Facile and Efficient Decontamination of Thorium from Rare Earths based on Selective Selenite Crystallization

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Ten SI pages containing 4 tables and 12 figures, as cross referenced through the main article:

1. Table S1. Crystallographic data for lanthanide selenite/selenate.
2. Figure S1 to S5. PXRD for unitary lanthanide elements reaction with SeO_2.
3. Figure S6. PXRD for binary lanthanide except for Ce elements reaction with SeO_2.
4. Figure S7. PXRD for binary lanthanide La/Ce reaction with SeO_2.
5. Figure S8 and S9 PXRD for binary lanthanide Ce/Pr reaction with SeO_2. PXRD for binary Th/La, Th/Eu Th/Yb reaction with SeO_2.
6. Figure S10. PXRD for $Th^{4+}Ce^{4+}$/simulated monazite solid products at different reaction conditions.
7. Table S2. Result summary of Ln_1/Ln_2 separation experiment.
8. Table S3. Result summary of simulated monazite separation experiment.
10. Figure S11. Separation factor for binary La/Ce and Ce/Pr under different amounts of SeO_2.
11. Table S4. The coordination bond populations in **LnSeO-2** and **ThSeO-2**.
12. Figure S12. The calculated incorporation energies of different center atoms in **LnSeO-2**.

Table S1. Crystallographic data for $La_2(SeO_3)_3$ (LnSeO-1), $Ce(SeO_3)_2$ (LnSeO-2), $Pr_2(SeO_3)_3$ (LnSeO-3), $Eu_3(SeO_3)_4(OH)$ (LnSeO-4), and $Nd_2(SeO_4)(SeO_3)_2(H_2O)_2$ (LnSeO-5)

Compound	$La_2(SeO_3)_3$ (LnSeO-1)	$Ce(SeO_3)_2$ (LnSeO-2)	$Pr_2(SeO_3)_3$ (LnSeO-3)*	$Eu_3(SeO_3)_4(OH)$ (LnSeO-4)	$Nd_2(SeO_4)(SeO_3)_2(H_2O)_2$ (LnSeO-5)
Mass	658.70	394.04	658.70	979.72	721.39
Color and habit	Colorless, Sheet	Orange, Rod	Colorless, Sheet	Colorless, Pole	Purple, Rod
Space group	*Pnma*	$P2_1/n$	*I*4/*mcm*	$P6_3mc$	*C*2/*c*
a (Å)	8.4508(5)	7.0232(7)	15.956(4)	10.4435(9)	12.276(1)
b (Å)	14.2493(8)	10.5912(10)	15.956(4)	10.4435(9)	7.0783(5)
c (Å)	7.1024(5)	7.3081(7)	21.395(5)	6.9878(6)	13.329(1)
α(deg)	90	90	90	90	90
β(deg)	90	107.077(3)	90	90	104.276(7)
γ(deg)	90	90	90	120	30
V (Å^3)	855.26(9)	519.64(9)	5447(3)	660.03(13)	1122.4(2)
Z	4	4	4	2	4
T(K)	296(2)	296(2)	153(2)	296(2)	293
λ (Å)	0.71073	0.71073	/	0.71073	0.71073
Maximum 2θ(deg)	27.417	27.465	/	27.467	58.7
ρ calcd (g cm^{-3})	5.116	5.037	/	4.930	4.27
μ(Mo Ka)	22.647	22.720	/	25.169	189
R_1	0.0290	0.0194	/	0.0170	0.022
wR_2	0.0993	0.0460	/	0.0431	0.029

* The crystals of $Ln_2(SeO_3)_3$ (**LnSeO-3**) are seriously twinning, even after we tried many synthetic modifications. The unit cell data is available at the present work, and a rough structure model can be resolved and provided in the main text.

