Synthesizing stable actinide intermetallic materials for nuclear waste storage

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Introduction

Nuclear energy is crucial to provide the energy requirement; however, the lack of an ideal method to permanently store this highly radioactive waste is a pressing issue that scientists are currently working to rectify. Metal flux synthesis has proven to be an excellent method to generate actinide intermetallic materials. This technique uses an excess of one or more metals with low melting points to grow crystals of intermetallic phases. This allows to form kinetically stable complex materials at lower temperatures than those used in traditional solid-state synthesis. Actinide compounds also exhibit interesting magnetic properties. The current work focuses on synthesizing refractory actinide materials with unusual magnetic properties. In this study, actinide (U/Th/Np/Pu), transition metal (Ni/Co) silicide compounds were synthesized using the flux growth method. The obtained crystals were characterized using single-crystal X-ray diffraction, SEM/EDS and magnetic susceptibility measurements. For some products, stability in different media and at high temperatures was explored.

Objective

- Synthesizing stable actinide intermetallic materials suitable for long term radioactive waste storage using flux growth synthesis
- Analyzing the stability properties of these materials
- Exploring unique magnetic behaviors

Methods

Synthesis

Uranium and thorium compounds

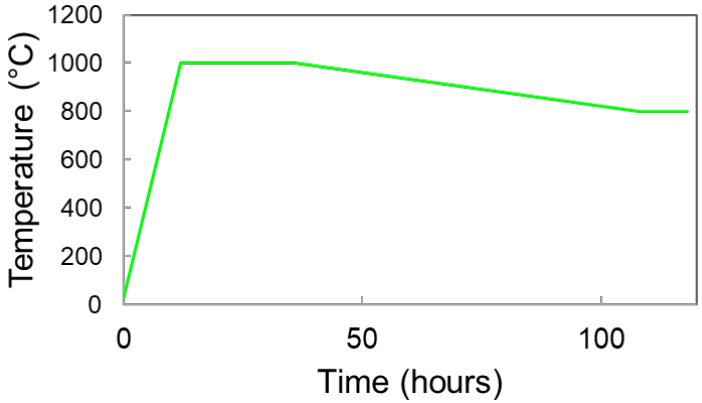
- UO_2/ThO_2, T (Ni/Co), Si, Ga, and Al 0.5, 1, 1, 10, and 10 mmol were mixed in an alumina crucible
- Crucibles placed in quartz tube and sealed under vacuum
- Ampules heated according to the temperature profile shown below
- Ampules inverted and centrifuged to remove excess flux and isolate crystals

Neptunium and plutonium compounds

- NpO_2/PuO_2, T (Ni/Co), Si, Ga, and Al 0.037, 0.074, 0.074, 0.741, and 0.741 mmol were mixed and the previous procedure was followed

Characterization

- SEM/EDS
- Single crystal and powder X-ray diffraction
- SQUID
- TGA/DSC



Heating profile

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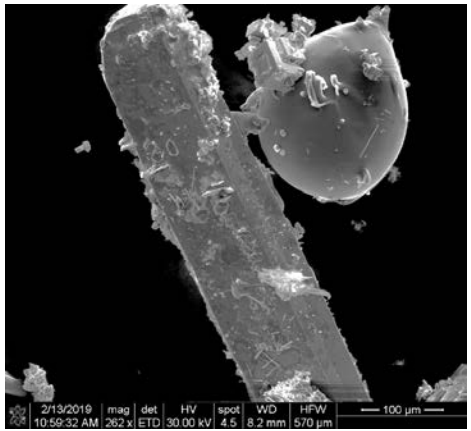
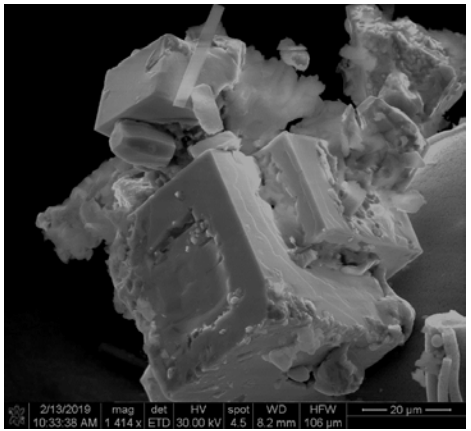
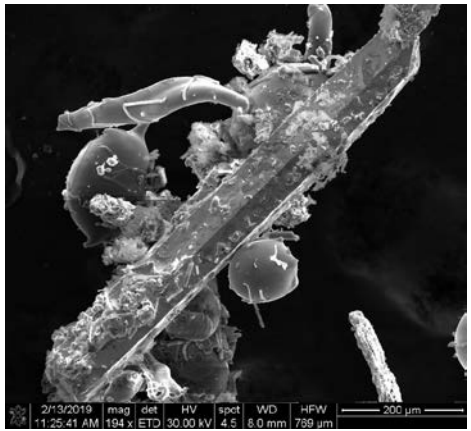
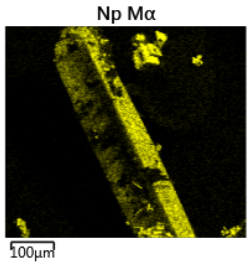
Results

