

Article

Thermodynamic Prehistory in the Formation of the Internal Structure of Highly Stable Ferroelectric Materials

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Received: 11 September 2018; Accepted: 7 October 2018; Published: 12 October 2018



Abstract: We investigated and presented our results for the dependence of the characteristics of the crystalline and grain structures of the PCR-13 material (based on the lead zirconate titanate (PZT) system), which was sintered in various ways, on the regulations for its preparation. The data from the microfluorescence analysis of the surface of ceramic materials were provided, which allowed us to state that micro X-ray fluorescence spectrometry (MICRO-XRF), supplemented by mathematical statistics, allows us to trace even small changes in the chemical composition of ceramic samples, reliably characterize the degree of surface homogeneity and provide strict mathematical conclusions related to the reproducibility of the properties of manufactured piezoelectric ceramic materials. Based on the obtained data, the optimal conditions for ceramics have been selected, which ensure homogeneity, high-density structure and reproducibility of the characteristics. This allows us to reliably use the material in frequency-selective equipment.

Keywords: PCR-13; PZT; sintering; crystal structure; grain structure; MICRO-XRF

1. Introduction

The present time is characterized by the intellectualization of the science of materials [1] as there has been a transition from the instrumental and technological aspect to the creation of basic principles and the foundations of molecular design, which corresponds to modern trends that have emphasized the necessity of supporting the breakthrough development of science into a powerful fundamental component [2–11].

In this connection, the studies that we are undertaking are aimed at establishing the role of thermodynamic prehistory (phase formation conditions) in the formation of the internal structure (crystalline, grained) of highly stable ferroelectric materials, which are in high demand in the real sector of the economy. Furthermore, these are intended for use in frequency-selective (filter) devices.

The demand for these materials in this equipment imposes strict requirements on the homogeneity of its internal structure, primarily the chemical composition of materials. Hence, the reproducibility and stability of macro-responses obtained by various methods (conventional ceramic technology, hot pressing, sintering in an oxygen atmosphere) during the variation of technological parameters (sintering temperature) is also essential.

Considering all the aforementioned points, the purpose of this study is to determine the dependence of the characteristics of the crystal and grain structures of the PCR-13 material (the abbreviation PCR stands for rostov piezoceramic) [12] intended for the above-mentioned purposes (based on the lead zirconate titanate (PZT) system), which is sintered in various ways, on the regulations for its preparation, including the thermal conditions of processing of the synthesized dispersed-crystalline products during the formation of the ceramic skeleton. Furthermore, we conducted an evaluation of the degree of their surface homogeneity by the microfluorescence analysis method (MICRO-XRF).

2. Materials and Methods

The modified material PCR-13, which corresponded to the formula $\text{PbTi}_{0.512}\text{Zr}_{0.385}\text{Nb}_{0.093}\text{Zn}_{0.006}\text{Mn}_{0.004}\text{O}_3$ (developed at the Research Institute of Physics SFU [13]), was used as the object of the research.

The samples were obtained by a two-stage solid-phase synthesis, followed by sintering with conventional ceramic technology (CCT) with a variation in the sintering temperature ($T_{\text{sint.}}$) and with a Pb-containing backfilling. This was achieved by the hot pressing (HP) of small ($\text{Ø}10 \times 1$ mm) disks in the air atmosphere (laboratory technology, the HP-lab.) and hot pressing of large blocks ($110 \times 110 \times 25$ mm, the HP-block) and in oxygen (HP + O₂) [14].

In terms of specific technological procedures for each method, the synthesis— $T_{\text{synt.1}} = 1140$ K, $\tau_{\text{synt.1}} = 6$ h, $T_{\text{synt.2}} = 1120$ K, $\tau_{\text{synt.2}} = 4$ h (for all methods); sintering: (CCT)— $T_{\text{sint.}} = (1500 \div 1520)$ K, $\tau_{\text{sint.}} = 2 \div 5$ h; (HP-lab.)— $T_{\text{sint.}} = 1450$ K, $\tau_{\text{sint.}} = 2$ h, $P_{\text{sint.}} = 200$ kg/cm²; (HP-block)— $T_{\text{sint.}} = 1430$ K, $\tau_{\text{sint.}} = 2$ h, $P_{\text{sint.}} = 100$ kg/cm²; (HP + O₂)— $T_{\text{sint.}} = 1430$ K, $\tau_{\text{sint.}} = 2$ h, $P_{\text{sint.}} = 200$ kg/cm².

The oxides of the following qualifications were used as starting reagents: PbO, ZrO₂, TiO₂, Nb₂O₅, MnO₂—“c” and ZnO—“c.f.a.” of the supplier in Rostov-on-Don LLC ROSTEKHNOHIM (where “c” is clean, “c.f.a.” is clean for analysis).

