DETERMINATION OF THE CHEMICAL COMPOSITION AND HETEROGENEITY RANGE OF HIGHLY DENSE PLZT CERAMICS BY ELECTRON-PROBE MICROANALYSIS

DOLOČANJE KEMIJSKE SESTAVE IN NIVOJA HETEROGENOSTI GOSTE PLZT-KERAMIKE Z ELEKTRONSKO MIKROANALIZO

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Dense, lead-lanthanum-zirconate-titanate $(Pb,La)(Zr,Ti)O_3$ ceramics (PLZT) were prepared by hot isostatic pressing and analyzed in an electron-probe microanalyzer. The chemical composition of the PLZT material was measured using wavelength-dispersive X-ray spectroscopy (WDXS) with an improved analytical sensitivity and accuracy. Quantitative WDXS analysis was performed for all cations as well as for oxygen, using appropriate standards. Results showed that the composition of the sintered PLZT sample is close to the nominal starting composition. A statistical analysis of the X-ray data from the heterogeneity measurements confirmed the minimal extent of the heterogeneity for the measured cations Pb, La, Zr and Ti (below 1 % relative) over the entire surface of this PLZT sample. The sample is compositionally homogeneous within the usually accepted criteria of 95% confidence limits, and can be used as a reference material for the analysis of other PLZT materials and related compounds.

Key words: electron-probe microanalysis, WDXS, PLZT ceramics

Gosto $(Pb,La)(Zr,Ti)O_3$-keramiko(PLZT), ki je bila pripravljena z vročim izostatskim stiskanjem, smo analizirali z elektronskim mikroanalizatorjem. Kemijsko sestavo materiala smo določili z valovno disperzijsko spektroskopijo rentgenskih žarkov (WDXS). S kvantitativno WDXS-analizo in ustreznimi standardi smo določili koncentracije kationov Pb, La, Zr in Ti kot tudi koncentracijo kisika. Rezultati so pokazali, da sestava sintranega PLZT-vzorca ustreza začetni sestavi vzorca. Meritve heterogenosti PLZT-vzorca so pokazale minimalne variacije sestave s standardno deviacijo manj kot 1 % za vse analizirane katione: Pb, La, Zr in Ti. V intervalu 95-odstotne statistične gotovosti je analizirani PLZT-vzorec po sestavi homogen in ga lahko uporabimo kot referenčni material za kvantitativno analizo drugih PLZT in podobnih materialov.

Ključne besede: elektronska mikroanaliza, WDXS, PLZT-keramika

1 INTRODUCTION

Lead-lanthanum-zirconate-titanate (PLZT) ceramics, or $(Pb,La)(Zr,Ti)O_3$ solid solutions have been studied as high-performance ferroelectric materials for electro-optical applications, non-volatile memories and actuators, as well as for high-speed electrophoretic printing, utilizing their memory effect [1,2]. Such applications generally require dense, homogeneous material with a well-defined chemical composition. However, elemental concentrations in sintered PLZT ceramics can often vary from the nominal ones as a consequence of the preparation process.

Electron-probe microanalysis (EPMA) with energy-dispersive X-ray spectroscopy (EDXS) and/or wavelength-dispersive X-ray spectroscopy (WDXS) can be used to determine the chemical composition of various PLZT (PZT) materials [3]. For the case of PLZT material, quantitative EDXS analysis is not accurate enough because of the partial overlap of the ZrL with the PbM spectral lines and the TiK with the LaL spectral lines in the EDX spectra. In addition, low elemental concentrations of Ti and La in the material (< 5 wt%) reduce the accuracy of the EDXS method. In contrast, a WDXS analysis with appropriate standards and precisely adjusted experimental conditions can be used for a more accurate quantitative elemental analysis of PLZT. In this work the composition of highly dense, optically transparent, PLZT bulk material was determined by WDXS. EPMA heterogeneity tests were performed to evaluate the compositional homogeneity of the material and its suitability as a useful reference material for the analysis of other PLZT and related compounds.

