Electron probe microanalysis of the dopant concentrations in complex perovskite ferroelectrics

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Abstract. Quantitative EPMA-WDS microanalyses were applied for the compositional characterisation of complex perovskite ferroelectrics based on cerium-doped barium titanate, a solid solution between lead-magnesium-niobate/lead-titanate and niobium-doped barium-bismuth-titanate. The analyses were optimized for high analytical sensitivity, precision and an ultimate accuracy of $\pm 1\%$ relative. The inherent problem with the WDS peak overlap of the Ce-L$_{α1}$ and Ba-L$_{β1,4}$ spectral lines was solved by introducing overlap-correction methods in order to obtain consistent quantitative results for the Ce-doped BaTiO$_3$. The quantitative results made it possible to obtain accurate chemical formulae for these materials, to determine the solubility of the dopants as well as to define the mode of the dopant incorporation and the charge-compensation mechanisms.

1. Introduction
Complex perovskite ferroelectrics belong to the group of oxide ceramic materials with a ternary ABO$_3$ crystal structure where the ions on the A and/or B sites are partially substituted by doping with other ions, thus forming numerous solid-solution compounds [1]. Among the large number of such compounds, many electroceramic dielectrics are based on a modified barium-titanate (BaTiO$_3$) ceramic host, which was one of the first synthetic perovskites [2]. Following the crystal chemistry of perovskites, a multiple ion substitution on the same structural site was also involved [3]. With an appropriate change in the composition, using various types and amounts of dopants, the properties of these materials can be tailored and modified for a wide range of electroceramic devices with different dielectric, piezoelectric, electro-optic, microwave and related applications [4]. Since small quantities of dopants can significantly change the ferroelectric properties, the structure-composition-property relations have to be accurately defined. Therefore, an important part of the studies of complex ferroelectrics is associated with an accurate analysis of their chemical composition. For this reason, quantitative electron probe microanalysis (EPMA) has a key role and can be applied for the compositional analysis of ferroelectric ceramics in forms of multi-phase or single-phase polycrystalline materials and single crystals.

In this work, selected case studies of EPMA for complex perovskite ferroelectrics based on Ce-doped BaTiO$_3$ (BTC), the solid solution between lead-magnesium-niobate and lead-titanate Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$-PbTiO$_3$ (PMN-PT) and the layer-structure (Aurivillius type) perovskite barium-bismuth-titanate (BaBi$_4$Ti$_4$O$_{15}$) doped with Nb (BBTN) were presented, demonstrating the usability and power of a quantitative EPMA in these cases. The aim of the work was to achieve reliable, accurate, quantitative analyses of the elemental concentrations in these materials in order to...
study the solubility and the incorporation of the dopants in the host perovskites. In order to achieve this, the ultimate quantitative microanalysis was carried out using wavelength-dispersive X-ray spectroscopy (WDS) that was optimized to achieve a high analytical sensitivity, precision and accuracy.

2. Experimental

The microstructures of selected polished ceramic samples are shown in figure 1, revealing that the BTC and BBTN materials are polycrystalline, multiphase samples, while the PMN-PT material is single phase with a polycrystalline and a single-crystal part. For a consistent microanalysis of the doped-perovskite matrix phases in multiphase microstructures it is necessary to perform precise positioning of the focused electron beam in order to avoid the influence of adjacent secondary phases and/or pores.

Figure 1. SEM compositional contrast micrographs of the microstructures of the analysed samples: (a) BTC; (b) PMN-PT with polycrystalline part (p.) and single-crystal part (s.c.); (c) BBTN.

Preliminary analyses using energy-dispersive X-ray spectroscopy (EDS) revealed several problems that show why quantitative EDS analyses in these cases cannot be sufficiently accurate. The problems are related to the poor detection limits of the method and to several peak overlaps, i.e., between the Ba-L and Ti-K spectral lines, the more complicated overlap of both the Ba-L and Ti-K with the Ce-L line, and the partial overlap of the Pb-M and Bi-M lines with the Nb-L line. These overlaps are especially difficult to deconvolute properly when the dopant concentrations are low/minor, as is the situation in the selected materials. The parts of the EDS spectra from the BTC and BBTN samples showing the current peak overlaps are presented in figure 2.

