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Temperature stability of the piezoelectric properties of Li-modified KNN ceramics

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Abstract

Presently, the most promising family of lead-free piezoelectric ceramics is based on $K_{0.5}Na_{0.5}NbO_3$ (KNN). Lithium doped KNN ceramics show high piezoelectric properties at room temperature. An issue of particular interest for medical applications is the temperature stability of the properties because of the need for repeated sterilization process at around 140 °C. A concern with Li-doped KNN is that the properties may not be thermally stable because the orthorhombic–tetragonal phase transition temperature is close to the room temperature. We report on electromechanical properties of KNN-modified with 3–6 atomic % Li, measured by resonance technique in function of temperature from 20 to 140 °C, during two heating and cooling cycles. The piezoelectric coefficients d_{31} and radial coupling coefficients k_p are decreased up to 30% of their initial value after the first heating cycle. However, after the second cycle, the properties stabilize. The depoling is smaller in compositions that do not undergo a phase transition in the examined temperature interval.

Keywords: Lead-free ceramics; Dielectric properties; Piezoelectric properties; Biomedical applications

1. Introduction

The most widely used piezoelectric ceramics are lead oxide based ferroelectrics, especially $Pb(Zr,Ti)O_3$ (PZT). PZT exhibits high piezoelectric properties close to a morphotropic phase boundary (MPB) between rhombohedral and tetragonal phases. Typical compositions can contain up to 60% lead by weight.

Because of lead toxicity, the current legislations in Europe[1] require gradual removal of lead from electronic components. Good candidates to replace the lead based piezoelectric ceramics, are compositions based on potassium sodium niobate family (K, Na)NbO_3 or KNN. This solid solution exhibits an MPB between two different orthorhombic phases at around 50:50 K–Na, accompanied with an increase in the piezoelectric properties.[2,3] Nevertheless, the electromechanical properties of KNN ceramics are significantly lower to those of PZT.

Recently, modified KNN ceramics, obtained by replacing the A and/or the B site cation of the ABO_3 perovskite structure, have shown to exhibit properties comparable to those of PZT ceramics.[4] In particular, KNN ceramics modified by $LiNbO_3$,[5,6] $LiTaO_3$[6,7] or $SrTiO_3$ exhibit a thickness coupling coefficient $k_t > 50\%$ and the converse piezoelectric coefficient d_{33} around 200 pm/V for the Li substituted ceramics, and a $k_t > 50\%$ and d_{33} over 300 pm/V for the Li and Ta-modified compositions.[4] A d_{33} over 400 pm/V has been reported in textured (K,Na,Li)(Nb,Ta)O_3 ceramics.[6]

In doped materials, the maximum properties were reported in compositions containing about 6% Li[4–6] and this maximum has been attributed to the presence of an MPB between an orthorhombic and a tetragonal phase. On the other hand, the thermally induced phase transition between these phases for this composition occur close to the room temperature.[4] Two questions can be posed: first, whether the high properties reported in these materials are due to a thermally induced phase transition near room temperature, or are due, as in PZT, to the presence of a phase transition in function of composition, independent of the temperature. The second, and closely related question concerns the fact that the domain configuration changes on crossing the orthorhombic–tetragonal phase transition temperature during temperature cycling. This may lead to partial depoling of samples, which is of a considerable practical importance. For medical applications, for example, the probes containing piezoelectric transducer sometimes need to be sterilized at temperatures close to 140 °C. Comparable temperatures

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may be encountered during the probe fabrication. Ideally, for transducers operating at room temperature, the initial room temperature properties should be recovered after repeated thermal cycling.

The goal of this paper is to investigate the thermal behaviour of the electromechanical properties of KNN ceramics that show elevated properties near the room temperature. Successive thermal cycles similar to those used during the sterilization processes are performed and piezoelectric properties are measured during the cycling using the resonance technique.

2. Experimental

Lithium-modified KNN ceramics of compositions $(K_{0.5-x/2}Na_{0.5-x/2}Li_x)NbO_3$ (with $x = 0.03, 0.05, 0.06, 0.07$) were prepared by solid state synthesis from K_2CO_3 (99.997%), Na_2CO_3 (99.997%), Li_2CO_3 (99.999%) and Nb_2O_5 (99.9985%,) starting powders, which were dried at 200 °C prior to use. After separate milling, the powders were mixed together with the aid of ZrO_2 balls for 24 h in isopropanol. Two calcinations at 825 °C for 4 h, separated by attrition milling, were then performed to get a good compositional homogeneity. Finally, the powders were pressed into 15 mm diameter pellets and sintered in air, at temperatures between 1065 and 1095 °C, with a short dwell time of 10 min to avoid grain growth.

