Dielectric and piezoelectric properties of KCT added $(\text{Li}_{0.02}(\text{Na}_{0.56}\text{K}_{0.46})_{0.98}(\text{Nb}_{0.81}\text{Ta}_{0.15}\text{Sb}_{0.04})\text{O}_3$ ceramics

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Abstract In this study, $[\text{Li}_{0.02}(\text{Na}_{0.56}\text{K}_{0.46})_{0.98}(\text{Nb}_{0.81}\text{Ta}_{0.15}\text{Sb}_{0.04})\text{O}_3 + x \text{ mol\% K}_{5.4}\text{Cu}_{1.3}\text{Ta}_{10}\text{O}_{29}$ ceramics were fabricated by conventional solid-state solution processes. Then, their dielectric and piezoelectric properties were investigated. Sinterability of all samples was enhanced because $\text{K}_{5.4}\text{Cu}_{1.3}\text{Ta}_{10}\text{O}_{29}$ (abbreviated as KCT) acted as sintering aids. As the result of XRD, phase structure showed orthorhombic symmetry when $\text{KCT} \leq 0.2 \text{ mol\%}$. Whereas, the phase structure changed from orthorhombic symmetry to tetragonal symmetry when $\text{KCT} \geq 0.4 \text{ mol\%}$. The results suggest that the orthorhombic and tetragonal phases co-exist in the composition ceramics with $0.2 \text{ mol\%} < \text{KCT} < 0.4 \text{ mol\%}$ at room temperature. The effects of the addition of KCT on the dielectric and piezoelectric properties were investigated. As the result, excellent properties of density $= 4.81 [\text{g/cm}^3]$, electromechanical coupling factor (k_p) $= 0.48$ and piezoelectric constant (d_{33}) $= 252 [\text{pC/N}]$ were obtained in the composition ceramics with $0.4 \text{ mol\% KCT}$.

Keywords Dielectric · Piezoelectric · KCT · NKN · Electromechanical coupling coefficient (k_p) · Piezoelectric constant (d_{33})

1 Introduction

Piezoelectric ceramics have been developed from BaTiO_3 -based compositions to $\text{Pb}(\text{Zr,Ti})\text{O}_3$ -based compositions. Among them, Lead zirconate titanate-based (abbreviated as PZT) ceramics have been widely used in actuator, sensors, resonator, transducer, and energy harvesters due to their excellent piezoelectric and dielectric properties. However, these lead-based ceramics can cause serious environmental pollution and damage human health due to generation of toxic PbO during the process of manufacturing. Thus, electrical waste and electronic equipment (WEEE) and restriction of hazardous substances (RoHS) have been enforced to new electronic products for the environmental production and human health. Therefore, lead-free piezoelectric ceramics such as BNT-based materials, and NKN-based materials have been studied during the past decade.

Among these, $(\text{N}_{0.5}\text{K}_{0.5})\text{NbO}_3$ (abbreviated as NKN) ceramics is a promising candidate for replacing lead-free ceramics due to their strong piezoelectricity and ferroelectricity. Typically, well sintered KNN ceramics have excellent physical properties such as a piezoelectric constant (d_{33}) $= 80 \text{ pC/N}$, electromechanical coupling factor (k_p) $= 36\text{--}40 \%$, mechanical quality factor (Q_m) $= 130$ and high curie temperature ($T_c \sim 420^\circ\text{C}$). However, the physical properties of the ceramics are still weak for application in piezoelectric devices.

Recently, special sintering processes such as Spark Plasma sintering (SPS), Hot pressing, Hot forging, and RTGG (Reactive template grain growth) have been utilized for

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manufacturing high performance ceramics [1]. However, the methods using these special sintering processes have high manufacturing costs. Therefore, new methods for manufacturing high performance ceramics have been introduced by using sintering aids such as CuO [2], ZnO, Ta₂O₅, [3–6] KNbO₃ [7], LiNbO₃, and K_{5.4}Cu_{1.3}Ta₁₀O₂₉ (KCT) [8–14]. They can be added in the basic composition ceramics to form a solid solution. Ta₂O₅ can be not only good sintering aids by the formation of K_{5.4}Cu_{1.3}Ta₁₀O₂₉ (KCT) [8–14] but also may act as the Ta⁵⁺ ion substituted at the B-site of the ABO₃ perovskite structure which make phase transition temperature orthorhombic-tetragonal phase transition (T_{O-T}) and tetragonal-cubic phase transition (T_C) decrease toward room temperature. In addition, potassium (K) of KCT acted as the compensating material for the volatilization of potassium.

