Kovine, zlitine, tehnologije, 31, 1997, 1-2, 63-67

# Electron Probe Microanalysis in Materials Characterization

## Karakterizacija materialov z metodami elektronske mikroanalize

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Prejem rokopisa - received: 1996-10-04; sprejem za objavo - accepted for publication: 1996-11-22

*Energy dispersive (EDS) and wavelength dispersive (WDS) X-ray spectroscopy as electron probe microanalytical (EPMA) techniques, are used for the determination of chemical composition of solid materials. EDS is suitable for fast qualitative and quantitative analysis. It has however limited sensitivity in quantitation. WDS quantitative analysis, with appropriate reference standards, has better sensitivity and accuracy. WDS procedure is especially suitable for quantitative analysis of elements which overlap in the EDS spectra, in the case of low elemental concentrations in the samples, and for analysis of light elements. In general, quantitative analysis with both EDS and WDS is performed on the micro-level where the analyzed volume of the material is about 1 $\mu m^3$. Results of the analyses of selected lead glass samples, $BaTiO_3$ - doped ceramics, and ALNICO magnets are presented and discussed.*

*Key words: electron probe microanalysis*

*Energijsko disperzijsko spektroskopijo (EDS) in valovno disperzijsko spektroskopijo (WDS) rentgenskih žarkov smo uporabili kot tehnike elektronske mikroanalize (EPMA) za določanje kemijske sestave materialov. EDS je primerna za hitro kvalitativno in kvantitativno analizo, ima pa omejeno občutljivost pri kvantitativni analizi. WDS kvantitativna analiza z uporabo referenčnih standardov ima višjo občutljivost in natančnost. WDS je posebej primerna za kvantitativno analizo elementov, ki jih ne moremo ločiti v EDS spektrih zaradi prekrivanja, v primeru elementov nizkih koncentracij in za analizo lahkih elementov. Kvantitativno analizo z EDS ali WDS naredimo na področju velikosti nekaj mikronov. Pri tem analiziramo približno 1 $\mu m^3$ materiala. V prispevku poročamo o rezultatih analiz izbranih vzorcev stekla, dopirane $BaTiO_3$ keramike ter ALNICO magnetov.*

*Ključne besede: elektronska mikroanaliza*

### 1 Introduction

Electron probe microanalysis (EPMA) deals with the analysis of characteristic X-rays, emited from the region of the solid material where the electron beam impinges. The analysis yields compositional information of both qualitative and quantitative nature. X-ray spectral measurement can be performed by energy dispersive spectroscopy (EDS) with solid state Si(Li) detector or by wavelentgh dispersive spectroscopy (WDS) with crystal spectrometers. In modern commercial instruments EDS and WDS are integrated with the scanning electron microscope (SEM). This combination allows to obtain SEM micrographs of samples which contain topographic and compositional informations and to perform chemical analysis (EDS or WDS) in selected regions by measuring the energy and intensity distribution of the X-rays. EPMA is integrated with modern computers and software support for all data acquisition and manipulation, including digital image processing, qualitatitive and quantitative elemental analysis, automatization of the measurements, etc.. The major advantage of EPMA techniques is the possibility to carry out chemical analysis on a micrometer scale. The analyzed volume (about 1 $\mu m^3$) contains small amount of material, typically in order of $10^{-10}$ - $10^{-11}$ g.

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Nowdays these techniques are not restricted to basic scientific research but also common in laboratories devoted to the development of "high-tech" products, quality control in production, failure analysis, enviromental care, etc. In the Ceramics department of the "Jožef Stefan" Institute SEM, EDS, and WDS techniques are used for the characterization of different materials including ceramics, metals, alloys, composites, polymers, thin films, glasses, etc. A short list of the EPMA capabilities is shown in **Table 1**.

This paper reports on the results of applied EPMA methods using examples of analysis of lead glass, $BaTiO_3$ based ceramics, and ALNICO magnets.