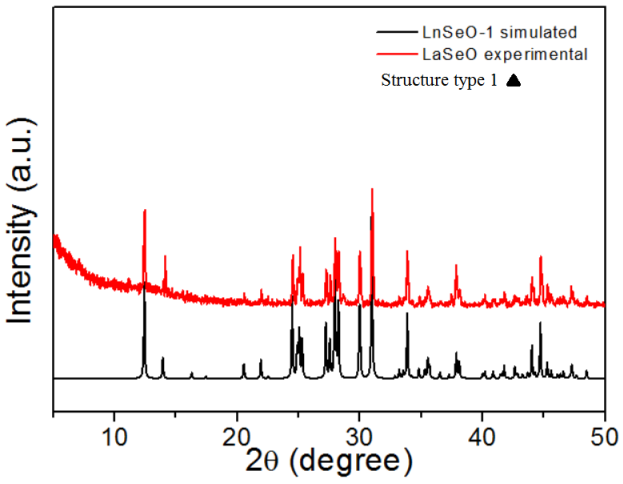

Figure S1. Simulated PXRD pattern for **LnSeO-1** and experimental PXRD pattern for LaSeO solid product.

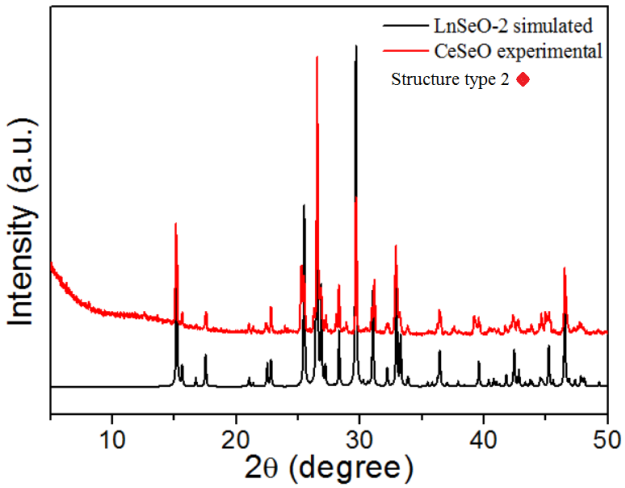

Figure S2. Simulated PXRD pattern for **LnSeO-2** and experimental PXRD pattern for CeSeO solid product.

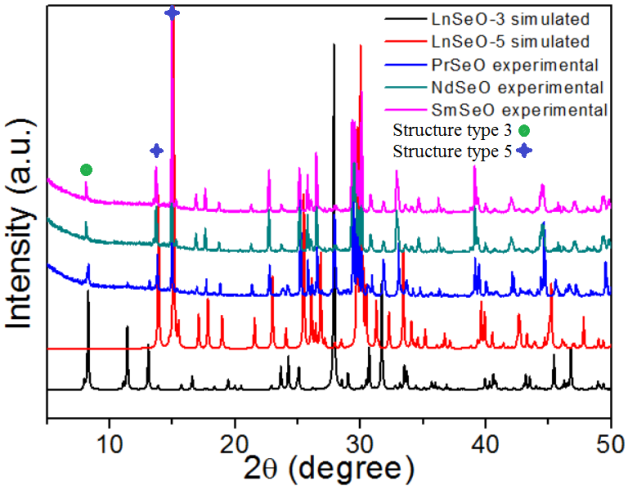

Figure S3. Simulated PXRD patterns for **LnSeO-3, LnSeO-5** and experimental PXRD patterns for LnSeO (Ln = Pr, Nd, and Sm) solid products.

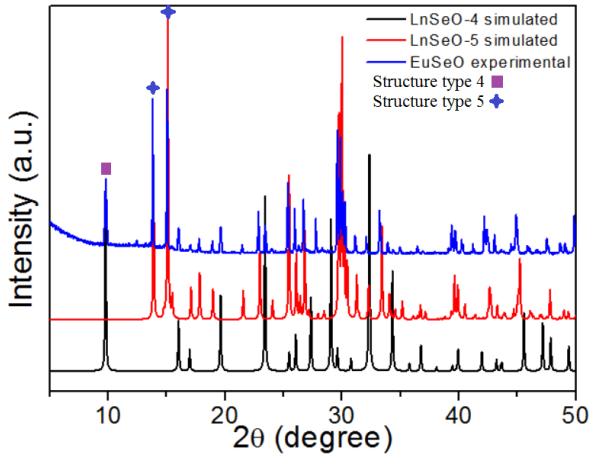

Figure S4. Simulated PXRD patterns for **LnSeO-4, LnSeO-5** and experimental PXRD pattern for EuSeO solid product.

