Fabrication and properties of technetium-bearing pyrochlores and perovskites as potential waste forms

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Abstract

Technetium-99 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+, for isolation and encapsulation in solid waste forms for storage in a nuclear repository. We report here results regarding the incorporation of Tc-99 into ternary oxides of different structure types: pyrochlore (Nd₂Tc₂O₇), perovskite (SrTcO₃), and layered perovskite (Sr₂TcO₄). The goal was to determine synthesis conditions of these potential waste forms to immobilize Tc-99 and to harvest crystallographic, thermophysical and hydrodynamic data. Within these studies, Rietveld structure refinement was applied to allow for crystallographic characterization, while a physical property measurement system (PPMS) was used to determine thermophysical properties. The ternary oxides exhibited good crystallinity and their lattice parameters and atomic coordinates could be refined to high accuracy. Low refinement residuals (R_Bragg) of 2.0, 2.4, and 3.9 % were achieved for Nd₂Tc₂O₇, SrTcO₃, and Sr₂TcO₄, respectively. The strontium technetates, SrTcO₃ and Sr₂TcO₄, show superconductivity at rather high critical temperatures of T_c = 7.8 K and 7 K, respectively. Nd₂Tc₂O₇ did not show any changes in magnetic properties above 3 K.

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1. Introduction

Technetium-99 (t½ = 2.13x10^5 years) is important from a nuclear waste perspective and is one of the most abundant, long-lived radioisotopes 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. Immobilization of Tc-99 by a durable solid waste form is a challenge. To date, scientists have investigated immobilization of Tc-99 e.g. in metallic waste forms (Tc-Zr alloys [2]), and borosilicate-based waste glass [3]. In the envisioned technical process to vitrify high-level radioactive waste effluents, part of the technetium inventory will be oxidized or will be subject to disproportionation and will consequently volatilize as heptoxide. An alternative idea for immobilizing Tc-99 is to incorporate the cation in a solid state refractory oxide with a reduced valence state. In so doing, it may be possible to avoid the highly-mobile, pertechnetate, TcO$_4^-$ species.

Pioneering research on the crystal chemistry of technetium-containing oxides was published by Muller et al. [4] and a series of simple binary and ternary Tc-containing oxide structures are reported, including a variety of spinel, perovskite and pyrochlore compounds, among them is the perovskite SrTcO$_3$. In a study by Wassilopulos [5], the oxides SrTcO$_3$ and Sr$_2$TcO$_4$ were synthesized and characterized by XRD. Hereby the perovskite (SrTcO$_3$) was described as cubic, and a K$_2$NiF$_4$ structure type was proposed for the layered perovskite Sr$_2$TcO$_6$. In a more recent study, Rodriguez et al. [6] have characterized SrTcO$_3$ by neutron diffraction data and indexed the pattern based on a GdFeO$_3$-type lattice with space group Pnma. The authors observed high magnetic ordering temperature for SrTcO$_3$ with G-type antiferromagnetic ordering and an unusually high Néel point at 750 °C. Electron calculations on this distorted perovskite structure showed mixing between Tc 4$d$ states and oxygen states proximal to the Fermi level. Thorogood et al. [7] determined phase transitions and magnetic order in SrTcO$_3$ by means of neutron diffraction and synchrotron X-ray diffraction experiments. The perovskite SrTcO$_3$ exhibits three phase transitions with increasing temperature and its structure changes at ~400 K from space group Pnma to space group Inma, at ~600 K to the tetragonal space group I4/mcm, and at ~800 K to a structure type with space group Pm-3m. This sequence of transition is also observed for isostructural SrRuO$_3$. In another study in continuation of the research by Muller et al. [4] Hartmann et al. [8] have reported results of a systematic structural investigation of the incorporation of Tc into pyrochlore oxide structures, Ln$_2$Tc$_2$O$_7$, where Ln represents trivalent lanthanides.

