Na₂Co₃ and Er₂O₃ Modified Lead Free Knn Piezoelectric Ceramic Obtained by Hot Pressing

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Abstract

Analysis of dense KNN ceramic obtained by hot pressing (HP) method at 1100°C are presented in this paper. The synthesis of KNN-based piezoelectrics meets following challenges: low density of material, uncontrolled K/Na ratio, multiphase composition and formation of different KNN structures. Classical hot pressing approach results in contamination by carbon originating from graphite moulds. The proposed h-BN protection layer between green sample and graphite mould prevented carbon reaction with powder. Additionally, h-BN presence may decrease formation of oxygen vacancies which allows to maintain semiconductor features of KNN structure. Remaining issues were addressed with the addition of excess Na and Er_2O_3 doping. The results showed that excess Na addition allowed to compensate evaporation of sodium during the synthesis and sintering. Er_2O_3 was added as sintering aid to limit abnormal grain growth. The modification of amount of Na and Er_2O_3 addition resulted in high purity KNN samples with tetragonal structure and apparent density higher than 97%. Finally, piezoelectric features of prepared dense samples were measured and presented.

1. Introduction

Ferroelectric materials are widely used as a piezoelectric ceramics, serving as sensors, motors, energy harvesters or parts of advance measurement devices among many others applications [1–4]. Their prominent piezo- and ferroelectric properties derived from the perovskite crystal structure are still utilized in new emerging fields of engineering, leading to new solutions and possibilities. However, those materials are also a current challenge for many researchers as their most commonly used element, lead, is proven to be dangerous to natural environment [5]. Therefore Pb-based piezoelectrics, such as $\text{PbZr}_x\text{Ti}_{(1-x)}\text{O}_3$ (PZT), $\text{Pb}_{1-x}\text{La}_x(\text{Zr}_{1-y}\text{Ti}_y)_{1-x/4}\text{O}_3$ (PLZT) or $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ although dominating at this moment, are aimed to be replaced with lead-free solutions.

There are many possible replacements considered by various scientific associations, specialized in functional ceramics:

1. Barium-titanate ceramic (BT) systems – those materials are among the very first developed lead-free piezoelectrics, that could potentially replace lead-based systems. They are advantageous mainly due to their easier appliance in industry, as they are very stable at room temperatures and are said to possess low dielectric loss. However, because of their limitations, new, optimized solutions utilizing barium are required, to compensate for low Curie temperature (T_c) and relatively small deformation coefficients (d_{33}), including: $\text{BaZr}_x\text{Ti}_{(1-x)}\text{O}_3$ - $\text{Ba}_x\text{Ca}_{(1-x)}\text{TiO}_3$ (BZT-BCT) and BaTiO_3 – BiFeO_3 (BF-BT) materials[6].
2. Bismuth layer-structured (BLSF) systems – those materials are generally based on the layered structure in which Bi-based layer occurs interchangeably with other elements oxides, such as K, Na, Ca, Ti, Nb, Bi. Their target applications include aerospace and nuclear industries, because of relatively high T_c . However their d_{33} coefficients are magnitude smaller than any other popular lead-

free piezoelectrics, regardless of method or dopants and therefore are decisively limiting their usage. Recent materials include $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BLSF), $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BLaT) and $\text{Bi}_{3.1}\text{Nd}_{0.9}\text{Ti}_3\text{O}_{12}$ (BNdT) layers, obtained by solid-state reactions [7].

