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Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x www.rsc.org/

Ultra-High Seebeck Coefficient and Low Thermal Conductivity of Centimeter-sized Perovskite Single Crystal Acquired by a Modified Fast Growth Method

Tao Ye,^{a,b†} Xizu Wang,^{a†} Xianqiang Li,^c Alex Qingyu Yan,^c Seeram Ramakrishna,^{b*} Jianwei Xu^{a*}

A centimeter-sized organic–inorganic hybrid lead-based perovskite $CH_3NH_3PbI_3$ (MAPbI₃) single crystal was obtained by using a modified fast and inverse-temperature growth method. The optical properties of this single crystal at room and low temperatures were studied in terms of optical absorption and photoluminescence measurements. The single crystal exhibited optical properties with a band-gap of 1.53 eV, which is comparable to a reported value. Temperature-dependent UV-vis spectra of this perovskite single crystal showed a unique structural phase transition as the temperatures varied. The thermoelectric properties of this MAPbI₃ single crystal were studied, showing that the Seebeck coefficient of 920 ± 91 μ V/K almost remained unchanged from room temperature to 330 K and it progressively increased with the increase in temperature and reached to 1693 ± 146 μ V/K at 351 K. In contrast, there was no very clear trend for thermal conductivities with the temperature range of 298 – 425 K. These thermoelectric characteristics would be of useful for the potential thermoelectric applications if its electrical conductivity is improved by tuning its composition.

Introduction

The organic-inorganic hybrid lead-based perovskite CH₃NH₃Pbl₃ (MAPbI₃) has recently attracted considerable attention for optoelectronics applications in solar cells and photo-detector due to its superior characteristics including high absorption coefficient, direct band-gap, long carrier lifetime, and high balanced hole and electron mobility, etc.^{1,2} These perovskites materials have emerged as a strong candidate in photovoltaic and solar cells. In particular, lead halide perovskite $APbB_3$ (A = methylammonium (MA) and formamidium (FA); B = CI, Br and I) solar cells have reached a record high efficiency of 22.1% in the past 5 years.³⁻¹⁰ Based on unique properties of these hybrid lead-based perovskites such as high charge carrier mobility and high diffusion length, they have attracted intense attention for possible thermoelectric (TE) applications.¹¹⁻¹³ Low thermal conductivity, high carrier mobility and Seebeck coefficient are desirable for promising thermoelectric materials.¹⁴ Compared with inorganic-based thermoelectric material, polymer and organic-inorganic perovskite materials have attracted more attention for potential thermoelectric application due to their lower thermal conductivity and density.^{15,16} The high scattering parameter at the inorganic-organic interface provided the solid evidence for the energy filtering effect, which is in conjugation with the enhancement of the thermal Seebeck coefficient and power factor.¹⁷ In addition, the enhanced density of states of energy levels also led to increase in Seebeck coefficient in the inorganic-organic material interface.¹⁵

Thermoelectric materials play a vital role in energy harvesting applications due to their great potential in transforming a temperature gradient into thermoelectricity.^{18,19} The oxide-based thermoelectric materials such as SrTiO₃, ZnO, TiO₂, CaMnO₃, and Ca₃Co₄O₉ were fully studied as alternatives to expensive or toxic tellurium-based and selenium-based traditional thermoelectric compounds.²⁰ La doped SrTiO₃ inorganic perovskites have been developed and their optimized figure-of-merit value of 0.41 (at 973 K) for an n-type $Sr_{1-3x/2}La_xTiO_{3\square\delta}$ ceramics with $0.125 \le x \le 0.175^{21}$ has been achieved. With the help of advanced ab initio calculations, researchers reported that the MAPbl₃ exhibits a large value of carrier mobility, which is ascribed to a small effective mass and a long diffusion length, while a large value of the Seebeck coefficients is due to the multi-degenerated conduction and valence bands.^{11,12} This intense interest in the lead halide perovskite APbB₃ is mostly due to their long electron and hole transport length, tunable optoelectronic properties and high absorption coefficients. Meanwhile, these organometallic halide perovskites are low-cost and can be fabricated through facile deposition techniques.²² Moreover, perovskite single crystals have shown to possess various merits when compared with their thin film counterparts.²⁵⁻²⁷ More precisely, a remarkably low trap-state density of perovskite single crystals is comparable to that of the best quality silicon in the photovoltaic field and it is five orders of magnitude lower than that of microcrystalline perovskites. Firstly, the carrier mobility in single crystalline perovskites increases with carrier diffusion length. Secondly, the light absorption onset of it is red-shifted, resulting in a large theoretic current density for the crystalline perovskites. As a result, the electrical conductivity and stability of single-crystalline perovskite are expected to be improved. Recently, it was reported

