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Determination of Chemical Composition of (Pb,La)(Zr,Ti)O₃ Type Ferroelectric Ceramics by WD-XRF and ED-EPMA

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The stoichiometry determination of lanthanum doped lead zirconate titanate (PLZT) by the wavelength-dispersive X-ray fluorescence spectrometry (WD-XRF) and energy-dispersive-electron-probe microanalysis (ED-EPMA) is presented. For WD-XRF measurements the analyzed material was mixed with boric acid in the ratio 1:20 and pressed into pellets. The multielement standard samples were prepared by mixing appropriate amounts of analyte oxides (PbO, TiO₂, ZrO₂ and La₂O₃) with boric acid. The obtained results were compared with the analysis of PLZT performed by ED-EPMA. The matrix effects were corrected using theoretical influence algorithm for intermediate-thickness samples (WD-XRF) and ZAF method (ED-EPMA).

Przedstawiono metodę oznaczania stechiometrii tytanianu i cyrkonianu ołowiu domieszkowanego lantanem (PLZT) z wykorzystaniem rentgenowskiej spektrometrii fluorescencyjnej z dyspersją długości fali (WD-XRF) i mikroanalizy rentgenowskiej z dyspersją energii (ED-EPMA). Do pomiarów WD-XRF analizowany materiał był mieszany z kwasem borowym w stosunku 1:20 i prasowany w pastylkę. Wielopierwiastkowe próbki wzorcowe były przygotowane przez zmieszanie odpowiednich ilości tlenków analitów (PbO, TiO₂, ZrO₂ i La₂O₃) z kwasem borowym. Uzyskane rezultaty porównano z wynikami ED-EPMA. Efekty matrycy korygowano za pomocą algorytmu teoretycznych współczynników wpływów dla próbek o grubości pośredniej (WD-XRF) oraz metodą ZAF (ED-EPMA).

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Many ferroelectric ceramic materials such as $(\text{Ba,Sr})\text{TiO}_3$ (BST), $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT), $(\text{Pb,Lu})(\text{Zr,Ti})\text{O}_3$ (PLZT) are already applied in electronics and other branches of technology. Lanthanum doped lead zirconate titanate is a particularly interesting material because of its transparency. The method of PLZT preparation, both the solid-state reaction and the sol-gel method require the use of high temperatures. Because under these conditions oxygen and lead can be lost, the stoichiometry of the final product has to be determined. Various analytical methods are applied for the determination of major and trace elements in ferroelectric ceramics. The analysis of thin BST layers was performed by XRF before chemical dissolution and by inductively coupled mass spectrometry (ICP-MS) after digesting [1, 2]. The authors described the difficulties in stoichiometry determination of these thin layers as a consequence of the inhomogeneous element distribution. Several trace elements were determined in BST layers using ICP-MS after digestion in HNO_3/HF acid mixture. The ICP-MS was also utilized for the determination of traces of uranium and thorium in BST using two step separation technique: leaching and anion-exchange [3]. The PZT and PZT doped with $\text{Pb}(\text{Nb,Mn})\text{O}_3$ and Bi_2O_3 were analyzed using WD-XRF after digesting and pipetting obtained solution onto a substrate [4, 5]. The RMSs ranged from *ca* 1% for major elements to 3% for minor elements when internal standard was used for the minimization of the error resulting from inhomogeneity of the mass per unit area. In the analysis without internal standard, RMSs were slightly higher. The PZT bulk materials can be also analyzed using XRF after fusion with $\text{Li}_2\text{B}_4\text{O}_7$. Then, standard samples can be prepared from oxides of determined elements [6]. For matrix correction Raspberry and Heinrich algorithm was used. The methods which allow performing the analysis of solid materials directly are applied for element distribution and depth profile examination. The wavelength-dispersive X-ray spectrometry (WD-XRF), secondary ion mass spectrometry (SIMS) and sputtered neutral mass spectrometry (SNMS) were used for the analysis of BST dielectric thin films [7]. The thickness and stoichiometry of these materials were determined by WD-XRF (matrix effects were neglected), whereas depth profiles were examined by SIMS and SNMS. The electron-probe microanalysis (EPMA) was used for the analysis of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ ceramic doped with Nb and Fe [8]. The results were calculated from the ZAF and PAP matrix correction programs. Unfortunately, the information about stoichiometry determination of PLZT is rather general and not very detailed. In the previous paper, the authors analyzed PLZT using WD-XRF after collection of the powdered material on the membrane filter and also using inductively coupled plasma optical emission spectrometry (ICP-OES) after digesting [9]. This time the authors present the energy-dispersive-electron-probe microanalysis (ED-EPMA) of PLZT and WD-XRF analysis after pressing powdered material into pellet with boric acid.

