Supporting Information

Photoluminescence Enhancement Study in Bi-doped $Cs_2AgInCl_6$ Double Perovskite by Pressure and Temperature-Dependent Self-Trapped Exciton Emission

Kashyap Dave,[a,b] Wen-Tse Huang,[a] Tadeusz Leśniewski,[c] Agata Lazarowska,[c] Dawid Jankowski,[c] Sebastian Mahlik[c] and Ru-Shi Liu [a,d]*

[a]Department of Chemistry and Advanced Research Center of Green Materials Science and Technology, National Taiwan University, Taipei 106, Taiwan.

[b]Nanoscience and Technology Program, Taiwan International Graduate Program, Academia Sinica and National Taiwan University, Taipei 115, Taiwan.

[c] Institute of Experimental Physics, Faculty of Mathematics, Physics and Informatics, University of Gdańsk, 80-308 Gdańsk, Poland.

[d] Advanced Research Center of Green Materials Science and Technology, National Taiwan University, Taipei 106, Taiwan.

E-mail: rsliu@ntu.edu.tw

Experimental Section

Materials and method

Materials

The following reagents were used in the synthesis process. CsCl (99.9%) was purchased from SIGMA Aldrich. AgCl (99.9%), $InCl_3$ (99.9%), and BiCl3 (99.9%) were purchased from Alfa Aeaser. HCl (37%) was purchased from Merck. Anhydrous ethanol (99.9%) was purchased from ECHO.

Synthesis of Bi-doped $Cs_2AgInCl_6$

The acid-based precipitation method was used to synthesize $Cs_2AgInCl_6$ and its derivatives with Bi using the method mentioned in a previous report with some modifications.[1] For the reaction, 1.5 mmol of AgCl and 1.5 mmol of $InCl_3$ were mixed into the 3 mL of HCl and stirred at 70–80 °C for 20 min. Afterward, 3 mmol of CsCl was added into the reaction, which was continued until a white precipitate was formed. The reaction was further cooled down to room temperature. The precipitate was washed by ethanol and centrifuged five times at 5000 rpm for 6 min. The washed sediment was further dried at 60 °C for 24 h. To perform the substitution of Bi into the $Cs_2AgInCl_6$ structure, the same reaction process was used; only the $BiCl_3/InCl_3$ ratio was changed.

Characterizations

Synchrotron powder X-ray diffraction patterns of $Cs_2AgIn_{1-x}Bi_xCl_6$ (x = 0, 0.02, 0.04, 0.08, 0.16, 0.64, 1) were acquired from the National Synchrotron Radiation Research Center (NSRRC, Taiwan). BL01C2 beamline was performed at room temperature using a Debye-Scherrer camera at a wavelength of 0.82657 Å. The pattern was then subjected to Rietveld analysis using Total Pattern Analysis Solutions software (TOPAS 4.2). The internal quantum efficiency was measured by using Hamamatsu Quantaurus. Before measuring the specimen, we calibrated the system by using YAG: Ce^{3+}. Scanning electron microscopy from ZEISS was used for analyzing $Cs_2AgInCl_6$ and Bi derivatives. The particle size was measured for all the samples by Multisizer 3 Beckman Coulter. Raman spectra were recorded on a Horiba Jobin Yvon Lab Ram Aramis spectrometer with a He-Ne laser, which provided excitation light at 633 nm with 1200 l/mm grating. Fluoromax 4P spectrofluorometer was used to measure photoluminescence (PL) and photoluminescence excitation (PLE) spectra. The diffuse reflectance and absorption (ABS) were measured using a Quantaurus-QY absolute PL quantum yield spectrometer (Hamamatsu) with an integrating sphere. For the photocurrent excitation spectra (PCE) measurement, the powder samples were pressed into pellets 10 mm in diameter. Gold electrodes were deposited by magnetron sputtering process using NanoPVD-S10A vacuum deposition system (Moorfield Nanotechnology). The PCE was acquired using a setup consisting of a B2987A electrometer (Keysight) with an internal voltage source and 150 W Xe light source coupled with Omni-λ 150 mm grating monochromator (LOT Oriel). The measurements were carried out under 50 V in a vacuum. The temperature and pressure-dependent PL spectra were recorded using a Shamrock SR750 grating spectrometer with an iDus 420 CCD detector (Andor Technology). The temperature and pressure-dependent PLE spectra were recorded using a self-made spectrofluorometer consisting of a 200W Xe lamp, two SPM2 prism monochromators (one on the excitation side and one on the detection side), and two R928P photomultiplier tubes (for signal detection and lamp reference measurement). The samples were held in the THMS600 cooling or heating stage (Linkam Scientific).

