Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary Information

Understanding the Interplay between Crystal Structure and Charge Transport in Alloyed Lead-free Perovskites

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Table S1. Average P, R, D characteristics of the studied lateral devices (symbols in brackets show standard deviation). Bandgaps were estimated using Tauc plot, * denotes for indirect bandgap.

Material	Dimansionality	Bandgap (ass)	405 nm			532 nm			650 nm		
		eV	P %	R mA/W	D Jones	P %	R mA/W	D Jones	P %	R mA/W	D Jones
$MA_3Bi_2I_9$	0D	1.91*	51.4 (8.2)	2.8 (0.0925)	$1.8\cdot10^{8}$ (0.0925)	2.15 (48.8)	0.0041 (48.8)	$2.4\cdot10^{5}$ (48.8)	-	-	-
$MA_3(Bi_{0.6}Sb_{0.4})_2I_9$	0D	1.89*	25 (8.2)	1.3 (0.0925)	$8.4\cdot10^{7}$ (0.0925)	3.9 (48.8)	0.0067 (48.8)	$4.1\cdot10^{5}$ (48.8)	-	-	-
$MA_3Sb_2I_9$	**0D**	**1.91***	**314 (8.2)**	**19 (0.0925)**	**$1.2\cdot10^{9}$ (0.0925)**	**8.0 (48.8)**	**0.13 (48.8)**	**$2.6\cdot10^{6}$ (48.8)**	**4.6 (63.2)**	**0.4 (0.38)**	$7.4\cdot10^{6}$ (0.38)
$MA_3Bi_2(I_{0.6}Br_{0.4})_9$	2D	2.25	3.6 (8.2)	0.16 (0.371)	$1\cdot10^{7}$ (0.371)	-	-	-	-	-	-
$MA_3(Bi_{0.6}Sb_{0.4})_2(I_{0.6}Br_{0.4})_9$	2D	2.23	55.3 (8.2)	2.4 (0.371)	$1.6\cdot10^{8}$ (0.371)	6.8 (48.8)	0.012 (48.8)	$7.3\cdot10^{5}$ (48.8)	-	-	-
$MA_3Sb_2(I_{0.6}Br_{0.4})_9$	**2D**	**2.28**	**315 (8.2)**	**19 (0.0925)**	**$1.2\cdot10^{9}$ (0.0925)**	**8.9 (48.8)**	**0.016 (48.8)**	**$1.0\cdot10^{6}$ (48.8)**	-	-	-
$MA_3Bi_2Br_9$	2D	2.74	-	-	-	-	-	-	-	-	-
$MA_3(Bi_{0.6}Sb_{0.4})_2Br_9$	2D	2.71	6.2 (8.2)	0.17 (0.371)	$1.1\cdot10^{7}$ (0.371)	-	-	-	-	-	-
$MA_3Sb_2Br_9$	2D	2.75	58.9 (8.2)	4.2 (0.0925)	$2.7\cdot10^{8}$ (0.0925)	-	-	-	-	-	-

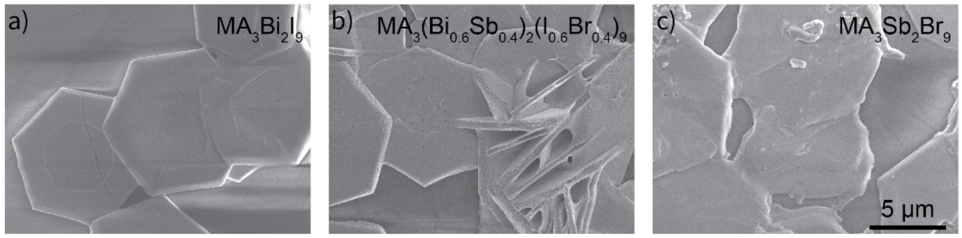

Figure S1. SEM images of 3 characteristic samples prepared on quartz showing micrometer size hexagonal grains and the resulting material exhibited the same carrier mobility but improved carrier lifetime.

Table S2. – THz measurements for 2 set of samples, prepared on quartz. (set #1 – bare perovskite solutions, #2– solutions with NH_4SCN additive).

