Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

One-step freezing temperature crystallization of layered rare-earth hydroxide ($Ln_2(OH)_5NO_3\cdot nH_2O$) nanosheets for a wide spectrum of Ln (Ln=Pr-Er, and Y), anion exchange with fluorine and sulfate, and microscopic coordination probed via photoluminescence

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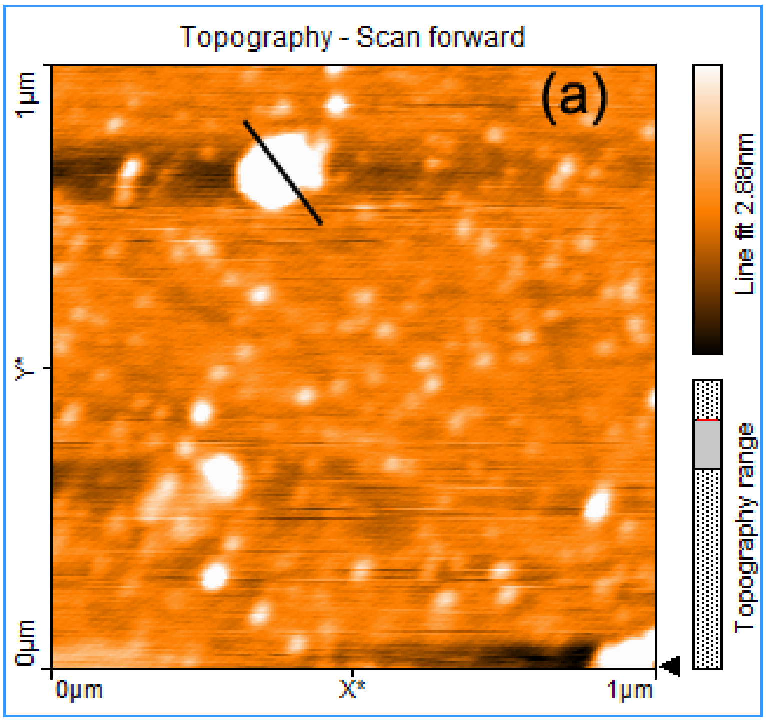

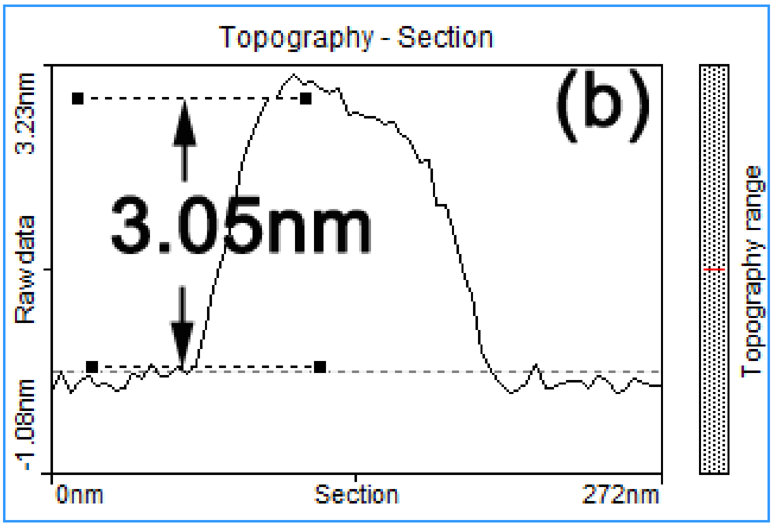

Figure S1. AFM observation of the $Y_2(OH)_5NO_3 \cdot nH_2O$ LRH nanosheets, with (a) the scan mode and (b) height profile analysis of the marked object. The very thin nature and limited lateral size of the nanosheets make clearer imaging rather challenging.

