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FOCUS ISSUE

THERMODYNAMICS OF COMPLEX SOLIDS

Introduction

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Oxides have been materials of choice for ceramic, optoelectronic, magnetic, and catalytic applications for decades because of their tunable properties, ease of fabrication, and environmental stability. Now there is increasing interest in non-oxide materials, including: robust high melting carbides and nitrides for aerospace applications; halide perovskites for solar energy conversion; chalcogenides for magnetic and electronic applications; hybrid organic–inorganic materials and metal organic frameworks for catalysis and separations; and many new and as-yet poorly understood layered materials for quantum computing. This wealth of new materials, often synthesized by specialized deposition techniques or under extreme conditions, has freed materials science from the "tyranny of equilibrium." Indeed, metastable materials often have desirable properties. Understanding the pathways that lead to desired products combines thermodynamic and kinetic considerations, the former delineating what is possible, the latter how fast those possibilities occur. Thermodynamics forms the fundamental underpinning for materials synthesis, reactivity, compatibility, and degradation, and thus pervades all aspects of materials science. There is much interest in elucidating, modeling, and classifying fundamental pathways of materials formation, in advancing thermodynamic characterization of energy landscapes and multivariable phase diagrams, including both stable and kinetically stabilized materials, in integrating in situ characterization and theoretical approaches to understand reaction thermodynamics and dynamics at multiple length and time scales, and in exploiting surfaces and interfaces as drivers of synthesis and functionality.

Nature follows conditional cause and effect—the synthesis of a solid material, particularly starting with dissolved species, often goes through a series of steps creating different intermediates that form "branch-points" in a complex energy landscape in a further progression toward or away from the desired product. This dependence of product formation on specific synthesis conditions is well known in the field of zeolite synthesis, but generally needs systematic study for other systems. Such product control has both thermodynamic and kinetic drivers that must be separated and understood.

Metastable phases and those near the edge of thermodynamic stability fields often have unique and interesting functionality. High T_c superconductors and hybrid lead halide perovskites manifest such behavior, but it is probably much more general.

Surfaces and interfaces can control thermodynamics and structure, especially at high surface area, and in turn can be controlled by dopants. Both chemical and mechanical properties are controlled by the same assemblage of defects and their energetics. Nanoscale materials have different thermodynamic properties from their bulk counterparts and show distinct phase diagrams, including the stabilization of polymorphs that are metastable in bulk. Such nanomaterials can be persistent and technologically useful, especially in catalysis.

In structurally complex materials, both cation and anion order–disorder can lead to a series of structures with different ordering on short, medium, and long range scales. The persistence, over long times and at high temperatures, of metastable states leads to a complex and closely spaced free energy landscape of structures with distinct properties. Such complexity in multi-major-component oxides, sometimes referred to as "high entropy oxides," diminishes their configurational entropy. Nevertheless, the different local atomic environments lead to the ability to tailor new physical properties.

In equilibrium, distribution of ions, vacancies, and oxidation states depends on composition, temperature, and pressure. In addition, a wealth of out-of-equilibrium states can be accessed using various techniques: quenching from high temperature or pressure, low temperature aqueous or solvothermal synthesis of disordered nanomaterials, vapor deposition, grinding, and radiation damage. These metastable states can sometimes persist indefinitely at ambient conditions and, perhaps surprisingly, at higher temperatures as well.

This wealth of new materials, new approaches to characterization, improved thermodynamic measurements, and rapidly evolving computational capabilities make a Focus Issue on Thermodynamics of Complex Solids timely. Our contributions are focused on a variety of materials studied by both experimental and theoretical thermodynamic techniques, complemented by

detailed structural studies emphasizing the complexities of order–disorder on different length and time scales.

We would like to thank the authors and all reviewers who made the Focus Issue possible and we hope our readers find the collection intriguing and useful.

On the cover

The surface energetics of complex solid state materials, such as carbon nanotubes grown on different substrates, can be explored by adsorption calorimetry with different molecular probes.