2 EXPERIMENTAL

Dense PLZT ceramics were prepared by a complex solid-state synthesis and hot-isostatic pressing from the mixed constituent oxides according to the formula $Pb_{1-3x/2}La_xZr_{0.65}Ti_{0.35}O_3$ ($x = 0.08$) [4]. After removing the edges of the raw sintered material (a cylinder of about 80 mm in diameter and 40-mm high), the bulk specimen

was sliced parallel to the diameter into disks of 75 mm in diameter and 0.5-mm thick. After polishing on both sides, these disks were optically transparent. Because of the large size of such samples, a single disk was prepared for microanalysis. The polished surface of the PLZT disk was evaporated with carbon in a Cressington 208 Carbon Coater in a turbo-pumped vacuum of $2 \cdot 10^{-3}$ Pa, with rotating specimen substrate (2 rotations per second), 160-mm distance between the carbon source and the specimen surface, no tilting of the specimen and with a 2.5 s evaporation time. Under these conditions an uniform carbon film of 22 ± 1 nm thickness was evaporated onto the specimen to ensure the electrical conductivity of the whole disk surface in the EPMA. The standards for microanalysis were evaporated with carbon together with the specimen.

The PLZT disk was analyzed in a JEOL Superprobe JXA 8600 electron-probe microanalyzer equipped with five wavelength spectrometers. The X-ray intensities for the $PbM\alpha_1$, $LaL\alpha_1$, $TiK\alpha_1$, $ZrL\alpha_1$ and $OK\alpha$ spectral lines for the quantitative analysis were measured at a 15-kV accelerating voltage, a 100-nA beam current, a 40° take-off angle and a focused point beam. A PET crystal was used for Pb, Zr, La, and Ti whereas a LDE1 synthetic multilayer was used for O. The experimental settings for the pulse-height analyzers and the pro-portional X-ray counters were carefully optimized to achieve high peak-to-background ratios and to increase the analytical sensitivity for the analyzed elements. The counting times were set to ensure a relative standard counting deviation σ_c^{rel} below 0.5 % ($\sigma_c^{rel} = [\sqrt{N}/N] \times 100$, N-number of counts). The standards were PbSe and K-456 glass for Pb, $La_2Ti_2O_7$ for La and Ti, pure Zr and SiO_2 for O. The composition of the sample was determined from measured elemental k-ratios using the ZAF and $\Phi(\rho z)$ matrix-correction methods [5].

The heterogeneity of the PLZT disk was tested for cations (Pb, Zr, Ti, La) using fixed WD spectrometers at a 25-kV accelerating voltage, a 100-nA beam current, a 20-s counting time and a point beam. $TiK\alpha_1$, $LaL\alpha_1$ and $ZrL\alpha_1$ were analyzed on a PET crystal, $PbL\alpha_1$ was analyzed on a LiF crystal. Micro-step heterogeneity tests were performed using eight pairs of line profiles normal to each other from 8 different locations on the disk. For every line profile, x-ray counts from 50 points with a 2-μm step were collected. With such a setup, measurements were made in the grains as well as across the grain boundaries. Since the PLZT specimen was 75 mm in diameter, a macro-pattern was defined to do tests on the whole surface of the specimen. The disk was masked into 44 squares of approximately 9.3x9.3-mm each, excluding partial squares near the edge of the disk. In each square the center point and three additional random points were tested, recording the x-ray counts from each point three times. The positions of the experimental points for both the quantitative analysis and the heterogeneity tests are shown in **figure 1**.

Heterogeneity data consisted of 800 point measurements from micro-step line-profile tests and 528 point measurements from a macro-pattern test, with four elements measured in every point. Data were taken over a period of two days. X-ray intensities were corrected for any changes in beam current. The data were evaluated statistically with the usually accepted 95% confidence limits of $N \pm 3\sigma_c$ to estimate the variations in elemental concentrations [3].

3 RESULTS AND DISCUSSION

An electron micrograph of the PLZT material (**figure 2**) reveals a dense, polycrystalline microstructure consisting of grains 5 to 20 μm in size. The gray level differences are due to a random crystallographic orientation of the individual grains. No secondary phases were observed in the grains and/or at the grain boundaries.

