

## Metal Thio/Selenophosphates: A Novel Two-Dimensional Materials System

Matthew Cheng<sup>1</sup>, Roberto do Reis<sup>1,3</sup>, Daniel Chica<sup>2</sup>, Mercouri Kanatzidis<sup>2</sup> and Vinayak P. Dravid<sup>1,3\*</sup>

<sup>1</sup> Department of Materials Science and Engineering, Northwestern University, Evanston, IL, USA.

<sup>2</sup> Department of Chemistry, Northwestern University, Evanston, IL, USA.

<sup>3</sup> NUANCE Center, Northwestern University, Evanston, IL, USA.

\* Corresponding author: v-dravid@northwestern.edu

Ever since the discovery of graphene in 2004, interest in van der Waals materials have increased exponentially. This material system, which includes black phosphorus (BP), hexagonal boron nitride (h-BN), and the transition metal dichalcogenides (TMD) are found to possess many interesting properties when reduced to the 2D limit that can both complement and supplement that of graphene. For example, due to the extreme spatial confinement present in these structures, MoS<sub>2</sub> undergoes an indirect to direct bandgap transition.

This fascination with van der Waals materials has brought upon renewed interest in the layered metal thio(seleno)phosphates (MTSPs) family, as well. First discovered in the late 1980s, MTSPs adopt either a M<sub>2</sub><sup>2+</sup>P<sub>2</sub>X<sub>6</sub> or M<sup>1+</sup>M<sup>3+</sup>P<sub>2</sub>X<sub>6</sub> stoichiometry with a similar crystallographic structure to the TMDs. A layer of metal cations with a phosphorus dimer is sandwiched in between two layers of chalcogen (S, Se) atoms. Many of the MTSPs have been shown to exhibit either an antiferroelectric (AFE) or ferroelectric (FE) ordering and/or ferromagnetic (FM) or antiferromagnetic (AFM) ordering at lower temperatures [1]. This unique property of a material to possess both FE and FM ordering or multiferroicity has promising applications in the fields of spintronics and nonvolatile memory storage.

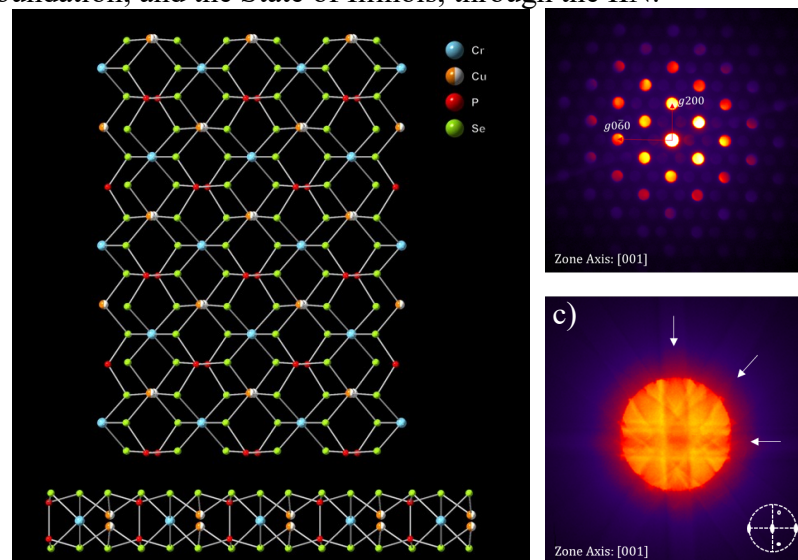
In the mixed cation MTSPs, M<sup>1+</sup>M<sup>3+</sup>P<sub>2</sub>X<sub>6</sub>, special interest is paid toward the Cu containing systems as a distortion of the Cu<sup>1+</sup> site due to a Jahn-Teller distortion gives rise to a ferroelectric response as is shown with CuInP<sub>2</sub>S<sub>6</sub> [2]. Further, by using a magnetic element in the second metallic site such as Cr or V, the resulting MTSP system can in turn exhibit ordered magnetic phases as is reported with CuCrP<sub>2</sub>S<sub>6</sub> [3]. Electronic and magnetic polarization are due to the spontaneous formation of dipoles and spin, respectively. Electron microscopy, thus, offers a route to probe the atomic structure in order to better understand the mechanisms giving rise to ordering in these systems.

