ESRF	XAFS study of single crystalline $Ce_{1-x}Pr_xO_{2-\delta}$ mixed ternary rare earth thin films on Si (111)	Experiment number: HC-1010
Beamline: BM 08	Date of experiment: from: 6/9/13 to: 12/9/13	Date of report: 5/9/2016
Shifts: 18	Local contact(s): F. d'Acapito	

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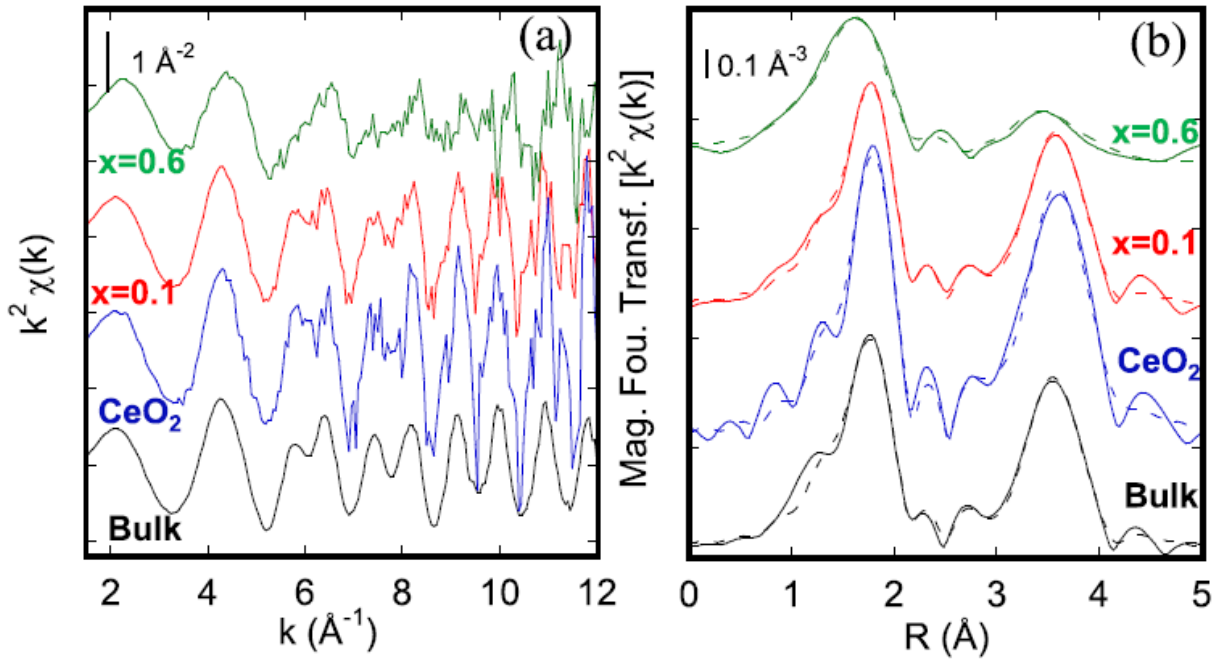
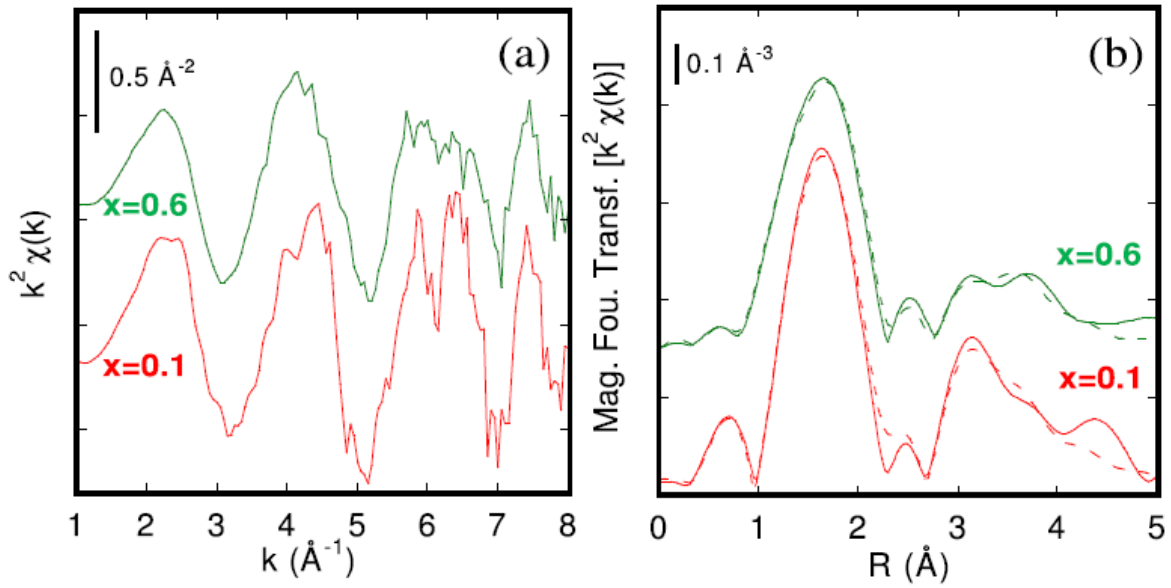
Report:

The local electronic and atomic structure of (111)-oriented, single crystalline mixed $Ce_{1-x}Pr_xO_{2-\delta}$ (x= 0, 0.1 and 0.6) epitaxial thin films on silicon substrates have been investigated in view of engineering redox properties of complex oxide films. X-ray absorption near edge structure reveals that Pr shows only +3 valence and Ce shows only nominal +4 valence in mixed oxides. Extended x-ray absorption fine structure (EXAFS) studies were performed at K edges of Ce and Pr using a specially designed monochromator system for high energy measurements. They demonstrate that the fluorite lattice of ceria (CeO_2) is almost not perturbed for x=0.1 sample, while higher Pr concentration (x=0.6) not only generates a higher disorder level (thus more disordered oxygen) but also causes a significant reduction of Ce–O interatomic distances. The valence states of the cations were also examined by techniques operating in highly reducing environments: scanning transmission electron microscopy-electron energy loss spectroscopy and X-ray photoemission spectroscopy; in these reducing environments, evidence for the presence of Ce3+ was clearly found for the higher Pr concentration. Thus, the introduction of Pr3+ into CeO_2 strongly enhances the oxygen exchange properties of CeO_2. This improved oxygen mobility properties of CeO_2 are attributed to the lattice disorder induced by Pr mixing in the CeO_2 fluorite lattice, as demonstrated by EXAFS measurements. Thus, a comprehensive picture of the modifications of the atomic and electronic structure of $Ce_{1-x}Pr_xO_{2-\delta}$ epitaxial films and their relation is obtained.

These results have been published in Niu et al., Jour. Appl. Phys. **116**, 123515 (2014).



Ce K-edge XAFS data. (a) back ground subtracted and (b) Fourier Transform and fits.



Pr K-edge XAFS data. (a) back ground subtracted and (b) Fourier Transform and fits.

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On the local electronic and atomic structure of $Ce_{1-x}Pr_xO_{2-\delta}$ epitaxial films on Si

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