Quantitative microanalysis of the PMNT single crystal

Zoran Samardžija[a], Jae-Ho Jeon[b], Miran Čeh[a]

[a] *Jožef Stefan Institute, Jamova cesta 39, Ljubljana, Slovenia*

[b] *Korea Institute of Machinery and Materials, 66 Sangnam-Dong, Changwon, South Korea*

Compositional analysis and assessment of the micro-scale and macro-scale homogeneity of the PMNT single crystal were carried out using advanced quantitative electron-probe microanalysis (EPMA) with wavelength-dispersive X-ray spectroscopy (WDS). Special experimental sampling design was applied for ANOVA statistical data evaluation [1]. PMNT single crystal grew from polycrystalline precursor $Pb(Mg_{1/3}Nb_{2/3})_{0.7}Ti_{0.3}O_3$ (70PMN-30PT), employing the seeded polycrystal conversion using $BaTiO_3$ single crystal as a seed (*Ceracomp Co., Ltd*.). The composition of the crystal was determined with high precision and accuracy using optimized WDS quantitative analysis with ultimate experimental uncertainty better than ±1%. It was given by $Pb_{0.994\pm0.004}(Mg_{0.220\pm0.003}Nb_{0.447\pm0.005})Ti_{0.334\pm0.007}O_3$, i.e. $Pb(Mg_{1/3}Nb_{2/3})_{1-x}Ti_xO_3$, where x=0.33 (67PMN-33PT). The assessment of compositional homogeneity revealed that PMNT crystal is homogeneous on the micro-scale with variations below ± 0.5 % for all elements. On the macro-scale statistically significant compositional variations were found for perovskite B-site ions being ± 2.3% for Ti, ± 1.3 % for Nb and ± 1.4 % for Mg, whereas the concentration of Pb (A-site ion) remained uniform within homogeneity level of $\leq \pm 0.5$ % [2]. Concentration variations for Ti^{4+}, Nb^{5+} and Mg^{2+} indicate that an unequal distribution of the B-site ions occurred during crystal growth, showing an opposite trend between the competing Ti and Mg–Nb ions. Calculated relative occupancy of the B-site ions gave an average atomic ratio of Ti/(Mg+Nb) = 0.50, however it can vary across the crystal between 0.48 and 0.53 (± 5 % relative). WDS microanalysis gave excellent, reliable and accurate quantitative compositional analysis as well as quantitative homogeneity assessment of the PMNT single crystal.

Acknowledgement: The research leading to these results has received funding from the European Union Seventh Framework Programme [FP7/2007-2013] under grant agreement n°312483 (ESTEEM2).

1. Z. Samardžija, J-H. Jeon, M. Čeh, *Mater. Charact.* **2007**, 58, 534-543

2. Z. Samardžija, EMAS 2014, *Book of Tutorials and Abstracts*, 241-252