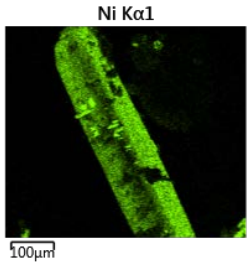
SEM/EDS data of products from NpO_2/Ni/Si/Al/Ga reactions

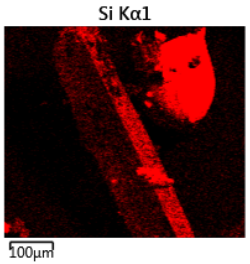


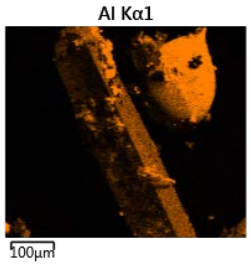


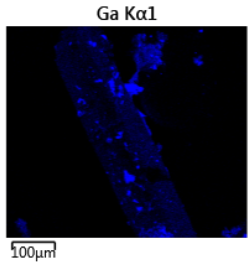












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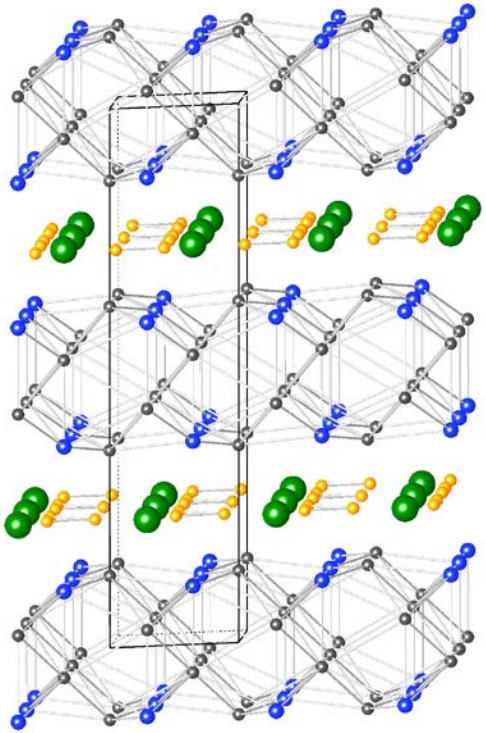
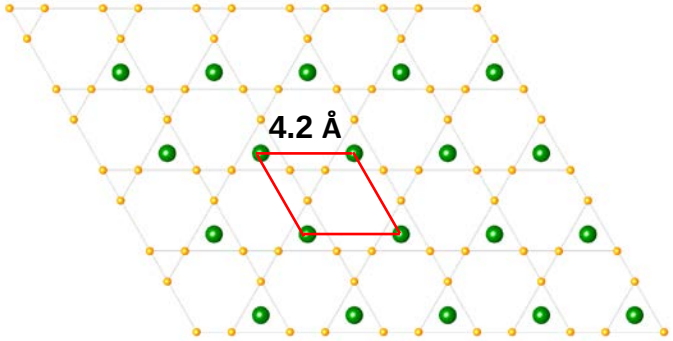
Rod - Np: Ni: Si: Al: Ga – 5.9(0.1): 18.8(0.6): 11(1): 55(1) 8.5(0.6)

Cube - Np: Si: Al: Ga – 17.1(2.8): 9.8(1.7): 38.2(2.7): 34.5(1.5)

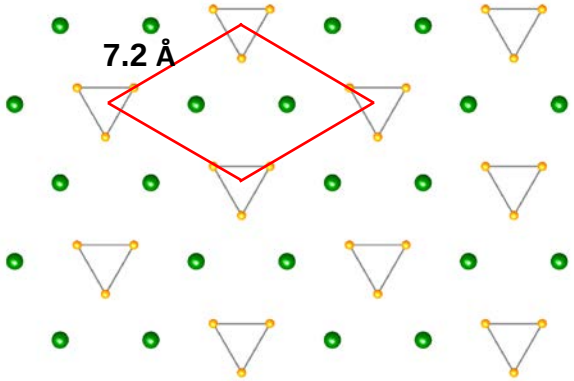
Crystal structure and disorder of $An_{1.33}T_4Al_8Si_2$ (An = Th, U, Np; T = Ni, Co)



