

XRF Microanalysis of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ Type Nanocrystalline Ferroelectric Powders by Thin Layer Method

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A method of wavel-dispersive XRF analysis of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ type nanocrystalline ferroelectric powders (PZT) has been presented. Matrix effects have been minimized by using the thin layer method. Preparation of the nature sample has consisted in digesting 25 mg of the materials in hydrochloric acid and 30% hydrogen peroxide (1+1), diluting up to 25 mL, and placing 0.5 mL of the obtained solution on a substrate. Standard samples of the same chemical composition but varied masses have been prepared to simplify calibration. Determined elements in nature samples occur within the following concentration ranges: Pb from 66.72% to 69.84%, Zr from 8.54% to 14.04%, and Ti from 3.68% to 9.16%. The detection limits for 0.5 mg samples were obtained: Pb = 1.1×10^{-3} mg (0.22%), Zr = 1.3×10^{-3} mg (0.26%), Ti = 2.3×10^{-4} mg (0.05%).

Opracowano metodę mikroanalizy XRF nanokrystalicznych proszków ferroelektrycznych typu $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT). W celu wyeliminowania efektów matrycy zastosowano technikę cienkiej warstwy. Przygotowanie próbek naturalnych do analizy sprowadza się do rozтворzenia 25 mg badanego materiału w kwasie chlorowodorowym i 30% nadtlenu wodoru (1+1), rozcieńczeniu do objętości 25 mL i nakropleniu 0.5 mL uzyskanego roztworu na podłoże. Do kalibracji wykorzystano wielopierwiastkowe wzorce syntetyczne o tym samym składzie jakościowym lecz różnych masach. Oznaczane pierwiastki występowały w zakresach stężeń: Pb od 66.72% do 69.84%, Zr od 8.54% do 14.04% i Ti od 3.68% do 9.16%. Granice wykrywalności dla 0.5 mg próbki wynoszą: Pb = 1.1×10^{-3} mg (0.22%), Zr = 1.3×10^{-3} mg (0.26%), Ti = 2.3×10^{-4} mg (0.05%).

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The development of technology of ferroelectrics requires not only investigating their microstructure, physical and optical properties but also determination of the product composition and the synthesis control. Ferroelectrics are widely used in practice. Their use includes, *inter alia*, the construction of capacitors, surface acoustic wave transducers, electromechanical sensors, micro-servomotors, spatial optical modulators and memory elements.

The sol-gel method which was used to obtain polycrystalline thin layers and nanocrystalline powders of PbTiO_3 , BaTiO_3 , LiNbO_3 and numerous other compounds is one of those used in the synthesis of ferroelectrics of any chemical composition [1]. The sol-gel method is also widely used to obtain $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ type solid solutions [2–5]. The manufacturing of PZT ferroelectrics, irrespective of their chemical composition, is time-consuming and entails many stages. It includes, among other things, the following stages: hydrolysis, homogenisation, solution condensation, gel drying and ageing, and also burning of organic components and the final controlled heat treatment. All these stages may result in a change of materials composition. Hence there is a need to control the chemical composition of not only the final product, but also the products of certain technological stages [6].

The crystalline structure and thereby the physical properties of $(x)\text{PbTiO}_3$ - $(1-x)\text{PbZrO}_3$ solid solution depend on the quantitative ratio of both compounds. For $x > 0.042$ (mole fraction) the PZT maintains ferroelectric properties at room temperature and its application depends strictly on the ratio of titanium and zirconium concentrations [7]. Therefore the issue of such materials technology and the preservation of their chemical composition and the necessity to control this composition is important and difficult. The papers of Bochenek *et al.* [8] and Surowiak *et al.* [9] present the results for nanocrystalline powders and nanocrystalline $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ceramics production, where $0.35 \leq x \leq 0.65$, as well as the results of the studies on their crystal structure, microstructure, and basic physical properties. The technology of ceramic powders was based on the sol-gel synthesis. The material examinations comprised the X-ray diffraction (XRD), electron microscopy (TEM, SEM, RESEM), differential scanning calorimetry (DSC), differential thermal analysis (DTA), Raman scattering (RS) and the electric methods typical for ferroelectrics.

