

Electronic Supplementary Information

Synthesis.

$\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ (98%, International Bio-Analytical Industries), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.998 %, Alfa-Aesar), $\text{Pr}(\text{NO}_3)_3$ (99.9 %, Alfa-Aesar), $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9 %, Alfa-Aesar), $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9 %, Alfa-Aesar), $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9 %, Alfa-Aesar), I_2O_5 (98 %, Alfa-Aesar), SeO_2 (99.4 %, Alfa-Aesar), and V_2O_5 (99.6 %, Alfa-Aesar) were all used as received. Reactions were run in PTFE-lined Parr 4749 autoclaves with 23 mL internal volume autoclaves. Distilled and Millipore filtered water was used in all reactions.

$\text{Th}(\text{VO}_3)_2(\text{SeO}_3)$. $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ (0.25 mmol, 0.1425 g), SeO_2 (0.25 mmol, 0.0277 g), V_2O_5 (0.25 mmol, 0.0455 g), and water (2 mL) were loaded into a 23 mL PTFE-lined autoclave liner. The autoclave was sealed and heated to 230 °C in a box furnace for 3 days followed by slow cooling to room temperature at a rate of 5 °C/h. The products were washed with DI water to remove soluble solids, followed by rinsing with ethanol. The products consists of yellow columnar crystals of $\text{Th}(\text{VO}_3)_2(\text{SeO}_3)$. Powder X-ray diffraction studies reveal that $\text{Th}(\text{VO}_3)_2(\text{SeO}_3)$ can be made with an average yield of 60 % based on Th, coexisting with V_2O_5 and SeO_2 .

$\text{Ln}(\text{VO}_3)_2(\text{IO}_3)$ (Ln = Ce, Pr, Nd, Sm, and Eu). $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.5 mmol, 0.2171 g for $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 0.1635 g for $\text{Pr}(\text{NO}_3)_3$, 0.2192 g for $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 0.2222 g for $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and 0.2230 g for $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), V_2O_5 (0.5 mmol, 0.0909 g), I_2O_5 (0.25 mmol, 0.0835 g) and water (3 mL) were loaded into a 23 mL PTFE-lined autoclave liner. The autoclave was sealed and heated to 180 °C for 3 days. The autoclave was then cooled to room temperature at a rate of 5 °C/h. The products were washed with DI water to remove soluble

solids, followed by rinsing with ethanol. $\text{Ce}(\text{VO}_3)_2(\text{IO}_3)$ forms dark-red columnar crystals. $\text{Pr}(\text{VO}_3)_2(\text{IO}_3)$, $\text{Nd}(\text{VO}_3)_2(\text{IO}_3)$, $\text{Sm}(\text{VO}_3)_2(\text{IO}_3)$, and $\text{Eu}(\text{VO}_3)_2(\text{IO}_3)$ are yellow columnar crystals. Powder X-ray diffraction studies reveal that $\text{Ce}(\text{VO}_3)_2(\text{IO}_3)$, $\text{Pr}(\text{VO}_3)_2(\text{IO}_3)$, and $\text{Eu}(\text{VO}_3)_2(\text{IO}_3)$ can be made with a yield of 40 %, 55 %, and 40 %, respectively. The main byproducts for those reactions are $\text{Ln}(\text{IO}_3)_3$ ($\text{Ln} = \text{Ce}, \text{Pr}, \text{and Eu}$). For $\text{Nd}(\text{VO}_3)_2(\text{IO}_3)$ and $\text{Sm}(\text{VO}_3)_2(\text{IO}_3)$, the main products are $\text{Ln}(\text{IO}_3)_3$ ($\text{Ln} = \text{Nd and Sm, respectively}$). The yield of $\text{Nd}(\text{VO}_3)_2(\text{IO}_3)$ and $\text{Sm}(\text{VO}_3)_2(\text{IO}_3)$ is approximately 5 % and 10%, respectively, based on a visual estimation.

Crystallographic Studies. Single crystals of all compounds were mounted on CryoLoops with Krytox oil and optically aligned on a Bruker D8 QUEST X-ray diffractometer using a digital camera. Initial intensity measurements were performed using an $I\mu\text{SX}$ -ray source, a 30 W microfocused sealed tube ($\text{MoK}\alpha$, $\lambda = 0.71073 \text{ \AA}$) with high-brilliance and high-performance focusing Quazar multilayer optics. Standard APEXII 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 four 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 . A total of 1464 frames were collected with an exposure time per frame of 10 to 30 s, depending on the crystal. The SAINT software was used for data integration including Lorentz and polarization corrections. Semi-empirical absorption corrections were applied using the program SADABS or TWINABS. Selected crystallographic information is listed in Table 1. Atomic coordinates and additional structural information are provided in the Supporting Information (CIFs).

