MATERIAL STRUCTURE CONTROL AS ONE OF THE PERSPECTIVE APPROACHES TO OPTIMIZE PHYSICAL AND TECHNICAL CHARACTERISTICS OF PIEZOELECTRIC CERAMIC MATERIALS

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Abstract. The paper reviews the state of art in the development of new lead-free piezoelectric ceramic materials. Piezoceramic materials are used in a wide field of applications, most of them are based on lead titanate-zirconate. However, modern human health and environmental requirements make necessary the use of alternative lead-free materials. Advantages and drawbacks of perspective piezoceramics are discussed, possible approaches to increase their piezoelectric properties (texturing and template grain growth method) are considered.

1. INTRODUCTION

The development of new effective piezoelectric ceramic materials providing interconversion between mechanic and electric energies gives rise to the significant increase in a number of engineering projects for a wide range of applications. New types of generators, sensors, actuators (piezodrives), convertors, and complex systems are manufactured using these materials. In spite of active investigations both in theory and technology of piezoelectric ceramic materials performed in the second half of XX century, piezoceramics is still considered as one of the perspective materials nowadays; it is due to the fact that its complete range of potential characteristics and applications is not still realized.

At present, most of piezoceramic materials produced are based on lead titanate-zirconate (LTZ) possessing rather high piezoelectrical characteristics. However, its application contradicts The European Parliament directives from July 01, 2006. These directives regulating the wastes of electric and electronic equipment prohibit the use of some hazardous compounds in such equipment as well as the recycling of such materials. The use of alternative materials is prescribed in order to decrease the dangerous effects of hazardous compounds on human health and the environment [1].

The above prohibition includes a number of types of household and industrial equipment, including medical instruments, control and monitoring devices, as well as spare parts for previously manufactured products. For all these items, the maximal content of lead, mercury, hexavalent chromium, and polybrominated bifinyl is stated as 0.1 wt.%, while for cadmium it is 0.01 wt.%. It should be mentioned that the exceptions are considered for some equipment due to the absence of proper safe materials;

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Table 1. BaTiO$_3$ based piezoceramic materials.

Base	Name	Manufacturer	Characteristics					
			$\varepsilon_{33}^{T}/\varepsilon_0$	tgδ,	$|d_{31}|$, pC/N	d_{33}, pC/N	Q_M	Tc,°C
BaTiO$_3$	TBK-3	ELPA Research Institute, Russia	1000-14000	≤0.02	43.3	83.3	≤300	≥95
	300	Chanxel Ind. Inc., USA	1250	0.008	58	145	450	>115
	600	Chanxel Ind. Inc., USA	625	0.03	33	82	1200	>140
	1300	Chanxel Ind. Inc., USA	1350	0.08	56	145	600	>115
	EC-21 EDO	Ceramics, USA	1070	0.005	49	117	1400	130
	EC-31 EDO	Ceramics, USA	1170	0.007	59	152	400	115
	EC-55 EDO	Ceramics, USA	1220	0.005	58	150	550	115
	PC3	Morgan Matross Ltd., USA	1100	0.006	42	127	500	130

at the moment, piezoceramic materials with high lead content are still legal. However, the list of exceptions is revised each 4 years (at least); obviously, as soon as the alternative for LTZ piezoceramics will be found, the situation will change dramatically.

For this reason, the task of the development of lead-free piezoceramic materials with high physical and technical properties is very important. The present review discusses the state of art in the field of perspective lead-free piezoceramic materials.

2. MATERIALS BASED ON BARIUM TITANATE (BaTiO$_3$)

At present, more that 500 ferroelectric compounds based on barium titanate are known. BaTiO$_3$ has a number of modifications. The cubic one is stable at temperatures over 120 °C, the tetragonal modification is stable in the temperature range from 5 to 120 °C, rhombic modification is stable in the temperature range from -90 to 5 °C, while rhombohedrical phase is stable at lower temperatures. In its paraelectric state, barium titanate possesses cubic structure: perovskit-like ABO$_3$ [2].

A number of piezoceramic materials based on BaTiO$_3$ were developed. However, typical drawbacks of these materials are: (1) restricted temperature range of exploitation, (2) the decrease in piezoelectric properties (depolarization) in case when a strong electric field directed against the polarization field

is applied (low coercive field), (3) fatigue effect (depolarization in strong electrical and mechanical fields), (4) high synthesis and annealing temperatures. The addition of some dopants is considered as a possible pathway to overcome these drawbacks. Some materials based on barium titanate solid solutions modified by dopants were developed. Table 1 presents a list of widely used piezoceramic materials.

