**Room-Temperature Synthesis, Growth Mechanisms and Optical Properties of Organic-Inorganic Halide Perovskite CH$_3$NH$_3$PbX$_3$ (X= I, Br and Cl) Single Crystals**

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Room-Temperature Synthesis, Growth Mechanisms and Optical Properties of Organic-Inorganic Halide Perovskite CH$_3$NH$_3$PbX$_3$ (X= I, Br and Cl) Single Crystals

Maryam Bari $^a$, Hua Wu $^{b,a}$, Alexei A. Bokov $^a$, Rana Faryad Ali $^b$, Hamel N. Tailor $^a$, Byron D. Gates $^a$, and Zuo-Guang Ye $^a$*

Single crystals of the organic-inorganic halide perovskites are well needed in order to fully explore their potential in optoelectronic applications and to gain a fundamental understanding of their intrinsic properties. Previously, inverse temperature crystallization (ITC) was used to grow halide perovskite crystals at high temperatures ($\approx 100 ^\circ$C). Here, we develop an effective synthetic technique by which the CH$_3$NH$_3$PbX$_3$ (X= I, Br, and Cl) crystals are grown in polar solvents at room temperature (except for CH$_3$NH$_3$PbI$_3$ grown at 45 $^\circ$C) in a relatively short time. A constant supersaturation during the crystal growth is created to produce large single crystals, which is achieved during room temperature crystallization (RTC) through controlled solvent evaporation. We investigate the effects of the temperature and supersaturation level on the nucleation kinetics of CH$_3$NH$_3$PbI$_3$, as an example, and propose and compare the different growth pathways. The crystal structural analysis, steady-state absorption, photoluminescence, and charge-transport properties demonstrate excellent long-term stability (over 2 years) of the RTC-grown CH$_3$NH$_3$PbX$_3$ (X= Br, Cl) crystals against environmental degradation and moisture. The crystal optical properties are studied by polarized light microscopy, revealing birefringent ferroelastic domain structures characteristic of the tetragonal (X = Br) or orthorhombic (X = Cl) symmetry and high optical quality. This work presents a general strategy for designing, controlling, and optimizing the growth of high-quality halide perovskite crystals, which is an important step forward toward realizing high-end and stable optoelectronic devices such as nonlinear absorbers, photocatalyst, and micro- electromechanical actuators.

Introduction

Organic-inorganic halide perovskites have rapidly emerged at the forefront of photovoltaic devices exhibiting a power conversion efficiency of over 22% for the CH$_3$NH$_3$PbI$_3$ solar cells, with a relatively low cost and simple processing technique, making them a serious competitor in commercial photovoltaics. As a part of the ABX$_3$ perovskite family, MAPbX$_3$ (MA = CH$_3$NH$_3$; X = I, Br and Cl) have shown unprecedented potential for the various single crystal (SC)-based devices such as photon, X-ray and gamma-ray detectors, owing to their high photosensitivity and detectivity with fast response features. More recently, such perovskites were found to be high-performance nonlinear absorbers (e. g., MAPbBr$_3$ SC), making them a viable alternative to silicon in optical communication and information processing, and to exhibit a large electrostriction response (e. g., MAPbI$_3$ SC), potentially useful for such technologies as sonar transducers and micro- electromechanical systems. For many applications, the use of halide perovskite SC with high purity and low defect concentrations could lead to enhanced device performance and stability over their polycrystalline counterparts. These crystals also appear to be crucial for investigating the intrinsic nature of structural and photo-physical/chemical properties.

So far, several approaches have been developed to grow halide perovskite crystals, including the solution temperature lowering (STL), antisolvent vapor-assisted crystallization (AVC), and inverse temperature crystallization (ITC) methods. STL is a relatively simple process that involves cooling a preheated solution, e. g., a hydroiodic acid (HI) solution for the growth of MAPbI$_3$ SC. Seed-assisted growth such as bottom-seeded solution growth (BSSG) and top-seeded solution growth (TSSG) techniques were applied to increase the size and quality of the crystals, in which a small crystal is used as seed, followed by the STL process. Large MAPbI$_3$ and MASnI$_3$ single crystals were obtained using these methods, but growing centimeter-sized crystal usually takes about one month. The other hand, the solubility of halide perovskites decreases with increasing temperature in certain polar solvents such as γ-butyrolactone (GBL), dimethyl sulfoxide (DMSO), and N, N-dimethylformamide (DMF). Based

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on this feature, ITC was designed to grow the MAPbX₃ (X = I, Br, and Cl) crystals at high temperatures over several hours. ITC can produce large crystals (up to a two-inch size) by seed-induced heterogeneous nucleation approach, which have been used to fabricate various devices of high performance, such as SC solar cells with a power conversion efficiency (PCE) ~ 21%. SC photodetectors.

High temperature (HT) growth may induce some invisible or visible defects such as inclusions, dislocations, strain, and growth steps in the crystals especially when the thermal gradient during the growth cannot be minimized, which may negatively impact their carrier properties, as evidenced in the literature with different values of carrier mobility and lifetime. More recently, attention has been paid to the low temperature (LT) growth to improve the structural perfection, and a number of approaches have been developed such as low-temperature gradient crystallization (LTGC), low temperature (45 °C) rapid crystallization, room-temperature (RT) liquid-diffused separation induced crystallization (LDSIC), RT growth of MAPbCl₃, and antisolvent assisted inverse temperature growth of MAPbI₃. The LT-grown crystals exhibited better carrier performance (an increase by ~3 times in charge mobility and lifetime) with the density of defect traps almost half of that of the HT-grown crystals.

In terms of processing, the precursor solution typically needs to be replaced several times to obtain large crystals by ITC, which results in low efficiency and a time-consuming process. This issue also appears in the LT growth methods by which it often takes several weeks to grow large crystals with precise temperature control. For instance, the MAPbCl₃ crystals of medium size were lately grown at RT by solvent evaporation in four weeks.

Given the challenges of the currently used methods, it is necessary to develop a rapid and effective technique to grow the MAPbX₃ single crystals at room temperature, in order to meet the increasing demand for halide perovskite single crystals both for scientific investigations and device applications and to understand the complex growth mechanisms. In this work, we have successfully grown the MAPbX₃ crystals at room temperature (except for X = I at 45 °C) via controlled solvent evaporation. By this optimized room-temperature crystallization (RTC) process, a large quantity of the crystals of several millimeters in size can be grown in just several hours for X = I & Br, and a few days for X = Cl without the need for crystal seeding. More importantly, the first MAPbBr₃ and MAPbCl₃ crystals grown by RTC in 2018 demonstrate excellent long-term stability against environmental degradation and moisture. In addition, the crystallization kinetics of MAPbCl₃ at room temperature and high temperature is investigated in detail. The solubility behaviour, induction time, interfacial energy, and some important nucleation parameters are determined. The absorption, photoluminescent (PL), and PL decay time properties and ferroelastic domain structures of the RTC-grown crystals are characterized. From the experimental results, the crystal growth mechanisms of MAPbCl₃ at 25 °C and 110 °C are proposed and compared. Based on this analysis, the factors controlling the size and quality of crystals are discussed, providing the optimum conditions for the RT growth of halide perovskite crystals.

