Supplementary materials

Table S1 Solubility data and calculations for dissolution experiments of $NaEu(CO_3)_2{\cdot}xH_2O$(s) in Na_2CO_3-$NaClO_4$ solutions.

t /weeks	$[Na_2CO_3]$[a] /mol l^{-1}	$[NaClO_4]$[a] /mol l^{-1}	p /l kg^{-1}	I_m /mol kg^{-1}	pH[b]	-log$[H^+]$[c]	log$[CO_3^{2-}]$[d]	log[Eu]
10	2.00	0.00	1.2039	7.22	12.23	11.50	0.30	-4.18[e]
14[f]	1.00	0.00	1.0554	3.17	11.73	11.51	0.00	-4.50[e]
10	1.00	1.00	1.1670	4.67	11.88	11.34	0.00	-4.71
10	0.30	2.40	1.1752	3.88	11.58	11.03	–0.53	–5.45
10	0.10	2.80[g]	1.0687	3.31	11.24	10.37	–1.03	–5.84
10	0.03	2.94	1.1692	3.54	11.05	10.50	–1.55	–6.05
10	0.01	2.98	1.1686	3.52	10.81	10.27	–2.05	–6.75[e]
10	0.30	0.40	1.0437	1.36	11.40	11.12	–0.53	–4.96
10	0.10	0.80	1.0508	1.16	11.17	10.81	–1.02	–5.28
10	0.01	0.98	1.0508	1.06	10.67	10.35	–2.04	–6.94
10	0.30	0.00	1.0082	0.91	11.39	11.25	–0.53	–4.51
10	0.03	0.00	1.0025	0.09	11.10	10.62	–1.57	–5.91
16	2.00	0.00	1.2039	7.22	12.23	11.44	0.30	–4.19
20[f]	1.00	0.00	1.0554	3.17	11.73	11.46	0.00	–4.55[e]
16	1.00	1.00	1.1670	4.67	11.88	11.27	–0.01	–4.74
16	0.30	2.40	1.1752	3.88	11.58	10.95	–0.53	–5.49
16	0.10	2.80[g]	1.0687	3.31	11.24	10.33	–1.04	–5.89
16	0.03	2.94	1.1692	3.54	11.05	10.28	–1.57	–6.10
16	0.01	2.98	1.1686	3.52	10.81	10.08	–2.07	–6.63
16	0.30	0.40	1.0437	1.36	11.40	11.06	–0.53	–5.10
16	0.10	0.80	1.0508	1.16	11.17	10.75	–1.02	–5.35
16	0.01	0.98	1.0508	1.06	10.67	10.29	–2.05	–6.67
16	0.30	0.00	1.0082	0.91	11.39	11.20	–0.53	–4.60
16	0.03	0.00	1.0025	0.09	11.10	10.70	–1.56	–5.92[e]

[a] Initial concentration.
[b] Calculated pH : pH = 0.5 (pK_w + log K_1 + log$[CO_3^{2-}]$), where K_w is the ionic product of water ($pK_w° = 14.00$, $\Delta z^2 = 2$, $\varepsilon_{H^+ClO_4^-} = 0.14$ kg mol^{-1}; $\varepsilon_{Na^+OH^-} = 0.04$ kg mol^{-1}, $\phi_{NaClO_4} = -0.015_3$) and K_1 the equilibrium constant for $CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$ ($pK_w° = -10.329$, $\Delta z^2 = -4$, $\varepsilon_{Na^+HCO_3^-} = -0.03$ kg mol^{-1}, $\varepsilon_{H^+ClO_4^-} = 0.14$ kg mol^{-1}, $\varepsilon_{Na^+CO_3^{2-}} = -0.08$ kg mol^{-1}).[4]
[c] Errors in the response of the electrodes may occur for values higher than about 11 due to alkaline effect.
[d] $[CO_3^{2-}] = ([Na^+] + [H^+] - K_w / [H^+]) / (2 + K_1 [H^+])$ (K_w and K_1 are defined in footnote [b]).
[e] The nature of the solid, $NaEu(CO_3)_2{\cdot}xH_2O$(s), was confirmed by XRD analysis.
[f] Initial solution in which $NaEu(CO_3)_2{\cdot}xH_2O$(s) precipitated.
[g] ClO_4^- was replaced by Cl^-.

Table S2 Bragg reflections of non-altered and altered $NaEu(CO_3)_2 \cdot xH_2O$(s), in comparison with literature data.