3. MATERIALS BASED ON BISMUTH-SODIUM TITANATE (BNT)

Bismuth-sodium titanate Bi$_{0.5}$(Na$_{0.5}$K$_{0.5}$)TiO$_3$, discovered by Smolenski et al., could be considered as an alternative to LTZ piezoceramics. BNT is characterized by perovskite-like rhombohedral structure. BNT based piezoceramics demonstrate high piezoelectrical properties, rather high residual polarization, P_r=38 μC/cm^2, and high value of Curie temperature T_C=320 °C. In should be mentioned that BNT-based ceramics has one additional phase transition below T_C, the temperature of this transition (depolarization temperature T_d) is usually below 200 °C. Depolarization occurring during this phase transition results in some insignificant decrease in piezoelectric properties. In addition to this disadvantage, a number of drawbacks typical to BNT-based ceramics should be mentioned. High values of coercive field and high conductivity hinders proper polarization, thus, the complete realization of piezo-

Table 2. Basic characteristics reported for BNT-based piezoceramics.

Composition	Density(kg/m³)	d_{33}(pC/N)	tgδ	K	T_C(°C)
$Bi_{0.5}(Na_{0.5}K_{0.5})TiO_3$	5.32	64	1.752	302	310
$Bi_{0.5}(Na_{0.5}K_{0.5})TiO_3$	-	57	0.011	240	350
$Bi_{0.5}(Na_{0.5}K_{0.5})TiO_3$	-	61	4.11	467	-

Table 3. Characteristics of piezoceramic materials based on BNT-BKT solid solutions.

Composition	ε_r	tgδ	d_{33}pC/N	k_p (%)	k_t (%)	T_C (°C)
$0.85BNT-0.15(Bi_{0.5}Li_{0.5})TiO_3$			110	18		
$0.99BNT-0.005Ba(Cu_{0.5}W_{0.5})O_3$	328	1.5	80	18.1		308
$0.98BNT-0.02NaNO_3$	624	5.9	88	17.9		
$0.82BNT-0.18BKT$	893	3.7	144	29		
$0.77BNT-0.23BKT+1\%$îîëBi$_2O_3$	1261	5.1	207	29.8		330
$0.88BNT-0.12BKT+0.2\%$ââñ CeO$_2$			132	27.8		
$0.82BNT-0.16BKT-0.02KN$	1437	4.0	215	35		
$0.79BNT-0.18BKT-0.03BiFeO_3$			170	36.6		
$0.805BNT-0.18BKT-0.015BiCrO_3$			168			
$0.7BNT-0.2BKT-0.1(Bi_{0.5}Li_{0.5})TiO_3$	1190	4.47	231	36.8	50.5	
$0.7BNT-0.2BKT-0.1(Bi_{0.5}Li_{0.5})TiO_3+Na^+$			171	30.0		334
$0.9(0.79BNT-0.21BKT)-0.1(Bi_{0.5}Ag_{0.5})TiO_3$	1110	5.2	160	30	38	

electric properties is not possible. High temperatures (over 1200 °C) necessary to manufacture dense BNT-based ceramics complicates production technology and makes it less cost-effective. So, conventional BNT materials still could not successfully replace LTZ piezoceramics.

A number of studies were carried out recently aiming at studying of the dopant effect. Rather small amounts of such doping compounds as Ba, Pb, Ca, Sr, Ce, Se, NaNbO$_3$, etc. (cationic modificators) were introduced into BNT-ceramics, it was shown that this modification gives an opportunity to overcome the above discussed disadvantages [4,5]. So, one can consider that, in spite of some problems, BNT-based piezoceramics is the perspective lead-free material possessing well-balanced piezoelectric properties. Table 2 lists the basic properties of such piezoceramics (data for a number of species synthesized by different groups via conventional approach, see [6] for details).