3. Bismuth-sodium-titanate (BNT) systems – known for its relatively high piezoelectric polarization (P_r), those materials are based on following lead-free structure: $(\text{BiNa}_{0.88}\text{K}_{0.08}\text{Li}_{0.04})_{0.5}\text{Ti}_{0.995}\text{Mn}_{0.015}\text{O}_3$, which can be doped towards better sinterability by addition of other Bi-based ferroelectric such as $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ (BKT), as shown by Taghaddos et al.[8]. It also occurs in $((\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3)_{1-x}(\text{BaTiO}_3)_x$ (NBBT) system and could be very promising in variants with relatively high T_c and decreased dielectric loss, that often occurs[6].
4. Piezoelectric nanomaterials are considered due to their improved sinterability, high density of polycrystals and homogeneous microstructure. For example, properly sintered and processed n-ZnO is a prominent material within this category, with promising piezoelectric and functional features in general[9]. However, nanomaterial piezoelectrics applications are limited due to difficulties in spontaneous polarization alignment by applied electric field, which is crucial for piezoelectric properties[10].
5. Organic lead-free piezoelectrics – most prominent organic lead-free piezoelectric is Polyvinylidene fluoride (PVDF), which is developed mainly for energy harvesters as it possesses high conversion efficiency due to high coupling factor and easy manufacturing for such applications[11].
6. Sodium-potassium-niobate (KNN) systems – widely recognized, due to their versatile properties and generally prominent piezoelectric performance, derived from phase composition in case of 1:1:2 stoichiometric ratio ($\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$). Both P_r and T_c parameters are relatively high when compared to other piezoelectrics with large coupling factor to follow but main issue is proper synthesis and densification of polycrystals.

Ferroelectric materials, such as described above (except for PVDF), used as piezoelectrics have the crystalline structure of perovskite, which is commonly known as a structure similar to BaTiO_3 . It's specific positioning combined with proper compositions stands for many functional properties, including ferromagnetism or thermoelectricity. KNN materials consist of two phases: ferroelectric potassium niobate ($\text{K}_{1-x}\text{NbO}_3$) and antiferroelectric sodium niobate (Na_xNbO_3) which differ in transition but crystallize in the almost the same perovskite structure. The basic transition dependency of K/Na ratio results in possibility of obtaining functional perovskite structure with outstanding piezoelectric properties, given that mentioned stoichiometric proportions are preserved, because of morphotropic phase boundary (MPB) that it creates in the tetragonal - rhombohedral transition[12].

The main challenge of implementing KNN lead-free piezoelectric materials is the proper synthesis. While material can be relatively simply obtained by high temperature processing of uniaxially pressed samples, it's expected properties could be decreased due to the small density of samples. Amongst possible reasons of this situation, most possible are: evaporation of sodium, alkali vacancies created during sintering and lack of liquid phase in the microstructure of pure KNN[13–15].

In face of those problems, a proper solutions were pursued by many researching teams experimenting with both environment and composition. Shimizu et al. showed that pure alkali niobate ferroelectric and dielectric properties can be significantly improved using only low oxygen partial pressure processes[16]. Those studies were inspired by articles on KNN ceramics sintered under low oxygen partial pressure[17], which showed suppressing of vacancies formation in used process, both proving that reducing oxygen interaction with those materials is desired on every step of technological process. Studies concerning sintering in H_2 and Ar atmospheres respectively showed, that similar improvements of properties can be obtained by changing the environment[18]. Moreover, similar studies shown that different atmospheres can affect dopants behavior[15].

Yang et al. while obtaining transparent lead-free ferroelectric ceramics, went one step further, employing sealed sintering process and comparing it to sintering in air. Although used KNN materials were differing due to the doping of $Ca(Sc_{0.5}Nb_{0.5})O_3$ (CSN), it was shown, that sealed ceramic samples were denser than their unsealed counterparts. The overall improvement of electrical properties was also noted[19]. Additionally, more advanced, alternative processes were involved including, for example, spark plasma sintering (SPS), and while reducing volatility of obtained samples and offering overall better performance, they are still more technologically demanding[20].

