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# (K,Na)NbO$_3$-based ceramics with excess alkali oxide for piezoelectric energy harvester

J.H. Kim[a], J.S. Kim[b], S.H. Han[c], H.-W. Kang[c], H.-G. Lee[c], C.I. Cheon[a,*]

[a]Department of Materials Science and Engineering, Hoseo University, Baebang, Asan, Chungnam 336-795, Republic of Korea
[b]Department of Digital Display Engineering, Hoseo University, Baebang, Asan, Chungnam 336-795, Republic of Korea
[c]Electronic Materials and Device Research Center, Korea Electronics Technology Institute, Bundang-gu, Seongnam, Kyeonggi 463-816, Republic of Korea

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## Abstract

$(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.1}Sb_{0.04})O_3$ (KNLNTS) ceramics were prepared by a solid-state reaction. The effect of excess $(K,Na)_2O$ alkali oxide on the densification, phase evolution, microstructure development, and piezoelectric properties was investigated. The figure of merit (FOM) ($d_{33} \cdot g_{33}$) for piezoelectric energy harvesting applications was also compared between the samples with and without excess alkali oxide. The addition of the excess alkali oxide changed the tetragonal crystal structure to orthorhombic and decreased the sintering temperature by about 100 °C. The dielectric constant of the orthorhombic phase is much lower than that of the tetragonal phase. The orthorhombic sample with excess alkali oxide sintered at 1020 °C demonstrated higher FOM in spite of having a smaller piezoelectric constant ($d_{33}$) than the stoichiometric sample sintered at 1100 °C. This result indicates that a KNN ceramic with an orthorhombic composition near the MPB with a moderate piezoelectric constant and smaller permittivity is more advantageous for an energy harvesting application than that with a morphotropic phase boundary (MPB) or a tetragonal composition.

*Keywords:* (K,Na)NbO$_3$-based; Excess alkali; Piezoelectricity; Energy harvester

## 1. Introduction

The wide range of piezoelectric material applications includes actuators, sensors, and transducers. Recently, piezoelectric energy harvesters that generate electrical energy from environmental vibrations have been developed for applications such as wireless self-powered sensor nodes [1–5]. A piezoelectric material with high energy density for energy harvesting applications is characterized by the figure of merit (FOM), which is the product of the piezoelectric voltage constant ($g$) and piezoelectric strain constant ($d$) [4,5]. A piezoelectric ceramic with a large $d$ and a small permittivity ($\varepsilon$) is favorable for energy harvesting applications because $g$ is defined by $d$ divided by $\varepsilon$ [4,5].

Global interest in the environment has been increasing, and many efforts have been made to develop lead-free piezoelectric ceramics such as (K,Na)NbO$_3$ (KNN) and (Bi,Na)TiO$_3$(BNT) in order to replace Pb(Zr,Ti)O$_3$ (PZT)-based ceramics [1–3,6–10]. KNN-based ceramics are one of the most promising candidates among various lead-free piezoelectric materials due to a large piezoelectric constant and a high Curie temperature [1–3]. KNN-based binary compositions such as (K,Na)NbO$_3$–LiSbO$_3$ demonstrate the best piezoelectric activity around the morphotropic phase boundary (MPB) between the orthorhombic and tetragonal phases [10]. However, the most favorable composition with a large $d$ and a small $\varepsilon$ for energy harvesting applications would be orthorhombic or tetragonal rather than the MPB because both $d$ and $\varepsilon$ decrease when the composition moves away from the MPB [1–3,10].

A multilayered piezoelectric ceramic is required for an actuator with a large displacement [11]. A piezoelectric material with a low sintering temperature is favorable for multilayered ceramics for

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*Corresponding author. Tel.: +82 41 540 5763; fax: +82 41 548 3502.
*E-mail address:* cicheon@hoseo.edu (C.I. Cheon).

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reducing the amount of expensive noble metal in the inner electrode (Ag/Pd) [12]. KNN-based ceramics have been successfully fabricated at low sintering temperature around 1000 °C by adding sintering aids such as excess alkali oxide, CuO, ZnO, or $LiBiO_2$ [12–17]. Excess of an alkali oxide like $Na_2O$ has been reported to reduce the sintering temperature and compensate for the alkali metal that evaporates during the sintering process [14].

In this work, stoichiometric $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.1}Sb_{0.04})O_3$ (KNLNTS) ceramics with high piezoelectric activity were prepared by a solid state reaction. The KNLNTS ceramic has been reported to show comparable piezoelectric properties to PZT-based piezoelectric ceramics [10]. Excess alkali oxide was added to the KNLNTS composition to decrease the sintering temperature. Excess alkali oxide was expected to change the crystal structure of the KNLNTS, which is tetragonal at room temperature, into MPB or orthorhombic. The densification, phase evolution, and microstructure development were investigated with respect to the sintering temperature. The effects of the excess alkali oxide on the sintering temperature and crystal structure were investigated. The piezoelectric properties and FOM for energy harvesting applications were compared between the samples with and without excess alkali oxide.

