Supporting information

Kinetically-determined crystal structures of undoped and La^{3+}-doped LnF_3

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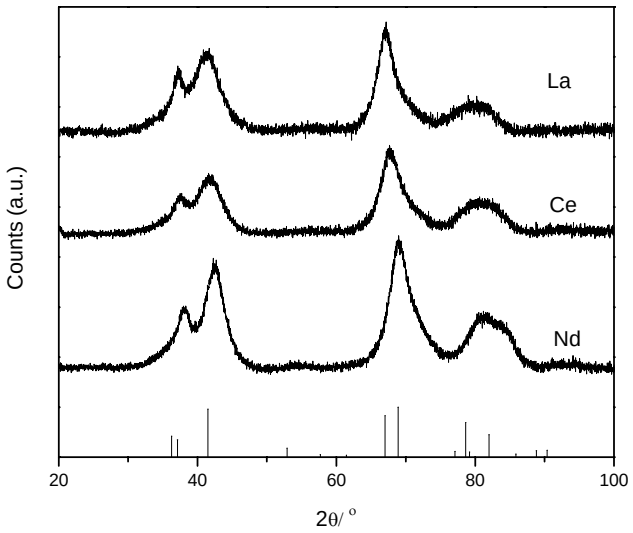

Figure S1. Comparison of XRD patterns of LaF_3, CeF_3, and NdF_3 nanoparticles with all the Bragg reflections of LaF_3 (vertical lines at the bottom).

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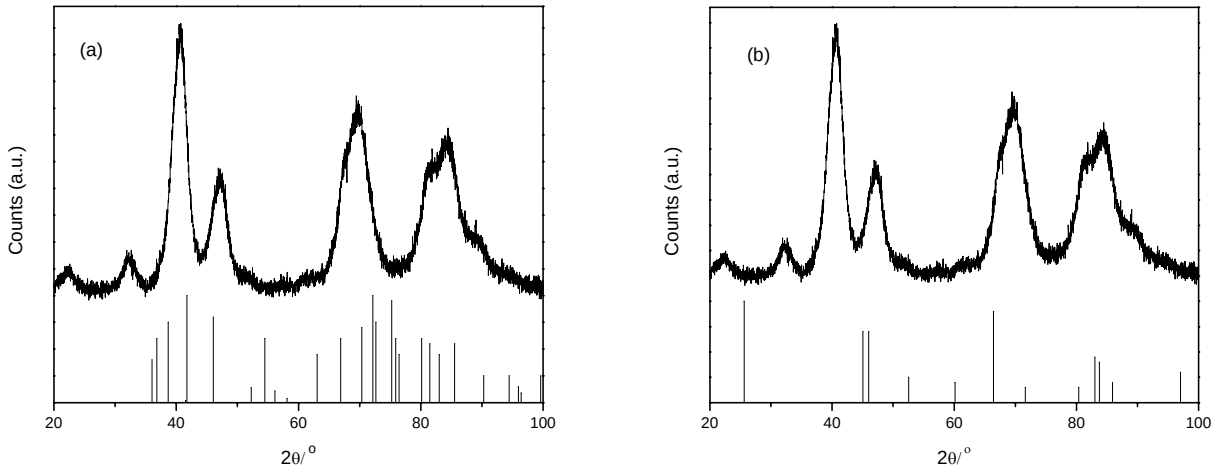

Figure S2. Comparison of XRD pattern of dysprosium fluoride nanoparticles with all the Bragg reflections of (a) DyF_3 and (b) stoichiometric $NaDyF_4$ (vertical lines at the bottom).

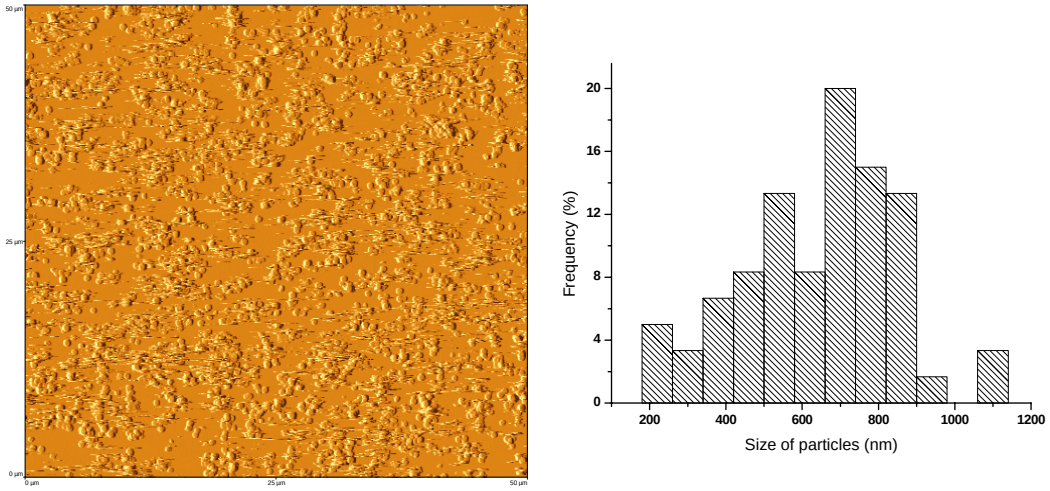

Figure S3. AFM image and size distribution of the submicron-sized GdF_3 particles

