Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

First-principles calculations of strain engineering in $NaYF_4$-based nanocrystals with hydroxyl impurities

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Determination of the chemical potential range for each species. Under thermal equilibrium growth conditions, stable cubic-phase $NaYF_4$ can form when the chemical potentials of each species follow

$$\Delta\mu_{Na} + \Delta\mu_Y + 4\Delta\mu_F = \Delta H^f(NaYF_4) \quad \text{(S1)}$$

where $\Delta H^f(NaYF_4)$ is the formation enthalpy of cubic $NaYF_4$ obtained from first-principles calculations. $\Delta\mu_{Na}$, $\Delta\mu_Y$, and $\Delta\mu_F$ are the relative chemical potentials of Na, Y, and F, referenced to the energy per atom of sodium bulk, yttrium bulk, and a gas-phase fluorine diatomic molecule, respectively. These relative chemical potentials can be written as

$$\Delta\mu_{Na} = \mu_{Na} - \mu_{Na}^{Bulk} \quad \text{(S2)}$$

$$\Delta\mu_Y = \mu_Y - \mu_Y^{Bulk} \quad \text{(S3)}$$

$$\Delta\mu_F = \mu_F - \mu_F^{Gas} \quad \text{(S4)}$$

To avoid the formation of the aforementioned elemental substances, relative chemical potentials should follow

$$\Delta\mu_{Na} \leq 0 \quad \text{(S5)}$$

$$\Delta\mu_Y \leq 0 \quad \text{(S6)}$$

$$\Delta\mu_F \leq 0 \quad \text{(S7)}$$

where $\Delta\mu = 0$ denotes Na-rich, Y-rich, or F-rich conditions.

To avoid the precipitation of secondary phases of fluoride-based compounds, relative chemical potentials should follow

$$\Delta\mu_{Na} + \Delta\mu_F \leq \Delta H^f(NaF) \quad \text{(S8)}$$

$$\Delta\mu_Y + 3\Delta\mu_F \leq \Delta H^f(YF_3) \quad \text{(S9)}$$

With DFT-calculated energies of each atom species in their bulk/gas phase and the formation enthalpy of each inorganic compound, the stability diagram of cubic $NaYF_4$ was obtained (**Fig. 1**).

Additionally, the relative chemical potential of OH species was referenced to the energy of a gas-phase, isolated OH^- ion, which can be written as

$$\Delta\mu_{OH} = \mu_{OH} - \mu_{OH}^{Gas} \quad \text{(S10)}$$

Similarly, to avoid the formation of the elemental substance and the corresponding second phases, the relative chemical potential of OH species was limited by

$$\Delta\mu_{OH} \leq 0 \quad \text{(S11)}$$

$$\Delta\mu_{Na} + \Delta\mu_{OH} \leq \Delta H^f(NaOH) \quad \text{(S12)}$$

$$\Delta\mu_Y + 3\Delta\mu_{OH} \leq \Delta H^f(Y(OH)_3) \quad \text{(S13)}$$

Table S1 Calculated formation enthalpy of each inorganic compound. Note that disordered cubic $NaYF_4$ crystal was converted to ordered tetragonal $NaYF_4$ crystal for DFT calculations.

Compound	Calculated ΔHf (eV/chemical formula)
$NaYF_4$ (I41/amd)	-22.862
NaF (Fm3m)	-5.637
YF_3 (Pnma)	-17.017
NaOH ($P2_1$)	-4.536
$Y(OH)_3$ ($P6_3/m$)	-15.324

Table S2 Bond length between F^-/OH^- and its first neighboring ions in pristine/OH-incorporated unstrained cubic $NaYF_4$. The number assigned to each atom is illustrated in **Figs. 2a** and **b**.

Pristine lattice		OH-incorporated lattice	
Bond name	**Bond length (Å)**	**Bond name**	**Bond length (Å)**
F_0–Y_1	2.31	O–Y_1	2.29
F_0–Y_2	2.31	O–Y_2	2.29
F_0–Na_1	2.44	O–Na_1	2.59
F_0–Na_2	2.44	O–Na_2	2.59
F_0–F_1	2.53	O–F_1	2.57
F_0–F_2	2.72	O–F_2	2.76
F_0–F_3	2.97	H–F_3	1.81
F_0–F_4	2.72	O–F_4	2.76
F_0–F_5	2.75	O–F_5	2.81
F_0–F_6	2.75	O–F_6	2.81
		O–H	0.99