**Results and discussion**

**Crystal Growth of MAPbX₃, Structural Characterization, and Long-Term Stability.** To grow the MAPbX₃ (X=I, Br and Cl) crystals, a saturated precursor solution was prepared, then cooled down and left at room temperature (at 45 °C for X = I) in a semi-closed vial for several hours (see the details in the Experimental Section). The solvents were selected based on their ability to dissolve both inorganic and organic halide precursors. Various combinations of solutes and solvents were examined, and the best results were obtained by dissolving CH₃NH₃X and PbX₂ (X = I, Br, and Cl) into GBL to grow MAPbI₃, into DMF to grow MAPbBr₃ and into DMSO to grow MAPbCl₃. The schematic diagrams of the RTC method along with the resultant crystals are presented in Fig. 1a-c. A large number of crystals were grown simultaneously (see Supporting Information, Fig. S1), and Fig. 1a shows a relatively large MAPbI₃ crystal that was grown in just 3 hours. Similarly, many transparent MAPbBr₃ crystals of orange colour with sizes between ~ 2 and 20 mm³ were obtained at room temperature in less than 12 hours, as shown in Fig. 1b and Fig. 1S. Fig. 1c shows one of the grown MAPbCl₃ crystals with a size of ~ 4 mm³ obtained by RTC after two days of growth. Interestingly, the crystals grew up to ~ 70 mm³ after three more days, while maintaining good transparency.

The required supersaturation for RTC crystallization was attained by controlled evaporation of the solvent, and the evaporation rate determines the growth time. The growth time for the MAPbI₃ and MAPbBr₃ crystals was much shorter than for MAPbCl₃, which could be due to strong coordination of DMSO with the halide perovskite, leading to slower evaporation of DMSO. In addition, DMSO has a lower vapor pressure (~ 0.42 Torr) than DMF (~ 2.7 Torr) and GBL (~ 1.5 Torr) at room temperature, which is also an important contributor to its lower solvent evaporation rate. To compare the RTC growth with the HT growth, we used ITC to grow the MAPbCl₃ crystals at high temperatures. A saturated solution of the precursors was prepared in DMSO at 60 °C and the solution was then heated to 110 °C in a fully closed vial over 12 hours. Due to the negative solubility of MAPbCl₃ in polar solvents such as DMSO, a supersaturation was induced in the solution, leading to crystallization at 110 °C. Fig. 1d shows a sketch of the ITC process and selected large grown crystals [while many smaller (≤ 6 mm³) crystals were formed in 12 hours]. Then, the seed-assisted method was used to grow larger crystals. In this process, a spontaneously grown crystal was selected as the nucleation seed and placed into a fresh precursor solution at 110 °C for an additional 12 hours to form a larger crystal (Fig. 1d). Our results confirm the literature reports that the ITC method is a fast-growing process which can lead to high-quality small to medium size crystals and that, generally, the transparency of the HT-grown crystal drops in the second run (of seeded) growth as the crystal size increases. In terms of yield, with no need for seeding, the RTC technique results in yields of ~40 wt%, 60 wt% and 15 wt% for...
X = I, Br, and Cl, respectively, making it a more efficient and cost-effective method compared to the HT growth with the yields of 5 wt% for MAPbCl$_3$ from this work, and 11 wt% and 35 wt% for X = I and Br, respectively, according to a previous report.\textsuperscript{28}

Fig. 1e-g shows the powder and single-crystal X-ray diffraction patterns of the halide perovskite crystals grown using the RTC method. As displayed in the lower panels of Fig. 1e-g, the results of a Pawley refinement analysis confirmed the formation of a perovskite structure with a cubic symmetry ($Pm\bar{3}m$ space group) for the MAPbBr$_3$ and MAPbCl$_3$ crystals and a tetragonal symmetry (I4/$mcm$ space group) for the MAPbI$_3$ crystals. These refinements yield the lattice parameters of $a = 5.665$ Å and 5.918 Å for MAPbCl$_3$ and MAPbBr$_3$, respectively, and $a = 8.877$ Å and $c = 12.628$ Å for MAPbI$_3$, consistent with previously reported data.\textsuperscript{26} Furthermore, the single-crystal XRD patterns of the as-grown MAPbCl$_3$ and MAPbBr$_3$ crystals show the presence of the (100), (200), (300), and (400) peaks with strong diffraction intensities, indicating that the naturally developed facets of the crystals belong to the (h00) planes (Upper panels of Fig. 1f and 1g). The MAPbI$_3$ crystal shows sharp peaks of (112) and (224), belonging to the (112) plane of the tetragonal structure (Upper panel of Fig. 1e). The full width at half maximum (FWHM) of the first two peaks was calculated for MAPbX$_3$ (X = I, Br, and Cl). The FWHM values of the (112) and (224) peaks are 0.040° and 0.045°, respectively, for MAPbI$_3$. The FWHM values of the (100) and (200) peaks are 0.026° and 0.031° for MAPbBr$_3$, and 0.034° and 0.039° for MAPbCl$_3$, respectively. These values are in the narrow range of ~ 0.026° - 0.045°, indicating that the RTC-grown single crystals are well-orientated and of good crystallinity, comparable to the quality of the MAPbX$_3$ crystals reported in the literature.\textsuperscript{36,38,43} Fig. S2 shows the result of energy-dispersive X-ray spectroscopy (EDX) analyses obtained from the MAPbX$_3$ crystals. The Pb: X ratio averaged from several EDX experiments at different points on a crystal surface is found to be 1: 3 (± 0.06), in close agreement with the nominal composition of the perovskite phase.
The long-term stability of the crystals, grown by RTC more than two years earlier, against environmental degradation and moisture was also investigated and no decomposition was observed from the PXRD patterns of the MAPbX₃ (X = Br, Cl) crystals, indicating that no degradation had happened over that period of time. These crystals have fully preserved their crystal structure, phase, morphology, and transparency (Fig. S3). However, the PXRD pattern of the MAPbI₃ crystals, which were grown a year earlier, shows some additional peaks corresponding to the yellow layer formed on the surface, which was identified to be \((\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}\) (Fig. S4). As reported previously, the MAPbI₃ crystals can absorb ambient moisture to form a hydrate phase such as \((\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}\). Note that the crystals were not stored in a sealed dry condition but rather kept in an ordinary container in ambient condition.

