Mechanistic insight of $ABiQ_2$ (A = alkali metal, Q = S, Se) using panoramic synthesis towards synthesis-by-design

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Solid-state synthesis has historically focused on reactants and end products; however, knowledge of reaction pathways, intermediate phases and their formation may provide mechanistic insight of solid-state reactions. With an increased understanding of reaction progressions, design principles can be developed, affording more predictive power in materials synthesis. In pursuit of this goal, *in-situ* powder X-ray diffraction is employed to observe crystalline phase evolution over the course of the reaction, thereby constructing a "panoramic" view of the reaction. *In-situ* diffraction studies were conducted in the A-Bi-Q (A = alkali metal, Q = S, Se) system to understand the formation of known phases in this system as well as to correlate these observations to structural analogues. Three new phases were discovered, including a metastable intermediate phase. Panoramic synthesis showed that this intermediate phase serves an important mechanistic role as a structural intermediate in the reaction to form the $ABiQ_2$ structure. The formation of the two new thermodynamically-stable products, both of which crystallize in the $NaCrS_2$ structure type, show a boundary where the structure can be disordered or ordered with regards to the alkali metal and pnictogen. A cation radius tolerance for six-coordinate cation site sharing is proposed. The mechanistic insight this technique provides in the A-Bi-Q system is progress towards the overarching goal of synthesis-by-design.