The sintered samples were ground and polished to obtain an aspect ratio suitable for resonance measurements. Cr–Au electrodes were sputtered onto both parallel surfaces of the disks. The samples were subsequently poled at 50 °C and under 50 kV/cm for different times (ranging from 5 to 15 min), optimized for the different compositions. To minimize aging effects, the resonance measurements were performed at least 3 days after the poling. Thin copper wires were glued with silver paste on each electroded surface, and the samples were supported only by these wires during the resonant measurements. Two thermal cycles from 20 to 140 °C were made with each sample, and properties were measured during the heating and cooling.

Radial mode electromechanical coupling coefficients k_p, piezoelectric coefficient d_{31}, permittivity and mechanical coefficients s_{11}^E, s_{12}^E and Poisson's coefficient were determined by the IEEE resonance method[8] using an impedance analyzer HP 4194 (Agilent, USA). Piezoelectric d_{31} and k_p were determined using resonance method described in detail in Ref.[9]

The thickness mode coupling coefficient could not be reliably measured with the IEEE technique because of numerous spurious modes that interfered with the thickness mode resonance at high temperatures.

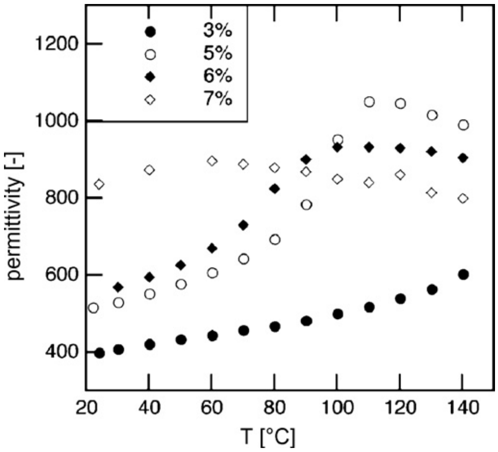

Fig. 1. Dielectric properties of lithium-modified KNN ceramics for (●) 3% Li, (◯) 5% Li, (♦) 6% Li and (() 7% Li.

3. Results and discussion

As shown in Table 1, the initial electromechanical properties at room temperature are in good agreement with the previous reports,[5] confirming the enhancement of the properties in this composition region. Note that, as is the case with PZT, the properties do not peak at the same composition.[10] The dielectric permittivity at room temperature increases with Li concentration, indicating the decrease of the orthorhombic–tetragonal phase transition temperature with increasing Li concentration. This is also an indication that the effect of the phase transition temperature shift on the permittivity is probably stronger than an MPB effect.

The temperature dependence of the permittivity, shown in Fig. 1, confirms the presence of a phase transition in the temperature region between 20 and 140 °C for compositions with 5% and 6% Li. The composition containing 3% lithium has a phase transition temperature from the orthorhombic to the tetragonal structure higher than 140 °C. In the case of 7% lithium ceramics, the orthorhombic to tetragonal phase transition temperature is located below room temperature. The apparent peak in permittivity visible for this composition in Fig. 1 between 40 and 60 °C is present only in poled samples and powder diffraction indicates the tetragonal structure at room temperature. The ceramics with 3% and 7% Li thus do not change crystal structure and remain, respectively, orthorhombic and tetragonal over the examined temperature interval.

The temperature dependence of the electromechanical properties of the MPB composition $(K_{0.47}Na_{0.47}Li_{0.06})NbO_3$ are

Table 1
Electromechanical properties of the $(K_{0.5-x/2}Na_{0.5-x/2}Li_x)NbO_3$ ceramics at room temperature obtained with the resonance technique before thermal cycling

Li (%)	3	5	6	7
ε	418	420	480	760
s_{11}^E (m^2/N)	10.5×10^{-12}	10.5×10^{-12}	11.4×10^{-12}	12.8×10^{-12}
s_{12}^E (m^2/N)	-4.27×10^{-12}	-3.60×10^{-12}	-4.21×10^{-12}	-5.54×10^{-12}
k_p	0.348	0.520	0.474	0.486
d_{31} (pC/N)	−38	−59	−59	−76
k_{31}	0.189	0.299	0.266	0.259