2 Experimental

The specimens were manufactured using a conventional mixed oxide process. The compositions used in this study were as follows [15, 16];

$$[\text{Li}_{0.02}(\text{K}_{0.5}\text{Na}_{0.5})_{0.98}](\text{Nb}_{0.81}\text{Ta}_{0.15}\text{Sb}_{0.04})\text{O}_3 + x \text{ mol\% K}_{5.4}\text{Cu}_{1.3}\text{Ta}_{10}\text{O}_{29} \quad (x = 0, 0.2, 0.4, 0.6, 0.8)$$

The raw materials, Na₂CO₃ (99.5 %), K₂CO₃ (99.5 %), Sb₂O₅ (99.9 %), Nb₂O₅ (99.9 %), CuO (99.9 %), Li₂CO₃ (99 %) and Ta₂O₅ (99.95 %) for the given composition were weighted by mole ratio and the powders were ball-milled for 24 h. After drying, they were calcined at 900 °C and 950 °C for 6 h and 5 h, respectively. Thereafter, KCT was added as sintering aids and then the specimens were ball-milled and dried again. Polyvinyl alcohol (PVA: 5 wt.% aqueous solution) was subsequently added to the dried powders. The powders were molded under pressure of 2,000 kg/cm², burned out at 600 °C for 3 h, and then sintered at 1100–1120 °C for 5 h. The dimensions of the specimens were 17.2 Φ (diameter) × 1 mm (thickness). Poling was carried out at 100 °C in a silicon oil bath by applying a field of 3 kV/mm for 30 min. In order to investigate the dielectric properties, capacitance was measured at 1 kHz using an LCR meter (ANDO AG-4034) and the dielectric constant (ϵ_r) was calculated. Piezoelectric constants were obtained using a d_{33} meter (APC 8000 piezo d_{33} tester). For investigating the piezoelectric properties, the resonant and anti-resonant

frequencies were measured by an Impedance Analyzer (Agilent 4294A) according to the IEEE standard and then k_p and Q_m were calculated [17].

An X-ray diffractometer (XRD) (Rigaku, D/MAX 2500V) with CuK α 1 radiation ($\lambda=1.5406$ Å) was utilized to identify the crystal structure.

3 Results and discussion

Figure 1 presents the X-ray diffraction pattern as a function of KCT addition. The XRD analysis showed a typical perovskite structure. The XRD pattern of the ceramics in the range of 2θ from 43° to 48° indicated that the specimens have orthorhombic symmetry when $\text{KCT} \leq 0.2$ mol%, and then phases structure was changed from orthorhombic symmetry to tetragonal symmetry when $\text{KCT} \geq 0.4$ mol% because of the excess addition

Fig. 1 X-ray diffraction pattern as a function of KCT addition in the range 2θ ((a) 20°–65°, (b) 43°–48°)

of KCT. At room temperature, the crystal structures of all samples showed the pure perovskite without any secondary phases (indexed by JCPDS card no. 71–2171).

Figure 2 illustrates the microstructures of specimens as a function of KCT addition. It was observed that all samples had dense microstructures. The grain size gradually increased from 0 mol%KCT to 0.8 mol%KCT. The average grain size was obtained as approximately 2.6 μm , 2.89 μm , 3.86 μm , 3.94 μm and 4.5 μm , respectively. The grain size reached the maximum value at 0.8 mol%KCT. The pores were gradually decreased

by KCT addition. This may be due to the liquid phase that formed during the sintering process.

Figure 3 shows the bulk density and relative density of specimens as a function of KCT addition. As shown in Fig. 3, the (bulk) density gradually increased from 4.71 g/cm^3 to 4.81 g/cm^3 . This can be due to the improved sinterability as a function of KCT addition, and then little changed. The little change of density above 0.4 mol%KCT was attributed to the suppression of grain growth by excess KCT. The densities were researched as 4.71 g/cm^3 , 4.81 g/cm^3 , 4.82 g/cm^3 and 4.83 g/cm^3 , respectively.

