# Atomistic Models of Structural Relaxations in Ceria Nanoparticles from Neutron Total Scattering

## Scientific Motivation

Ceria nanoparticles can store, release, and transport oxygen ions efficiently which makes them attractive for active components in applications ranging from automotive catalytic converters to solid-oxide-fuel-cells. These useful properties are intimately linked to the point-defect chemistry of ceria. Despite the practical significance, types of dominant defects (e.g., oxygen vacancies, Frenkel pairs, cerium interstitials) and their effects on lattice distortions, both static and dynamic, remain uncertain. The structure of ceria nanoparticles has been studied on several occasions [1, 2] but the conclusions were either contentious or vague. As a basic example, at room temperature, these nanoparticles appear to exhibit oxygen atomic displacement parameters that are considerably larger than those measured for bulk ceria [2]; however, the origins of such "enhanced disorder" have not been identified.

## Proposed Study

We are planning to address this uncertainty by performing whole-nanoparticle atomistic structure refinements from neutron total scattering using the Reverse Monte Carlo (RMC) method as implemented in the RMCProfile software. Recently, the NIST group has been successful in using this approach (with X-ray total scattering) to determine the structure of brookite titania nanorods in mixed-phase brookite-anatase nanoparticle samples; the RMC results were validated by first principles calculations [3]. The case of ceria nanoparticles is simultaneously simpler and more complex. The simpler part is that ceria samples are single phase. The complexity comes from likely deviations from stoichiometry and a spherical shape of the available ceria nanoparticles in hand. We propose to perform measurements on two nanoparticle samples having similar particle sizes and shapes but distinct stoichiometries; the latter difference will be achieved via annealing under controlled reducing conditions to convert a portion of $Ce^{4+}$ into $Ce^{3+}$. The measurements will be performed at several temperatures between 300 K and 10 K to enable the separation of the dynamic and static atomic displacements which is expected to facilitate the determination of the effects of finite size and point defects on atomic arrangements relative to the bulk. Furthermore, we hope to use the lattice-dynamics information to obtain an insight into oxygen diffusion via the Einstein equation (linking atomic disorder to diffusion coefficient) and Arrhenius equation (linking diffuse coefficient with activation energy for diffusion) [4]. This study, if successful, will provide key inputs to the understanding of the origins of electrical transport and catalytic properties of nano-ceria.

## Preliminary Work

In 2018, we measured neutron total scattering for the pure and doped (Zr, La) ceria nanoparticle samples; the particle sizes for the three samples were different. These data were compromised by the high incoherent-scattering background from the residual organic molecules capping the particles. Nevertheless, we managed to remove this background and obtain a signal of quality suitable for RMC refinements. An example of the RMC refinements for the pure ceria particles having the diameter of about 6 nm (smallest of all the samples) are summarized in Fig. 1. Fig. 1 (bottom right) illustrates the results of the microstrain analysis, which compares the effective local and average lattice parameters for the concentric shells of increasing radii (the shell thicknesses were adjusted to maintain the same number of the unit cells per shell). The microstrain appears to be the largest near the particle center; the reasons for such a trend remain uncertain. One goal of the proposed measurements is to obtain data of improved quality and scope that would help to clarify these microstrain effects. Since the last round, we developed a procedure for eliminating the residual hydrocarbons without affecting particle sizes and morphologies. Thus, new data should be devoid of

hydrogen backgrounds as can be judged from the neutron-diffraction measurements that were performed on the improved samples using the BT-1 instrument at NCNR (NIST). Having samples with similar particle sizes but distinct stoichiometries should provide additional comparison points for assessing the origins and spatial distributions of local distortions.

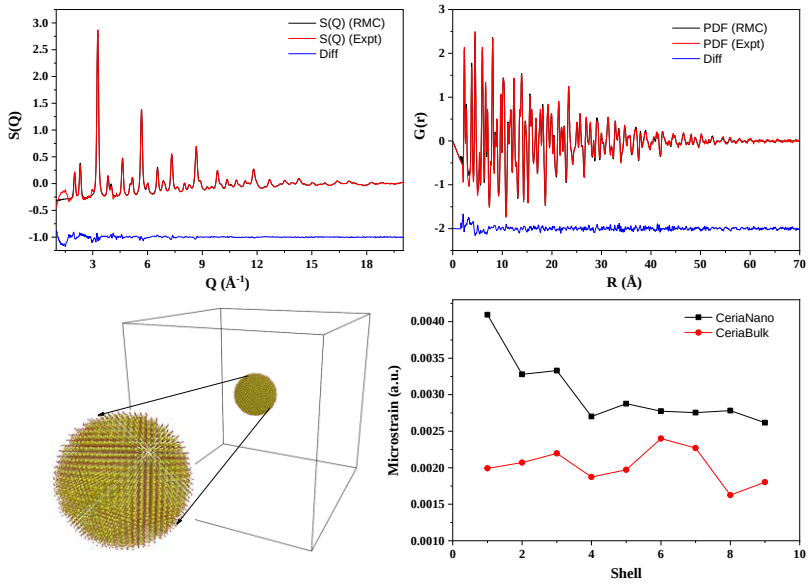


**Figure. 1**. Results from the preliminary study of nanoceria using neutron total scattering and RMC. The top two figures summarize the results of the real (left) and reciprocal (right) space fitting, respectively. The bottom left figure displays the structural model used, while the bottom right figure presents the microstrain calculated for the refined nanoparticle model as a function of distance from the particle center (squares/black). A similar analysis was also performed for the refined bulk-ceria model (circles/red).

## Choice of Instrument

We request time on NOMAD because it is optimized for neutron total scattering measurements on small samples**.**

## Experiment Plan

We will collect total-scattering data on 2 nanoparticle (6 nm) and 1 bulk-ceria samples. The powders will be loaded in 3 mm (in radius) PAC can. We expect to have 300 mg for each nanoparticle sample. The data will be collected at 300 K, 150 K, and 10 K. From previous experience and given the relatively small volumes and nanoscale nature of the powders, which makes it difficult to achieve high packing densities, we expect that each run will take about 6 hours to obtain adequate counting statistics with high real- and reciprocal-space resolution (54 hours). Including the calibration runs, time for cooling and sample changing we request 3 days of beam time.

## References

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