High-quality bulk hybrid perovskite single crystals within minutes by inverse temperature crystallization

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Single crystals of methylammonium lead trihalide perovskites (MAPbX3; MA = CH₃NH₃⁺, X = Br⁻ or I⁻) have shown remarkably low trap density and charge transport properties; however, growth of such high-quality semiconductors is a time-consuming process. Here we present a rapid crystal growth process to obtain MAPbX₃ single crystals, an order of magnitude faster than previous reports. The process is based on our observation of the substantial decrease of MAPbX₃ solubility, in certain solvents, at elevated temperatures. The crystals can be both size- and shape-controlled by manipulating the different crystallization parameters. Despite the rapidity of the method, the grown crystals exhibit transport properties and trap densities comparable to the highest quality MAPbX₃ reported to date. The phenomenon of inverse or retrograde solubility and its correlated inverse temperature crystallization strategy present a major step forward for advancing the field on perovskite crystallization.
Organic-lead trihalide hybrid perovskites (MAPbX$_3$; MA = CH$_3$NH$_3^+$, $X$ = Br$^-$ or I$^-$) have been widely investigated for solar cells$^{1-9}$, lasing$^9$, light-emitting diodes$^{10}$, photodetectors$^{11}$ and hydrogen production$^{12}$. This considerable interest in organic-lead trihalide perovskites is because of their tunable optical properties, high-absorption coefficients, long-ranged balanced electron and hole transport$^{11}$, low cost and facile deposition techniques$^{14-16}$. In particular, single crystals of MAPbBr$_3$ and MAPbI$_3$ were shown to possess long carrier diffusion lengths and a remarkably low trap-state densities, which is comparable to the best photovoltaic-quality silicon$^{17}$. These properties provide a view of the ultimate potential of hybrid perovskites, and make single crystals of MAPbX$_3$ a highly desirable semiconductor for optoelectronic applications that are much broader than their polycrystalline thin film counterpart. However, the reported solution crystallization processes for perovskite single crystals suffer from very slow growth rates and no shape control over the resultant crystals$^{17-21}$. The highest reported growth rate was estimated to be $\sim 26$ mm$^3$ per day ($\sim$1 mm$^3$ h$^{-1}$) for a MAPbI$_3$ crystal with the dimensions of 10 mm $\times$ 10 mm $\times$ 8 mm that took a month to grow$^{20}$. A radically faster crystallization technique that could also address the need for a diverse variety of crystal geometries will allow more extensive use of hybrid perovskite single crystals.

The choice of a suitable solvent medium has always been a defining factor for the quality of the ensuing crystals. In the case of hybrid perovskites, the most widely used solvents are N,N-dimethylformamide (DMF) and dimethylsulphoxide (DMSO). The solubility of PbX$_2$ and MAX in these solvents or their mixtures was found to vary; hence, it was previously reported that MAPbBr$_3$ crystallized more aptly from DMF while MAPbI$_3$ crystallized better from GBL$^{11}$. Perovskite crystallization from aqueous solution was also reported, in which crystals were formed, classically, on cooling a preheated solution$^{20}$. It is generally the norm that solutes tend to have a higher degree of solubility at higher temperatures; hence, a good solvent for crystallization will dissolve more precursors when hot, while cooling down induces supersaturation commencing the crystallization. On the other hand, a decrease of solute solubility in solvents with increasing temperature (that is, inverse temperature or retrograde solubility) is a rare occurrence, that is, only displayed by a few materials$^{22}$.

Here we show that MAPbX$_3$ perovskites exhibit inverse temperature solubility behaviour in certain solvents. This novel phenomenon in hybrid perovskites enabled us to design an innovative crystallization method for these materials, referred to here as inverse temperature crystallization (ITC), to rapidly grow high-quality size- and shape-controlled single crystals of both MAPbBr$_3$ and MAPbI$_3$, at a rate that is an order of magnitude faster than the previously reported growth methods$^{17-21}$. The versatility of our approach provides the continuous enlargement of crystals, through replacement of the depleted growth solution, and the use of templates for controlling their shapes.

