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High-sensitivity piezoceramic elements for medical ultrasonic examination equipment

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Results of investigation for production of piezoelectric ceramic elements (PCE) with high values of piezosensitivity g_{33} are discussed. Industrial materials ЦТССт-2М, ЦТС-46 based on the lead titanate-zirconate solid solutions were used for fabrication of PCE. Model solid solution $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT 52/48) doped with various chemical elements was used, too. The advantage of semiceramic method for ceramic elements fabrication has been shown.

Обсуждаются результаты исследований производства пьезоэлектрических керамических элементов (ПКЭ) с высокими значениями пьезочувствительности g_{33}. Для изготовления ПКЭ использованы промышленные материалы ЦТССт-2М, ЦТС-46 на основе твердых растворов титаната-цирконата свинца. Использован также модельный твердый раствор $Pb(Zr_{0,52}Ti_{0,48})O_3$ (ЦТС 52/48), легированный различными химическими элементами. Показано преимущество полукерамического метода для производства керамических элементов.

Ultrasonic examination methods are used widely for diagnostic purposes in cardiology, surgery, obstetrics, ophthalmology, dentistry, and other fields of medicine. Such methods are realized using various types of ultrasonic apparatuses based on magnetostrictive or piezoelectric transducers. The main requirement to ultrasonic medical diagnostic equipment is minimization of the ultrasound action on human organism. The safety degree of ultrasonic apparatuses is defined by the technical characteristics thereof. As to devices based on piezoelectric transducers, such characteristics include piezoelectric sensitivity, g_{33}, of working piezoceramic elements (PCE). The higher is the g_{33} value, the weaker acoustic signal can be used for ultrasonic examination.

The piezoelectric transducers used in diagnostic ultrasonic equipment belong to reversible devices, i.e. to the ones which can act both as emitters and receivers of radiation. The manufacturing of PCE requires materials with low mechanical quality Q_m as well as with high values of piezoelectric modulus d_{ij} and piezoelectric sensitivity g_{ij} simultaneously, such as the ceramics ЦТССт-2М, ЦТССт-9 (produced by Reaktivelektron, Ukraine) [1], ПКР-89, ЦТСНВ-1 (made in Russia) [2]. The development of materials characterized by the above-mentioned combination of properties is a complex task, as the parameters d and g ($d \sim \varepsilon^{1/2}$, $g \sim \varepsilon^{-1}$) are antagonistic. The existing PCE have piezoelectric sensitivity values g_{33} of at most 40 mV/Pa [3]. To obtain the required set of properties, special attention is being paid to the development of new methods for the making of ceramic elements and to the study of the material structure state influence on the performance characteristics of ceramic materials. As shown recently, nanoscale structures give rise to the effects changing radically the physical properties of materials, the chemical composition remaining unchanged [4–6].

In this work, reported are the results of the studies aimed at the obtaining of piezoceramic elements with high g_{33} values. The investigated PCE were produced from industrial materials based on lead zirconate-titanate (PZT) solid solutions such as ЦТССт-2М, ЦТС-46, as well as the model solid solution of the $Pb(Zr_{0.52}Ti_{0.48})O_3$ composition with small amounts of doping additives (PZT 52/48). The electrophysical properties of these PCE were optimized using traditional approaches (e.g. doping of the material) and new methods based on the change of the material structure state, in particular, dispersity and morphology of the synthesized powder, as well as peculiarities of its compacting.

The PZT powders were prepared by the semi-ceramic synthesis (SCS). At first, the co-precipitation method was applied to obtain precursors in the form of titanium and zirconium hydroxides which were heat treated to obtain crystalline powder. Then the obtained powder was mixed with lead oxide and the doping additive oxides. The raw material so prepared was ground in a vibratory mill and subjected to the final heat treatment to obtain a monophase product. The conditions for the raw material synthesis and sintering of the ceramic samples were chosen basing on the results of thermogravimetric, dilatometric, and X-ray investigations. The powdered products of heat treatment were controlled by of X-ray phase analysis using a DRON-3 diffractometer (filtered $CuK\alpha$ radiation) and transmission electron microscopy. The determination accuracy of quantitative phase analysis was 3 %.

The synthesized powders were used to produce PCE shaped as 0.35 to 1.00 mm thick disks of 6–15 mm diameter. The ceramic preforms were shaped by uniaxial compacting under a pressure of 1–6 t/cm^2 using surface-active substances (SAS) and organic binder. The preforms were sintered at temperatures ranging between 950 and 1300°C together with lead-containing charge in closed alundum containers. The isothermal holding duration was 15 minutes to 3 hours. For comparison, the similar samples were also obtained using the traditional ceramic technology (CT).

