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Core-shell Grain Structures and Dielectric Properties of $Na_{0.5}K_{0.5}NbO_3$-$LiTaO_3$-$BiScO_3$ Piezoelectric Ceramics

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Abstract

The origins of distinctive compositional dependence of relative permittivity, ε_r, in the Pb-free piezoelectric system (1-x)$Na_{0.5}K_{0.5}NbO_3$-x$LiTaO_3$, x≤ 10 mol% modified with $BiScO_3$ have been revealed using transmission electron microscopy with energy dispersive X-ray analysis (TEM-EDX). As the $LiTaO_3$ content increased the Curie peak at ~370°C in ε_r –T plots became more diffuse, and at x= 5 mol% an additional higher temperature peak occurred. TEM-EDX analysis showed the change in dielectric properties at x= 5 mol% was due to a change in microstructure: micron-scale grains were replaced by submicron grains exhibiting core-shell chemical segregation. The outer shell was similar to the target solid solution composition, slightly enriched in Bi, Sc and Ta, whilst the core approximated to (Na, K, Li)NbO_3 and was responsible for the additional dielectric peak. Examples of a novel three-tier metastable grain structure were observed for certain compositions.

Keywords: core-shell structure, lead-free, NKN-based, dielectric, TEM.

1. Introduction

Lead zirconate titanate, PZT, has dominated the commercial piezoelectric market for several decades due to its superior properties and ease of manufacture. However PZT is likely to face legislative restrictions in future, and research is underway to develop Pb-free alternatives. Some of the most promising Pb-free piezoelectrics for resonator applications are solid solutions based on sodium potassium niobate, $Na_{0.5}K_{0.5}NbO_3$ (NKN), notably $Na_{0.5}K_{0.5}NbO_3$-$LaTiO_3$ (NKN–LT) and its derivatives.[1-5] An optimal d_{33} piezoelectric charge coefficient of ≥200 pC/N was reported for NKN-LT at 5–6 mol% LT.[6-10] A study of the NKN-LT phase diagram has shown that increasing the LT content to 7 mol% favourably shifts the temperature of the monoclinic-tetragonal polymorphic phase transition which permits piezoelectric properties to be retained over a wider temperature range with a relatively high depolarisation temperature T_d~ 200°C for the lead-free piezoelectrics being explored as PZT replacements.[11] Further enhancements in the piezoelectric properties of NKN-based ceramics have been achieved through various compositional modifications.[12-15] For example modification of NKN-LT with $CaZrO_3$ increases d_{33} to 320 pC/N and improves fatigue performance, but the Curie temperature is moderate, ~190°C.[16] The piezoelectric properties of NKN-LT modified with $BiScO_3$ have also been investigated due to its high Curie temperature, with a maximum d_{33} ~215 pC/N at a composition $[(1-x)(Na_{0.5}K_{0.5}NbO_3) -x(LiTaO_3)]_{0.98}-(BiScO_3)_{0.02}$ (x= 2 mol%) corresponding to tetragonal and orthorhombic (monoclinic) phase co-existence at the ambient measurement temperature.[5, 17-19] Unusual trends in dielectric behaviour were observed for $[(1-x)(Na_{0.5}K_{0.5}NbO_3)–x(LiTaO_3)]_{0.98}–(BiScO_3)_{0.02}$ as the LT content is increased to 5 mol%, in that ε_r-T plots indicated a change from a slightly broad Curie peak at ~ 370°C, for $x \leq 2$ mol% , to a diffuse peak for x= 3-4 mol% compositions and an additional peak at ~ 470°C for x= 5 mol% ceramics. Here we report the results of a transmission electron microscopy (TEM) study which examines the reasons for these distinctive dielectric properties.

2. Experimental

Ceramics of $(1-y)[(1-x)Na_{0.5}K_{0.5}NbO_3 – xLiTaO_3] – yBiScO_3$ (x= 0-10 mol%; y= 0-10 mol%) were synthesized from the starting regents, Na_2CO_3, K_2CO_3, Nb_2O_5 (Sigma–Aldrich, UK, 99.9% purity); Bi_2O_3, Sc_2O_3, Ta_2O_5, and Li_2CO_3 (Sigma–Aldrich, 99% purity). The compositions are abbreviated as NKN-xLT-yBS, in the remainder of the text mole fractions are expressed as percentages. The major part of the study focussed on the solid solution series NKN-xLT-2BS, the location of the compositions in the NKN-LT-BS ternary are shown in **Fig. 1**; nominal compositions are listed in **Table. 1**.

