$[Ag_2M(Te_2O_5)_2]SO_4$ (M = Ce^{IV} or Th^{IV}): A New Purely Inorganic *d/f*-Heterometallic Cationic Material

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Supporting Information

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Experimental Section

Synthesis.

Caution! Th-232 used in this study is an α-emitter, producing the radioactive Ra-228 daughter. All of the thorium experiments were conducted in a laboratory dedicated for actinide element studies with approved safety operating procedures.

ThO_2 (99.99%, Puratrem), CeO_2 (99.5%, Alfa Aesar), TeO_2 (99.99%, Alfa Aesar), $AgNO_3$ (99.9+%, Alfa Aesar), H_2SO_4 (ACS Reagent Grade, 18 M, Pharmco-Aaper) were all reagent grade and used as received with no further purification. Reactions were run in PTFE-lined Parr 4749 autoclaves with a 23 mL internal volume. Distilled and Millipore filtered water was used in all reactions.

$[Ag_2M(Te_2O_5)_2]SO_4$ (M = Ce^{IV}, Th^{IV}). TeO_2 (1.00 mmol, 0.1596 g), $AgNO_3$ (1.00 mmol, 0.1699 g), 1.0 M H_2SO_4 (1.00 mmol, 1.00 mL), 1.00 mL H_2O, and either CeO_2 (1.00 mmol, 0.1721 g) or ThO_2 (1.00 mmol, 0.2640 g) were charged into a PTFE-lined Parr 4749 autoclave with a 23 mL internal volume. This provides a M:Te:Ag molar ratio of 1:1:1. The autoclave was sealed and heated to 230 °C for three days under autogenous pressure followed by cooling at a rate of 3 °C hr $^{-1}$. The resulting crystalline materials were washed extensively with boiling deionized water to remove any excess reactants. The products consisted of either orange (Ce) or colorless (Th) columnar crystals and were present in *ca.* 70% yield for both reactions. It should be noted that the cerium analogue can also be produced by replacing CeO_2 with $(NH_4)_2Ce(NO_3)_6$ under the conditions listed above.

Crystallographic Studies. Crystals of both compounds were mounted on CryoLoops with Krytox oil and optically aligned on a diffractometer using a digital camera.

[Ag₂Th(Te₂O₅)₂]SO₄. Crystallographic analysis of this compound was performed on a Bruker D8 Quest x-ray diffractometer. Initial intensity measures were performed using a IμS x-ray source (Mo Kα, λ = 0.71073 Å) with high-brilliance and high-performance focusing multi-layered optics. QUEST software was used for determination of the unit cells and data collection control. The intensities of reflections of a sphere were collected by a combination of multiple sets of exposures (frames). Each set had a different φ angle for the crystal and each exposure covered a range of 0.5 ° in ω. Single crystals of this compound were run at 273 K. SAINT software was used for data integration including Lorentz and polarization corrections. Semiempirical absorption corrections were applied using the program SCALE (SADABS).[1] Solutions were checked for missed symmetry and solvent accessible voids using PLATON.[2] Selected crystallographic information is listed in Table 1.

[Ag₂Ce(Te₂O₅)₂]SO₄. Crystallographic analysis of this compound was performed on a Rigaku SCX-Mini Single-Crystal X-ray diffractometer equipped with a Mercury2 (2x2 bin mode) diffractometer. The crystal was kept at 293 K during data collection. Initial matrix

images were collected to determine the unit cell and proper exposure time. Three hemispheres (where $\varphi = 0.0$, 120.0, and 240.0) of data were collected with each consisting of 180 images each with 1.00° widths and 1.00° steps. Using Olex2, the structure was solved with the ShelXT[3] structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization.[4-6]

Solutions for both compounds were checked for missed symmetry and solvent accessible voids using PLATON.[2] Selected crystallographic information is listed in Table S1. Atomic coordinates for both compounds are provided in Tables S3 and S4. The Crystallographic Information File (CIF) is available from the Cambridge Crystal Structure Database Center: 1819474 ($[Ag_2Ce(Te_2O_5)_2]SO_4$) and 1819475 ($[Ag_2Th(Te_2O_5)_2]SO_4$)

