Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Band-Bowing Effects in Lead-Free Double $Cs_2AgBi_xSb_{1-x}Cl_6$ Perovskites and Their Anion-Exchanged Derivatives

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Tables

Table S1. Composition of Cs-Ag-Bi-Sb-Cl perovskites from EDX analysis

Nominal Bi fraction x	Actual Bi fraction x_a	Cl/(Bi+Sb)	Cs/(Bi+Sb)	Ag/(Bi+Sb)
0	0	5.56	1.96	1.00
0.05	0.06	5.55	2.02	1.00
0.10	0.12	5.36	1.93	0.98
0.25	0.26	5.06	1.91	0.92
0.50	0.50	4.92	1.87	0.92
0.75	0.76	5.18	1.86	0.90
0.90	0.91	5.02	2.02	0.91
1.00	1.00	5.42	1.96	0.96

Table S2. Composition of the products of Cl-to-Br anionic exchange in CABSC perovskites

Bi(Bi+Sb)	Cs/(Bi+Sb)	Ag/(Bi+Sb)	Na/(Bi+Sb)	(Br+Cl)/(Bi+Sb)	Br/(Br+Cl)
0	1.51	0.68	0.13	4.70	0.64
0.07	1.53	0.86	0.12	4.45	0.65
0.12	1.47	0.36	0.14	4.60	0.65
0.25	1.68	1.04	0.19	5.55	0.66
0.47	1.89	0.97	0.27	5.90	0.68
0.82	1.96	1.02	0.18	6.00	0.67
0.94	1.97	1.00	0.25	6.05	0.68
1.00	2.01	1.04	0.21	5.80	0.68

Table S3. Composition of Cs-Bi-Sb-I perovskites from EDX analysis

Nominal Bi fraction x	Actual Bi fraction x_a	I/(Bi+Sb)	Cs/(Bi+Sb)
0	0	4.57	1.48
0.05	0.07	4.24	1.47
0.10	0.12	4.27	1.44
0.25	0.29	3.94	1.43
0.50	0.52	4.50	1.52
0.75	0.78	4.61	1.54
0.90	0.88	4.75	1.55
1.00	1.00	4.87	1.59

Figures

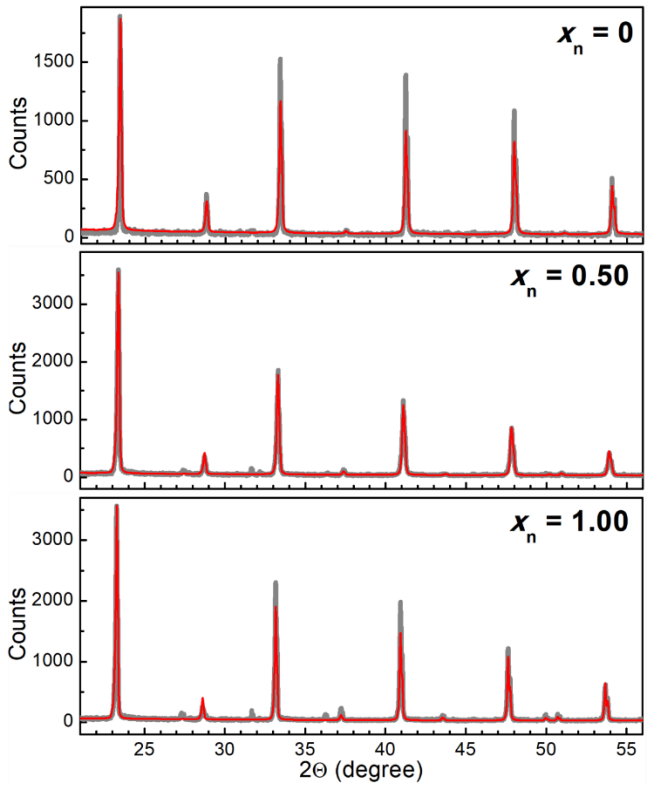
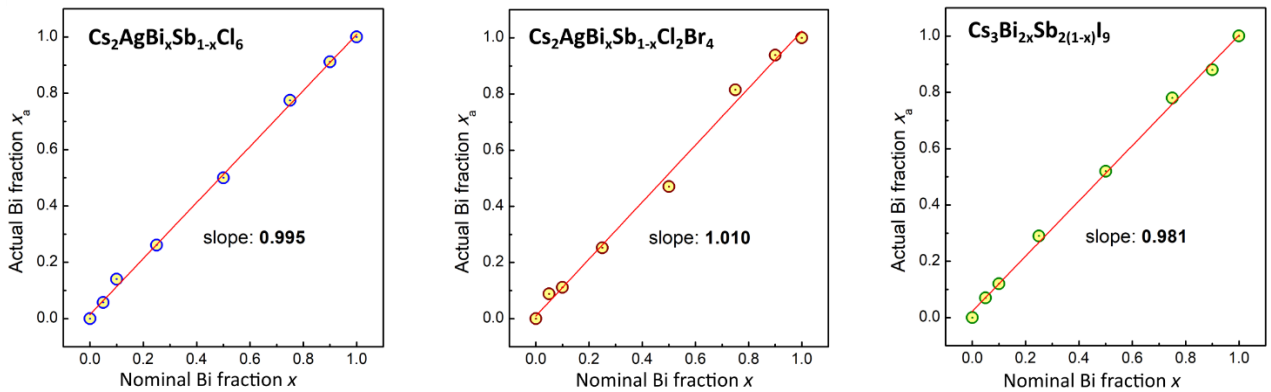


Figure S1. XRD patterns of $Cs_2AgBi_xSb_{1-x}Cl_6$ perovskites with a nominal Bi fraction x_n of 0, 0.50, and 1.00 (gray lines) and Rietveld refinement of the experimental data (red lines).



a b c

Figure S2. Actual Bi fraction x_a versus nominal Bi fraction x for original $Cs_2AgBi_xSb_{1-x}Cl_6$ double perovskites (a) and the products of anion exchange with NaBr (b) and NaI (c).

