Electrical and structural characterization of
(K_xNa_{1-x})NbO₃ ceramics modified with Li and TaHenry E. Mgbemere,^a Manuel Hinterstein^b and Gerold A. Schneider^{a*}^aInstitute of Advanced Ceramics, Hamburg University of Technology, Denickestrasse 15, 21073 Hamburg, Germany, and ^bInstitut für Werkstoffwissenschaften, Technische Universität Dresden, Helmholtzstrasse 7, 01069 Dresden, Germany. Correspondence e-mail: g.schneider@tu-harburg.deReceived 8 April 2011
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(K_xNa_{1-x})NbO₃ ceramics modified with Li⁺ and Ta⁵⁺ have been produced using the mixed-oxide synthesis method. Synchrotron X-ray diffraction measurements were made on the samples from 12 K to temperatures above their ferroelectric–paraelectric transition points with 10 K measurement steps. Rietveld refinement was used to refine the patterns. Depending on the composition and temperature, rhombohedral phases, orthorhombic phases, tetragonal phases, cubic phases and two-phase mixtures were obtained. Space groups *R3c* (161), *Amm2* (38), *P4mm* (99) and *Pm3̄m* (221) and their combinations were used to refine the rhombohedral, orthorhombic, tetragonal, cubic and mixed phases, respectively. Li⁺ addition suppressed the formation of the rhombohedral low-temperature phase and increased the Curie temperature. This is attributed to the size difference in ionic radii of the *A*-site elements, which leads to increased atomic polarizability and increased interaction with the *B*-site element. Li⁺ and Ta⁵⁺ co-doping led to a wide temperature range of coexistence between the orthorhombic and tetragonal phases. Electrical characterizations by dielectric and hysteresis measurements were used to compare with the results from the structural studies.

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1. Introduction

Lead zirconate titanate (PZT)-based ceramics are the most frequently used piezoelectric ceramics in devices for sensing, electromechanical and actuation purposes. Environmental safety awareness and legislation against continuing the use of lead has made it necessary that lead-free piezoelectric ceramic alternatives are used to replace PZT-based ceramics. The potential lead-free alternatives include BaTiO₃-based ceramics (Hippel, 1950), (Bi_{0.5}Na_{0.5})TiO₃-based ceramics (Take-naka *et al.*, 1997; Ichinose & Udagawa, 1995) and (K_xNa_{1-x})NbO₃ (KNN)-based ceramics (Egerton & Dillion, 1959). KNN is a solid solution of ferroelectric KNbO₃ and antiferroelectric NaNbO₃. It undergoes a series of phase transitions, just like BaTiO₃, and the structure of this composition has been well investigated (Shirane *et al.*, 1954; Lufaso *et al.*, 2006; Egerton & Dillion, 1959). It has a relatively high Curie temperature *T*_c (~693 K) and moderate piezo-electricity (~80 pC N⁻¹) (Egerton & Dillion, 1959). When other elements are added to this composition in the form of dopants, its sinterability and piezoelectric properties are improved, while the phase transition temperatures are lowered in most cases (Saito *et al.*, 2004; Noheda *et al.*, 2000; Hagh *et al.*, 2008).

The effect of doping KNN with Li⁺ has been investigated by a lot of researchers. Guo *et al.* (2004) studied Li⁺ addition from 4 to 20 mol% and reported an improvement in the piezo-electric properties but also showed that, above 8 mol%, an

extra phase (K₃Li₂Nb₅O₁₅) begins to form. High-temperature dielectric studies (Zhao *et al.*, 2007; Klein *et al.*, 2007; Du *et al.*, 2007) have been used to investigate the changes in phase transition temperature with Li⁺ addition, while thermal cycling (Hollenstein *et al.*, 2007) was used to study its effect on the properties of KNN. Raman spectroscopy and dielectric and piezoelectric measurements were used to construct a phase diagram for Li⁺-doped KNN ceramics, and the authors reported the occurrence of a rhombohedral phase at very low temperatures (Klein *et al.*, 2007). Rietveld refinement using a two-phase model with space groups *Amm2* and *P4mm* was used to refine the crystal structure of this composition up to 6 mol% Li⁺ at room temperature (Lee *et al.*, 2007).

Ta⁵⁺ was reported to lower both the electromechanical quality factor and the phase transition temperatures when added to KNN (Mgbemere *et al.*, 2010). It also decreased the grain size of KNN ceramics owing to the high temperatures required for the sintering (Zuo *et al.*, 2009). There are some reports in the literature about the doping of KNN with both Li⁺ and Ta⁵⁺ (Saito *et al.*, 2004; Hollenstein *et al.*, 2005). In one of the reports on KNN modified with 7 mol% LiTaO₃, space group *P1m1* was used as a reference for the refinement of the patterns and the temperature-dependent lattice parameters were obtained. An extra phase, however, can be observed in the diffraction pattern used for the Rietveld refinement (Skidmore *et al.*, 2009). The piezoelectric and electro-mechanical properties of the samples are reported to be

Table 1

OES–ICP analysis data and calculated molar amounts of the elements in our composition.