Sample Set #1	**THz mobility, cm²/V/s**	**THz lifetime, ps**
$MA_3Bi_2Br_9$, (2D)	0.4	8.7
$MA_3Sb_2Br_9$, (2D)	0.5	4.8
$MA_3(Bi_{0.6}Sb_{0.4})_2(I_{0.6}Br0_{.4})_9$, (2D)	0.6	6.6
$MA_3Bi_2I_9$ (0D)	0.3	2.8
$MA_3Sb_2I_9$, (0D)	0.4	1.2
Sample Set #2	**THz mobility, cm²/V/s**	**THz lifetime, ps**
$MA_3(Bi_{0.6}Sb_{0.4})_2(I_{0.6}Br0_{.4})_9$, (2D)	0.4	12
$MA_3Sb_2Br_9$, (2D)	0.4	10
$MA_3Bi_2I_9$ (0D)	0.3	9

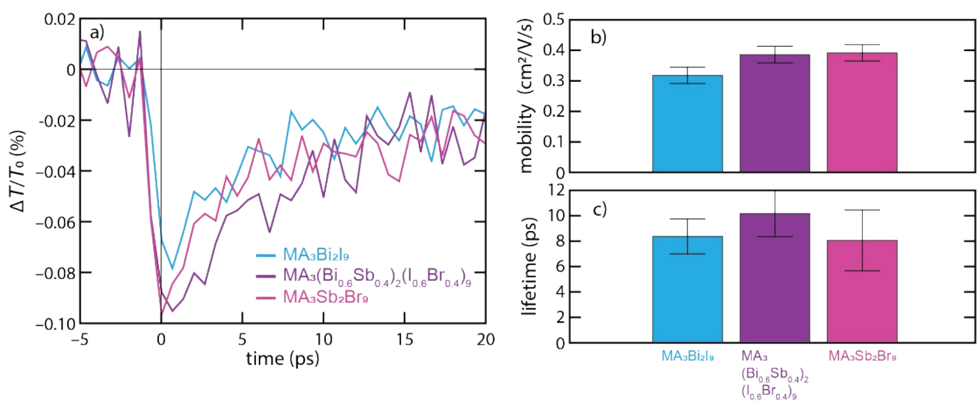

Figure S2. THz mobility and lifetime of samples prepared on quartz with the increased grain size, carrier lifetime increased to >9 ps for all samples while carrier mobilities remain the same.