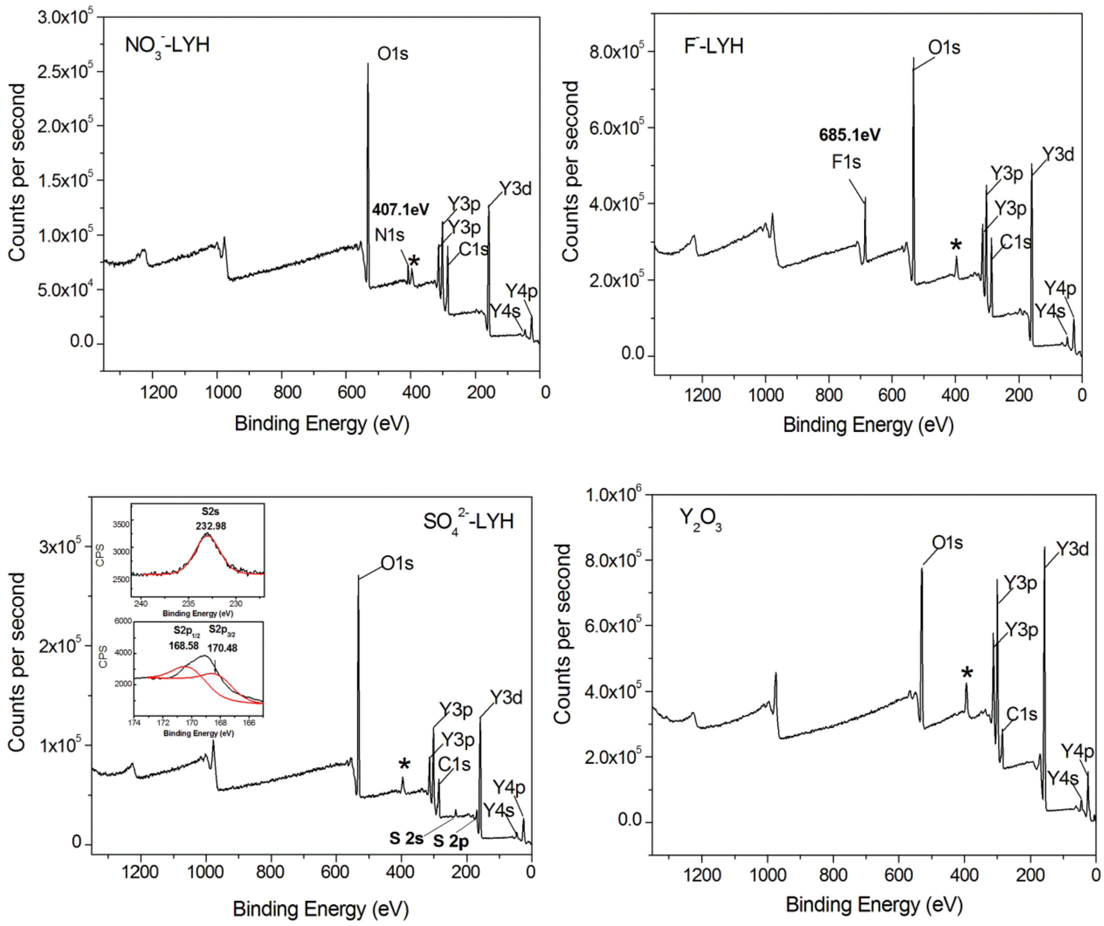

Figure S2. XPS survey spectra for the pristine LYH (NO_3^--LYH) and the products anion exchanged with F^- (F^--LYH) and SO_4^{2-} (SO_4^{2-}-LYH). The peak (~396 eV) indicated with an asterisk is also for N-1s, but possibly comes from nitride contamination of the equipment or protective N_2 gas since it is similarly found for an high purity Y_2O_3 powder (99.99%, Kanto Pure Chemicals, Tokyo, Japan). The XPS results indicate that anion exchange of the interlayer NO_3^- is essentially complete, as evidenced by the disappearance of the N-1s signal as in nitrate at 407.1 eV and the emergence of the F-1s signal at 685.1 eV and the S-2s (~233 eV) and S-2p (~165-173 eV) signals.