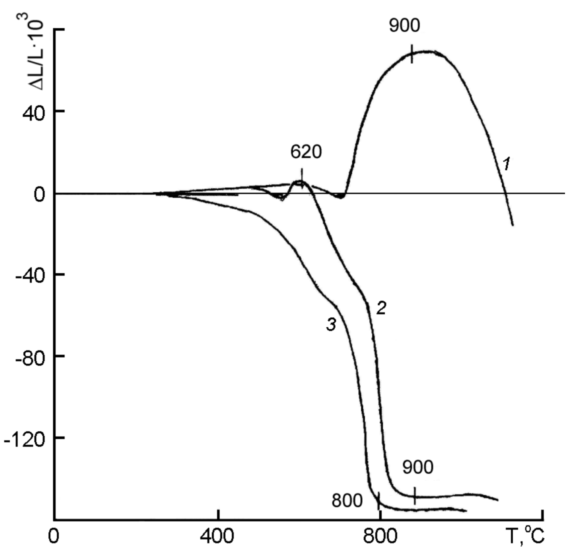

Fig. 1. Dilatometry curves for different processes of ЦТССт-2М synthesis: *1*, traditional ceramic method; *2*, semi-ceramic method; *3*, co-precipitation of the components.

The electrophysical properties of the samples were studied using electrodes formed by burning-in the silver paste into the sample surface. The samples were polarized in DC electric field with the intensity $E = 4$ kV/mm by holding at 120°C for one hour. The electrophysical parameters of the PCE were controlled according to the standard technique, the piezoelectric modulus d_{33} was measured by the static method [7]. The PCE were tested in medical ultrasonic apparatuses at a number of enterprises such as "Eskulap-UZT", "Kvant" (Keiv, Ukraine) and other PCE users.

Shown in Fig. 1 are the dilatometric investigation results of the ЦТССт-2М material synthesis by the traditional ceramic method from the mechanical mixture of PbO, TiO_2, ZrO_2, and Bi_2O_3 (curve *1*) and by the SCS method from the mechanical mixture of the Ti and Zr hydroxides with PbO and Bi_2O_3 (curve *2*). Curve 1 is characterized by a pronounced maximum at approximately 900°C, which is due to the solid-phase reaction of the solid solution formation. To obtain the monophase product, the synthetic process is to be realized at temperatures at least 1000°C. Curve *2* shows an insignificant anomalous widening at 590–620°C which is connected with decomposition of the initial precursors and the formation of the final product. At 800°C, the curve reaches a plateau, thus evidencing the completion of the material synthesis. The powder synthesized at 800°C was examined by XPA. The analysis showed the absence of any initial and intermediate phases: the X-ray diffraction patterns contained only the lines corresponding to the PZT structure. The average size of the coherent scattering regions (CSR) is d_{av}≈11.5 nm. The powdered materials ЦТС-46 and PZT 52/48 also have highly dispersed CSR: 11 nm and 17.5 nm, respectively. According to the data of microscopic examination, the average grain size for the powder synthesized by the traditional method is 1350 nm, the CSR size being 9.6 nm. So, the obtained results point even at this stage to advantages of the SCS method over the traditional ceramic method for the obtaining of PZT system piezoelectric materials.

The stage of powder compaction is very important for the formation of the final material structure. The finely dispersed powders are especially sensitive to the compaction conditions, in particular, to those of pressing. This is explained by their specific features, e.g. domination of the surface properties over other physicochemical characteristics. As the dispersity degree rises, the interaction of the powder particles becomes more intense and results in their aggregation and the formation of a skeleton structure which hinders the powder compaction when the applied external pressure increases. The pressing problem of fine-dispersed powders may be solved by changing the surface properties of the powder particles, e.g. using SAS. The influence of uniaxial pressing of ЦТССт-2М powders obtained by the two methods mentioned above is illustrated by Table 1 as well as the influence of SAS on the quality of the pressings.

The presented data testify that the technique we have developed for press-powder preparation makes it possible to increase the tolerable pressures of powder compaction from 1.0 up to 6.0 t/cm^2 and to raise the quality of the pressings.

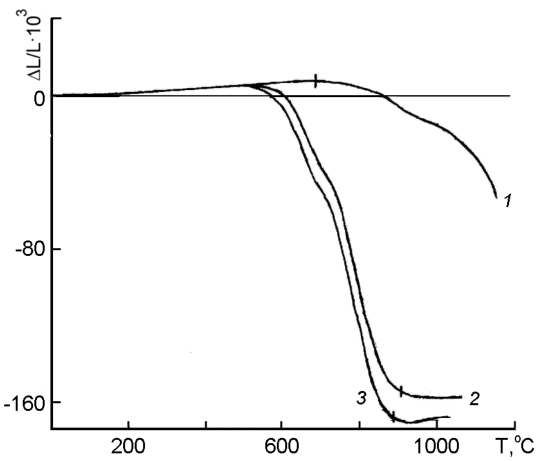

Fig. 2. Dilatometry curves for different processes of ЦТССт-2М sintering: *1*, traditional ceramic method; *2*, semi-ceramic method; *3*, co-precipitation of the components.