### 2 Experimental

In general it is required that samples for EPMA analysis are flat, polished and electroconductive[1]. An exception is the SEM examination of rough surfaces, fractures, etched samples and particles where the information is focused on topography and microstructure. Standard metallographic techniques are usually applied for sample preparation. Non-conductive ceramic and glass samples are coated with a thin film of carbon or metal to prevent charging. Samples for elemental analysis (EDS, WDS) were coated with carbon to reduce absorption of the emitted X-rays.

Preliminary investigations of the samples by SEM-EDS is usually recommended to specify the microanalytical problem, as far as possible, with regard to the fol-

**Table 1:** List of SEM-EPMA methods applied for materials characterization
**Tabela 1:** Pregled SEM-EPMA metod za karakterizacijo materialov

| SEM | EDS analysis | | WDS analysis |
|---|---|---|---|
| microstructure, grain size | qualitative: | quantitative: | qualitative: X-ray maps |
| topography | element identification | standardless | qualitative: line profile |
| compositional images | | with standards | quantitative with standards |
| particle size, morphology | line profile | ZAF, PRZ | quantitative: line analysis |
| image analysis | X-ray maps | corrections | ZAF, PROZA corrections |

lowing application of more sophisticated techniques, such as WDS. A JEOL JXA 840A electron probe microanalyzer equipped with EDS, two WD spectrometers and Tracor Series II X-Ray Microanalysis System was used for overall analysis of the samples.

## 3 Results and discussion

### *3.1 Defects in lead glass*

The aim of work was SEM examination and EDS qualitative and quantitative analysis of defects in lead glass. SEM micrographs of the defects in lead glass were recorded using both secondary (SE) and backscattered (BSE) electrons, emphasizing the Z-contrast of different phases present in the sample. A micrograph displaying a defect is shown in **figure 1**. The right side of the micrograph is recorded at a higher magnification showing the presence of four phases, which are marked as A, B, C, and D, respectively. Phases in the region containing defects differ in gray-level contrast. EDS analyses of the matrix M and phases A, B, C, and D were done at 15 keV, 0,5 nA, take off angle 40°, and acquisition time 100 s. EDS spectra were quantified using PRZ matrix correction programs[2]. Both standardless and analysis using oxide standards were performed. Calculated quantitative results for unknown oxide compounds are given in **Table 2**.

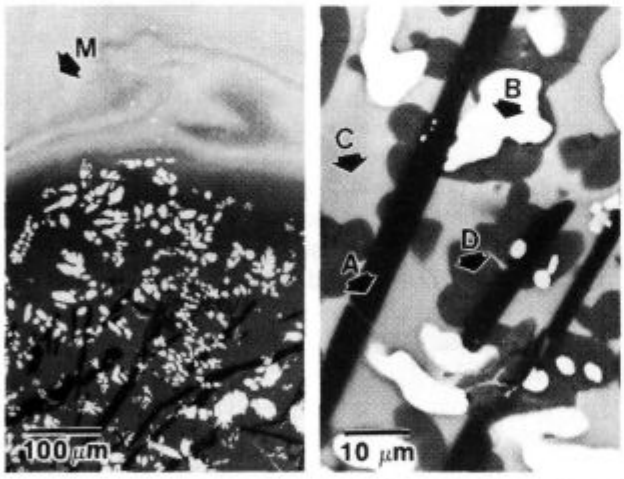


**Figure 1:** Combined SE/BSE electron micrograph of the defects in lead glass: M - glass matrix; A, B, C, D: glass defect phases
**Slika 1:** Posnetek SEM (s sekundarnimi in odbitimi elektroni) defektov v svinčevem steklu: M - matrica stekla; A, B, C, D: faze prisotne v področju defekta

When analyzing alkaline glass matrices containing Na and K one should take into account possible migration of alkaline ions, induced by the electron beam during microanalysis. Experimental parameters for EDS spectra acquisition should be carefully determined in order to minimize this migration and to obtain reasonable analytical results. The stability of the standards and sample material under the electron beam could often be different, and may cause problems in the quantitative analysis with standards. These problems are avoided in the standardless procedure. The comparison of quantitative results shows quite satisfactory standardless analysis. In the case of well-defined EDS spectral peaks, without spectral interference, good analytical precision was achieved with r.m.s. (root mean square) errors for calculated element concentrations up to 5%[3].

