RIGA TECHNICAL UNIVERSITY
Faculty of Material Science and Applied Chemistry

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Doctoral program „ Material Science”

LEAD-FREE FERROELECTRIC CERAMICS BASED ON ALKALI NIOBATES

Summary of the Doctoral Thesis

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The thesis for doctoral degree in engineering sciences is to be publicly defended on June 5th 2013, at 14^{00} at the Riga Technical University, Faculty of Material Science and Applied Chemistry 14/24, room 272.

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CONFIRMATION

I confirm that I have developed the present Doctoral Thesis, which is submitted for consideration at Riga Technical University for scientific degree of the doctor of engineering sciences. The Doctoral Thesis has not been submitted at any other university for the acquisition of a scientific degree.

Ilze Smeltere .....

Date .....

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I send my deepest love to my parents and brothers family as well as to all of my friends for the support and believing in me.

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CONTENT

GENERAL DESCRIPTION

Introduction

Ferroelectric ceramics are used in different devices since 1940's. Hence the market of ferroelectric ceramics has developed enormously. Ceramics with different compositions have been produced and modified to adapt the material for a specific purpose. Lead zirconate titanate PZT having outstanding electromechanical properties is mentioned for the first time in 1952. Until now materials based on PZT have dominated the industry of piezoelectric ceramics. However lead is toxic and the measures for safe utilization need to be taken. Furthermore lead oxide evaporates easily causing the environmental pollution. European Union directives released in 2004 restrict the use of toxic elements in electric and electronic devices. A lot of literature sources about lead-free ferroelectric ceramics are available nowadays however the deeper research is needed in order to substitute lead-based materials.
Lead-free ferroelectric ceramics based on alkali niobates is one of the most promising material classes. An advantage is higher phase transition temperatures (around 400°C) compared to other lead-free materials with perovskite structure. Potassium sodium niobate KNN also possess higher piezoelectric properties. The main difficulty is to obtain fully dense ceramic body; pure densification of KNN sets a limit for the electrical properties. Therefore there are many studies about possibilities to improve the densification process. There are several new sintering methods for example spark plasma sintering or capacitor discharge sintering available but they are much more expensive than solid state sintering. For industrial production conventional ceramic technology is more convenient.

The challenge of the topic

Despite the many studies on lead-free ferroelectric ceramics potassium sodium niobate KNN is still behind the lead-based materials. The main disadvantage is the pure density compared to lead-based materials. Besides it is difficult to obtain fully dense ceramic samples via conventional ceramic technology.

Aim of the work

The aim of the doctoral thesis is to produce dense ferroelectric ceramics based on alkali niobates using conventional ceramic technology.
According to the aim the tasks for the thesis were highlighted:

- to obtain dense ceramics based on alkali niobates whilst guided by the literature data on producing and modifying ferroelectric ceramics;
- to research the solid state synthesis process;
- to carry out the structure examination;
- to investigate the dielectric, ferroelectric and piezoelectric properties of obtained materials;
- to analyze and interpret the obtained results.

Conferences and Publications

The results of the doctoral thesis have been reported at 24 international and local scientific conferences, 10 SCI publications and 3 full text scientific papers in conference proceedings have been published. One patent of Republic of Latvia has been received.

CONTENT OF THE DOCTORAL THESIS

Overview on the literature

Piezoelectric and ferroelectric materials belong to the class of smart materials it means their properties can be significantly changed by external stimuli [1]. Lead zirconate titanate PZT and PZT-based ceramics have dominated the market of ferroelectric materials for the last five decades. However, they contain up to 60 wt% lead which is toxic and should be replaced wherever it is possible [2]. This is the reason for present tendency to develop new lead free ferroelectric materials replacing Pb-based ones [3-5]. Potassium sodium niobate $(K_{0.5}Na_{0.5})NbO_3$ (KNN) is one of the most promising candidates with perovskite structure for this aim. KNN exhibits a morphotropic phase boundary (MPB) at K/Na 50/50. Compositions close to this MPB have the best dielectric, ferroelectric and piezoelectric properties [6]. Potassium sodium niobate has perovskite structure; ABO_3 unit cell has a monoclinic symmetry with lattice parameters $a_m=c_m>b_m$, and $\beta>90°$ as shown in Fig.1 [7].

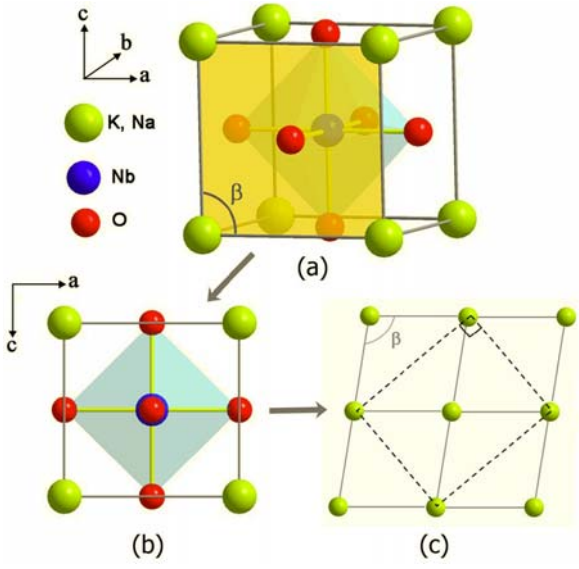


Fig. 1. Cell structure: a) $(K,Na)NbO_3$ subcell;
b) The projection of the subcell along *b* axis;
c) Four adjacent subcell projections, while omitting Nb and O atoms [7]

Diffusion couple studies confirmed that Na^+ and K^+ ions diffuse into Nb_2O_5 and not vice versa. XRD analysis of product layers declared several intermediate compounds like $Na_2Nb_4O_{11}$, $K_4Nb_6O_{17}$, $K_6Nb_{10.88}O_{30}$, $K_{5.75}Nb_{10.85}O_{30}$. It is found that Na^+ ions diffuse into Nb_2O_5 more quickly than K^+ ions which can be explained with differences in ionic radii of Na^+ and K^+, respectively 1.39 Å and 1.64 Å [8].

The properties of the final ceramic product could be changed or improved with the modification of the solid solution. There are several opportunities:

a) the addition of different oxides as sintering aids,

b) by A- or B-site ion substitution with the same valence ions,

c) by A- or B-site ion substitution with different valence ions.