**Solubility and Supersaturation Studies.** Our experiments demonstrate that the halide perovskite crystals can be grown in polar solvents at room temperature via solvent evaporation. To explain the RT and HT crystallizations of halide perovskites, it is necessary to understand the underlying mechanisms involved in the processes, which are closely related to saturation and solubility behaviour. Since the supersaturation is the main driving force for crystallization from solution, determining the optimum supersaturation is crucial for the RT growth of MAPbX₃, and it can be achieved by manipulating temperature, solution concentration, and solvent evaporation.

The solubility limit as a function of temperature enables us to find the supersaturation at different temperatures. The solubility of MAPbX₃ in polar solvents was determined by measuring the equilibrium concentration \(C^*\) between 25 °C and 120 °C, as shown in Fig. 2a-c. The actual precursor concentration \(C\) for the prepared solutions of MAPbI₃, MAPbBr₃, and MAPbCl₃ is 6.2 g/mL, 7.2 g/mL, and 7.0 g/mL, respectively (as marked by the red dashed lines in Figure 2a-c). The solubility of MAPbI₃ and MAPbCl₃ increases linearly with increasing temperature from 25 °C to 60 °C, followed by a decrease from 60 °C to 120 °C. The inverse solubility between 60 °C and 110 °C results in, upon heating, a decrease by 11% and 30% in the solubility of X = I and Cl, respectively. This is equivalent to the creation of 11% (for X = I) and 30% (for X = Cl) supersaturation due to solubility reduction \(S_{sr}\). In contrast, the normal solubility behaviour existing between 60 °C and 25 °C results in, upon cooling, a solubility reduction by 11% (for X = I) and 12.5% (for X = Cl), giving rise to the corresponding supersaturation \(S_{co}\). The MAPbBr₃ shows an absolute inverse solubility, as its solubility decreases monotonically with increasing temperature (Fig. 2b). While the supersaturation at high temperatures due to the negative solubility trend explains the principle of ITC, the supersaturation at 25 °C suggests that it is possible to grow the MAPbI₃ and MAPbCl₃ crystals at room temperature, justifying the feasibility of the RTC method. To test this hypothesis, we first cooled a saturated solution of X = I and Cl from 60 °C to 25 °C in a fully sealed vial and kept it at room temperature for several hours. No crystals were obtained for X = Cl. Some yellowish crystals were formed at the bottom of the flask containing the X = I solution, which were found to be an intermediate product of \((\text{MA})_3\text{[PbI}_4\text{]}\) from the Pawley refinement of the PXRD pattern. This result is consistent with the intermediate adduct of perovskite precursors and GBL precipitated at RT, as previously found (Fig. S5). To avoid the undesired formation of the adduct, the growth temperature of MAPbI₃ was adjusted to 45°C.

This observation also shows that the 12.5% supersaturation was insufficient to trigger nucleation of MAPbCl₃ crystals at RT. Thus, an additional approach must be taken to increase supersaturation at room temperature, namely by solvent evaporation, which was also applied for X = Br and X = I (at 45 °C). The solutions were then transferred to a half-closed cap vial to allow the solvent to evaporate to produce more supersaturation (Fig. 1a-c). Various solvent evaporation conditions were investigated in which 0, 25, 50, 75, and 100 % of vial cap was closed and the optimum crystal growth was achieved using a vial with a half (50%-closed) cap (a 50 mL vial was used with a surface area of ~16 cm²) for X = Br and Cl, and fully open vial for X = I. We further calculated the total (optimal) supersaturation \(S_{total}\) in our experimental conditions by combining the three different contributions to the supersaturation, i.e., \(S_{total} = S_{se} + S_{sr} + S_{cg}\), where \(S_{se}\) corresponds to the solubility reduction (Fig. 2a-c), \(S_{sr}\) results from the solvent evaporation and \(S_{cg}\) is the negative supersaturation arising from crystal growth due to the decrease in solute concentration (see the detailed calculations in the Experimental Section). All the three individual factors \((S_{se}, S_{sr}, S_{cg})\) together with the total supersaturation \(S_{total}\) were calculated versus growth time as shown in Fig. 2d-f. For example, \(S_{total}\) of MAPbCl₃ increases above 12.5 % at the early stage due to solvent evaporation, leading to nucleation and growth. As the growth proceeds, \(S_{total}\) reaches a value of 16 % after 2 days and maintains that level until day 5, providing an optimum window for the growth of MAPbCl₃ crystals at room temperature. The growth process slows down after five days when the total supersaturation drops to 11 % due to the formation of the crystals (Fig. 2f). Similar work was carried out for MAPbBr₃ and MAPbI₃ to find the desirable supersaturation for the RT growth, from which \(S_{total}\) was measured to be 13 % and 12 % for X = Br and I, respectively. It takes 2 h and 3 h for the nucleation onset to occur, and the growth process slows down after 12 h and 6 h for X = Br and I, respectively. For MAPbI₃, the actual concentration \(C\) of the solution (0.62 gr/mL) is lower than the equilibrium concentration \(C^* \approx 0.83\) gr/mL at the growth temperature of 45 °C (marked by the red arrow in Fig. 2a), implying that solvent evaporation is needed first to compensate for the negative solubility reduction \(S_{sr} \approx -25\)%, and then to produce supersaturation for crystalization (Fig. 2d). MAPbBr₃ has retrograde solubility behaviour in the DMF solvent (Fig. 2b), and no \(S_{sr}\) exists at room temperature, hence, \(S_{total}\) is the sum of \(S_{se}\) and \(S_{cg}\) (Fig. 2e).
Nucleation Mechanisms of MAPbCl₃ in RTC & ITC. As shown in Fig. 1c & 1d, the size of the grown crystals can be affected by the growth temperature. Here, we use classical homogeneous nucleation theory⁴⁶ to deduce the nucleation kinetics of the MAPbCl₃ crystals at 25 °C by RTC and 110 °C by ITC.

