Reliable structure determination of K-intercalated $RuCl_3$ 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-$RuCl_3$ is a spin ½ honeycomb material that exhibits exotic magnetic ground states both in bulk[1] and exfoliated[2] forms. Its flakes and intercalates feature high environmental stability and retain the in-plane honeycomb structure during wet-chemistry functionalization[2]. $RuCl_3$ 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 $RuCl_3$ 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 $K_{0.5}RuCl_3$ layered intercalate (sp. gr. *P*-31*m*) is stacked differently than the α-$RuCl_3$ parent compound (sp.gr. *C*2/*m*): the K atoms in the interlayer space are coordinated by six equivalent Cl atoms to form the [KCl_6] octahedra that share corners with the six equivalent [$RuCl_6$] 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 fusion[3] 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-$RuCl_3$ matrix together with the K^+ cations.

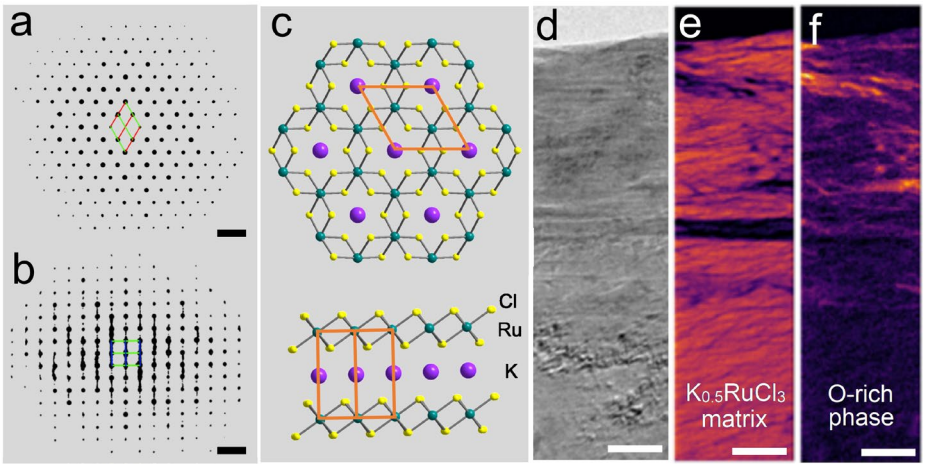

Figure 1. a,b Reconstructed 3D reciprocal lattice of the K-doped α-$RuCl_3$, scale bar is 4 nm^{-1}, c In-plane and out-of-plane structure of $K_{0.5}RuCl_3$ found by 3DED, d TEM overview image, e,f Abundance maps from fused EDX and EELS data. Scale bar is 200 nm.

[1] Roslova, M., Hunger, J., Bastien, G., Pohl, D., Haghighi, H. M., Wolter, A. U. B., Isaeva, A., et al. (2019). *Inorg. Chem.* **10**, 6659-6668; Bastien, G., Roslova, M., Haghighi, M. H., Mehlawat, K., Hunger, J., Isaeva, A., et al. (2019). *Phys. Rev. B.* **99**, 214410.

[2] Weber, D., Schoop, L. M., Duppel, V., Lippmann, J. M., Nuss, J., Lotsch, B. V. (2016). *Nano Lett.* **16(6)**, 3578–3584.

[3] Thersleff, T., Budnyk, S., Drangai, L., Slabon, A. (2020). *Ultramicroscopy*. **219**, 113116; Thersleff, T., Jenei, I. Z., Budnyk, S., Dörr, N., Slabon, A. (2021). *ACS Appl. Nano Mater.* **4 (1)**, 220–228.

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