Supplementary Information

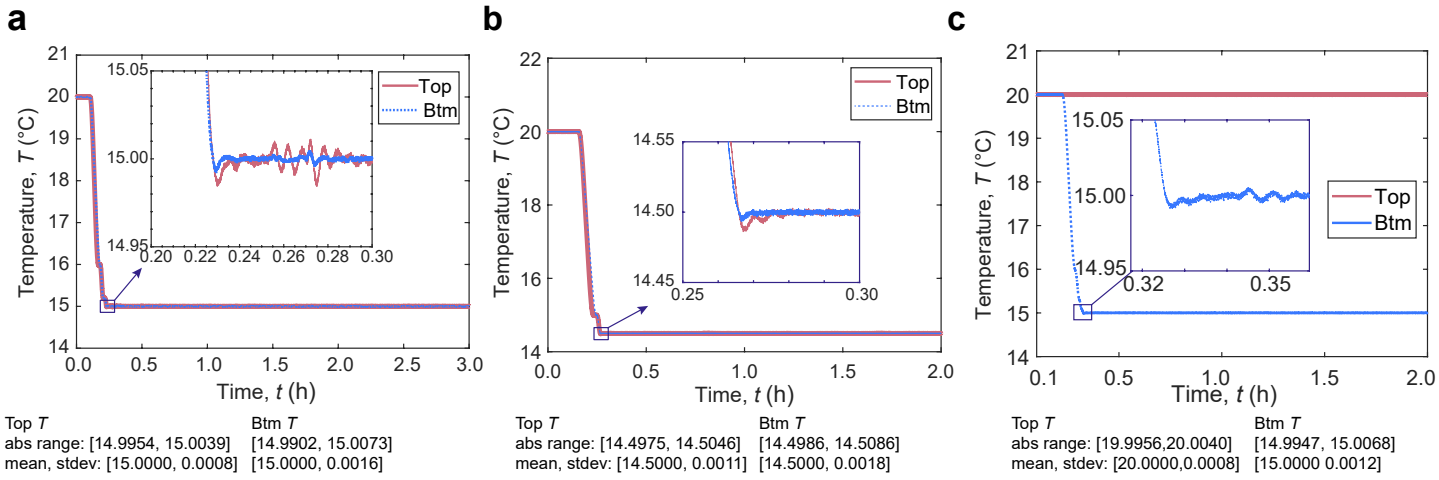
Crystallisation triggered by mass diffusion at a lower local supersaturation

Shuqi Xu[1] and Juan F. Torres[1]

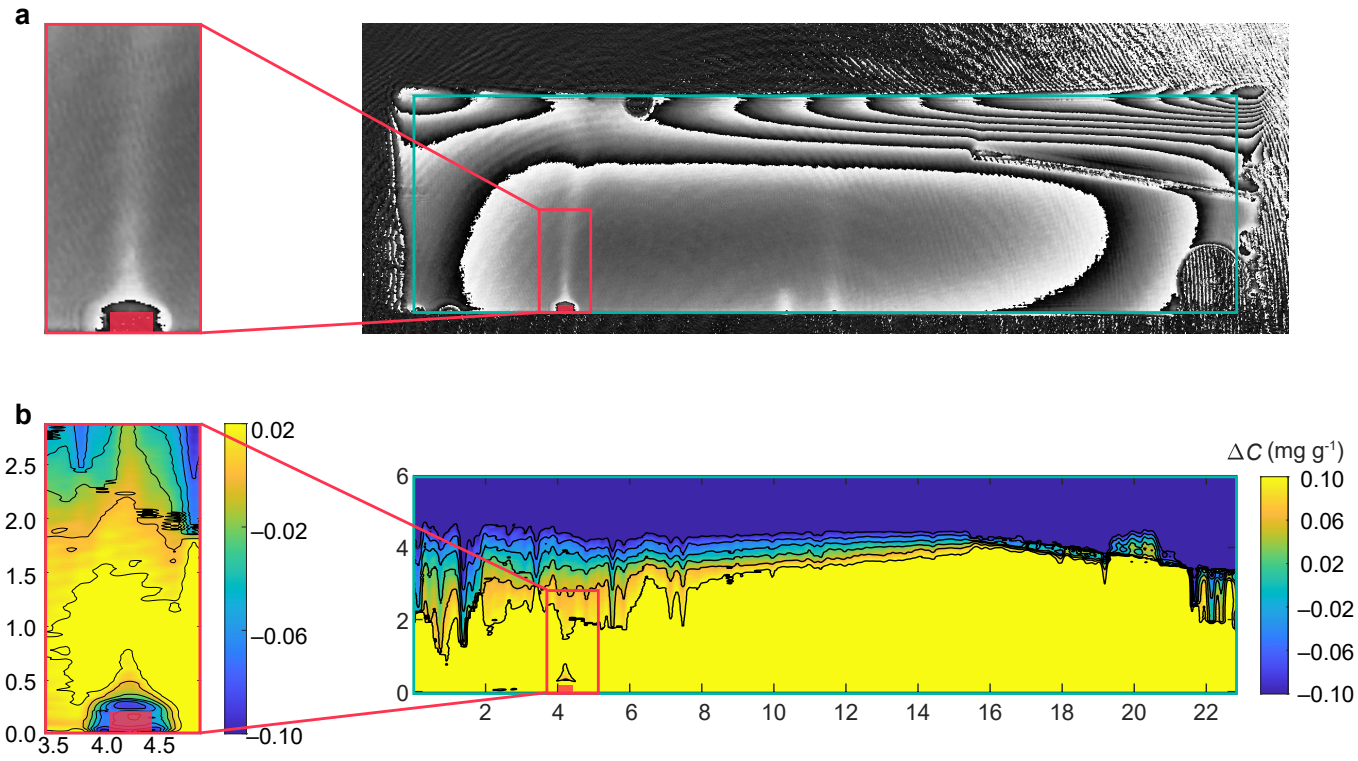
[1]ANU HEAT Lab, School of Engineering, Australian National University, Canberra, Australia

