Structural phase transitions and electrical properties of $(K_xNa_{1-x})NbO_3$ -based ceramics modified with Mn

Henry E. Mgbemere^a, Manuel Hinterstein^b, Gerold A. Schneider^{a,*}

^a Institute of Advanced Ceramics, Hamburg University of Technology, Denickestraße 15, 21073 Hamburg, Germany

^b Institut für Werkstoffwissenschaft, Technische Universität Dresden, Helmholtzstraße 7, 01069 Dresden, Germany

Received 28 March 2012; received in revised form 4 July 2012; accepted 26 July 2012

Available online 13 August 2012

Abstract

$(K_{0.5}Na_{0.5})NbO_3$ (KNN) ceramics and KNN containing Li, Ta modified with 2 mol% of manganese have been produced using the mixed-oxide ceramics synthesis route. The structure and properties of these piezoelectric ceramics modified with manganese have been investigated using high resolution X-ray diffraction and electrical characterisation. The structural information about the ceramics was determined by Rietveld refinement with Fullprof. The phase transition temperatures observed with X-ray diffraction compares well with the values from dielectric studies. The addition of Mn slightly reduced the phase transition temperatures and for the sample containing only Li, the phase changed from orthorhombic to monoclinic phase with space group *Pm*. The dielectric, piezoelectric and ferroelectric properties of the samples decreased with Mn addition due to hard doping effects resulting from oxygen vacancies in the perovskite lattice.

© 2012 Elsevier Ltd. All rights reserved.

Keywords: Powders-solid state reaction; X-ray methods; Ferroelectric properties; Perovskites; Actuators

1. Introduction

Researches into lead-free KNN-based piezoelectric ceramics have increased in the last 10 years because of the need to find piezoelectric ceramic compositions with good piezoelectric properties and are also environmentally harmless. The properties of unmodified KNN ceramics have been reported in the literature.^{1,2} It has a high Curie temperature (T_c) ~ 420 °C, phase boundaries which resemble the morphotropic phase boundary in $Pb(Zr_xTi_{1-x})O_3$ (PZT) ceramics but a low piezoelectric coefficient (~ 80 pC/N) and other electromechanical properties which do not meet the requirements for industrial applications.

Substitution in KNN ceramics with isovalent elements has been used by many researchers to improve both the piezoelectric properties and the sintering process. When used in their optimum amounts to dope KNN ceramics, Sb,³ Li,^{4,5} Ta⁶ alone or in combination^{7–11} have all been reported to improve the piezoelectric properties.

Manganese is an interesting element because of its multivalent ions (Mn^{2+} , Mn^{3+} , Mn^{4+}) and its ability to improve sintering, resistivity and quality mechanical factor (Q_m) of piezoelectric ceramics. It acts as a domain pinning element in $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics¹² and with more than 0.5 wt.% in $Pb(Zr_{1-x}Ti_x)O_3$ – $Pb(Zn_yNb_{1-y})O_3$ ceramics, densification deteriorates and the crystal structure changes from tetragonal to rhombohedral.¹³ It changes the crystal structure from tetragonal to rhombohedral in $(Bi_{0.5}Na_{0.5})TiO_3$ – $BaTiO_3$ (BNT–BT) ceramics^{14–17} and the piezoelectric response decreases with ≥ 0.8 wt.%.¹⁶ In a BNT single crystal with increasing amounts of Mn, the sequence of phase transition is not altered but the transition temperature is lowered.¹⁷ Based on results of the dielectric, piezoelectric and electromechanical properties, Mn is believed to enter both A- and B-sites of the lattice in $(CaSr)Bi_4Ti_4O_{15}$ ceramics.¹⁸ The Mn^{3+} is believed to play a critical role in the soft and hard doping effects. When used to dope $BaTiO_3$ ceramics (0.5–1.7 mol%), the crystal structure changes from tetragonal to hexagonal.¹⁹ Jahn Teller distortions by Mn_{Ti}^{3+} were proposed to be the driving force for the phase transition.

Mn also promotes densification and slightly lowers the remanent polarisation (P_r) and coercive field (E_c) in $(K_xNa_{1-x})NbO_3$ ceramics.²⁰ Decreased leakage current and high current densities

* Corresponding author. Tel.: +49 04042878 3037; fax: +49 04042878 2647.
E-mail address: g.schneider@tu-harburg.de (G.A. Schneider).

Table 1
OES-ICP data and the calculated molar amounts of the elements in the samples.

Element	Li	Na	K	Nb	Ta	Mn	O	Zr*
(K_{0.5}Na_{0.5})NbO₃								
OES-ICP values (g/kg)	–	78.1 (2)	125 (2)	587 (8)	–	–	271	<0.5
Element amount (mol)	–	0.53737	0.50682	1	–	–	3	<0.00075
(K_{0.50}Na_{0.50})(Nb_{0.98}Mn_{0.02})O₃								
OES-ICP values (g/kg)	–	72.7(1)	121 (1)	581 (16)	–	6.4 (1)	284	<0.5
Element amount (mol)	–	0.49523	0.48469	0.98	–	0.01917	2.92174	<0.00075
(K_{0.48}Na_{0.48}Li_{0.04})(Nb_{0.98}Mn_{0.02})O₃								
OES-ICP values (g/kg)	1.52 (1)	72.6 (3)	120 (1)	577 (1)	–	6.04 (1)	286	0.5
Element amount (mol)	0.03446	0.49853	0.4827	0.98	–	0.01794	2.91646	0.0009
(K_{0.50}Na_{0.50})(Nb_{0.88}Ta_{0.1}Mn_{0.02})O₃								
OES-ICP values (g/kg)	–	66.4 (3)	113 (7)	423 (5)	109 (1)	5.69 (1)	270	<0.5
Element amount (mol)	–	0.51723	0.51689	0.81487	0.10812	0.01853	3.02436	<0.00075
(K_{0.48}Na_{0.48}Li_{0.04})(Nb_{0.88}Ta_{0.1}Mn_{0.02})O₃								
OES-ICP values (g/kg)	1.28 (8)	66.3 (4)	115 (17)	476 (35)	113 (8)	5.57 (6)	272	0.5
Element amount (mol)	0.03198	0.50017	0.5088	0.88784	0.10845	0.01757	2.94419	0.00075

