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Li_2O excess $(Na_{0.51}K_{0.47}Li_{0.02})(Nb_{0.8}Ta_{0.2})O_3$ lead free piezoelectric ceramics

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Abstract

1 mol% Li_2O excess $(Na_{0.51}K_{0.47}Li_{0.02})(Nb_{0.8}Ta_{0.2})O_3$ ceramics were prepared by the conventional mixed oxide method and sintered from 950 to 1200 °C. Also, Li_2O was employed as a sintering aid for high densification and low temperature sintering process. X-ray diffraction results of 1 mol% Li_2O excess $(Na_{0.51}K_{0.47}Li_{0.02})(Nb_{0.8}Ta_{0.2})O_3$ lead free piezoelectric ceramics indicated that the specimens were well crystallized and have tetragonal structure. The specimens which sintered at 1050 °C showed the highest piezoelectric properties compared with others. The measured piezoelectric constant and electromechanical coupling coefficient were 231 pC/N and 38.9%, respectively. Curie temperature of $(Na_{0.51}K_{0.47}Li_{0.02})(Nb_{0.8}Ta_{0.2})O_3$ ceramics was 344.32, 344.4 and 344.5 °C at 1, 10 and 100 kHz, respectively.

Keywords: A. Sintering; C. Piezoelectric properties; D. Perovskites; NKN–LT

1. Introduction

The piezoelectric ceramic materials play an important role in electronic and microelectronic devices. In these days, lead free piezoelectric ceramics such as $Pb(Ni,Nb)O_3$–$Pb(Zr,Ti)O_3$ (PNN–PZT), $Pb(Mg,Nb)O_3$–$Pb(Zr,Ti)O_3$ (PMN–PZT), $Pb(Ni,Nb)O_3$–$Pb(Zn,Nb)O_3$ (PNN–PZN) and $0.7Pb(Mg,Nn)O_3$–$0.3PbTiO_3$ (PMN–PT) have been intensively investigated due to their excellent piezoelectric, mechanical, and dielectric properties. Even if lead oxide based piezoelectric ceramics have excellent electrical properties, the generation of toxic PbO during the sintering process have created serious pollution problems. The best way to solve this problem is to search lead free piezoelectric ceramic materials which will replace the lead based materials. Recently, several lead free piezoelectric materials such as $BaTiO_3$, $Bi_{0.5}Na_{0.5}TiO_3$ (hereafter BNT), and $Na_{0.5}K_{0.5}NbO_3$ (hereafter NKN) are being considered as attractive alternatives to lead oxide based piezoelectric ceramic systems. In the case of $BaTiO_3$ which was the first polycrystalline piezoelectric ceramics, although it shows high electromechanical properties ($k_p = 36\%$), the development of practical applications was limited due to its low Curie temperature ($T_C = 115$ °C). Thus, the researches on lead free piezoelectric are focused on $Bi_{0.5}Na_{0.5}TiO_3$ and NKN system. BNT has been considered as a good candidate for lead free piezoelectric ceramic due to its strong ferroelectricity with large remanent polarization ($P_r = 38$ μC/cm^2). However, pure BNT ceramics have weak points of high coercive field ($E_c = 73$ kV/cm) and low phase transition temperature. Recently NKN, the solid solution of antiferroelectric $NaNbO_3$ and ferroelectric $KNbO_3$ at room temperature, has been considered as the most promising candidate for a lead free piezoelectric ceramics due to its outstanding piezoelectric properties such as high Curie temperature, and large electromechanical coupling coefficient. However, volatility of sodium potassium based ceramics makes it difficult to obtain high densed and well sintered NKN ceramics using conventional sintering process under atmospheric pressure. On the other hand, pure NKN ceramics prepared by hot pressing and plasma sintering method showed high densification and good sinterability [1]. While pure NKN ceramics fabricated by conventional sintering process have relatively lower piezoelectric constant ($d_{33} = 80$) and electromechanical coupling coefficient ($k_p = 0.360$) [2], the hot pressed pure NKN ceramics have high

