Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Probing the Emissive Behaviour of Lead-free $Cs_2AgBiCl_6$ Double Perovskite with Cu (II) Doping

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Instrumentation details

1. **Absorption and emission spectroscopy**

Optical spectra, i.e., absorption and emission studies, were done on a UV-vis spectrophotometer at room temperature. Shimadzu UV-vis 2450 spectrophotometer was used for recording UV-vis absorption spectra in the range of 200-800 nm. Photoluminescence spectra were collected by the Horiba scientific Fluoromax-4C spectrophotometer. A quartz cuvette of 10 mm path length and volume 3.0 ml was used for taking the spectra in the range of 350-700 nm wavelengths. Slit widths and step size of excitations and emissions were 5.0, 5.0, and 1.0, respectively. We have added 200 μL of perovskite solution into 3 mL isopropanol for each cases and then recorded the spectra.

2. **Fourier Transform Infrared Spectroscopy (FTIR) studies**

FTIR spectra of double perovskites were recorded by using Thermo scientific Nicolet 6700. The experiments were performed using the KBr pellet making technique with a scan range between 400 to 4000 cm^{-1} over 64 scans at a resolution of 4 cm^{-1} and an interval of 1 cm^{-1}.

3. **Powder XRD (P-XRD)**

Powder XRD was carried out on Rigaku having Target Cu Kα radiation of wavelength 1.54 Å and accelerating voltage 9 kW. Samples were scanned in the range of 10º to 50º. Samples were prepared in the form of a thin film on silica glass by the drop-casting method.

4. **Field Emission Scanning Electron Microscopy (FE-SEM)**

FE-SEM Carl Zeiss Ultra Plus and Gemini 300 have been used to know about the surface morphology of double perovskites by making a thin film on a glass slide through drop casting technique. Glass slides were gold coated, and the experiment was performed at an operating voltage of 20 kV.

5. **Transmission Electron Microscopy (TEM)**

TEM study was done by FEI TECHNAI G2 20 S-TWIN. A drop of diluted samples was deposited on a carbon-coated copper grid. Again a drop was added after drying it, and drying was carried at ambient temperature.

6. **X-Ray Photoelectron Spectroscopy (XPS)**

Surface analysis of thin film of double perovskites has been studied on XPS with model no. PHI 5000 Versa Probe III.

7. **Thermogravimetric analysis (TGA)**

Thermal analyses were performed on SII 6300 EXSTAR. All the samples were heated in a temperature range of 0 ºC - 900 ºC at a 10 ºC/min heating rate under an inert atmosphere. We have spread the residue of the samples on a glass slide and dried it overnight in an oven at 80 ℃ to collect the powder form of samples for the TGA experiment.

8. **Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)**

Inductively coupled plasma mass spectroscopy was studied on an Inductively Coupled Plasma Quadrupole Mass Spectrometer with model ELAN DRC-e. Samples were prepared by digesting the materials in aqua-regia and then diluted with distilled water for ICP-MS study.

9. **Solid State Nuclear Magnetic Resonance Spectroscopy (NMR)**

Solid-State Nuclear Magnetic Resonance (NMR) spectroscopy was performed in a JEOL NMR spectrometer with model ECZR Series 600 MHz NMR SPECTROMETER.

10. **Electro Paramagnetic Resonance Spectroscopic (EPR)**

Electron paramagnetic resonance (EPR) spectroscopy was studied in Electro Paramagnetic Resonance Spectrometer with model EMXmicro A200-9.5/12/S/W at room temperature. Both the solid and liquid samples were analyzed.

11. **Microwave plasma atomic emission spectroscopy (MP-AES)**

Microwave plasma atomic emission spectroscopy was studied on a Microwave plasma atomic emission Spectrometer with model 4210-MP-AES. Double perovskites were first digested in aqua-regia and then diluted with distilled water for the MP-AES study.

Table S1: PLQY data of pristine and all the doped samples.

Samples	PLQY (%)
P1	8
P2	1.114
P3	0.829
P4	0.0139
P5	0.0088
P6	0.0069

Table S2: XRD data of $Cs_2AgBiCl_6$.

2Θ	Θ	sinΘ	$\sin^2 \Theta$	Ratio	*d*(A˚)	(h k l)
16.90	8.45	0.146	0.0213	1	5.24	(2 0 0)
23.86	11.93	0.206	0.0424	1.99	3.73	(2 2 0)

33.78	16.89	0.290	0.0841	3.94	2.65	(4 0 0)
41.52	20.76	0.354	0.1253	5.88	2.17	(4 2 2)
48.33	24.165	0.409	0.1672	7.85	1.88	(4 4 0)

a = 10.56Å

Table S3: XRD data of 10% Cu doped $Cs_2AgBiCl_6$.

2Θ	**Θ**	**sinΘ**	**sin² Θ**	**Ratio**	***d*(A°)**	**(h k l)**
16.90	8.45	0.146	0.0213	1	5.24	(2 0 0)
23.90	11.95	0.207	0.0428	2.00	3.71	(2 2 0)
33.78	16.89	0.290	0.0841	3.94	2.65	(4 0 0)
41.52	20.76	0.354	0.1253	5.88	2.17	(4 2 2)
48.33	24.165	0.409	0.1672	7.85	1.88	(4 4 0)

a = 10.49Å

Table S4: XRD data of 20% Cu doped $Cs_2AgBiCl_6$.

2Θ	**Θ**	**sinΘ**	**sin² Θ**	**Ratio**	***d*(A°)**	**(h k l)**
17.06	8.53	0.148	0.0219	1	5.19	(2 0 0)
24.01	12.005	0.208	0.0432	1.97	3.70	(2 2 0)
33.96	16.98	0.292	0.0852	3.89	2.64	(4 0 0)
41.63	20.815	0.355	0.1260	5.75	2.17	(4 2 2)
48.37	24.38	0.412	0.1697	7.75	1.86	(4 4 0)

a = 10.47Å

Table S5: XRD data of 30% Cu doped $Cs_2AgBiCl_6$.

