

Fabrication and Properties of Technetium-Bearing Pyrochlores and Perovskites as Potential Waste Forms – 13222

Thomas Hartmann *, Ariana J. Alaniz ** and Daniel J. Antonio ***

* *University of Nevada – Las Vegas, Harry Reid Center, 4505 S. Maryland Parkway, Box 4009, Las Vegas, NV 89154-4009, USA, thomas.hartmann@unlv.edu.*

** *University of Nevada – Las Vegas, Howard R. Hughes College of Engineering, 4505 S. Maryland Parkway, Box 4009, Las Vegas, NV 89154-4009, USA, alaniza2@unlv.nevada.edu*

*** *University of Nevada – Las Vegas, Department of Physics & Astronomy, 4505 S. Maryland Parkway, Box 4002, Las Vegas, NV 89154-4002, USA, antonio@physics.unlv.edu*

ABSTRACT

Technetium-99 ($t_{1/2} = 2.13 \times 10^5$ 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+, 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 ($\text{Nd}_2\text{Tc}_2\text{O}_7$), perovskite (SrTcO_3), and layered perovskite (Sr_2TcO_4). The goal was to determine synthesis conditions of these potential waste forms to immobilize Tc-99 as tetravalent technetium and to harvest crystallographic, thermophysical and hydrodynamic data. The objective of this research is to provide fundamental crystallographic and thermophysical data on advanced ceramic Tc-99 waste forms such as pyrochlore, perovskite, and layered perovskite in support of our current efforts on the corrosion of technetium-bearing waste forms. The ceramic Tc-99-bearing waste forms exhibit good crystallinity. The lattice parameters and crystal structures of the technetium host phases could be refined with high accuracies of ± 3 , ± 4 , and ± 7 fm (10^{-15} m), for $\text{Nd}_2\text{Tc}_2\text{O}_7$, SrTcO_3 , and Sr_2TcO_4 , respectively. The associated refinement residuals (R_{wp}) 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. Thermophysical properties of the oxides SrTcO_3 , Sr_2TcO_4 , and $\text{Nd}_2\text{Tc}_2\text{O}_7$ were analyzed using AC magnetic susceptibility measurements to further harvest information on the critical temperature (T_c) for superconductivity. In our experiments the strontium technetates, SrTcO_3 and Sr_2TcO_4 , show superconductivity at rather high critical temperatures of $T_c = 7.8$ K and 7 K, respectively. On the other hand $\text{Nd}_2\text{Tc}_2\text{O}_7$ did not show any changes in magnetic properties above 3 K.

INTRODUCTION

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. 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), and borosilicate-based waste glass. 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 formation of the highly-mobile, pertechnetate TcO_4^- species under conditions of waste processing and within the long-term aspects of a generic repository.

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 Wassilopoulos [5], the oxides SrTcO_3 and Sr_2TcO_4 were synthesized and characterized by XRD. Hereby the perovskite (SrTcO_3) was described as cubic, and a K_2NiF_4 structure type was proposed for the layered perovskite Sr_2TcO_4 . 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 4d 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 $Imma$, 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, $\text{Ln}_2\text{Tc}_2\text{O}_7$, 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 ($\text{Nd}_2\text{Tc}_2\text{O}_7$), perovskite (SrTcO_3), and layered perovskite (Sr_2TcO_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.

METHODS

Preparation on TcO_2

Ammonium-pertechnetate (NH_4TcO_4) was obtained from Oak Ridge National Laboratory and was purified by recrystallization. Anhydrous crystalline TcO_2 was obtained by thermal decomposition of NH_4TcO_4 at up to 700°C under argon atmosphere for about 8 hrs. For the set of experiments ~350 mg NH_4TcO_4 were decomposed in a fused silica boat while raising the temperature stepwise to 700 °C.

