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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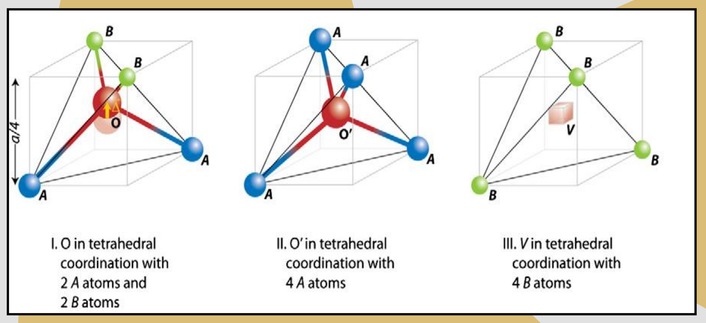
Introduction

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 ^{99}Tc (half-life, $t_{1/2}$ = 2.13 x 10^5 years). ^{99}Tc is one of the most abundant, long-lived radiotoxic isotopes 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,Tc_2O_7, wherein the Tc^{7+} cations are in tetrahedral (4-fold, IV) coordination. In aqueous solution, Tc_2O_7 readily reacts with water to form the pertechnetate ion, TcO_4.The TcO_4 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 Tc^{7+}. 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–Zr 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, $Ln_2Tc_2O_7$, where Ln represents trivalent lanthanide (rare earth) Ln^{3+} cations, while Tc is a tetravalent, Tc^{4+}, metal cation. Pyrochlore compounds are high-melting temperature oxides and are recognized for their durability [8]. 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, $Nd_2Tc_2O_7$. This is one of the pyrochlores that was investigated in this study.

Pyrochlore Fundamental Structural Units



I. O in tetrahedral coordination with 2 *A* atoms and 2 *B* atoms

II. O′ in tetrahedral coordination with 4 *A* atoms

III. *V* in tetrahedral coordination with 4 *B* atoms

Materials & Methods

Ammonium-pertechnetate (NH_4TcO_4) 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 Arcos. To synthesize Ln–Tc pyrochlores, stoichiometric amounts of Ln_2O_3 were ground up with TcO_2. 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 Ln–Tc oxide samples.

Stoichiometry configuration for lanthanide technetium pyrochlore structure

$$Ln_2O_3 + 2TcO_2 \rightarrow Ln_2Tc_2O_7$$

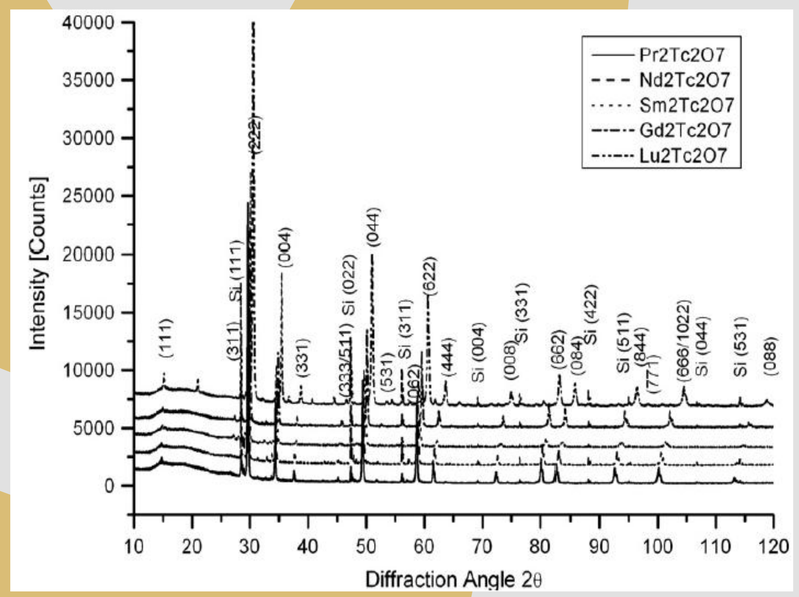
Results

Powder XRD results for the synthesized $Ln_2Tc_2O_7$ pyrochlore phases, where *Ln* = Pr, Nd, Sm, Gd, and Lu.