Consequently, the EPMA-WDS method was employed for the spectroscopic measurements of the elemental analytical spectral lines in the selected samples, taking advantage of the high spectral resolution and the high peak-to-background (P/B) ratios that can be achieved using properly optimized WDS. A JEOL JXA-840A electron-probe microanalyser with two wavelength spectrometers and a TN5600 system with TASK programme were used for the X-ray data acquisition and processing. For all the WDS measurements the designated diffracting crystals were tuned to peak and background positions that were accurately determined from precise, slow wavelength scans performed on standards and additionally re-checked on the samples. In the case of the PMN-PT and BBTN samples, the Nb-Lα, Pb-Mα and Bi-Mα spectral lines were easily separated and measured without any interference using the PET crystal. For the determination of the relatively low (1 - 2 m.f.%) dopant concentration of Mg in the PMN-PT, the Mg-Kα line was measured using a TAP crystal with the background positions (B1, B2) that were carefully determined, taking into account that the multiple-λ (n = 2) peak from the Pb-Mβ line emerges close to the Mg-Kα peak, as illustrated in figure 3a. When
analysing the samples containing Ba and Ti (BTC, BBTN), the Ba-Lα and Ti-Kα spectral lines were well separated and correctly measured using the LiF crystal, as shown in figure 3b.

Figure 2. Characteristic EDS peak overlaps of the spectral lines in the spectra acquired from the doped-perovskite phases in the BTC and BBTN materials.

Figure 3. (a) TAP wavelength scans for the Mg-Kα line on the MgO standard and PMN-PT sample; (b) LiF wavelength scan for the Ba-Kα and Ti-Kα lines on the BaTiO₃ standard.

However, a specific situation occurs when the BaTiO₃ is doped with cerium, and the spectral interference between the Ce-Lα₁ and the Ba-Lβ₁,₄ lines also causes a peak overlap when using the WDS and a high-resolution LiF crystal, as shown in figure 4a. This overlap introduces a systematic error in the quantification of the concentrations of the Ce dopant in the BaTiO₃. The evaluation of the Ba-Lβ₁,₄-Ce-Lα₁ peak overlap for the BTC material that was obtained by deconvolution using pseudo-Voigt peak-profiles is shown in figure 4b. Here, it is clear that the measured Ce-Lα₁ intensity (I) is always greater than its true intensity (I'), i.e., the k-ratios obtained for the Ce are too high, leading to an overestimated and erroneous quantification.
In order to obtain the true Ce-Lα₁ intensity (I*) a correction of the existing peak overlap has to be performed. Basically, the contribution of the Ba-Lβ₁,4 at the peak position for Ce-Lα₁ has to be estimated and then subtracted from the measured Ce intensity. In order to achieve this, three approaches were proposed to provide a reliable quantitative analysis of the BTC material:

A) Correction of the Ce-Lα₁-Ba-Lβ₁,4 peak overlap using the method based on relative spectral line intensities. Here we assume that the ratio between the Ba-Lα₁ intensity and the intensity of the Ba-Lβ₁,4 measured at the Ce-Lα₁ peak position is the same in the BaTiO₃ standard (BT) and in the Ce-doped BaTiO₃ sample (BTC). Then the true Ce-Lα₁ intensity (I*) corrected for the contribution of the Ba-Lβ₁,4 is calculated using equation

\[ I_{\text{Ce-L}}^{* \text{BTC}} = \frac{I_{\text{Ce-L}}^{\text{BTC}}}{I_{\text{Ba-L}}^{\text{measured}}} - \left[ I_{\text{Ba-L}}^{\text{BTC}} \text{ at Ce-L}_1 \text{ position} \times \left( \frac{I_{\text{BTC}}^{\text{Ba-L}}}{I_{\text{Ba-L}}^{\text{BTC}}} \right) \right] \]  