The presence of $Al_2O_3$ (phase A) and $ZrO_2$ (phase B) inclusions in the glass a due to the erosion of furnace refractory material. Phases C and D were formed by the reaction of the aggressive alkaline glass melt with pieces of refractories. These glassy phases differ in the concentrations of $Na_2O$, $ZrO_2$, PbO, and $K_2O$, whereas the $Al_2O_3$ and $SiO_2$ content remains practically the same.

**Table 2:** Average results of quantitative EDS analysis of glass and defects (oxides, wt%)
**Tabela 2:** Rezultati EDS kvantitativne analize stekla in defektov (oksidi, mas.%)

| | $Na_2O$ | | $Al_2O_3$ | | $SiO_2$ | | $ZrO_2$ | | PbO | | $K_2O$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PHASE | I | II | I | II | I | II | I | II | I | II | I | II |
| matrix M | 3,2 | 3,1 | - | - | 59,7 | 58,8 | - | - | 28,4 | 27,9 | 8,7 | 10,2 |
| A | - | - | 100 | 100 | - | - | - | - | - | - | - | - |
| B | - | - | - | - | - | - | 100 | 100 | - | - | - | - |
| C | 5,4 | 5,4 | 32,1 | 32,4 | 33,1 | 33,2 | 1,2 | 1,4 | 18,0 | 17,9 | 10,2 | 9,7 |
| D | 3,4 | 3,2 | 32,3 | 32,4 | 32,5 | 33,0 | 4,2 | 4,3 | 7,5 | 7,4 | 20,2 | 19,7 |

I - standardless analysis, II - analysis with standards

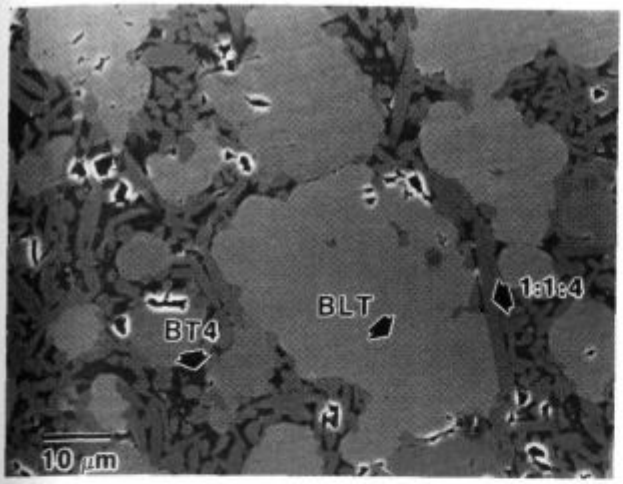


**Figure 2:** BSE electron micrograph of La-doped $BaTiO_3$; phase marks: 1:1:4 - $BaLa_2Ti_4O_{12}$ lamellae, BT4 - polytitanate $BaTi_4O_9$, BLT - La-doped $BaTiO_3$ grains

**Slika 2:** Slika odbitih elektronov mikrostrukture keramike $BaTiO_3$ dopirane z La; oznake faz: 1:1:4 - lamele $BaLa_2Ti_4O_{12}$, BT4 - polititanat $BaTi_4O_9$, BLT - zrna $BaTiO_3$ dopirana z La

### *3.2 La-doped $BaTiO_3$ ceramics*

The microstructure and grain size of a La-doped $BaTiO_3$ sample is shown in **figure 2**. It is important that the size of the analyzed phase is quite large (minimum 5-10 µm of average diameter) in order to avoid the generation of X-rays from adjacent phases. Because of peak overlapping of the most intense Ba, Ti, and La spectral lines in the EDS spectrum, quantitative analysis based on EDS (resolution 150 eV) is not possible. The better resolution of the WD spectrometer (5-10 eV) allows analysis of the $BaL\alpha_1$, $TiK\alpha_1$, and $LaL\alpha_1$ lines without spectral interference. Furthermore, higher X-ray collection efficiency and better analytical sensitivity improve the accuracy of quantitative analysis[4].