In this study, we report structural analysis of the CuCrP<sub>2</sub>Se<sub>6</sub> system at both room and cryogenic temperatures. The crystal symmetry of CuCrP<sub>2</sub>Se<sub>6</sub> (Fig.1) [4] is probed by Kossel-Möllenstedt (K-M-) and Kossel (K-) Convergent Beam Electron Diffraction (CBED) patterns taken along the [001] direction (Figs 1b and 1c). At the [001] zone axis, the local symmetry for monoclinic C<sub>2</sub> (space group #5) is expected to be *C1m1*.

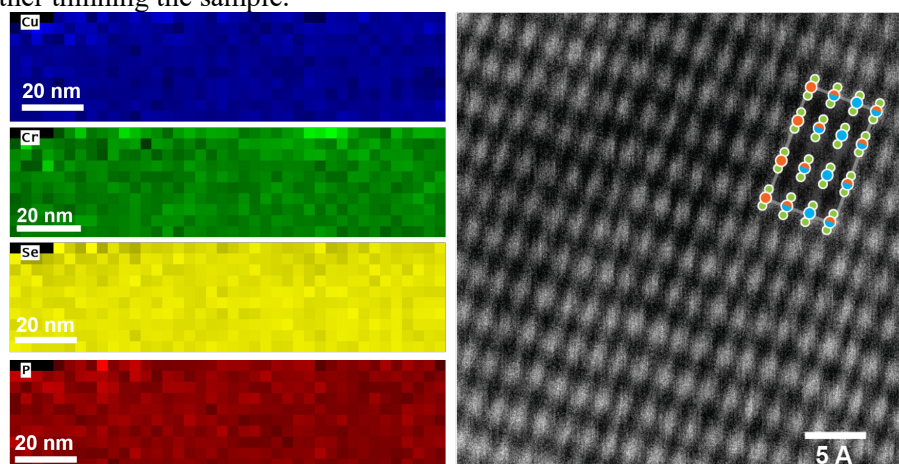
High resolution scanning transmission electron microscopy (STEM) images were taken along the [001] direction at room temperature in order to both compare with the diffraction patterns but also to visualize any distortions or changes in the crystal lattice. The crystallographic and structural characterization is supplemented by electron energy loss spectroscopy (EELS). Further, we endeavor to capture the break of symmetry of different materials in the metal seleno(thio)phosphate family [4,5].

## References:

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**Figure 1.** a) Top (c-axis) and side view (a-axis) of the theoretical CuCrP<sub>2</sub>Se<sub>6</sub> structure. Note that the Cu sites would be expected to have half filled sites on both sides of the mid-plane. b) K-M CBED pattern ( $\alpha = 1.5$  mrad) showing the monoclinic structure of the materials. c) Energy filtered K-CBED pattern ( $\alpha = 24.8$  mrad) with visible Kikuchi lines shows the whole-crystal symmetry (see inset for symmetry representation). Note the presence of extra symmetry elements that may be attributed to offset layers present in the sample. This will likely be resolved by further thinning the sample.



**Figure 2.** (Left) Energy Dispersive Spectroscopy (EDS) Maps exhibiting a uniform distribution of Cu, Cr, P, and Se in the CuCrP<sub>2</sub>Se<sub>6</sub> structure. (Right) High Resolution STEM image of the CuCrP<sub>2</sub>Se<sub>6</sub> system. The presence of offset layers in the sample likely accounts for the “extra” atoms that are visible in the HRSTEM image.