According to the classical nucleation theory, the relation between the induction time and the supersaturation ratio can be expressed as:

\[
\ln{\tau} = K + \frac{16\pi\sigma V_m^2 N_A}{3RT^2(\ln{S_r})^2}, \tag{1}
\]

where \( \tau \) is the induction time, \( K \) is a constant, \( \sigma \) is the interfacial energy, \( V_m \) is the molar volume (= \( M/p \), with \( M \) being the molar mass and \( p \) the density of MAPbCl₃), \( N_A \) is the Avogadro’s number, \( R \) is the universal gas constant, \( S_r \) is the supersaturation ratio (\( S_r = C/C^* \) with \( C \) being the actual concentration and \( C^* \) the equilibrium concentration), and \( T \) is the temperature. The induction time (\( \tau \)), the time required for the crystallization of critical nuclei with a detectable size is important for evaluating the nucleation kinetics in this work. The experimental values of the induction time were measured at various supersaturation ratios (\( S_r \)) at two different temperatures (25 °C & 110 °C) and are plotted in Fig. 3a. At a given temperature, \( \tau \) decreases with increasing supersaturation ratio. \( \tau \) is found to be 300 minutes at the maximum \( S_r (= 1.15) \) at 25 °C, while only 103 minutes at the maximum \( S_r (= 1.44) \) at 110 °C. According to Equation 1, a small \( \tau \) value was obtained by ITC, favouring a fast crystal nucleation.

In the RTC process, it is believed that several precursor-solvent complexes are formed, which cannot be easily dissociated at room temperature (to be discussed in detail in the following section). Thus, the solubility reduction (supersaturation) is small, leading to a slower nucleation process and a longer induction time. Figure 3b shows the \( \ln{\tau} \) versus \( 1/(\ln{S_r})^2 \) plots of MAPbCl₃ at 25 °C and 110 °C, where the dashed lines are the least-square linear fittings of the experimental data. \( K \) and \( V_m \) in Equation 1 can be considered as constants. Then, the interfacial energy \( \sigma \) of the crystal can be calculated using the following equation:

\[
\sigma = RT\left(\frac{3m}{16\pi V_m^2 N_A}\right)^\frac{3}{2}, \tag{2}
\]

when \( m \) is the slope of the linear fitting between \( \ln{\tau} \) and \( 1/(\ln{S_r})^2 \). As shown in Fig. 3b, the linear behaviour of \( \ln{\tau} \) versus \( 1/(\ln{S_r})^2 \) consists of two segments with different slopes, indicating two different nucleation mechanisms in the respective supersaturation regions. The higher supersaturation region (lower \( 1/(\ln{S_r})^2 \)) in Fig. 3b with a steeper linear slope corresponds to a homogeneous nucleation, while the shallower linear relation in the lower supersaturation region (higher \( 1/(\ln{S_r})^2 \)) indicates a heterogeneous nucleation. The interfacial energy of the homogeneous nucleation was calculated by using the steeper slope of the linear fitting, and it is found to be 2.5 mJ/m² for the RTC process and only 1.7 mJ/m² for the ITC one. These interfacial energy values agree well with the values reported for the growth of other organic compounds.⁴⁷,⁴⁸ The smaller value in ITC implies a lower
interfacial energy needed for nucleation and consequently the formation of more nuclei with small sizes at high temperatures. Based on the homogeneous nucleation theory, the nucleation parameters for 25 °C and 110 °C, such as the critical radius of nuclei ($r_c$), the Gibbs free energy per volume unit ($\Delta G_v$), and the critical free energy barrier ($\Delta G_c$) as a function of supersaturation, were calculated and the results are listed in Table 1 (detailed calculations of these parameters are provided in the Supporting Information). According to Table 1, $\Delta G_c$ decreases with the increase of supersaturation, and the $\Delta G_c$ values at 110 °C are much smaller than those at 25 °C, indicating that the temperature and the supersaturation are two main factors that determine the crystal nucleation process. The critical radius of the nucleus ($r_c$) of the MAPbCl$_3$ crystals as a function of supersaturation is plotted in Figure S6. It can be seen that the $r_c$ values at 110 °C are significantly smaller than those at 25 °C, which indicates that the higher temperature and the resultant higher supersaturation favour a decrease in the interfacial energy and the critical free energy barrier, leading to easier nucleation and smaller critical nuclei. In RTC, the large critical energy barrier allows only the crystals with nucleus radii larger than the critical one to grow, limiting the number of nuclei. Consequently, only a few large crystals are formed. These calculations and analysis are in good agreement with our experimental observations of the crystal growth by RTC and ITC (see Fig. 1c & d), respectively.

**Growth Mechanisms of MAPbCl$_3$ by ITC and RTC.** The analysis of the nucleation process allows us to deduce the growth mechanisms of MAPbCl$_3$ at high temperatures (ITC) and at room temperature (RTC), and to determine the factors influencing the quality, quantity, and size of the grown crystals. Figure 4a and 4b depicts the growth mechanisms for ITC and RTC, respectively. In ITC (Fig. 4a), in the initial stage (I), the precursor solution prepared at 60 °C may contain two types of ions: the solute ions of Pb$^{2+}$, Cl$^-$ and MA$^+$ and the precursor-solvent complex ions such as PbCl$_3$ and [PbCl$_3$((CH$_3$)$_2$SO$_3$]$^-$. In RTC, the large critical energy barrier allows only the crystals with nucleus radii larger than the critical one to grow, limiting the number of nuclei. Consequently, only a few large crystals are formed. These calculations and analysis are in good agreement with our experimental observations of the crystal growth by RTC and ITC (see Fig. 1c & d), respectively.

**Table 1.** Interfacial energy ($\sigma$) and nucleation parameters (the critical radius of the nuclei ($r_c$), the Gibbs free energy per volume unit ($\Delta G_v$), and the critical free energy barrier ($\Delta G_c$)) for the growth of MAPbCl$_3$ crystals with different supersaturation ratios ($S_r$) at 25 °C and 110 °C.

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With the increase of temperature from 60 °C to 110 °C in ITC, the ionic complexes can extensively dissolve into the solution and produce a high concentration of ions (Intermediate Stage (II) in Fig. 4a), resulting in a high supersaturation, and hence a lowered interfacial energy and enhanced nucleation. By abruptly inducing a large supersaturation at a high temperature, many small crystals are formed quickly, accompanied by a decrease in the solute concentration (Final Stage (III) in Fig. 4a). The lowered concentration of solute ions prevents the crystals from growing to larger dimensions via spontaneous crystallization from the solution, which is no longer supersaturated. Therefore, to grow large crystals by ITC, it is necessary to use seed-assisted growth in which a high-quality pre-grown crystal is placed in a fresh supersaturated solution to grow further. In contrast, in the RTC process, by cooling from 60 °C to room temperature (Fig. 4b), the complexes do not dissociate as much as they do at high temperatures since the thermal energy is insufficient to break down completely the strong coordination bonds between DMSO and the precursor ions (Intermediate Stage (II) in Fig. 4b). Thus, the concentration of the precursor ions is lower in the solution at room temperature, which leads to lower interfacial energy, a small number of nuclei, and thereby larger crystals. To confirm the presence of those complex ions in the solution. The term "colloid" was previously used and it was shown that the colloid contains Pb$^{2+}$ and halide ions, which can be broken down by increasing the acidity of the solution. As expected, the dissociation of complex ions at room temperature is less favoured than at high temperatures, giving rise to a lower degree of supersaturation, and thereby a retarded crystallization process. Therefore, in the RTC process, the crystallization initiation or induction takes a longer time due to a higher critical energy barrier, leading to a larger critical nucleus size (see Table 1). From this stage on, the controlled solvent evaporation provides additional supersaturation to feed a sustainable growth over a period of up to 5 days (Final Stage (III) in Fig. 4b). The experimental data and analysis show that our designed RTC process provides a nearly constant total supersaturation of about 16% for the growth of MAPbCl$_3$ crystals.