are the results of doping KNN single crystals with Mn.^{21,22} When used to dope (K_{0.5}Na_{0.5})_{0.935}Li_{0.065}NbO₃ ceramics, no significant change on the crystal structure was observed and hard ferroelectric effects were observed due to oxygen vacancies.²³ A change of valence state from Mn⁴⁺ to Mn³⁺ has been observed using synchrotron X-ray absorption spectroscopy for (K_{0.5}Na_{0.5}Li_{0.065})NbO₃ doped with Mn and the phase was identified to be tetragonal.²⁴ With 0.8 mol% Mn in 0.98(K_{0.5}Na_{0.5})NbO₃–0.02(BiScO₃) ceramics, the optimum values of piezoelectric and dielectric properties were obtained.²⁵ Both acceptor and donor doping effects and phase coexistence are reported in Mn-doped 0.94(K_{0.5}Na_{0.5})NbO₃–0.06Ba(Zr_{0.05}Ti_{0.95})O₃ ceramics.²⁶

Most of these studies on Mn doped KNN-based ceramics mainly concern electrical properties. There is very little information on its effect on the structure and phase coexistence in these KNN ceramics. Synchrotron diffraction was used in this work to study the effect of Mn doping on the structure of KNN based ceramics. The objective of this work therefore, is to study the effect of Manganese on KNN-based ceramics and to correlate the results of structural studies with the electrical properties of these ceramics.

2. Experimental details

2.1. Sample preparation

The compositions intended to be produced are (K_{0.5}Na_{0.5})NbO₃, (K_{0.50}Na_{0.50})(Nb_{0.98}Mn_{0.02})O₃, (K_{0.48}Na_{0.48}Li_{0.04})(Nb_{0.98}Mn_{0.02})O₃, (K_{0.50}Na_{0.50})(Nb_{0.88}Ta_{0.1}Mn_{0.02})O₃, (K_{0.48}Na_{0.48}Li_{0.04})(Nb_{0.88}Ta_{0.1}Mn_{0.02})O₃. K₂CO₃, Na₂CO₃, Li₂CO₃ (99%), Nb₂O₅ and Ta₂O₅ (99.9%) (Chempur Feinchemikalien und Forschungs GmbH, Karlsruhe, Germany) and MnO₂ (Merck chemicals Darmstadt, Germany) are the raw powders used for the synthesis. The powders were first dried in the oven at 220 °C for 4 h to remove any moisture present. Stoichiometric amounts of the starting oxide-based

powders were measured while 2 mol% excess powders were added for the carbonates. The powders were milled using an attrition mill operating at 500 rpm for 2 h with ethanol as solvent and 3 mm Ø zirconia balls as grinding media. Solvent extraction was carried out to separate the ethanol from the powder while the powders were calcined at 850 °C for 4 h with a heating rate of 3 °C/min. The milling process was repeated to homogenise the powders and to reduce the average particle size of the powders to below 1 µm. A cold isostatic press operating at 300 MPa was used to press the samples for 2 min. The samples were sintered in air for 1 h with a heating rate of 2 °C/min and a cooling rate of 10 °C/min at different temperatures as indicated in the brackets [(K_{0.5}Na_{0.5})NbO₃ 1085 °C, (K_{0.50}Na_{0.50})(Nb_{0.98}Mn_{0.02})O₃ 1060 °C, (K_{0.48}Na_{0.48}Li_{0.04})(Nb_{0.98}Mn_{0.02})O₃ 1050 °C, (K_{0.50}Na_{0.50})(Nb_{0.88}Ta_{0.1}Mn_{0.02})O₃ 1085 °C, (K_{0.48}Na_{0.48}Li_{0.04})(Nb_{0.88}Ta_{0.1}Mn_{0.02})O₃ 1070 °C]. The densities of the samples were measured using the Archimedes method. The samples for chemical analysis and synchrotron diffraction measurements were ground and annealed at 900 °C for 4 h. The samples were polished while those used for microstructural investigations were chemically etched using Mastermet (Al₂O₃-based suspension) and also thermally etched at 950 °C for 30 min at 10 °C/min heating and cooling rates. The grain size measurements were determined using the mean intercept length method from a minimum of six different area of the micrograph. The samples were poled at room temperature with a field of 2 kV/mm. Polarisation 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 coefficient (d_{33}^*) values.

Optical emission spectroscopy-inductive coupled plasma (OES-ICP (PE-Optima 7000 DV)) analysis was used to determine quantitatively the amount of each element present. A mean value was obtained from four separate measurements and the element amounts in moles are shown in Table 1. Small amounts of

some elements were lost while a small amount of Zr was introduced through the grinding balls made from ZrO_2 . The slight increase in the amounts of some elements could be due to their presence as impurities in other powders. The final compositions were adjusted to reflect the changes observed after the chemical analysis. Finally, the actual compositions were adjusted to be:

$(\text{K}_{0.507}\text{Na}_{0.537})\text{NbO}_3$	(KNN)
$(\text{K}_{0.485}\text{Na}_{0.495})(\text{Nb}_{0.98}\text{Mn}_{0.019})\text{O}_{2.92}$	(KNN-2Mn)
$(\text{K}_{0.483}\text{Na}_{0.499}\text{Li}_{0.04})(\text{Nb}_{0.98}\text{Mn}_{0.018})\text{O}_{2.96}$	(KNNLi-2Mn)
$(\text{K}_{0.517}\text{Na}_{0.517})(\text{Nb}_{0.815}\text{Ta}_{0.108}\text{Mn}_{0.019})\text{O}_{3.024}$	(KNNTa-2Mn)
$(\text{K}_{0.509}\text{Na}_{0.5}\text{Li}_{0.032})(\text{Nb}_{0.888}\text{Ta}_{0.108}\text{Mn}_{0.018})\text{O}_{2.944}$	(KNNLiTa-2Mn)