All carbonates and oxides were dried at 300°C for at least 12 h then stored at room-temperature under reduced pressure in desiccators to avoid compositional errors related to the hygroscopic nature of alkali metal carbonates. Ternary formulations were prepared from pre-calcined NKN-xLT and BS precursor components. Powder mixtures were processed in a high energy bead-mill for 30 min using 0.5 mm yttria-stablized zirconia grinding media and isopropyl alcohol (WAB, Dyno-Mill, KDLA Basel, Switzerland). Each NKN–LT composition was calcined at 850°C for 5 h. Powders of Bi_2O_3 and Sc_2O_3 were mixed in equi-molar ratios and calcined at 750°C. As $BiScO_3$ does not exist as a stable phase under normal processing conditions;[20] the term '$BiScO_3$ precursor' is used to describe the calcined Bi_2O_3 and Sc_2O_3 powders. The calcined powders were each passed through a 300 µm mesh-size nylon sieve; the NKN–xLT powders were mixed with the $BiScO_3$ precursor powders, followed by calcination in alumina crucibles at 850°C for 5 h, with a 300°C/h heating rate and a 600°C/h cooling rate. The NKN–xLT–yBS powders were uniaxially compacted into 12 mm diameter pellets and isostatically pressed at 300 MPa to increase green density. The pellets were placed in an alumina crucible surrounded by powder of the same composition, and a lid fitted to help minimize loss of volatile oxide vapours from the pellets during sintering at 1100°C for 4 h.

X-ray diffraction (XRD) was used for routine phase analysis (PANalytical B.V., Almelo, Netherlands, Cu Kα radiation). Powders for XRD analysis were obtained by crushing sintered discs. For electrical measurements, ceramics were polished to achieve parallel smooth faces and electrodes applied using silver paint. The relative permittivity was determined as a function of temperature by using an impedance analyser (HP Agilent 4194A Hewlett Packed) with computerized control and data collection systems, over the temperature range 20°C to 600°C.

Specimens were prepared for TEM by using focused ion beam (FIB) milling and in situ lift out. A FEI Nova 200 Nanolab dual-beam SEM/FIB (FEI Co., Hillsboro, OR) fitted with a Kleindiek micromanipulator (Kleindiek Nanotechnik GmbH, Reutlingen, Germany) was used. All the sectioned ceramic samples were first sputter coated with 5 nm of platinum. Milling was performed at 30 kV with beam currents between 0.1 and 5 nA, with a final cleaning step of 5 kV and 29 pA. TEM analysis was carried out using an FEI Tecnai F20 field emission gun (FEG) TEM (200 kV) fitted with a high angle annular dark field (HAADF) detector, a Gatan SC600 Orius CCD camera (Gatan Inc., Pleasanton, CA) and an Oxford Instruments 80 mm^2 X-max energy dispersive X-ray (EDX) spectroscopy SDD (Oxford Instruments plc, Abingdon, UK). Prior to examination, samples were cleaned for 5 min using a Fischione model 1020 plasma cleaner (E. A. Fischione Instruments Inc., Monroeville, PA). Scanning (S)TEM-HAADF imaging has the benefit that contrast is approximately proportional to atomic number squared (Z^2), and largely excludes diffraction effects.[21] It is commonly applied for imaging chemical segregation, and especially useful for providing information on core-shell grain structures.[22] In addition to this, bright field imaging was also performed in order to identify any crystallographic structure/orientation variations in the specimens. For the further identification of chemical segregation, EDX was used in both spot mode (with a static electron probe approximately 10-20 nm in diameter), and in STEM mode to produce elemental maps. During STEM-EDX mapping, the software collects an entire EDX spectrum for each scan point, and after successive scans these spectra are summed to give a single cumulative spectrum for each scan point. This allows for post-acquisition generation of maps of different elements, also allows for the extraction of summed spectra from specified areas of the sample. Integrating spectral data was an effective method to macroscopically average the composition of individual regions and was particularly useful in the study of chemically segregated core-shell grains. Semi-quantitative compositional ratios were calculated from spectra using a standardless procedure available in the EDX software, which uses a library of pre-installed correction k-factors. Semi-quantitative TEM-EDX data are expressed as atomic percent (at. %), which is same unit of the theoretical values being used for comparison, excluding Li as it cannot be detected by EDX. For example, the mole fractions in the solid solution formulae for x= 5 mol% $(Na_{0.4655}K_{0.4655}Li_{0.049}Bi_{0.02})(Nb_{0.931}Ta_{0.049}Sc_{0.02})O_3$ were divided by 1.951 to give a common point of cross reference with EDX data in **Table. 2**.