**Crystal Morphology, Optical Quality, and Ferroelastic Domains.** The control of crystallization kinetics and thermodynamics, including thermal conditions and supersaturation, is known to determine the quality of the crystals.
grown crystals in terms of crystallinity and transparency.\textsuperscript{56-58} The quality of the HT- and RT-grown MAPbX$_3$ (X = Cl and Br) crystals were examined by optical microscopy, which revealed a rough surface with dark spots arising from defects/strains and inclusions on the MAPbCl$_3$ crystal grown by the seeded ITC method (Figure S8a). A much smoother surface with lower strain or inclusions was observed for the RT-grown crystals of MAPbCl$_3$ and MAPbBr$_3$, as shown in Fig. S8b-c, respectively. The sharp increase in supersaturation at high temperatures can cause an unstable growth that in turn leads to the uneven development of the growing layers, as observed in the HT-grown MAPbCl$_3$ crystals. In particular, the formation of new layers before a previous layer reaches the edge of the crystal due to the unstable growth condition results in the incompletely developed layers and thereby uneven growth steps. As the crystal grows, a sudden decrease in supersaturation occurs due to a high nucleation rate in the ITC process, which facilitates the nucleation in the regions with low surface energy such as the edges or corners of the crystals, and leads to the formation of the raised edges. In contrast, the good transparency and smooth surface of the RTC-grown crystals with less internal strains can be attributed to a more stable growth under a moderate constant supersaturation, leading to more complete layer-by-layer growth at room temperature.

Of note, a number of factors may affect the quality and morphology of the MAPbX$_3$ grown by RTC. For instance, the MAPbBr$_3$ crystals exhibit mixed cuboid and dodecahedral morphologies. This can be explained by the different growth rates along the main crystallographic directions, e.g. [100]$_{cub}$, [110]$_{cub}$ and [111]$_{cub}$, since a cuboid shape results from the fact that the growth rate is the slowest along the [100]$_{cub}$, while a dodecahedron forms when the growth rates are comparable along the three main directions, giving rise to visible (100)$_{cub}$, (110)$_{cub}$ and/or (111)$_{cub}$ facets. The growth conditions are known to affect the crystal morphology. It was reported that a higher X/PbX$_2$ ratio may favour the growth of cuboids over dodecahedral morphology.\textsuperscript{59} In the RTC method, the formation of complex ions in the MAPbBr$_3$ and MAPbCl$_3$ solutions or evaporation of the CH$_3$NH$_3$ ions from the MAPbI$_3$ solution at 45°C may change the solute ratios and consequently affect the quality and morphology of the crystals. On the other hand, the crystal growth rate is determined by the deposition rate of the solute onto the crystal surface and the diffusion rate of the solute in the solution where the deposition rate is controlled by temperature and solution concentration, while the diffusion rate is determined by the concentration gradient of the solution. There must be a balance between the deposition rate and the diffusion rate to grow a high-quality single crystal. In the RTC method, both temperature and concentration of the solution are constant, while the solvent evaporation can affect the concentration of the solution and its gradient. For MAPbBr$_3$ and MAPbI$_3$, the diffusion rate can be higher than the deposition rate because the evaporation rates of DMF and GBL are relatively high, especially GBL at 45°C. This condition creates oversupplied solutes, which can lead to imperfect crystals with twins and scars. Thus, limiting the solute diffusion process could control the crystal growth rate and thereby improve the quality of the grown crystals. The optical transparency of the RTC-grown crystals allows us to observe and analyse their domain structures and crystal symmetry by polarized light microscopy (PLM) in transmission. Figure 5a and 5b shows selected PLM micrographs for X = Cl and X = Br, respectively. Both the MAPbCl$_3$ and MAPbBr$_3$ crystals appear to be dark (complete extinction) under crossed polarizers (0° < δ < 45°), indicating that they are optically isotropic at room temperature, consistent with the cubic symmetry (α phase) [Fig. 5a(1) & 5b(1)]. Upon cooling, the MAPbCl$_3$ crystal undergoes a phase transition from the cubic to an orthorhombic (β) phase at 178 K with the development of ferroelastic twin domains [Fig. 5a(2)] and then to another orthorhombic (γ) phase at a lower temperature of 172 K [Fig. 5a(3)]. Note that the PLM image of Fig. 5a(2) was taken with a first-order red (FOR) plate (λ = 530 nm) placed between the sample and the analyzer to distinguish the domain walls, which are orientated at the angles of 0/90° and 45°. The analysis of the domain structure and domain wall orientations reveals that the intermediate β phase of MAPbCl$_3$ belongs to the side-centred orthorhombic O$_3$ symmetry,\textsuperscript{20} rather than the tetragonal symmetry reported previously.\textsuperscript{26} The γ-phase is of primitive orthorhombic O$_2$ symmetry. On the other hand, the MAPbBr$_3$ crystal transforms, upon cooling, from the cubic to a tetragonal phase at 236 K, which appears as a single domain [Fig. 5b(2)], then to an orthorhombic O$_2$-phase at 152 K [Figure 5b(3)], and finally to another orthorhombic O$_2$-phase at 148 K [Figure 5b(4)]. More detailed information on the optical crystallography principles used for domain structure and crystal symmetry analysis can be found in our recent work.\textsuperscript{20} The characterization of other structural and physical properties of our crystals, especially for X = Cl, including crystal symmetry and domain configuration, ferroelasticity, Raman spectroscopy, neutron scattering, and dielectric constant also confirm the high quality of the RTC-grown crystals.\textsuperscript{20-22, 60}