2.2. Synchrotron X-ray data collection and refinement

The X-ray data were collected at the synchrotron facility (beamline B2, HASYLAB/DESY) in Hamburg from 26 °C to 500 °C in steps of either 10 °C or 20 °C. High temperature measurements were performed using a capillary furnace from Stoe & Cie type 0.65.3 and the data were recorded on heating by a position sensitive image plate detector (OBI, *ortsfest auslesbarer Bildplattendetektor*)²⁷ at a wavelength of 0.6881 Å. More details about the experimental setup at the beamline can be found in the literature.^{27,28}

All the collected data were analysed by the Rietveld refinement method using the Fullprof software.²⁹ 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 T–C–H pseudo-Voigt profile function which is convoluted with asymmetry due to axial divergence as formulated by Laar and Yelon³⁰ and using the method of Finger et al.^{31,32} The atomic positions and the isotropic atomic displacement parameters B_{iso} were refined. The anisotropic peak broadening model in the general strain formulation from Stephens was used to refine the strain in the sample.³³

2.3. Temperature-dependent measurement of dielectric properties

The dielectric property measurements were carried out from room temperature to temperatures above the respective T_c of the samples. The surfaces of the pellets were coated with silver paints which acted as electrodes for the dielectric measurements. The measurements were done with an LCR meter (HP 4284A, Agilent Technologies, Inc., Palo Alto, USA) connected to a heating chamber at 5 °C. The dielectric properties plots were made with data obtained at a frequency of 100 kHz.

3. Results and discussion

3.1. Structural characterisation

Fig. 1 shows the measured and calculated diffraction profiles and the difference curves taken at 27 °C for KNN-based ceramics modified with Mn. KNN, KNN-2Mn and KNNTa-2Mn samples in Fig. 1a, b and d, respectively, have orthorhombic symmetry

at 27 °C, while KNNLi-2Mn (Fig. 1c) has monoclinic symmetry and KNNLiTa-2Mn (Fig. 1e) has a two-phase coexistence between an orthorhombic and a tetragonal phase. The inset in each figure shows the enlarged section of the patterns with higher 2θ regions (35–55°). The refinement was carried out from 27 °C to temperatures above the respective T_c of the samples.

In order to show the difference between the orthorhombic and the monoclinic phase, an enlargement of the patterns between 2θ angles (19–24°) is shown in Fig. 2 and a representation of the two structures is shown in Fig. 3. The clear splitting of the 200_c reflection at ~20° shows a threefold splitting for KNNLi-2Mn which means that all three axes in the pseudo-cubic cell are of different length. This indicates at least orthorhombic symmetry. A ferroelectric orthorhombic structure like *Amm*2 is setup in a way so that the b_o and c_o axes are the $[1\ 1\ 0]_c$ axes (Fig. 3a). If $b_o \neq c_o$ this results in a rhombic distortion of the $(0\ 0\ 1)_c$ plane with two equal a_{pc} (or $[1\ 0\ 0]_c$) axes. To reproduce the resulting angle α together with three different $\langle 1\ 0\ 0 \rangle_c$ directions, monoclinic symmetry is necessary. In this case we used *P11m* with the mirror plane perpendicular to the c -axis and gamma (γ) as the monoclinic angle (Fig. 3b). The effect of the monoclinic angle can be observed at the 110_c reflection in Fig. 2. It shows a fourfold splitting into $1\ 1\ 0$, $-1\ 1\ 0$, $1\ 0\ 1$ and $0\ 1\ 1$. The setup of the *P11m* space group shows that the atomic positions in the a – b plane are restricted due to the mirror plane perpendicular to the c -axis. Therefore the polar displacement is only possible in the mirror plane and the refinement results in an alignment close to the $[1\ 1\ 0]_c$ direction. The angle γ results in the rhombic distortion of the $(0\ 0\ 1)_c$ plane but due to the monoclinic setup, the $1\ 0\ 0_c$ reflection is not equal to the $0\ 1\ 0_c$ but the structure still shows a pseudo-orthorhombic character.

Orthorhombic, tetragonal, monoclinic and cubic phases were observed with changes in temperature and space groups *Amm*2, *P4mm*, *Pm* and *Pm* $\bar{3}m$, respectively, were used for the refinement. Single phase and sometimes mixed phases were observed in the diffraction patterns. When phase coexistence is observed, two-phase refinement models which are a combination of the space groups involved were used. The refinement parameters for KNN, KNN-2Mn, KNNLi-2Mn, KNNTa-2Mn and KNNLiTa-2Mn ceramics for the lowest temperatures of each model used are shown in Tables 2, 3, 4, 5 and 6, respectively.

Fig. 4 shows the lattice parameters of the samples as a function of temperature. The subscripts ‘o’, ‘t’, ‘m’ and ‘c’ represent the orthorhombic, tetragonal, monoclinic and cubic phases, respectively. The orthorhombic cell parameters b_o and c_o were divided by $(2)^{1/2}$ for better representation in the diagrams. The plot for KNN ceramics (Fig. 4a) shows that from 27 °C to 180 °C, only the orthorhombic phase is present and between 200 °C and 220 °C, a coexistence of an orthorhombic and a tetragonal phase is present. From 240 °C to 400 °C the tetragonal phase exists, with coexistence between the cubic and the tetragonal phase at 420 °C. Above 420 °C, the cubic phase is observed. The plot for KNN-2Mn ceramics (Fig. 4b) shows that the orthorhombic phase is present up to 160 °C and from 180 °C to 200 °C, orthorhombic–tetragonal coexistence is observed. The tetragonal phase is present from 220 °C to 420 °C, and above this temperature, the cubic phase is present.

Fig. 1. Measured and calculated X-ray diffraction profiles and their difference plot at 27 °C for (a) KNN, (b) KNN-2Mn, (c) KNNLi-2Mn, (d) KNNTa-2Mn and (e) KNNLiTa-2Mn ceramics.

