Solution-processed lead halide perovskite single crystal scintillators

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**NANYANG
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SINGAPORE

**SOLUTION-PROCESSED LEAD HALIDE PEROVSKITE
SINGLE CRYSTAL SCINTILLATORS**

XIE AOZHEN

SCHOOL OF ELECTRICAL & ELECTRONIC ENGINEERING

2020

SOLUTION-PROCESSED LEAD HALIDE PEROVSKITE SINGLE CRYSTAL SCINTILLATORS

XIE AOZHEN

School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2020

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarized materials and has not been submitted for a higher degree to any other University or Institution.

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accordance with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

13/07/2020

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Date

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Asst. Prof. Cuong Dang

Authorship Attribution Statement

This thesis contains material from three papers published and one paper submitted in the peer-reviewed journals where I am listed as an author

Chapter 2 is published as Maddalena, F., Tjahjana, L., Xie, A., Zeng, S., Wang, H., Coquet, P., Drozdowski, W., Dujardin, C., Dang, C. and Birowosuto, M.D. Inorganic, organic, and perovskite halides with nanotechnology for high-light yield X- and γ -ray scintillators. *Crystals* **9**, 88 (2019).

The contributions of the co-authors are as follows:

- Dr. Francesco Maddalena contributed the most to prepare the manuscript.
- The others helped revise the manuscript.

Chapter 4 is published as Xie, A., Nguyen, T.-H., Hettiarachchi, C., Witkowski, M.E., Drozdowski, W., Birowosuto, M.D., Wang, H. and Dang, C. Thermal quenching and dose studies of X-ray luminescence in single crystals of halide perovskites. *J. Phys. Chem. C* **122**, 16265-16273 (2018).

The contributions of the co-authors are as follows:

- I prepared all the crystal samples and the manuscript drafts. This investigation required high-quality perovskite single crystals, but by simply following the reported receipts did not always grant successful synthesis and I tried to modify those receipts, sometimes a small change in temperature or concentration. After a few trials, I summarized the results and found the optimized conditions for high-quality single crystals. Besides, I analyzed all the data, correlated the experimental phenomena with the crystal structures/properties and got the useful conclusions with the help from others.
- Dr. Tien Hoa Nguyen assisted in the collection of powder X-ray diffraction (XRD) data.
- Chathuranga Hettiarachchi contributed to the temperature-dependent photoluminescence (PL).

- Prof. Marcin E. Witkowski and Prof. Winicjusz Drozdowski collected the temperature- and dose-dependent X-ray luminescence and X-ray thermoluminescence. They also offered aid in data analysis.
- Dr. Danang and Asst. Prof. Cuong Dang conceived and supervised the project. The manuscript was revised based on suggestions from them.
- Dr. Danang and I prepared the answers for referees' comments, then thoroughly discussed with Asst. Prof. Cuong Dang.

Chapter 5 is published as Xie, A., Hettiarachchi, C., Maddalena, F., Witkowski, M.E., Makowski, M., Drozdowski, W., Arramel, A., Wee, A.T.S., Springham, S.V., Vuong, P. Q., Kim, H.J., Dujardin, C., Coquet, P., Birowosuto, M.D. and Dang, C. Lithium-doped two-dimensional perovskite scintillator for wide-range radiation detection. *Comms. Mater.* **1**, 37 (2020).

The contributions of the co-authors are as follows:

- I performed the crystal synthesis, X-ray imaging, most of the data analysis and manuscript writing. After hearing the new idea about ^6Li -doped perovskite scintillator for thermal neutron, I began searching all available source to purchase all chemicals. I have to say it was not an easy task since ^6Li compound was a restrict product in US. After dealing with many paper works, the chemical preparation was finally finished. For this paper, it was another challenge to obtain high-quality 2D perovskite single crystal, a more difficult task than to obtain 3D ones. None of our group members had related experience at that time. Thus I had to spend more time in searching for optimal growing conditions, such as the solvents, the rate of solvent evaporation, concentration and so forth. After almost half year, I finally acquired some good crystals suitable for following characterizations. During the analysis, we found some unusual emission behaviors. I searched other similar works and found a nice model that could well explain these behaviors. For the X-ray imaging part, I prepared a home-made setup for all the images collections.
- Dr Danang. and Asst. Prof. Cuong Dang. conceived the idea and supervised the project.

- Chathuranga Hettiarachchi carried out the XRD measurement.
- Dr. Francesco Maddalena contributed to the X-ray imaging.
- Prof. Marcin E. Witkowski, Michał Makowski and Prof. Winicjusz Drozdowski contributed to the temperature-dependent X-ray luminescence, thermoluminescence and gamma-ray characterizations.
- Dr. Arramel and Prof. Andrew Wee performed the XPS measurement.
- Prof. Stuart Victor Springham carried out the alpha particle pulse height measurement.
- Phan Quoc Vuong and Prof. Hong Joo Kim contributed to the pulse-shape discrimination, thermal neutron measurements and the related data analysis.
- Prof. Christophe Dujardin and Prof. Philippe Coquet contributed to the data analysis.
- Dr. Francesco Maddalena, Dr. Danang and I prepared the answers for referees' comments, then thoroughly discussed with Asst. Prof. Cuong Dang.

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The contributions of the co-authors are as follows:

- I prepared the first draft of manuscript. At first, the raw characterization data of a series of perovskite single crystals were relatively loose and not very useful. However, I did a screen and found a clue that could integrate all the important data. Based on the clue, I finished the first version by focusing on comparing the effect of controlled variances, like anions and organic cations, on scintillating performance among eleven different 2D perovskite single crystals. After the first version, more supporting data was added by others and the conclusion became

stronger.

- Dr. Francesco performed most of the crystal synthesis, XRD and UV absorption.
- Dr. Danang carried out the PL and TRPL.
- Prof. Marcin E. Witkowski, Michał Makowski and Prof. Winicjusz Drozdowski contributed to the temperature-dependent X-ray luminescence, thermoluminescence and gamma-ray characterizations.
- Prof. Stuart Victor Springham contributed to the X-ray imaging.
- Dr. Benoit Mahler and Prof. Christophe Dujardin provided the TRXL data.
- Prof. Philippe Coquet contributed to the data analysis.
- Dr Danang. and Asst. Prof. Cuong Dang. conceived the idea and supervised the project.

30 Jun 2020

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Date

XIE AOZHEN

Acknowledgments

I can still recall the first day on which I came to Singapore. That day was sunny and I was excited to live and study in a new country. All in a sudden, four years just passed somehow. Recently, I have been learning and developing my academic skills. There were many people who helped me a lot in my PhD period and I would like to express my gratitude to them in this acknowledgement section.

To begin with, wish to thank my advisor, Prof. Cuong Dang. I am impressed by his professional knowledge and all those useful suggestions he provided since the day we met. His easy-going personality allows us to communicate easier. In addition, he always enlightens us when we are confused and he often uses examples and analogies to illustrate his point of view. I think it is, at least to me, very convincing. Moreover, the financial support from him gives us the opportunity and freedom to explore any idea or experimental instruments and method. This is actually crucial to me, who focuses a lot on chemistry and characterizations in the school of EEE. Prof. Dang provided us the chance to conduct overnight experiments in ERI@N after he knew our problem and it helped enormously in the start-up stage in my first year. It could be a long story if I mentioned all the kindness he showed in these years. I shall never forget how lucky I was to have such a great advisor. He taught me not only how to solve a specific problem, but the methodology to tackle different obstacles in the future.

Dr. Muhammad Danang Birowosuto, whom we usually called Dr. Danang, is really the guide who led me all the way in this perovskite scintillator field. To be honest, I knew nothing about scintillators and I initially I had not even heard the word ‘scintillator’. Dr. Danang was working on scintillators for his PhD and he is very experienced in this direction. His wide-reaching connections provided the experimental conditions that had

not existed in NTU. None of the characterizations under high energy radiation in this thesis could have been done without him. He is very nice and willing to answer all questions I asked. Besides, he seems to be all-mighty in optics. We communicate and share a lot in daily life and he is like a good friend to me.

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Lionel Messi, my favorite, and the best football player in the world, inspires me to work harder and go further every weekend when I watch his matches. Congratulations to his recent sixth Ballon d'Or reward.

Thank you for the publishers to allow me to reuse my published data in the Chapter 4-6 in this thesis.

At last, I really appreciate my wife, Fengyin Chen and my son Yunqian Xie. My wife has been in a full-speed mode since the birth of my son and she seldom got rest physically or mentally. Taking care of our baby should be our shared responsibility, but

she now takes all the burdens alone and also does the job of a father in China. However, she has continued to support me. I feel so sorry for her and want to accompany her as soon as possible. My son is one year old now but I have spent only slightly more than a month with him. His birth indeed gave me motivation to be a better man, and I hope to be a decent example for him.

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Summary

Perovskite scintillators have been a rising research topic after the zeal on promoting perovskite solar cell efficiency. Heavy element Pb, low fabrication cost and relatively strong emission make some of perovskite scintillators (like $(\text{PEA})_2\text{PbBr}_4$ and $(\text{BA})_2\text{PbBr}_4$ in this thesis) potentially competitive in comparison to current commercial scintillators. In this thesis, the focus will be on the how different components, including organic cation, halide anion and dopant affect the scintillator performance. A series of characterizations were systematically carried out to correlate the perovskites' properties to their behavior and performance. Based on these characterization results, corresponding conclusions and predictions will be provided.

To begin with, we synthesized and characterized 3D perovskite MAPbX_3 ($\text{X}=\text{Cl}$, Br or I) single crystals that have been well studied in solar cell and optoelectronic areas but relatively new in the scintillator field. My first work (Chapter 4) demonstrated the effect of halide anions on thermal quenching behavior of perovskite under X-ray. The thermal quenching activation energy and the ratio between the thermal quenching rate and the radiative transition rate are decreasing from MAPbCl_3 to MAPbI_3 in 3D MAPbX_3 family. The conclusion could be reasonably extrapolated to 3D perovskites beside methylammonium lead halide perovskites.

After mastering the synthesis of 3D perovskite crystals and the related characterization analysis, we further explored the 2D perovskite crystals, which were predicted to be better compared to 3D counterpart. In my second work (Chapter 5), we found that Li doping can enhance the scintillating performance of 2D perovskite $(\text{PEA})_2\text{PbBr}_4$, such as higher light yield and smaller light yield difference caused by temperature change. In addition, for the first time we utilized the Li dopant strategy to extend the detection

energy range by demonstrating the detection of alpha particle and thermal neutron with our Li-doped (PEA)₂PbBr₄ crystals. With such strategy, there are numerous chances to develop new functionalities based on available perovskite scintillators.

Furthermore, we explored the similarities and differences in 2D perovskite crystals made of varied cations and anions as my last work (Chapter 6). We synthesized eleven 2D perovskites with different cations and anions to compare the influence they brought. Bromide perovskite crystals are better over the chloride and iodide ones in terms of high chemical stabilities in ambient as well as their emission wavelengths that match the high quantum efficiency ranges of Si-based detectors. Simple linear alkyl and small bulky ring-containing cations tend to introduce (100) type which typically exhibits narrow emission and more likely to show negative thermal quenching behavior (stronger emission upon higher temperature). Cations containing O and N elements (beside ammonium group) usually lead to (110)-orientated perovskites which show broad emissions in visible light range because of self-trapped excitons. We believe our conclusions in this thesis could shed light on similar scintillator design investigations.

At last, based on my experimental skills and knowledge learnt from other perovskite scintillator references, I ended up my thesis with the comparison of 2D and 3D perovskite single crystal scintillators. 3D perovskite scintillators (especially thick crystal samples) are easy to obtain due to early synthesis investigations. This provides a good way to predict, modify and test the properties and performances of 3D perovskite scintillators. Ultimately, we should focus on 2D ones due to their theoretically higher performances although the current synthetic method is inefficient. 2D perovskite single crystal scintillators are potential candidates to compete with current commercial scintillators in the future market.

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Chapter 1 Introduction

1.1 Motivation

Currently there are two types of radiation detections using perovskites, direct detection and indirect detection as shown in Figure 1-1. Direct detection takes advantage of the gammapoltaic effect which convers high-energy photons to detectable electrons. This semiconductor type of detector is straightforward and only needs one conversion from radiation photons to electrons. However, other components beside perovskites like electron and hole transport layers for efficient exciton dissociation are also necessary. The deposition of these extra layers increases the cost and the difficulty in fabrication. That is one reason why in this thesis we are more interested in the other indirect scintillator detection. Another reason is that the free carrier extraction efficiency is low if the perovskite layer is thick. Indirect detection requires a scintillator, an active material that can convert high-energy radiations, such as X-ray, gamma-ray, ions, electrons, and neutrons into visible light photons. After the radiation to visible light photons conversion, visible light photons will be detected by a coupled photodetector. Although indirect detection needs two conversions, i.e., radiation photons - visible light photons - electron, the device component can be integrated into commercial Si technology. Most current X-ray detection equipment are based on this indirect scintillator detection. Majority of the cost lies in the high-temperature-grown scintillators since the coupling commercial photodetectors array are relatively low-cost. Therefore it is of practical and commercial interest to find a new type of scintillator that avoids the use of high temperatures in order to substantially reduce the cost in energy consumption.

Figure 1-1 Scheme of direct and indirect detections.

The history of scintillators began at the time of the discovery of X-rays¹. After a century of development, a variety of scintillators have been commercialized. Different types of scintillators for different radiation detection have been intensively studied and widely employed in different fields. In current days, depending on the radiations, different scintillators are used. For example, NaI:Tl and CsI:Tl scintillators perform well in typical X- and gamma-ray detection and their cost are relatively low. BGO ($\text{Bi}_4\text{Ge}_3\text{O}_{12}$) scintillators are useful in cases where thin scintillators are needed under high energy gamma-ray. Lithium glass scintillators are specific for neutron detection while co-doped NaI:(Tl+Li) scintillators can even detect and distinguish gamma-ray and thermal neutrons.

Figure 1-2 Emissions from scintillators under radiation².

It is reported that the global scintillator market reached a value of \$425 million in 2018³. Medical imaging amounts to a considerable portion in this value. Healthcare and clinical applications are the two principal driving forces. Though current knowledge of different diseases is much richer than before, increasing occurrence of some diseases like cancer, stroke and cardiovascular diseases are still huge threats to people. Minimally invasive surgery compared to open surgery for these diseases requires an efficient integrated system for real-time diagnosis. X-ray imaging, including radiography, mammography, myelography and so forth, is one of these minimally invasive techniques. In principle, all these systems require the application of scintillators. Because most current commercial silicon-based photodetectors cannot (or are very inefficient to) ‘see’ X-rays, scintillators are needed to assist the detection by converting X-rays to visible light that can be efficiently detected by silicon-based photodetectors. Figure 1-3 demonstrates an

application of scintillators in medical imaging equipment⁴.

Figure 1-3 Application of scintillators in chest radiograph⁴.

X-rays are one energetic ionizing radiation that can damage our organs by destroying the DNAs, therefore it is beneficial to the human body to have a lower dose of X-rays. That is one reason why researchers are interested in finding sensitive scintillator so that a lower dose of X-rays can be used, whilst maintaining the imaging quality. In a real-time medical spectroscopic mode, each X-ray image is recorded in a short period and to avoid the signal pile-up, a fast luminescence decay is necessary for a high scintillator on/off frequency. Beside medical applications, other areas such as astronomy demand a scintillator with high sensitivity to radiation, selectivity to different radiation types or possibly equal detectivity to a single type of radiation but at different energy levels⁵. Security is also one area where scintillators are particularly useful. For example, Cargo NII (non-intrusive inspection) systems, especially for large cargo inspection, require relatively large-size scintillators for fast detections⁶. In this case, the sensitivity

requirement for scintillators is lower but the low cost of scintillators is the priority.

Figure 1-4 X-imaging in cargo inspection⁷.

There is no single all-mighty scintillator that can serve all purposes⁸. However, in general, we want a scintillator to be sensitive (bright under radiation and able to discriminate between different radiation energy levels) and low-cost. Traditional scintillators are grown using the Czochralski or Bridgman method, for instance, bulk crystalline CsI:Tl (621 °C), bismuth germanium oxide (BGO, 1050 °C), CaWO₄ (1600 °C) and Lu₂SiO₅:Ce³⁺ (LSO, 2050 °C). Substantially high temperatures are needed to melt all the precursors so the energy consumption is high. Therefore, a large-size scintillator-based detector system would be rather expensive. The demand for low-cost scintillators has been motivating new discoveries of low-temperature solution-processing methods to fabricate high-quality and large-area scintillators. Also, it will be attractive to improve the performance or extend the detection range of scintillators at the beginning of solution-processing fabrication by using simple strategies like doping other metal elements.

A group of materials known since the nineteenth century, known as halide perovskites, have recently regained researchers' attention. The superior performance, as well as the low cost of perovskite-based solar cells, led to new investigations of perovskites in other fields. Perovskites for X-ray/gamma-ray detection is one of the hot topics. The intrinsic heavy lead element ($Z = 82$) is beneficial for perovskites to strongly absorb high-energy radiation as higher Z allows more electrons/ nuclei to involve in radiation attenuation. The principal merit of perovskite is the possibility of large-scale solution-processing fabrication. Thanks to early developments in perovskite solar cells, development of the solution-processed perovskite scintillator does not begin from zero. Scientists have shown comparable performances of certain perovskite scintillators to traditional ones. Given the combination of good scintillator performance and low-cost solution-processing fabrication, it is of practical and commercial interest to investigate the subject of this thesis; the solution-processed perovskite single crystal scintillators.

1.2 Objectives

Primary objectives of this project are listed below.

- Synthesize a series of 3D and 2D perovskite single crystals with solution-processing method.
- Investigate the effect of halide anions on thermal quenching behavior (weaker emission upon higher temperature) of 3D MAPbX_3 ($X = \text{Cl, Br or I}$) perovskite single crystal scintillators.
- Study the effect of Li dopant on the performance of 2D phenethylammonium lead bromide perovskite single crystal scintillator and the possibility of Li-doped perovskite scintillator for alpha particle and thermal neutron detection.
- Compare the effect of different organic cations in 2D perovskite single crystal on X-ray scintillating performance.

These goals are more related to fundamental investigations and demonstrate potential X-ray imaging applications since most perovskite single crystal scintillators are at an early development stage whose scintillating performance is far from their limit. The Li-doped perovskite scintillator is a proof of our concept that doping can extend the detection range. The library of 2D perovskites comparatively investigate their properties and scintillation performance. Our research results will be useful in future perovskite scintillator design

1.3 Approach

The traditional method to grow a halide perovskite single crystal is by the Czochralski or Bridgman method. However, recently researchers developed a series of low-temperature solution-processing methods⁹⁻¹¹. One breakthrough for the MAPbX₃ perovskite single crystal is the inverse temperature crystallization (ITC) method¹². It now takes just a few hours to obtain a high-quality MAPbX₃ single crystal. Compared to commercial scintillators, the cost of perovskite scintillator production with ITC method is much lower and the efficiency is tremendously improved^{13,14}. In this perovskite scintillator project, we will take advantage of such efficient single crystal growth of MAPbX₃ and focus on single crystal scintillator characterizations. MAPbX₃ single crystal scintillators with mixed halide anions and polycrystalline film scintillators will not be discussed.

We also investigate the performance of 2D perovskites. The growth of 2D or so-called layered perovskite dates to 1970s^{15,16} and after almost five decades' development, researchers summarized more techniques and skills to acquire crystals of superior quality. In this project, we adopted the most widely applicable but relatively less efficient method, slow solvent evaporation¹⁷. As long as there is a solvent that can dissolve all the precursors, this method will work. However, it may take up to more than

one month to obtain a crystal of sufficient size for measurement purposes. Thus, it is necessary to prepare a bunch of vessels loaded with precursor solution at the same time.

All these 3D and 2D perovskites can be obtained at low temperatures by using wet chemistry. After the synthesis, we performed material characterizations and measured different scintillating properties with traditional scintillator characterization equipment.

1.4 Major contribution of the thesis

Lead halide perovskites have been receiving increasing attention since researchers discovered the superior performance in perovskite solar cells. However, the biggest advantage of perovskite lies in its solution-processing, which could bring the possibility of low-cost mass production. This advantages still holds true in case of perovskite scintillators. The current understanding of perovskite scintillators is based on studies on previous traditional scintillators and luminescence mechanisms under UV-vis excitation. In this thesis, we investigate the fundamental mechanism of perovskite and employ the idea of doping to expand the functionality of perovskite.

The first contribution of this thesis is the systematic study on the effect of halide anions and cations on the thermal quenching of single crystal methylammonium lead halide (MAPbX_3 , $\text{X}=\text{Cl}$, Br or I) and cesium lead bromide (CsPbBr_3). These four 3D perovskite crystals are the most representative ones in current perovskite scintillator study and our contribution may help predict the anion effect on thermal quenching in other halide perovskites. These crystals are synthesized by the inverse temperature crystallization method are all in high quality and stable enough for different characterizations. We compared these representative perovskites and concluded the difference brought by different halides and cations. MAPbCl_3 has both largest thermal quenching activation

energy (ΔE_q) and the ratio between the thermal quenching rate and the radiative transition rate (Γ_0/Γ_v) while MAPbI₃ has the lowest. In other words, the emission of MAPbCl₃ is the least subject to increasing temperature when temperature is relatively low, but it will show faster quenching than Br and I ones as temperature continues increasing. Substitution of cation (like MA with Cs in our experiment) changes Γ_0/Γ_v but has little influence on ΔE_q .

The second contribution is to prove our idea that extra scintillator function of 2D perovskite can be introduced by doping. In this case, 2D perovskite (PEA)₂PbBr₄ was doped by Li. We carefully examined the effect of Li dopant on X-ray luminescence, light yield and decay time. Li doping enhances while broadens the emissions of (PEA)₂PbBr₄ crystals compared to undoped ones. Such effect is stronger upon higher Li doping level. The light yields of highest 1:1 Li-doped (PEA)₂PbBr₄ crystal and undoped one are 11,000 and 8,000 photons/MeV, respectively. But we found the Li doping has little impact on the decay time. Successful pulse shape discrimination between alpha particle and gamma-ray is presented using our 1:1 Li-doped (PEA)₂PbBr₄ crystal and it indicates the potential of thermal neutron detection because alpha particles are the reaction product of ⁶Li and thermal neutron. Thermal neutron pulse height measurement was carried out and the full energy peak was found although its energy resolution was poor. We consider the result can meet our expectation if optimization of crystal growth is successful. In addition, we proved our idea that doping in 2D perovskite scintillators can extend their detection range.

The third contribution is related to compare and summarize the effect of organic cation on 2D perovskite scintillators. A series of 2D bromide and iodide perovskite crystals with different organic cations were grown. These perovskites were systematically

compared and their characteristics were summarized. We found that usually organic cations can be catalogized into two types depending on the orientation of the corresponding 2D perovskites ((001) or (110)). Simple linear alkyl and small bulky (phenethylammonium and cyclohexylammonium) cations tend to introduce (001) type which typically exhibits narrow emission. Negative thermal quenching behavior was found in perovskites with butylammonium (BA), octylammonium (OA) and phenethylammonium (PEA) cations. While long linear containing oxygen or nitrogen element beside carbon and hydrogen cations tends to introduce (110) type whose emission is likely to be broad and this broad emission can be explained by self-trapped excitons. In addition, we found that butylammonium lead bromide showed the highest light yield of 40,000 photons/MeV. This information could be useful for other researches in 2D perovskites.

1.5 Organization of the thesis

The next chapters are arranged as follows:

Chapter 2 focuses on the scintillator review, including a brief history and the advantages/disadvantages of inorganic and organic scintillators. Then the structures of 3D and 2D perovskites are discussed to provide the necessary information to understand how their structures and optical properties correlate in Chapter 4-7. At last, we introduce the recently fast development of perovskite scintillators and highlight their most attractive merit that perovskites can be solution-processed at low temperature in low cost.

Chapter 3 details most of the experimental method and characterization techniques in this thesis. The growth method of perovskite crystals and the mechanisms behind them

will be highlighted. Concise introductions and mechanisms of characterization techniques are necessary for understanding why these characterizations are needed.

Chapter 4 is dedicated to scintillator characterizations of four most representative perovskite single crystals, MAPbCl₃, MAPbBr₃, MAPbI₃ and CsPbBr₃. In this chapter, we explore the influence on thermal quenching brought by different halide anions and cations under X-ray radiation. We conclude that both thermal quenching activation energy and ratio between thermal quenching rate and radiative transition rate decrease from Cl to I. The quenching effect of bismuth doping in MAPbBr₃ is also investigated. This chapter sheds light on the halide effect in perovskite scintillator applications and explores the possibility of metal ion doping to achieve certain results.

Chapter 5 aims to characterize one most representative 2D perovskite scintillator, phenethylammonium lead bromide (PEA)₂PbBr₄. In this experiment, we prepared the lithium-doped (PEA)₂PbBr₄ single crystal by mixing Li precursor in the (PEA)₂PbBr₄ precursor solution. Our goal is to investigate the effect of Li dopant in X-ray luminescence, scintillation light yield and scintillation decay under gamma-ray radiation. Information were highlighted about negative thermal quenching behavior (i.e., stronger emission upon higher temperature, opposite to typical thermal quenching in 3D perovskite scintillators and many other light-emitting materials) in 2D perovskites since such behavior may allow scintillators to have maximized emission without cooling to low temperature. Finally, we also introduce a new strategy of ⁶Li doping for thermal neutron detection and carry out the X-ray imaging experiment with our (PEA)₂PbBr₄ scintillator screen.

Chapter 6 is a comparison and summary of the effect of a series of organic cations and different anions on 2D perovskite scintillating performance under X-ray. Though there

is still unclear mechanism, we managed to extract some useful information that are beneficial to reasonable 2D perovskite crystal design and prediction of new perovskite scintillator performance.

Chapter 7 is the summary of the project and prospect of perovskite scintillator. We conclude the previous results and propose some future works to further this project. Perovskite scintillator is still a new field and hopefully our proposal could pave way to deeper understanding in the luminescence mechanism, improving the scintillating performance and enabling new functionalities of scintillators.

The last chapter is the list of all publications with my involvement.