The objective of this research as presented is to provide fundamental crystallographic and thermophysical data on advanced ceramic Tc-99 waste forms such as pyrochlore (Nd$_2$Tc$_2$O$_7$), perovskite (SrTcO$_3$), and layered perovskite (Sr$_2$TcO$_4$). In our current efforts we are setting-up ASTM-based leaching and corrosion test experiments to compare hydrodynamic data of these Tc-99 host phases with those of borosilicate-based standard glasses.

2. Experimental Procedure

2.1. Preparation on TcO$_2$

Ammonium-pertechnetate (NH$_4$TcO$_4$) was obtained from Oak Ridge National Laboratory and was purified by recrystallization. Anhydrous crystalline TcO$_2$ was obtained by thermal decomposition of NH$_4$TcO$_4$ at up to 700°C under argon atmosphere for about 8 hrs. For the set of experiments ~350 mg NH$_4$TcO$_4$ were decomposed in a fused silica boat while raising the temperature stepwise to 700 °C.

2.2. Synthesis of SrTcO$_3$ perovskite, Sr$_2$TcO$_4$ layered perovskite, and Nd$_2$Tc$_2$O$_7$ pyrochlore

Strontium oxide (99.5 %) was purchased from Alfa Aesar while Nd$_2$O$_3$ (99.9 %) was purchased from Arcos. The oxides were dried at 400 °C overnight in air prior to be used. To synthesize SrTcO$_3$, Sr$_2$TcO$_4$ and Nd$_2$Tc$_2$O$_7$ stoichiometric amounts of the oxides were mixed and ground with up to 30 mg TcO$_2$ in an agate mortar with the addition of ethanol. The dry powder mixtures were wrapped in platinum foil (Alfa Aesar, 99.9 %) and folded to envelopes which were vacuum sealed in fused silica. The pyrochlore was synthesized by annealing at 1150 °C for 48 hrs in vacuum. The perovskite structure type was synthesized after annealing at 770 °C for 7 days, and the
layered perovskite structure after annealing at 550 °C for 10 days. The oxide Sr₂TcO₄ decomposes at temperatures of >570 °C. For the synthesis of Sr₂TcO₄ in the tetragonal K₂NiF₄ structure type the following reaction equation can be postulated: 2 SrO + TcO₂ → (450°C < T < 570°C) → Sr₂TcO₄ → (T >570°C) → SrTcO₃ + SrO. This is in agreement with the observation by Wassilopulos [5].

2.3. Characterization of SrTcO₃, Sr₂TcO₄, and Nd₂Tc₂O₇

Powder X-ray diffraction (XRD) and Rietveld structure refinement were used to quantify the crystalline phase content of the oxides. Hereby ~30 mg of specimens were ground and mixed with ~6 mg of silicon line standard (NIST SRM 640c, a = 0.54311964(92) nm). These mixtures were placed on an air-tight low background sample holder. Powder XRD patterns were collected from 10° to 120° (step size 0.008°) 2θ. Measurements were performed using Cu Kα₁ emission (λ = 0.154063 nm) on a Bruker D8 Advance equipped with a Johansson-type monochromator (Ge) and a LynxEye® silicon strip detector. The data were analyzed using Rietveld analysis (Bruker AXS, Topas 4.2). AC magnetic susceptibility of the Tc-containing oxides were measured on a physical property measurement system (PPMS, Quantum Design) in the temperature range 300 to 1.7 K applying a magnetic field of 0.1 Tesla. Hereby ~10 mg of the oxide powders were inserted in medical capsules and the remaining capsule void was filled with cotton wool. The capsules were carefully sealed with Kapton® tape and inserted into a secondary plastic tube which served as sample carrier for the AC magnetic susceptibility measurements.

