

Electret properties of $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ with five-layered perovskite-like structure

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It is found that ceramic thermoelectret based on $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ with five-layered slab perovskite-like structure is characterized by high values of potential external electric field V_S which demonstrates enhanced stability in time both under normal and high humidity conditions. In particular, the initial value V_{S_0} of the surface potential for $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ polarized ceramics ($F_{pol.} = 15$ kV/cm, $T_{pol.} = 493$ K, $\tau_{pol.} = 2$ h) is equal to 480 V, the decreasing of V_S/V_{S_0} under normal conditions does not exceed 20 % for 316 days and under 100 % of humidity reaches 73 % for 7 days.

Keywords: ceramic thermoelectret, compounds with slab perovskite-like structure.

Установлено, що керамічний термоелектрет на основі $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ з п'ятишаровою слоистою перовскітоподібною структурою характеризується високими значеннями потенціала зовнішнього електричного поля V_S і має високу стабільність V_S во часі як в нормальних умовах, так і в умовах високої вологості оточуючої середовища. Так, величина початкового поверхневого потенціала V_{S_0} для заполяризованої ($F_{пол.} = 15$ кВ/см, $T_{пол.} = 493$ К, $\tau_{пол.} = 2$ ч) кераміки $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ складає 480 В, спад V_S/V_{S_0} в нормальних умовах не перевищує 20 % за 316 суток, а в умовах 100 % вологості становить 73 % за 7 суток.

Електретні властивості $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ з п'ятишаровою перовскітоподібною структурою. *Ю.О.Тітов, М.С.Слободяник, Н.М.Білявіна, О.І.Наконечна, В.В.Чумак, Р.М.Кузьмін.*

Встановлено, що керамічний термоелектрет на основі $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ із п'ятишаровою шаруватою перовскітоподібною структурою характеризується високими значеннями потенціалу зовнішнього електричного поля V_S та має високу стабільність V_S у часі як за нормальних умов, так і в умовах високої вологості оточуючого середовища. Зокрема, величина початкового поверхневого потенціалу V_{S_0} для заполяризованої ($F_{пол.} = 15$ кВ/см, $T_{пол.} = 493$ К, $\tau_{пол.} = 2$ год.) кераміки $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ складає 480 В, спад V_S/V_{S_0} у нормальних умовах не перевищує 20 % за 316 діб, а в умовах 100 % вологості становить 73 % за 7 діб.

1. Introduction

Structure features of slab perovskite-like structure (SPS) of AnBnO_{3n+2} compound and phases, including the presence of BO_6 distorted octahedra that are joined vertices as

infinite two-dimensional layers [1, 2], gave reason to expect a residual polarization phenomenon. Beyond that the emergence of the new, specific just to this structure, trap types on the boundaries between the perovskite-like slabs through their originat-

ing on interphase boundaries is possible [3]. This can significantly improve the electret properties of materials based on the slab compounds.

These assumptions have been confirmed by the study of electret properties of a number of phases based on the four-layered $\text{La}_4\text{Ti}_4\text{O}_{14}$. It should be noted that thermal and moisture capacity of the external field for these phases are essentially higher than those for industrial T-150-type electret materials based on CaTiO_3 [3–5]. Accordingly, there were reasons to expect the presence of electret properties for the rest of the AnBnO_{3n+2} family of compounds, in particular for the AnBnO_{3n+2} ($n = 5$) five-layered compounds.

2. Experimental

To study the origin of residual polarization and its features the five-layered $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$, in SPS of which the B-position is occupied by niobium and titanium ions (Fig. 1) [6], was chosen as an object of research. Dimensional differences in crystal radii of the six-coordinated Ti^{4+} and Nb^{5+} ions and different deformation degree of BO_6 octahedra (depending on their location in a perovskite-like slab) had to determine, in our opinion, the formation of a significant number of additional minimum of potential energy and to provide the high electret parameters of material obtained.

Since the electret characteristics of oxide ceramics also significantly affect its physical and mechanical parameters (density, number and size of pores), the initial stage of our research was connected with definition of the conditions to obtain the $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ high-quality ceramic samples. Synthesis of the $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ polycrystalline powder was carried out by co-precipitation method [7] since it allows to obtain the high-stoichiometric fine-grained material with a size of microcrystals one order less than those obtained by solid-phase ceramic technology. This fact essentially facilitates the further powder sintering.