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piezoelectric constant (d_{33} = 160) and electromechanical coupling coefficient (k_p = 0.45) [3]. However, hot pressing and plasma sintering methods are not easy to use for industry due to high processing cost. For these reasons, a number of researches have been focused to improve the densification and piezoelectric properties at the atmospheric pressure by using various additives such as CuO, ZnO, $LiTaO_3$, $BaTiO_3$, $LiSbO_3$ and $LiNbO_3$. It was reported that textured $Na_{0.52}K_{0.44}Li_{0.04}Nb_{0.86}Sb_{0.04}Ta_{0.10}O_3$ system (hereafter (Li, Ta, Sb) modified NKN) has high piezoelectirc constant d_{33} of 400 pC/N, which comparable with that of PZT [4]. However, (Li, Ta, Sb) modified NKN has several shortcomings. The serious problem is the toxicity of antimony. Moreover, the price of Sb_2O_5 powders is expensive compared with those of Ta_2O_5 and Nb_2O_5. Especially, the price of Sb_2O_5 is at least 3 times higher than that of Nb_2O_5. Therefore in this work, our goal is to obtain excellent piezoelectric materials based on NKN system without any toxic materials. Also, we have investigated the effect of Li_2O as sintering aid. Recently, Kim et al. reported the effect of Li_2O to improve the sinterability, densification and piezoelectric properties of $0.95(Na_{0.5}K_{0.5})NbO_3$–$0.05LiTO_3$ (NKN–LT) ceramics. Li_2O can improve the piezoelectric properties and dielectric permittivity [5]. For the first time, we will report Curie temperature of Li_2O excess NKN–LT ceramics. After adding the 0.1 wt.% Li_2O, piezoelectric coefficient and electromechanical coupling coefficient of PMN–PZT ceramics are increased by 29% and 12%, respectively.

2. Experimental

1 mol% Li_2O excess $(Na_{0.51}K_{0.47}Li_{0.02})(Nb_{0.8}Ta_{0.2})O_3$ ceramics were fabricated by traditional ceramic process. The sintering temperature was varied from 950 to 1200 °C. The crystal structure was investigated by X-ray diffraction (XRD) patterns (θ–2θ scans with Cu-Kα source). Scanning electron microscopy (SEM) images were observed through NOVA 200. Frequency dependent dielectric dispersions were analyzed through HP 4284 precision LCR meter from 1 kHz to 1 MHz at room temperature. The temperature dependent dielectric permittivities of samples were studied at 1, 10 and 100 kHz using FLUKE PM6304 programmable automatic RCL meter. The piezoelectric constant d_{33} was measured using quasi-static meter of Berlincourt type.

3. Results and discussion

Fig. 1 shows X-ray diffraction scans of 1 mol% Li_2O excess NKN–LT ceramics sintered from 950 to 1200 °C. As shown in Fig. 1, we found that 1 mol% Li_2O excess NKN–LT ceramics were crystallized and have tetragonal structure. From the 950 to 1150 °C, 1 mol% Li_2O excess NKN–LT ceramics have similar crystalline properties. However, as the sintering temperature was increased up to 1200 °C, 1 mol% Li_2O excess NKN–LT ceramics lose their crystalline properties and pyrochlore phases were observed. The calculated lattice parameters c, and a of 1 mol% Li_2O excess NKN–LT ceramics sintered at 1050 °C were 4.01, and 3.94 Å, respectively. The observed tetragonality (c/a) of 1.018 is higher than those of other specimens sintered at different temperatures. Therefore, we expect that the 1 mol% Li_2O excess NKN–LT ceramics sintered at 1050 °C has the excellent piezoelectric properties. Since the 1 mol% Li_2O excess NKN–LT ceramics sintered at 1050 °C have increased tetragonality (c/a) compared with other specimen, the increased displacement of dipole moment induce large polarization compared with other specimen. Moreover, the spontaneous strain X_s is related with the spontaneous polarization P_s as follow, $X_s = QP_s^2$ (where X_s is spontaneous strain, Q is the charge, and P_s is the spontaneous polarization). As a result, we can expect that 1 mol% Li_2O excess NKN–LT ceramics sintered at 1050 °C has the higher piezoelectric properties compared with other specimen.