3. Results

3.1 Dielectric Properties

Trends in dielectric properties for NKN-xLT-2BS ceramics as a function of LT content are summarized in **Fig. 2**.[15] The compositions NKN-1LT-2BS and NKN-2LT-2BS displayed a Curie peak at ~ 350°C with slight broadening relative to a classic ferroelectric such as $BaTiO_3$. For the end member phase, NKN-2BS, a discontinuity in ε_r-T plots occurred at 100°C signifying a polymorphic transition between orthorhombic (or monoclinic) and tetragonal phases;[19] the temperature of this anomaly decreased to ~ 25°C for NKN-2LT-2BS, which is the composition with maximum piezoelectric charge coefficient, d_{33}= 215 pC/N.[18] The Curie peak became more diffuse for the 3 and 4 mol% LT samples (NKN-3LT-2BS and NKN-4LT-2BS) and T_c decreased slightly to ~ 350°C. For 5 mol% LT (NKN-5LT-2BS), an additional dielectric peak occurred at ~ 470°C. These compositionally-dependent dielectric properties are labelled as:

Type I - single slightly broad Curie peak at ~ 350°C (when $x \leq 2$ mol% LT);

Type II - diffuse Curie peak at ≤ 350°C (when x= 3-4 mol% LT);

Type III - a very diffuse peak centred around 350°C, with a second sharper peak, at ~ 470°C for x=5 mol% LT, which is not visible in the 6 mol% LT sample.

Increasing the LT content to 6 mol% LT sharpened the lower temperature peak and shifted Tc to 380°C, there was no clear 470°C peak but main peak profile was asymmetric possibly due to overlap of the high temperature tail with a residual 470°C peak. Higher LT contents produced a sharper single peak with T_c ~ 350-370°C.[23] All samples displayed ferroelectric character in polarisation-electric field measurements, **Fig. DB1**.

3.2 TEM Investigations for NKN-LT-BS Ternary System

Compositions ≤ 4 mol% LT (Types I and II as defined above) each showed similar microstructures, with grain sizes of ~ 2-5 µm.[18] STEM-EDX mapping indicated no detectable variation in composition within or between grains. This was also confirmed by taking a number of individual spot-EDX spectra from the inner and outer parts of a grain, **Fig. DB2**. Semi-quantitative compositional ratios were calculated from the integrated mapping spectral data using a standardless procedure available in the EDX software, which uses a library of pre-installed correction k-factors. The resulting value for grains within the 4 mol%, 5 mol% and 6 mol% LT samples are presented in **Table. 2**. On this basis the analytical data for the 4 mol% LT ceramic are in agreement with the target composition with no segregation.[24]

Increasing the LT content to 5 mol% (Type III) produced a marked decrease in grain size to ~0.5 μm; and grains were of a cuboid shape. Bright field TEM and STEM-HAADF images revealed a contrast variation between the core and outer shell regions in ~ 90% of the grains, **Fig. 3** and **4**. Data from EDX mapping, **Fig. 4**, indicated the core-shell structure was associated with an enrichment of Sc, Ta and Bi in the outer shell regions when compared to the grain cores. The areas delineated as core and shell on this basis are indicated in **Fig. 5** (inset) and the corresponding integrated compositional analysis values (semi-quantitative) are presented in histogram form in the main figure. Peaks for all of the elements of interest (Na, K, Ta, Bi, Sc and Nb) were present in the integrated EDX spectra from both the core and the shell regions, and so a semi-quantitative procedure was performed for all of the elements from both regions. The compositional data show Ta increasing from 1.4 at. % in the core to 4.1 at. % in the outer shell regions for sample NKN-5LT-2BS, **Table. 2**. The Bi and Sc compositions were both 0.4 at. % in the core, increasing to 1.8 at. % Bi and 1.0 at. % Sc in the shell. The compositions of the other elements were consistent across the grain (within the level of precision of the technique).