Fig. 2 Microstructure as a function of KCT addition. (a) 0 mol%KCT, (b) 0.2 mol%KCT, (c) 0.4 mol%KCT, (d) 0.6 mol%KCT, (e) 0.8 mol%KCT

Fig. 3 Sintered density as a function of KCT addition

Fig. 5 Mechanical quality factor(Q_m) as a function of KCT addition

Figures 4 and 5 show the electromechanical coupling factor (k_p) and piezoelectric constant (d_{33}) as a function of KCT addition. The k_p values showed similar d_{33} values. k_p and d_{33} gradually increased. k_p and d_{33} showed the maximum values of 0.48 and 252[pC/N], respectively, at 0.4 mol%KCT addition. However, k_p and d_{33} decreased above 0.4 mol%KCT addition due to pores formed by the excess addition of KCT.

Figure 6 shows the dielectric constant (ϵ_r) as a function of KCT addition. The dielectric constant (ϵ_r) gradually increased from 1693 at 0.2 mol% KCT to 2789 at 0.6 mol% KCT, and then decreased. It is found that the dielectric constant (ϵ_r) was increased

due to the T_{o-t} shifted toward room temperature by Ta substitution.

Figure 7 shows the mechanical quality factor (Q_m) according to the amount of KCT addition. The mechanical quality factor (Q_m) increased from 80 at 0.2 mol%KCT to 141 at 0.4 mol% KCT because of the oxygen vacancies formed by Cu^{2+} ion substituted into the B-site in the ABO_3 perovskite structure. A similar tendency was observed for k_p and d_{33} .

Figure 8(a) shows the temperature dependence of the dielectric constant at 10 kHz. The Curie temperature T_c shifted toward the lower temperature region as a function of KCT addition. The orthorhombic–tetragonal phase transition temperature (T_{o-t}) appeared at room temperature as shown

Fig. 4 Electromechanical coupling factor (k_p) with the amount of KCT addition

Fig. 6 Dielectric constant(ϵ_r) as a function of KCT addition

Fig. 7 Piezoelectric constant(d_{33}) as a function of KCT addition

Fig. 9 Effect of KCT addition level on P-E hysteresis loop

Fig. 8 Dielectric constant as a function of KCT concentration

in Fig. 8(b). The substitution of Ta^{5+} ions in the B-site caused the phase transition shift toward the lower temperature range.

Figure 9 presents the P - E hysteresis loop of LKNTNS ceramics with $x=0, 0.2, 0.4, 0.6$ and 0.8 mol% sintered at 1100 – 1120 °C. The remnant polarization (P_r) rapidly increased from $3.54 \mu\text{C}/\text{cm}^2$ to $12.95 \mu\text{C}/\text{cm}^2$, and then gradually decreased from $12.95 \mu\text{C}/\text{cm}^2$ to $6.26 \mu\text{C}/\text{cm}^2$ as a function of KCT.

Table 1 shows the physical characteristics of the specimens as a function of KCT addition.

4 Conclusion

Lead-free $[\text{Li}_{0.02}(\text{K}_{0.5}\text{Na}_{0.5})_{0.98}](\text{Nb}_{0.81}\text{Ta}_{0.15}\text{Sb}_{0.04})\text{O}_3$ piezoelectric ceramics were prepared as a function of KCT addition by the conventional solid state reaction and normal sintering processes. Their piezoelectric and dielectric properties were investigated as a function of KCT addition. The results obtained from the experiment are as follows:

1. The grain size gradually increased from 0 mol%KCT to 0.8 mol%KCT.
2. The density gradually increased from $4.71 \text{ g}/\text{cm}^3$ to $4.81 \text{ g}/\text{cm}^3$ due to the improved sinterability with KCT addition.
3. The Curie temperature T_c shifted toward the lower temperature region with KCT addition.
4. Excellent physical properties of density= $4.81[\text{g}/\text{cm}^3]$, the electromechanical coupling factor (k_p)= 0.48 and the

Table 1 Physical characteristics of the specimens of LNKNTS ceramics as a function of KCT addition

Sintering Temp. [°C]	mol[%]	ρ [g/cm ³]	k_p	Q_m	d_{33} [pC/N]	Dielectric constant	To-t	Tc
1120 °C	0	4.78	0.42	70	170	1100	152	324
	0.2	4.71	0.41	80	171	1693	74	310
	0.4	4.81	0.48	141	252	2205	59	310
1100 °C	0.6	4.82	0.41	108	222	2789	70	290
	0.8	4.83	0.34	98	177	2554	85	280

piezoelectric constant(d_{33})=252[pC/N] were obtained in the composition ceramics with 0.4 mol%KCT.

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