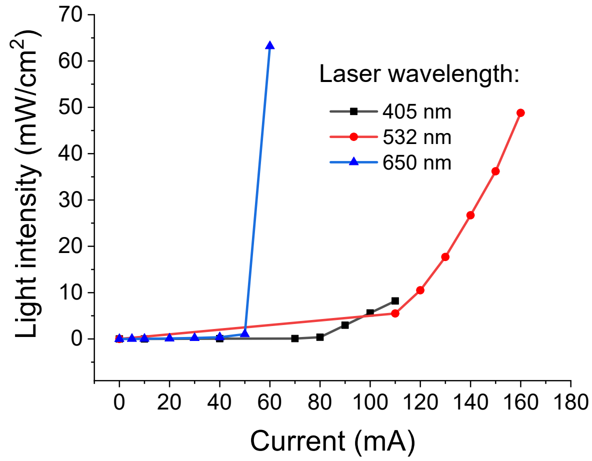

Figure S3. – Relation between laser light intensity and current

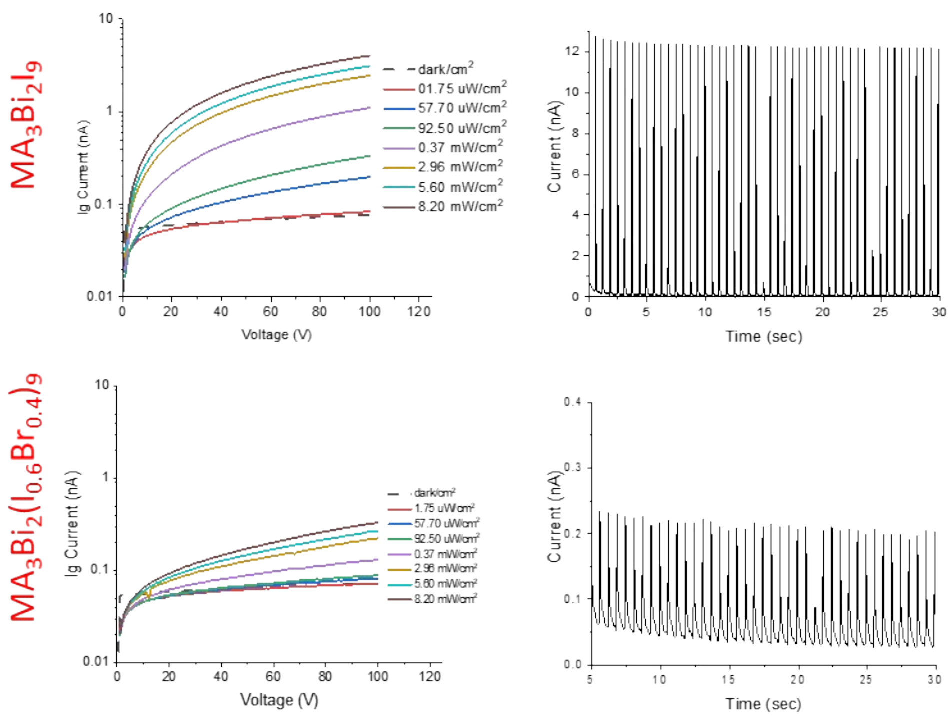

Figure S4. IV characteristics and transient photoresponse of Bi- systems ($MA_3Bi_2Br_9$ did not respond)