(1)

B) Correction of the Ce-Ba overlap using the calibration-curve method [5]. Here we assume that the Ba-Lβ₁,4 intensity measured at the Ce-Lα₁ peak position increases linearly with an increase of the Ba concentration. This intensity was then measured versus the Ba-Lα₁ peak intensity in three Ba-Ti-O compounds (without Ce) and the linear calibration curve presented in figure 5a was obtained. The slope of this curve gave a correction factor that was used to estimate the contribution of the Ba-Lβ₁,4 to the Ce-Lα₁ in the Ce-doped BaTiO₃ matrix (BTC). The true Ce-Lα₁ intensity is then calculated using

\[ I_{\text{Ce-L}}^{* \text{BTC}} = \frac{I_{\text{Ce-L}}^{\text{BTC}}}{I_{\text{Ba-L}}^{\text{measured}}} - 0.066 \times I_{\text{Ba-L}}^{\text{BTC}} \]  

(2)

C) An analysis using an alternative spectral line for Ce that is not interfered with by other lines, i.e., the Ce-Lβ₁ line, as illustrated in figure 5b. Here, two background positions (B1, B2) have to be precisely determined because of the presence of the Ba-Lβ₂,1₅ and Ce-Lβ₁ peaks in the vicinity of the Ce-Lβ₁.

For the WDS measurements the elemental P/B ratios were maximized to obtain a high analytical sensitivity (i.e., low detection limits) using optimized conditions for the analysing crystals (P and B positions, slit size and position) and the detector’s electronics (pulse-height analyser settings: bias,

Figure 4. (a) Merged wavelength scans for the Ba-Lβ₁,4 and Ce-Lα₁,2 lines, showing their mutual overlap that exists in the wavelength spectrum; (b) deconvolution of the wavelength spectrum acquired from the BTC matrix using pseudo-Voigt profiles, revealing the difference between the measured (I) and true (I*) Ce-Lα₁ intensity.
The BTC and BBTN were analysed at 20 kV / 40 nA and the PMN-PT at 15 kV / 60 nA. A high analytical precision was achieved, with the counting times set to be sufficiently long so as to ensure a relative counting error $\sigma_c \leq 1\%$ for all the elements. In the case of BTC the corrected $k$-ratios for Ce-L$\alpha_1$ were firstly calculated using true net Ce-intensities obtained from Eqs. (1) and (2) and then processed within the matrix correction. The quantification was performed using the $\Phi(\rho z)$-PROZA (Bastin) matrix correction with the oxygen content being calculated using the stoichiometry to nominal cation valencies [6]. To improve the accuracy and to minimise the matrix effects, stable stoichiometric oxide compounds were chosen as the standards [7]. A summary of the experimental conditions for the WDS analyses is given in table 1. The corresponding detection limits ($C_{DL}$) were calculated using the Ziebold equation [8].

![Figure 5.](image)

**Figure 5.** (a) Calibration curve used for the estimation of the Ba-L$\beta_{1,4}$ contribution to the Ce-L$\alpha_1$ intensity (data for 15 nA and 20 nA were corrected to nominal current of 40 nA); (b) LiF wavelength scans for the Ce-L$\beta_1$ line on the CeO$_2$ standard and on the BTC sample.

| Element | Line | Crystal | P/B ratio | $C_{DL}$ (m.f.% | Standard |
|---------|------|---------|-----------|----------------|----------|
| Ba      | L$\alpha_1$ | LiF | 143 | 0.058 | BaTiO$_3$ |
| Ti      | K$\alpha_1$ | LiF | 162 | 0.012 | BaTiO$_3$ |
| Ce      | L$\alpha_1$ | LiF | 120 | 0.058 | CeO$_2$ |
| Ce      | L$\beta_1$ | LiF | 57 | 0.101 | CeO$_2$ |
| Pb      | M$\alpha$ | PET | 150 | 0.044 | PbO |
| Ti      | K$\alpha$ | PET | 107 | 0.005 | SrTiO$_3$ |
| Bi      | M$\alpha$ | PET | 150 | 0.035 | Bi$_2$O$_3$ |
| Nb      | L$\alpha$ | PET | 360 | 0.023 | Nb$_2$O$_5$ |
| Mg      | K$\alpha$ | TAP | 800 | 0.003 | MgO |
3. Results and discussion