3. Results and Discussion

Powder XRD measurements revealed the successful synthesis of three potential host phases for Tc-99 immobilization: pyrochlore-type Nd₂Tc₂O₇, the perovskite-type SrTcO₃, and the layered perovskite structure Sr₂TcO₄. The applied dry chemical synthesis route produced high yields of >99 %. As main impurities, the oxides SrO and TcO₂ in concentrations <1 wt.-% were identified. The Tc-99-bearing oxides exhibit good crystallinity with calculated crystallite sizes of 120 nm for the strontium technetates, and ~10,000 nm for the pyrochlore. The lattice parameters of the phases could be refined with high accuracies of ±3, ±4, and ±7 fm (10⁻¹⁵ m), for Nd₂Tc₂O₇, SrTcO₃, and Sr₂TcO₄ respectively. The associated refinement residuals (RWP) for the patterns are 4.1 %, 4.7 % and 6.7 %, and the refinement residuals for the individual phases (R_Bragg) are 2.0 %, 2.4 % and 3.9 %, respectively (tables 1-3).

Thermophysical properties of the oxides SrTcO₃, Sr₂TcO₄, and Nd₂Tc₂O₇ were analyzed using a physical property measurement system (PPMS). Hereby we performed AC magnetic susceptibility measurements to further harvest information on the critical temperature (Tc) for superconductivity. The critical temperature for superconductivity Tc is determined by the temperature when changes in the magnetic moment become apparent (Meissner effect). In our experiments the strontium technetates, SrTcO₃ and Sr₂TcO₄ show superconductivity at rather high critical temperatures of Tc = 7.8 K and 7 K, respectively. On the other hand Nd₂Tc₂O₇ did not show any changes in magnetic properties above 3 K (fig. 2).

3.1. Pyrochlore Nd₂Tc₂O₇

The pyrochlore phase Nd₂Tc₂O₇ crystallizes in the cubic space group Fd-3m and its crystal structure was refined applying Rietveld structure refinement (fig. 1, table 2). Considering the pyrochlore structure of the unit cell (Z=8) as:

\[
(A_{12II}^{1+}B_{12II}^{1+})_{6}(X_{I})_{48}(X_{II})_{8}
\]

(1)
We positioned the octahedral coordinated $A^{3+}$ lanthanide position on the origin of the unit cell ((0,0,0), Wyckoff position 16c), and the tetrahedral coordinated $B^{4+}$ technetium position to $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ on Wyckoff position 16d. Oxygen occupies two different structure positions, hereby 48 oxygen occupy the 48f Wyckoff position at $(x,\frac{1}{2},\frac{1}{2})$, and eight oxygen the 8a position at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$. The atomic coordinate “x” in the 48f position in this pyrochlore setting is defined as:

$$x = \frac{3}{8} + \Delta, \text{ for } 0 \leq \Delta \leq \frac{1}{16}$$  \hspace{1cm} (2)

The value $\Delta = 0$ represents an ideal, fluorite-like oxygen sub-lattice, while the maximum possible oxygen displacement, $\Delta = 1/16$ (0.0625), is for an ideal, “pyrochlore-like” oxygen sub-lattice. A more comprehensive discussion of the $Ln_2Tc_2O_7$ structure is described in [8]. Using Rietveld structure refinement on X-ray powder data the lattice parameter of Nd$_2$Tc$_2$O$_7$ was refined to $a = 1.040629(3)$ nm, and the atomic coordinate x to 0.4206(4) to define the oxygen derivation parameter as $\Delta = 0.0456(4)$. In an additional effort to understand this oxygen derivation parameter in the series of $Ln_2Tc_2O_7$ lanthanide technetium pyrochlore we collected neutron diffraction time-of-flight (TOF) data and could extract the atomic coordinate x = 0.4222(1) (48f) for Nd$_2$Tc$_2$O$_7$. This defines the oxygen derivation parameter derived by neutron TOF data as $\Delta = 0.0472$. This small but significant increase, compared with the X-ray diffraction data, is also confirmed by computational DFT (density-function-theory) data [8]. In the series of $Ln_2Tc_2O_7$ pyrochlores from Pr to Lu the oxygen derivation parameter shows a steady decline [8]. The crystal structure of Nd$_2$Tc$_2$O$_7$ pyrochlore was refined to low refinement residuals ($R_{WP} = 4.1\%$) and is displayed in fig.1. The pyrochlore phase does not show any evidence of superconductivity above 3 K and AC magnetic susceptibility measurements do not reveal notable changes in the magnetic moment (fig. 2). This is not surprising due to the cubic nature of its crystal structure (space group Fd-3m).