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Chapter 2 Literature survey

2.1 Scintillator overview

2.1.1 Inorganic scintillators

In the late 19th century, Roentgen discovered the emission from Ba[Pt(CN)₄] under X-ray radiation¹. After decades of development, other ionizing radiation were discovered gradually, accompanied by a variety of scintillators. Figure 2-1 demonstrates the history of discovery of major inorganic scintillators. CaWO₄ and ZnS being first scintillators showed up in the early 20th century². CaWO₄ are still being used in gamma-ray detection due to its satisfactory light yield and energy resolution³ and with the activator Ag, ZnS: Ag is reported to be a good neutron scintillator⁴. Most of current inorganic scintillators are ionic bulk crystal that are synthesized in high-temperature furnace. In the 1940s, NaI crystal with Tl ion impurity was found to be a good scintillation counter by Hofstadter⁵. Later on Tl ion and other ion impurities like Na⁺ and other divalent or trivalent rare earth metal effectively enhanced the light yield or alter the emission. These impurities are called ‘activator’. Activators, though their concentrations are low, are able to create new energy levels between bandgap of those host scintillators and hence maximizing electron-hole recombination and reducing reabsorption of the emission. Table 2-1 lists some common inorganic X-ray and gamma-ray scintillators. NaI:Tl and CsI:Tl are still the most widely used gamma-ray scintillators nowadays because of their satisfying light yield and energy resolution though they are hygroscopic. Besides, the cost of mass production of these two scintillators are relatively low because of their low melting points (< 700 °C). These factors make them dominators in the market. Besides mentioned tungstate scintillator, some heavy metal oxide scintillators like lutetium yttrium orthosilicate (LYSO) and bismuth germanate (BGO) also show superior

performance. But due to their high prices due to their melting points in fabrication, they are not widely employed as NaI:Tl and CsI:Tl. But one big merit of oxide scintillators is that they are not hygroscopic, hence they can survive well in ‘bad environment’.

Figure 2-1 History of major inorganic scintillators (from Webber et al.⁶).

Table 2-1 Overview of some common inorganic scintillator in X- and gamma-ray detection (from Maddalena et al.⁷).

Scintillator	Density (g/cm ³)	Effective atomic umber	LY (ph/MeV)	Energy resolution (%) at 662 keV)	Emission wavelength (nm)	Decay time (ns)	Refs.
NaI:Tl	3.7	50.8	43,000	6.7	415	230	^{8,9}
CsI:Tl	4.5	54	66,000	6.6	560	1000	⁹
CsI:Na	4.5	54	43,000	7.4	425	-	¹⁰
CsF	4.6	53.2	1,900	19	390	2-4	¹¹
BaF ₂	4.9	52.7	1,430	10	175	0.8	¹¹
CaWO ₄	6.1	75.6	15,800	6.2	425	6,800	³
PbWO ₄	8.3	75.6	140	-	~475	~10	¹²
CdWO ₄	7.9	64.2	19,700	6.5	495	104	¹³
Bi ₄ Ge ₃ O ₁₂ (BGO)	7.1	75.2	8,200	27	505	300	¹⁴
Lu _{2-2x} Y _{2x} SiO ₅ (LYSO)	7.4	66	32,000	7.1	420	45	¹⁵
CdS:Te	4.8	48	17,000	24	640	270-3,000	¹⁶
ZnS:Ag	4.1	27.4	73,000	-	450	105	¹⁷

2.1.2 Organic scintillators

Organic scintillator are typically conjugated molecules which demonstrate fluorescence emission. Table 2-2 lists some commercial organic scintillator. The first organic scintillator naphthalene dates back the same late 1940s where NaI:Tl and CsI:Tl were discovered¹⁸. Within the next few years, anthracene¹⁹ and stilbene²⁰ were found be useful as scintillation counters. Organic scintillators can be in a variety of forms, liquid solutions, plastics and solid crystals²¹. They can detect charged radiations like alpha and beta radiations well as electromagnetic radiations (like X- and gamma-ray²²). As organic component, flexibility can be complied for special cases where rigid scintillators do not work well. Extrusion, injection molding and glass mode casting are mature techniques in standard production²³⁻²⁵. In addition, the production cost of organic scintillator can be of low price since the synthesis and engineering process do not require high temperature as inorganic ones. Similar to oxide scintillators, organic scintillators are not hydroscopic. Optical emission tuning can be achieved readily as well because chemical functional group design is quite mature in current days. The most important character of organic scintillators is their fast decay, typically < 5 ns, due to absence of trapping process that usually occurs in case of inorganic scintillators, especially ones with activators. However, being completely organic indicates organic scintillators do not have sufficiently high density and high Z for X- and gamma-ray absorption. But still they can be practical in charged particle detection. In general, the average light yields and energy resolutions of commercial scintillators are not good as those of commercial inorganic ones.

Table 2-2 Overview of some commercial organic scintillators

Scintillator	Density (g/cm ³)	Molecular weight	Emission wavelength (nm)	Light yield (ph/MeV)	Decay time (ns)	Refs.
Anthracene	1.25	178	445	20,000	30	²⁶
Stilbene	1.22	180	290	14,000	3.5	²⁶
Doped p- terphenyl	1.23	280	420	27,000	3.7	²⁶
polystyrene	0.96-1.04	Depends	390-480	~10,000	3.3	²⁶

2.2 Perovskite crystal structure and scintillator applications

2.2.1 3D perovskites structure

Perovskite, named after a Russian mineralogist Lev Perovski, is a group of compounds that share the same structure ABX_3 as calcium titanate ($CaTiO_3$). In this thesis, perovskite indicates the group of lead halide perovskite ($APbX_3$, A = organic cation or Cs and X = Cl, Br or I) instead of traditional oxide perovskite. We will introduce three classes of perovskite here, three-dimensional bulk $APbX_3$ perovskite and two-dimensional bulk A_2PbX_4 perovskite.

To begin with, $APbX_3$ perovskite is first class of perovskite that were studied for its photoconductivity ($CsPbX_3$) in the late 50s²⁷. In the late 70s, methylammonium (MA) was in with Cl-, Br- and I- as anion by Weber and co-workers²⁸. In this part, the most

representative organic-inorganic hybrid halide perovskite MAPbX_3 ($\text{X} = \text{Cl}, \text{Br}$ and I) is discussed. Three typical crystal structures of MAPbX_3 perovskites, cubic, tetragonal and orthorhombic phases, are shown in Figure 2-2 and the detail of phase transition is listed in Table 2-3. All MAPbX_3 crystals share the same three types of crystal system, i.e., cubic, tetragonal and orthorhombic with slightly different space group. From Cl to I, the lattice constant increases and thus the volume. Lead chloride and bromide perovskites usually are in cubic structure with the $Pm3m$ space group at high temperature. Therefore, cubic crystal of MAPbCl_3 and MAPbBr_3 is usually the product obtained after synthesis either by high temperature melting or solution processing.

Figure 2-2 Scheme of three crystallographic structures of perovskite MAPbX_3 ($\text{X} = \text{Cl}, \text{Br}$ and I) (from Liu et al.²⁹).

Table 2-3 Temperature-dependent phase of $\text{CH}_3\text{NH}_3\text{PbX}_3$ (X = Cl, Br and I)

Phase	Temperature (K)	Crystal system	Space group	Lattice (pm)
MAPbCl ₃				
α	> 178.8	Cubic	<i>Pm3m</i>	a = 567.5
β	172.9 – 178.8	Tetragonal	<i>P4/mmm</i>	a = 565.6 c = 563.0
γ	< 172.9	Orthorhombic	<i>P222</i>	a = 565.6 b = 562.8 c = 1118.2
MAPbBr ₃				
α	> 236.9	Cubic	<i>Pm3m</i>	a = 590.1 (1)
β	155.1 – 236.9	Tetragonal	<i>P4/mcm</i>	a = 832.2 (2) c = 1183.2 (7)
γ	149.5 – 155.1	Tetragonal	<i>P4/mmm</i>	a = 589.4 (2) c = 586.1 (2)
δ	< 144.5	Orthorhombic	<i>Pna2</i>	a = 797.9 (1) b = 858.0 (2) c = 1184.9 (2)

MAPbI ₃				
α	> 327.4	Cubic	$Pm\bar{3}m$	$a = 632.85$ (4)
β	$162.2 - 327.4$	Tetragonal	$P4/mmm$	$a = 885.5$ (6) $c = 1265.9$ (8)
γ	< 162.2	Orthorhombic	$Pna2$	$a = 886.1$ (1) $b = 858.1$ (2) $c = 1262.0$ (3)

However, because of much larger ion size of iodide, at room temperature the cubic MAPbI₃ cannot tolerate the existence of I⁻. Thus, tetragonal structure is formed by slight distortion of the PbI₆ octahedra around the c axes²⁸. And that is why the MAPbI₃ is varied from the other two at room temperature.

It should be pointed out here the importance of fixation of CH₃NH₃⁺ cation. In either cubic or tetragonal symmetry, the non-spherical cation cannot be fixed because tetrahedral coordinated carbon and nitrogen atom show random distribution. Such behavior causes orientational disorder and polarization. In orthorhombic phase, for MAPbBr₃ and MAPbI₃, the CH₃NH₃⁺ cation can be fixed in position whereas for MAPbCl₃, CH₃NH₃⁺ cation is still in a twofold disordered position. However, there is no such behavior for spherical Cs⁺.

The most famous application of MAPbX₃ is the photovoltaics, especially MAPbI₃. The strong absorption of UV-vis light allows the active material to be relative thin, typically

within 500 nm^{30,31}. Perovskite solar cells are considered to be a potential competitor to the current silicon solar cell because of their much low cost in raw material and fabrication while comparable performance. MAPbI₃ has a small exciton binding energy, in the range of 19- 50 mV and a carrier diffusion length over 175 μ m determined from a high-quality single crystal³². These characteristics makes MAPbI₃ very attractive in solar cell field³³⁻³⁵.

2.2.2 2D perovskites structure

2D halide perovskites in history can be categorized into three types, (001), (110) and (111)-orientated perovskites depending on the stacking orientation with respect to ideal cubic perovskites³⁶ as shown in Figure 2-3. They can be considered cut from the 3D structures by replacing small organic cations with large organic spacer.

Figure 2-3 Three different 2D halide perovskite structures: (001), (110) and (111) (from

Ma et al.)

Among the (001) perovskites, there are Ruddlesden-Popper phase, Dion-Jacobson phase and alternating cation in the interlayer space type³⁶. Ruddlesden-Popper phase is the most common structure while Dion-Jacobson phase is less common³⁸. These two perovskite structures can be found in nature but alternating cation in the interlayer space type is only available in specially designed perovskites³⁹. Here we only focus on (110) perovskites and (001) ones (Ruddlesden-Popper phase and Dion-Jacobson phase). In terms of ammonium function group numbers in the organic cations, there are two kinds of organic-inorganic compounds, $(R-NH_3)_2PbX_4$ and $(NH_3-R-NH_3)PbX_4$, where $R-NH_3$ is an aliphatic or aromatic derivatives ammonium cation and X is the halogen anion. Figure 2-4 demonstrates these two possible ideal structures, where $R-NH_3$ is an aliphatic or aromatic derivatives ammonium cation and X is the halogen anion. In the monoammonium (staggered) compounds, the successive layers are held together by van der Waals force among the organic cation interdigitation, i.e., Ruddlesden-Popper phase. Octahedral covalent PbX_4^{2-} is the framework forming the inorganic layer and there are ionic bonds between the ammonium cations and the halogen anions connecting the inorganic layer and the organic layer. The ideal diammonium compounds have an eclipsed configuration where the octahedral frameworks align vertically, i.e., Dion-Jacobson phase. The biggest difference is that in the eclipsed configuration two adjacent inorganic sheets are directly hydrogen bonded to the organic cations. In this configuration, the interdigitation of cations no longer exists and now one inorganic sheet can ideally stack on another inorganic sheet without displacement. However, actual details will influence the distinction between these two structures, for instance, the PbI_4^{2-} of much larger volume than the chloride or bromide counterparts and the manner of how organic cation bonds to inorganic layer.

Figure 2-4 Two ideal 2D perovskite crystal structures, staggered (monoammonium) and eclipsed (diammonium) (from Arend et al.⁴⁰).

The length of the organic chain substantially determines the spacing between two adjacent inorganic sheets and this spacing can be determined by XRD. As mentioned above, at room temperature the actual structures deviate from the ideal cases, where the PbX_4^{2-} frameworks tilt to adapt to the bulky organic parts or hydrogen bonds. In this work, our 2D perovskites are relatively complicated so that we cannot consider them in ideal structures. Figure 2-5 shows the structure of $(BA)_2PbI_4$, one of the 2D perovskite we investigated in this thesis at room temperature. We can see the real structure is far from ideal case but still it belongs to the staggered configuration. $(PEA)_2PbBr_4$ is more or less similar but less distorted because the $PbBr_4^{2-}$ is less bulky.

Figure 2-5 Structure of actual $(\text{BA})_2\text{PbI}_4$ at room temperature (from Arend et al.⁴⁰).

2.2.3 Perovskite Scintillators

Perovskite scintillator is a quite broad concept. So here we only limit it to organic-inorganic hybrid perovskite with heavy metal Pb or Bi and fully inorganic perovskite with heavy metal Pb or Bi. These heavy elements allow perovskite scintillator to be advantageous in absorbing high-energy radiation compared to organic scintillator. Also, we limit the concept to the scope where perovskites are obtained by solution-processing instead of high-temperature Bridgman or Czochralski growth⁶. Therefore, oxide perovskites like $\text{Lu}_3\text{Al}_5\text{O}_{12}$ (LuAG), YAlO_3 (YAP), and above LYSO are excluded here. The idea of solution-processing fabrication is what researchers and the market values most compared to current commercial inorganic scintillators because such fabrication could save large amount of money by avoid huge energy cost in high-temperature oven. At last, smaller bandgap and relatively higher photoluminescence quantum efficiency of perovskite result in a larger theoretical light yield maximum compared to traditional scintillators⁴¹.

At the moment, perovskite scintillators could be categorized into two-dimensional (2D) perovskite scintillator, three-dimensional (3D) perovskite scintillator and perovskite nanocrystal scintillator. The beginning of 2D perovskite research, to the best of our knowledge, dates back to 2006, in which the idea of organic/inorganic perovskite for picosecond X-ray scintillator was developed.⁴² The authors in this work saw the possible low cost brought by solution-processing scintillator fabrication but there is no experimental data such as scintillating light yield or decay except UV emission. In 2008, 2D perovskite phenethylammonium lead bromide ((PEA)₂PbBr₄) crystal obtained by slow solvent evaporation, was for the first time investigated as a gamma-ray scintillator^{43,44}. The light yield and the major decay time were 10,000 ph/MeV and 9.4 ns, respectively. But it did not receive immediate attention at that time. After the emergence of organolead halide perovskite solar cell, researcher reexplored the possibility of high-energy radiation detection application of perovskites. Due to early development in time-efficient synthesis of bulk 3D perovskites, especially methylammonium lead halides (MAPbX₃, X= Cl, Br or I), researchers at first focused on the semiconductor-type direct detection of X-and gamma-ray using methylammonium lead halides (MAPbX₃, X= Cl, Br or I), i.e., the detection of photocurrent generated from the perovskite under X-ray radiation⁴⁵⁻⁵¹. Later on, researches on perovskite scintillators emerged and climbed up. Single crystal perovskite scintillators are preferred over thin film for the sake of sufficient thickness required to absorb energetic radiation. Because of strong thermal quenching at room temperature, MAPbX₃ perovskites usually require low temperature to exhibit high light yield. MAPbBr₃ single crystal has a light yield of a few thousand ph/MeV at room temperature while 90,000 ph/MeV at 77 K with a fast decay of less than 1 ns⁵² as shown in Figure 2-6. MAPbI₃ shares a similar case, where its light yield can be up to 50,000 ph/MeV at

50 K⁵³.

Figure 2-6 Temperature-dependent X-ray scintillation light yield of MAPbBr₃. (from Mykhaylyk et al.⁵²)

In 2016, Birowosuto et al. reported the X-ray luminescence comparison among 3D MAPbBr₃, MAPbI₃ and 2D perovskite, 2,2'-(ethylenedioxy)bis(ethylammonium) lead bromide ((EDBE)PbBr₄)scintillator crystals. He concluded that 2D perovskite holds more promises as perovskite scintillator due to their large exciton binding energy compared to that of MAPbBr₃ and MAPbI₃ at relatively higher temperature (> 150 K)⁵³ as shown in Figure 2-7. Large exciton binding energy favors exciton recombination and enhances the luminescence quantum efficiency, and ultimately improves the light yield. My work of this perovskite scintillator project inherited the idea from his work and continued further investigation.

Figure 2-7 Temperature dependent light yield of (EDBE)PbBr₄. (from Birowosuto et al.⁵³)

Finally, another perovskite scintillator of particular interest is perovskite nanocrystal, especially cesium lead halide nanocrystals (CsPbX₃, X= Cl, Br or I). The readiness to fabricate perovskite nanocrystal by either hot injection^{54,55} or ligand assisted reprecipitation^{56,57} allows possible mass production. The major merits of perovskite nanocrystal lie in the solution-processing, tunable emission (400-700 nm), fast decay (~10 ns) and high quantum efficiency. Currently, researches on perovskite nanocrystal scintillator focus on CsPbBr₃, whose emission under X-ray is 520 nm with a quantum efficiency close to unity⁵⁸⁻⁶⁰. Figure 2-8 shows some recent CsPbBr₃-nanocrystal-scintillator-based X-ray imaging detector. The integration of CsPbBr₃ nanocrystal scintillator and mature multichannel photodetector array provides satisfying X-ray images compared to current commercial CsI:Tl-based system.

Figure 2-8 (a) Scheme of X-ray detector based on CsPbBr₃ nanocrystal scintillator. (b) X-ray images (bottom) shows the structures of normal and defective ball pens (top). (c)

Scheme of a flat-panel X-ray imaging system. (d) Comparison of X-ray images of an Apple iPhone with and without perovskite scintillator. (e) Image of CsPbBr₃ nanocrystal solution and a large-area scintillator screen. (f) Optical and X-ray images of a transistor panel of a cell phone. (a) and (b) are from Heo et al.⁵⁸. (c) and (d) are from Chen et al.⁵⁹. (e) and (f) are from Zhang et al.⁶⁰.

In summary, perovskite scintillators are still in early laboratory stage and yet to compete with available commercial scintillators. However, the preliminary results are promising and exciting. Fundamental investigation into their emission mechanism and expanding their functionality would be beneficial to reasonable scintillator design in molecular level and a further step towards future commercialization.

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Chapter 3   Methods and characterization techniques

3.1 Perovskite synthesis and single crystal growth

3.1.1 General perovskite synthesis with self-assembly (SA) method

Perovskite materials can be generally described using following reactions:

where A is organic or inorganic cations with relatively small radii, like methylammonium (MA), formamidinium (FA) and cesium (Cs), X is the halide anions, mainly Cl, Br and I, and L is the organic cations with large radii (superscript 1 represents connects with single halide anion at one end while 2 connects with two halide anions at both ends), like phenethylammonium (PEA), butylammonium (BA), octylammonium (OA) and 2,2'-(ethylenedioxy)bis(ethylammonium) (EDBE). Since we are focusing on solution-processing perovskites, solid-state reactions (Czochralski or Bridgman methods) will not be discussed in this thesis in detail. For perovskite single crystal growth by wet chemistry, there is a general method, self-assembly method¹. The basic idea is that atoms will make up the structure with a high degree of order as a result of ionic interactions, or at times hydrogen bonding. It requires that there is one solvent which can dissolve all the organic or inorganic precursors. Therefore, organic solvents with high dielectric constants are preferred, including dimethylformamide (DMF), dimethyl sulfoxide (DMSO), γ -butyrolactone (GBL) and N-Methyl-2-pyrrolidone (NMP). Mixed solvent strategy is also an option^{2,3}. As solvent slowly evaporates and concentration becomes

high, nucleation occurs and crystallization begins. Since the solvents are of high dielectric constants, they are of high boiling point and hence difficult to evaporate at room temperature. It may take up to months or even longer to obtain a good crystal with desire size. Any disturbance should be avoided during the crystal growth. However, such self-assembly method is adopted more in case of 2D perovskites⁴. And in this project, most of the 2D perovskite crystals were obtained by this method. An example is shown in Figure 3-1 to illustrate the simplicity of this method.

Figure 3-1 Image of 2D perovskite crystal precipitated from the solution upon solvent evaporation.

Acid precipitation method in Chapter 7 is one special case of this SA method. Depending on the halide anion, all solid and liquid precursors are dissolved in the corresponding concentrated acid (like Br perovskite using HBr). If necessary, the solution will be heated to dissolve solid precursors. Upon cooling, crystals will slowly

precipitate and grow in the solution. The idea of acid precipitation is same as the general method above except the acid solvent is used instead.

3.1.2 Antisolvent vapor-assistant crystallization (AVC) method

Antisolvent vapor-assistant crystallization (AVC) method here is only applied in 2D perovskite crystal synthesis because there is a very efficient method to obtain MAPbX_3 crystals. The basic idea to choose one good solvent (solvents with high solubilities of precursors, DMF, DMSO or GBL) to dissolve the all the precursors necessary for the crystal formation and an evaporative bad solvent (solvents with low solubilities of perovskite crystals, chlorobenzene, nitrobenzene, dichloromethane or diethyl ether) in which the crystals has low solubilities. Then by putting precursor solution in good solvent in the environment of the bad solvent vapor, the vapor will slowly diffuse into the good solvent and results in crystal nucleation and growth as the solubility of perovskite becomes lower. It is a much faster growth method compared to the above self-assembly method. With the optimal choice of solvents, only a few days are needed to obtain crystals in reasonable sizes. However, in the case of $(\text{PEA})_2\text{PbBr}_4$ crystal growth, the product crystal were thin flakes that are not suitable for high energy radiation characterizations. Nevertheless, this AVC method is able to provide crystals in suitable sizes for single crystal XRD characterization, which is useful to determine the crystal structure of any new perovskite.

3.1.3 Inverse temperature crystallization (ITC) method for MAPbX_3

In my opinion, inverse temperature crystallization (ITC) method^{5,6} is one of the most important breakthroughs in the area of MAPbX_3 single crystal growth. Retrograde or inverse solubility refers to lower solubility of one solid solute in a solvent upon higher temperature. This behavior is rare because in most cases solubilities of solids increase

with increasing temperature. This ITC method takes advantage of the unusual retrograde solubility of MAPbX_3 in certain solvents or solvent mixtures^{5,7}. For instance, the temperature-dependent solubilities of MAPbBr_3 and MAPbI_3 are shown in Figure 3-2. Their solubilities decrease with temperature in certain ranges and these temperature windows allow us to precipitate the perovskite crystals by simply heating.

Figure 3-2 Temperature-dependent solubilities and yields of MAPbBr_3 and MAPbI_3 . Higher temperature increases the perovskite crystal product yield (from Saidaminov et al.⁷)

Figure 3-2b also shows general procedure of ITC method. The first step is to dissolve

all precursors in a chosen solvent, like DMF for MAPbBr₃. The second step is to heat up the solution to a set temperature (from 20 to 100 °C). And the last step to increase the temperature to allow crystals to grow in bigger sizes. Our experimental setup of ITC method to obtain MAPbBr₃ is shown in Figure 3-3. All precursors are dissolved in DMF in the left bottle and the solution are clear before heating. After heating, crystal formation starts due to lower solubility at higher temperature and we can see the crystals in the right bottle. The crystals continue growing bigger upon gradually increasing temperature. At last, once the crystal size is sufficient for characterizations, the crystal will be taken out, washed, and stored.

Figure 3-3 Image of experimental ITC method. Bottle in the left is before crystal formation and that in the right is after crystal formation.

For MAPbCl₃, a solvent mixture (DMF/DMSO, v/v = 1/1) is used. For MAPbBr₃ and MAPbI₃, pure DMF and GBL are employed, respectively. Pure DMSO is proved to be ineffective in MAPbX₃ single crystal growth. The mechanism of ITC method is clearly

demonstrated and shown in Figure 3-4, which includes four steps, initial dissolution, dissolution of colloids, super-saturation of perovskite solution and growth of perovskite crystal. However, unlike DMF or GBL, DMSO solely does not provide the acidic environment for dissolution of lead halide colloids even at elevated temperature which are formed after initial dissolution of lead halide precursor. Therefore DMSO only is not applicable in ITC method and but the reason to use DMSO in MAPbCl_3 crystal growth is because DMSO can dissolve the precursor methylammonium chloride (MACl) while DMF cannot. Typically, 1 M concentration is suitable and easy to handle. From my experience, higher concentration allows a lower growth temperature but may result in too many nucleations. The optimal temperatures for MAPbCl_3 , MAPbBr_3 and MAPbI_3 single crystal growth from 1 M precursor solutions are 50 °C, 80 °C and 110 °C. Gradual increasing the synthesis temperature helps enhance the product yield because of lower perovskite solubility. And this strategy is very useful in practice to obtain a large-size single crystal for high-energy radiation related characterizations.

Figure 3-4 Four stages in the ITC method in the MAPbX_3 single crystal growth. The bars on top represent the concentrations of different component (not to scale) in the solution and the spheres below represent each species (from Nayak, P.K. et al.⁸).

Unfortunately, there is no such efficient single crystal growth method for 2D perovskites. Fast growth of high-quality 2D perovskite will be a topic of interest since the long duration to acquire crystals of reasonable sizes hinders more intensive investigation into their useful properties.

3.1.4 Mixed halide perovskite single crystal growth

One of biggest merits of perovskite is the emission tunability. Most of the emission tuning can be achieved by simply adjusting or mixing the halide anions. Method of mixed halide perovskite single crystal growth is almost the same as the one for perovskite without mixed halides. In most case, the solubility of precursors with different halide components will not cause any problem since precursors can dissolve easily solvents like DMF or DMSO. However, the reactivities of different halides are not the same. Therefore, the halide ratio of the precursor usually differs a lot from the ratio of the product crystal. The product halide ratio can be determined by simple either X-ray photoelectron spectroscopy (XPS) or energy-dispersive X-ray spectroscopy (EDS). Lattice and emission wavelength of mixed halides can be obtained by X-ray diffraction (XRD) and photoluminescence (PL) spectroscopy characterizations, respectively.

3.2 Structural and chemical composition characterization techniques

3.2.1 X-ray diffraction (XRD)

Generally, there are two types of X-ray diffraction (XRD), powder XRD and single crystal XRD. XRD is a nondestructive and rapid technique to unambiguously identify and characterize unknown crystals. With specialized techniques, quantitative

investigation can be achieved also. To begin with, we will focus on the power XRD, where finely grounded, homogenized powders of bulk crystals were characterized. XRD technique is based on constructive interference of collimated monoenergetic characteristic X-ray. In XRD, only X-ray photons from Rayleigh scattering are considered while their absorption is ignored. In a certain volume in crystalline materials, X-ray photons scatter in all direction after impinging with all the atoms. Constructive inferences show up only when scattering X-ray photons satisfy the Bragg's law,

$$n\lambda = 2d_{hkl}\sin \theta \quad (1)$$

where n is the order of diffraction, λ is the incident X-ray wavelength, d_{hkl} is the lattice spacing and θ is the angle of diffracted X-ray beam. The XRD patterns contains useful information including peak positions and peak intensities (or more specifically, peak intensity ratios)⁹. Peak positions provide the lattice parameters, chemical compositions and qualitative phase analysis while peak intensities offer quantitative phase analysis¹⁰. Peak linewidths also allow analysis of crystal grain size and macrostrains^{11,12}. In this thesis, most of the XRD experiments are carried out with the Burker D8 Discover HR-XRD machine as shown in Figure 3-5. Cu K α ($\lambda = 1.5406 \text{ \AA}$) is used as the X-ray source and Ni is the filter. The details of experiments can be found in respective experimental methods in Chapter 4-6.