WDS analyses were performed on ten La-doped $BaTiO_3$ grains using a PET crystal, at 20 keV, 10 nA, and 40° take off angle. Measured X-ray intensities in the samples were transformed into k-ratios relative to calibrated X-ray intensities from the $BaTiO_3$ and $La_2Ti_2O_7$ standards. Quantitative analysis was performed through the ZAF matrix correction procedure, transforming the measured k-ratios into element concentrations. The printout of WDS-ZAF results for measurement performed on one point of sample 2 is given in **Table 3**.

**Table 3:** Printout of the results of quantitative WDS-ZAF analysis
**Tabela 3:** Izpis rezultatov kvantitativne WDS-ZAF analize

| element | wt% | norm wt% | at% | oxides | wt% | norm wt% |
|---|---|---|---|---|---|---|
| Ba | 47,73 | 47,77 | 16,20 | BaO | 53,30 | 53,38 |
| Ti | 19,74 | 19,76 | 19,22 | $TiO_2$ | 32,93 | 32,98 |
| La | 11,62 | 11,63 | 3,90 | $La_2O_3$ | 13,62 | 13,64 |
| O* | 20,83 | 20,84 | 60,68 | total | 99,85 | 100,00 |
| total | 99,92 | 100,00 | 100,00 | *by difference | | |

An unnormalized analytical total of 99.85% for oxide wt%, indicates a very good result (totals between 99 in 101% are treated as good analytical results[1]) of the applied microanalytical method. In **Table 4** the average results, of measurements of cation concentrations, in three La-doped $BaTiO_3$ samples are presented. Oxygen content was calculated by difference, which is the usual approach in the analyses of oxide compounds. Data were calculated to the perovskite $ABO_3$ formula taking into account that $La^{3+}$ substitutes on $Ba^{2+}$ sites with the formation of Ti-site vacancies[5].

**Table 4:** WDS results for La-doped $BaTiO_3$ samples
**Tabela 4:** Rezultati WDS mikroanalize vzorcev La-dopiranega $BaTiO_3$

| | Composition of La-doped $BaTiO_3$ phase: $Ba_{1-x}La_xTi_{1-x/4}(V_{Ti})''''_{x/4}O_3$ | | | |
|---|---|---|---|---|
| Sample | Ba (at%) | La (at%) | Ti (at%) | X (mol% La) |
| 1 | 17,35 ± 0,28 | 2,53 ± 0,04 | 19,43 ± 0,25 | 13 |
| 2 | 16,24 ± 0,20 | 3,97 ± 0,04 | 19,58 ± 0,25 | 20 |
| 3 | 14,69 ± 0,23 | 5,84 ± 0,09 | 18,63 ± 0,24 | 28 |

The quoted standard deviations are related to data measured on the various analyzed grains, in the samples, with r.m.s. errors for calculated element concentrations between 1-2%. As an illustration of the achieved analytical precision the La-doped $BaTiO_3$ sample 3 can be considered as an example. The starting composition of the sample was expressed by the formula $Ba_{0.715}La_{0.285}Ti_{0.928}(V_{Ti})''''O_3$. The sintered sample was monophase material and the calculated formula based on the results of WDS microanalysis was $Ba_{0.715}La_{0.285}Ti_{0.907}(V_{Ti})''''O_3$.

The results allow the determination of solid solubility and investigation of the mode of dopant incorporation in $BaTiO_3$. The basic advantages of WDS microanalysis are direct analysis of phases of interest in the chosen samples and quantitative analysis with improved analytical sensitivity and precision.

### *3.3 ALNICO magnets*

ALNICO magnets were analyzed. SEM examination of a polished cross section of the sample reveals the presence of inclusions in the matrix and defects on the surface. The matrix composition was determined by quantitative EDS standardless analysis using five different points along the matrix. Results are given in **Table 5**. Good reproducibility of the quantitative results was obtained for major constituents of the matrix (Al, Ni, Co, and Fe) with r.m.s. errors between 1,5% and 3%. Ti, Cu, and Nb are present in lower concentrations consequently increasing r.m.s. error from 7% (Ti) to 15% (Cu), due to poor X-ray counting statistics and possible variation in element concentrations from point to point. Nevertheless, results affirmed the use of EDS standardless analysis as a fast method to determine the elemental composition of the sample.