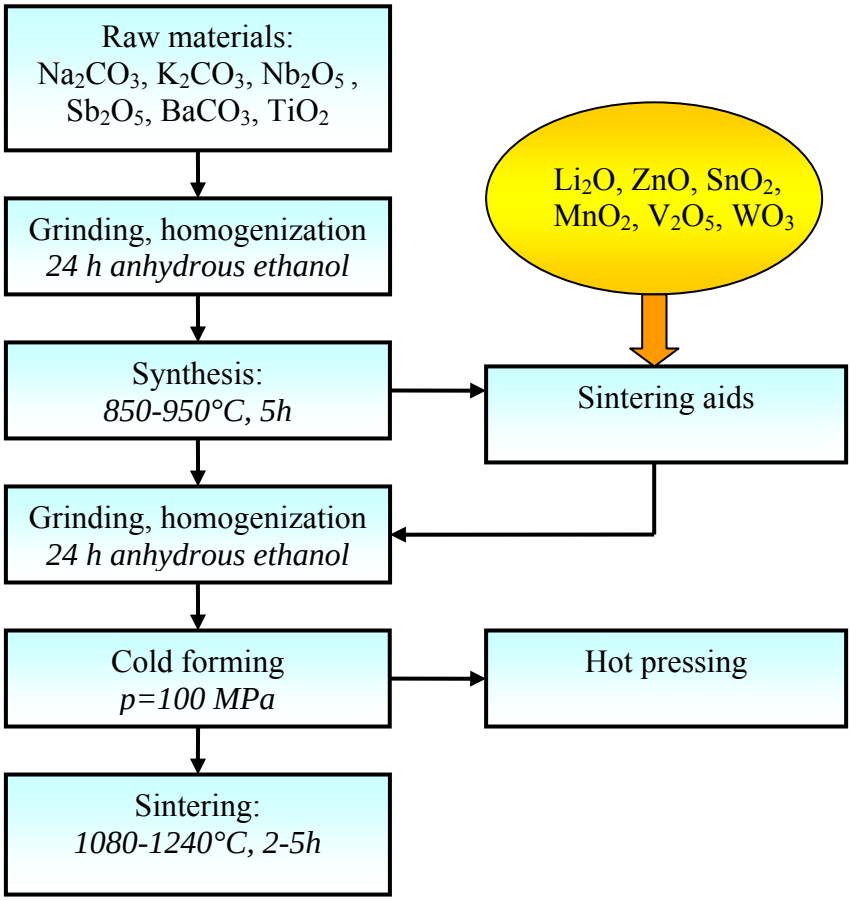
KNN ceramics is a good candidate for substituting lead-based ferroelectric ceramics in high frequency dielectric devices [9-11]. Solid solutions based on KNN could also be a potential implant material. Electric charge promotes osteogenesis and the proliferation of the cells on the material surface what helps in the bone regeneration process. Tests proved that cytotoxicity of KNN is not considerable, cell growth on the surface of material is very good [12].

Experimental

Potassium sodium niobate ceramics $(K_{0.5}Na_{0.5})NbO_3$ (KNN) were made by conventional solid-state sintering method from high purity oxides and carbonates. KNN was modified:

1. Using different oxides (Li_2O, ZnO, SnO_2, MnO_2, V_2O_5, WO_3) of 1 mass % as sintering aids;
2. By substituting B-site lattice Nb^{5+} for Sb^{5+};
3. By making solid solutions from substituted KNN and $BaTiO_3$ (BT).

Technological scheme of lead-free KNN processing is shown below (Fig.2).



2. att. KNN ceramic processing technological scheme

Differential scanning calorimetry (DSC) and thermogravimetry (TG) analysis were performed in SiC oven within a temperature interval from room temperature to 1200°C with a heating-cooling rate of 20°C/min (NETZSCH STA 449 F3 Jupiter®). Synthesis kinetic measurements were performed at different temperatures 400°, 450°, 500°, 550°, 600°, 650°C and different holding times 5, 7, 10, 15, 20, 30 min. One gram of $(K_{0.5}Na_{0.5})NbO_3$ was used for each experimental series. The outcome of the solid state synthesis is measured with parameter α, which is the amount of the reacted material in time. For the evaluating the sintering process high-temperature microscope HTM analysis was used (EMO-1750-30-K). Densities of the samples were measured by Archimedes method. The phase structure was investigated with an

X-ray diffraction (XRD) analysis (X'Pert Pro MPD, Cu Kα radiation). The microstructures of ceramics were studied with scanning electron microscope SEM (Mira/Tescan). Material constants: the Young′s modulus *E*, the shear modulus *G* and the Poisson′s ratio *ν* were measured by an ultrasonic method (UZP-1 INCO-VERITAS).

For the dielectric measurements silver or golden electrodes were carried up and burned at 700°÷750°C. Temperature and frequency dependence of dielectric permittivity ε and losses tanδ was measured on an impedance analyzer HP4194A precision LRC meter. P-E hysteresis loops were measured using Sawyer-Tower circuit. The samples for piezoelectric measurements were poled and piezoelectric parameters were determined through resonance – anti-resonance technique.

Results and discussion

KNN ceramics synthesis

KNN ceramic samples were prepared by conventional ceramic technology from powders synthesized via solid state synthesis as showed in equation 1:

$$½\ K_2CO_3 + ½\ Na_2CO_3 + Nb_2O_5 \rightarrow 2(K_{0.5}Na_{0.5})NbO_3 + CO_2\uparrow \quad (1)$$

DSC showed the synthesis process of the solid solution. Endothermic reaction at lower temperatures is associated with absorbed (85°C) and conjugated water (200°C) evaporation (Fig. 3). Endothermic peaks above 460°C are linked with a beginning of the solid state reactions when structural changes occur with decomposing of the carbonates and CO_2 evaporation. Synthesis kinetic measurements confirmed these results. Further follow reactions at ~690° and 745°C, corresponding to niobium oxide polymorphic transitions and the end of alkali niobate formation.

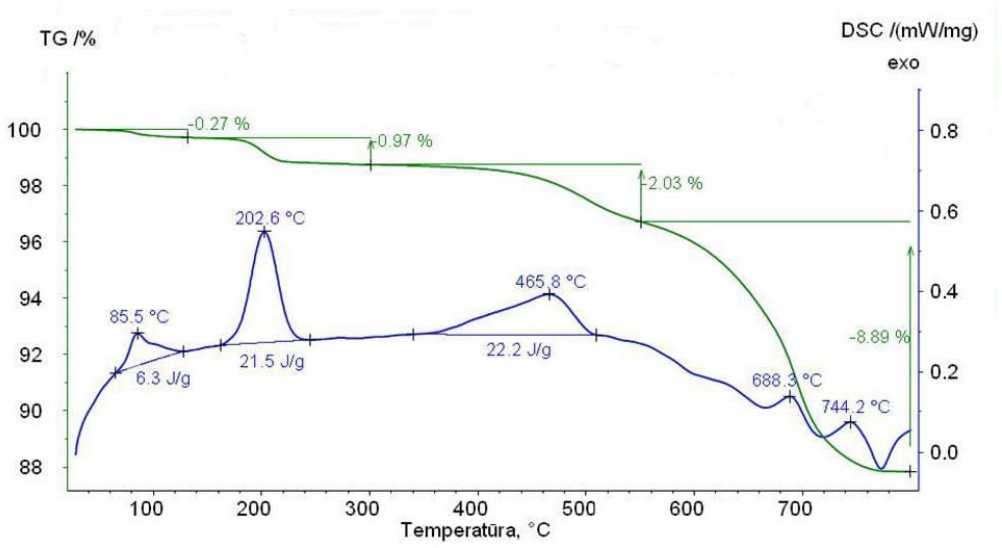


Fig. 3. DSC and TG analysis for $(K_{0.5}Na_{0.5})NbO_3$

From thermogravimetry results (TG) it can be seen that starting from 400°C there is continuous loss of mass associated with CO_2 vaporization. Synthesis kinetic measurements were performed to define more precisely the data from DSC. The outcome of the solid state synthesis is measured with parameter α, which is the amount of the reacted material in time. At 400°C α is only a little above 10 %, at 450°C α is about four times higher. At 650°C after holding sample for 30 min amount of the reacted material is already 100%. Reaction occurs fast in the first few minutes because the speed depends on reagent concentration. The reaction speed decreases simultaneously with a decrease in reagent concentration. XRD analysis confirmed the formation of perovskite phase with a small amount of intermediate compounds only for samples sintered at 650°C with holding time 30 min.