The extended structure along *a* axis

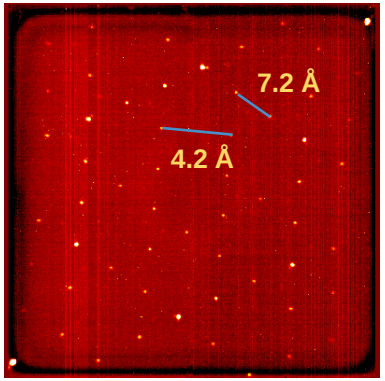


An-Si layer modeled with all the sites completely occupied viewed down *c* axis

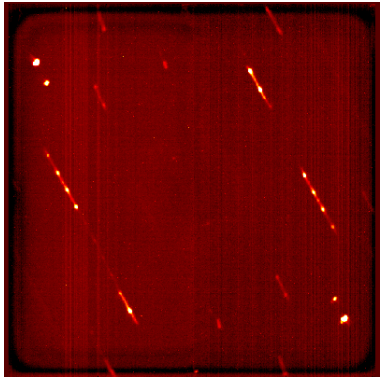


An-Si layer modeled with sites partially occupied in a super cell

(a)



(b)



Zone photos collected on $Np_{1.33}Co_4Al_8Si_2$ (a) along *c* axis (b) along *a* axis

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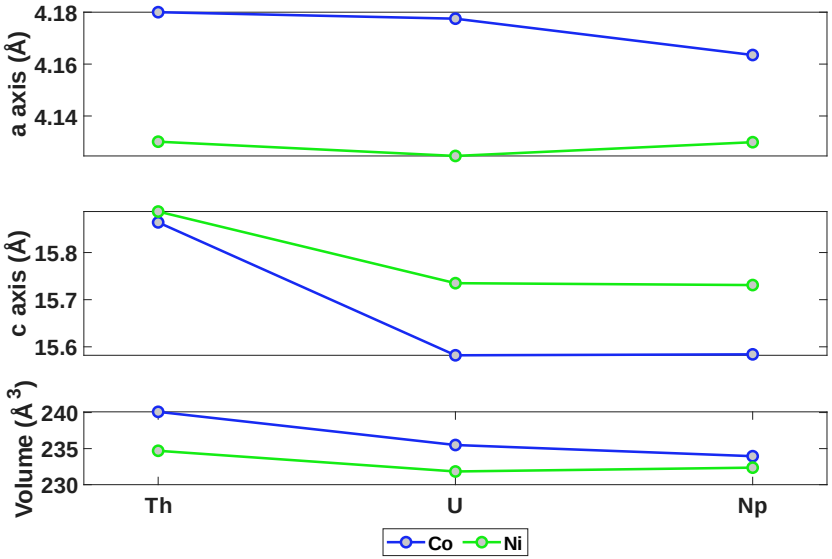
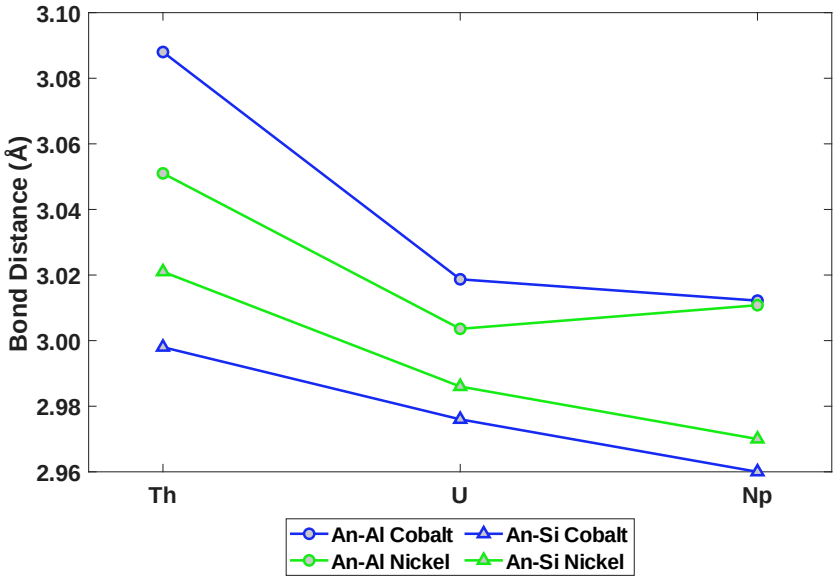
Unit cell parameters and bond distances of $An_{1.33}T_4Al_8Si_2$ (An = Th, U, Np; T = Ni, Co)