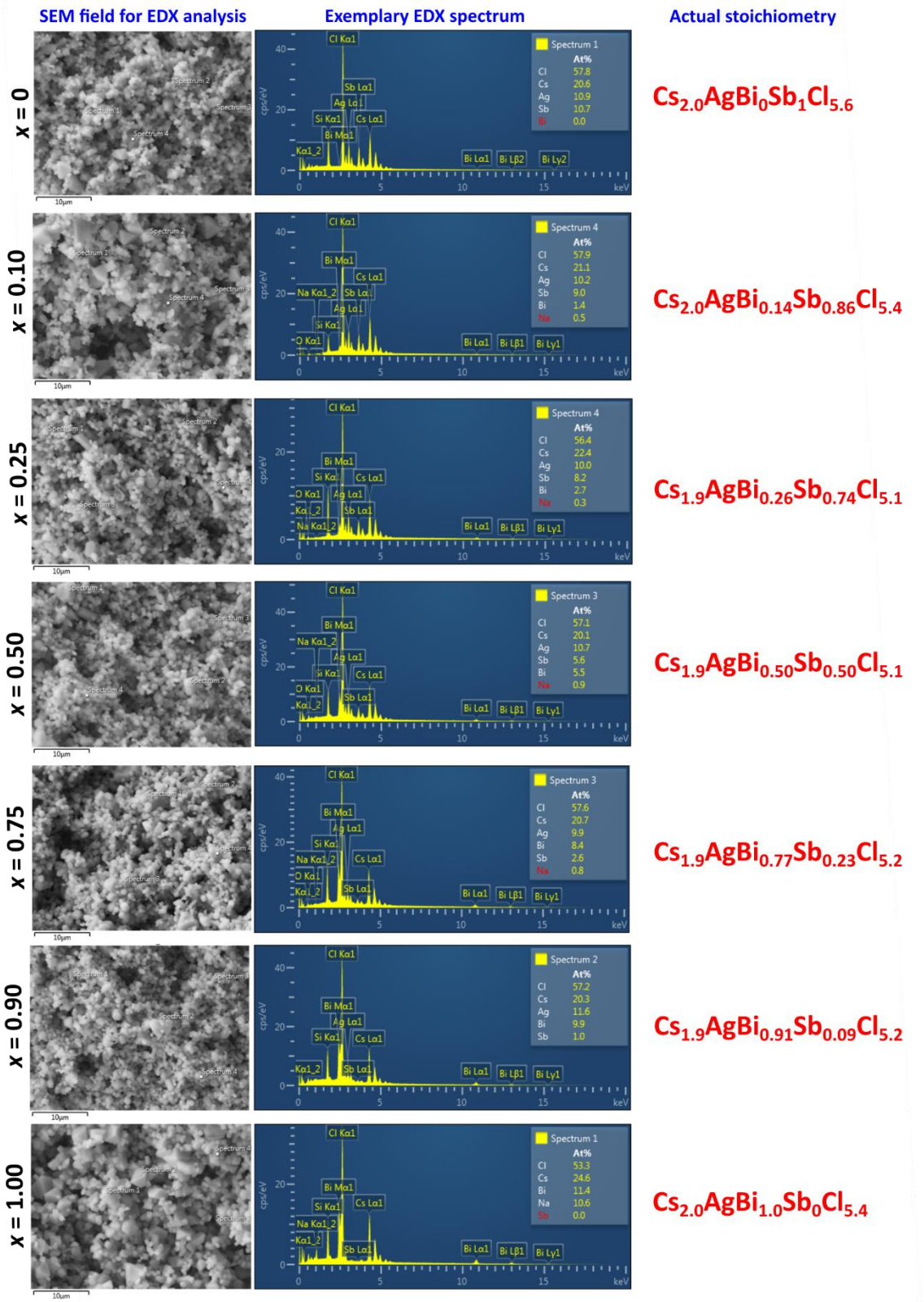


Figure S3. SEM of sample areas used for the EDX analysis, exemplary EDX spectra, and actual stoichiometries derived from EDX data for $Cs_2AgBi_xSb_{1-x}Cl$ perovskites.