Pure KNN

Theoretical density of pure KNN is 4.51 g/cm^3. Density of air sintered KNN sample does not exceed 93%. Dielectric permittivity ε of pure KNN reaches the maximum at temperature 410°C, which is the phase transition temperature from cubic to tetragonal T_C (Curie temperature). One more phase transition from tetragonal to orthorhombic structure T_{O-T} occurs at 193°C (Fig. 4).

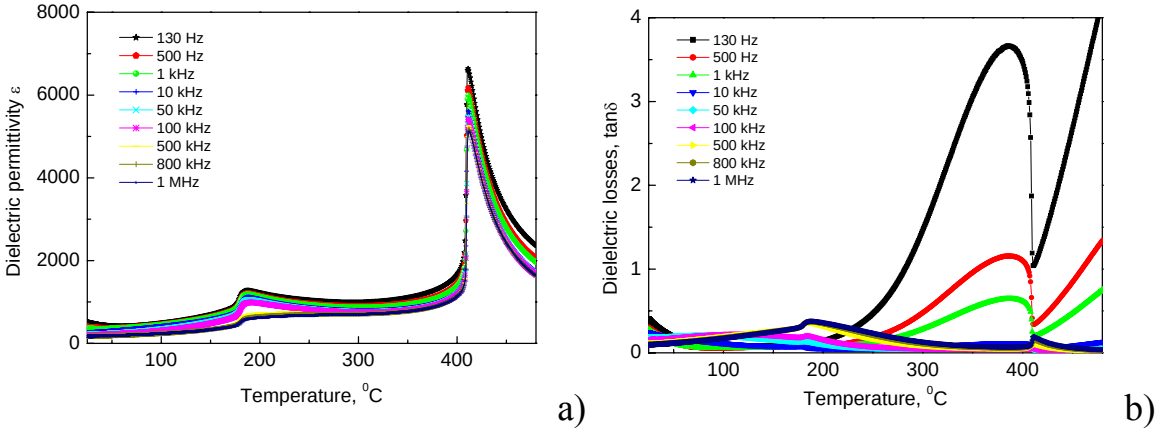


Fig. 4. Temperature and frequency dependence on a) dielectric permittivity ε and b) dielectric losses tanδ

KNN with oxide dopants

Oxide additives decrease the optimal sintering temperature of KNN ceramics from 1170°C to 1100 – 1130°C. XRD analysis showed that the addition of sintering aids did not affect the crystallographic structure of the ceramics significantly. In all the samples perovskite structure is confirmed, no secondary phase is observed.

The fracture morphology of KNN ceramics containing different kinds of oxide dopants is demonstrated on Fig. 5. Pure KNN has inhomogeneous structure with bimodal grain size distribution. It can be seen that all of the doping elements have different effects on the microstructure of the ceramic samples.

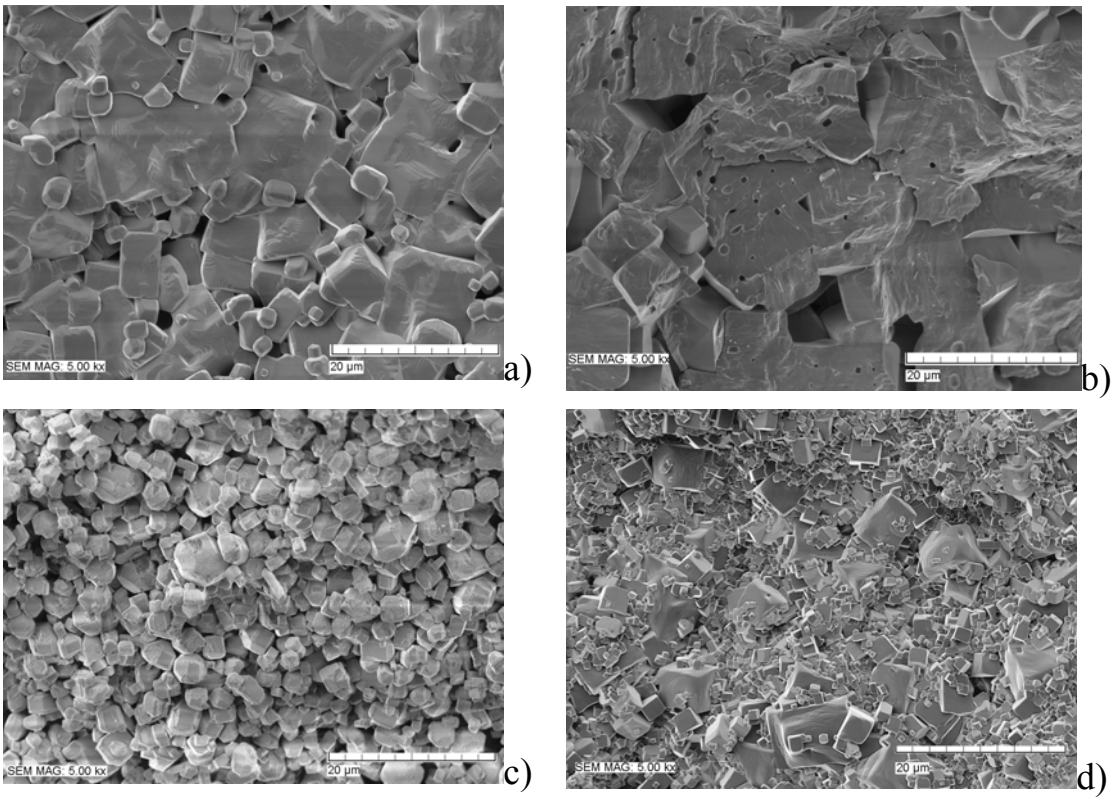


Fig. 5. SEM microstructure: a) pure KNN, b) KNN+Li_2O; c) KNN+V_2O_5; d) KNN+MnO_2

Cubic or rectangular morphology of the grains with clear grain boundaries can be seen in ceramics except those, doped with V_2O_5 and WO_3. The addition of V_2O_5 causes the growth of fine grains with lamellar grain structure. The addition of MnO_2 suppresses the grain growth and gives rather homogenous microstructure with grain sizes of 1-4 µm which can be explained also by lower sintering temperatures.

The temperature dependence of dielectric permittivity ε at 1 kHz frequency is shown in Fig.6.