Luminescence kinetics measurements were carried out using a 2501S grating spectrometer (Bruker Optics) combined with a C4334-01 streak camera (Hamamatsu). The pulsed excitation of tunable wavelength was provided by PL2251A picosecond YAG: Nd laser coupled with PG 401/SH Optical Parametric Generator (EKSPLA). For temperature-dependent measurements, the sample was held in DE202 closed-cycle helium cryostat (ARS Cryo). All high-pressure measurements were carried out using Merill-Bassett type Diamond Anvil Cell (DAC) with polydimethylsiloxane as the pressure transmitting medium. The pressure inside the DAC was determined using the ruby fluorescence method.

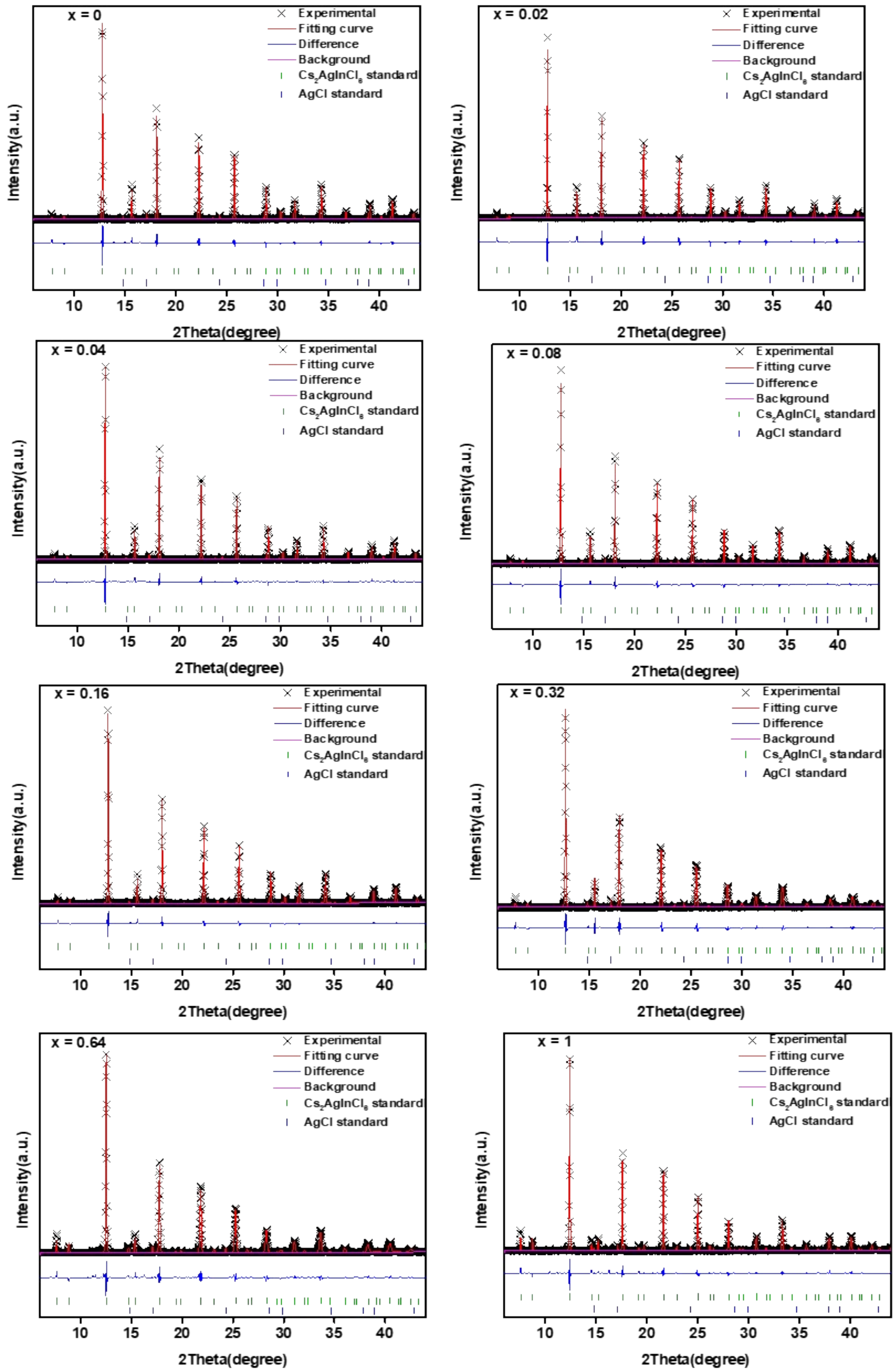

Fig. S1 Rietveld refinement of $Cs_2AgIn_{1-x}Bi_xCl_6$ (x = 0, 0.02, 0.04, 0.08, 0.16, 0.32, 0.64, 1.0).

