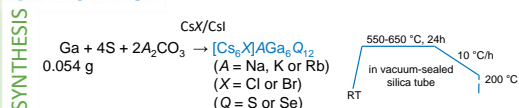
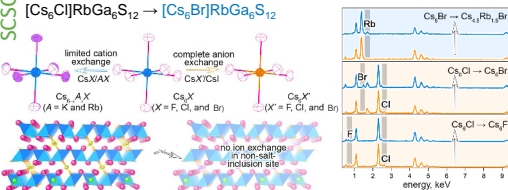
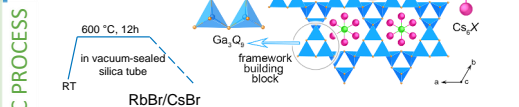
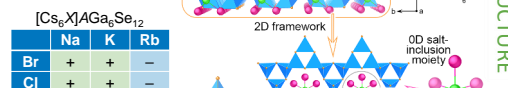
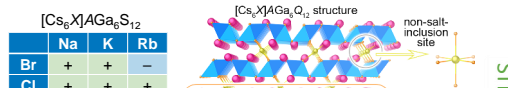


Chalcogenides are the cornerstone of the semiconductor and thermoelectric industries and are up-and-coming materials for superconductors, catalysis, and battery applications. Challenges in synthesizing those materials emerge from the chalcogen's volatility and the tendencies of chalcogenides to react with even trace quantities of oxygen. Many techniques have been applied to the growth of chalcogenide single crystals, which are convenient for structure determinations and intrinsic property measurements. One of the recent advances in chalcogenide chemistry is the intriguing single-crystal-to-single-crystal (SCSC) transformation, leading to new metastable compositions. Post-synthetic transformations are well-known and studied for chalcogenide powders; however, examples of post-synthetic conversions that retain single crystallinity are rare. To date, the scope of SCSC reactions includes (de)intercalation in the layered compositions and ion exchange in open-framework materials, salt-inclusion chalcogenides, and layered structures. This poster will discuss the successful examples of SCSC modifications monitored by single-crystal X-ray diffraction (SC-XRD), emphasizing how post-synthetic transformations affect materials' properties.

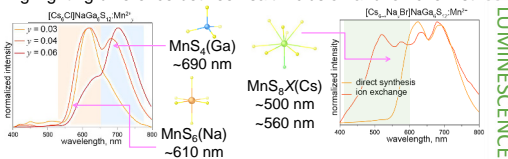
ION EXCHANGE



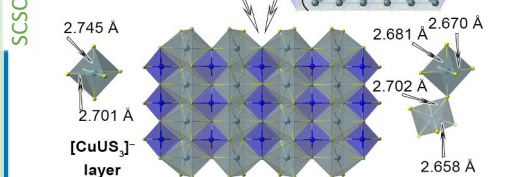
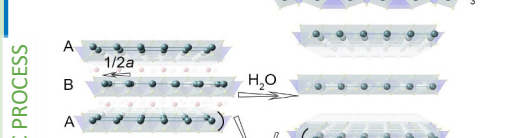
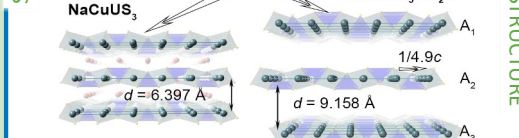
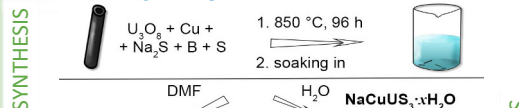
Using polychalcogenide/halide flux, we obtained single crystals of salt-inclusion chalcogenides $[\text{Cs}_x\text{X}]_n\text{AGa}_6\text{Q}_{12}$. This structure consists of 0D $[\text{Cs}_x\text{X}]^{5+}$ fragment, 2D $[\text{Ga}_6\text{Q}_{12}]^{6-}$ honeycomb layers, and A cations between the layers.