Quantitative analysis of the PLZT disk was performed at 20 points (see **figure 1**). The results are presented in **table 1**. A comparison of the quantitative matrix-correction procedures showed that the best analytical results are obtained using $\Phi(\rho z)$ methods, where the non-normalized analytical totals are close to 100%. The conventional ZAF method gave systema-tically higher analytical totals (up to 104 %), which is the consequence of the insufficient absorption correction within the ZAF calculations. The mathematical
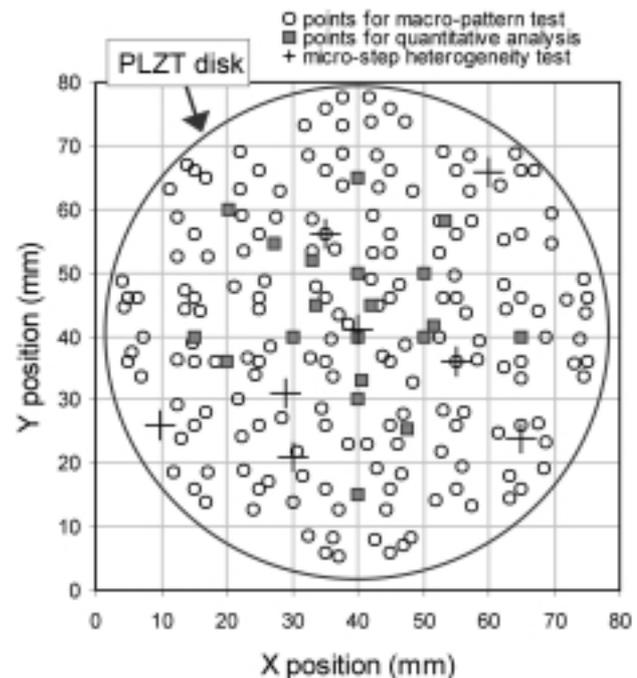
Figure 1: Chart illustrates the strategy for the positions of experimental points on the PLZT disk for the quantitative analysis and heterogeneity tests
Slika 1: Risba ponazarja način postavitve eksperimentalnih točk na PLZT-disku za kvantitativno analizo in preskus heterogenosti
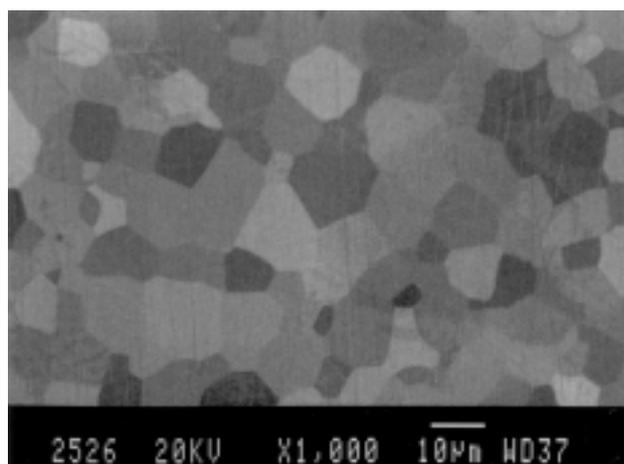
Figure 2: Backscattered electron micrograph of the microstructure of PLZT sample

Slika 2: Slika mikrostrukture PLZT-vzorca, ki je bila narejena s povratno sipanimi elektroni

normalization of the ZAF results was done assuming that the error (4 %) is distributed between the analyzed elements relative to their concentrations. This assumption is generally not completely correct; however, normalization helps in the cases where analytical totals differ slightly from 100 %. The normalized ZAF results were comparable to those obtained with the $\Phi(\rho z)$ method.