2Θ	**Θ**	**sinΘ**	**sin² Θ**	**Ratio**	***d*(A°)**	**(h k l)**
17.33	8.665	0.150	0.0225	1	5.11	(2 0 0)
24.23	12.115	0.209	0.0436	1.94	3.67	(2 2 0)
34.12	17.06	0.293	0.0858	3.81	2.62	(4 0 0)
41.86	20.93	0.357	0.1274	5.66	2.15	(4 2 2)
48.60	24.30	0.411	0.1689	7.51	1.87	(4 4 0)

a = 10.39Å

Table S6: XRD data of 40% Cu doped $Cs_2AgBiCl_6$.

2Θ	Θ	sinΘ	$\sin^2 \Theta$	Ratio	*d*(A°)	(h k l)
17.51	8.755	0.152	0.0231	1	5.06	(2 0 0)
24.35	12.175	0.210	0.0441	1.91	3.65	(2 2 0)
34.23	17.115	0.294	0.0864	3.74	2.62	(4 0 0)
41.97	20.985	0.358	0.1281	5.54	2.15	(4 2 2)
48.71	24.355	0.412	0.1697	7.34	1.87	(4 4 0)

a = 10.33Å

Table S7: XRD data of 50% Cu doped $Cs_2AgBiCl_6$.

2Θ	Θ	sinΘ	$\sin^2 \Theta$	Ratio	*d*(A°)	(h k l)
17.62	8.81	0.153	0.0234	1	5.03	(2 0 0)
24.57	12.285	0.212	0.0449	1.92	3.62	(2 2 0)
34.44	17.22	0.296	0.0876	3.74	2.60	(4 0 0)
42.20	21.10	0.359	0.1288	5.50	2.13	(4 2 2)
48.82	24.41	0.413	0.1705	7.29	1.86	(4 4 0)

a = 10.24Å

Table S8: Composition of $Cs_2AgBiCl_6$ using EDX analysis.

Element	Weight %	Atomic %
Cs (L)	32.93	20.21
Ag (L)	27.11	10.58
Bi (M)	14.71	11.12
Cl (K)	25.25	58.09

Table S9: SEM-EDX of all the doped samples.

Sample	Atomic%	Atomic%	Atomic%	Atomic%	Atomic%	Ratio of

name	of Cs	of Ag	of Bi	of Cl	of Cu	Cu/Ag
P2	17.91	13.21	10.82	57.77	0.30	0.0227
P3	17.98	11.76	9.83	60.06	0.37	0.0314
P4	19.31	11.61	10.00	58.50	0.57	0.0491
P5	20.06	10.89	9.40	59.03	0.62	0.0569
P6	19.00	9.52	9.77	61.08	0.63	0.0662

Table S10: ICPMS data for all the doped samples.

% of Cu taken in the precursor	% of Cu present in the product
10	1.18
20	2.82
30	3.42
40	6.04
50	6.41

Table S11: Cu/Ag ratio in the double perovskites in MP-AES data.

Sample name	Cu/Ag ratio
P1	0
P2	0.100
P3	0.108
P4	0.134
P5	0.144
P6	0.185

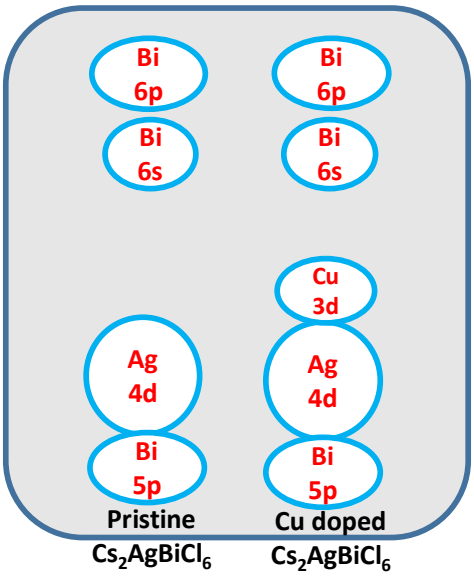

Fig. S1: Schematic representation of orbital interaction in undoped and Cu doped double perovskite.

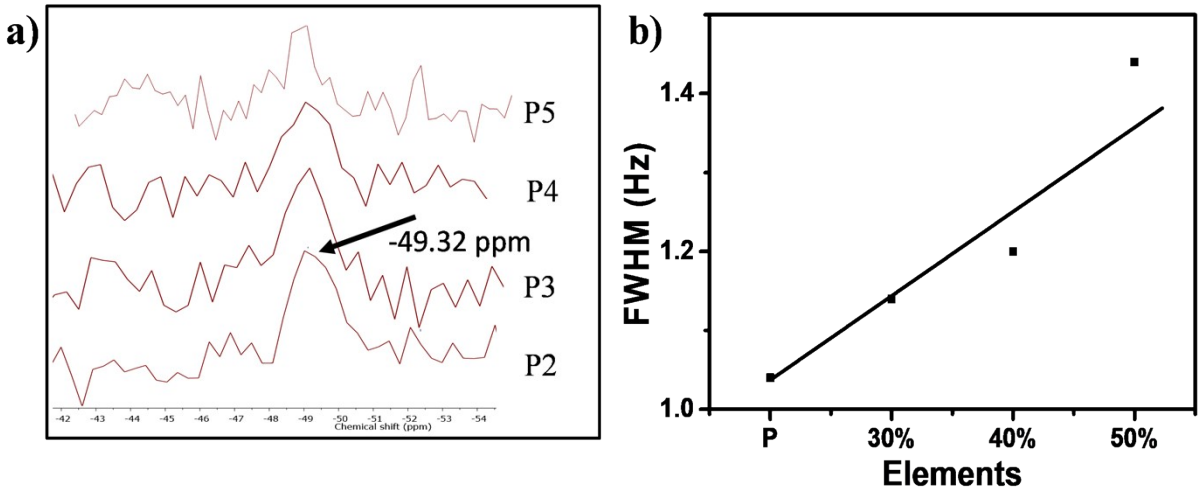

Fig. S2: a) ^{133}Cs NMR spectra of Cu doped samples, b) FWHM of Cs peak at 78 ppm.

