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Layered hybrid lead perovskite single crystals: phase transformations and tunable optical properties[†]

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Based on the disadvantages of crystal processing and device fabrications of 3D halide perovskites, there is a need to introduce aromatic ammonium into $CH_3NH_3PbI_3$ to address these concerns. Herein, we report the controllable growth of layered perovskite $(C_6H_5CH_2CH_2NH_3)_2(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$ (n = 1-3) single crystals realised by controlling the proper molar ratio of reactants in the ambient atmosphere. Interestingly, two polymorphs of $(C_6H_5CH_2CH_2NH_3)_2PbI_4$ single crystals coexisted, and their phase transformation were achieved by different strategies. Moreover, the crystal structure determinations, band gap, optical properties, and thermal stability of the $(C_6H_5CH_2CH_2NH_3)_2(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$ (n = 1-3) single crystals were studied in detail. The $(C_6H_5CH_2CH_2NH_3)_2(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$ (n < 3) single crystals with quantum well structures exhibited strong photoluminescent properties. These intriguing features may lay the foundation for optoelectronic applications of the layered perovskite materials.

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Introduction

Organic-inorganic hybrid lead layered perovskite materials have gained significant attention in the field optoelectronics due to their high stability and optical tunability.^{1–7} Contrary to three-dimensional hybrid perovskites ABX₃, Ruddlesden-Popper layered perovskite materials $A_2MA_{n-1}Pb_nI_{3n+1}$ (where A is *n*-butyl-ammonium (BA) phenethyl-ammonium (PEA); MA or is methylammonium; M is ordinarily Sn²⁺ or Pb²⁺; X is usually Cl⁻, Br⁻ or I⁻, and n is an integer) exhibit the excellent stability and have thus attracted considerable interest. In 1957, the Ruddlesden-Popper layered perovskite structured models were put forward by S. N. Ruddlesden and P. Popper.⁴ Later, Mitzi et al. reported the synthesis and properties of layered perovskite materials $BA_2MA_{n-1}Sn_nI_{3n+1}$.⁵ Subsequently,

syntheses, crystal structure determinations, and optoelectronic properties research of layered perovskites BA2- $MA_{n-1}Pb_nI_{3n+1}$ (*n* = 1–3) were investigated by Kanatzidis *et al.*^{6a} Recently, $BA_2MA_{n-1}Pb_nI_{3n+1}$ based solar cells, reported by Mohite et al. exhibited the PCE of 12.52% with high stability.^{6b} However, there have been only few reports available on the PEA₂MA_{n-1}Pb_nI_{3n+1} material. Karunadasa et al. have reported enhanced moisture-stable PEA2MA2Pb3I10 solar cells with the PCE of 4.73%.7 Kanatzidis group have reported the whitelight emission and structural distortions based on the two polymorphs of $(DMEN)PbBr_4$ (DMEN = 2-(dimethylamino) ethylamine) single crystals as well as the structural diversity perovskite single crystal of lavered materials.8 Photoconductors based on $PEA_2MA_{n-1}Pb_nI_{3n+1}$ (*n* = 1-3) single crystals with significant light-detection have been investigated in detail by Bakr et al.9 Photosensors based on a large-area flexible single-crystalline membrane (SCM) and bulk singlecrystals of PEA₂PbI₄ were investigated.¹⁰ In many cases, the layered perovskite-based optoelectronic devices such as solar cells,^{7,11} field-effect transistors (FETs),¹² light-emitting diodes (LEDs),^{13–15} and photodetectors are based on powders and thin films. In particular, PEA2MAn-1PbnI3n+1 materials with quantum well structures are extensively utilized in perovskite lightemitting diodes (LEDs) due to their strong photoluminescence.