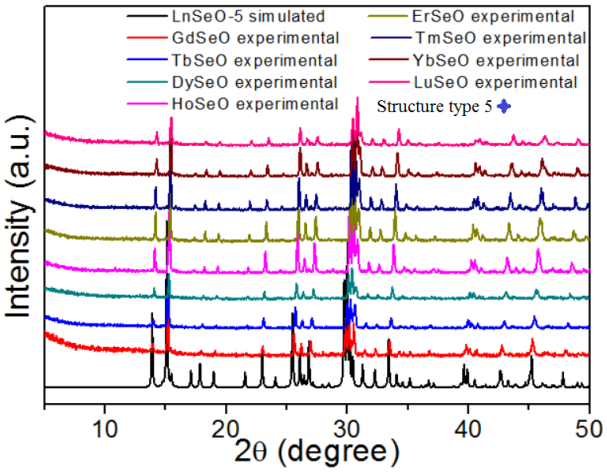

Figure S5. Simulated PXRD pattern for **LnSeO-5** and experimental PXRD patterns for LnSeO (Ln = Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) solid products.

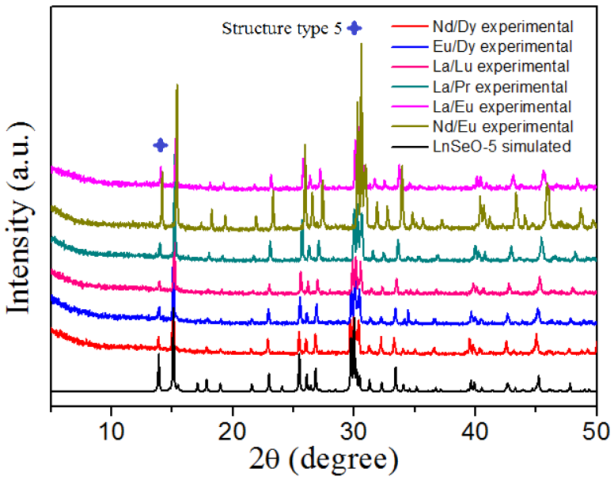

Figure S6. Simulated PXRD pattern for **LnSeO-5** and binary Nd/Dy, Eu/Dy, La/Lu, La/Pr, La/Eu, Nd/Eu experimental PXRD patterns.

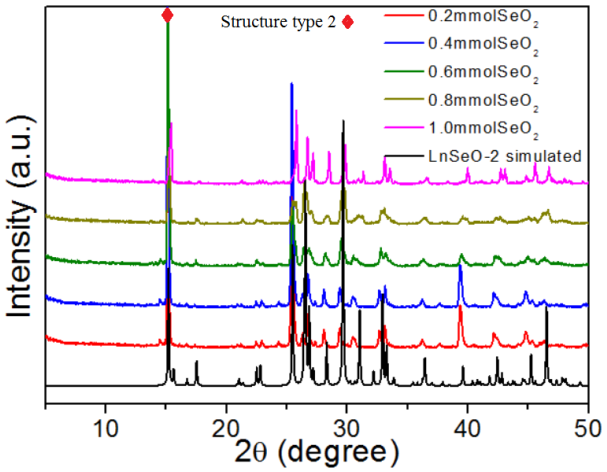

Figure S7. Simulated PXRD pattern for **LnSeO-2** and experimental PXRD patterns for La/Ce solid products at different reaction conditions (the reactant of SeO_2: 0.2 mmol, 0.4 mmol, 0.6 mmol, 0.8 mmol, or 1.0 mmol).