^{a.} Institute of Materials Research and Engineering (IMRE), Agency for Science, Technology and Research (A*STAR), #08-03, 2 Fusionopolis Way, Innovis, 138634, Singapore. Email: jw-xu@imre.a-star.edu.sq

^{b.} Department of Mechanical Engineering and Centre of Nanofibers and

Nanotechnology (NUSCNN), National University of Singapore, Singapore 117576, Singapore. Email: seeram@nus.edu.sg

^c School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore.
[†]Equal contribution

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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that MAPbl₃ single crystal has a low thermal conductivity, which is mainly attributed to the MA rotations in the system. ^{11,12} Moreover, the ultra-low thermal conductivity of ~ 0.4 Wm/K and high Seebeck coefficient of 820 μ V/K were also obtained for 3 – 5 mm sized MAPbl₃ crystal drusy facets at a low temperature region (from 200 to 300 K).¹³ Polycrystals and amorphous perovskite structures, however, cannot be reliably characterized because of their geometries. For instance, the presence of many grain boundaries in polycrystals and amorphous perovskites cannot result in accurate measurement of the thermal conductivity. Therefore, large single crystal perovskites may be necessary to explore their detailed thermoelectric properties.

The perovskite single crystals growth by using solution crystallization processes always suffers from a slow growth rate.^{2t} A fast crystallization technique-inverse temperature crystallization (ITC) has been introduced to address the need for fast and massive fabrication of perovskite single crystals.²⁵ In our study, we optimized a similar MAPbl₃ crystal growth method to obtain a perfect centimeter-sized organic-inorganic hybrid perovskite (MAPbl₃) single crystal. The growth rate of the resulting single crystal can be further enhanced without compromising its quality. Herein, the physical properties of this single crystal in a wide temperature range have been studied by low-temperature optical absorption and photoluminescence measurements. The thermoelectric behaviour of a MAPbI₃ single crystal grown by a fast and solutionbased method was examined at above room temperature for the first time. The results exhibited a high and positive Seebeck coefficient in the above room temperature region, thus suggesting holes are the majority carriers in this kind of MAPbl₃ single crystal. In addition, the thermal conductivity of the single crystal was measured and it had a very lower thermal conductivity than reported inorganic perovskites. Apart from the superior photovoltaic characteristics of centimeter-sized perovskite crystals, it revealed unexpected thermoelectric characteristics including a high Seebeck coefficient and low thermal conductivity at room temperature. In addition, it was found that the increase in temperature led to significant increase in the Seebeck coefficient.

EXPERIMENTAL SECTION

Materials

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Unless specified otherwise, all materials were purchased from either Alfa Aesar or Sigma-Aldrich. All chemicals were used as purchased without any further purification.

Synthesis of MAI

Methylammonium iodide was prepared by reacting methylamine,

33 wt% in ethanol, with hydroiodic acid (HI) 57 wt% in water, at 0 $^{\circ}$ C for 4 h. HI was added dropwise while stirring. Upon drying at 100 $^{\circ}$ C on a hotplate to remove the solvent and make methylammonium iodide crystallize, the precipitate was washed with diethyl ether and ethanol three times. The resulting white powder was dried on a hotplate at 65 $^{\circ}$ C for 6 h in air.

