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Modified potassium-sodium niobate based lead-free piezoceramics

L.G.Gusakova, V.M.Ishchuk, N.G.Kisel, D.V.Kuzenko, N.A.Spiridonov

Science and Engineering Center "Reaktivelektron", National Academy of Sciences of Ukraine, 17-A Bakinskih komissarov St. Donetsk, Ukraine

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Influence of doping elements Li, Mg, Sr, Mn on synthesis conditions, and sinterability, and electrophysical properties of lead-free $(K_{0.5}Na_{0.5})NbO_3$ based piezoelectric ceramics is studied. The effects revealed are correlated well with the adopted concepts of soft and hard doping elements for ferroelectric substances. On the base of the it is obtained A lead free piezoelectric ceramics with the Curie point T_c = 410°C has been obtained based on manganese modified $(K_{0.5}Na_{0.5})NbO_3$ solid solution. The piezoelectric constant d_{33} of the said ceramics exceeds the well-known analogs and the piezoelectric sensitivity g_{33} exceeds almost 4 times that of the best lead zirconate-titanate based ceramics.

Исследовано влияние легирующих элементов Li, Mg, Sr, Mn на условия синтеза, спекаемость и электрофизические свойства бессвинцовой пьезокерамики на основе твердого раствора $(K_{0.5}Na_{0.5})NbO_3$. Полученные эффекты хорошо согласуются с развитыми представлениями о сегнетомягких и сегнетожестких добавках. На основе модифицированного марганцем твердого раствора ниобата калия-натрия $(K_{0.5}Na_{0.5})NbO_3$ получена бессвинцовая пьезокерамика с высокой температурой Кюри (410°C), пьезомодулем d_{33}, превосходящим значения известных аналогов, и пьезочувствительностью g_{33}, почти в 4 раза превосходящей лучшие образцы керамики на основе цирконата-титаната свинца.

1. Introduction

Piezoelectric ceramics is among materials of high importance for different areas of technical applications such as electronics, telephony, hydroacoustics, atomic engineering, automatics, the space and aviation engineering, medicine, etc. Among existing piezoelectric ceramic materials, the most widely used is that based on the lead zirconate-titanate (PZT) solid solutions due to its unique properties and high technological effectiveness. Its only disadvantage is the lead presence in composition.

The system of sodium-potassium niobate ($KNbO_3$–$NaNbO_3$) solid solutions is considered as one of the most prospective lead-free systems [1–3]. $(K,Na)NbO_3$ based piezoceramics shows numerous valuable properties concerning first of all to high Curie point (~ 400°C) and a combination of low dielectric constant value and relatively high piezoelectric modules.

Unlike PZT solid solutions, the $KNbO_3$–$NaNbO_3$ system is less comprehensively studied. It is less practically feasible because of the natural trend to formation of secondary phases [4], very narrow (about 50°C) sintering temperature interval and high volatility of potassium oxide resulting in poor reproducibility of the ceramics properties and level thereof. Therefore, now investigations are carried out directed to elimination of said disadvantages. One way to control the ceramics properties is modification of its chemical composition. The purpose of this work is to study the influence of one-, bivalent doping elements as well as

elements with variable valence on the $(K_{0.5}Na_{0.5})NbO_3$ solid solution (KNN) synthesis process, sinterability of the synthesized powders, and electrophysical properties of piezoceramics obtained.

2. Experimental

To prepare the unmodified and modified sodium-potassium niobate ($(K_{0.5}Na_{0.5})NbO_3$, the solid state synthesis technique was used. The oxides and carbonates of corresponding metals were used as starting materials. The synthesis was carried out at 850–1100°C during 4–10 h, depending on the material composition. After synthesis, the specific surface of powders was determined by the BET method [5]. The effective diameter of powder particles was determined from the formula

$$d_{cp} = \frac{6}{\rho \cdot S_{ud}}$$

where ρ is the powder density (g/m^3), S_{ud}, the specific surface (m^2/g).

The 1 mm thick ceramic samples of 10 mm diameter were sintered in the temperature range of 1050–1150°C (depending on doping elements) during 1–2 h at the heating rate 100°C/h. The quality of ceramic elements was controlled by determining the geometrical density, as well as the apparent density and porosity by hydrostatic weighing. Li, Mg, Sr, Mn were used as doping elements in the amount of 1 at. %.

The X-ray analysis was carried out using a DRON-3 diffractometer in filtered CuKα radiation. Microscopic researches were carried out using transmission electron microscopy (TEM) (JEM-200microscope) and scanning electronic microscopy (SEM) (JSM-6490LV microscope, JEOL, Japan). The dielectric constant and dielectric losses in weak AC electric fields were measured at 1 kHz frequency. The piezoelectric parameters were measured by the resonance method according to [6]. The piezoelectric module d_{33} was determined by the static (Berlincourt) method according to the same standard [6].