In addition to process changes, various dopants were reported to improve KNN synthesis processes and were considered as a possible solution to this problem. The simplest idea of doping with alkaline earth metals was proposed by Malič et al. but was generally lacking significant, if any, positive effect on densification of samples[21]. Previously mentioned articles on low oxygen partial pressure in KNN processes involved addition of LiF, to furthermore improve the densification by usage of Lithium[17] with similar solution proposed by Saito et al. but additionally involving alkaline earth metals, resulting in advanced systems, such as: $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.10}Sb_{0.04})O_3$ in which lithium subtracts either potassium or sodium atoms, while alkaline earth metals are in niobium positions[22] and resulting in additional improvements of piezoelectric charge coefficients (d_{33}) with relatively high conversion ratios. Due to those findings, later iterations of solution were to follow[23, 24], showing similar increase of the same coefficients. Important process distinction was provided in studies, in which KNN was firstly annealed, and then milled with different doping oxides. Such process improved densities of sample with relatively small additions of dopants [25].

Another chance of improvement came with involvement of rare earth metals oxides. Those materials were expected to improve samples, based on previous research, performed to improve PZT material systems. Those studies showed that Yb^{3+} substitution in perovskite structure could reduce coupling factor of materials, but greatly improve its other piezoelectric properties [26]. In case of KNN materials, coupling factor is considered high, and therefore such dopant was considered in our previous studies prior to this paper [27] alongside Er_2O_3 which was investigated by Zhao et al. and shown that it could result in creation of highly desired liquid phase during sintering [28].

It is worth mentioning that reversed approach, in which KNN serves as dopant was also considered, to obtain ternary systems with MPB compositions based on BNT materials. However, as of this day, this solution did not had a big impact on the lead-free piezoelectrics, as it is merely opening opportunities on further improving of BNT-based systems, which are already considered inferior due to the complicity of processes, when compared to KNN materials [10, 29, 30].

The aim of this study was to obtain a dense KNN-based material, using industrially applicable process, using the listed findings and preliminary studies performed prior to this paper, which would be tested in stress sensor. To achieve this task, dopants of rare-earth elements, namely Er_2O_3 , were employed. Additionally, the process was improved by numerous factors. Usage of hot pressing in h-BN form would expectedly improve the density of material in comparison to commonly used techniques, additionally texturing the microstructure of samples, which is desirable in case of piezoelectrics [31]. Moreover, the decrease of sintering temperature may reduce the overall alkali evaporation, allowing to manufacture stoichiometric 0.5 KNN material when combined with additional sodium in initial powder mixture.

2. Materials And Methods

To synthesize KNN ($\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$), the following commercial reactants were used: Nb_2O_5 powder of CHANGSHA EASCHEM CO. Ltd (China), and K_2CO_3 , Na_2CO_3 carbonate powders produced by Lach-Ner (Czech Republic). In the first step of KNN synthesis, the carbonate reactants were annealed at 150 °C for 24 hours in order to remove residual water. Then K_2CO_3 , Na_2CO_3 and Nb_2O_5 powders with 5 wt. % and 10 wt. % excess of sodium carbonate were mixed in ceramic mortar. The extra amount of Na_2CO_3 was added to compensate sodium evaporation process during synthesis. Thus prepared powders were dry homogenized in ball mill using 10,0 mm diameter silicon nitride milling media for 24 hours. The reactants mixture were placed into alumina crucible with lid and heated up in air atmosphere to temperature of 950 °C, in which they were annealed for 2 hours. The crushed and grinded KNN reaction bed was analyzed by X-ray diffraction method. The qualitative and quantitative XRD/Rietveld phase composition analysis was made using PANalitycal diffractometer, equipped with Cu anode supported by X-pert HighScore software for quantitative analysis of the samples.