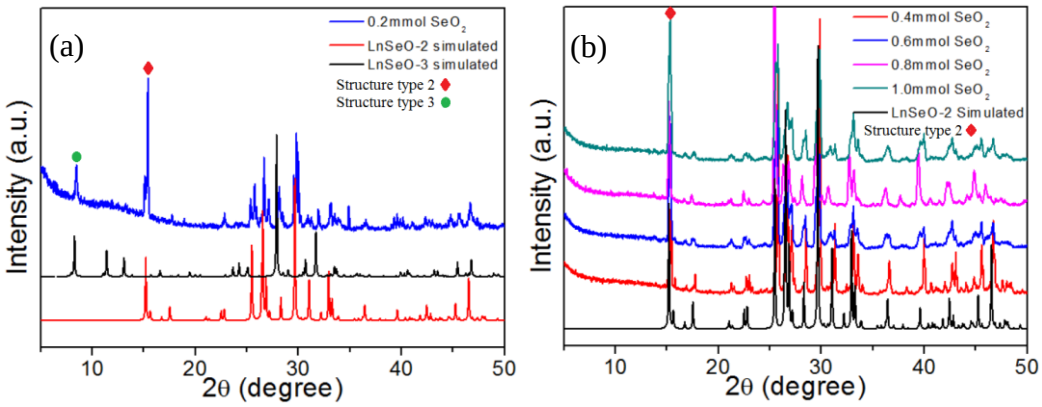

Figure S8. Simulated PXRD pattern for **LnSeO-2** and experimental PXRD patterns for Ce/Pr solid products at different reaction conditions (the reactant of SeO_2: 0.2 mmol, 0.4 mmol, 0.6 mmol, 0.8 mmol, or 1.0 mmol).

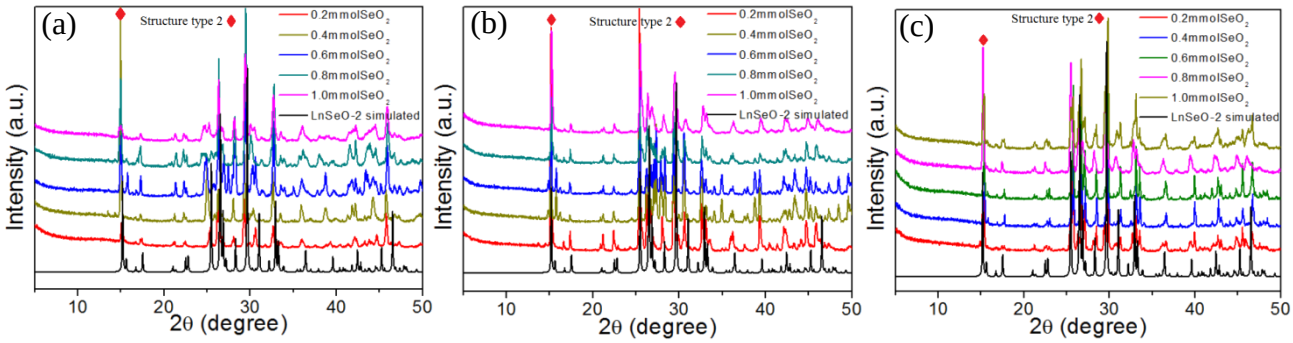

Figure S9. Simulated PXRD pattern for LnSeO-2 and experimental PXRD patterns for (a) Th/La (b) Th/Eu (c) Th/Yb solid products at different reaction conditions (the reactant of SeO_2: 0.2 mmol, 0.4 mmol, 0.6 mmol, 0.8 mmol, 1.0 mmol).