**Table 5:** Results of EDS quantitative analysis: composition of ALNICO matrix
**Tabela 5:** Rezultati kvantitativne analize EDS: sestava matrice ALNICO

| Point | Al(wt%) | Ni(wt%) | Co(wt%) | Fe(wt%) | Cu(wt%) | Ti(wt%) | Nb(wt%) |
|---|---|---|---|---|---|---|---|
| 1 | 8,1 | 14,9 | 35,1 | 33,0 | 1,9 | 5,9 | 1,1 |
| 2 | 8,1 | 14,5 | 35,9 | 33,2 | 1,4 | 5,9 | 0,9 |
| 3 | 7,8 | 15,7 | 34,9 | 33,4 | 2,0 | 5,2 | 1,1 |
| 4 | 7,7 | 15,0 | 35,6 | 32,9 | 2,2 | 5,6 | 1,0 |
| 5 | 8,3 | 15,8 | 36,3 | 32,0 | 1,5 | 5,0 | 1,1 |
| average | 8,0±0,2 | 15,2±0,5 | 35,6±0,5 | 32,9±0,5 | 1,8±0,3 | 5,5±0,4 | 1,0±0,1 |

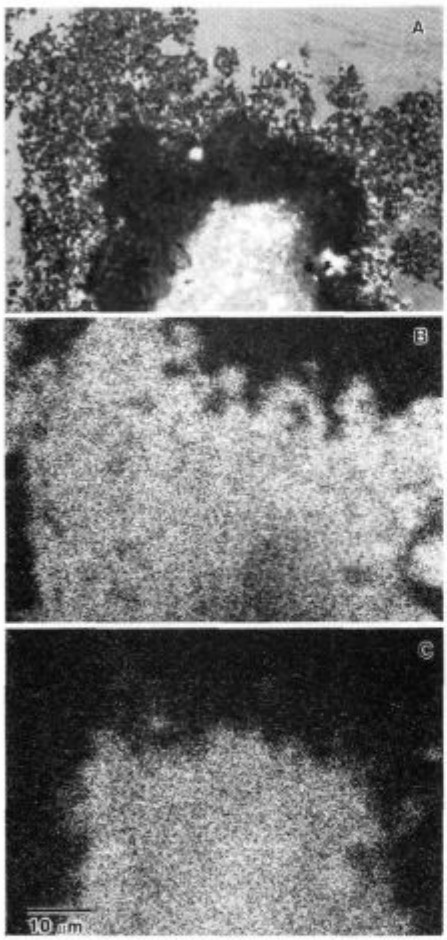


**Figure 3:** Defect near the surface of ALNICO magnet: (A) SEM micrograph, (B) X-ray dot map for Ti, (C) X-ray dot map for O
**Slika 3:** Defekt pri površini ALNICO magneta: (A) posnetek SEM, (B) slika porazdelitve titana, (C) slika porazdelitve kisika

Defects were analyzed qualitatively by WDS X-ray mapping. X-ray maps are generally used to show the distribution of a particular element on a selected area of sample. A SEM micrograph and the corresponding X-ray maps, of the defect, near the surface of the magnet are shown in **figure 3**. Surface defects contain Ti and O and were identified as titanium oxide layer on the sample surface. Oxygen is present only near the surface whereas titanium is distributed over a wider area inside the matrix, in form of titanium-carbides and/or titanium-carbo-

