Atomic-resolution Measurement of Oxygen Concentration in Twin Domain Boundaries in $BaTiO_3$

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Thin films of Ba-based perovskites have great potential for electronic applications. This is the background to intensive research efforts to explore the intrinsic and defect-related properties of this class of materials. This work has shown that the electronic properties are very sensitive to variations in chemical composition. In particular, the formation of oxygen vacancies associated with extended lattice defects such as grain boundaries and interfaces has recently attracted great attention. A new tool to contribute to a solution of defect related problems is aberration-corrected transmission electron microscopy. In this report it will be applied to measure for the first time the oxygen concentration in a perovskite at atomic resolution.

In thin films of $BaTiO_3$ a high density of {111} twin domain lamellae with $\Sigma 3\{111\}\langle 111\rangle$ coincident site lattice boundaries is frequently observed. Their habit plane was identified as the {111} BaO_3 plane. Across the boundary oxygen octahedra change from corner- to face-sharing forming a Ti_2O_9 group unit. This is also the basic structural element of the hexagonal high-temperature phase of $BaTiO_3$ formed from the cubic phase at about 1460 °C. In a study of the near-edge structure of the L_{23} ionization edge of Ti by electron-energy loss spectroscopy it was found that the Ti atoms adjacent to the boundary plane occur in an oxidation state lower than the +4 in the stoichiometric compound and, as a consequence, the boundary plane should be oxygen- deficient. In the present work $\Sigma 3\{111\}\langle 110\rangle$ twin boundaries occurring naturally in thin films of $BaTiO_3$ are investigated using the novel technique of negative-C_S imaging (NCSI) in an aberration corrected transmission electron microscope.

On the basis of an investigation of the quantum mechanical background by computer calculations and detailed investigation of the dependence of oxygen intensity on imaging parameters we are able to measure the oxygen concentration in the boundary plane. We derive a mean value for the occupancy of 0.68, i.e. an oxygen concentration substantially lower than the stoichiometric value. We also observe a reduction of the BaO column spacing accompanied of an increase of the Ti-Ti atom spacing across the boundary. Our results are in excellent agreement with those of a chemical study employing X-ray diffraction and Ti-Fe substitution in the structurally equivalent hexagonal $Ba(Ti_{1-x}Fe_x)O_3$ phase.

References

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