Single crystals with the absence of grain boundaries and low density traps provide an ideal test platform for fundamental studies on properties of layered perovskites. However, there has been previous reports^{16–19} focused on the preparation, ¹³C-CP/MAS NMR, ionic motion, and local structures as well as confinement effects of the

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Paper

 $PEA_2MA_{n-1}Pb_nI_{3n+1}$. Recently, based on the previous research, ^{20–23} the layered perovskite $PEA_2MA_{n-1}Pb_nI_{3n+1}$ in the form of nano- or micro-crystals, polycrystalline powders, and thin films have been thoroughly investigated. Until now, there have been only few reports on the bulk crystal growth and relevant intrinsic properties of the layered perovskite PEA2- $MA_{n-1}Pb_nI_{3n+1}$. In this work, we reported the bulk growth and crystal structure determinations of $PEA_2MA_{n-1}Pb_nI_{3n+1}$ (n = 1-3) single crystals in detail. Interestingly, we observed that PEA₂PbI₄ had two polymorphs (monoclinic and triclinic lattice structures) with green and red emissions, when exposed to UV irradiation. The phase transformation processes of PEA₂PbI₄ polymorphs by different strategies demonstrated that the two polymorphs get transformed mutually. Further, their tunable bandgap, PL and PL decay time, and thermal stability were also systematically investigated. The interesting results may provide chances of further study on optoelectronic device applications of these layered hybrid perovskite single crystals.

Experimental

Reagents

All starting reagents including PbO, CH_3NH_2 , $C_6H_5CH_2CH_2$ -NH₃Cl (PEACl), and HI solution obtained from Sino-pharm Co. Ltd were of analytical grade and used without further purification.

Syntheses and crystal growth

The synthesis of MAI and crystal growth procedure was performed according to previously reported methods.^{24–26} PEACl (9.458 g, 0.06 mol) and PbO (6.696 g, 0.03 mol) were dissolved in 200 ml HI mixed solution at 75 °C under constant stirring, forming a yellow transparent solution. Solutions were saturated at 55 °C. Two polymorphs of orange-layered PEA₂PbI₄ single crystals were grown *via* the temperature-lowering method in an ambient atmosphere for about two weeks, as evidenced in Fig. 1(a).

The mixtures of two polymorphous PEA_2PbI_4 single crystals (0.500 g) were weighed, dissolved in 6 ml CH₃OH solution and then added into 10 ml HI solution, which resulted in a light-yellow solution. Green emissive PEA_2PbI_4 single crystals appeared at the bottom of the flask under UV irradiation condition at room temperature by the slow evaporation method, as shown in Fig. 2 and S2.[†]

The mixtures of the two polymorphous PEA_2PbI_4 single crystals (2.00 g) were weighed and dissolved in 10 ml HI solution, forming a light-yellow solution at 100 °C. Red emissive PEA_2PbI_4 single crystals appeared at the bottom of the flask under UV irradiation condition *via* the temperature-lowering method, as shown in Fig. 2 and S3.[†]

PEACl (4.729 g, 0.03 mol), MAI (4.77 g, 0.03 mol), and PbO (6.696 g, 0.03 mol) were dissolved in 200 ml HI solution at 75 °C under constant stirring, forming a yellow transparent solution. The solutions were saturated at 55 °C. Red plate MA: PEAPbI₄ single crystals were grown by using the



Fig. 1 Bulk single crystals of $PEA_2MA_{n-1}Pb_nI_{3n+1}$ (n = 1-3) obtained by the control of molar ratio. (a) PEA_2PbI_4 single crystals; (b) MA: PEA_2PbI_4 single crystals; (c) $PEA_2MAPb_2I_7$ single crystals; (d) $PEA_2MA_2Pb_3I_{10}$ single crystals. Inset: Scale bar: mm.



Fig. 2 The phase transformation processes of red and green emissive PEA_2PbI_4 single crystals. (a and f) The mixture of red and green emissive PEA_2PbI_4 single crystals or only green emissive PEA_2PbI_4 single crystals turned to red emissive *via* high temperature and high concentration PEA_2PbI_4 -HI solutions. (b–e) The mixture of red and green emissive PEA_2PbI_4 single crystals or only the red emissive PEA_2PbI_4 single crystals or only the red emissive PEA_2PbI_4 single crystals turned to green emissive via CH₃OH and HI mixed solutions.



Fig. 3 (a–e) Diagrams of crystal structures of $PEA_2MA_{n-1}Pb_nI_{3n+1}$ (n = 1-3) at room temperature. (a) Along the [100] direction, the layered monoclinic crystal structure of PEA_2PbI_4 ; (b–e) Along the [001] direction, the layered triclinic crystal structures of $PEA_2MA_{n-1}Pb_nI_{3n+1}$ (n = 1-3); hydrogen atoms bonded to C or N atoms were omitted for clarity.

temperature-lowering method in an ambient atmosphere for about two weeks, as shown in Fig. 1(b).