Analysis of a 6 mol% LT sample indicated ~ 50% of the grains had core-shell grain structure; grain size remained at ~ 0.5 μm. The STEM-HAADF imaging revealed some of the core-shell grains in NKN-6LT-2BS displayed a 'three-tier' grain structure**,** consisting of a core and two outer shell regions, **Fig. 6**. EDX mapping was performed for this sample, and again integrated spectral data taken from each of the core and shell regions showed peaks for each of the elements of interest, **Fig. DB3**. Semi-quantitative analysis indicated the core regions of 6 mol% LT to be similar in composition to the core of the 5 mol% sample, but with a higher Nb content for the 6 mol% LT sample, **Table. 2**. The outermost shell (labelled as Shell 2) was higher in Bi, Sc and Ta relative to the inner shell (Shell 1) and there was also a difference in the K content. Despite some of the grains possessing a core shell structure, this sample displayed a single, broad dielectric peak (and is considered as Type III).

3.3 Effect of Sintering Time and Excess Alkali Metal Carbonates.

The existence of chemical segregation in the 5 and 6 mol% LT samples could be the result of slow diffusion and incomplete reaction. As the standard sintering temperature of 1100°C was close to the melting temperature of NKN; it was decided to extend the sintering time from 4 to 9 h and 48 h, rather than to increase sintering temperature, for the purpose of promoting more complete reaction. There was little variation in the resulting dielectric plots between the 4 and 9 h sintering times, **Fig. 7**. Indeed the additional dielectric peak at 470°C remained even after 48 h prolonged sintering; however the ε_r values were reduced - possibly due to changes in polarisation linked to higher losses of volatile oxides and alterations to defect chemistry.

In another experiment, the effect of adding excess of Li, K, Na carbonates to offset volatilisation loss (in samples sintered for 4 h) was investigated by adding 3 wt% of each of the component Li, Na, K carbonate precursors to a 6 mol% LT formulation (named as Excess NKN-6LT-2BS). This resulted in the disappearance of the core-shell grain structure (**Fig. DB4**), and in ε_r-T plots the diffuse dielectric peak was replaced by a much sharper transition peak, **Fig. 8**. The addition of excess starting reagents may have introduced a transient liquid phase which promoted inter-diffusion of the components which prevented core-shell structures developing, and the improved level of chemical homogeneity was such that the Curie peak was much sharper. The increase in grain size may also contribute to peak sharpening. Dielectric loss at temperature below 450°C was lower in Excess samples, but increased sharply in both sample types at temperatures >450°C consistent with the effects of thermally activated ionic conduction at elevated temperatures.

4. Discussion

The core-shell grain structures of NKN-LT-BS ceramics are very different from the faceted core-shell grains reported for NKN based-piezeoelectric ceramics which were composed of aligned nano-crystals in the core, with larger sub-crystals around the shell.[25] Instead the NKN-LT-BS microstructures of 5 mol% LT and 6 mol% LT samples are similar to those of certain compositionally modified $BaTiO_3$ ceramics.[26-28] Chemical inhomogeneity and strain effects linked to fine grain size and to core-shell grain structures are well known phenomena in chemically modified $BaTiO_3$ and give rise to diffuse Curie peaks.[29, 30] The precise mechanism for the formation of core-shell grain structures in $BaTiO_3$ doped with, for example, Nb, Zn and/or Cd is still subject to debate. Liquid phase sintering and secondary grain growth (re-crystallization) are considered to promote multi-component inter-diffusion and minimise chemical inhomogeneity. By contrast, in the absence of diffusion-enhancing liquid dissolution mechanisms, chemical segregation occurs and results in core-shell grain structures.

By analogy, a minor amount of liquid phase at sintering temperatures is expected to promote component inter-diffusion, secondary grain growth and reduce chemical inhomogeneity in NKN-LT-BS ceramics, assuming microstructural development is similar to other ferroelectrics.[15] By inference from the observation of core-shell microstructure in 5 mol% LT and 6 mol% LT standard samples liquid phase sintering mechanisms are absent. Additional of an excess of low-melting point alkali metal carbonates induces liquid phase which avoids chemical segregation and core-shell grain structures; it also leads to enhanced grain growth.