UV–vis–NIR Spectroscopy. UV–vis–NIR data were acquired from single crystals using a Craic Technologies microspectrophotometer. Crystals were placed on quartz slides under Krytox oil, and the data was collected from 200 to 1500 nm.

Scanning Electron Microscopy and Energy-Dispersive X-Ray Spectrometry (SEM-EDS) Analysis. SEM-EDS images and data were collected using a JEOL 5900 with an XRF energy-dispersive X-ray spectrometer. The energy of the electron beam was set at 29.02 kV, and the spectrum acquisition time was 60 s.

Powder X-Ray Diffractometer. Powder patterns were collected from 5° to 80°, with a step of 0.5°, and the data collection time was 0.5 s using a Panalytical X'PERT Pro powder diffractometer.

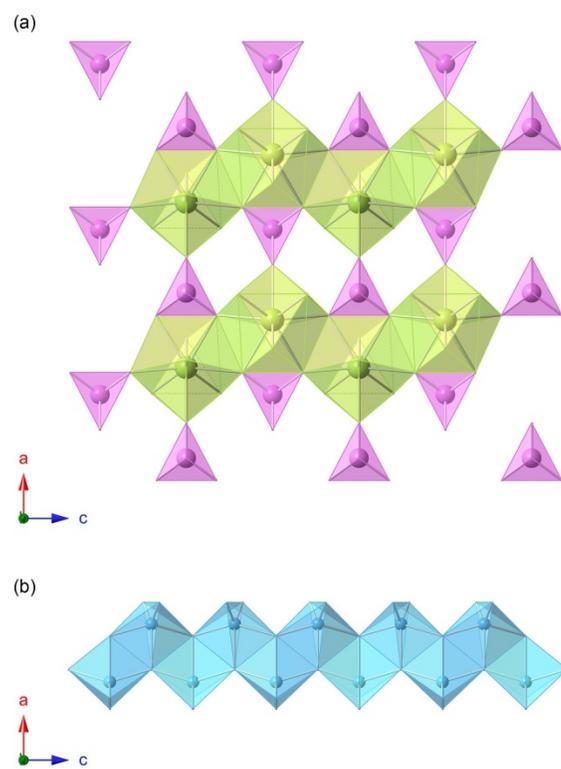


Figure S1. A view of $\text{Th}(\text{SeO}_3)^{2+}/\text{Ln}(\text{IO}_3)^{2+}$ layer and $\text{V}_2\text{O}_6^{2-}$ chains.