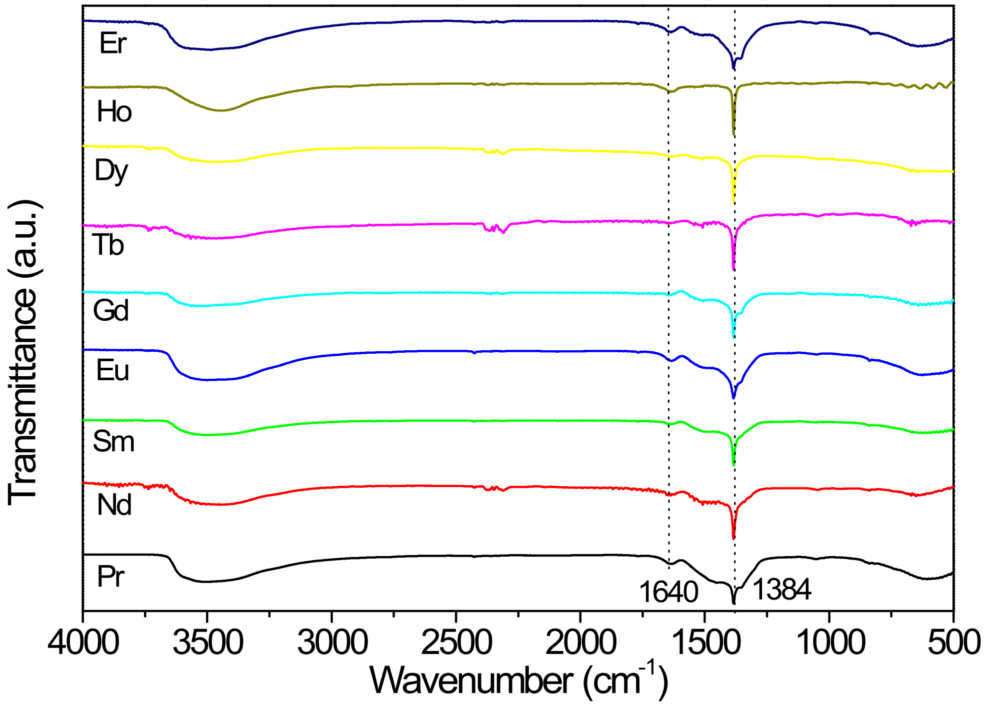

Figure S3. FT-IR spectra of the $Ln_2(OH)_5NO_3 \cdot nH_2O$ nanosheets crystallized at ~4 °C, with the type of Ln indicated.

Table S1. Results of chemical analysis for $Ln_2(OH)_5NO_3 \cdot nH_2O$ and the derived chemical formula. Carbon was assumed to solely come from CO_3^{2-} and CO_3^{2-} was assumed to replace OH^-. The amount of OH^- was derived from molecular neutrality.