Figure 3-5 Bruker D8 Discover HR-XRD machine for powder XRD.

Single crystal XRD was also applied to determine the crystal structure of single crystal MAPbBr_3 in Chapter 4. The basic mechanism of single crystal XRD is very similar to powder XRD. Bruker Smart APEXII SC-XRD was employed, as shown in Figure 3-6.

Figure 3-6 Bruker Smart APEXII SC-XRD for single crystal XRD.

The major difference lies in the number of goniometers, where single crystal XRD uses

three or four goniometers while powder XRD uses only two. More goniometers allow collection of diffracted X-ray beams from four angles, 2θ (2-theta), Φ , χ and Ω to construct a three-dimensional crystal structure. These four angles define the relationship between the crystal lattice, the incident ray and detector as shown in Figure 3-7. The X-ray source is Mo K_α ($\lambda = 0.7107 \text{ \AA}$) and Zr is the filter. The crystal structure needed to be model using computer software using the data collected in single crystal XRD measurement. And after the modeling, a crystallographic information file will be generated containing all the crystallographic information.

Figure 3-7 Scheme of 4-circle diffractometer showing the angles (2θ , Φ , χ and Ω)⁹.

3.2.2 Scanning electron microscopy (SEM) equipped with Energy dispersive X-ray spectroscopy (EDS)

Scanning electron microscopy (SEM) is very useful in direct observation of specimens' morphologies. Compared to traditional optical microscope, SEM offers a much higher resolution due to the much shorter wavelength of accelerated electron beam ($\sim 0.01 \text{ nm}$, 124 keV)¹⁰. The primary electron beam interacts with atoms of specimens and a variety

of signals are produced. Figure 3-8 shows the possible signals. The most widely used mode in SEM imaging is secondary electron (SE) mode. By collecting secondary electrons after electron-atom interaction, surface topology and morphology can be reconstructed and directly observed. Although SE mode is limited to surface (usually < 10 nm) due to a strong absorption of charged electrons by the samples, its high resolution and great depth of field capabilities make SE mode the first choice in SEM imaging. Backscattered electrons from deeper surface (10-100 nm) contain valuable information about contrast between different compositions or phases. SEM (SE mode) was used to observe the morphology of perovskites. Besides, there are other useful signals including cathodoluminescence (CL), X-rays and Auger electrons. For instance, CL signal can provide information about impurities or mechanical defects in the crystals due to their different colors. X-ray signal is useful in Energy dispersive X-ray spectroscopy (EDS) which will be discussed in the next section. Auger electron signal can quantify element and chemical states from sample surfaces. The SEM is JEOL FESEM 7800F Prime equipped with INCA-XAct 10 mm² / XMax 50 mm² (TED) Energy dispersive X-ray spectroscopy (EDS) system.

Figure 3-8 Possible signals after interaction between primary electron beam and

specimen from SEM.

Figure 3-9 Field emission SEM equipped with EDS

Energy dispersive X-ray spectroscopy (EDS) is semi-quantitative technique to determine the elemental composition. EDS detects the characteristic X-ray from the sample and uses these ‘fingerprints’ to search the possible elements from the database. Although densities with from one sample to another, the depth resolution can usually reach 1 μm . Hence EDS provides the elemental composition of the bulk instead of the surface. Besides, it can be used to obtain a spatially resolved element mapping in a selected area. However, due to low intensities of characteristic X-ray from light elements and the absorption of low energy X-ray by protective beryllium window, light elements ($Z < 11$, i.e., ahead of sodium in the periodic table) are hard to be analyzed¹¹.

This unfortunately caused a problem in the lithium content determination in Chapter 6 so we turned to another technique for element characterization, X-ray photoelectron spectroscopy which we are about to discuss in the next section. This EDS technique proves to be useful in halide content determination, especially in mixed halide perovskites.

3.2.3 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS), also called electron spectroscopy for chemical analysis (ESCA) roots in the photoelectric effect. If the kinetic energy of the photoejected electrons is measured, one can calculate the hole-electron binding energy, or short for binding energy ($E_{binding}$), using the following equation according to the law of conservation of energy,

$$E_{binding} = h\nu - E_{kinetic} - \Phi \quad (2)$$

where $h\nu$ is the X-ray photon energy, $E_{kinetic}$ is the detected kinetic energy of the photoejected electron and Φ is work function. $E_{binding}$ is also an element ‘fingerprint’, similar to the characteristic X-ray in the case of EDS. By matching the $E_{binding}$ peaks in established database and knowing the expected elements, we can determine qualitatively if certain elements exist in the sample. Moreover, XPS is known to be a quantitative technique, whose accuracy can be $\pm 10\%$ if experimental conditions and operations are optimized. However, the most important reason we choose XPS is that it can probe the content of Li, which cannot be detected in EDS. Compared to EDS, XPS is a very surface-sensitive (a few nm) measurement. Therefore surface contamination or inhomogeneous specimen would cause problems in result analysis. If possible, different spots should be measured for comparison and averaging.

3.3 Optical characterization techniques

3.3.1 Photoluminescence (PL) and X-ray luminescence (XL) spectroscopy

In this section, photoluminescence (PL) spectroscopy and X-ray luminescence (XL) are combined and discussed together since their mechanisms behind are the same. PL is the probably most widely used characterization technique in studying the electronic structure of materials. Excitation light is directed to and partially or fully absorbed by the sample. The photon energy absorbed will excite electrons within the sample in the low energy state to permitted high energy state (excited state), and the relaxation of excited electrons could dissipate the excess energy through emission of photons or luminescence. In the case of photoexcitation described above, such luminescence is called photoluminescence. Luminescence can be formally divided into two categories, fluorescence and phosphorescence depending on the nature of excited state¹². In the fluorescence (excited singlet states), the excited electron has an opposite spin to the second electron in the ground state so it can return to the ground state and release a photon rapidly (lifetime in the range of 10^{-7} - 10^{-9} s). In phosphorescence (excited triplet states), the excited electron has the same spin as the other in ground state so transition is forbidden and the lifetime usually is 10^{-3} - 10^0 s. Figure 3-10 shows the scheme of PL process. Not all excited electron relaxations will give out photons, nonradiative relaxation by releasing heat is the competing process, like the internal conversion. PL has quite a few applications, including bandgap determination, impurity level and defect detection. Bandgap determination is the major application in this thesis and based on the bandgap change, we have our hypothesis and models. PL is a relatively simple measurement in terms of operation since PL systems nowadays are commercially mature and compact setups with user-friendly software.

In this thesis, multiple PL systems are employed for PL measurements. A HORIBA Fluorolog 3 ® Fluorescence system is useful in thin film and nanocrystal measurements at room temperature. The combination of the xenon lamp and the monochromator inside can be the excitation source with tunable wavelength. Nevertheless, the cm-size spot from the monochromator is too large for small samples. Also, the excitation intensity is relatively low so only strongly emissive samples are suitable for this Fluorolog 3 ® Fluorescence system. For few-mm-size single crystal perovskite PL measurement, an ACCENT Nanometric RPM200 system is used instead because we would like to take advantage of the high power 325-nm laser and small laser spot that can be focus on the crystal surface (especially useful for MAPbCl₃ single crystal). Figure 3-11 and Figure 3-12 show the PL systems of HORIBA Fluorolog 3 ® Fluorescence and ACCENT Nanometric RPM200. The detail experimental method about PL can be found in Chapter 4 to 6.

Figure 3-10 Scheme of PL processes. (from Lakowicz¹²)

Figure 3-11 HORIBA Fluorolog 3 ® Fluorescence PL system.

Figure 3-12 ACCENT Nanometric RPM200 PL system.

Typical PL systems use white light or lasers in UV or visible range wavelength as excitation sources, so the photon energy is relatively low, usually lower than 4 eV. While XL applies soft X-ray as excitation, the photon energy is typical 8-15 keV, which is much higher than laser used in PL. Hence the electron excitation and relaxation processes are more completed in the case of XL where ionization occurs. XL is a catalog of radioluminescence (RL), whose luminescence can be induced by alpha particle, fast electron, X-ray, gamma-ray and so forth¹³. In this thesis, XL spectra of our perovskite scintillators are detailed. Because scintillator converts high energy radiation into UV or visible light photons, XL spectra of scintillators is similar to PL spectra of typical emissive semiconductors. In the scenario of perovskites, XL and PL spectra shares very similar main features except that XL spectra contain more other information. The high-energy excitation in XL leads to beyond band gap excitation, resulting in other phenomena such as core-valence or Auger-free luminescence. In addition, as XL can originate from deep-in-side of the materials due to in-depth penetration of X-ray, it also can provide information about surface reabsorption, emission properties, estimation of scintillator performance, stability over X-ray and so forth.

3.3.2 UV-vis absorption spectroscopy

UV-vis absorption spectroscopy is valuable in bandgap material determination. In a UV-vis transmission mode, a beam of white light covering the UV-Vis region passes through a sample, and then it is collected by a spectrometer after light-sample interactions and compared to the origin beam intensity to calculate the absorbance or transmittance. There are three possible light-sample interactions, absorption, reflection and transmission. Influence of reflection is typically constant (so small change) in the spectral range of interest so that it can be neglected for perovskites bandgap determinations. Therefore if the sample absorb part of the light, the amount of

absorption can be calculated by measuring the intensity difference of the incident and transmitted light. If the intensity difference based on wavelength, we can learn the information about what wavelength of light and how much light at that wavelength the sample absorbs. This is the basic idea of the UV-vis absorption spectroscopy. In principle, this technique can quantitatively determine the amount or concentration of active materials that need to be measured based on the well-known Beer–Lambert law¹⁴,

$$A = \varepsilon lc \quad (3)$$

where A , ε , l and c are absorbance, molar attenuation coefficient, optical path length (solution thickness) and concentration of the solution, respectively. Beer-Lambert law states that there is a linear relationship between the absorbance and the concentration of the solute. But in this work, we do not utilize this function. When studying light emitting semiconductors like perovskites with this technique, edge of large absorption (where absorption begins) in the spectrum usually indicates their bandgaps. In practice, a sample and a reference (the reference should be the same as the sample except no active material) are needed at the same time to perform the measurement. A Shimadzu UV-2450 ® UV-Vis spectrometer (Figure 3-13) was used to collect the absorption spectra for this work.

Figure 3-13 Shimadzu UV-2450 ® UV-Vis spectrometer for UV-Vis absorption.

However, for perovskite with Pb element, the absorption coefficient to UV or visible light is very high,

3.3.3 Time-resolved photoluminescence (TRPL) and gamma-luminescence spectroscopy

PL/XL and UV-Vis absorption techniques are in the second time scale, which is much longer than the process of fluorescence and they are considered to be steady-state measurements. If one wants to study to the dynamics of fluorescence, time-domain measurements are preferred. Time-resolved photoluminescence (TRPL), also called PL decay is most widely tool for semiconductor fluorescence in time-domain. And for scintillators, time-resolved X-ray or gamma-ray luminescence, which also called XL decay or GL decay are utilized. In principle, in these PL decay or GL decay

measurement, a pulse of excitation light (laser or gamma-ray in this work) will be splitter into two. One will go straight to the photodetector and generate a timestamp marking the arrival of excitation photons. This timestamp could be considered as the starting point of the luminescence process. Meanwhile, the other will excite the sample and produce emission photons. These emission photons after being focused, selected by monochromator will collected by photodetector. Such detection will also generate an arrival timestamp for emission photons. As photons with different arrival times are detected, a series of timestamps will be generated, categorized and counted. Therefore we can see the number change of emission photons upon time changes (in picosecond or nanosecond scale). After accumulation over multiple pulses, the pattern will emerge. Because one electron in excited state will rapidly relax to lower energy state through emission of a photon. The number of detected emission photons indicates the number of relaxed electrons. Thus as excited electrons relax and their number decreases gradually, i.e., the number of photons decreases as time passes, we always observe a decay pattern in PL decay or GL decay. Interpretation of decays are more important and complicated. Single exponential decay is the simplest case but sometimes samples could display nonexponential or multiexponential decays. In case of perovskite, biexponential decay will be good enough to decay data interpretation of 3D perovskite while triexponential decay is needed for 2D perovskite in this work.

3.3.4 X-ray thermoluminescence spectroscopy (TL)

At the early stage of thermoluminescence spectroscopy, the major application of this technique lies in radiation dosimetry since emission from the material was found to be proportional to the absorbed dose. Later this technique was found be useful in studying material defects or impurities¹⁵. The basic mechanism of TL is the trapping of free carriers excited by radiation. Heating of the material results in release of trapped free

carriers and the following electron-hole recombination¹⁶. A simplified model is shown in Figure 3-14. (a), (b), (c) and (d) represent the process of generation of free carriers, trapping of the free carriers, release of trapped carriers and recombination of free carriers, respectively. E is the trap depth or activation energy we will discuss in Chapter 4 to 6. In this work, we explored the defect/impurity density using this TL technique since a density of 10^7 cm^{-3} can produce observable TL signal, which is much lower than other techniques in measuring defect density. Using the fitting of Randall-Wilkins equation¹⁷, we can extract useful information, mainly concentration of trap and trap depth. Randall-Wilkins equation is shown below,

$$I = \sum_{i=1}^j n_{0i} s_i \exp\left(-\frac{E_i}{k_B T}\right) \exp\left(-\frac{s_i}{\beta} \int_{T_0}^T \exp\left(-\frac{E_i}{k_B T'}\right) dT'\right) \quad (4)$$

where I is the TL intensity, j is the number of deconvoluted peaks, n_{0i} is the initial trap concentration, s_i is the frequency factor, E_i is the trap depth, k_B is the Boltzmann constant, β is the heating rate, T is the temperature and T_0 is the initial temperature.

Figure 3-14 A simplified model of TL. (a), (b), (c) and (d) represent the process of generation of free carriers, trapping of the free carriers, release of trapped carriers and recombination of free carriers, respectively. E is the trap depth or activation energy.

3.3.5 Temperature-dependent photoluminescence and X-ray luminescence spectroscopy

PL and XL at room temperature are able to provide useful information. However, to better understand how temperature affects the luminescence or luminescence mechanism, it is necessary to obtain PL and XL at different temperature. That's where temperature-dependent PL or XL will be applied. This measurement is essentially recording the luminescence spectra at a range of temperature so the mechanism of this measurement will not be detailed here. Figure 3-15 shows the scheme of temperature-dependent PL setup (temperature-dependent XL setup not shown here). This is similar to a typical low temperature PL setup with the temperature controller and the cryogenic chamber where the sample is cooled down. The computer collects both temperature and emission spectrum at the same time. The collection of temperature-dependent XL is similar to

temperature-dependent PL except that laser excitation is replaced by X-ray excitation. In temperature-dependent PL or XL spectra, we usually search the emission differences as temperature changes, including peak position, peak intensity, peak linewidth and additional peaks. Generally, as temperature goes down, we can observe the following phenomena, higher emission intensity and smaller linewidth because of the weaker phonon-exciton interaction. In most case of hybrid perovskites, the emission peak shifts towards shorter wavelength since the bandgap becomes larger which is opposite to many semiconductors^{18,19}.

There are similarities in XL and TL (Section 5.3.3), for example, X-ray radiation is applied and emissions are recorded upon changing temperature. However, there are major differences between these two techniques in this thesis. To begin with, the origins of emissions are different in XL and TL. Emission in XL is from exciton recombination in perovskites and the excitons are excited by X-ray. While emission in TL originates from trapped carrier recombination activated thermally and there is no involvement with X-ray. Secondly, XL provides wavelength-dependent emission intensity while TL provides collective emission intensity in this thesis. At last, the temperature change in XL is from 350 to 10 K while that in TL is in reversed direction since the target emissions are different.

Figure 3-15 Scheme and image of temperature-dependent PL and XL setup in this work.

3.3.6 Pulse height spectrometry (PHS)

Pulse height spectrometry (PHS) is used to examine the amplitudes of signals from a radiation detector to determine the energies of radiations

A typical PHS system consists of the following components, radiation detector (scintillator and detector in this work), high-voltage supply, preamplifier, shaping amplifier and pulse height analyzer (PHA), as shown in Figure 3-16. High-voltage supply provides the voltage for the photodetector, which is typically a PMT. The charges created within the detector are firstly collected by the preamplifier. The main function

of a preamplifier is to extract the weak signal from the detector without significantly degrading the intrinsic signal-to-noise ratio and generate a tail pulse. The following shaping amplifier converts the tail pulse from the preamplifier to a symmetrical Gaussian pulse. Another important feature of the shaping amplifier is to filter much of the noise and therefore to improve the signal to noise ratio. The Gaussian pulses are recorded digitally by the PHA with the help of analog-to-digit converter (ADC) embedded in the PHA. The PHA provides the acquisition, storage, event counting and data interpretation. A PHS spectrum usually displays the number of counts/events versus the amplitudes of these events (or channels).

Figure 3-16 Scheme of standard scintillation spectrometer setup.

The basis of this technique is that the number of emitted photons after scintillator-radiation interaction and thus the voltages generated by the coupled photodetectors are proportional to the radiation energy. Take an ideal gamma-ray pulse height spectrum as an example in Figure 3-17. There are three gamma-ray/scintillator interactions: photoelectric absorption, Compton scattering and pair production provided that the energy is higher than 1.02 MeV. If the radiation energy is below 1.02 MeV, only

photoelectric absorption, Compton scattering are considered. A scintillator will be excited by the deposition of energy from these two interactions and emit photons. The coupled photodetector generates voltage amplitudes as outputs accordingly. After signal processing, a number of voltage amplitude outputs are converted to pulse amplitudes which are collected by PHA in a set time. As most of the photoelectric interactions result in full deposition of the gamma-ray energy in the scintillator, the scintillator has the strongest emission. Then the voltage amplitude generated by coupled photodetector is the highest and thus after signal processing PHA collects pulses with the largest and same amplitudes from the photoelectric interactions in Figure 3-17A. The Compton scattering does not fully deposit its energy in the scintillator while its energy deposition is continuous in a range of energy. Therefore, the pulse amplitude from Compton scattering is not greater than photoelectric absorption and varies in Figure 3-17A. There are single and multiple Compton scatterings but these two are beyond the scope of this thesis. After counting the number of these two interaction events, a typical PHS spectrum (Figure 3-17B) is histogram of pulse amplitude (or channel). If a standard radiation source is applied for energy calibration and single electron response to determine the energy represented by a channel, we can convert all pulse amplitudes/channels to energies. In Figure 3-17B, the photopeak corresponds to the photoelectric interaction thus indicating the radiation energy while the curve on the left corresponds to the Compton scattering interaction. Ideally the photopeak is a line because of same pulse amplitude (full energy deposition) and the curve should be continues as the pulse amplitudes from the Compton scattering is continues in a range of energy mentioned above. In most experiments, the photopeaks will be Gaussian peaks instead and other peaks from other interactions that are not discussed. Therefore, the analysis will be more complicated.

Figure 3-17 An ideal gamma-ray pulse height spectrum. A) Pulses from the detector representing different types of gamma-ray interactions in the detector. B) Histogram of pulses amplitude²⁰.

This technique is very powerful in acquisition of scintillator light yield and energy resolution under specific radiation. Besides, it can reveal details of scintillator-radiation interaction. This scintillator performance characterization will be discussed a lot in Chapter 6 and the experimental details can be found accordingly.

3.4 References

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Chapter 4   Thermal quenching and dose studies of

X-ray luminescence in single crystals of halide

perovskites

4.1 Introduction

Lead halide perovskites in recent years have shown promises in new generation optoelectronics because of their outstanding solar cell¹⁻³ and photodetector^{4,5} performances and their low fabrication cost. The intrinsic high carrier mobility and long carrier lifetime as well as the high atomic number element Pb allow lead halide perovskites to be potential X-ray detectors with high absorption efficiency. There have been quite a few reports on the successful applications of MAPbI₃ for X-ray detectors⁶⁻⁹. From all studies, the single crystals are more efficient in converting X-ray into current as they have fewer defects and grain boundaries⁷⁻⁹. Beside the direct conversion from X-ray to current, halide perovskites being employed as scintillators could also be equally practical in X-ray detection due to their intrinsic X-ray fluorescence, but it has been rarely explored¹⁰⁻¹². The photoluminescence (PL) studies using ultraviolet (UV) or visible laser as excitation sources has already proved bright emission in perovskite¹³⁻¹⁵. Thus, the high energy excitations such as X-ray are expected to yield the same result¹⁶. Additionally, the light yield of scintillator is inversely proportional to the bandgap¹⁷ and thus, the relatively low bandgap of halide perovskites (1.6-3.1 eV) compared to traditional scintillators (CsI: 6.4 eV, NaI: 5.9 eV, CaWO₄: 4.6 eV)¹⁸ offers the advantage of much higher theoretical light yield of 129,000 - 250,000 photons/MeV.

However, the previous studies on the scintillation light yield only report maximum 1,000

and 10,000 photons/MeV for three-dimensional (3D) and two-dimensional (2D) perovskite single crystals respectively^{10,11}. The 3D perovskite single crystals at room temperature have lower light yield than the 2D ones since the loosely bounded excitonic states in the 3D perovskite are much prone to thermal quenching than tightly bounded excitons in the 2D perovskite at room temperature (without consideration of perovskite configurations).¹¹ However, the 3D perovskite single crystals are still interesting due to much faster growth in comparison to the 2D ones, i.e. less than one day compared to about one month for a single crystal of $5 \times 5 \times 5 \text{ mm}^3$ size^{11,19}.

In this work, we investigate the X-ray excited luminescence (XL) of a variety of halide perovskite single crystals APbX_3 ($\text{A} = \text{Methylammonium (MA) or Cs}$, $\text{X} = \text{Cl, Br or I}$). First, we vary the halides in MAPbX_3 ($\text{X} = \text{Cl, Br or I}$). It is apparent that the largest bandgap perovskite (Cl) has the slowest quenching behavior. Then, we fit the temperature-dependent integrated intensities of XL with Arrhenius equation. For Cl, although the ratio between the attempt rate of the nonradiative process in the Arrhenius equation and the radiative transition rate (Γ_0/Γ_v) is 100-160 folds of those in Br and I, the large thermal quenching activation energy (ΔE_q) of about 7-10 folds from Br and I prevents the quenching at low temperature. Then, we replace the cation MA with Cs and we find the quenching worsens with Γ_0/Γ_v is about 4-7 folds while ΔE_q is similar. In addition, the full width at half maximum (FWHM) of the X-ray luminescence emission peaks from single crystals of MAPbX_3 and CsPbX_3 is very narrow of about 1 nm at low temperature. Finally, we doped the MAPbBr_3 single crystal with Bi^{3+} . We observe luminescence quenching with the increase of Bi^{3+} concentration. Only Γ_0/Γ_v increases with the concentration and we address this quenching caused by polaronic effect²⁰. Our XL studies with different halides, cations, and Bi^{3+} concentrations in the perovskite single crystals can be useful in future analysis and design of potential high-performance

perovskite scintillators.

4.2 Experimental Section

For the synthesis of hybrid perovskite crystals, the following chemicals and reagents were purchased from Sigma-Aldrich: lead(II) chloride (PbCl_2 , 98 %), lead(II) bromide (PbBr_2 , 98 %) and lead(II) iodide (PbI_2 , 99 %), methylammonium chloride (MACl , 99 %), methylammonium bromide (MABr , 99 %), methylammonium iodide (MAI , 99 %), dimethylsulphoxide (DMSO) (99 %), dimethylformamide (DMF) (anhydrous, 99.8 %), γ -butyrolactone (GBL) (99 %). Inverse temperature crystallization method was applied for single crystal growth as the following^{19,21}: the precursors were first prepared by dissolving proper materials in corresponding solvents. While one molar precursor of MAPbCl_3 was prepared by dissolving $\text{PbCl}_2/\text{MACl}$ (0.8/1 by molar) in DMSO/DMF (1/1 by volume) at room temperature, MAPbBr_3 and MAPbI_3 precursor solutions of $\text{PbBr}_2/\text{MABr}$ (0.8/1 by molar) and PbI_2/MAI (0.8/1 by molar) were prepared in DMF and GBL at room temperature and 60 °C, respectively⁸. The molar ratios and solvents in this report are different than those previously reported by one of us in Ref. 11. The precursor was filtered by a polytetrafluoroethylene (PTFE) filter (0.22 μm pore size) and placed in a vial. Then the vial was kept in a silicone oil bath undisturbed for 6 hours at 50 °C, 80 °C and 110 °C for perovskites of MAPbCl_3 , MAPbBr_3 , and MAPbI_3 , respectively. Finally, the perovskite single crystals were rinsed in corresponding solvents that were used in the crystal growth and then kept in hexane for later use.

For the synthesis of inorganic perovskite single crystals of CsPbBr_3 , the precursor solution of 0.5 M of CsPbBr_3 was first prepared by dissolving an equimolar amount of PbBr_2 and CsBr in DMSO at 50 °C for 2 hours. The solution was then saturated by adding an appropriate amount of methanol ($\text{DMSO}/\text{CH}_3\text{OH} = 1/0.55$ by volume) at

room temperature. Subsequently, the saturated solution was heated at 50 °C for 24 hours followed by heating at 80 °C for 8 hours. The precursor was filtered (0.22 µm PTFE) and placed in a vial. The vial was kept undisturbed with temperature increasing gradually from room temperature to 80 °C for crystal growth. The crystals were collected and stored in hexane for further use²².

Bi-doped MAPbBr₃ was synthesized by addition of BiBr₃ into same precursor solution for MAPbBr₃²³. In our experiment, the amount of added BiBr₃ depends on expected molar ratio between Bi and Pb. Herein two ratios, Bi/Pb = 1/10 and Bi/Pb = 1/100 by molar doping were carried out. After the addition of BiBr₃ in the precursor solution, the remaining synthesis was the same as undoped MAPbBr₃ above. Since we grew the crystals using different compositions, we characterized the crystal structures through typical powder X-ray diffraction (XRD) measurements and compared the results with those in Ref. 11. The XRD measurements were performed on a BRUKER D8 ADVANCE with Bragg-Brentano geometry using Cu K α radiation ($\lambda = 1.54056$ Å), step increment of 0.01° and 1 s of acquisition time. Besides, single crystal X-ray diffraction (SCXRD) was also carried out to confirm the single-crystal quality of our samples (see Supporting Information for detail).