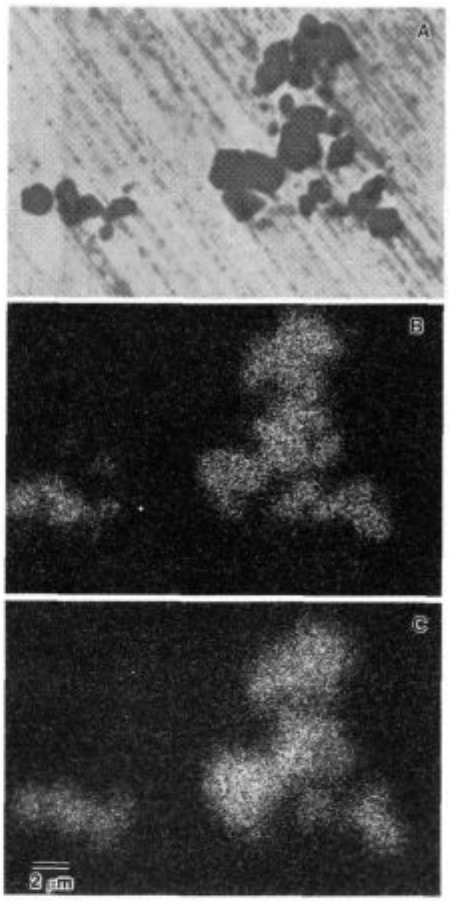


**Figure 4:** Inclusions in ALNICO matrix: (A) SEM micrograph, (B) X-ray dot map for Ti, (C) X-ray dot map for C
**Slika 4:** Vključki v ALNICO matrici: (A) posnetek SEM, (B) slika porazdelitve titana, (C) slika porazdelitve ogljika

nitrides. The presence of C and N was confirmed by WDS mapping. Similar analysis was performed for defects-inclusions which are found in the ALNICO matrix (**figure 4**). X-ray maps reveal the presence of Ti and C in inclusions. These defects were identified as titanium carbides.

Results of EPMA analysis of ALNICO magnets showed a regular composition of the matrix and the presence of defects containing light elements (C, O, N). These defects are identified qualitatively by WDS X-ray maps as a titanium oxide layer, on the sample surface, and titanium carbide inclusions in the matrix. Analysis allows the determination of the defects' origin and consequently their elimination with improvements in the production process.

## 4 Conclusions

Microanalytical methods EDS and WDS in combination with SEM were applied to characterize three different types of materials: lead glass, ceramics, and alloys. The microstructures of the samples were investigated on a SEM using both secondary electron and backscattered

electron imaging. Usually information of elemental composition is obtained first by EDS qualitative analysis. Chemical composition of the samples or phases in the samples was determined by EDS quantitative analysis with and/or without standards. WDS quantitative analysis with appropriate reference standards allows to measure the elemental concentration with better sensitivity and accuracy. WDS procedure is especially suitable for the quantitative analysis of elements which overlap in the EDS spectra, in the case of low elemental concentrations in the samples, and for light element analysis.

The relative accuracy of EDS quantitative analysis achieved is between 3-10% whereas in the WDS quantitative analysis accuracy between 1-2% is obtained. EDS analysis has a limited sensitivity (detection limit about 0.1 wt%) and limited quantification in situations of complex materials with spectral interference (overlap) and ultralight elements. However, combination of SEM-EDS regarding to its flexibility, ease of operation, and data interpretation is widely used. WDS technique is time consuming but more sensitive and accurate (detection limit about 0.01 wt%) quantitative procedure suitable for wide range of microanalytical problems.

**Acknowledgements**

This publication is based on work partially sponsored by the U.S. - Slovene Science and Technology Joint Fund in cooperation with the Ministry of Science and Technology of Slovenia under Project Number US-SLO 95/6-05.

## 5 References

[1] J. I. Goldstein et al., *Scanning Electron Microscopy and X-Ray Microanalysis*, Plenum Press, New York, 1992

[2] G. F. Bastin, H. J. M. Heijligers, F. J. J. van Loo, A further improvement in the Gaussian $\phi(\rho z)$ approach for matrix correction in quantitative electron probe microanalysis, *Scanning*, 8, 1986, 45-67

[3] J. L. Pouchou, Standardless X-Ray Analysis of Bulk Specimens, *Mikrochimica Acta*, 114/115, 1994, 33-52

[4] J. S. B. Reed, *Electron Microprobe Analysis*, Cambridge University Press, 1975

[5] D. Makovec, Z. Samardžija, U. Delalut and D. Kolar, Defect Structure and Phase Relations of Highly La-Doped $BaTiO_3$, *Journal of American Ceramic Society*, 78, 1995, 8, 2193-2197