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Determination of Atomic Structures of Crystal Defects, Interfaces and Surfaces via Aberration-Corrected Transmission Electron Microscopy

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Understanding of the structure/property relations of crystal defects, interfaces and surfaces in advanced materials is key to providing needed control and enhancement of the behavior that is critical to the usages. Knowledge of the chemistry and structure of defects, interfaces and surfaces in crystal on an atomic level is therefore essential for understanding changes in performance. Recently, the developed hardware with objective-lens aberration correction technique has successfully pushed the point resolution of a transmission electron microscope (TEM) with field-emission gun up to its information limit [1]. Furthermore, a novel imaging technique called negative-C_S-imaging (NCSI) enables the direct imaging of light elements in materials [2]. In this study we investigated the core structures of dislocations in $BaTiO_3$ perovskite, the domain walls in $(K_{1-x}Na_x)NbO_3$ lead-free ferroelectric ceramics, the size-morphology dependence relation of faceted face-centered cubic (fcc) Fe nanoparticles and the surface structures of zigzag SnO_2 nanobelts by using NCSI and associated image simulations.

Oxides with perovskite structure have been the topic of intensive research on account of their wide variety of physical properties including piezoelectricity, ferroelectricity, magnetoresistance and superconductivity. Due to strong lattice distortions and local changes of the stoichiometry around the defects, the electrical properties in the vicinity of the defect area usually significantly deviate from those of the perfect area. Here we determined the atomic configurations of the core structures of two types of $<001>_{PC}\{110\}_{PC}$ edge dislocations (subscript PC stands for pseudo-cubic) and a $<001>_{PC}\{100\}_{PC}$ mixed dislocation in $BaTiO_3$ by using NCSI. The $<001>_{PC}\{110\}_{PC}$ edge dislocation dissociated into two collinear partials by a short-distance climb of $(100)_{PC}$ Ti-O_2 or Ba-O plane. The mixed dislocation had also the Burgers vector of <001>, but the glide plane of {100}. The experimental images of the core structures matched with the simulation results with the proposed atomic configurations. Local stoichiometry indicated the oxygen deficiencies in the compressive region.

Recently increasing efforts have been devoted to searching for new lead-free ferroelectric and piezoelectric materials from the perspective of environmental protection. One of the most promising lead-free candidates is the doped $(K_{0.5}Na_{0.5})NbO_3$-based ceramics [3]. As domain walls play a significant role in influencing the macroscopic properties of ferroelectrics, the atomic configurations of domain walls is important for understanding and optimizing the properties. The cation-oxygen dipoles across the 60°/120° domain walls in orthorhombic $(K_{0.46}Na_{0.54})NbO_3$ (KNN) ferroelectric ceramics were experimentally determined via NCSI. The orientation of the polarization changed very abruptly cross the 60°/120° domain walls in KNN, which was in consistent with the first-principles calculation results. The width across the wall was measured to be ~ 1.1 nm.

Metal nanoparticles have attracted great attention due to their great potential to modulate electronic, magnetic, optic, and catalytic properties. The size and shape of metal nanoparticles play an important role in determining their chemical and physical properties. Here we successfully synthesized face-centered cubic (fcc) Fe nanoparticles with diverse morphologies including icosahedron, decahedron, 5-fold twinned nanorod, tetrahedron and cube [4]. With the aberration-corrected high-resolution TEM, the unique icosahedral structure's pseudo-2-fold, 3-fold, and pseudo-5-fold axes were directly observed for the first time and verified by computer simulation [5]. Small sizes (5-13 nm) favor icosahedral nanoparticles; decahedron and 5-fold twinned nanorods are favored at intermediate sizes (12-164 nm), and triangular plate and cube at large sizes (~200 nm). This size-morphology dependence relation of faceted fcc-Fe nanoparticles can be well explained by thermodynamic calculations.

Tin oxide is widely used as a solid state gas sensor material, oxidation catalyst, and transparent conductor. Tin oxide nanobelts and nanowires have been fabricated and applied as novel materials for gas sensing nanodevices. The surface structures of tin oxide play a significant role in gas adsorption in devices, Using NCSI and image simulations, we identified that most of the {101} surfaces of zigzag SnO_2 nanobelts, synthesized by a solid-vapor process, were the reduced surfaces with termination of Sn atoms. The Sn-terminated surface was a non-polar surface. Since both reduced SnO and stoichiometric SnO_2 (101) surfaces were neutral terminations, the polar surface model was not suitable for the (101) type surface of rutile SnO_2 nanobelts.

Here we have demonstrated that the NCSI and associated image simulations are powerful tools for determining the atomic configurations of the crystal defects, interfaces and surfaces in materials. Increased knowledge of the structures of defects, interfaces and surfaces on an atomic level provides information useful in developing the advanced materials with desired performance.

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