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Journal of the European Ceramic Society 32 (2012) 2381–2387

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Low temperature sintering of ZnO and MnO_2-added $(Na_{0.5}K_{0.5})NbO_3$ ceramics ☆

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Received 13 October 2011; received in revised form 25 January 2012; accepted 30 January 2012
Available online 3 March 2012

Abstract

ZnO was used to decrease the sintering temperature of 1.5 mol% MnO_2-added $(Na_{0.5}K_{0.5})NbO_3$(MNKN) ceramics. When a small amount of ZnO (≥2.0 mol%) was added, a dense microstructure was observed for specimens sintered at 960 °C, with high relative density of 96.0% of the theoretical density. The liquid phase, which was considered to be an Nb_2O_5–MnO–ZnO related phase, was formed in the ZnO-added MNKN ceramics and abnormal grain growth occurred in its presence. Therefore, although a very small amount of ZnO might enter the matrix of the MNKN, most of the ZnO was used to form the liquid phase and assisted the densification of the specimens, indicating that the hardening effect of Zn^{2+} was insignificant. The 2.0 mol% ZnO-added MNKN (ZMNKN) ceramics sintered at 960 °C exhibited the high piezoelectric properties of $k_p = 37\%$, $\varepsilon_3^T/\varepsilon_0 = 297$, $d_{33} = 120$ pC/N, and $Q_m = 200$. In addition, the reaction between the Ag electrode and the ZMNKN ceramic sintered at 960 °C was negligible.

Keywords: Piezoelectric properties; Grain growth; Perovskite; Grain size; Low temperature sintering

1. Introduction

$Pb(Zr,Ti)O_3$ (PZT)-based ceramics have been widely used for piezoelectric actuators, sensors and resonators because of their excellent piezoelectric properties.[1] However, since PZT-based ceramics contain more than 60.0 wt% of PbO, which is toxic and evaporates during the sintering process, they pose serious environmental problems. Therefore, $(Na_{0.5}K_{0.5})NbO_3$ (NKN) lead-free piezoelectric ceramics, which are solid solutions of ferroelectric $KNbO_3$ and anti-ferroelectric $NaNbO_3$, have been extensively investigated as a replacement for PZT-based ceramics because they exhibit promising piezoelectric properties with a high Curie temperature.[2–4]

The sintering temperatures of NKN-based ceramics are generally high (>1060 °C).[5–9] Since the evaporation of Na_2O was observed during sintering at temperatures higher than 1000 °C,[6,9] their sintering temperature should be reduced to below 1000 °C to produce homogeneous NKN ceramics. Moreover, if NKN ceramics are to be used in piezoelectric multilayer devices, the sintering temperature should be decreased to 960 °C because Ag, with a melting temperature of 960 °C, is commonly used as an electrode in multilayer devices. According to previous works, CuO-containing NKN-based ceramics have been successfully sintered at 950–960 °C, due to the presence of a CuO-related liquid phase.[10–12] Moreover, CuO and ZnO co-doped NKN ceramics can be sintered at 900 °C. However, Cu^{2+} ions entered the B-sites (Nb^{5+} sites) of the perovskite unit cell of the NKN-based ceramics and behaved as hardeners, increasing the Q_m value but reducing the d_{33} value to below 100 pC/N.[11,12] Therefore, the CuO-added NKN-based ceramics can be used as hard piezoelectric materials but it would be difficult to utilize these materials for multilayer actuators. V_2O_5 was also used to

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doi:10.1016/j.jeurceramsoc.2012.01.030

reduce the sintering temperature of the NKN ceramics to 900 °C without reducing the d_{33} value.[13] However, since a KVO_3 secondary phase, which dissolved in water, was formed, it was difficult to form a homogeneous NKN phase.[13] Therefore, it is necessary to find a new additive which can decrease the sintering temperature to below 960 °C without reducing the piezoelectric properties such as the d_{33} and k_p values. According to previous work, the addition of MnO_2 improved the piezoelectric properties of 0.95NKN–0.05$BaTiO_3$ ceramics by improving their sinterability.[14] The effect of MnO on the (K,Na,Li)(Nb,Ta,Sb) was also investigated.[15] Moreover, ZnO addition decreased the sintering temperature of CuO-added NKN-based ceramics without causing a hardening effect.[12] In this work, therefore, MnO_2 and ZnO were co-doped into NKN ceramics to decrease the sintering temperature without degrading the piezoelectric properties, particularly the d_{33} and k_p values. Moreover, variations in the microstructure and their effect on the piezoelectric properties of the ZnO- and MnO_2-doped NKN ceramics have been investigated.

