Electronic Supplementary Material (ESI) for Materials Advances.

Supplementary Information

Experimental evidence of ion migration in unbiased aged inorganic perovskite solar cells using non-destructive RBS depth profiling

Taimoor Hussain [1,2], Kalsoom Fatima [1], Arfa Anjum [2], Turab Ali Abbas [3], Ishaq Ahmad [3], Azhar Fakharuddin [4], *Muhammad Sultan [1,*]*

[1] National Centre for Physics, Quaid-i-Azam University Campus, 44000 Islamabad, Pakistan

[2] Department of Physics, Quaid-i-Azam University, 45320 Islamabad, Pakistan

[3] Experimental Physics Department (EPD), National Centre for Physics, Quaid-i-Azam University Campus, 44000 Islamabad, Pakistan

[4] Department of Physics, University of Konstanz, D-78457 Konstanz, Germany

Layers	**Thickness (10^{15} atoms/cm^2)**	**Br**	**I**	**Cs**	**Pb**	**O**	**Si**	**Ca**
Layer 1 (IHP)	278.192	(0.399-0.420)	(0.125-0.441)	(0.130-0.140)	(0.200-0.201)			
Layer 2 (IHP)	291.286	(0.394-0.413)	(0.125-0.484)	(0.130-0.138)	(0.201-0.207)	0	0	0
Layer 3 (Interface)	213.719	(0.194-0.195)	(0.113-0.190)	(0.300-0.305)	(0.258-0.263)	(0.06-0.12)	0	0
Layer 4 (Interface)	70	0.16	0.330	0.018	0.180	0.210	0.100	0.002
Layer 5 (Glass)	21375.964	0	0	0	0	0.602	0.342	0.056

Depth profile table S1. Percentage concentration of various elements in different layers of Glass/ IHPF ($CsPbI_2Br$).

Layers	**Thickness (10^{15} atoms/cm^2)**	**Br**	**Pb**	**I**	**Cs**	**O**	**Ni**	**Sn**	**In**	**Si**	**Ca**
Layer 1 (IHP)	197.753	0.249	0.179	0.300	0.272						
Layer 2 (IHP)	479.987	(0.230 - 0.231)	(0.168-0.179)	(0.310-0.343)	(0.278-0.289)	0	0	0	0	0	0
Layer 3 (Interface)	214.846	(0.278-0.383)	(0.083-0.085)	(0.350-0.403)	(0.09-0.119)	(0.133-0.189)	(0.08-0.095)	0	0	0	0
Layer 4 (Interface)	165.285	(0.263-0.275)	(0.079-0.081)	(0.164-0.292)	(0.04-0.07)	(0.317-0.437)	(0.088-0.09)	0	0	0	0
Layer 5 (Interface)	44.165	0	0	0	0	(0.424)	(0.116)	(0.457)	(0.002)	0	0