3.1. Materials based on bismuth-sodium titanate (BNT) and bismuth-potassium titanate (BKT)

Binary BNT-BKT system should be especially mentioned among BNT-based systems since it was thoroughly studied due to the fact that it possess high piezoelectric properties near the rhombohedral-tetragonal morphotropic phase boundary (MPB). The study of this ceramics began in 1978 in China, Wang with coauthors investigated piezoelectric and ferroelectric characteristics of xBNT - $(1-x)$BKT $(0.73 \leq x \leq 1.0)$ and yBNT - $(1-y)$BT $(0.81 \leq y \leq 0.99)$ compositions [7,8]. It was found that MPB between tetragonal and rhombohedral phases is located at x=0.81 and y=0.94, respectively. In addition, the doping effect of $(Bi_{0.5}Li_{0.5})TiO_3$, $Ba(Cu_{0.5}W_{0.5})O_3$, NaNbO$_3$, and Er$_2O_3$ was investigated.

Recent works of Yang et al. demonstrated MPB formation for BNT-BKT solid solutions in the range of BKT content between 0.16 and 0.2 [9]. Piezoelectric modulus for this MPB was 144 pC/N, k_p value was 0.29, and dielectric permittivity was 893. Table 3 summarizes the results obtained for a number of BNT-BKT solid solutions.

3.2. Materials based on bismuth-sodium titanate (BNT), bismuth-potassium titanate (BKT) and barium titanate

Along with above discussed BNT and BKT, barium titanate is also a well-known lead-free piezoelectric material. Ternary BNT-BKT-BT system, possessing high Curie temperature and good piezoelectrical

Table 4. Bi(Na, K)TiO$_3$-BaTiO$_3$ system properties.

Composition	d_{33}, pC/N
Na$_{0.5}$Bi$_{0.5}$TiO$_3$-K$_{0.5}$Bi$_{0.5}$TiO$_3$-BaTiO$_3$ (1-3x)NBT - 2xKBT – xBT	150
(1-5x)NBT - 4xKBT – xBT	145

properties near MPB, is an object of especial interest. Sakai et al. [10] investigated piezoelectrical characteristics of BNT-BT and BNT-BKT materials. Lee et al. demonstrated that the formation of ternary BNT-BKT-BT system occurring at BKT and BT introduction into BNT results in high piezoelectric properties. Ternary (1-3δ)BNT - 2xBKT - xBT system at constant BKT and BT content was studied [11,12], basic results of these investigations are presented in Table 4.

4. MATERIALS BASED ON POTASSIUM-SODIUM TITANATE (KNN)

Increased interest in KNN-based piezoceramics is due to a number of its unique characteristics: high value of Curie temperature (>400 °C), and a combination of a low value of the dielectric constant with comparatively high values of piezomodules and electromechanical coupling coefficients. In addition, (K,Na)NbO$_3$ solid solutions are of high scientific interest since they are complex multiphase systems with a lot of phase transitions including morphotropic phase transitions. This allows the development of new effective lead-free piezoceramics with controlled properties [13].

KNN ceramics synthesized by the conventional approach without any dopants demonstrates Curie temperature of 420 °C and high ferroelectric char-

acteristics (P_r=33 μC/cm^2), however, piezoelectric properties are rather low (d_{33}=80 pC/N). It should be mentioned that KNN ceramics synthesis is complicated due to instability of KNN phase and essential alkali oxides volatility at high temperatures, thus, the production of materials with high density is difficult [14].

Table 5 summarizes recent results on KNN-based piezoceramics properties. Zen et al. studied the possibility of the introduction of some additional amount of alkali metals in the material in order to compensate the losses due to alkali oxide evaporation during the ceramics high temperature synthesis. As a result of such addition, the increase in the piezoelectric properties was shown for 0.058LiNbO$_3$-0.942Na$_{0.535}$K$_{0.480}$NbO$_3$ ceramics: T_C=490 °C, d_{33}=314 pC/N, and k_p=41.2% were reported. Additional dopants, e.g. K$_4$CuNb$_8$O$_{23}$, K$_{5.4}$Cu$_{1.3}$Ta$_{10}$O$_{29}$, and CuO, were used to decrease synthesis temperature; as was discussed above, such a decrease could increase the material density. The authors of [15,16] stated the density increase up to >96% as a result of the above approach. Sintering conditions could be also improved by ZnO, CdO, Sc$_2$O$_3$, and SnO$_2$ addition, while CeO$_2$, Y$_2$O$_3$, and WO$_3$ complicate material manufacturing [17].