	Chemical analysis (wt%)			Chemical formula
	Ln	NO_3^-	C	
Pr	62	13.7	0.37	$Pr_2(OH)_{4.72}(NO_3)_{1.0}(CO_3)_{0.14} \cdot 1.23H_2O$
Nd	62.8	13.5	0.37	$Nd_2(OH)_{4.74}(NO_3)_{0.98}(CO_3)_{0.14} \cdot 1.17H_2O$
Sm	63.7	13.1	0.35	$Sm_2(OH)_{4.74}(NO_3)_{0.98}(CO_3)_{0.14} \cdot 1.20H_2O$
Eu	64	13.1	0.35	$Eu_2(OH)_{4.74}(NO_3)_{0.98}(CO_3)_{0.14} \cdot 1.18H_2O$
Gd	64.8	12.8	0.35	$Gd_2(OH)_{4.72}(NO_3)_{1.0}(CO_3)_{0.14} \cdot 1.12H_2O$
Tb	65	12.7	0.34	$Tb_2(OH)_{4.72}(NO_3)_{1.0}(CO_3)_{0.14} \cdot 1.14H_2O$
Dy	65.5	12.5	0.34	$Dy_2(OH)_{4.54}(NO_3)_{1.0}(CO_3)_{0.14} \cdot 1.31H_2O$
Ho	66	12.4	0.28	$Ho_2(OH)_{4.76}(NO_3)_{1.0}(CO_3)_{0.12} \cdot 1.10H_2O$
Er	66	12.3	0.28	$Er_2(OH)_{4.74}(NO_3)_{1.02}(CO_3)_{0.12} \cdot 1.18H_2O$
Y	51	17.8	0.48	$Y_2(OH)_{4.72}(NO_3)_{1.0}(CO_3)_{0.14} \cdot 1.12H_2O$