The uncertainity expressed by the relative standard deviation of 20 measurements is below 1 % for Pb, Zr, La and O, and around 1.10 % for Ti. The achieved analytical sensitivity was quite high, with minimum

detectability limits for the analyzed elements of 0.066 wt% for Pb, 0.032 wt% for Zr, 0.040 wt% for La, 0.038 wt% for Ti and 0.040 wt% for O [6]. Taking into account the experimental uncertainity and the errors, which are the consequence of matrix-correction calculations, the measured elemental concentrations agree well with the expected ones from the nominal formula $Pb_{1-3x/2}La_xZr_{0.65}Ti_{0.35}O_3$ (x=0.08). The slight difference from the nominal composition of the PLZT solid solution after sintering is possible as a consequence of material loss during the sintering process. In addition, small local variations of the elemental concentrations between the polycrystalline grains in the material cannot be excluded.

Data from the micro-step heterogeneity tests were collected from 16 line profiles for each element. The concentration trends for the Pb, Zr, La and Ti were studied by plotting the corresponding X-ray intensities, corrected for beam-current drift, versus the distance of the line profile for each element (**figure 3 - a,b,c,d**). The data for Ti showed the largest scattering. Considering the high X-ray intensities measured for Ti, about 191000 cts, and that the Ti concentration in the material is only 5 wt%, this scattering may occur as a result of X-ray counting error as well as because of small compositional variations in the material. The data for Pb, Zr and La fall mostly within the interval of $N \pm 3\sigma_c$. No significant difference in the X-ray data collected within the PLZT grains and at the grain boundaries suggests that the PLZT material is a single-phase solid solution with little heterogeneity on the micrometer level.

The results from the macro-pattern heterogeneity test are shown in **figure 4 – a,b,c,d**. Measured X-ray

Table 1: Results of quantitative WDXS analysis of PLZT disk - average from 20 measurements

Tabela 1: Rezultati kvantitativne WDXS-analize PLZT-diska - povprečje 20 meritev

| matrix correction procedure	PLZT disk	elemental concentrations in weight %					
		Pb	Zr	La	Ti	O	total
$\phi(\rho z)$ Armstrong	average	**57.59**	**19.07**	**3.62**	**5.19**	**14.80**	100.27
	σ (±)	0.33	0.16	0.03	0.06	0.08	0.37
	σ_r (%)	0.58	0.87	0.73	1.07	0.57	0.36
	normalized	**57.44**	**19.02**	**3.61**	**5.18**	**14.76**	100
$\phi(\rho z)$ Bastin	average	58.44	19.24	3.54	5.00	14.56	100.76
	σ (±)	0.32	0.17	0.03	0.05	0.08	0.35
	σ_r (%)	0.54	0.86	0.75	1.07	0.57	0.34
	normalized	**58.00**	**19.09**	**3.51**	**4.95**	**14.45**	100
ZAF conventional	average	59.89	19.26	3.64	5.21	15.89	103.89
	σ (±)	0.33	0.17	0.03	0.06	0.09	0.35
	σ_r (%)	0.55	0.86	0.74	1.07	0.55	0.34
	normalized	**57.65**	**18.54**	**3.50**	**5.01**	**15.30**	100
composition proposed by nominal formula		**57.47**	**18.69**	**3.50**	**5.21**	**15.13**	100