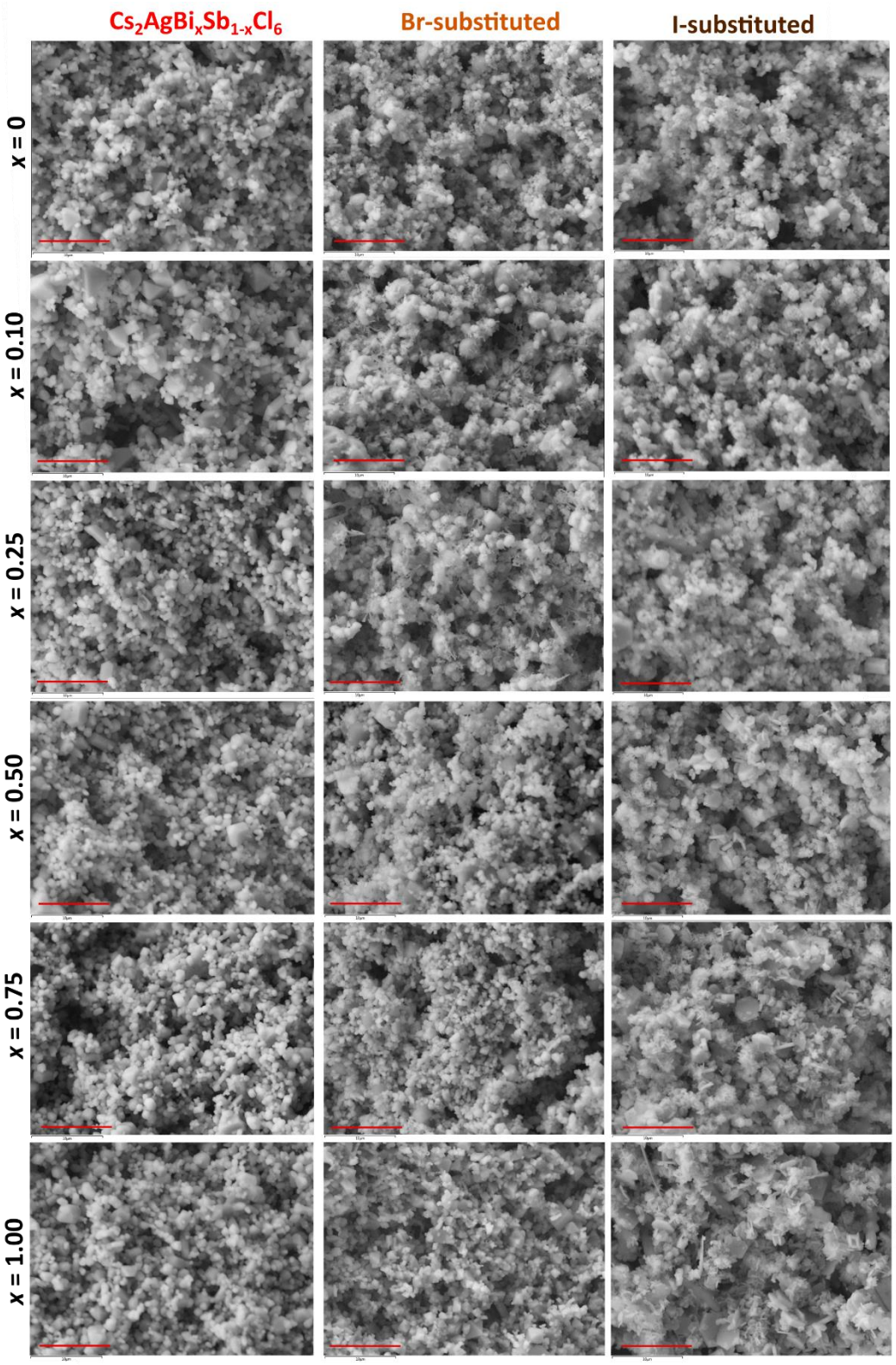


Figure S4. SEM images of $Cs_2AgBi_xSb_{1-x}Cl_6$ double perovskites with varied x and corresponding products of Br-to-Cl and I-to-Cl substitution. The scale bar is 10 μm.

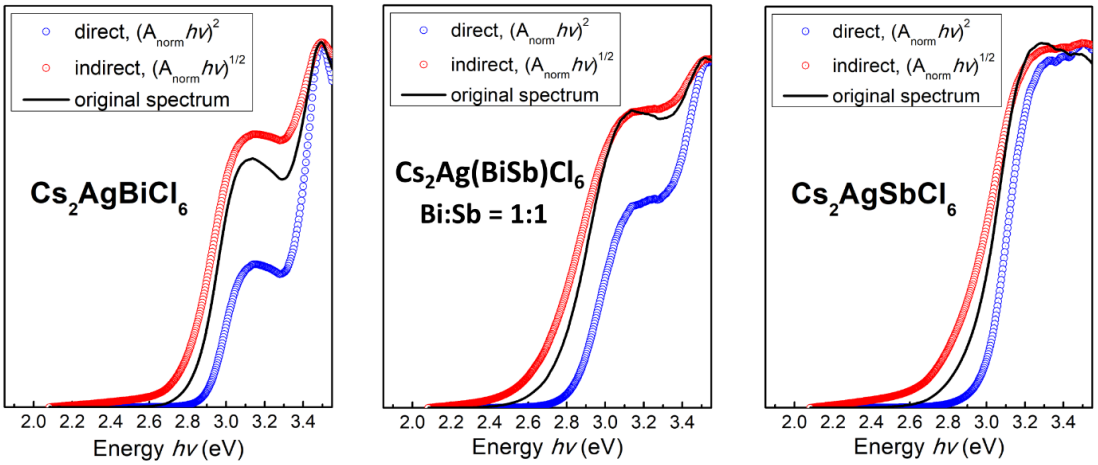


Figure S5. Normalized absorption spectra of $Cs_2AgBiCl_6$, $Cs_2AgBi_{0.5}Sb_{0.5}Cl_6$, and $Cs_2AgSbCl_6$ double perovskites presented in original form (solid black lines) and in Tauc coordinates for direct transitions (blue open rings) and indirect transitions (red open rings).

