Electronic Supplementary Material (ESI) for Dalton Transactions.

Structural distortion induced broad emission in vacancy-ordered halide triple perovskites

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Electronic Supplementary Information

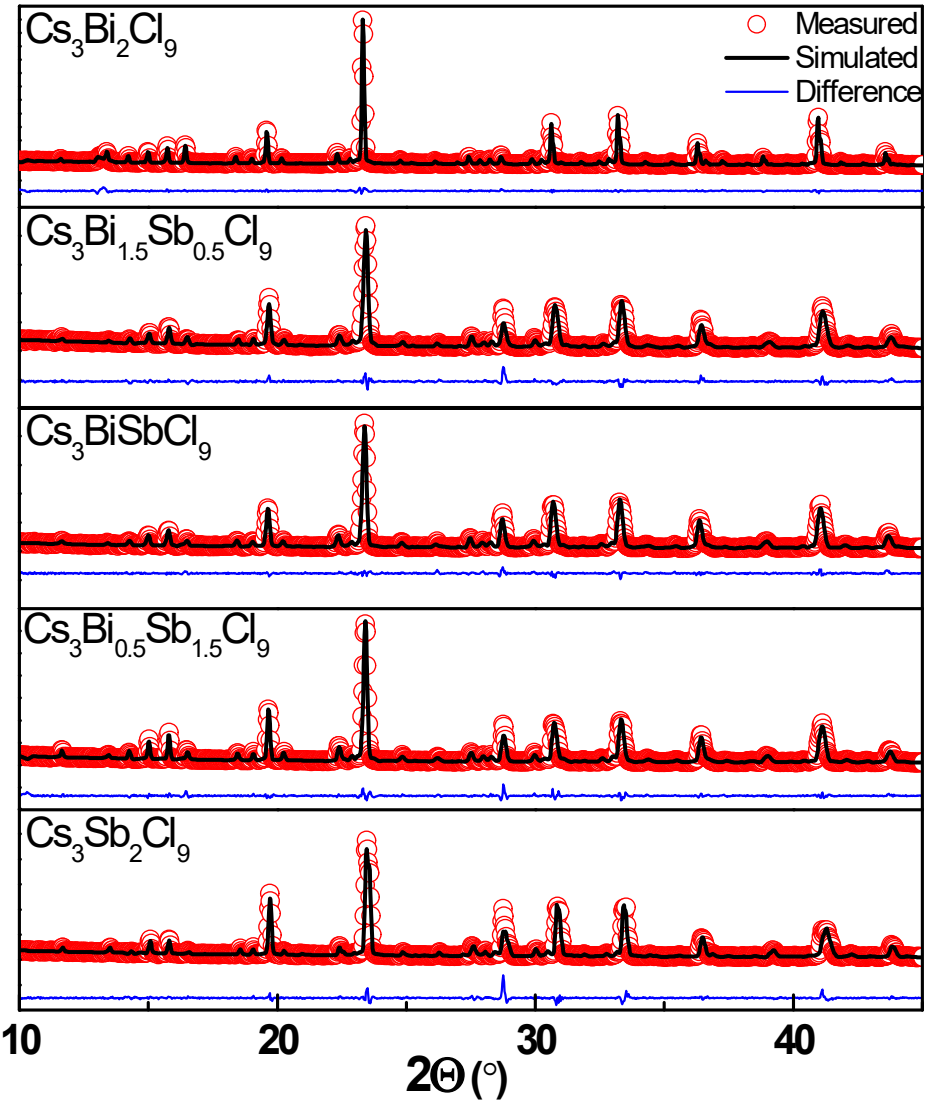

Figure S1. Rietveld refinement plots of $Cs_3M_2Cl_9$ powders