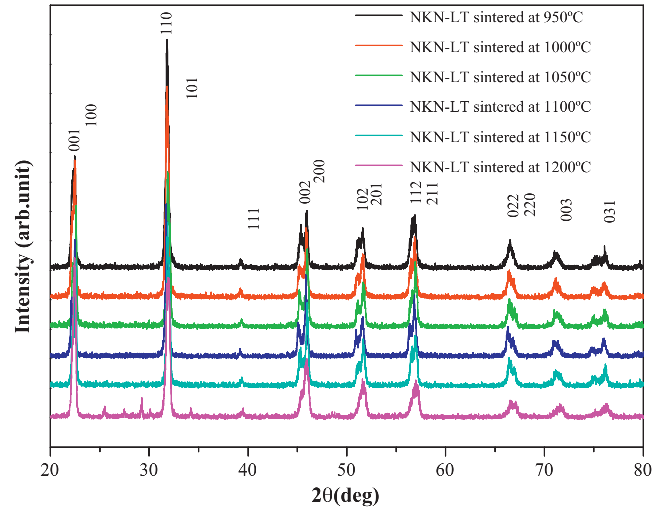

Fig. 1. XRD 2θ scans of 1 mol% Li_2O excess $(Na_{0.51}K_{0.47}Li_{0.02})(Nb_{0.8}Ta_{0.2})O_3$ ceramics, which sintered at the various temperatures from 950 to 1200 °C.

Fig. 2 shows the SEM images of 1 mol% Li_2O excess NKN–LT ceramics with different sintering temperature from 950 to 1200 °C. As increasing the sintering temperature, the grain size of NKN–LT ceramics was increased. The estimated grain size of 1 mol% Li_2O excess NKN–LT ceramics sintered at 1200 °C was approximately 10 μm. It is about nine times larger than that of specimen sintered at 950 °C. The gain size of 1 mol% Li_2O excess NKN–LT ceramics sintered at 1200 °C was the bigger compared with others. Densification of 1 mol% Li_2O excess NKN–LT ceramics sintered at 1200 °C was relatively porous than those of other specimens which sintered at lower temperatures. The bulk density reaches maximum value of 4.972 g/cm^3 as sintering temperature was increased up to 1050 °C, then drop to 3.950 g/cm^3 at 1200 °C. The measured density of 1 mol% Li_2O excess NKN–LT ceramics sintered from 950 to 1200 °C was 4.252, 4.253, 4.972, 4.310, 4.045 and 3.950 g/cm^3, respectively. Decreased density of specimens may be explained as volatility of cation at high temperature [6]. Because the phase stability is limited less than 1100 °C for potassium sodium niobate system. High temperatures of sintering process more than 1100 °C create volatile problems. 1 mol% Li_2O excess NKN–LT ceramics sintered at 1050 °C