Results

Single crystal growth and structural characterization. We noticed the rapid formation of small MAPbBr$_3$ perovskite precipitates at high temperatures in some concentrated solutions (for example, DMF) and not in others (for example, DMSO). On the other hand, GBL could not be used as a solvent because of the very low solubility of MAPbBr$_3$ (<0.05 g ml$^{-1}$ at both room temperature and 80°C). The effect of the different solvents could be related to their varying degrees of coordination with the precursors, as it was previously reported that DMSO may retard the crystallization process because of its strong binding to the lead precursor$^{23-25}$.

Consequently, DMF was chosen for MAPbBr$_3$ ITC. Through studying the solubility of MAPbBr$_3$ in DMF, we observed that it drops markedly from 0.80 ± 0.05 g ml$^{-1}$ at room temperature to 0.30 ± 0.05 g ml$^{-1}$ at 80°C. This inverse solubility phenomenon was used to crystallize MAPbBr$_3$ rapidly in hot solutions as illustrated in Fig. 1a. Through balancing both temperature and concentration of precursors in DMF, only a few crystals were formed. For instance, by setting the temperature of the heating bath at 80°C usually <5 crystals are formed in case of 1 M solution of PbBr$_2$ and MAPb (Supplementary Fig. 1). Inspired by this observation, we repeated the same procedure and studied different solvents that could lead to the same effect in MAPbI$_3$. Unlike MAPbBr$_3$, ITC of MAPbI$_3$ was only possible in GBL solution, while no precipitates were observed in the case of DMF or DMSO.

As expected, we observed that the crystallization process in both MAPbBr$_3$ and MAPbI$_3$ is reversible and the crystals dissolve back when cooled to room temperature. It is also worth mentioning that individual precursors PbX$_2$ and MAX did not show any inverse solubility behaviour (that is, saturated solutions of the individual precursor did not show precipitation on heating), implying that the phenomenon is tied to the perovskite structure.

The growth process of MAPbI$_3$ crystal using the ITC technique was recorded on video using time-accelerated mode (Supplementary Movie 1), several snapshots of which are shown in Fig. 1b. Individual MAPbI$_3$ crystal was calculated to grow at a rate of ~3 mm$^3$ h$^{-1}$ for the first hour, a rate that significantly increases to ~9 mm$^3$ h$^{-1}$ for the second hour and to ~20 mm$^3$ h$^{-1}$ for the following hour. This value is an order of magnitude greater than the previously reported highest growth rate$^{20}$. An even faster growth rate was observed for MAPbBr$_3$ crystals, reaching up to 38 mm$^3$ h$^{-1}$ for the third hour (Fig. 1c), resulting in a higher yield in comparison with MAPbI$_3$. Powder X-ray diffraction patterns of the ground crystals demonstrate pure perovskite phase for both MAPbBr$_3$ and MAPbI$_3$ (Fig. 1d,e). Single-crystal X-ray diffraction analysis showed a good match with previous single crystals grown at room temperature using antisolvent vapour-assisted crystallization$^{17}$ (Supplementary Table 1). Scanning electron microscopy images of the cleaved crystals show the absence of any grain boundaries, indicating the single-crystalline nature of both crystals (Supplementary Fig. 2).

Further growth of the crystal was achieved by carefully removing the crystal and placing it in a fresh 1 M solution of the precursors (Fig. 2a). As shown in Supplementary Movie 2 for MAPbBr$_3$, we observed a possible shape control of the crystal by the geometry of the crystallization vessel. Hence, single crystals of MAPbBr$_3$ and MAPbI$_3$ were synthesized with a number of different shapes by changing the geometry of the vessel in which crystallization takes place (Fig. 2b).