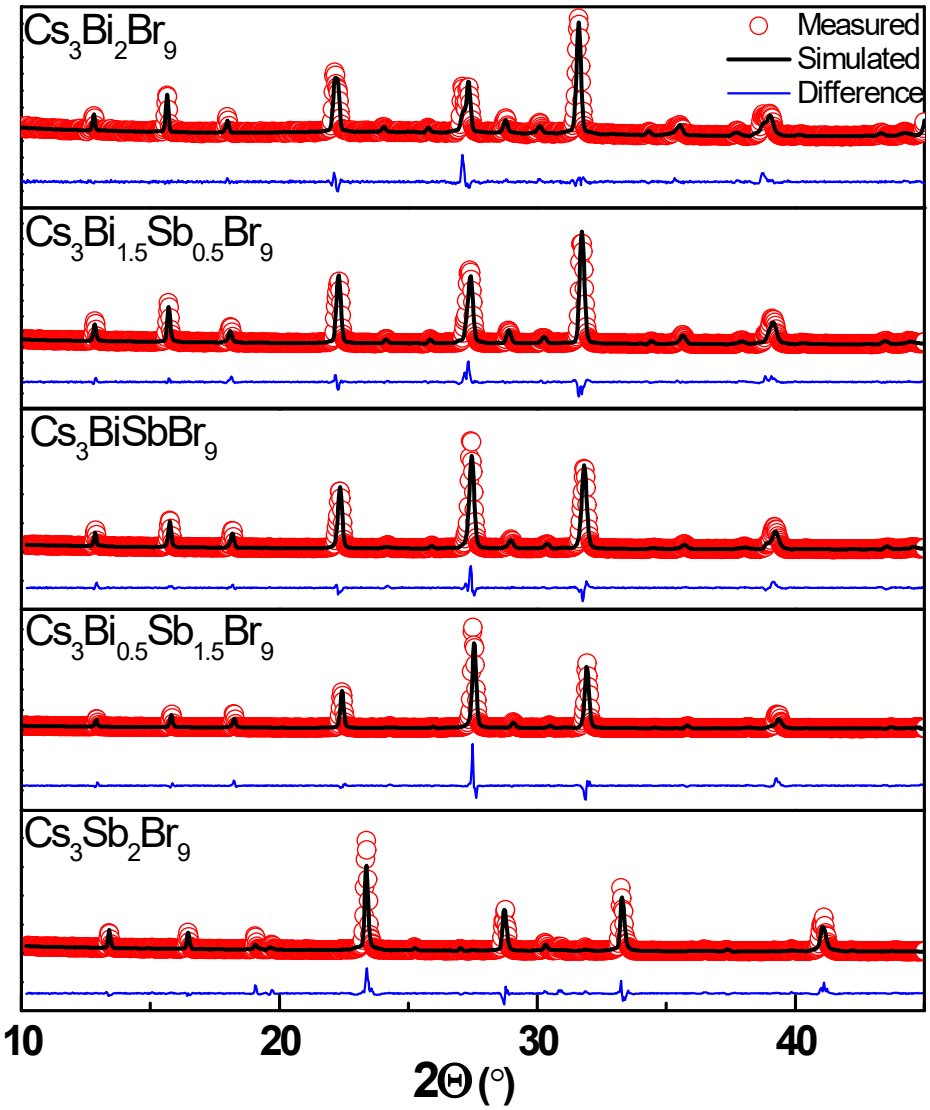

Figure S2. Rietveld refinement plots of $Cs_3M_2Br_9$ powders

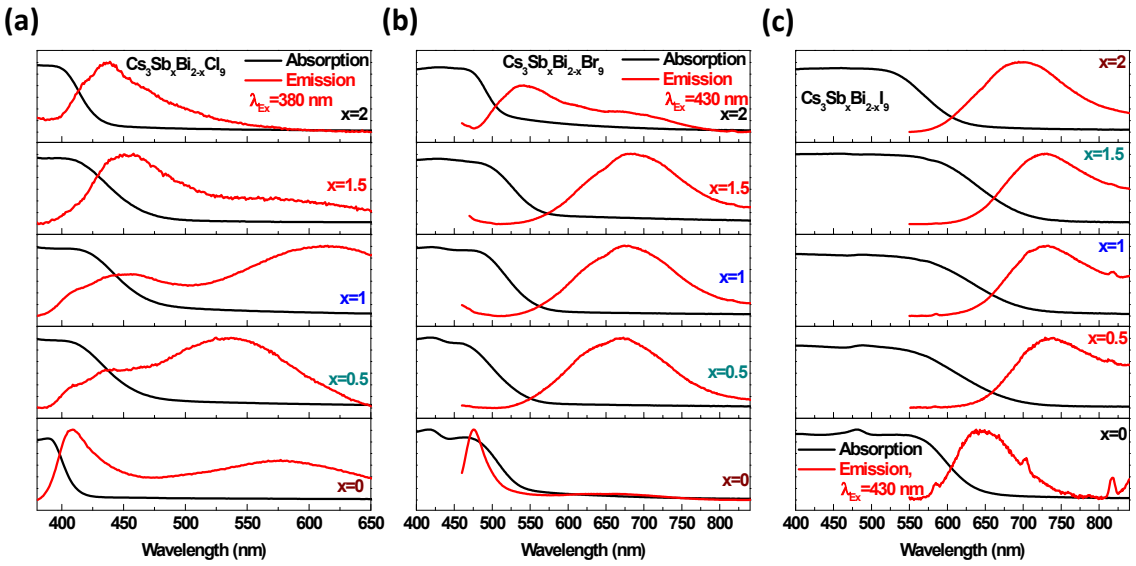

Figure S3. Comparison of absorption and emission spectra of (a) $Cs_3M_2Cl_9$ (b) $Cs_3M_2Br_9$ and (c) $Cs_3M_2I_9$ samples at different wavelengths (M = Sb and Bi).