3.1. Nb-doped \( \text{BaBi}_4\text{Ti}_4\text{O}_{15} \) (BBTN)

The results of the quantitative analysis for the BBTN samples that were prepared with the nominal addition of 5, 8 and 10 mol\% of Nb are given in table 2, with the analysis of the undoped sample (BBT) added for comparison.

| Sample  | Ba    | Bi   | Ti    | Nb    | Ti+Nb | Ba+Bi |
|---------|-------|------|-------|-------|-------|-------|
| BBT     | 4.26 ± 0.12 | 16.71 ± 0.16 | 16.57 ± 0.08 | -     | 16.57 | 20.97 |
| BBTN5   | 4.93 ± 0.23 | 15.94 ± 0.17 | 15.72 ± 0.15 | 0.90 ± 0.14 | 16.62 | 20.87 |
| BBTN8   | 5.21 ± 0.24 | 15.71 ± 0.21 | 15.20 ± 0.15 | 1.34 ± 0.16 | 16.54 | 20.92 |
| BBTN10  | 5.56 ± 0.13 | 15.33 ± 0.18 | 14.85 ± 0.07 | 1.72 ± 0.12 | 16.57 | 20.89 |

The results reveal that the concentrations of the Ti and Nb in the doped samples agree well with the nominal composition described by the formula \( \text{BaBi}_4\text{Ti}_{4-x}\text{Nb}_x\text{O}_{15} \); however, the Ba- and Bi-concentrations differ significantly from the nominal values. The change of the Ba- and Bi-concentrations in the BBTN samples versus the dopant concentration is shown in figure 6a. It is clear that the Ba-concentration increases and the Bi decreases in proportion to the Nb-concentration. Consequently, a systematic change in the Ba/Bi ratio with an increase in the dopant concentration is present, as shown in figure 6b, whereas the total \([\text{Ti}^4]+[\text{Nb}]\) remains practically constant and equal to the Ti-concentration in the undoped sample (see table 2), directly verifying that the Nb\(^{5+}\) incorporates/substitutes at the Ti\(^{4+}\) sites. The excess charge introduced by the substitution of Ti\(^{4+}\) with Nb\(^{5+}\) is thus compensated by the change in the Ba\(^{2+}\)/Bi\(^{3+}\) ratio [9]. According to the obtained elemental concentrations, the composition of the BBTN solid solution is reliably described by the general formula \( \text{Ba}_{1-x}\text{Bi}_{4-x}\text{Ti}_{4-x}\text{Nb}_x\text{O}_{15} \).

![Figure 6](image)

**Figure 6.** (a) Change of the Bi and Ba concentrations in the BBTN samples; (b) variation of the Ba/Bi ratio versus the Nb-dopant concentration.
3.2. Solid-solution Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}–PbTiO\textsubscript{3} (PMN-PT)

The PMN-PT single crystal was produced from the starting 70PMN-30PT polycrystalline precursor. After the synthesis, the final composition of the PMN-PT single crystal, which was several millimetres in size, was analysed in 10 microscopic areas that were positioned randomly over the crystal. In each of these areas 10 analytical points were selected within a circle of about 20 \( \mu \)m in diameter. This sampling made it possible to study the composition of the crystal on both the macroscopic mm-scale (between the areas) and the microscopic \( \mu \)m-scale (within the areas). The total experimental uncertainty was then calculated from the corresponding components of variance as

\[
\sigma_{\text{exp}} = \left[ (\sigma_{\text{wp}})^2 + (\sigma_{\text{bp}})^2 + (\sigma_{\text{ba}})^2 \right]^{1/2}
\]

where \((\sigma_{\text{wp}})^2\) is the variance within the points associated with the counting statistics, \((\sigma_{\text{bp}})^2\) is the variance between the points within an individual area, and \((\sigma_{\text{ba}})^2\) is the variance between the areas [10]. The quantitative results for one representative microscopic area on the PMN-PT sample are presented in table 3.