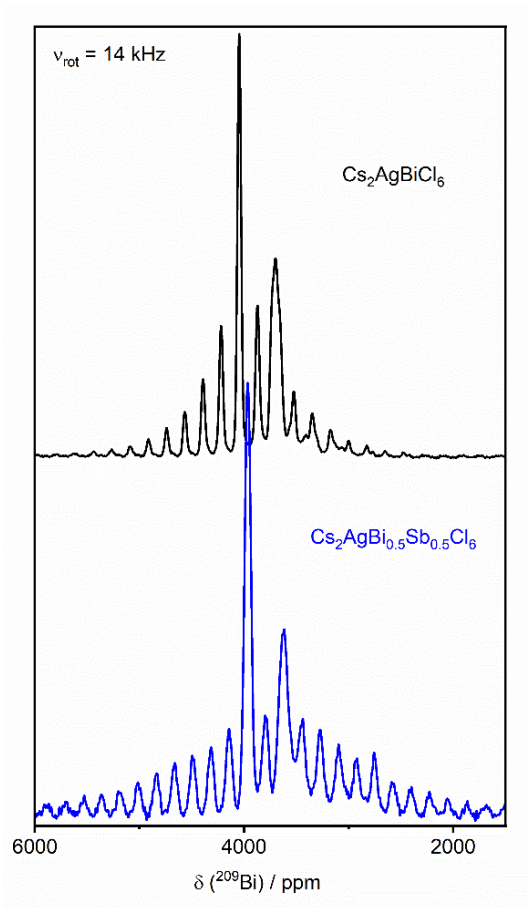


Figure S6. ^{209}Bi MAS NMR spectra of $Cs_2AgBiCl_6$ (upper black trace) and mixed $Cs_2AgBi_{0.5}Sb_{0.5}Cl_6$ (lower blue trace) double perovskites. The presence of an unidentified secondary Bi phase is observed between 3600-3800 ppm, unfortunately overlapping with the residual first-order spinning sideband of the dominant double perovskite.

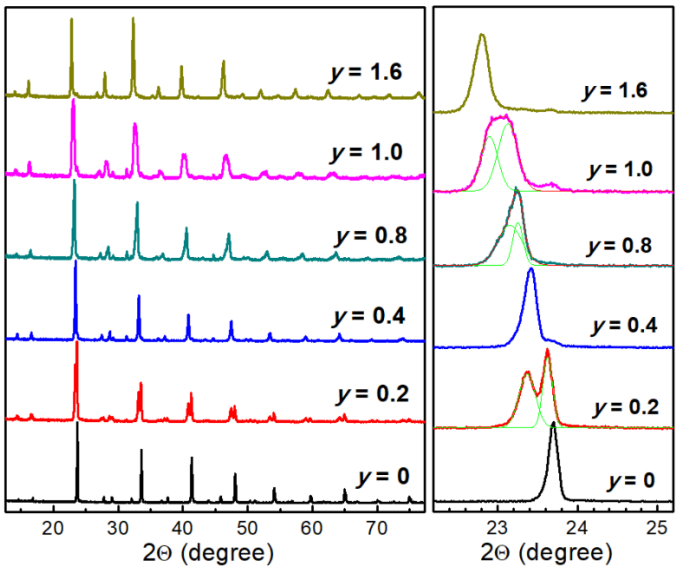


Figure S7. XRD patterns of the products of Cl-to-Br substitution in CABC double perovskites with a varied nominal ratio of *y* = Br/(Cl+Br).

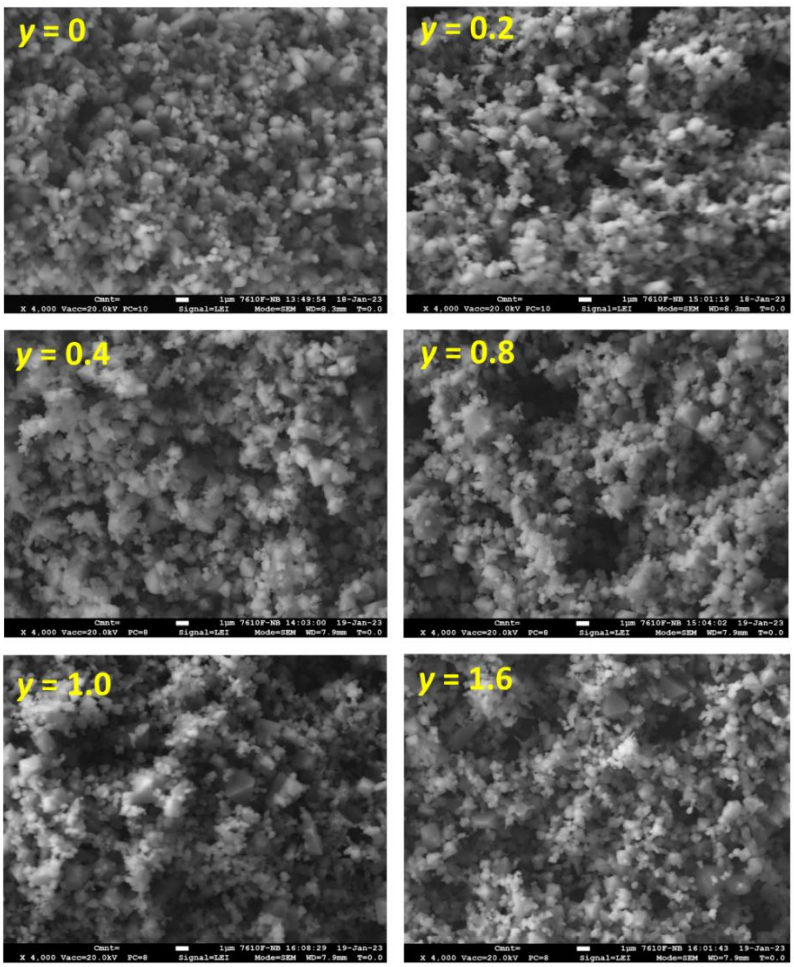


Figure S8. SEM images of the products of Cl-to-Br substitution in CABC double perovskites with a varied nominal ratio of *y* = Br/(Cl+Br).