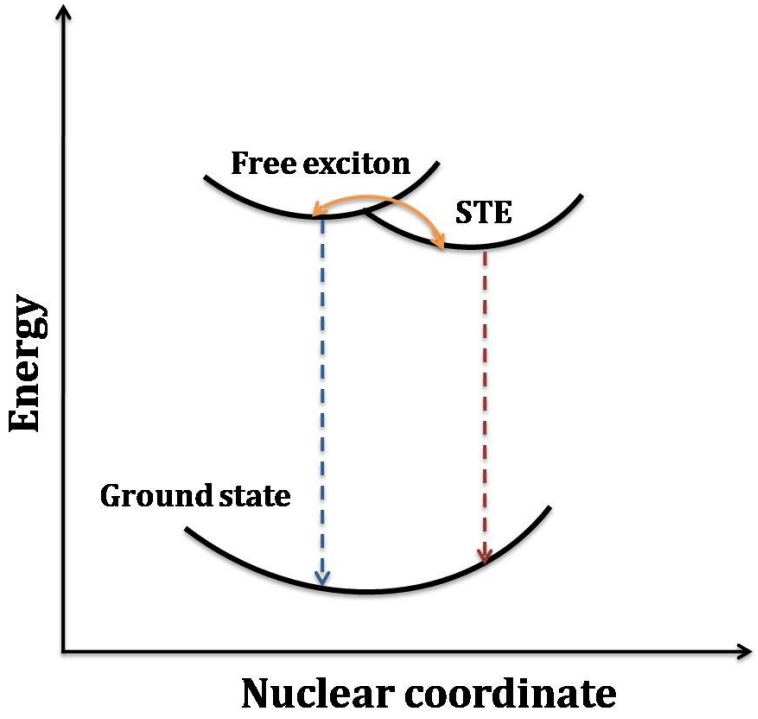

Figure S4. Schematic representation of STE

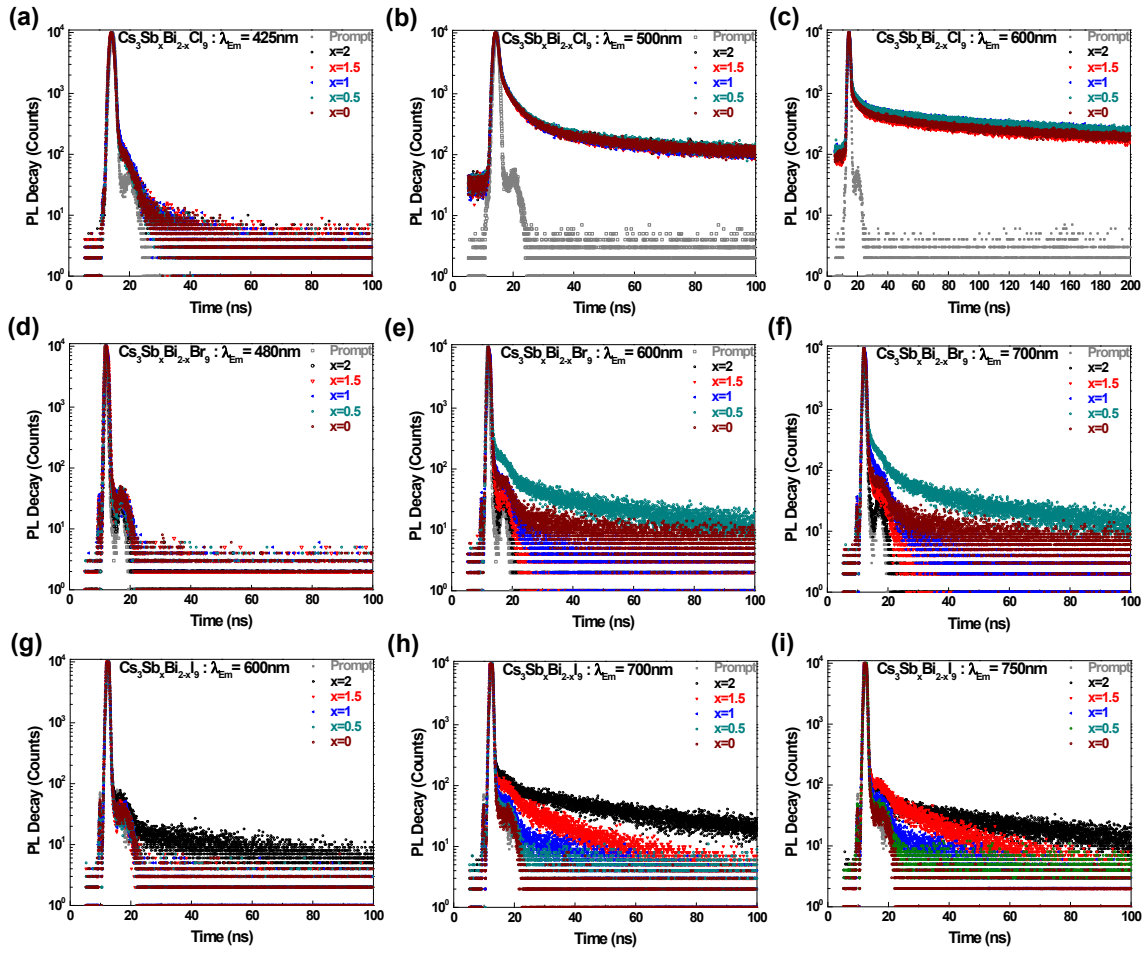

Figure S5. Time resolved PL spectra of (a-c) $Cs_3M_2Cl_9$ (d-f) $Cs_3M_2Br_9$ and (f-g) $Cs_3M_2I_9$ samples at different wavelengths (M=Sb and Bi).