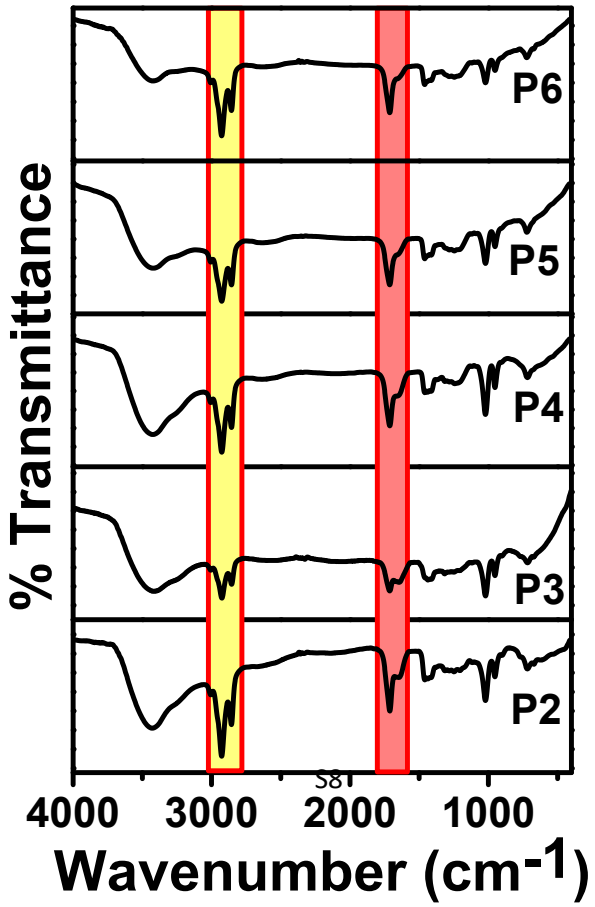

Fig. S3: IR spectra of all the doped samples.

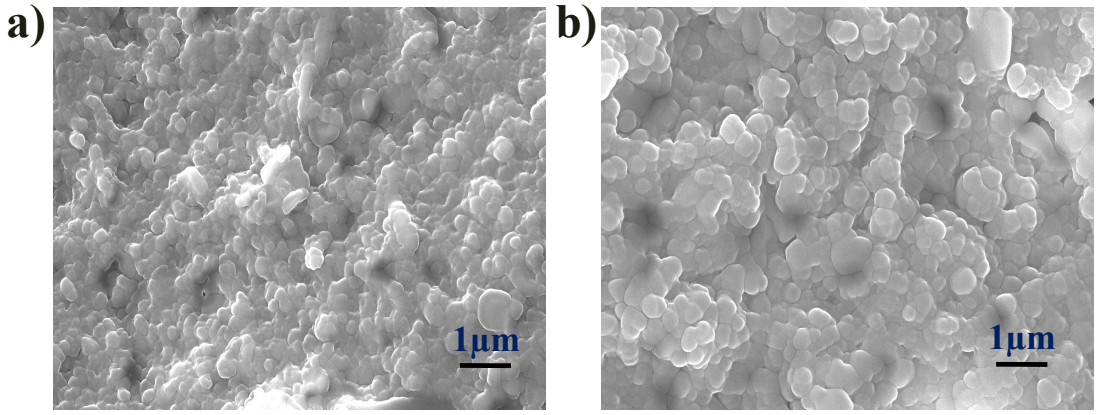

Fig. S4: SEM images of 20 % (a) and 40 % (b) Cu doped in $Cs_2AgBiCl_6$ respectively.

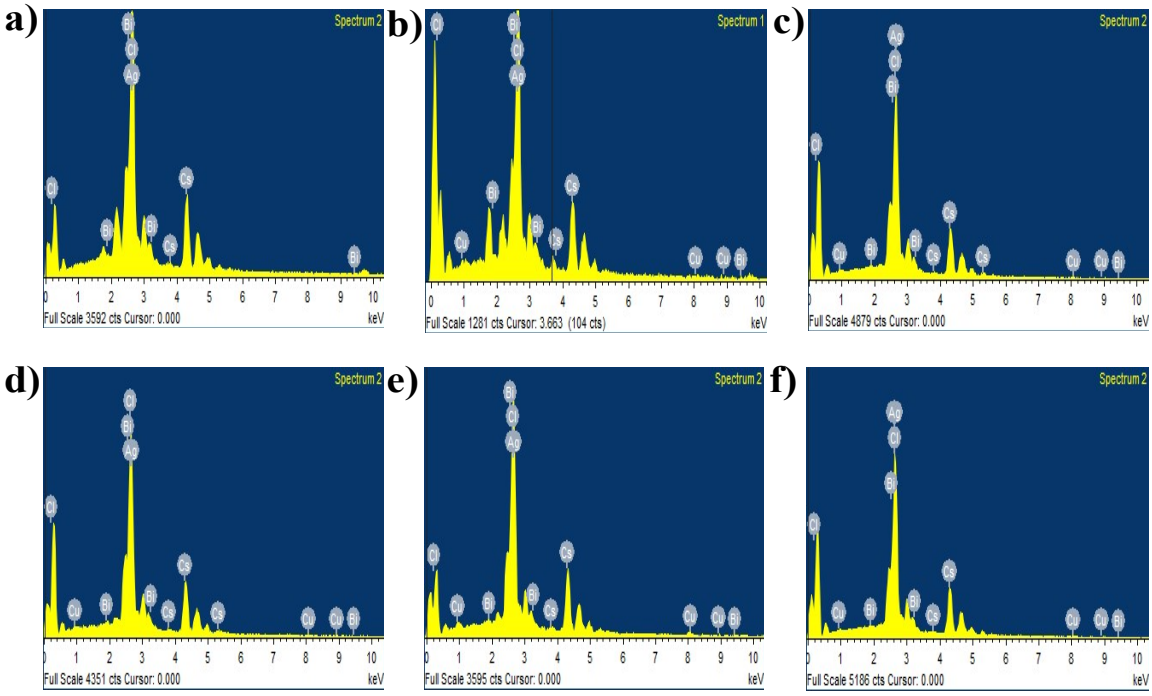

Fig. S5: SEM-EDX of pristine and all the doped (10%, 20%, 30%, 40%, 50%) samples respectively.