Absorption, Photoluminescent (PL), and Time-resolved PL Properties. For potential optoelectronic applications, the optical properties of the MAPbX$_3$ crystals were investigated under ambient conditions in terms of absorption and photoluminescence (PL) response. Fig. 6 shows that the crystals exhibit a narrow PL peaks (blue curves) located at 445 nm, 545 nm, and 745 nm for MAPbCl$_3$, MAPbBr$_3$, and MAPbI$_3$, respectively, very close to the values reported previously.\textsuperscript{7,18,28} From the steady-state absorption measurements, a sharp band edge is observed at 420 nm, 547 nm and 780 nm for MAPbCl$_3$, MAPbBr$_3$, and MAPbI$_3$, respectively. The corresponding to a direct bandgap of 2.50 eV for MAPbCl$_3$, 2.10 eV for MAPbBr$_3$, and 1.47 eV for MAPbI$_3$, which is calculated from the Tauc plots (Inset in Fig. 6). Of note, the MAPbCl$_3$ and MAPbBr$_3$ crystals used for the optical investigation were grown more than two years ago, and their decent optoelectronic behaviour demonstrates the long-term stability of the crystals in terms of physical properties, in addition to the stability of composition, structure, and phase.

\textsuperscript{20} J. Name., 20xx, 00, 1-3
Fig. 5. Optical micrographic images of the (001)-oriented CH$_3$NH$_3$PbX$_3$ crystals (a: X = Cl, thickness = 100 μm; B: X = Br; Thickness = 140 μm) obtained by polarized light microscopy in transmission. a(1) and b(1): Both MAPbCl$_3$ and MAPbBr$_3$ crystals appear to be dark (in complete extinction) under crossed polarizers ($0^\circ < \delta < 45^\circ$), indicating that they are optically isotropic at room temperature, consistent with the cubic symmetry ($\alpha$ phase). a(2) and a(3): Ferroelastic twin domains and domain walls developed in the intermediate ($\beta$) phase with a side-centred orthorhombic (Os) phase at 177 K, and in the low-temperature ($\gamma$) phase with a primitive orthorhombic (Op) symmetry at 171 K, respectively, of the MAPbCl$_3$ crystal; a(2) was taken with a first-order red plate ($\lambda = 530$ nm) inserted between the crystal and the analyzer. b (2): Single domain state in the tetragonal ($\beta$) phase of the MAPbBr$_3$ crystal at 235 K. b(3) and b(4): Ferroelastic twin domains and domain walls developed in the intermediate ($\beta'$) phase with a side-centred orthorhombic (Os) symmetry at 150 K, and in the low-temperature ($\gamma$) phase also with a side-centred orthorhombic (Os) symmetry at 147 K, respectively, of the MAPbBr$_3$ crystal. Note: The PLM pictures of a (2-3) and b (2-4) were taken with the [100]-direction of the crystals oriented at an angle of 45° to the directions of the crossed polarizers. The temperature, crystallographic directions and polarizer/analyzer directions are indicated. Scale bars: 200 μm.

Fig. 6 Absorption and steady-state photoluminescence spectra of the MAPbX$_3$ (X = I, Br and Cl) single crystals grown by RTC. Insets show the determination of optical band gap using the Tauc plots.

Time-resolved photoluminescence (PL) spectra were acquired using the time-correlated single photon counting (TCSPC) setup to investigate the dynamics of exciton recombination in the MAPbBr$_3$ and MAPbI$_3$ crystals. The PL spectra were fit with a four-exponential decay, as shown in Fig. 7. Very short-lived components $\tau_1 \approx 0.35$ ns and $\approx 0.15$ ns were observed for the MAPbBr$_3$ and MAPbI$_3$ crystals, respectively, which were limited by the instrument response of TCSPC. The PL decay times of both crystals measured under ambient conditions showed a short-lived PL lifetime ($\tau_1$), long-lived PL lifetime ($\tau_2$), and ultralong-lived component ($\tau_4$), as shown in Table S1. A relatively large contribution of the longer PL lifetimes indicates the good optical properties of the crystals compared to the PL decay lifetimes of the previously reported ITC crystals.$^{61,62,63}$ Remarkably, the crystals grown recently (the fresh crystals), and the crystals grown two years ago for MAPbBr$_3$ and six months ago for MAPbI$_3$ (the old crystals) showed similar PL lifetime properties, indicating a good long-term stability of the RTC-grown crystals. In particular, the $\tau_4$ values in MAPbBr$_3$ with ~ 48% of the total PL contribution are 115 ns and 153 ns for the old and fresh crystals, respectively, and the $\tau_4$ values in MAPbI$_3$ with ~ 36% of the total PL contribution are 111 ns and 117 ns for the old and fresh crystals, respectively.

Fig. 7 Time-resolved PL spectra of the fresh RTC-grown crystals of (a) MAPbBr$_3$ and (b) MAPbI$_3$, and of the old RTC-grown crystals of (c) MAPbBr$_3$ and (d) MAPbI$_3$. 
We have characterized the charge-transport properties of MAPbX$_3$ (X= I, Br, Cl) crystals, including the trap density and (hole) carrier mobility from the dark current-voltage ($J$-$V$) characteristics, using the standard space charge-limited current (SCLC) model. As shown in Fig. 8, the $J$-$V$ relation exhibits the Mott-Gurney's power-law dependence, where an Ohmic behaviour ($J \propto V$) is observed at low voltages. By increasing the voltage above the trap-filled limited voltage ($V_{TFL}$), a sharp increase in the current is found with a non-linear behaviour ($J \propto V^{n>3}$). This is an indication of the trap-filled limit (TFL) process, in which the trap states are filled by the charge carriers. The trap density ($n_{\text{trap}}$) can be determined using the following equation:

$$V_{TFL} = \frac{en_{\text{trap}}L^2}{\varepsilon\varepsilon_0},$$

where $e$ is the elementary charge, $L$ is the thickness of the crystal, $\varepsilon_0$ is vacuum permittivity, and $\varepsilon$ is the dielectric constant ($\approx 25.5$ for MAPbI$_3$, $23.9$ for MAPbBr$_3$, and $23.9$ for MAPbCl$_3$). From Equation 3, the values of trap density ($n_{\text{trap}}$) are calculated to be $1.36 \times 10^{10}$ cm$^{-3}$ for MAPbI$_3$, $2.06 \times 10^{10}$ cm$^{-3}$ for MAPbBr$_3$, and $4.27 \times 10^9$ cm$^{-3}$ for MAPbCl$_3$ and the $V_{TFL}$ values are extracted from the $J$-$V$ characteristics, as indicated in Fig. 8a-c. At higher voltage (the Child region), the current shows a quadratic dependence on voltage ($J \propto V^2$) and the relation can be stated as:

