Chemical instability in the surface layer of the lead hafnate single crystal

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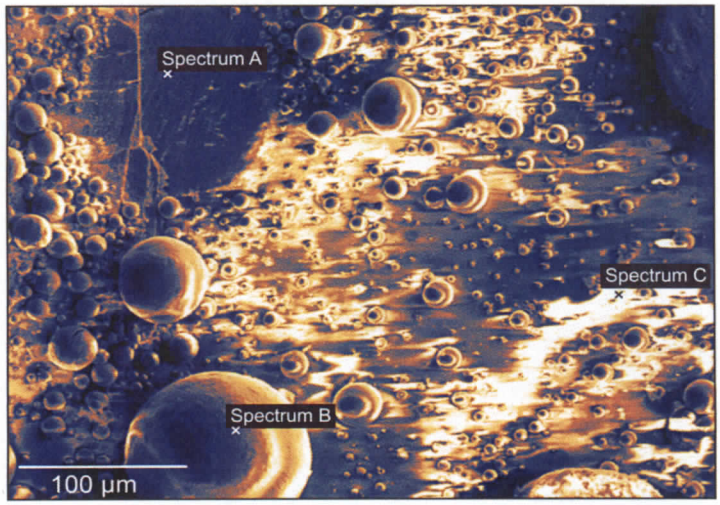
Lead hafnate $PbHfO_3$, as lead zirconate $PbZrO_3$, is an antiferroelectric perovskite oxide, which is a promising material for electric energy storage in high power applications. In order to elucidate the basic properties of this material the crystallographic and optical properties [1], lattice dynamics [2] and dielectric properties [3] have been investigated in a wide temperature range for single $PbHfO_3$ crystals. All of those investigations were conducted on crystals grown by means of spontaneous crystallization from the high-temperature solution in Pb_3O_4–B_2O_3 solvent [3].

We will present studies on the modifications of the surface layer of the lead hafnate crystals after exposition to various external conditions, such as high temperatures, oxidation and reduction processes. The thermogravimetric measurement method was used to define the stability of the crystal during oxidation at 600 °C and reduction at 500 °C. X-ray photoelectron spectroscopy was used to verify the modification in the electronic states after heating from room temperature to 700 °C, with a 100 °C step. Energy-dispersive x-ray analysis with a scanning electron microscope was used to identify topography and chemical composition of the surface layer after redox reactions. Figure 1 presents an electron microscopy image of the crystal after the reduction process. It shows areas with lead-deficiency (Spectrum A) and lead-rich exsolutions agglomerated with a bubbles-shaped structures (Spectrum B).



Area	Atomic concentration [%]		
	Pb	Hf	O
Average	15.5	18.4	66.1
Spectrum A	5.0	30.9	64.1
Spectrum B	40.0	0.7	59.3
Spectrum C	5.9	26.7	67.4

Figure 1. SEM-EDX measurement of surface of lead hafnate single crystal after reduction.

References

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