Optical and transport properties. Further, we investigated optical and transport properties of the crystals, demonstrating that MAPbX$_3$ obtained using ITC in few hours are comparable quality to previously reported crystals grown in several weeks. From the steady-state absorption measurements a sharp band edge is observed (Fig. 3a,b). Band gaps extracted from Tauc plots show values of 2.18 and 1.51 eV for MAPbBr$_3$ and MAPbI$_3$, respectively. The band gap values for crystals grown using ITC are in a good agreement with the values reported for single crystals grown at room temperature through antisolvent vapour-assisted crystallization$^{17}$. The photoluminescence peak position of MAPbBr$_3$ and MAPbI$_3$ single crystals is located at 574 and
820 nm, respectively, matching the values reported earlier for the same single crystals grown using antisolvent vapour-assisted crystallization\(^\text{17}\).

To investigate the excited-state lifetime of these single crystals, we monitored both the ground-state bleach recovery and the excited-state absorption in the nano- and microsecond time regime using nanosecond transient absorption spectroscopy with broadband capabilities. Two time components are observed for both single crystals. A fast component of \(t_E^{28\pm5\text{ ns}}\) and \(t_E^{18\pm6\text{ ns}}\) together with a slower decay of \(t_E^{300\pm26\text{ ns}}\) and \(t_E^{570\pm69\text{ ns}}\) were measured for MAPbBr\(_3\) and MAPbI\(_3\) crystals, respectively. These measured surface (fast component) and bulk (slow component) carrier lifetimes are in good agreement with the ones reported recently for the same kinds of single crystals\(^\text{17}\).

The carrier mobility \(\mu = \mu_p \approx \mu_n\), where \(\mu_p\) and \(\mu_n\) are hole and electron mobility, respectively, as MAPbX\(_3\) is an intrinsic semiconductor\(^\text{26}\) of MAPbX\(_3\) (X = Br\(^-\), I\(^-\)) was estimated from the dark current–voltage (I–V) characteristics, following the standard space charge-limited current model. The I–V traces showed the Mott–Gurney’s power law dependence, for instance, an Ohmic region at the lower and a space charge-limited current model at higher bias. A quadratic dependence of the transition from the Ohmic to Child’s law through the trap filled limit (TFL) was observed in both MAPbBr\(_3\) and MAPbI\(_3\) crystals, respectively. The carrier mobilities and the trap densities (\(n_{\text{traps}}\)) were estimated to be 24.0 cm\(^2\) V\(^{-1}\) s\(^{-1}\) and \(3 \times 10^{10}\) cm\(^{-3}\) for MAPbBr\(_3\) crystals (Fig. 4c), as well as 67.2 cm\(^2\) V\(^{-1}\) s\(^{-1}\) and \(1.4 \times 10^{10}\) cm\(^{-3}\) for MAPbI\(_3\) crystals (Fig. 4d).

We calculated the carrier diffusion length by combining carrier lifetime with mobility \(L_D = (\mu \tau k_B T/e)^{1/2}\) (where \(k_B\) is Boltzmann’s constant and \(T\) is the sample’s temperature). By using the longer carrier lifetime (bulk component), a best-case carrier diffusion...
length was calculated to be \(\sim 4.3\) \(\mu\)m for MAPbBr\(_3\) and \(\sim 10.0\) \(\mu\)m for MAPbI\(_3\). A worst-case diffusion length could be estimated from the shorter carrier lifetime, corresponding to the surface component: \(\sim 1.3\) and \(\sim 1.8\) \(\mu\)m for MAPbBr\(_3\) and MAPbI\(_3\), respectively. Hence, despite the rapid rate with which crystals were grown via ITC, their transport characteristics together with trap-state densities are comparable to single crystals prepared with classical techniques, which were grown over a much longer period of time.