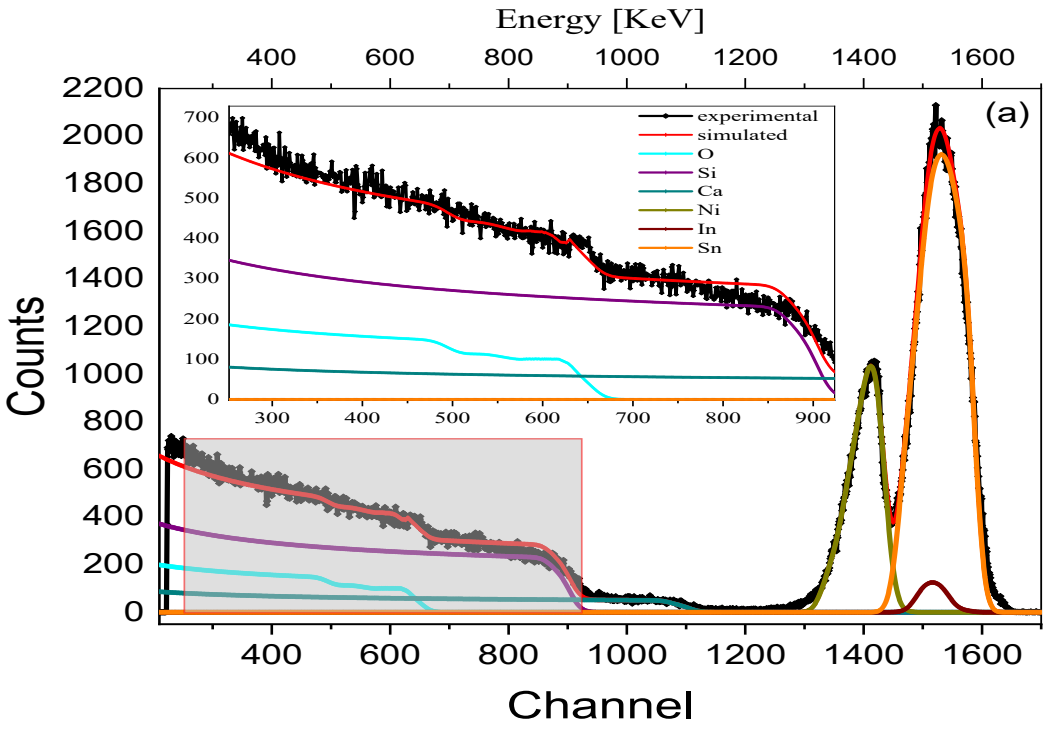
Layer 6 (Interface)	52.334	0	0	0	0	(0.491)	(0.111)	(0.406)	(0.002)	0	0
Layer 7 (Interface)	111.667	0	0	0	0	0.684	0.111	0.203	0.002	0	0
Layer 8 (Interface)	653.498	0	0	0	0	(0.821-0.898)	0	(0.170-0.174)	(0.002-0.003)	0	0
Layer 9 (Interface)	1212.118	0	0	0	0	(0.653-0.714)	0	(0.069-0.075)	(0.002-0.003)	(0.201-0.220)	(0.023-0.025)
Layer 10 (Glass)	21296.362	0	0	0	0	0.58	0	0	0	0.33	0.09

Depth profile table S2. Percentage concentration of various elements in different layers of IHPF ($CsPbI_2Br$) is deposited on NiO (HTL) which is coated on ITO/glass that is Glass/ITO/NiO/$CsPbI_2Br$.

Layers	**Thickness (1015 atoms/cm2)**	**Cu**	**C**	**Br**	**I**	**Cs**	**Pb**	**O**	**Sn**	**In**	**Ni**	**Si**	**Ca**
Layer 1 (Electrode)	195.737	1.00	0	0	0	0	0	0	0	0	0	0	0
Layer 2 (Interface)	70.563	0.17	0.83	0	0	0	0	0	0	0	0	0	0
Layer 3 (ETL)	90	0.12	0.88	0	0	0	0	0	0	0	0	0	0
Layer 4 (Interface)	291.022	0.09	(0.149-0.180)	(0.095-0.107)	(0.242-0.348)	(0.267-0.277)	(0.155-0.157)	0	0	0	0	0	0
Layer 5 (IHP)	395.034	0	0	(0.226-0.261)	(0.387-0.530)	(0.203-0.208)	(0.140-0.142)	0	0	0	0	0	0
Layer 6 (IHP)	296.00	0	0	(0.293-0.333)	(0.386-0.530)	(0.296-0.319)	(0.071-0.073)	0	0	0	0	0	0
Layer 7 (Interface)	82.00	0	0	0.063	0.499	0.035	0.021	0.393	0	0	0.006	0	0
Layer 8 (Interface)	209.336	0	0	0	0	0	0	0.540	0.379	0.043	0.037	0	0
Layer 9 (Interface)	687.310	0	0	0	0	0	0	(0.611-0.667)	(0.246-0.250)	0.043-0.045	0.03-0.04	0	0

Layer 10 (Interface)	86.150	0	0	0	0	0	0	0.636	0.294	0.004	0.001	0.094	0.020
Layer 11 (Interface)	1110	0	0	0	0	0	0	(0.684-0.716)	(0.06-0.10)	(0.001-0.002)	(0.002-0.004)	(0.144-0.200)	(0.03-0.04)
Layer 12 (Glass)	20000	0	0	0	0	0	0	0.635	0	0	0	0.327	0.037

Depth profile table S3. Percentage concentration of various elements in different layers of IHPF ($CsPbI_2Br$) which is sandwich between ETL (C_{60}) and HTL (NiO) deposited on ITO/soda-lime glass along with Cu contact *i.e.* (Glass/ITO/NiO/$CsPbI_2Br$/C_{60}/Cu).


