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# Reversible Pt Nanoparticle Formation in Pt-doped $BaCeO_3$

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Engineered nanocomposites – solids consisting of a matrix containing nanoparticles with tailored orientation, surface chemistry, and size – are of considerable interest for potential application in areas such as photonics, photovoltaics and thermoelectrics [1-3]. In this work, we report a reversible process of Pt nanoparticle formation in Pt-doped $BaCeO_3$, a phenomenon that may be exploited to create and control engineered nanocomposites. An application of this phenomenon, to lower the thermal conductivity of oxide materials, whose potential in thermoelectrics has been inhibited by their relatively high thermal conductivities, is presented as an example. We believe this phenomenon can be expanded to a number of oxides as a common recipe to explore other new applications and elucidate the underlying physics, as well.

In our study, we considered thin films of $BaCeO_3$ (BCO), doped with 5% Pt, grown by pulsed laser deposition (PLD) on (001) MgO substrates. An STEM image of the as-grown film ($BaCe_{0.95}Pt_{0.05}O_{3+x}$) is shown in Figure 1 (a) with Pt dopants presumed to occupy B sites of the perovskite matrix. After 1 hour's reduction at 800 °C in 10% $H_2$ balanced with $N_2$, bright features, identified below as Pt nanoparticles, were expelled from the perovskite lattice, appearing uniformly dispersed throughout the film, at grain boundaries, and on the free surface, as shown in Figure 1 (b). The reduced film was then subjected to an oxidation treatment in dry air at 800 °C for one hour. At this stage, almost all the Pt particles, including those as large as 7-8 nm, disappeared, apparently having completely dissolved back into the perovskite lattice, and the system itself has essentially returned to the initial, as-grown state. We next conducted a second reduction treatment on the oxidized film, again at 800 °C for 1 hour, and found that Pt particles were again expelled, but now exhibiting a more uniform size and spatial distribution. A comparison of Pt particle sizes observed after the first and second reduction step is provided by the histograms shown on the right side of Figure 1. The Pt particles larger than 4 nm after the first reduction treatment have apparently been completely eliminated by one redox cycle, and the resulting distribution of Pt particles is more tightly peaked around 1 nm. A reversible change of Pt valence state, between 4+ (or 2+) after oxidation and metallic after reduction, was confirmed by XPS.

Aberration-corrected (Cs-corrected) high-angle annular dark-field (HAADF)-STEM images provide atomic structure with atomic-number sensitivity that can be used to determine the location and identity of heavy atoms and clusters in a lighter matrix. One of the interesting features we found in the reduced film is the epitaxial nature of sub-nanometer Pt particles relative to their perovskite host. Small precipitates often form epitaxially with a shape that can minimize strain energy against the anisotropic elastic constants of the crystal matrix. The elastic energy increases dramatically with the size of the coherent particle, and eventually a coherent interface becomes unstable and relaxes. The initial stage of the above scenario is shown in Figure 2. Because Pt (1.373Å) is ~80% larger than $Pt^{4+}$ (0.765 Å), the compressive strain induced by the precipitation of the epitaxial metal clusters, together with the energy created by the interface between the metal and the oxide, can modify electronic and thermal properties of the oxide without the nanostructures. For example, a reversible change of the thermal conductivity in this system has been observed when bulk ceramic samples were cycled between reduction and oxidation treatment. The lowered thermal conductivity after the segregation of the particles may indicate extra phonon scattering due to the strain field and the metal oxide interface within the oxide matrix. This demonstration of a new method to manipulate the thermal conductivity of a material through in situ creation and inhibition of compressive strain fields via a reversible redox process may pave the way to a high figure of merit in thermoelectric materials.

References
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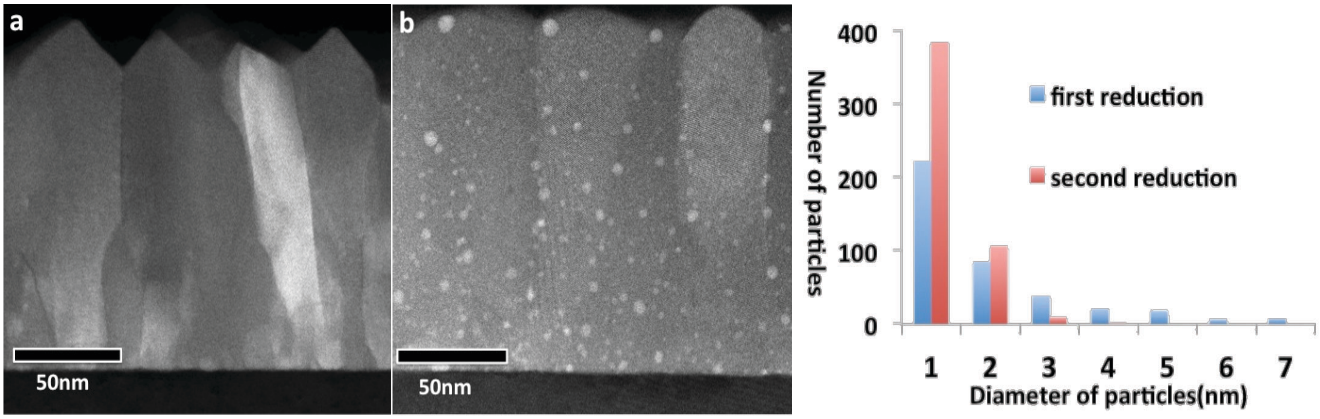

**Figure 1.** Comparison of the Pt-doped $BaCeO_3$ thin film, as grown and after thermal treatments: (a) As grown (b) As grown, then reduced. The histograms on the right correspond to the particle size distribution after this first reduction (400 sample points included), shown in blue, together with that following a second redox cycle (500 sample points included), shown in red.

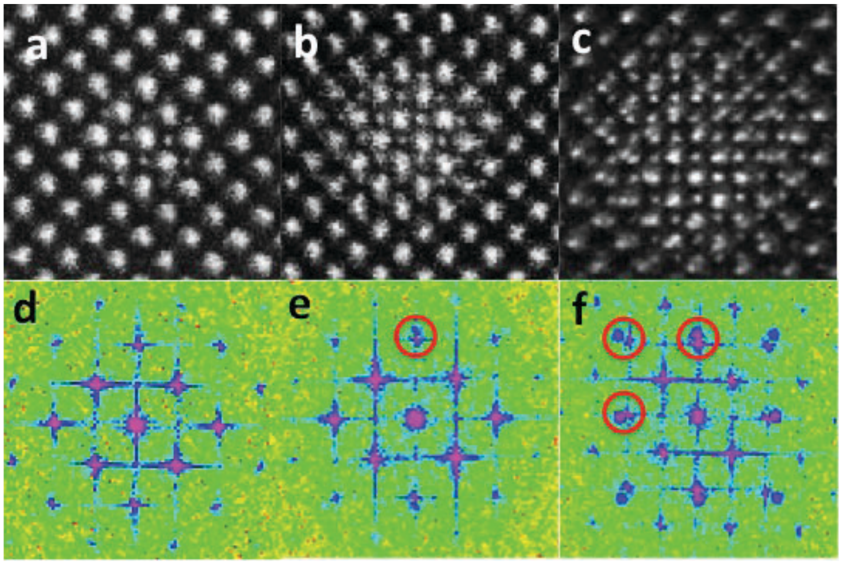

**Figure 2**. HAADF-STEM image showing embedded Pt nano clusters of different sizes and the corresponding Fast Fourier Transform (FFT).