For X-ray excited luminescence (XL), a typical set-up consisting of an Inel XRG3500 Xray generator (Cu-anode tube, 45 kV / 10 mA), an Acton Research Corporation SpectraPro-500i monochromator (500 nm blazed grating), a Hamamatsu R928 photomultiplier, and an APD Cryogenics Inc. closed-cycle helium cooler with a Lake Shore 330 programmable temperature controller, was used to record XL spectra at various temperatures between 10 and 350 K. We note that the measurements were carried out starting at 350 K (unless indicated) and terminating at 10 K to avoid a

possible contribution from thermal release of unwanted frozen charge carriers at low temperature to the emission yield.

To investigate the effect of the radiation power to the linewidth and intensity of XL, we have recorded XL as a function of the X-ray tube high voltage from 15 to 45 kV with a current of 5 and 10 mA. For the dose, using Eq. 1 below we calculated the dose output D_{out} , in the unit of microsievert per hour ($\mu\text{Sv/h}$),

$$D_{out} = K \times h \times V^2 \times I \times t \times \frac{1}{d^2} \quad (1)$$

where K is the constant value ($K = 3.265$, in the unit of $(\mu\text{Sv} \cdot \text{mm}^2)(\text{mA} \cdot \text{s} \cdot \text{kV}^2)^{-1}$), h is the second-to-hour conversion factor ($h = 720 \text{ h}^{-1}$. The exposure time is 5 s and the unit of D_{out} is microsievert per hour, thus $3600/5 = 720$), V is the peak tube voltage (kV), I is the current supply (mA), t is the exposure time (5 s), and d is the distance (500 mm).

4.3 Results and discussion

4.3.1 X-ray Diffraction

In our experiment, inverse temperature crystallization (ITC) was used to grow the single crystal perovskites since this method provides faster growth rates¹⁹. The images of single crystals are shown in Figure 4-1. In order to demonstrate the superior quality of our crystals, XRD characterization was first carried out in room temperature. The four XRD patterns of powder grounded from corresponding crystals are shown in Figure 4-2 and they match well with the standard structure. The pure phases of these perovskites matched well with those reported earlier grown by varied methods²⁴⁻²⁶. MAPbCl₃ and MAPbBr₃ single crystals are consistent with the perovskite structure

having a cubic crystal system, space group $Pm3m$ while $MAPbI_3$ single crystal has the perovskite structure with a tetragonal crystal system, space group $I4/mcm$ at room temperature²⁷. Additionally, $CsPbBr_3$ is related to the space group $Pnma$ ²². Finally, the results of SCXRD measurement demonstrate our single-crystalline quality of $MAPbBr_3$ which is in excellent agreement with reported single crystal structure (See Table 4-1 for the crystal analysis of $MAPbBr_3$)²⁸ and substantiates the single-crystalline quality of our samples.

Figure 4-1 Images of $MAPbCl_3$ (left), $MAPbBr_3$ (center) and $MAPbI_3$ (right) single crystals using ITC method.

Figure 4-2 X-ray diffraction (XRD) pattern of a) MAPbCl₃, b) MAPbBr₃, c) MAPbI₃, and d) CsPbBr₃ powders of single crystals and simulation from published single crystal information²⁸⁻³¹. The extra peaks in MAPbI₃ may come from the side product after decomposition in ambient.

Table 4-1 Crystallographic data for α -MAPbBr₃ at ambient pressure

Empirical Formula	CH ₃ NPbBr ₃
Wavelength, Å	0.71073
Formula Weight, g/mol	478.99
Temperature, K	296(2)
Crystal system	Cubic
Space group	<i>Pm3m</i>
a, Å	5.932(2)
b, Å	5.932(2)
c, Å	5.932(2)
$\alpha = \beta = \gamma, ^\circ$	90
Volume, Å ³	208.7(3)
Z	1
Density (calculated), g/cm ³	3.811
Absorption coefficient, /mm	34.64
<i>F</i> (000)	206
Crystal size, mm ³	0.44 * 0.36 * 0.3
θ range, °	5.96 to 34.64
Index ranges	-5 ≤ h ≤ 8, -9 ≤ k ≤ 4, -4 ≤ l ≤ 5
Completeness	100 %
Final R index (all data)	0.0418
Largest diff. peak and hole, e/ Å ³	1.682, -1.676

4.3.2 X-ray Thermoluminescence

In addition to the typical XRD measurement, the energy traps in these perovskite single crystals are also investigated with thermal luminescence (TL). Representative curves are plotted in Figure 4-3. We monitor any possible emission up to thousands of seconds after the termination of X-ray excitation at 10 K. A temperature ramp to 350 K at a rate of 0.14 K/s is set at 3,600 s. This duration was chosen because we want to make sure samples were well stabilized. The fall of the TL signal could be attributed to damage of the crystal caused by X-ray or loss of focus. While the rise of signal is from the activation of traps or other impurities. Surprisingly, there is no afterglow during the temperature increase, confirming the absence of the energy traps. This observation shows significant improvement in our crystal quality from previous report in which very-shallow traps from 10 to 90 meV were observed using the same experimental setup. Similar small adjustments in precursor ratio $\text{PbX}_2/\text{MAX} = 0.8/1$ by molar (as opposed to 1/1)¹¹ in corresponding solvents were also reported for higher crystal quality⁸. It is noted that there is an intensity drop in Figure 4-3b in the first steady-state stage (before 730 s) and it is also common in other scintillators though theoretically an increase is expected³²⁻³⁴. Such decrease could be attributed to radiation damage to the whole sample or only to the surface, where the former leads to the drop of luminescence and the latter lowers gradually the light collection efficiency. Considering the stability of other perovskite samples in Figure 4-3, we consider that it is more likely due to the worse light collection efficiency.

Figure 4-3 Low temperature thermoluminescence curves of (a) MAPbCl₃, (b) MAPbBr₃, (c) MAPbI₃ and (d) CsPbBr₃ single crystals showing no afterglow and energy trap for all crystals. The data are presented on a time scale starting at temperature of 10 K and increasing to 350 K after 3600 s (except 1800 s for CsPbBr₃), as indicated by the red dashed line in the right panel (temperature scale on the right axes).

4.3.3 X-ray Luminescence

Organic-inorganic hybrid lead halide perovskites

With the high-quality perovskite single crystals, we study the temperature- and power-dependent XL of the perovskite. First, we would like to investigate the effect of halides (Cl, Br, and I) to the XL properties. Under constant X-ray excitation, the comparisons of temperature-dependent luminescence spectra of MAPbX₃ are demonstrated in Figure 4-4. The main emission peak shift occurs for these three perovskites and the trend of peak shift coincides with other studies^{13,35}. We note that the strongest emission at 405 nm of MAPbCl₃ is at 60 K rather than 10 K and the mechanism is not yet clear. The FWHM of the deconvoluted emission peak for MAPbCl₃ (Figure 4-4a) is as narrow as 1 nm, where the resolution limit of our spectrometer is reached. It should be pointed out that although here the spectra are displayed in wavelength scale, peak deconvolution was actually completed by Gaussian fitting in energy scale and recalculated into wavelength scale throughout this work. When reaching 150 K, the narrow emission peak

barely exists. For MAPbBr₃ in Figure 4-4b, there is one bump at around 625 nm besides the main emission peak at 560 nm but completely quenched at 150 K. This agrees well with typical PL of orthorhombic (< 144.5 K) MAPbBr₃^{27,35}. It has been reported that the 560 nm emission peak and the 625 nm emission bump originate from the surface defect and the bulk defect states, respectively³⁶. The narrowing emission peak is also observed in MAPbI₃ except with larger linewidth and peak shift (Figure 4-4c). The narrowing emissions can be attributed to weaker electron–phonon coupling upon lower temperature³⁸.

Figure 4-4 Luminescence spectra under X-ray excitation for (a) MAPbCl₃, (b) MAPbBr₃, and (c) MAPbI₃ at low temperatures (white area) of 60, 10, and 10 K,

respectively and at high temperatures (blue shaded area) of 150 K. All spectra were normalized with those measured at low temperatures. The blue numbers beside the spectra at 150 K exhibit the multiplication for the clarity of the spectra. The dotted red lines correspond to the Gaussian fits of the narrowing peaks. All Gaussian peaks are fitted in energy scale and recalculated into wavelength scale.

To better illustrate the influence of temperature on luminescent properties, temperature dependences of the integrations from total spectrum and peak intensities are shown in Figure 4-5. In this work, we aimed to investigate halide perovskites as scintillators. Therefore, we focused on the main emissions (also the peak intensity) since they contribute the most to the full-spectrum integrations which represent the total emission. As the temperature decreases from 160 to 10 K, both integrated total spectrum and peak intensities increase generally. Linewidth narrowing is also exhibited upon decreasing temperature. There is a temperature threshold in evolution of FWHM for each perovskite. For MAPbCl₃, below 100 K, the FWHM is around 1 nm, and the FWHM hikes up to 12 nm for temperature above 100 K. Similarly, the threshold of MAPbI₃ is 60 K. Though the linewidth is not as narrow as MAPbCl₃, the effect of narrowing from 35 to 10 nm is still apparent. Such narrowing emission is also common in MAPbX₃ as it is also observed in their temperature-dependent PL spectra^{13,37}. To quantize and compare intrinsic difference of hybrid halide perovskites, temperature-dependent intensities are further analyzed. Employing the Arrhenius fitting equation below (Eq. 2), plots in Figure 4-5a-c are fitted and result is presented in Table 4-2,

$$I_{norm} = \frac{1}{1 + \Gamma_0/\Gamma_v \exp(-\Delta E_q/k_B T)} \quad (2)$$

where Γ_0/Γ_v , ΔE_q and k_B are the ratio between thermal quenching rate at $T = \infty$ (attempt rate) and the radiative transition rate, the thermal quenching activation energy and

Boltzmann constant, respectively. Both ΔE_q and Γ_0/Γ_v decrease from MAPbCl₃ to MAPbI₃. On the one hand, we observe that with the decrease of ΔE_q from Cl to I, the XL quenching starts at higher temperature in MAPbCl₃ compared to MAPbBr₃ and MAPbI₃. On the other hand, the decrease of Γ_0/Γ_v in the same sequence implies the faster quenching rate in MAPbCl₃ compared to the other two in our experiments. The influence of halide on quenching behavior is strong and we speculate that this can be relevant to the bandgap and exciton binding energy. Bandgaps of halide perovskites are mainly contributed by Pb-halide bonds (MAPbCl₃: 3 eV, MAPbBr₃: 2.3 eV and MAPbI₃: 1.6 eV). The different quenching behavior of MAPbX₃ is also common in other traditional inorganic halide scintillators³⁹. Besides, the PL and XL share the same exciton recombination luminescence and the exciton binding energy becomes smaller from Cl to I (MAPbCl₃: 107 meV, MAPbBr₃: 45 meV and MAPbI₃: 17 meV)⁴⁰. Therefore exciton becomes easier to dissociate into free carrier compared to recombination when halide changes from I to Cl, that is, easier to be quenched thermodynamically since the possibility of luminescence from exciton recombination is lower. We found that the tendency of thermal quenching activation energy ΔE_q might follow that of exciton binding energy from Cl to I. For the kinetics term Γ_0/Γ_v , it is more complex. The radiative transition rate Γ_v decreases from Cl to I as it is inversely proportional to the emission wavelength according to Fermi-Golden rule¹⁷. This trend increases Γ_0/Γ_v in the same sequence. However, the thermal quenching rate Γ_0 has to become much smaller in comparison with Γ_v to reverse the trend. This behavior is strongly related to the scintillation mechanism as previously observed for different halide systems¹⁷.

Figure 4-5 Normalized total spectrum integrated X-ray excited luminescence intensities at various temperatures, from 10 to 160 K for (a) MAPbCl₃, (b) MAPbBr₃, and (c) MAPbI₃. Narrow-peak integrated intensities and its full width at half maximum (FWHM) for (d)MAPbCl₃, (e) MAPbBr₃, and (f) MAPbI₃. Narrow-peak intensities were normalized with the maximum of total integrated intensities. The red lines exhibit the Arrhenius fits explained in the text.

Table 4-2 Thermal quenching activation energy (ΔE_q) and the ratio between the thermal quenching rate (Γ_0) and the radiative transition rate (Γ_v).

Hybrid Perovskite	ΔE_q (meV)	Γ_0/Γ_v
MAPbCl ₃	53 ± 3	$1,427 \pm 513$
MAPbBr ₃	8 ± 1	15 ± 1
MAPbI ₃	6 ± 1	9 ± 1

To investigate the effect of X-ray radiation power, i.e., dose (unit in $\mu\text{Sv/h}$), X-ray excitation power-dependent luminescence was carried out at 10 K by tuning the acceleration voltage. Mappings of dose versus wavelength for MAPbX_3 are shown in Figure 4-6a-c. No apparent emission peak shift is observed. For MAPbBr_3 and MAPbI_3 , apart from main peaks, long tails show up in long wavelength, and these tails become stronger as dose increases. Figure 4-6d and e plot the comparison of integrated intensity and FWHM versus X-ray radiation dose. There is a linear relation between integrated intensity and dose in the double-log scale plot for all hybrid halide perovskites and their overall inclinations show no strong saturation. The linewidth narrowing resulted from increasing dose of FWHM for MAPbCl_3 , MAPbBr_3 and MAPbI_3 are not the same. FWHM of MAPbCl_3 is dose-independent, 1 nm. The linewidth narrowing upon dose is stronger for MAPbBr_3 and the strongest for MAPbI_3 . However, since the general linewidth narrowing is not significant and not associated with increase in intensity compared to the amplified spontaneous emission (ASE) although it is reported that high fluence X-ray pulse can induce ASE in GaAs⁴¹, we cannot address those narrow lines as the ASE process upon the high-energy excitation, which is similar to that upon the near bandgap excitation^{13,36}.

Figure 4-6 X-ray excited luminescence spectra mapping at different accelerating X-ray tube voltages and 10 mA tube current for (a) MAPbCl₃, (b) MAPbBr₃, and (c) MAPbI₃. d) Normalized total spectrum integrated intensities and e) FWHM of the narrow-peak are presented as function of doses.

4.3.4 All inorganic lead halide perovskite CsPbBr₃

All inorganic halide perovskite CsPbBr₃ is also included in this study. Figure 4-7 shows the result of X-ray luminescence characterizations and analysis similar to MAPbX₃. As seen in Figure 4-7a, a sharp emission peak arises at 543 nm, a weak one at 532 nm and a broad emission at 552 nm at 10 K while only a very broad hump exists at 150 K. There three emissions at 10 K are attributed to free exciton, bound exciton and donor-acceptor pair. Redshift of both free exciton and bound exciton upon lower temperature from 10 to 60 K as well as existence of donor-acceptor pair only at below 60 K agree well with other reports^{42,43}. The mapping in Figure 6b demonstrates the monotone XL intensity of the peak at 543 nm increase over decreasing temperature and emergence of the peak at 532 nm below 50 K. The free exciton peak at above 30 K becomes stronger and dominant while the bound exciton peak is gradually quenched at higher temperature. It

is consistent with the report of switching excitonic recombination at different temperature⁴². Figure 6c shows the representative visible laser (488 nm) excited PL spectra at 30 and 150 K. The general peak attribution and evolution upon lower temperature is similar to that in XL. The major difference between PL and XL is the different positions and intensity ratios of the two emission peaks. There is a blue shift from XL to PL for both free exciton and bound exciton peaks (535 to 532 nm and 543 to 540 nm). This can be explained by different emissions from the bulk and the surface. Bulk emission usually has a lower energy while surface emission has a higher one due to the shorter bond lengths of the molecules near the surface. Deeper penetration of X-ray than visible light provides a larger portion of bulk emission in XL. We do not have convincing data to conclude the different intensity ratios between XL and PL. One explanation based on our experiment is that the bulk crystal has a larger population of bound exciton than the free exciton. X-ray penetrates deeper as mentioned and thus XL provides a more collective information of the bulk. Another explanation is that thick CsPbBr₃ with a small Stokes shift could show stronger self-absorption effect²². The free exciton emission of higher energy is more reabsorbed in the path from bulk to surface than the bound exciton of lower energy. At last, the difference between pristine structure inside a crystal and its surface together with the different XL and PL setup configurations might be another reason for their luminescence deviation. In addition to the major difference, the donor-acceptor pair luminescence at longer wavelength (552 nm in XL) disappears which may be attributed to insufficiently low temperature (lowest 30 K in PL while 10 K in XL) or crystal quality difference. Plot of integrated intensity versus temperature in Figure 6d can be again fitted well with Eq. 2. ΔE_q and Γ_0/Γ_v from CsPbBr₃ of are 10 ± 1 meV and 66 ± 14 , respectively. ΔE_q is quite similar to 8 ± 1 meV of MAPbBr₃ while Γ_0/Γ_v is four folds of 15 ± 1 of MAPbBr₃. When substituting MA by

Cs cation, the thermal activation energy ΔE_q does not change much but because of larger Γ_0/Γ_v , quenching is stronger upon the same increasing temperature. The reason for such behavior is not clear yet. There are a few possible reasons. To begin with, Cs^+ is smaller than MA^+ though the difference is not much, but this could lead to slight distortion in crystal structure. Secondly, hydrogen bonds are reported in MAPbI_3 while not in CsPbI_3 and hydrogen bonds cause crystal tilting and we could reasonably expect the similar effect also occurs when comparing MAPbBr_3 and CsPbBr_3 ⁴⁴. These possible changes of crystal structure and therefore the band structure. But it is interesting that by changing different cations, it is likely to tune the Γ_0/Γ_v without changing ΔE_q much. In Figure 4-7e, linewidth as a function of temperature shows apparent narrowing effect, from 23 down to 2 nm below 100 K (even 1.5 nm below 40 K). The result of dose dependent measurement is shown in Figure 6d. Similar to MAPbCl_3 , the integrated intensity of CsPbBr_3 is linearly dependent while the FWHM independent upon dose. In general, CsPbBr_3 shares similar performance in XL as hybrid halide perovskite MAPbX_3 .

Figure 4-7 X-ray excited luminescence spectra from CsPbBr₃. (a) Low- (10 K) and high temperature (150 K) X-ray excited luminescence spectra shown by white and blue-shaded area, respectively. (b) Temperature mapping of XL spectra from 10 to 160 K. (c) 30- and 150-K PL spectra shown by white and blue-shaded area, respectively. All spectra were normalized with those measured at low temperatures. The blue numbers beside the spectra in a) and (c) at 150 K exhibit the multiplication for the clarity of the

spectra while the dotted red lines correspond to the Gaussian fits. The asterisks show the same narrowing peaks at low and high temperature. (d) Normalized total spectrum integrated intensities as a function of temperatures with the Arrhenius fittings shown by the red lines and (e) Narrow-peak integrated intensities and its FWHM derived from temperature-dependent spectra. (f) Normalized total spectrum integrated intensities and FWHM derived from dose-dependent spectra at different tube voltages and 5 mA tube current.

4.3.5 Bi³⁺-doped MAPbBr₃

Doping is a popular method to endow scintillators new properties or enhance their performances¹⁷. Here we tried to explore perovskite scintillator further by doping with Bi³⁺. There are several reports on that incorporation of Bi²⁺ or Bi³⁺ in metal oxide matrices offers deep red or near infrared emission (NIR), which can be useful in white lighting and bioimaging⁴⁵⁻⁴⁷. Inclusion of Bi³⁺ in halide perovskite has been reported to provide similar NIR emission^{20,48}. Beside of that, the Bi-doped perovskite is more stable in air compared to undoped one⁴⁹. Therefore, the investigation of Bi³⁺-doped MAPbBr₃ under X-ray could be interesting. According to reported result, Bi concentration in final product determined by energy-dispersive X-ray spectroscopy (EDX) is almost two orders of magnitude lower than in precursor solution prepared²³. In this case, the error in dopant concentration determination could be relatively large using EDX. Therefore for clarification, here we still use Bi/Pb ratio in precursor solution as notation for our samples. The difference in PL (Figure 4-8) and the decrease in sheet resistance (Table 4-3) upon increasing Bi doping concentration indicate the successful doping. Figure 4-9a (Bi/Pb = 1/100 by molar) and b (Bi/Pb = 1/10 by molar) show the emission difference at 10 K and 40 K. The emissions from these two doped MAPbBr₃ at 40 K become very weak compared to 10 K. Both emission spectra also do not exhibit

emission from the bulk defect state at 625 nm in MAPbBr₃, see Figure 4-10. The quenching of this emission bump maybe attributed to the insertion of Bi³⁺. Once more, Arrhenius fitting is applied for further analysis. Here we try to compare three samples, undoped, 1/100 and 1/10 and the result is in Figure 4-9c. The ΔE_q and Γ_0/Γ_v from 1/100 Bi-doped MAPbBr₃ are 8 meV and 35 ± 3 , respectively. The ΔE_q is the same as undoped MAPbBr₃ while the Γ_0/Γ_v is two times larger, which explains stronger quenching at ~ 120 K than in undoped samples. When we grew the crystals in higher concentration Bi/Pb = 1/10, the quenching becomes even more significant at ~ 80 K and the Γ_0/Γ_v increases to 78 ± 18 . Such quenching effect in XL can be explained by polaronic effect²⁰. The atomic size mismatch causes structure distortion after substitution of Pb²⁺ by Bi³⁺ and thus creates polaron traps that can capture excited free electrons and inhibit radiative recombination. The afterglow in TL spectrum of 1/100 Bi-doped MAPbBr₃ confirms the existence of the possible polaron traps (Figure 4-11). As Bi³⁺ concentration increases, that is, number of trap increases, quenching is stronger. The absence of possible NIR emission might be associated with the large excitation energy of Bi³⁺. The emission of Bi³⁺ strongly depends on the host and it comes from the localized $^3P_{1,0} \rightarrow ^1S_0$ transition⁵⁰. Accordingly, the smallest excitation energy is by far 3.3 eV, which is much larger than the bandgap of 2.3 eV from the perovskite host. Therefore, excitation at Bi³⁺ will result in perovskite host emission (no Bi³⁺ emission) while adding more Bi³⁺ concentration may yield more quenching of the host emission⁵¹. Later there were other similar investigations about Bi³⁺-doped MAPbBr₃ and the mechanism of emission quenching and NIR emission from Bi doping is better understood now. Bi³⁺ doping introduces higher level of microstrain and electronic disorder and thus increases nonradiative recombination⁵². But there is another possibility of energy transfer taking the NIR emission into account. The new PL peak at 1080 nm in the NIR region could

be attributed to energy transfer to the in-band state induced by Bi^{3+} ion⁵³. We consider both explanations are reasonable. Higher Bi doping results in stronger quenching at around 550 nm, but stronger NIR emission unproportionally as reported. This result indicates that increasing nonradiative recombination center and energy transfer to new energy states (lead to NIR emission) from Bi doping coexist. We compared our methods and measurements to those in this report as well as the Bi^{3+} -doped CsPbI_3 powder and nanocrystals. The differences in synthesis are considered to be small so the missing NIR emission in this work is likely due to the experimental setup difference. Our PL system (including the grating and photodetector) has a relatively low detection efficiency in NIR region and the NIR emission might from our doped crystals were weak. At that moment we did not realize that and concluded the absence of NIR emission incorrectly.

Figure 4-8 Photoluminescence spectra of undoped, 1:100 and 1:10 Bi-doped MAPbBr_3 at room temperature. The absence of PL in 1:100 and 1:10 doped samples verify the Bi doping.

Table 4-3 Four-point probe measurement for Bi-doped MAPbBr₃

Sample	Sheet resistance
Undoped	No reading (too large)
1:100	$4.2 \pm 1.0 \text{ M}\Omega/\text{sqr}$
1:10	$0.208 \pm 0.082 \text{ M}\Omega/\text{sqr}$

The decrease in sheet resistance upon higher Bi concentration also confirms the successful Bi doping.

Figure 4-9 X-ray excited luminescence spectra from Bi³⁺ doped MAPbBr₃. (a) Low- (10 K) and (b) high-temperature (40 K) X-ray excited luminescence spectra of Bi³⁺ doped MAPbBr₃ single crystal shown by white and blue-shaded area, respectively. The Bi³⁺ concentrations of (a) 1/100 and (b) 1/10 were introduced in the precursor solution. (c) Normalized total spectrum integrated intensities as a function of temperatures with the Arrhenius fittings shown by the red lines.

Figure 4-10 XL comparison of undoped and 1/10 Bi-doped MAPbBr₃ at 10K.

Figure 4-11 TL spectrum of 1:100 Bi-doped MAPbBr₃. Traps can be determined from the afterglow emission¹¹. Such afterglow partly verifies the possible polaron traps caused by the Bi doping since there is no afterglow in undoped MAPbBr₃.

4.4 Conclusions

Here we performed XL measurements for different types of perovskite from halide variation, hybrid, all-inorganic, and transition metal, Bi³⁺ doped perovskite single crystals. Temperature-dependent XL measurements demonstrate spectrum intensity

rising and emission linewidth narrowing occurs for all MAPbX₃ and CsPbBr₃ perovskites upon decreasing temperature. In MAPbX₃ family, thermal quenching activation energy (ΔE_q) and ratio between the thermal quenching rate (Γ_0) and the radiative transition rate (Γ_r) are decreasing from MAPbCl₃ to MAPbI₃. Regarding to halide choices for perovskite scintillator, perovskite with Cl holds more potential since its ΔE_q is the highest and therefore allows operation at higher temperature. Notably, linewidth of MAPbCl₃ and CsPbBr₃ can be down to 1 and 1.5 nm for temperature below 100 K. For changing MA with Cs, we found that CsPbBr₃ quenches stronger than MAPbBr₃ and it is due to the increase Γ_0/Γ_r by four folds but without much change of ΔE_q . This phenomenon demonstrates one way to finely tune the thermal quenching behavior of perovskite scintillators by simply changing the cation. Finally, we found that inclusion of Bi³⁺ into MAPbBr₃ causes strong quenching effect in XL which may not be beneficial for scintillator practically. However, it suggests a method for exploring other dopants, such as Eu²⁺ and Ce³⁺ which are famous in scintillator doping. For dose, all perovskite single crystals show linear intensity-dose dependences with no strong saturation. There is no significant linewidth narrowing with the increase of the dose. Our contribution might pave the way to develop perovskite-based scintillator with low-cost and fast solution-processing method.

4.5 References

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Chapter 5   Lithium-doped two-dimensional perovskite scintillator for wide-range radiation detection

5.1 Introduction

The research on lead halide perovskite (referred to here as ‘perovskite’) for X-ray or gamma-ray detection has been rapidly expanding. Methylammonium lead iodide (MAPbI₃) as the active material in a solar cell configuration shows good performance in X-ray photon to electron conversion taking advantage of gamma voltaic effect¹⁻⁴ and it brought back the idea of perovskite scintillator again, which emerged as early as 2008 but did not receive much attention⁵.