The obtained KNN powders were then mixed with 1 wt.% and 2 wt. % of Er_2O_3 used as sintering activator produced by Ganzhou HongDe New Technology Development Ltd. having 0.65 m^2/g specific surface area, 99.5% purity and 8.69 g/cm^3 helium density. Due to company information average grain size of powder was estimated to $d_{50} = 1.4 \mu\text{m}$. The powder batches were dry homogenized in rotary mill using 5,0 mm Si_3N_4 grinding media for 24 hours. Then mixtures were screened by 0.5 mm mesh sieve and placed in 25.0 mm diameter hot pressing graphite moulds. To prevent excessive contamination of green samples by carbon, the graphite parts of the mould were covered by graphite foil and next it was sprayed by hexagonal boron nitride (h-BN) powder, as schematically showed in Fig. 1. The additional positive effect of the h-BN usage is stimulation of KNN densification process [32].

Prepared powders were hot pressed (HP) under 25 MPa of pressure for 2 hours at 1100 °C in argon flow with heating/cooling rate of 10 °C/min and 8°C/min. respectively. The applied pressure accelerated sintering, polycrystal texturing and reduced evaporation of sodium. The obtained dense KNN sinters had diameter of 25.0 mm and thickness of 5.0 mm. Additionally, polycrystalline KNN reference sample without sintering activator and Na₂CO₃ extra addition was manufactured in larger size of 75 mm diameter in order to check: density, microstructure formation, phase composition and texturing of thus prepared sinters. Cooling rate of HP process for those materials was very low of 3 °C/min. to reduce internal stresses caused by phase transformation and polycrystal formation during heat treatment.

The water contact with sample is harmful due to hygroscopic feature of KNN, with this reason all samples handling was carefully proceeded in dry and no moisture conditions. The density measurements of KNN polycrystals was conducted in helium pycnometer AccuPyc II 1340 produced by Micrometrics Company. An average density value was calculated based on 30 measurement points. For microscopic observation purposes the sintered samples were included in resin and then polished by Struers polisher TegraPol-21 equipped with TegraForce-5 grinding discs under set load of 35 N and rotation speed of 300 rpm. The process was carried out in isopropanol environment. Surface preparation was done by diamond discs followed by final polishing with 0.25 µm colloidal silica, which enabled mechanical etching of polycrystal to reveal microstructure details. Microstructural examinations were performed by scanning electron microscope NOVA NANO SEM 200 equipped with EDAX EDS analyzer. In order to confirm influence of HP applied pressure on material texturing, the reference sample was taken for ultrasonic measurement of longitudinal wave propagation in parallel and perpendicular directions to pressing axis. The ultrasonic examination was made by UZP-1 (INCO - VERITAS) apparatus equipped with 1 MHz heads. In order to measure piezoelectric properties, selected materials were subjected to poling process in custom built apparatus for 1 hour in

2 kV/mm in silicon oil environment. Electric signal generated by those samples was measured by automatic apparatus for cyclic compression with force 150 N and 200 N for 2000 cycles. The analysis of these signals was performed by DasyLab software.

3. Result and discussion for KNN polycrystal without sintering aids

The most researches reports are focused on KNN samples manufacturing having limited sizes e.g. 20 mm – 25 mm of diameter. This paper shows preparation much larger – 75 mm diameter polycrystalline KNN characterized by high density, which can be potentially used in production of piezoelectric generators. To prevent material cracking, cooling process was very low rate 3°C/min. The X-ray diffraction patterns obtained for KNN reference sample revealed presence of two major phases: K₄Nb₁₀O₃₀ in quantity of 83.5 wt. % and NaNbO₃ in quantity of 11.5 wt. %, while planned stoichiometric K_xNa_{1-x}NbO₃ existed as minor phase in quantity of approximately 5.0 wt. %. That may be caused by deficiency of sodium in the system, due to evaporation occurred at both synthesis and hot-pressing steps. Figure 2a and 2b shows image size and XRD pattern of prepared polycrystal, respectively.