We investigated any differences in melting temperatures across the NKN-xLT-2BS series by heating compacts of selected compositions in a tube-furnace which was designed such that photographic images could be recorded at different temperatures, **Fig. DB5**. NKN compacts fully melted at 1230°C, 2 mol% LT and 10 mol% LT pellets slumped by 1260°C, but the 5 mol% LT pellets retained a cylindrical shape with only minor deformation consistent with partial melting (as opposed to complete melting for 2 mol% and 10 mol% LT samples). The higher melting temperature for 5 mol% LT inferred from these experiments ceramics may infer less liquid is present during sintering at 1100°C, the standard temperature adopted, compared to other compositions with lower melting (slumping) temperature. Indeed an absence of significant amounts of liquid phase during sintering would account for the sub-micron grain size and core-shell segregation in 5 mol% and 6 mol% LT samples, consistent with concepts of microstructural development in other ceramics.[31-33] This interpretation provides a framework for interpreting microstructure development and dielectric properties of all NKN-LT-BS compositions:

- Type I samples densify in the presence of a transient liquid phase; re-crystallisation/grain growth mechanisms produce micron-scale grain sizes, and liquid-phase diffusion restricts chemical non-uniformity to a scale below the resolution of the STEM-EDX analysis technique. However chemical disorder on the lattice scale is present, and leads to Curie peaks which are slightly broader than for a classic ferroelectric such as $BaTiO_3$.
- Type II samples have similar microstructures to Type I, but dielectric properties specifically more diffuse Curie peaks than Type I infer an increased level of chemical inhomogeneity, again unresolved by standard TEM-EDX.
- Type III samples, 5 mol% LT (and 6 mol% LT), sinter in the absence of liquid phase densification mechanisms and result in core-shell segregation and restricted grain growth. Core-shell structures persist even after extended sintering, but additions of liquid-phase forming excess alkali metal oxides prevent core-shell formation. For 5 mol% LT two distinct dielectric peaks are visible, the peak at ~ 470°C arising from the core. A minor second peak may exist in 6 mol%

LT (fewer core-shell grains exist in 6 mol% LT), but is obscured by the high temperature tail of the lower temperature dielectric peak derived from the shell compositions.

Chemical inhomogeneity in a related compositions, NKN-LT, including a high concentration of Ta in the outer regions have been reported and can be overcome by pre-calcining the two refractory components Nb_2O_5 and Ta_2O_5 at high temperatures.[34] In the present NKN-LT-BS materials, the existence of a three-tier grain structure in 6 mol% and the persistence of core-shell features after prolonged sintering highlight the increased complexity in forming a homogeneous perovskite solid solution (Li, Na, K, Bi)(Nb, Ta, Sc)O_3 involving four different cation types (1^+ and 3^+ charges) on A sites and three cation types (3^+ and 5^+ charges) on the B sites of the perovskite lattice.

However gross segregation linked to unreacted components was absent after sintering. No secondary phases were detected by X-ray powder diffraction. The XRD peaks of the product showed increased broadening in the Type III 5 mol% LT sample but tetragonal peak splitting was still evident,[18, 23] indicating only a slight difference in lattice dimensions of the core and shell grain material. For most of the NKN-LT-BS samples (excluding 5 mol% and 6 mol% LT), the scale of any localised segregation was below the sensitivity of the EDX analysis technique.

Core-shell segregation in 5 mol% LT and 6 mol% LT could be eliminated by incorporating excess alkali metal oxides, highlighting the importance of liquid-phase forming additions (5 and 6 mol% LT melted at higher temperatures than adjacent compositions, **Fig. DB5**). The ability to manipulate processing conditions to eliminate core-shell segregation highlights the remarkable adaptability of the perovskite crystal structure in accommodating a diverse range of ion sizes and valences.

Supporting evidence for our assertion that the core materials is responsible for the 470°C peak in NKN-5LT-2BS Type III ceramics is found in the literature on bulk ceramics of similar composition to that identified by EDX in the grain core: (Li, Na, K)NbO_3 (with very minor amounts of other elements). Most modified NKN ceramics reported in the literature have Curie temperature well below 470°C. However Li modification raises T_c. For example Paula et al. report T_c= 474°C for a nominal bulk composition $(Na_{0.47}K_{0.47}Li_{0.06})NbO_3$.[34**]** Guo et al. studied the compositional series $(1-x)(Na_{0.5}K_{0.5})NbO_3$–$xLiNbO_3$, x= 0.04-0.2 and reported Curie temperatures ranging from 452ºC to 510ºC (T_c ~ 470ºC corresponded to a composition x= 0.06).[10] Hence, although there is no dielectric data for the nano-regions of the core-shell grains it is reasonable to assume based on EDX and literature values of T_c for bulk (Li, Na, K)NbO_3 ceramics that the core in NKN-5LT-2BS is responsible for the 470°C dielectric peak.