Energy [KeV]
400
600
800
1000
1200
1400
1600
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
Counts
(a)
experimental
simulated
O
Si
Ca
Ni
In
Sn
700
600
500
400
300
200
100
0
300
400
500
600
700
800
900
400
600
800
1000
1200
1400
1600
Channel

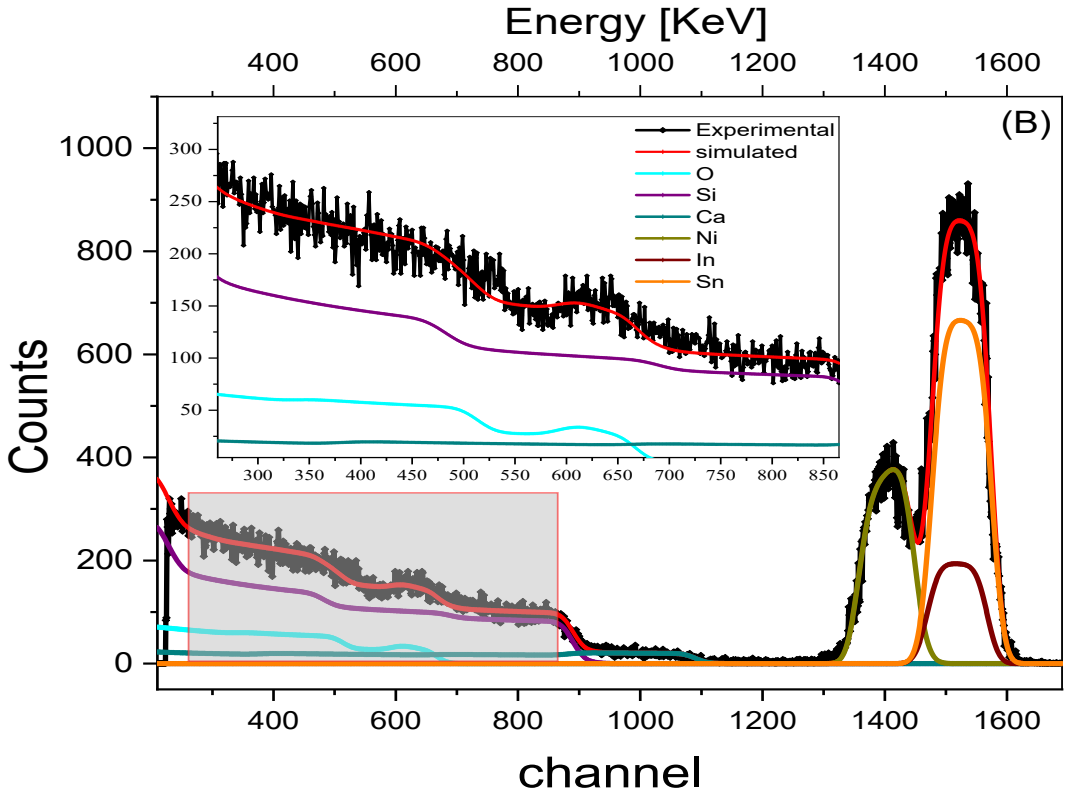

Energy [KeV]
400
600
800
1000
1200
1400
1600
1000
800
600
400
200
0
Counts
(B)
Experimental
simulated
O
Si
Ca
Ni
In
Sn
300
250
200
150
100
50
300
350
400
450
500
550
600
650
700
750
800
850
400
600
800
1000
1200
1400
1600
channel

Figure S1. RBS spectrum of NiO which is deposited on glass/ITO (a) after 3- month (b) after1-year.

