

Two-dimensional Dion-Jacobson oxides: reducing the size to improve the functionality

Authors: Y. Leibas^{1,2}, Y. Thomas¹, L. Joanny³, S. Ollivier¹, G. Ciatto², C. Cochard¹, V. Demange^{*1}

¹ Univ Rennes, CNRS, ISCR – UMR 6226, Rennes, France

² Synchrotron Soleil, SIRIUS Beamline, Saint-Aubin, France

³ ScanMAT - UAR 2025, Rennes, France

Abstract

Ferroelectrics are materials that exhibit spontaneous polarization that can be reversed by the application of an external electric field. This bistability makes them attractive for applications such as non-volatile memories, while reducing their dimensions can enable further miniaturization and potentially new functionalities. For a long time, ferroelectricity was not expected to persist in ultrathin, two-dimensional (2D), systems. However, recent advances have demonstrated ferroelectric behavior in layers below 10 nm and have shown that reducing the dimensionality of non-ferroelectric bulk materials can also lead to emergent functional properties. Dion–Jacobson (DJ) layered perovskites are particularly promising in this context because their intrinsically layered structure enables chemical exfoliation into 2D nanosheets. Recent studies have reported local ferroelectric behavior in $\text{Ca}_2\text{Na}_2\text{Nb}_5\text{O}_{16}$ nanosheets obtained from $\text{KCa}_2\text{Na}_2\text{Nb}_5\text{O}_{16}$ (5KCNN), belonging to the $\text{KCa}_2\text{Na}_{n-3}\text{Nb}_n\text{O}_{3n+1}$ family ($n=3-6$). Nevertheless, the structural features governing the stability and ferroelectric response of these exfoliated layers remain incompletely understood.

My work focuses on the synthesis and structural characterization of $\text{KCa}_2\text{NaNb}_4\text{O}_{13}$ (4KCNN) and $\text{KCa}_2\text{Na}_2\text{Nb}_5\text{O}_{16}$ (5KCNN), synthesized through a step by step high-temperature solid-state reaction using previously prepared $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ and NaNbO_3 as precursors. The resulting layered crystals were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS), with preliminary Le Bail refinements performed to determine their lattice parameters, while further structural analyses are ongoing. These samples were subsequently subjected to protonation and liquid-phase exfoliation to investigate the associated structural changes. The resulting protonated phases were studied by XRD, SEM, and EDS, while the resulting nanosheets were characterized by atomic force microscopy (AFM) and transmission electron microscopy (TEM). To complement the average structural information obtained by laboratory XRD, a proposal for pair distribution function (PDF) measurements at the CRISTAL beamline has been submitted to investigate the atomic structure. Preliminary grazing incidence (GI) X-ray absorption spectroscopy (XAS) measurements performed at the SIRIUS beamline provide complementary information on the local environment of selected cations, with quantitative analysis currently in progress. A second proposal for performing GI-XAS and X-ray linear dichroism on nanosheets has been submitted for the SIRIUS beamline. This combined approach aims to establish the structural evolution of 4KCNN and 5KCNN from layered bulk crystals to 2D nanosheets and to identify structural features potentially related to the emergence of ferroelectricity in the 2D limit. Future work will extend this study to the 6KCNN member of the family.