| Point | Pb  | Mg | Nb  | Ti  | O\textsuperscript{a} | Total\textsuperscript{b} |
|-------|-----|----|-----|-----|----------------|---------------------|
| 1     | 65.25 | 1.69 | 13.20 | 4.97 | 15.12 | 100.23 |
| 2     | 65.29 | 1.70 | 13.15 | 4.93 | 15.09 | 100.16 |
| 3     | 65.39 | 1.70 | 13.20 | 4.95 | 15.10 | 100.34 |
| 4     | 65.65 | 1.71 | 13.15 | 4.96 | 15.07 | 100.54 |
| 5     | 65.46 | 1.70 | 13.12 | 4.95 | 15.08 | 100.31 |
| 6     | 64.99 | 1.69 | 13.13 | 4.95 | 15.11 | 99.87  |
| 7     | 65.24 | 1.69 | 13.20 | 4.97 | 15.12 | 100.22 |
| 8     | 65.56 | 1.69 | 13.13 | 4.97 | 15.07 | 100.42 |
| 9     | 65.43 | 1.70 | 13.14 | 4.96 | 15.09 | 100.32 |
| 10    | 65.30 | 1.71 | 13.14 | 4.95 | 15.10 | 100.20 |
|       | **65.36** | **1.70** | **13.16** | **4.96** | **15.09** | **100.26** |

\(\sigma_{\text{exp}}\) ± 0.23  ± 0.01  ± 0.04  ± 0.02  ± 0.02  ± 0.18  
\(\pm \sigma_{\text{exp}}\)\textsuperscript{rel} (%) 0.35  0.75  0.34  0.34  0.11  0.18

| Point | Pb  | Mg | Nb  | Ti  | O\textsuperscript{a} | Total\textsuperscript{b} |
|-------|-----|----|-----|-----|----------------|---------------------|
|       | **65.36** | **1.70** | **13.16** | **4.96** | **15.09** | **100.26** |

\(\sigma_{\text{exp}}\)\textsuperscript{2} 0.01760  0.00010  0.00101  0.00013  
\(\sigma_{\text{exp}}\)\textsuperscript{2} 0.03463  0.00006  0.00100  0.00016  

|    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|
|    |    |    |    |    |    |    |
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|    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|
|    |    |    |    |    |    |    |
|    |    |    |    |    |    |    |

*By stoichiometry.*

**Non-normalized analytical total.**

Within the microscopic areas all the elemental concentrations are uniform, with minimal scattering between the points and with the relative analytical uncertainties \(\sigma_{\text{exp}}\)\textsuperscript{rel} below 1 %, indicating that the composition of the PMN-PT material within the areas is homogeneous. The achieved, non-normalized analytical totals close to 100 % verify the correctness of the analyses. In addition to this, another parameter for the consistency of the analytical procedure was introduced on the basis of the crystal chemistry of the PMN-PT perovskite. Namely, in this case the B-sites in the perovskite structure are occupied by multiple ions Ti\textsuperscript{4+}, Mg\textsuperscript{2+} and Nb\textsuperscript{5+}, and the Ti\textsuperscript{4+} ions are substituted for the complex \((\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}\). Thus, it is reasonable to expect that the atomic ratio Mg/Nb = 0.5 should remain
unchanged. The Mg/Nb ratio was then calculated and monitored as a significant parameter for the quantitative data [11]. For the results given in table 3, this ratio is $0.493 \pm 0.003$, which is, taking into account the experimental uncertainty, in very good agreement with expected ratio of 0.5. The elemental atomic fractions fit perfectly to the ABO$_3$-type perovskite formula for the PMN-PT solid solution, given by Pb$_{1.000\pm0.002}$(Mg$_{0.221\pm0.001}$Nb$_{0.449\pm0.001}$)Ti$_{0.328\pm0.001}$O$_3$.