Fig. 4c shows the lattice parameters for KNNLi-2Mn ceramics. The monoclinic phase is present from 27 °C to 70 °C and between 80 °C and 150 °C, a mixture of monoclinic and tetragonal phase is observed. From 160 °C to 440 °C, only the tetragonal phase is present and from 450 °C, the cubic phase is present. For the KNNTa-2Mn sample (Fig. 4d), the orthorhombic phase is present from 27 °C to 140 °C and orthorhombic–tetragonal phase coexistence is observed from 160 °C to 180 °C. The tetragonal phase is present from 200 °C to 360 °C while a tetragonal–cubic phase coexistence is present

from 380 °C to 400 °C and at 420 °C, the cubic phase is present. The plot for the KNNLiTa-2Mn sample (Fig. 4e) shows orthorhombic–tetragonal phase coexistence from 27 °C to 140 °C and from 160 °C to 360 °C, only the tetragonal phase is observed. The cubic phase is observed from 380 °C and above.

In *Amm2*, the different values of the orthorhombic lattice parameters b_o and c_o lead to a rhombic distortion of the $(001)_c$ plane resulting in an expansion along $[110]_c$. The plot of the pseudo-monoclinic angle as a function of temperature for samples with the orthorhombic phase is shown in Fig. 5. As the

Table 2

Experimental details and refinement results for KNN at 27, 200, 240, 420 and 440 °C.

Phase type	Single	Two-phase		Single	Two-phase		Single
Crystal system	Orthorhombic	Orthorhombic	Tetragonal	Tetragonal	Tetragonal	Cubic	Cubic
Space group	<i>Amm2</i>	<i>Amm2</i>	<i>P4mm</i>	<i>P4mm</i>	<i>P4mm</i>	<i>Pm3m</i>	<i>Pm3m</i>
Temperature (°C)	27	200		240	420		440
<i>a</i> (Å)	3.94455(3)	3.95598(3)	3.96372(5)	3.96471(2)	3.97726(3)	3.98679(3)	3.986603(18)
<i>b</i> (Å)	5.64377(4)	5.64421(6)	–	–	–	–	–
<i>c</i> (Å)	5.67647(4)	5.66918(6)	4.02863(7)	4.02684(3)	4.00854(4)	–	–
<i>V</i> (g/cm ^{−3})	126.3705(15)	126.584(2)	63.2941(16)	63.2976(7)	63.4094(9)	63.3678(9)	63.3591(5)
<i>Z</i>	2	2	1	1	1	1	1
<i>Refinement</i>							
<i>R_B</i> (%)	5.37	4.9	7.5	5.89	7.71	4.75	11.1
<i>R_f</i> (%)	4.82	3.83	6.39	5.22	7.98	3.79	12.5
GOF	4.5	4.4	–	4.8	4.7	–	6
χ^2	20.6	19.5	–	23.1	22.1	–	36.3
No. of parameters	29	36	–	28	28	–	19

Table 3

Experimental details and refinement results for KNN-2Mn at 27, 180, 220 and 420 °C.

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 (°C)	27	180	180	220	420
<i>a</i> (Å)	3.94514(3)	3.95503(4)	3.96390(8)	3.96391(2)	3.98607(3)
<i>b</i> (Å)	5.64309(5)	5.64372(7)	–	–	–
<i>c</i> (Å)	5.67440(5)	5.66869(7)	4.02631(14)	4.02730(3)	–
<i>V</i> (g/cm ^{−3})	126.3278(19)	126.532(2)	63.263(3)	63.2794(7)	63.3336(7)
<i>Z</i>	2	2	1	1	1
<i>Refinement</i>					
<i>R_B</i> (%)	5.92	5.45	7.31	6.61	7.33
<i>R_f</i> (%)	5.53	4.4	6.05	6.64	6.4
GOF	3.9	3.8	–	4.1	5.8
χ^2	15.2	14.3	–	16.1	34.2
No. of parameters	31	36	–	31	26

Table 4

Experimental details and refinement results for KNNL-2Mn ceramics at 27, 80, 170, 450 and 460 °C.

Phase type	Single	Two-phase		Single	Two-phase		Single
Crystal system	Monoclinic	Monoclinic	Tetragonal	Tetragonal	Tetragonal	Cubic	Cubic
Space group	<i>P11 m</i>	<i>P11 m</i>	<i>P4mm</i>	<i>P4mm</i>	<i>P4mm</i>	<i>Pm3m</i>	<i>Pm3m</i>
Temperature (°C)	27	80	80	170	450	450	460
<i>a</i> (Å)	4.01097(4)	4.01379(5)	3.95549(10)	3.959406(20)	3.97763(8)	3.986710(20)	3.986167(16)
<i>b</i> (Å)	3.98931(4)	3.98693(6)	–	–	–	–	–
<i>c</i> (Å)	3.94495(3)	3.94842(3)	4.02963(18)	4.03278(3)	4.00474(17)	–	–
γ (°)	89.6881(6)	89.7182(7)	–	–	–	–	–
<i>V</i> (g/cm ^{−3})	63.1223(11)	63.1846(13)	63.047(4)	63.2214(6)	63.361(3)	63.3642(5)	63.3383(4)
<i>Z</i>	1	1	1	1	1	1	1
<i>Refinement</i>							
<i>R_B</i> (%)	5.31	4.72	8.43	5.43	4.73	10	6.53
<i>R_f</i> (%)	4.6	3.58	5.95	5.1	5.75	9.77	7.21
GOF	4.1	4.4	–	4.8	4.8	–	5.1
χ^2	17.1	19.4	–	23.3	22.7	–	25.9
No. of parameters	36	47	–	33	32	–	21

Table 5

Experimental details and refinement results for KNNT-2Mn ceramics at 27, 140, 200, 380 and 420 °C.

Phase type	Single	Two-phase		Single	Two-phase		Single
Crystal system	Orthorhombic	Orthorhombic	Tetragonal	Tetragonal	Tetragonal	Cubic	Cubic
Space group	<i>Amm2</i>	<i>Amm2</i>	<i>P4mm</i>	<i>P4mm</i>	<i>P4mm</i>	<i>Pm3m</i>	<i>Pm3m</i>
Temperature (°C)	27	140	140	200	380	380	420
<i>a</i> (Å)	3.94846(4)	3.95607(4)	3.9627(2)	3.96453(3)	3.97731(5)	3.98400(5)	3.98384(2)
<i>b</i> (Å)	5.63831(6)	5.63893(7)	–	–	–	–	–
<i>c</i> (Å)	5.66623(7)	5.66222(7)	4.02745(2)	4.01762(4)	4.0005(2)	–	–
<i>V</i> (g/cm ^{−3})	126.145(2)	126.313(3)	63.245(5)	63.1471(9)	63.284(4)	63.2349(14)	63.2272(7)
<i>Z</i>	2	2	1	1	1	1	1
<i>Refinement</i>							
<i>R</i> _B (%)	4.89	5.11	11.7	5.69	7.08	5.54	5.94
<i>R</i> _f (%)	4.62	3.63	6.99	4.49	6.74	5.99	6.38
GOF	4.1	4.3	–	20.4	4.9	–	4.9
χ^2	16.6	18.4	–	4.5	24.3	–	24.5
No. of parameters	34	29	–	29	27	–	20

Table 6

Experimental details and refinement results for KNNLT-2Mn ceramics at 27, 140 and 400 °C.