## 2. Experimental

$K_2CO_3$ (Aldrich, 99%), $Na_2CO_3$ (Aldrich, 99%), $Li_2CO_3$ (Aldrich, 99%), $Nb_2O_5$ (Aldrich, 99.9%), $Ta_2O_5$ (High Pure Chemicals, 99.9%), and $Sb_2O_5$ (High Pure Chemicals, 99.9%) powder were weighed in a desired mole ratio for $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.1}Sb_{0.04})O_3$ (KNLNTS). These were mixed by ball-milling for 24 h in plastic bottles with anhydrous ethanol and yttria-stabilized zirconia (YSZ) balls. After drying, the mixed powder was calcined at 900 °C for 4 h. The calcined powder was ball-milled again after adding 0.5 wt% polyvinyl butyral (PVB). 0.75 atomic% excess $(K, Na)_2O$ alkali oxide was added as a mixture of $K_2CO_3$ and $Na_2CO_3$ to the calcined powder before ball milling. The disk-type compacts with a diameter of 12 mm were formed by uniaxial pressing and heat-treated at 600 °C for 5 h for binder burn-out. The stoichiometric KNLNTS sample (ST) was sintered at 1100 °C for 3 h, and the sample with excess alkali (EX) was sintered at 960–1040 °C for 3 h.

The phases of the calcined and sintered samples were identified by X-ray diffraction analysis (XD-D1, Shimadzu). The surface morphologies were observed by a scanning electron microscope (SEC, SNE-4500E). The densities of the sintered samples were measured using Archimedes' principle. Silver paste was printed on the sintered sample and fired at 750 °C for 10 min for electrical measurements. A DC electric field of 3–5 kV/mm was applied to the samples for 30 min at 100 °C for dipole alignment (poling). The dielectric properties and electromechanical coupling factor of the samples were measured using an impedance analyzer (HP 4192A), and the piezoelectric constant $d_{33}$ was measured using a Berlincourt-type $d_{33}$ meter (YE2730A, APC International Ltd.).

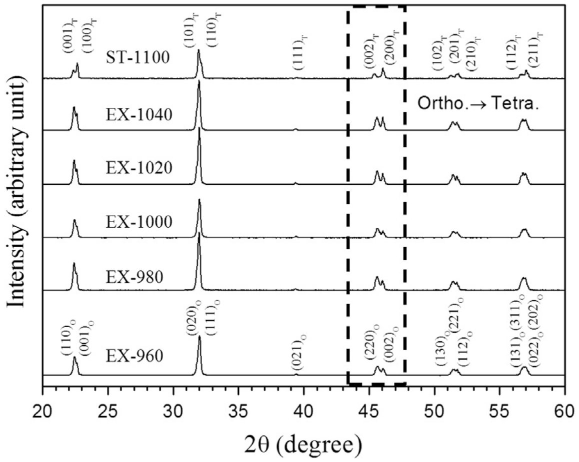

Fig. 1. X-ray diffraction patterns of the stoichiometric (ST) and alkali-excess (EX) samples sintered at various temperatures.

## 3. Results and discussion

Fig. 1 displays the X-ray diffraction patterns of the ST sample sintered at 1100 °C (ST-1100) and EX samples sintered at 960–1040 °C (EX-960–EX-1040). The ST-1100 sample has a tetragonal structure, which is in accordance with a previous report [10], whereas the EX sample sintered at 960 °C has an orthorhombic structure. The crystal structure of Li-doped KNN ceramics has been reported to vary from orthorhombic to tetragonal with the increase of Li content [18]. The orthorhombic nature of the EX samples (lower part in Fig. 1) indicates that the excess alkali oxides penetrated into the grains and actually increased the (Na+K)/Li ratio in the lattice. Fig. 1 also demonstrates that the EX sample starts to change its structural characteristics from orthorhombic to tetragonal at above 1020 °C. This suggests that a part of the excess alkali evaporated during the sintering process above this temperature and that the amount of excess alkali was actually reduced.

Fig. 2 shows that the sintered density increases with the sintering temperature in the alkali-excess sample and becomes larger at sintering temperature above 1020 °C than that of the ST-1100 sample. This indicates that the excess alkali reduces the sintering temperature of the KNLNTS ceramic effectively by forming a liquid phase and facilitating the densification, which agrees with previous reports [14].

Surface morphologies of EX samples sintered at 1000–1040 °C are displayed in Fig. 3. That of the ST-1100 sample is also shown in Fig. 3 for comparison. The EX-1000 has a uniform microstructure with grain sizes of 1–2 µm or smaller, as shown in Fig. 2(a) and (e). When the sintering temperature increases above 1000 °C, some grains grow abnormally, resulting in a bimodal size distribution of large 20–30-µm grains and small 1–2-µm grains, as shown in Fig. 3(a)–(c).

The changes of the density and piezoelectric properties with the increase of the sintering temperature are displayed in Table 1. The piezoelectric properties of the EX-960 sample could not be measured due to a low insulating resistivity. When the sintering temperature increases, the density and the piezoelectric