Synthesis of MAPbl₃ single crystal and TE sample. One molar solution containing Pbl₂ and MAI was prepared in DMF. The solution was filtered using PTFE filters with 0.2 μ m pore size. Five milliliters of the filtrate were placed in a vial and the vial was kept in

an oil bath undisturbed at 120 °C for crystal formation, N₂ air flow (or using a vacuum pump to keep the pressure in the inner vial is 0.7 atm.) is utilized to increase the solvent evaporation and take away the solvent vapour. All the crystal synthesis procedures were carried out under ambient conditions. The crystals used for measurements were grown within 2-3 h. Then two 100 nm-gold electrodes were deposited on the same surface of perovskite single crystal with a space distance of 1 cm through a thermal evaporator within a N₂ filled glove box.

Characterization

A conventional four-point technique was employed to measure the resistivity (MCP-T610, MITSUBISHI CHEMICAL ANALYTECH). The optical absorption spectra were measured on a PerkinElmer Lambda 950UV/VIS/NIR spectrometer. PL spectra were obtained from a triple-grating micro-Raman spectrometer (Horiba-JY T64000). Liquid nitrogen was utilized for the cooling the samples. X-ray diffraction experiments were conducted by a Bruker AXS (D8 ADVANCE GADDS) X-ray diffractometer with Cu K α radiation (λ = 1.54 Å), the beam diameter for this instrument can range from 0.05 to 0.8 mm. Carrier concentration and mobility of the perovskite single crystal was determined by the Hall measurement (Bio Rad HL5500) with a four-point-probe using van der Pauw geometry. Four 100 nm-gold electrodes were deposited on the same surface of perovskite single crystal through a thermal evaporator within a N_2 filled glove box. The measurements of the thermal diffusivity (κ) were carried out with a Netzsch Microflash system (LFA 457), the density (p) were calculated by the measured volume and mass of materials, and the specific heats (Cp) was measured using a Differential Scanning Calorimetry (DSC, Mettler Toledo) at room temperature. The TE properties were measured through a custommade setup. More precisely, the sample was put on two substrates (as shown in Figure 3a) with a built-in resistive heater, and the setting temperature can be adjusted by the resistive heater that were driven by direct current power supply (PWS2721, Tetronix). The temperature differences of measuring points were documented by two thermometers (RS 1319A, Taiwan) and the voltage differences at same points were collected by a Keithley 2400 source meter.

Results and discussion

The solubility behaviour of MA-based perovskite in N,Ndimethylformamide (DMF) is different from common organicinorganic crystals. It has a high solubility at room temperature, but its solubility decreases with increase in temperature.²⁵ This inverse solubility effect can be used to crystallize MAPbI₃ rapidly by heating the precursor solution as illustrated in Figure 1a. A temperaturecontrollable hot plate was used to heat the oil bath and only a few crystals were formed within the first 10 min. By using the N₂ air flow (or vacuum) to remove the evaporated DMF solvent promptly, the crystal growth rate can be increased to $\sim 5 \text{ mm}^3/\text{h}$ for the first hour and the rate would reach ~20 mm³/h for the following hours. The crystal used for thermoelectric measurement with a suitable size (more than 1 cm in the length direction) can be fabricated within 2 \sim 3 h (Figure 1b). By carefully removing the small crystals from the old solution and placing them in a newly prepared perovskite precursor solution, the crystals can grow further with a large dimension. X-ray diffraction of the perovskite crystal demonstrates high purity as evidenced by similar diffractions of perovskite MAPbl₃