Phase type	Two-phase		Single	Single
Crystal system	Orthorhombic	Tetragonal	Tetragonal	Cubic
Space group	<i>Amm2</i>	<i>P4mm</i>	<i>P4mm</i>	<i>Pm3m</i>
Temperature (°C)	27	27	140	400
<i>a</i> (Å)	3.94760(5)	3.95606(9)	3.95875(3)	3.98034(2)
<i>b</i> (Å)	5.63459(10)	–	–	–
<i>c</i> (Å)	5.66034(9)	4.0079(2)	4.01800(4)	–
<i>V</i> (g/cm ^{−3})	125.903(3)	62.726(4)	62.9688(10)	63.0610(6)
<i>Z</i>	2	1	1	1
<i>Refinement</i>				
<i>R</i> _B (%)	5.27	5.15	5.64	7.32
<i>R</i> _f (%)	4.33	4.75	4.39	7.78
GOF	4.0	–	4.2	4.6
χ^2	16.1	–	17.4	21.2
No. of parameters	36	–	31	20

Fig. 2. Enlarged section of the diffraction patterns showing the difference in 110_c and 200_c reflections between the KNN ceramics (orthorhombic phase) and the KNNLi-2Mn ceramics (monoclinic phase).

temperature increases, the pseudo-monoclinic angles decrease in the following order: KNN, KNN-2Mn, KNNLi-2Mn, KNNTa-2Mn and KNNLiTa-2Mn. As the pseudo-monoclinic angle decreases, the tendency to form the orthorhombic lattice increases.

The percentages of each phase present in the samples are calculated through their scale factors which comprise a product of mass and volume of the unit cell of each phase. The weight fraction of the phases in percentage is presented in Fig. 6. The temperature range of phase coexistence for KNN, KNN-2Mn and KNNTa-2Mn in Fig. 5a, b and d, respectively, are narrow and are restricted to the phase transition region. For KNN and KNNTa-2Mn samples, the tetragonal phase and the cubic phase also coexist close the *T_c* of the samples. For KNNLi-2Mn sample (Fig. 6c) at 70 °C, only the monoclinic phase is present and as the temperature increases the monoclinic phase decreases while the phase is completely tetragonal at 160 °C. For KNNLiTa-2Mn (Fig. 6e) sample, approximately 70% of the orthorhombic phase is present up to 60 °C and above this temperature; there is a gradual decrease in this phase while the tetragonal phase increases up to 100% at 160 °C.

Fig. 3. Graphical representation of the orthorhombic structure model *Amm2* and the monoclinic structure model *Pm* used in the refinements. The arrow indicates the direction of spontaneous polarisation (P_s).

The SEM images of the polished and etched surfaces of the samples are shown in Fig. 7. In all the samples, the grains and the pores can be clearly seen with the latter located mainly at the grain boundary junctions. The grinding and polishing process is believed to have contributed to some of the pores through grain pull-out. For KNN ceramics (Fig. 7a), grains with smooth and rough surfaces are observed and this is possibly due to different crystallographic planes. A steeped/rough surface results when the higher energetic planes try to revert to the lower energetic planes. The KNN sample has small grains and the average grain size is $1.8 \pm 1.0 \mu\text{m}$. The average grain size of the samples increases with the addition of 2 mol% Mn. The average grain size for KNN-2Mn (Fig. 7b) ceramics is $5.5 \pm 2.4 \mu\text{m}$ while it is $8.0 \pm 3.5 \mu\text{m}$ for KNNLi-2Mn (Fig. 7c). The average size for KNNTa-2Mn (Fig. 7d) is $3.3 \pm 1.5 \mu\text{m}$ while it is $3.0 \pm 1.3 \mu\text{m}$ for KNNLT-2Mn ceramics. A few big grains and many small grains are observed for KNNLT-2Mn ceramics.

3.2. Electrical characterisation

The dielectric constant values of the samples as a function of temperature are shown in Fig. 8a and the insets highlight the low temperature part of the graph which shows the ferroelectric–ferroelectric phase transition. With the exception of the KNN sample, the other samples show signs of a diffuse phase transition at their dielectric peak. The phase transition temperatures observed for the samples at the T_c with X-ray diffraction are similar to those from dielectric measurements as shown in Table 7. The only exception is the KNNTa-2Mn sample with a difference of up to 30° . It should be pointed out that at 360°C a mixture of cubic and tetragonal phase is present in the diffraction pattern. The KNNLiTa-2Mn sample has the highest dielectric constant and lowest dielectric loss at temperatures below 100°C . The tetragonal to orthorhombic phase transition temperature (T_{T-O}) for the KNN sample is $\sim 207^\circ\text{C}$ while the T_c occurred at 421°C with a dielectric peak value of ~ 3740 . For KNN-2Mn sample, the T_{T-O} is 192°C while the T_c occurred at 421°C with a dielectric peak value of ~ 4855 . The monoclinic to orthorhombic transition temperature (T_{M-O})

for KNNLi-2Mn sample is at 105°C while the T_c occurred at 453°C with a dielectric peak of ~ 4601 . The T_{T-O} for KNNTa-2Mn sample is $\sim 160^\circ\text{C}$ while the T_c occurred at 362°C with a dielectric peak of ~ 4145 and the T_{T-O} for KNNLiTa-2Mn sample is $\sim 83^\circ\text{C}$ while the T_c occurred at 403°C with a dielectric peak of ~ 3285 . The plot of dielectric loss values (Fig. 8b) shows that the KNN sample has the highest dielectric loss value below 120°C . The presence of Li and Ta in the ceramic seems to play a role in the loss values because the KNN-2Mn sample has higher loss values between 120°C and 250°C .