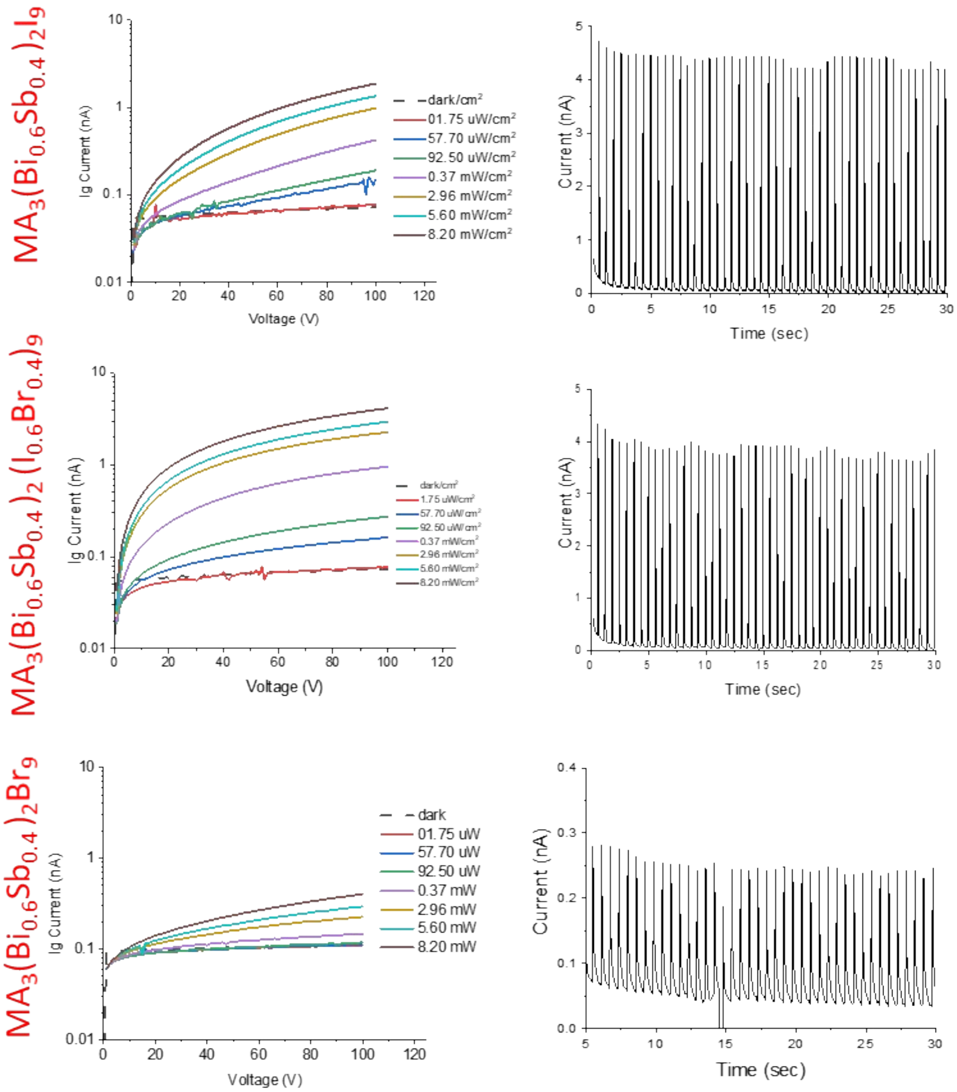

Figure S5. IV characteristics and transient photoresponse of Bi-Sb systems

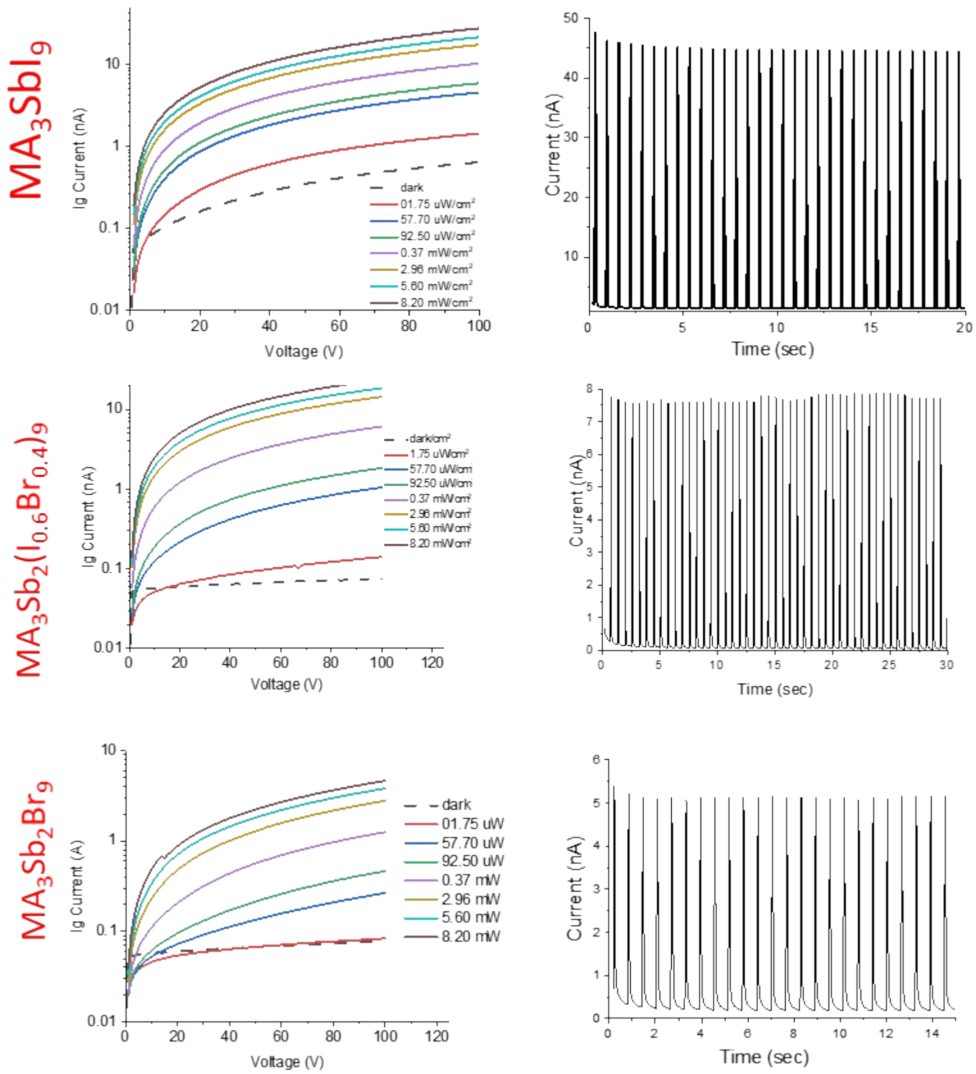