In the instrumental solution analysis it is necessary to digest ceramic powders [10]. Various methods of PZT digestion are used, *inter alia* using hydrochloric acid (digestion is then conducted under increased pressure at 160°C for 16 h), digestion under increased pressure at 160°C using hydrofluoric acid and sulfuric(VI) acid, digestion in a platinum vessel by means of sulfuric(VI) acid with the addition of ammonium sulfate(VI), and the fusion with sodium carbonate and sodium tetraborate [11]. XPS methods are used in the analysis of ceramic materials [12], and in the analysis of minerals and sinters also classical methods [13,14].

This paper presents the results of investigations on the quantitative composition of nanocrystalline ferroelectric $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ type powders which was done using the thin layer method in the XRF analysis and applying the digestion of samples by means of concentrated hydrochloric acid and 30% hydrogen peroxide.

EXPERIMENTAL

Apparatus and conditions

A wavelength-dispersive sequential X-ray spectrometer; excitation: an X-ray tube with a Mo anode, 50 kV, 40 mA; a LiF200 crystal, a fine collimator, vacuum, rotation of sample. Detailed measurement conditions are presented in Table 1.

Table 1. Apparatus conditions for measurements; fl — flow counter, sc — scintillation counter

Element	Analytical lines	2Θ	Counter	Detection time
Pb	L_α	33.93	fl + sc	20 s
Zr	K_α	22.55	sc	40 s
Ti	K_α	86.14	fl	100 s

Preparation of natural samples

Nanocrystalline $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ powders obtained with the sol-gel method were disintegrated to grains smaller than 100 μm in diameter, then 25 mg was weighed on a microbalance with accuracy of 0.001 mg and transferred to a 25 mL beaker. The weighed amount was then digested in concentrated hydrochloric acid with the addition of 30% hydrogen peroxide (at 1+1 ratio). The cooled-down solution was transferred to a 25 mL measuring flask, 0.5 mL of concentrated hydrochloric acid was added (to prevent hydrolysis of salts) and water was added up to the mark. As a result a solution of 1 mg mL^{-1} concentration was obtained. 0.5 mL of solution (0.5 mg sample) was taken for the XRF analysis and dropped on a 'Synpor' membrane filter (manufactured by Barva a Laky company). The filter was glued on PVC disk and covered by means two-sided adhesive tape. The sample was dried under an IR radiator and protected with a Mylar foil. The diagram of the substrate, on which the studied solutions were placed and analysed in the X-ray spectrometer, is presented in Figure 1.