The quantitative results for 10 analysed areas are given in table 4. Increased scattering $\sigma_{\text{exp}}$ between the area averages is evidently present for the Ti ($\pm 2.3\%$), for the Mg ($\pm 1.4\%$) and for the Nb ($\pm 1.3\%$); however, it remains as only $\pm 0.5\%$ for the Pb, indicating that the Pb-concentration is uniform over the entire single crystal. The between-the-area variances $\sigma_{\text{ba}}^2$ for the Mg, Nb and Ti were considerably higher, revealing that a certain degree of heterogeneity over the crystal is present for the B-site cations. The statistical evaluation of the $\sigma_{\text{bp}}^2$ and $\sigma_{\text{ba}}^2$ variances has also shown that the differences between the area averages for the Mg, Nb and Ti were statistically significant, while the differences for the Pb were found to be insignificant. The PMN-PT solid-solution formula calculated from the overall average values is given by Pb$_{0.994\pm0.004}$(Mg$_{0.220\pm0.003}$Nb$_{0.447\pm0.005}$)Ti$_{0.334\pm0.007}$O$_3$ with a consistent Mg/Nb ratio of $0.494 \pm 0.005$.

Table 4. Average quantitative results for 10 areas over the PMNT crystal.

| Area | Pb  | Mg  | Nb  | Ti  | O  |
|------|-----|-----|-----|-----|----|
| 1    | 65.86 | 1.72 | 13.08 | 5.28 | 15.18 |
| 2    | 65.36 | 1.70 | 13.16 | 4.96 | 15.09 |
| 3    | 65.71 | 1.70 | 13.31 | 5.08 | 15.15 |
| 4    | 65.47 | 1.70 | 13.27 | 5.22 | 15.22 |
| 5    | 65.76 | 1.73 | 13.37 | 5.05 | 15.15 |
| 6    | 65.89 | 1.71 | 13.29 | 5.09 | 15.14 |
| 7    | 65.76 | 1.68 | 12.95 | 5.25 | 15.13 |
| 8    | 65.40 | 1.74 | 13.44 | 4.97 | 15.17 |
| 9    | 66.01 | 1.68 | 13.11 | 5.10 | 15.08 |
| 10   | 65.60 | 1.73 | 13.37 | 5.05 | 15.16 |
| Grand average | **65.68** | **1.71** | **13.23** | **5.10** | **15.15** |

$\sigma_{\text{exp}} \pm 0.33$ $\pm 0.02$ $\pm 0.17$ $\pm 0.12$ $\pm 0.04$

$\pm \sigma_{\text{exp}}^{\text{rel}}/\%$ **0.50** **1.43** **1.28** **2.27** **0.26**