PEACl (9.458 g, 0.06 mol), MAI (7.155 g, 0.045 mol), and PbO (20.088 g, 0.09 mol) were dissolved in 300 ml HI solution at 75 °C under constant stirring, forming a yellow transparent solution. The solutions were saturated at 60 °C. Dark red PEA₂MAPb₂I₇ single crystals were grown *via* the temperature-lowering method in an ambient atmosphere for about two weeks, as shown in Fig. 1(c).

PEACl (9.458 g, 0.06 mol), MAI (11.925 g, 0.075 mol), and PbO (33.480 g, 0.15 mol) were dissolved in 500 ml HI solution at 75 °C under constant stirring, forming a yellow transparent solution. The solutions were saturated at 65 °C. Black PEA₂MA₂Pb₃I₁₀ single crystals were grown *via* the temperature-lowering method in an ambient atmosphere for about two weeks, as shown in Fig. 1(d).

Characterizations

The measurements from single-crystal and powder X-ray diffractions, TGA/DSC, PL spectroscopy, PL lifetime decay, and UV-vis spectroscopy are described in detail in the ESI.[†]

Result and discussions

The bulk PEA₂MA_{*n*-1}Pb_{*n*}I_{3*n*+1} (n = 1-3) single crystals obtained in ambient atmosphere *via* the temperature-lowering method are shown in Fig. 1. Based on the disadvantages of obtaining bulk-layered PEA₂MA_{*n*-1}Pb_{*n*}I_{3*n*+1} (n = 1-3) single crystals, it is essential to master the proper molar ratio of PEACl, MAI, and PbO in the HI solution to obtain bulk PEA₂MA_{*n*-1}Pb_{*n*}I_{3*n*+1} (n = 1-3) single crystals. First, PEACl was reacted with PbO in HI solutions at 75 °C in air. Subsequently, MAI was added into the formed PEA₂PbI₄ solution to obtain different PEA₂MA_{n-1}- Pb_nI_{3n+1} single crystals. Recently, Yin *et al.* reported the modulation of broadband emissions of PEA2PbI4; the different emission peaks resulted from different precursor materials (PbO and PbI₂) due to the concentration of lead iodide species in the reaction mixture that affected the final product and contributed to the generation of iodine vacancies.²⁷ In our results, the two polymorphs of PEA₂PbI₄ easily crystallized in coexistence and exhibited green and red fluorescence when exposed to UV irradiation, as shown in Fig. 2. Under the UV irradiation, the red emissive PEA₂PbI₄ single crystals first appeared, followed by the green emissive PEA₂PbI₄ single crystals that covered the surface of the red emissive PEA₂PbI₄ single crystals, as shown in Fig. 2(a) and S1.† The results indicated that the solubility of the red emissive PEA₂PbI₄ single crystals was lower than that of the green emissive PEA₂PbI₄ single crystals. More importantly, PEA₂PbI₄ polymorphs were completely and mutually transformed by different strategies (Fig. 2). The red emissive PEA₂PbI₄ single crystals completely transformed into green emissive PEA₂PbI₄ single crystals by the slow evaporation method using CH₃OH and HI mixed solutions at room temperature (Fig. 2 and S2[†]). Previously, Yang et al. employed methanol as an additive in diethyl ether to control the morphology and investigate the growth mechanism of MAPbI₃ perovskite films.²⁸ As described above, the CH₃OH solvent helps accelerate the perovskite crystallization due to the lower Gibbs free energy, which possibly combines with PEA₂PbI₄ to produce the intermediate complex to promote the formation of green emissive PEA₂PbI₄ single crystals. However, the green emissive PEA₂PbI₄ single crystals were completely transformed into the red emissive PEA₂PbI₄ single crystals with a high concentration PEA₂PbI₄-HI solution or at high temperature (Fig. 2 and S3[†]). Moreover, the two polymorphous phases of PEA₂PbI₄ single crystals were stable at room temperature in the ambient atmosphere. These phase transformations could provide guidance for the controlled crystal growth of the multi-component perovskite materials. Besides, $PEA_2MA_{n-1}Pb_nI_{3n+1}$ (n = 1-3) single crystals exhibited an oriented morphology; the PXRD patterns were same as their calculated XRD diffraction patterns, as shown in Fig. S4.†