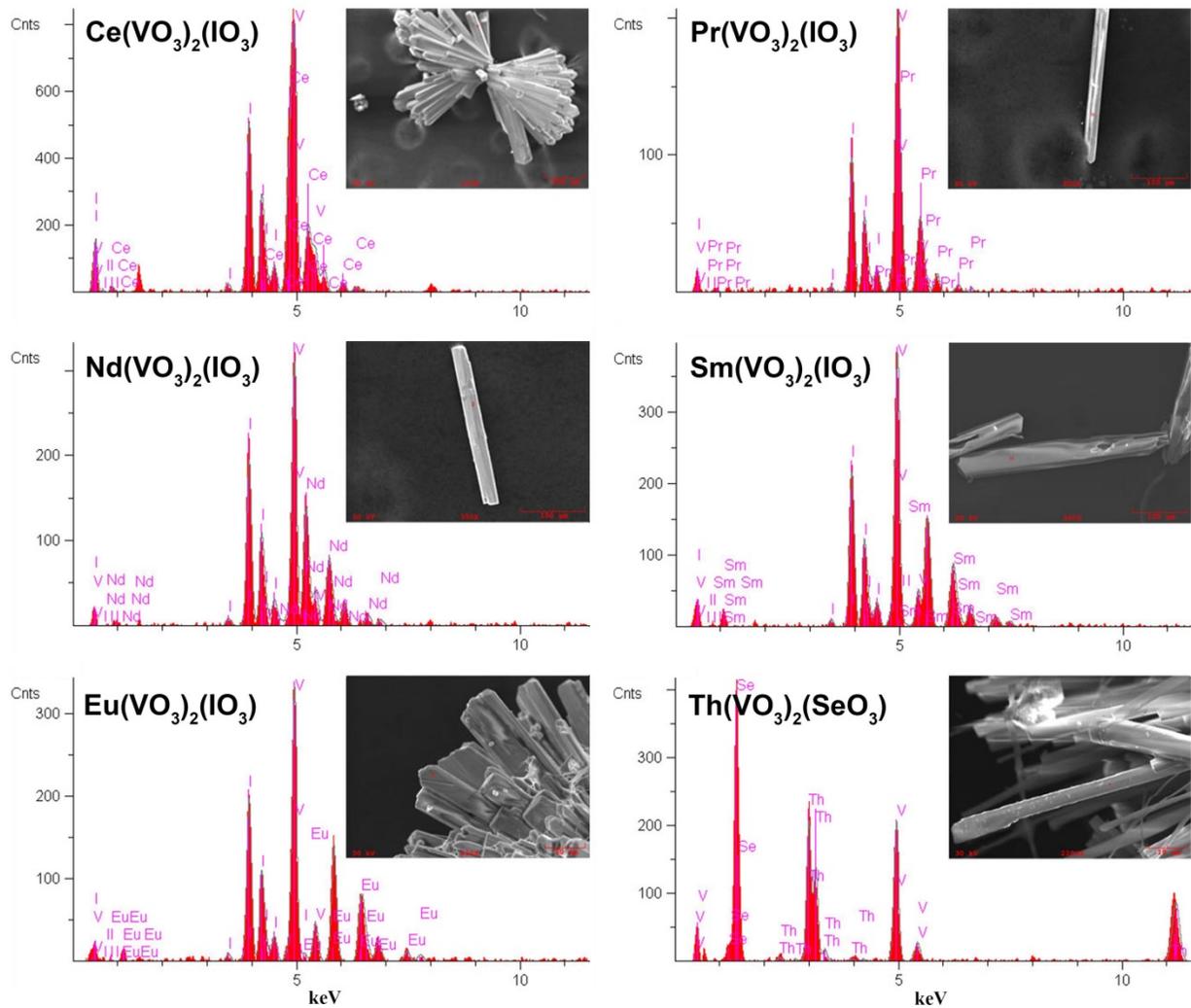


Figure S2. SEM images and EDS spectra of $\text{Ln}(\text{VO}_3)_2(\text{IO}_3)$ ($\text{Ln} = \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{and Eu}$) and $\text{Th}(\text{VO}_3)_2(\text{SeO}_3)$. The $\text{Ln} : \text{V} : \text{I}$ and $\text{Th} : \text{V} : \text{I}$ molar ratio of 1:2:1 was verified using EDS.