The polarisation hysteresis curves for the samples in Fig. 9 show that 2 mol% Mn reduces the ferroelectric activity in the samples. The KNN sample looks to be slightly conductive and show a P_r value of $\sim 25 \mu\text{C}/\text{cm}^2$ with a coercive field of $\sim 12 \text{ kV}/\text{cm}$. The P_r and E_c values of the doped samples are strongly reduced possibly due to the high content of Mn. It is not clear if the curve for KNN-2Mn sample indicate the presence of ferroelectricity. The decreasing value of both E_c and P_r indicates both soft and hard doping effects occurring in the samples. The relative density of the sintered samples is shown in Table 7 and they indicate good values for samples sintered in air. The piezoelectric coefficient of the samples obtained from the slope of the unipolar strain hysteresis curves show that low d_{33}^* values are obtained compared to when there is no Mn present.⁹

3.3. Discussion

The result of chemical analysis using OES-ICP shows that the amounts of Li, K and Mn are slightly lower than expected in some samples. This is possibly due to their high vapour pressure which makes them to be volatile during the sintering process. It also shows that synthesis of polycrystalline ceramics which involves milling of powders is not completely free of impurities.

The A- and B-site elements have valence states of +1 and +5, respectively, while oxygen has -2 . Based on the result from electron paramagnetic studies on KNN ceramics, Mn is believed to be incorporated to the B-site of the perovskite lattice.^{21,23} It therefore acts as an acceptor and the possible defect chemical

Fig. 4. Lattice parameters (Å) of the samples as a function of temperature. a_o , b_o and c_o represent the parameters for the orthorhombic phase, a_m , b_m and c_m represents the parameters for the monoclinic phase, a_t and c_t represent the parameters for the tetragonal phase while a_c represents the cubic phase, respectively. The graphs are for (a) KNN ceramic, (b) KNN-2Mn, (c) KNNLi-2Mn, (d) KNNTa-2Mn and (e) KNNLiTa-2Mn.

reactions for +3 and +4 valence states are shown in Eqs. (1) and (2), respectively.

Oxygen vacancies are formed and when they combine with Mn ions, defect dipoles are created. These defect dipoles move along

the direction of polarisation and are based on the principle of symmetry conforming of point defects and lead to hard doping effects.³⁴

The phase transition temperatures of the samples are lowered with doping and this is possibly due to the introduction of inhomogeneous electric field generated by the vacancies created.³⁵ The X-ray diffraction patterns for KNN, KNN-2Mn and KNNTa-2Mn samples show that at 27 °C, only the

Table 7

Relative density, piezoelectric coefficient (d_{33}^*), first order transition temperature and Curie temperature (T_c) for KNN-based ceramics modified with Mn.

Sample	Relative density (%)	d_{33}^* (pm/V)	T_{T-O} or T_{M-O} (°C)		T_c (°C)	
			Dielectric		X-ray	Dielectric
KNN	94.5 ± 1.5	100 ± 15	207		420–440	421
KNN-2Mn	92.4 ± 1	119 ± 11	192		420–440	421
KNNLi-2Mn	92.1 ± 1	147 ± 15	105		440–450	453
KNNTa-2Mn	95 ± 0.5	205 ± 12	160		400–420	362
KNNLiTa-2Mn	93 ± 0.5	152 ± 10	83		380–400	403

Fig. 5. Pseudo-monoclinic angles as a function of temperature for KNN, KNN-2Mn, KNNLi-2Mn, KNNTa-2Mn and KNNLiTa-2Mn ceramics. The angle for KNNLi-2Mn was obtained by subtracting the monoclinic angles from 180° to ensure a uniform plot.

orthorhombic phase is present. The sequence of phase transitions with increasing temperature is also similar; from the orthorhombic phase to the tetragonal phase and finally to the cubic phase, but the difference lies in the temperature of phase transitions. Mn appears to have very little effect on the phase coexistence of

the KNNLiTa-2Mn sample because the sequence and temperature of the phase transitions are similar with and without it.⁹ Composition fluctuation which in a way is due to compositional inhomogeneities is believed to be the main reason for phase coexistence in the samples.³⁶ The change in slope of the lattice parameters observed at certain temperatures for the samples correspond to a phase transition.

KNN ceramics modified with Li has an orthorhombic structure at 27 °C⁹ but when 2 mol% of Mn is introduced, a monoclinic phase with space group *Pm* is formed from 27 °C to 70 °C. This monoclinic phase also coexists with the tetragonal phase from 80 °C to 150 °C. A possible reason for the structural phase transition is the lattice instability due to forces which determine the interaction of the ions being displaced. A possible change in the valence state of Mn from +4 to +3 introduces a pseudo-Jahn Teller effect which is related to low symmetry distortion of the lattice.³⁷ When Mn is added to KNN containing Ta (KNNTa-2Mn), the phase did not change possibly because the lattice instability introduced is low. When Nb and Ta have the same coordination number, the values of their ionic radius are similar.

At temperatures below 100 °C, KNN-2Mn had the lowest dielectric constant values which corresponds with the low d_{33}^* values and the poor hysteresis curve. KNNLiTa-2Mn ceramic has the highest permittivity values below 100 °C and this may

Fig. 6. Weight fraction of the phases (%) as a function of temperature for (a) KNN, (b) KNN-2Mn, (c) KNNLi-2Mn, (d) KNNTa-2Mn and (e) KNNLiTa-2Mn ceramics.

Fig. 7. Scanning electron microscope (SEM) images of the polished and etched surfaces of (a) KNN, (b) KNN-2Mn, (c) KNNLi-2Mn, (d) KNNTa-2Mn and (e) KNNLT-2Mn ceramics.

be due to phase coexistence. Although a new monoclinic phase with Pm space group is observed for KNNLi-2Mn sample, the dielectric properties did not greatly improve. The coexistence of the monoclinic and the tetragonal phase over a wide temperature range also did not lead to a significant improvement in the dielectric constant values probably because of the hard doping effects. The diffuseness of the dielectric constant peaks at the phase transition temperatures of the samples is mainly due to an increase in site disorder as a result of the doping in the samples. The energy barriers decrease due to the vacancies and promote enhanced fluctuations between the energy minima below the T_c . The addition of Mn to the samples also led to a reduction in the dielectric loss values compared to KNN sample which had higher loss values.