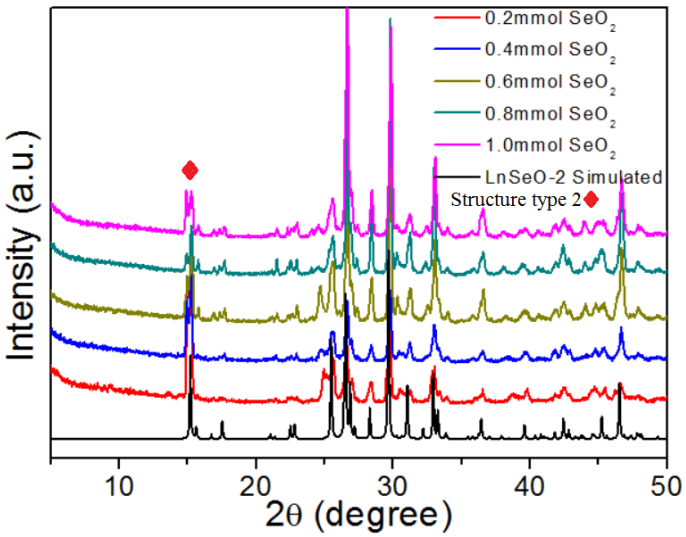

Figure S10. Simulated PXRD pattern for LnSeO-2 and experimental PXRD patterns for $Th^{4+}Ce^{4+}$/simulated monazite solid products at different reaction conditions (the reactant of SeO_2: 0.2 mmol, 0.4 mmol, 0.6 mmol, 0.8 mmol, or 1.0 mmol).

Table S2. Result summary of Ln_1/Ln_2 separation experiment (the separation factors were calculated using the solid/aqueous model and the molar ratio of Ln_1: Ln_2: Se in original reactions is 1:1:n, n = 2, 4, 6, 8, 10).

SeO_2	Element	The molar mass in reactants / mmol	The molar mass in products / mmol	The molar mass in wash solutions / mmol	Crystallization purity	Crystallization yield	Separation factor
0.2mmol	La	0.1±0.01	0.0007±2.9E-5	0.0951±0.0013	0.9915±0.0002	0.7867±0.0073	515.65±28.67
	Ce	0.1±0.01	0.0750±0.0015	0.0213±0.0007			
	Ce	0.1±0.01	0.0367±0.0010	0.0627±0.0019	0.9886±0.0015	0.3730±0.0196	128.47±13.26
	Pr	0.1±0.01	0.0004±6.1E-5	0.0924±0.0011			
0.4mmol	La	0.1±0.01	0.0007±4.2E-5	0.0926±0.0011	0.9921±0.0003	0.9341±0.0034	1746.05±38.30
	Ce	0.1±0.01	0.0912±0.0015	0.0066±0.0003			
	Ce	0.1±0.01	0.0632±0.0008	0.0346±0.0008	0.9794±0.0011	0.6538±0.0075	125.75±3.24
	Pr	0.1±0.01	0.0013±7.8E-5	0.0906±0.0018			
0.6mmol	La	0.1±0.01	0.0010±6.2E-5	0.0915±0.0020	0.9884±0.0027	0.9760±0.0012	3677.22±306.36
	Ce	0.1±0.01	0.0942±0.0004	0.0024±0.0001			
	Ce	0.1±0.01	0.0828±0.0026	0.0159±0.0007	0.9831±0.0010	0.8410±0.0066	339.12±11.34
	Pr	0.1±0.01	0.0014±7.8E-5	0.0918±0.0011			
0.8mmol	La	0.1±0.01	0.0010±0.0002	0.0904±0.0002	0.9896±0.0011	0.9837±0.0005	5078.55±221.65
	Ce	0.1±0.01	0.0941±0.0042	0.0017±0.0002			
	Ce	0.1±0.01	0.0817±0.0020	0.0119±0.0002	0.9826±0.0008	0.8805±0.0018	433.46±25.22
	Pr	0.1±0.01	0.0014±5.2E-5	0.0907±0.0021			
1.0mmol	La	0.1±0.01	0.0012±0.0001	0.0906±0.0020	0.9878±0.0010	0.9855±0.0010	5038.02±329.95
	Ce	0.1±0.01	0.0965±0.0011	0.0015±0.0001			
	Ce	0.1±0.01	0.0843±0.0024	0.0066±4.5E-5	0.9817±0.0008	0.9336±0.0004	740.92±39.91
	Pr	0.1±0.01	0.0016±5.9E-5	0.0894±0.0007			