Table S1. Rietveld refinement results of $Cs_2AgIn_{1-x}Bi_xCl_6$ (x = 0, 0.02, 0.04, 0.08, 0.16, 0.32, 0.64, 1.0).

x = 0					
Site	*x*	*y*	*z*	*Occ*	*Beq(Å²)*
Cs1	0.25	0.25	0.25	1	1.375(70)
Ag1	0	0	0	1	3.55(17)
In1	0.50	0.50	0.50	1.000(16)	0.94(13)
Bi1	0.50	0.50	0.50	0.000(16)	0.94(13)
Cl1	0.26604(60)	0	0	1	1.57(11)

x = 0.02					
Site	*x*	*y*	*z*	*Occ*	*Beq(Å²)*
Cs1	0.25	0.25	0.25	1	1.425(77)
Ag1	0	0	0	1	3.92(18)
In1	0.50	0.50	0.50	0.969(17)	1.19(10)
Bi1	0.50	0.50	0.50	0.031(17)	1.19(10)
Cl1	0.26594(58)	0	0	1	1.89(13)

x = 0.04					
Site	*x*	*y*	*z*	*Occ*	*Beq(Å²)*
Cs1	0.25	0.25	0.25	1	1.600(60)
Ag1	0	0	0	1	3.26(16)
In1	0.50	0.50	0.50	0.954(18)	1.01(11)
Bi1	0.50	0.50	0.50	0.046(18)	1.01(11)
Cl1	0.26570(56)	0	0	1	1.54(11)

x = 0.08					
Site	*x*	*y*	*z*	*Occ*	*Beq(Å²)*
Cs1	0.25	0.25	0.25	1	1.642(68)
Ag1	0	0	0	1	3.43(15)
In1	0.50	0.50	0.50	0.934(13)	1.013(77)
Bi1	0.50	0.50	0.50	0.066(13)	1.013(77)
Cl1	0.26587(39)	0	0	1	1.79(11)

x = 0.16					
Site	*x*	*y*	*z*	*Occ*	*Beq(Å²)*
Cs1	0.25	0.25	0.25	1	1.754(53)
Ag1	0	0	0	1	3.23(10)
In1	0.50	0.50	0.50	0.851(10)	1.088(80)
Bi1	0.50	0.50	0.50	0.149(10)	1.088(80)
Cl1	0.26618(41)	0	0	1	1.648(77)

x = 0.32					
Site	*x*	*y*	*z*	*Occ*	*Beq(Å²)*
Cs1	0.25	0.25	0.25	1	1.59(11)
Ag1	0	0	0	1	4.18(23)
In1	0.50	0.50	0.50	0.559(16)	1.84(14)
Bi1	0.50	0.50	0.50	0.441(16)	1.84(14)
Cl1	0.26425(92)	0	0	1	2.17(17)

x = 0.64					
Site	*x*	*y*	*z*	*Occ*	*Beq(Å²)*
Cs1	0.25	0.25	0.25	1	1.67(11)
Ag1	0	0	0	1	5.08(20)
In1	0.50	0.50	0.50	0.268(16)	1.37(12)
Bi1	0.50	0.50	0.50	0.732(16)	1.37(12)
Cl1	0.26151(81)	0	0	1	2.45(16)

x = 1					
Site	*x*	*y*	*z*	*Occ*	*Beq(Å²)*
Cs1	0.25	0.25	0.25	1	2.35(10)
Ag1	0	0	0	1	4.03(16)
In1	0.50	0.50	0.50	0.000(14)	0.760(82)
Bi1	0.50	0.50	0.50	1.000(14)	0.760(82)
Cl1	0.25731(80)	0	0	1	2.67(17)

Table S2. Rietveld refinement results of $Cs_2AgIn_{1-x}Bi_xCl_6$ (x = 0, 0.02, 0.04, 0.08, 0.16, 0.32, 0.64, 1.0).