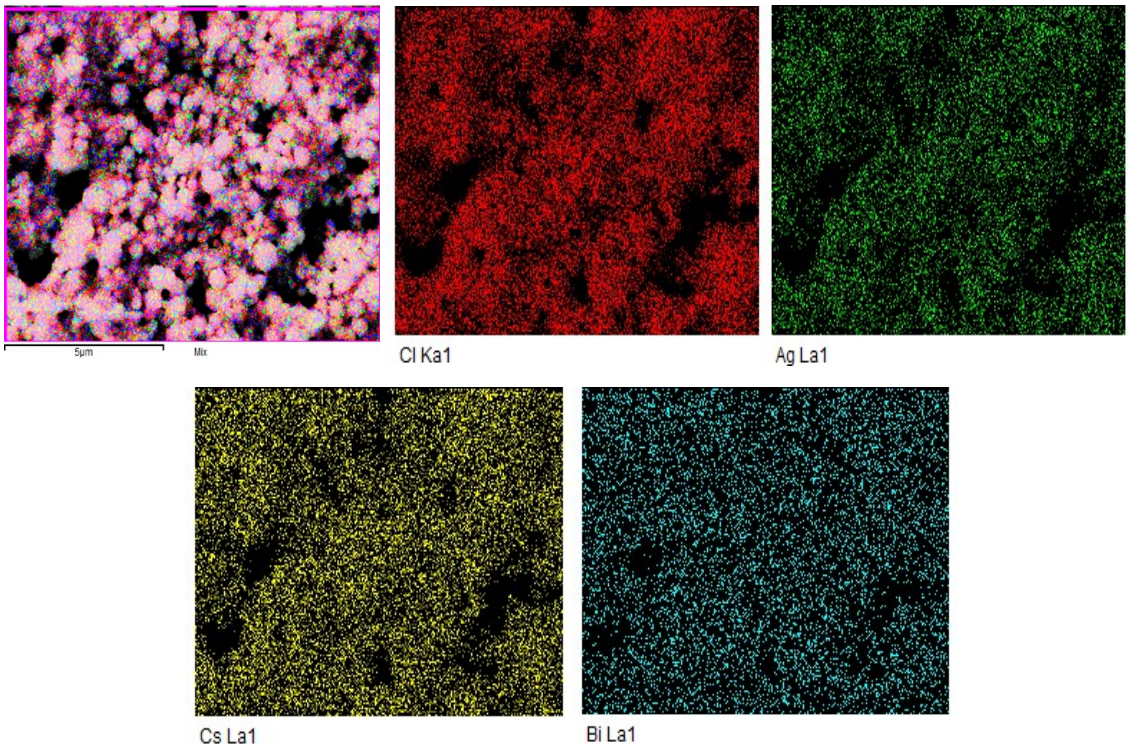

Fig. S6: Elemental mapping of $Cs_2AgBiCl_6$ by SEM analysis.

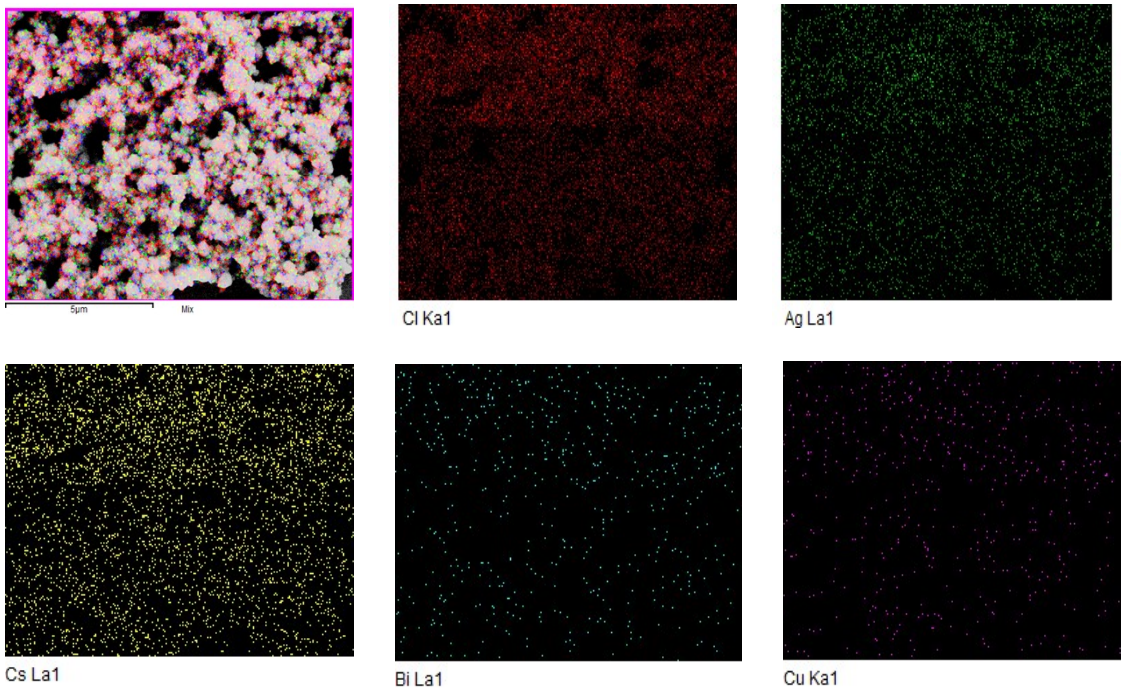

Fig. S7: Elemental mapping of 10% Cu doped $Cs_2AgBiCl_6$ by SEM analysis.