In order to avoid the lead losses associated with fusibility, volatility and consequently high diffuse activity of the lead oxide during the technological process, an excess amount ($(1 \div 2)$ wt %) of PbO was additionally introduced into the material composition and a lead-containing atmosphere was created in the working chamber of the furnace due to the firing in the backfilling of the synthesized material. In addition, taking into account the possibility of the presence of a small (~ 1 wt %) amount of unreacted PbO in the charge, a two-stage synthesis with intermediate grinding of the reaction products and subsequent granulation of sintered powders provides a breakdown of the reaction product layer on the “coated” refractory particles (TiO₂, ZrO, Nb₂O₅) in addition to the homogenization of the composition. Thus, this allows the “coating” (PbO) reagent to access the unreacted volumes of the refractory low-active oxides. Preservation of the stoichiometry of a given composition of the material was also ensured by using finely dispersed raw materials ($0.5 \div 2.0$ μm) that did not contain coarse fractions. This allowed us to significantly increase the reaction surface of the particles, to accelerate their diffusion and, as a consequence, to ensure the completeness of the reaction and prevent losses of lead.

X-ray studies were performed by powder diffraction on a DRON-3 diffractometer using $\text{Co}_{K\alpha}$ radiation. The cell parameters were calculated in accordance with the standard procedure. The measurement error of the parameters was: $\Delta a = \Delta b = \Delta c = \pm 0.003$ Å, $\Delta V = \pm 0.05$ Å³, where a , b and c are the parameters, V is the volume of the tetragonal, T , cell, δ is a homogeneous strain

parameter characterizing the value of the spontaneous strain, which is calculated from the formula for the T phase $2/3(\frac{\epsilon}{a} - 1)$ [15].

A scanning electron microscope JSM-6390L (JEOL Ltd., Tokyo, Japan) with a microanalyzer system from Oxford Instruments (Abingdon, UK) was used to study the microstructure of the samples of the chips. The resolution of the microscope is up to 1.2 nm with an accelerating voltage of 30 kV (the image in secondary electrons); the limits of the accelerating voltage are from 0.5 to 30 kV; the increase is from $\times 10$ to $\times 1,000,000$; and the beam current is up to 200 nA.

The samples were analyzed on the M4 TORNADO microfluorescence spectrometer (Bruker, Billerica, MA, USA). The microfluorescence analysis is performed by focusing a polycapillary lens of primary radiation excited by a microfocus X-ray tube with a rhodium anode. The X-ray emission is registered by an energy-dispersive detector with an energy resolution of 130 eV. The registration of the X-ray spectrum is a time process of accumulation, which is subject to the laws of statistics. The “Multipoint” mode allows us to analyze the selected areas of the sample surface. According to a given number of points, statistics are collected, averaging and quantitative analysis are used for the determination of the concentrations of different chemical elements.

3. Results

3.1. The Role of Thermodynamic Prehistory in the Formation of the Internal Structure of Samples Produced by Various Technologies

Figure 1 shows the X-ray diffraction patterns of the PCR-13 material manufactured by different methods in the range of the angles $2\theta = (22 \div 55)^\circ$, in which there are the lines of the original compounds or impurity phases that are usually formed in the material during its synthesis (a); and the X-ray fragment, including the line $(200)_c$ (b). The lines of the ballast phases are absent on the X-ray patterns of CCT0 samples (CCT, $T_{sint.} = 1500$ K and $\tau_{sint.} = 5$ h) and the HP-block.

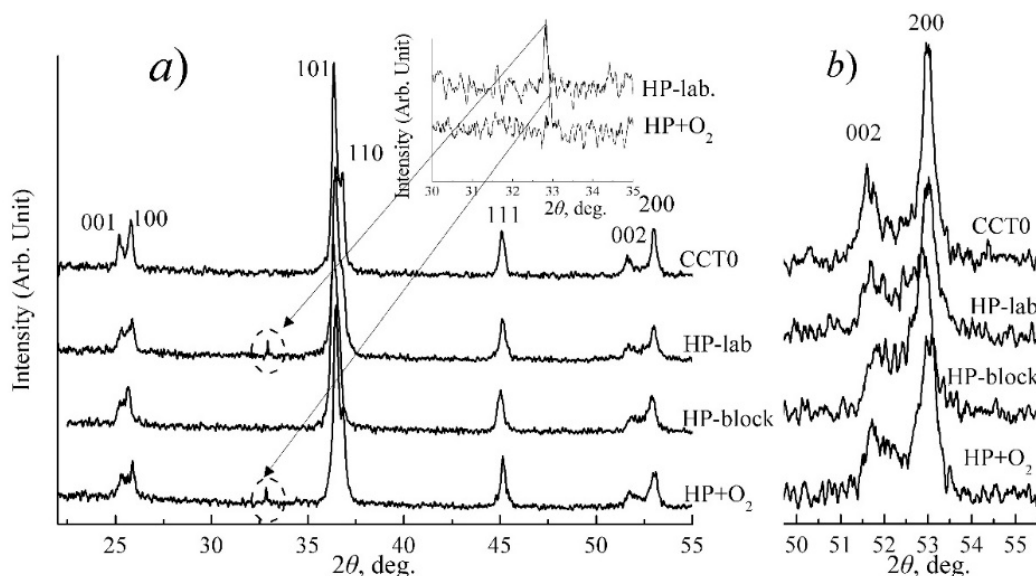


Figure 1. (a) X-ray patterns of PCR-13 material manufactured by different methods; and (b) X-ray fragments comprising lines $(200)_c$.