Supplementary Figures

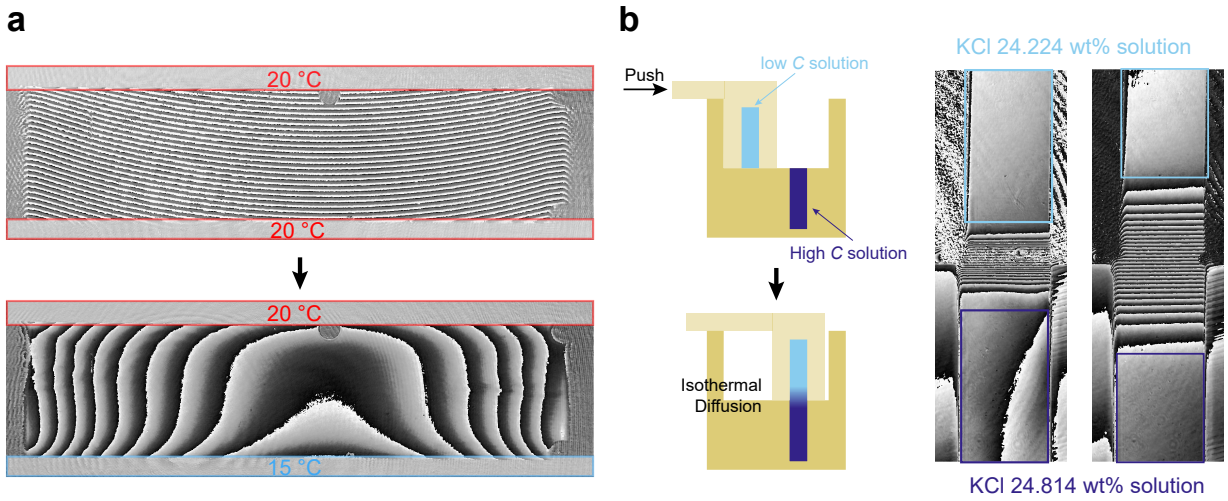
Fig. 1 Temperature control 2
Fig. 2 Cooling crystallisation at 1980 s 2
Fig. 3 Contrast factor measurement 3
Fig. 4 KCl thermodiffusion without crystallisation 3
Fig. 5 Evaporation suppression for the crystallisation cell 4
Fig. 6 Phase-shifting interferometry (PSI) 4