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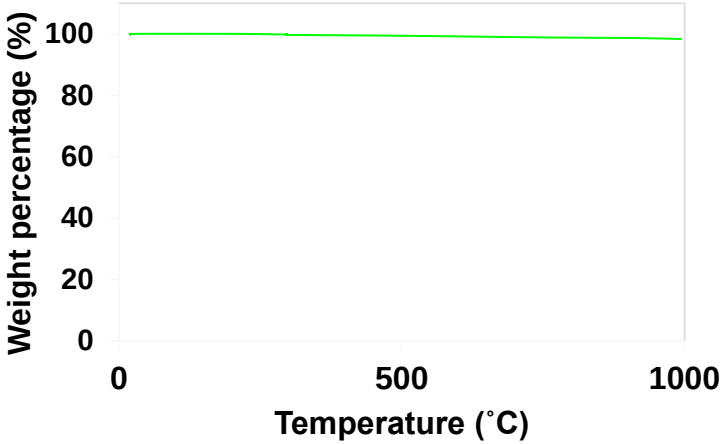
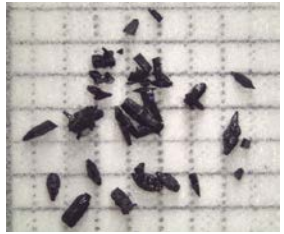
Thermal stability and chemical stability of the crystals in different media

	$U_{1.33}Ni_4Al_8Si_2$	$U_{1.33}Co_4Al_8Si_2$
Air	✓	✓
Water	✓	✓
6 M NaOH	✓	✓
1 M HCl	✓	✗
1 M HNO_3	✗	✗
10% NaCl	✓	✓



Thermogravimetric analysis (TGA) of $U_{1.33}Co_4Al_8Si_2$

Before



After TGA

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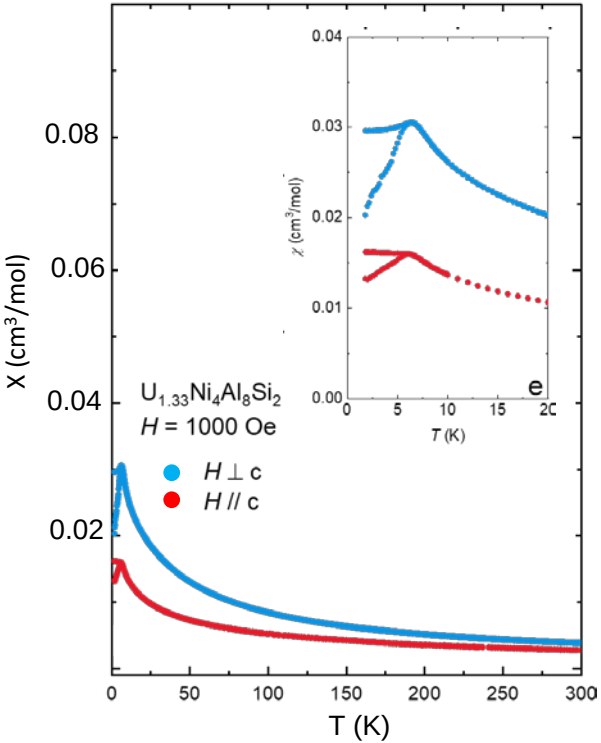
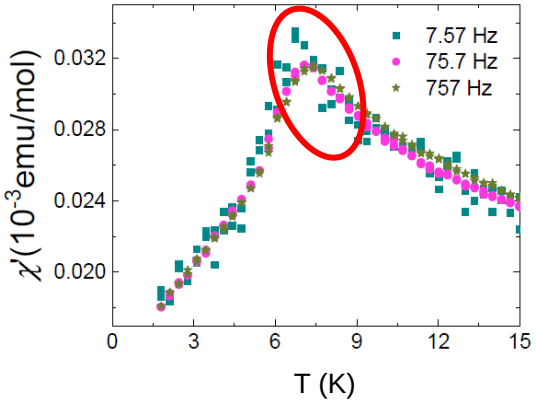
$U_{1.33}Ni_4Al_8Si_2$ magnetic data