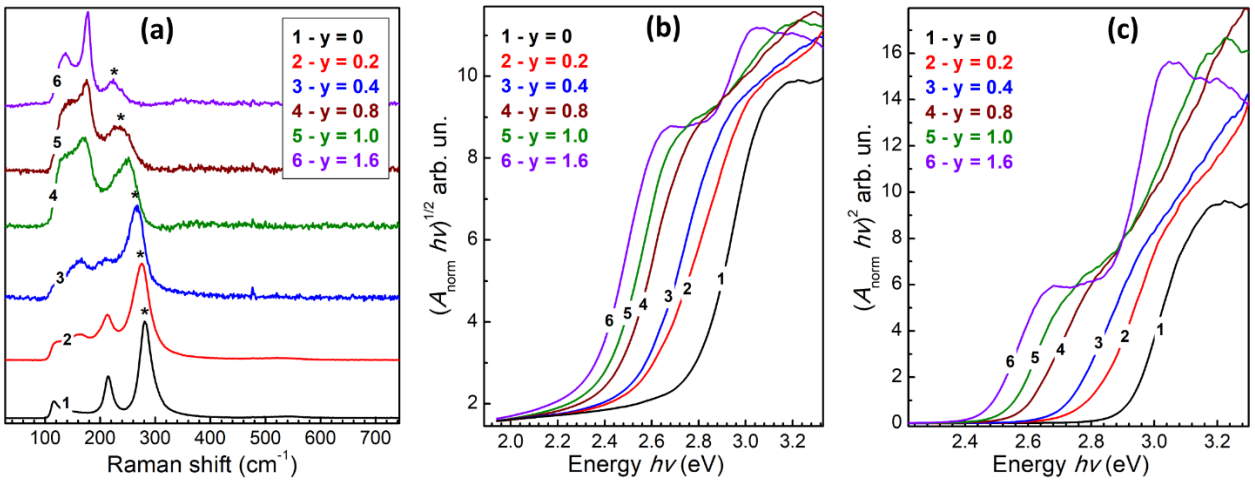


Figure S9. Raman spectra (a) and absorption spectra (b,c) of the products of Cl-to-Br substitution in CABC double perovskites with a varied nominal ratio of *y* = Br/(Cl+Br). In (a) the position of the highest-energy peak *v* is marked by an asterisk. Absorption spectra are presented in Tauc coordinates for indirect transitions (b) and direct transitions (c).

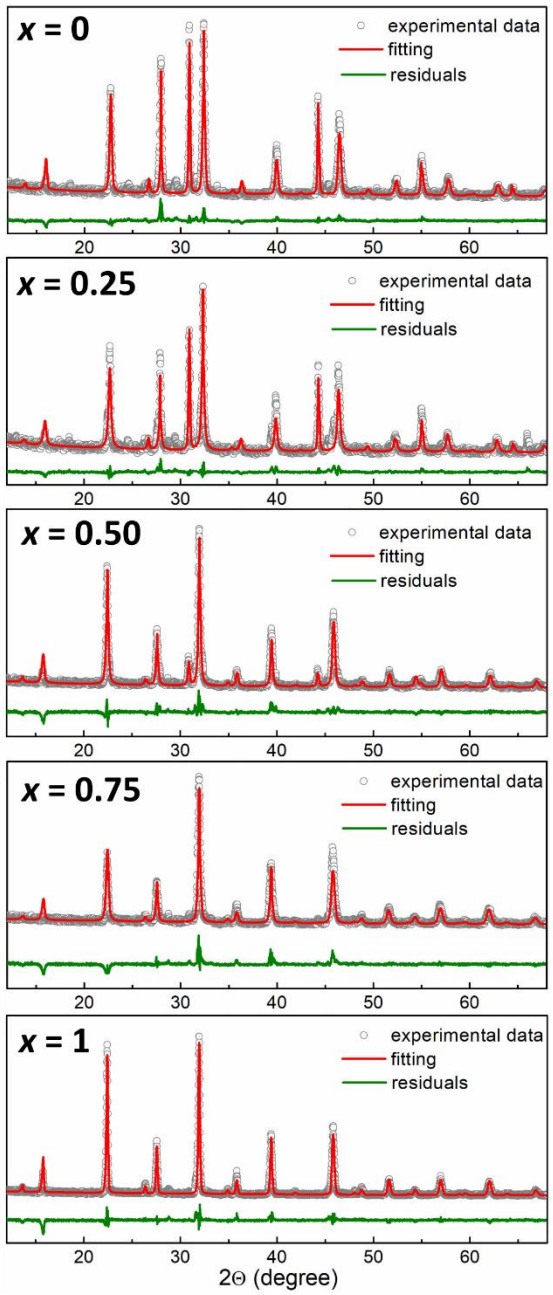


Figure S10. XRD profiles for the products of interaction between NaBr and $Cs_2AgBi_xSb_{1-x}Cl_6$ (CABSC) double perovskites with varied nominal Bi fraction x: gray scatter shows experimental data, solid red lines represent Rietveld refinement of the XRD patterns, green line shows the difference between experimental data and fitting curves (residuals).