A small background increase, which can be treated as the traces of the line of a given oxide that are present in the sample as an impurity phase, is seen on the X-ray diffraction patterns of the HP-lab and HP + O₂ samples (Figure 1a) in the region of $2\theta = 32.8^\circ$, where there is a strong ZrO₂ line. If a small part of Zr is not present in the structure, the prescribed stoichiometry of the solid solution, SS, is violated with an increase in the Ti concentration, which means a shift of the SS into the T -region of

the phase diagram and a consequent decrease in its volume. This is reflected in Table 1, which shows a decrease in the cell volume in the HP-lab and HP + O₂ samples as compared to the other two. Figure 1b shows the fragments of the X-ray diffraction patterns shown in Figure 1a, including the lines (200)_c.

Table 1. Parameters = a and c ; volume = V ; degree of distortion = c/a ; for tetragonal cells, homogeneous strain parameter = δ ; experimental = ρ_{exp} ; X-ray = ρ_{x-ray} ; and relative = ρ_{rel} , densities of PCR-13 produced by different methods.

Sample	a , Å	c , Å	$c/a \times 10^3$	V , Å ³	$\delta \times 10^3$	ρ_{exp} , g/cm ³	ρ_{x-ray} , g/cm ³	ρ_{rel} , %
CCT0	4.021	4.123	25.4	66.66	17.0	7.79	8.08	96.45
HP-lab.	4.020	4.115	23.5	66.50	15.7	8.00	8.10	98.80
HP-block	4.040	4.121	20.1	67.25	13.4	8.00	8.01	99.87
HP + O ₂	4.017	4.113	23.7	66.37	15.8	7.30	8.11	89.99

It can be seen that the SS lines produced by HP, especially 002, are very blurred and in fact, represent a superposition of several lines, which indicates the inhomogeneity of the SS. The most homogeneous composition was found in the material produced by the CCT. The practically limiting value for the CCT is 96.45 (Table 1) [16] and the largest value of δ provides an ultrahigh mechanical quality factor ($Q_m = 2800$ [14]) for the material and a fine grain structure (Figure 2), which was formed under conditions of the increased spontaneous strain of the object [17].

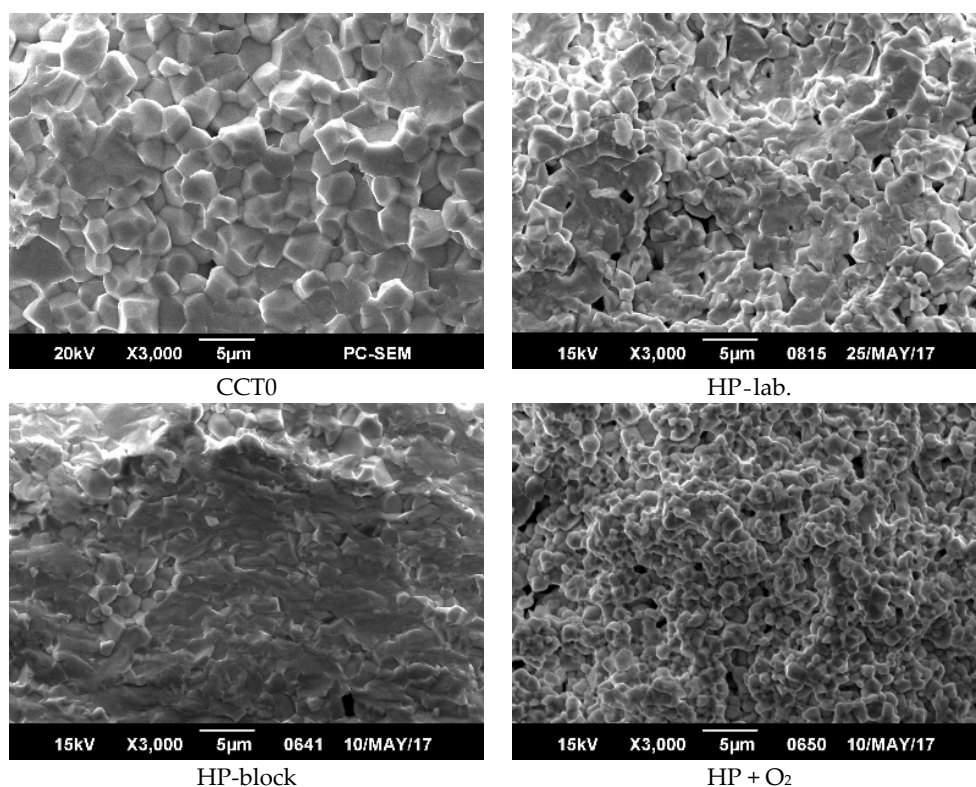


Figure 2. Fragments of microstructures of SS ceramics, produced by CCT0, HP-lab, HP-block and HP + oxygen.