2. Experimental procedures

The NKN ceramics were prepared using conventional solid-state synthesis. The oxide compounds K_2CO_3, Na_2CO_3 and Nb_2O_5 (all from High Purity Chemicals, >99%, Saitama, Japan) were mixed for 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 for 72 h, the calcined NKN powders were re-milled with MnO_2 and ZnO additives. The ZnO-added NKN + 1.5 mol% MnO_2 (MNKN) powders were dried and pressed into discs under a pressure of 100 kgf/cm^2 and sintered at 960–1060 °C for 4 h. The structural properties of the specimens were examined by using X-ray diffraction (XRD: Rigaku D/max-RC, Tokyo, Japan) and scanning electron microscopy (SEM: Hitachi S-4300, Osaka, Japan). The densities of the sintered specimens were measured by a water-immersion technique. A silver electrode was printed on the lapped surfaces, and the specimens were poled in silicone oil at 120 °C by applying a DC field of 4–5 kV/mm for 60 min. The polarization versus electric field (*P*–*E*) behavior was determined using a modified Sawyer–Tower circuit. The piezoelectric and dielectric properties and electromechanical coupling factor were determined using a d_{33} meter (Micro-Epsilon Channel Product DT-3300, Raleigh, NC, USA) and an impedance analyzer (Agilent Technologies HP 4294A, Santa Clara, CA, USA) according to IEEE standards.

3. Results and discussion

Fig. 1 shows the XRD patterns of MNKN + $x$mol% ZnO ceramics with $0.0 \leq x \leq 3.0$ which were sintered at 980 °C for 4 h. The Si powders were used as reference powders against which we measured the lattice parameter of the specimens. A homogeneous perovskite NKN phase was formed for the specimens with $x < 2.0$. However, peaks for an unknown phase (indicated by the asterisks) were observed for the specimens with $x \geq 2.0$. Therefore, a very small amount of Zn ions was considered to have entered the matrix of the MNKN ceramics. However, when a large amount of ZnO was added into the specimen, most of the Zn ions reacted with the ions in the matrix and formed the second phase. According to previous work, the addition of ZnO changes the lattice parameters of the (K,Na,Li)(Nb,Ta,Sb)O_3 ceramics.[16] Therefore, the variations of the lattice parameters (*a*, *b* and *c*) of MNKN ceramics with the addition of ZnO were also studied, as shown in Fig. 2. The lattice parameters of MNKN ceramics did not change significantly with the addition of ZnO content, indicating that few Zn^{2+} ions entered the matrix of the MNKN ceramics. On the contrary, most of the Zn^{2+} ions were considered to be used to form the liquid phase and assisted in the densification of the

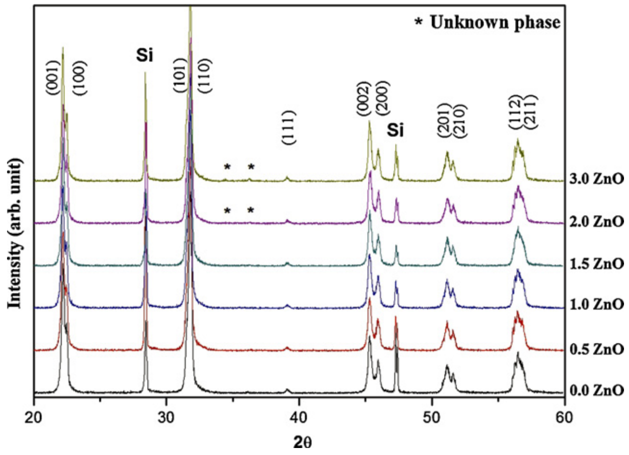

Fig. 1. XRD patterns of MNKN + $x$mol% ZnO ceramics sintered at 980 °C for 4 h.