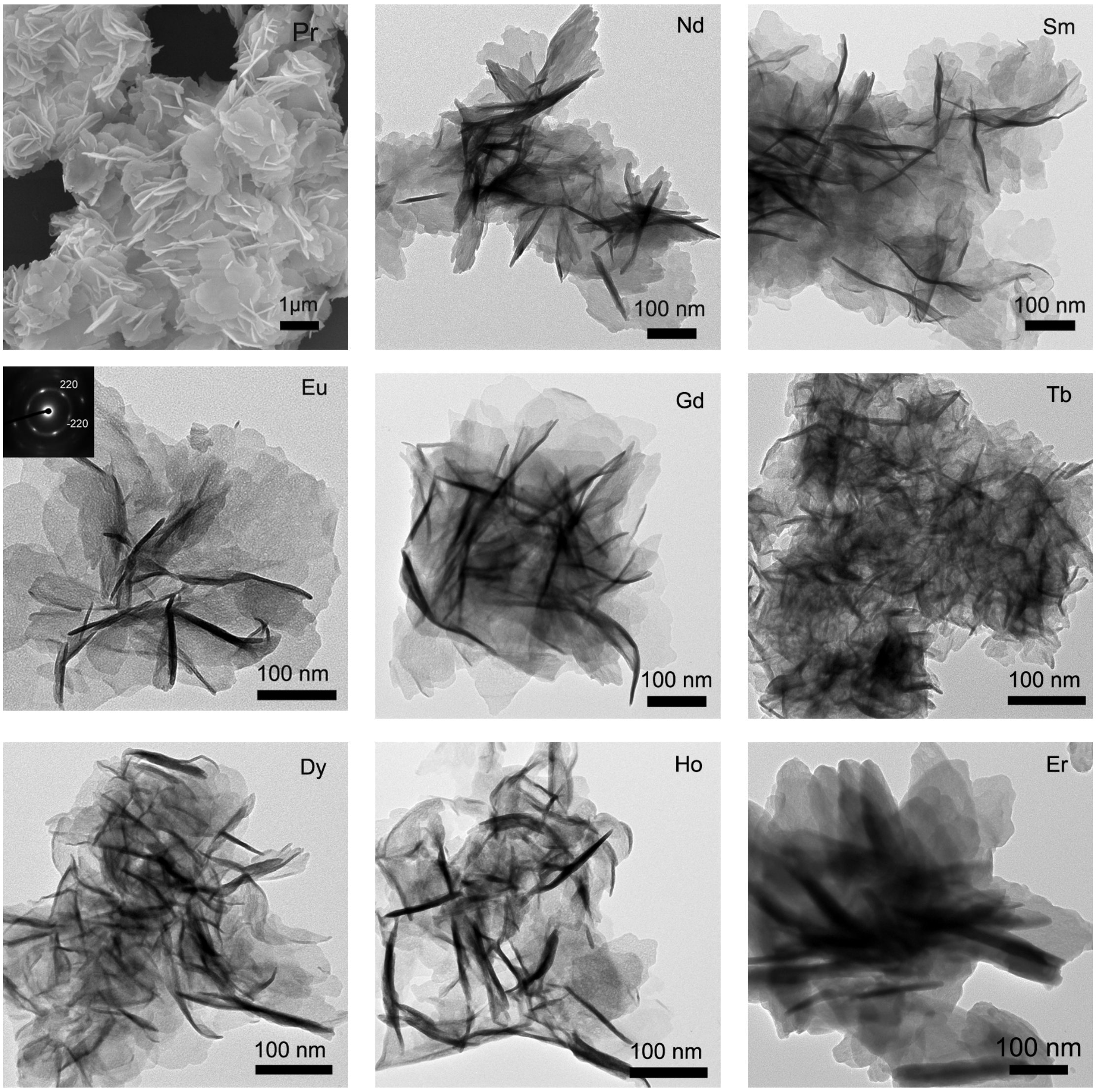

Figure S4. FE-SEM (for Pr) and TEM (for the rest) morphologies of the $Ln_2(OH)_5NO_3 \cdot nH_2O$ nanosheets.

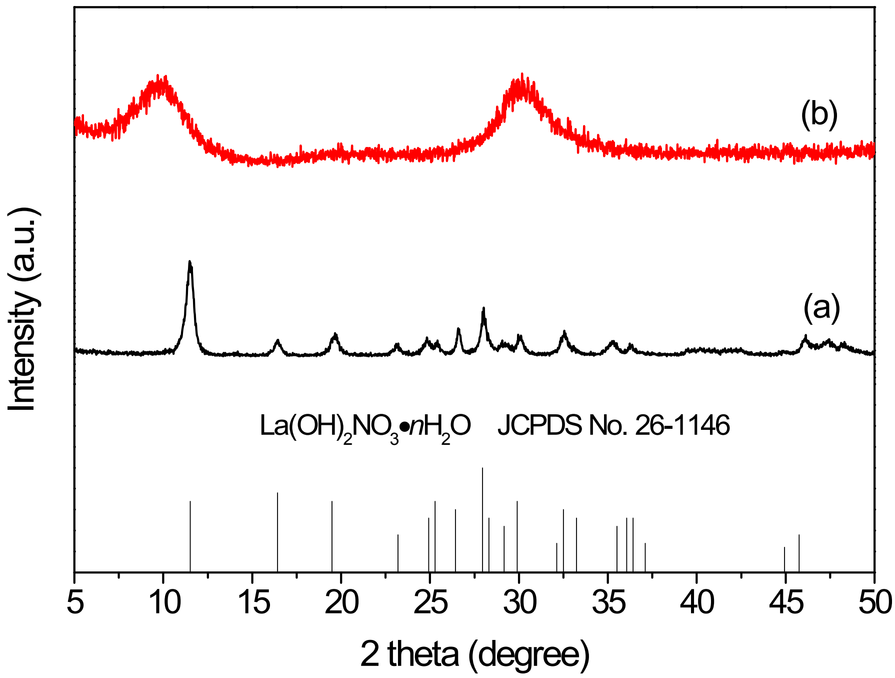

Figure S5. XRD patterns of the products precipitated at 4 °C for La (a) and Tm (b).