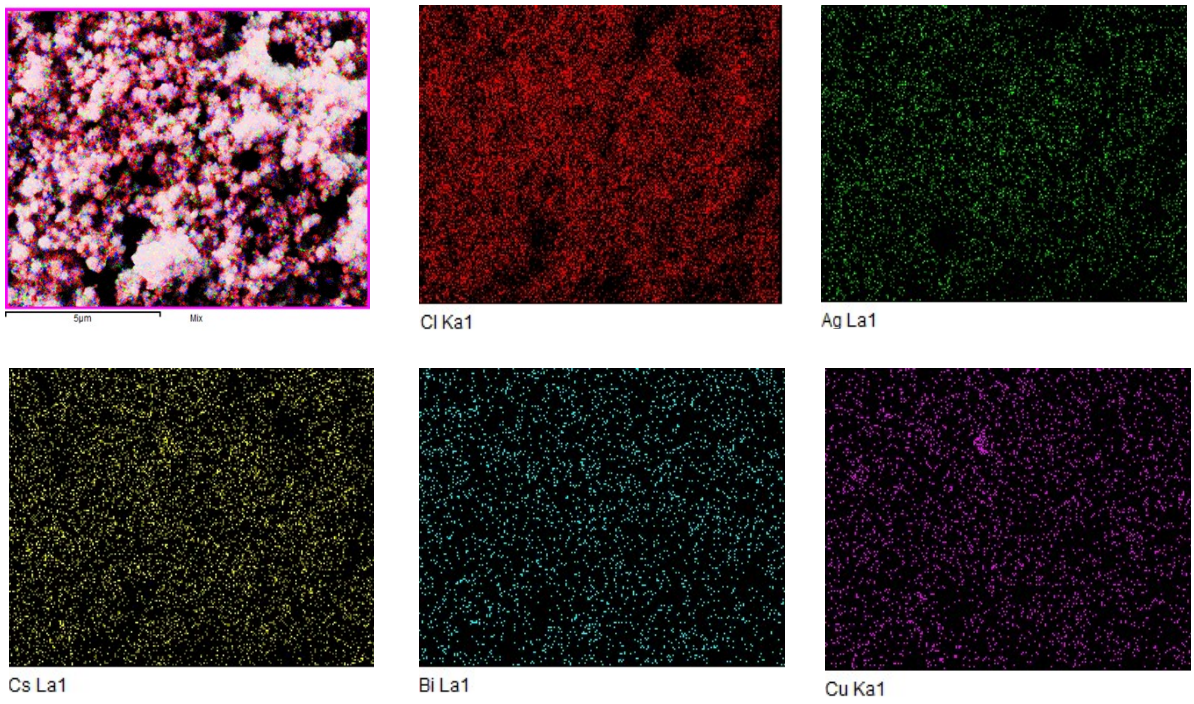

Fig. S8: Elemental mapping of 20% Cu doped $Cs_2AgBiCl_6$ by SEM analysis.

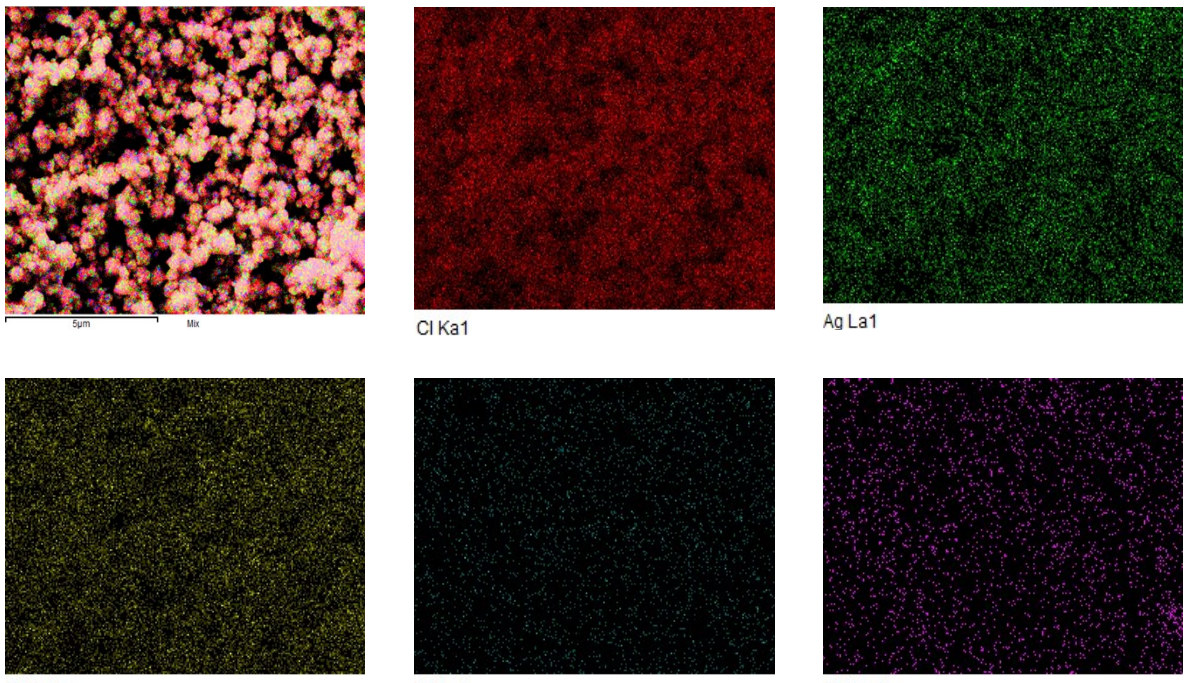

Fig. S9: Elemental mapping of 30% Cu doped $Cs_2AgBiCl_6$ by SEM analysis.