Table S1. Lattice parameters and other fit data for various vacancy-ordered halide triple perovskites.

	a	b	c		α	β	γ	χ^2
$Cs_3Sb_xBi_{2-x}Br_9$								
x=0	7.986	7.986	9.867		90	90	120	3.11
x=0.5	7.959	7.959	9.804		90	90	120	5.64
x=1	7.949	7.949	9.759		90	90	120	5.41
x=1.5	7.925	7.925	9.727		90	90	120	10.3
x=2	7.618	7.618	9.303		90	90	120	8.81
$Cs_3Sb_xBi_{2-x}Cl_9$								
x=0	18.669	7.633	13.209		90	90	90	2.14
x=0.5	18.612	7.620	13.105		90	90	90	2.23
x=1	18.643	7.635	13.144		90	90	90	1.79
x=1.5	18.610	7.624	13.130		90	90	90	2.96
x=2	18.624	7.582	13.052		90	90	90	3.01

References for crystal structure data shown in Figure 1 of main content.

Crystallographic Information File (CIF) for all $Cs_3M_2X_9$compounds, where bond length is taken from those CIF files.

Spring materials: https://materials.springer.com/

Material	Dataset ID	Reference link
$Cs_3Sb_2Cl_9$	sd_1938701	https://materials.springer.com/isp/crystallographic/docs/sd_1938701
$Cs_3Sb_2Br_9$	sd_0551881	https://materials.springer.com/isp/crystallographic/docs/sd_0551881
$Cs_3Sb_2I_9$	sd_1200175	https://materials.springer.com/isp/crystallographic/docs/sd_1200175

Crystallography open database: http://www.crystallography.net/cod/index.php

Material	COD ID	Reference link
$Cs_3Bi_2Cl_9$	8000483	http://www.crystallography.net/cod/8000483.html
$Cs_3Bi_2Br_9$	2106377	http://www.crystallography.net/cod/2106376.html
$Cs_3Bi_2I_9$	2106275	http://www.crystallography.net/cod/2106275.html

Spring materials: https://materials.springer.com/

Material	Dataset ID	Reference paper
$Cs_3Sb_2Cl_9$	sd_1938701	Kihara K., Sudo T.: *Two structure types of cesium antimony nonachloride, $Cs_3Sb_2Cl_9$*. Zeitschrift für Kristallographie,Kristallgeometrie, Kristallphysik, Kristallchemie 134 (1971) 155-158
$Cs_3Sb_2Br_9$	sd_0551881	Kun S.V., Lazarev V.B., Peresh E.Y., Kun S.V., Voroshilov Y.V.: *Phase equilibria in RbBr-Sb(Bi)Br3 systems and type crystal structure of compounds of $A(I)_3B(V)_2C(VI)_9$ type (A(I)= Rb, Cs; B(V)= Sb, Bi; C(VII)= Br, I)*. Inorganic Materials (translated from NeorganicheskieMaterialy) 29 (1993) 445-450
$Cs_3Sb_2I_9$	sd_1200175	Ho D., Riley W.C., Jacobson R.A.: *The crystal and molecular structure of $Cs_3Sb_2I_9$*. Crystal Structure Communications 7 (1978) 111-114

Crystallography open database: http://www.crystallography.net/cod/index.php

Material	COD ID	Reference paper
$Cs_3Bi_2Cl_9$	8000483	Tailor, Naveen Kumar; Maity, Partha; Saidaminov, Makhsud I.; Pradhan, Narayan; Satapathi, Soumitra. *Dark Self-Healing-Mediated Negative Photoconductivity of a Lead-Free $Cs_3Bi_2Cl_9$ Perovskite Single Crystal*. The journal of physical chemistry letters, 2021, 12, 2286-2292
$Cs_3Bi_2Br_9$	2106377	Lazarini, F. *Cesiumenneabromodibismuthate(III)* Acta Crystallographica B (24,1968-38,1982), 1977, 33, 2961-2964
$Cs_3Bi_2I_9$	2106275	Chabot, B.; Parthe, E. *$Cs_3Sb_2I_9$ and $Cs_3Bi_2I_9$ with the hexagonal Cs3Cr2Cl9 structure type.* Acta Crystallographica B (24,1968-38,1982), 1978, 34, 645-648