Figure S6. IV characteristics and transient photoresponse of Sb-systems

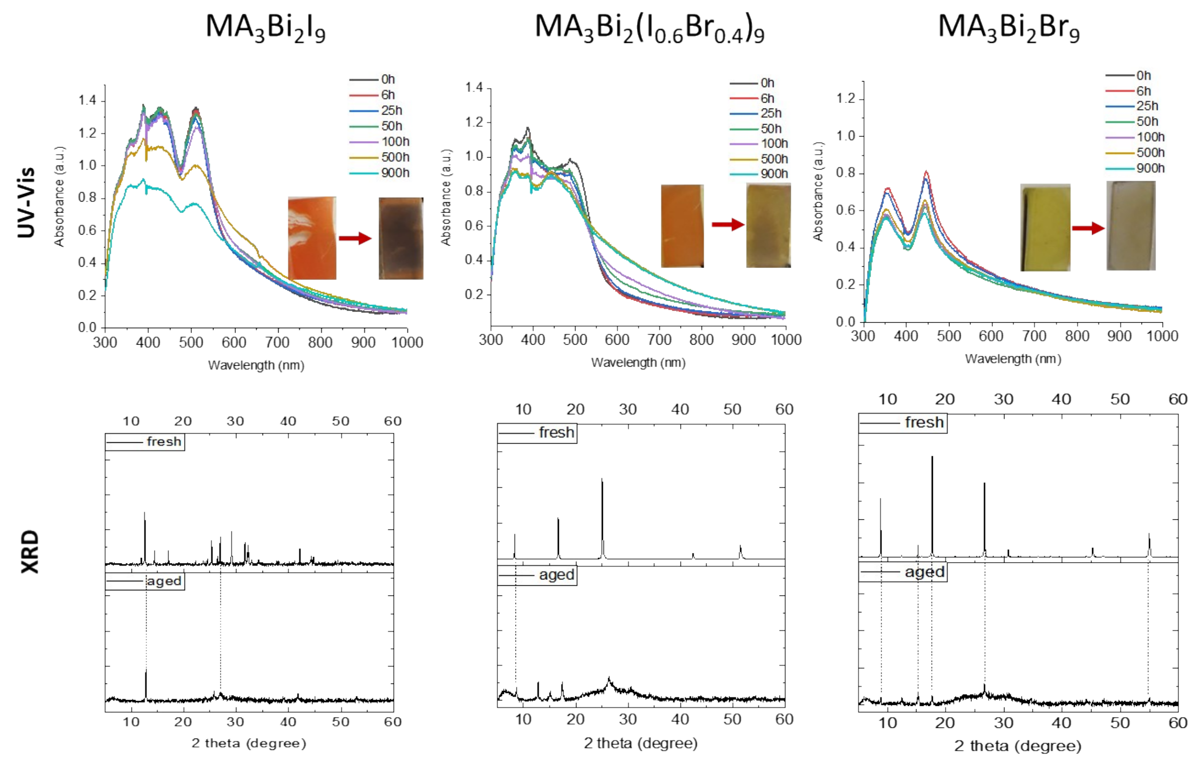

Figure S7. Change of UV-vis spectra(a) and XRD patern(b) of Bi-rich- systems.