Magnetic susceptibility measurements



AC susceptibility measurements

	(H ⊥ c)	(H // c)
Weiss constant (K)	-76	-137
Magnetic moment (μ_B)	3.0	3.3

$\gamma \approx 210$ mJ mol^{-1} K^{-2} for both Co and Ni compounds

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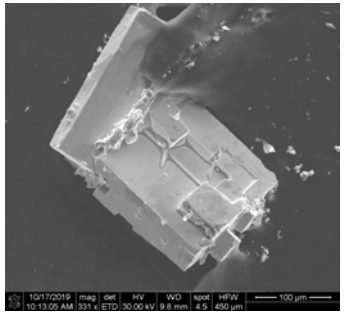
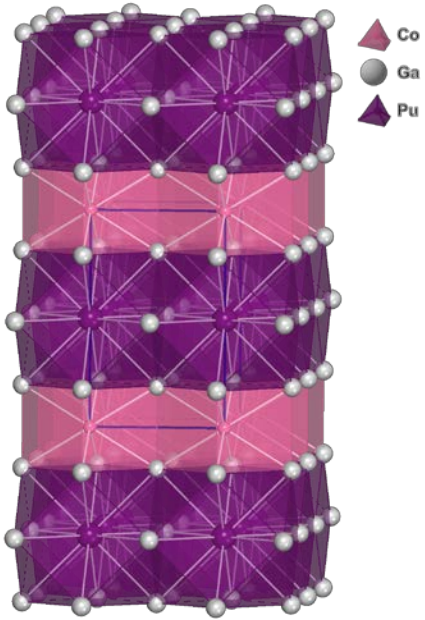
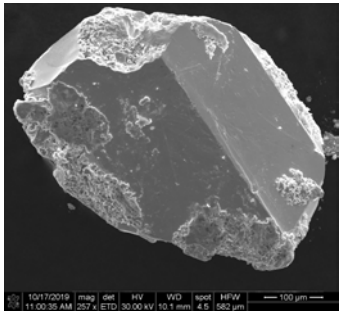
Similar reactions with Pu produced different products

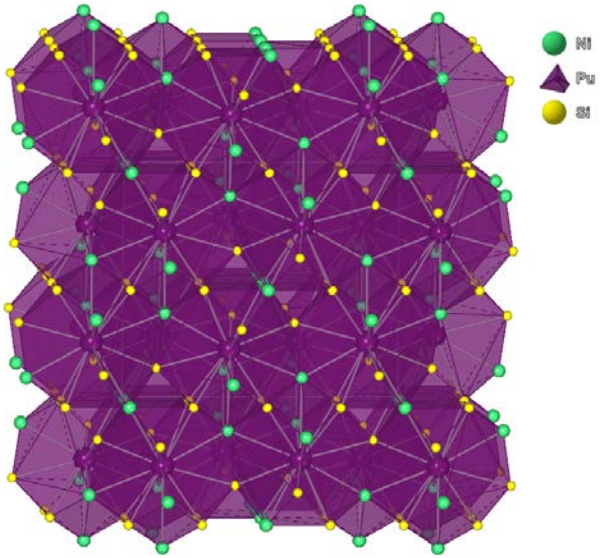




Pu: Co: Ga
14.9(3): 15.1(3): 70.0(4)

a **= 4.2078(3) Å** ***c*** **= 6.7491(4) Å**
P4/mmm
Final R [I>2σ(I)] = 1.49





Pu: Ni: Si: Ga: Al
18.3(0.5): 29(2): 45(2): 5(1): 1.7(0.2)

a **= 9.5974(5) Å** ***b*** **= 11.2377(6) Å** ***c*** **= 5.6619 Å**
Ibam
Final R [I>2σ(I)] = 1.09

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Conclusions and Future Work

- Flux growth synthesis provide an effective method to grow actinide intermetallic crystals
- Properties vary based on the transition metal used
- The synthesized materials are stable in different media and have high thermal stability
- With Pu, it does not form $Pu_{1.33}T_4Al_8Si_2$ analog, instead $PuCoGa_5$ and $Pu_2Ni_5Si_6$ compounds are formed
- The unit cell parameters and An-Al bond distances do not decrease as expected from Th – U – Np
- EXAFS data are required to analyze whether the previous anomaly is due to change in the oxidation state of the actinide
- U/T (T = Ni, Co) eutectic fluxes will be used to attempt to synthesize more novel stable materials

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