Relatively high P_r is obtained for the KNN sample and it is clear that there is a small contribution due to leakage current to the curve. When Mn is added to the samples, low P_r values

are obtained. The shape of the curve for KNN-2Mn indicates that the ferroelectric behaviour in the sample has been greatly lowered. This is probably because the rate of migration of the defects due to doping is low and this creates an inner biased field which tends to reverse the switched polarisation. A pinning of the domains is created because the defect dipoles do not respond to the motion of the polarisation as fast as possible. There is no difference in the piezoelectric coefficient d_{33}^* values for KNN and KNN-2Mn samples. Although a new Pm phase is obtained for KNNLi-2Mn composition, the d_{33}^* value is not very high while the KNNTa-2Mn sample gave the highest values. The KNNLiTa-2Mn composition has a two-phase coexistence between the orthorhombic and the tetragonal phase but the value of d_{33}^* is not high which may be explained by the fact that although there is phase coexistence, the degree of defects introduced by doping with 2 mol% Mn may have affected the properties adversely.

Fig. 8. Temperature-dependent plots of (a) dielectric constant and (b) dielectric loss ($\tan \delta$) measured at 100 kHz for KNN-based ceramics doped with Mn.

Fig. 9. Polarisation – electric field hysteresis curves for KNN-based ceramics modified with Mn.

4. Conclusion

The effect of Mn doping on the structure and piezoelectric properties of KNN-based ceramics has been investigated. The chemical analysis on the samples shows that Li, K and Mn

amounts were less than intended due to their high vapour pressure during sintering and also that small amounts of impurities are always introduced during processing.

A new monoclinic phase with Pm space group is obtained with the KNNLi-2Mn sample from 27 °C to about 150 °C probably due to the Jahn Teller effect on Mn in valence changes from +4 to +3. Mn is believed to be incorporated to the B-site of the perovskite lattice and this leads to the formation of oxygen vacancies. When these O^{2-} vacancies combine with Mn ions, defect dipoles are created and because they do not respond fast enough to the movement of the domains, they pin the domains leading to hard ferroelectric effects. An inner biased field is also believed to be formed which tends to reverse the switched polarisation leading to low values of P_r , d_{33}^* , dielectric constant and dielectric loss. The phase transition temperatures of the samples are lowered probably due to inhomogeneous electric field generated by the vacancies.

Acknowledgements

The research leading to these results has received financial support from Deutsche Forschungsgemeinschaft under Grant No. SCHN 372/16-2 and the Bundesministerium für Bildung und Forschung under Grant No. 05K100DA.

References

1. Egerton L, Dillion DM. Piezoelectric and dielectric properties of ceramics in the system potassium–sodium niobate. *J Am Ceram Soc* 1959;**42**(9):438–42.
2. Jaeger RE, Egerton L. Hot pressing of potassium–sodium niobates. *J Am Ceram Soc* 1962;**45**(5):209–13.
3. Mgbemere HE, Schneider GA, Stegk TA. Effect of antimony substitution for niobium on the crystal structure, piezoelectric and dielectric properties of $(K_{0.5}Na_{0.5})NbO_3$ ceramics. *Funct Mater Lett* 2010;**3**(1):25–30.
4. Klein N, Hollenstein E, Damjanovic D, Trodahl HJ, Setter N. A study of the phase diagram of $(K,Na,Li)NbO_3$ determined by dielectric and piezoelectric measurements, and Raman spectroscopy. *J Appl Phys* 2007;**102**(1):014112.
5. Guo Y, Kakimoto K-I, Ohsato H. Phase transitional behavior and piezoelectric properties of $(Na_{0.5}K_{0.5})NbO_3$ – $LiNbO_3$ ceramics. *Appl Phys Lett* 2004;**85**(18):4121–3.
6. Matsubara M, Yamaguchi T, Kikuta K, Shin-Ichi H. Synthesis and characterization of $(K_{0.5}Na_{0.5})(Nb_{0.7}Ta_{0.3})O_3$ piezoelectric ceramics sintered with sintering Aid $K_{5.4}Cu_{1.3}Ta_{10}O_{29}$. *Jpn J Appl Phys* 2005;**44**:6618–23.
7. Saito Y, Takao H. High performance lead-free piezoelectric ceramics in the $(K,Na)NbO_3$ – $LiTaO_3$ solid solution system. *Ferroelectrics* 2006;**338**:17–32.
8. Guo Y, Kakimoto K-I, Ohsato H. $(Na_{0.5}K_{0.5})NbO_3$ – $LiTaO_3$ lead-free piezoelectric ceramics. *Mater Lett* 2005;**59**(2–3):241–4.
9. Mgbemere HE, Hinterstein M, Schneider GA. Electrical and structural characterization of $(K_xNa_{1-x})NbO_3$ ceramics modified with Li and Ta. *J Appl Crystallogr* 2011;**44**:1080–9.
10. Mgbemere HE, Herber R-P, Schneider GA. Investigation of the dielectric and piezoelectric properties of potassium sodium niobate ceramics close to the phase boundary at $(K_{0.35}Na_{0.65})NbO_3$ and partial substitutions with lithium and antimony. *J Eur Ceram Soc* 2009;**29**:3273–8.
11. Hollenstein E, Davis M, Damjanovic D, Setter N. Piezoelectric properties of Li and Ta modified $(K_{0.5}Na_{0.5})NbO_3$ ceramics. *Appl Phys Lett* 2005;**87**:182905.
12. Park J-H, Park J-G, Kim B-K, Je H-J, Kim Y. Effect of MnO_2 addition on the piezoelectric properties in $Pb(Mg_{1/3}Nb_{2/3})O_3$ relaxor ferroelectrics. *Mater Res Bull* 2002;**37**(2):305–11.