The noted heterogeneity of the HP ceramics can be a consequence of the directional (anisotropic) application of pressure. Under the conditions of the practically always existing temperature gradient in a chamber intended for firing synthesized products, this can lead to changes in the local kinetics of the sintering of the objects with the appearance of the textured dislocations and their ordering up to

the formation of macrodefects acting as the sources of heterogeneity of the samples. The process is exacerbated by the absence of the liquid phases in the material that perform the transport function in this case. To a certain extent, this dampens the violations in the internal structure (crystalline, grained) of the media under investigation.

It should be noted that using the CCT (and not to HP as it is commonly assumed [16]) forms the most uniformly grained, close-packed structure with the crystallites of the regular geometric shape and the rectilinear boundaries in materials (Figure 2). Within the framework of the CCT, varying $T_{sint.}$, $\tau_{sint.}$ and the sintering conditions (in the backfilling of sintering product and without it), the influence of these parameters on the structure of PCR-13 was traced and we determined the optimal conditions for the preparation of the PCR-13.

For each of the used technologies, a series of the images, $8 \div 10$ pieces each, were made. It was established that the highest reproducibility of the properties corresponds to the CCT.

3.2. The Role of the Thermodynamic Prehistory in the Formation of the Internal Structure of the Samples Made Using Conventional Ceramic Technology

Figure 3 shows the X-ray diffraction patterns of the PCR-13 material, which was sintered according to the CCT under various conditions (Figure 3a) and the X-ray fragments, including the lines $(200)_c$ (Figure 3b). It is seen in Figure 3a that there is a line at $2\theta = 32.8^\circ$, the diffraction angle of which corresponds to the strong ZrO_2 line. This means a violation of the stoichiometry of the material towards an increase in the Ti concentration and a consequent shift into the T-region of the phase diagram of the PZT system. It can be seen in Figure 3b that the most homogeneous material was obtained at $T_{sint.} = 1500$ K and $\tau_{sint.} = 2$ h (X-ray diffraction pattern CCT4), with the same sample practically not containing ZrO_2 . Table 2 shows the structural characteristics and density of the ceramic material PCR-13 under different sintering modes. It can be seen from the table that in the samples made in backfilling (CCT1-CCT3 samples), the degree of the T-cell distortion (c/a) is greater than in the samples produced by the HP, which indicates a greater shift of the first ones into the T-region. The density of the ceramic is higher in the samples obtained using CCT at 1500 K in the backfill for 5 h.

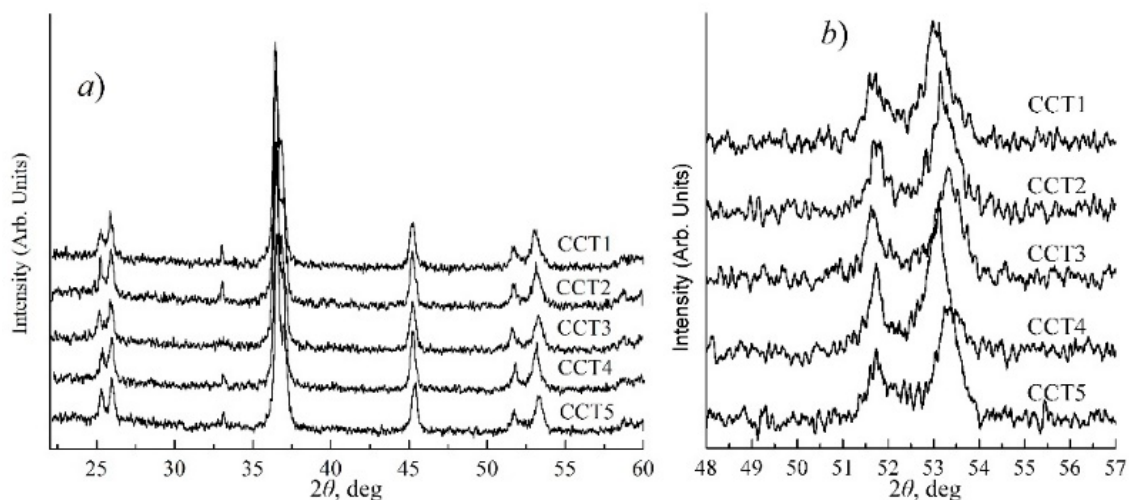


Figure 3. X-ray diffraction patterns of PCR-13 material produced by CCT under different sintering conditions: CCT1 at $T_{sint.} = 1520$ K for 2 h with backfill; CCT2 at $T_{sint.} = 1500$ K for 2 h with backfill; CCT3 at $T_{sint.} = 1500$ K for 5 h with backfilling; CCT4 at $T_{sint.} = 1520$ K for 2 h without backfill; CCT5 at $T_{sint.} = 1520$ K for 5 h without backfill (a); fragments of X-ray patterns, including lines $(200)_c$ (b).