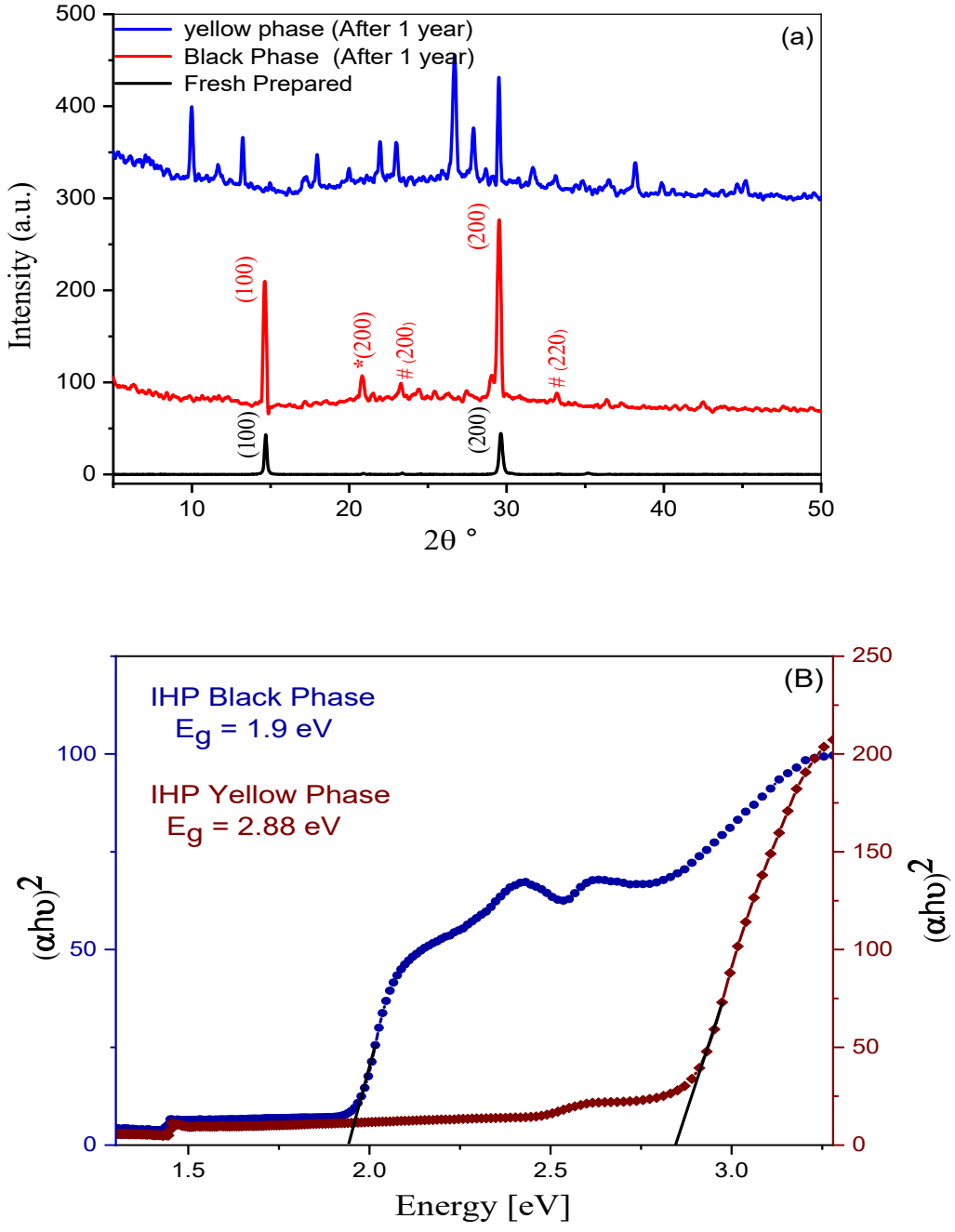


Figure S2. (a) XRD spectrum of freshly prepared (bottom), annealed after one year to 150 °C (Center) and Yellow phase after one year (Top) of IHP coated on glass (b) Bandgap of IHP coated on glass in black and yellow phase.

Detail of Experimental Method

A powerful ion beam-based analytical technique the Rutherford Back Scattering (RBS) was used which not only estimates the thickness and composition of the surface regime with high accuracy up to 1%[1] but also can inspect depth effectively from few nm up to a few μm^{2}-^{3} (depending on the matrix of elements) to understand the ion migration and interfacial diffusion between various layers of perovskite solar cells. The composition and concentration of elemental target constituents can be measured and determined as a function of depth using this technique. It also allows for the determination of areal density and impurity distribution. RBS is an ion scattering technique that is commonly used for IBA[4] that outperforms other techniques since it quantifies without the use of a reference or standard. The schematic of RBS is shown in fig 6. High energy (MeV) ions i.e. He+,++, Li+, D+, and H+[4] are guided onto the sample during an RBS study which is elastically backscattered due to Coulomb repulsion force between target and incoming ion. The energy distribution of backscattered ions at a given angle is measured which is used to determine the quantitative compositional depth profile of target nuclei. It is a non-destructive, quantitative nuclear analytical technique that has high sensitivity and accuracy which is used to examine not only thin layers but also multi-layer structures[5]. RBS usually entails using high-energy helium ions (He++) with energies ranging from 0.5 to 2.0 MeV for high Z elements ($Z \geq 6$) but sometimes even low mass elements can be detected by doing RBS with H+ depending on the concentration level of that low mass element and the matrix of elements in the corresponding sample[6, 7]. The precision of Rutherford scattering cross sections is almost greater than 99 % along with some limitation i.e. limited detector resolution (inability to differentiate the elements with the low atomic mass difference due to relatively alike Kinematic factors)[8]. Incident ions while traversing through the target encounter a large number of collisions and thus lose their energy and no longer remain