**Discussion**

We observed experimentally that perovskite crystals formed in the precursor solution at elevated temperatures dissolved back when the solution temperature was decreased to room temperature. This observation demonstrates that the thermodynamic stability of a precipitated hybrid perovskite compound has seemingly paradoxical temperature dependence, since simple monomolecular compounds are expected to dissolve at higher temperatures. Therefore, it is instructive to analyse how such a situation may arise. We hypothesize that this phenomenon might be related to the formation of complexes of precursors (whose nature is not the subject of this report and is under intensive study) or their products with the solvent.\(^{23,27,28}\) The theory presented below illustrates how these complexes can affect the temperature-dependent stability of the precipitate and reverse its effect depending on the different parameters of the system.

Suppose there is only one type of molecular precursor controlling the crystallization of a complex compound such as a perovskite, then the formation of complexes involving the precursor molecule and solvent molecules may significantly affect the precipitation of the compound. To illustrate this situation we analyse the thermodynamic stability of a monomolecular precipitate made of molecules A in the solution, where molecules

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**Figure 3** | **Steady-state absorption and photoluminescence.** (a) MAPbBr\(_3\) single crystal. (b) MAPbI\(_3\) single crystal. Insets: corresponding Tauc plots displaying the extrapolated optical band gaps.

**Figure 4** | **Carrier lifetime measurements and \(I-V\) traces.** (a,b) Transient absorption of (a) MAPbBr\(_3\) and (b) MAPbI\(_3\) crystals. (c,d) \(I-V\) of perovskite crystals exhibiting different regions obtained from the log \(I\) versus log \(V\) plots. The regions are marked for Ohmic (\(I \sim V^n\)), TFL (\(I \sim V^n > 3\)) and Child’s regime (\(I \sim V^n - 2\)). The trap densities were calculated from the Child’s regime shown in (c,d).
A can form complexes with solvent molecules, the complex’s binding energy being $\varepsilon_C$. As an ultimate stable state always contains only one precipitated particle, and to avoid secondary issues related to crystal facets, we assume that a single precipitated A-particle is placed in a unit volume of solution and has a spherical shape.

In general, the stability of precipitated solids in a solution is determined by several conditions based on the balance of chemical potentials of all its molecular or atomic constituents present in the solution and in the solid form. These conditions must also take into account the presence of complexes formed by the constituents in the solution. In our case, these conditions are the equality of the chemical potentials of A-molecules in the precipitated number of A-molecules, as observed by experimentally for hybrid perovskites. This effect, as can be seen from equation (4), takes place if

$$\varepsilon_C > \varepsilon \cdot \left(1 + \frac{v_C}{v_A} \cdot \left(n_{SA} \cdot v_S / v_A\right) \cdot e^{\frac{\varepsilon_C - \varepsilon}{T}}\right),$$

or if we accept that $\frac{\varepsilon}{T} \cdot \left(n_{SA} \cdot v_S / v_A\right) \cdot e^{\frac{\varepsilon}{T}} \ll 1$ (that is, large enough $\varepsilon_C/T$ ratio), then the inequality given by equation (5) reduces to $\varepsilon_C > \varepsilon$. These analytical relation can be further understood in physical terms as follows: at low temperatures most of the A-molecules are bound in the complexes with the solvent; therefore, the solution has no supersaturation in terms of concentration of unbound A-molecules. When the temperature increases, the concentration of unbound A-molecules increases (because of dissociation of the complexes) and may reach the supersaturation, thus triggering the precipitation of A-particles. Conversely, when the temperature of the solution containing the precipitated A-particle is decreased, the concentration $n_A$ of unbound A-molecules is also decreased because of formation of many more complexes with solvent. This decrease in $n_A$ makes the solution too diluted in A-molecules such that the particle has to transfer some molecules to the solution, that is, it dissolves. It should be noted that the process of crystallization is endothermic with respect to A-molecules, as a molecule moves from the complex with higher binding energy to the precipitate, where its binding (cohesive) energy is lower. Therefore, the crystallization reaction consumes thermal energy.

The temperature behaviour described by equation (5) provides a qualitative framework to explain the effects observed experimentally for perovskite materials. A quantitative analysis requires a detailed investigation of the molecular content of the precursor solution, a subject of future research.