Table 2. Parameters = a , c and c/a ; volume = V ; ceramic densities: experimental = ρ_{exp} ; X-ray = ρ_{x-ray} ; and relative = ρ_{rel} of PCR-13 material under different sintering conditions.

Sample	$T_{sint.}$, K	τ , h. (Sample)	a , Å	c , Å	V , Å ³	$(c/a - 1) \times 10^3$	$\delta \times 10^3$	ρ_{exp} , g/cm ³	ρ_{x-ray} , g/cm ³	ρ_{rel} , %
CCT2	1500 (with	2	4.005	4.112	65.95	26.7	17.8	7.18	8.16	87.94
CCT3	backfilling)	5	3.997	4.120	65.83	30.7	20.4	7.87	8.18	96.21
CCT1	1520 (with	2	4.018	4.118	66.47	25.0	16.6	7.07	8.10	87.29
CCT4	backfilling)									
CCT4	1520 (without	2	4.012	4.112	66.19	25.0	16.6	6.71	8.13	82.48
CCT5	backfilling)	5	3.998	4.112	65.73	28.4	18.9	7.09	8.19	86.56

It can be seen that at $2\theta = 32.8^\circ$ (Figure 3a), there is a line, which has a diffraction angle that corresponds to the strong ZrO_2 line. This means a violation of the stoichiometry of the material, which increases the Ti concentration and consequently shifts it to the T-region of the PZT system phase diagram. As seen in Figure 3b, the most homogeneous material was obtained at $T_{sint.} = 1500$ K and $\tau_{sint.} = 2$ h (CCT3), with the same sample containing the smallest amount of ZrO_2 . Table 2 shows the structural characteristics and density of the ceramic material PCR-13 under different sintering regimes. It can be seen that in the samples made in backfill (samples CCT1–CCT3), the degree of T-cell distortion (c/a) is greater than in the samples produced by the HP method, which indicates a greater shift of the former in the T region. The density of the ceramic is higher in the samples obtained at 1520 K in the backfill for 5 h.

Figure 4 shows the fragments of the microstructures of the PCR-13 material obtained under various technological regulations, which also indicates that the optimal method to obtain the PCR-13 material is by using CCT at $T_{sint.} = 1500$ K and $\tau_{sint.} = 5$ h in a backfill since under these conditions, the most dense perfect microstructure is formed with grains of a practically regular geometric shape that are packed in a mosaic way. Exclusion of backfill and enhancement of $T_{sint.}$ (Figure 4) lead to a loosening of the structure (the appearance of channel-like pores) and as a consequence, a decrease in the density (Table 2) of the samples.

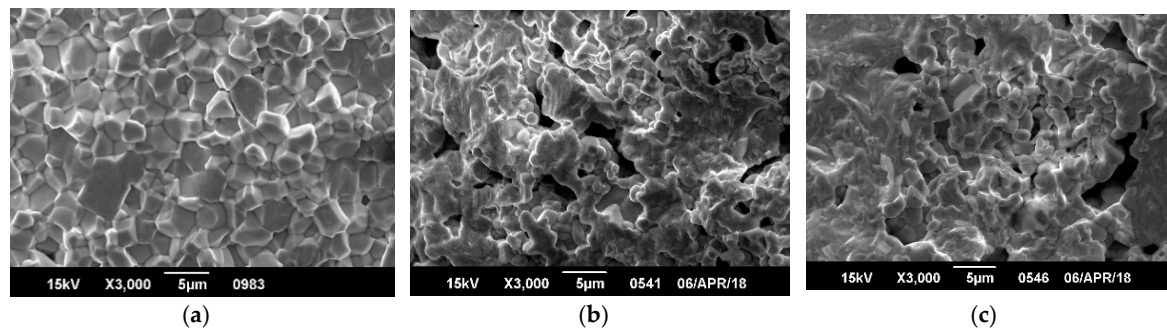


Figure 4. Fragments of microstructures of SS ceramics obtained in backfill ($T_{sint.} = 1500$ K (a); $T_{sint.} = 1520$ K (b)) and without it ($T_{sint.} = 1520$ K (c)).

3.3. On Elemental Homogeneity

Figure 5 shows the images of the analyzed region of the surface of the ceramic sample with different magnifications ($\times 10$ and $\times 100$). With reference to the investigated objects, the measurements of X-ray fluorescence intensities were obtained in this work and the calculations of the concentrations of chemical elements located on the surface of the samples were performed. Based on a large volume of experimental data on the concentrations of basic chemical elements, the methods for the statistical determination of the homogeneity degree of the surface of the studied ceramic samples were developed. The calculated metrological characteristics of the ceramic materials, which were obtained during the statistical processing of MICRO-XRF data, allowed for the evaluation and comparison of the investigated ferroelectric ceramics produced under various technological conditions.