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(Figure 1c) to some previous results.²⁵⁻²⁷ High-resolution XRD was used to examine the quality of the CH₃NH₃Pbl₃ single crystal. Figure S1 shows the 2θ scan profile with only two very sharp diffractions corresponding to the 200 and 400 planes, indicating the singlecrystalline nature of the sample.²⁷ The quality of crystal grown within a few hours is comparable to these which were grown within several weeks.²⁴ The optical absorption and photoluminescence properties of the MAPbl₃ single crystal were investigated at room temperature. According to the steady state optical absorption spectrum, it is easy to find a sharp band edge in the spectrum (Figure 1d). Based on the UV-vis absorption of MAPbI₃, its band-gap is estimated to be 1.53 eV. The magnitude of band-gap of the MAPbI₃ single crystal grown by using the N₂ flow-assisted ITC method is in good agreement with that of the single crystals grown by an ITC or anti-solvent crystallization method at room temperature.^{25,28} The narrow and blue-shifted PL peak (~ 65 nm) indicates a low trap density in MAPbI₃ crystal and the PL peak width was determined by the intensity difference crossing the first derivative of the PL spectrum. The excellent overlapping of the PL spectrum with the optical absorption spectrum of the MAPbl₃ single crystal allows photon recycling in the thick crystal by reabsorbing the emission, which is beneficial to the solar thermoelectric generation, an emerging technology combining concentrated solar power and thermoelectric effect (the corresponding optical properties of MAPbl₃ thin film can be found in Figure S2).



Figure 1. (a) Schematic graph showing the single crystal growth setup in this study. (b) Image of 1.3 cm-sized single crystal. (c) X-ray diffraction of the MAPbl₃ crystal. (d) Optical absorption (red), smoothed curve (black) and PL (blue) of a 2 mm-sized MAPbl₃ crystal at room temperature.

Original single crystals instead of powder (mechanically fabricated from single crystals) ²⁵⁻²⁸ were used for this experiment. To study the ratio of free charges over the total photo-excitation in this single crystal, temperature-dependent optical absorption spectra are recorded from 340 K to 77 K.³² The absorption edge (valance band maximum) of MAPbl₃ single crystal is 1.53 eV. Generally, the tetragonal phase of MAPbl₃, in which the methylammonium moiety is disordered, exists from 160 K to room temperature. In contrast, the orthorhombic phase, in which the methylammonium unit is ordered, exists below 160 K.^{29,32} As can be seen from Figure 2a, the spectra of the MAPbl₃ single crystal show a remarkable structural phase transition during the cooling period.

More precisely, there is a significant shift of the absorption edge through 170 - 210 K in a single crystal. This behaviour can be regarded as a crystal phase transition of the perovskite single crystal from a tetragonal to an orthorhombic structure at ~170 K, inducing a blue shift in the MAPbl₃ material absorption edge of ~ 34 meV. As the temperature decreases, the absorption band edges of the sample show blue shifts called 'Varshni' trend (a positive thermal expansion coefficient), which has been observed in many lead composite semiconductors.³²⁻³⁴ Different from the perovskite thin film, no typical exciton peak was observed in the wide temperature range (Figure 2a), thus implying that the exciton binding energy of this single crystal is much less than that in the film, resulting in a high free carrier generation ratio within the crystal.