$$J_0 = \frac{4e\varepsilon^2L^3}{\varepsilon_0},$$

where $J_0$ and $\varepsilon$ are the current density, the applied voltage, and the hole carrier mobility, respectively. According to Equation 4, the carrier mobility values are calculated to be $\approx 410$ cm$^2$V$^{-1}$s$^{-1}$ for MAPbI$_3$, $47$ cm$^2$V$^{-1}$s$^{-1}$ for MAPbBr$_3$, and $12$ cm$^2$V$^{-1}$s$^{-1}$ for MAPbCl$_3$. Furthermore, having the carrier lifetime ($\tau$) and mobility ($\mu$), one can calculate the carrier diffusion length ($L_D$) of the crystals from the following equation:

$$L_D = \frac{\mu e^2}{k_B T e},$$

where $K_B$ is the Boltzmann constant, and $T$ is the temperature. The $L_D$ values of the crystals are calculated to be $10.75$ μm for MAPbI$_3$ and $3.72$ μm for MAPbBr$_3$ for a long recombination time ($\approx 110$ ns). Therefore, the charge-transport characteristics and trap densities obtained for the RTC-grown crystals are comparable to those of the single crystals grown by the other methods.$^7,18,28,38$ In particular, the RTC-grown MAPbI$_3$ crystal exhibits an ultra-high carrier mobility $\mu$ of $410$ cm$^2$V$^{-1}$s$^{-1}$ and an ultra-long diffusion length $L_D$ of $10.75$ μm, suggesting that it could be a promising material for high-performance optoelectronic devices. To the best of our knowledge, this is the first report on the long-term carrier properties of the halide perovskite single crystals.

![Figure 8](image-url) Fig. 8. Characteristic current-voltage (J-V) curves of the RTC-grown CH$_3$NH$_3$PbX$_3$ crystals, (a) CH$_3$NH$_3$PbI$_3$, (b) CH$_3$NH$_3$PbBr$_3$, (c) CH$_3$NH$_3$PbCl$_3$, exhibiting three different regions, corresponding to the Ohmic, trap filling limit (TFL), and Child, as shown by different colours.
Experimental

All chemicals and reagents were purchased from Sigma-Aldrich and used as received without further treatment.

Growth of MAPbX₃ (X= I, Br and Cl) single crystals by the RTC method. A homogenous saturated solution was first prepared by continuous stirring at 60 °C (except for X=Br at room temperature) for two hours. Specifically, 1.6 g of methylammonium iodide (> 98%) and 4.6 g of lead(II) iodide (> 99%) were dissolved in 10 mL GBL solvent for X= I, 1.7 g of methylammonium bromide (> 98%) and 5.5 g of lead(II) bromide (> 99%) were dissolved in 10 mL DMF solvent for X= Br, 1.4 g of methylammonium chloride (> 98%) and 5.6 g of lead(II) chloride (> 99%) were dissolved in 10 mL DMSO solvent for X= Cl. In the next step, the solutions were cooled down to room temperature (20 to 25 °C) for of X= Br, Cl, or to 45 °C for X= I. In the next step, the solutions were cooled down to room temperature (20 to 25 °C) for of X= Br, Cl, or to 45 °C for X= I and then transferred into a 50 % closed, partially capped vial for X= Br, Cl, and into a 100 % open vial for X= I, and then kept therein at these temperatures. As shown in Fig. S1, many MAPbI₃, MAPbBr₂, and MAPbCl₃ single crystals were grown after 6, 12 hours, and 5 days, respectively.

Growth of CH₃NH₃PbCl₃ crystals by the seed-assisted ITC method. Stoichiometric amounts of chloride precursors, i.e., 1.4 g of methylammonium chloride (> 98%) and 5.6 g of lead(II) chloride (> 99%), were dissolved into 10 mL DMSO solvent by continuous stirring on a heating plate at 60 °C for two hours. Stoichiometric amounts of chloride precursors, i.e., 1.4 g of methylammonium chloride (> 98%) and 5.6 g of lead(II) chloride (> 99%), were dissolved into 10 mL DMSO solvent by continuous stirring on a heating plate at 60 °C for two hours. The solution was poured into a vial, which was then fully sealed, and heated from 60 °C to 110 °C in a mineral oil bath. The sealed vial remained at the temperature of 110 °C in the undisturbed mineral oil bath for the single crystals to grow. After 12 hours of growth, single crystals of various sizes were obtained in the vial. A crystal of high quality was selected to serve as the seed for the second round of growth by seed-assisted ITC. The seed was placed into a fresh solution, heated to, and kept at, 110 °C for 12 hours. The original 2 mm³ seed was grown into a larger one in the second run (Fig. 1d).

Powder & single-crystal X-ray diffraction (XRD): Powder X-ray diffraction (PXRD) patterns were obtained using a Rigaku diffractometer equipped with the Cu Kα radiation (λ = 1.5405Å). Powders of MAPbX₃ (X= I, Br and Cl) and intermediate compounds of X=Cl and I were prepared by grinding large crystals into fine powders. A yellow layer formed on the MAPbI₃ crystal was scratched out for XRD analysis. The MACI and PbCl₂ powders were also analyzed as references. The resultant diffraction data were collected for Pawley structural analysis and refinement of lattice parameters by using TOPAS software package. A Bruker D8 Advance Diffractometer equipped with a Goebel mirror for a parallel X-ray beam for high-resolution diffraction was used to perform single-crystal X-ray diffraction of MAPbX₃ (X= I, Br, Cl) crystals grown by RTC.

Energy-dispersive X-ray spectroscopy (EDX) and Infrared spectroscopy (IR) measurements: The chemical composition of the CH₃NH₃PbX₃ crystals prepared by RTC was determined by using a FEI Nova NanoSEM 430 system equipped with an EDX spectrometer. The infrared spectroscopy measurement was carried out in the wave number range of 4000 - 500 cm⁻¹ on both pure CH₃NH₃PbCl₃ and the intermediate compound formed by the RTC method and the data were recorded on a Spectrum Two FT-IR spectrophotometer at room temperature.

Solubility and supersaturation characterizations: The solubility behaviour of CH₃NH₃PbX₃ in polar solvents was studied by changing the temperature of the solution from 25 °C to 120 °C with a step of 10 °C. At each given temperature, 0.2 g of CH₃NH₃PbX₃ powder prepared by heating the precursor solution to 60 °C to evaporate the solvent, was added into 20 mL of solvent step-by-step and the solution was continuously stirred until the chemicals were dissolved completely in the solvent. The solution was considered to have reached saturation when the CH₃NH₃PbX₃ powder could no longer dissolve in the solvent upon the further addition of the solute. The solubility is described by the equilibrium concentration (C*) at a given temperature, and C* is the ratio of the mass of the dissolved MAPbX₃ powder to the volume (ml) of the solvent. The supersaturation arising from solubility reduction is defined as:

\[ S_{gr} = \frac{|C_{final} - C_{initial}|}{C_{initial}} \times 100, \]  

where \( C_{final} \) and \( C_{initial} \) are the equilibrium concentration at growth and initial concentrations, respectively.

