Kovine, zlitine, tehnologije / letnik 29 / 1995 / številka 1–2 / strani 200 do 202

Determination of the Solubility of Ce and La in $BaTiO_3$ by Quantitative WDS Electron Probe Microanalysis

Določanje topnosti Ce in La v $BaTiO_3$ s kvantitativno WDS elektronsko mikroanalizo

Samardžija Z.[1], D. Makovec, D. Kolar, Jožef Stefan Institute, Ljubljana

Quantitative wavelength dispersive (WDS) electron probe microanalysis was applied for determination of Ba, Ti, Ce and La concentrations in Ce and La doped $BaTiO_3$ ceramics. The high resolution and analytical sensitivity of the wavelength dispersive spectrometer allowed accurate quantitative measurements of cation concentrations in doped $BaTiO_3$. Pure $BaTiO_3$, CeO_2 and $La_2Ti_2O_7$ were used as verified standard compounds. The experimental parameters of an electron probe microanalyzer were optimized to achieve the maximum sensitivity and precision of analysis. K-ratios were determined for the $BaL\alpha_1$, $TiK\alpha_1$, $CeL\alpha_1$ and $LaL\alpha_1$ spectral lines. Because of multiple peak overlapping of the $CeL\alpha_{1,2}$ and $BaL\beta_{1,4}$ lines, which introduces substantial error in the measured $CeL\alpha_1$ intensity, k-ratios for $CeL\alpha_1$ were corrected using the empirical calibration curve method. Element concentrations were calculated by ZAF and/or PROZA matrix correction procedures. Results were calculated to the perovskite ABO_3 formula considering different modes of dopant incorporation and donor charge compensation.

Key words: quantitative electron probe microanalysis, wavelength dispersive analysis, solid solubility of Ce and La in $BaTiO_3$

S kvantitativno valovno disperzijsko (WDS) elektronsko mikroanalizo smo določali koncentracije Ba, Ti, Ce in La v keramiki $BaTiO_3$ dopirani s cerijem in lantanom. Visoka ločljivost in analitična občutljivost valovnega disperzijskega spektrometra omogoča natančno kvantitativno meritev koncentracij kationov. Kot standardi so bile uporabljene čiste spojine $BaTiO_3$, $La_2Ti_2O_7$ in CeO_2. Eksperimentalni parametri elektronskega mikroanalizatorja so bili optimizirani za dosego visoke občutljivosti in natančnosti analize. K-razmerja smo določali za spektralne linije $BaL\alpha_1$, $TiK\alpha_1$, $CeL\alpha_1$ in $LaL\alpha_1$. Pri tovrstni analizi prihaja do prekrivanja spektralnih linij $CeL\alpha_{1,2}$ in $BaL\beta_{1,4}$, kar povzroča napako pri merjenju intenzitete linije $CeL\alpha_1$. Z uporabo empirične umeritvene krivulje smo korigirali k-razmerja za $CeL\alpha_1$. Koncentracije elementov smo izračunali z uporabo ZAF in/ali PROZA matrične korekcijske metode. Podani rezultati so preračunani na formulo perovskita ABO_3 z upoštevanjem različnega načina vgradnje dopantov in kompenzacije donorskih nabojev.

Ključne besede: kvantitativna elektronska mikroanaliza, valovna disperzijska analiza, trdna topnost Ce in La v $BaTiO_3$

1. Introduction

$BaTiO_3$ ceramics modified with donor dopants, such as La^{3+} or Nb^{5+}, are extensively studied because of their interesting dielectric and semiconducting properties. Donor dopants may be incorporated into the $BaTiO_3$ perovskite lattice differently as regards their site of incorporation and donor charge compensation[1]. A knowledge of the quantity and modality of dopant incorporation is of fundamental importance in the optimization of the processing of materials. Characterization methods usually applied such as XRD, TGA, DTA and electrical measurements give information about solid solubility indirectly by measuring changes in material properties. Quantitative wavelength dispersive (WDS) electron probe microanalysis (EPMA) is the best appropriate direct method[2] for determination of the mode and amount of dopant incorporation. The information about sample composition is taken at the micro-level (from a micro-volume of approximately 1 μm^3) giving the possibility of analyzing multiphase ceramic samples. In this paper a detailed study of the optimal experimental procedure for WDS quantitation in the Ba-Ce-Ti-O and Ba-La-Ti-O systems is presented.

