Thermoelectric properties such as thermopower, electronic and thermal conductivity are governed by the underlying bonding interactions and local structural arrangements. This presentation will provide examples on how changing the local structural situation in materials affects thermoelectric transport directly. For instance, in the quaternary Cu$_2$MGeQ$_4$ ($M = \text{Zn, Fe;}$ $Q = \text{S, Se}$), the local bonding situation on the one hand leads to moving valence and conduction bands as well as enhanced point defect scattering on the other hand. Further examples include materials such as Yb$_{1-x}$Zn$_2$Sb$_2$ and CoSb$_3$. Understanding the underlying structure, defect chemistry, and temperature dependent structural changes helps to understand effects such as doping efficiencies and apparent band convergence.