x	0	0.02	0.04	0.08	0.16	0.32	0.64	1
a (Å)	10.48764(16)	10.49327(18)	10.49840(15)	10.51135(12)	10.53564(14)	10.58381(36)	10.68437(42)	10.78584(21)
V (Å³)	1153.541(53)	1155.401(59)	1157.095(51)	1161.383(39)	1169.454(46)	1185.57(12)	1219.68(15)	1254.765(74)
$Cs_2AgInCl_6$(%)	97.06	99.15	97.33	97.21	97.68	96.17	96.99	96.53
AgCl(%)	2.94	0.85	2.67	2.79	2.32	3.83	3.01	3.47
χ^2	1.84	1.57	1.36	1.07	0.98	1.80	1.98	1.38
R_{wp} (%)	11.49	13.17	10.23	8.77	7.82	12.14	10.85	9.22
R_p (%)	7.99	9.61	7.34	6.02	5.31	7.95	7.81	6.68

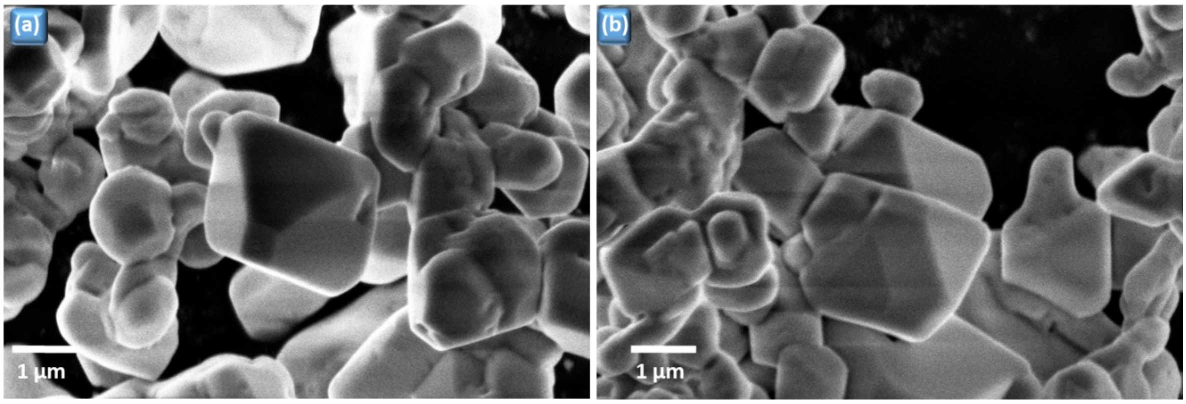

Fig. S2 Scanning electron microscopy images of (a) $Cs_2AgInCl_6$ and (b) $Cs_2AgIn_{0.92}Bi_{0.08}Cl_6$.

Table S3. Particle size analyzer results of $Cs_2AgIn_{1-x}Bi_xCl_6$ (x = 0, 0.02, 0.04, 0.08, 0.16, 0.32, 0.64, 1.0).

Compound	d_{10} (µm)	d_{50}(µm)	d_{90}(µm)	$(d_{90}-d_{10})/d_{50}$
$Cs_2AgInCl_6$	3.65	6.77	12.28	1.27
$Cs_2AgIn_{0.98}Bi_{0.02}Cl_6$	3.04	4.18	7.66	1.10
$Cs_2AgIn_{0.96}Bi_{0.04}Cl_6$	3.52	5.21	13.51	1.91
$Cs_2AgIn_{0.92}Bi_{0.08}Cl_6$	3.57	6.20	9.67	0.98
$Cs_2AgIn_{0.84}Bi_{0.16}Cl_6$	4.13	6.49	29.14	3.85
$Cs_2AgIn_{0.68}Bi_{0.32}Cl_6$	4.03	6.56	30.97	4.10
$Cs_2AgIn_{0.36}Bi_{0.64}Cl_6$	2.55	5.95	35.61	5.55
$Cs_2AgBiCl_6$	5.22	9.12	21.28	1.76