13. Lee S-M, Lee S-H, Yoon C-B, Kim H-E, Lee K-W. Low-temperature sintering of MnO₂-doped PZT–PZN piezoelectric ceramics. *J Electroceram* 2007;**18**(3–4):311–5.
14. Aksel E, Jakes P, Erdem E, Smyth DM, Ozarowski A, Tol JV, et al. Processing of manganese-doped [Bi_{0.5}Na_{0.5}]TiO₃ ferroelectrics: reduction and oxidation reactions during calcination and sintering. *J Am Ceram Soc* 2011;**94**(5):1363–7.
15. Li X-J, Wang Q, Li Q-L. Effects of MnO₂ addition on microstructure and electrical properties of (Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO₃ ceramics. *J Electroceram* 2008;**20**(2):89–94.
16. Fan G, Lu W, Wang X, Liang F. Effects of manganese additive on piezoelectric properties of (Bi_{1/2}Na_{1/2})TiO₃–BaTiO₃ ferroelectric ceramics. *J Mater Sci* 2007;**42**(2):472–6.
17. Ge W, Li J, Viehland D, Luo H. Influence of Mn doping on the structure and properties of Na_{0.5}Bi_{0.5}TiO₃ single crystals. *J Am Ceram Soc* 2010;**93**(5):1372–7.
18. Li G, Zheng L, Yin Q, Jiang B, Cao W. Microstructure and ferroelectric properties of MnO₂-doped bismuth-layer (Ca,Sr)Bi₄Ti₄O₁₅ ceramics. *J Appl Phys* 2005;**98**(6):064108.
19. Langhammer HT, Mueller T, Felgner K-H, Abicht H-P. Crystal structure and related properties of manganese-doped barium titanate ceramics. *J Am Ceram Soc* 2000;**83**(3):605–11.
20. Lin D, Kwok KW, Chan HLW. Piezoelectric and ferroelectric properties of K_xNa_{1-x}NbO₃ lead-free ceramics with MnO₂ and CuO doping. *J Alloys Compd* 2008;**461**(1–2):273–8.
21. Kizaki Y, Noguchi Y, Miyayama M. Defect control for low leakage current in K_{0.5}Na_{0.5}NbO₃ single crystals. *Appl Phys Lett* 2006;**89**(14):142910.
22. Noguchi Y, Miyayama M. Effect of Mn doping on the leakage current and polarization properties in K_{0.14}Na_{0.86}NbO₃ ferroelectric single crystals. *J Ceram Soc Jpn* 2010;**118**:711–6.
23. Zuo R, Fu J, Su S, Fang X, Cao J-L. Electrical properties of manganese modified sodium potassium lithium niobate lead-free piezoelectric ceramics. *J Mater Sci Mater Electron* 2009;**20**(3):212–6.
24. Wongsanmai S, Kanchiang K, Chandarak S, Laosiritaworn Y, Ruji-rawat S, Yimnirun R. Crystal structure and ferroelectrics of Mn-doped ((K_{0.5}Na_{0.5})_{0.935}Li_{0.065})NbO₃ lead-free ceramics. *Curr Appl Phys* 2012;**12**(2):418–21.
25. Li X, Jiang M, Liu J, Zhu J, Zhu X, Zhu J, et al. Enhanced piezoelectric properties in Mn-doped 0.98 K_{0.5}Na_{0.5}NbO₃–0.02BiScO₃ lead-free ceramics. *J Am Ceram Soc* 2009;**92**(7):1625–8.
26. Lin D, Kwok KW, Chan HLW. Effects of MnO₂ on the microstructure and electrical properties of 0.94(K_{0.5}Na_{0.5})NbO₃–0.06Ba(Zr_{0.05}Ti_{0.95})O₃ lead-free ceramics. *Mater Chem Phys* 2008;**109**(2–3):455–8.
27. Knapp M, Joco V, Baehtz C, Brecht HH, Berghaeuser A, Ehrenberg H, et al. Position-sensitive detector system OBI for high resolution X-ray powder diffraction using on-site readable image plates. *Nucl Instrum Methods Phys Res A* 2004;**521**(2–3):565–70.
28. Knapp M, Baehtz C, Ehrenberg H, Fuess H. The synchrotron powder diffractometer at beamline B2 at HASYLAB/DESY: status and capabilities. *J Synchrotron Radiat* 2004;**11**(4):328–34.
29. Rodríguez-Carvajal J. Recent advances in magnetic structure determination by neutron powder diffraction. *Phys B: Condens Matter* 1993;**192**(1–2):55–69.
30. Laar BV, Yelon WB. The peak in neutron powder diffraction. *J Appl Crystallogr* 1984;**17**:47–54.
31. Finger LW, Cox DE, Jephcoat AP. A correction for powder diffraction peak asymmetry due to axial divergence. *J Appl Crystallogr* 1994;**27**:892–900.
32. Finger LW. PROFVAL: functions to calculate powder-pattern peak profiles with axial divergence asymmetry. *J Appl Crystallogr* 1998;**31**:111.
33. Stephens PW. Phenomenological model of anisotropic peak broadening in powder diffraction. *J Appl Crystallogr* 1999;**32**:281–9.
34. Lin D, Guo MS, Lam KH, Kwok KW, Chan HLW. Lead-free piezoelectric ceramic (K_{0.5}Na_{0.5})NbO₃ with MnO₂ and K_{5.4}Cu_{1.3}Ta₁₀O₂₉ doping for piezoelectric transformer application. *Smart Mater Struct* 2008;**17**(3):035002.
35. Bellaiche L, Íñiguez J, Cockayne E, Burton BP. Effects of vacancies on the properties of disordered ferroelectrics: a first-principles study. *Phys Rev B* 2007;**75**:014111.
36. Frantti J, Ivanov S, Eriksson S, Rundlöf H, Lantto V, Lappalainen J, et al. Phase transitions of Pb(Zr_xTi_{1-x})O₃ ceramics. *Phys Rev B* 2002;**66**(6):064108.
37. Aksenov VL, Plakid NM, Stamenkovic S [Pontekorvo DB, Trans.] Neutron Scattering by Ferroelectrics. *World Scientific* 1989:1–67.