It is generally believed that 2D perovskite scintillators have theoretically higher light yields and faster decays due to their higher exciton binding energies (hundreds of meV) compared to 3D ones (tens of meV)^{10,11}. Although 2D perovskite single crystal scintillators in X-/gamma-ray detections have been reported^{12,13}, high energy alpha particle detection and the potential X-ray imaging applications with 2D perovskite single crystal scintillators have never been reported. 2D bulk perovskite crystals in this work are preferred over perovskite nanocrystals that have also higher exciton binding energy because they possess the benefits mentioned above and they are free from inherent chemical instability and low density of composite made of nanomaterials^{14,15}. Doping could be a useful approach to modify or boost some scintillator performance¹⁶. Li dopant has been reported for alternation of optical properties¹⁷ and reduction of nonradiative loss in perovskite exciton recombination¹⁸. Electrochemical doping of Li

was achieved to lower the threshold voltage for perovskite LED¹⁹. The introduction of ⁶Li can bring a completely new functionality, thermal neutron detection because of the intrinsic high thermal neutron capture of ⁶Li isotope. Thermal neutron detection plays an important role in neutron scattering research²⁰, landmine detection²¹ and oil logging²². However, current thermal neutron scintillator also suffers from the high cost of the high-temperature processing. A recent report of 2D semiconductor ⁶LiInP₂Se₆ for first-time direct thermal neutron detection provided a new direction but this direct detection mode is still far from commercialization and wide application for neutron imaging²³. It will be of interest to combine the merits of 2D perovskite and Li dopant to develop low-cost X-/gamma-ray scintillators with extra thermal neutron detection capability and investigate the property changes or develop new scintillator behaviors.

In this work, we synthesized Li-(PEA)₂PbBr₄ perovskite crystals which are characterized under different radiation. We also tested its capability to discriminate the gamma-ray and alpha particle. Finally, we demonstrate the employment of our perovskite in X-ray imaging. After temperature-dependent X-ray luminescence and X-ray thermoluminescence characterizations, it is concluded that Li ion being trapped in the crystal poses its impact on enhancing while broadening the emission. Under 662 keV gamma-ray, the light yield of Li-(PEA)₂PbBr₄ is up to 11,000 photons/MeV (ph/MeV) with a fast primary decay time of 11 ns. Successful detection of alpha particle, in conjunction with reasonable discrimination between gamma-ray and alpha particle, demonstrates the potential of Li-(PEA)₂PbBr₄ crystal in neutron detection. With 8 keV soft X-ray, X-ray phase-contrast images were obtained using our perovskite as the scintillator screen. Our study suggests the potential of Li-(PEA)₂PbBr₄ as a versatile scintillator in wide-range energy radiation detection.

5.2 Experimental section

Li-(PEA)₂PbBr₄ crystals and film preparation. Dimethyl sulfoxide (DMSO, anhydrous), phenethylammonium bromide ((PEA)Br, 98 %), lead bromide (PbBr, 98%) and lithium bromide (LiBr, $\geq 99\%$) were purchased from Sigma-Aldrich. Undoped precursor solution was prepared by dissolving equal molar amount of (PEA)Br and PbBr₂ in DMSO under stirring at 100 °C for 2 h under N₂. Crystals were obtained by evaporating DMSO from 3 M precursor solution in ambient environment slowly; it could take a few weeks. The crystal precipitate was then washed with diethyl ether and dried under vacuum for future characterizations. For Li-(PEA)₂PbBr₄ crystals, the procedure was the same as that of the undoped one except for the addition of LiBr to the precursor solution. The amount of LiBr depends on the molar ratio between Li and Pb. In our experiment, one undoped and three doping concentration were prepared, i.e., molar ratio Li:Pb = 0, 1:100, 1:10 and 1:1 (denoted as undoped, 1:100, 1:10 and 1:1). The concentration of the precursor solution is 3 M except 1:1 Li-(PEA)₂PbBr₄ (2 M due to limited solubility of LiBr). Here, it should be noted that the ratio is from the precursor instead of the final product. For the film preparation, precursor solution (1:1, 2 M concentration for high viscosity) was spin-coated on a UV-ozone treated cover glass substrate with 500 rpm for 60 s (acceleration: 100 rpm/s). In the last 30 s, a heat gun was applied right on top of the film to blow-dry the film with hot air flow. The film was baked at 100 °C on a hotplate for another 20 min.

Structure and composition characterization. The structure was determined by powder X-ray diffraction (XRD) measurement. The XRD measurements were carried out on a Bruker D8 Discover with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). Step increment and acquisition time were 0.05° and 1 s, respectively. The element composition was determined by X-ray photoemission spectroscopy (XPS) and inductively coupled plasma mass spectrometer (ICPMS) measurement.

XPS measurements were performed in an integrated VG ESCA Lab system using an X-ray source of Magnesium $K\alpha$ with typical excitation energy output of 1,254 eV. The entire experiments were carried out in an ultrahigh vacuum (UHV) system with typical base pressure in the range of $\sim 10^{-10}$ mbar and the whole acquisition data were taken at room temperature. The impinging spot size on the sample is about 1 mm in diameter. The XPS Li/Pb ratios of $\text{Li}(\text{PEA})_2\text{PbBr}_4$ are calculated by the integration of Li 1s signal over the integration of Pb 4f signal in full XPS spectra. ICPMS samples were prepared by dissolving respective crystals in deionized water (18 M Ω) and the ICPMS equipment model was PerkinElmer ELAN DRC-e.

Temperature-dependent X-ray luminescence measurement. The experiment was carried out in a similar way as our previous one²⁴. A typical setup consisting of an Inel XRG3500 X-ray generator (Cu-anode tube, 45 kV/10 mA), an Acton Research Corporation SpectraPro-500i monochromator (500 nm blazed grating), a Hamamatsu R928 photomultiplier, and an APD Cryogenics Inc. closed-cycle helium cooler with a Lake Shore 330 programmable temperature controller was used to record XL spectra at various temperatures between 10 and 350 K. The measurements were carried out starting at 350 K (unless indicated) and terminating at 10 K to avoid a possible contribution from thermal release of charge carriers to the emission yield.

X-ray thermoluminescence (TL) measurement. The same setup was used as the one in temperature-dependent X-ray luminescence measurement. Prior to the TL runs, the sample was exposed for 10 min to X-ray at about 10 K. The glow curve was recorded up to 350 K at a heating rate of about 0.14 K/s.

Gamma-ray pulse height and excited decay measurement. We used ^{137}Cs (662 KeV) radioisotope for gamma-ray source and various photomultipliers (PMT) (Hamamatsu R2059, Hamamatsu R878, and Photonis XP Series) for detecting the converted photons.

To operate the PMT, we applied a voltage between 1.25 and 1.7 kV. The corresponding output signal from PMT is integrated with a charge sensitive pre-amplifier. The output then feeds a spectroscopic amplifier with a shaping time of 2 μ s and an analog-to-digital converter (Ortec series). The photoelectron yield was obtained by comparing the position of photopeak to the position of the mean value of the single electron response in pulse high spectra measurements. The actual light yield for the radiation conversion in photons per MeV was obtained after the photoelectron yield was divided by the quantum efficiencies of the PMT.

Scintillation decay measurements were performed by the delayed coincidence single photon counting method, originally proposed by Bollinger and Thomas²⁵. The idea of this method is to use two PMT to record the scintillation events to correct the dead time resulting from the detection. One PMT is to record the zero-time of the signal by just collecting one photoelectron per signal from scintillator while the other is to collect many photoelectrons per signal. By counting the time difference, a histogram of time difference can be plotted and the curve of decay is obtained. A ¹³⁷Cs radioactive source, two Hamamatsu photomultiplier tubes (R1104 and R928 for "starts" and "stops", respectively), a Canberra 2145 time-to-amplitude converter, and a TUKAN-8K-USB multichannel analyzer were used.

Alpha particle pulse height measurement. Four alpha-emitting sources were used: ²⁴¹Am (5,486 keV), ²⁴⁴Cm (5,805 keV), ²²⁸Th (with progeny ²¹²Po: 8,785 keV), ²³⁰Th (4,687 keV). To perform alpha particle spectroscopy, the crystal was mounted on the window of a Hamamatsu R9880U-20 photomultiplier tube (PMT), with a thin layer of silicone grease to provide optical coupling. This PMT has a fast time response (0.6 ns rise time), a broad spectral sensitivity (230–920 nm), and an 8 mm diameter photocathode sensitive area. The PMT was operated at a voltage of -750 V for these

measurements. The PMT anode signal was input directly to a Caen DT5720D digital pulse processing (DPP) unit which integrated the anode charge pulses over a 92 ns gate. Caen's CoMPASS software was used to control the DPP parameters and accumulate pulse-height (proportional to energy) spectra for each radioactive source. These radioactive sources were positioned (in air) at 2 mm distance from the surface of the crystal.

Pulse shape discrimination (PSD) between alpha particle and gamma-ray. The PSD capability of 1:1 Li-(PEA)₂PbBr₄ crystal was tested under alpha particle and gamma-ray signals using ¹³⁷Cs and ²⁴¹Am source, respectively. The crystal was mounted on a Hamamatsu multiplier tube R6233-100 and covered with several Teflon layers, except a small hole was opened to enable alpha particle irradiation. The PMT anode signal was digitized directly by a fast analog-to-digital-converter (FADC400 Notice Korea) with recording length of 2.56 μs for each pulse. A ROOT-based C++ program was used to record data to a Linux-based PC used for further analysis. The optimum filter method was employed for PSD study with detail information can be found in this reference²⁶.

X-ray imaging setup. The X-ray source was PHYWE XR 4.0 expert unit (Cu anode, 35 kV, 1 mA) and the camera was Chameleon CMLN-13S2C (exposure time depends on varied samples, usually 1 to 3 s). The equipment was placed as shown in the scheme in Figure 5-17a. The envelop with the safety pin inside was put at the aperture of the X-ray tube where the uncollimated X-ray came out. The envelop, the perovskite film and the camera were placed as close as possible to reduce light scattering.

5.3 Results and discussion

5.3.1 Crystal structure characterization and doping analysis

Compared to 3D perovskite, the layered structure of $(\text{PEA})_2\text{PbBr}_4$ introduces the quantum confinement effect¹¹. In this case, large binding energy (hundreds of meV versus tens of meV in the 3D counterpart) favors excitonic recombination and thus theoretically enhances luminescence²⁷. The key to transforming a 3D lead halide perovskite into a 2D one is the introduction of a long alkyl chain or bulky organic cation, such as n-butylammonium, 2,2'-(ethylenedioxy)bis(ethylammonium)¹² and 3,4,5-Trifluoroaniline ammonium²⁸. In our experiment, phenethylammonium cation is chosen due to its high chemical stability, commercial availability and fast scintillation^{5,13}. The structure of $(\text{PEA})_2\text{PbBr}_4$ is shown in Figure 5-1a. The alternating inorganic/organic layers effectively confine the exciton inside the inorganic layer and thus benefit the scintillation under high energy radiation like gamma-ray¹³. Figure 5-1a shows the optical images of the 1:1 Li- $(\text{PEA})_2\text{PbBr}_4$ crystals. The size of the tilted hexagonal-shape crystal can be up to $1 \times 0.7 \times 0.2 \text{ cm}^3$ by the slow evaporation method. Although some grains and boundaries exist, the transparency is still satisfactory as all the assigned letters below the crystal can be seen clearly. Under UV (365 nm) and X-ray (Cu $K\alpha$, 8 keV) excitation, the crystal shows a bright purple-blue emission which indicates high crystal quality. Our blue emission brightness is comparable to that of recent 1D Rb_2CuBr_3 under 30 keV X-ray radiation²⁹. The powder X-ray diffraction (XRD) result is demonstrated Figure 5-1c. The experimental XRD pattern is comparable to the powder diffraction pattern simulation from the corresponding crystallographic information file (Figure 5-2)³⁰. No substantial peak shift can be found except a slight intensity ratio of the (020) peak at 15.4° and the (003) peak at 15.9° decreases from

undoped to highest 1:1 Li-(PEA)₂PbBr₄ crystals. The absence of large difference in XRD implies Li dopant induced little lattice distortion. There are two reasons behind this observation. On the one hand, Li is a light element and its X-ray cross section is smaller than the other elements. On the other hand, Li atom is so small that unlikely to cause large lattice distortion while the Li concentration is relatively low in the crystal, which is confirmed by the X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma mass spectrometry (ICPMS) result demonstrated in Figure 5-1d. In our experiment, we used (PEA)₂PbBr₄ crystals with different Li doping concentrations at comparable size and thickness, allowing us to make direct qualitative and quantitative comparisons. As the Li/Pb precursor ratio increases, the Li/Pb XPS integrated intensity ratio from the crystals rises from undoped to 1:100 and then gradually reaches a plateau. According to integration of different elements, we estimate that the Li/Pb ratio is 5% in the highest doping 1:1 Li-doped crystal. Inductively coupled plasma mass spectrometry (ICPMS) suggests also a similar 4% Li/Pb ratio in the highest doped 1:1 crystal but they are variations in 1:100 and 1:10 crystals compared to XPS result (See Table 5-1).. The differences can be attributed to different element detection sensitivity because of varied detection mechanisms, but we consider that they are still reasonable, because the absolute differences are not large as well as the low concentration and intrinsic light atom properties of Li may cause insensitivity in these characterizations. The natural abundance of ⁶Li, of interest for thermal neutron capture is 7.59 % and thus the ⁶Li percentage is around 0.38% in 1:1 Li-doped crystal. In Figure 5-1d, a huge increase in the Li/Pb XPS integration signal can be seen from undoped to 1:100. In our experiment, while we increased the Li/Pb ratio exponentially in the precursor solutions, the Li/Pb ratio in the corresponding crystals increased only marginally. We suggest that it is difficult to control the actual Li doping level as we expect by simply add more dopant

precursor.

Figure 5-1 Crystals structure, luminescence and Li dopant concentration characterization. (a) Crystal structure of (PEA)₂PbBr₄^{31,32}. (b) Bright-field, UV and X-ray images of 1:1 Li-(PEA)₂PbBr₄ single crystal. Scale bars, 1 cm. (c) Powder XRD pattern of four different Li-doped crystals. (d) Li to Pb XPS and ICPMS signal ratios as a function of precursor ratio.

Figure 5-2 Comparison of experimental and simulated powder XRD pattern of undoped $(\text{PEA})_2\text{PbBr}_4$. The experimental curve is from single crystal powder. Thin film powder curve is also included to demonstrate that there is little change of crystal phase after spin-coating. The simulated result is based on the crystallographic information file reported by Shibuya³⁰. The characteristic XRD peaks of our crystal matches well with the simulation.

Table 5-1 Result of ICPMS to estimate Li/Pb ratio of the all crystals.

Li/Pb precursor ratio	Li concentration (ppb)	Pb concentration (ppb)	Li:Pb sample ratio (%)
Undoped	1.74	11600	0%
1:100	2.22	150	1%
1:10	3.31	146	2%
1:1	6.99	160	4%

5.3.2 Temperature-dependent X-ray luminescence

Based on the above XPS result, the existence of Li dopant within the perovskite is verified. Therefore, we proceed to investigate the influence of Li in temperature-dependent X-ray luminescence (XL) spectra. Here the undoped and the 1:1 Li-doped crystals are chosen and compared because their representative emission contrast is quite distinctive under X-ray excitation. a and b show the XL comparison between two representative high and low temperatures (330 K and 10 K) from undoped and 1:1 Li-doped crystals (1:100 and 1:10 in Figure 5-4). Both free exciton (FE) emissions at 418 nm are shifted to 436 nm from 10 to 330 K³³. XL spectra at 10 K from both crystals show a bump ranging from 450 to 750 nm. We consider this bump corresponds to the self-trapped exciton (STE) emissions although STE in (001) type 2D perovskite is scattered. STE is a result of strong photogenerated electron-phonon interaction. The interaction is so strong that surrounding lattice are distorted elastically. In this case, the electrons and holes will be self-trapped quickly once they are photogenerated and this trapping state is more stable than the one where the electrons and holes are free to move. The energy of STE is much smaller than that of the free carrier or free exciton recombination generally and the broad emission of STE can be explained by in-gap trap states in the bulk³⁴. There are two reasons we attribute the broad peaks at low temperature to STE. Firstly, STE in (001) type can be temperature-dependent in which STE only emerges at low temperature³⁵, and that is what we observed in the spectra. Secondly, dopant in 2D perovskite could possibly trigger the occurrence of STE³⁶. However, the intensity ratio between FE emission and the STE emission (denoted as FE/STE ratio) is much higher in a 1:1 crystal than in undoped one. Theoretically, higher Li concentration should create more traps and thus more likely to have stronger STE emission. In fact, Li being traps is indeed confirmed by the following X-ray

thermoluminescence measurement. In this case, Li dopant could bring three possible effect on FE and STE quenching or enhancement at 10 K. The first possibility is Li dopants enhance both FE and STE but impose stronger effect on FE. The second possibility is Li dopants quench both FE and STE but have stronger effect on STE. The final possibility is Li dopant enhances FE while quench STE. Figure 5-5 demonstrates that all doped crystals have higher intensity than undoped ones at 10 K, so it is unlikely for Li dopant to quench both FE and STE. Then we can compare the normalized 2D map temperature-dependent XL of undoped and 1:1 Li-doped crystals in Figure 5-3c and d (1:100 and 1:10 in Figure 5-6). We can see the bump in from 1:1 crystal survives up to 200 K and thus Li dopant does not quench STE. Our first preposition of Li dopant may enhance both FE and STE seems more suitable to our observations. The emission peaks at 330 K are asymmetric, which we believe it is due to part of the emission being re-absorbed and confirmed by the UV absorption and emission spectrum (see Figure 5-7) since the X-ray luminescence shares a similar exciton emission mechanism to the UV photoluminescence. The emission peak is shifted from 405 nm in PL to 436 nm in XL. This redshift behavior also occurs for three-dimensional CsPbBr₃ perovskite single crystal. In addition, we can find the full width half maximum (FWHM) of undoped is smaller than that of 1:1. By comparison of this series of crystals, FWHM at 330 K increases gradually from undoped to 1:1 (undoped: 30 nm, 1:100 doped: 41 nm, 1:10 doped: 46 nm and 1:1 doped: 50 nm). The effect of Li is apparent in broadening the emission, besides enhancing the emission intensity. From 200 to 10 K, both emission peaks are narrow and almost symmetric and STE emissions exist. But the difference in peak position or FWHM is quite small between undoped and doped due to strong narrowing effect by lowering temperature²⁴. Figure 5-3e plots the quantitative comparison of FWHM evolution upon cooling. No substantial variation can be seen

below 200 K and above 200 K, the slope starts differing as a result of Li dopant. A simple linear fitting can be employed to quantify the difference. The slope values increase considerably from undoped to 1:1 but level off (undoped: 0.15, 1:100 doped: 0.24, 1:10 doped: 0.25 and 1:1 doped: 0.28, unit, nm/K) and such behavior agrees well with the integrated ratio profile in XPS analysis in Figure 5-1d.

The more interesting part of the 2D maps is the stronger emission upon higher temperature, as shown in Figure 5-3f. Such behavior has been reported earlier in photoluminescence (PL) of n-type GaAs and n-type ZnS and it was termed as the negative thermal quenching effect³⁷. This effect is commonly originated from thermally excited traps from the electron eigenstate between the ground state and final eigenstate where excited electrons will relax and generate PL emission³⁸. A similar phenomenon in temperature-dependent PL of (PEA)₂PbBr₄ microplate was observed³⁷. Negative thermal quenching is almost the opposite to the thermal quenching in our previous report on methylammonium lead halide perovskite single crystals using the same setup, where the emissions become stronger monotonically as temperature goes down to 10 K²⁴. In this scenario, the strongest emission occurred at 350 K, the highest temperature in this experiment. As cooling continues, the emissions reach their minima at around 220 to 200 K. Below 200 K, slowly the emissions become slightly stronger compared to their minima and the STE emissions begin to appear. This effect is enhanced with Li doping. The curves of Li-doped crystals are “lifted up” compared to the undoped one. The integrated intensity ratios between the minima and the maxima (~350 K) can be a parameter to define the enhancement induced by Li. The other parameters for the fitting of the negative thermal quenching are presented in Table 5-2. With increasing Li concentration, this ratio increases from lowest undoped to highest 1:1 doped (undoped: 0.23, 1:100 doped: 0.25, 1:10 doped: 0.32 and 1:1 doped: 0.42). Although the magnitude

of enhancement is small, it indicates the relative wide-range emission stability of our Li-(PEA)₂PbBr₄. The strongest emission is rarely above 300 K in lead halide perovskite because thermal quenching dominates and prevents excitonic recombination at that temperature. It is reported that most of the strongest emission from materials with negative thermal quenching behavior occurs at around 100-200 K for typical II-VI or III-V semiconductor composite³⁸; while it is considerably lower than 300 K for other 3D perovskites or perovskite nanocrystals/quantum dots without extra protection^{37,39,40}. Such stronger emission upon higher temperature characteristics allows (PEA)₂PbBr₄-based detector to operate at up to 350 K or even higher. The continuous luminescence change suggests the absence of temperature-induced phase transition⁴¹. Instead of making it worse upon rising temperature, the addition of Li dopant increases the stability of the intensity or the radiation-converted photons with the temperature. Beside the later function of Li dopant with other radiation detection, the addition of concentration already makes Li-(PEA)₂PbBr₄ even more competitive compared to the other perovskites mentioned above (3D or nanocrystals) since a Li-(PEA)₂PbBr₄ scintillator performs well at a wide-range of temperature, and no extra cooling is required to maximize its emission and light yield.

Figure 5-3 Temperature-dependent X-ray luminescence. X-ray luminescence spectra at representative temperature, 10 K and 330 K from (a) undoped and (b) 1:1 Li-(PEA)₂PbBr₄. Temperature-dependent X-ray luminescence spectra from 10 K and 350 K from (c) undoped and (d) 1:1 Li-(PEA)₂PbBr₄. (e) Comparison of FWHM versus temperature among different Li-doped crystals. (f) Comparison of the negative thermal quenching behavior.

Figure 5-4 Comparison of normalized XL spectra between 10 K and 330 K from undoped, 1:100, 1:10 and 1:1 Li-doped crystals. At 10 K, all four crystals show STE emissions after the FE emissions. The STE emissions seems to be affected by Li dopant concentration. In addition, we can see the tendency of FE emission broadening.

Figure 5-5 Comparison of XL at 10 K. The absolute emission counts of Li-doped crystals are all higher than undoped one.

Figure 5-6 Comparison of temperature-dependent 2D map from undoped, 1:100, 1:10 and 1:1 Li-doped crystals. The tendency of emission broadening is apparent from undoped to highest-doped crystal. Negative thermal quenching can be observed as well.

Figure 5-7 UV-Vis Absorption and PL excited by 360 nm UV in ambient. There is an overlap in the absorption and emission at around 410 nm, which induces the reabsorption at this overlapped region. It follows that the emission peak is asymmetric

and sharp at the lower wavelength.

Table 5-2 Parameters of negative thermal quenching.

Item	D	C	E'_1 (meV)	E_1 (meV)
Undoped	6.69×10^5	2.46×10^6	4.38	4.30
Li:Pb = 1:100	5.82×10^6	1.28×10^7	5.33	5.07
Li:Pb = 1:10	9.05×10^5	2.04×10^6	4.85	4.69
Li:Pb = 1:1	3.01×10^6	5.93×10^6	4.87	4.87

5.3.3 X-ray thermoluminescence

After a detailed discussion on the emission properties of Li-(PEA)₂PbBr₄, we continue presenting an insight on the role of Li as trap agent using X-ray excited thermoluminescence (TL) characterization. Figure 5-8a demonstrates the comparison of normalized TL curves. After 10 min X-ray exposure at 10 K, the emission was monitored for 100 minutes. We find two changes induced by Li doping. The most prominent change is that we find that the thermoluminescence peaks (after 3,600 s) become more intense upon higher Li doping. To analyze these TL peaks, classic Randall-Wilkins equation⁴² can be employed to deconvolute the peaks:

$$I = \sum_{i=1}^3 n_{0i} s_i \exp\left(-\frac{E_i}{k_B T}\right) \exp\left(-\frac{s_i}{\beta} \int_{T_0}^T \exp\left(-\frac{E_i}{k_B T'}\right) dT'\right) \quad (1)$$

where I is the TL intensity, 3 is the number of deconvoluted peaks, n_{0i} is the initial trap concentration, s_i is the frequency factor, E_i is the trap depth, k_B is the Boltzmann constant, β is the heating rate, T is the temperature and T_0 is the initial temperature. The

The TL peaks of the undoped samples do not exhibit any appreciable fitting. For the other crystals, the TL peaks can be deconvoluted into three peaks and the parameters are listed in Table 5-3. Figure 5-8b displays the concentration of three types of trap with different energy depths. It is clear that there are more traps at different energy depths with higher Li doping from 1:100 to 1:1. The total number of traps is comparable to the reported value from by photocurrent measurement ($10^5 \sim 10^7 \text{ cm}^{-3}$)³. Shallow traps (10.8 meV) are the major contribution to the total increase of traps induced by Li-doping, while deep traps (124 meV) show a smaller contribution. The other difference is that small afterglow effect (the tails showing the slow transition from bright to dark state) can be barely seen in undoped and 1:100 doped crystals, while they become more pronounced in 1:10 and 1:1 (Figure 5-9). We attributed this behavior to additional trap generated by Li doping. After these characterizations, we establish that Li serves as traps in the (PEA)₂PbBr₄ scintillation under X-ray irradiation and it could enhance performance while broadening the luminescence.

Figure 5-8 Thermoluminescence and energy traps. (a) X-ray thermoluminescence plots of undoped, 1:100, 1:10, and 1:1 Li-(PEA)₂PbBr₄. The dashed line indicates the rise of temperature. (b) Initial trap concentration at corresponding energy from 1:100, 1:10, and 1:1 Li-(PEA)₂PbBr₄. For clarity, the symbols of 1:10 and 1:1 are intentionally separated

due to their close values.

Table 5-3 Parameters of low-energy traps

Item	T_{max} (K)	E (meV)	n_0	σ_i
Li:Pb = 1:100	37	10.8	1.04×10^5	0.285
	78.5	41.74	6.27×10^4	4.348
	120	124	8.81×10^4	1.87×10^3
Li:Pb = 1:10	39	10.8	2.72×10^5	0.213
	78.5	41.74	1.06×10^5	4.328
	117	123	1.95×10^5	2.83×10^3
Li:Pb = 1:1	45	10.8	6.95×10^5	0.101
	78	41.74	3.17×10^5	4.541
	114	124	1.94×10^5	4.11×10^3

Figure 5-9 Zoom-in TL spectra show the increasing afterglow upon higher Li concentration. The afterglow effect in undoped crystal is weaker than the other Li-doped ones and it is a result of traps generated by Li dopant.

