

# Temperature-dependent photoluminescence characteristics of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite thin film

F. J. Cheng<sup>1</sup>, S. Y. Hu<sup>2,\*</sup>, L. Y. Chen<sup>3</sup>, Y. C. Lee<sup>4,\*\*</sup>, G. Z. Yin<sup>5</sup>, K. K. Tiong<sup>5</sup>, and J. L. Shen<sup>6</sup>

<sup>1</sup> Department of Electrical Engineering, Tunghan University, Shenkeng, New Taipei City, Taiwan

<sup>2</sup> Department of Digital Technology Design, Tungfang Design Institute, Kaohsiung, Taiwan

<sup>3</sup> Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan

<sup>4</sup> Department of Electronic Engineering, Tunghan University, Shenkeng, New Taipei City, Taiwan

<sup>5</sup> Department of Electrical Engineering, National Taiwan Ocean University, Keelung, Taiwan

<sup>6</sup> Department of Physics, Chung Yuan Christian University, Chungli, Taiwan

Corresponding author's e-mail: \* [shenghu2729@gmail.com](mailto:shenghu2729@gmail.com)

\*\*[jacklee@mail.tnu.edu.tw](mailto:jacklee@mail.tnu.edu.tw)

**Abstract.** Recently, organometal halide perovskites are widely considered as promising materials in light emitting and lasing devices due to their potential optical properties. The luminescence characteristics of  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  perovskite material have investigated by temperature-dependent PL measurements. We suggest that the tetragonal inclusions in the orthorhombic phase of  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  thin film at low temperature result in the 12 K PL spectrum with a broad emission band. In addition, the PL peak of  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  thin film as a function temperature shows a tendency of blueshift, which is contrary to the typical tendency of redshift for traditional semiconductor materials.

## 1. Introduction

Methylammonium lead iodide perovskite material  $\text{CH}_3\text{NH}_3\text{PbI}_3$  have attached much attention, because it has unique optical of a direct bandgap with high absorption coefficients over the visible to near-infrared range and small exciton binding energies for the application of solar cells [1-3]. Comparing to the widely used  $\text{CH}_3\text{NH}_3\text{PbI}_3$  material, the mixed halide  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  material has further been used as the active layer of the highly efficient solar cells owing to its improved optical properties [4-5]. The wavelength emission of  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  material can be tunable from ultraviolet to near infrared by substituting iodine with chlorine and bromine, and these perovskite films can possess significant photoluminescence (PL) characteristics, which make them potential candidates for use in light-emitting devices [5-6]. However, only a few studies of the temperature dependence of the photo-physics of organic-inorganic perovskites present. Temperature-dependent steady state PL measurements allow the depiction of a complex photoexcitation performance, and the low-temperature PL spectra are also used to elucidate the basic photophysical properties of the perovskite materials. In



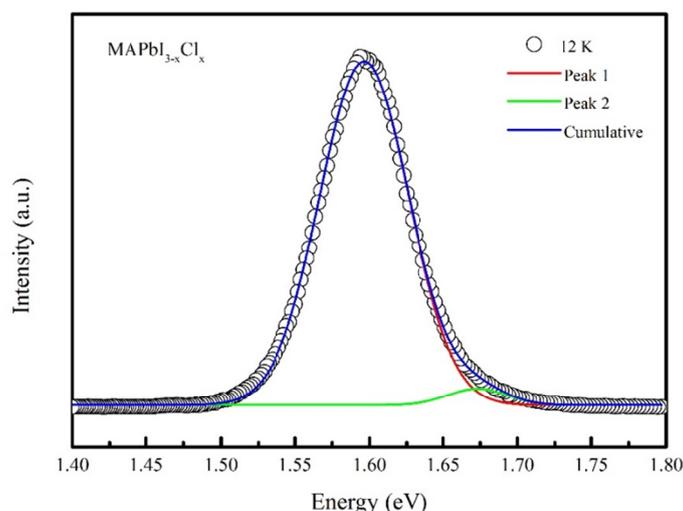
this work, we investigate the luminescence properties of solution-processed  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  material from temperatures ranging from 10 to 300 K using PL measurement with temperature dependence.

## 2. Experimental

The  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  perovskite material was synthesized with a mixture of  $\text{PbCl}_2$  and  $\text{CH}_3\text{NH}_3\text{I}$  (1:3 molar ratio) dissolved in dimethylformamide (DMF) as the precursor solution. The synthesized  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  perovskite material was spin-coated on the quartz substrates and heated to form a thin film. The temperature-dependent PL spectra were measured by using a diode laser with an excitation wavelength of 686 nm (PicoQuant). The diode laser produces light pulses with 50 ps duration and a repetition rate of 1 MHz. PL measurement was setup using a spectrometer (Zolix omni- $\lambda$  500) with a grating of 1200 grooves/mm, and detected using a photomultiplier tube (PMT). Janis Research Model CCS-150 and LakeShore Model 321 temperature controller were used to carry out the temperature-dependent PL measurement.

