Complex oxides are one of the largest and most technologically important materials families. The ABO$_3$ perovskite oxides in particular display an unparalleled variety of physical properties. The microscopic origin of these properties (how they arise from the structure of the material) is often complicated, but in many systems previous research has identified simple guidelines or ‘rules of thumb’ that link structure and chemistry to the physics of interest. For example, the tolerance factor is a simple empirical measure that relates the composition of a perovskite to its tendency to adopt a distorted structure. First-principles calculations have shown that the tendency towards ferroelectricity increases systematically as the tolerance factor of the perovskite decreases. Can we uncover a similar set of simple guidelines to yield new insights into the ionic and thermal transport properties of perovskites? I will discuss recent research from my group on the link between crystal structure and chemistry, soft phonons and ionic transport in a family of layered perovskite oxides, the Ln$_2$NiO$_{4+δ}$ Ruddlesden-Popper phases. In particular, we show how the lattice dynamical properties of these materials (their tendency to undergo certain structural distortions) can be correlated with oxide ion transport properties. Ultimately, we seek new ways to understand the microscopic origins of complex transport processes and to develop first-principles-based design rules for new materials based on our understanding.