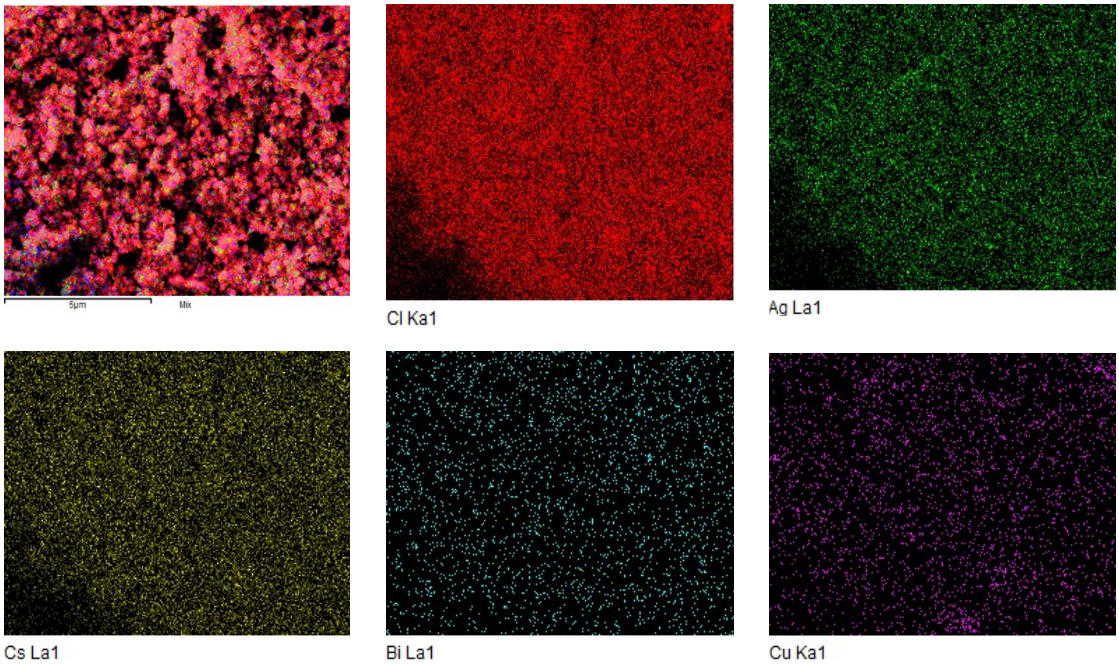

Fig. S10: Elemental mapping of 40% Cu doped $Cs_2AgBiCl_6$ by SEM analysis.

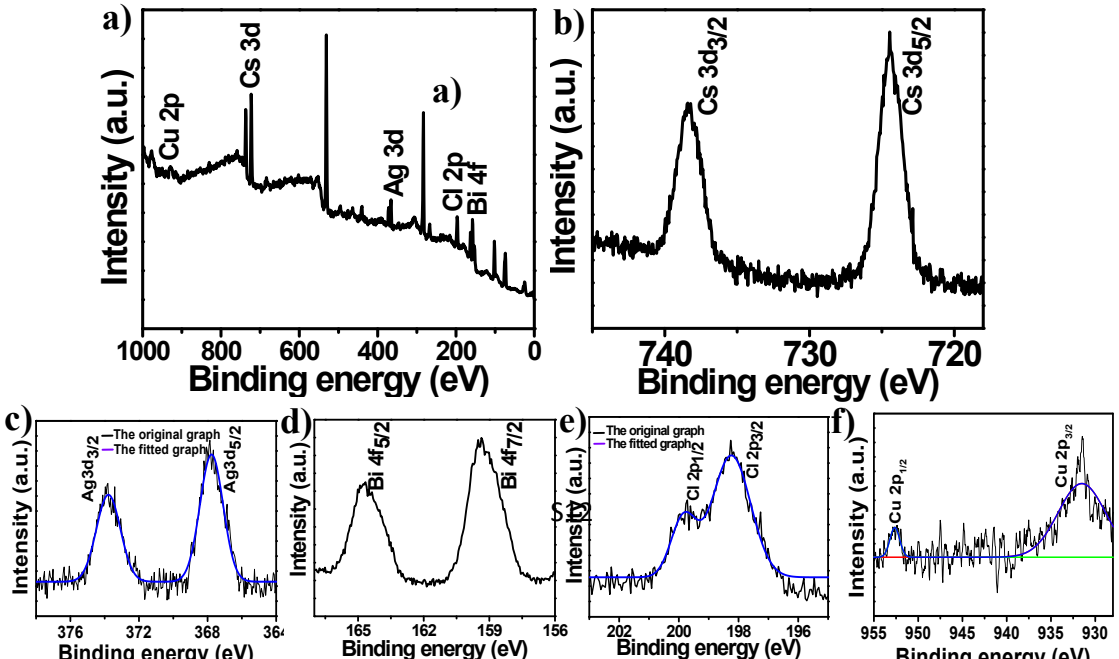

Fig. S11: a) XPS survey scan of 10% Cu doped $Cs_2AgBiCl_6$, b) narrow scan of Cs^+, c) narrow scan of Ag^+, d) narrow scan of Bi^{3+}, e) narrow scan of Cl^-, f) narrow scan of Cu^{2+}.