Relative density of manufactured KNN material was estimated to 98.4% based on theoretical one 4.55 g/cm³ measured by helium method on polycrystalline grinded sample. The material was microstructurally and chemically examined by SEM and EDS techniques. The morphological observations of KNN fracture are presented in Fig. 3. It showed presence of coarser approx. 50 µm size grains and of ten times smaller approximately 5 µm grains in close proximity to each other. Thus SEM observation of hot pressed KNN reference sinter presented in Fig. 3, confirmed existence of bi-modal grain size distribution. Those larger grains are textured which can suggested favored formation under uniaxial load applied by hot pressing.

Table 1
An average elemental composition measured by EDS for KNN taken from Fig. 3.

Point	Chemical composition									
	Nb		Na		K		O		B	
	[wt. %]	[at. %]	[wt. %]	[at. %]	[wt. %]	[at. %]	[wt. %]	[at. %]	[wt. %]	[at. %]
1	50.6	14.3	2.1	2.3	9.7	6.5	18.0	29.4	19.6	47.5
2	68.1	30.2	2.0	3.5	11.4	12.0	13.5	34.8	5.1	19.5

EDS analysis results collected in Table 1 indicated similar content of Na and K in coarse and fine grains. However, these data showed higher amount of boron, which is the reason of extensive grain growth leaded to sizes of 50 microns as shown in Fig. 3(a)(b). Smaller particles exhibited 4 times lower concentration of B. The atomic ratio of Na/K for all observed grains is about 0.3 which further confirmed Na depletion due to its evaporation from material during the thermal processing. The nucleation rate of fine grains was previously confirmed to be enhanced by excess amount of Na₂CO₃ introduced to the system [27]. The observed texturization leads to improved piezoelectric properties of material. In order to check texturization level, ultrasonic measurement was applied to reference sample.

The ultrasonic analysis of longitudinal wave propagation examined in perpendicular directions of the sinter confirms texturing influence of HP process, what is visible in the wave propagation anisotropy reaching 25%. The measurement directions and wave velocity are collected in Table 2. Investigations carried out on the large samples showed that it is possible to manufacture KNN polycrystals with large oriented grains but the size of sample has to be lower due to internal stresses and material possible cracking. As mentioned before for larger samples lower cooling rate is required to prevent material destruction. That is why it was decided do reduce diameter of samples to 25 mm. These samples were additionally modified by erbium oxide sintering aid.

Table 2
Results of ultrasonic measurements

Measurement direction	Wave velocity	Standard deviation (SD)	z/x wave velocity relation	Young modulus	Standard deviation (SD)	z/x Young modulus relation
	[m/s]	[m/s]		[GPa]	[GPa]	
x	4243	12	1.33	80	0.1	1.78
z	5660	181		145	0.2	

4. Results And Discussion For Erbium Oxide Doped Knn

In order to obtain materials containing $K_{0.5}Na_{0.5}NbO_3$, Er_2O_3 sintering activator was added because of its positive effect in formation of both orthorhombic and tetragonal structures which enhance piezoelectric properties of obtained sinters [27]. The hot pressed KNN samples containing 5 wt. % or 10 wt. % excess amount of Na_2CO_3 and addition of 1 wt. % or 2 wt. % of Er_2O_3 were subjected to density measurements. The helium density was above 4.43 g/cm^3 , which confirmed that all of samples have more than 97% of relative density which is enough for piezoelectric generator manufacturing. This suggests, that material may be strengthened because of low concentration of microstructure defects. Complete density data is presented in Table 3 and it indicates that increased amounts of Er and Na in the material might lead to a slight decrease in material density.