$\sigma_{\text{ba}}^2$ 0.04811 0.00044 0.02394 0.01292

Average atomic f. % | **19.90** | **4.42** | **8.94** | **6.69** | **60.05**

$\sigma_{\text{exp}} \pm 0.08$ $\pm 0.05$ $\pm 0.10$ $\pm 0.14$ $\pm 0.03$

Mg/Nb ratio 0.494 $\pm 0.005$

Taking into account all the quantitative results, the composition of the PMN-PT single crystal is described by the formula Pb(Mg$_{1/3}$Nb$_{2/3}$)$_{0.67}$Ti$_{0.33}$O$_3$, i.e., 67PMN-33PT, which is significantly different from the starting formula. The variations that were measured for the B-site cation concentrations between the analysed areas over the crystal indicate that an opposite trend in the occupancy between the Ti$^{4+}$ ions, on the one hand, and the Mg$^{2+}$ and Nb$^{5+}$ ions, on the other, is present, as shown in figure 7a. The graph of the relative B-site occupancy, calculated by means of the Ti/(Mg+Nb) atomic ratio (figure 7b), confirms that a slightly unequal occupation of the B-sites is present over the entire grown PMN-PT crystal, with an average ratio of 0.50 and a variation of $\pm 5\%$ relative. The unequal B-site occupation is a known phenomenon that takes place in Pb-based relaxor ferroelectrics. In this work the fluctuations observed for Ti (and also for Mg and Nb) were quantitatively evaluated by
EPMA, so directly verifying the suggestion of an inhomogeneous distribution of the Ti$^{4+}$ concentration in the PMN-PT, as given in [12].

![Figure 7](image)

**Figure 7.** (a) The occupancy of the Ti$^{4+}$, Mg$^{2+}$ and Nb$^{5+}$ B-site ions between 10 areas; (b) the relative occupancy between the areas, given by the Ti/(Mg+Nb) ratio.

### 3.3. Ce-doped BaTiO$_3$ (BTC)

A summary of the quantitative results for 10 randomly selected BTC grains is given in table 5, where the correction of the Ba-Ce peak overlap was performed using equation (1). The good counting statistics achieved ($\sigma_{\text{c,rel}} < 1\%$) and the high analytical sensitivities ensured that the elemental concentrations were measured with great precision and accuracy. The between-the-grains scattering ($\sigma_{\text{bg}}$) for the Ba and Ce is evidently larger than the uncertainty within the individual grains ($\sigma_{\text{wg}}$), whereas the values of $\sigma_{\text{bg}}$ and $\sigma_{\text{wg}}$ for Ti remain similar. This suggests that certain compositional variations for Ba and Ce between the grains are present, whereas the Ti-concentration remains uniform, as shown in detail in figure 8.

| Table 5. Quantitative analysis of 10 BTC grains. |
|-----------------------------------------------|
| n = 10 grains & Mass fractions % |
| & Ba | Ce | Ti |
| average C $\pm \sigma_{\text{wg}}$ | 54.38 $\pm$ 0.17 | 4.63 $\pm$ 0.08 | 20.13 $\pm$ 0.10 |
| between grains $\sigma_{\text{bg}}$ | $\pm$ 0.59 | $\pm$ 0.67 | $\pm$ 0.12 |
| analytical sensitivity | 0.14 | 0.03 | 0.05 |
| relative $\sigma_{\text{wg}}$ | 0.3 % | 1.5 % | 0.5 % |
| rel. count. error $\sigma_{\text{c,rel}}$ | 0.3 % | 0.8 % | 0.3 % |

Since the sum [Ba]+[Ce] remains constant (within the range $\pm \sigma_{\text{wg}}$) the observed opposite trend between the Ba and Ce variations indicates that in this sample Ce ions incorporate at the Ba-sites in the BaTiO$_3$. The results of the WDS quantitative analyses obtained using the three, above-described analytical approaches (A), (B) and (C) as well as using the analysis of the Ce-L$\alpha_1$ line without an overlap correction (D) are given in table 6.
Figure 8. Elemental concentrations between the BTC grains showing an opposite change between the Ba- and Ce-values, and uniform Ti-values.

Table 6. Comparison of the quantitative results of the BTC sample obtained with different methods of analysis.

| Method | Mass fractions (%) | Atomic fractions (%) |
|--------|--------------------|----------------------|
|        | Ba     | Ti    | Ce    | O  | Totala | Ba     | Ti    | Ce    | O  |
| (A)    | 54.38  | 20.13 | 4.63  | 20.64 | 99.78 | 18.54  | 19.69 | 1.55  | 60.23 |
| (B)    | 54.37  | 20.13 | 4.73  | 20.64 | 99.87 | 18.52  | 19.67 | 1.58  | 60.23 |
| (C)    | 54.69  | 20.16 | 4.39  | 20.63 | 99.88 | 18.62  | 19.69 | 1.47  | 60.22 |
| (D)    | 54.16  | 20.13 | 7.22  | 20.49 | 102.00| 18.10  | 19.30 | 2.36  | 60.24 |

a Non-normalized analytical total (m. f. %).