The resulting batch of the hydroxycarbonates co-precipitated with a ratio of $\text{Ca}:\text{Nb}:\text{Ti} = 5:4:1$ was drained at 370 K and heat treated at 1170 K for 2 h. Then the powder was accurately grinded with further addition of plasticizer (polyvinyl alcohol). The disc samples (1 mm of thickness and diameter of 10 mm) were formed by a cold pressing ($1\text{--}1.5 \cdot 10^7$ Pa) from the batch obtained. Analysis of the temperature dependences of shrinkage and hydrostatic density

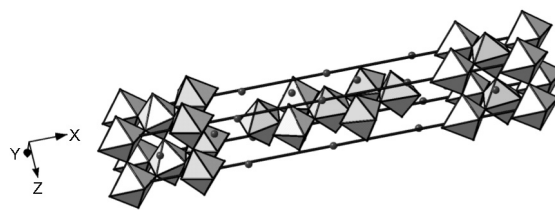


Fig. 1. Five-layered perovskite-like structure of $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ in a form of $(\text{Nb,Ti})\text{O}_6$ octahedra and Ca atoms (circles) [6].

of the $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ cold pressed discs (heat treated at different temperatures) has showed that the optimal sintering mode is the heat treatment at 1670 K for 2 h. For the $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ ceramic samples with SPS obtained in this way the density values comprise 96–98 % of the X-ray, and the value of open porosity do not exceed 0.7 %.

Creation of the residual polarization in the $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ ceramic samples with SPS was performed by thermopolarization using aluminum electrodes pressed and dielectric mylar spacers of 7.5 μ thickness ($\epsilon = 2.3\text{--}2.8$, $\rho > 10^{16}$ $\Omega\cdot\text{cm}$). The value of surface potential of the external field was measured by compensation method.

3. Results and discussion

As shown by the authors of [4, 5], the optimum temperature of termopolyarization of the four-layered $\text{La}_4\text{Ti}_4\text{O}_{14}$ -based thermoelectrets is 480–500 K, and the values of the initial surface potential V_{S0} essentially depend on the strength of polarizing field. Therefore, in this work the electret characteristics of $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ ceramics have been studied on the samples polarized at different strengths of polarizing field ($F_{pol.} = 10\text{--}25$ kV/cm, exposition for 2 h) and polarizing temperature of 493 K with further cooling of the ceramics in the field. As shown in Fig. 2, with the polarizing field strength increases the initial surface potential V_{S0} of the $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ ceramics increases, and dependence $V_{S0} = f(F_{pol.})$ is exponential. Thus, the highest V_{S0} value (525 V) is detected at polarization of the $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ ceramics in the field of 25 kV/cm but at the same time the sample polarized under these conditions is shown one of the biggest trends to V_S/V_{S0} decrease.

The highest stability in time of the relative surface potential of $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ ceramics is observed after its polarization at $F_{pol.} = 15$ kV/cm, $T_p = 493$ K, the exposure time $\tau_{pol.}$ is 2 h. For the $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ ce-

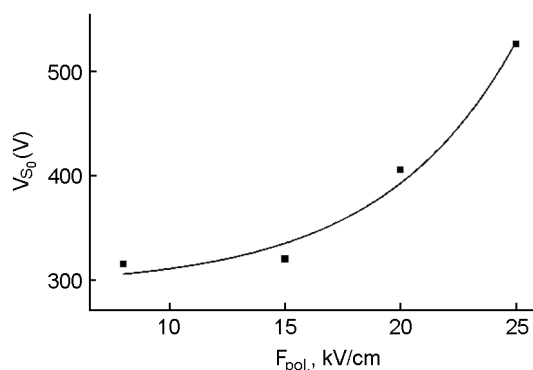


Fig. 2. Dependence of initial surface potential V_{S0} of external field of $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ ceramics on polarizing field strength ($F_{pol.}$).