mono-energetic. This causes the energy to spread and fluctuate which is manifested by the energy loss calculations.

The quantitative analysis of the RBS spectra is done by using XRUMP[9] and SIMNRA[9, 10]. SIMNRA is a Microsoft Windows 95/Windows NT program that simulates Rutherford backscattering (RBS), nuclear reaction analysis (NRA), and elastic recoil detection analysis (EDA) with MeV ions and has a completely graphical user interface[11]. By comparing the experimental data with the SIMNRA computer simulations, the composition profiles are figured out. To calculate its simulated spectrum, SIMNRA exploits parameters such as scattering angle, the solid angle of the detector, incident ion energy, incident angle, total charge deposited by incident beam, and Rutherford backscattering cross-section. After that, the thickness of layers and composition of elements are systematically wavered to get the best fit. The obtained data can be either plotted in-depth profile format or in yield versus energy format. Moreover, SigmaCalc calculates the cross-section data for different ion-target combinations Rutherford backscattering spectrometry (RBS) is used to calculate the composition of the sample with 2 MeV He^{++} ions using an ion accelerator (3 MeV NEC Tandem Ion Accelerator). At the scattering angle of 170 degrees, the helium ions that are backscattered were collected and detected using a surface barrier detector [12].

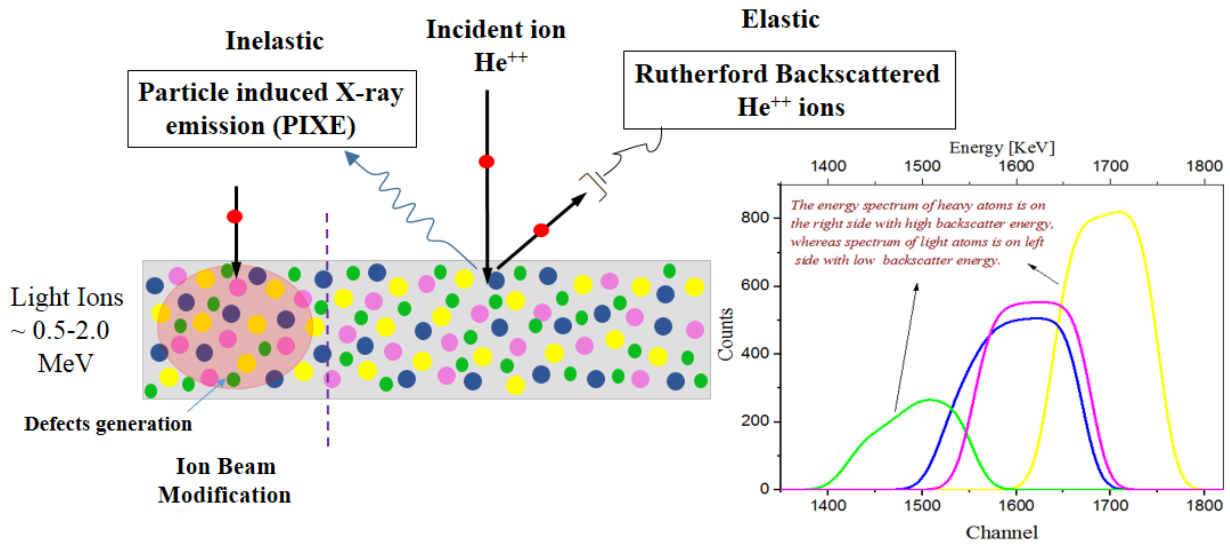
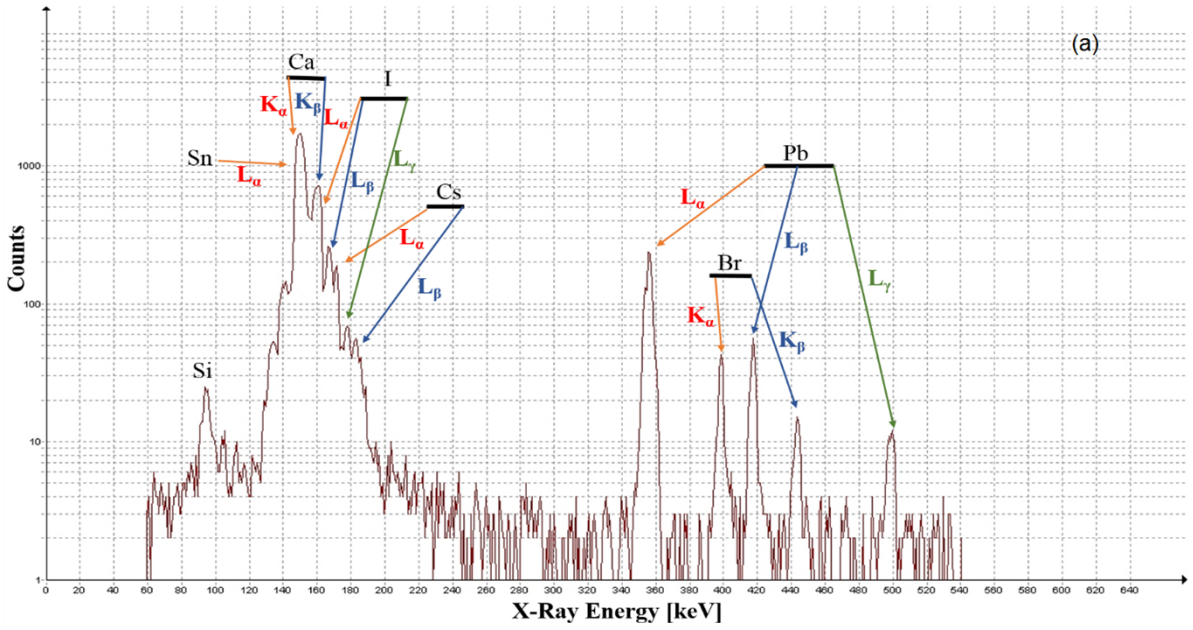