The PEA₂MA_{*n*-1}Pb_{*n*}I_{3*n*+1} (n = 1-3) single crystals mostly represented a triclinic lattice structure at room temperature, as revealed by the single-crystal X-ray diffraction technique and is listed in Table S1.† More importantly, there have been no reports about the crystal structures of MA: PEAPbI₄ and PEA₂MA₂Pb₃I₁₀. Previously, Calabrese *et al.* determined and refined the crystal structures of PEA₂PbI₄ and PEA₂MAPb₂I₇ to the *C*2/*m* (no. 12) and *P*I (no. 2) space groups at -70 °C.²⁰ In our results, the green and red emissive PEA₂PbI₄ single crystals exhibited the monoclinic and triclinic space groups, which was determined to be *C*2/*m* (no. 12) and *P*I (no. 2) at room temperature, respectively. Especially, the new crystal





Fig. 4 (a) Fluorescence photos and PL spectra of monoclinic PEA_2PbI_4 (1), triclinic PEA_2PbI_4 (2), and MA: $PEAPbI_4$ (3) single crystals; (b) PL decay lifetime of monoclinic PEA_2PbI_4 under 445 nm irradiation and emission at 520 nm; (c) PL decay lifetime of triclinic PEA_2PbI_4 under 445 nm irradiation and emission at 710 nm; (d) PL decay lifetime of MA: $PEAPbI_4$ under 445 nm irradiation and emission at 710 nm; (d) PL decay lifetime of MA: $PEAPbI_4$ under 445 nm irradiation and emission at 710 nm.

structures of the red emissive PEA2PbI4, MA: PEAPbI4, and PEA2MA2Pb3I10 at room temperature were determined and refined to be the triclinic system with the space group $P\bar{1}$ (no. 2). For triclinic PEA₂PbI₄, the cell parameters were a =8.7350(16) Å, b = 8.7359(16) Å, c = 16.673(3) Å, V = 1248.6(4)Å³, $\alpha = 99.694(5)^{\circ}$, $\beta = 95.220(6)^{\circ}$, $\gamma = 90.393(5)^{\circ}$, and Z = 2. The cell parameters for MA: PEAPbI₄ were a = 8.7497(8) Å, b =8.7510(8) Å, c = 16.6830(15) Å, V = 1253.4(2) Å³, $\alpha =$ 99.7643(10)°, $\beta = 95.2258(10)°$, $\gamma = 90.3394(10)°$ and Z = 2, and PEA2MA2Pb3I10 exhibited the layered perovskite crystal structure with cell parameters a = 8.8201(14) Å, b = 8.8198(14)Å, c = 29.038(5) Å, V = 2245.0(6) Å³, $\alpha = 93.198(2)^{\circ}$, $\beta =$ $95.495(2)^{\circ}$, $\gamma = 90.123(2)^{\circ}$ and Z = 2. The ball and stick diagrams of $PEA_2MA_{n-1}Pb_nI_{3n+1}$ (n = 1-3) crystal structures are shown in Fig. 3, in which all diagrams include the $\{PbI_6\}$ octahedral structured units. Moreover, PEA⁺ and MA⁺ organic cations were so disordered that the benzene ring and MA⁺ cation could be hardly distinguished. Further, the monoclinic PEA₂PbI₄ single crystals showed a layered crystal structure along the [100] direction (Fig. 3(a)), while the layered crystal

structures of triclinic PEA₂MA_{*n*-1}Pb_{*n*}I_{3*n*+1} (n = 1-3) were in array along the [001] direction (Fig. 3(b-d)). All the I–Pb bond lengths in the crystal structures of PEA₂MA_{*n*-1}Pb_{*n*}I_{3*n*+1} (n = 1-3) were found to be in perfect alignment, which made all crystal structures of PEA₂MA_{*n*-1}Pb_{*n*}I_{3*n*+1} (n = 1-3) symmetric.