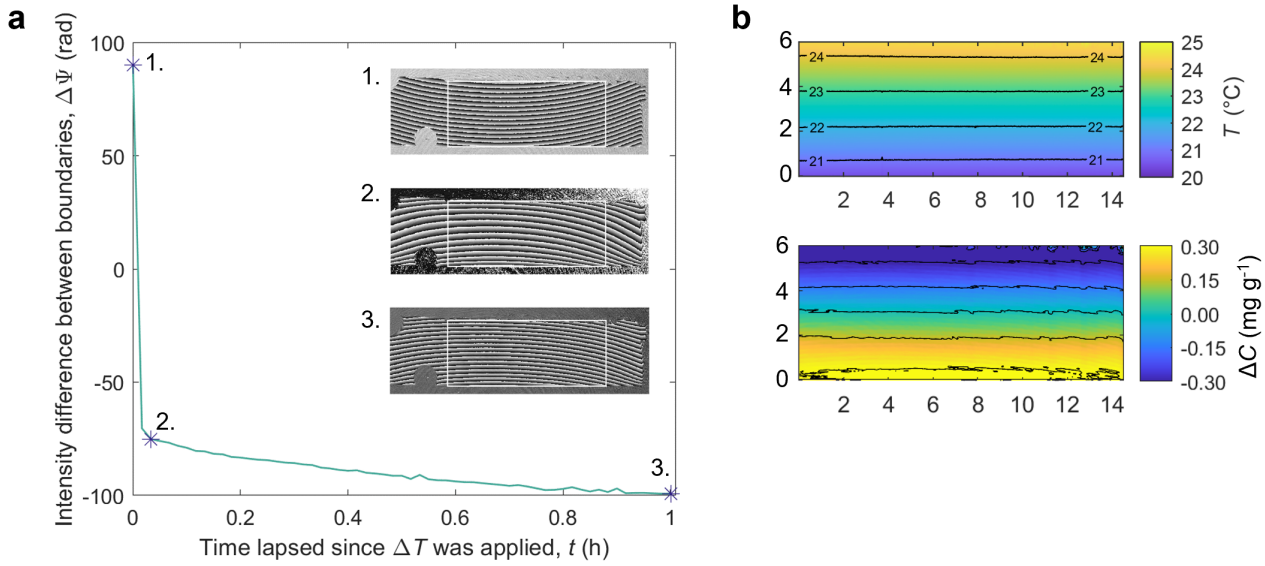
Supplementary Fig. 1 | **Temperature control. a,** Top and bottom boundaries cool from $20\,^{\circ}\mathrm{C}$ to $15\,^{\circ}\mathrm{C}$). **b,** Top and bottom boundaries cool from $20\,^{\circ}\mathrm{C}$ to $14.5\,^{\circ}\mathrm{C}$. **c,** Top boundary remains at $20\,^{\circ}\mathrm{C}$ and bottom boundary cools from $20\,^{\circ}\mathrm{C}$ to $15.0\,^{\circ}\mathrm{C}$.



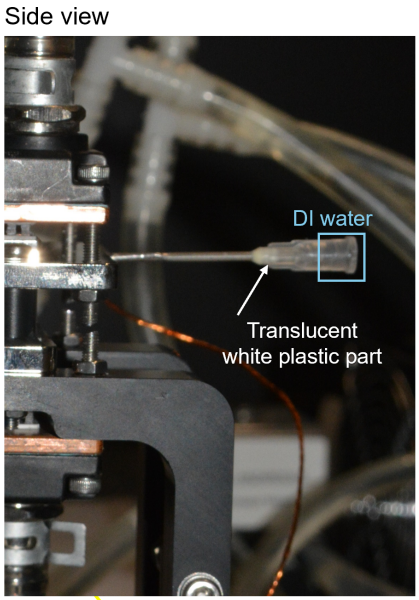
Supplementary Fig. 2 | **Cooling crystallisation at** $1980\,\mathrm{s}$**. a,** Phase-shifted data, with one growing crystal magnified on the left. **b,** Concentration profile, with the same growing crystal magnified. Solute depletion is evident near the growing crystal, generating a rising plume that reduces the solute concentration in the upper half of the cell during active crystal growth.