DOI: 10.1039/C6TC04594D

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We also present a temperature-dependent study of PL emission of the perovskite single crystal to explore the nature of recombination channels within the MAPbl₃ single crystal at a wide temperature range.^{35,36} Figure 2b shows the PL spectra at a wide temperature range from 77 K to 340 K with a laser excitation at 532 nm. The PL spectral profile is independent on the excited laser intensity and photon energy of the excitation in this study. At room temperature, a broad peak at ~ 1.62 eV can be seen in the PL spectrum. The PL intensity shows a rapid increase by more than one order of magnitude when temperature decreases to 200 K and the peak position red-shifts to ~ 1.61 eV (P1 of Figure 2c). According to a previous work, the estimated $\mathsf{MAPbI}_3\,\mathsf{band}\text{-}\mathsf{gap}$ energy is 1.61 eV,³⁵ only a very small Stokes shift occurs here, and thus the PL of the single crystal is generated from the radiative recombination [conduction band (electrons) to valence band (holes)]. At T \leq 160 K, a new blue-shifted PL peak appears at ~ 1.64 eV, it grows rapidly with temperature decreases (one order of magnitude in a 20 K temperature range) and it becomes the main feature at 77 K (P2 of Figure 2c). The evolution of PL spectra in the single crystal with decreasing temperature is due to a tetragonal-to-orthorhombic phase transition, in good agreement with the optical absorption result. The tetragonal phase at the high temperature with the PL peak at 1.61-1.64 eV is ascribed to the collective rotation (around the c-axis) of each Pbl₆ octahedron from its symmetric position in the cubic structure. In contrast, the low temperature phase (orthorhombic) with PL peak at 1.59-1.64 eV is derived from the tilting of the PbI₆ octahedral out of the *ab* plane.³⁶⁻³⁸ Since the orthorhombic MAPbI₃ is a direct-band-gap crystal,³⁹⁻⁴¹ multiple PL peaks indicate the coexistence of the tetragonal and orthorhombic phases of MAPbI₃ in the temperature range of 200-160 K. When the temperature continues to go down to 110 K, a new PL peak appears at 1.67 eV, which may originate from free excitons and donoracceptor-pair transition. A peak intensity decrease can be observed in this period (PE of Figure 2c) as the new peak enhances with decrease in temperature. Further modelling and experiments are needed to understand the inter-conversion among the thermal activation of the trap states into band-gap excitons, the broad distribution of trap states, and competing for radiative and nonradiative recombination rates from these states.^{36,42}

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Energy (eV) а 1.76 1.68 1.60 1.52 ntensity (a.u.) 110 K 130 K 77 K 150 K 160 K 170 K 210 H 250 k 296 K 720 760 800 840 Wavelength (nm) b 77 K PE 110 K 140 K /P2 (a.u.) 150 K intensity 160 K PT 200 K 250 K Ч 296 K 340 K P1 680 720 760 800 840 С Wavelength (nm) 100000 PF 10000 (a.u.) 1000 Intensity 100 10 1 ∟ 50 100 150 200 250 300 350 Temperature (K)

Figure 2. Optical results of the MAPbl₃ single crystal. (a) Temperature-dependent optical absorption spectra of the single crystal at different temperatures; (b) Temperature-dependent PL spectra of the single crystal at different temperatures; (c) The PL intensity of MAPbl₃ single crystal vs. temperature. P: Process, PT: Phase transition and PE: Process with abnormal exciton behaviour.

The Hall effect is another important method to examine the quality of the perovskite single crystal.^{26,27} It was found that the MAPbI₃ single crystal shows a high carrier mobility of 59 cm² V⁻¹ s⁻¹ and a free hole concentration of 4.72 \times 10¹¹ cm⁻³. The thermoelectric properties of the perovskite single crystal were measured with a custom-made setup. Specifically, using a voltage controllable DC power supply and electric resistance elements to create a temperature gradient, and two thermometers together with two copper points (wires) were used to measure the temperature gradient. The voltage difference at the same points was collected by another two copper points (wires) and a Keithley