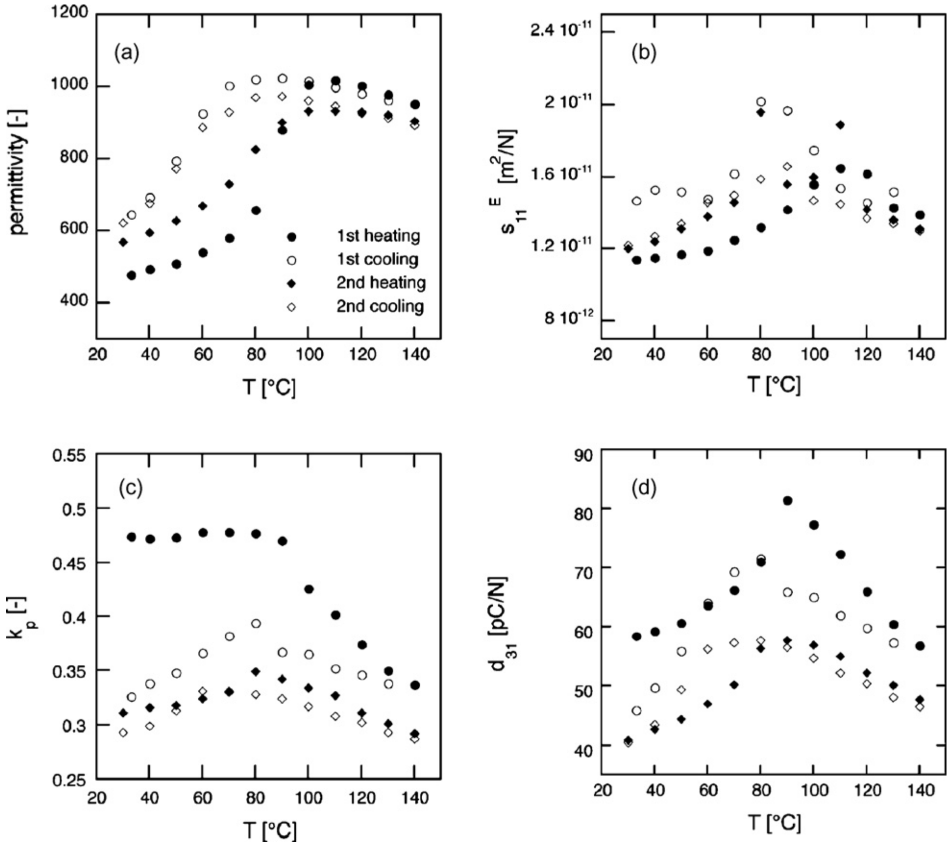

Fig. 2. Electromechanical properties of $(K_{0.47}Na_{0.47}Li_{0.06})NbO_3$ ceramics: (a) permittivity, (b) mechanical compliance s_{11}^{E}, (c) radial mode coupling coefficient k_p and (d) piezoelectric coefficient d_{31}.

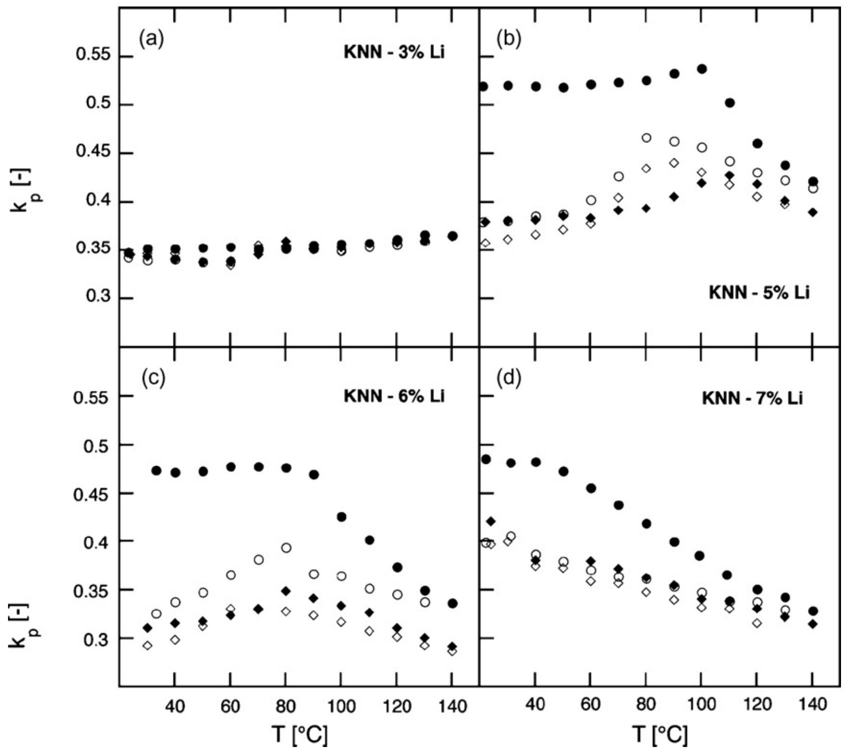

Fig. 3. Planar coupling coefficient of Li-modified KNN ceramics around orthorhombic–tetragonal phase transition temperature, for (a) 3% Li, (b) 5% Li, (c) 6% Li and (d) 7% Li.

