

Tailoring Orbital Symmetry and Ordering: *A new route in searching for new materials*

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CaCu₃Ti₄O₁₂ (CCTO), a perovskite oxide, exhibits unusually high dielectric constant ($\epsilon \sim 10^5$) [1], the highest ever measured in non-ferroelectrics over a wide range of temperature and frequency. Although this intriguing property offers promising technological applications, such as the miniaturization of static- and dynamic-random access memories, the underlying mechanism was unknown since Density Functional Theory (DFT) calculations suggest $\epsilon \sim 40$ for a perfect CCTO. Many researchers speculated that extrinsic defects such as grain boundaries act as “Internal Barrier Layer Capacitance” (IBLC) responsible for this anomalous behavior, but similar dielectric behavior was observed even in single crystals, so raising major doubts about the IBLC mechanism.

To understand the origin of the gigantic dielectric response in CCTO, we studied single crystals (originally studied with neutron diffraction and optical reflectivity [1]) using a quantitative electron-diffraction method (PARODI) we developed at Brookhaven that allows us to map the distribution of valence electrons. We focused on obtaining accurate measurements of the electron structure factors of low-order reflections that are very sensitive to the small change of bonding electrons, in combination with the structure factors of high-order reflections from synchrotron x-rays (at X7B beam-line, National Synchrotron Light Source, NSLS). Our charge density study, along with the high-resolution imaging and selected area diffraction, suggests possible atomic disorder and local symmetry breaking (see Fig.1 (a) and (b)). To confirm the disorder, which may not be sensitive to x-ray and neutron diffraction, we conducted extended x-ray absorption fine structure spectroscopy (EXAFS, also at NSLS), an approach that is ideal for revealing bond coordination number, bond length, and short-range-order. With these complementary methods, we uncovered the existence of significant local atomic substitution in the otherwise ordered CCTO single crystals, involving the replacement of Ca by Cu, and vice versa. DFT-based calculations revealed that when Cu occupies the Ca site in the insulating matrix, the region becomes metallic-like due to orbital degeneracy (Fig.1(c)), yielding the mystifying dielectric response. We demonstrated that a small disturbance of local symmetry can significantly alter the static- and dynamic-electronic behaviors in strongly correlated electron systems, thus pointing to a new route in searching for such fascinating properties of materials, especially high-dielectric ones, by tailoring orbital symmetry and ordering [2].

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References

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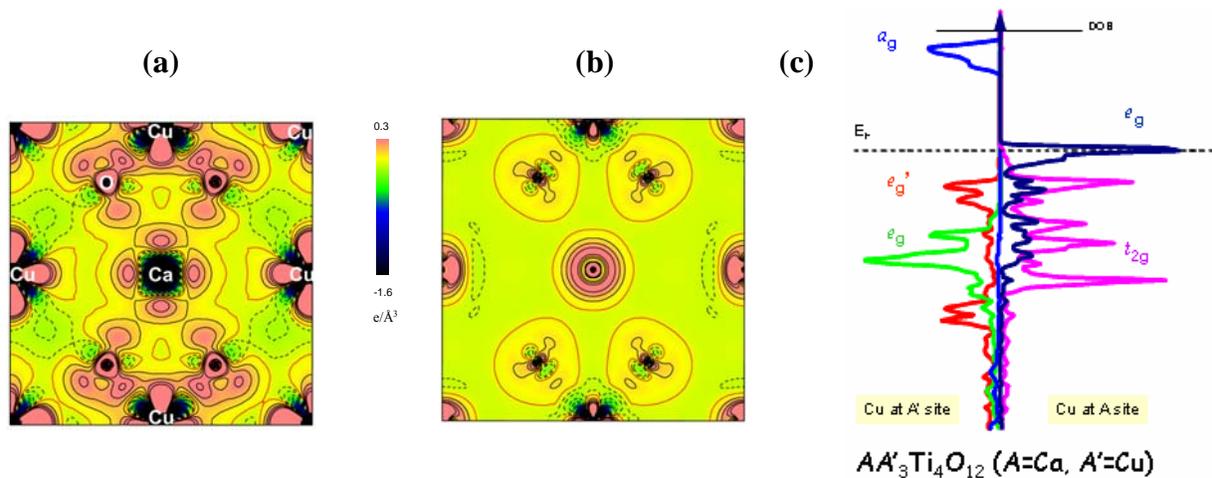


Fig1(a) Experimental map of bonding-electron distribution of A-site (Ca) in CCTO, based on structure factor measurements using combined electron and x-ray diffraction, showing anisotropy of e_g electrons due to the partial substitution of Cu. (b) DFT calculation of the same site in perfect CCTO, showing a spherical orbital symmetry. (c) Partial density of spin-minority states (states/eV cell spin) of Cu based on DFT calculations (LSDA+U, $U=4\text{eV}$) of the periodic systems. In perfect CCTO (left), the orbital ordering associated with the O-octahedral tilt breaks the degeneracy of t_{2g} , while in the disordered region (right) the cubic-like symmetry at the A' site retains the e_g -degeneracy, and thus, exhibits metallic-like behavior so enabling a large local dielectric response.