Element	Li	Na	K	Nb	Ta	O	Zr†
$(\text{K}_{0.48}\text{Na}_{0.48}\text{Li}_{0.04})\text{NbO}_3$							
OES–ICP values (g kg^{-1})	1.27 (3)	68.9 (14)	108 (22)	526 (11)	–	281 (6)	0.40
Element amount (mol)	0.03136	0.51369	0.47346	0.97041	–	3.01034	<0.00075
$(\text{K}_{0.5}\text{Na}_{0.5})(\text{Nb}_{0.90}\text{Ta}_{0.1})\text{O}_3$							
OES–ICP values (g kg^{-1})	–	64.5 (13)	105 (2)	452 (9)	98.2 (20)	266 (5)	0.40
Element amount (mol)	–	0.50957	0.48777	0.88364	0.09857	3.01966	<0.00080
$(\text{K}_{0.48}\text{Na}_{0.48}\text{Li}_{0.04})(\text{Nb}_{0.9}\text{Ta}_{0.1})\text{O}_3$							
OES–ICP values (g kg^{-1})	0.96 (2)	64.6 (13)	101 (2)	451 (9)	101 (2)	267 (5)	0.40
Element amount (mol)	0.02502	0.5083	0.46736	0.87825	0.10098	3.01922	<0.00079

† Zr is an impurity that was introduced into the sample during processing.

increased, while their phase transition temperatures decreased.

There is not much information in the literature with regard to structural studies of modified KNN ceramics at either cryogenic or elevated temperatures. Synchrotron diffraction is a very important tool for studying structures of crystalline substances. In this investigation, KNN modified with Li^+ , Ta^{5+} , and a combination of Li^+ and Ta^{5+} was synthesized and analyzed from 12 K to temperatures above their respective T_c . Dielectric and hysteresis measurements were also carried out on the samples. The objective of this article is to determine in these ceramics the relative amount of phases present, their lattice parameters and phase transition temperatures from cryogenic temperatures to temperatures above their ferroelectric paraelectric transition temperatures, and to compare these results with those obtained through electrical characterization.

2. Experimental details

2.1. Sample preparation

The intended compositions to be produced using the conventional synthesis method are $(\text{K}_{0.48}\text{Na}_{0.48}\text{Li}_{0.04})\text{NbO}_3$, $(\text{K}_{0.5}\text{Na}_{0.5})(\text{Nb}_{0.9}\text{Ta}_{0.1})\text{O}_3$ and $(\text{K}_{0.48}\text{Na}_{0.48}\text{Li}_{0.04})(\text{Nb}_{0.9}\text{Ta}_{0.1})\text{O}_3$. K_2CO_3 , Na_2CO_3 , Li_2CO_3 (99%), Nb_2O_5 and Ta_2O_5 (99.9%) (Chempur Feinchemikalien und Forschungs GmbH, Karlsruhe, Germany) were the raw powders used for the synthesis. The powders were dried at 473 K, mixed, attrition milled for 4 h and calcined in air at 1023 K for 4 h. The milling step was repeated to ensure that a homogenous powder was obtained and to reduce the particle size. They were pressed into pellets with a cold isostatic press at 300 MPa for 2 min. The pellets were sintered in air at temperatures ranging from 1343 to 1373 K for 1 h with a heating and cooling rate of 2 and 10 K min^{-1} , respectively. The pellets were ground for both chemical analysis and synchrotron X-ray diffraction measurements. In order to reduce residual stresses, the samples were annealed at 1023 K for 30 min.

The optical emission spectroscopy/inductive coupled plasma (OES–ICP; PE–Optima 7000 DV) analysis technique was used to determine the quantitative amount of each

element present and search for possible impurities that may have been introduced during processing. A mean value was obtained from four separate measurements, and the OES–ICP values as well as the element amounts in moles are shown in Table 1. Owing to sublimation during the sintering process as a result of the high volatility of some elements, small amounts of some elements were lost.

The amounts of Na^+ , Ta^{5+} and O^{2-} in most cases either remained the same or were slightly higher than the calculated amounts before the synthesis, while the amounts of Li^+ and K^+ were lower. Since the starting powders were not 100% pure, it is possible

that some of the powders contained small amounts of these elements in excess. The final compositions were adjusted to reflect the changes in the amounts of elements present after the chemical analysis. Grinding balls made from zirconia were used during the milling process and the chemical analysis showed that small amounts were introduced into the samples. Finally, we concluded that our compositions are actually $(\text{K}_{0.47}\text{Na}_{0.51}\text{Li}_{0.03})(\text{Nb}_{0.97})\text{O}_{3.01}$ abbreviated as KNN-L, $(\text{K}_{0.49}\text{Na}_{0.51})(\text{Nb}_{0.88}\text{Ta}_{0.1})\text{O}_3$ denoted as KNN-T and $(\text{K}_{0.47}\text{Na}_{0.51}\text{Li}_{0.025})(\text{Nb}_{0.88}\text{Ta}_{0.1})\text{O}_{3.02}$ abbreviated as KNN-LT.