The outer shell regions were similar by EDX analysis to the target NKN-LT-BS composition (slightly enriched in Bi, Sc, Ta) and the very diffuse peak centred at ~350°C is thus attributed to the outer shell.

The diffuseness of the dielectric peaks in the NKN-LT-BS samples will be dependent on grain size effects as well as compositional effects. The suppression of dipole reorientation due to size-related strain effects, and/or the presence of metastable non-ferroelectric phases within sub-micron grains have been reported for other perovskite ferroelectrics.[35] In the present Type III samples, the distinctive core-shell structure produces nano-scale features, well below the size of the constituent grains. Strain associated with the nano-scale grain sub-structure will contribute to broadening and suppression of Curie peaks. The loss of polarisation in P-E loops at 5 mol% LT is also indicative of this effect of restricted dipole re-orientation in nanostructured core-shell Type III samples.

For Type I and II, dielectric peak broadening is only due to the effects of short-range (non-core shell) chemical inhomogeneity without any grain size related strain effects. Hence the ~350°C dielectric peak is less diffuse in Types I and II than in Type III samples.

The NKN-6LT-2BS sample exhibited irregular character, as core-shell grains and compositional segregation were detected by STEM-EDX but only a single, diffuse dielectric peak was present in ε_r–T plots. The proportion of core-shell grains in 6 mol% LT was smaller than for NKN-5LT-2BS (~ 50% versus ~ 90%) and the size of the core region was reduced. Therefore, the dielectric peak at ~ 470°C would be anticipated to be smaller in 6 mol% LT samples. Moreover, the peak in 6 mol% LT may have been obscured by the tail of the more intense 380°C dielectric peak (T_c increased from 350 to 380°C between 5 and 6 mol% LT which will add to overlap issues).

Along the binary join (NKN-xLT) as compositions increase to 7-10 mol% Type I behaviour re-presented. Extended our study to compositions lying off of the NKN-xLT-2BS join, with behaviour being characterised principally by dielectric measurements, allowed us to define a broader ranges of Type I, II and III compositions, as summarised in **Fig. 9**. Summary dielectric plots and schematic illustrations of the characteristic grain structures for each sample type are also shown.

5. Conclusions

The $Na_{0.5}K_{0.5}NbO_3$ rich region of the ternary solid-solution system $Na_{0.5}K_{0.5}NbO_3$ –$LiTaO_3$–$BiScO_3$ has been studied using STEM-EDX analysis and dielectric property measurements. Evolution of relative permittivity-temperature response from a near-normal ferroelectric Curie peak to a diffuse peak and then to twin peaks as the $LiTaO_3$ increased from 0-5 mol% LT is attributed to a reduction in grain size (single diffuse dielectric peak) and the existence of core-shell grain structure (at 5 mol% LT). Semi-quantitative EDX analysis indicated the core to be similar in composition to (Li, Na, K)NbO_3 and the outer shell to a composition similar to the nominal target composition but enriched in Bi and Sc. Comparison of reported Curie temperatures for bulk ceramics of closely related compositions to the core composition indicated the core was responsible for the additional dielectric peak in the 5 mol% $LiTaO_3$ sample.

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References

[1] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya and M. Nakamura, Lead-free piezoceramics, Nature 432 (2004) 84-87.

[2] T.R. Shrout, S.J. Zhang, Lead-free piezoelectric ceramics: Alternatives for PZT?, J. Electroceram. 19 (2007) 111-124.

[3] M.D. Maeder, D. Damjanovic, N. Setter, Lead Free Piezoelectric Materials, J. Electroceram. 13 (2004) 385-392.

[4] J.-F. Li, K. Wang, F.-Y. Zhu, L.-Q. Cheng, F.-Z. Yao, (K, Na)NbO_3-Based Lead-free Piezoceramics: Fundamental Aspects, Processing Technologies, and Remaining Challenges, J. Am. Ceram. Soc. 96 (2013) 1-20.

[5] R.Z. Zuo, C. Ye, X.S. Fang, Dielectric and Piezoelectric Properties of Lead Free $Na_{0.5}K_{0.5}NbO_3$-$BiScO_3$ Ceramics, Jpn. J. Appl. Phys. 46 (2007) 6733-6736.