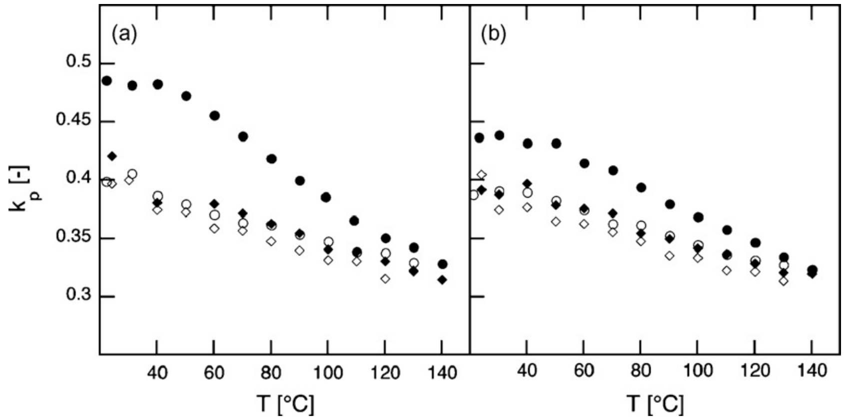

Fig. 4. Planar coupling coefficient of ($K_{0.465}$, $Na_{0.465}$, $Li_{0.07}$)NbO_3 ceramics for two different poling conditions: (a) at 50 °C, 50 kV/cm for 15 min and (b) at 150 °C, 30 kV/cm for 15 min with field cooling.

shown in Fig. 2. Thermal hysteresis of the dielectric permittivity of about 30 °C during heating and cooling cycles is indicative of the first-order phase transition between the orthorhombic and tetragonal phases. It should be noted that for each measurement, the temperature was stabilized for at least 10 min. All the other electromechanical properties measured show a maximum at the temperature of the phase transition. A decrease of about 30% of the piezoelectric coefficient d_{31} and the radial coupling coefficient k_p can be noticed after the first cycle. Considering the properties after the first and the second heating and cooling cycle, no additional significant decrease in properties is observed.

The radial coupling coefficient in function of the temperature for all the compositions is shown in Fig. 3. The depoling (decease in k_p between 20% and 30%) during the first heating cycle is stronger for the two compositions, 5% and 6% Li, going through a phase transition in the temperature range of the measurement. The same behaviour is also seen in the case of the piezoelectric coefficient d_{31}. In the case of the ceramic with 3% Li, the thermal cycling doesn't affect the radial coupling coefficient, as well as the other properties obtained. Considering the tetragonal ceramic (7% Li), a small depoling (a decrease of about 10% of the piezoelectric properties) in observed. After the second heating and cooling cycle, when the properties are stabilized, this composition exhibit the best properties among the examined ceramics with $d_{31} = -69$ pC/N and $k_p = 0.41$.

The poling conditions (50 °C, 50 kV/cm) used were the best found for these ceramics, however, as the poling temperature lies in the temperature range of the measurements, there is a concern that depoling may be related to a relatively low poling temperature. Another poling has been performed on a 7% Li ceramic, at 150 °C, with a field of 30 kV/cm applied for 15 min, with field cooling. The electromechanical properties after poling are not as good as for the low temperature poling, as can be seen in the case of the radial coupling coefficient in Fig. 4. After cycling the two samples up to 140 °C, the properties stabilize at the same values. At least for this composition the poling conditions do not seem to affect the thermal stability of the electromechanical properties.

4. Summary and conclusions

The electrochemical properties of lithium-modified KNN ceramics have been measured as a function of temperature in the interval from room temperature to 140 °C during two heating and cooling cycles. For the compositions, which cross orthorhombic–tetragonal phase transition at the examined temperature range, the depoling is strong (piezoelectric properties being decreased by about 20–30%) while the decrease of the piezoelectric properties in the case of ceramics which remain tetragonal or orthorhombic in the examined temperature range is lower than 10%. After cycling, the best piezoelectric properties are obtained for composition with $x = 0.07$: $d_{31} = -69$ pC/N and $k_p = 0.41$. As the decrease of the properties is significant, there is a need to look for new compositions with a better thermal stability of the electromechanical properties.

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