2.2. Synchrotron X-ray data collection and refinement

The synchrotron X-ray diffraction data were collected at the synchrotron facility (beamline B2, HASYLAB/DESY) in Hamburg from 12 to 773 K (well above the paraelectric cubic phase transition) in steps of 10 K. Low-temperature (12–300 K) measurements were performed in a closed cycle capillary cryostat (Cryophysics) (Ihringer & Küster, 1993), while the high-temperature measurements were performed using a capillary furnace from Stoe & Cie (type 0.65.3). Data were recorded by a position-sensitive image-plate detector (OBI, *ortsfest auslesbarer Bildplattendetektor*) (Knapp, Bahtz *et al.*, 2004) at wavelengths between 0.6880 and 0.6888 Å. More details about the experimental setup at the beamline can be found in the literature (Knapp, Joco *et al.*, 2004; Knapp, Bahtz *et al.*, 2004).

All the collected data were refined by the Rietveld method using the software package *FULLPROF* (Rodríguez-Carvajal, 1990). In *Amm2*, the different values of b_o and c_o lead to a rhombic distortion of the (001)_c plane resulting in an expansion along [110]_c. The subscripts 'c', 'o', 't' and 'h' denote the pseudo-cubic, orthorhombic, tetragonal and rhombohedral unit cells, respectively. Because of symmetry restrictions, the number of refinable parameters in *Amm2* is smaller than in *Pmm2* and so *Amm2* was used instead of *Pmm2*. *Amm2* is set up in such a way that the polarization vector is aligned along [110]_c.

The background under the peaks was refined using a linear interpolation between points from the regions in which no reflections contributed to the intensity. The model used was based on a Thompson–Cox–Hastings pseudo-Voigt profile

function, which is convoluted with asymmetry owing to the axial divergence as formulated by Laar & Yelon (1984) and using the method of Finger and co-workers (Finger *et al.*, 1994;

Finger, 1998). The atomic positions and the isotropic atomic displacement parameters B_{iso} were refined. Efforts to refine the structure using anisotropic displacement parameters were not successful. The anisotropic peak broadening model in the general strain formulation following Stephens (1999) was used to refine the strain in the sample.

2.3. Temperature-dependent measurement of electric properties

In order to compare the phase transition temperatures observed from the X-ray measurements with dielectric properties, dielectric measurements were carried out at elevated temperatures. The surfaces of the pellets were coated with silver paint, which acted as electrodes for the dielectric measurement. The temperature dependence of the dielectric properties of the ceramics was measured with an LCR meter (HP 4284A, Agilent Technologies Inc., Palo Alto, USA) connected to a heating chamber. The measurements were made from room temperature up to temperatures above the ferroelectric–paraelectric transitions for the respective samples using 5 K temperature steps. The dielectric properties plots were constructed with data obtained at a frequency of 100 kHz.

Polarization and strain hysteresis measurements were carried out at room temperature using the standard Sawyer–Tower circuit, and a complete dipolar hysteresis measurement was performed in 200 s. Unipolar strain hysteresis measurement was used to determine the piezoelectric charge coefficient values.

3. Results and discussion

3.1. Structural characterization

The measured and calculated diffraction profiles and their difference curves for the KNN-L, KNN-T and KNN-LT ceramics taken at 20 K are shown in Fig. 1. KNN-L and KNN-LT (Figs. 1*a* and 1*c*) show an orthorhombic $Amm2$ phase, while KNN-T (Fig. 1*b*) shows a rhombohedral $R3c$ phase. The insets in the figures are enlarged sections of the patterns with higher 2θ regions (35–55°). The clear splitting of the 200_c reflection at approximately 20° (Figs. 1*a* and 1*c*) shows that the phase present is orthorhombic, while for the rhombohedral phase (Fig. 1*b*) the 200_c reflection shows no splitting. This indicates that the presence of Li⁺ in KNN ceramics stabilizes the orthorhombic phase at lower temperatures by suppressing the orthorhombic to rhombohedral phase transition.

The refinement parameters for KNN-L, KNN-T and KNN-LT ceramics for the lowest temperatures of each model used for the refinement are shown in Tables 2, 3 and 4, respectively.¹ The lattice parameters for KNN-L, KNN-T and KNN-LT ceramics as a function of temperature are shown in Fig. 2. Depending on the composition, a series of phase transformations were observed from 12 K to temperatures above the respective T_c of the samples. Orthorhombic, rhombohedral,

Figure 1 Measured and calculated synchrotron X-ray diffraction profiles and their difference curves for (a) KNN-L measured at 20 K showing the orthorhombic phase, (b) KNN-T measured at 20 K showing the rhombohedral phase and (c) KNN-LT measured at 20 K showing the orthorhombic phase.

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: CG5189). Services for accessing these data are described at the back of the journal.

Table 2

Experimental details and refinement results for KNN-L at 12, 373, 393 and 753 K.

