Abstract

This dissertation describes the synthesis, processing, and fundamental insights into chemical processing of high-entropy oxides (HEOs) and high-entropy sulfides (HESs) using metal alkoxides and thiolates. The central hypothesis is that not only thermodynamic entropy effects, but in particular the chemistry of the precursors used play a decisive role in achieving homogeneity, phase stability, and structural control in multicomponent inorganic materials. One of the aims was to systematically investigate how different precursor chemistries influence the formation of entropy-stabilized phases.

The central focus of the dissertation is based on the multi-source precursor-based synthesis of high entropy materials. Part of this is the polymer-assisted electrospinning of high entropy oxide fibers using PVP as viscous matrix. By adapting a polymer-supported process to multicomponent metal systems, continuous $(MnFeNiCoZn)_3O_4$ nanofibers with homogeneous element distribution could be produced. The results prove that classic electrospinning strategies are also suitable for modern high-entropy materials, provided that spinning parameters, polymer content, and thermal treatment are carefully coordinated.

A systematic investigation of alkoxide-based high-entropy oxides allowed control over hydrolysis and condensation reactions to precisely achieve different M:O stoichiometries, including MO_2, M_2O_3, and mixed-valence systems of the type $(M^{IV}{}_3M^{III}M^{V})O_2$. This precursor-based approach allowed clear correlations between precursor reactivity, oxidation state compatibility, and phase formation. Particularly noteworthy is the successful stabilization of mixed-valent HEOs that go beyond classical equimolar systems.

In contrast to the synthesis of high entropy materials as powders, fabrication of thin films with homogeneous dispersion of metals is challenging. Within this work, HEO thin films were successfully prepared by employing a mixture of molecular alkoxides in a commercial vaporizer. This technical system enables the controlled injection of multi-metallic precursor solutions and bridges the gap between solution-based chemistry

and plasma-assisted thin film deposition. The characterization of the resulting thin films showed that precursor-based high-entropy concepts can be successfully transferred to functional coatings.

Finally, the precursor concept for high entropy materials was extended to chalcogenides through the synthesis of tetravalent metal thiolates and their use in thiol-based sol-gel routes to obtain high entropy sulfides. The non-hydrolyte thio-sol-gel process is a less-studied field, with results showing that thiolate precursors are an effective source of sulfur and at the same time they enable homogeneous metal distribution.

The work reported in this dissertation illustrates that high-entropy materials are not formed by purely thermodynamic driven phenomenon and precursor chemistry, reaction kinetics, and process control are decisive factors for their successful synthesis.