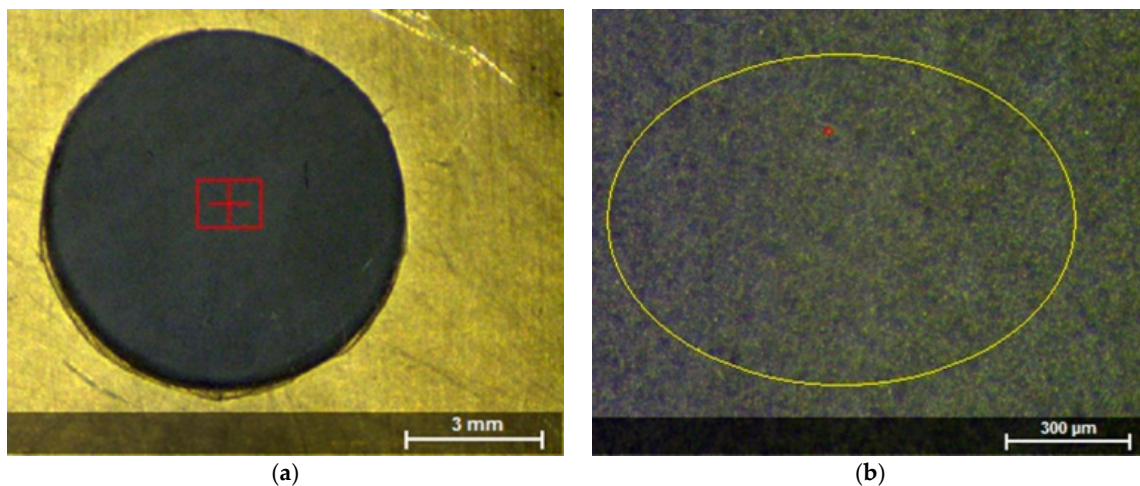


Figure 5. The image of the analyzed region of the surface for the ceramic sample (CCT3) with different magnifications ($\times 10$ (a) and $\times 100$ (b)).

In particular, a statistical analysis of the degree of the homogeneity/heterogeneity of the surface was performed according to the chemical composition of the main components, which were namely Ti, Zr, Nb and Pb. The total sample size for a single sample for each chemical element was $N = 1000$. This corresponds to ten local areas ($1 \times 1.5 \text{ mm}^2$), inside which there were 100 measurements taken of the intensities of the analytical lines of the spectrum at different points.

For the ceramic samples and for those in the stage preceding the ceramic annealing, the values of the confidence intervals ($\bar{x} \pm \Delta\bar{x}$) of the concentrations of these chemical elements were obtained, for which the condition $(\bar{x} - \Delta\bar{x}) \leq \mu \leq (\bar{x} + \Delta\bar{x})$ is satisfied with a given confidence probability. The calculation of the boundary values of the confidence intervals was performed according to the Student's criterion, assuming that the concentration values included in the sample are normally distributed:

$$(\bar{x} \pm \Delta\bar{x}) = \bar{x} \pm (t(P, f) \bullet S) / n^{1/2} \quad (1)$$

where $t(P, f)$ are the table values of the Student's criterion.

At the confidence level $P = 95\%$, a statistical comparison of the dispersion equation (according to Fisher's F-criterion) was performed, while we obtained the reliability of the differences in mathematical expectations based on Student's t -criterion.

Figure 6 shows the concentration distributions for two samples (Rand-1 and Rand-2) obtained by the fluorescence excitation of the characteristic radiation by the surface of the analyzed ceramic sample (CCT3). The statistical analysis has shown that the sample variances and calculated average values at a given confidence probability level have no significant differences.

The performed statistical analysis has shown reliable reproducibility of the production of the ceramic samples produced using a single technology at different times. According to the Fisher and Student criteria, the differences in the values of the variances and average values of the basic chemical elements (Ti, Zr, Nb and Pb) had insignificant differences, which is typical for single crystals of the same composition.

Figure 7 shows the concentration distributions for the samples obtained using the micro-PCFA of two ceramic samples (CCT2 and CCT1), with the sintering temperature having differed by less than 5%.

