Structure studies on lanthanide technetium pyrochlores as prospective host phases to immobilize 99-technetium and fission lanthanides from effluents of reprocessed used nuclear fuels

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Corresponding Article Featured in The Journal of Nuclear Materials (2011)

Introduction

Technetium (Tc) is an artificial element produced by nuclear fission, spallation, or other transmutation processes. There are three long-lived isotopes of Tc: the most important from a nuclear waste perspective being ⁹⁹Tc (half-life, 2.13 x 10⁹ years). ⁹⁹Tc is one of the most abundant, long-lived radionuclides in used nuclear fuel (UNF). As such, it is targeted in UNF separation strategies such as UREX+ [1], for isolation and encapsulation in solid waste forms for storage in a nuclear repository. In terms of compound formation, the preferred valence for Tc is +7. Tc reacts with oxygen to form the heptoxide,TcO₇, wherein the Tc⁷⁺ cations are in tetrahedral (4-fold, IV) coordination. In aqueous solution, TcO₇ readily reacts with water to form the pertechnetate ion, TcO₄⁻. The TcO₄⁻ pertechnetate ion is a highly-mobile aqueous species. Consequently, it is a potential threat to the biosphere. Note that the technetium in the pertechnetate ion is in oxidation state Tc⁴⁺. Immobilization of Tc in a durable solid waste form is a challenge of great importance to the nuclear waste community. To date, scientists have investigated immobilization of Tc in both metallic waste forms (e.g., Tc-zirconium alloys) [3], and borosilicate-based waste glass [4]. The purpose of this study is to perform a systematic investigation of the incorporation of Tc into pyrochlore oxide structures, Ln₂TcO₇, where Ln represents trivalent lanthanides (rare earth) Ln³⁺ cations, while Tc is a tetravalent, Tc⁴⁺, metal cation. Pyrochlore compounds are high-melting temperature oxides and are recognized for their durability [5]. Interestingly, in a complex oxide such as a pyrochlore, two or more fission products may be incorporated simultaneously into the same crystal structure. For instance, neodymium (Nd), a prominent lanthanide fission product, can be incorporated with Tc in a pyrochlore with formula, Nd₂TcO₇. This is one of the pyrochlores that was investigated in this study.

Materials & Methods

Ammonium-pertechnetate (NH₄TcO₄) was obtained from Oak Ridge National Laboratory and had to be purified before further use. The lanthanide (Ln) oxides, were purchased from Alfa Aesar and Alcoss. To synthesize Ln₂TcO₇ pyrochlores, stoichiometric amounts of Ln₂O₃ were ground up with TcO₂. The dry powder mixtures were wrapped in platinum foil and folded to cold sealed envelopes. These envelopes were sealed in silica ampoules under vacuum. After decontamination, the ampoules were inserted in a tube furnace and annealed at 1150°C for 48 hours under a constant flow of Argon (99.99%). The ampoules were opened, the Pt envelopes unfolded, and the powders analyzed. Powder X-ray diffraction (XRD) and Rietveld analysis were used to determine and characterize the crystalline phase content of the Ln₂TcO₇ samples.

Results

X-Ray Diffraction Patterns

Measured X-ray diffraction (XRD) patterns obtained from various Ln₂TcO₇ pyrochlore compounds synthesized in this study. The pyrochlore XRD patterns are plotted (bottom to top) for Ln = Pr, Nd, Sm, Gd, and Lu. The 2θ positions for similar (hkl) reflections in the various Ln pyrochlore phases shift steadily towards larger 2θ values, from pyrochlores with lighter lanthanides (e.g., Pr) to the heavier lanthanides (e.g., Lu).

Microstructures of Nd₂TcO₇, Pyrochlore

XRD patterns revealed pyrochlore-type phases in all of the binary Ln₂O₃/ TcO₂ oxide systems examined in this report, i.e., for Ln = Pr, Nd, Sm, Gd, and Lu. Using the diffraction patterns obtained from each oxide sample, the lattice parameters of the Ln₂TcO₇ pyrochlores were refined to high accuracy.

Conclusion

Technetium (Tc) metal was successfully incorporated into a series of complex oxides with general composition given by Ln₂TcO₇ (Ln = Pr, Nd, Sm, Gd, Lu). Each of these compounds was found to crystallize into a pyrochlore-type crystal structure. Within this series, X-ray diffraction (XRD) structural analyses and Rietveld crystal structure refinements produced highly accurate lattice parameters ranging from 0.4437(6)Å (mm for Pr₂TcO₇, to 0.10377(22) Å for Lu₂TcO₇. In the series of Ln₂TcO₇ pyrochlore phases examined in this study, Nd₂TcO₇ is noteworthy because neodymium is based on fission yields, the most prominent lanthanide generated in reactors for fissioning HU. In this study, we demonstrated successful synthesis of Nd₂TcO₇, applying a fairly simple, up-scalable synthesis route. This technique offers the opportunity to stabilize and immobilize the oxides of two major fission products, Tc and Nd, in what may prove to be a highly durable crystalline oxide host phase.

Acknowledgements

This project was funded under the auspices of the US Department of Energy, Office of Nuclear Energy (DOE-NE), cooperative Agreement No. DE-AC52-08NA25596. The funding of this research was provided through the subcontract No. 76398-001-09 with Los Alamos National Laboratory. Valdez, Tang, Jervinen and Sickaffs were sponsored by a DOE-NE program at Los Alamos National Laboratory on advanced waste forms for fission products. We also thank the kind efforts of the UNLV Radiochemistry radiation safety team.