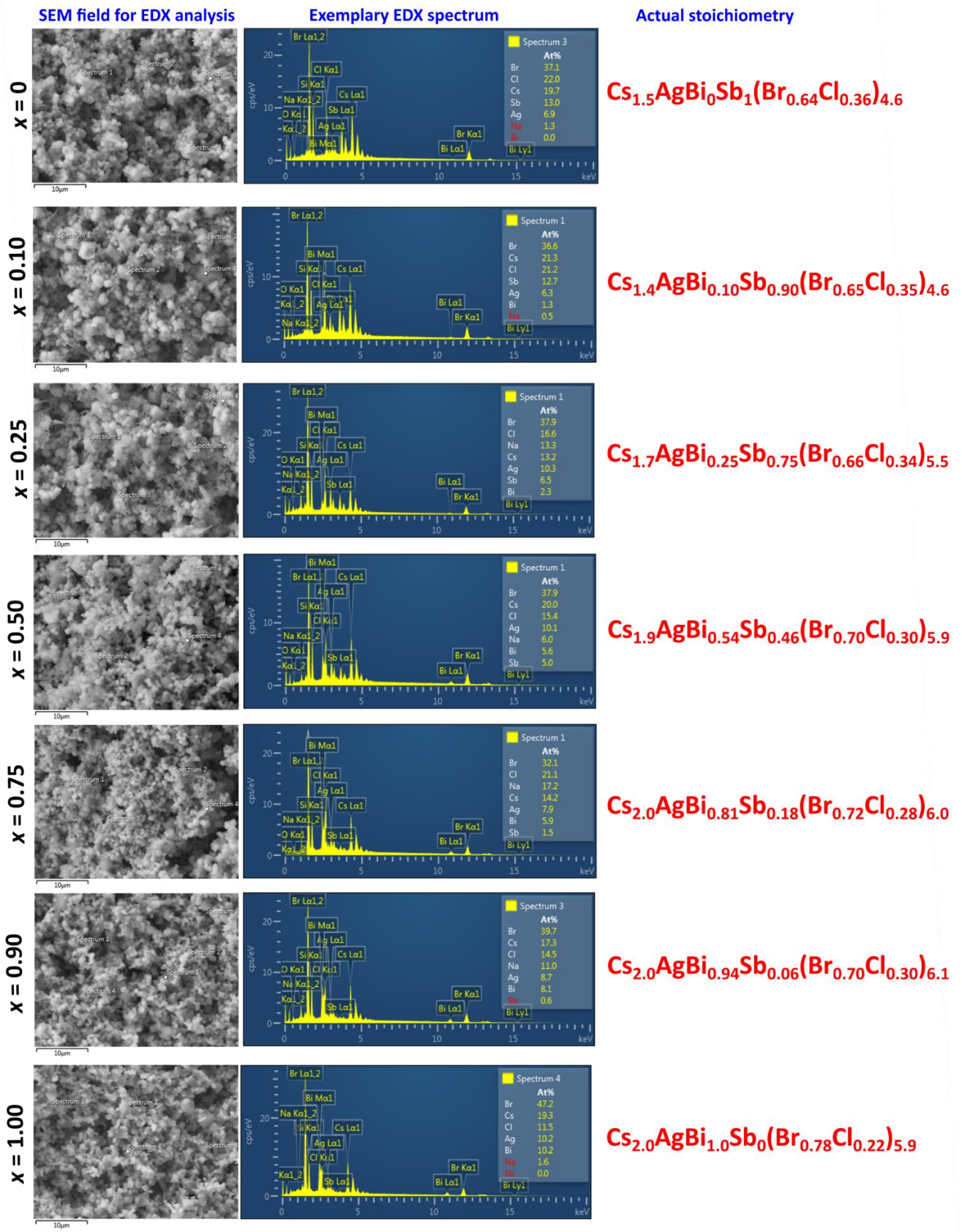


Figure S11. SEM of sample areas used for the EDX analysis, exemplary EDX spectra, and actual stoichiometries derived from EDX data for the products of Cl-to-Br substitution in CABSC perovskites.

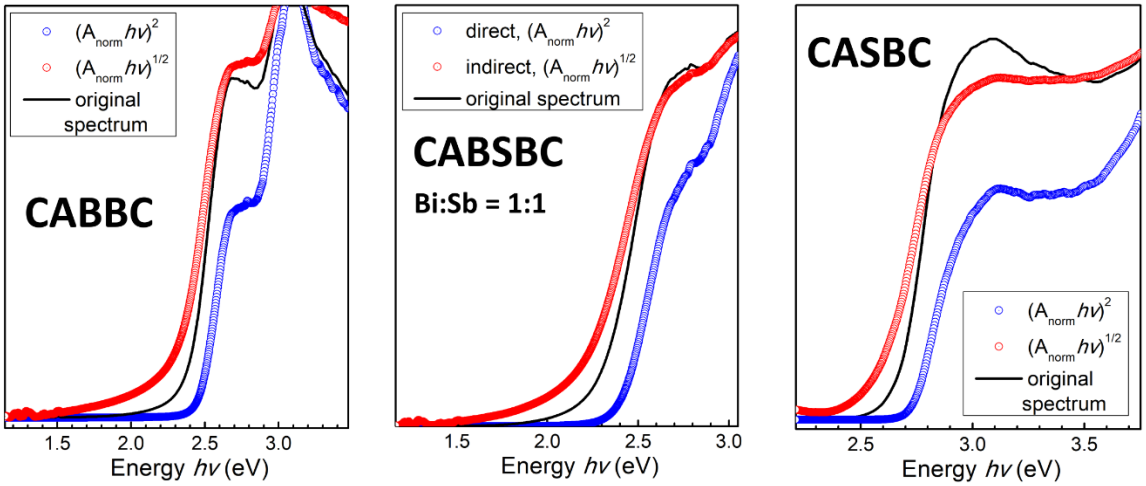


Figure S12. Normalized absorption spectra of CABBC, CABSBC (Bi:Sb = 1:1), and CASBC presented in original form (solid black lines) and in Tauc coordinates for direct transitions (blue open rings) and indirect transitions (red open rings).