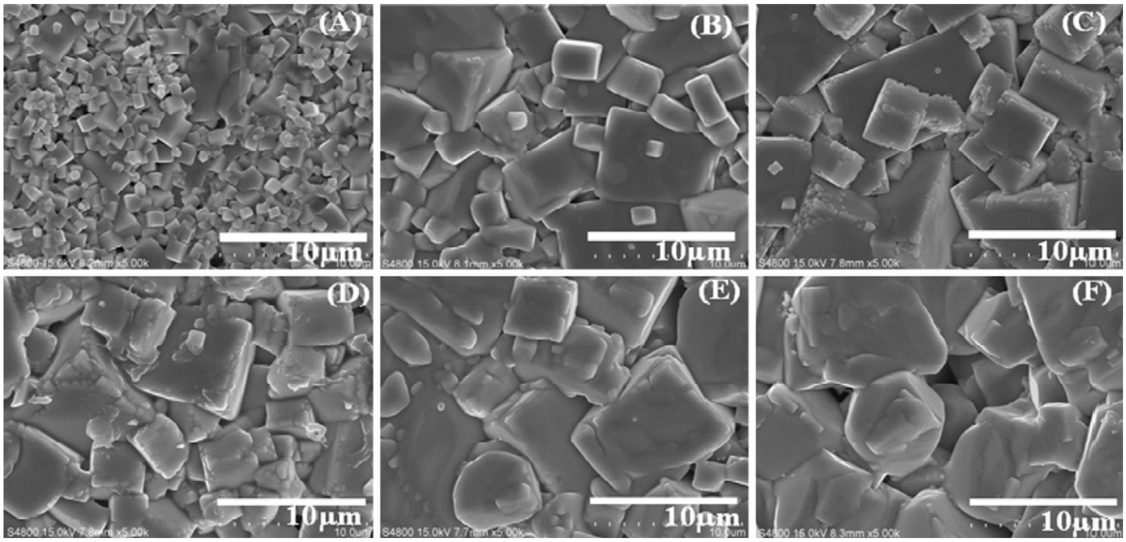

Fig. 2. SEM images of 1 mol% Li_2O excess $(Na_{0.51}K_{0.47}Li_{0.02})(Nb_{0.8}Ta_{0.2})O_3$ ceramics sintered at (A) 950 °C, (B) 1000 °C, (C) 1050 °C, (D) 1100 °C, (E) 1150 °C, and (F) 1200 °C for 4 h.

show the form of square or rectangular shapes. However, when the sintering temperature was increased above 1100 °C, grain shapes of 1 mol% Li_2O excess NKN–LT ceramics were deformed into round corner form. This phenomenon means that sintering temperature over 1100 °C leads over-sintered states. Therefore, grain size of Li_2O excess NKN–LT ceramics was continuously increased during the over-sintering process.

Fig. 3 shows piezoelectric properties of 1 mol% Li_2O excess NKN–LT ceramics with different sintering temperatures from 950 to 1150 °C. The piezoelectric coefficient d_{33} and electromechanical coupling coefficient were gradually increased as the sintering temperature up to 1050 °C and then decreased. Among the measured samples, 1 mol% Li_2O excess NKN–LT ceramics sintered at 1050 °C showed the highest piezoelectric constant of 231 pC/N and electromechanical coupling coefficient of 0.389. This result was well coincided with the X-ray diffraction analysis as we have discussed. We believe that these outstanding electrical properties including piezoelectric and electromechanical coupling coefficient may be associated with microstructure including densification, uniformity, grain size, and grain shapes.

Fig. 4 displays sintering temperature dependent dielectric permittivity and loss tangent of 1 mol% Li_2O excess NKN–LT ceramics measured at 1 MHz. The dielectric permittivity was increased as sintering temperature up to 1050 °C and then decreased. In the contradiction to dielectric permittivity, loss tangent was slightly decreased with increasing the sintering temperature and then increased from 1100 °C again.

Fig. 5 reveals the temperature dependent dielectric permittivity ε' of 1 mol% Li_2O excess NKN–LT ceramics sintered at 1050 °C. It has been hardly reported the Curie temperature of NKN–LT piezoelectric ceramics. As shown in Fig. 5, 1 mol% Li_2O excess NKN–LT showed tetragonal–cubic transition temperature (T_C) of 344.32, 344.4, and 344.5 °C at 1,

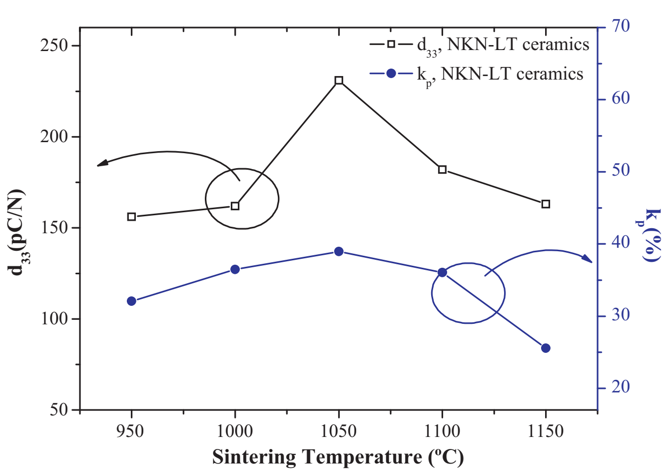

Fig. 3. The piezoelectric constant (d_{33}) and electromechanical coupling coefficient (k_p) of 1 mol% Li_2O excess $(Na_{0.51}K_{0.47}Li_{0.02})(Nb_{0.8}Ta_{0.2})O_3$ ceramics for various sintering temperatures.