2. Experimental

La and Ce doped $BaTiO_3$ ceramic samples were prepared by conventional ceramic technology. Oxides were mixed, pressed

[1] Zoran SAMARDŽIJA, dipl. fiz.
Institut Jožef Štefan
Jamova 39, 61000 Ljubljana

into pellets and sintered at 1400°C in air for a longer period (5 days) with intermittent cooling, crushing and mixing to promote homogeneity. Samples were polished and coated with a thin film of carbon in order to assure electrical conductivity and prevent charging under the electron beam.

A JEOL JXA 840A SEM/EPMA scanning electron microscope and electron probe microanalyzer equipped with a Tracor Z-Max 30 EDS analyzer and two JEOL WD spectrometers controlled by a Tracor Series II X-Ray Microanalysis System were used for overall analysis of the samples.

Preliminary information about the ceramic microstructure and grain size of the doped $BaTiO_3$ samples was obtained by SEM observations. In the WDS microanalysis it is important that the grain size of the phase analyzed is quite large (min. 5-10 μm average diameter) in order to avoid the influence of neighbouring phases during the analysis. Electron micrographs of the samples were recorded using compositional backscattered electron imaging based on atomic number contrast.

Because of strong and multiple peak overlapping of the most intense Ba, Ti, La and Ba, Ti, Ce spectral lines in the EDS spectra, accurate quantitative analysis based on EDS (resolution 150eV) was not possible. The better resolution achieved in the WD spectrometer (5-10 eV) allowed separate analysis of $BaL\alpha_1$, $TiK\alpha_1$, $LaL\alpha_1$ and $CeL\alpha_1$ spectral lines without spectral interference. At the same time a high X-ray collection efficiency and higher peak to background ratios were achieved.

The experimental parameters in EPMA were optimized according to data based on a Monte Carlo electron trajectory simulation, Kanaya-Okayama calculations for electron range and $\Phi(\rho z)$ curve calculations for X-rays generated by electron-solid interactions. Taking into account the excitation energies of characteristic X-rays, absorption and fluorescence processes in the material, the optimal conditions were found to be 20 kV voltage and 10/15 nA electron beam current. X-rays were diffracted on the high resolution and reflectivity crystals: PET ($2d_{002}$=0.40267nm), was used for Ba, La, Ti and LiF ($2d_{200}$=0.87420 nm), was used for the Ba, Ce, Ti element combination. Diffracted X-rays were detected by a sealed xenon filled gas proportional counter. Accurate peak positions for the spectral lines analyzed as well as background positions were determined by slow wavelength scans. Counting time was set to assure less than 1% standard counting deviation. Peak to background ratios were maximized setting the pulse height analyzer parameters, bias and pulse voltage discriminators, to the optimum values. This lead to improved analytical sensitivity due to the decreased minimum detectability limit, which was calculated according to Ziebold criterion and was found to be in the range of 100 to 300 ppm element concentration (0.01 to 0.03wt%) in the samples.

Homogeneity of standards and samples is required in EPMA. It was checked and confirmed according to the criterion[2] that all the measured peak intensity counts, N, from the analyzed points, should fall within $N+/-3N^{1/2}$, where $N^{1/2}=\sigma$ is the standard counting deviation.

Specimen surface contamination, which may occur during the analysis, was reduced using a liquid nitrogen cold trap in the vacuum system and mounting the cold finger above the samples. Analysis was performed point by point on selected doped $BaTiO_3$ grains. The programmed software controlled and automated the multi-point analysis, with a complete quantitative routine was applied in the case of long data-collection times. In such cases the electron beam current stability was confirmed to be better than 0.5% of the nominal value.

Measured intensities of generated characteristic X-rays in the samples were transformed into k-ratios relative to known element concentrations in the appropriate standards consisting of $BaTiO_3$, $La_2Ti_2O_7$ and CeO_2. The systematic error which appeared in the measurements of Ce concentration was due to $BaL\beta_{1,4}$ and $CeL\alpha_{1,2}$ spectral interference causing overlap of the corresponding spectral peaks even in the WDS analysis. This problem was solved by using the empirical calibration curve method for correction of the $CeL\alpha_1$ intensity[3]. Corrected k-ratios for Ce were then processed in the quantitation routine. Quantitative analysis was performed through the ZAF and/or PROZA matrix correction programs, transforming the measured k-ratios into element concentrations.