3. Results and discussion

The XRD analysis shows the presence of Na_2CO_3, K_2CO_3, and Nb_2O_5 (initial components) in the reaction mixtures sintered at temperatures lower than 450°C. At the further sintering temperature elevation, the individual compounds $KNbO_3$ and $NaNbO_3$ appear. At 600°C (Fig. 1), a reaction mixture

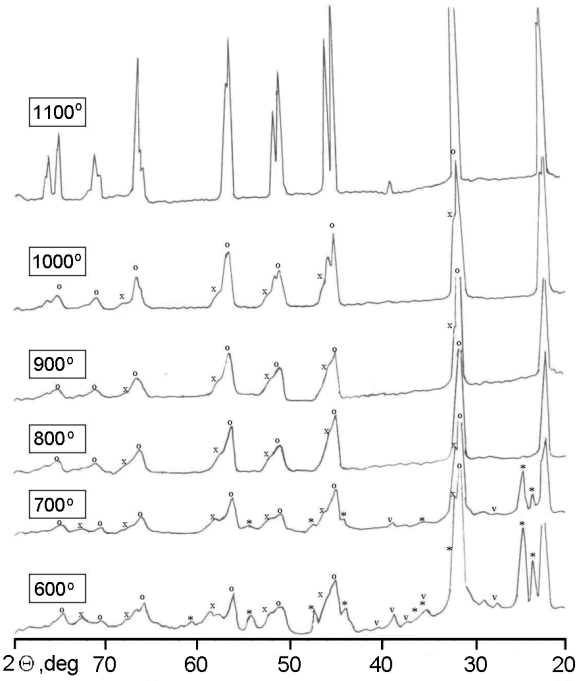

Fig. 1. X-ray patterns of KNN powders synthesized at different temperatures. Sintering temperatures are marked near the patterns. The sintering time is 1 h. Notations: *o*, $KNbO_3$ based sold solution; *x*, $NaNbO_3$ based solid solution; *v*, Na_2CO_3.

contains considerable amounts of the solid solution with pseudo-cubic perovskite $KNbO_3$ based structure with the lattice period $a = 4.00$ Å. Another $NaNbO_3$ based solid solution (with pseudo-cubic perovskite structure, too) with the lattice period $a = 3.92$ Å appears also. Significant amounts of Nb_2O_5 are still present as well as Na_2CO_3 (in smaller amounts). At 700°C, the fraction of perovskite components in the reaction mixture increases. In the temperature interval 800–900°C, chemical interaction process between two solid solutions is continued. At 1000°C, the fraction of $KNbO_3$ based solid solution increases at the expense of $NaNbO_3$ based one. The cubic structure of crystal lattice turns to orthorhombic. The solid solution on the base of $NaNbO_3$ still remains, but its amount is rather small. At 1100°C, interaction between two solid solution systems becomes completed. The single-phase product of the $(Na_{0.5}K_{0.5})NbO_3$ composition with well expressed crystal structure and the orthorhombic lattice parameters $a = 5.651$ Å, $b = 5.680$ Å, $c = 3.948$ Å is obtained. Table 1 presents characteristics of obtained KNN powder annealed at two different tempera-

Table 1. Synthesis conditions and properties of KNN powders

Synthesis conditions		Method of measurement		
Temperature, °C	Time, *h*	BET		TEM
		S_{ud}, m^2/g	d_{cp}, μm	d_{cp}, μm
900	1	2.55	0.52	0.60
1100	1	1.86	0.70	0.80

tures. Electronic TEM images of the powder annealed at 1100°C are shown in Fig. 2.

As X-ray analysis has shown, during the synthesis of $(K_{0.5}Na_{0.5})NbO_3$ based solid solution modified with Li, Mg, Sr or Mn, the same sequence of solid state reactions is observed as in the case of unmodified solid solution. The powders synthesized at 1100°C are single-phase products with rhombic perovskite crystal structure. The density and microstructure of unmodified and modified potassium-sodium niobate ceramics sintered at 1100°C are presented in Table 2 and in Fig. 3, respectively.

The maximum ceramics density after sintering is attained in case of Sr and Mn doping, whereas, in contrast, Mg reduces density of sintered ceramics. As follows from Fig. 3, the ceramics grains show a morphology close to cubic and are arranged chaotically. The largest and well formed grains-crystallites are observed in the case of ceramics modified by Sr and Mn.

