

Formation of ferroelectric nanostructures by solid-state diffusion.

Nanoscale reaction engineering using reactive templates

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Nanostructures with different dimensionality are usually fabricated using liquid-phase chemical methods or growth from the vapour phase. Opposite, the solid-state synthesis route is often considered in a negative way because it is said that it produces coarse particles with broad size distribution and uncontrolled morphology. In this investigation we have shown that, in contrast, solid-state reactions can be used to fabricate high-quality nanowires and nanotubes of two well-known ferroelectric materials, BaTiO₃ and Bi₄Ti₃O₁₂, using suitable reactive templates. The templates have a coaxial, core-shell structure and are obtained using wet chemistry methods, such as precipitation and hydrothermal synthesis. Nanowires of one of the reactants are first grown from solution and then coated with a layer of the second reactant. For example, for the synthesis of BaTiO₃ nanorods, layered hydrogen titanate fiber-like crystals are first obtained by hydrothermal synthesis at 200°C and then coated with BaCO₃ nanocrystals. The intimate contact of the parent compounds in the core-shell templates results in low reaction temperatures (500-700 °C), overcoming the morphological instability problem of one-dimensional (1D) templates. The final morphology depends on the predominant diffusion mechanism and the arrangement of the parent compounds in the core-shell template. If the growth of the reaction product is dominated by the outward diffusion of the core material, the constrained geometry of the system does not allow for an efficient annihilation of the resulting vacancies and will enhance the formation of Kirkendall porosity inside the core. Pore coarsening and coalescence by surface diffusion then determine the formation of a single central cavity. In contrast, when the diffusivity of the shell material in the reaction product is higher than that of the core material, this will result in the formation of dense nanowires because the Kirkendall porosity is efficiently removed during the course of the reaction. Therefore, the final morphology, nanowire or nanotube, can be controlled by changing the arrangement of the parent oxides in the template. Nanoscale reaction engineering by means of reactive templates represent an effective strategy for the design and synthesis of ferroelectric nanostructures. Composite nanostructures, such as ferroelectric-magnetic core shell particles, can be obtained by a generalization of the foregoing approach.