Reliable structure determination of K-intercalated RuCl₃ nanoflakes by 3D electron crystallography and multivariate analysis of fused EELS and EDX spectrum images

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2D nanosheets are intensely researched as new quantum materials and components of next-generation electronic and spintronic devices with unprecedented magnetic, transport and optical properties. In particular, the thickness-dependency of structural and physical properties is subject of close scrutiny. α-RuCl₃ is a spin ½ honeycomb material that exhibits exotic magnetic ground states both in bulk¹ and exfoliated² forms. Its flakes and intercalates feature high environmental stability and retain the in-plane honeycomb structure during wet-chemistry functionalization². RuCl₃ nanosheets are a robust test-bed for fabrication of new nanocomposites in both acidic or basic aqueous solutions, and their performance as electrodes for electrochemical reduction/ion transfer reactions can be further optimized. Reliable structural and compositional characterization during downscaling and intercalation is one of the goals that will enable well-controlled nanosheet functionalization. We synthesized K-intercalated RuCl₃ by electrochemistry in an aqueous KCl solution. Conventional X-ray diffraction methods fail to characterize such intercalates due to the presence of multiple nm-sized domains, stacking faults and other defects associated with the layered morphology. Instead, we for the first time determine the local structure and capture the essential properties on the nm-length scale by collecting the multimodal 3DED–STEM–EELS–EDX data. The 3DED method is one of the very few that provides both in-plane and out-of-plane structural information, which is indispensable for layered materials. The K₀.₅RuCl₃ layered intercalate (sp. gr. P-31m) is stacked differently than the α-RuCl₃ parent compound (sp.gr. C₂/m): the K atoms in the interlayer space are coordinated by six equivalent Cl atoms to form the [KCl₆] octahedra that share corners with the six equivalent [RuCl₆] octahedra. As a hallmark of STEM, EELS, and EDX spectroscopy, spatial mapping techniques were used to trace local changes in the chemical composition. A multimodal data fusion³ helped to overcome the severe spectral overlap and high sparseness of EDX data. The retrieved abundance profiles revealed spatially resolved phases with differing in the K:Ru:Cl ratio, the Ru oxidation state and in the oxygen content. This microinhomogeneity is a rather local disorder, which might cause only minor local symmetry changes, and could be associated with concomitant water molecules co-intercalating into the α-RuCl₃ matrix together with the K⁺ cations.

Figure 1. a,b Reconstructed 3D reciprocal lattice of the K-doped α-RuCl₃, scale bar is 4 nm⁻¹, c In-plane and out-of-plane structure of K₀.₅RuCl₃ found by 3DED, d TEM overview image, e,f Abundance maps from fused EDX and EELS data. Scale bar is 200 nm.


Keywords: 3DED; electron crystallography; multimodal data fusion; EELS; EDX; multivariate analysis; α-RuCl₃

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