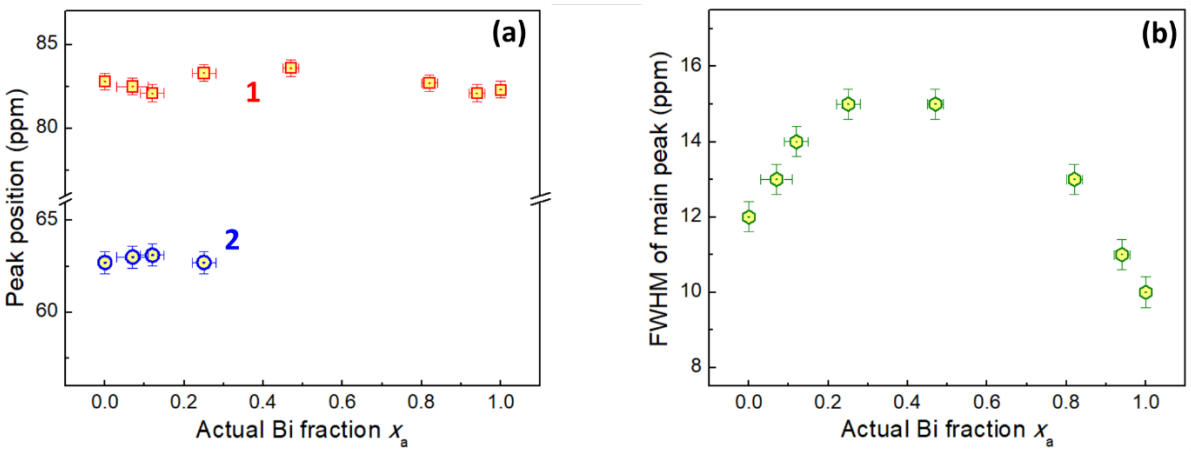


Figure S13. Positions of peaks (a) and FWHM of the main peak at 82-84 ppm (b) in ^{133}Cs MAS NMR spectra of the products of anion exchange of CABSC perovskites with NaBr.

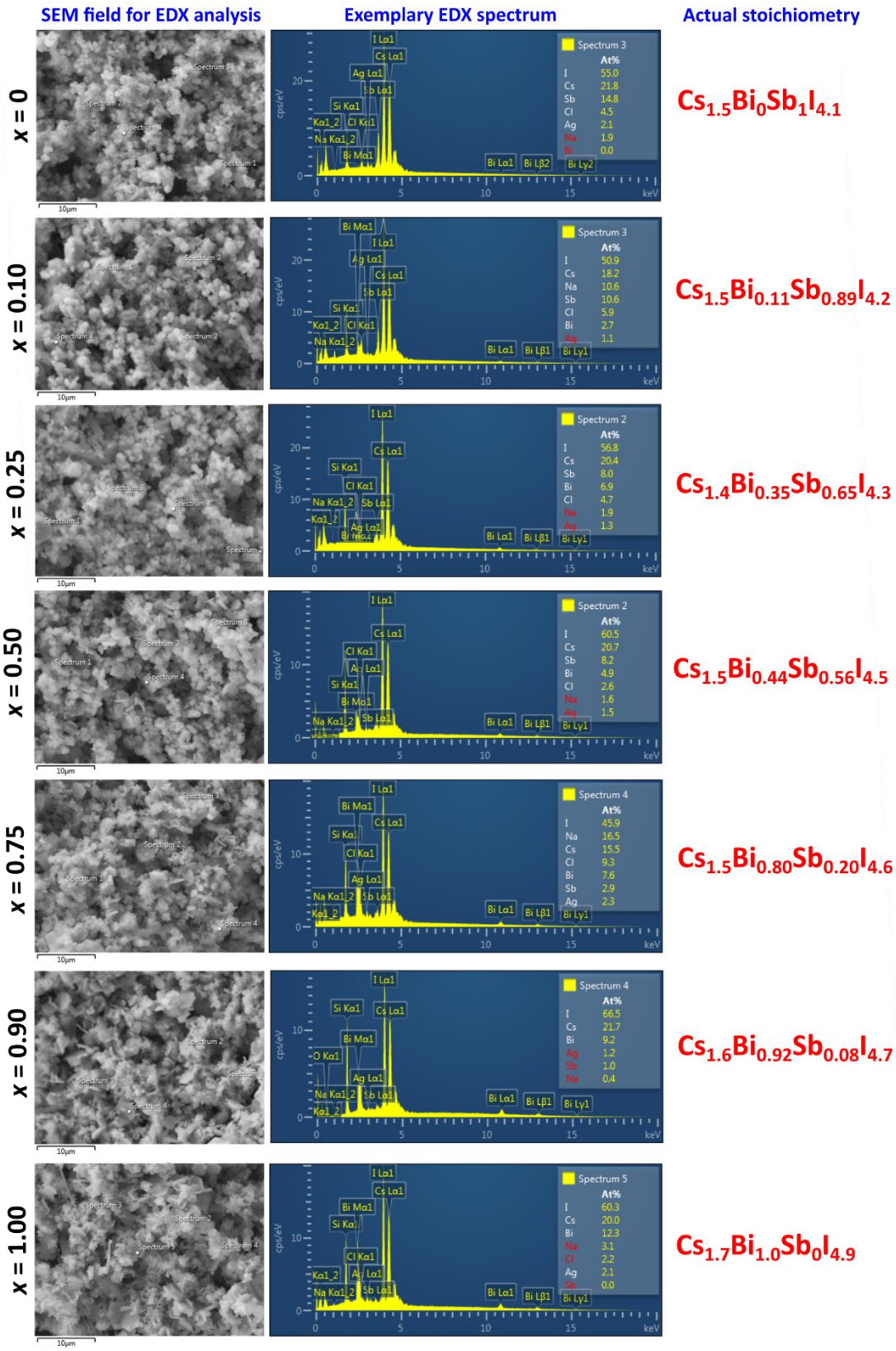


Figure S14. SEM of sample areas used for the EDX analysis, exemplary EDX spectra, and actual stoichiometries derived from EDX data for the products of Cl-to-I substitution in CABSC perovskites.

