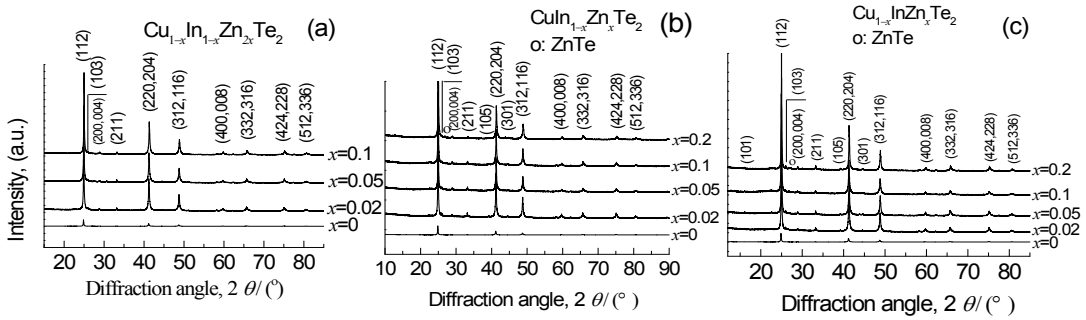


Supplementary Figure 1 X–ray diffraction patterns of the powders (a) $Cu_{1-x}In_{1-x}Zn_{2x}Se_2$, and (b) $CuIn_{1-x}Zn_xSe_2$, (c) $Cu_{1-x}InZn_xSe_2$

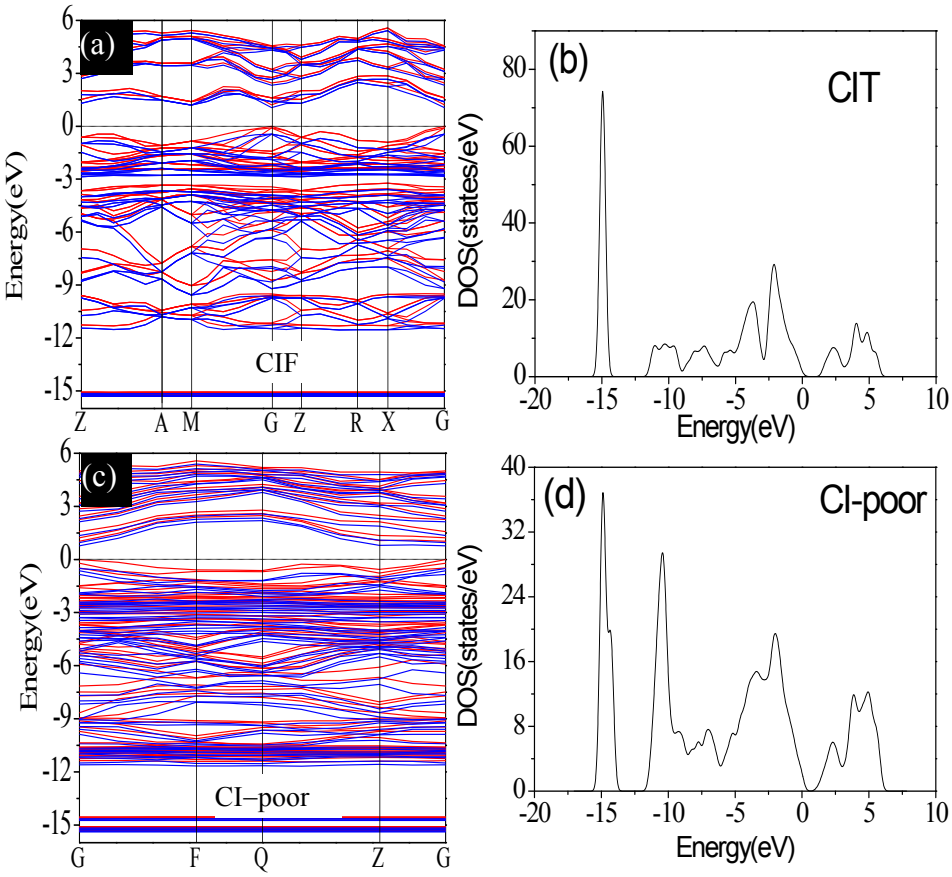


Fig.S2 Calculated band structures and DOS (a) intrinsic $CuInTe_2$ (CIT); (b) DOS of CIT, (c) Zn substitutions for Cu and In simultaneously (CI–poor); (d) DOS of CI–poor.