[6] T.A. Skidmore, T.P. Comyn, A.J. Bell, F. Zhu, S.J. Milne, Phase Diagram and Structure-Property Relationships in the Lead-Free Piezoelectric System: $Na_{0.5}K_{0.5}NbO_3$-$LiTaO_3$, IEEE Trans. Ultrason. Ferroelectr. Freq. Control. 58 (2011) 1819-1825.

[7] T.A. Skidmore, T.P. Comyn, S.J. Milne, Temperature stability of ($[Na_{0.5}K_{0.5}NbO_3]_{0.93}$-$[LiTaO_3]_{0.07}$) lead-free piezoelectric ceramics, Appl. Phys. Lett. 94 (2009) 222902-1-3.

[8] R. Zuo, J. Fu, G.Z. Yin, X.L. Li and J.Z Jiang, Electric field induced phase instability in typical (Na, K)(Nb,Sb)O_3-$LiTaO_3$ ceramics near orthorhombic and tetragonal phase boundary, Appl. Phys. Lett. 101 (2012) 092906-1-4.

[9] Y. Dai, X. Zhang and G. Zhou, Phase transitional behaviour in $K_{0.5}Na_{0.5}NbO_3$-$LiTaO_3$ ceramics, Appl. Phys. Lett. 90 (2007) 262903-1-3.

[10] Y. Guo, K. Kakimoto, H. Ohsato, $(Na_{0.5}K_{0.5})NbO_3$-$LiTaO_3$ lead-free piezoelectric ceramics, Mater. Lett. 59 (2005) 241-244.

[11] A. Zeb and S.J. Milne, Stability of High-Temperature Dielectric Properties for (1-x)$Ba_{0.8}Ca_{0.2}TiO_3$-xBi$(Mg_{0.5}Ti_{0.5})O_3$ Ceramics, J. Am. Ceram. Soc. 96[9] (2013) 2887-2892.

[12] C. Liu, D. Xiao, T. Huang, J. Wu, F. Li, B. Wu, J. Zhu, Composition induced rhombohedral-tetragonal phase boundary in $BaZrO_3$ modified $(K_{0.445}Na_{0.5}Li_{0.055})NbO_3$ lead-free ceramics, Mater. Lett. 120 (2014) 275-278.

[13] W. Liang, W. Wu, D. Xiao, J. Zhu, J. Wu, Construction of new morphotropic phase boundary in 0.94$(K_{0.4-x}Na_{0.6}Ba_xNb_{1-x}Zr_x)O_3-0.06LiSbO_3$ lead-free piezoelectric ceramics, J. Mater. Sci. 46 (2011) 6871-6876.

[14] B. Zhang, J. Wu, X. Cheng, X. Wang, D. Xiao, J. Zhu, X. Wang and X. Lou, Lead-free Piezoelectrics Based on Potassium-Sodium Niobate with Giant d_{33}, ACS Appl. Mater. Inter. 5 (2013) 7718-7725.

[15] Z. Wang, D. Xiao, J. Wu, M. Xiao, F. Li, and J. Zhu, New Lead-Free (1-x)$(K_{0.5}Na_{0.5})NbO_3$–x$(Bi_{0.5}Na_{0.5})ZrO_3$ Ceramics with High Piezoelectricity, J. Am. Ceram.

Soc. 97[3] (2014) 688-690.

[16] K. Wang, F.-Z. Yao, W. Jo, D. Gobeljic, V.V. Shvartsman, D.C. Lupascu, J.-F. Li and J. Rödel, Temperature-Insensitive (K, Na)NbO_3-based Lead-free Piezoactuator Ceramics, Adv. Funct. Mater. 23 (2013) 4079-4086.

[17] X. Sun, J. Chen, R. Yu, C. Sun, G. Liu, X. Xing and L. Qiao, BiScO3 Doped $(Na_{0.5}K_{0.5})NbO_3$ Lead-Free Piezoelectric Ceramics, J. Am. Ceram. Soc. 92[1] (2009) 130-132.

[18] F. Zhu, M.B. Ward, T.P. Comyn, A.J. Bell and S.J. Milne, Dielectric and Piezoelectric Properties in the Lead-Free System $Na_{0.5}K_{0.5}NbO_3$-$BiScO_3$-$LiTaO_3$, IEEE Trans. Ultrason. Ferroelectr. Freq. Control. 58[9] (2011) 1811-1818.