EXPERIMENTAL

Wavelength-dispersive X-ray fluorescence spectrometry

A wavelength-dispersive X-ray spectrometer with LiF(200) analyzing crystals was used for the measurements. The molybdenum target X-ray tube was operated at 45 kV. The incidence and take-off angles were 60° and 40°, respectively. The measurements were performed in vacuum with rotation of the sample. Net intensities were determined for each sample by the measurement of the fluorescent radiation of the analyte (peak) and the measurement of the continuum close to the peak. The analytical lines and measurement conditions are given in detail in Table 1.

Table 1. WD-XRF measurements conditions

Analytical line	Wavelength, nm	Two-theta angle	X-ray tube current, mA	Counting time, s	Detector ^a
Pb L _{α1}	0.1175	33.93	14	10	fl + sc
La L _{α1}	0.2665	82.91	50	20	fl
Zr K _α	0.0788	22.55	25	10	fl + sc
Ti K _α	0.2750	86.14	50	20	fl

^a fl – flow-proportional counter, sc – scintillation counter.

The analyzed material was pulverized (in the case of sintered PLZT, the sample was initially crushed) in agate mortar. Then the material was weighed on an analytical balance with an accuracy 0.01 mg in amounts from 300 to 600 mg. In the next step, the analyzed material was mixed with boric acid (in amounts from 6 to 12 g) in agate ball mill during 20 min to obtain a homogeneous mixture. In all cases, the ratio of analyzed material to boric acid was 1:20. Finally, the mixture was pressed (50 MPa) into pellet of 4 cm diameter. The mass per unit area of the samples depended on the quantity of the material available and ranged from 0.5 to 1 g cm⁻².

Multielement standard samples were prepared by mixing appropriate amount of analyte oxide (PbO, TiO₂, ZrO₂ and La₂O₃) with boric acid to obtain a homogeneous mixture and then pressing in the form of pellets of 4 cm diameter. Two series of standards were prepared – one with a wide concentration range: 55–75% PbO, 0–8% La₂O₃, 15–35% ZrO₂, 5–14.5% TiO₂ and the other with a narrow concentration range: 61–66% PbO, 2–6% La₂O₃, 23–25% ZrO₂, 7–10% TiO₂.

Energy-dispersive-electron-probe microanalysis

The microstructure observation and the chemical composition of calcined and sintered PLZT were performed by scanning electron microscopy Hitachi S-4700 and Noran Vantage EDS system. Accelerating voltage was 20 keV; take-off angle 30°; high resolution detector 134 eV; counting time 100 s; analyzing area 50 × 50 μm. L lines were used for Pb, La, Zr determination, K line for Ti.

The powder of calcined PLZTs were spread on an adhesive tape and coated with a conducting carbon film to avoid charging effects. The sintered materials were broken and fracture surface was also coated with a conducting carbon film before the measurements.

RESULTS AND DISCUSSION

Both powder and bulk ferroelectric materials were analyzed. For XRF measurement, the powder ferroelectric ceramics were pressed into pellets with boric acid. In this method, the standard samples can be easily obtained from oxides in the similar way to the analyzed material. In these materials, titanium was determined which emits radiation of the lowest energy among all analyte elements. For Ti K_{α} , depth penetration in high-Z matrix materials (Pb) is very small: in the case of pellets with boric acid 1:20, it is *ca* 170 μm and in the case of „pure” PLZT, it is only *ca* 40 μm . Thus, to obtain accurate results of XRF analysis, the sample must be milled into very fine powder, otherwise particle size effects can be a source of additional error in quantitative analysis. Particle size distribution of the powdered materials was controlled using Laser-Particle-Sizer Analysette 22 (Fritsh, Germany). Analysis shows that 70% of particles have a diameter of up to 20 μm , whereas only 10% of particles have diameters above 40 μm [9]. In the case of ferroelectrics pressed into pellets with boric acid, the surface of the specimen should be representative for the bulk composition. Thus, the repeatability of pressed sample preparation has been tested. The obtained relative standard deviations RSDs characterizing specimen preparation, both for standards and unknown specimens, are satisfactory and they equal to 0.15%, 0.66%, 0.23%, 0.75% for Pb, La, Zr and Ti, respectively. It confirms the composition homogeneity of the specimens after mixing the oxides or analyzed materials, with boric acid. The comparatively high RSDs for lanthanum and titanium result from small contents of these elements in the specimens. Low-absorption dilution with boric acid allows minimizing the matrix effects, both absorption and enhancement. Nevertheless, for obtaining the best results, the matrix correction using theoretical influence coefficients has been performed. The algorithm [10] for intermediate-thickness samples was used because if mass per unit area of the pellet was too small, the specimen was not thick enough for Zr K_{α} radiation.