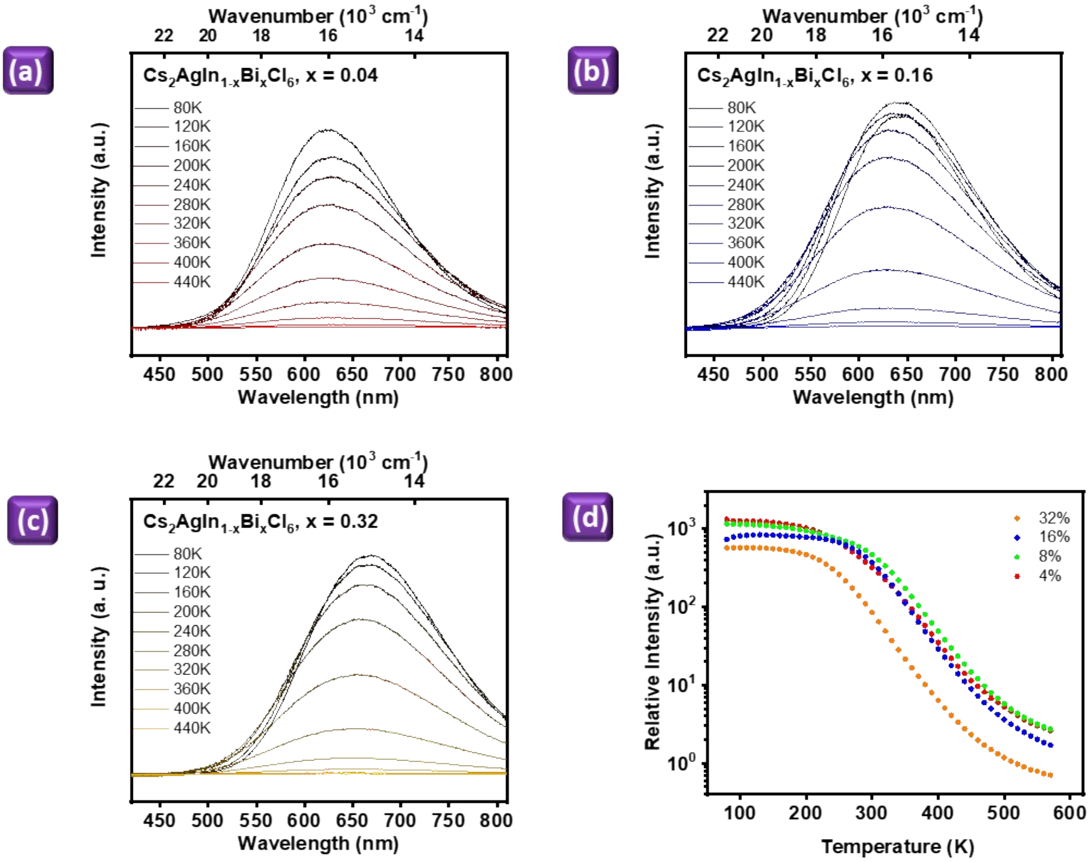

Fig. S3 Temperature-dependent PL spectra of $Cs_2AgIn_{1-x}Bi_xCl_6$ (a) x = 0.04, (b) x = 0.16, (c) x = 0.32 and (d) Normalized and integrated emission intensity based on results.

Table S4. Fitting parameters of temperature-dependent photoluminescence spectra.

x	0.04	0.08	0.16	0.32
ΔE (cm^{-1})	1320	1490	2140	1500
p_{nr}/p_r	1.8×10^3	2.2×10^3	3.8×10^4	7.3×10^3

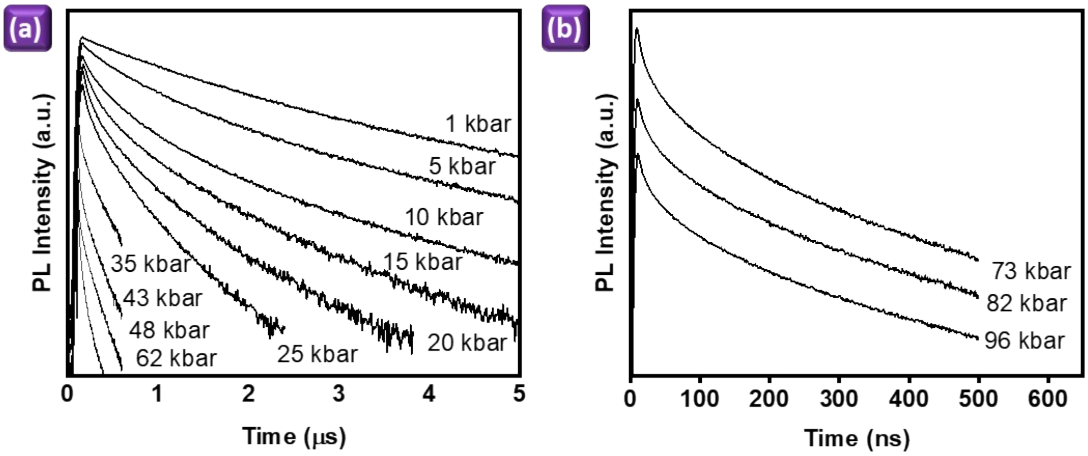

Fig. S4 Pressure dependence of PL decay curves $Cs_2AgIn_{0.92}Bi_{0.08}Cl_6$ (a) before and (b) after phase transition at above 70 kbar.

Reference

1. K, N. N.; Nag, A., Synthesis, and Luminescence of Mn-doped $Cs_2AgInCl_6$ Double Perovskites. *Chem. Comm.* **2018,** *54*, 5205–5208.