Phase type	Single	Two-phase		Single	Single
Crystal system	Orthorhombic	Orthorhombic	Tetragonal	Tetragonal	Cubic
Space group	<i>Amm2</i>	<i>Amm2</i>	<i>P4mm</i>	<i>P4mm</i>	<i>Pm3m</i>
Temperature (K)	12	373	373	393	753
<i>a</i> (Å)	3.93132 (3)	3.94646 (4)	3.95257 (8)	3.95531 (3)	3.97596 (16)
<i>b</i> (Å)	5.63895 (5)	5.64422 (7)	—	—	—
<i>c</i> (Å)	5.68307 (5)	5.67812 (7)	4.03856 (15)	4.03898 (4)	—
<i>V</i> (Å ³)	125.9851 (17)	126.478 (3)	63.094 (3)	63.1878 (10)	62.8532 (4)
ρ (g cm ⁻³)	4.451	4.436	—	4.438	4.424
<i>Z</i>	2	2	1	1	1
Refinement					
<i>R</i> _p (%)	7.19	10.1	—	12.5	11.7
<i>R</i> _{wp} (%)	9.25	12.7	—	16.8	14.7
<i>R</i> _{exp} (%)	2.04	2.28	—	2.31	2.36
GOF	4.5	5.5	—	7.1	6.2
χ^2	20.6	30.8	—	53.2	38.9
No. of parameters	35	43	43	30	24

Table 3

Experimental details and refinement results for KNN-T at 12, 170, 190, 443 and 643 K.

Phase type	Single	Two-phase		Single	Single	Single
Crystal system	Rhombohedral	Rhombohedral	Orthorhombic	Orthorhombic	Tetragonal	Cubic
Space group	<i>R3c</i>	<i>R3c</i>	<i>Amm2</i>	<i>Amm2</i>	<i>P4mm</i>	<i>Pm3m</i>
Temperature (K)	12	170	170	190	443	643
<i>a</i> (Å)	5.61271 (4)	5.61662 (5)	3.94036 (6)	3.94128 (2)	3.96331 (2)	3.98276 (19)
<i>b</i> (Å)	—	—	5.63778 (12)	5.63739 (4)	—	—
<i>c</i> (Å)	13.83390 (4)	13.83255	5.67068 (10)	5.67081 (4)	4.02016 (3)	—
<i>V</i> (Å ³)	377.417 (4)	377.905 (5)	125.974 (4)	125.9970 (14)	63.1479 (6)	63.1758 (5)
ρ (g cm ⁻³)	4.726	4.720	—	4.719	4.709	4.704
<i>Z</i>	6	6	2	2	1	1
Refinement						
<i>R</i> _p (%)	6.38	6.50	—	6.34	8.33	9.22
<i>R</i> _{wp} (%)	8.38	8.56	—	8.23	10.6	12.1
<i>R</i> _{exp} (%)	1.91	3.76	—	1.89	2.14	2.20
GOF	4.4	4.5	—	4.4	7.1	5.5
χ^2	19.2	20.66	—	19.0	24.6	30.2
No. of parameters	27	35	—	35	30	20

Table 4

Experimental details and refinement results for KNN-LT at 12, 293, 383 and 693 K.

Phase type	Single	Two-phase		Single	Single
Crystal system	Orthorhombic	Orthorhombic	Tetragonal	Tetragonal	Cubic
Space group	<i>Amm2</i>	<i>Amm2</i>	<i>P4mm</i>	<i>P4mm</i>	<i>Pm3m</i>
Temperature (K)	12	293	293	383	693
<i>a</i> (Å)	3.93602 (3)	3.94594 (5)	3.95505 (12)	3.95496 (2)	3.96519 (2)
<i>b</i> (Å)	5.63331 (6)	5.6418 (2)	—	—	—
<i>c</i> (Å)	5.67188 (6)	5.66929 (11)	4.0038 (5)	4.02479 (3)	4.01483 (3)
<i>V</i> (Å ³)	125.761 (2)	126.212 (5)	62.629 (8)	62.9544 (7)	63.1240 (7)
ρ (g cm ⁻³)	4.709	4.701	—	4.703	4.693
<i>Z</i>	2	2	1	1	1
Refinement					
<i>R</i> _p (%)	6.26	4.50	—	6.08	6.17
<i>R</i> _{wp} (%)	8.06	5.70	—	8.05	7.85
<i>R</i> _{exp} (%)	1.81	1.51	—	1.21	1.75
GOF	4.4	3.8	—	6.6	4.5
χ^2	19.7	14.3	—	44.1	20.2
No. of parameters	35	46	—	30	30

tetragonal and cubic phases were observed, and for these phases, the space groups *Amm2*, *R3c*, *P4mm* and *Pm3m* were used for the refinement. There are temperature ranges where

phase coexistence occurred, and for such phase mixtures, a combination of the respective models was used for the refinement.

The orthorhombic cell parameters *b*_o and *c*_o for all the graphs in Fig. 2 were divided by 2^{1/2}, while the rhombohedral cell parameters *a*_h and *c*_h were divided by 2^{1/2} and 12^{1/2}, respectively, for better representation so that they will fit well with *a*_t and *c*_t from the tetragonal phase.