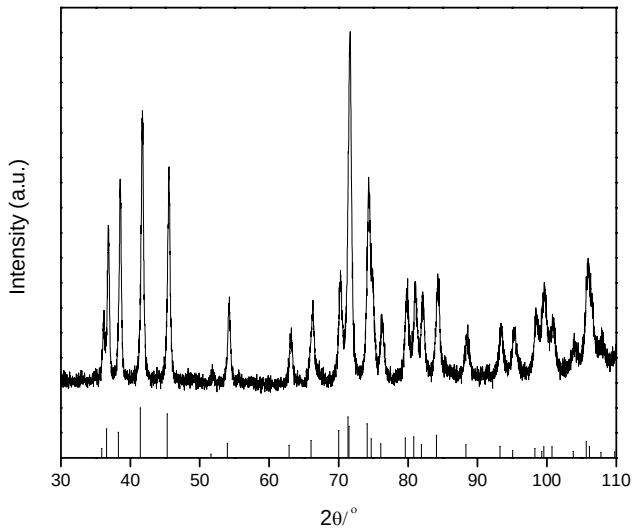

Figure S4. XRD pattern of the baked sub-micro GdF_3 particles (vertical bars at bottom are positions of all the Bragg reflections for the orthorhombic GdF_3).

Calculation of the lattice energies of LnF_3

The lattice energies of LnF_3 were calculated using the Born-Haber cycle (Figure S5).

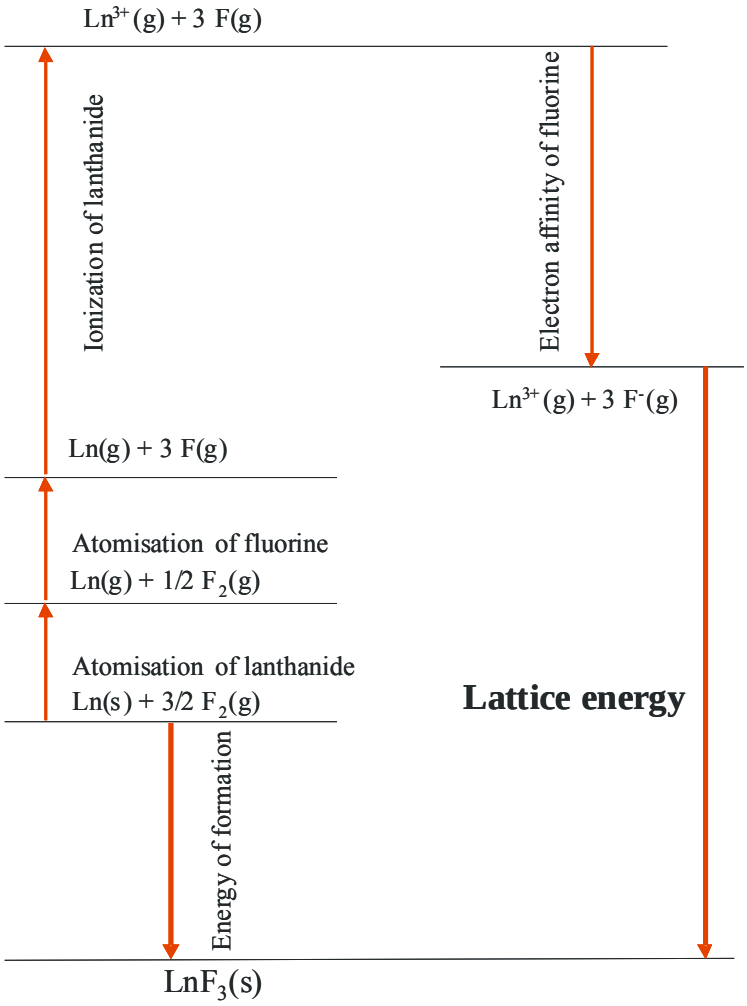

Figure S5. Born-Haber cycle used to calculate the lattice energies of LnF_3

From the above diagram, the following formula is deduced:

$$\Delta H_f = V + \frac{3}{2}B + IE_M - 3EA_X - U_L$$

ΔH_f is the standard enthalpy of formation

V is the heat of sublimation of Ln metal

IE_M is the ionization energy of Ln

EA_x is the electron affinity of F_2

B is the bond energy of F_2

U_L is the lattice energy

Using this formula, the lattice energies of LnF_3 are calculated and tabulated in Table S1.