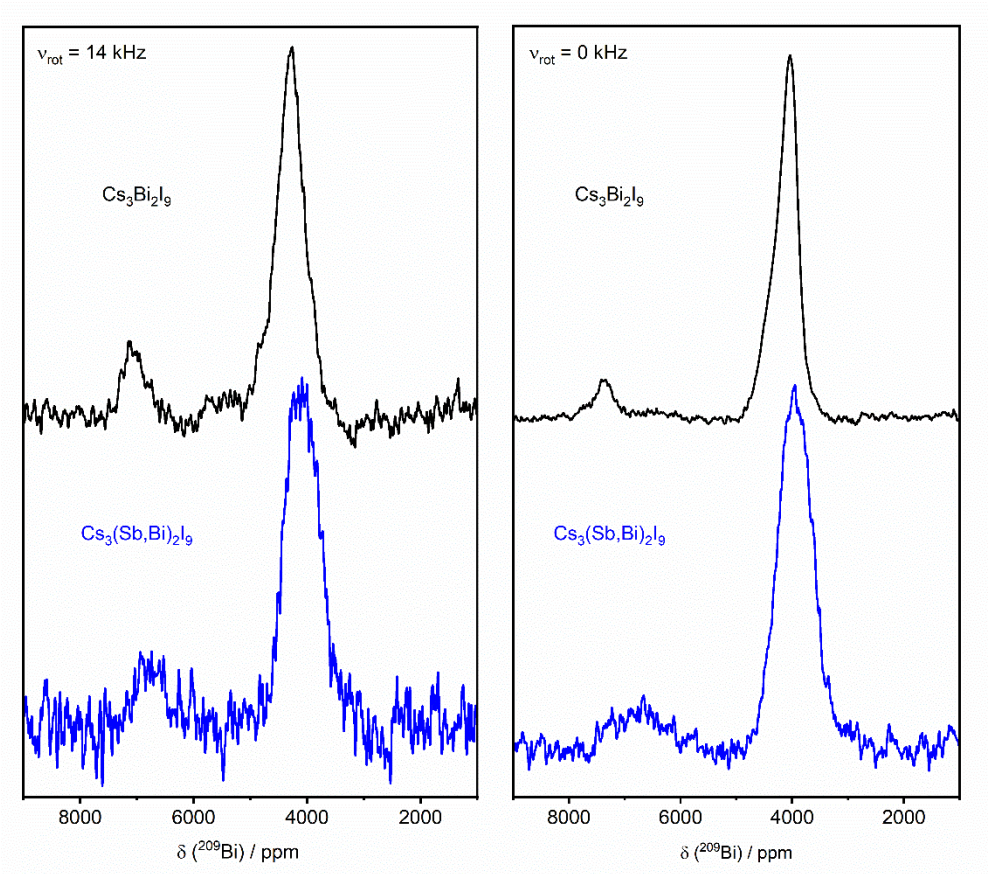


Figure S15. ^{209}Bi MAS (left) and non-spinning (right) NMR spectra of $Cs_3Bi_2I_9$ (upper black trace) and mixed $Cs_3(Sb,Bi)_2I_9$ (lower blue trace) compounds.

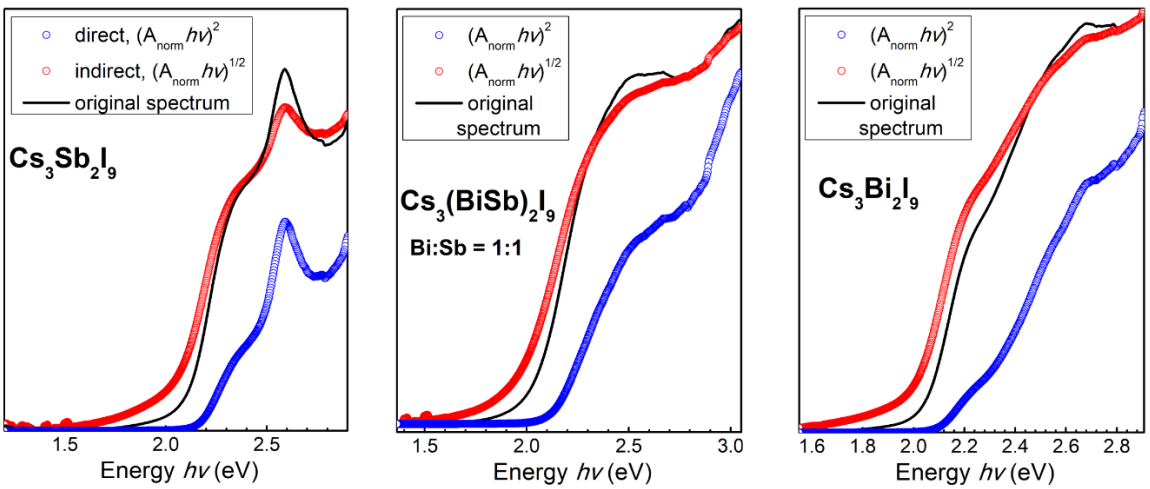


Figure S16. Normalized absorption spectra of CSI, CBSI (Bi:Sb = 1:1), and CBI presented in original form (solid black lines) and in Tauc coordinates for direct transitions (blue open rings) and indirect transitions (red open rings).