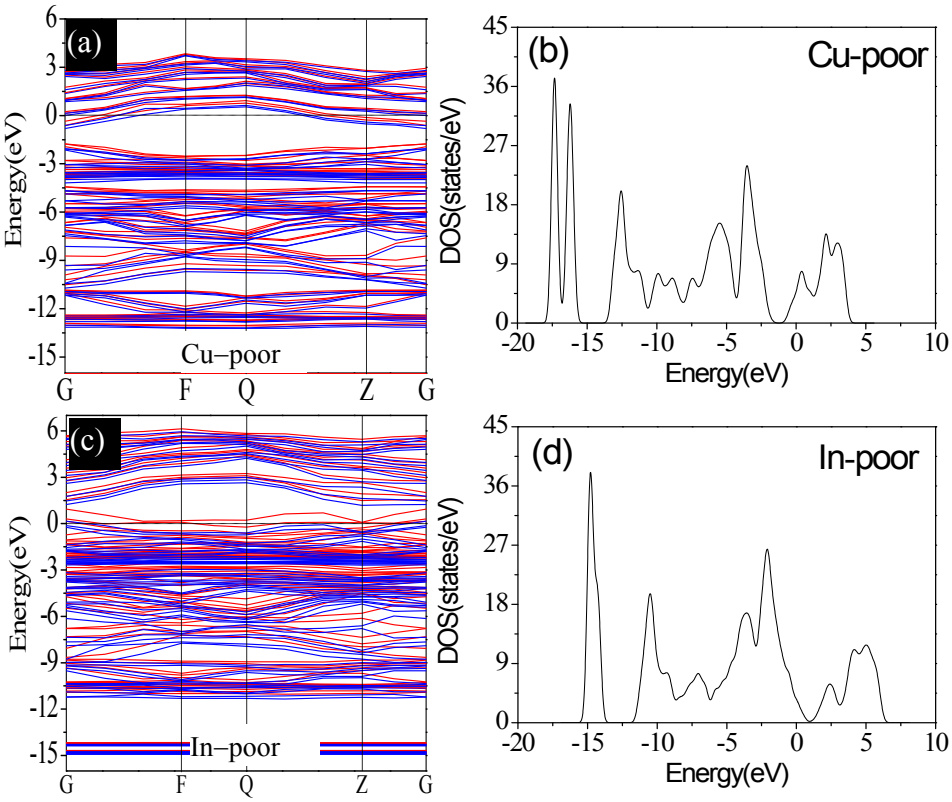
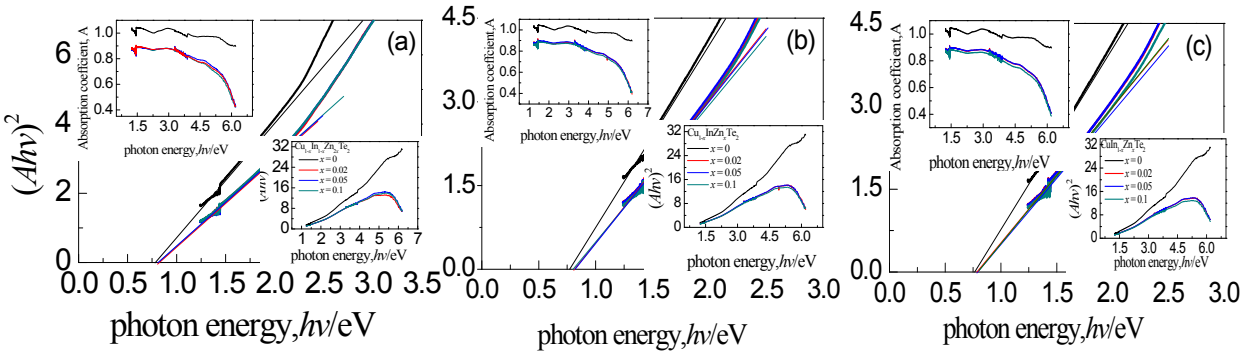
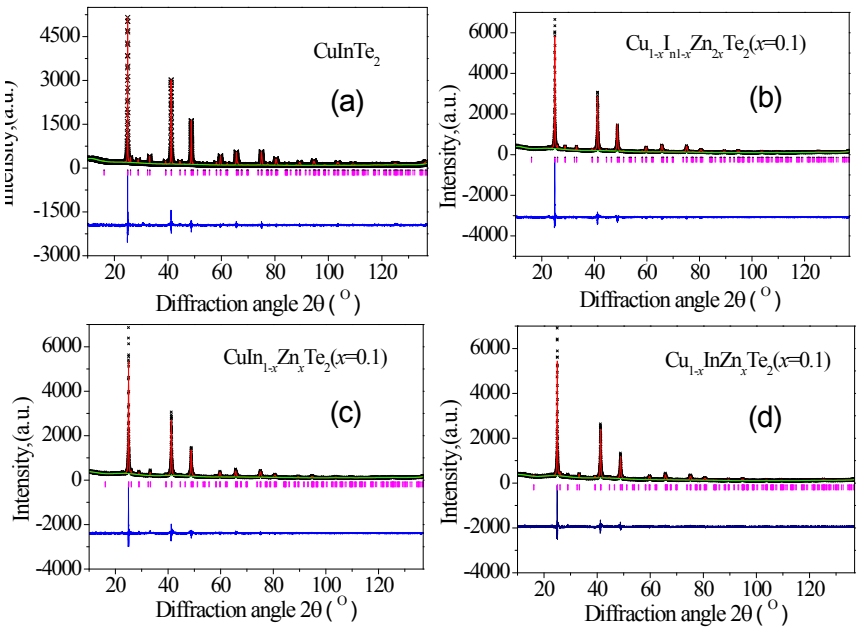