Table 3
Density of hot pressed KNN with Er_2O_3 addition

Sample ID	Sodium carbonate excess [wt. %]	Er_2O_3 Sintering Aid [wt. %]	Helium density [g/cm^3]	Standard deviation (SD) [g/cm^3]	Relative density [%]
N5E1	5	1	4.4989	0.0069	98.8
N5E2	5	2	4.4492	0.0043	97.5
N10E1	10	1	4.4527	0.0082	97.8
N10E2	10	2	4.4327	0.0235	97.1

The quantitative and qualitative XRD analysis presented in Table 4 showed that both: excess amount of Na_2CO_3 and Er_2O_3 sintering aid allowed to obtain almost pure KNN material in the tetragonal crystallographic structure. The increase of Er_2O_3 from 1wt. % to 2 wt. % content and excess of Na_2CO_3 addition from 5 wt% to 10wt. % led to orthorhombic structure of $K_{0.5}Na_{0.5}NbO_3$ and small quantities of

KNN doped by erbium. However, the same mixture with both additions of 10 wt. % of Na_2CO_3 and 2% Er_2O_3 resulted in shift to undesired monoclinic structure.

Table 4
Phase composition and crystallographic structure of obtained KNN polycrystals

Sample ID	Na_2CO_3 excess [wt. %]	Er_2O_3 amount [wt. %]	Major KNN crystallographic structure	Phase composition [wt. %]			
				KNN	Er doped KNN	KNbO_3	Process graphite
N5E1	5	1	Tetragonal	100	-	-	-
N5E2	5	2	Orthorhombic	97.5	2.5	-	-
N10E1	10	1	Orthorhombic	93.6	1.2	-	5.2
N10E2	10	2	Monoclinic	90.5	1.8	7.3	-

The obtained KNN sinters were taken for morphological SEM - EDS investigation. The material fracture appearance with addition of 1 wt.% and 2 wt.% of Er_2O_3 is presented in Fig. 4 and Fig. 5 respectively. SEM – EDS area element concentration analysis is presented in Table 5. All of the images confirmed high density of samples. The N5E1 polycrystal is characterized by some elongated and geometrically oriented grains as marked in Fig. 4 (a,b). The other parts exhibited fine grains with size of about 1.0 μm . Higher addition of erbium oxide reduced number of elongated grains towards more uniform particles having well defined sharp edges as shown in Fig. 4 (c,d). However in both samples N5E1 and N5E2 there are same fine grains existed between those larger particles. Based on the result of our previous work [27] it can be concluded that those fine grains of tetragonal $\text{K}_x\text{Na}_{1-x}\text{NbO}_3$ were formed due to higher sodium content which was enhanced by excess amount of Na_2CO_3 introduced to the system [27].

Table 5
Sodium and potassium chemical analysis of obtained KNN sinters

Sample ID	Na ₂ CO ₃ excess [wt. %]	Er ₂ O ₃ amount [wt. %]	Figure	Analysis point	Na [at %]	K [at %]	Average Na/K ratio
N5E1	5	1	4b	1	14.43	5.56	0.90
				2	12.09	19.06	
				3	3.44	15.79	
				4	2.91	21.23	
N5E2	5	2	4d	1	11.12	12.47	0.94 ± 0.04
				2	9.45	9.78	
				3	9.69	10.22	
N10E1	10	1	5b	1	11.59	10.37	1.08 ± 0.09
				2	10.58	10.85	
				3	11.06	9.67	
N10E2	10	2	5d	1	11.38	10.04	1.06 ± 0.13
				2	11.00	9.65	
				3	8.54	9.45	

Higher content of Na₂CO₃ excess from 5 wt. % to 10 wt. % resulted in much more uniform fractures appearance as shown in Fig. 5. Those grains have regular shapes with size of approx. 10 µm - orthorhombic K_xNa_{1-x}NbO₃. There is no significant changes in microstructure details by increased addition of Er₂O₃ from 1 wt% to 2 wt% as can be noticed in Fig. 5(b) and 5(d). However, fine grains are still existed between larger one as minor phase.

The elemental concentration analysis was conducted in selected areas for each material. For samples shown in Fig. 4 and Fig. 5, the average Na/K atomic ratio was close to 1 as seen in Table 4. It agreed with XRD phase composition analysis presented in Table 4.