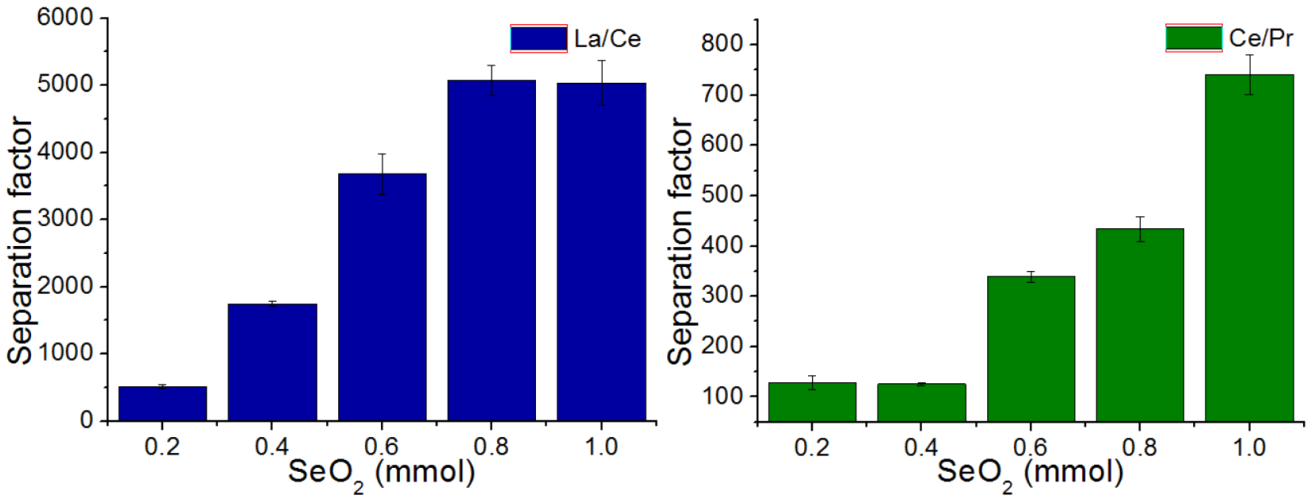

Figure S11. Separation factors for binary La/Ce and Ce/Pr under different amounts of SeO_2.

Table S3. Result summary of simulated monazite separation experiment (the separation factors were calculated using the solid/aqueous model and the molar ratio of (Ln+An) : Se in original reactions is 1: n, n = 1, 2, 3, 4, 5). (Solid samples treatment with dilute nitric acid)

SeO_2	Element	The molar mass in reactants / mmol	The molar mass in products / mmol	The molar mass in wash solutions / mmol	Crystallization purity	Crystallization yield	Separation factor
0.2mmol	La	0.04±0.004	0.0013	0.0393±0.0008	0.9434±0.0011	0.6100±0.0211	31.96±1.52
	Ce	0.086±0.0086	0.0485	0.0413±0.0022			
	Pr	0.009±0.0009	0.0005	0.0085±0.0006			
	Nd	0.032±0.0032	0.0010	0.0326±0.0020			
	Sm	0.006±0.0006	0.0007	0.0059±0.0001			
	Eu	0.0002±0.0001	1.8E-5	0.0002±1.6E-5			
	Gd	0.003±0.0003	0.0005	0.0023±0.0001			
	Dy	0.0012±0.0006	0.0002	0.0013±0.0002			
	Er	0.0004±0.0002	3.8E-6	0.0004±6.2E-5			
	Yb	0.0002±0.0001	7.4E-5	0.0001±7.6E-6			
	Y	0.005±0.0005	0.0006	0.0041±9.3E-5			
	Th	0.02±0.002	0.0195	1.3E-5±9.0E-7			