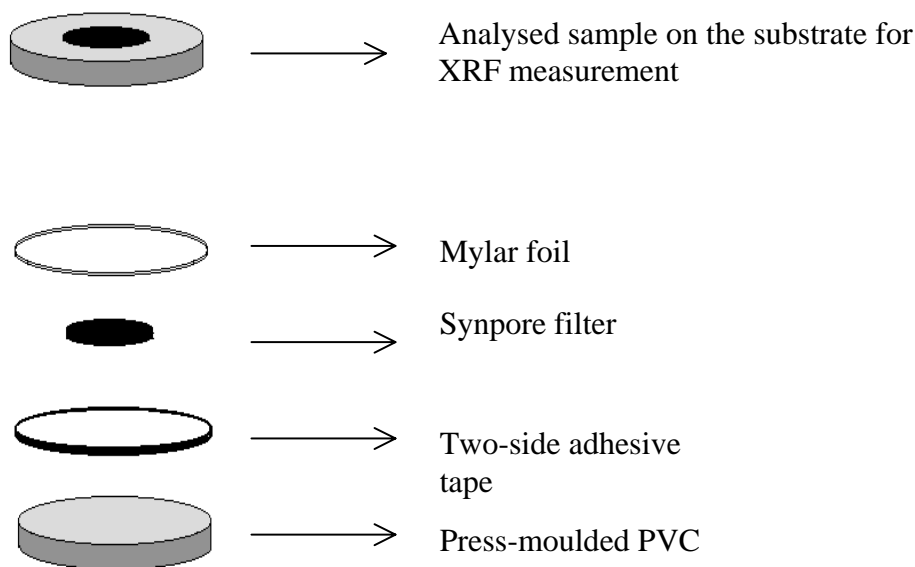


Figure 1. Substrate for the analysed samples of solutions

Preparation of synthetic standard samples

30.0 mg of metallic lead was weighed with accuracy of 0.001 mg and then digested in a 50 mL beaker in nitric acid (1+2), dry evaporated and 23.0 mg of K_2ZrF_6 and 25.3 mg of K_2TiF_6 were added to the residue. The whole was digested in a mixture of concentrated hydrochloric acid and 30% hydrogen peroxide (1+1). Cooled-down solution was transferred to a 50 mL measuring flask and then 1 mL of concentrated hydrochloric acid was added (to prevent the hydrolysis of the salts), and water was added up to the mark. To prepare the standardisation graphs, multielement solutions were dropped on ten 'Synpor' filters (glued on the PVC disk covered with a two-sided adhesive tape) at amounts from 0.30 mL to 0.75 mL. The samples were dried with an IR radiator at 70°C and protected with a Mylar foil (6 µm). The standardisation curve was drawn up on the basis of 10 synthetic multielement standards of the same composition and varied masses. The standardisation curve was designed in such a way that 0.5 mL of the standard solution corresponds with the quantitative composition of 0.5 mg of the analysed ceramic material.

Preparation of blank samples

Press-moulded PVC substrates with glued two-sided adhesive tape, on which a 'Synpore' filter with digested substances was centrally placed, were used as blank samples. After drying with an IR radiator the samples were protected with a Mylar foil.

RESULTS AND DISCUSSION

The studies were aimed at working out an XRF semimicroanalysis method with the use of small analytical weighed amounts of selected ferroelectric powders. Table 2 presents the assumed composition of ferroelectric powders after the digestion, converted to approx. 0.5 mg analytical weighed amount.

Table 2. Assumed composition of ferroelectric material after the process of digestion (analytical weighed amount ~0.5 mg)

The baked material (without organic matrix)	PbCl ₂ , mg	ZrCl ₄ , mg	TiCl ₄ , mg	Mass per unit area, mg cm ⁻²
Pb(Zr _{0.65} Ti _{0.35})O ₃	0.420	0.229	0.100	0.166
Pb(Zr _{0.55} Ti _{0.45})O ₃	0.425	0.196	0.131	0.166
Pb(Zr _{0.35} Ti _{0.65})O ₃	0.437	0.128	0.194	0.168

Table 3 shows average mass absorption coefficients $\bar{\mu}_i$ for lines of determined elements and the molybdenum line of the X-ray tube necessary to calculate average mass absorption coefficients, χ_i , taking into account the measuring system geometry and, in addition, the relative difference of average mass absorption coefficients, $\Delta\bar{\mu}_i$, for various materials. The relative difference of average mass absorption coefficients, $\Delta\bar{\mu}_i$, between various Pb(Zr_xTi_{1-x})O₃ type materials, where x ranges from 0.35 to 0.65, does not exceed 3%. This indicates a small influence of the matrix [15,16] even in the case of thick samples, and a possibility to use one calibration straight line for the materials of so diversified compositions.

Table 3. Average mass absorption coefficients

The baked material (without organic matrix)	Average mass absorption coefficients $\bar{\mu}_i$, cm ² g ⁻¹			
	L _{α1} Pb	K _α Zr	K _α Ti	K _α Mo
Pb(Zr _{0.65} Ti _{0.35})O ₃	82	70	762	62
Pb(Zr _{0.55} Ti _{0.45})O ₃	83	70	759	62
Pb(Zr _{0.35} Ti _{0.65})O ₃	84	72	750	63
$\Delta\bar{\mu}_i$	2.4%	2.8%	1.6%	1.6%

Table 4 presents summary absorption coefficients χ_i (K_αMo line) and the errors resulting from the absorption effects, Abs_{error,i}. These errors were calculated for the mass

per unit area equal to 0.17 mg cm^{-2} corresponding to the average sample mass of 0.752 mg fallen to 4.52 cm^2 of the filter. $\text{Abs}_{\text{error},i}$ allows to estimate the deviations from the linear relationship between the radiation intensity and the mass of the element in a thin sample and so the approximation error, $\exp(-\chi_i \cdot m_s) \approx (1 - \chi_i \cdot m_s)$, which is assumed for thin samples.

Table 4. Average mass absorption coefficients taking into account the geometry of the measuring system and errors resulting from absorption effects.