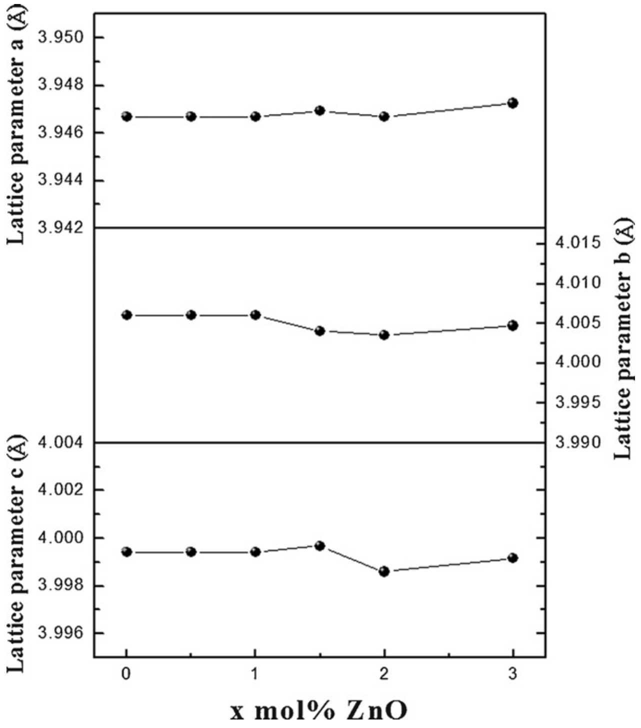

Fig. 2. Variations of the lattice parameters with respect to x for MNKN + $x$mol% ZnO ceramics sintered at 980 °C for 4 h.

MNKN ceramics at low temperatures, which will discussed in detail later.

The microstructures of the MNKN + $x$mol% ZnO ceramics sintered at 980 °C for 4 h were investigated using SEM, as shown in Fig. 3(a)–(d). The MNKN ceramic exhibited a porous microstructure with a small grain size (~0.7 μm). When ZnO was added into the MNKN ceramics, a dense microstructure was developed and some of the grains had a large grain size, as indicated by the arrows in Fig. 3(b)–(d). Moreover, the number of large grains increased as the ZnO amount was increased so that two types of grains, small grains with an average grain size of 0.7 μm and large grains with an average grain size of approximately 10.0 μm, coexisted in the specimens with $x = 1.5$–3.0. All of the large grains showed faceted surfaces instead of round surfaces, indicating that the increase of the grain size in the ZnO-added MNKN ceramics could be explained by an abnormal grain growth mechanism.[17] Therefore, it can be suggested that the addition of ZnO expedited the densification and abnormal grain growth in the MNKN ceramics.

Fig. 4(a)–(d) show the variation of the microstructures of the 2.0 mol% ZnO-added MNKN (ZMNKN) ceramics with respect to sintering temperature. All the specimens exhibited dense microstructures. Some of the grains had already grown abnormally in the specimen sintered at 960 °C and the number and size of the grains increased as the sintering temperature was increased. In particular, the specimen sintered at 1040 °C for 4 h had very large grains with an average grain size of ~20.0 μm, as shown in Fig. 4(c). However, the average grain size suddenly decreased to 6.0 μm as the sintering temperature was raised to 1060 °C, as shown in Fig. 4(d). Abnormal grain growth generally occurred in the presence of the liquid phase and a small amount of the liquid phase was already observed in the 2.0 mol% ZnO-added specimen sintered at 980 °C, as indicated by the arrows in Fig. 4(b). The amount of liquid phase was considered to increase with increasing ZnO content and a large amount of liquid phase could be formed for the specimen sintered at 1060 °C. Moreover, the large amount of liquid phase produced many nuclei for abnormal grain growth, which impinged on each other and eventually inhibited grain growth, resulting in a microstructure with small grains, as shown in Fig. 4(d). Therefore, the decreased grain size observed in the specimen sintered at 1060 °C could be explained by the formation of numerous nuclei of abnormal grains due to the presence of a large amount of liquid phase; similar results were also observed in other systems.[6,17–19]

Energy dispersive spectroscopy (EDS) analysis was conducted on the 3.0 mol% ZnO-added MNKN ceramics sintered at 1060 °C to identify the composition of the liquid phase. Fig. 5(a) shows an SEM image of the thermally etched surface of the 3.0 mol% ZnO-added MNKN ceramic sintered at 1060 °C for 4 h. The liquid phase was formed along the grain boundary as indicated by the arrow and EDS analysis was conducted on the matrix and the liquid phase. The EDS spectra of the matrix and the liquid phase are shown in Fig. 5(b) and (c). Table 1(a) and (b) shows the chemical composition of the matrix and the liquid phase of the specimen, respectively. The composition of the matrix was very similar to that of NKN. A few Mn ions were also observed in the matrix, revealing the incorporation of these ions into the matrix of the specimen. On the other hand, Zn ions were not detected in the matrix, confirming that few Zn^{2+} ions enter the matrix of the MNKN ceramics. Numerous Nb, Mn and Zn ions were observed in the liquid phase, indicating that the liquid phase could be an Nb_2O_5–MnO–ZnO related phase.

Table 1
The chemical compositions of the (a) matrix and (b) liquid phase of the 3.0 mol% ZnO-added MNKN ceramics sintered at 1060 °C.