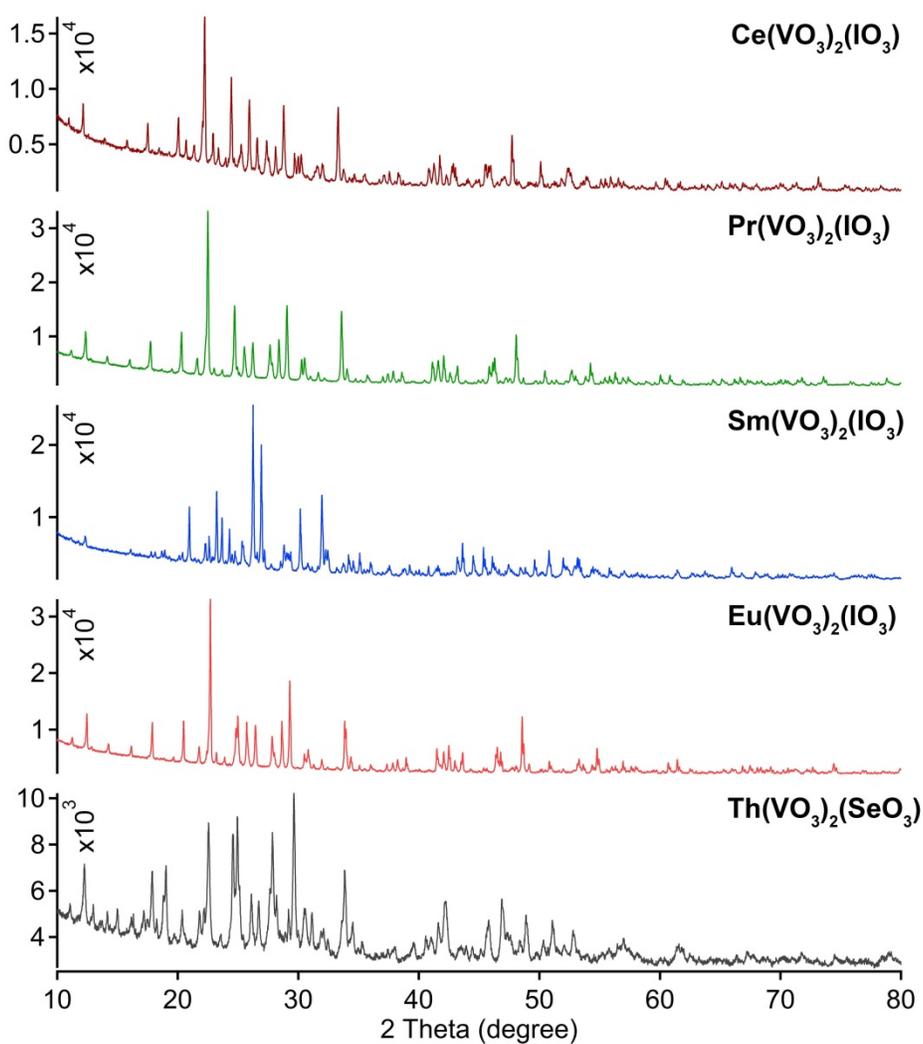


Figure S3. Powder X-Ray Diffraction data of Ln(VO₃)₂(IO₃) (Ln = Ce, Pr, Sm, and Eu) and Th(VO₃)₂(SeO₃) reveal that Ce(VO₃)₂(IO₃), Pr(VO₃)₂(IO₃), Eu(VO₃)₂(IO₃) and Th(VO₃)₂(SeO₃) can be made with a yield of 40 %, 55 %, 40 %, and 60 %. The main product for reactions of Nd(VO₃)₂(IO₃) and Sm(VO₃)₂(IO₃) is Nd(IO₃)₃ and Sm(IO₃)₃, respectively.

Table S1. Crystallographic data for Th(VO₃)₂(SeO₃), Ce(VO₃)₂(IO₃), Pr(VO₃)₂(IO₃), Nd(VO₃)₂(IO₃), Sm(VO₃)₂(IO₃) and Eu(VO₃)₂(IO₃).

Compound	Th(VO ₃) ₂ (SeO ₃)	Ce(VO ₃) ₂ (IO ₃)	Pr(VO ₃) ₂ (IO ₃)	Nd(VO ₃) ₂ (IO ₃)	Sm(VO ₃) ₂ (IO ₃)	Eu(VO ₃) ₂ (IO ₃)
Formula Mass	556.88	512.9	513.69	517.02	523.14	524.75
Color	Yellow	Dark-red	Yellow	Yellow	Yellow	Yellow
Habit	Columnar	Columnar	Columnar	Columnar	Columnar	Columnar
Space Group	<i>Pbcm</i>	<i>Pbcm</i>	<i>Pbcm</i>	<i>Pbcm</i>	<i>Pbcm</i>	<i>Pbcm</i>
<i>a</i> (Å)	6.839(2)	7.0352(6)	7.0009(7)	6.9863(11)	6.9439(10)	6.9278(4)
<i>b</i> (Å)	14.481(5)	14.5215(11)	14.4453(14)	14.422(2)	14.303(2)	14.2624(9)
<i>c</i> (Å)	7.149(3)	7.2665(6)	7.2344(7)	7.2237(11)	7.188(1)	7.1720(5)
α (deg)	90	90	90	90	90	90
β (deg)	90	90	90	90	90	90
γ (deg)	90	90	90	90	90	90
<i>V</i> (Å ³)	708.0(4)	742.36(10)	731.62(12)	727.83(19)	713.90(17)	708.64(8)
<i>Z</i>	4	4	4	4	4	4
<i>T</i> (K)	100	100	100	100	100	100
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Maximum 2 θ (deg.)	27.510	27.550	27.550	27.630	27.570	27.560
ρ_{calcd} (g cm ⁻³)	5.224	4.589	4.664	4.718	4.867	4.919
μ (Mo K α) (cm ⁻¹)	28.702	12.674	13.298	13.807	15.029	15.705
R(F) for F _o ² > 2 σ (F _o ²) ^a	0.0239	0.0147	0.0147	0.0200	0.0207	0.0155
R _w (F _o ²) ^b	0.0530	0.0330	0.0327	0.0409	0.0574	0.0350

$${}^a R(F) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \cdot {}^b R_w(F_o^2) = \left[\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum wF_o^4} \right]^{1/2}$$

Table S2. Selected bond distances (Å) for Th(VO₃)₂(SeO₃), Ce(VO₃)₂(IO₃), Pr(VO₃)₂(IO₃), Nd(VO₃)₂(IO₃), Sm(VO₃)₂(IO₃) and Eu(VO₃)₂(IO₃).

