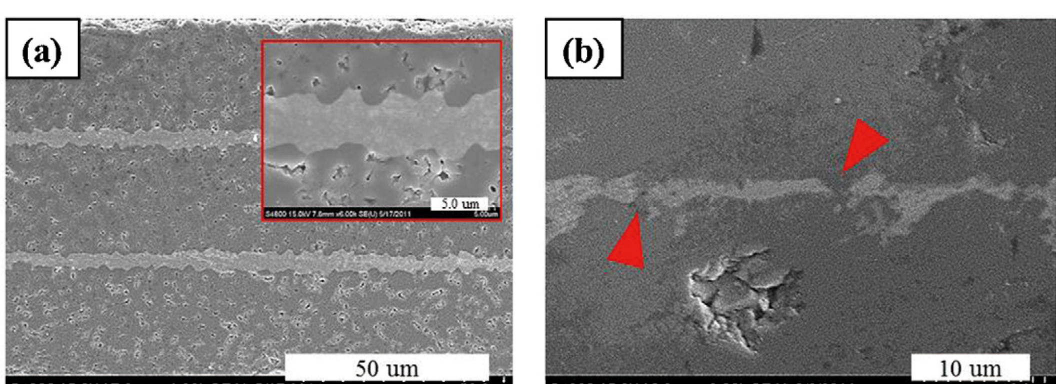

Fig. 5. Cross-sectional SEM images of the CNKN MLCs with inner electrodes sintered at 960 °C for (a) 2 h and (b) 4 h.