5.3.4 Gamma-ray pulse height and decay spectrum

Beside from soft X-ray characterization, we further explored scintillation properties under gamma-ray radiation. As temperature-dependent XL shows that the radiation-converted photons are optimized at room temperature, we still need to determine the scintillation light yield. This number is obtained through the comparison of the photopeak signals in the pulse height spectra at certain energy of gamma-ray radiation with the scintillator single electron response. Figure 5-10a exhibits the pulse height spectra of 1:1 crystal with ^{137}Cs (662 keV). The light yield and the energy resolution are $11,000 \pm 500$ ph/MeV and 12.4%, respectively. For the other doped crystals, the light yield of 1:100 and 1:10 are $6,300 \pm 300$ and $9,100 \pm 400$ ph/MeV, while their energy resolutions are 32.6% and 36.8%, respectively (Figure 5-11). The light yield of undoped crystal is $8,000 \pm 800$ ph/MeV. Our light yield values here are determined by traditional

gamma-ray pulse height measurements compared to those estimated by the integral of the X-ray luminescence intensities demonstrated previously for perovskite scintillators^{14,29}. We can see a general tendency of increasing light yield with higher Li concentration although the light yield of undoped is marginally higher than 1:100. We consider that it is due to slightly different crystal quality. Crystal quality, including crystal morphology, transparency and homogeneity plays a critical role on quality-sensitive pulse height measurement. Unfortunately, crystal quality control is not easy since there has been not a mature 2D perovskite crystal growth technique from solution method compared to 3D ones⁴³. However, it is reasonable that there is no dramatic increase in light yields with more Li since the XPS result manifest close Li concentration in all doped crystals. The energy resolution is also affected by crystal quality. According to our calculation based on Poisson statistics of the photoelectron, the energy resolution of 1:1 crystal can be as low as 6% theoretically^{41-43,44-46} (See Section 5.6 for theoretical limit of energy resolution) and hence there is considerable room for energy resolution improvement. Gamma-ray excited decay measurement result of 1:1 is shown in Figure 5-10b. A three-component exponential decay was adopted in the fitting. We also tried to take into account the bimolecular recombination, but the fittings did not converge well⁴⁷. The percentages of decay in this experiment are all in amplitude. The primary (fast) decay time (11 ns) is similar to early reports (9-11 ns)^{13,48}. At this stage, it is difficult to confirm the doping effect on decay time and we tentatively see no significant effect is induced by the Li content since their values are comparable to one another and to other reports (See Figure 5-12). Compared to the popular commercial NaI:Tl scintillator, the highest light yield of our Li-(PEA)₂PbBr₄ is lower (11,000 vs. 38,000 ph/MeV), while the primary decay time is one order smaller (11 vs. 250 ns) at room temperature⁸. It indicates that the time density of photon at early stage of the pulse is

significantly higher, making Li-(PEA)₂PbBr₄ advantageous for fast timing applications such as high-speed imaging and image processing application.

Figure 5-10 Gamma-ray excitation characterizations. (a) Gamma-ray pulse height spectra and (b) gamma-ray excited decay of 1:1 Li-(PEA)₂PbBr₄. Black line in (a) is the Gaussian fitting for extraction of light yield and energy resolution and in (b) is the three-component exponential decay fitting.

Figure 5-11 Gamma-ray pulse height measurements of undoped, 1:100, 1:10 and 1:1 Li-doped crystals. Gaussian fittings were employed to extract the light yields and energy resolutions. At the first glance, the photopeak of the undoped crystal seems indistinguishable as the others doped crystals so we put it in log-log scale. Its light yield and energy resolution are $8,000 \pm 800$ ph/MeV (based on the channel difference (~ 500 as shown in other figures) between the Compton edge (1,100) and photopeak ($1,100 + 500 = 1,600$)) and 55.4%, respectively. We also compare here our light yield result to

early reports of undoped (PEA)₂PbBr₄ crystals (9,400 and 14,000 ph/MeV) although the characterization method might be different^{13,43}. In our experiments, the light yield increases as Li concentration increases from 1:100 to 1:1. The best energy resolution is from the highest 1:1 Li-doped crystal.

Figure 5-12 Comparisons of gamma-ray excited decay of undoped, 1:100, 1:10 and 1:1 Li-doped crystals. Primary (fast) decay time from early researches are reported to be 9

and 11 ns^{13,43}.

5.3.5 Discrimination of alpha particle, gamma-ray and thermal neutron radiations

In addition to X- and gamma-ray, we took a step further to test our Li-(PEA)₂PbBr₄ crystals for alpha particle ($\frac{4}{2}\alpha$) detection. Figure 5-13a displays the result of alpha particle pulse height characterization of 1:1 Li-doped crystal using ²⁴¹Am (5,486 keV) and ²⁴⁴Cm (5,805 keV) as the alpha particle sources. Results of other radioisotope sources are also presented in Figure 5-14. We can easily distinguish the two full-energy peaks although they are relatively broad. To the best of our knowledge, this is the first time the successful application of 2D perovskite scintillator in alpha particle detection has been reported⁴⁹⁻⁵¹. The full-energy peaks indicate the potential thermal neutron detection on the alpha particle as a product from the ⁶Li (n, α) reaction⁵². Also, there is an opportunity for fast neutron detection by virtue of the considerable amount of hydrogen and Li dopant in the future Li-doped perovskite crystal⁵². However, the discrimination with other radiations will be more complicated if we add more hydrogen amounts in the crystals. It can be a choice of material for neutron diagnostics in inertial confinement fusion requiring fast neutron detection and back scattering on Li ions⁵³. Figure 5-13b shows the first sign for pulse shape discrimination (PSD) with our Li-(PEA)₂PbBr₄ crystal using the optimum filter method⁵⁴ based on the significant difference between the scintillation decay under alpha particle and gamma-ray excitation (Figure 5-13b inset). Alpha particle signals in high energy channels is quite well separated from gamma-ray ones. However, the alpha particle full-energy peak was broad and the tail at low energy channel is slightly overlapped with the gamma-ray signals. It can be a result of insufficiently high crystal quality and aggravated by the defect layer on the surface of the crystal as the crystal could be degraded through long-

time MeV alpha particle bombardment in this measurement. In our previous report of 3D halide perovskite scintillators, dose-dependent XL measurements reveal that radiation dose up to 1,000 microsievert per hour has a weak impact on the light yields of bromide perovskite scintillators²⁴. And we could reasonably expect a similar X-ray radiation hardness of our (PEA)₂PbBr₄ crystals and good stability over time at low dose. However, decreases in light yields and energy resolutions in pulse height spectra were indeed observed after long time exposure of much energetic radiation (see Figure 5-15). Despite the small signal overlap, the demonstration of PSD discrimination between alpha particle and gamma-ray verifies the potential of thermal neutron detection with our Li-doped 2D perovskite. It is known that thermal neutron detection usually requires the detection of neutron-induced secondary radiation, especially for readily detected charged particles like alpha particle⁵². However, the process of neutron generation is usually accompanied by gamma-ray background. That is the reason why it is critical to exploit the capability of discriminating between alpha particle and gamma ray using the PSD method^{55,56}, which is not demonstrated by the recent neutron semiconductor detection²¹. The quenching factor (α/β ratio), which is determined by the number of photon/MeV produced by one alpha particle over the number of photon/MeV produced by one electron (photoelectric effect by gamma-ray in this case), was estimated to be 0.24⁵⁷. Using this result, we can also discriminate between thermal neutrons and gamma-ray and it is expected that the thermal neutron signal will appear at energy larger than 1.5 MeV. However, as ⁶Li is only 7.59% in natural abundance⁴¹ while the Li content in this crystal is only 5%, it is expected that we cannot observe the strong thermal neutron full-energy peak but only a bump in our experiment as demonstrated in Figure 5-13c. In addition, at this current stage, the crystal quality also needs to be improved so that it can compete with the energy resolution of Cs₂LiYCl₆:Ce³⁺ crystal⁵⁸. Besides, the

theoretical thermal neutron detection efficiency maximum of natural and ^6Li -enriched 1:1 $\text{Li}-(\text{PEA})_2\text{PbBr}_4$ are 7% and 48%, respectively (see calculation in Section 5.6). The 48% efficiency is still comparable to natural Li-containing elpasolite single crystal scintillators in an early report⁵⁹. Therefore, further growth of cm-scale thicker crystals with higher ^6Li content are necessary to improve the thermal neutron detection. Figure 5-16 shows the XPS and PSD matrix of 1:1 $^6\text{Li}-(\text{PEA})_2\text{PbBr}_4$ prepared by using 95% enriched $^6\text{LiBr}$ precursor. In Figure 5-16a, the difference between ^6Li and ^7Li 1s signals are small since they overlapped the same binding energy range. Figure 5-16b-d show the pulse height spectra under gamma-ray and neutron radiations. We can see the gamma-ray photopeak can be distinguished easily at 662 keV and but the energy resolution is still large in Figure 5-16b. We should observe thermal neutrons signal at 4.8 MeV and fast neutrons signal below 1 MeV. Here thermal neutrons react with ^6Li while fast neutrons interact with hydrogen in the atoms in the crystal. In our samples, thermal neutron signal will appear around 1-1.5 MeV since the nonproportionality is high at 4.8 MeV and we have a low alpha/beta ratio so there is an interference from the fast neutron.

Figure 5-13 (a) Alpha particle pulse height spectra, (b) pulse shape discrimination (PSD) matrix with the shape indicator on y-axis and the measured energy (electron equivalent) on x-axis and (c) pulse height spectra measured with graphite-moderated Am-Be

neutrons source of 1:1 Li-(PEA)₂PbBr₄ crystal. The inset with the green and the blue curves shows the normalized average waveforms from both alpha particle and gamma-ray radiation of ¹³⁷Cs and ²⁴¹Am sources, respectively. The pulse height spectra of neutron and ¹³⁷Cs sources are indicated by red and blue dots, respectively. The red arrow indicates the weak thermal neutron full-energy peak.

Figure 5-14 Alpha particle pulse height spectra of ²⁴¹Am, ²⁴⁴Cm, ²¹²Po and ²³⁰Th. Relatively broad photopeaks correspond to varied radioisotopes can be discriminated. Poor energy resolution could be attributed to crystal morphology and inhomogeneity.

Figure 5-15 Pulse height spectra of ^{137}Cs measured before and after thermal neutron exposure of 4.8 MeV. The light yield drops from 10,500 to 7,000 ph/MeV after thermal neutron measurement while the energy resolution increases from 17.6 to 25.9.

Figure 5-16 (a) X-ray photoelectron spectrum of 1:1 ^6Li -doped $(\text{PEA})_2\text{PbBr}_4$ crystal showing ^6Li peaks with binding energies between 52 and 56 eV. PSD matrix of ^6Li doped crystals measured with (b) ^{137}Cs source, (c) 5-cm-organic glass moderated Am-Be neutrons source, and (d) direct neutron source. The insets in (b) and (d) exhibit the pulse height spectra with the gaussian fits and projection on y-axis for neutron signal, respectively. A huge number of events with PSD ratio center at 0.66 observed for the neutron measurements is a clear evidence for neutron interaction with ^6Li doped crystals. Most neutrons are fast due to large amount of hydrogen in crystal. The figure of merit (FoM) based on PSD is expected to be 0.57. Theoretically, we have acceptable gamma rejection of 3-sigma (99.7%) with FoM of 1.27.

5.3.6 X-ray imaging

Finally, to demonstrate the X-ray scintillation imaging application, X-ray phase-contrast imaging of a ubiquitous safety pin was carried out using Li-(PEA)₂PbBr₄ as a scintillator film. The schematic setup is displayed in Figure 5-17a. The safety pin was put inside an envelope as the test subject. The 1:1 Li-(PEA)₂PbBr₄ spin-coated film with a thickness of 67 μm (Figure 5-18) that was prepared by our new technique shows high transparency and satisfying homogeneity, despite some small surface ripples (Figure 5-17b). Typical spincoating and baking techniques were found to be ineffective in acquisition of a homogeneous thick film (up to 50 μm or above for effective X-ray stopping), which is required in the X-ray characterization (See Section 5.6 for calculation detail)⁶⁰. To get a thick film, spincoating at low speed (< 500 rpm) usually results in an inhomogeneous film. Inspired by a reported spincoating technique by introducing N₂ flow during spincoating, we modified it and blow-dried the film with hot air flow in the last stage of spincoating⁶¹. This technique proved to be very useful and a relatively thick and homogeneous film on glass substrate was obtained. One great merit in (PEA)₂PbBr₄ should be highlighted here; that is, its intrinsic readiness to form on average mm-size large single crystal flakes upon drying. It follows that the film is composed of large orientated single crystal 2D flakes instead of the small un-orientated small crystals which are common in 3D perovskite spin-coated film. The powder XRD verifies the same crystal phase of the spin-coated film as the single crystal (see Figure 5-2). Longer exposure time (3 s) for the spin-coated film was needed to achieve comparable brightness to the thick crystal in Figure 5-1b (~400- μm -thickness, 1 s) under X-ray radiation. Despite such circumstance, decent X-ray pictures can be secured as the thickness of 67 μm is enough to stop X-ray radiation, see Figure 5-19. Due to the substantial difference in X-ray stopping power (Cu K α , 8 keV) between the envelope

and the stainless steel, the fine structure of the safety pin, like a 250- μm slit, is revealed clearly by an ordinary camera as shown in Figure 5-17c. Here, the black and white mode was utilized for better contrast. Other items like a spring or a paper clip can be clearly imaged under X-ray as well (Figure 5-20). Though there are quite a few researches on the scintillation properties of $(\text{PEA})_2\text{PbBr}_4$ under X-ray or gamma-ray^{13,43}, here we demonstrate the first imaging using this perovskite material. The quality of the imaging compared to those of CsPbBr_3 ^{14,15} is still lower as our camera is not optimized for the blue emission of scintillators. Moreover, the configuration of the imaging is different as we did not couple the scintillator directly on the photodetector. However, the convenient coupling of our cost-efficient film with the commercial camera is already applicable in high-throughput security inspection. The film can be even further optimized for a smoother surface and higher thickness in the future and a performance improvement can be expected, such as higher and more homogeneous scintillating brightness and shorter exposure time for reduced noise.

Figure 5-17 X-ray imaging performance. (a) Scheme of X-ray imaging setup using 1:1 Li- $(\text{PEA})_2\text{PbBr}_4$ as scintillator. The safety pin is inside the envelope. (b) Bright-field image of the safety pin and the Li- $(\text{PEA})_2\text{PbBr}_4$ film on glass substrate with high transparency. Scale bar is 1 cm. (c) X-ray image (background corrected) of the safety pin. Black and white mode was applied for better contrast. Scale bar, 5 mm.

Figure 5-18 Cross-section view of the spin-coated 1:1 Li-(PEA)₂PbBr₄ film (right) on a glass cover substrate (left). The thickness is around 67 μm. Flat surface of the film can be seen.

Figure 5-19 Photon energy dependent attenuation coefficient of $(\text{PEA})_2\text{PbBr}_4$.

Figure 5-20 Luminescence of the 1:1 $\text{Li}-(\text{PEA})_2\text{PbBr}_4$ film and bright-field and X-ray images of a spring and a paper clip. The blue emission of the spin-coated film under X-ray was bright. The details of a paper clip and a spring inside an envelope can be seen in the X-ray images.

5.4 Conclusion

In summary, we demonstrated successful Li doping in $(\text{PEA})_2\text{PbBr}_4$ crystal synthesis using a solution-processing method. Li dopant serving as traps is capable of enhancing the intensity while broadening the X-ray luminescence. The intrinsic negative thermal quenching behavior of $(\text{PEA})_2\text{PbBr}_4$ allows it to maintain its scintillating performance at a relatively wide range of temperature; however, with additional Li dopant, the performance stability could be even more improved. We found that Li ion dopant could increase the light yield up to 11,000 ph/MeV while maintain a primary decay time (11 ns) under 662 keV gamma-ray radiation. Good numbers of converted photons and especially significantly fast scintillation response compared to commercial NaI: Tl could be propitious in low-cost and large-size scintillator fabrication. Moreover, for the first time we successfully employed our Li- $(\text{PEA})_2\text{PbBr}_4$ scintillator in alpha particle detection and in discrimination between alpha particle and gamma-ray. Based on the thermal neutron results for crystals doping with natural Li and ^6Li , our Li-doped crystal will be a promising thermal neutron scintillator provided more ^6Li is included as it is low cost and it can be deposited in large-area arrays of photodetectors. Finally, we carried out low-dose X-ray imaging using high-quality Li- $(\text{PEA})_2\text{PbBr}_4$ film prepared by our new technique and obtained first satisfactory X-ray imaging pictures using $(\text{PEA})_2\text{PbBr}_4$ perovskite. Here we show promising characterization results and prove that our Li- $(\text{PEA})_2\text{PbBr}_4$ scintillator may hold promise as a low-cost and versatile radiation detector covering a wide range of energy from keV up to MeV.

Appendix I

Negative thermal quenching behavior analysis

In this case, we can apply the model in the simplest case,

$$I(T)_{norm} = \frac{1 + D \exp(-E'_1/k_B T)}{1 + C \exp(-E_1/k_B T)} \quad (1)$$

where $I(T)_{norm}$ is the integrated emission intensity at absolute temperature T normalized to the maximum integrated intensity, D is the negative thermal quenching coefficient which describes the contribution from thermally excited electrons, C is the thermal quenching coefficient related to non-radiative electron excitation, E'_1 and E_1 are the activation energies for negative thermal quenching and typical thermal quenching and k_B is the Boltzmann constant. The fitting parameters are listed in Table 5-2.

Theoretical limit of energy resolution^{45,46,60}

Then energy resolution can be calculated by the following equation,

$$R^2 = \left(\frac{\Delta E}{E}\right)^2 = R_{np}^2 + R_{inh}^2 + R_p^2 + R_M^2 \quad (2)$$

where ΔE is the full width at half maximum of the total absorption peak in the gamma-ray pulse height spectrum, R_{np} is the contribution of the non-proportional response of the scintillator, R_{inh} is related to inhomogeneities of the scintillator, which causes fluctuations in the scintillation light yield, R_{inh} is connected to the fluctuation in the transfer efficiency, which results in the arrival of a photoelectron at the first dynode and subsequently undergoes the full multiplication in the PMT. R_M is determined by Poisson statistics in the number of detected photons N_{dph} , which is equal to the number of photoelectrons from the photocathode in case of a PMT. This resolution is also the

fundamental limit for the energy resolution. It is given by

$$R_M = 2.35 \sqrt{\frac{1+v(M)}{N_{dph}}} \quad (3)$$

where $v(M)$ is the variance in the PMT gain which usually is 0.1-0.2. Theoretically, if the scintillator is a perfect one, then the first three terms can be neglected and the final term R_M is the only consideration while $v(M) = 0.1$. In this case,

$$R = R_M = 2.35 \sqrt{\frac{1+0.1}{N_{dph}}} \quad (4)$$

In our experiment, N_{dph} of 1:1 Li-(PEA)₂PbBr₄ is 1655, the product of number of photoelectron/energy (2500 phe/MeV) and the energy of the radiation source (0.662 MeV). After calculation of Eq. (4), we can obtain theoretical limit of energy resolution,

$$R = 6\%$$

Calculation for thickness-dependent attenuation coefficient of 1:1 Li-(PEA)₂PbBr₄ with natural Li precursor and enriched ⁶Li precursor.

Here we assume atomic 5% Li/Pb LiBr dopant in 1:1 Li-(PEA)₂PbBr₄ crystal using XPS result and we calculated the difference in thickness-dependent attenuation coefficient.

Element	number of atoms n_i per molecule	Thermal neutron cross section σ_i (barn, 10^{-24} cm^2)	Total thermal neutron cross section (barn, 10^{-24} cm^2)
C	16	0.00353	0.05648
H	24	0.3326	7.9824
Br	4	6.9	35.535
N	2	1.9	3.8
Pb	1	0.171	0.171
⁶ Li	-	940	
⁷ Li	-	0.0454	
Natural Li precursor (7.59% ⁶ Li and 92.41% ⁷ Li)	0.05	70.5 ^a	3.525
Commercial enriched ⁷ Li precursor (95% ⁶ Li and 5% ⁷ Li)	0.05	893 ^a	44.65

a. Calculated from percentage average from ⁶Li and ⁷Li.

The thermal neutron cross section of $\text{Li}_{0.05}(\text{C}_8\text{H}_{12}\text{N})_2\text{PbBr}_{4.05}$ is the summation of the products of respective element cross sections σ_i and their number of atoms n .

For natural Li crystal (1:1)

$$\sigma_{\text{natural}} = \sum \sigma_i * n_i = 51.07 \text{ barn}$$

For enriched ^6Li crystal (1:1),

$$\sigma_{\text{enriched}} = \sum \sigma_i * n_i = 92.2 \text{ barn}$$

The detection efficiency maximum E is quotient of the cross section of Li dopant and the cross section of the molecule⁵⁷,

$$E_{\text{natural}} = 3.525/51.07 = 7\%$$

$$E_{\text{enriched}} = 44.65/92.2 = 48\%$$

The number of molecule per unit volume N can be calculated by the density (ρ , 2.276 g/cm³), molecular weight (M_W , 771.19 g/mol) and the Avogadro constant (N_A , 6.02×10^{23}),

$$N = \rho / M_W * N_A = 2.276 / 771.19 * 6.02 * 10^{23} = 1.78 * 10^{21} \text{ cm}^{-3}$$

Macroscopic cross section (attenuation coefficient) Σ_{natural} and Σ_{enriched} are the product of number N and microscopic σ_{natural} and σ_{enriched} , respectively. Therefore, we have

$$\Sigma_{\text{natural}} = N * \sigma_{\text{natural}} = 0.09 \text{ cm}^{-1}$$

$$\Sigma_{\text{enriched}} = N * \sigma_{\text{enriched}} = 0.16 \text{ cm}^{-1}$$

The attenuation length L is,

$$L_{\text{natural}} = 1 / \Sigma_{\text{natural}} = 11 \text{ cm}$$

$$L_{\text{natural}} = 1 / \Sigma_{\text{enriched}} = 6.1 \text{ cm}$$

Charge integration method and optimum filter method

Charge integration method is commonly used for pulse shape discrimination by comparing the integration charge ratio between the slow decay component and total decay. The pulse shape discrimination ratio (PSD ratio) is defined as,

$$PSD\ ratio = \frac{Q_1}{Q_1 + Q_2} = \frac{Tail}{Total}$$

where Q_1 and Q_2 are integrated charge of the tail and the total decay. The selection of tail needs to be optimized for better discrimination. Fraction of luminescence in slow component depends on nature of incoming particle. For gamma-ray and neutron discrimination, the slow decay component in a neutron induced decay takes a larger portion so the neutron peak has a higher PSD ratio than the gamma-ray peak in PSD matrix (Figure 5-16).

Optimum filter method can be considered as the mathematic treatment of the charge integration method to push the discrimination to theoretical limit. Shape indicator (Figure 5-14) is a result of treatment of PSD ratio by taking into account of average decay time in a time interval. Shape indicator (SI) is defined as,

$$SI = \frac{\sum A_i P(t_i)}{\sum A_i}$$

where $P(t_i)$ is the weight factor at the time interval i calculated based on exponential decay functions of the average decay time of gamma-ray and neutron signals.

Therefore, both PSD ratio and SI can be considered parameters showing the positions of the gamma and neutron peaks. The PSD ratio and SI peak differences (gamma and neutron) in a PSD matrix are more important than the absolute PSD ratio and SI value.

The figure of merit (FOM) is used to quantify the how good the peak discrimination is, which is defined as,

$$FOM = \frac{\langle n \rangle - \langle gamma \rangle}{FWHM_n + FWHM_{gamma}}$$

where $\langle n \rangle$ and $\langle gamma \rangle$ are the neutron and gamma peak positions in PSD ratio or SI, $FWHM_n$ and $FWHM_{gamma}$ are FWHM of the neutron and gamma peaks. Usually, we have acceptable gamma rejection of 3-sigma (99.7%) with FoM of 1.27. Our current result is 0.57 as shown in Figure 5-16, which does not meet the acceptable discrimination criteria.

Thickness-dependent X-ray attenuation of spincoated film

With the aid of XCOM web tool⁵⁸, the photon energy-dependent linear attenuation coefficient of (PEA)₂PbBr₄ (dopant LiBr neglected) is plotted in Figure 5-19. X-ray attenuation within an absorber follows the single exponential decay,

$$\frac{I}{I_0} = e^{-\mu t}$$

where I is the number of transmitted photon and I_0 is the photon number without absorber (the term $\frac{I}{I_0}$ can be considered as transmission), μ is the linear attenuation coefficient and t is the thickness of the absorber. The linear attenuation coefficient of (PEA)₂PbBr₄ at 8 keV (Cu K α , 1.54 Å) is 222 cm⁻¹ and the film thickness is 67 µm while single crystal 400 µm. Therefore, the respective transmission of film and single crystal are 22% and 0.014%. That's why the single crystal is brighter under the same condition in our X-ray imaging and thus why thicker film or crystal is needed.

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Chapter 6   Library of two-dimensional hybrid lead halide perovskite X-ray scintillator crystals

6.1   Introduction

The platform for light manipulation offered by two-dimensional (2D) organic/inorganic hybrid perovskites has boosted the extensive investigation in their light emitting applications¹⁻⁴. In addition to intrinsic heavy Pb element that can enhance the absorption of high-energy X-ray and gamma-ray (see energy-dependent attenuation length in Figure 6-1), 2D perovskites are able to show high scintillation light yield and different emission patterns depending on the combination of organic cations and halide anions^{5,6}. Depending on practical demands, their emissions can be tuned by composition to be either narrow thus displaying high-purity color^{7,8} or broad therefore rendering white-emissions^{9,10}. Several recent reports regarding 2D perovskite scintillators have shown very promising preliminary X-ray scintillation results¹¹⁻¹⁴. Perovskite scintillators have manifested several merits, for instance, comparable light yield to commercial scintillators^{11,12}, fast decay, and more importantly, low cost from low-temperature solution-processing synthesis. In addition, 2D perovskites have shown remarkable environmental, thermal stability, and large Stokes' shifts, usually coupled with very broad emission compared to their 3D and quantum dot counterparts^{15,16}. These advantages qualify 2D perovskites to be superior scintillators and hold the commercialization potential provided through optimal crystal and synthetic design.

Figure 6-1 Attenuation length of the investigated 2D perovskites and two commercial scintillators, CsI:Tl and LaBr₃:Ce. Due to the presence of lead, the 2D perovskites have relatively short attenuation length, in the same order of magnitude of the fully inorganic commercial scintillators.