KNN-L (Fig. 2*a*) exhibits an orthorhombic phase from 12 to 363 K. Between 373 and 383 K, phase coexistence between the orthorhombic and the tetragonal phases could be observed. The tetragonal phase existed from 393 to 743 K, and above this temperature the cubic phase was present. In KNN-T (Fig. 2*b*) the rhombohedral phase was observed from 12 to 160 K, with a two-phase coexistence of the rhombohedral and the orthorhombic phases between 170 and 180 K. From 190 to 423 K the orthorhombic phase was present, showing a two-phase coexistence of the orthorhombic and the tetragonal phases at 433 K. From 453 to 633 K the tetragonal phase was observed, and above 643 K the sample was cubic. In KNN-LT (Fig. 2*c*) the orthorhombic phase was present from 12 to 240 K, with a broad two-phase coexistence of the orthorhombic and the tetragonal phases between 273 and 373 K. The tetragonal phase was present from 383 to 693 K, and above this temperature the cubic phase was present.

Different values of *b*_o and *c*_o in space group *Amm2* lead to a rhombic distortion of the (001)_c plane, which results in an expansion along [110]_c. The pseudo-cubic lattice parameter *a*_{pc} was calculated using

$$a_{pc} = (b_o^2 + c_o^2)^{1/2}/2. \quad (1)$$

The pseudo-monoclinic angle β was derived from equation (2):

$$\beta = 2 \arcsin[c_o/(2a_{pc})]. \quad (2)$$

The plot of the pseudo-monoclinic angle as a function of temperature for KNN-L, KNN-T and KNN-LT is shown in Fig. 3. In all cases, the pseudo-monoclinic angle decreases with

Figure 2

Temperature dependence of the lattice parameters ($\text{\AA}$) a_h , c_h for the rhombohedral phase, a_o , b_o , c_o for the orthorhombic phase, a_t , c_t for the tetragonal phase and a_c for the cubic phase for (a) KNN-L ceramics with coexistence of the orthorhombic and tetragonal phase between 373 and 383 K, (b) KNN-T ceramics with phase coexistence between the rhombohedral and orthorhombic phase between 170 and 180 K and orthorhombic and tetragonal phases at 433 K, and (c) KNN-LT ceramics with coexistence of the orthorhombic and tetragonal phases from 273 to 373 K.

increasing temperature. The pseudo-monoclinic angle increased in the following order: KNN-T, KNN-LT and KNN-L, which shows that such lattice deformation does not require monoclinic symmetry. The scattering of the values obtained for the KNN-LT composition from ~ 280 K corresponds to the two-phase coexistence between the orthorhombic and the tetragonal phases.

The percentage of the constituent phases in the samples was calculated through the scale factors, which involve the product of mass and volume of the unit-cell contents of each phase. The weight fraction of the phase (W_P) was obtained using

$$W_P = \frac{S_P(Z, M, V)_P \tau_j}{\sum_j S_j(Z, M, V)_j \tau_P}, \quad (3)$$

where W_P is the relative weight fraction of phase P in a mixture of j phases, while S , Z , M , τ and V are the Rietveld scale factors obtained from the refinement, the number of formula units per unit cell, the mass of the formula unit, the Brindley particle absorption contrast factor and the unit-cell volume, respectively.

The weight fractions of the phases present in the samples as a function of temperature are shown in Fig. 4. In KNN-L (Fig. 4a) the rhombohedral phase was not observed at low temperatures, and the phase coexistence between the orthorhombic and the tetragonal phase occurred within a narrow temperature range between 373 and 383 K. The temperature range of phase coexistence in KNN-LT was wider than that in the other compositions. The coexistence ranges from 240 to 383 K. The temperature range of phase coexistence is even wider (up to 453 K) when Sb^{5+} is added to the sample (Mgbemere *et al.*, 2011). In KNN-T (Fig. 4c) two different phase coexistence regions are observed. The first is between the rhombohedral and orthorhombic phases, while the second is between the orthorhombic and tetragonal phases. They occurred at between 170 and 180 K for the former and at 433 K for the later. The rhombohedral phase was observed in the KNN-T composition from 12 to 180 K, and to calculate the rhombohedral angle α_{pc} in the pseudo-cubic cell, the lattice

Figure 3

Pseudo-monoclinic angle as a function of temperature for KNN-L, KNN-T and KNN-LT ceramics.

parameters (a_h and c_h) of the hexagonal cell are used, as shown in equation (4):

$$\cos \alpha_{pc} = (c_h^2 - 6a_h^2)/(c_h^2 + 12a_h^2). \quad (4)$$

The lattice strain is the deviation of the rhombohedral angle from 90° (Thomas, 1996; Zhang *et al.*, 2009), and the corresponding plot for KNN-T ceramics is shown in Fig. 5. As the temperature increased, the lattice strain gradually decreased and remained constant at the phase boundary.

Figure 4
Weight fractions of the phases in percent as a function of temperature for (a) KNN-L, (b) KNN-LT and (c) KNN-T ceramics.

Domain formation and mechanical treatments on the ceramics during the synthesis and sample preparation steps are expected to introduce stresses and strains in the samples. Although the samples were annealed prior to being measured, all the stresses and strains may not be relieved and they contribute to lattice distortion. The distortions of the lattice (%) for the rhombohedral, orthorhombic and tetragonal phases were calculated using equations (5), (6) and (7), respectively:

$$\eta(r) = \left\{ \left[c_h / (6^{1/2} a_h) \right] - 1 \right\} 100, \quad (5)$$

$$\eta(o) = \left\{ \left[c_o / (2^{1/2} a_o) \right] - 1 \right\} 100, \quad (6)$$

$$\eta(t) = \left\{ \left[c_t / a_t \right] - 1 \right\} 100. \quad (7)$$

The lattice distortion (%) as a function of temperature for the samples is shown in Fig. 6. The largest lattice distortions in both the orthorhombic and the tetragonal phase were obtained from the KNN-L composition. In the orthorhombic phase, the distortion is $\sim 2.25\%$, and as the temperature

Figure 5
Lattice strain for KNN-T ceramics.