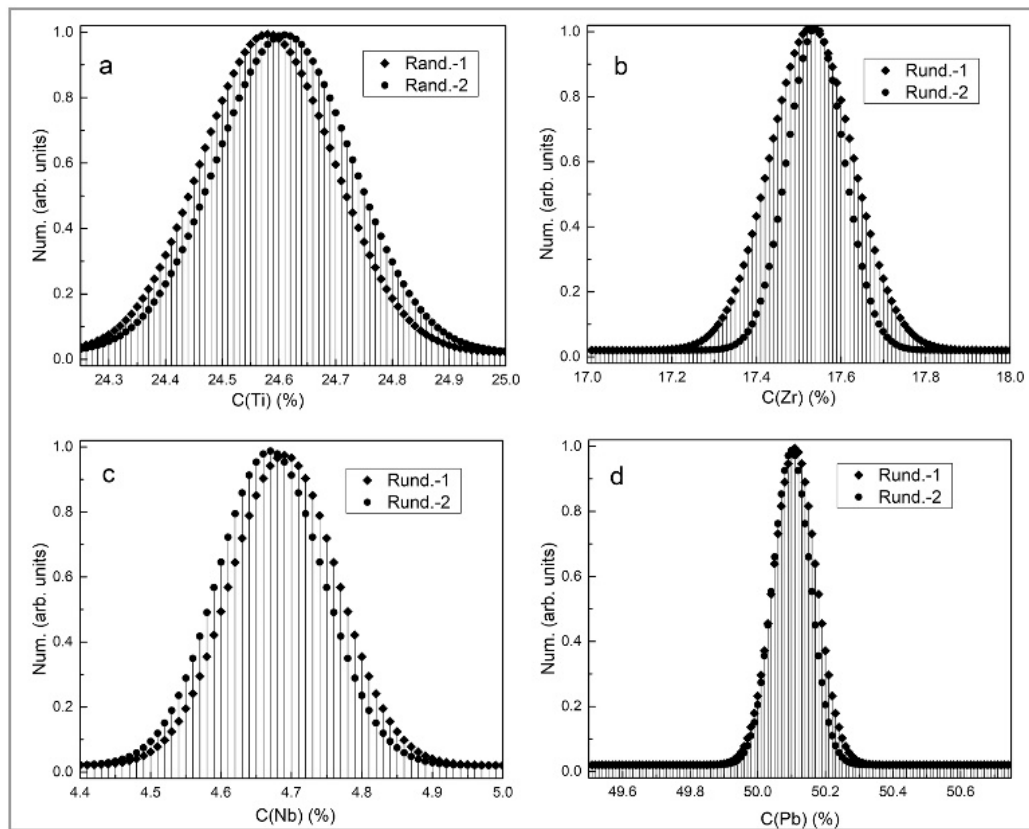


Figure 6. The concentration distributions for two samples (Rand-1, Rand-2) obtained by fluorescence excitation of the characteristic radiation by the surface of the analyzed ceramic sample (CCT3).

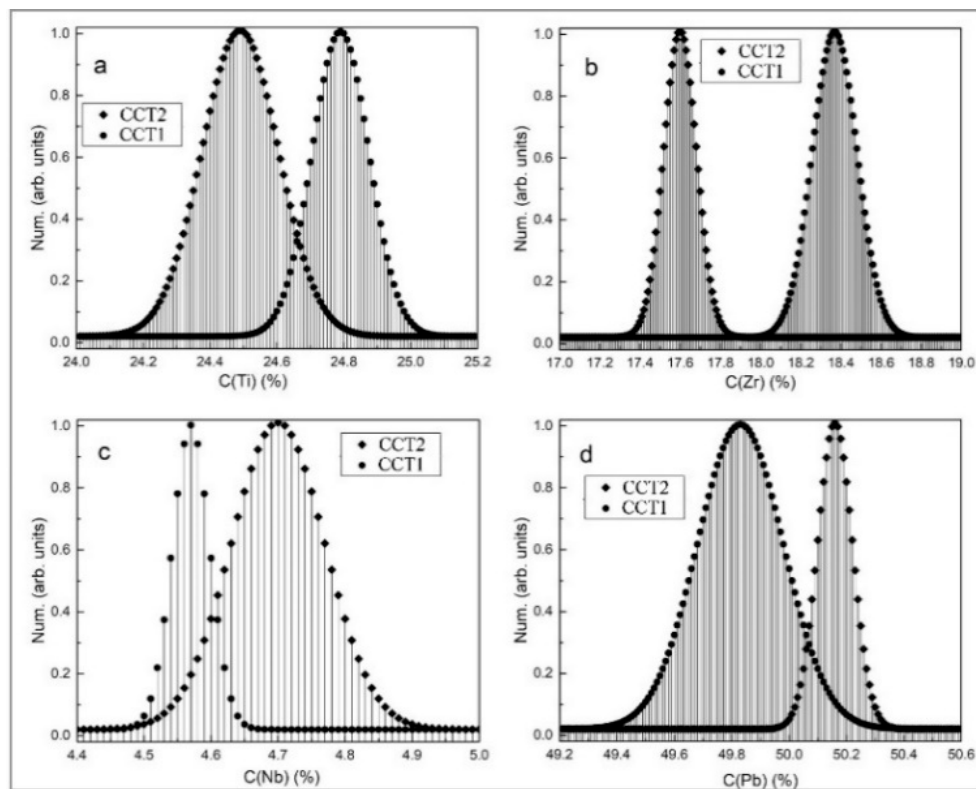


Figure 7. The concentration distributions for the samples obtained using micro-PCFA of two ceramic samples (CCT2 and CCT1).

The statistical analysis of the corresponding concentrations has shown that the variances and the calculated average values have significant differences for all chemical elements at a given confidence probability level $P = 95\%$.

Figure 8 presents the results of the statistical analysis and the distribution of concentrations of the basic chemical elements obtained for a sample (CCT3) prepared by the standard technology at a stage just before the sintering process. According to the Fisher criterion, the statistical analysis of the dispersion of the concentrations of chemical elements (Ti, Zr, Nb and Pb) distributed on the surface has shown significant differences in the variances of two independent samples. In this case, the calculation of the boundary values of the confidence interval according to Equation (1) shows that the values of the deviations of the concentrations from the average value can exceed 10%. This is an unacceptably high dispersion, which significantly exceeds the corresponding value after the sintering of the ceramic samples.