σ - standard deviation of twenty measurements

σ_r - relative standard deviation
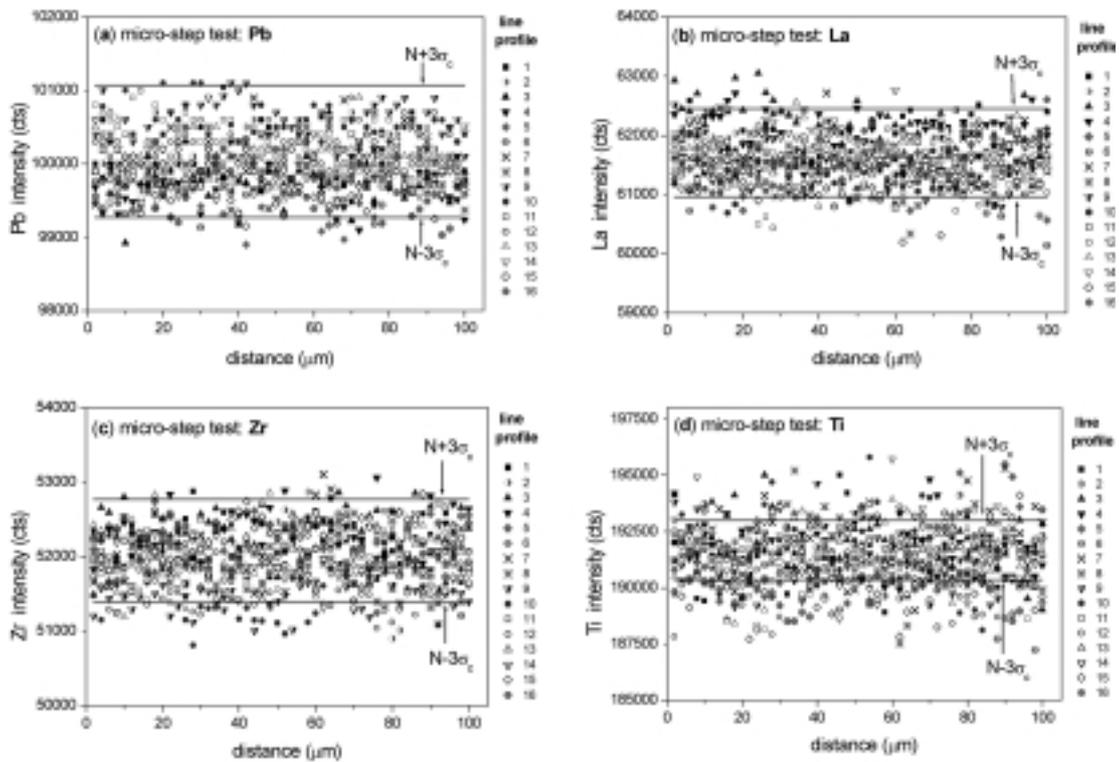
Figure 3: Line-profile micro-step heterogeneity tests for Pb (a), La (b), Zr (c) and Ti (d). Lines representing the $N \pm 3\sigma_c$ values correspond to the 95% confidence limits.

Slika 3: Linijski profili za mikropreskus heterogenosti za Pb (a), La (b), Zr (c) in Ti (d). Linije, ki pomenijo vrednosti $N \pm 3\sigma_c$, ustrezajo intervalu 95-odstotne statistične gotovosti.
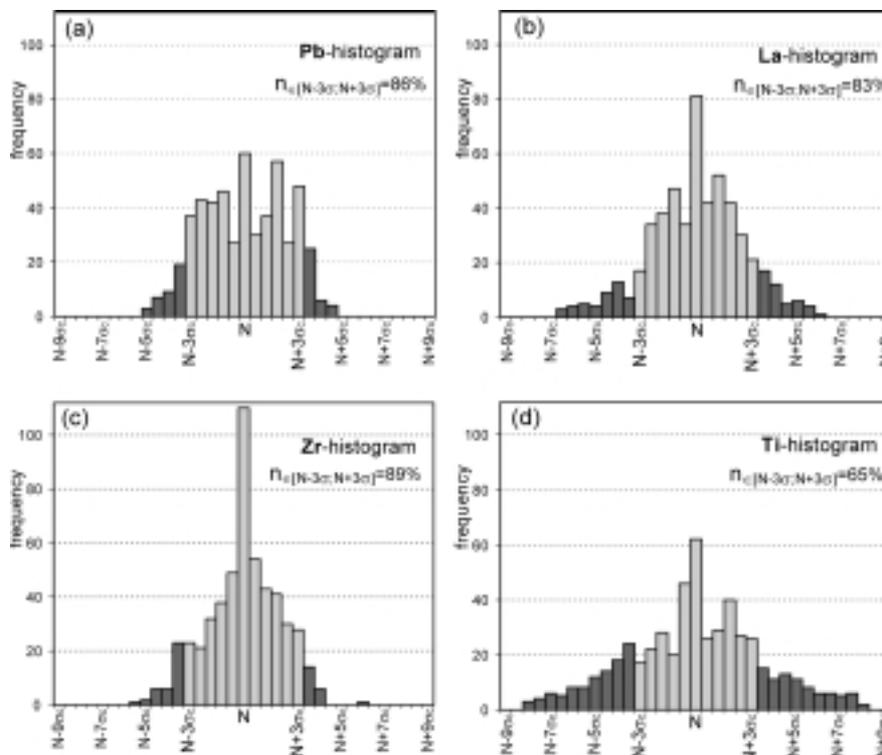
Figure 4: Histograms show the distribution of the macro-pattern heterogeneity test results for Pb (a), La (b), Zr (c) and Ti (d). Light-grey bars correspond to the fraction of data $\mathbf{n}_{\in [N-3\sigma, \, N+3\sigma]}$, which fall within the $N \pm 3\sigma_c$ interval.