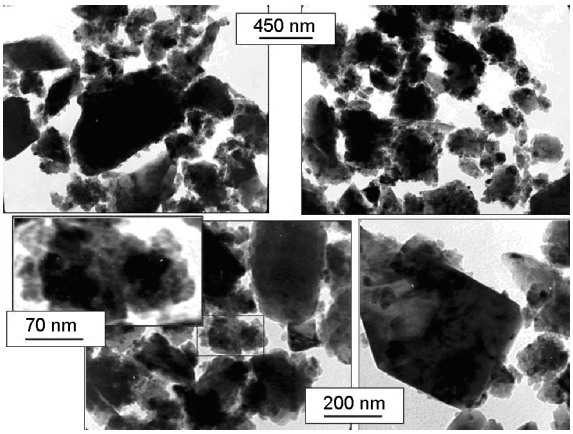

Fig. 2. TEM images of KNN powder synthesized at 1100°C.

The electrophysical characteristics of pure and modified $(K_{0.5}Na_{0.5})NbO_3$ based piezoelectric ceramics are presented in Table 3. It is seen that strontium is a typical soft ferroelectric doping element. It raises the dielectric constant ε, piezoelectric modules d_{31} and d_{33}, the electromechanical factor k_r,

Table 2. Density of KNN ceramics with different doping elements

Doping element	Li	Mg	Sr	Mn	Without doping elements
Density, g/cm^3	4.19	4.02	4.27	4.29	4.14
Relative density, %	92.9	89.1	94.7	95.1	91.8

Table 3. Electrophysical properties of $(K_{0.5}Na_{0.5})NbO_3$ based piezoelectric ceramics

Composition	$\varepsilon_{33}/\varepsilon_0$ (1 kHz)	tgδ, % (1 kHz)	d_{31}, pC/N	k_r	d_{33}, pC/N	g_{33}, $mV \cdot m \cdot N^{-1}$	$V_{sound.}$, m/s	T_c, °C	ρ, g/cm^3
Lead-free piezoelectric ceramics (results from this work)									
KNN	250	5.66	27	0.31	160	72	3890	405	4.14
KNN+Li	245	4.97	25	0.28	180	74	3472	425	4.19
KNN+Sr	293	4.85	33	0.36	220	84	3570	395	4.27
KNN+Mn	182	2.13	13	0.15	300	186	3488	410	4.29
Lead-contained piezoelectric ceramics (commercial)									
$CTCC_T$-9 soft FE	2000±200	≤2	≥200	≥0.65	≥600	35–50	2200	≥265	≥7.5
$CTCC_T$-3 hard FE	1400±140	≤0.55	≥140	≥0.55	270–350	35–50	2900	290	≥7.5

piezosensitivity g_{33}, as well as reduces the Curie point. Sr^{2+} cation has a higher valency than the ions being replaced (K^+, Na^+) and results in formation of vacancies in *A*-sublattice of perovskite crystal cell with general formula ABO_3, giving the general formula of substance as $(K_{0.5}Na_{0.5})_{1-2x}Sr_x\square_xNbO_3$.

The isovalent Li^+ also promotes soft ferroelectric properties of ceramics. But in this case, the said properties are less pronounced. Unlike Sr^{2+}, lithium cation has $2S^1$ electron structure. The entry of lithium ions into the crystal lattice causes formation of the solid solution with the chemical formula $(K_{0.5}Na_{0.5})_{1-x}Li_xNbO_3$.

Mn ions increase the piezoelectric module d_{33} as a soft ferroelectric additive, but reduce ε and tg δ as a hard ferroelectric one. At manganese oxidation degree +(3–4), the substitution of niobium ions with manganese ones is most probable (on the basis of crystal chemistry). The manganese dissolution process in a potassium-sodium niobate crystal lattice can be expressed by the formula $(K_{0.5}Na_{0.5})Nb_{1-x}Mn_{x-\alpha}^{4+}Mn_{\alpha}^{3+}O_{3-\delta}$. An interstitial position of Mn^{4+} is also posiible due to its small ionic radius.

The manganese doped $(K_{0.5}Na_{0.5})NbO_3$ ceramics shows the piezoelectric module d_{33} larger then for foreign analogs [7]. The piezoelectric sensitivity g_{33} exceeds almost 4 times that of both the best foreign lead-free analogs and the best piezoelectric materials on the base of PZT solid solutions [7]. The obtained results are of a high practical importance. The lead-free piezoelectric ceramics with high sensitivity in a combination with the high degree of ecological safety is especially prospective for application in the medical diagnostic techniques as well as in devices for nondestructive control, high-temperature sensors, high-frequency converters and other engineering devices.