The results of TGA and DSC of $PEA_2MA_{n-1}Pb_nI_{3n+1}$ (n = 1-3) are shown in Fig. S5.[†] All the single crystals showed relatively good thermal stability. This advantage may promote realistic optoelectronic applications of layered perovskite temperature-variable environment. materials in the Subsequently, the optical band gap (E_g) was calculated from the UV-vis absorption spectra combined with the Kubelka-Munk function (Fig. S6[†]).^{29–31} The as-determined optical E_{g} was 2.13 eV, 1.97 eV, 1.86 eV, and 1.55 eV for PEA₂PbI₄, MA: PEAPbI₄, PEA₂MAPb₂I₇, and PEA₂MA₂Pb₃I₁₀, respectively. It is demonstrated that $PEA_2MA_{n-1}Pb_nI_{3n+1}$ (n = 1-3) single crystals exhibit an obvious tunable band gap. Due to the weak red fluorescence of PEA2MAPb2I7 and PEA2MA2Pb3I10 single crystals (Fig. S4[†]), we focused on PL spectra and the PL decay time of the monoclinic phase of PEA₂PbI₄ and the triclinic

phase of PEA₂PbI₄ and MA: PEAPbI₄ single crystals. The thick single crystals exhibited shoulder and broad PL peaks, which were similar to previous reports.³²⁻³⁴ Interestingly, when MA⁺ cation was added into PEA-Pb-I systems, all the PEA₂MA_{n-1}- Pb_nI_{3n+1} (*n* = 1-3) single crystals exhibited red emission. With the increase in the number of MA^+ cation, $PEA_2MA_{n-1}Pb_nI_{3n+1}$ (n = 1-3) single crystals gradually exhibited weaker emissions. The monoclinic phase of PEA₂PbI₄ was positioned at 520 nm. Surprisingly, the triclinic PEA₂PbI₄ and MA: PEAPbI₄ had two fluorescent peak positions at 520 nm and 710 nm, respectively, as shown in Fig. 4(a), which possibly resulted from edges of the layered perovskite single crystals, as reported by Blancon et al.³⁵ According to a previous report,³⁰ the TRPL spectra of the layered perovskites were well fitted by bi-exponential decays, as shown in Fig. 4(b-d) and S7.⁺ We found that the PL decay time (τ) of monoclinic PEA₂PbI₄ bulk crystals was 0.32 ns and 1.58 ns at 520 nm emission peak position. For triclinic PEA₂PbI₄and MA: PEAPbI₄ bulk crystals, the decay time was reduced to 0.12 or 0.01 ns, and 0.63 or 0.44 ns at 520 nm emission peak position, while their decay time at 710 nm emission peak position was 1.81 or 1.64 µs and 9.39 or 9.41 µs, respectively. The decreased band gaps and redshifted PL spectra compared with PEA₂PbI₄ may be attributed to the reduced disorder in dipoles of MA⁺ cations within the crystal lattice.^{36,37} As mentioned above, it is concluded that $PEA_2MA_{n-1}Pb_nI_{3n+1}$ (n < 3) single crystals exhibit the strong photoluminescent properties, which may benefit the light-emitting diode (LED) applications.

Conclusions

In summary, we investigated the bulk growth, crystal structure determinations, and tunable optical properties of layered hybrid perovskite PEA₂MA_{*n*-1}Pb_{*n*}I_{3*n*+1} (n = 1-3) single crystals. More importantly, we observed that PEA₂PbI₄ had two polymorphs (monoclinic and triclinic lattice structures) with green and red emissions when exposed to UV irradiation. The phase transformations of PEA₂PbI₄ by different strategies demonstrated that the two polymorphs transformed mutually. Further, the tunable bandgap, PL spectra and PL decay time, and thermal properties of PEA₂MA_{*n*-1}Pb_{*n*}I_{3*n*+1} (n = 1-3) single crystals were investigated due to the changes in the compositional concentration of PEA⁺ and small MA⁺ cations. This work provides an insightful guidance for the controlled growth of layered hybrid perovskites and paves way for achieving high-performance and stable layered perovskite optoelectronic devices.

Conflicts of interest

There are no conflicts of interest to declare.

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