Supplementary Information

***In-situ* observation of epitaxial growth during evaporative simultaneous crystallization from aqueous electrolytes in droplets**

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1. NaCl-H2O seeded with NaCl

Behaviour of an NaCl seed growing in a NaCl aqueous solution can be observed in Figure 1SI. Evidence of Hopper growth is clear after 14 minutes of evaporation. Overgrown edges are seen to increase in size along time.
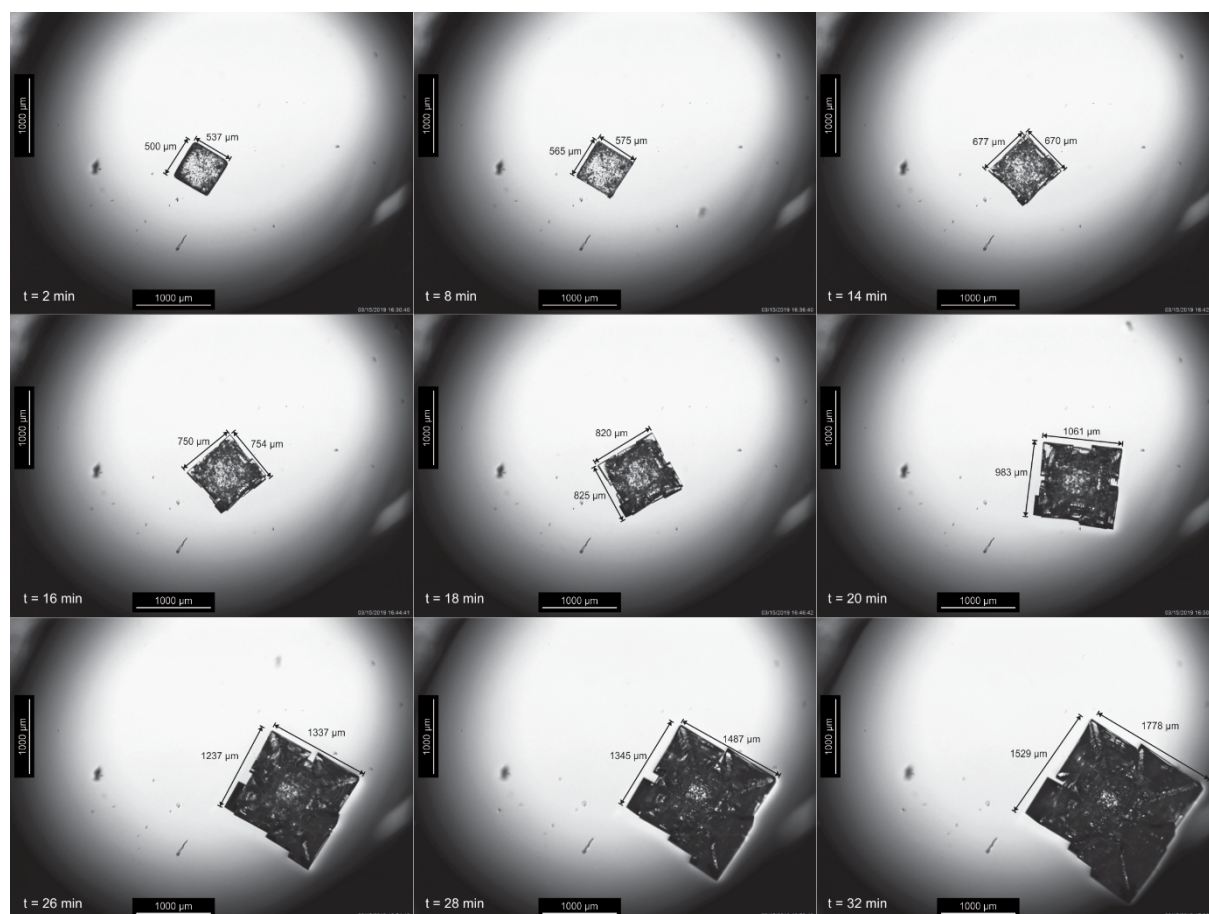
Figure S1 Optical photomicrographs along time of the NaCl-H_2O droplet under evaporation seeded with NaCl.

2. 2D Lattice matching calculations

Lattice matching calculations were performed using MATLAB, according to the method devised by Hillier and Ward[6]. The method is based on a rationale that epitaxial growth can be induced if the planes of substrate and an overlayer of the deposit – consisting of periodicities of lattices – may match at certain azimuthal angle (which defines the orientation of both lattices). Hence, geometric matching is computationally more efficient than conventional potential energy calculations since it is based on structural fitting between substrate and deposit, whereas potential energy calculations rely on optimizing the interaction energy of substrate-deposit atom over various azimuthal angle[7].