Figure 6
Lattice distortion (%) as a function of temperature (12–773 K) for KNN-L, KNN-T and KNN-LT ceramics. Depending on the composition, rhombohedral, orthorhombic and tetragonal distortions were observed.

Table 5
Comparison of the reported phase transition temperatures obtained in this work with those reported in the literature for similar compositions.

Composition	Reference	T_c (K)		T_{T-O} (K)
		X-ray	Dielectric	Dielectric
(K _{0.47} Na _{0.51} Li _{0.03})(Nb _{0.97} O _{3.01}) (KNN-L)	This work	~753	~730	~416
0.97(K _{0.5} Na _{0.5})NbO ₃ -0.03LiNbO ₃	Klein <i>et al.</i> (2007)	–	~700	~420
0.96(Na _{0.5} K _{0.5})NbO ₃ -0.04LiNbO ₃	Guo <i>et al.</i> (2004)	–	~728	~398
0.95(Na _{0.5} K _{0.5})NbO ₃ -0.05LiNbO ₃	Du <i>et al.</i> (2007)	~773	~753	~298
(K _{0.49} Na _{0.51})(Nb _{0.88} Ta _{0.1})O ₃ (KNN-T)	This work	~643	~631.7	~450
(KNa) _{0.97} (Nb _{0.9} Ta _{0.1})O ₃	Matsubara <i>et al.</i> (2005)	–	~633	~443
(Na _{0.5} K _{0.5})(Nb _{0.9} Ta _{0.1})O ₃	Lin <i>et al.</i> (2008)	–	~633	~453
(K _{0.47} Na _{0.51} Li _{0.025})(Nb _{0.88} Ta _{0.1})O _{3.02} (KNN-LT)	This work	~693	~666	–
(Na _{0.535} K _{0.48}) _{0.942} -Li _{0.058} (Nb _{0.9} Ta _{0.1})O ₃	Zhao <i>et al.</i> (2008)	–	~703	~323
(KNb) _{0.975} Li _{0.025} (Nb _{0.9} Ta _{0.1})O ₃	Saito & Takao (2006)	–	~648	–
(K _{0.46} Na _{0.5} Li _{0.04})(Nb _{0.85} Ta _{0.15})O ₃	Chang <i>et al.</i> (2009)	–	~643	~293

increases, the distortion decreases. When a new phase is formed, the distortion jumps to a higher value and gradually decreases with increasing temperature. When the temperature approaches T_c , the distortion rapidly drops to near zero. The same trend was observed for the KNN-LT composition with the difference that the distortions are lower. The scattering of the distortion values corresponds to the two-phase coexistence in the sample. For the KNN-T composition the degree of distortion in the rhombohedral phase is the smallest.

3.2. Electrical characterization

Plots of the dielectric properties for KNN-L, KNN-T and KNN-LT ceramics from room temperature to temperatures above their T_c are shown in Fig. 7. The enlarged insets highlight the behavior near the tetragonal to orthorhombic phase transition temperature (T_{T-O}). The temperatures at which the phase transitions occurred in the samples are slightly higher than those obtained from X-ray diffraction. A possible reason could be the differences in strain constraints in the samples used for the measurements. The samples for X-ray diffraction were ground and annealed prior to the measurements, while the samples used for dielectric measurements were in pellet form. The powders for X-ray diffraction were rotated during measurement to ensure that averaged results were obtained, while fixed bulk ceramic pellets were used for the dielectric measurement. In a related article by Pramanick *et al.* (2011) polycrystalline constraints, domain wall motion and interphase boundary motion were said to have significant effects on the properties of the ceramics.

For the KNN-L composition, the value of T_c , corresponding to a peak value of ~10 000, was found to be ~753 K in the dielectric measurement and ~730 K with X-ray diffraction. In the KNN-T composition, the dielectric peak has a value of ~5000 and the corresponding T_c was observed at 631 K, whereas a value of ~643 K was obtained with X-ray diffraction, while for the KNN-LT composition, it was observed at ~666 K (~5000) in the dielectric measurement and ~693 K by X-ray diffraction. The variations in the reported T_c and T_{T-O} values for similar compositions in the literature are shown in Table 5. For the KNN-L composition, a T_{T-O} value between

~393 and 423 K and T_c in the range 713–733 K with lower dielectric peak were reported (Du *et al.*, 2007; Klein *et al.*, 2007; Hollenstein *et al.*, 2005). For KNN-T-like compositions, the reported T_{T-O} and T_c values were ~460 and 623–633 K, respectively (Matsubara *et al.*, 2005; Lin *et al.*, 2008), while for KNN-LT-like compositions, the reported T_{T-O} and T_c values were ~293 and 623–713 K (Chang *et al.*, 2009; Zhao *et al.*, 2008). The shape of the peak at T_{T-O} appears to be more diffuse with increasing temperature range of the phase coexistence in the material.