3. Results and discussion

Microstructures of typical Ce-doped and La-doped $BaTiO_3$ samples are shown in **Figures 1 and 2**.

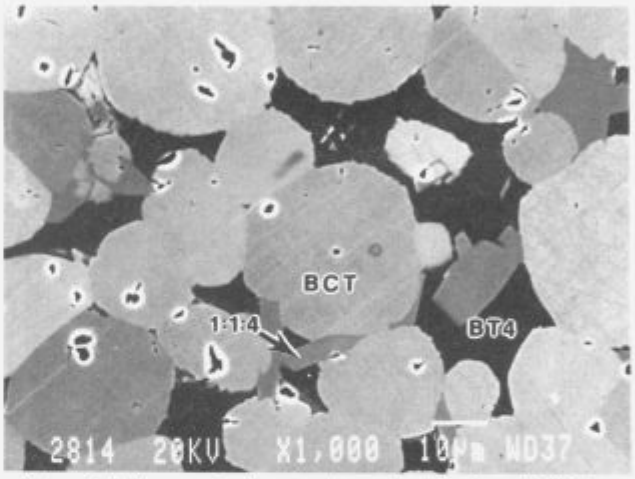

Figure 1: Backscattered electron micrograph of Ce-doped $BaTiO_3$; phase identification: 1:1:4 lamellae - $BaCe_2Ti_4O_{12}$, BT4 - polytitanate $BaTi_4O_9$, BCT - Ce-doped $BaTiO_3$ grains
Slika 1: Slika odbitih elektronov mikrostrukture keramike $BaTiO_3$ dopirane s Ce; oznake faz: 1:1:4 lamele - spojina $BaCe_2Ti_4O_{12}$, BT4 polititanat $BaTi_4O_9$, BCT - zrna $BaTiO_3$ dopirana s Ce

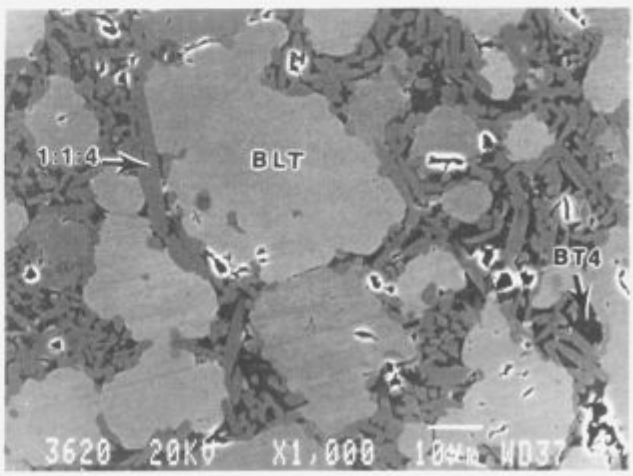

Figure 2: Backscattered electron micrograph of La-doped $BaTiO_3$; phase identification: 1:1:4 lamellae - $BaLa_2Ti_4O_{12}$, BT4 - polytitanate $BaTi_4O_9$, BLT - La-doped $BaTiO_3$ grains
Slika 2: Slika odbitih elektronov mikrostrukture keramike $BaTiO_3$ dopirane z La; oznake faz: 1:1:4 lamele - spojina $BaLa_2Ti_4O_{12}$, BT4 polititanat $BaTi_4O_9$, BLT - zrna $BaTiO_3$ dopirana z La

In every sample at least 10 doped $BaTiO_3$ grains were analyzed. Data obtained from counting statistics confirmed the homogeneity of the phases analyzed within the range N+/-σ, better than required N+/-3σ. In **Tables 1** and **2** the average results of measurements of cation concentrations in 4 Ce-doped and 3 La-doped characteristic samples are presented. Data were calculated to the perovskite ABO_3 formula considering different modes of Ce and La incorporation[4,5]. It should be noted that the oxygen content was not measured but calculated by difference from 100%, which is the usual approach in the analysis of oxide compounds.