Element	Atomic (%)
(a) Matrix	
O	73.10
Na	5.51
K	5.26
Mn	0.59
Zn	0
Nb	15.54
(b) Liquid phase	
O	70.64
Na	0
K	1.82
Mn	9.01
Zn	10.32
Nb	8.22

Fig. 6 shows the P–E curves of the ZnO-added MNKN ceramics sintered at 980 °C for 4 h. The P–E curve of the MNKN ceramics could not be measured because of its low relative density. The P_r value increased with increasing ZnO content and a maximum value of 38 μC/cm^2 was observed for the MNKN ceramics containing 2.0–3.0 mol% of ZnO. The E_c value also improved with the addition of a small amount of ZnO because of the increase of the relative density, but it was not further increased when the ZnO content exceeded 0.5 mol%. Therefore, it is expected that the hardening effect of the Zn ions was not significant in the MNKN ceramics.

Fig. 7 shows the relative density, $\varepsilon_3^T/\varepsilon_0$, k_p, d_{33}, and Q_m values of the MNKN + $x$mol% ZnO ceramics with $0.0 \le x \le 3.0$ that were sintered at 960 °C and 980 °C for 4 h, as well as those of the NKN ceramics sintered at 1070 °C, which are indicated by the asterisks. The relative density of the MNKN ceramic sintered at 960 °C was low: approximately 87.5% of the theoretical density. The density increased with increasing ZnO content and a saturated value of 96.1% of the theoretical value was obtained from the specimens with $x \ge 2.0$. Even though the specimens sintered at 980 °C exhibited a higher relative density, the variation of the density with respect to ZnO content was similar to that of the specimens sintered at 960 °C. In particular, the specimens with $x \ge 1.0$ sintered at 980 °C exhibited a high relative density (≥97.0% of the theoretical density). The $\varepsilon_3^T/\varepsilon_0$ values of MNKN ceramics sintered at 960 and 980 °C were low because of their low relative density. This value increases with the addition of ZnO due to the increased relative density. Moreover, the $\varepsilon_3^T/\varepsilon_0$ values of specimens sintered at 960 and 980 °C did not decrease when 3.0 mol% of ZnO was added, indicating that the hardening effect of ZnO was considered to be insignificant in the ZnO-added MNKN ceramics. The k_p values were also low for MNKN ceramics and increased with increasing ZnO, due to the increase in the density. A saturated value of 39% was obtained