SeO_2	Element	The molar mass in reactants / mmol	The molar mass in products / mmol	The molar mass in wash solutions / mmol	Crystallization purity	Crystallization yield	Separation factor
0.4mmol	La	0.04±0.004	0.0019±0.0001	0.0369±0.0003	0.9217±0.0041	0.8892±0.0041	78.26±6.12
	Ce	0.086±0.0086	0.0789±0.0036	0.0117±0.0004			
	Pr	0.009±0.0009	0.0009±0.0002	0.0084±0.0001			
	Nd	0.032±0.0032	0.0034±0.0007	0.0289±0.0003			
	Sm	0.006±0.0006	0.0010±0.0001	0.0055±6.6E-5			
	Eu	0.0002±0.0001	1.9E-5±6.3E-6	0.0002±3.1E-5			
	Gd	0.003±0.0003	0.0007±6.6E-5	0.0021±6.6E-5			
	Dy	0.0012±0.0006	0.0005±9.8E-5	0.0011±0.0002			
	Er	0.0004±0.0002	2.0E-5±2.4E-6	0.0004±8.8E-5			
	Yb	0.0002±0.0001	7.5E-5±2.5E-5	0.0001±1.1E-5			
	Y	0.005±0.0005	0.0008±0.0001	0.0040±0.0002			
	Th	0.02±0.002	0.0195±0.0002	4.8E-6±2.7E-7			
SeO_2	Element	The molar mass in reactants / mmol	The molar mass in products / mmol	The molar mass in wash solutions / mmol	Crystallization purity	Crystallization yield	Separation factor
0.6mmol	La	0.04±0.004	0.0028±0.0001	0.0360±0.0008	0.8918±0.0028	0.9869±0.0012	435.62±26.86
	Ce	0.086±0.0086	0.0867±0.0013	0.0014±0.0001			
	Pr	0.009±0.0009	0.0012±0.0002	0.0080±7.2E-5			
	Nd	0.032±0.0032	0.0057±0.0007	0.0258±0.0034			
	Sm	0.006±0.0006	0.0019±8.5E-6	0.0045±2.0E-5			
	Eu	0.0002±0.0001	1.9E-5±8.7E-6	0.0002±4.6E-5			
	Gd	0.003±0.0003	0.0009±5.2E-6	0.0019±4.7E-5			
	Dy	0.0012±0.0006	0.0005±5.8E-6	0.0011±0.0001			
	Er	0.0004±0.0002	5.7E-5±9.3E-6	0.0004±4.7E-5			
	Yb	0.0002±0.0001	8.5E-5±4.1E-5	0.0001±1.1E-5			
	Y	0.005±0.0005	0.0012±0.0001	0.0035±9.7E-5			
	Th	0.02±0.002	0.0193±0.0003	2.5E-6±1.5E-7			
SeO_2	Element	The molar mass in reactants /	The molar mass in products /	The molar mass in wash solutions /	Crystallization purity	Crystallization yield	Separation factor