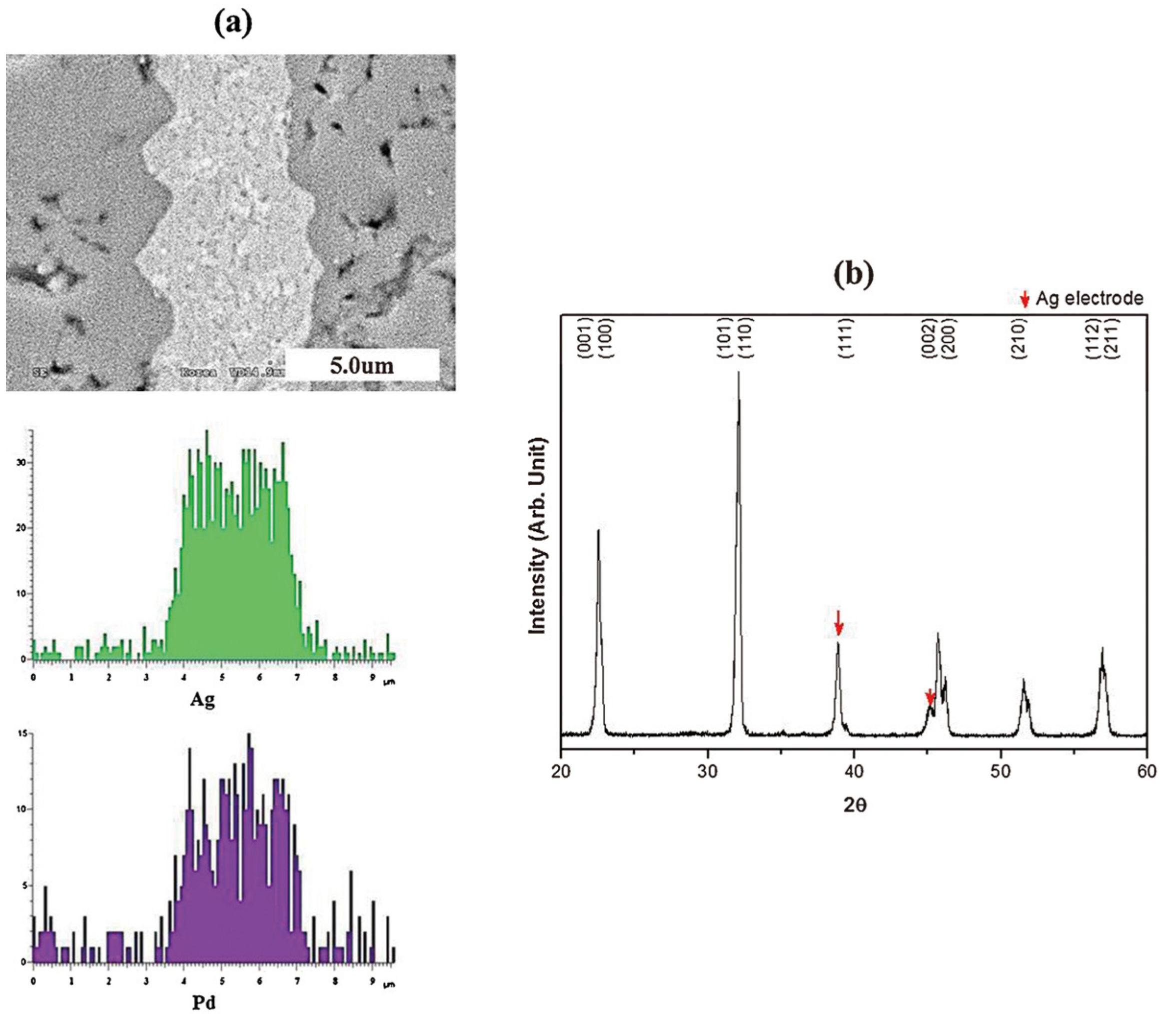

Fig. 6. (a) EDX line scan images and (b) XRD patterns of CNKN MLCs with the 80Ag/20Pd inner electrodes sintered at 960 °C for 2 h.

to the Ag and Pd metals. Therefore, it is considered that the MLCs with 80Ag/20Pd electrodes were well formed when they were sintered at 960 °C for 2 h. Furthermore, the 6-layers MLCs synthesized under these conditions show a high capacitance of 67 nF, confirming that the 80Ag/20Pd internal electrodes were well developed inside the MLC.

A piezoelectric speaker was fabricated using a MLC with six layers of CNKN tape and its schematic diagram is shown in Fig. 1. Fig. 7 shows the SPL curve of this piezoelectric speaker at 5 V and a maximum SPL of 90 dB was obtained at a resonance frequency of 7000 Hz. The SPL of the speaker is expressed by the following equations[22]:

$$\mathrm{SPL} = 10 \log 10 \left(\frac{I}{I_{\mathrm{ref}}} \right)$$

where I is the intensity of the sound and I_{ref} is the intensity of the reference, which is 20 μPa. Moreover, $I = (P_{\mathrm{m}}/2^{1/2})^2/(\rho c)$, where P_{m} is the maximum amplitude of the sound wave which is generated by the vibrating plate, i.e. the piezoelectric ceramics, while ρ is the density of the medium and c is the velocity of the sound wave in the medium. Therefore, SPL was increased with the increase of the amplitude of the vibration of the piezoelectric ceramics, which can be expressed by the d_{33} values of the piezoelectric materials. The capacitance of a single NKN tape used in this work was calculated to be 15–17 nF. On the other hand, the capacitance of the MLCs with 6 layers was measured to be 67 nF, indicating that the capacitance

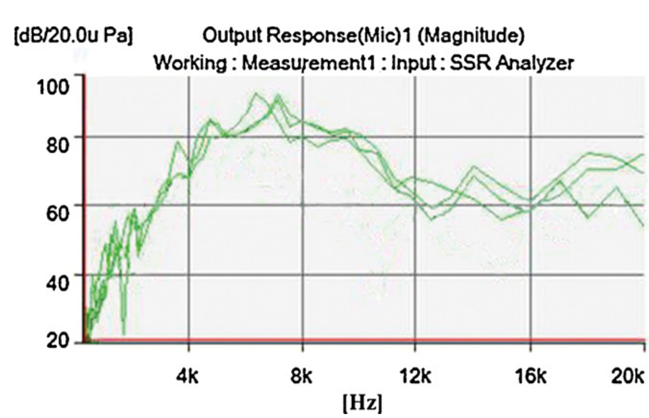

Fig. 7. SPL curve of the piezoelectric CNKN MLC speaker obtained at 5 V.