5. MATERIALS BASED ON LAYERED BISMUTH-CONTAINING STRUCTURES

Layered bismuth-containing ferroelectrics can be generally described as Bi$_2$A$_{n-1}$B$_n$O$_{3n+3}$, they consist of n perovskite layers with bismuth oxide layers (Bi$_2$O$_2$)$^{2+}$ between them. In the above formula, A is mono-, bi- or tri-valent ions or their mixture; B is the combination of cations forming an octahedron, n can be 1,2,3,4 or a combination of adjacent values. At

Table 5. KNN-based piezoceramics properties.

Composition	K	d_{33}, pC/N	k_p (%)	k_t (%)	T_C (°C)
K$_{0.48}$Na$_{0.52}$NbO$_3$	~600	160		47	~410
K$_{0.5}$Na$_{0.5}$NbO$_3$ (SPS)	606	148	38.9		395
K$_{0.5}$Na$_{0.5}$NbO$_3$+1 mol.% CuO		82	39	47	421
K$_{0.5}$Na$_{0.5}$NbO$_3$+0.75 mol.% K$_{5.4}$Cu$_{1.3}$Ta$_{10}$O$_{29}$	360	90	41	46	383
K$_{0.5}$Na$_{0.5}$NbO$_3$+1 wt.% K$_4$CuNb$_8$O$_{23}$		100	40		
0.92Na$_{0.535}$K$_{0.48}$NbO$_3$-0.08LiNbO$_3$		280	48.3		475
0.92Na$_{0.535}$K$_{0.48}$NbO$_3$-0.08LiNbO$_3$ (textured)	324				
(K$_{0.55}$Na$_{0.45}$)$_{0.965}$Li$_{0.035}$Nb$_{0.8}$Ta$_{0.2}$O$_3$	1290	262	53		325
0.948K$_{0.48}$Na$_{0.52}$NbO$_3$-0.052LiSbO$_3$	1372	286	51		385
K$_{0.38}$Na$_{0.58}$Li$_{0.04}$Nb$_{0.91}$Ta$_{0.05}$Sb$_{0.04}$O$_3$	1327	306	48	49	337

Table 6. Dopants effect on BLSF ceramics properties.

Composition	ε_r	tgε %	d_{33}, pKl/N	T_C (ºC)	PmC/cm^2
$CaBi_2NbTiO_9$	97	1.5	5	936	
$Ca_{0.9}(K, Ce)_{0.05}Bi_2NbTiO_9$	118	0.18	16	868	
$Bi_4Ti_3O_{12}$	176	0.95	4	672	
$Bi_4Ti_3O_{12}$+4%ìîë Nb_2O_5	224	0.23	18	630	
$Bi_4Ti_{2.98}V_{0.02}O_{12.01}$	170		20	674	6
$Bi_4Ti_{2.975}W_{0.025}O_{12.025}$+0.2%âåñ Cr_2O_3	178	2	22	658	
$Bi_{3.84}Nd_{0.16}Ti_{2.98}V_{0.02}O_{12.01}$		1.8		648	13.5

present, five types of such materials are known: materials based on Bi_3TiNO_9, $Bi_4Ti_3NO_{12}$, $MBi_2Nb_2O_9$, $MBi_4Ti_4O_{15}$, and bismuth-containing layered ferroelectrics (BLSF). M here can be Sr^{2+}, Ca^{2+}, Ba^{2+} $(Bi_{0.5}Na_{0.5})^{2+}$, $(Bi_{0.5}K_{0.5})^{2+}$, while N can be Nb^{5+} and Ta^{5+}.

BLSF are characterized by low dielectric constant, low values of the dielectric loss tangent, high Curie temperature, and high level of the electromechanical coupling factor anisotropy. Hence, BLSF can be considered as promising candidate for high temperature applications. Since BLSF ceramics demonstrates high stability of piezoelectrical modulus d_{33} at elevated temperatures [18], it is suitable for the exploitation at temperatures over 600 °C.

However, piezoelectric activity of BLSF ceramics is rather low due to the existence of a two-dimensional orientational prohibition of the allowed values of spontaneous polarization and due to relatively low resistance. A lot of studies were carried out in order to improve the physical properties of BLSF ceramics and its high-temperature stability; usually, some substitute was introduced in A and B sublattices of the perovskite layers, while substitution in bismuth oxide levels was used very rarely. Such rare ions as La^{3+}, Nd^{3+}, Sm^{3+} were used as substitutes in A sublattice, Nb^{5+}, V^{5+}, and W^{6+} were used for B sublattice. Table 6 analyzes the effect of these dopants [19] on BLSF ceramics properties.

