Supporting information

Cation Exchange in Lanthanide Fluoride Nanoparticles

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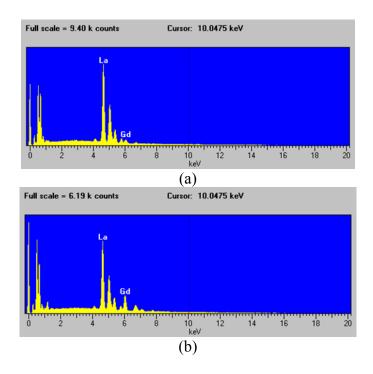


Figure S1. EDX spectra of nanoparticles made (a) by exposing GdF_3 nanoparticles to La^{3+} and (b) by exposing LaF_3 to Gd^{3+} .

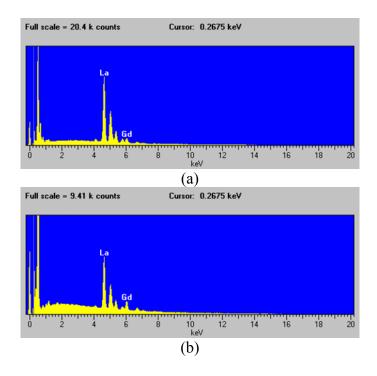


Figure S2. EDX spectra of nanoparticles made (a) by exposing GdF₃ nanoparticles to La³⁺ and (b) by exposing LaF₃ to Gd³⁺.

Calculation of solubility product¹

For the reaction

$$M_m A_n(s) \implies mM^+(aq) + nA^-(aq)$$

Where $M_m A_n$ is the slightly soluble substance and M^+ and A^- are the dissociated ions, then the Gibbs energy change is

$$\Delta G^{0} = m \Delta_{f} G^{0} (M^{+}, aq) + n \Delta_{f} G^{0} (A^{-}, aq) - \Delta_{f} G^{0} (M_{m} A_{n}, s)$$

Where $\Delta_f G^0$ (M⁺, aq) is the free energy of formation of M⁺ ion, $\Delta_f G^0$ (A⁻, aq) the free energy of formation of A⁻ ion and $\Delta_f G^0$ (M_mA_n, s) the free energy of formation of M_mA_n. The solubility product was calculated from:

$$\ln K_{\rm sp} = -\Delta G^0/RT$$

where R is the gas constant and T is temperature in Kelvin.

The calculated K_{sp} and the data used are tabulated in Table S1.

Table S1. Data from literature $^{1-3}$ and the calculated solubility product K_{sp} (unit: kJ/mol)

	$\Delta_{\rm f}G^0({ m M}^+,{ m aq})$	$\Delta_{\rm f}G^0$ (A ⁻ , aq)	$\Delta_{\rm f}G^0\left({\rm M_mA_n,s}\right)$	ΔG^0	Calculated K _{sp}
YF_3	-693.8	-278.8	-1644	113.8	1.16×10^{-20}
ScF ₃	-586.6	-278.8	-1554	131	1.09×10^{-23}
LaF ₃	-683.7	-278.8	-1625	104.9	4.26×10^{-19}
GdF ₃	-661	-278.8	-1624	126.6	4.30×10^{-23}

The calculated K_{sp} of YF₃ and ScF₃ are 1.16×10^{-20} and 1.09×10^{-23} , respectively, which are very close to data from literature (8.62×10^{-21} and 5.81×10^{-24} , respectively¹).

References

- (1) Lide, D. R. Handbook of Chemistry and Physics; CRC press: Boca Raton, 1996.
- (2) Greis, O.; Haschke, J. M. Handbook on the Physics and Chemistry of Rare Earths; Gschneidner, K. A., Eyring, L., Eds.; Elsevier North-Holland: Amsterdam, 1982; Vol. 5.
- (3) Marcus, Y. Ion Properties; Marcel Dekker: New York, 1997.