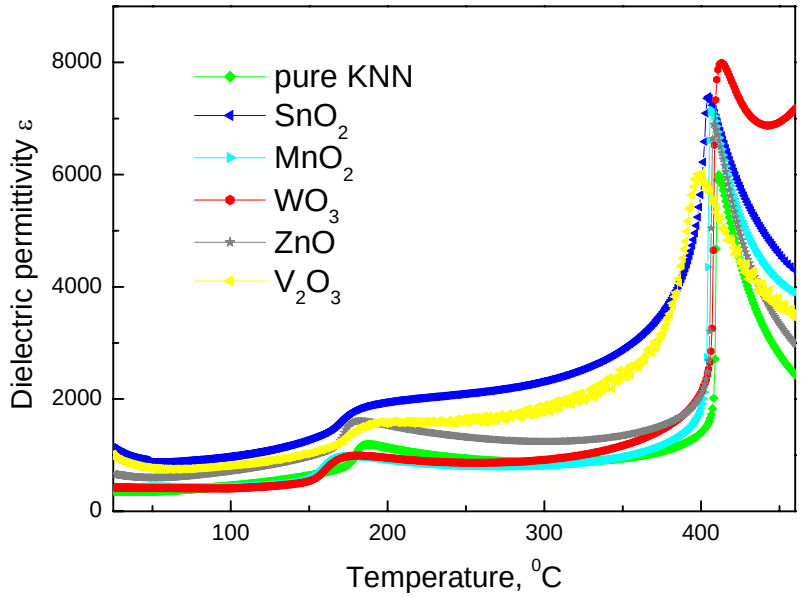


Fig. 6. Temperature dependence on the dielectric permittivity ε for $(K_{0.5}Na_{0.5})NbO_3$ ceramics with different sintering aids at 1 kHz

The properties of KNN ceramics depend a lot on sintering conditions. We obtained an interesting result in ferroelectric properties for the ceramics samples KNN+MnO_2 sintered at the same temperature with different holding times (Fig. 7). The tendency to make antiferroelectric like double hysteresis loop occurs for a sample with sintering regime 1100°C for 5 h. KNN consists equally from ferroelectric potassium niobate $KNbO_3$ (KN) and antiferroelectric sodium niobate $NaNbO_3$ (NN). KN evaporates at lower temperature than NN and it is possible that after a longer holding time NN dominates in the ceramic composition what causes the observed effect.

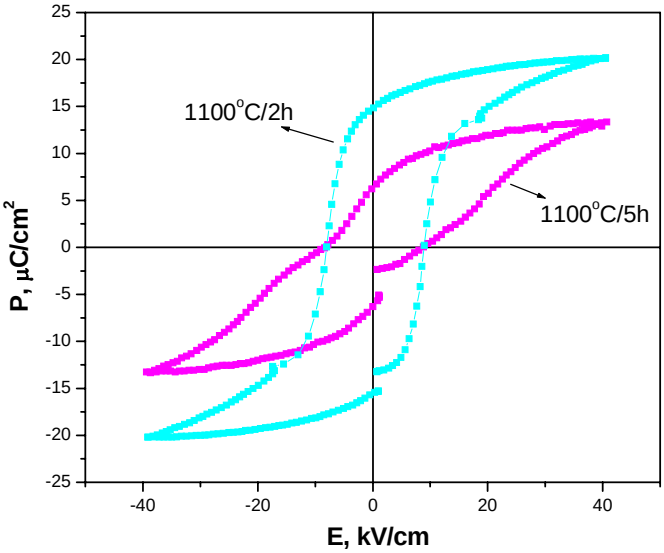


Fig. 7. P-E hysteresis loops for KNN+MnO_2 samples depending on sintering time

Pure KNN has modest piezoelectric properties. A small amount (0.5 wt%) of MnO_2 improves the properties considerably, increasing d_{33} from 80 pC/N to 110 pC/N, k_p from 0.3 to 0.38, Q_m from 60 to 190. The reason for this first of all is that in the presence of MnO_2 the microstructure becomes more homogeneous. Introducing manganese dioxide in the KNN composition it changes to Mn_3O_4 while sintering at high temperature. Mn_3O_4 is a compound of $MnO{\cdot}Mn_2O_3$, and has two values Mn^{2+} and Mn^{3+} with different ionic radii 0.67 Å, and 0.58 Å, respectively. Mn ions enter into the B-site lattice causing distortion of crystal lattice and oxygen vacancies what restricts the domain wall motion. We assume that Mn ions and oxygen vacancies form the defect dipoles. These dipoles align to the polarization direction forming the local fields.

$(K_{0.5}Na_{0.5})Nb_{1-x}Sb_xO_3$

B-site ion Nb^{5+} partial substitution for Sb^{5+} and addition of MnO_2 as a sintering aid leads to obtaining of high density ceramic samples.

The chemical composition affects the microstructure of ceramic sample as well as the sintering conditions. The influence of antimony Sb^{5+} substitution level on the microstructure of the samples sintered at the same temperature is shown in Fig. 8.

With increasing Sb^{5+} content ceramics get more dense and with more homogeneous microstructure.

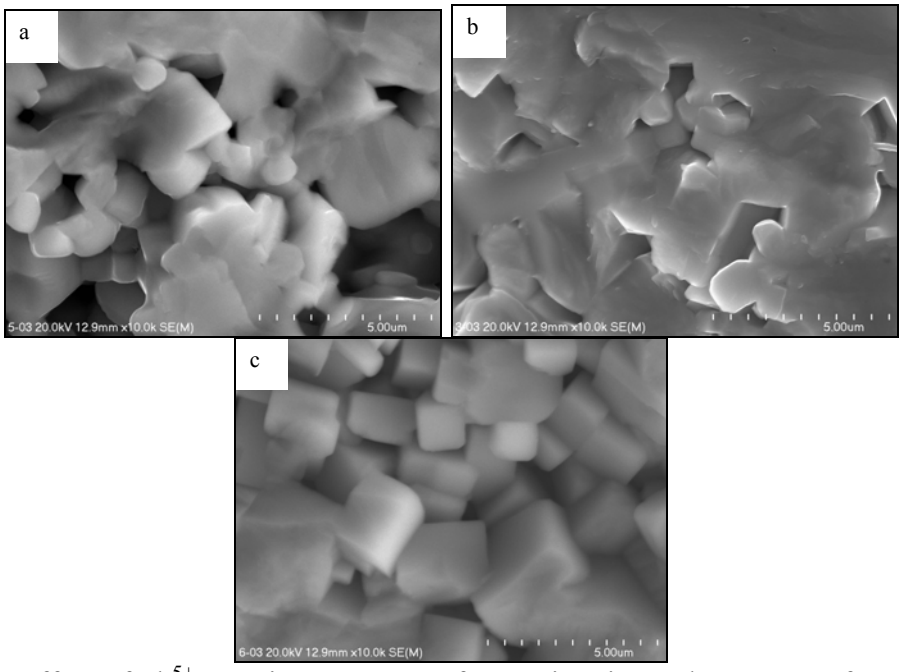


Fig. 8. The effect of Sb^{5+} on microstructure of ceramics sintered at 1130°C for x=0.04 (a), x=0.05 (b) and x=0.06 (c)

For undoped KNN ceramic two sharp phase transitions are observed at 190° and about 410°C, corresponding to the phase transitions from orthorhombic to tetragonal (T_{O-T}) and from ferroelectric tetragonal to paraelectric cubic (T_c), respectively. After the partial substitution of Sb^{+5} for Nb^{+5} both of these phase transitions are shifted to lower temperatures (Fig. 9).