Figure S3. Schematic representing the backscattering of ions from the specimen under test and ion matter interactions.

PIXE is done with He++ instead of proton (H+) because of higher energy loss factor of He++ in thin films as compared to H+. Moreover, as the film is not thick to significantly detect by PIXE. Hence, sample was exposed at grazing angle of 70° to the incident He++ ions to increase the thickness of the film. The Beam of He++ ion is used with Energy 1 MeV, charge collection 2 μC and current is 2 nA.



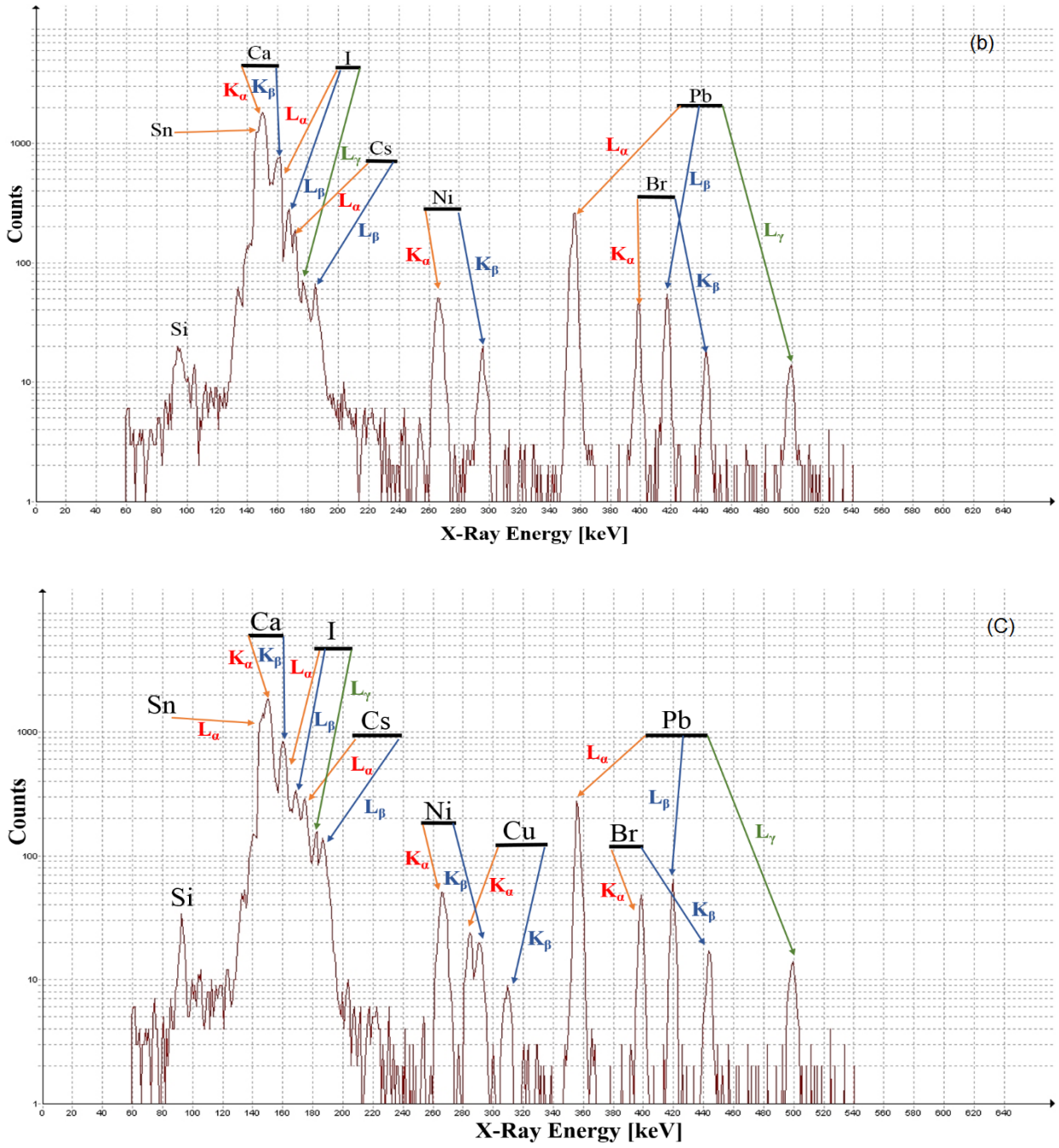


Figure S4. PIXE spectrum for (a) IHP (CsPbI2Br) deposited on glass (b) IHP (CsPbI2Br) coated on NiO (HTL) deposited on ITO/glass and (c) IHP (CsPbI2Br) which is sandwiched between ETL (C60) and HTL (NiO) deposited on ITO/ glass with Cu contact.

References

1. Colaux, J. L.; Jeynes, C. *Analytical Methods* **2014,** 6, (1), 120-129.
2. J. R. Tesmer and M. Nastasi. *Materials*

Research Society, Warrendale, **1995**, 1-342.
3. Malmqvist, K. G. *Radiation Physics and Chemistry* **2004,** 71, 817.