$$W_i = K_i I_i \left(\frac{a_i}{m} + c_i + \sum \alpha_{ij}^* W_j \right) + B_i$$

where K_i and B_i are calibration constants calculated using least-squares method on the basis of standard samples, W_i and W_j are weight fractions of analyte i and matrix element j , respectively, I_i is net radiation intensity of analyte, m is mass per unit area

of the sample, a_i and c_i are the coefficients dependent on the total mass-attenuation coefficient and the thickness of the specimen (for thick specimen c_i and a_i equal 1 and 0, respectively, and then the influence coefficients do not depend on specimen thickness), α_{ij}^* is the multielement influence coefficient for matrix element j dependent on the full matrix composition and mass per unit area of the specimen:

$$\alpha_{ij}^* = \frac{\alpha_{ij} c_i - S_{ijq} \left(\frac{a_i}{m} + c_i \right)}{1 + \sum_j S_{ijq} W_j}$$

where α_{ij} is the absorption influence coefficient, S_{ijq} is the enhancement term for each line q of the matrix element j , which enhances analyte i .

Table 2 presents residual errors RMS (root of the mean square of the sum of the differences between the measured values and the calculated values) before and after matrix correction for two concentration ranges. The results after the correction of matrix effects are satisfactory taking into consideration the precision of sample preparation and requirements set according to the accuracy of the analysis. In the analysis of unknown samples, the calibration of wide concentration range was used first. If narrow calibration covered the concentration of analytes calculated from wide calibration, this calibration was used next.

Table 2. Values of RMSs before and after matrix correction

Analyte	Concentration range, %	Before correction	After correction	Concentration range, %	Before correction	After correction
PbO	55–75	1.58	0.61	62–68	0.42	0.21
La ₂ O ₃	0–8	0.13	0.095	2–6	0.057	0.044
ZrO ₂	15–35	0.42	0.41	20–25	0.11	0.11
TiO ₂	5–14.5	0.12	0.11	7–10	0.091	0.082

The matrix correction in the electron-probe microanalysis was performed using the classical ZAF method. Table 3 presents exemplary results of WD-XRF and ED-EPMA of two PLZT ceramics. ED-EPMA was performed for one selected area of dimension 50 × 50 μm and the uncertainty intervals presented in Table 3 correspond to one standard deviation of measurement (counting statistic). For WD-XRF analysis three specimens were prepared and three measurements were carried out for

each analyte. Therefore, the uncertainty intervals (one standard deviation) presented for WD-XRF in Table 3 characterize both measurement and sample preparation precision. In general, the results are comparable. Nevertheless, zirconium concentration determined by ED-EPMA is somewhat overestimated in comparison with WD-XRF analysis of both materials, while lead and lanthanum concentration is underestimated for 9/65/35 material. These differences can appear due to calibration, standards used in WD-XRF and ED-EPMA and by matrix correction (uncertainty of the atomic parameters used for calculation of theoretical coefficients and used in ZAF method). Moreover, the uncertainty of the WD-XRF analysis can result from particle size effects, reference and unknown sample preparation. PLZT ceramics were also analyzed after digestion using ICP–OES [9]. The obtained results between WD-XRF and ICP–OES were insignificant. The uncertainty of the ED-EPMA result from measurement precision (the number of counts is much smaller than in WD-XRF) and spectrum evaluation because of low resolution of the solid-state detector *e.g.* overlapping of Ti K_{α} (4.51 keV) and La L_{α} (4.64 keV). The exemplary energy-dispersive X-ray spectrum of PLZT and spectral interferences in ED-EPMA are presented in Figure 1.

Table 3. Analysis of exemplary PLZT in % (m/m)

Material	Analyte	EPMA	WDXRF
6/65/35	PbO	65.0 ± 2.18	66.2 ± 0.17
	La ₂ O ₃	2.51 ± 0.20	2.73 ± 0.021
	ZrO ₂	23.7 ± 0.30	22.4 ± 0.14
	TiO ₂	8.8 ± 0.23	8.9 ± 0.063
9/65/35	PbO	66.2 ± 1.49	68.7 ± 0.20
	La ₂ O ₃	3.59 ± 0.25	4.02 ± 0.018
	ZrO ₂	22.2 ± 0.22	20.1 ± 0.10
	TiO ₂	8.0 ± 0.17	7.8 ± 0.080