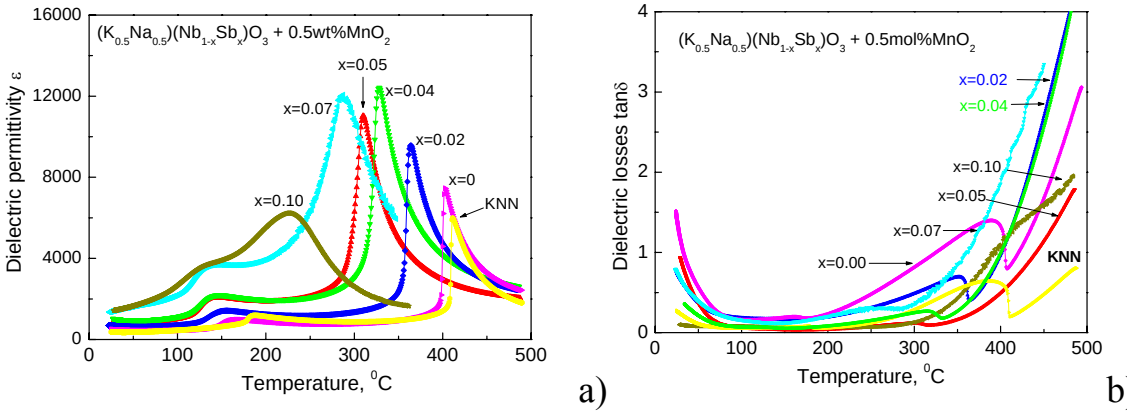


Fig. 9. Temperature dependence on dielectric permittivity ε (a) and dielectric loss tanδ (b) at 1 kHz

Fig. 10 demonstrates the changes of both phase transitions with increasing Sb^{5+} level more clearly.

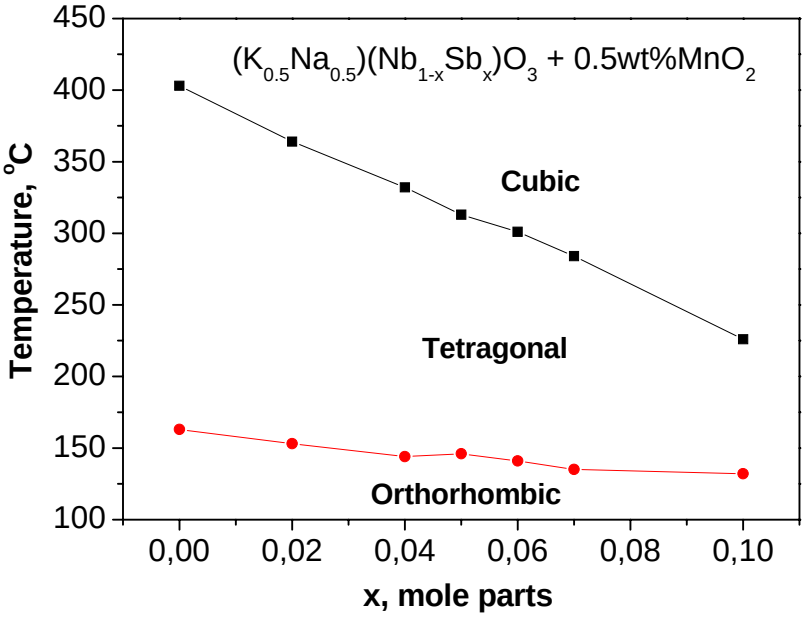


Fig. 10. Phase transition temperatures depending on Sb^{5+} substitution level

Ceramics with small amount of Sb^{5+} retain the classic ferroelectric characteristics, and undergo sharp ferroelectric tetragonal to paraelectric cubic T_c phase transition. The phase transition peak at T_c becomes broadened gradually with increasing x indicating the appearance of a diffuse phase transition.

Shoulders emerging on the ε(T) curves at lower frequencies may be an evidence of a structural transition between the orthorhombic phases or a rotational phase transition related to turning of oxygen octahedrons [$a^-b^+a^-$].

The obtained results are characteristic for that observed in complex compounds or solid solutions, in which foreign ions occupy crystallographically equivalent lattice sites. The break of translational invariance caused by foreign ions/lattice imperfections leads to extreme broadening of the transition anomalies in these materials. The phase transition occurs in the temperature range rather than one specific temperature value and therefore is called diffused phase transition. The substitution of B-site ions Nb^{5+} by Sb^{5+} introduces additional disorder in this site. As this substitution is isovalent, it does not affect drastically the charge state of the material. However, the Sb^{5+} ion size is smaller than Nb^{5+} ions, it may cause internal compressive stress and the random elastic fields are expected from this substitution. These elastic fields, which promote formation of polar regions, are very likely to be responsible for improvement of dielectric as well as ferroelectric properties of investigated ceramics. These results are characteristic for complex solid solutions in which the substitution is performed with the ions of the same value. Those foreign ions have different radii and atomic mass such deforming the crystal lattice despite the same value.

The temperature dependence of the remnant polarization P_r obtained from pyroelectric measurements is shown in Fig. 11. Both Sb or Sb and MnO_2 doping causes a significant increase of P_r. It should be noted that the remnant polarization remains nonzero up to temperature higher the structural phase transition temperature

for KNNS6 and KNNS6+0.5%MnO_2, indicating an possible existence of polar regions above the structural phase transition.

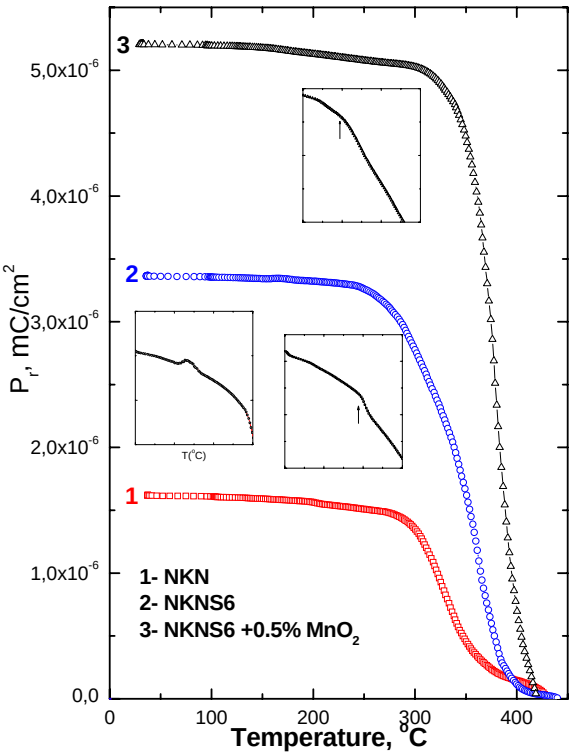


Fig. 11. P_r dependence on temperature

P-E hysteresis loops of all Sb^{5+} substituted $(K_{0.5}Na_{0.5})(Nb_{1-x}Sb_x)O_3$ + 0.5 wt% MnO_2 ceramics are well saturated (Fig. 12). Coercitive field E_C did not exceed 10 kV/cm, meaning this kind of material is easy to polarize. The highest P_r values have compositions which showed the best dielectric properties. Different compositions have different remnant polarization P_r and the highest P_r values reached the same compositions with the highest ε_{max}.