$NaEu(CO_3)_2 \cdot xH_2O$		Altered $NaEu(CO_3)_2 \cdot xH_2O$		$NaEu(CO_3)_2 \cdot 5H_2O$ [21]		$NaEu(CO_3)_2 \cdot 6H_2O$ [22]
d /Å	Rel. int. (%)	d /Å	Rel. int. (%)	d /Å	Rel. int. (%)	d /Å
12.72	100	12.89	100	13.01	60	12.0752
		9.82	80			
6.43	30	6.48	30	6.49	30	6.265
		5.68	30			
		5.11	60			
		4.92	10			
4.55	20	4.57	10	4.57	100	
		4.49	<10			
4.31	40	4.32	20	4.31	70	4.221
		3.80	40			
		3.72	10			
3.29	<10	3.28	50	3.3	60	3.2466
				3.21	60	
3.20	<10			3.19	50	
3.16	<10	3.16	40	3.16	40	
3.07	10	3.07	<10	3.07	80	
		2.99	<10	3.01	10	
				2.95	20	
2.91	<10	2.92	<10	2.92	20	
2.84	<10	2.86	<10	2.86	30	
		2.73	40			
2.63	<10	2.65	30			
2.59	10	2.60	<10			
2.55	<10	2.57	10	2.57	<10	2.5631
		2.48	60			
		2.33	20			
		2.28	10	2.28	<10	
2.26	<10	2.26	10	2.25	10	
2.16	<10	2.15	10	2.16	20	2.1371
2.08	<10	2.11	30	2.08	30	
		2.08	<10	2.05	30	
		2.06	30			
2.02	<10	2.03	<10	2.02	<10	
2.00	<10			2.01	10	

Fig. S1 XRD powder patterns for the solubility-controlling phase, $NaEu(CO_3)_2{\cdot}xH_2O(s)$, analysed (a) immediately after filtration and (b) few days after, resulting in alteration of $NaEu(CO_3)_2{\cdot}xH_2O(s)$ to $Eu_2(CO_3)_2{\cdot}yH_2O(s)$ and $Na_2CO_3(s)$. Only a few peaks (noted with *) could be assigned to $Eu_2(CO_3)_2(s)$ from the comparison with oven dried $Eu_2(CO_3)_3(s)$ as reported in Appendix 5.3 of Ref. 37 (p.376). The others were consistent with the previous measurements although, as in Ref. 37, they could not be easily assigned.

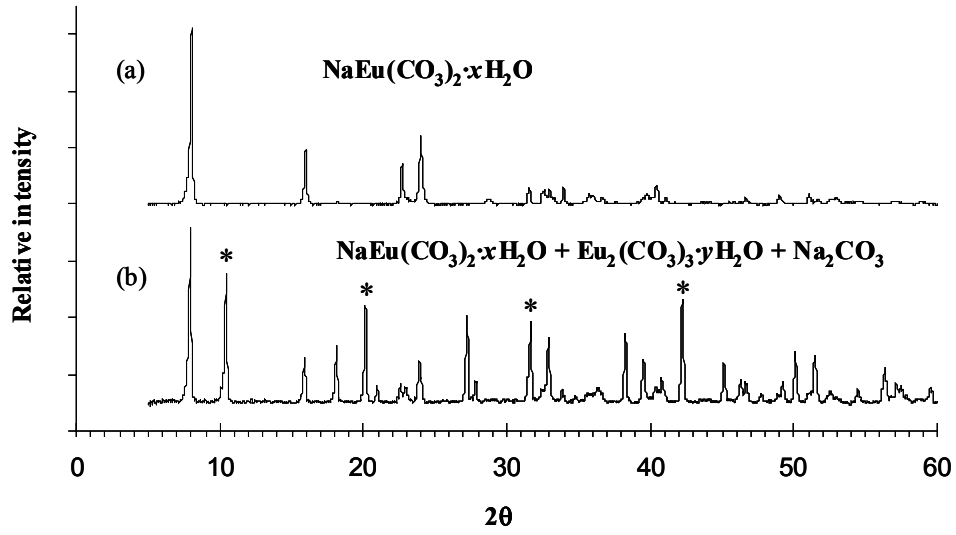

Fig. S2 Infra-red spectrum of precipitated $NaEu(CO_3)_2{\cdot}xH_2O(s)$.