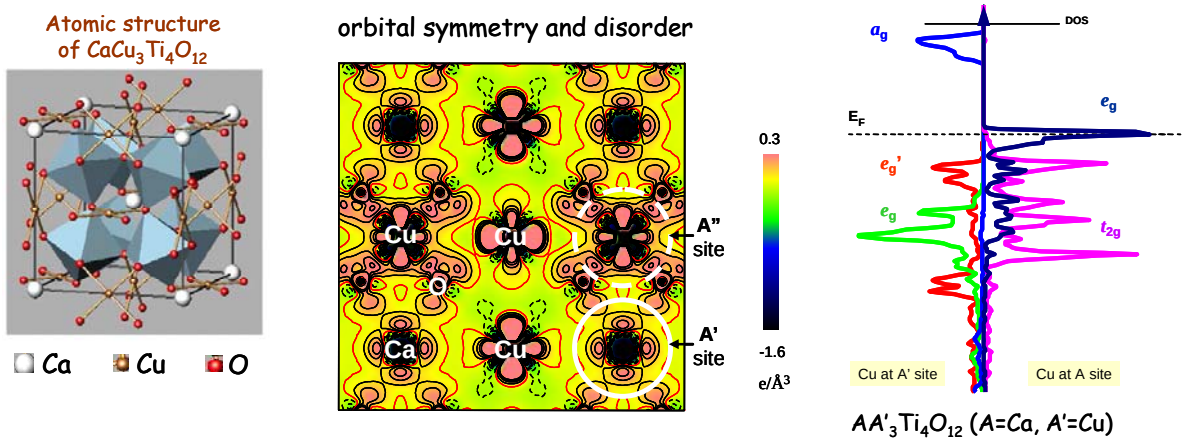
TAILORING ORBITAL SYMMETRY AND ORDERING :
A novel route to search for new functional materials

The recent discovery of the extremely high dielectric constant of $CaCu_3Ti_4O_{12}$ over a wide range of temperature and frequency, the highest ever measured in non-ferroelectrics, offers promising technological applications, including the possible miniaturization of random-access-memories for wireless communications. The puzzling aspect of the discovery is that while theoretical calculations suggest the dielectric constant in perfect $CaCu_3Ti_4O_{12}$ is four-orders-of-magnitude smaller than experimental measurement, structural defects conventionally expected for such unusual behavior were never found in the system. The origin of this high dielectric property soon became a "Holy Grail" for researchers.

An integrated study combining quantitative electron and synchrotron-x-ray diffraction, imaging and spectroscopy, as well as first-principles calculations reveals the existence of a small amount of nanoscale disorder of Cu/Ca substitution and its remarkable effect on the electronic properties of the material. In particular, the change of Cu orbital ordering leads to a unique electronic environment with drastically enhanced local dielectric response. We have demonstrated that a small disturbance of local orbital symmetry could significantly alter the static and dynamic electronic behavior of the material. This provides a new route in the search for novel materials by opening the door to understanding substitutional and orbital symmetry-driven properties and functionalization of various complex oxides.



The bonding-electron distribution of $CaCu_3Ti_4O_{12}$ in the basal plane, derived from quantitative electron and x-ray diffraction data at 90K. Density of state calculations on the effect of orbital symmetry and ordering shown on the right with Cu at A' site (perfect crystal) and Cu substitute Ca.

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