As seen from the table, the introduction of dopants into A sublattice is more effective for the improvement of piezoelectric modulus d_{33} and for the increase in the residual polarization than dopants introduction into B sublattice.

The synthesis of piezoactive phases is one of the important tasks at new lead-free piezomaterials development since manufacturing of high quality complex oxide ceramics is a complicated task both in science and in industry. In addition to oxygen, the composition of such materials includes two or more elements, their ratio and synthesis conditions give an opportunity to produce different stable compounds from the same initial reagents. Hence, the directed synthesis of monophase product with the strictly defined stoichiometry requires specific technological methods. Dopants introduction here usually complicates the process since it can be accompanied by secondary phase formation; moreover, it affects the functional properties of the final product [20]. At present, solid state chemistry considers a number of approaches for complex oxide ceramics manufacturing: high temperature solid phase synthesis [21], mechanochemical synthesis [22], complex-formation method [23], sol-gel synthesis [24], hydrothermal method [25], synthesis in a supercritical aqueous fluid [26].

As was mentioned above, lead-free materials are usually characterized by low piezoelectric characteristics. Ceramic texturing (the grain arrangement in order to obtain the required structure) is known as an approach providing the increase in these properties. Texturing gives an opportunity for ceramic polycrystallites to arrange their analogues of monocrystals in such a way that forms the preferable domain location increasing the piezoelectric characteristics of the material.

Two texture types should be mentioned - morphological and orientational. The first one (morphological) is connected with the outer form of the grain – habit, while the second one (orientational) – with the ordered orientation of grains or grain crystal lattices relative to each other.

Starting from 1960-th and up to the first half of 1980-th, texturing has been widely studied in bismuth-based layered ferroelectrics (bismuth titanate) and in potassium-tungsten bronzes. The basic texturing technology was the directed pressuring with simultaneous heating, i.e. hot pressing. The possibility of such texturing in these materials is possible due to the existence of crystallographic anisotropy in layered materials: one of the lattice parameters value is some times higher than the typi-

cal values of other parameters. This significant difference in lattice parameters causes the existence of lamellar structures in the synthesized materials. Such structures can be arranged by mechanical approaches, the meaning result here can be obtained relatively quickly and without additional labor. Generally, texturing of polycrctalline materials can be performed using mechanical stresses: hot pressing, rolling, extrusion, as a result of temperature gradient or magnetic field application. However, these methods considers the morphologic texture formation [27], their practical application is limited. Texturing provides the significant increase in piezoelectric properties; sometimes, it is more effective than chemical modifications (doping, material composition, etc.). At that, the increase in piezoelectric characteristics is quite important for the compositions near MPB.

Regretfully, most modern piezoelectric materials possess perovskite-like structure, i.e. there is no significant anisotropy in their elementary cells. That was the main reason for the decline in interest in texturing technique in 1990th. However, the studies were again intensified in the end of 1990th, due to the following reasons. First, it was the requirement to develop lead-free piezoceramics with high piezoelectric properties. Second, a new texturing approach, the template grain growth method, providing texture formation in the materials with perovskite-like structures was developed.

As was discussed above, perovskite-like structures do not show significant anisotropy of the elementary cell. In other words, these materials do not contain crystallites that can be mechanically arranged in order to form textured structure. The aim of any template method is to provide the presence of the growth centers for the grains of ceramics forming crystallites with required habit. Being applied to the task of new piezoceramics development, the main aim of the template method can be stated as the intentional increase of one of the crystallographic axes in each grain.

Nowadays, there exist a number of template grain growth approaches: template grain growth, multitemplate grain growth, and reactive grain growth.

5.1. Template grain growth (TTG)

Template grain growth (TTG) is widely used in textured ceramics production due to the convenience of its realization. The basics of the approach can be described as follows. At the preliminary step of the synthesis, small highly anisotropic crystals (plate, fibrous or needle) are prepared; they are called the template crystals. These crystals are added to the initial reagents mixture before baking sintering. At the next step, molding of this mixture is carried out by pressing, extrusion, slip casting or by magnetic, mechanic, or temperature field application. At that, the template crystals are oriented in the specific direction resulting in the required structure in the baked ceramics [28]. Usually, template crystals are the materials with the nature different from the manufactured functional material, they can be considered as some addition, the negative effect of such addition can prevail over the positive texturing effect. However, sometimes it is possible to remove these template crystals from the ceramic powder by dissolution.

