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# Electron Energy Loss Spectroscopy of $CeO_{2-x}$ Nanoparticles

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Ceria has been widely studied due to its applications, such as a catalyst in vehicle emissions system and an electrolyte material in solid oxide fuel cells. Recently, it has been reported that $CeO_{2-x}$ nanoparticles exhibit lattice expansion and valence reduction of Ce ions with decreasing particle size[1]. In this study, we use electron energy loss spectroscopy (EELS) to study the valence of Ce ions in $CeO_{2-x}$ nanoparticles. The advantage of using EELS in a high resolution transmission electron microscope (TEM) is that the size and crystal structure of the individual particle is precisely determined. Other macro techniques require a substantial quantity of material with unavoidable variations in size.

The $CeO_{2-x}$ nanoparticles were synthesized using thermal evaporation in a helium atmosphere. For comparison, micron-size $CeO_2$ and $Ce_2(WO_4)_3$ samples were prepared by grinding commercial powder. The EELS measurements were carried out in a 300 keV JEOL-3000FEG transmission electron microscope equipped with Gatan imaging filter.

Fig. 1(a-d) show the EELS spectra of micron-size $CeO_2$ and $Ce_2(WO_4)_3$ particles. The valences of Ce ions in micron-size $CeO_2$ and $Ce_2(WO_4)_3$ are nominally $4^+$ and $3^+$, respectively. The EELS spectra of $Ce^{4+}$ and $Ce^{3+}$ are quite different as shown in the figure, e.g. there are three peaks after zero loss in $Ce^{4+}$, while only two peaks in $Ce^{3+}$. A shoulder indicated by the arrow is present in the $M_4$ edge of $Ce^{3+}$, but absent in the $M_4$ edge of $Ce^{4+}$, and the tail in $Ce^{4+}$ is higher than that in $Ce^{3+}$. Moreover, the intensity of $M_4$ edge is higher than that of $M_5$ edge in $Ce^{4+}$, reversed in $Ce^{3+}$. We also performed x-ray absorption spectroscopy (XAS) for micron-size $CeO_2$ and $Ce_2(WO_4)_3$ at NSLS NIST/Dow U7A. The XAS spectra (Fig. 2) are similar to the corresponding EELS. However, with the higher energy resolution, a small peak indicated by the arrow before the $M_4$ edge in $Ce^{3+}$ is resolved, and both $M_4$ and $M_5$ peaks in $Ce^{3+}$ are split in the XAS spectra.

Fig. 3 shows the high resolution image and its corresponding electron diffraction pattern of the $CeO_2$ nanoparticles. In general, the particles are single crystals and their diameters $3<d<4$ nm. Both lattice image and diffraction show that the particles are cubic with lattice constant 0.549 nm, which is consistent with that reported by Tsunekawa et al.[1] EELS spectrum from a particle with $d$=3.4 nm is shown in Fig. 1(e). Comparing to the $Ce^{3+}$ and $Ce^{4+}$, the spectrum of the nanoparticle is very close to that of $Ce^{3+}$ as it has a similar shoulder indicated by the arrow at the $M_4$ edge and an $M_4$ edge intensity lower than that of the $M_5$ edge. This indicates that the valence of Ce ions in the nanoparticle is very close to $Ce^{3+}$. The quantitative measurement about the $Ce^{3+}/Ce^{4+}$ ratio in $CeO_{2-x}$ nanoparticles is underway.

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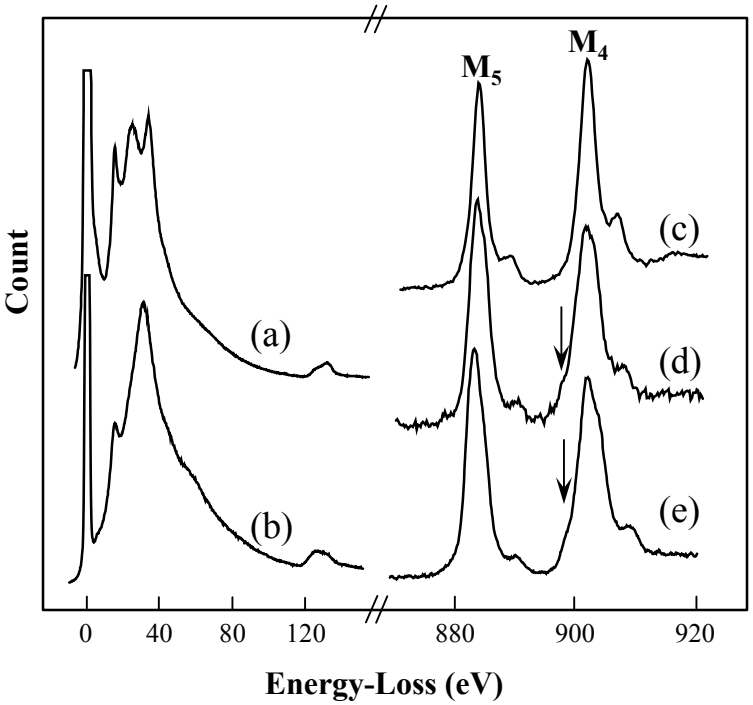



