

The Energy Landscape of Framework Materials

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Framework minerals display a complex set of behaviors traceable to the inherent flexibility of the framework that encompasses a number of phenomena in crystalline, amorphous, and liquid states. These phenomena include polymorphism, negative volumes of fusion, very low to negative thermal expansion, pressure-induced amorphization, and polyamorphism. Taken together, this combination of behavior defines the energy landscape of framework materials as a function of pressure (P), temperature (T) and composition (X) via the “flexibility syndrome”. In this presentation we address the factors that influence the P-T-X energy landscape of tetrahedral frameworks (e.g. zeolites), octahedral frameworks (e.g. perovskites) and tetrahedral-octahedral frameworks (e.g. garnets). Crystallographic studies, combined with spectroscopic studies (Raman, Inelastic Neutron Scattering), at variable P-T-X, reveal details about the structural, elastic properties and vibrational density of states of frameworks that, in turn, are related to their thermodynamic properties. The relative compressibilities of the framework and extra-framework cations control the high-pressure behavior of the frameworks. Phonon modes present at low energies are linked to the distortion of the framework and determine the stability of the framework. This overview provides important insights about how the stronger rigid bonds of the framework and weaker, more flexible modes affect the lattice dynamics, energetics and stabilities of the structures.