Exploratory materials chemistry seeks to uncover new compounds, which increasingly are formed under some non-traditional chemical potential. This deviation from thermally-driven solid-state reaction processes can be seen in our syntheses of semiconducting or magnetic materials. Sulfides, for example, can behave as oxides, with slow, thermally-driven diffusion reactions governed by phase diagrams. However their synthesis becomes more complex by melting, and confluence of these processes offers some opportunities for synthetic control. In the case of the semiconductor Fe$_2$SiS$_4$, in situ diffraction reveals mechanisms (e.g. a peritectic onset of ternary compound formation) that bridge the solid state and melt scenarios. The ability to tune these material by metathesis reactions is also valuable. The defect-forming character and correlated-electron properties can be changed in situ, as in charge-doping superconductors. We will discuss recent results from our lab on redox reactions in magnetic materials.

**Keywords:** powder diffraction, magnetism, materials discovery