High Spatial and Energy Resolution Analytical Scanning Transmission Electron Microscopy for Quantum Materials

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The functional properties of materials are increasingly controlled and tuned through structural or chemical architectures whose engineering takes place quite literally at the atomic level. This enables so-called emergent properties relying on the interplay between charge, spin, chemistry, etc…, which if understood and controlled should find many applications in crucial fields such as information or energy sciences. One of the most powerful means of characterization of these subtle physico-chemical effects arguably lies within a combination of high resolution scanning transmission electron microscopy and energy loss spectroscopy (STEM-EELS) and *ab initio* modeling. Recent instrumentation advances have pushed the spatial resolution of these instruments below 0.1nm, while providing energy resolution for spectroscopy of under 10meV, thus truly realizing the promise of placing a 'synchrotron in a microscope' [1]. This contribution will highlight a number of recent applications of high spatial, energy (and momentum) resolution STEM-EELS.

A first example concerns pyramidal quantum dots (QDs), which thanks to highly symmetrical pyramidal site-controlled QDs at smaller scales than previously possible, offer a unique system for non-classical light emission and therefore represent a highly promising candidate for photonic quantum information applications [2,3]. The pyramidal QD system studied here consists of differently composed III-V (Al)GaAs layers and an $In_xGa_{1-x}As$ QD layer (typically <1nm) which are grown by metal-organic vapor-phase epitaxy (MOVPE) between GaAs inner barriers and AlGaAs outer barriers. The high symmetry of the (111)B site-controlled pyramids allows for smaller shape asymmetries in the QDs formation, compared to other systems resulting in an exceptionally high density of entangled-photon emitters by means of both optical and electrical excitation [2,3]. Atomically-resolved STEM-EELS is key to not only confirm the chemistry and structure of these extremely thin quantum layers, but also to probe directly the electronic and optical response of individual QDs, including variations in the measured band gap compared to that of the surrounding matrix, thanks to monochromated EELS [4].

The ability of monochromated STEM-EELS to reveal the close interplay between structure, chemistry and transport properties is also evident in complex A-site deficient perovskite oxides for thermoelectric applications. Here, the presence of a large number of cation vacancies generates different degrees of structural ordering, such as cation-vacancy ordering or oxygen octahedral tilting domain ordering. These structural features, which can be tailored via specific growth strategies, can significantly affect the base material's electronic structure (for instance by introducing electronic states in the vicinity of the Fermi

level), or reduce lattice thermal conductivity. Here we focus on a $La_{1/3}NbO_3$ ceramic, that presents the highest vacancy content among the A-site-deficient perovskite family (whereby 2/3 of the A sites are vacant), a feature which may promote glasslike low thermal conductivity [5]. Atomically resolved imaging and EELS analysis reveals the presence of a layered structure in addition to A-site cation vacancy pairing along the $[\bar{1}11]$ and $[11\bar{1}]$ crystallographic directions. The near-edge fine structure of the O K edge observed at high energy resolution in the distinct layers of the structures is compared with first-principles electronic structure calculations, which are in turn used to link the temperature dependence of the Seebeck coefficient measured experimentally to the evolution of the density of states with electronic doping concentration. These experimental findings point to possible avenues for further optimization through electron doping and control of the A-site occupancies [6].

References:

[1] Q Ramasse, Ultramicroscopy **180** (2017), p. 41.
[2] G Juska *et al.*, Nature Photonics. **7** (2013), p. 527.
[3] TH Chung *et al.*, Nature Photonics **10** (2016), p. 782.
[4] K Holsgrove *et al.*, Submitted (2019).
[5] D Kepaptsoglou *et al.*, Inorganic Chemistry **57** (2018), p.45.
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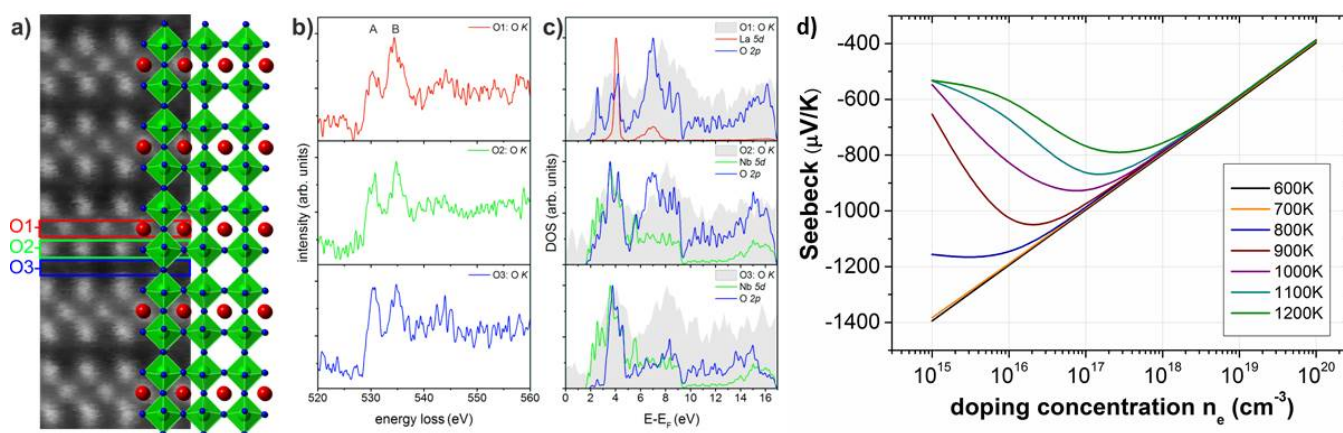
Figure 1. a) HAADF STEM signal and b) background subtracted O K EELS spectra from the regions marked in (a) and (c) calculated DOS of $La_{1/3}NbO_3$ projected onto La, Nb and O. The Fermi level is set at 0eV. The pDOS is plotted against the experimental O K edges for the corresponding layers. d) calculated Seebeck coefficient dependence on the doping concentration, which can be controlled by tailoring the A-site deficiency in the structure. The calculations are provided at various temperatures, using a rigid-band model that assumes no shape change in the band structure, but only a shift in the Fermi energy due to the changing electron doping concentration. [5]