of MLCs was approximately 4 times larger than that of the single NKN tape. Moreover, the d_{33} of the MLCs was also considered to be 4 times amplified. Therefore, the high SPL value of our MLC device could be explained by the amplified d_{33} value of the MLCs, which also showed increased capacitance. Moreover, the average SPL of this device was 75 dB in the frequency range between 300 and 20,000 Hz, which is part of the audible frequency range. This SPL value is comparable to that of a loud stereo radio and it is also very similar to that of Pb-based piezoelectric speakers.[23,24] Therefore, the CNKN piezoelectric MLC speaker is a good candidate for lead-free audible sound devices. However, the SPL was relatively low at the frequencies below 2000 Hz. This low SPL value can be increased by changing the size and the shape of the speaker but more investigation is required to understand this behavior.[25]

4. Conclusions

CNKN MLCs were well formed with a dense and homogeneous microstructure when they were sintered at temperatures ≥960 °C. The average grain size of these MLCs was approximately 5.0 μm, which is much larger than that of bulk CNKN ceramics sintered under the same conditions. The k_p and Q_m values of the MLC sintered at 960 °C for 2 h were 0.34 and 793, respectively, which are similar to those of CNKN ceramics sintered under similar conditions. Their d_{33} and $\varepsilon^T_{33}/\varepsilon_0$ values were114 pC/N and 709, respectively, which are higher than those of bulk ceramics, and this is probably due to the increased grain size. The 80Ag/20Pd electrodes were not homogeneously formed on the MLCs when they were co-fired with MLCs at temperatures ≥960 °C for 4 h due to the large shrinkage of the 80Ag/20Pd electrode. However, when they were sintered at 960 °C for 2 h, the 80Ag/20Pd electrodes were well developed without diffusion of Ag or Pd ions into the CNKN layer. A piezoelectric speaker was fabricated using an MLC that consisted of six layers of CNKN tape. A maximum SPL of 90 dB was obtained at a resonance frequency of 7000 Hz and the average SPL of this device was 75 dB in the frequency range between 300 and 20,000 Hz. Therefore, the CNKN MLC is considered to a good Pb-free piezoelectric material for piezoelectric speakers.