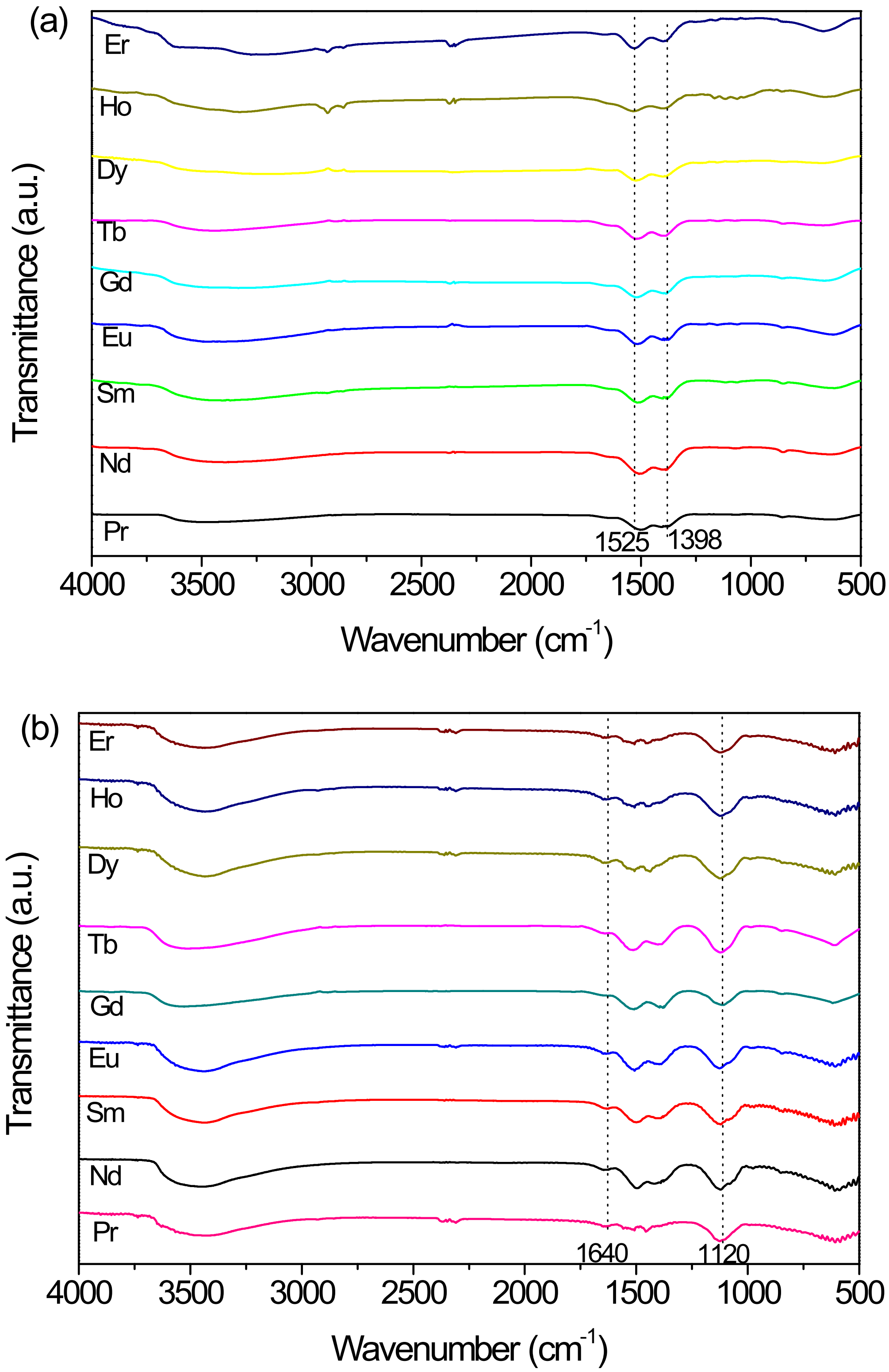

Figure S6. FT-IR spectra of the products obtained via anion exchange of $Ln_2(OH)_5NO_3 \cdot nH_2O$ with F^- (a) and SO_4^{2-} (b).