4. Moro, M. V.; Holeňák, R.; Zendejas Medina, L.; Jansson, U.; Primetzhofer, D. *Thin Solid Films* **2019,** 686, 137416.
5. Raja, P. M. V.; Barron, A. R., Rutherford Backscattering of Thin Films. 2021.
6. Frost, R. J. W.; De La Rosa, N.; Elfman, M.; Kristiansson, P.; Nilsson, E. J. C.; Pallon, J.; Ros, L. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **2021,** 494-495, 34-45.
7. Ma, X.; Wang, Q.; Wang, Z.; Wan, X. *Fusion Science and Technology* **2021,** 77, (6), 446-453.
8. Jeynes, C.; Colaux, J. L. *Analyst* **2016,** 141, (21), 5944-5985.
9. Mayer, M. **1997**.
10. Silva, T. F.; Rodrigues, C. L.; Mayer, M.; Moro, M. V.; Trindade, G. F.; Aguirre, F. R.; Added, N.; Rizzutto, M. A.; Tabacniks, M. H. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **2016,** 371, 86-89.
11. Mayer, M. *AIP Conference Proceedings* **1999,** 475, (1), 541-544.
12. Stojanović, M. S.; MilosavljeviĆ, M.; Subotić, K. M.; Boreli, F.; Wilson, I. H.; Novković, D. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **1990,** 50, (1), 102-104.