Slika 4: Histogrami porazdelitve rezultatov preskusa heterogenosti iz makrovzorca za Pb (a), La (b), Zr (c) in Ti (d). Svetlo sivi pravokotniki pomenijo delež podatkov $\mathbf{n}_{\in [N-3\sigma, \, N+3\sigma]}$, ki so v intervalu $N \pm 3\sigma_c$.

Table 2: Results of macro-pattern heterogeneity test of the PLZT disk
Tabela 2: Rezultati preskusa heterogenosti PLZT-diska iz makrovzorca

macro-pattern test	Pb	Ti	La	Zr
n	528	528	528	528
$n_{\pm 3\sigma}$	454	343	438	469
$P = (n_{\pm 3\sigma}/n) \times 100$	86 %	65 %	83 %	89 %
N_{ave} (cts)	99402	190833	61469	51886
σ_c^{rel}	0.32 %	0.23 %	0.40 %	0.44 %
$\sigma_r^{\mathrm{total}}$	0.68 %	0.76 %	0.92 %	0.82 %

n - number of measurements
$n_{\pm 3\sigma}$ - number of measurements within the interval (N+3σ_c, N-3σ_c)
p - fraction of $n_{\pm 3\sigma}$ in percents
N_{ave} - average number of counts
σ_c^{rel} - relative counting error
$\sigma_r^{\mathrm{total}}$ - relative standard deviation of n-measurements

intensities for Pb, La, Zr and Ti were plotted in the form of histograms showing the distributions of data versus multiple σ_c deviation from the average intensity N. Some data fall outside the $N \pm 3\sigma_c$ interval, indicating the presence of a certain amount of heterogeneity in the PLZT sample. As in the case of the micro-step test, the largest scattering occured for the Ti data. A summary of the macro-pattern test results and a statistical evaluation is given in **table 2**. The relative standard deviation for the population of 528 measurements is below 1% for all cations. These results confirmed the minimal extent of the heterogenity for the analyzed elements over the entire surface of the PLZT disk.

4 CONCLUSIONS

An electron probe WDXS microanalysis was undertaken to determine the composition of dense PLZT ceramics. The achieved analytical sensitivity allowed very accurate quantitative analysis for all cations and oxygen, with a relative uncertainity $\leq$ 1%. Such results verified the correctness of the whole analytical approach. The comparision of quantitative matrix-correction procedures showed that modern $\Phi(\rho z)$ methods give the best results and should be used instead of the classical ZAF

approach. The choice of standards for microanalysis has to be carefully considered - the use of appropriate standards can improve the accuracy of the analysis. Heterogeneity tests on the micro- and macro-level revealed little heterogeneity in the composition of the PLZT solid solution. However, these variations in elemental composition are still under 1% of the relative standard deviation. The largest part of the heterogeneity results fall within the usually accepted homogeneity criteria of 95% confidence limits. Within this criteria the analyzed dense PLZT material can be accepted as compositionally homogeneous and can be used as an internal reference material for the analysis of other PLZT materials and related compounds.

5 REFERENCES

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