UV-vis-NIR Spectroscopy. Solid state UV-vis-NIR data were collected on clusters of single crystals using a Craic Technologies 508 PV Microscope Spectrophotometer equipped with a 1.3 MP high sensitivity digital imaging system. Samples were mounted onto glass slides and data collected from 350 – 850 nm (Figure S1). Exposure time and sampling rate were auto-optimized using Craic's Lambdafire Control and Analysis software.

Scanning Electron Microscopy (SEM)/Energy-Dispersive Spectroscopy (EDS). Scanning electron microscopy (SEM) images and Energy-dispersive spectroscopy (EDS) data were collected using a FEI Nova nanoSEM 400 with an Oxford INCA x-sight EDS detector. The energy of the electron beam was 3.00 kV for the SEM images and 20.0 kV for EDS data. The spectrum acquisition time was 60 s. All data were calibrated with standards and the EDS results for $[Ag_2Ce(Te_2O_5)_2]SO_4$ is provided in the Figure S2. The observed weight percent of each element help to confirm the overall chemical formula for the structure.

Table S1. Crystallographic Data for $[Ag_2Ce(Te_2O_5)_2]SO_4$ and $[Ag_2Th(Te_2O_5)_2]SO_4$.

Compound	$[Ag_2Ce(Te_2O_5)_2]SO_4$	$[Ag_2Th(Te_2O_5)_2]SO_4$
Mass	1122.32	1214.24
Color and habit	Orange, Column	Colorless, Column
Space group	*Cmca*	*Cmca*
a (Å)	15.5581(4)	15.6795(13)
b (Å)	10.7450(3)	10.8699(2)
c (Å)	15.6309(4)	15.7334(13)
V (Å^3)	2613.05(13)	2681.5(4)
Z	8	8
T (K)	293(2)	273(2)
λ(Å)	0.71073	0.71073
Maximum 2θ(deg.)	30.505	34.938
ρcalcd (g cm^{-3})	5.706	6.015
μ(Mo $K\alpha$)	15.383	22.718
$R(F)$ for $F_o{}^2 > 2\sigma(F_o{}^2)^a$	0.0322	0.0458
Rw$(F_o{}^2)^b$	0.0711	0.0923

$^aR(F) = \Sigma \,||\,F_0\,|-|\,F_c\,||\,/\Sigma\,|\,F_0\,|$

$^bR(F_0^2) = [\Sigma w(F_0^2 - F_c^2)^2 \,/\, \Sigma w(F_0^4)]^{1/2}$

Table S2. Selected bond distances (Å) for [Ag$_2$Ce(Te$_2$O$_5$)$_2$]SO$_4$ and [Ag$_2$Th(Te$_2$O$_5$)$_2$]SO$_4$.

	Distance (Å)				Distance (Å)		
Ce(1)-O(2)	2.350(4)	Ag(1)-O(2)	2.209(4)	Th(1)-O(2)	2.413(6)	Ag(1)-O(2)	2.217(7)
Ce(1)-O(3)	2.332(4)	Ag(2)-O(5)	2.315(4)	Th(1)-O(3)	2.370(6)	Ag(2)-O(5)	2.314(7)
Ce(1)-O(4)	2.290(4)	Ag(2)-O(6)	2.423(6)	Th(1)-O(4)	2.357(6)	Ag(2)-O(6)	2.489(10)
Ce(1)-O(5)	2.377(4)			Th(1)-O(5)	2.426(6)		
Te(1)-O(1)	1.925(2)	S(1)-O(7)	1.460(9)	Te(1)-O(1)	1.903(3)	S(1)-O(7)	1.449(16)
Te(1)-O(2)	1.868(4)	S(1)-O(8)	1.465(7)	Te(1)-O(2)	1.867(6)	S(1)-O(8)	1.479(11)
Te(1)-O(3)	1.885(4)	S(1)-O(9)	1.476(8)	Te(1)-O(3)	1.872(6)	S(1)-O(9)	1.440(14)
Te(2)-O(4)	1.886(4)			Te(2)-O(4)	1.871(6)		
Te(2)-O(5)	1.858(4)			Te(2)-O(5)	1.868(6)		
Te(2)-O(6)	1.946(2)			Te(2)-O(6)	1.928(4)		