The presented results reveal that both methods that were introduced for the correction of the Ba-Lβ1,4–Ce-Lα1 peak overlap, i.e., (A) with eq. (1) and (B) with eq. (2), provide similar quantitative results. The elemental concentrations fit perfectly to the perovskite solid-solution formula Ba$_{0.923±0.004}$Ce$_{0.077±0.001}$Ti$_{0.981±0.002}$O$_3$ or in general form by Ba$_{1-x}$Ce$_x$Ti$_{1-x/4}$V$_{Ti}$O$_3$, where $x = 0.08$ and V$_{Ti}$ are the vacancies at the Ti-sites. This result directly confirms that in the selected sample Ce incorporates into the BaTiO$_3$ as donor Ce$^{3+}$ at the Ba$^{2+}$ sites. In this case, the excess donor charge is compensated with the formation of ionized vacancies at the Ti-sites, V$_{Ti}$ [13]. Direct evidence for this mechanism of charge compensation is that the measured deficit (from the nominal 20.00 at.f. %) for the Ti-concentration, which is attributed to [V$_{Ti}$], is equal to [Ce$^{3+}$]/4.

The non-normalized analytical totals close to 100 % verify the correctness of the WDS analytical procedures with the proposed methods (A), (B) and (C). However, it should be noted that the quantification of the Ce-Lβ$_1$ (method C) is less correct and gives a slightly underestimated (by 6 % relative) Ce-concentration, which is believed to be due to an inaccurate absorption correction caused by the uncertainty in the MAC values for the Ce-Lβ$_1$ line. The analysis performed by measuring the Ce-Lα$_1$ line without applying the peak-overlap correction (method D) is obviously erroneous, with a significantly overvalued Ce concentration and, consequently, an excessive analytical total.
4. Conclusion
Quantitative EPMA-WDS microanalyses were applied to determine the chemical compositions of selected complex perovskite ferroelectric materials that were modified by dopants. It was shown that each material requires specific and detailed optimisation of the analytical procedure in order to achieve the best results in terms of the precision and accuracy. The results made it possible to obtain accurate chemical formulae for the compounds/solid-solutions, to define the solubility of the dopants in the host materials, and, indirectly, to evaluate the mode of dopant incorporation and the charge-compensation mechanisms as well. Reliable quantitative compositional data are very important for studies of the structure-composition-property relations of these materials and to provide a correct interpretation of their ferroelectric properties.

References
[1] Bhalla A S, Guo R and Roy R 2000 Mater. Res. Innovat. 4 2-26
[2] Jonker G H and Havinga E E 1982 Mater. Res. Bull. 17 345-350
[3] Roy R 1954 J. Am. Ceram. Soc. 37 581-588
[4] Xu Y 1991 Ferroelectric materials and their applications. (Amsterdam: North Holland)
[5] Samardžija Z, Čeh M, Makovec D and Kolar D 1996 Mikrochim. Acta Suppl. 13 517-523
[6] Bastin G F, Dijkstra J M and Heijligers H J M 1998 X-ray Spectrom. 27 3-10
[7] Lifshin E and Gauvin R 2001 Microsc. Microanal. 7 168-177
[8] Ziebold T O 1967 Anal. Chem. 39 858-861
[9] Samardžija Z, Makovec D and Čeh M 2002 Mikrochim. Acta 139 159-163
[10] Marinenko R and Leigh S 2004 Microsc. Microanal. 10 491-506
[11] Samardžija Z, Jeon J-H and Čeh M 2007 Mater. Charact. 58 534-543
[12] Tu C-S, Chen L-F, Schmidt V H and Tsai C-L 2001 Jpn. J. Appl. Phys. 40 4118-4125
[13] Makovec D, Samardžija Z and Kolar D 1996 J. Solid State Chem. 123 30-38