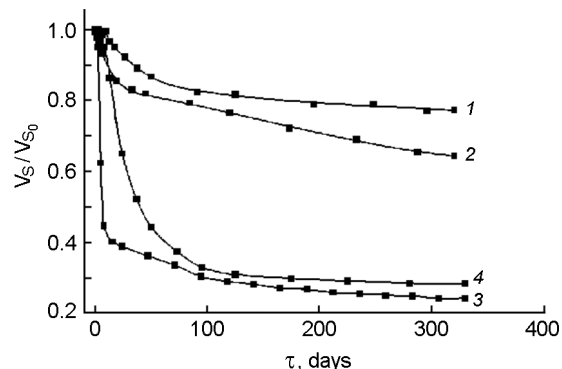


Fig. 3. Dependences of relative surface potential (V_S/V_{S0}) of $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ ceramics (1 — $F_{pol.} = 15$ kV/cm, 2 — $F_{pol.} = 20$ kV/cm, 3 — $F_{pol.} = 25$ kV/cm) and T-150 (on the base of CaTiO_3 [5]) (4 — $F_{pol.} = 10$ kV/cm) on time.

ramic samples polarized in these conditions the decrease of V_S/V_{S0} does not exceed 20 % for a quite long period (316 days), and V_{S0} value was equal to 480 V, while the V_S/V_{S0} parameter for the industrial T-150 electret exceeds 70 % for the same period (Fig. 3).

In addition to the potential value of external electric field and its stability over time, the stability of the surface potential of the external field to high humidity environment is one of the most important functional characteristics of the electret materials.

Stability of the surface potential of the $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ ceramic electret's electric field toward humidity action is controlled by the following algorithm: V_S of the ceramic sample is measured immediately before immersion into humid atmosphere, the sample is placed into a desiccator with a relative humidity of 100 %; V_S measurements are provided after the sample being kept in the humid atmosphere for 10 min, 1 day, etc. Decrease of the potential of the ceramic sample is determined by the formula:

$$\% \text{ decrease} = \frac{100 \cdot (V_S \text{ before test} - V_S \text{ after test})}{V_S \text{ before test}}$$

Data on stability of the external electric field potential for the $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ ceramics under conditions of 100 % humidity and for known ceramic electrets based on sodium niobate, lithium and strontium titanate [8] and CaTiO_3 ceramics are listed in Table.

From Table it is seen that the $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ ceramics has output values of the external electric field potential close to the known ceramic material [8], but demonstrates much greater stability V_S under the conditions of high humidity. So, % decrease of V_S for the $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ ceramics after 10 min exposure under 100 % of relative humidity is ~3 %, while this value is (31.4–45.6) % for the known ceramic material [8] and is equal to 78 % for CaTiO_3 ceramics. After 24 h of keeping in such a humid atmosphere CaTiO_3 absolutely loses

Table. Stability of the external field potential V_S of $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ ceramics with SPS, known ceramic material [8] and CaTiO_3 ceramics at relative humidity of 100 %

Ceramic electret material	External field potential (V_S , V), after 10 days of polarization	Exposition at relative humidity of 100 %					
		10 min		1 day		7 days	
		V_S , V after testing	% decrease V_S	V_S , V after testing	% decrease V_S	V_S , V after testing	% decrease V_S
$\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$	300	290	3.3	280	6.7	80	73.3
Known ceramic material [8]	246–297	134–204	31.4–45.6	–	–	–	–
CaTiO_3	90	20	78	0	100	–	–

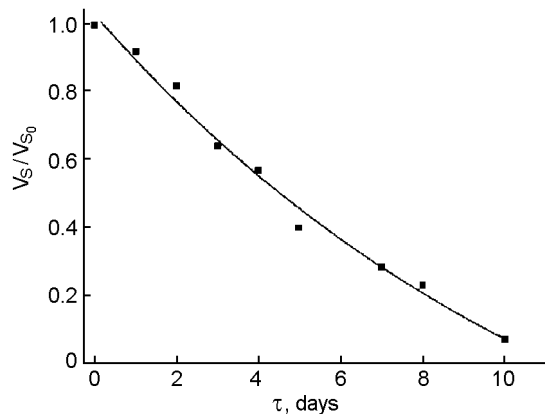


Fig. 4. Dependence of relative surface potential (V_S/V_{S_0}) of $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ ceramics on time of keeping the sample in conditions of 100 % relative humidity.

its charge while the potential decreases on ~ 7 % on the $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ ceramic disks (Table), total discharge of the $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ electret ceramics arrives on the 15th day of the sample keeping at 100 % humidity.

4. Conclusions

Thus, our studies have experimentally confirmed the expected ability of creation

of stable residual polarization in the $\text{A}_n\text{B}_n\text{O}_{3n+2}$ five-layered family of compounds with SPS. The $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$ -based ceramic electrets with SPS are characterized by enhanced values of the external electric field potential and its high stability over the time. Besides, such functional requirements as stability in the high humidity V_S is much higher than that for not only other known electrets but also for the industrial ceramic electret material on the base of CaTiO_3 .

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