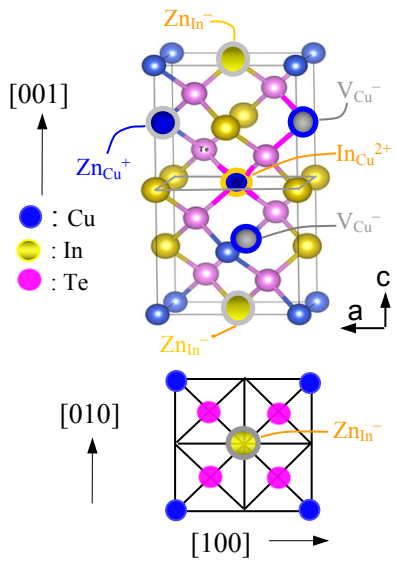
Fig.S3 Calculated band structures and DOS (a) Zn substitution for Cu (Cu–poor); (d) DOS of Cu–poor; (c) Zn substitution for In (In–poor); (d) DOS of In–poor.



Supplementary Figure 4 Experimentally determined bandgap E_g: (a) $Cu_{1-x}In_{1-x}Zn_{2x}Se_2$, and (b) $Cu_{1-x}InZn_xSe_2$, (c) $CuIn_{1-x}Zn_xSe_2$. An upper left insert is the absorption coefficient spectra A ($h\nu$), A is the absorption coefficient, $h\nu$ is the photon energy, and low right insert is the full relations of $(Ah\nu)^2 = (h\nu - E_g)$.



Supplementary Figure 5 Rietveld refinement using X-ray diffraction data for (a) CIT, (b) CI–poor, (c) In–poor, and (d) Cu–poor with x = 0.1. Observed (×××) and calculated (solid line) X-ray powder diffraction patterns are shown.



Supplementary Figure 6 The schematic model of the single cell upon creations of multiple defects in $CuInTe_2$ chalcopyrite.