For KNN-T, the dielectric constant *versus* temperature curve shows a phase change T_{T-O} at 443 K. As the degree of phase coexistence increases, the shape of the curve becomes diffuse and the exact transition temperature cannot be clearly determined, especially for the KNN-LT composition (Fig. 7*a*). The dielectric loss in the samples is shown in Fig. 7*b*). In the KNN-L and KNN-T

Figure 7
Variation of (a) the dielectric constant and (b) the dielectric loss ($\tan \delta$) as a function of temperature for KNN-L, KNN-T and KNN-LT ceramics measured at 100 kHz.

compositions, high loss values were obtained compared to that for the KNN-LT composition. As the measurement temperature increases, the loss values for KNN-L and KNN-T also increase, but the loss values for KNN-LT remain approximately the same. This shows that the properties of KNN-LT can be stable over a wide temperature range.

The polarization hysteresis curves for the samples are shown in Fig. 8(a). When a field of $\sim 20 \text{ kV cm}^{-1}$ is applied, hysteresis loops with near saturation polarization were obtained for some samples. A remnant polarization P_r value of $25 \mu\text{C cm}^{-2}$ was obtained for the KNN-L composition, while the coercive field E_C was $\sim 8 \text{ kV cm}^{-1}$ for all compositions. For the KNN-T composition, P_r was $\sim 16.5 \mu\text{C cm}^{-2}$, and it was $\sim 13 \mu\text{C cm}^{-2}$ for the KNN-LT composition. P_r values in the literature ($17\text{--}19 \mu\text{C cm}^{-2}$) for compositions close to KNN-T are similar; the only difference is that we used lower applied fields (Matsubara *et al.*, 2005). For KNN-LT compositions, slightly higher P_r values ($25 \mu\text{C cm}^{-2}$) were reported in the literature (Chang *et al.*, 2009).

The strain hysteresis loops for the samples showing the typical butterfly shape that indicates ferroelectricity are shown in Fig. 8(b). High remnant strain S_r (0.0013) was obtained for the KNN-L composition, which corresponds to the high lattice distortion for the sample in Fig. 6. Moderately high S_r was

Figure 8
Variation of (a) polarization-field hysteresis loops and (b) strain-field hysteresis loops measured at room temperature for KNN-L, KNN-T and KNN-LT ceramics.

Table 6

Density, remnant polarization P_r , coercive field E_C , remnant strain S_r and piezoelectric coefficient d_{33}^* values for KNN-L, KNN-T and KNN-LT ceramics studied at room temperature.

Composi- tion	Density (g cm^{-3})	Theoretical density at 293 K (g cm^{-3})	P_r ($\mu\text{C cm}^{-2}$)	E_C (kV cm^{-1})	S_r	d_{33}^* (pm V^{-1})
KNN-L	4.12 (4)	4.44	25.0	8.0	0.0013	206.7 (80)
KNN-T	4.40 (7)	4.71	16.5	7.8	0.000136	103.5 (151)
KNN-LT	4.23 (3)	4.70	13.0	7.8	0.00047	228.0 (64)

obtained for KNN-LT (0.00047), while a very low S_r (0.000136) was obtained for the KNN-T composition. There are very few reports in the literature on strain hysteresis of KNN-based ceramics with similar composition to ours and so it is difficult to make a comparison of S_r values. The asymmetry in the loop for the KNN-L composition is possibly due to uneven distribution of charges, as the field is applied in opposite directions (Robels *et al.*, 1995; Lupascu & Rabe, 2002). The piezoelectric charge coefficient (d_{33}^*) values for the samples obtained using unipolar strain hysteresis measurements are shown in Table 6. The highest value [$228 (6) \text{ pm V}^{-1}$] is obtained with the KNN-LT composition, followed by KNN-L with a value of $206 (8) \text{ pm V}^{-1}$. The highest relative density value of $\sim 93\%$ was obtained with the KNN-T composition, but the d_{33}^* value was the lowest [$103 (15) \text{ pm V}^{-1}$]. A slightly higher d_{33}^* value was reported for the KNN-T composition, and this increment was attributed to 'softening' of the ceramic due to the presence of KTaO_3 (Lin *et al.*, 2008). For KNN-L compositions a slightly lower value was reported (Du *et al.*, 2007; Guo *et al.*, 2004), and for KNN-LT-like compositions, a range of values were reported depending on the composition (Chang *et al.*, 2009; Hollenstein *et al.*, 2005; Zhao *et al.*, 2008). A summary of the density, P_r , E_C , S_r and d_{33}^* values is given in Table 6.

3.3. Discussion

Materials that undergo a first-order phase transition exhibit a discontinuity in the polarization, lattice parameters and other properties (Boettger, 2004). The lattice parameters for all the samples show discontinuities at the phase transitions (Fig. 2), indicating that they all undergo a first-order phase transition. Noheda *et al.* (2002) reported that, when there is a second-order phase transition, no phase coexistence should be observed, thereby confirming the first-order phase transition. It is not clear if the phase coexistence is an intrinsic feature of modified KNN ceramics or just a compositional fluctuation over a small range of temperature or composition. More research needs to be done to clarify this.