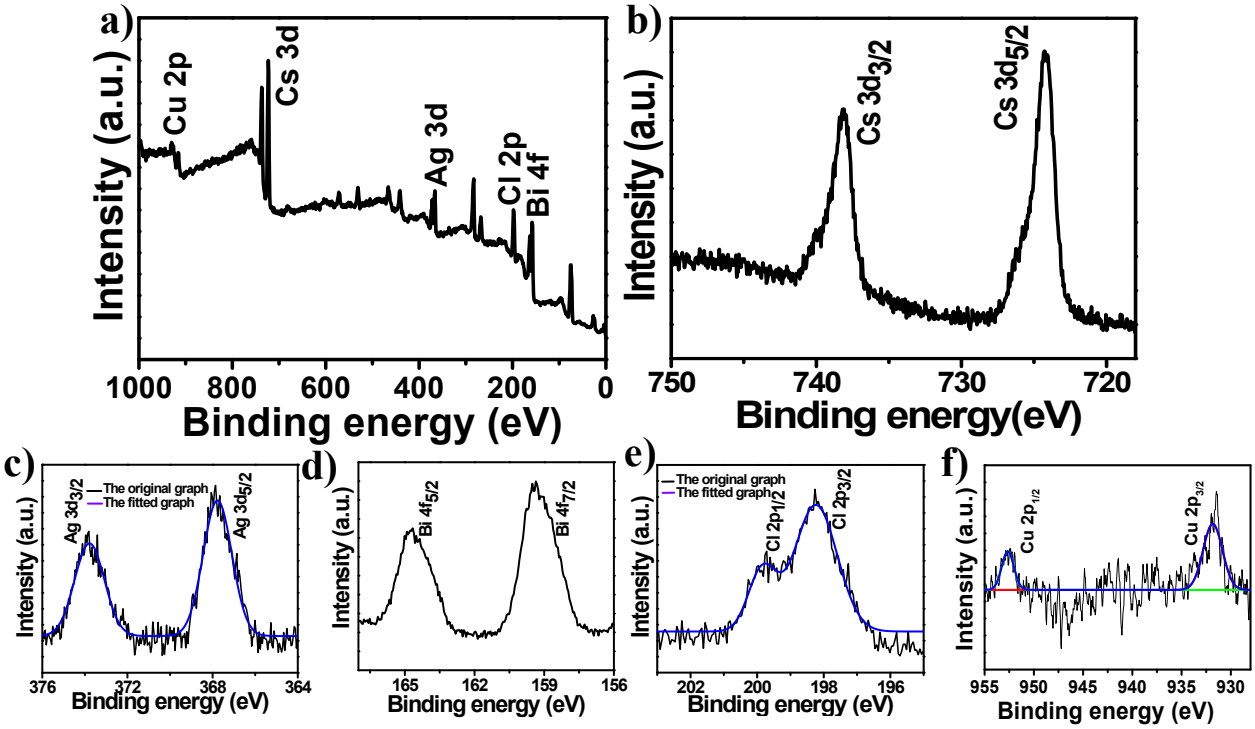

Fig. S12: a) XPS survey scan of 20% Cu doped $Cs_2AgBiCl_6$, b) narrow scan of Cs^+, c) narrow scan of Ag^+, d) narrow scan of Bi^{3+}, e) narrow scan of Cl^-, f) narrow scan of Cu^{2+}.

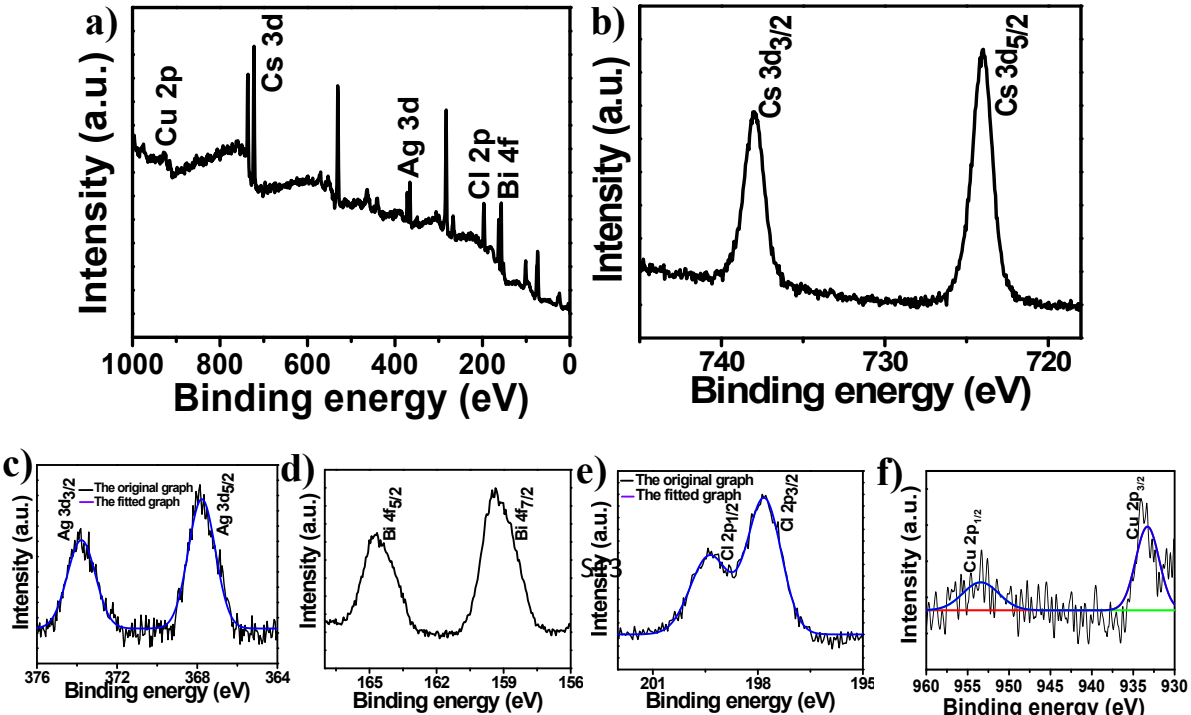

Fig. S13: a) XPS survey scan of 30% Cu doped $Cs_2AgBiCl_6$, b) narrow scan of Cs^+, c) narrow scan of Ag^+, d) narrow scan of Bi^{3+}, e) narrow scan of Cl^-, f) narrow scan of Cu^{2+}.