In summary, we report the novel observation of inverse solubility of hybrid organo-lead trihalide perovskites. A careful choice of solvent, temperature and other parameters made it possible to utilize this method to rapidly grow single crystals of MAPbBr₃ and MAPbI₃ in hot solutions via ITC. Despite the fact that these crystals grow very fast, they exhibit carrier transport properties comparable to those grown by the usual cooling or antisolvent vapour-assisted crystallization techniques. The ‘quantum leap’ in crystal growth rates in ITC, over the previously reported growth methods so far used for single crystal-hybrid perovskites, represents a major breakthrough in the field of perovskite single crystals for enabling the wide applications of these remarkable semiconductor materials.

Methods
Chemics and reagents. Lead bromide (≥98%), lead iodide (99.999% trace metal basis), DMF (anhydrous, 99.8%) and GBL (≥99%) were purchased from Sigma Aldrich. MAPbBr₃ and MAPbI₃ were purchased from Dyexol Limited (Australia). All salts and solvents were used as received without any further purification.

Synthesis of MAPbX₃ single crystals. One molar solution containing PbX₂ and MAX was prepared in DMF or GBL for X = Br-, I⁻, respectively. The bromide solution was prepared at room temperature, whereas the iodide solution was heated up to 60°C. The solutions were filtered using PTFE filter with 0.2-µm pore size. Two milliliters of the filtrate were placed in a vial and the vial was kept in an oil bath undisturbed at 80 and 110°C for Br- and I- based perovskites, respectively. All procedures were carried out under ambient conditions and humidity of 55–57%. The crystals used for measurements were grown for 3 h. The reaction yield for MAPbBr₃ and MAPbI₃ was calculated to be 35 and 11 wt %, respectively.

Measurement and characterization. Powder X-ray diffraction was performed on a Bruker AXS D8 diffractometer using Cu-Kα radiation. Single-crystal X-ray diffraction was performed on Bruker D8 Venture, CMOS detector, microfocus copper source. The steady-state absorption and photoluminescence were recorded using Cary 6000i spectrophotometer with an integrating sphere and Edinburgh Instrument spectrophluorometer, respectively. Time-resolved transient absorption decays were measured with a femto-nanosecond pump – probe set-up. The excitation pulse at 480 nm was generated using a spectrally tunable optical Parametric Amplifier (Light Conversion LTD) integrated to a Ti:sapphire femtosecond regenerative amplifier operating at 800 nm with 35 fs pulses and a repetition rate of 1 kHz. The white light probe pulse, on the other hand, was generated by a super continuum source<sup>53</sup>. The pump and probe beams were overlapped spatially and temporally on the sample, and the transmitted probe light from the samples was collected and focused on the broad-band ultraviolet-visible-near-infrared detectors to record the time-resolved excitation-induced difference spectra, $I_V$.
was sandwiched between the rectangular electrodes (3 mm × 2 mm) Au (100 nm), deposited on both sides of the single crystal, by an Angstrom thermal evaporator at a 0.5 Å s⁻¹ deposition rate. The thickness and rate of deposition during the evaporation of Au contact was monitored by an Inficon thickness monitor. The thickness of MAPbBr₃ and MAPbI₃ crystals were measured as 2.32 and 2.49 nm, respectively, by the digital Vernier caliper. The typical nonlinear dark current, voltage plots followed the Lambert’s theory, where the current was found to be limited by the trap-assisted space charge conduction. Onset voltage (VTFL) for the TFL was used for the calculation (equation (6)) of density of traps (ntraps) in the perovskite crystals

\[
n_{\text{traps}} = \frac{2 \varepsilon V_{\text{TFL}}}{d \varepsilon_0}
\]

where \( q \) is the electronic charge, \( d \) is the thickness of the crystal, \( \varepsilon \) is the dielectric constant of the material (25.5 for MAPbBr₃ and 32 for MAPbI₃) [18,31] and \( \varepsilon_0 \) is the vacuum permittivity.

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