Table SI Structural parameters and refinement details for CI–poor compounds ($Cu_{1-x}In_{1-x}Zn_{2x}Te_2$) obtained by Rietveld refinements

Parameters	x=0.02		x=0.05		x=0.1
	Model A	Model B	Model A	Model B	Model A
			Cation 4*a*		
SOF(Cu)	1.0470	0.9800	1.0673	0.9500	0.9227
SOF(In)	–0.0008	0.0678	0.0070	0.1664	–0.0003
SOF(Zn)	0.0204	–0.0478	0.0496	–0.1164	0.0996
100Uiso (Å ^{2})	1.8580	1.8770	1.3270	1.3480	1.0030
			Cation 4*b*		
SOF(In)	0.9665	0.9141	0.9123	0.9175	0.8248
SOF(Cu)	–0.0046	0.0000	0.0003	0.0000	–0.0021
SOF(Zn)	0.0200	0.0859	0.0500	0.0825	0.0980
100Uiso (Å ^{2})	1.2620	1.2620	1.4510	1.4580	2.3280
			Anion 8*d*		
SOF(Te)	1.0682	0.9873	0.9797	1.0025	1.0000
100Uiso (Å ^{2})	2.3610	2.2143	2.4320	2.4350	2.1580
x_{Te}	0.2268	0.2268	0.2305	0.2304	0.2246
			Reliability factors		
χ^2	1.487	1.493	1.614	1.614	1.880
WRp	0.0898	0.0900	0.0870	0.0870	0.0966
Rp	0.0691	0.0694	0.0679	0.0679	0.0737

Table SII Structural parameters and refinement details for Cu–poor compounds ($Cu_{1-x}In\ Zn_xTe_2$) obtained by Rietveld refinements

Parameters	x=0.02		x=0.05		x=0.1
	Model A	Model B	Model A	Model B	Model A
			Cation 4*a*		
SOF(Cu)	1.0536	0.9800	1.0309	0.9500	0.9029
SOF(In)	0.0004	0.1242	0.0007	0.1389	0.0012
SOF(Zn)	0.0197	–0.1042	0.0499	–0.0889	0.1875
100Uiso (Å ^{2})	1.1820	1.2250	1.1190	1.1680	1.3490
			Cation 4*b*		
SOF(In)	0.9759	0.9605	0.9618	0.9280	0.9517
SOF(Cu)	–0.0003	0.0000	–0.0007	0.0000	0.0007
SOF(Zn)	0.0001	0.0395	0.0000	0.0720	0.0010
100Uiso (Å ^{2})	1.4520	2.4400	1.3060	2.2720	1.6590
			Anion 8*d*		
SOF(Te)	0.9962	1.0054	0.9964	1.0100	0.9970
100Uiso (Å ^{2})	1.8930	2.0450	2.1240	2.2980	1.9890
x_{Te}	0.2298	0.2294	0.2296	0.2297	0.2299
			Reliability factors		
χ^2	1.7450	1.7520	1.6180	1.6130	1.6430
WRp	0.0917	0.0919	0.0896	0.0894	0.0891
Rp	0.0701	0.0703	0.0694	0.0692	0.0691

Table SIII Structural parameters and refinement details for In–poor compounds ($CuIn_{1-x}Zn_xTe_2$) obtained by Rietveld refinements

Parameters	x=0.02		x=0.05		x=0.1
	Model A	Model B	Model A	Model B	Model A
Cation 4*a*					
SOF(Cu)	1.0592	1.0000	1.0959	1.0000	1.0746
SOF(In)	0.0001	0.0947	0.0003	0.1299	–0.0002
SOF(Zn)	–0.0001	–0.0947	–0.0003	–0.1299	0.0000
100Uiso (Å ^{2})	1.1180	1.1390	1.0990	1.1480	1.0090
Cation 4*b*					
SOF(In)	0.9509	0.9443	0.9223	0.9313	0.9004
SOF(Cu)	–0.0002	0.0000	–0.0005	0.0000	0.0002
SOF(Zn)	0.0200	0.0557	0.0501	0.0687	0.0989
100Uiso (Å ^{2})	1.3550	2.3140	1.2230	2.0687	1.8290
Anion 8*d*					
SOF(Te)	0.9863	1.0043	0.9816	1.0010	0.9994
100Uiso (Å ^{2})	2.0890	2.0690	1.9250	1.9220	2.1030
x_{Te}	0.2279	0.2279	0.2277	0.2277	0.2271
Reliability factors					
χ^2	1.7240	1.6930	1.6970	1.7590	1.8740
WRp	0.0942	0.0934	0.0918	0.0935	0.0975
Rp	0.0730	0.0723	0.0708	0.0720	0.0752