Material	Element	$\chi_i, \text{ cm}^2 \text{ g}^{-1}$	$\text{Abs}_{\text{error},i}, \%$
$\text{Pb}(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$	Pb	199	0.058
	Zr	180	0.048
	Ti	1257	2.636
$\text{Pb}(\text{Zr}_{0.55}\text{Ti}_{0.45})\text{O}_3$	Pb	201	0.060
	Zr	180	0.048
	Ti	1252	2.614
$\text{Pb}(\text{Zr}_{0.35}\text{Ti}_{0.65})\text{O}_3$	Pb	203	0.061
	Zr	185	0.050
	Ti	1239	2.556

$$\text{Abs}_{\text{error},i} = \frac{e^{-m_s \cdot \chi_i} - (1 - m_s \cdot \chi_i)}{e^{-m_s \cdot \chi_i}} \cdot 100\%$$

$$\text{where} \quad \chi_i = \frac{\bar{\mu}_{\text{K}\alpha\text{M}}}{\sin\varphi} + \frac{\bar{\mu}_i}{\sin\psi}$$

m_s is mass per unit area of the sample, φ is angle of incident radiation beam on the sample and ψ is angle of discharge radiation beam from the sample. For the considered system φ and ψ amount to 60° and 40° , respectively.

In the case of the application of *e.g.* Rhodes criterion for thin samples [17] $m_s < 0.1/\chi_i$ (mass per unit area are given in Table 2), which allows the error resulting from the absorption effects to be not greater than 0.5%, is not fulfilled only for titanium. For Ti the error amounts to approx. 2.6%, what results in the classification of the sample as an intermediary sample. Taking into account the relative standard deviations for titanium, which characterise mainly the precision of the sample preparation, equal to from 2.4 to 4.4%, the error resulting from absorption effects may be neglected. For the other elements the errors resulting from the absorption neglect are smaller by an order of magnitude than the value adopted by Rhodes and allow classification the prepared samples as thin samples.

The calibration was performed on the basis of the multielement synthetic standards, common for the concentration range of elements in the studied material. The calibration curves were prepared on the basis of the standards of the same chemical com-

position but varied masses [18]. The composition of the standards presented in Table 5 covers the average composition of examined ferroelectric powders, *i.e.* containing approx. 60% Pb, 15% Zr, and 7% Ti, what converted to 0.5 mg of weighed amount of the sample equals to ~0.30 mg Pb, ~0.075 mg Zr, and ~0.05 mg Ti, respectively.

Table 5. Composition of synthetic series of calibration samples

Standard	Amount of dropped standard solution, mL	Chemical composition, mg		
		Pb	Zr	Ti
W1	0.30	0.1798	0.0446	0.0303
W2	0.35	0.2098	0.0520	0.0354
W3	0.40	0.2397	0.0594	0.0404
W4	0.45	0.2697	0.0668	0.0454
W5	0.50	0.2997	0.0742	0.0505
W6	0.55	0.3296	0.0817	0.0556
W7	0.60	0.3596	0.0891	0.0606
W8	0.65	0.3896	0.0965	0.0656
W9	0.70	0.4195	0.1040	0.0707
W10	0.75	0.4495	0.1114	0.0758

Table 6 presents the linear regression equations, standard deviations (rstd) that characterise the residual errors of linear functions, and the correlation coefficients, *r*.

$$\text{rstd} = \sqrt{\frac{\sum_{k=1}^n (m_{\text{standard},k} - m_{\text{reg},k})^2}{n - p}}$$

n is number of standards, *p* is number of coefficients in the equation (for linear regression *p* = 2), $m_{\text{standard},k}$ is mass of elements in the *k*-th standard and $m_{\text{reg},k}$ is mass of element calculated from the regression equation for the *k*-th standard.

Table 6. Obtained calibration equations and correlation coefficients

Element	Equation	rstd, mg	<i>r</i>
Pb	$I = 379904 \text{ mgPb} + 41731$	0.0117	0.997
Zr	$I = 610478 \text{ mgZr} + 65922$	0.0022	0.993
Ti	$I = 816733 \text{ mgTi} + 7410$	0.0020	0.992

In all the cases the linear regression coefficients exceed 0.99, what confirms the linear relationship between the radiation intensity and the mass of the elements being determined.

