High-resolution structural analysis of cation-mixed (Fe,Mn,Ni)PS3 van der Waals single crystals

Dr. Tatiana Smoliarova[1], B.Sc. Moritz Küster[1], Dr. Apoorva Chaturvedi[2], Prof. Edwin-Hang-Tong Teo[2], Prof. Michael Farle[1], Dr. Anna Semisalova[1]
[1]Faculty of Physics and Center of Nanointegration (CENIDE), University of Duisburg-Essen, Duisburg, Germany, [2]Center for Programmable Materials, School of Materials Science and Engineering, Nanyang Technological University, Singapore, Singapore

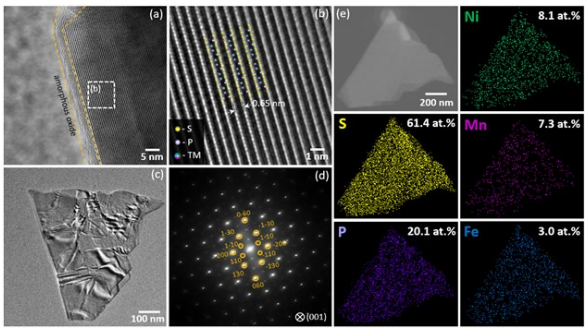
Transition-metal (TM)-based van der Waals (vdW) materials ("2D – materials") recently received particular attention due to their tunable magnetic properties arising from unpaired magnetic moments due to the partially filled d-shells of the TM ions. The subclass of TM phosphorous trisulfides (TMPS3) has attracted significant interest due to its wide range of TM elements, resulting in diverse properties [1]. The structure of TMPS3 is defined by its vdW nature. Layers exhibit the monoclinic crystal structure, space group 3 C2/m, and are only bound by weak vdW forces [2], which allows for easy exfoliation and leads to 2D-like properties being observable in 3D crystals.

In this study, transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), electron energy loss spectroscopy (EELS), and continuous rotation electron diffraction (cRED) have been combined to study the cation-mixed (Fe,Mn,Ni)PS3 van der Waals single crystals with different Fe, Mn, and Ni concentrations produced in a bulk state by chemical vapor transport (CVT) [3].

The high-resolution (HR) TEM image (a) shows the cross-section of a (Fe,Mn,Ni)PS3 single crystalline sample, prepared by Cryo-Ultramicrotome. An amorphous oxide layer formed on the edge of the sample is highlighted with a yellow dashed line. It has a thickness of 5 nm. The magnified HRTEM image (b) shows the layered structure with a layer distance of 0.65 ± 0.02 nm. Bright spots (atomic columns) correspond to S and P. The darker lines are the planes of TM ions. Ultrasonically exfoliated layers are shown on TEM image (c) on which selected area electron diffraction (SAED) (d) and EDX mapping (e) have been performed. The lattice parameters a = 0.647 nm, b = 1.072 nm, c = 0.698 nm, α = γ = 90° and β = 111.22° were estimated from the SAED pattern and slightly deviate from earlier reported FePS3, MnPS3 and NiPS3 mono-compounds [4,5].

Work is funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Project-ID 405553726 – TRR 270, Z02"

Graphic:



Keywords:

3D ED, cRED, 2D-materials, TMPS3

Reference:

[1] Burch, K. S., Mandrus, D., & Park, J. G. "Magnetism in two-dimensional van der Waals materials." Nature, vol. 563, no. 7729, 2018, pp. 47–52.

[2] Mayorga-Martinez, C. C., et al. "Layered Metal Thiophosphite Materials: Magnetic, Electrochemical, and Electronic Properties." ACS Applied Materials & Interfaces, vol. 9, no. 14, 2017, pp. 12563–12573.

[3] Samal, Rutuparna, et al. “Two-dimensional transition metal phosphorous trichalcogenides (MPX3): a review on emerging trends, current state and future perspectives”. In: Journal of Materials Chemistry A, vol. 9, no. 5, 2021, pp. 2560–2591.

[4] Ouvrard, G., Brec, R., & Rouxel, J. “Structural determination of some MPS3 layered phases (M = Mn, Fe, Co, Ni and Cd)”. In: Materials Research Bulletin, vol. 20, no. 10, 1985, pp. 1181–1189. ISSN: 0025-5408.

[5] Saito, Shozo, Ko Kurosawa, & Yasuo Yamaguchi. “Neutron Diffraction Study on MnPS3 and FePS3”. In: Journal of the Physical Society of Japan, 1985, pp. 3919–3926.