In short, three types of 2D lattice matching can be observed: (i) commensurism, where the lattice sites of the substrate and deposit fully overlap each other; (ii) coincidence, where the lattices of the deposit overlaps on a certain lattice vector of the substrate, but not all; and (iii) incommensurism, where no overlap between the lattices of the substrate and deposit are seen. These three types can be correlated with the dimensionless potential energy (V/V_0) such that if $V/V_0 \approx 0$ indicates commensurism; $V/V_0 \approx 0.5$ indicates coincidence; and $V/V_0 \approx 1$ indicates incommensurism.

The dimensionless potential energy (V/V_0), shown in Equation 1, can be calculated at the substrate-deposit interface associated with a characteristic lattice match. Mathematically, the calculation matches the substrate and deposit lattice vectors (a_1, a_2, α for substrate and b_1, b_2, β for the overlayer) over a range of azimuthal angle (μ) between them, such that the global minimum of V/V_0 at an azimuthal angle can be used to infer the epitaxial relation.

$$\frac{V}{V_0} = 1 - \frac{1}{2MN} \times \frac{\sin(M\pi p_x)\sin(N\pi q_x)}{\sin(\pi p_x)\sin(\pi q_x)} - \frac{1}{2MN} \times \frac{\sin(M\pi q_y)\sin(N\pi p_y)}{\sin(\pi q_y)\sin(\pi p_y)} \qquad \text{Equation 1}$$

Where p_x, p_y, q_x, q_y are parameters that relate lattice vectors of substrate and deposit and M, N are the number of deposit lattices along two dimensions.

The possibility of 2D lattice match between the pairs of crystals was explored for all combinations of substrate and deposit faces.
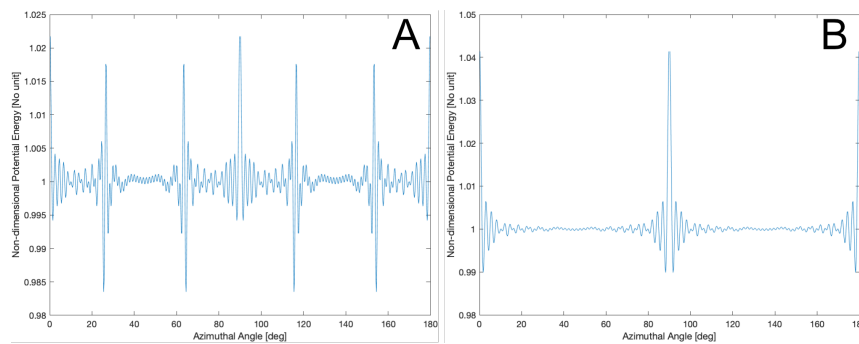

Figure S2 Plots of the non-dimensional potential energy at the NaCl-KCl interface versus the orientation angle for (A) NaCl as the substrate and KCl as deposit and for (B) KCl as the substrate and NaCl as deposit.
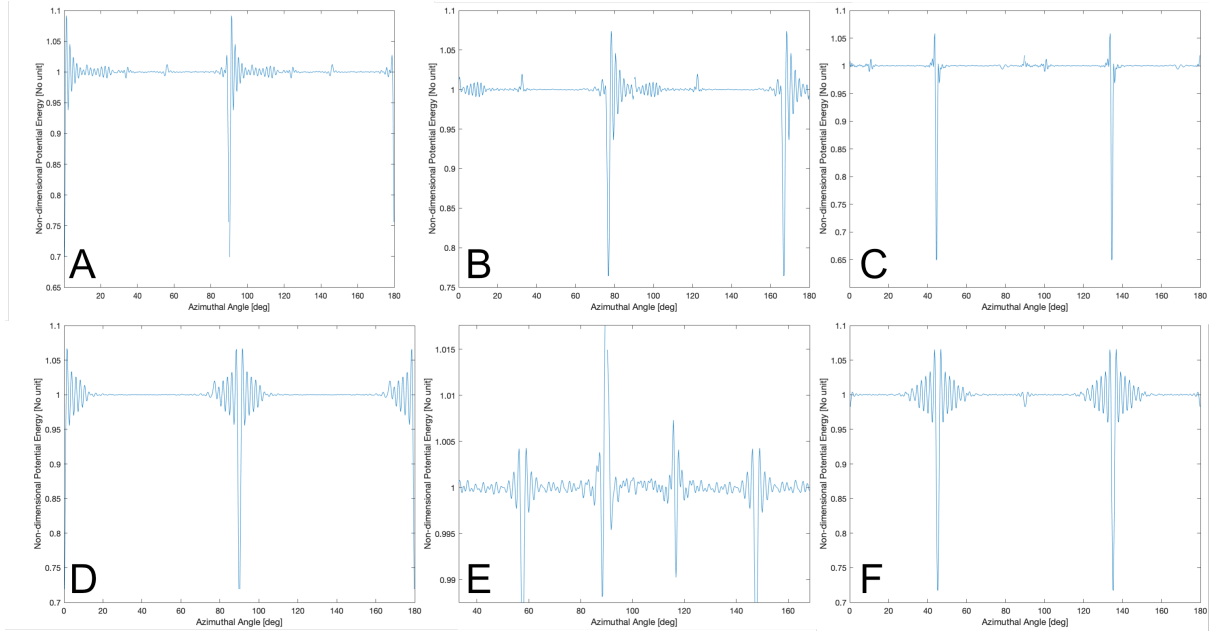
Figure S3 Plots of the non-dimensional potential energy at the NaCl-Na₂SO₄ interface, considering all possible combinations of the face of NaCl and each face of Na₂SO₄, versus the orientation angle for (A, B, C) NaCl as the substrate and Na₂SO₄ as deposit and for (D, E, F) Na₂SO₄ as the substrate and NaCl as deposit.