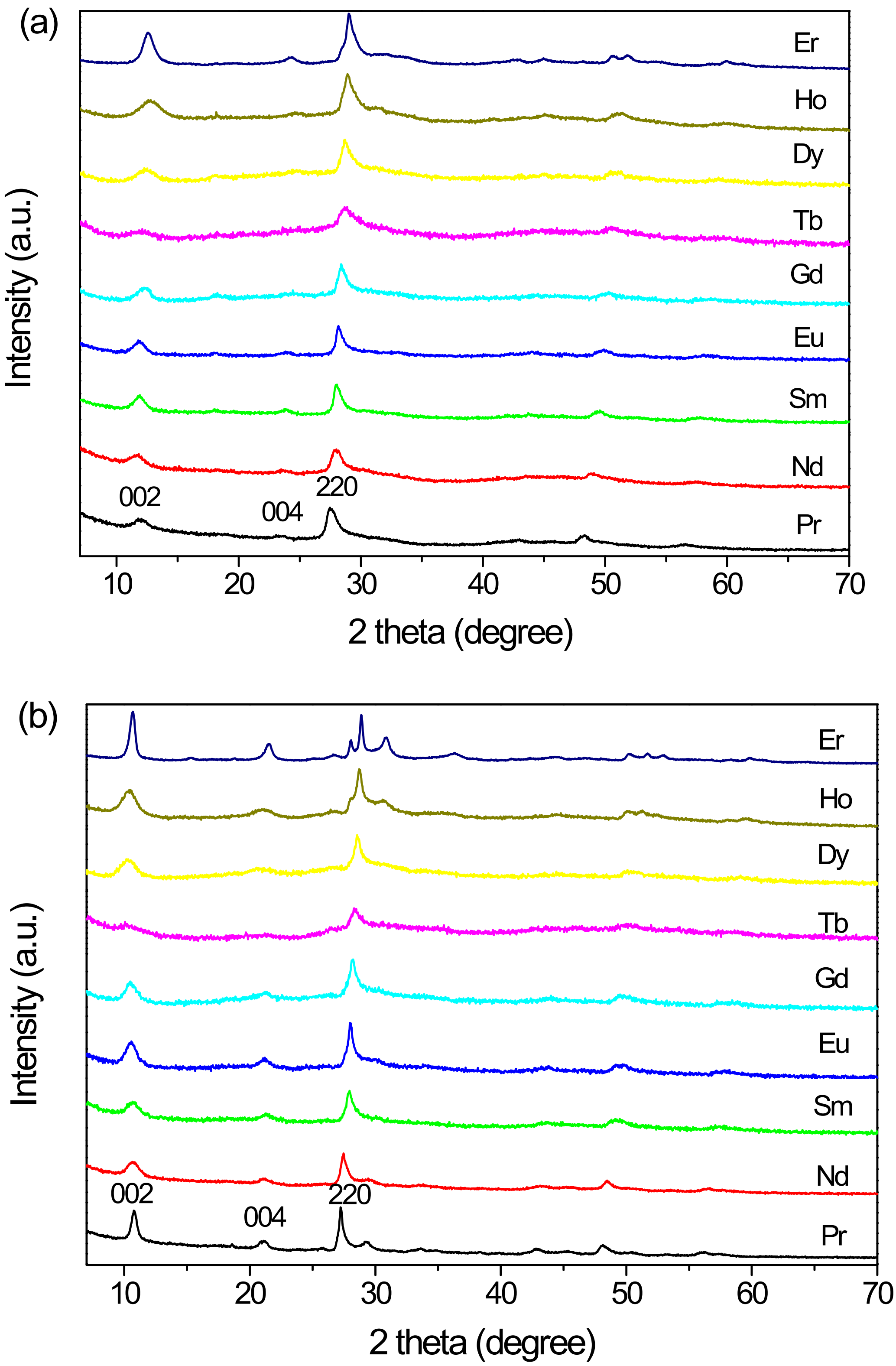

Figure S7. Powder XRD patterns for the products obtained via anion exchange of $Ln_2(OH)_5NO_3 \cdot nH_2O$ with F^- (a) and SO_4^{2-} (b).