Intergranular Chemistry and Sintering of Metal Oxide Particle Powders

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Configurations of composite metal oxide nanoparticles are typically far off their thermodynamic equilibrium state. As such they represent a versatile but so far overlooked source material for the intergranular solid-state chemistry inside ceramics. Moreover, Ion exsolution can be instrumental to engineer intergranular regions inside ceramic microstructures that are derived from nanocomposites. We explored the potential of vapor phase-grown MgO nanoparticles hosting Ba²⁺, In³⁺ and Fe³⁺ admixtures as precursors for engineered intergranular regions.[1,2]

During annealing-induced exsolution from the nanocrystal bulk into the grain interfaces, the impurity admixtures impact grain coarsening and powder densification, effects that were compared for the first time using an integrated characterization approach. The comprehensive structural analysis with XRD and electron microscopy enabled us to draw conclusions on the structure-property-relationships that are controlled by the impurity dispersion inside the MgO grain network.

Depending on the concentration of admixed Ba²⁺ ions, isolated impurity ions either become part of low-coordinated surface structures of the MgO grains where they give rise to a characteristic bright photoluminescence emission profile around λ = 500 nm, or they aggregate to form nanocrystalline BaO segregates at the inner pore surfaces to produce an emission feature centered at λ = 460 nm.[3]

A substantially less soft magnetic behavior was observed for samples with iron admixtures and a reduced fraction of the intergranular MgFe₂O₄ phase. Respective phenomenon is attributed to a nanodispersion effect describing size-dependent magnetic properties of Fe³⁺-doped MgO ceramics. Percolating networks of semiconducting MgIn₂O₄ were derived from MgO nanoparticles with admixtures of 20 at% In³⁺ that gives rise to an enhancement of dc conductivity values by more than 5 orders of magnitude in comparison to the insulating host.

The here presented approach is general and applicable to the synthesis of a variety of functional nanostructured spinel structures embedded inside ceramic matrices. Densification of vapor phase-grown nanoparticle powders with extremely well-defined bulk and surface properties to generate ceramics can lead to a high abundance of structurally and compositionally uniform intergranular regions that emerge from the interrelated effects of segregation and grain growth.