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ABSTRACT:

Elucidating Grain-Boundary–Driven Ionic Conduction in Perovskite Solid Electrolytes via 4D-STEM and Multimodal Spectroscopy

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Understanding ionic conduction and diffusion in solid electrolytes requires direct insight into how grain-boundary (GB) structure, chemistry, and electrostatics govern ion transport. While bulk transport in perovskite oxides is well studied, GBs often dominate total resistance yet remain poorly understood due to the lack of nanoscale measurements of charge distribution and local electric fields. Here, we combine four-dimensional scanning transmission electron microscopy (4D-STEM), atomic-resolution X-ray energy dispersive spectroscopy (EDS) and electron energy-loss spectroscopy (EELS), and first-principles simulations to directly correlate GB electrostatics with Li-ion transport in perovskite solid electrolytes, including $(Li_{0.375}Sr_{0.4375})(Ta_{0.375}Nb_{0.375}Zr_{0.125}Hf_{0.125})O_3$ and $Li_{0.375}Sr_{0.4375}Ta_{0.75}Zr_{0.25}O_3$, which exhibit distinct bulk- and GB-limited conduction regimes.
4D-STEM measurements reveal that air-quenched samples exhibit pronounced asymmetric charge accumulation across GBs, forming built-in electric fields analogous to nanoscale p–n junctions, in contrast to the commonly assumed symmetric space-charge model. These internal fields extend from the boundary and are expected to influence ion migration pathways. Correlative STEM-EDS and EELS analysis shows that this electrostatic asymmetry originates from B-site cation segregation, with Nb preferentially enriched at GBs and Ta redistributed into adjacent grain interiors, while Li concentration remains largely uniform. First-principles calculations and ab initio molecular dynamics simulations further demonstrate that these compositional gradients modify the local electrostatic landscape and bonding environment, leading to enhanced Li-ion diffusivity in Ta-rich regions where Li–cation interactions are weaker. These results establish that GBs can function as active electrostatic interfaces that regulate ionic diffusion, rather than passive barriers or simple vacancy-rich pathways.