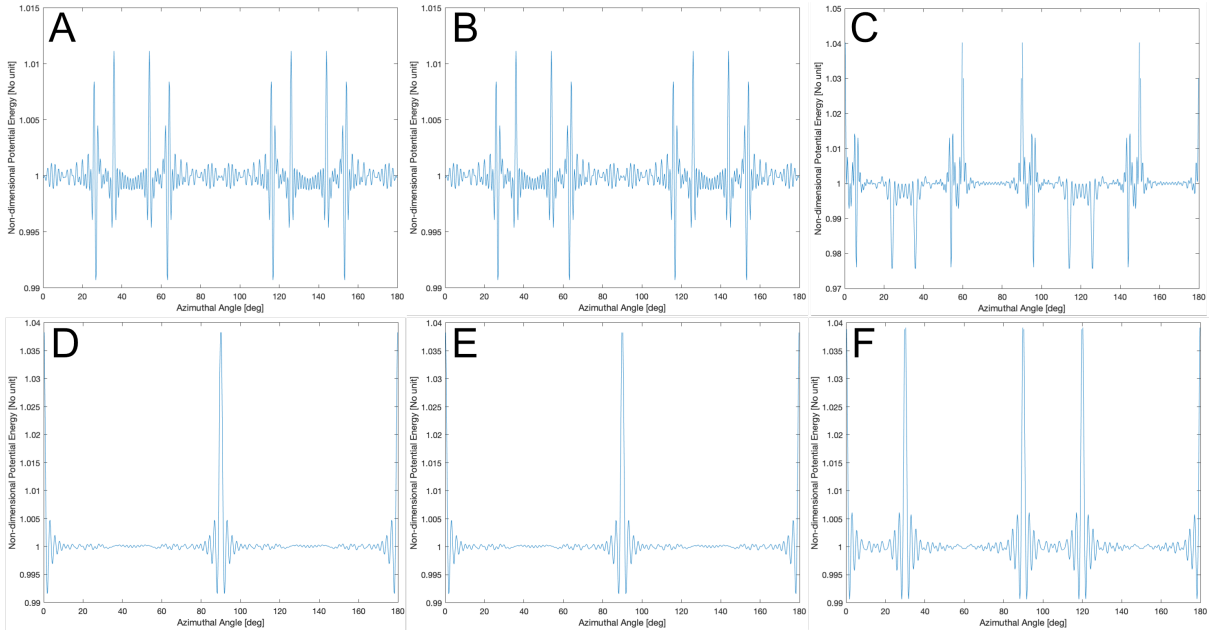
Figure S4 Plots of the non-dimensional potential energy at the NaCl-CaSO₄ interface, considering all possible combinations of the face of NaCl and each face of CaSO₄, versus the orientation angle for (A, B, C) NaCl as the substrate and CaSO₄ as deposit and for (D, E, F) CaSO₄ as the substrate and NaCl as deposit.

The results obtained in Figures S2, S3 and S4 show that no characteristic match could be observed between the pairs of crystals analyzed, as most of the non-dimensional potential energy value always

lies close to 1. The minimum value for all the pairs was seen between NaCl and two of the Na_2SO_4 faces (Figure S3 A, C, D and F), yet the dimensionless potential energy is still 0.7. Hence, lattice matching is not inducing epitaxial growth in any of the cases.