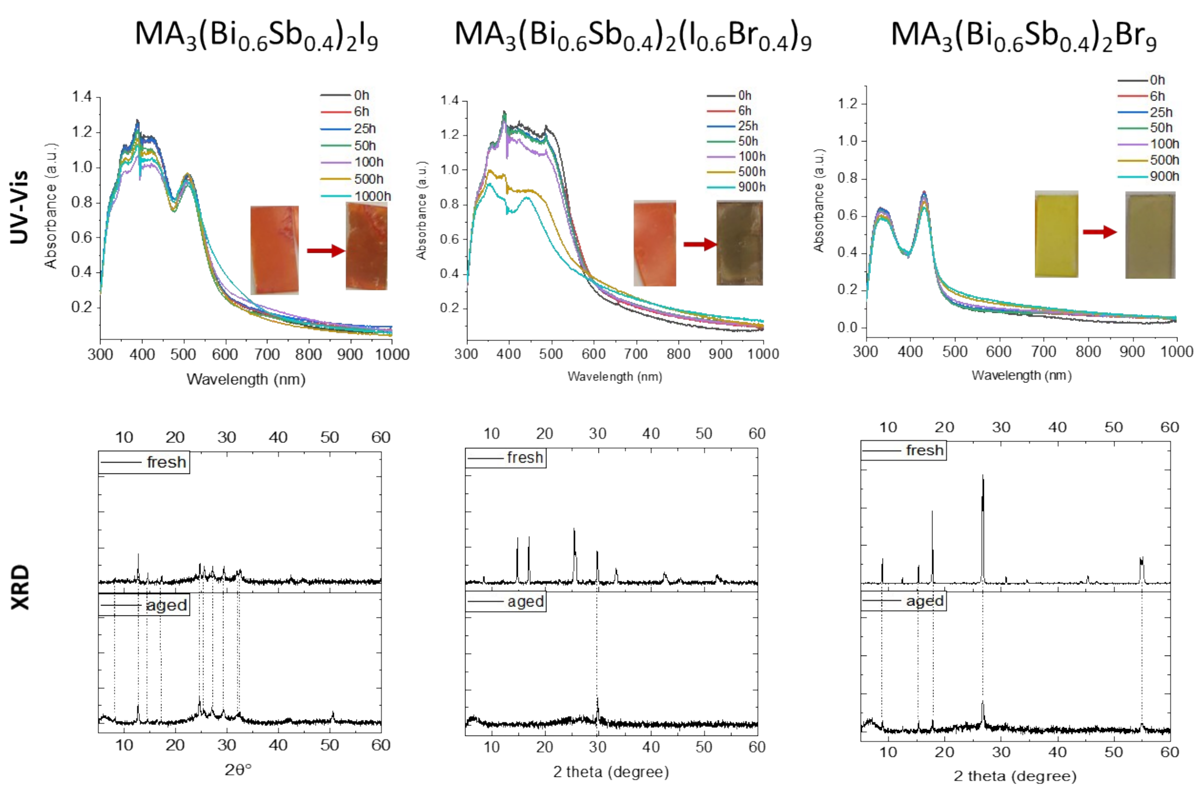

Figure S8. Change of UV-vis spectra(a) and XRD patern(b) Bi-Sb systems.

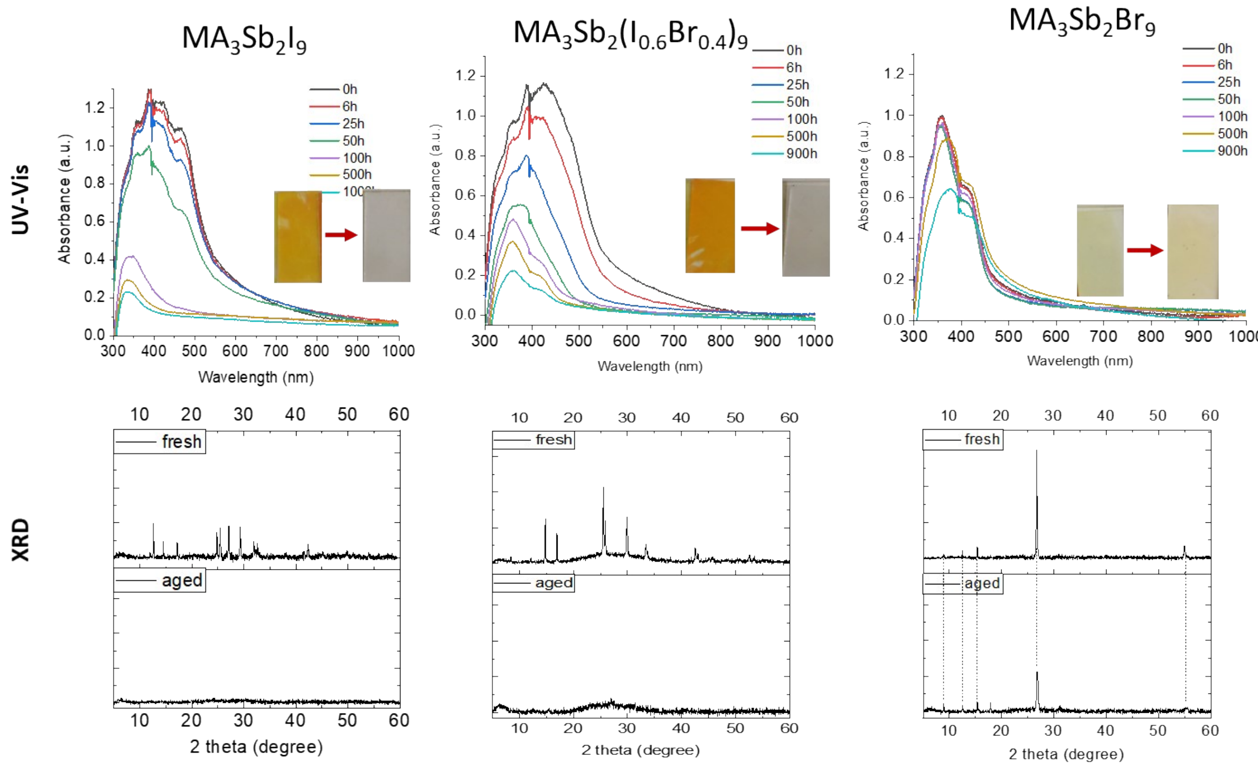

Figure S9. Change of UV-vis spectra(a) and XRD patern(b) of Sb-rich systems.