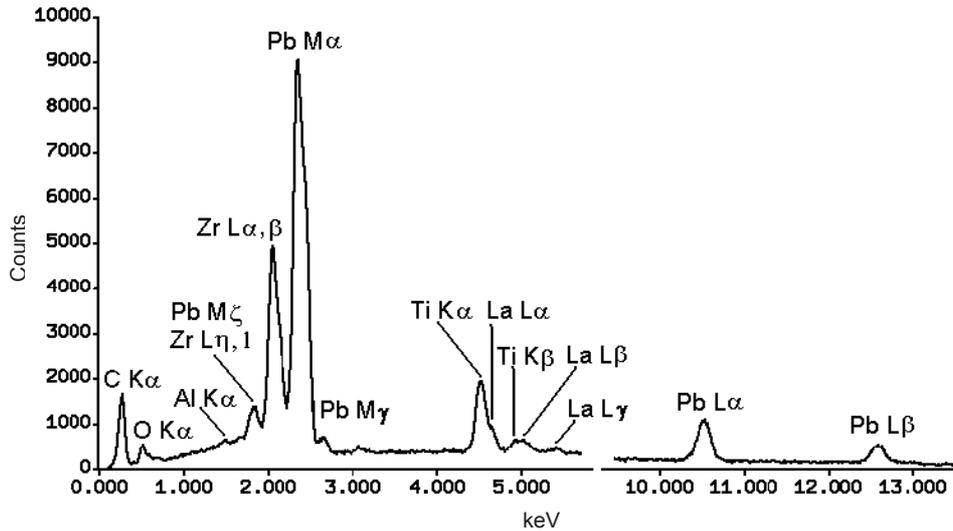


Figure 1. The energy-dispersive X-ray spectrum of PLZT

Much of uncertainty of ED-EPMA can result from the inhomogeneous composition because of small volume of the analyzed material. Table 4 presents results of ED-EPMA of various areas of dimension $50 \times 50 \mu\text{m}$. The differences between results obtained for various areas of 6/65/35 PLZT can be explained by measurement precision and geometric effects. However, for PLZT of assumed stoichiometry of 9/65/35 microheterogeneity is observed. Therefore, the measurements of several areas have to be performed to obtain accurate result of bulk composition. Because analysis was performed in various areas of the samples the standard deviations presented in Table 4 characterize both measurement and inhomogeneity of the material.

Table 4. ED-EPMA of various areas of PLZT. Results in % (m/m)

Material	Analyzed area	PbO	La ₂ O ₃	ZrO ₂	TiO ₂
6/65/35	1	65.0	2.51	23.7	8.8
	2	65.6	2.58	23.6	8.2
	3	66.8	2.12	22.8	8.3
	4	65.6	2.24	23.6	8.7
	5	65.3	2.09	23.9	8.7
	Mean ± SD	65.7 ± 0.69	2.3 ± 0.22	23.5 ± 0.42	8.5 ± 0.27
9/65/35	1	66.2	3.59	22.2	8.0
	2	64.6	4.94	22.8	7.7
	3	70.0	3.65	19.1	7.3
	4	69.0	3.79	19.9	7.4
	5	71.3	3.31	18.1	7.3
	Mean ± SD	68.2 ± 2.75	3.9 ± 0.63	20.4 ± 2.00	7.5 ± 0.32

The electron-probe microanalysis (mean values for five analyzed areas of dimension $50 \times 50 \mu\text{m}$) of sintered 9/65/35 material indicates that the stoichiometry calculated from the determined composition is $\text{Pb}_{0.868}\text{La}_{0.076}\text{Zr}_{0.662}\text{Ti}_{0.348}\text{O}_3$. It is close to theoretical stoichiometry: $\text{Pb}_{0.865}\text{La}_{0.09}\text{Zr}_{0.65}\text{Ti}_{0.35}\text{O}_3$. The difference in the above formulas result from the ED-EPMA accuracy and from the fact that the PLZTs are prepared by means of a solid-state reaction with *ca* 5% excess of Pb because these materials lose lead in high temperatures. Moreover, in these conditions PLZT can lose oxygen. Nevertheless, the oxygen vacancies can be difficult to detect taking into consideration the precision of ED-EPMA results. The final composition of ceramics is rather impossible to predict theoretically. Therefore, quantities of oxides have to be experimentally selected and the composition of the product has to be controlled.

CONCLUSION

RSDs do not exceed 1% (0.2–0.8%) for all elements determined by WD-XRF. The precision of results obtained by ED-EPMA is slightly worse and RSDs are in the range 1–3% for Pb, Zr, Ti, and 5–7% for La. This results mainly from the fact that the counting rates obtained in ED-EPMA are much lower than those observed in WD-XRF method. In general, ED-EPMA and WD-XRF results are comparable taking precision into account (sample preparation, inhomogeneity of the material, counting statistics). Nevertheless, using ED-EPMA, the measurements of several areas have to be performed to obtain accurate result for the bulk composition. If the inhomogeneity of the material is significant, the EPMA results should be very carefully interpreted.

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