Epitaxial growth of template grains occurs during texturing, these grains are located along the direction of the applied elastic deformations in the matrix powder. This fact is very important for the development of textured lead-free piezoceramics. As an example, let us consider the application of this approach for $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) ceramics texturing. The most suitable template for BNT-ceramics texturing are BNT grains. However, BNT is characterized by the cubic symmetry of the elementary cell that results in high symmetry of the crystallites forms at high temperatures. Thus, these uniform symmetric crystallites can not be arranged by casting method or by any other mechanical impact. Some highly anisotropic forms should be used for BNT structuring, so, it is necessary to produce BNT templates with highly anisotropic form. Topochemical conversion of $Bi_4Ti_3O_{12}$ (BIT) templates is carried out for this task since BIT templates possess high lattice parameters ratio. The use of molten salts method gives the possibility to produce the required qualitative composition with an isotropic form. BNT templates synthesized via such topochemical reaction are longitudinally arranged in the matrix base due to shear stresses during the slip casting [29]. Non-annealed ceramic films composed of the arranged grains are croped in order to fit the required dimensions and piled up to required thickness. At the next step, annealing is carried out in order to remove binder. Note that monocrystal BNT templates can transform into polycrystals in case when binder removal annealing results in low density material. In turn, such polycrystal BNT templates cause low texturing level in the ceramics with oriented grains resulting in low piezoelectric response. For this reason, high density of the ceramics before high tem-

perature baking is necessary to obtain high texturing level.

To avoid these problems (to eliminate cavities and empty space), ceramics after the binder removal are subjected to cold isostatic pressing. The next synthesis step is the high temperature baking resulting in the epitaxial growth of $[001]_{pc}/[012]_{Rh}$ (ps: pseudocubuc, Rh: rhombohedral) oriented surfaces of the template grains [30].

5.2. Reactive template grain growth (RTGG)

RTGG is a version of the template grain growth, the difference is in the texture forming mechanism and in the driving force of the process. In this method, oriented crystallites play a role of crystallization centers and determine the crystallographic orientation in the textured ceramics. The driving force of the epitaxial RTGG on the template grains is the free energy of formation of the required phase, it can be increased by the decrease in the energetic barrier of the grain formation on the template surface. This case significantly differs from the above discussed template grain growth since the epitaxial matrix growth on the template grains is caused by the difference in the free energies of the matrix material powder particles and higher values of this energy typical for template grains [31].

It should be mentioned that technical realization of both technological processes (TGG and RTGG) is quite similar, the idea is in the introduction of highly anisotropic template grains into the matrix powder.

5.3. Multitemplate or heterotemplate grain growth (MGG)

The other version of template grain growth is MGG approach. Two or more compounds are used here as the templates determining the directed grain growth that forms the final material structure. MGG is used when proper homogeneous reactive templates are unavailable. Similar to usual homogeneous templates, heterotemplates are asymmetric particles with the structure different from the perovskite matrix structure. The increased grain growth rate is typical for MGG process due to the presence of heterogeneous particles. Another typical feature of the process is the change in the matrix particle shape in the presence of the template particles. In particular, the change in the particle form from equilibrium to the plate one occurs due to the energy decrease on the phase boundary caused

by the (001) plane formation with the lower surface energy. Heterotemplate particles determine the growth direction for (001) plane and, in turn, the direction of texture formation <001> [32].

6. TEMPLATES ARRANGEMENT

Templates arrangement providing their required orientation is the complicated technological task, a number of modern approached will be discussed below.

6.1. Film casting

The main advantage of film casting is the possibility to form large, thin, and flat surfaces. The process of film casting in case of textured ceramics formation is similar to those in case of conventional film casting: a slip composed of matrix powder with templates is poured into a reservoir. Then the slip is poured onto the substrate located on a moving belt and flattened by a blade [31].