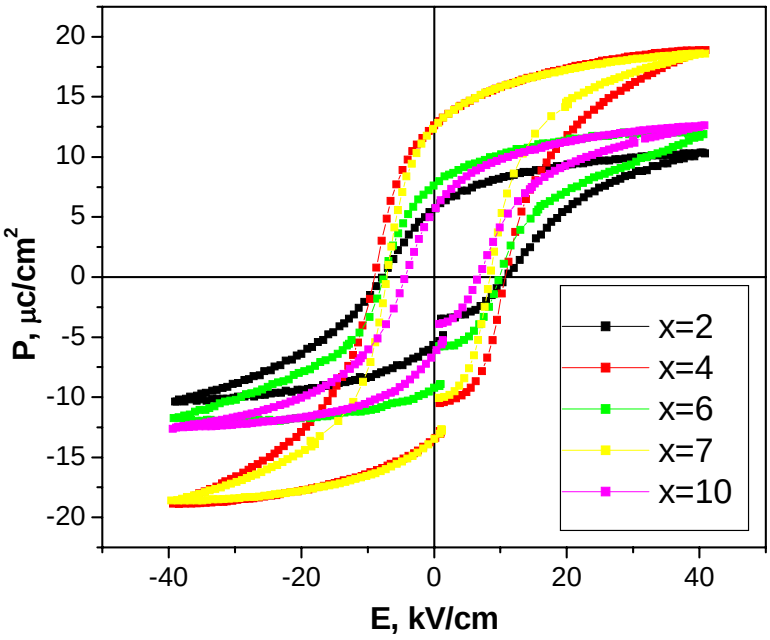


Fig. 12. P-E hysteresis loops

The samples in composition range from x = 0.02 to 0.07 exhibited excellent piezoelectric properties: piezoelectric coefficient of d_{33} = 92 ÷ 192pC/N, electromechanical planar and thickness coupling coefficients of k_p = 0.32 ÷ 0.46 and k_t = 0.34 ÷ 0.48, respectively (Fig. 13).

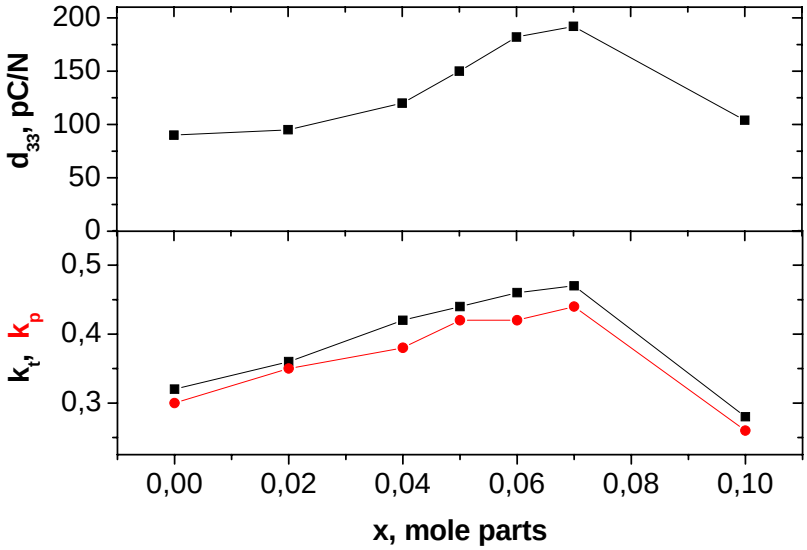
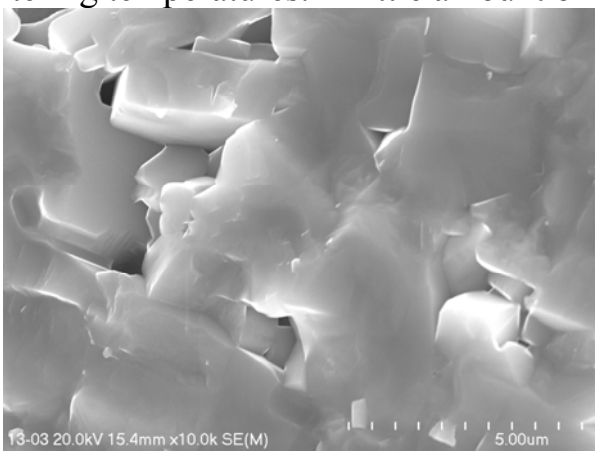


Fig. 13. Piezoelectric properties depending on Sb^{5+} substitution level

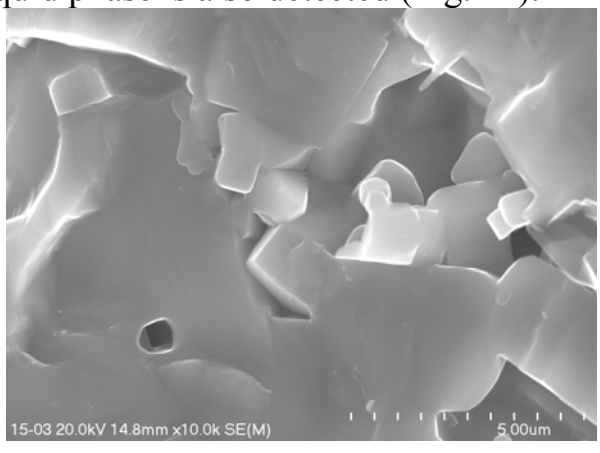
(1-x)($K_{0.5}Na_{0.5}$)$Nb_{1-y}Sb_yO_3$-x$BaTiO_3$

New solid solutions with chemical formula (1-x)($K_{0.5}Na_{0.5}$)$Nb_{1-y}Sb_yO_3$-x$BaTiO_3$ (x=0.01; 0.015; 0.02; 0.04; y=0.04; 0.07) (KNNSy%-xBT) were made by conventional solid state sintering. Phase structure changes from monoclinic to tetragonal with increasing x in NS4. Lattice parameters changes could be related with smaller cations entering crystal lattice: K^+ - 1.64 Å, Na^+ - 1.39 Å, Ba^{2+} - 1.61 Å for A-site, Nb^{5+} - 0.64 Å, Sb^{5+} - 0.60 Å, Ti^{4+} - 0.605 Å for B-site.