The chemical composition and radii of the ions influence how ferroelectric phases are formed. Li^+ has a very small ionic radius (76 pm) compared to either K^+ (138 pm) or Na^+ (102 pm). Ta^{5+} , being a transition element, has a lot of valence states with different ionic radii. If the valence state is +5, the ionic radius is similar to that of Nb^{5+} (64 pm), but as the valence state decreases, the ionic radius increases (Shannon,

1976). The huge difference in the ionic radius of Li^+ compared to the A -site elements that it replaces may explain why the rhombohedral low-temperature phase is suppressed while T_c is shifted to higher temperatures. Similar results have been reported for Ca^{2+} - and Pb^{2+} -doped BaTiO_3 , where T_c increased with doping while other phase transition temperatures decreased (Mitsui & Westphal, 1961). Both elements have a smaller ionic radius than Ba^{2+} , giving them more space and higher atomic and electronic polarizability, respectively, which intensifies the interactions between the Ti^{4+} ions (Mitsui & Westphal, 1961).

Addition of dopants is known to result in the lowering of the phase transition temperatures (Zhang *et al.*, 2007). Instead of the normal morphotropic phase boundary that is observed in PZT, a polymorphic phase transition occurs, and this is both a composition- and a temperature-dependent phenomenon. Phase coexistence leads to the formation of a polymorphic phase boundary, which results in higher piezoelectricity than is possessed by pure KNN, especially for isovalent dopants (Zhang *et al.*, 2007). The increase in the number of possible polarization directions is also a possible reason for the enhanced piezoelectric properties. A total of 18 possible polarization directions of the domains are therefore available for a mixture of orthorhombic (12 $[110]_c$) and tetragonal phases (6 $[001]_c$).

As the temperature range of the phase coexistence becomes wider, the piezoelectric coefficient becomes higher, especially for KNN with Li, Ta and Sb (Saito *et al.*, 2004; Mgbemere *et al.*, 2009), but unlike in PZT, the d_{33}^* value is not greatly increased at the phase boundary.

The dielectric constant values always peak at T_c because the polarizability of the lattice is higher and is also associated with the increased density of free conducting electrons (Damjanovic, 2005). The highest value of dielectric constant at T_c was obtained with the KNN-L composition (Fig. 7a), and it also has the highest dielectric loss values. As the temperature increases, it is probable that there is motion of Li^+ ions in the lattice, which creates interfacial ionic polarization within the Nb—O framework, giving rise to large dielectric constants (Glass *et al.*, 1977). This motion of the Li^+ ions also accounts for the high dielectric loss in the KNN-L composition. It can also be explained in terms of the mobility of the free electronic or ionic charges in the sample, leading to ease of domain wall movement and therefore high dielectric loss. When Ta^{5+} is added to the Li^+ (KNN-LT), it appears that this motion is reduced in the lattice, leading to reduced dielectric constant and loss values.

A decrease in the lattice distortion also results in a reduction of both the spontaneous polarization and the strain (Hoffmann *et al.*, 2004). The high P_r value for KNN-L is related to the high lattice distortion at all temperatures. Addition of Ta^{5+} to the Li^+ (KNN-LT) decreases the lattice distortion, the spontaneous polarization and S_r . The KNN-T composition has low distortion values, possibly because Ta^{5+} inhibits the domain wall movement owing to the presence of a large concentration of defects (Saito & Takao, 2006). This reduces the average grain size in KNN, which results in higher

relative density values. The uneven strain hysteresis loop for KNN-L (Fig. 8b) is possibly due to inhomogeneities in the charge carrier densities in the sample (Robels *et al.*, 1995). The d_{33}^* value for the KNN-T composition is low even when the relative density is higher than that for other compositions, possibly because of the difficulty of aligning the domains when the electric field is applied.

4. Conclusion

Synchrotron X-ray diffraction was used to characterize KNN ceramics modified with Li^+ and Ta^{5+} from 12 K to temperatures above their respective T_c using a 10 K measurement step. OES–ICP analysis showed that, after sintering, the presence of elements with high vapor pressure (Li^+ and K^+) is lower than the intended compositions and that small amounts of ZrO_2 are introduced into the samples. Li^+ in KNN suppresses the formation of the rhombohedral low-temperature phase, and this is attributed to the size difference between the ionic radii of the A -site elements. When only Ta^{5+} is added to KNN, the rhombohedral to octahedral phase transition is observed at ~ 170 K. With co-doping of Li^+ and Ta^{5+} in KNN, a wide temperature range of phase coexistence is observed with a slightly higher piezoelectric coefficient owing to the higher number of possible polarization directions. High dielectric constant peaks, lattice distortion, spontaneous polarization, and strain and dielectric constants are obtained with Li^+ -doped KNN ceramics. This is attributed to the ease of domain wall movement and the high mobility of the free electrons or ionic charges in the sample. A higher density value does not always translate to enhanced piezoelectric properties as there are other determining factors involved.

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