The template arrangement during the film casting occurs due to shear stress and due to templates sliding relative each other. Up to some time, most of textured ceramics was produced using slip casting from the ceramic powder with the template grains introduced into this powder. However, this approach has certain disadvantages. First, the effective template grain orientation is possible when the gap between the blade edge and the substrate is minimal. In this case, drying and baking results in a very thin film. Hence, the direction with the best ceramics properties (especially in case of needle templates) is parallel to slip casting direction and lies in the plane of minimal thickness. Thus, the plane with the required properties in the ceramics synthesized by this approach is very thin; this fact significantly restricts the application of such ceramics.

6.2. Extrusion

The above drawback of film casting gives rise for extrusion application since it provides relatively thick ribbons and fibers with crystallographic structure. It was shown that shear stresses here are more effective for a long time period and at larger surface areas as compared to film casting. However, since the extruded slip is more viscous than the casting one, the process realization needs higher pressures. A new approach suggested recently considers the application of water-based slip with lower viscosity, the specific feature of this process is a rapid congealing of the green units. The rate of the process is provided by an ion-exchange reaction between
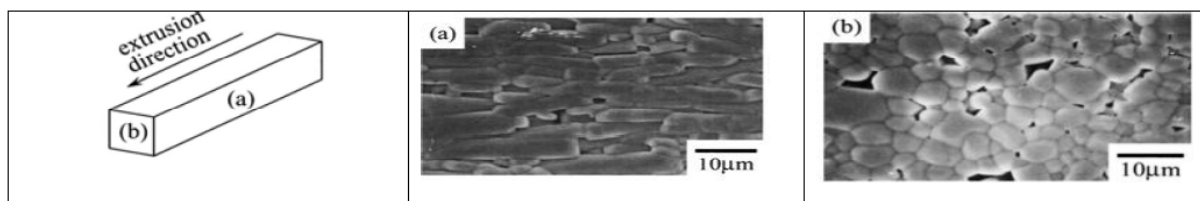
Fig. 1. Microstructure of textured $K_2Sr_4Nb_{10}O_{30}$ ceramics: a direction – along the extrusion direction, b – perpendicular to the extrusion direction.

Table 7. The comparison of textured and untextured piezoceramics properties.

Piezoceramics composition	Property	Sample with random crystallites orientation	Sample with ordered crystallites orientation
$Na_{0.5}Bi_{4.5}Ti_4O_{15}$	k_{33} (%)	14.7	32.5
	d_{33} (pC/N)	15.6	33.7
	g_{33} (10^{-3} Wm/N)	12.6	25.6
$Na_{0.475}Ca_{0.05}Bi_{4.475}Ti_4O_{12}$	k_{33} (%)	13.3	49
	d_{33} (pC/N)	13	44
	g_{33} (10^{-3} Wm/N)	9.1	33.5
$Sr_{0.3}Bi_{3.7}Ti_{2.7}Ta_{0.3}O_{12}$	k_{33} (%)	12.8	37.1
	d_{33} (pC/N)	14.6	45.3
$Sr_{0.53}Ba_{0.47}Nb_2O_6$	d_{33} (pC/N)	30	83
$94.5Bi_{0.5}Na_{0.5}TiO_9–5.5BaTiO_3$	d_{33} (pC/N)	110	200
$0.675Pb(Mg_{0.25}Nb_{0.75})O_3$	k_{33} (%)	376	525
$– 0.325PbTiO_3$	d_{33} (pC/N)	0.673	0.755

the salt cation and the alkali metal ions containing in a binder copolymer. As a result, the decrease in the slip viscosity gives an opportunity to vary the geometry of die openings and to arrange the template particles without high pressure application [31], see an example in Fig. 1.

6.3. Directed pressing

Monodirected pressing is the additional operation which is used to produce dense textured structures. This approach considers the preliminary preparation of raw units containing asymmetric particles oriented in a certain direction, film casting or extrusion can be used for this task [31]. It should be mentioned that monodirected pressing can be used without such preliminary preparation for some composition. First of all, we are talking about materials with the Aurivillius structure characterized by the presence of crystallites with highly anisotropic form due to high anisotropy of the elementary cell. Such materials provides an opportunity to achieve some texturing level, however, usually, it is less than 60% [33].

7. SUMMARY

The analysis of the results obtained by different authors shown in Table 7 demonstrates the advantages of textured piezoceramics. Thus, such ceramics can be considered as a perspective material to replace lead-containing piezoceramics.

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