Despite promising results, practical issues for potential commercialization still need to be addressed; for instance, high quantum efficiency and tuning of the emission wavelength to maximize the coupled commercial photodetector efficiency. In this work, we synthesized 11 different 2D bromide and iodide perovskite crystals and created a library of X-ray 2D perovskite scintillators. These include butylammonium lead bromide ((BA)₂PbBr₄), cyclohexylammonium lead bromide ((CHA)₂PbBr₄), octylammonium lead bromide ((OA)₂PbBr₄), 1,4-diaminobutane lead bromide ((DAB)PbBr₄), *N*-(3-aminopropyl)imidazole lead bromide ((API)PbBr₄), 2-(2-aminoethyl)isothioureia lead bromide ((AEIU)PbBr₄), phenethylammonium lead bromide ((PEA)₂PbBr₄), 2,2'-(ethylenedioxy)bis(ethylammonium) lead bromide ((EBDE)PbBr₄), butylammonium lead iodide ((BA)₂PbI₄), cyclohexylammonium lead iodide ((CHA)₂PbI₄) and octylammonium lead iodide ((OA)₂PbI₄). The information

regarding the molecular formula, volume, mass density and atomic effective number is presented in Table 6-1. Our focus is on the bromide and iodide perovskites as they typically emit in the visible region, while most chloride 2D perovskites have their strongest emission in the UV or near-UV region, which is not maximizing the efficiency of the coupled CCDs in X-ray detection^{17,18}. We first confirmed the crystals structure with X-ray diffraction (XRD) characterizations and then carried out photoluminescence (PL) measurement to demonstrate the narrow emission and the broad emission from these perovskites at room temperature (RT). Based on our available results, we extract the effect of the organic cations and the halide anions on narrow or broad emission. Temperature-dependent XL spectra of perovskite scintillators provide the detailed information on emission from 10 to 350 K. (BA)₂PbBr₄, (OA)₂PbBr₄ and (PEA)₂PbBr₄ show the negative thermal quenching behavior,^{19,20} i.e. stronger luminescence emissions are observed as the temperature increases, which could be practically useful, such as in reducing cooling necessities for the scintillator and improved performance at higher temperatures. Regarding the scintillating performance, the light yield of (BA)₂PbBr₄ is the highest at of 3.7 times than that of (PEA)₂PbBr₄ (~40,000 photons/MeV at RT), as well as being more stable from 10 to 350 K compared to the others. In conjunction with the 5.3 ns fast decay time, (BA)₂PbBr₄ could be a potential superior scintillator. For pulse height spectra, we report the best energy resolution of 5.7% at 662 keV of gamma-ray excitation for high-quality lithium doped (PEA)₂PbBr₄ scintillator showing the potential applications in spectroscopy.

Table 6-1 Concise formula, molecular formula, volume, mass density, and atomic effective numbers for our 2D perovskite halide crystals.

Concise formula	Molecular formula	Volume (Å ³)		Mass density (g/cm ³)		Atom. Effect. Number	
		Bromide	Iodide	Bromide	Iodide	Bromide	Iodide
(BA) ₂ PbX ₄	(CH ₃ (CH ₂) ₃ NH ₃) ₂ PbX ₄	1840.34	2094.34	2.437	2.736	33.85	37.45
(CHA) ₂ PbX ₄	(C ₆ H ₁₁ NH ₃) ₂ PbX ₄	2031.50	2238.00	2.378	2.716	32.31	35.75
(DAB)PbX ₄	H ₃ N(CH ₂) ₄ NH ₃ PbX ₄	1362.45	1550.49	3.008	3.376	37.83	41.86
(OA) ₂ PbX ₄	(CH ₃ (CH ₂) ₇ NH ₃) ₂ PbX ₄	2635.22	2925.24	2.052	2.215	30.03	33.22
(API)PbX ₄	(C ₃ N ₂ H ₃ (CH ₂) ₃ NH ₃)PbX ₄	1432.85	1630.61	3.032	3.404	33.43	36.99
(AEIU)PbX ₄	H ₃ NCNHS(CH ₂) ₂ NH ₃ PbX ₄	1362.06	1550.05	3.16	3.546	38.64	42.75
(EDBE)PbX ₄	C ₆ H ₁₈ O ₂ N ₂ PbX ₄	1557.09	1772.00	2.888	3.242	35.29	39.05
(PEA) ₂ PbX ₄	(C ₆ H ₅ (CH ₂) ₂ NH ₃) ₂ PbX ₄	2250.60	2498.29	2.362	2.550	32.31	35.75

6.2 Experimental Section

Two-dimensional perovskite synthesis. The amines were converted into the corresponding ammonium salts by reaction with concentrated HX acid (X= Br, I) in presence of PbX₂. The mixture was heated to a high temperature (> 150 °C) in order to obtain a clear solution. Afterwards, the temperature was lowered to 120 °C slowly and the crystals were allowed to form in the period of 12-24 h. Finally, the temperature was gradually lowered to room temperature. The crystals were then collected by filtering the solution and washed with diethyl ether.

PL, time-resolved PL and PLE measurements. PL and lifetime measurements were

performed using a free-space home-built micro-PL setup in an ambient environment at room temperature. 266 and 355 nm pulsed lasers (VisUV, PicoQuant) with a pulse width of 15 ps and a repetition rate of 10 MHz were focused on samples with a microscope objective (Olympus, 40 $\times$ objective, NA = 0.65, focused laser beam diameter $\approx$ 1 μ m). The PL signal was collected by a Peltier cooled photomultiplier tube (Hamamatsu H7422 series) coupled with a grating spectrometer (Edinburgh Instruments, Model F900 and Bentham, Model TMS300) and the PL image was collected by a silicon charge-coupled device (CCD). TRPL measurement was performed using a time-correlated single-photon counting acquisition module (MicroPhoton Devices MPD series) at selected peak wavelengths with a bandwidth of 20 nm. Other PL and PLE measurements were also performed with standard commercial system of Fluoromax 4C from Horiba.

Temperature-dependent XL measurement. The experiments were carried out in a similar way to our previous one.[18] A typical setup consisting of an Inel XRG3500 X-ray generator (Cu-anode tube, 8.04 keV at 45 kV and 10 mA), an Acton Research Corporation SpectraPro-500i monochromator (1200 gr/mm 500 nm blazed grating), a Hamamatsu R928 photomultiplier, and an APD Cryogenics Inc. closed-cycle helium cooler with a Lake Shore 330 programmable temperature controller was used to record XL spectra at various temperatures between 10 and 350 K. The measurements were carried out starting at 350 K (unless indicated) and terminating at 10 K to avoid a possible contribution from thermal release of charge carriers to the emission yield.

X-ray afterglow and TL measurements. The same setup was used as the one in temperature-dependent XL measurements. Prior to the TL runs, the sample was exposed for 10 min to X-ray at about 10 K. The glow curve was recorded up to 350 K at a heating rate of about 0.14 K/s.

Time-resolved X-ray luminescence measurement. TRXL measurements were obtained with a time correlated single photon counting (TCSPC) system composed by a fast photomultiplier (SMA650) and TCSPC electronics (PicoHarp 300) both from PicoQuant. The excitation was performed with a Hamamatsu N5084 light-excited X-ray tube set at 30 kV as irradiation source. The optical excitation of the tube was done with a Horiba-Delta diode at 405 nm (DD-405-L). The emission wavelengths were selected by using a Thorlabs FEL450 long-pass interferential filter.

6.3 Results and Discussion

Our perovskite crystals were prepared by using a modified version of the acid precipitation method²¹. XRD spectra of our 2D perovskites are shown in Figure 6-2a. The prominent peaks in the 4-9° range are the representatives of the (001)-orientated layer structures as displayed in Figure 6-2b (except (API)PbBr₄, (AEIU)PbBr₄ and (EDBE)PbBr₄ are in (110) configuration)^{9,22}, where two inorganic sheets are separated by a layer of organic molecules. These organic cations attach to the inorganic sheets by hydrogen bonding and Coulomb interactions, attaching to the halides and acts like cations. According to Bragg's law, peaks at the lower angle indicate a larger space between two inorganic sheets which is determined by the size or length of the organic cations rather than that of the inorganic sheets. Therefore, both (OA)₂PbBr₄ and (OA)₂PbI₄, with the longest chains show XRD peaks at the lowest 4°, though iodine is bigger than bromine, while the shorter BA counterparts display peaks at the higher value of 6°. The bulky PEA cation can also considerably increase the layer spacing. From these XRD patterns, we can directly compare the different size or the length of the organic cations in respective (001) or (110). We also note that for the AEIU, API and DAB perovskites variants the peak in the 4-9° range is rather weak. This might be the consequence of

preferred orientation of the micro-crystals in the powder XRD samples and the possible presence of amorphous phases, which might lead to the attenuation of the small angle Bragg's reflection peak. Figure 6-2c shows the images of four representative 2D perovskites with relatively strong brightness under UV excitation. As seen in the figure, the average size of the crystals is smaller than 5 mm and it is usually very thin, as two-dimensional perovskites prefer a lateral orientation growth. A picture of larger crystals is shown in Figure 6-3. Among these perovskites, we find that (AEIU)₂PbBr₄ shows white color emission, while (BA)₂PbBr₄, (OA)₂PbI₄ and (CHA)₂PbBr₄ exhibit clear blue, green and red emissions. In addition, to demonstrate our perovskite scintillators, we prepared a (PEA)₂PbBr₄ scintillating screen by spin-coating and used it in X-ray imaging. Figure 6-2d shows the blue emission from the (PEA)₂PbBr₄ film and Figure 6-2e shows the X-ray imaging of a paper clip inside an envelope. Due to stronger absorption of X-ray by the stainless steel, the paper clip can be easily distinguished by shadow-induced contrast. At last, high brightness from the (PEA)₂PbBr₄ ensures the high and clear contrast between the emitting scintillator screen and paper clip shadow.

Figure 6-2 Crystallographic properties and X-ray imaging a) X-ray diffraction patterns of all the investigated two-dimensional (2D) perovskite crystals. a) X-ray diffraction patterns of all investigated the two-dimensional (2D) perovskite crystals. b) Crystal

structure representation of one of 2D perovskite crystals: $(\text{BA})_2\text{PbX}_4$ ($\text{X} = \text{Br}, \text{I}$). c) Different color emissions of four representative perovskite crystals under UV lamp. Scale bar is 5 mm. d) Blue emission $(\text{PEA})_2\text{PbBr}_4$ film on glass substrate. e) X-ray imaging image of a paper clip inside an envelope using film in e). Scale bars in d) and e) are 1 mm.

Figure 6-3 Centimeter size crystals for a) $(\text{PEA})_2\text{PbBr}_4$ and b) $(\text{BA})_2\text{PbBr}_4$.

Figure 6-4a shows the PL spectra at room temperature. To gauge the stability of our perovskites, we carried out preliminary measurements of the PL under ambient conditions (RT, humidity > 65%). We observed a loss of luminescence for the crystals of only 6 ± 2 % after one week of exposure to environmental conditions for $(\text{BA})_2\text{PbBr}_4$ and $(\text{PEA})_2\text{PbBr}_4$. The PL excitation (PLE) spectra are shown in Figure 6-6. For bromide perovskites, only $(\text{BA})_2\text{PbBr}_4$ and $(\text{PEA})_2\text{PbBr}_4$ exhibit narrow emission whose full wide at half maximum (FWHM) is less than 30 nm, while the others exhibit broad emission whose FWHM is larger than 40 nm. It is reported that the broad emissions of $(\text{API})\text{PbBr}_4$, $(\text{AEIU})\text{PbBr}_4$ and $(\text{EDBE})\text{PbBr}_4$ originate from their (110) corrugated crystal structures, which is common in early found white-light emission perovskites)^{9,22}. The (110) corrugated structures often result in self-trapped excitons. Also, (001)-type flat $(\text{CHA})_2\text{PbBr}_4$ have two emissions, one free excitonic emission at 425 nm, and another very broad emission peaking at 520 nm. Self-trapped excitons again can be also the hypothesis to explain these broad emissions in the case of (001)-

orientated structure, though this phenomenon is rare²³. In the self-trapped exciton theory, photo-induced excitons can generate transient lattice distortions and the excitons themselves can interact with the lattice ‘trap’. The large amplitude of distortion and energy release after stabilization of the trapped excitons often result in a large Stokes shift and broad emission.

Perovskites with narrow emission usually have relatively small Stokes shift like (BA)₂PbBr₄ (0.16 eV)²⁴ and (PEA)₂PbBr₄ (0.07 eV)²⁵. The linear alkyl chains in BA and OA differ in length leading to a difference in emission width, both crystals have a main peak around 420 nm, with OA having a significantly larger towards longer wavelengths. The difference might originate from a larger octahedral geometry distortion in OA, which also results in broader emission²⁶⁻²⁸. PEA and CHA have both relatively bulky ring structures but they also demonstrate a significant emission difference, with narrow and broad emissions respectively.

Diammonium variant (DAB)₂PbBr₄ with linear alkyl chain has a very similar narrow emission pattern to monoammonium variants (BA)₂PbBr₄ and (OA)₂PbBr₄ except different peak positions. So far, there has been still no decisive conclusive explanation for such significant differences resulting from very similar organic cations, making it very difficult to conduct reliable *a priori* predictions, and we must still mainly rely on experimental data to discern the optoelectronic properties of 2D perovskite crystals. The broad emission in iodide perovskites seems to be quenched somehow compared to their bromide counterparts although peaks or shoulders can be seen by comparing emissions of (BA)₂PbBr₄, (CHA)₂PbBr₄, (OA)₂PbBr₄ and their iodide counterparts in Figure 6-4. The quenching of broad emission upon high iodide content occurs in other layered perovskites as well^{9,10,29}. We also observe evidence of a dual bandgap structure, which

characterized by a double peak, in $(\text{BA})_2\text{PbBr}_4$ and $(\text{BA})_2\text{PbI}_4$ (see Figure 6-5), as it was also previously reported in literature³⁰. The OA and DAB variants show this feature as well, albeit weakly, with the OA variant also having been previously reported³¹. The dual bandgap could be explained by the surface and bulk emissions as a result of reabsorption and partial transparency to their own luminescence³². Crystals that are only a few monolayer thin exhibits thus a blue shifted peak compared to large bulk crystals. Since the synthesized crystals were rather thin, both the surface and bulk emission are observed in the PL spectra in Figure 6-4a for the BA variants. The OA and DAB variants showed a less pronounced double peak, probably because they were thicker, and the surface states become less prominent.

Figure 6-4b shows the time-resolved PL (TRPL) decay curves of the perovskites, with the average decay times are also tabulated in Table 6-5, which were calculated from the three exponential decay fits³³ and their components with their contributions are shown in Table 6-2. Most perovskite crystals show a fast decay, below 6.4 ns, except $(\text{EDBE})\text{PbBr}_4$, whose decay is up to 12.4 ns. The longer decay for $(\text{EDBE})\text{PbBr}_4$ is related to the substantially long lifetime of the exciton self-trapping process which also explains its very broad PL spectrum. In addition, bromide perovskites exhibit longer decay times than their iodide counterparts. Based on our observations, the bromide variants also have brighter emission than iodide counterparts under the same excitation conditions. It is likely that fast non-radiative decay processes dominate in the iodide variants, causing a quenching in PL and faster decay times. At last, we note that the decay times of films and crystals are not much different (Figure 6-7).

Figure 6-4 a) Photoluminescence (PL) spectra of 2D perovskite bromide and iodide single crystals at room temperature (RT). For bromide and iodide crystals, the excitation wavelengths for PL spectra are 260 and 400 nm, respectively. b) Time-resolved PL (TRPL) of all 2D perovskite crystals with excitation and emission wavelengths respectively at 266 and 425 nm for bromide crystals, while these values being at 355 and 500 nm for iodide crystals. White solid lines indicate three exponential fits and Table 6-2 shows their components.

Figure 6-5 Comparison between the crystal photoluminescence, the crystal radioluminescence and photoluminescence of nano-crystalline films for $(\text{BA})_2\text{PbBr}_4$ (left) and $(\text{BA})_2\text{PbI}_4$ (right) at room temperature.

Figure 6-6 PL excitation spectra at room temperature of the investigated 2D perovskites taken at the peak of emission wavelength and PL spectra excited at 260 and 400 nm for bromide and iodide crystals, respectively.

Figure 6-7 Time resolved PL of single crystals and thin films (~ 70 nm) of $(\text{BA})_2\text{PbBr}_4$ and $(\text{PEA})_2\text{PbBr}_4$ with excitation at 266 nm with monitoring emission at 425 nm. The decay times of the films are faster than those of single crystals. The respective decay components (and % contributions) for $(\text{BA})_2\text{PbBr}_4$ and $(\text{PEA})_2\text{PbBr}_4$ thin films are 0.4 (24%), 1.5 (32%), 4.8 ns (44%) and 2.3 (34%), 5.4 (61%), 12.0 (5%). The average decay times are 2.7 and 4.6 ns for $(\text{BA})_2\text{PbBr}_4$ and $(\text{PEA})_2\text{PbBr}_4$ thin films, respectively. They are slightly faster than those in crystals (Table 6-5).

Table 6-2 Decay components, their averages and their contributions from three-exponential fits of time-resolved PL (TRPL) and time-resolved XL (TRXL). The values of components and averages are in nanoseconds.

Compounds	Decay components (%) [Average]	
	TRPL	TRXL
(BA) ₂ PbBr ₄	0.7 (33%), 2.2 (47%), 7.8 (20%) [2.8]	1.3 (12%), 4.5 (81%), 20.8 (7%) [5.3]
(CHA) ₂ PbBr ₄	1.0 (13%), 2.9 (68%), 9.2 (19%) [3.9]	0.4 (4%), 1.9 (33%), 5.5 (63%) [4.1]
(OA) ₂ PbBr ₄	0.3 (43%), 0.4 (43%), 2.5 (14%) [0.7]	0.2 (15) 0.6 (42%) 1.9 (43%) [1.1]
(DAB)PbBr ₄	0.4 (43%), 0.5 (44%), 4.9 (13%) [1.0]	0.4 (13%), 1.6 (32%), 7.1 (55%) [4.5]
(API)PbBr ₄	1.5 (26%), 4.0 (59%), 9.6 (15%) [4.2]	1.4 (6%), 5.5 (36%), 17.3 (58%) [12.1]
(AEIU)PbBr ₄	0.7 (46%), 2.5 (37%), 10.3 (17%) [3.0]	0.5 (4%), 2.2 (29%), 6.9 (67%) [5.2]
(PEA) ₂ PbBr ₄	2.6 (37%) 6.9 (54%) 19.2 (9%) [6.4]	1.1 (2%), 5.0 (22%), 14.6 (76%) [12.3]
(EDBE)PbBr ₄	0.3 (2%), 0.4 (2%), 12.9 (96%) [12.4]	1.1 (5%), 17.0 (88%), 36.0 (7%) [17.0]
(BA) ₂ PbI ₄	0.3 (3%), 0.5 (89%), 1.0 (8%) [0.5]	0.3 (49%), 1.3 (47%), 2.1 (4%) [0.8]
(CHA) ₂ PbI ₄	0.3 (9%), 1.0 (85%), 9.7 (6%) [1.4]	0.3 (21%), 1.5 (75%), 8.3 (4%) [1.5]
(OA) ₂ PbI ₄	0.4 (36%), 0.6 (59%), 1.6 (5%) [0.6]	0.3 (49%), 0.9 (43%), 2.0 (8%) [0.6]

We further investigated the temperature-dependent radioluminescence from 10 to 350

K. Figure 6-8 plots the 2D maps of some representative perovskites to illustrate their

different patterns and the others can be found in Figure 6-9. It is reported that broad emission in (001)-oriented perovskites is not rare, but actually temperature-dependent²⁶. This may hold true for (BA)₂PbBr₄ and (OA)₂PbBr₄ which differ only in the alkyl chain length. The difference in alkyl chain length does not cause a significant difference the emission at room temperature. Both show a main peak around 420 nm, with (OA)₂PbBr₄ showing a broader tail at longer wavelengths, similar to their PL profiles. (BA)₂PbBr₄ and (OA)₂PbBr₄ have similar FWHM as temperature goes down. Notably, emissions from (BA)₂PbX₄ and (OA)₂PbX₄ do not monotonically increase upon cooling down and reach their maxima at around 250-300 K rather than at the lowest 10 K. Such behavior could be attributed to a trap-assisting emission process or negative thermal quenching^{34,35}. The dominant factor in determining emission peak wavelength is the anion (Br, 420 nm and I, 520 nm) while length of organic cation within the same group (BA and OA are both linear alkyl chains) has little effect on the peak wavelength itself. At low temperature below 50 K, extra broad emissions (although very weak in (BA)₂PbBr₄) at 500-600 nm occur and it is likely due to bound excitons which can only be stabilized at low temperature. On the other hand, (CHA)₂PbBr₄ and (CHA)₂PbI₄ behave distinctly where (CHA)₂PbBr₄ has much broader emission than (CHA)₂PbI₄ in the whole temperature range. (CHA)₂PbBr₄ and (CHA)₂PbI₄ represent the more universal trend in perovskites, where thermal quenching behavior dominates and strongest emissions occur at lowest temperature. In terms of cation, (CHA)₂PbBr₄ and (PEA)₂PbBr₄ have similar bulky cation, but these two cations result in different configurations of their inorganic layers and therefore their spectra are completely different. It should be pointed out that the crystal phases are temperature-dependent as well, which explains discontinuous emissions in (BA)₂PbI₄ and (OA)₂PbI₄. Moreover, we also observe dual emissions in (BA)₂PbBr₄, (DAB)₂PbBr₄, (OA)₂PbBr₄ and

(BA)₂PbI₄, which was also previously reported in literature.³⁰ The dual emissions arise from the difference in environment and distortion of the crystal between surface and bulk layers, resulting in two different bandgaps. Crystals surface with a-few-layer thickness exhibits a blue shifted peak compared to large bulk crystals. The intensity ratio of these two peaks are crystal thickness dependent. (DAB)PbBr₄ and (OA)₂PbBr₄ are thicker in our experiment so the peaks from crystal surface are less pronounced. This behavior is verified by the comparison of PL and XL of the same crystals, (BA)₂PbBr₄ and (BA)₂PbI₄ in Figure 6-5. Since the X-ray penetrates through the crystals while UV is attenuated within few tens of nm surface, we can see the bulk emissions almost dominate in XL while surface emissions are much prominent in PL¹¹.

Because excitation under X-ray involves charge carriers, and thus potential trapping effects, we further investigated the temperature-dependent XL from 10 to 350 K. Figure 6-8 plots the temperature-dependent XL 2D maps of some representative perovskites to illustrate their different patterns and the others can be found in Figure 6-9. It is reported that the broad emissions in some (001)-oriented perovskites are temperature-dependent²⁶. This may hold true for BA and OA, which differ only in the alkyl chain length. The difference in alkyl chain length does not cause a significant difference for the emission at room temperature. Both spectra show a main peak around 420 nm, with OA showing a broader tail at longer wavelengths, similar with their PL profiles. OA and BA have a similar FWHM as temperature decreases. Notably, emissions from (BA)₂PbX₄ and (OA)₂PbX₄ do not monotonically increase upon cooling down and reach their maxima at around 250-300 K rather than at the lowest possible value of 10 K. Such behavior could be attributed to a trap-assisting emission process or negative thermal quenching^{34,35}. The dominant factor in determining emission peak wavelength is the anion (Br, 420 nm and I, 520 nm), while the length of the organic cation within the same

group (BA and OA are both linear alkyl chains) has little effect on the peak wavelength itself. At low temperatures below 50 K, extra broad emissions (although very weak in $(\text{BA})_2\text{PbBr}_4$) at 500-600 nm occur and it is likely due to bound excitons which can only be stabilized at low temperature. On the other hand, $(\text{CHA})_2\text{PbBr}_4$ and $(\text{CHA})_2\text{PbI}_4$ behave distinctively where $(\text{CHA})_2\text{PbBr}_4$ has much broader emission than $(\text{CHA})_2\text{PbI}_4$ in the whole temperature range. $(\text{CHA})_2\text{PbBr}_4$ and $(\text{CHA})_2\text{PbI}_4$ represent the more universal trend in perovskites, where thermal quenching dominates at high temperatures and strongest emissions occur at the lowest temperatures. Regarding cations effects, $(\text{CHA})_2\text{PbBr}_4$ and $(\text{PEA})_2\text{PbBr}_4$ have similar bulky cation, but these two cations result in different configurations of their inorganic layers and therefore their spectra are completely different. We should point out that the crystal phases are temperature dependent as well, which may explain the distinctive sharp emissions at 500 nm below 203 K in $(\text{BA})_2\text{PbI}_4$ and $(\text{OA})_2\text{PbI}_4$. Comparison of the PL and XL at room temperature is shown in Figure 6-10. Generally, the XL emissions of most perovskites we examined resemble closely their PL emissions. Some of the smaller wavelength peaks are absent in the XL spectra, particularly those of $(\text{BA})_2\text{PbX}_4$ and $(\text{CHA})_2\text{PbX}_4$, which is to be attributed to the lack of XL emission from surface states, as we explained previously and shown in Figure 6-5. $(\text{PEA})_2\text{PbBr}_4$ and $(\text{OA})_2\text{PbI}_4$ show clearly red-shifted XL compared to their PL, which might possibly be attributed to the same phenomenon.

Figure 6-8 Temperature-dependent radioluminescence spectra under X-ray excitation of a) $(\text{BA})_2\text{PbBr}_4$, b) $(\text{BA})_2\text{PbI}_4$, c) $(\text{OA})_2\text{PbBr}_4$, d) $(\text{OA})_2\text{PbI}_4$, e) $(\text{CHA})_2\text{PbBr}_4$ and f) $(\text{CHA})_2\text{PbI}_4$ at temperatures ranging from 10 to 350 K.

Figure 6-9 Temperature-dependent radioluminescence of (DAB)PbBr₄, (API)PbBr₄, (AEIU)PbBr₄, (PEA)₂PbBr₄, and (EDBE)PbBr₄.

Figure 6-10 Comparison between the photoluminescence (PL) and X-ray luminescence (XL) spectra at 290 K.

