## Designing Complex Semiconductors: Tunable Mixed-Halide Chalcohalides and Transition Metal Dichalcogenides for Optoelectronic Applications

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Part 1. Chalcohalides are desirable semiconducting materials due to their enhanced lightabsorbing efficiency and stability compared to lead halide perovskites. However, unlike perovskites, tuning the optical properties of chalcohalides by mixing different halide ions into their structure remains to be explored. We present an effective strategy for halide-alloying  $Pb_3SBr_xl_{4-x}$  ( $1 \le x \le 3$ ) using a solution-phase approach and study the effect of halide-mixing on structural and optical properties. We employ a combination of X-ray diffraction, electron microscopy, and solid-state NMR spectroscopy to probe the chemical structure of the chalcohalides and determine mixed-halide incorporation. The absorption onsets of the chalcohalides blue-shift to higher energies as bromide replaces iodide within the structure. The photoluminescence maxima of these materials mimic this trend at both the ensemble and single particle fluorescence levels, as observed by solution-phase and single particle fluorescence microscopy, respectively. These materials exhibit superior stability against moisture compared to traditional lead halide perovskites, and IR spectroscopy reveals that the chalcohalide surfaces are terminated by both amine and carboxylate ligands. Electronic structure calculations support the experimental band gap widening and volume reduction with increased bromide incorporation, and provide useful insight into the likely atomic coloring patterns of the different mixed-halide compositions.

Part 2. Layered, transition metal dichalcogenides (TMDCs) such as MoS<sub>2</sub> and WSe<sub>2</sub> are under intense investigation due to their structural flexibility and optoelectronic tunability. The extent of mixing and alloying between two or more TMDCs is critical to their properties, yet elucidating these chemical transformations at the atomic scale remains difficult. To address this challenge, we probe TMDC mixing and alloying by using a combination of powder X-ray diffraction (XRD) and <sup>77</sup>Se solid-state nuclear magnetic resonance (SSNMR) spectroscopy. We find that the specific material and atmosphere used for ball milling and annealing strongly impact the formation of oxides during the mixing of TMDCs. Static wideband, uniform rate, smooth truncation (WURST)-quadrupolar Carr-Purcell-Meiboom-Gill (QCPMG), magic angle spinning (MAS), and dynamic nuclear polarization (DNP) SSNMR techniques allow us to detect and resolve <sup>77</sup>Se resonances in mixed bulk, exfoliated, and nanoscale TMDCs. Together, powder XRD and static WURST-QCPMG <sup>77</sup>Se SSNMR provide conclusive evidence for the formation of new alloyed multinary TMDCs, where all elements are intimately mixed at the atomic level, upon ball milling and subsequent annealing.