Figure 6 presents two typical SEM images of microstructure and domain patterns for a dense KNN polycrystals obtained. Majority of visible grains have an average size of about 10–12 µm, but there are also fine particles in size of less than 2 µm. Those coarse grains show simple parallel domain stripes that run through the whole grain in the etching plane. It is well known that the dielectric and piezoelectric properties of a ferroelectric ceramics could be resolved into intrinsic and extrinsic contributions. The intrinsic one is attributed to the relative ion shift that preserves the ferroelectric crystal structure, whereas

the extrinsic one is related to the movement of domain walls [33]. Thus domain structure may have significant influences on the piezoelectric and dielectric properties of a ferroelectric ceramics. It was expected that obtained dense polycrystals poses high piezoelectric feature. As evidence of sodium evaporation during processing, some spherical pores remained in the microstructure as shown in Fig. 6.

Microstructure of sample N5E1 should have the best piezoelectric properties from all prepared samples thanks to its tetragonal crystallographic structure as shown in Table 4. Presented results were subjected to signal filtering in order to minimize effect of interference from electrical network. It was confirmed by measurements of electric signal generated by obtained samples shown in Fig. 7. Results shows that N5E1 material generated highest voltage under compression for both 150 N and 200 N load. The second best was N10E1 which signals were slightly lower. Both samples with 10 wt. % excess of Na_2CO_3 exhibited much lower values. This proves that small overabundance of Na in materials can be beneficial for piezoelectric properties but must be carefully optimized.

5. Summary

1. Modification of reagents stoichiometry together with addition of Er_2O_3 sintering aid showed promising results when combined with hot pressing manufacturing method.
2. The excess amount of Na_2CO_3 during sintering have beneficial effect in keeping desired tetragonal $\text{K}_x\text{Na}_{1-x}\text{NbO}_3$ stoichiometry.
3. Addition of Na_2CO_3 excess and Er_2O_3 sintering aid assured high density of samples having large geometrical dimensions which can be applied for industrial use.
4. Material with 5 wt. % excess of Na_2CO_3 and 1 wt. % of Er_2O_3 which possess domain microstructure generated highest electric signal of all samples for both 150 N and 200 N load cyclic compression, combination of 10 wt. % Na_2CO_3 and 2 wt. % Er_2O_3 additions led to extensive formation of monoclinic KNN with low piezoelectric properties.
5. Hexagonal boron nitride partially blocked material contamination by carbon which originated from graphite mould.
6. The hot pressing process applied in KNN manufacturing stimulated texturing of microstructure, which was confirmed by ultrasonic measurements indicating anisotropy of properties. In case of reference KNN sample, addition of hexagonal boron nitride lead to sintering intensification and extensive grain growth up to 50 μm .

Declarations

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Figures

Figure 1

The hot-press graphite mould protected by graphite foil and sprayed h-BN layer.

Figure 2

(a) Appearance of KNN reference hot-pressed sample (b) XRD patterns showing its phase composition.

Figure 3

Fracture appearance of KNN reference sample (a) bimodal feature of grain size distribution (b) microstructure details of coarse grains.

Figure 4

KNN polycrystal with addition of 5 wt. % of Na₂CO₃ excess; (a,b) fracture appearance of sample with 1 wt. % of Er₂O₃; and (c,d) with 2 wt. % of Er₂O₃.

Figure 5

KNN polycrystal with addition of 10 wt. % of Na_2CO_3 excess; 4(a,b) fracture appearance of sample with 1 wt. % of Er_2O_3 ; (c,d) with 2 wt. % of Er_2O_3 .

Figure 6

Microstructure domain appearance of N5E1 sample with 5% of Na_2CO_3 and 1% of Er_2O_3 addition revealed on polished and mechanically etched surface; (a) bimodal character of grain distribution (b) details of spherical porosity caused by sodium evaporation

Cyclic compression ($F = 150\text{ N}$)

Cyclic compression ($F = 200\text{ N}$)

Figure 7

Signal generated by obtained samples under cyclic compression of 150 N and 200 N.

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