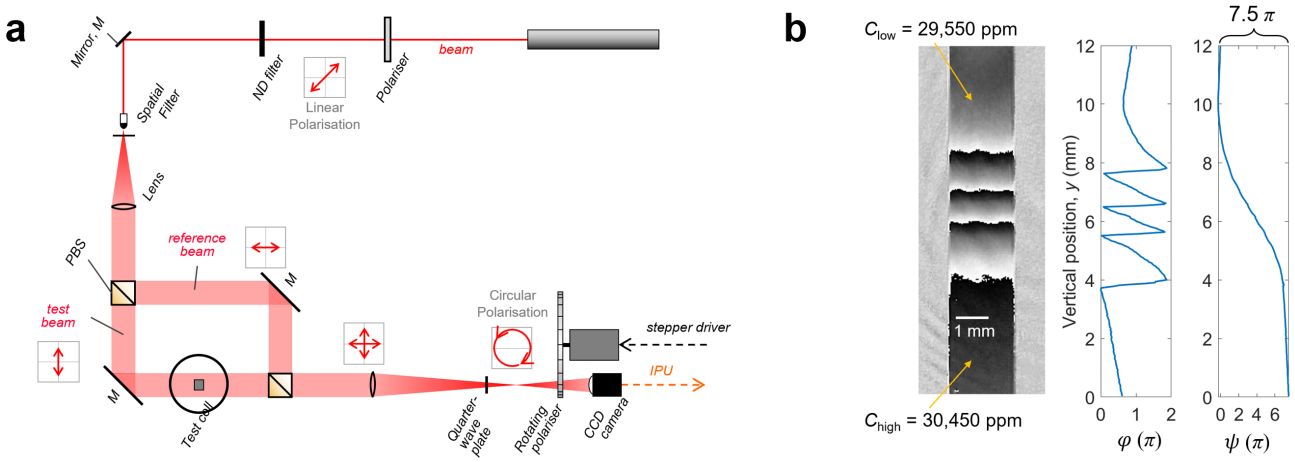
Supplementary Fig. 3 | **Contrast factor measurement. a,** Contrast factor $\delta\Psi/\delta T_{C=C_0}$ is measured by applying a known temperature difference to solution $C = C_0$. The boundary temperatures are measured with thermistors and $\delta\Psi/\delta T_{C=C_0}$ is assumed to be a constant when ΔT is small. Thus $\delta\Psi/\delta T_{C=C_0} = \frac{\Delta\Psi}{\mathrm{OP}\Delta T}$ where OP is the optical path length. **b,** Contrast factor $\delta\Psi/\delta C_{T=\text{constant}}$ is measured by performing an isothermal diffusion experiment. The isothermal diffusion experiment was done through sliding the top part containing low C solution onto the bottom part containing the high C solution. Diffusion occurs from the high and low C solution interface. $C_{\text{high}} = 24.814\,\text{wt}\%$ and $C_{\text{low}} = 24.224\,\text{wt}\%$. We assume that the contrast factor at $C_0 = 25.36\,\text{wt}\%$ is the same. From the top to bottom, the concentration increases while the phase Ψ decreases, i.e., each fringe changes from bright to dark. Thus the contrast factor $\delta\Psi/\delta C$ is negative and $\delta\Psi/\delta C_{T=T_0} = \frac{\Delta\Psi}{\mathrm{OP}\Delta C}$.



Supplementary Fig. 4 | **KCl thermodiffusion without crystallisation. a,** The unwrapped phase change Ψ as time progresses. The thermodiffusion is nearly constant after $0.8\,\text{h}$. Between **1** and **2** is the temperature development phase and between **2** and **3** is the concentration development phase. **b,** The temperature map is obtained by subtracting unwrapped PSI image in **a1** from **a2** and the concentration difference map is obtained by subtracting unwrapped PSI image in **a2** from **a3**. The maximum ΔC is $0.3097\,\text{mg}\,\text{g}^{-1}$ and the minimum ΔC is $-0.3422\,\text{mg}\,\text{g}^{-1}$.



Supplementary Fig. 5 | **Evaporation suppression for the crystallisation cell.** Photo showing the side view with a glued needle used to suppress evaporation from the solution injection hole. The KCl solution was removed from the white plastic part by a lint-free tissue, and then the DI water was injected slightly forming a seal. The white part is translucent to confirm that there is air between the KCl solution in the needle and the injected DI water. This produced a tight seal of the crystallisation cell.



Supplementary Fig. 6 | **Phase-shifting interferometry (PSI). a,** Layout of the polarising Mach–Zehnder interferometer with rotating polariser, which is the basis for the PSI technique with a temporal phase-shifting algorithm, as described in Torres et al. *Optics and Laser in Engineering* **50**, 1287–1296 (2012). Adapted with permission of Elsevier. **b**, On the left is a typical phase-shifted data, which describes the diffusion field between a low and high concentration solution, C_{high} and C_{low}, respectively. The phase φ and the unwrapped phase Ψ are plotted against the cell height on the right. The unwrapped phase map Ψ connects discrete values of φ.