	Th(VO ₃) ₂ (SeO ₃)		Ce(VO ₃) ₂ (IO ₃)	Pr(VO ₃) ₂ (IO ₃)	Nd(VO ₃) ₂ (IO ₃)	Sm(VO ₃) ₂ (IO ₃)	Eu(VO ₃) ₂ (IO ₃)
Th(1)-O(1)	2.553(4)	Ln(1)-O(1)	2.693(2)	2.669(2)	2.652(3)	2.634(3)	2.620(2)
Th(1)-O(1)#5	2.465(5)	Ln(1)-O(1)#5	2.482(2)	2.468(2)	2.467(3)	2.447(3)	2.441(2)
Th(1)-O(1)#6	2.465(5)	Ln(1)-O(1)#6	2.482(2)	2.468(2)	2.467(3)	2.447(3)	2.441(2)
Th(1)-O(1)#7	2.553(4)	Ln(1)-O(1)#7	2.693(2)	2.669(2)	2.652(3)	2.634(3)	2.620(2)
Th(1)-O(2)#1	2.328(6)	Ln(1)-O(2)#1	2.403(3)	2.384(3)	2.376(5)	2.340(5)	2.328(3)
Th(1)-O(3)#3	2.450(4)	Ln(1)-O(3)#3	2.546(2)	2.524(2)	2.508(3)	2.479(3)	2.467(2)
Th(1)-O(3)#4	2.450(4)	Ln(1)-O(3)#4	2.546(2)	2.524(2)	2.508(3)	2.479(3)	2.467(2)
Th(1)-O(6)#2	2.415(7)	Ln(1)-O(6)#2	2.420(3)	2.398(3)	2.398(4)	2.372(5)	2.361(3)
Th(1)-O(7)	2.483(7)	Ln(1)-O(7)	2.565(3)	2.526(3)	2.512(4)	2.478(5)	2.462(3)
Se(1)-O(1)	1.741(5)	I(1)-O(1)	1.825(2)	1.827(2)	1.829(3)	1.827(3)	1.829(2)
Se(1)-O(1)#7	1.741(5)	I(1)-O(1)#7	1.825(2)	1.827(2)	1.829(3)	1.827(3)	1.829(2)
Se(1)-O(2)	1.679(7)	I(1)-O(2)	1.773(3)	1.776(3)	1.776(5)	1.782(5)	1.782(3)
V(1)-O(3)	1.642(4)	V(1)-O(3)	1.655(2)	1.657(2)	1.662(3)	1.657(3)	1.658(2)
V(1)-O(3)#8	1.642(4)	V(1)-O(3)#8	1.655(2)	1.657(2)	1.662(3)	1.657(3)	1.658(2)
V(1)-O(4)	1.908(2)	V(1)-O(4)	1.9249(10)	1.9189(10)	1.9200(15)	1.9141(16)	1.9110(11)
V(1)-O(4)#9	1.908(2)	V(1)-O(4)#9	1.9249(10)	1.9189(10)	1.9200(15)	1.9141(16)	1.9110(11)
V(1)-O(5)	1.947(6)	V(1)-O(5)	1.924(3)	1.929(3)	1.931(4)	1.932(5)	1.933(3)
V(2)-O(4)#9	1.984(6)	V(2)-O(4)#9	2.014(3)	2.022(3)	2.021(4)	2.020(5)	2.030(3)
V(2)-O(5)	1.8913(19)	V(2)-O(5)	1.9228(8)	1.9161(8)	1.9148(12)	1.9068(14)	1.9044(9)
V(2)-O(5)#7	1.8913(19)	V(2)-O(5)#7	1.9228(8)	1.9161(8)	1.9148(12)	1.9068(14)	1.9044(9)
V(2)-O(6)	1.646(7)	V(2)-O(6)	1.635(3)	1.640(3)	1.638(5)	1.637(5)	1.638(3)
V(2)-O(7)	1.656(7)	V(2)-O(7)	1.644(3)	1.652(3)	1.655(4)	1.654(5)	1.653(3)

Table S3. Bond valence sums of Th, Ce, Pr, Nd, Sm, Eu, Se, I, and V ions.

	Th		Ce	Pr	Nd	Sm	Eu
Th(1)	4.114	Ln(1)	3.283	3.333	3.251	3.229	3.222
Se(1)	3.845	I(1)	5.056	5.024	5.007	4.995	4.978
V(1)	5.274	V(1)	5.135	5.141	5.093	5.154	5.157
V(2)	5.205	V(2)	5.124	5.084	5.087	5.129	5.125