Table 1. Crystallographic data of Nd$_2$Tc$_2$O$_7$ pyrochlore

| Site | Wyckoff | x | y | z | Atom | Occupancy | $B_{iso}$ |
|------|---------|---|---|---|------|-----------|---------|
| Nd-1 | 16c     | 0 | 0 | 0 | Nd$^{+3}$ | 1         | 0.314(2) |
| Tc-1 | 16d     | 0.5 | 0.5 | 0.5 | Tc$^{+4}$ | 1         | 0.06(2)  |
| O-1  | 48f     | 0.4206(4) | 0.125 | 0.125 | O-2 | 1         | 0.01     |
| O-2  | 8a      | 0.125 | 0.125 | 0.125 | O-2 | 1         | 0.01     |

3.2. Perovskite SrTcO$_3$ and layered perovskite Sr$_2$TcO$_4$

The strontium technetates SrTcO$_3$ (perovskite) and Sr$_2$TcO$_4$ (layered perovskite) were originally synthesized by Muller et al [4] and Wassilopulos [5]. While the structure of SrTcO$_3$ in its four different temperature-dependent modifications from orthorhombic to cubic was determined by Thorogood et al. [7], current or peer-reviewed structure data and thermophysical property data of the layered perovskite Sr$_2$TcO$_4$ are lacking. The reason therefore might be the difficulties of its synthesis due to the thermal instability of Sr$_2$TcO$_4$ above 570 °C. However, we can report here the successful synthesis of orthorhombic SrTcO$_3$ perovskite and tetragonal Sr$_2$TcO$_4$ layered perovskite (fig. 1).
Table 2. Crystalline data of SrTcO₃ perovskite

| Lattice parameters | Space group | Refinement residuals |
|--------------------|-------------|----------------------|
| \( a = 0.557503(5) \) nm | \( \text{Imma (}I\overline{2}m2/m2/m\alpha)\) | \( R_{\text{Bragg}} = 2.4 \% \) |
| \( b = 0.788808(7) \) nm | Space group \#74 | \( R_{\text{wp}} = 4.7 \% \) |
| \( c = 0.560296(5) \) nm | | |

| Site | Wyckoff | \( x \) | \( y \) | \( z \) | Atom | Occ | \( B_{\text{iso}} \) |
|------|---------|-------|------|------|------|-----|---------|
| Sr-1 | 4e      | 0     | 0.25 | 0.5014(5) | Sr\(^{2+}\) | 1 | 0.45(2) |
| Tc-1 | 4a      | 0     | 0    | 0    | Tc\(^{4+}\) | 1 | 0.19(2) |
| O-1  | 4e      | 0     | 0.25 | 0.043(2) | O-2 | 1 | 0.01(2) |
| O-2  | 8g      | 0.25  | 0.024(1) | 0.25 | O-2 | 1 | 0.3(1) |

The crystal structures of the strontium technetates were refined to high accuracies (tables 2, 3). While SrTcO₃ crystallizes in the orthorhombic SrRuO₃ lattice (e.g. space group \( \text{Imma} \) at RT), \( \text{Sr}_2\text{TcO}_4 \) crystallizes in the tetragonal structure type of \( \text{K}_2\text{NiF}_4 \) (space group \( \text{I}4/m\text{mm} \)). Furthermore, \( \text{Sr}_2\text{TcO}_4 \) is isostructural with \( \text{Sr}_2\text{RuO}_4 \). Among other structures, the \( \text{K}_2\text{NiF}_4 \) structure type is realized in the technologically interesting oxide system Ba-La-Cu-O, which is subject to intensive research in the arena of high-temperature superconductivity since the 1980s [9].