Fig. 1. EELS spectra of $CeO_2$ and $Ce_2(WO_4)_3$ particles. (a,b) are the spectra of micron-size (a) $CeO_2$ and (b) $Ce_2(WO_4)_3$ particles for Energy 0<E<140eV. (c-e) show the $M_4$ and $M_5$ edge of micron-size (c) $CeO_2$, (d) micron-size $Ce_2(WO_4)_3$ and (e) nano-size $CeO_2$ particles with its *d*=3.4nm. The arrows in (d) and (e) indicate the shoulder in $Ce_2(WO_4)_3$ and $CeO_2$ nanoparticles, respectively.

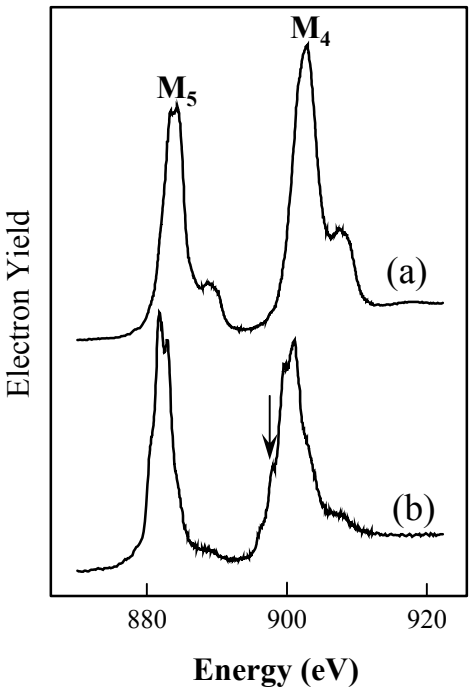
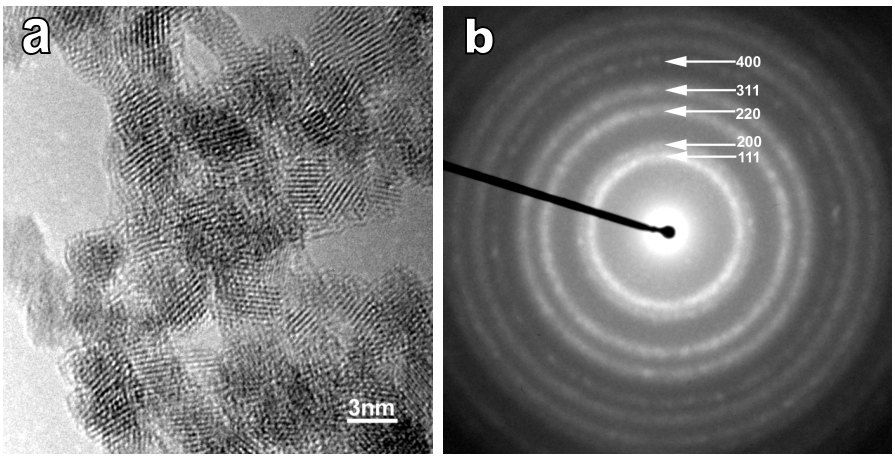



Fig. 2. XAS of micron-size (a) $CeO_2$ and (b) $Ce_2(WO_4)_3$ particles. Note, the arrow indicates the small peak before $M_4$ edge in $Ce_2(WO_4)_3$.

Fig. 3. High resolution image (a) and diffraction pattern (b) of $CeO_2$ nanoparticles. The size of $CeO_2$ particles varies from 3nm to 4nm. Both lattice image and diffraction show that the structure of $CeO_2$ nanoparticles is cubic with a=0.549nm.




Reference

[1] S. Tsunekawa et al., Phys. Rev. Lett. **85**, (2000) 3440.

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