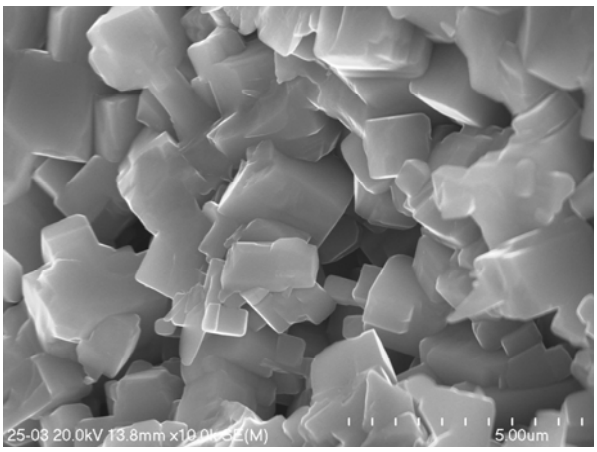
Solid solutions with $BaTiO_3$ addition have smaller average grain sizes; the shape of grains is a little rounded. MnO_2 addition suppresses the grain growth even more and the microstructure is more homogenous which could be the result of lower sintering temperatures. A little amount of liquid phase is also detected (Fig. 14).



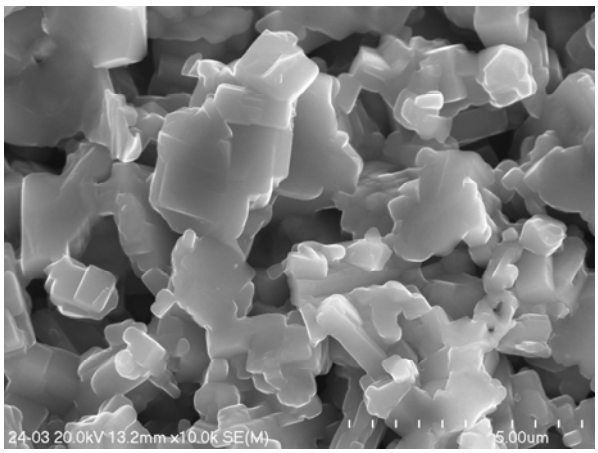
a) 0.99($K_{0.5}Na_{0.5}$)$Nb_{0.96}Sb_{0.04}O_3$ – 0.01BT



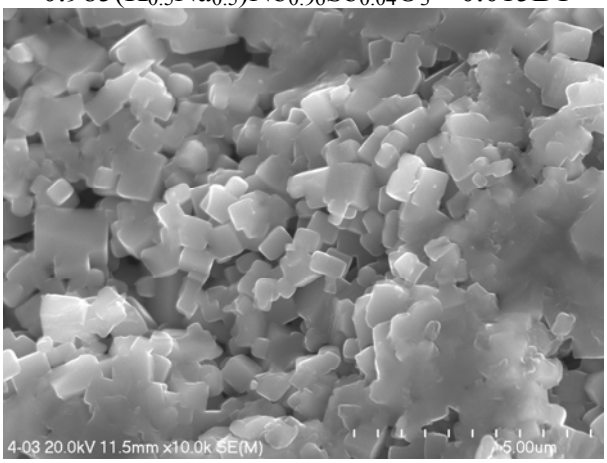
b) 0.99($K_{0.5}Na_{0.5}$)$Nb_{0.93}Sb_{0.07}O_3$ - 0.01BT



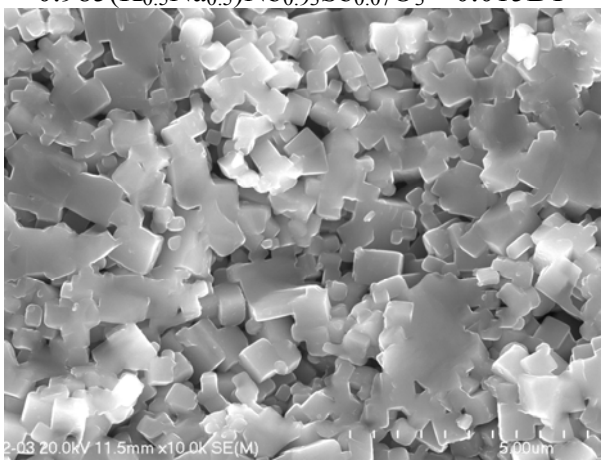
$0.985(K_{0.5}Na_{0.5})Nb_{0.96}Sb_{0.04}O_3 - 0.015BT$



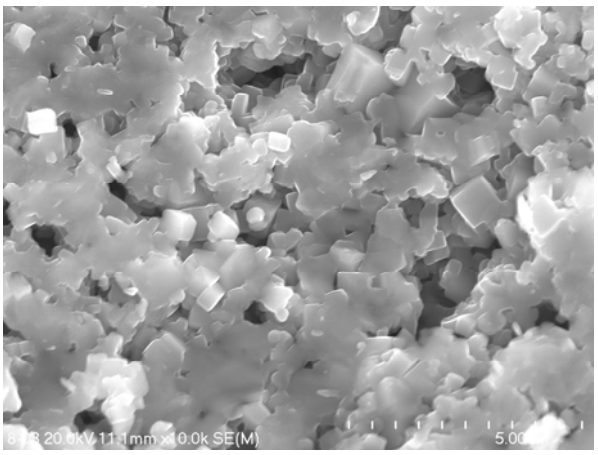
$0.985(K_{0.5}Na_{0.5})Nb_{0.93}Sb_{0.07}O_3 - 0.015BT$



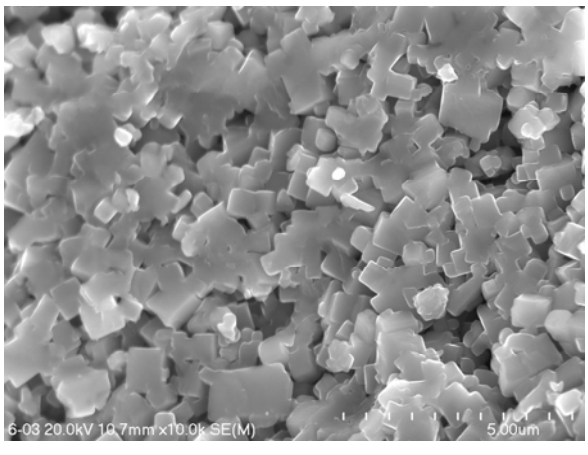
c) $0.98(K_{0.5}Na_{0.5})Nb_{0.96}Sb_{0.04}O_3$-$0.02BaTiO_3$



d) $0.98(K_{0.5}Na_{0.5})Nb_{0.93}Sb_{0.07}O_3$-$0.02BaTiO_3$



e) $0.96(K_{0.5}Na_{0.5})Nb_{0.96}Sb_{0.04}O_3$-$0.04BaTiO_3$



f) $0.96(K_{0.5}Na_{0.5})Nb_{0.93}Sb_{0.07}O_3$-$0.04BaTiO_3$

Fig. 14. SEM microstructure for $(1\text{-}y)(K_{0.5}Na_{0.5})Nb_{1-x}Sb_xO_3$-$yBaTiO_3$+ 0.5wt%$MnO_2$

The EDS and EPMA (Electron probe micro-analyzer) made in the chosen microregions of the sample surface analysis confirmed the purity and experimentally assumed qualitative and quantitative composition.