Synthesis of SrTcO_3 perovskite, Sr_2TcO_4 layered perovskite, and $\text{Nd}_2\text{Tc}_2\text{O}_7$ pyrochlore

Strontium oxide (99.5 %) was purchased from Alfa Aesar while Nd_2O_3 (99.9 %) was purchased from Arcos. The oxides were dried at 600 °C overnight in air prior to be used. To synthesize SrTcO_3 , Sr_2TcO_4

and $\text{Nd}_2\text{Tc}_2\text{O}_7$ 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 Sr_2TcO_4 decomposes at temperatures of >570 °C. For the synthesis of Sr_2TcO_4 in the tetragonal K_2NiF_4 structure type the following reaction equation can be postulated: $2 \text{SrO} + \text{TcO}_2 \rightarrow (450^\circ\text{C} < T < 570^\circ\text{C}) \rightarrow \text{Sr}_2\text{TcO}_4 \rightarrow (T > 570^\circ\text{C}) \rightarrow \text{SrTcO}_3 + \text{SrO}$. This is in agreement with the observation by Wassilopoulos [5].

Characterization of SrTcO_3 , Sr_2TcO_4 , and $\text{Nd}_2\text{Tc}_2\text{O}_7$

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 $\text{Cu } K\alpha_1$ emission ($\lambda = 0.154063$ 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.

RESULTS and DISCUSSION

Powder XRD measurements revealed the successful synthesis of three potential host phases for Tc-99 immobilization: pyrochlore-type $\text{Nd}_2\text{Tc}_2\text{O}_7$, the perovskite-type SrTcO_3 , and the layered perovskite structure Sr_2TcO_4 . The applied dry chemical synthesis route produced high yields of >99 %. As main impurities, the oxides SrO and TcO_2 in concentrations <1 wt.-% were identified. After sintering, the fused silica ampoules did not show any condensation of volatile technetium species such as Tc_2O_7 . 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 $\text{Nd}_2\text{Tc}_2\text{O}_7$, SrTcO_3 , and Sr_2TcO_4 , respectively. The associated refinement residuals (R_{wp}) 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.

Thermophysical properties of the oxides SrTcO_3 , Sr_2TcO_4 , and $\text{Nd}_2\text{Tc}_2\text{O}_7$ were analyzed using a physical property measurement system (PPMS). Hereby we performed AC magnetic susceptibility measurements to further harvest information on the critical temperature (T_c) for superconductivity. The critical temperature for superconductivity T_c is determined by the temperature when changes in the magnetic moment become apparent (Meissner effect). In our experiments the strontium technetates, SrTcO_3 and

Sr_2TcO_4 , show superconductivity at rather high critical temperatures of $T_c = 7.8$ K and 7 K, respectively. On the other hand $\text{Nd}_2\text{Tc}_2\text{O}_7$ did not show any changes in magnetic properties above 3 K.

Pyrochlore $\text{Nd}_2\text{Tc}_2\text{O}_7$

The pyrochlore phase $\text{Nd}_2\text{Tc}_2\text{O}_7$ crystallizes in the cubic space group $Fd-3m$ and its crystal structure was refined applying Rietveld structure refinement (figure 1, table I). Considering the pyrochlore structure of the unit cell ($Z=8$) as:



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 $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$. The atomic coordinate “x” in the 48 f position in this pyrochlore setting is defined as:

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

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 $\text{Ln}_2\text{Tc}_2\text{O}_7$ structure is described in [8]. Using Rietveld structure refinement on X-ray powder data the lattice parameter of $\text{Nd}_2\text{Tc}_2\text{O}_7$ was refined to $a = 1.040629(3)$ nm, and the atomic coordinate x to 0.4206(4) to define the oxygen deviation parameter as $\Delta = 0.0456(4)$. In an additional effort to understand this oxygen dilation parameter in the series of $\text{Ln}_2\text{Tc}_2\text{O}_7$ lanthanide technetium pyrochlore we collected neutron diffraction time-of-flight (TOF) data and could extract the atomic coordinate $x = 0.4222(1)$ (48f) for $\text{Nd}_2\text{Tc}_2\text{O}_7$. This defines the oxygen dilation 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 $\text{Ln}_2\text{Tc}_2\text{O}_7$ pyrochlores from Pr to Lu the oxygen dilation parameter shows a steady decline [8]. The crystal structure of $\text{Nd}_2\text{Tc}_2\text{O}_7$ pyrochlore was refined to low refinement residuals ($R_{WP} = 4.1\%$) and is displayed in figure 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 (figure 2). This is not surprising due to the cubic nature of its crystal structure (space group $Fd-3m$).

