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Decoding the Structural Origin of Piezoelectric and Thermoelectric Materials with Aberration-Corrected STEM

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Aberration-corrected scanning transmission electron microscopy (STEM) has developed into a most powerful characterization and even fabrication platform for materials. This is especially so for functional materials with complex structural features that dynamically respond to external fields. Thoroughly understanding and tailoring structural defects is extremely significant for understanding the structure-property relations of existing high-performance materials, and more importantly, guiding the design of new materials with improved properties. Here we show examples of new insights obtained from two representative functional materials, piezoelectric and thermoelectric materials. Results were obtained with the newly set-up JEOL ARM200F STEM with ASCOR aberration corrector, cold field emission gun, UHR pole piece, Gatan Quantum ER spectrometer, OneView camera and Oxford Aztec EDS system at the National University of Singapore.

Piezoelectric materials interconvert between electrical energy and mechanical strain, and they are widely used for electronic and electro-mechanical devices. Owing to growing environmental concerns, the development of lead-free piezoelectric materials with enhanced properties becomes of great interest. Key to the academic problem is a lack of fundamental understanding of the actual mechanisms involved at the microscopic (unit cell) level. While it is understood that giant responses occur near structural phase boundaries, there has been no atomistic understanding of the origin of the response. New materials have therefore been synthesized largely by informed trial and error. We employed atomic-resolution polarization mapping to uncover the general structural origin: the coexistence of ferroelectric phases inside nanodomains and gradual polarization rotation between them. Guided from such structural origin, with systematic density functional calculations, our team has achieved notable breakthroughs in improving the properties of $(K,Na)NbO_3$ and $BaTiO_3$ based lead-free piezoceramics [1-2].

Thermoelectricity enables the direct inter-conversion between electrical energy and thermal energy, promising for scavenging electric power from sources of waste heat and for solid-state refrigeration to prevent electronic devices from overheating. Different scales of structural defects have strong influence on both thermal and electrical transport properties [3]. Nanostructuring has been widely acknowledged as the most universal strategy to enhance thermoelectric properties. However, atomic-scale defects have usually been ignored due to the difficulty of quantifying them via traditional methods. With the new generation of aberration-corrected STEM this has now become possible. For example, one of our recent achievements was to directly observe the intrinsic Pb vacancies and extrinsic Cu interstitials in the classic PbTe thermoelectric, so revealing the “magic” roles of Cu on synergistic optimization of phonon and carrier transport [4]. The structural origins of the new-generation “Phonon glass, electron crystal, PGEC” compounds (e.g., SnSe and $CoSb_3$) are thus proposed as static lattice distortion and dynamic lattice thermal vibration [5].

References:

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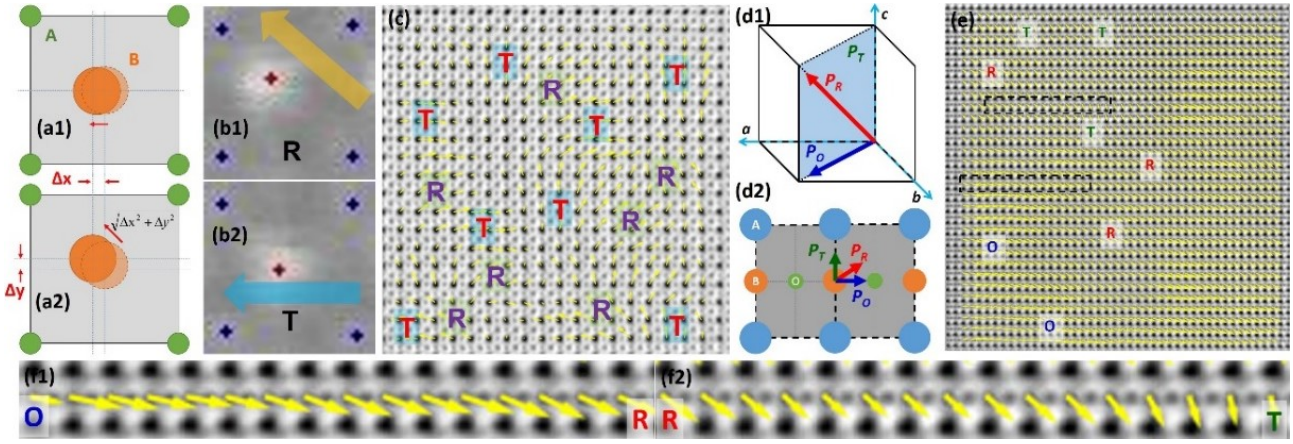

Figure 1. Structural models showing phase coexistence and gradual polarization rotation, (a1, a2) and (d1, d2); (b1,b2) STEM HAADF and (c) ABF images of KNN-based material with polarization map showing R+T phases; (e) ABF image of BT-based material with polarization map showing R+T+O; (f1,f2) Gradual polarization rotation between R, O, and T. Adapted from [2].

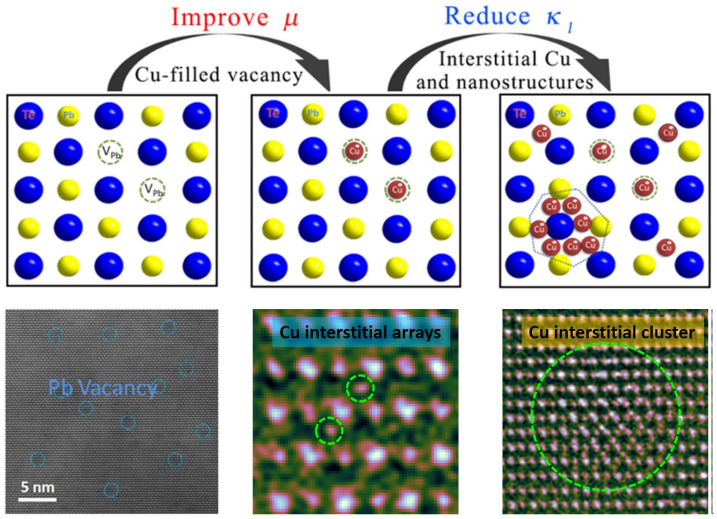

Figure 2. Schematic and structural evidence for the roles of Cu in PbTe: filling the intrinsic Pb vacancies to enhance carrier mobility and reducing the lattice thermal conductivity through scattering all-wavelength phonons via forming interstitials, clusters and precipitates. Reproduced from [4].