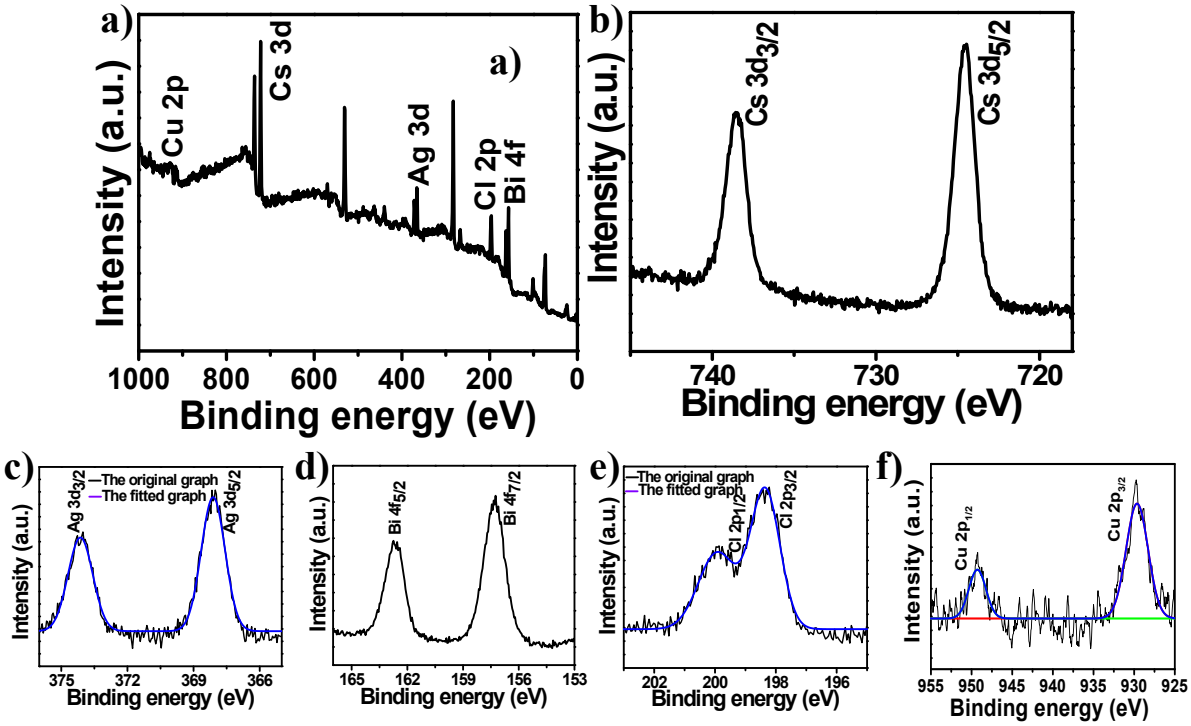

Fig. S14: a) XPS survey scan of 40% Cu doped $Cs_2AgBiCl_6$, b) narrow scan of Cs^+, c) narrow scan of Ag^+, d) narrow scan of Bi^{3+}, e) narrow scan of Cl^-, f) narrow scan of Cu^{2+}.

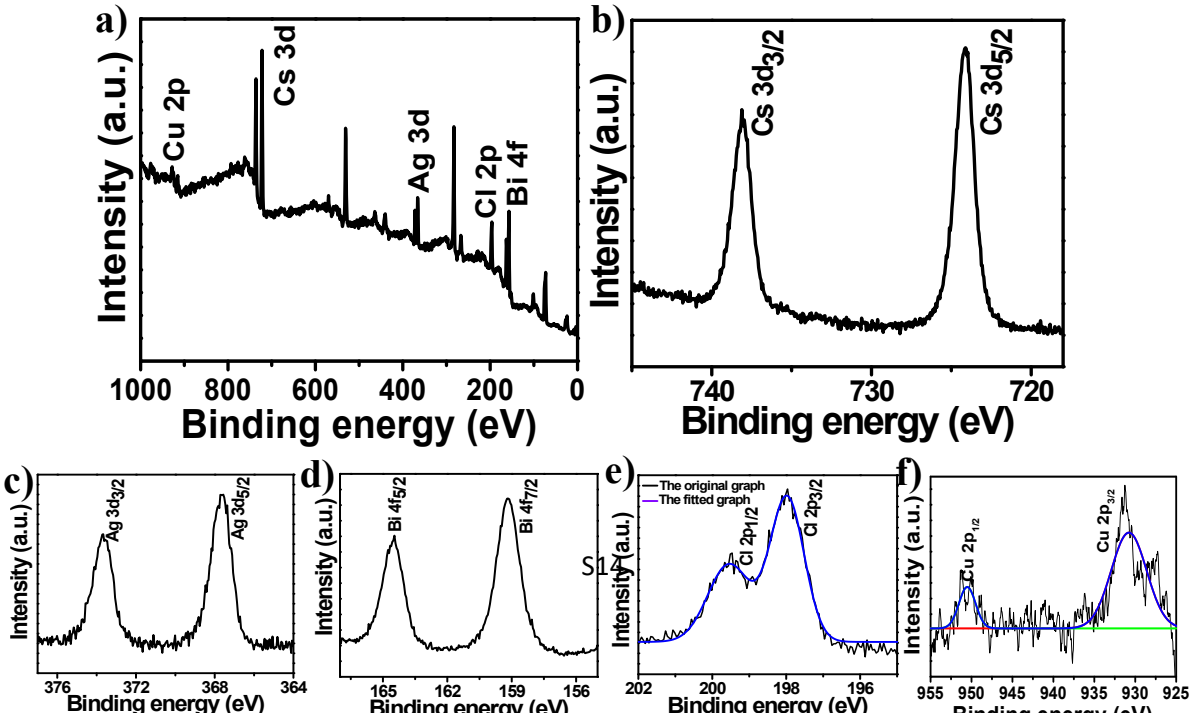

Fig. S15: a) XPS survey scan of 50% Cu doped $Cs_2AgBiCl_6$, b) narrow scan of Cs^+, c) narrow scan of Ag^+, d) narrow scan of Bi^{3+}, e) narrow scan of Cl^-, f) narrow scan of Cu^{2+}.

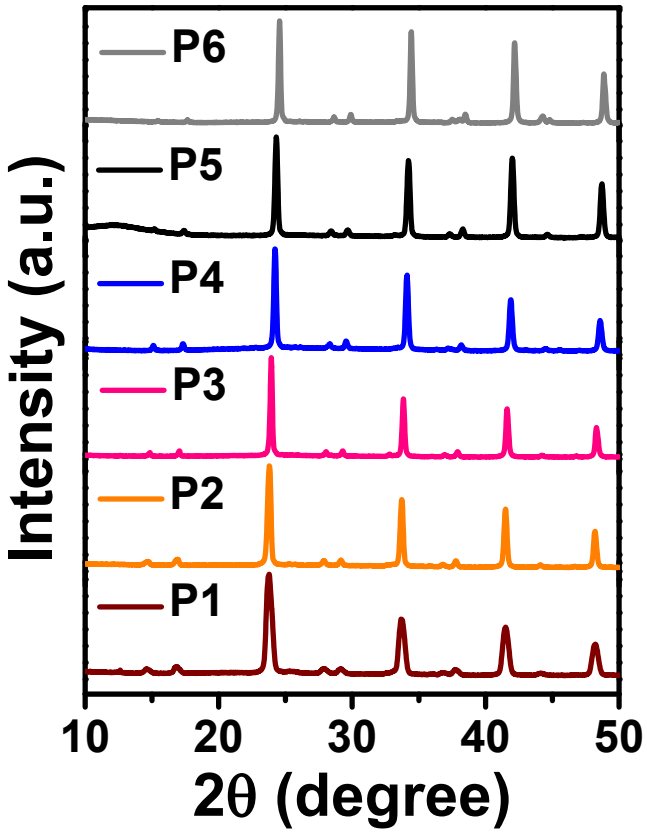

Fig. S16: P-XRD data of all the samples after two months.