The supersaturation of solvent evaporation for RTC was obtained from the equation:

\[ S_{se} = \frac{|m - m_{grown crystals}|}{m_{initial}} \times 100, \]  

where \( m \) initial is the initial mass of powder dissolved in the solvent (6.2 g for X=I, 7.2 g for X=Br and 7 g for X=Cl), \( V_{sol}(t) \) is the volume of solvent used in our experiment which was 10 mL at \( t = 0 \) and it varies with the time \( t \). The decrease in supersaturation due to crystal growth is obtained from the equation:

\[ S_{cg} = \frac{|m_{grown crystals} - m_{grown crystals}|}{m_{final}} \times 100 \]  

where \( m_{grown crystals} \) is the mass of the grown crystals and were calculated from the relation of \( m_{grown crystals} = \rho MAPbX₃ \times V \) crystals, where the density (\( \rho \)) of MAPbX₃ is 0.00312 g mm⁻³, 0.00383 g mm⁻³ and 0.00417 g mm⁻³ for X= Cl, Br, and I, respectively, and the volume (\( V \) crystals) of crystals was recorded during growth. Fig. 2 shows the average values of the solubility and supersaturation for MAPbX₃ during these measurements.

Induction period measurement. The induction period was measured experimentally at different supersaturation ratios (Sₚ = C*/C) for two temperatures: 25 °C and 110°C. First, the saturated solution was prepared at different temperatures according to the solubility values. Then, the solution was heated to 110 °C to obtain a desired supersaturation. The supersaturated solution was held isothermally at 110 °C until
the first crystal nuclei were observed. The time taken for the first crystal to appear from the supersaturated solution was recorded as the induction time. The same procedure was carried out to obtain induction time at 25 °C for different supersaturation ratios.

Optical characterization of MAPbX₃ single crystals. The surface roughness and morphology of the grown CH₃NH₃PbX₃ were examined by optical microscopy. The crystallographic orientation of the crystals was confirmed using SC diffraction, as shown in Fig. 1f-g, which confirmed that the naturally grown facets are the (100) surfaces. The domain structure and phase transitions of the RTC-grown CH₃NH₃PbCl₃ (~0.10 mm thick) and CH₃NH₃PbBr₃ (~0.12 mm thick) crystal platelets were investigated by polarized light microscopy (PLM) in transmission, using an Olympus BX60 polarizing microscope equipped with an Olympus UC 30 digital camera and a first order red (FOR) plate (530 nm). A Linkam HTMS600 heating/cooling stage was used for investigating the variations of domain structures and phase transitions in the temperature range of 80 K to 300 K at a heating and cooling rate of ~2 K min⁻¹.

Absorption, steady-state photoluminescence (PL), and Time-resolved PL measurements. The optical absorption spectra of the crystals were measured using an Ocean Optics Flame Spectrometer. The excitation was achieved using a DH-2000 light source equipped with both a deuterium and a halogen lamp passed through a Thorlabs bandpass optical filter. The steady-state photoluminescence measurements were carried out using a Photon Technology International (PTI) QuantaMaster spectrophuorometer. The time-resolved PL spectra were collected on a Horiba PTI spectrometer with a DeltaFlex time-correlated single photon counting (TCSPC) lifetime measurement system equipped with a 370 nm excitation laser pulse.

Space charge limited current (SCLC) measurement. The variation of current as a function of the voltage was measured using a Keithley 2401 source meter in the dark at room temperature. Hole-only devices were prepared by sputter-deposition of 80 nm gold layers on opposite sides of the crystals as electrodes with the surface areas of 2x1.1 mm² for MAPbI₃, 2x1.7 mm² for MAPbBr₃, and 1.7x1.7 mm² for MAPbCl₃. The J-V response was analysed based on the SCLC model.

Conclusions

An optimized room-temperature crystallization (RTC) process is designed upon examination of solubility behaviour, and successfully applied for the growth of organic-inorganic hybrid halide perovskite MAPbX₃ (X = I, Br and Cl) crystals from polar solvents with the aid of solvent evaporation. The crystals grown by RTC are comparatively large and transparent (except for the X = I ones which are opaque) with a regular cubic morphology. This growth process results in high yields (~40 wt%, 60 wt%, and 15% for the I, Br, and Cl-based perovskites, respectively). The optimum supersaturation (S(tot)) for a stable RT growth of MAPbX₃ crystals is found to be 12%, 13%, and 16% for X= I, Br, and Cl, respectively, from the assessment of the supersaturation components from solubility reduction (S(0)), solvent evaporation (S(w)) and grown crystal quantity (S(tot)). Based on classical nucleation theory, the nucleation parameters such as interfacial energies, critical nuclei radius, critical free energy barrier, and volume free energy change were calculated and compared for the crystal growth via RT and high temperature (HT) processes, which gives a deep insight into the nucleation processes. The small interfacial energy of HT growth results in a high nucleation rate, causing an abrupt decrease in supersaturation and preventing further crystal growth after a few hours. In contrast, the RTC method provides a relatively large interfacial energy and a longer induction time due to the slow dissociation of complex ions, resulting in a decreased nucleation rate, a retarded crystallization process, and a more stable and sustainable growth. The controlled evaporation in the RTC process helps achieve a constant supersaturation during the crystal growth and allows the crystals to grow continuously into a large size.

The polarized light microscopic studies reveal ferroelastic twin domains and domain walls characteristic of the orthorhombic and tetragonal phases of the MAPbCl₃ and MAPbBr₃ crystals, respectively. The absorption and photoluminescence, and charge-transport properties indicate excellent optoelectronic properties of the RTC-grown MAPbX₃ crystals. Of note, the crystals of X = Br and Cl demonstrate an excellent long-term (> two years) stability in terms of composition, structure, phase, and optoelectronic properties. Our investigation shows that the size and optical quality of the crystals can be controlled by temperature and supersaturation and the optimum thermodynamic and kinetic conditions attained in the RTC method are advantageous over the HT process. The RTC growth method developed in this work can be scaled up for cost-effective mass production of high-quality MAPbX₃ crystals, which will promote not only more in-depth investigations into the intrinsic optical, electrical properties of hybrid halide perovskites, but also the realization of single crystals-based optoelectronic devices of superior performance.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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