Supporting Information for

Controlling anion off-center positions through thermodynamics and kinetics in flexible perovskite-like materials

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Unit cells of the rhombohedral (α) and cubic (ReO_3) structures of FeF_3

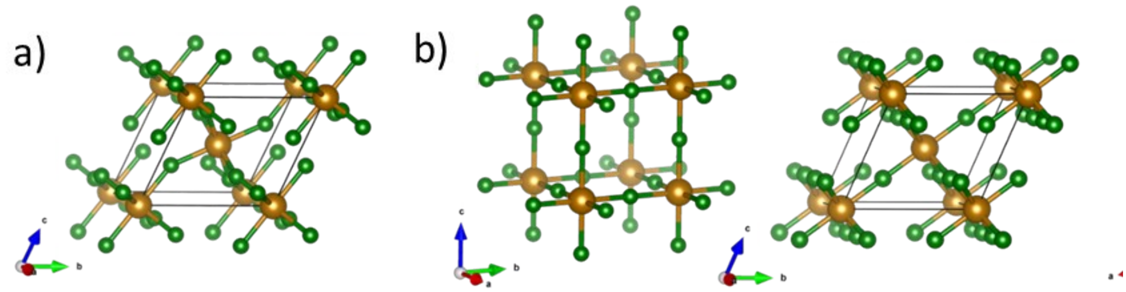

Figure S1. Conventional cells of the α (a) and ReO3 (b) structures of FeF_3.The rhombohedral setting is also shown for the cubic ReO3 structure. Brown and green balls stand for Fe and F, respectively.

Phonon-volume dependence of α-FeF_3

Since the unit cell of the rhombohedral structure contains two FeF_3 formula units, the total number of vibrational normal modes at the Γ-point is twenty-four. Three of these branches are acoustic and twenty-one are optic. According to group theory, the optical normal modes at the center of the Brillouin zone can be classified as follows:

$$\Gamma_{opt} = A_{1g} \oplus 2A_g \oplus 3E_g \oplus 2A_{1u} \oplus 2A_{2u} \oplus 4E_u$$

The frequencies at the Γ-point of the twenty-four vibrational modes were obtained for the α phase under the DFTP approach. Figure S2 collects the evolution with volume of the calculated twenty-four frequencies.

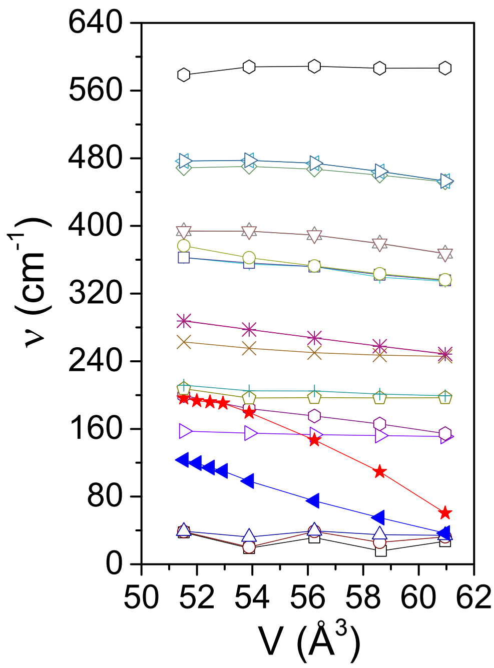

Figure S2. Volume dependence of the 24 vibrational modes of the α-FeF_3 phase. A_{1g} and E_g soft modes are highlighted as red filled starts and blue filled triangles, respectively.

Calculation of the attempt frequency in the classical kinetic modelling

The evaluation of the second derivative of the six order Landau potential at the minima (ω_{min}) gives the angular force constant associated with the rotational octahedral movements responsible for the α to ReO_3 transformation.

$$k_{tilt} = \left.\frac{d^2E}{d^2\omega_{tilt}}\right|_{\omega_{min}}$$

Assuming that the reduced mass for this rotational movement is given by the inertia moment (I_{FeF6}) of the FeF_6 octahedrons. We can calculate the attempt frequency as:

$$\nu = \sqrt{\frac{k_{tilt}}{I_{FeF6}}}$$

Where the I_{FeF6} is easily calculated in terms of the fluorine mass (m_F) and the Fe-F distance (r_{FeF}):

$$I = 4m_F {r_{FeF}}^2$$