The possibilities of improvement of the results accuracy, if any, have also been examined, having considered the interelement influences by the use of ‘mathematical models’ in the calculations, *i.e.* multiple regression (m.r.) [19], the Lucas–Tooth–Pyne (L.T.P.) intensities correction model [20], and the de Jongh (d.J.) concentrations correction model [21]. The obtained residual errors fall in the ranges: lead 0.0014 (d.J.)–0.0096 mg (L.T.P.), zirconium 0.0020 (L.T.P.)–0.0021 mg (d.J.) and titanium 0.0008 (d.J.)–0.0020 mg (L.T.P.). For the correlation coefficients the following ranges were obtained: lead 0.995 (L.T.P.)–0.999 (d.J.), zirconium 0.996 for all models, titanium 0.993 (L.T.P.)–0.999 (d.J.). The application of subsequent mathematical models did not show a significant improvement in the results connected with the magnitude of the residual errors and also the correlation coefficients for zirconium and titanium. However, for lead, the best results were obtained for de Jongh ‘model’, the application of which resulted in the improvement in residual error by one order of magnitude.

To determine the detection limit the following criterion was used: $C_{o,i} = 3S_b/a_i$ [22], where $S_b = \sqrt{N_b}$ is the standard deviation that characterises the reproducibility of the background and a_i is the slope of a straight line that characterises sensitivity of the method. The obtained values of detection limits for Pb, Zr and Ti, expressed in μg , amounted to 1.1, 1.3, and 0.23 μg , respectively. In each case the detection limit is by two orders of magnitude smaller than the determined contents of the selected elements, what possibly allows one to reduce the analysed weighed amount of the ferroelectric powder, subject to the maintenance of homogeneity of the analysed material and a good measurement precision (counting statistic).

Three various PZT types were analysed in the paper, featuring the same qualitative composition, but varied quantitative composition, *i.e.* $\text{Pb}(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$, $\text{Pb}(\text{Zr}_{0.55}\text{Ti}_{0.45})\text{O}_3$, and $\text{Pb}(\text{Zr}_{0.35}\text{Ti}_{0.65})\text{O}_3$ obtained by means of the sol-gel type method [8,9]. Each sample was analysed five times, and three measurements were done per analysis. The obtained results of analysis and the standard deviations characterising the precision of the sample preparation are given in Table 7.

$$\text{std} = \sqrt{\frac{\sum_{k=1}^n \sum_{j=1}^b (\bar{c} - c_{kj})^2}{n \cdot (b-1)}}$$

where $n = 5$ is number of samples, $b = 3$ is number of measurements for each sample, \bar{c} is average concentration, c_{kj} is concentration of element calculated from a single measurement.

The standard deviations for lead, zirconium and titanium fall in the ranges: 0.43–0.59%, 0.15–0.35%, and 0.16–0.28% of the element content, respectively, and

are higher than the accuracy of the counts. This is a primarily result of the inhomogeneity of mass per unit area and the errors caused by the dropping of the solutions dropping onto a filter.

Table 7. Results of elements determination in studied samples (n = 5)

Element		Pb(Zr _{0.65} Ti _{0.35})O ₃	Pb(Zr _{0.55} Ti _{0.45})O ₃	Pb(Zr _{0.35} Ti _{0.65})O ₃
Pb	Chemical composition, %	68.03	69.84	66.72
	std, %	0.46	0.43	0.59
Zr	Chemical composition, %	14.04	11.85	8.54
	std, %	0.15	0.35	0.15
Ti	Chemical composition, %	3.68	6.43	9.16
	std, %	0.16	0.28	0.22

CONCLUSIONS

The elaborated method with an analytical weighed amount equal to 25 mg, designed for measurement of 0.5 mg, enables a quick determination of Pb(Zr_xTi_{1-x})O₃ type ferroelectric material, where x ranges from 0.35 to 0.65, for the content of Pb, Zr and Ti. A possibility to transfer the sample to a solution at the specified conditions practically enables using also 0.5 mg analytical weighed amount (microanalysis), placed directly on the substrate, provided that material's homogeneity allows that. The direct use of 0.5 mg amounts in multicomponent XRF analysis of a ferroelectric material encourages investigations connected with the determination of the inhomogeneity of the obtained material also at certain stages of the technological manufacturing process.

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