To establish the sintering regimes for the ceramic elements, the dilatometric studies were performed under programmed heating (the heating rate of 10°C/min). Fig. 2 presents the shrinkage curves for the ЦТССт-2М powders prepared by three different methods. As seen from these dependences, for the samples obtained by the semi-ceramic technology the sintering temperature is essentially (by 250–300°C) lower than that for the samples prepared according to the standard ceramic technology, and is practically equal to the sintering temperature for the powders prepared by co-precipitation. Here it should be noted that the third method is extremely difficult to use in obtaining of multicomponent (with respect to cationic composition) products. The semi-ceramic technology allows to cope with this problem easily. The grain size of the ceramics prepared by the semi-ceramic technology ranges between 1150 and 1350 nm (Fig. 3). This provides high mechanical strength and long service life of the ceramic elements [8].

Table 1. Results for ЦТССт-2М powder compacting

Powder type	Press-powder composition	Compacting pressure, 10000 N/cm^2	Porosity, %
Traditional ceramic method (d_{av} = 1.2 μm)	Powder+binder	1.0	28.02
	Powder+binder+surface activator	6.0	17.82
Semi-ceramic method (d_{CSR} = 11 nm)	Powder+binder	1.0	49.60
	Powder+binder+surface activator	6.0	28.84

Table 2. Electrophysical parameters of ceramic elements

Powder description				Sintering temp., °C	Electro-physical parameters of ceramics				
Composition	Production technique	S_{sp}, m^2/g	RCS, nm		E_{33}^T/E_0	$d_{31}\cdot 10^{-12}$, C / N	$d_{33}\cdot 10^{-12}$, C / N	$g_{33}\cdot 10^{-3}$	V·m/Pa
ЦТССт-2М	SCM	–	13.5	1100	3000±300	260	800–1200	30–45	180
	Traditional ceramic	0.6	1200	1260	3000±300	≈240	≈630	≈24	180
ЦТС-46	SCM	–	11.0	1080	1100±200	120	1000–1200	100–120	380
	Traditional ceramic	0.6	1200	1140	1100±200	≈100	≈400	≈40	340
PZT 52/48	SCM	–	20	1050	1100±200	80–120	800–1200		385
	Traditional ceramic	–	1100	1300	1100±200	<70	<200		380

CSR — coherent scattering region, SCM — semi-ceramic method

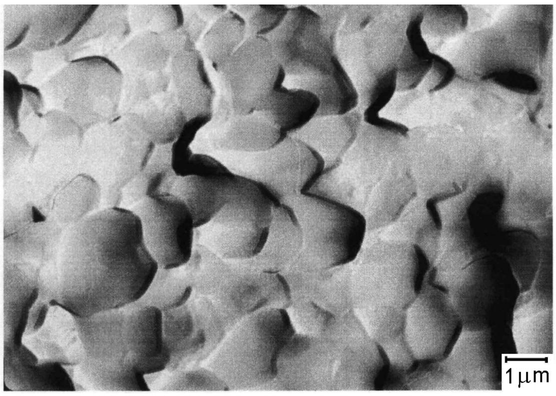

Fig. 3. Microstructure of ЦТССт-2М ceramics obtained by semi-ceramic method.

Table 2 presents the electrophysical characteristics of the PCE shaped as disks of 12 mm diameter and 0.76 mm thickness produced by the semi-ceramic technology. As seen from this Table, the PCE possess elevated g_{33} at high d_{33} values as compared to the elements obtained by the traditional technology and those produced at other companies in Ukraine and abroad.

The PCE were tested in medical ultrasonic apparatuses at a number of enterprises such as "Eskulap-UZT", "Kvant" (Kyiv, Ukraine). The PCE to be used in medical apparatuses must possess not only high piezosensitivity g_{33}, but also high stability and reproducibility of resonance frequency. The latter requirement is connected with the fact that a frequency mismatch between the master quartz oscillator and the natural resonance frequency of PCE lowers essentially the efficiency of the piezoelectric transducer both in sound emission and sound reception modes. This factor acquires a particular significance for the transducers containing a large number of PCE. The industrial PCE produced nowadays show a scatter of resonance frequency values of ±5 %. Attempts to diminish that scatter down to ±2.5 % result in a lower output of the finished products.

Testing of 120 PCE fabricated according to the results of the present investigation shows that the resonance frequency scatter does not exceed ±1 %. An analysis testifies that the obtained value can be improved considerably. The attained piezoelectric characteristics — high level of g_{33} and high reproducibility of the PCE frequency — offer an ample scope for using these elements as a base of medical ultrasonic examination apparatuses with technical characteristics comparing favorably with the best world analogs. Such devices will be able to work at very low levels of acoustic signal.

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Високочутливі п’єзокерамічні елементи для медичних УЗД-апаратів

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Обговорюються результати досліджень виробництва п’єзоелектричних керамічних елементів (ПКЕ) з високими значеннями п’єзочутливості g_{33}. Для виготовлення ПКЕ використано промислові матеріали ЦТССт-2М, ЦТС-46 на основі твердих розчинів титанату-цирконату свинцю. Використаний також модельний твердий розчин $Pb(Zr_{0,52}Ti_{0,48})O_3$, легований різними хімічними елементами. Показано перевагу напівкерамічного методу для виробництва керамічних елементів.