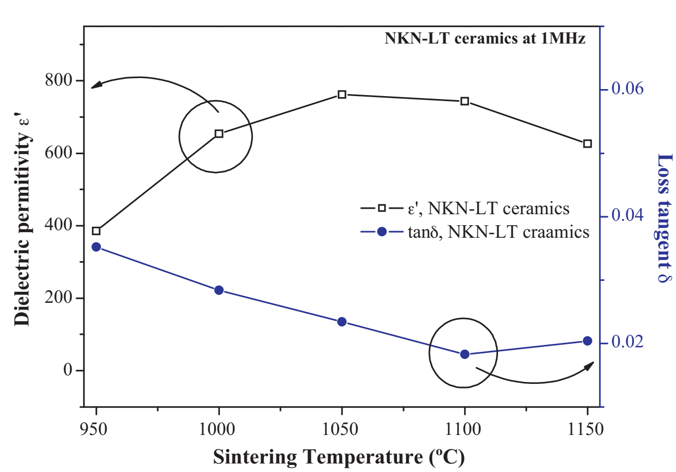

Fig. 4. Sintering temperature dependent relative dielectric permittivity and loss tangent of 1 mol% Li_2O excess $(Na_{0.51}K_{0.47}Li_{0.02})(Nb_{0.8}Ta_{0.2})O_3$ ceramics for various sintering temperatures measured at the 1 MHz.

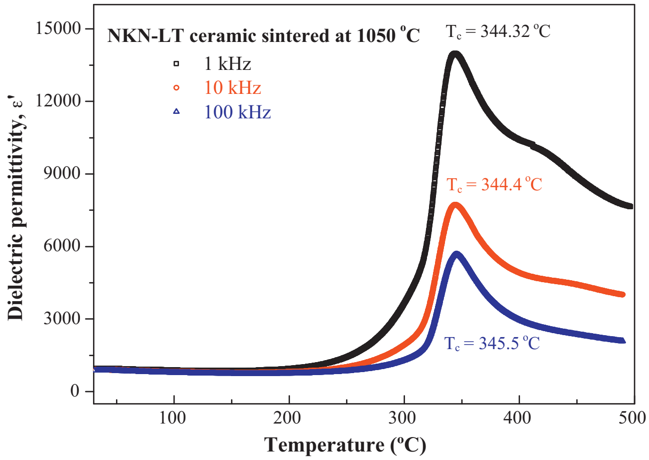

Fig. 5. Temperature dependent dielectric permittivity of 1 mol% Li_2O excess $(Na_{0.51}K_{0.47}Li_{0.02})(Nb_{0.8}Ta_{0.2})O_3$.

10, and 100 kHz, respectively. However, the small peak related to orthorhombic–tetragonal transitions ($T_{O\text{-}T}$) was hardly observed.

4. Conclusions

1 mol% Li_2O excess $(Na_{0.51}K_{0.47}Li_{0.02})(Nb_{0.8}Ta_{0.2})O_3$ lead free piezoelectric ceramics have been prepared by conventional sintering process. We found that NKN–LT ceramics were crystallized and they have tetragonal structure. 1 mol% Li_2O excess NKN–LT ceramics sintered at 1050 °C showed the remarkable piezoelectric performance such as piezoelectric constant of 231 pC/N, electromechanical coupling coefficient of 0.38, and Curie temperature around 344 °C. From our results we found that 1 mol% Li_2O excess NKN–LT ceramics which sintered at 1050 °C has the highest piezoelectric performance among with other samples.

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