References

1. Jaffe B, Cook WR, Jaffe H. *Piezoelectric ceramics*. 1st ed. New York: Academic; 1971.
2. Fujioka C, Aoyagi R, Takeda H, Okamura S, Shiosaki T. Effect of non-stoichiometry on ferroelectricity and piezoelectricity in strontium bismuth tantalate ceramics. *J Eur Ceram Soc* 2005;**25**:2723–6.
3. Yoshii K, Hiruma Y, Nagata H, Takenaka T. Electrical properties and depolarization temperature of $(Bi_{1/2}Na_{1/2})TiO_3$–$(Bi_{1/2}K_{1/2})TiO_3$ lead-free piezoelectric ceramics. *Jpn J Appl Phys* 2006;**45**:4493–6.
4. Nagata H, Yoshida M, Makiuchi Y, Takenaka T. Large piezoelectric constant and high Curie temperature of lead-free piezoelectric ceramic ternary system based on bismuth sodium titanate–bismuth potassium titanate–barium titanate near the morphotropic phase boundary. *Jpn J Appl Phys* 2003;**42**:7401–3.
5. Suzuki M, Nagata H, Ohara J, Funakubo H, Takenaka T. $Bi_{3-x}M_xTiTaO_9$ (M = La or Nd) ceramics with high mechanical quality factor Q_m. *Jpn J Appl Phys* 2003;**42**:6090–3.
6. Saito Y, Takao H, Tani T, Nonoyama T, Takatori K, Homma T, et al. Lead-free piezoceramics. *Nature* 2004;**432**:84–7.
7. Egerton L, Dillon DM. Piezoelectric and dielectric properties of ceramics in the system potassium sodium niobate. *J Am Ceram Soc* 1959;**42**:438–42.
8. Jaeger RE, Egerton L. Hot pressing of potassium–sodium niobates. *J Am Ceram Soc* 1962;**45**:209–13.
9. Haertling GH. Properties of hot-pressed ferroelectric alkali niobate ceramics. *J Am Ceram Soc* 1967;**50**:329–30.
10. Park HY, Ahn CW, Song HC, Lee JH, Nahm S, Uchino K, et al. Microstructure and piezoelectric properties of $0.95Na_{0.5}K_{0.5}NbO_3$-$0.05BaTiO_3$ ceramics. *Appl Phys Lett* 2006;**89**, 062906-1-3.
11. Cho KH, Park HY, Ahn CW, Nahm S, Uchino K, Park SH, et al. Microstructure and piezoelectric properties of $0.95(Na_{0.5}K_{0.5})NbO_3$–$0.05SrTiO_3$ ceramics. *J Am Ceram Soc* 2007;**90**:1946–9.
12. Song HC, Cho KH, Park HY, Ahn CW, Nahm S, Uchino K, et al. Microstructure and piezoelectric properties of $(1-x)(Na_{0.5}K_{0.5})NbO_3$–$x$LiNbO$_3$ ceramics. *J Am Ceram Soc* 2007;**90**:1812–6.
13. Park HY, Cho KH, Paik DS, Nahm S, Lee HG, Kim DH. Microstructure and piezoelectric properties of lead-free $(1-x)Na_{0.5}K_{0.5}NbO_3$–$x$CaTiO$_3$ ceramics. *Appl Phys Lett* 2007;**102**, 124101-1-5.
14. Park HY, Choi JY, Choi MK, Cho KH, Nahm S, Lee HG, et al. Effect of CuO on the sintering temperature and piezoelectric properties of $(Na_{0.5}K_{0.5})NbO_3$ lead-free piezoelectric ceramics. *J Am Ceram Soc* 2008;**91**:2374–7.
15. Park HY, Seo IT, Choi JH, Nahm S, Lee HG. Low-temperature sintering and piezoelectric properties of $(Na_{0.5}K_{0.5})NbO_3$ lead-free piezoelectric ceramics. *J Am Ceram Soc* 2010;**93**:36–9.
16. Seo IT, Park HY, Dung NV, Choi MK, Nahm S, Lee HG, et al. Microstructure and piezoelectric properties of $(Na_{0.5}K_{0.5})NbO_3$ lead-free piezoelectric ceramics with V_2O_5 addition. *IEEE Trans Ultra Ferro Freq Contr* 2009;**56**:2337–42.
17. Kim MS, Jeon SH, Lee DS, Jeong S.Jand Song JS. Lead-free NKN-5LT piezoelectric materials for multilayer ceramic actuator. *J Electroceram* 2009;**23**:372–5.
18. James S. *Reed principles of ceramics processing*. 2nd ed. New York: A Wiley-Interscience Publication; 1995.
19. Sumita S, Rhine WE, Kent Bowen H. Effects of organic dispersents on the dispersion, packing, and sintering of alumina. *J Am Ceram Soc* 1991;**74**:2189–96.
20. Lu W-H, Lee Y-C, Tsai P-R. Effect of sintering parameters on silver diffusion of (Zn,Mg)TiO_3 based multilayer ceramic capacitor. *Adv Appl Ceram* 2011;**110**:99–107.
21. Zuo R, Li L, Gui Z. Cofiring behaviors between BaTiO3-modified silver–palladium electrode and Pb-based relaxor ferroelectric ceramics. *Mater Chem Phys* 2001;**70**:326–9.
22. Yanagisawa T, Koike N. Cancellation of both phase mismatch and position errors with rotating microphones in sound intensity measurement. *J Sound Vib* 1987;**113**:117–26.
23. Schmette RM. Piezoelectric loudspeaker—its use in audio systems. *J Audio Eng Soc* 1972;**20**:687.
24. Lotton P, Bruneaua M, kvor ZS, Bruneaua AM. A model to describe the behaviour of a laterally radiating piezoelectric loudspeaker. *Appl Acoust* 1999;**58**:419–42.
25. Bai MR, Chen RL, Chuang CY, Yu CS, Hsieh HL. Optimal design of resonant piezoelectric buzzer from a perspective of vibration-absorber theory. *J Acoust Soc Am* 2007;**122**:1568–80.