Afterglow often appears under ionizing radiation. It is generally undesirable, particularly, for scintillators used for fast image processing applications. We thus performed thermoluminescence measurements (TL) to characterize the residual luminescence. Figure 6-11a shows the afterglow after the termination of X-ray irradiation at 720 s. The perovskite crystals were first kept at 10 K for 120 s and then exposed to X-ray for another 600 s at 10 K to stabilize the luminescence and minimize

potential interferences. 120 s and 600 s were chosen as they had previously proven time-efficient in meeting these two requirements. After terminating the X-ray radiation, the luminescence of $(\text{BA})_2\text{PbBr}_4$, $(\text{DAB})\text{PbBr}_4$, $(\text{PEA})_2\text{PbBr}_4$ and $(\text{BA})_2\text{PbI}_4$ drop from maximum to less than 1% within 5 s. The exponential fits to the afterglow are presented in Table 6-3. The curves for $(\text{CHA})_2\text{PbBr}_4$, $(\text{OA})_2\text{PbBr}_4$, $(\text{API})\text{PbBr}_4$, and $(\text{AEIU})\text{PbBr}_4$ have more than 2% residual luminescence after 5 s. The afterglow of $(\text{EDBE})\text{PbBr}_4$ is considerably higher than the other perovskites, exhibiting 16% residual luminescence, even after 5s. However, the afterglow effect of $(\text{EDBE})\text{PbBr}_4$ is much weaker than CsI:Tl whose residual luminescence can be more than 15% even after 900 s at room temperature³⁶. The average afterglow mean decay lifetimes of more than 280 s are recorded for $(\text{AEIU})\text{PbBr}_4$, $(\text{EDBE})\text{PbBr}_4$ and $(\text{OA})_2\text{PbI}_4$. Perovskites with stronger afterglow also exhibit distinctive thermoluminescence glow peaks emerging from 30 to 120 K, after increasing temperature as shown in Figure 6-11b. Different glow peak positions are as a result of different trap depths of these perovskites. After applying fittings to these glow peaks, the trap depths are found to vary from 20 to 250 meV (see Figure 6-12 and Table 6-4). These are much deeper energies in comparison with those in 3D perovskite crystals¹³. The traps in this case are considered as a result of transient exciton-lattice coupling and not necessarily, or exclusively, from permanent defects like impurity as reported earlier²³. Note that $(\text{OA})_2\text{PbI}_4$ seems to be an exception because it has narrow emission similar to $(\text{OA})_2\text{PbBr}_4$ but shows apparent residual luminescence and a clear afterglow peak.

Figure 6-11 Residual luminescence background and low-energy trap states after X-ray excitation. a) Residual luminescence recorded at 10 K and b) afterglow curves recorded after 12 min X-ray irradiation at 10 K and subsequent heating rate of 0.14K/s for all 2D perovskite single crystals. White solid lines in a) indicate single or double exponential fits and Table 6-3 shows their components.

Afterglow curve fits We fitted the intensity (I) in Figure 6-11a with single, double, or triple exponential decay components.

$$I = \sum_{i=1}^n \left(A_i e^{-\frac{t}{t_i}} \right), \quad n = 1 \text{ or } 2 \text{ or } 3 \quad (1)$$

and the contribution (C_i) of each decay components (t_i) is calculated as following

$$C_i = \frac{A_i \times t_i}{\sum_{i=1}^n A_i \times t_i}, \quad n = 1 \text{ or } 2 \text{ or } 3 \quad (2)$$

We also measured the average afterglow lifetimes ($\bar{t}$) through the multiplication of decay components and their contributions.

$$\bar{t} = \sum_{i=1}^n C_i \times t_i, n = 1 \text{ or } 2 \text{ or } 3 \quad (3)$$

Table 6-3 Afterglow decay time.

Perovskites	t_i (s) / C_i (%)	$\bar{t}$ (s)
(BA) ₂ PbBr ₄	Not observed	Not observed
(CHA) ₂ PbBr ₄	17.9 s / 100%	17.9 s
(OA) ₂ PbBr ₄	38.2 s / 83%; 290.6 s / 17%	63.8 s
(DAB)PbBr ₄	Not observed	Not observed
(API)PbBr ₄	30.7 s / 100%	30.7 s
(AEIU)PbBr ₄	51.0 s / 20%; 357.5 / 80%	296.2 s
(PEA) ₂ PbBr ₄	Not observed	Not observed
(EDBE)PbBr ₄	12.2 s / 18%; 69.7 s / 29%; 522.3 / 53%	299.2 s
(BA) ₂ PbI ₄	Not observed	Not observed
(CHA) ₂ PbI ₄	Not observed	Not observed
(OA) ₂ PbI ₄	21.9 s / 7%; 301.0 s / 93%	281.5 s

Figure 6-12 An example fitting procedure for glow peak of (OA)₂PbBr₄ for three trap depths.

Table 6-4 Trap parameters including the trap depth (E_t) and full width half maximum ($FWHM$) energies obtained from the fit.

Perovskites	E_t (meV) / $FWHM$ (meV)			
	Trap 1	Trap 2	Trap 3	Trap 4
(BA) ₂ PbBr ₄	-	-	-	-
(CHA) ₂ PbBr ₄	113.4 / 25.5	162.8 / 59.3	-	-
(OA) ₂ PbBr ₄	52.6 / 7.9	65.6 / 43.5	93.1 / 68.4	-
(DAB)PbBr ₄	-	-	-	-
(API)PbBr ₄	54.0 / 12.7	80.1 / 71.3	249 / 125	-
(AEIU)PbBr ₄	78.0 / 50.0	-	-	-
(PEA) ₂ PbBr ₄	-	-	-	-
(EDBE)PbBr ₄	20.0 / 9.2	30.0 / 11.6	70.0 / 16.3	110 / 18.2
(BA) ₂ PbI ₄	-	-	-	-
(CHA) ₂ PbI ₄	69.30 / 24.50	-	-	-
(OA) ₂ PbI ₄	62.5 / 24.7	94.7 / 101	-	-

We also compared the light yield and X-ray excited decay times of our 2D perovskites in Figure 6-13. The main method to determine the light yield in this work was done through the integrated intensity comparison from the XL spectra of some 1- μ m-size crushed perovskite crystals with a consideration of the perovskite amounts, see Figure

6-14. We used $(\text{PEA})_2\text{PbBr}_4$ as a reference, since we obtained on a crystal an absolute light yield values from the gamma-ray pulse height measurement at 300 K (Figure 6-15) in a previous work^{25,37}. We used this method since it will be more convenient to determine values for low light yield crystals. Another method based on the comparison between the positions of photopeaks in the gamma-ray pulse height spectra and the single electron responses is also performed, as demonstrated in Figure 6-15 and Figure 6-16. Since only three samples show photopeaks ($(\text{BA})_2\text{PbBr}_4$, $(\text{PEA})_2\text{PbBr}_4$, and $(\text{EDBE})\text{PbBr}_4$), we only can confirm the light yields from those samples. Figure 6-13a shows the temperature-dependent light yield normalized to that of $(\text{PEA})_2\text{PbBr}_4$ at 300 K. The light yield at each temperature was calculated by the integration of the corresponding XL. Due to the negative thermal quenching behaviors, $(\text{PEA})_2\text{PbBr}_4$ and $(\text{BA})_2\text{PbBr}_4$ have higher light yields at elevated temperature, while other perovskites suffer from the thermal quenching, so their light yields decrease. Between 250 and 350 K, $(\text{BA})_2\text{PbBr}_4$ exhibits the highest light yield of all the 2D perovskites investigated. Above 280 K, $(\text{EDBE})\text{PbBr}_4$ and $(\text{PEA})_2\text{PbBr}_4$ has almost the same light yield, while below $(\text{EDBE})\text{PbBr}_4$ and $(\text{CHA})_2\text{PbBr}_4$ show higher light yield than $(\text{PEA})_2\text{PbBr}_4$. By comparing the bromide and iodide variants with the same organic cation, for instance, $(\text{BA})_2\text{PbBr}_4$ and $(\text{BA})_2\text{PbI}_4$, it is apparent that bromide ones have higher light yields. Both curves of $(\text{OA})_2\text{PbBr}_4$ and $(\text{OA})_2\text{PbI}_4$ are on the bottom and it may imply that long alkyl cation ($n \geq 8$) perovskites are impractical as scintillators. All perovskites investigated show relatively little change in light yield in the range between 250 and 350 K, making them suitable for applications where variable temperature might be an issue. Because of their higher light yield, $(\text{BA})_2\text{PbBr}_4$, $(\text{PEA})_2\text{PbBr}_4$, $(\text{EDBE})\text{PbBr}_4$ are most worthy of further investigation for practical applications.

We also calculated the maximum theoretical light yield values of the investigated 2D

perovskites from the band gap of the materials: $LY = 10^6 \cdot SQ/(\beta E_g)$, where S is the efficiency of electron–hole transport to the optical center, Q is the is the luminescence quantum efficiency of the optical center and β is a constant, usually with a value of ~ 2.5 . The values were tabulated in Table 6-5. Assuming no losses in quantum efficiency and charge transport, putting S and Q equal to 1, the theoretical light yield of the perovskite bromides with a bandgap between 3 and 4 eV is around 100,000 ph/MeV, with slightly higher values for the API and AEIU which could reach higher values between 130,000 and 140,000 ph/MeV. For the iodide variants, having a smaller bandgap, the theoretical limits are around 160,000 ph/MeV. All those theoretical limit values need to be compared with the practical light yield from the experiments. To determine the experimental light yield in Table 6-5, here we used the integrated intensity comparison from the XL spectra with a consideration of the perovskite amounts, see Figure 6-14. However, regardless the proportionality, we found that the light yields obtained from XL is in the same order as those obtained from gamma-ray pulse height spectra. The number of the light yield is then normalized with (PEA)₂PbBr₄ intensity while the light yield of that crystal is 11,400 photons/MeV, see Figure 6-15. However, most perovskites show significant losses compared to the theoretical limit, while the light yields above 10,000 photons/MeV are only to be found in (PEA)₂PbBr₄, (EDBE)PbBr₄, and (BA)₂PbBr₄ crystals. Beside the highest integrated intensity sample of (BA)₂PbBr₄, which has a loss of light yield merely 60% compared to the theoretical maximum, most perovskites have a light yield of 13% or less, with the iodide variants showing less than 1% light yield, compared to the theoretical maximum. Since charge transport in 2D perovskites is usually efficient, showing good (in plane) mobilities and good exciton dissociation and lifetimes³⁸, the main bottleneck for the iodide-variants is probably luminescence quenching, as suggested from our luminescence lifetime measurements.

Overall, factors like trapping, concentration quenching, or auto ionization can also play a significant role in the scintillation efficiency of the 2D perovskites. Further charge carrier conduction studies and quantum yield analysis is however necessary for a more in-depth analysis of the bottlenecks of the 2D perovskite scintillator performance.

Beside light yield, decay time is another important scintillator parameter. Figures 5b-c display Time-Resolved XL (TRXL) decay curves of all investigated perovskites. The decay curves were fitted with three exponential decay components and the average decay time values are listed in Table 6-5³³. Most bromide perovskite variants have similar decay times of between 1.1-6.4 ns, except (API)PbBr₄, (PEA)₂PbBr₄, and (EDBE)PbBr₄. Iodide variants show usually faster decay times, below 2 ns. In general, perovskites here demonstrate faster PL decay than XL decay. The decay differences are larger in case of bromide perovskites than iodide variants. This is due to the different scintillation mechanisms for both perovskites in which iodide variants are dominated by direct electron hole recombination³⁹. In terms of the high light yield and fast decay we are aiming at, (BA)₂PbBr₄ has the best scintillating performance from 10 to 350 K. Due to the negative thermal quenching characteristics, (PEA)₂PbBr₄ can be a decent scintillator at room temperature or above. Other scintillators suffer from the thermal quenching and have lower light yield than the above two perovskites at higher temperature. The comparison of effect of different cations on light yield is limited to this library and we cannot predict the performance of other cations. Experimental data in that case is still required for a convincing comparison. In addition, compared to commercial NaI:Tl scintillator, our best 2D perovskite has comparable yield but decay times 2 orders of magnitude faster (<5 vs 500 ns). With such a light yield and fast decay, 2D perovskite scintillators can be quite very competitive for fast imaging applications. In addition to X-ray scintillators, 2D perovskite scintillators also work well for gamma-

ray spectroscopy. Pulse height spectra for different gamma-ray excitations show the energy resolution as low as 13% at 662 keV³⁸, with the light yield at 59.5 keV excitation energy increasing to 20% in comparison to that at 662 keV (Figure 6-16). The 20% nonproportionality at 59.5 keV shows that the light yields from X-ray measurements¹⁸ at tens keV do not give many differences in comparison with those obtained from pulse height spectra at 662 keV. However, for lithium doped two-dimensional perovskite scintillator⁴⁰, we can achieve the best energy resolution for Lithium doped (PEA)₂PbBr₄ of 7.7% at 662 keV from ¹³⁷Cs source of gamma-ray excitation, see Figure 6-13d. This is an improvement from the recent report of 12.4%⁴⁰ as the crystal is more transparent. Now, we can observe an escape peak due to K-shell absorption edge of lead close the photopeak as it was covered by poorer energy resolution. The resolution of the escape peak is about 8.7%, which is still the same with that of photopeak as both peaks overlap with similar error bars of ± 0.5 and $\pm 0.8\%$, respectively (Figure 6-15). But the crystal is too thin, the intensity of escape peak is therefore higher than that of photopeak. We also observe the improvement of light yield in this crystal from 11,400 to 22,900 ph/MeV. At first sight, this is similar with our previous observation but the general light yields in this report are also much improved due to the better crystal quality. However, we do expect the improvements of scintillation properties with lithium doped perovskite crystals as those crystals have less nonradiative parts in the exciton recombination in comparison with the undoped crystals. Additionally, the proportionality shown in Figure 6-13e is excellent with only 10% change in light yield at 59.5 keV in comparison with that at 662 keV.

Figure 6-13 Light yield and decay under X-ray excitation with gamma-ray spectroscopy. a) Temperature-dependent light yield (normalized to light yield of $(\text{PEA})_2\text{PbBr}_4$ at 300 K) for temperature between 250 and 350K. b, c) Time-resolved XL curves under pulsed X-ray excitation. For emission wavelength in decay measurements, we monitored 425 and 520 nm for bromide and iodide crystals, respectively. d) Pulse height spectra of Lithium doped $(\text{PEA})_2\text{PbBr}_4$ under 662 keV gamma-ray from ^{137}Cs source. e) Light yield and energy resolution as a function of photopeak energies for different gamma-ray sources of ^{241}Am , ^{22}Na , and ^{137}Cs .

Figure 6-14 X-ray luminescence spectra with direct comparison intensities among all 2D perovskite crystals. For this experiment, the samples were prepared with the same size, the measurements were initiated with the same setting for X-ray generator (Cu-anode tube, 8.04 keV at 45 kV and 10 mA), and performed at the same day.

Figure 6-15 a) Measured single electron response of the Hamamatsu R878 PMT. b, c) Pulse height spectra under gamma-ray excitation of ^{137}Cs source at 662 keV for b) undoped and c) Li doped $(\text{PEA})_2\text{PbBr}_4$ crystals. The energy resolutions for photopeaks are 10.23% and 5.70% while those for escape peaks are 6.07% and 10.11% measured in undoped and Li doped crystals, respectively.

Figure 6-16 a) Pulse height spectra under gamma-ray excitation with different energies for $(\text{BA})_2\text{PbBr}_4$. b) The nonproportionality of the light yields and the energy resolutions from pulse height spectra of four crystals.

6.4 Conclusions

In summary, we successfully prepared a library of eleven 2D lead perovskite crystals with different organic cations and halide anions. The optical and scintillation properties are presented in Table 6-5.

The effect of organic cations and anions on luminescence and scintillating performance were investigated via PL and XL related characterizations. The effect of anions on luminescence are the most obvious. Iodide substitution of the corresponding bromide perovskites with broad emission tends to quench the broadening in addition to redshift of the emission. Iodide perovskites usually have lower light yield than bromide ones due to quenching. The effect of organic cations on the optical and scintillation properties of the 2D perovskites is more complicated. Some cations like API and EDBE can template the inorganic sheet in (110) orientation which have broad emissions. (001) flat perovskites can have broad emission but might be temperature- and lattice-distortion-dependent. These broad emissions can be explained by the self-trapped excitons.

Perovskites with linear alkyl cations like BA and OA show negative thermal quenching behavior in case of both bromide and iodide. Since perovskites with this behavior are more practical, this information could be very important. When comparing the scintillating performance of this series, (BA)₂PbBr₄ performs the best as it has not only the highest and most stable light yield of 3.6 times that of (PEA)₂PbBr₄, but also show a fast XL decay time of 5.3 ns, and negligible afterglow. Although the Stokes shift of (BA)₂PbBr₄ (0.16 eV)²⁴ is relatively small compared to (EDBE)PbBr₄, there is no large influence to lowering light yield due to self-absorption³⁹. So far, available strategies for 2D perovskite emission manipulation have been empirical and far from decisive conclusion so more experimental data are needed. Although we cannot fully explain all the PL and XL behaviors in our perovskite library, our work does lead to a first classification for 2D perovskite scintillator design and property manipulation and can shed light on the further and deeper investigation. The scintillating properties can still be improved for producing the ultimate 2D perovskite scintillators.

Table 6-5 Overview of two-dimensional hybrid lead halide perovskite scintillators.

Perovskites	Theoretical Light Yield (est. from bandgap)	Light yield relative to (PEA) ₂ PbBr ₄ @290 K*	Absorption length @50 keV	Peak Emission Wavelength	Average lifetime		Refs.
	(Ph./MeV)	(a.u.)	(mm)	(nm)	TRPL (ns)	TRXL (ns)	
(BA) ₂ PbBr ₄	96,000	3.659	0.987	434	2.8	5.3	²⁴
(CHA) ₂ PbBr ₄	108,000	0.398	1.086	420**	3.9	4.1	⁴¹
(OA) ₂ PbBr ₄	98,000	~0.007	1.356	425	0.7	1.1	⁴²
(DAB)PbBr ₄	80,000	0.018	0.734	428	1.0	4.5	⁴³
(API)PbBr ₄	138,000	0.314	0.903	422**	4.2	12.1	²²
(AEIU)PbBr ₄	130,000	0.258	0.730	416**	3.0	5.2	⁴⁴
(PEA) ₂ PbBr ₄	95,000	1	1.156	414	6.4	12.3	^{6,25}
(EDBE)PbBr ₄	90,000	0.889	0.835	520**	12.4	17.0	^{12,45}
(BA) ₂ PbI ₄	160,000	~0.007	0.430	518	0.5	0.8	⁴⁶
(CHA) ₂ PbI ₄	163,000	~0.007	0.459	514**	1.4	1.5	⁴⁷
(OA) ₂ PbI ₄	158,000	~0.007	0.598	520	0.6	0.6	³¹

Appendix II

Light yield determination

We obtained light yields from the position of the 662 keV photopeak in pulse height spectra both recorded with the PMT. Using the PMT, the photoelectron yield (Y_{pe}), expressed in photoelectrons per MeV of absorbed gamma-ray energy (phe/MeV), is determined by comparing of the peak position of the 662 keV photopeak to the position of the mean value of the single electron response. The single electron response spectrum is shown in Figure 6-15a. The method to obtain the mean value of the single electron response can be found in the work¹. It was estimated that the position of the mean value of the single electron response is about 13% lower than the position of the top of the Gaussian function, see Figure 6-15a². The position as well as the energy resolution (full width at half maximum over position) of a photopeak is determined by fitting the photopeak with a Gaussian curve, see Figure 6-15b.

The absolute photon yield Y_{ph} in photons per MeV is derived from Y_{pe} as follows:

$$Y_{ph} = \frac{Y_{pe}}{QE_{eff}} \quad (4)$$

where QE_{eff} is the effective quantum efficiency of the PMT and grating obtained from the manufacturer. It is averaged over the profile of the X-ray excited emission spectra.

As an example of the complete pulse height spectrum, we calculate the light yield of the undoped, and Li-doped (PEA)₂PbBr₄ crystals in respective Figure 6-17b and c as following. The position of the mean value from single electron response is at channel of 72 while the positions of the photopeaks X_{pe} at 1150 ± 59 and 2270 ± 87 for undoped and Li-doped (PEA)₂PbBr₄ crystals, respectively. The positions at channel of 1052 ± 43

and 2039 ± 88 correspond to the escape peaks of undoped and Li doped crystals, respectively, due to K-shell absorption edge of lead. They are shifted by 72 keV at lower energy than the 662 keV photopeaks. The single electron response was measured at gain of 300 while the pulse height spectra of ^{137}Cs were at a gain of 3. Therefore, Y_{pe} for both samples should follow $(X_{pe}/72) * (300/3)$ and they are equal to $1,600 \pm 100$ and $3,200 \pm 100$ photoelectrons/MeV for undoped and Li-doped crystals, respectively. We obtain Q_{Eff} for our Hamamatsu R878 PMT of 14% at the emission wavelength and the light yield of undoped and Li doped $(\text{PEA})_2\text{PbBr}_4$ crystals are $11,400 \pm 700$ and $22,900 \pm 700$ photons/MeV, respectively.

Figure 6-17 a) Measured single electron response of the Hamamatsu R878 PMT. b, c) Pulse height spectra under gamma-ray excitation of ^{137}Cs source at 662 keV for b) undoped and c) Li-doped $(\text{PEA})_2\text{PbBr}_4$ crystals. The energy resolutions for photopeaks are 10.23% and 5.70% while those for escape peaks are 6.07% and 10.11% measured in undoped and Li doped crystals, respectively. This figure is the same as Figure 6-15 and for convenience.

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Chapter 7 Conclusion and Recommendations

7.1 Conclusion

Systematically we synthesized a series of 2D and 3D lead halide perovskites and investigated their performances as scintillators under different radiations. A series of characterization techniques are employed to study their material properties and scintillating performance from different angles. Also, we try to utilize these characterizations to correlate their performance to their corresponding properties. Their major advantages, disadvantages and a comparison between 3D and 2D perovskites in this work will be summarized in the following discussion.

At the current stage, the 3D perovskites are more ready and efficient to be grown in high quality using wet chemistry. They can be cm-scale thick, which is very useful as scintillators since they can then at least absorb most of the radiation energy. However, the exciton binding energies of 3D perovskites, especially iodide ones, are relatively small, usually in tens of meV. These small values indicate the high tendency of exciton dissociation rather than exciton recombination. Application of 3D perovskite scintillators in direct detection is more theoretically straightforward but then another problem will show up, the low efficiency in free carrier extraction in such thick semiconductors. Most of current 3D perovskite researches focus on the application of MAPbI_3 in direct detection. The results of MAPbI_3 are encouraging but the long-term chemical stability without extra protection remains a question. Chlorides and bromides in our experiments and other relevant reports, prove to be more stable but their performances are not impressive in either semiconductor or scintillator mode. In addition, 3D perovskite scintillators usually require low temperature to achieve

practically acceptable performance. The thermal quenching behavior imposes a substantial limit in the scintillator performance of 3D perovskites. In summary, large and thick 3D perovskites are very efficient to be obtained but their scintillator performances have a quite low upper limit at practical temperature due to the small exciton binding energy and strong thermal quenching behavior.

7.2 Recommendations for further research

After knowing the advantage and disadvantage of 3D and 2D perovskites, we can now search for new routes to circumvent the weakness if possible and boost the biggest merit. After all there is no single all-might scintillators that is capable of serving all detection purposes. All we need is to find a suitable application for each type of perovskite scintillators.

To begin with, although current theory suggests 3D perovskites scintillators have their intrinsic limit of low exciton binding energy, they are easiest high-quality samples that can be obtained for perovskite scintillator researches. The reason why we start with perovskite scintillators from 3D perovskites are because of their mature single crystal growth technique using solution-processing methods. These samples are reproducible and of high-quality in terms of trap concentration. In this case, effect of different dopants on 3D perovskite scintillators can be relatively easily accessed and, in some cases, the result can be reasonably extrapolated to 2D perovskite scintillator as well. For example, lanthanide dopants, which are quite useful in traditional scintillators, are one type of dopant we would like to further explore. However, as mentioned in the Chapter 5, the uniformity of 2D perovskite crystal quality (even from the same batch) could be one problem. This issue could pose unknown influence on quality-sensitive pulse height characterization while such issue could be alleviated in 3D perovskite crystals. In

addition, turning 3D bulk perovskite into nanomaterials (nanocrystal, quantum dot, nanoplate...), could be another choice to fundamentally alter the scintillating properties. CsPbBr₃ nanocrystal currently is the most intensively studied scintillator which shows superior performance compared to CsPbBr₃ bulk crystal. Beside shrinking the bulk crystal to nanomaterial, searching for novel 3D inorganic perovskite scintillator that could be synthesized from wet chemistry is always one hot topic in this field. But so far, the progress has been slow since most of the inorganic precursors are very difficult to be dissolved in organic solvents. In the end, as 3D perovskite scintillators are able to outperform 2D ones at relatively low temperature, under certain scenarios, like outer space where the temperature is very low. They may not serve general purpose in practice, but they could be useful in specific fields.

Regarding the future work of 2D perovskite scintillators, there are multiple directions we can take forward. Firstly, one of the interesting topics is the totally inorganic scintillators. Current 2D perovskites suffer from low densities because of the organic parts. It will improve the attenuation coefficient of either electromagnetic or particle radiation. As mentioned above, it is not easy due to low solubilities of many inorganic precursor. Transition metal salts usually are more soluble in DMF or DMSO, and they have the potential being the dopants or the Pb cation substitutions. Besides, to increase the density is beneficial to increase the radiation hardness, which makes perovskite scintillator more durable practically. Secondly, to develop a growth technique that can efficiently obtain a-few-mm thick crystal (not necessarily single crystal at first). It is the most useful research topic from my point of view. Relatively old reports in 1970s provide some hints to achieve this goal while their methods still take a long time (up to months) as well as some equipment are deeply customized. One key point in those early reports is to create a separate hot zone and a cold zone where the crystals are grown in

the cold zone. We can refer to such ideas and try to build our own setup. Finally, to substantially increase Li content in the compound for higher thermal neutron detection efficiency, it is best to synthesize Li-containing perovskite. Currently, there has been no report on this type of perovskites grown from wet chemistry. In my opinion, this could be a very useful and efficient perovskite scintillator dedicated to thermal neutron detection. Our work of Li-doped perovskite scintillator at the moment suffers from the low Li content in the compound since there is no chemical bonding or chemical/ionic absorption between the perovskite and the Li dopant. High-performance Li-containing scintillators grown by melting method are decent examples we can try to synthesize using wet chemistry. To obtain large and thick crystals similar to those from melting method is another challenge.

Perovskite scintillators is a relatively new topic but this topic has been receiving a number of attentions because of the huge potential and promising performance. It is hard to predict whether perovskite scintillators will come to a day when they will be commercialized and widely applied. As far as I am concerned, they are now indeed attractive and tempting. I hope my work will prove to be enlightening to other researches and one day perovskite scintillator will be a successful product in market.

List of publications

Thesis Contributions

1. **Aozhen Xie**, Tien Hoa Nguyen, Chathuranga Hettiarachchi, Marcin E. Witkowski, Winicjusz Drozdowski, Muhammad Danang Birowosuto, Hong Wang, and Cuong Dang. Thermal quenching and dose studies of X-ray luminescence in single crystals of halide perovskites. *J. Phys. Chem. C* 2018 122 (28), 16265-16273
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Other Contributions

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