



Contribution ID: 1043

Type: Verbal

Diffraction and Raman spectroscopy studies of zirconia solid phases containing cerium

Thursday, May 19, 2022 9:26 AM (18 minutes)

Zirconia (ZrO_2) doped with lanthanides or actinides has been extensively studied for several tailored applications, such as for the immobilization of actinides present in high-level radioactive waste streams (HLW) or as inert matrix fuel for the incineration of e.g. waste plutonium. Doped zirconia matrices have been reported to have a very high radiation tolerance, however, inconsistencies exist concerning the role of the different structural polymorphs in the high radiation resistance. In addition, the role of oxygen vacancies, which are formed for charge compensation when subvalent dopants are incorporated into the ZrO_2 crystal structure, have not been clarified. The lanthanide cerium is often used as a surrogate for plutonium due to its similar ionic radius and comparable chemical properties in the oxidation states +III and +IV. In this study, different Ce concentrations were incorporated in zirconia via the co-precipitation route, with the goal to stabilize the cubic zirconia polymorph. Due to the extraordinary luminescent properties of Eu, a trace amount of this lanthanide was added together with Ce in the synthesis process. A series of zirconia samples doped with 14 to 70 mol % Ce was prepared. Seven selected compositions are presented here, namely samples with 14, 22, 30, 42, 50, 62, 70 mol% Ce, as they demonstrate a clear phase transformation. The phase composition was evaluated by powder X-Ray diffraction (PXRD), and Raman spectroscopy. In the PXRD diffractograms, the monoclinic phase, characterized by diffraction peaks at 2θ of 28.2° and 31.3°, is dominant only in the composition with 14 mol % Ce. Above this concentration, a peak around 29.9°, assigned to the tetragonal phase, increases in intensity as a function of increasing Ce concentration in the zirconia matrix up to a concentration of 42 mol%. Beyond this, the cubic phase starts to dominate the phase composition, with the intensive characteristic peak around 29.3°. Additionally, the presence of a tetragonal metastable phase in samples with 30, 42, and 50 mol % Ce, and a trace of the tetragonal phase in the composition with 70 mol % Ce were identified. Generally, the diffraction peaks are shifted to lower 2θ angles as a result of the substitution of Zr^{4+} by the larger Ce^{4+} cation which increases the lattice parameters. The Raman results corroborate the assignment of the different phase compositions identified in the PXRD studies. However, a large band at 512 cm^{-1} becomes visible in the samples with 30 mol % Ce and grows in intensity with increasing Ce-doping. This band has been reported to arise from Frenkel-type defects, typically found in samples with oxygen vacancies or/and due to partial reduction of Ce^{4+} to Ce^{3+} occurring in the samples, and causing the formation of oxygen vacancies in the ZrO_2 structure for charge compensation. This, however, has to be verified in future XANES experiments. No solid phase separation was detected in both characterization analyses, PXRD and Raman. Luminescence spectroscopic studies, probing the Eu ion which has been incorporated together with Ce in all ZrO_2 solid phases, will be conducted in future studies. Preliminary results of these investigations will be shown at the RadChem conference.

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Session Classification: Nuclear Fuel Cycle

Track Classification: Chemistry of Nuclear Fuel Cycle, Radiochemical Problems in Nuclear Waste Management