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## XPS study of ion irradiated and unirradiated CeO<sub>2</sub> samples

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Cerium dioxide, CeO<sub>2</sub>, is a fluorite structure ceramic widely used as an inactive structural surrogate to UO<sub>2</sub> and PuO<sub>2</sub> to avoid difficulties associated when working with radioactive materials. This material is suggested to be used as an inert matrix for perspective nuclear fuels and highly radioactive waste disposal. Irradiation studies, where CeO<sub>2</sub> is exposed to ions with different mass and energy, are extensively taking place in the recent time. The attempt of these studies is to replicate the effect of radiation damage by fission fragments that is taking place in UO<sub>2</sub> based fuels. X-ray photoelectron spectroscopy (XPS) proved to be an effective tool for determination of the cerium ionic composition (Ce<sup>3+</sup> and Ce<sup>4+</sup>).

XPS determination of the cerium oxidation state in compounds faces difficulties due to the complex structure in the valence- and core- electron spectra. Therefore, this work employed an original technique for cerium oxidation state determination on the basis of the core- and valence electron fine spectral structure parameters. This work considers the effect of fission-energy ion irradiation on the electronic structure at the surface of bulk and thin film samples of CeO<sub>2</sub> as a simulant for UO<sub>2</sub> nuclear fuel. For this purpose, thin films of CeO<sub>2</sub> on Si substrates were produced and irradiated by 92 MeV <sup>129</sup>Xe<sup>23+</sup> ions to a fluence of  $4.8 \times 10^{15}$  ions/cm<sup>2</sup> to simulate fission damage that occurs within nuclear fuels along with bulk CeO<sub>2</sub> samples. The irradiated and unirradiated samples were characterised by X-ray photoelectron spectroscopy. The as-produced samples were found to contain mostly the Ce<sup>4+</sup> ions with a small fraction of Ce<sup>3+</sup> ions formed on the surface in the air or under X-rays. The core-electron XPS structure of CeO<sub>2</sub> was associated with the complex final state with vacancies (holes) resulted from the photoemission of an inner electron. A technique of the quantitative evaluation of cerium ionic composition on the surface of the samples has been successfully applied to the obtained XPS spectra. This technique is based on the intensity of only one of the reliably identifiable high-energy peak at 916.6 eV in the Ce 3d XPS spectra. This method yielded that the surface of unirradiated thin film sample AP1 contained Ce<sup>3+</sup> ions (AP1: 97% Ce<sup>4+</sup> and 3% Ce<sup>3+</sup>). A <sup>129</sup>Xe<sup>23+</sup> (92 MeV and  $4.8 \times 10^{15}$  ions/cm<sup>2</sup> fluence) irradiation was found to increase the Ce<sup>3+</sup> content in thin film sample AP2g (87% Ce<sup>4+</sup> and 13% Ce<sup>3+</sup>) and bulk samples AP4g (92% Ce<sup>4+</sup> and 8% Ce<sup>3+</sup>) and AP5g (93% Ce<sup>4+</sup> and 7% Ce<sup>3+</sup>). Concentration of Ce<sup>3+</sup> ions was shown to grow significantly as the film thickness decreased and the film fragmented (AP3g: 29% Ce<sup>4+</sup> and 71% Ce<sup>3+</sup>).

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