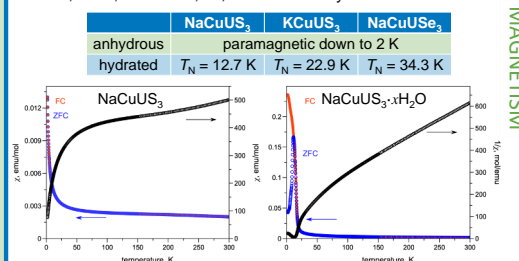
Single crystals of $[\text{Cs}_x\text{X}]_n\text{AGa}_6\text{Q}_{12}$ can further undergo SCSC ion-exchange reactions at melt. Novel $[\text{Cs}_x\text{F}]_n\text{NaGa}_6\text{S}_{12}$, $[\text{Cs}_x\text{Rb}_y\text{Br}]_n\text{NaGa}_6\text{S}_{12}$, $[\text{Cs}_x\text{Rb}_y\text{Br}]_n\text{NaGa}_6\text{S}_{12}$ compositions were synthesized, the structures were determined via SC-XRD and EDS. Ion exchange is possible for only $[\text{Cs}_x\text{X}]^{5+}$ and not A^+ , highlighting difference between salt-inclusion and ion chemistries.



WATER INTERCALATION

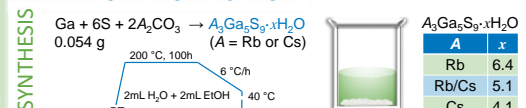


	NaCuUS_3	KCuUS_3	NaCuUS_3
anhydrous		paramagnetic down to 2 K	
hydrated	$T_N = 12.7 \text{ K}$	$T_N = 22.9 \text{ K}$	$T_N = 34.3 \text{ K}$

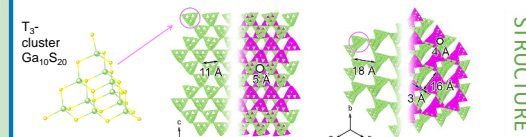


Magnetic measurements revealed the transformation from paramagnetism to canted antiferromagnetism upon hydration.

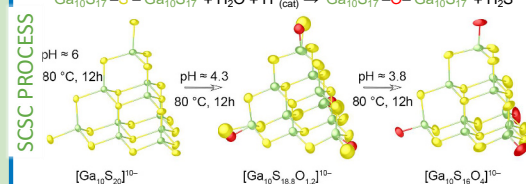
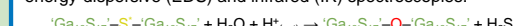
FRAMEWORK MODIFICATION



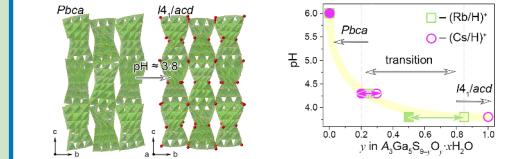
Using the mild hydrothermal synthesis approach, we crystallized the open-framework chalcogenides $\text{A}_3\text{Ga}_5\text{S}_9 \cdot x\text{H}_2\text{O}$ (A = Rb and Cs) starting from elemental gallium and sulfur, combined with cesium or rubidium carbonate in an ethanol/water solution.



The $\text{A}_3\text{Ga}_5\text{S}_9 \cdot x\text{H}_2\text{O}$ structure consists of a 2-fold interpenetrated diamond-like framework built with pseudo- T_3 supertetrahedra. The remaining 48% of the structural volume is occupied by disordered A^+ and water molecules, as determined by single-crystal X-ray diffraction (SC-XRD), thermo-gravimetric analysis, energy-dispersive (EDS) and infrared (IR) spectroscopies.



The $\text{A}_3\text{Ga}_5\text{S}_9 \cdot x\text{H}_2\text{O}$ open-framework structure can undergo a SC-SC framework transformation from $[\text{Ga}_5\text{S}_3]^{3-}$ to $[\text{Ga}_5\text{S}_3\text{O}]^{3-}$. Catalyzed by acidic solutions at very mild temperatures, and even at room temperature, under low pH (< 3) conditions, vertex S^* in the pseudo- T_3 supertetrahedral clusters could be replaced with O as determined by SC-XRD. During the SC-SC transformation, the structure changes symmetry from $Pbca$ to $I4_1/acd$.



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