

Linking Structure, Energetics and Fast-Ion Conduction

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The present review focuses on links between structure, energetics and ion transport in oxygen-deficient perovskite oxides, ABO_{3-d}. The perfect long-range-order, convenient for interpretations of the structure and properties of ordered materials, is evidently not present in disordered materials and highly defective perovskite oxides are spatially inhomogeneous on an intermediate length scale. Although this makes a fundamental description of these and other disordered materials very difficult, it is becoming increasingly clear that this complexity often is essential for the functional properties. In the present review we advocate a potential energy barrier description of the disordered state in which the possible local (or inherent) structures are seen to correspond to separate local minima on the potential energy surface. We interpret the average structure observed experimentally at any temperature as a time and spatial average of the different local structures which are energetically accessible. The local structure is largely affected by preferences for certain polyhedron coordinations and by the oxidation state stability of the transition metals and the strong long-range electrostatic interactions present in non-stoichiometric oxides imply that only a small fraction of the local minima are energetically accessible at most temperatures. Oxide-ion transport in the potential energy barrier description must be interpreted as due to the transformation of one energetically accessible local structure into another. Thus, strongly correlated transport mechanisms are expected; in addition to the movement of the oxygen ions giving rise to the transport, other ions are involved and even the A- and B-atoms move appreciably in a cooperative fashion along the transition path. Such strongly correlated or collective ionic migration mechanism should be considered for fast oxide ion conductors in general and in particular for systems forming superstructures at low temperatures. Structural criteria for fast ion conduction are discussed. A high density of low lying local energy minima is certainly a prerequisite and for perovskite-related A₂B₂O₅ oxides, those containing B-atoms that have energetic preference for tetrahedral coordination geometry are especially promising.