Table I. Crystallographic data of Nd₂Tc₂O₇ pyrochlore

Lattice parameter		Space group			Refinement residuals		
$a = 1.040629(3)$ nm		$Fd-3m$ (2 nd setting)			$R_{Bragg} = 1.99$ %		
		Space group #227			$R_{WP} = 4.1$ %		
Site	Wyckoff	x	y	z	Atom	Occ	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

Perovskite SrTcO₃ and layered perovskite Sr₂TcO₄

The strontium technetates SrTcO₃ (perovskite) and Sr₂TcO₄ (layered perovskite) were originally synthesized by Muller et al. [4] and Wassilopoulos [5]. While the structure of SrTcO₃ 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 Sr₂TcO₄ are lacking. The reason therefore might be the difficulties of its synthesis due to the thermal instability of Sr₂TcO₄ above 570 °C. However, we can report here the successful synthesis of orthorhombic SrTcO₃ perovskite and tetragonal Sr₂TcO₄ layered perovskite (figure 1).

Table II. Crystallographic data of SrTcO₃ perovskite

Lattice parameters		Space group			Refinement residuals		
$a = 0.557503(5)$ nm		$Imma$ ($I 2_1/m 2_1/m 2_1/a$)			$R_{Bragg} = 2.4$ %		
$b = 0.788808(7)$ nm		Space group #74			$R_{WP} = 4.7$ %		
$c = 0.560296(5)$ nm							
Site	Wyckoff	x	y	z	Atom	Occ	B _{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)

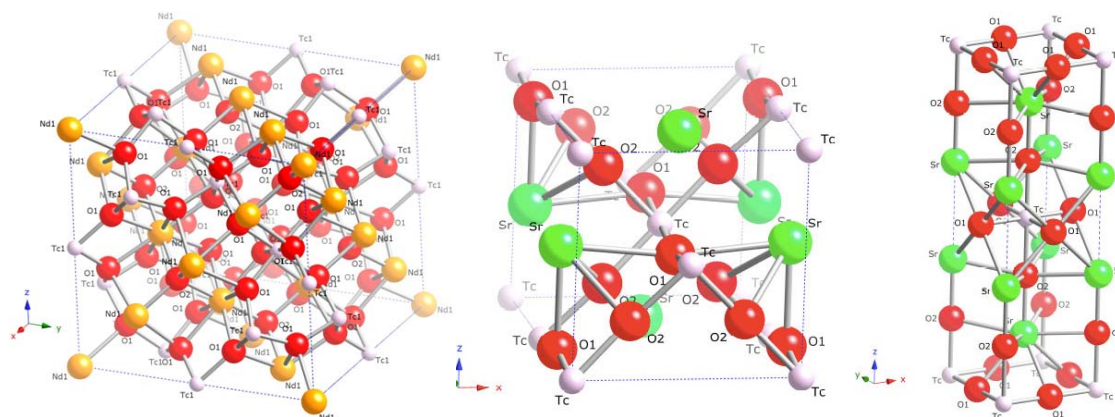


Figure 1. Refined crystal structures of potential host phases to immobilize Tc-99: (left) $\text{Nd}_2\text{Tc}_2\text{O}_7$ pyrochlore; (center) SrTcO_3 perovskite; (right) Sr_2TcO_4 layered perovskite