[19] F. Zhu, T.A. Skidmore, A.J. Bell, T.P. Comyn, C.W. James, M.B. Ward, S.J. Milne, Diffuse dielectric behaviour in $Na_{0.5}K_{0.5}NbO_3$-$LiTaO_3$-$BiScO_3$ lead-free ceramics, Mater. Chem. Phys., 129 (2011) 411-417.

[20] A.A Belik, S. Iikubo, K. Kodama, N. Igawa, S. Shamoto, M. Maie, T. Nagai, Y. Matsui, S.Y. Stefanovich, B.I. Lazoryak and E. Takayama-Muromachi, $BiScO_3$: Centrosymmetric $BiMnO_3$-type Oxide, J. Am. Chem. Soc. 128 (2006) 706-707.

[21] S.J. Pennycook, D.E. Jesson, High-resolution Z-contrast imaging of crystals, Ultramicroscopy 37 (1991) 14-38.

[22] S.J. Pennycook, L.A. Boatner, Chemically sensitive structure-imaging with a scanning transmission electron microscope, Nature 336[8] (1988) 565-567.

[23]F. ZHU, Lead-free Piezoelectric Ceramics. Institute for Materials Research, Ph.D. Thesis. Leeds: University of Leeds, 2012.

[24] L.-Q. Cheng, K. Wang, F.-Y. Yao, F. Zhu, J.-F. Li, Composition Inhomogeneity due to Alkaline Volatilization in Li-Modified (K, Na)NbO_3 Lead-free Piezoceramics, J. Am. Ceram. Soc. 96[9] (2013) 2693-2695.

[25] Y. Zhen and J.-F. Li, Abnormal Grain Growth and New Core-Shell Structure in (K,Na)NbO_3-Based Lead-Free Piezoelectric Ceramics, J. Am. Ceram. Soc. 90[11] (2007) 3496-3502.

[26] D. Hennings, Barium Titanate Based Ceramic Materials for Dielectric Use, Int. J. Technology Ceramics 3 (1987) 91-111.

[27] D. Hennings and G. Rosenstein, Temperature-Stable Dielectric Based on Chemically Inhomogeneous $BaTiO_3$, J. Am. Ceram. Soc. 67[4] (1984) 249-254.

[28] B.S. Rawal, M. Kahn and W.R. Buessem, Grain Core-Grain Shell Structures in Barium Titanate-Based Dielectrics, in Advances in Ceramics, Vol.1., Am. Ceram. Soc. Columbus, Ohio, 1981, pp.172-88.

[29] I. Burn, Temperature-stable Barium Titanate Ceramics Constaining Niobium Pentoxide, Electrocomponent Science and Technology 2 (1976) 241-247.

[30]P. Hansen, D. Hennings, H. Schreinemacher, Dielectric Properties of acceptor-Doped (Ba, Ca)(Ti, Zr)O_3, Electroceram 2:2, (1998) 85-94.

[31] S. Zhang, H.J. Lee, C. Ma, X. Tan, Sintering Effect on Microstructure and Properties of (K,Na)NbO_3 Ceramics, J. Am. Ceram. Soc. 94[11] (2011) 3659-3665.

[32] C.A. Randall, S.F. Wang, D. Laubscher, J.P. Dougherty, W. Huebner, Structure property relationships in core-shell $BaTiO_3$-LiF ceramics, J. Mater. Res. 8[4] (1993) 871-879.

[33] S.-C. Jeon, C.-S. Lee and S.-J.L. Kang, The Mechanism of Core/Shell Structure Formation During Sintering of $BaTiO_3$-Based Ceramics, J. Am. Ceram. Soc. 95[8] (2012)

2435-2438.
[34] A.J. Paula, R. Parra, M.A. Zaghete and J.A. Varela, Study on the $K_3Li_2Nb_5O_{15}$ formation during the production of $(Na_{0.5}K_{0.5})_{(1-x)}Li_xNbO_3$ lead-free piezoelectrics at the morphotropic phase boundary, Solid State Comm. 149 (2009) 1587-1590.
[35] M.H. Frey and D.A. Payne, Grain-size effect on structure and phase transformations for barium titanate, Phys. Rev. B 54[5] (1996) 3158-3168.

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