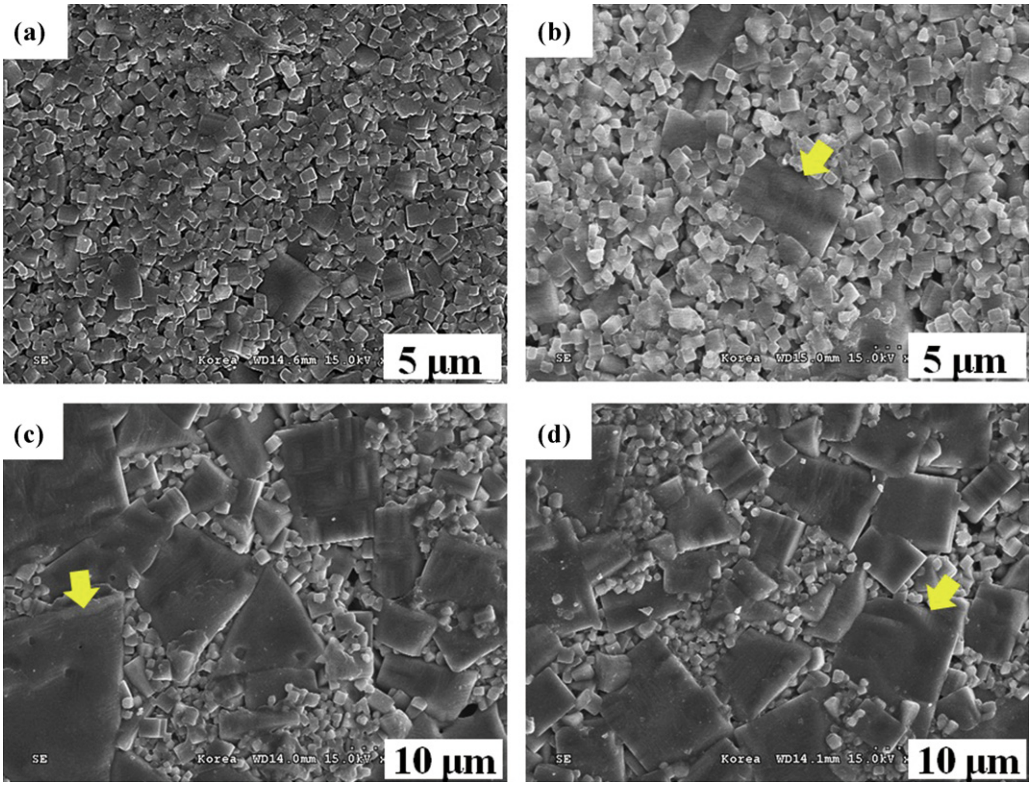

Fig. 3. SEM images of MNKN + $x$mol% ZnO ceramics sintered at 980 °C for 4 h with (a) $x = 0.0$, (b) $x = 0.5$, (c) $x = 1.5$ and (d) $x = 3.0$.

for the specimens with $x \geq 1.5$ sintered at 980 °C. Moreover, the specimens with $x = 2.0$ sintered even at 960 °C also exhibited a relatively high k_p value of 37%. The d_{33} value of the MNKN sintered at 960 °C was low (∼105 pC/N) due to the low density and this value increased with increasing ZnO content. In particular, the 2.0 mol% ZnO-added MNKN ceramic exhibited a d_{33} value of 117 pC/N, which is very similar to that of the NKN sintered at 1070 °C. On the other hand, all the specimens

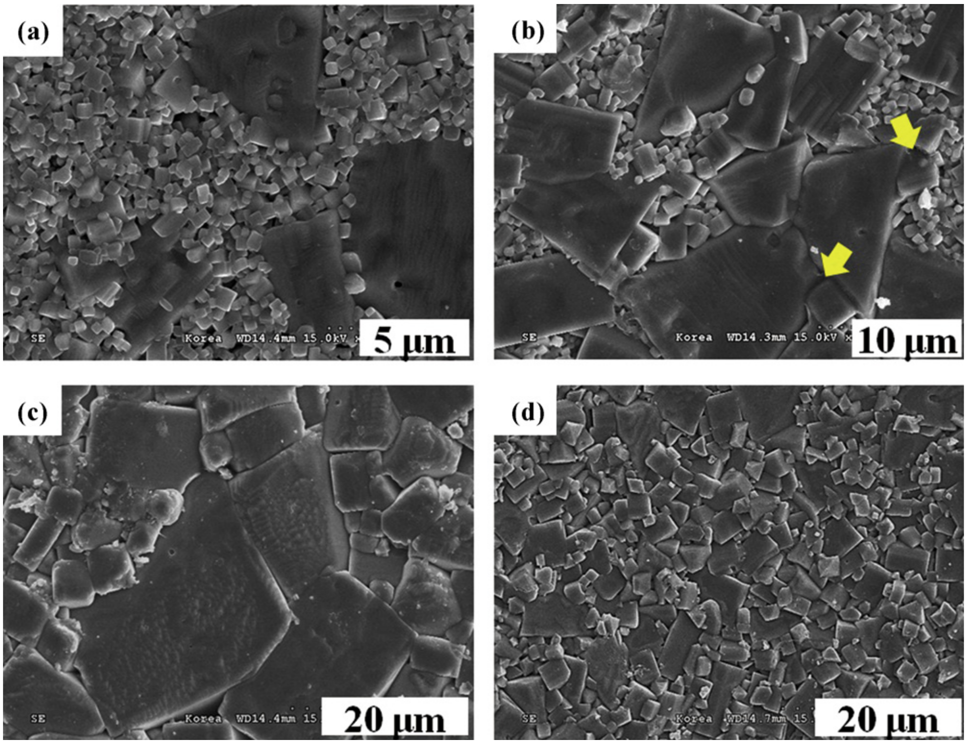

Fig. 4. SEM images of ZMNKN ceramics sintered at various temperatures for 4 h: (a) 960 °C, (b) 980 °C, (c) 1040 °C and (d) 1060 °C.