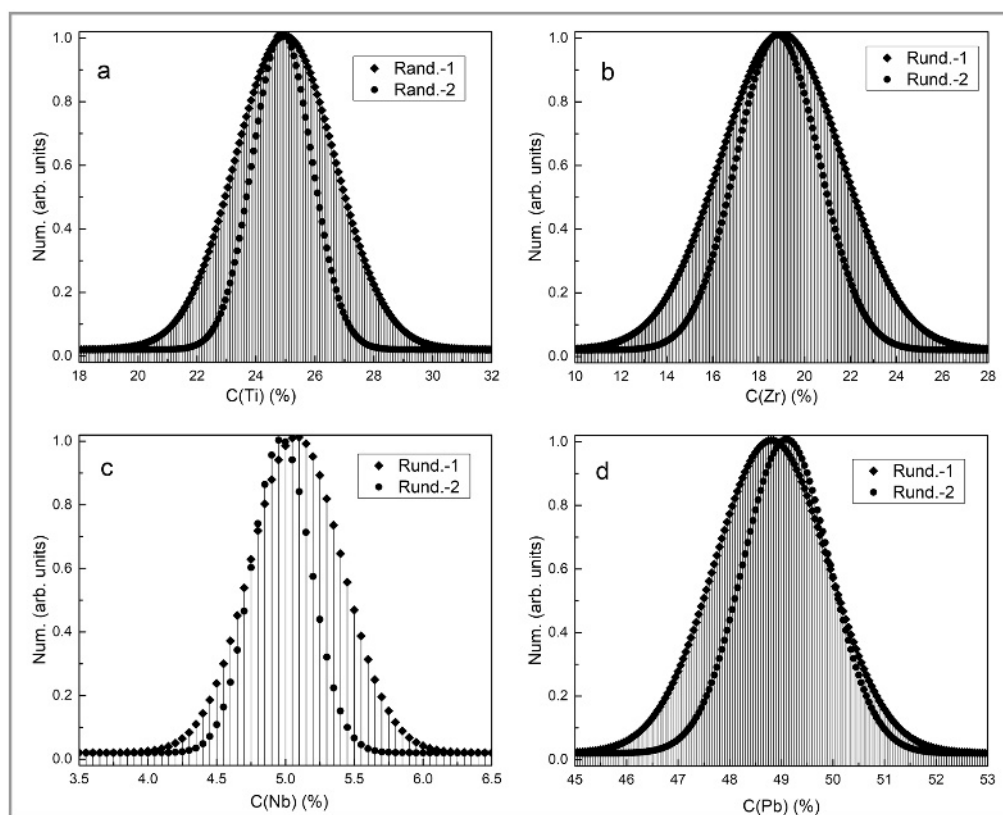


Figure 8. Results of the statistical analysis and the distribution of concentrations of the basic chemical elements obtained for a sample (CCT3) prepared by the standard technology at a stage just before the sintering process.

4. Conclusions

It has been established that the materials intended for frequency-selective (filter) devices are characterized by a critical dependence on the thermodynamic background (the conditions of production).

It has been detected that the most homogeneous (perfect) structure is realized using the conventional ceramic technology. In the HP samples, the structure is less uniform, which is explained by the anisotropy of the applied pressure. Due to the present temperature gradient in the chamber intended for firing the synthesized products, this leads to changes in the local kinetics of the sintering of objects with the appearance of the textured dislocations as well as the absence of liquid phases, which weaken the possibility of violations of the internal structure.

It has been shown that by choosing the optimal conditions for production, it is possible to fabricate a material with a homogeneous, high-density structure and reproducible characteristics.

The obtained results allow us to state that MICRO-XRF, supplemented by mathematical statistics, allows us to trace even small changes in the chemical composition of the ceramic samples, reliably characterize their degree of the surface homogeneity, and provide strict mathematical conclusions on the reproducibility of the manufacture of the piezoelectric ceramic materials.

Author Contributions: K.P.A.—original draft preparation and writing—review and editing; I.N.A.—validation; L.A.S.—X-Ray investigation; S.I.D.—data curation, I.A.V.—resources, L.A.R.—conceptualization, M.I.M.—micro-XRF investigation, A.V.N.—investigation of microstructures, I.A.P., S.-H.C., H.-Y.W.—discussion of results.

Funding: The work was funded by: the Ministry of Education and Science of the Russian Federation projects Nos. 3.6371.2017/8.9, 3.6439.2017/8.9 (the basic part of the state task); Grant of Russian Foundation for Basic Research No. 18-32-00552-mol-a; Ministry of Science and Technology of the Republic of China (Grant No. MOST 105-2923-E-992-302-MY3).

Acknowledgments: The equipment of the Center of Research Institute of Physics SFedU, “High-Tech” and Center of Research «Nanoscale structure of matter» SFedU was used.

Conflicts of Interest: The authors declare no conflict of interest.

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