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ([$Ag_2Ce(Te_2O_5)_2$]SO_4. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ce(1)	2500	2456(1)	7500	9(1)
Te(1)	3593(1)	-175(1)	6181(1)	10(1)
Te(2)	3833(1)	5147(1)	6418(1)	10(1)
Ag(1)	2500	-2500	5000	39(1)
Ag(2)	5000	7595(1)	7684(1)	36(1)
S(1)	5000	7521(2)	4895(2)	16(1)
O(1)	3262(5)	0	5000	21(1)
O(2)	2931(3)	-1626(4)	6205(3)	15(1)
O(3)	2684(3)	906(4)	6472(3)	15(1)
O(4)	3493(3)	3990(4)	7260(3)	16(1)
O(5)	3833(3)	6490(4)	7167(3)	14(1)
O(6)	5000	4685(6)	6733(4)	16(1)
O(7)	5000	6376(9)	5398(7)	55(3)
O(8)	4232(5)	7556(7)	4353(4)	55(2)
O(9)	5000	8572(8)	5504(6)	43(2)

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for ([Ag$_2$Ce(Te$_2$O$_5$)$_2$]SO$_4$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Th(1)	2500	2443(1)	7500	9(1)
Te(1)	3595(1)	-169(1)	6159(1)	12(1)
Te(2)	3849(1)	5120(1)	6412(1)	12(1)
Ag(1)	2500	-2500	5000	52(1)
Ag(2)	5000	7572(1)	7665(1)	42(1)
S(1)	5000	7525(3)	4897(2)	25(1)
O(1)	3266(7)	0	5000	32(2)
O(2)	2943(5)	-1605(6)	6187(4)	22(1)
O(3)	2703(4)	888(6)	6464(4)	19(1)
O(4)	3512(4)	4006(6)	7254(4)	21(1)
O(5)	3848(4)	6478(6)	7140(4)	21(1)
O(6)	5000	4680(10)	6718(7)	22(2)
O(7)	5000	6363(15)	5348(14)	76(6)
O(8)	4244(8)	7549(13)	4335(8)	68(4)
O(9)	5000	8559(14)	5469(13)	67(5)

Table S5. Bond Valence Sum (BVS) Data for $[Ag_2Ce(Te_2O_5)_2]SO_4$. BVS parameters provide complementary evidence supporting the oxidation state assignments. Specific parameters and values for each metal center were obtained from Refs. 7 and 8.

$vu = \exp[(R_0 - d)/b]$.

R(0) : Ce-O	2.094	Ce(1)-O(2)	d	vu
		Ce(1)-O(2)	2.35	0.501
b	0.37	Ce(1)-O(2)	2.35	0.501
		Ce(1)-O(3)	2.332	0.526
		Ce(1)-O(3)	2.332	0.526
		Ce(1)-O(4)	2.29	0.589
		Ce(1)-O(4)	2.29	0.589
		Ce(1)-O(5)	2.377	0.465
		Ce(1)-O(5)	2.377	0.465
		Ce(1) BVS		**4.161**

R(0) : Ag-O	1.805	Ag(1)-O(2)	d	vu
		Ag(1)-O(2)	2.209	0.336
b	0.37	Ag(1)-O(2)	2.209	0.336
		Ag(1) BVS		**0.671**

R(0) : Ag-O	1.805	Ag(2)-O(5)	d	vu
		Ag(2)-O(5)	2.315	0.252
b	0.37	Ag(2)-O(5)	2.315	0.252
		Ag(2)-O(6)	2.423	0.188
		Ag(2) BVS		**0.692**