		mmol	mmol	mmol			
0.8mmol	La	0.04±0.004	0.0031±0.0002	0.0351±0.0007	0.8859±0.0059	0.9964±0.0002	1466.78±65.07
	Ce	0.086±0.0086	0.0899±0.0012	0.0004±2.0E-5			
	Pr	0.009±0.0009	0.0011±0.0002	0.0083±0.0002			
	Nd	0.032±0.0032	0.0064±0.0003	0.0240±0.0010			
	Sm	0.006±0.0006	0.0021±3.0E-5	0.0043±9.2E-5			
	Eu	0.0002±0.0001	2.2E-5±4.1E-6	0.0002±4.5E-5			
	Gd	0.003±0.0003	0.0011±4.3E-5	0.0018±5.6E-5			
	Dy	0.0012±0.0006	0.0005±8.2E-5	0.0011±0.0002			
	Er	0.0004±0.0002	5.7E-5±8.5E-6	0.0004±9.7E-7			
	Yb	0.0002±0.0001	7.0E-5±5.0E-5	0.0001±1.6E-5			
	Y	0.005±0.0005	0.0012±0.0003	0.0037±0.0005			
	Th	0.02±0.002	0.0197±0.0005	4.2E-6±2.1E-6			
SeO_2	Element	The molar mass in reactants / mmol	The molar mass in products / mmol	The molar mass in wash solutions / mmol	Crystallization purity	Crystallization yield	Separation factor
1.0mmol	La	0.04±0.004	0.0037±0.0003	0.0349±0.0002	0.8732±0.0024	0.9976±9.1E-5	1886.73±99.09
	Ce	0.086±0.0086	0.0894±0.0036	0.0003±9.3E-6			
	Pr	0.009±0.0009	0.0016±0.0003	0.0077±0.0002			
	Nd	0.032±0.0032	0.0071±0.0002	0.0235±0.0016			
	Sm	0.006±0.0006	0.0021±6.0E-5	0.0043±0.0001			
	Eu	0.0002±0.0001	4.9E-5±6.1E-5	0.0002±6.5E-5			
	Gd	0.003±0.0003	0.0011±4.8E-5	0.0017±3.4E-5			
	Dy	0.0012±0.0006	0.0004±0.0002	0.0010±5.1E-5			
	Er	0.0004±0.0002	5.5E-5±1.8E-5	0.0004±8.3E-5			
	Yb	0.0002±0.0001	9.0E-5±3.5E-5	0.0001±5.1E-6			
	Y	0.005±0.0005	0.0015±0.0002	0.0034±0.0002			
	Th	0.02±0.002	0.0197±0.0005	1.8E-6±8.5E-7			

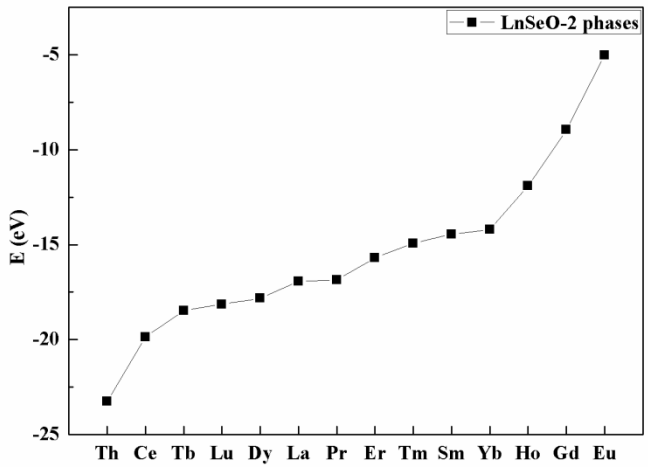

Figure S12. The calculated incorporation energies of different metal centers in **LnSeO-2**.

Table S4. The coordination bond populations in **LnSeO-2** and **ThSeO-2**.

Bond	Population	Bond	Population
O1—La	0.22	**O1-Ce**	0.36
O2—La	0.27	**O2-Ce**	0.35
O3—La	0.26	**O3-Ce**	0.29
O4—La	0.23	**O4-Ce**	0.17
O5—La	0.33	**O5-Ce**	0.36
O6—La	0.18	**O6-Ce**	0.31
O7—La	0.24	**O7-Ce**	0.35
O8—La	0.16	**O8-Ce**	0.16
O1—Eu	0.35	**O1—Yb**	0.30
O2—Eu	0.34	**O2—Yb**	0.33
O3—Eu	0.28	**O3—Yb**	0.32
O4—Eu	0.31	**O4—Yb**	0.29
O5—Eu	0.31	**O5—Yb**	0.30
O6—Eu	0.20	**O6—Yb**	0.23
O7—Eu	0.32	**O7—Yb**	0.30
O8—Eu	0.19	**O8—Yb**	0.16
O1—Th	0.40	**O5—Th**	0.38
O2—Th	0.39	**O6—Th**	0.18
O3—Th	0.31	**O7—Th**	0.35
O4—Th	0.30	**O8—Th**	0.19