Table 1: Results of WDS microanalysis of chosen Ce-doped $BaTiO_3$ samples

Sample	Ba (at%)	Ce (at%)	Ti (at%)	Calculated formula
1	19,51+/-0,41	6,79+/-0,43	12,31+/-0,30	$BaTi_{0.63}Ce_{0.37}O_3$
2	19,44+/-0,49	0,54+/-0,11	19,57+/-0,54	$Ba_{0.944}Ce_{0.016}Ti_{0.982}Ce_{0.018}(V_{Ti})''''_{0.964}O_3$
3	17,55+/-0,40	1,60+/-0,07	18,66+/-0,50	$Ba_{0.92}Ce_{0.08}Ti_{0.98}(V_{Ti})''''_{0.02}O_3$
4	18,72+/-0,44	1,02+/-0,09	19,44+/-0,46	$Ba_{0.962}Ce_{0.05}Ti_{0.981}(V_{Ti})''''_{0.01}O_3$

Table 2: Results of WDS microanalysis of chosen La-doped $BaTiO_3$ samples

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 from the average values relate to data measured on the various grains analyzed in the samples. Ce could be incorporated into the $BaTiO_3$ lattice in two different modes; substitutionally at Ti sites, as well as at Ba sites. It is generally accepted that the large trivalent rare earth cations La^{3+} and Ce^{3+} enter the $BaTiO_3$ lattice at Ba^{2+} sites and act as donors. In the present investigation, it is assumed that donor charge compensation takes place by creation of Ti^{4+} vacancies, $(V_{Ti})''''$[6].

Ce^{4+} ions enter the Ti^{4+} sites[7]. The distribution of Ce between Ba and Ti sites, expressed in the formulas given in **Table 1**, is calculated on the basis of WDS microanalysis of the (Ba+Ce)/Ti ratio. The chemical formulas of La containing $BaTiO_3$ solid solution listed in **Table 2** take into account La^{3+} on Ba^{2+} sites and the presence of Ti-site vacancies.

Correction of the Ba-Ce interference allows the correct analysis of samples with a low Ce concentration. Without correction the high Ba to Ce peak overlap ratio introduces a large error in the final quantitative analysis. Use of the ZAF and PROZA quantitative matrix correction programs gave practically the same results for calculated element concentrations within the range of statistical precision. Such a result is expected for the experimental conditions applied.

As an illustration of the analytical precision achieved the La-doped $BaTiO_3$ sample 3 can be presented as an example. 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 monophasic and the calculated formula based on the results of WDS microanalysis was $Ba_{0.715}La_{0.285}Ti_{0.907}(V_{Ti})''''O_3$. For the Ce-doped $BaTiO_3$ sample 4 can be used as an illustration of the analytical precision. Starting composition of the sample was expressed by the formula $Ba_{0.940}Ce_{0.060}Ti_{0.985}(V_{Ti})''''_{0.015}O_3$. The sintered sample was monophasic and the corresponding formula based on the results of WDS microanalysis was $Ba_{0.948}Ce_{0.052}Ti_{0.985}(V_{Ti})''''_{0.013}O_3$.

4. Conclusions

WDS quantitative microanalysis can be successfully applied for the investigation of oxide compound solid solutions. A detailed study and the optimization of WDS experimental EPMA procedure was performed for the analysis of Ce and La doped $BaTiO_3$ ceramics. 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 realized can be summarized as follows:direct analysis of phases of interest in the chosen samples, good analytical sensitivity and precision.

5. References

[1] H. M. Chan, M. P. Harmer and D. M. Smyth, Compensating Defects in Highly Donor Doped $BaTiO_3$, *J. Am. Ceram. Soc.*, 69, 1986, 6, 507-510

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

[3] M. Čeh, Z. Samardžija, D. Makovec, Study of Solid Solubility of Cerium in $BaTiO_3$ by Quantitative WDS Microanalysis, *Scanning*, Vol. 15, Supplement III, 1993, 94-95

[4] D. Makovec, Z. Samardžija and D. Kolar, Incorporation of Cerium into the $BaTiO_3$ Lattice, Third Euro-Ceramics Proc. 1, 1993, 961-966

[5] D. Makovec, Z. Samardžija, U. Delalut and D. Kolar, Defect Structure and Phase Relations of Highly La-Doped $BaTiO_3$, to be published

[6] G. H. Jonker and E. E. Havinga, The Influence of Foreign Ions on the Crystal Lattice of Barium Titanate, *Mat. Res. Bull.* 17, 1982, 345-350

[7] J. P. Guha, D. Kolar, Subsolidus Equilibria in the System BaO-CeO_2-TiO_2, *J. Am. Cer. Soc.* 56, 1973, 1, 5-6