From the high temperature microscope (HTM) measurements it can be seen what influence has $BaTiO_3$ on the sintering of the ceramic sample (Fig. 15). $BaTiO_3$ has much higher sintering temperatures than Sb-substituted KNN without BT. We assume that BT engages the sintering process later which is the reason of developing

of the shoulder. It also makes broader the ceramics sintering interval which is significant for KNN-based materials.

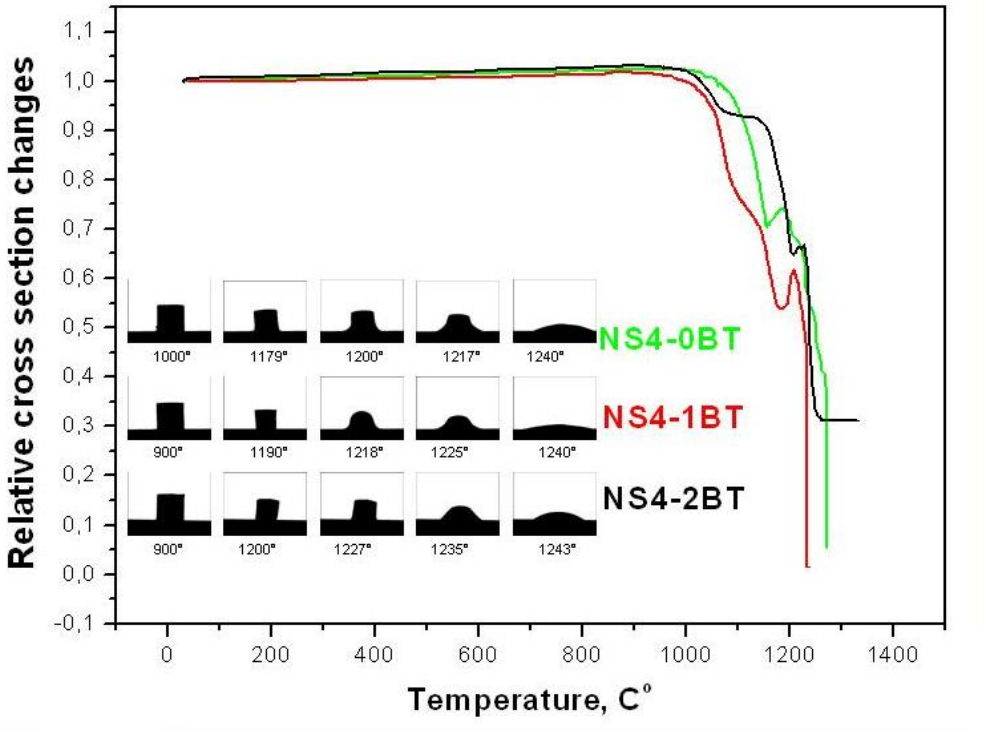


Fig. 15. HTM analysis

Material constants: the Young′s modulus *E*, the shear modulus *G* and the Poisson′s ratio *v* were measured by an ultrasonic method. The highest velocity of the longitudinal waves was observed for sample KNNS4-1.5BT (V_L = 4720.5 m/s). The transverse wave velocity for this sample is higher then for other samples (V_T = 2699.6 m/s). The values of both Young′s modulus E and the shear modulus G are relatively high taking into account modest densities of the samples (E = 64.96 GPa, G = 25.86 GPa).

The addition of 1 mol% of BT increases the value of dielectric permittivity ε and decreases T_C. In the same time BT decreases dielectric losses. Phase transition becomes more diffuse while increasing x. Table 1 summarizes the results of dielectric properties.

Table 1

Density and dielectric properties for different compositions

Composition	***Density g/cm^3***	***Dielectric permittivity ε (room T)***	***Dielectric loss tanδ (room T)***	***T_{max} (C°)***	***γ***
S4-1BT	4.51	1400	0.043	305	1.34
S4-2BT	4.44	1240	0.652	270	1.45
S4-4BT	4.34	1380	0.727	178	1.73
S7-1BT	4.31	1800	0.100	245	1.39
S7-2BT	4.34	940	0.490	211	1.57
S7-4BT	4.43	1400	0.549	129	1.76

CONCLUSIONS

1. KNN based ceramic powders were obtained by solid state synthesis from oxides and carbonates.
2. Synthesis kinetic analysis has been performed. Reactions start at 400°C when the carbonates start to decompose, however, perovskite phase was obtained at 650°C with the holding time of 30 min.
3. KNN ceramic samples were produced and modified a) using different oxides as sintering aids; b) substituting B-site cation Nb^{5+} for Sb^{5+}; c) making solid solutions from substituted KNN with barium titanate BT.
4. The addition of 1 wt% of different oxides (Li_2O, ZnO, MnO_2, V_2O_5) reduces sintering temperature of KNN (from 1170°C to ~1100°-1120°C). Dense ceramic samples were obtained resulting into the growth of dielectric permittivity at the same time phase transition temperature remained the same (T_C=410°C).
5. After the partial B-site Nb^{5+} substitution for Sb^{5+} dielectric permittivity values increased while phase transitions temperature T_C is shifted to lower temperatures with increasing antimony content.
6. The ferroelectric properties of KNN based ceramics are stable in the wide temperature range. The remnant polarization P_r remains constant up to temperature of ~300°C then rapidly drops to zero.
7. The samples in composition range from x = 0.02 to 0.07 exhibited excellent piezoelectric properties: piezoelectric coefficient of d_{33} = 92 ÷ 192pC/N, electromechanical planar and thickness coupling coefficients of k_p = 0.32 ÷ 0.46 and k_t = 0.34 ÷ 0.48, respectively.
8. Solid solutions with BT have high dielectric permittivity ε at room temperature reaching 1240 ÷1800.

THESIS

1. Manganese can change the value in the KNN composition while sintering at high temperature. The defects and oxygen vacancies appearing are pinning domain walls testified by triple increase in mechanical quality factor Q_m. Manganese ions and oxygen vacancies create defect dipoles along the polarization axes amplifying the appearance of the local fields. This results into increase of dielectric, ferroelectric and piezoelectric properties.
2. Because of higher Pauling electronegativity Sb^{5+} ion forms a stronger covalent bond with oxygen anion than Nb^{5+}. By substituting Nb^{5+} for Sb^{5+} in $(K_{0.5}Na_{0.5})NbO_3$ and optimizing the technological parameters dense ceramic samples are obtained with higher dielectric permittivity ε_{max}, P_r and piezoelectric coefficient d_{33} values than found in literature.
3. New solid solutions with chemical formula $(1\text{-}x)(K_{0.5}Na_{0.5})Nb_{1-y}Sb_yO_3\text{-}xBaTiO_3$ (x=0.01; 0.015; 0.02; 0.04; y=0.04; 0.07) were made by conventional solid state sintering. Dense ceramic samples were obtained with high dielectric permittivity ε at room temperature. Presented with a patent.

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