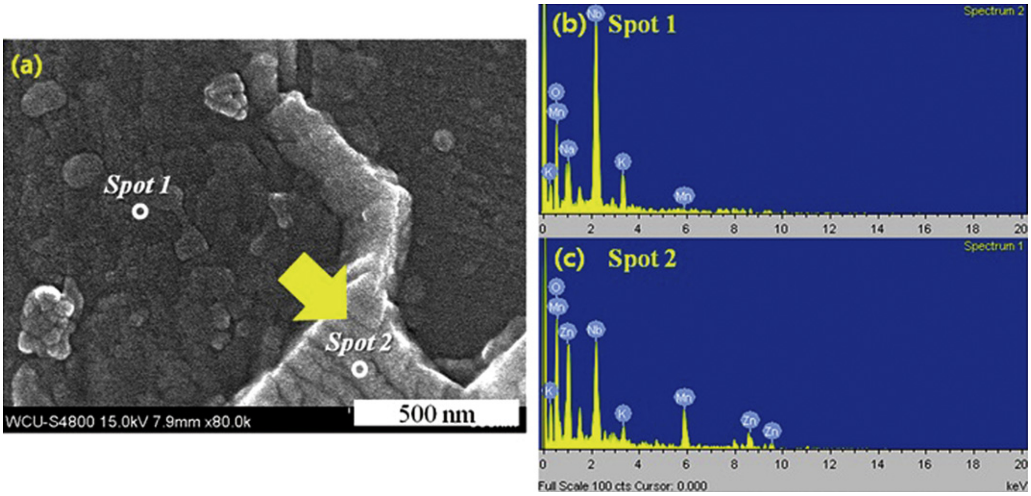

Fig. 5. (a) SEM image of the thermally etched surface of the 3.0 mol% ZnO-added MNKN ceramic sintered at 1060 °C for 4 h. A liquid phase (indicated by the arrow) was found in this specimen. EDS spectra of (b) the matrix and (c) the liquid phase taken from the specimen shown in Fig. 5(a).

sintered at 980 °C exhibited high d_{33} values which ranged between 115 and 120 pC/N. The Q_m value of MNKN ceramics sintered at 960 and 980 °C was approximately 200, which was higher than that of NKN (~80) due to the hardening effect of the Mn ions. When ZnO was added into the MNKN, the Q_m value was slightly increased, probably due to the increased density, but the variation was not significant, indicating that the hardening effect of ZnO was negligible.

Fig. 8 exhibits the relative density, $\varepsilon_3^T/\varepsilon_0$, grain size, k_p, d_{33}, and Q_m values of ZMNKN ceramics sintered at various temperatures for 4 h. The specimen sintered at 960 °C exhibited a high relative density of 96.1% of the theoretical density, a value which was slightly increased to 98.0% for the specimen sintered at 980 °C. The relative density was slightly decreased for the specimens sintered above 980 °C, probably due to the increased amount of liquid phase. The $\varepsilon_3^T/\varepsilon_0$ value of the specimen sintered at 960 °C was about 297, which increased to 354 for the specimen sintered at 980 °C due to the increased density and grain size. It slightly decreased when the sintering temperature exceeded 980 °C, probably due to the increased amount of liquid phase. The average grain size of the ZMNKN ceramics sintered at 960 °C was small, approximately 1.3 μm, and increased with increasing sintering temperature, showing a maximum value of 20.0 μm for specimens sintered at 1040 °C. However, it decreased to 6.0 μm for the specimens sintered at 1060 °C due to the presence of a large amount of the liquid phase. The k_p value of the specimen sintered at 960 °C was 37%, which was similar to that of the pure NKN ceramics, and

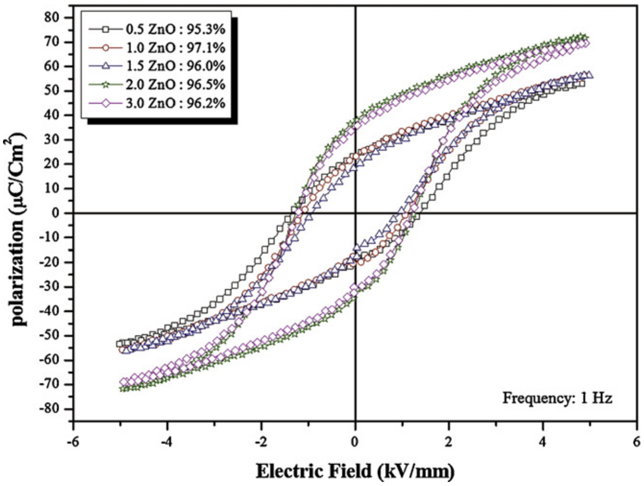

Fig. 6. A plot of the induced polarization versus electric field curves for the MNKN + xmol% ZnO ceramics sintered at 980 °C for 4 h.

