Microstructure evolution during $BaTiO_3$ formation by solid-state reactions on rutile single crystal surfaces

Andreas Graff, Stephan Senz, Dieter Völtzke*, Hans-Peter Abicht*, and Dietrich Hesse

Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany
*) Institut für Anorganische Chemie, AG Keramik, Kurt-Mothes-Str. 2, Martin-Luther-Universität Halle-Wittenberg, D-06120 Halle, Germany

During sintering of TiO_2-$BaCO_3$ core shell powders a modified sequence of chemical phases concerning the Ti/Ba ratio was observed compared to the common powder sintering process. To study this phenomenon model experiments concerning phase formation and microstructure evolution during $BaTiO_3$ genesis were performed. Reaction products between BaO vapor and TiO_2 (rutile) single crystals with different orientations were investigated by XRD texture analysis, high resolution TEM (HRTEM) and electron energy loss spectroscopy (EELS).
At substrate temperatures of 700°C nanocrystalline $BaTiO_3$ grows as a reaction product with a rough interface to the rutile substrate. At 900°C $BaTiO_3$ forms at the surface of the reaction layer. It has a well-defined orientation relation to the rutile substrate. In addition to $BaTiO_3$, Ti-rich phases and pores were identified at the $BaTiO_3$-TiO_2 interface. Ti-rich phases most probably form by a reaction between the substrate and the initially grown $BaTiO_3$ thin reaction layer. The pore formation is explained by an outdiffusion of titanium and oxygen from the $BaTiO_3$-TiO_2 interface through the reaction layer to the surface where again $BaTiO_3$ is formed.
For a more detailed study of the TiO_2-$BaTiO_3$ reaction behavior, reaction couples consisting of $BaTiO_3$ thin films on rutile single crystal substrates were prepared by laser ablation. The films show a well-defined orientation relation on (100), (110), and (101) surfaces of the rutile single crystal substrates. On the (001) oriented substrates a fiber texture of the $BaTiO_3$ film was found. Solid state reactions were initiated by heat treatment in air. Details of this $BaTiO_3$-TiO_2 solid-solid reaction are compared with the BaO-TiO_2 vapor-solid reaction, and with the phase evolution in the sintering process using core shell powders as starting material.