The crystal structures of the strontium technetates were refined to high accuracies (tables II, III). While SrTcO_3 crystallizes in the orthorhombic SrRuO_3 lattice (e.g. space group $Imma$ at RT), Sr_2TcO_4 crystallizes in the tetragonal structure type of K_2NiF_4 (space group $I4/mmm$). Furthermore, Sr_2TcO_4 is isostructural with Sr_2RuO_4 . Among other structures, the K_2NiF_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 III. Crystallographic data of Sr_2TcO_4 layered perovskite

Lattice parameters		Space group			Refinement residuals		
$a = 0.391831(4)$ nm		$I4/mmm$ ($I 4/m2/m2/m$)			$R_{\text{Bragg}} = 3.9\%$		
$c = 1.26867(2)$ nm		Space group #139			$R_{\text{WP}} = 6.7\%$		
Site	Wyckof f	x	y	z	Atom	Occ	B_{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	0.5	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_2TcO_4 , $T_c = 7.8$ K and 7 K, respectively, (figure 2) are in the vicinity of the Tc 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_2TcO_4 is significantly higher than the T_c of the isostructural homolog Sr_2RuO_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].

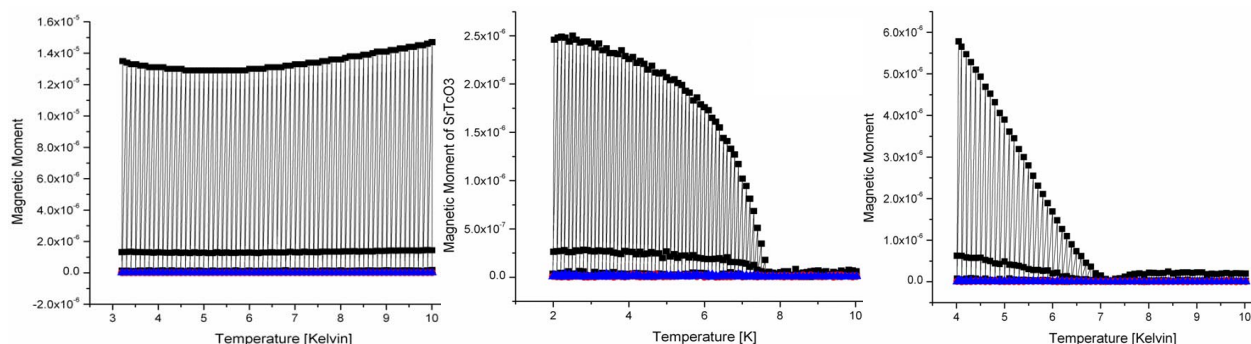


Figure 2. AC magnetic susceptibility of $\text{Nd}_2\text{Tc}_2\text{O}_7$ (left), SrTcO_3 perovskite (center) and Sr_2TcO_4 layered perovskite (right)

CONCLUSION

- 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 stabilize 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 ($\text{Nd}_2\text{Tc}_2\text{O}_7$, SrTcO_3 , and Sr_2TcO_4) can accommodate far superior waste loads than vitreous borosilicate waste forms and may potentially offer better leach resistance and improved corrosion resistance. Considering stoichiometric ceramic products, the loading of TcO_2 as high level waste content within $\text{Nd}_2\text{Tc}_2\text{O}_7$, SrTcO_3 , and Sr_2TcO_4 is 44, 56, and 39 wt.-%, respectively.
- 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 $\text{Nd}_2\text{Tc}_2\text{O}_7$, the perovskite-type SrTcO_3 , and the layered perovskite structure Sr_2TcO_4 . The synthesis of these Tc-99 waste forms in sub-gram quantities was performed on laboratory scale. While $\text{Nd}_2\text{Tc}_2\text{O}_7$ was obtained after sintering at 1150 °C, the strontium technetates SrTcO_3 and Sr_2TcO_4 were successfully synthesized at rather low temperatures (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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