4. Conclusions

The features of the potassium-sodium niobate formation process have been specified and temperature intervals of formation of individual solid solution components have been found. The influence of doping elements such as Li, Mg, Sr, and Mn on the sintering temperature and density of $(K_{0.5}Na_{0.5})NbO_3$ based ceramics has been established. The maximal densification of ceramics is attained at introduction of Sr and Mn as doping elements, whereas Mg, on the contrary, reduces the density of sintered ceramics. Said doping elements enter into perovskite crystal structure of potassium-

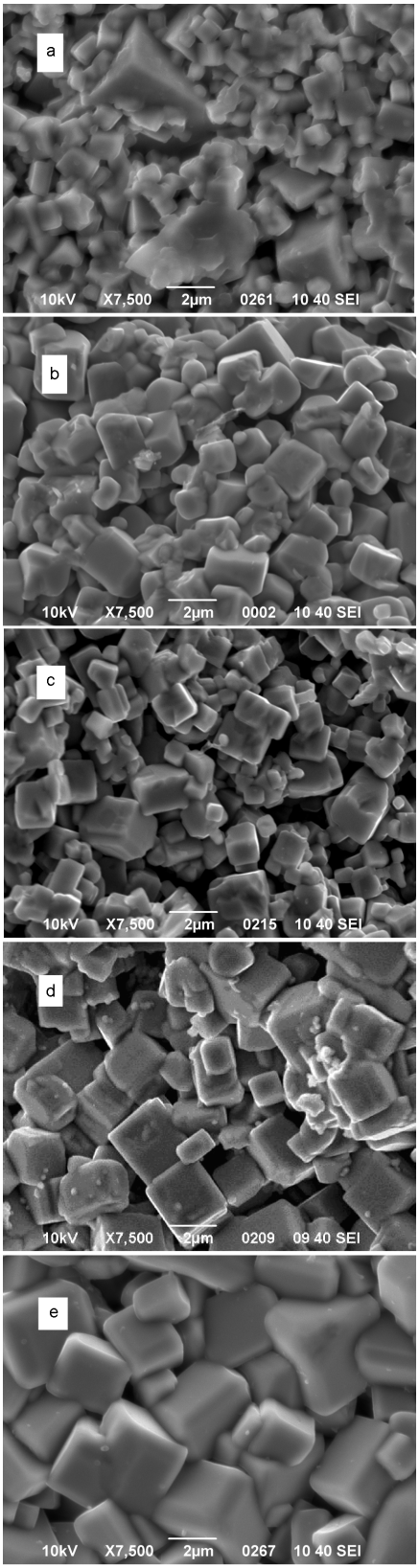

Fig. 3. Microstructure of KNN ceramics obtained by REM method: without doping elements (a), doped with – with Li (b), Mg (c), Sr (d), Mn (e).

sodium niobate. Li^+ and Sr^{2+} occupy most probably the lattice A-sites. Mn ions may occupy both A- and B-position, depending on oxidation degree, or interstitials. The potassium-sodium niobate ceramics with Sr^{2+} as doping element shows soft ferroelectric properties, and this ion reduces the Curie point. Li^+ ions, on the contrary, raise the ferroelectric hardness. Introduction of Mn ions promotes decreasing ε and tg δ, increasing piezoelectric modulus d_{33} and piezoelectric sensitivity g_{33}. The piezoelectric modulus d_{33} exceeds the values obtained in other researches, and piezoelectric sensitivity g_{33} is almost 4 times higher than that for the best samples of PZT-ceramics.

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Безсвинцева п'єзоелектрична кераміка на основі модифікованого ніобату калію-натрію

Л.Г.Гусакова, В.М.Іщук, М.Г.Кисіль, Д.В.Кузенко, М.А.Спірідонов

Досліджено вплив легуючих елементів Li, Mg, Sr, Mn на умови синтезу, спікливість та електрофізичні властивості безсвинцевої п'єзоелектричної кераміки на основі твердого розчину $(K_{0.5}Na_{0.5})NbO_3$. Отримані ефекти добре узгоджуються з сучасними уявленнями про сегнетожорсткі і сегнетом'які хімічні елементи. На базі модифікованого марганцем твердого розчину ніобату калію-натрію одержано безсвинцеву п'єзоелектричну кераміку з високою точкою Кюрі (410°C), п'єзоелектричним модулем d_{33}, що перевершує показники відомих аналогів, та п'єзоелектричною чутливістю g_{33}, що у чотири рази перевершує чутливість кращих зразків кераміки на основі цирконату-титанату свинцю.