Table 3. Crystalline data of \( \text{Sr}_2\text{TcO}_4 \) layered perovskite

| Lattice parameters | Space group | Refinement residuals |
|--------------------|-------------|----------------------|
| \( a = 0.391831(4) \) nm | \( \text{I}4\text{mmm (}I\overline{4}m2/m2/m\alpha\text{)}\) | \( R_{\text{Bragg}} = 3.9 \% \) |
| \( c = 1.26867(2) \) nm | Space group \#139 | \( R_{\text{wp}} = 6.7 \% \) |

| Site | Wyckoff | \( x \) | \( y \) | \( z \) | Atom | Occ | \( B_{\text{iso}} \) |
|------|---------|-------|------|------|------|-----|---------|
| Sr-1 | 4e      | 0     | 0    | 0.3525(1) | Sr\(^{2+}\) | 1 | 0.26(2) |
| Tc-1 | 2a      | 0     | 0    | 0    | Tc\(^{4+}\) | 1 | 0.57(3) |
| O-1  | 4c      | 0.5   | 0    | 0    | O-2 | 1 | 0.9(1) |
| O-2  | 4e      | 0     | 0    | 0.1737(5) | O-2 | 1 | 0.7(1) |
The critical temperatures of the strontium technetates SrTcO$_3$ and Sr$_2$TcO$_4$, $T_c = 7.8$ K and 7 K, respectively, (fig. 2) are in the vicinity of the $T_c$ for Tc-metal with 7.73(2) K [10]. However, in regard to the low sintering temperatures (770 °C, 550 °C), the formation of metallic Tc impurities caused by disproportionation of TcO$_2$ is unlikely. The $T_c$ of Sr$_2$TcO$_4$ is significantly higher than the $T_c$ of the isostructural homolog Sr$_2$RuO$_4$ ($T_c = 0.9$ K) and rather high for non-copper based oxides. We intend to further optimize the structure of the layered perovskite regarding oxygen deficiency to enhance electron-phonon interaction at the Fermi level, and to achieve metallic conductivity, and as a result, higher $T_c$'s, typical for type-II mixed-valence ceramic superconductors. Hereby we intend to investigate crystal chemistry and AC magnetic susceptibility in the system Sr-Ba-Nd-Tc-O. To further study hydrodynamic properties of these Tc-99 waste forms, such as Tc-leaching and matrix corrosion, a hot uniaxial press is currently in development to synthesize dense monolithic specimen [11].

Fig. 2. AC magnetic susceptibility of Nd$_2$Tc$_2$O$_7$ (left), SrTcO$_3$ perovskite (center) and Sr$_2$TcO$_4$ layered perovskite (right)

4. Conclusions

- Advanced separation strategies such as UREX+ allow the treatment of Tc-99 to be managed separately from the high-level waste stream. Therefore, these methods offer the opportunity to stabilized and immobilize Tc-99 by its structural fixation in a ceramic host phase. This is advantageous as the ceramic host phases presented in this study (Nd$_2$Tc$_2$O$_7$, SrTcO$_3$, and Sr$_2$TcO$_4$) can accommodate far superior waste loads (up to 44, 56, and 39 wt-%, respectively) than vitreous borosilicate waste forms and may potentially offer better leach resistance and improved corrosion resistance.

- As part of this ongoing research on novel ceramic Tc-99 waste forms, we report the successful synthesis of three potential host phases for Tc-99 immobilization using a dry-chemical synthesis route: pyrochlore-type Nd$_2$Tc$_2$O$_7$, the perovskite-type SrTcO$_3$, and the layered perovskite structure Sr$_2$TcO$_4$. The synthesis of SrTcO$_3$ and Sr$_2$TcO$_4$ is successful at rather low temperature (770 °C and 550 °C, respectively), therefore avoiding volatilization and disproportionation of TcO$_2$, as experienced in the vitrification process for high-level waste streams.

- Furthermore, the knowledge on synthesis conditions and precise crystallographic properties will be used to allow for glove-box based fabrication of ceramic Tc-99 waste forms in larger quantities. In subsequent experiments, Tc-99 leaching and matrix corrosion of these waste forms will be tested by applying ASTM-based procedures, and the results will be compared with leaching and corrosion of Tc-99 bearing borosilicate glass.
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