Table S1. Data from literature[1-3] and calculated lattice energies of LnF_3 (unit: kJ/mol)

	ΔH_f Standard enthalpy of formation	V Heat of sublimation of Ln metal	IE_M Ionization energy of Ln	EA_x electron affinity of F_2	B bond energy of F_2	U_L Lattice energy
LaF_3	1701	431	3474	328	159	4861
CeF_3	1703	423	3549			4930
PrF_3	1691	356	3650			4952
NdF_3	1681	328	3719			4983
SmF_3	1669	207	3904			5035
EuF_3	1571	175	4055			5056
GdF_3	1700	398	3769			5122
TbF_3	1708	389	3810			5162
DyF_3	1693	290	3927			5165
HoF_3	1698	301	3949			5203
ErF_3	1694	317	3953			5219
TmF_3	1695	232	4046			5228
YbF_3	1630	152	4215			5252
LuF_3	1701	428	3924			5308

Data processing for the thermodynamic cycle in Figure 9

Calculations of lattice energies of La^{3+} doped GdF_3 nanoparticles

To calculate the lattice energies of the doped materials, because the trigonal LaF_3 and the orthorhombic GdF_3 have different crystal structures, it is not correct to do a simple weighed average of them. Thus the lattice energies of "trigonal" GdF_3 and "orthorhombic" LaF_3 were calculated by using a least square fit and linearly extrapolating the lattice energies of LaF_3 to SmF_3 and of LuF_3 to EuF_3, respectively. The calculated lattice energies of the "trigonal" GdF_3 and the "orthorhombic" LaF_3 are 5108 kJ/mol, and 4926 kJ/mol, respectively. Specially, the lattice energy of the "trigonal" GdF_3 is very close to that of the orthorhombic GdF_3, 5122 kJ/mol (the difference is < 0.3%), suggesting the possibility of GdF_3 having two phases. To calculate the lattice energies of the doped materials, weighed averaging was applied to the trigonal LaF_3 and the "trigonal" GdF_3 for an assumed trigonal phase, as well as to the "orthorhombic" LaF_3 and the orthorhombic GdF_3 for an assumed orthorhombic phase. The calculated lattice energies are tabulated in Table S2.

Table S2. The calculated lattice energies of La^{3+} doped GdF_3. (unit: kJ/mol)

La^{3+} doping level in GdF_3	Lattice energies of La^{3+} doped GdF_3	
	If orthorhombic structure is taken	If trigonal structure is taken
5%	5112.2	4873.4
10%	5102.4	4885.7
15%	5092.6	4898.1
20%	5082.8	4910.4
50%	5024.0	4984.5
75%	4975.0	5046.3

Hydration energies

In Figure 9a, hydration energy of F^- is -472 kJ/mol, that of La^{3+} is -3155 kJ/mol, and that of Gd^{3+} -3385 kJ/mol.[3]

Entropies

All the standard entropies are available in the literature,[1,3] and the following equation was used to calculate the entropy change. The calculated entropy changes are tabulated in Table S3.

$LnF_3(s)$----$Ln^{3+}(g) + 3F^-(g)$

Table S3. The standard entropies and the entropy changes of LaF_3 and GdF_3 (unit: J/mol·K)

	Standard Entropy of LnF_3 (s)	Standard entropy of La^{3+} (g)	Standard entropy of F^- (g)	Standard entropy change (ΔS^0)
LaF_3	107	171	146	502
GdF_3	117	189		510

A weighed average of the standard entropy changes of LaF_3 and GdF_3 was used for the thermodynamic cycle.

Tabulation of the calculated standard Gibbs free energy

Table S4. The calculated Gibbs free energies based on the thermodynamic cycle. (unit: kJ/mol)

La^{3+} doping level in GdF_3	$\Delta G^0_{reac.}$ If orthorhombic structure is taken	$\Delta G^0_{reac.}$ If trigonal structure is taken
5%	-180.7	+68.2
10%	-172.4	+44.3
15%	-174.1	+20.5
20%	-175.8	-3.4
50%	-186.0	-146.0
75%	-194.5	-265.5

The data in Table S4 were used to make the plot in Figure 9b.

References

(1) *Handbook on the physics and chemistry of rare earths*; Elsevier North-Holland: Amsterdam, 1982; Vol. 5.

(2) Lide, D. R. *Handbook of Chemistry and Physics*; CRC press: Boca Raton, 1996.

(3) Marcus, Y. *Ion Properties*; Marcel Dekker: New York, 1997.