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New titanate matrices for immobilization of actinide high-level waste

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Uranium and plutonium extraction from spent nuclear fuel leads to formation of high-level waste (HLW) with complex composition. Actinides (An) from HLW due to their long half-lives (103-106 years) are the most dangerous elements for biosphere in long-term perspective. To enhance the effectiveness of waste handling it is expedient to extract from HLW An and rare earth elements (REE) in separate fraction. These elements can be incorporated in durable crystalline phases (matrices) and then disposed in geological repositories. Compounds with pyrochlore structure are considered as suitable An host phases [1,2]. Whereas in the system REE2O3-TiO2 pyrochlores are formedonly for REE with ionic radius smaller than Pm3+[3]. Titanates of large rare earths (La,Ce,Nd,Sm), which are dominated in HLW, crystallize in the monoclinic perovskite-type structure. Substitution of Ti4+ to Zr4+ stabilizes pyrochlore lattice. Therefore zirconate pyrochlores are one of the most well studied candidates for An host phases [4]. However the rate of phase formation in Zr systems during the process of synthesis is very slow even at high temperatures (1500oC)[5]. This results in presence of residual oxides in ceramics based on zirconate pyrochlores which deteriorates their matrix properties, e.g. corrosion stability in solutions. Phases with monoclinic and orthorombic structures are also formed in the system REE2O3-TiO2-ZrO2. These compounds are characterized by high REE concentrations [6].

The goal of our investigations was to prove the suitableness of monoclinic REE2(Ti,Zr)2O7 and orthorombic REE4Ti9O24 for use as An-REE host phases. The series of samples were prepared by cold pressing and sintering and inductive melting in cold crucible (IMCC) and studied by different analytical methods: X-ray difraction, scanning and transperent electron microscopy. One sample of monoclinic titanate was irradiated by 1 MeV Kr+.

Data obtained show that structures of REE2(Ti,Zr)2O7 and REE4Ti9O24 are characterized by high isomorphic capacity in respect to rare earth imitators of An-REE waste. Contents of REE2O3 in these phases reach 50 wt.%. There were not any additianal phases with REE in ceramics. All rare earths are occured only in. Thus ceramics based on target monoclinic and orthorombic titanates can be produced by two of the most suitable methods of matrices fabrication: cold pressing and sintering and IMCC.

Irradiation of monoclinic REE2Ti2O7 by Kr+ leads to gradual destruction of its structure. And full amorphization takes place at 2.5×1014 ion/cm2. Radiation resistance of REE2Ti2O7 with the monoclinic structure is close to titanate pyrochlore and ferrite garntes.

The future investigations will be aimed to the determination of Ce oxidation state in different phases by EXAFS and XANES. Irradiation experiments with REE4Ti9O24 and studying of chemical durability of monoclinic and orthorombic titanates will be also carried out.

Literature.

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