R(0) : Te-O	1.977	Te(1)-O(1)	d	vu
		Te(1)-O(1)	1.925	1.151
b	0.37	Te(1)-O(2)	1.868	1.343
		Te(1)-O(3)	1.885	1.282
		Te(1) BVS		**3.776**

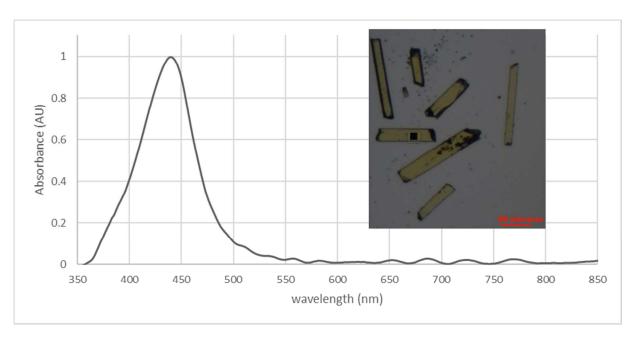| R(0) : Te-O	1.977	Te(2)-O(4)	d	vu
		Te(2)-O(4)	1.886	1.279
b	0.37	Te(2)-O(5)	1.858	1.379
		Te(2)-O(6)	1.946	1.087
		Te(2) BVS		**3.746**

Figure S1. Normalized UV-vis-NIR spectrum of [Ag$_2$Ce(Te$_2$O$_5$)$_2$]SO$_4$ showing the characteristic charge-transfer band of Ce(IV).
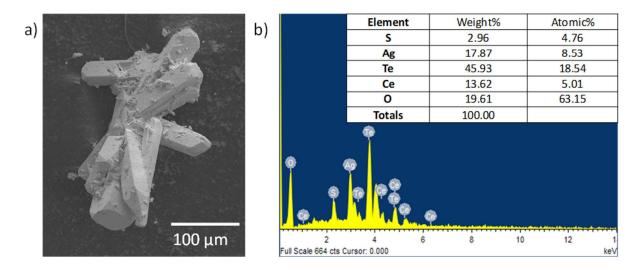
Element	Weight%	Atomic%
S	2.96	4.76
Ag	17.87	8.53
Te	45.93	18.54
Ce	13.62	5.01
O	19.61	63.15
Totals	100.00	

Full Scale 664 cts Cursor: 0.000

Figure S2. (a) Image of crystal surface obtained from Scanning Electron Miroscopy (SEM) and (b) elemental analysis of Energy Dispersive Spectroscopy (EDS) spectrum for $[Ag_2Ce(Te_2O_5)_2]SO_4$. Based on the EDS data, the measured composition is $Ag_{1.9}Ce_{1.1}Te_{4.0}O_{13.63}S_{1.0}$ which closely matches the theoretical composition of $Ag_2Ce_1Te_4O_{14}S$.
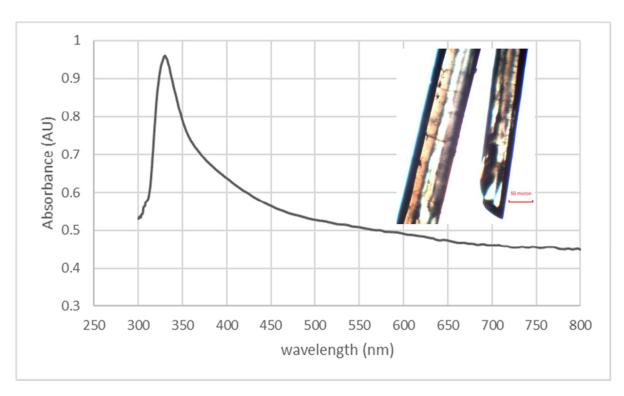
Figure S3. UV-vis-NIR spectrum of $[Ag_2Th(Te_2O_5)_2]SO_4$ showing the characteristic charge-transfer band of Th(IV).

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