Lanthanum oxides Ln_2O_3	Principal phase	Lattice parameter, *a* (nm)	Published lattice parameter (nm) Muller et al. [7]	Principal phase refinement residual R_{Bragg} (%)	Overall refinement residual R_{Wp} (%)	Impurities (1–5 wt.%, 20 wt.% for Lu_2O_3)
Pr_2O_3	$Pr_2Tc_2O_7$	1.0447156(83)	N/A	2.6	10.7	TcO_2 and Pr_2O_3
Nd_2O_3	$Nd_2Tc_2O_7$	1.041158(11)	N/A	2.4	11.4	TcO_2 and unknown phase
Sm_2O_3	$Sm_2Tc_2O_7$	1.035336(19)	1.0352(4)	3.1	8.4	TcO_2 and Sm_2O_3
Gd_2O_3	$Gd_2Tc_2O_7$	1.0299836(64)	N/A	1.1	5.0	TcO_2 and Gd_2O_3
Lu_2O_3	$Lu_2Tc_2O_7$	1.013777(22)	N/A	2.6	10.6	Lu_2O_3

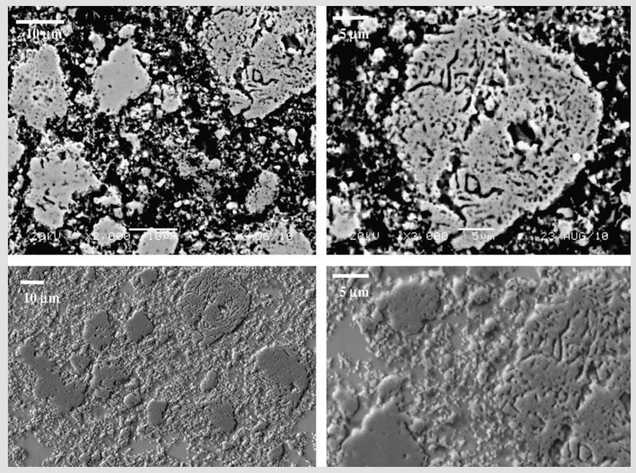
Powder XRD measurements revealed pyrochlore-type phases in all of the binary Ln2O3–TcO2 oxide systems examined in this report, i.e., for Ln = Pr, Nd, Sm, Gd, and Lu. Using the diffraction patterns obtained from each oxide sample, the lattice parameters of the Ln–Tc pyrochlores were refined to high accuracy.

X-Ray Diffraction Patterns



Measured X-ray diffraction (XRD) patterns obtained from various $Ln_2Tc_2O_7$ 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 $Nd_2Tc_2O_7$ Pyrochlore



Samples were imaged using secondary electron imaging (SEI) and backscattered electron imaging (BEI). Top left: 2000 SEI, top right: 3000 SEI, bottom left: 1000 BEI, bottom right: 3000 BEI. The microstructure is dominated by small, 1–4 µm particles as well as larger, up to 50 µm, aggregates with high porosity. In most cases, the larger particles exhibit spongy, "worm-hole" porosity as a result of pressure-less sintering. Based on BEI results, $Nd_2Tc_2O_7$ particles are chemically homogeneous and the formation of different chemical domains was not observed.

Conclusion

Technetium (Tc) metal was successfully incorporated into a series of complex oxides with general composition given by $Ln_2Tc_2O_7$ (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 analyzes and Rietveld crystal structure refinements produced highly accurate lattice parameters ranging from 1.0447156(83) nm for $Pr_2Tc_2O_7$ to 1.013777(22) nm for $Lu_2Tc_2O_7$. In the series of Ln–Tc pyrochlore phases examined in this study, $Nd_2Tc_2O_7$ is noteworthy because neodymium is based on fission yields, the most prominent lanthanide generated in reactors for fissioning ^{235}U. In this study, we demonstrated successful synthesis of $Nd_2Tc_2O_7$, 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

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