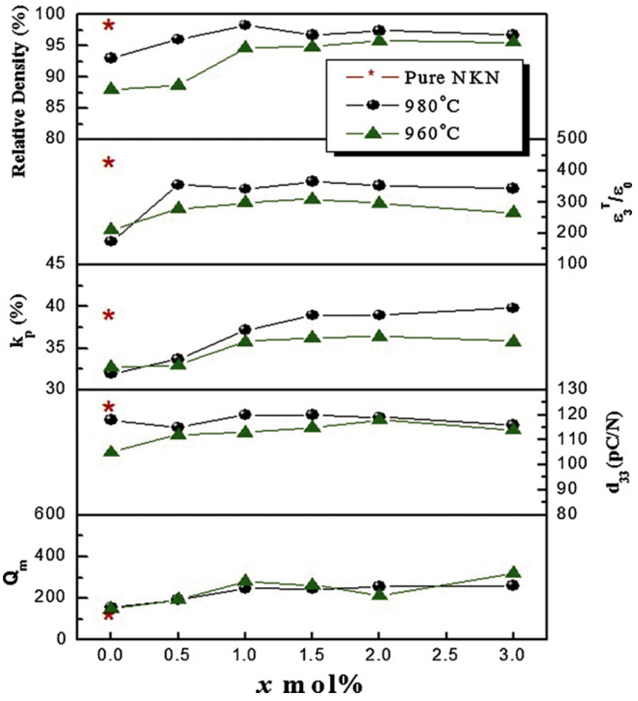

Fig. 7. Relative densities and $\varepsilon_3^T/\varepsilon_0$, k_p, d_{33}, and Q_m values of MNKN + xmol% ZnO ceramics with $0.0 \leq x \leq 3.0$ sintered at 960 and 980 °C for 4 h and those of NKN ceramics sintered at 1060 °C.

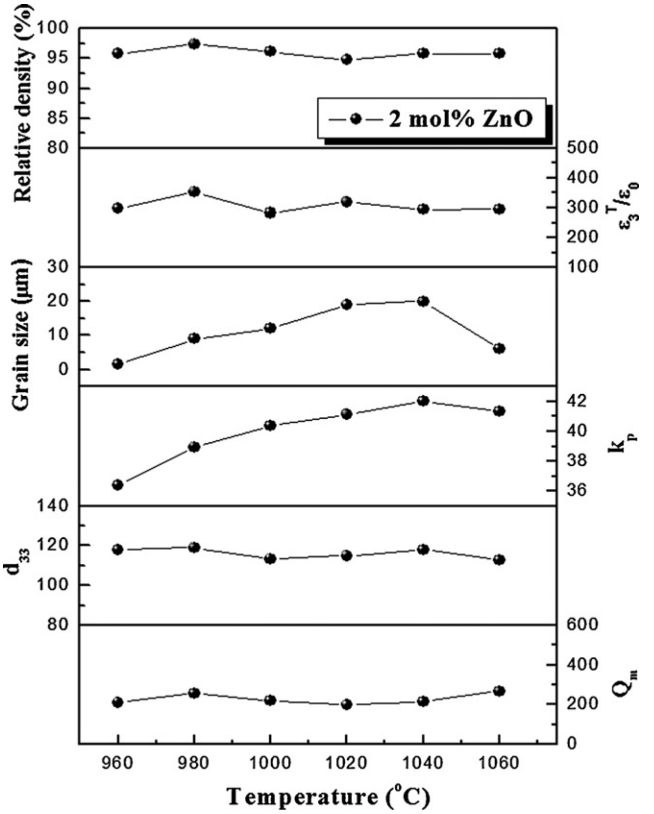

Fig. 8. Relative densities and $\varepsilon_3^T/\varepsilon_0$, grain size, k_p, d_{33}, and Q_m values of ZMNKN ceramics sintered at various temperatures for 4 h.

it increased with increasing sintering temperature to 42% for the specimen sintered at 1040 °C, but slightly decreased for the specimen sintered at 1060 °C. The variation of k_p with respect to sintering temperature was very similar to that of the grain size. Therefore, the k_p value was considered to be affected by the grain size of the specimen. The Q_m value of the specimen sintered at 960 °C was approximately 200 and its variation with sintering time was negligible. These results indicated that the ZnO-added MNKN ceramics were well sintered at low temperatures with promising piezoelectric properties. In particular, the ZMNKN ceramics sintered at 960 °C exhibited good piezoelectric properties of $k_p = 37\%$, $\varepsilon_3^T/\varepsilon_0 = 300$, $d_{33} = 120$ pC/N, and $Q_m = 200$.