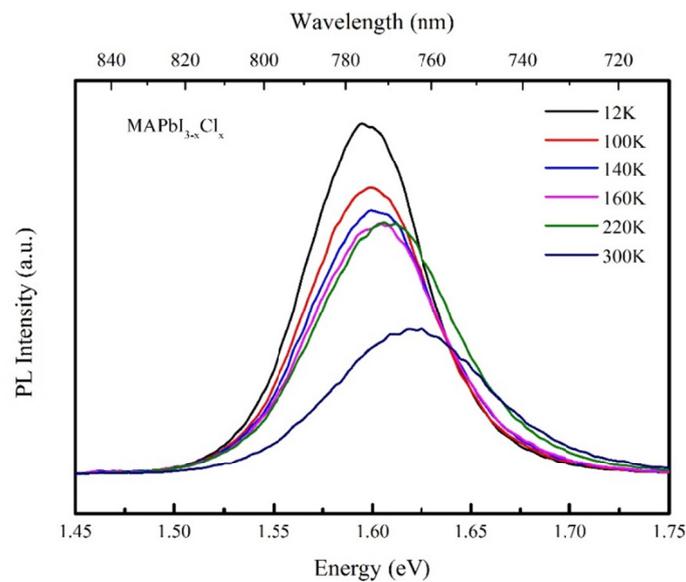
## 3. Results and discussion

Figure 1(a) shows the 12 K PL spectrum with a broad emission band, implying the existence of multi-band structures. By fitting with Gaussian function, the 12 K PL spectrum can be further decomposed into two peaks at 1.67 and 1.60 eV. According to the previous literatures [7-8], the higher peak at 1.67 eV and the lower peak at 1.60 eV are attributed to the low-temperature orthorhombic and the high-temperature tetragonal phase, respectively. It explains that the complex performance of PL spectrum in the  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  thin film at 12 K could be due to the coexistence of two structure phases.



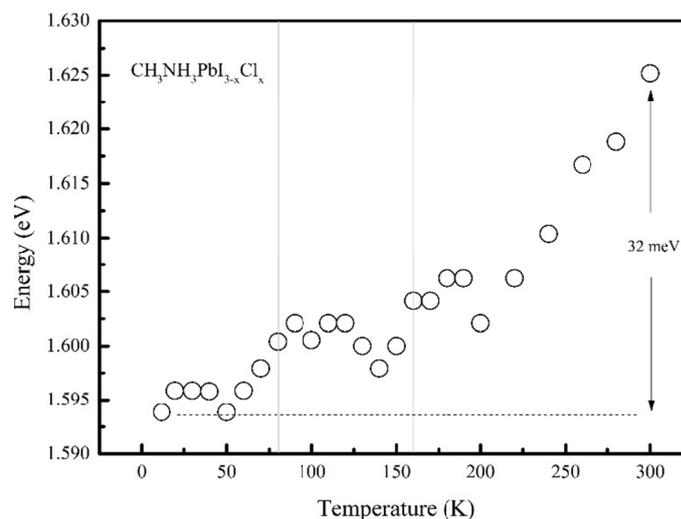
**Figure 1.** PL spectrum at 10 K for the  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  thin film. The spectrum is decomposed into two Gaussian peaks.

The PL spectra of  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  thin film taken at selected temperatures of 12, 100, 140, 160, 220, and 300 K are displayed in Figure 2. It is clear that the PL peak energy exhibits a blue-shifted tendency with increasing temperatures. The variations in the temperature-dependent PL peak of MAPbICl perovskite material is contrary to that of typical semiconductors, which shows a red-shifted PL peak with increasing temperature.



**Figure 2.** PL spectra of  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  thin film at selected temperatures.

Figure 3 display the PL peak positions as a function of temperature. The variations in the PL peak position could be discussed in three distinct regions separated by about 80 and 160K. Below 80 K, It can be observed that the PL peak position towards blueshift with increasing temperature to 50 K. In the temperature region of 80~160 K, the variations in the PL peak position shows a significant v-like shape. The performance could be attributed to the phase change from the orthorhombic to the tetragonal structure [9-10]. Above 160 K, the PL signal originated form the near-band-edge (NBE) transition in the  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  with tetragonal phase exhibits a continuous blueshift as the temperature increased to 300 K.



**Figure 3.** Temperature dependence of PL peak position for the  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  thin film.

#### 4. Summary

In this work, we have discussed the luminescence behavior of  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  perovskite material by temperature-dependent PL spectra. We suggests that the broad PL shapes are originated from the excitons transitions between the complication of orthorhombic and tetragonal phases in  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  thin film. The tendency of PL peak as a function temperature of  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  perovskite material presents a blueshift, which is contrary to that of traditional semiconductor materials belonging to redshift. Our results provide useful luminescence properties of hybrid perovskites to be applied in advanced optoelectronic devices.

#### 5. References

- [1] Sum T C, and Mathews N 2014 *Energy Environ. Sci.* **7** 2518.
- [2] Hsiao Y C, Wu T, Li M, Liu Q, Qin W, and Hu B 2015 *Mater. Chem. A* **3** 15372.
- [3] Sum T C, Chen S, Xing G, Liu X, and Wu B 2015 *Nanotechnology* **26** 342001.
- [4] Liu D, Wu L, Li C, Ren S, Zhang J, Li W and Feng L 2015 *ACS Appl. Mater. Interfaces* **7** 16330.
- [5] Wu K, Bera A, Ma C, Du Y, Yang Y, Li L and Wu T 2014 *Phys. Chem. Chem. Phys.* **16** 22476.
- [6] Xing G, Mathews N, Lim S S, Yantara N, Liu X, Sabba D, Grätzel M, Mhaisalkar S and Sum T C 2014 *Nat. Mater.* **13** 476.
- [7] Milot R L, Eperon G E, Snaith H J, Johnston M B and Herz L M 2015 *Adv. Funct. Mater.* **25** 6218.
- [8] Tahara H, Endo M, Wakamiya A and Kanemitsu Y, 2016 *J. Phys. Chem. C* **120** 5347.
- [9] Wehrenfennig C, Liu M, Snaith H J, Johnston M B and Herza L M 2014 *APL Mater.* **2** 081513.
- [10] Yamada Y, Nakamura T, Endo M, Wakamiya A and Kanemitsu Y 2014 *Appl. Phys. Express* **7** 032302.