2400 (Figure 3a). Plots of thermal voltage vs ΔT measured at room temperature (25 $^{\circ}$ C) and the Seebeck coefficients obtained at different average temperatures are shown in Figure 3b-c, respectively. The positive Seebeck coefficient indicates free holes are the majority carrier type in the MAPbI₃ single crystal, which is consistent with the Hall effect measurement, but the nonmonotonic temperature dependency of the Seebeck coefficient indicates that electrons also participate in the charge transport, and temperature-dependent mobility of electrons is different from the one of the holes.^{13,29} Moreover, the measured Seebeck coefficient value of 920 \pm 91 μ V/K for this perovskite single crystal at room temperature (297 K) is higher than that (820 μ V/K and or ~300 μ V/K) of the crystal facets made with a slow solvent evaporating method.^{13,29} The trend in Figure 3c suggests that it could reach even a larger value of 1693 \pm 146 μ V/K at 351 K, which is 5.4 ~ 33.9 times of that in the pure and La-doped SrTiO₃ inorganic perovskites.²⁰ This results seemed to conclude that with the temperature rise, the enhanced high energy carriers transport and increased density of state of energy levels within the single crystal perovskite lead to the improved Seebeck coefficient.^{15,17,43,44} The electrical conductivity of the single crystal was also measured at a temperature range of 296 to 350 K as shown in Figure 3d. The conductivity increases with the increase of temperature, which is consistent with a temperatureactivated transport thermal conductivity ~ exp(Ea/T) with an energy barrier of 128 meV (Figure S3).^{45,46}



Figure 3. Thermoelectric property characterization of the perovskite single crystal. (a) Schematic graph of the thermoelectric property measurement. (b) Thermal voltages at different applied temperature differences. The Seebeck coefficient can be obtained from the linear fit (dashed lines); (c) Seebeck coefficients at different average temperatures; (d) Conductivity at different temperatures and the dashed line is the linear fit.

A low thermal conductivity of around 0.30 - 0.42 Wm/K in a temperature range from 299 to 424 K was observed for this perovskite single crystal (Figure 4), and this value was much smaller than that of the pure or La doped SrTiO₃ perovskites (4.5 - 7 Wm/K).²⁰ Apart from the electrical conductivity, the ultrahigh Seebeck coefficient and low thermal conductivity were observed in this centimeter-sized perovskite single crystal, suggesting that the enhancement of electrical conductivity would be the key factor to achieve high thermoelectric performance of perovskite materials. Further increases in electrical conductivity can be achieved by doping some other metallic elements that can form more covalent

DOI: 10.1039/C6TC04594D

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bonds with the iodine ions in the perovskite crystal.⁴⁷⁻⁴⁹ It is noteworthy that the electrical conductivity is increased by 10 orders of magnitude in MASnl₃ with a value of 10^5 S/m.¹³ It shows a path towards significant improvements in MA based perovskites electrical conductivity. Holes are the majority carrier type for MAPbl₃ single crystal, but electrons also participate in the charge transport and thus influence the overall thermoelectric performance. This phenomenon is also called amphoterism,⁵⁰ which should be avoided in thermoelectric materials/applications. Therefore, improving the thermoelectric performance of the MAPbl₃ single crystal could be achieved by suppressing the amphoterism effect through heavy *p*-doping of this material.



Figure 4. Measured thermal conductivity as a function of the average temperature.

Conclusions

In conclusion, the large MAPbI₃ single crystal was grown using a modified fast growth method, and the Seebeck coefficient, electrical conductivity and thermal conductivity of the MAPbI₃ single crystals were measured. The Seebeck coefficients remained roughly constant in the temperature range of 298 - 330 K, and then significantly increased with the increase in temperature. A large and positive Seebeck coefficient of 920 \pm 91 μ V/K at room temperature and an ultra-high value of 1693 \pm 146 μ V/K at 351 K were observed. A low thermal conductivity of 0.30– 0.42 Wm/K, which is comparable to that of polymer materials, is obtained. It is envisioned that the MAPbI₃ single crystal could be considered as a new class of thermoelectric materials if proper elemental doping can be incorporated to improve the electrical conductivity and in turn increase the overall figure-of-merit value.

Acknowledgements

The authors acknowledge financial support from the A*STAR, Industry Alignment Fund, Pharos "Hybrid thermoelectric materials for ambient applications" Programme (Grant No.: 1527200021). This work is also supported by the Grantor Lloyd's Register Foundation (R-265-000-553-597) and T. Y. acknowledges the National University of Singapore for the research scholarship. The authors thank Mr. Xingzhi Wang from Nanyang Technological University for experiment assistance.

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