The reaction between the 80Ag/20Pd electrode and the ZMNKN ceramic was also investigated. Fig. 9(a) shows the XRD pattern of the specimen sintered with 80Ag/20Pd metal at 960 °C. Peaks for the ZnO-added MNKN ceramic and the Ag metal were observed without any secondary phase peaks. The interface between the 80Ag/20Pd metal and the ZMNKN ceramic was also studied using SEM and EDS line scanning, as shown in Fig. 9(b). This interface was well developed and the Ag and Pd profiles sharply decreased at the interface, indicating the absence of any silver diffusion into the ZMNKN ceramic. Moreover, the very low concentrations of Na, K, and Nb in the 80Ag/20Pd metal suggested the absence of any reaction between the 80Ag/20Pd metal and the ZMNKN ceramic. This demonstrated the potential of the ZnO-added MNKN ceramic as a promising lead-free piezoelectric material for piezoelectric multilayers.

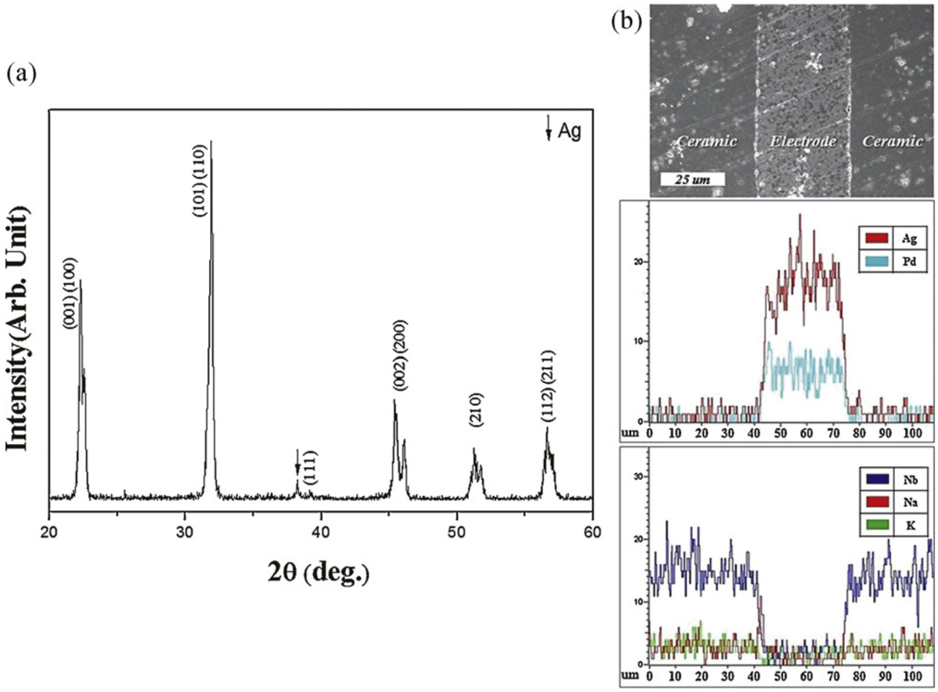

Fig. 9. (a) XRD pattern of the specimen sintered with 80Ag/20Pd metal at 980 °C and (b) SEM image and EDS line scan of the interface between the 80Ag/20Pd metal and the ZMNKN ceramic.

4. Conclusions

ZnO was added to MNKN ceramics to decrease their sintering temperature for piezoelectric multilayer applications. The MNKN ceramics sintered at 960 and 980 °C had a porous microstructure with small grains. When ZnO was added into the MNKN ceramics, however, a dense microstructure was developed and some of the grains had a large grain size. The enlarged grains showed faceted surfaces, indicating that the increase of the grain size in the ZnO-added MNKN ceramics could be explained by an abnormal grain growth mechanism. A liquid phase was also found in the ZnO-added MNKN ceramics where it was considered to be an Nb_2O_5–K_2O–ZnO related phase. The relative density of the MNKN ceramics was low when they were sintered at 960 and 980 °C but it increased with the addition of ZnO. The ZMNKN that was sintered at 980 °C for 4 h exhibited a high relative density of 97.5% of the theoretical density. Furthermore, the ZMNKN ceramics sintered at 960 °C also showed a high relative density of 96.1% of the theoretical density and they also exhibited promising piezoelectric properties of $k_p = 37\%$, $\varepsilon_3^T/\varepsilon_0 = 300$, $d_{33} = 120$ pC/N, and $Q_m = 200$. Moreover, the ZMNKN ceramics were sintered with Ag metal at 960 °C and no reaction between the Ag metal and the ZMNKN ceramics was found. Therefore, the ZnO-added MNKN ceramic is a good lead-free piezoelectric ceramic which can be applied to piezoelectric multilayer devices.

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