Supporting Information

Strong Infrared NLO Tellurides with Multifunction: $CsX^{II}_4In_5Te_{12}$ (X^{II} = Mn, Zn, Cd)

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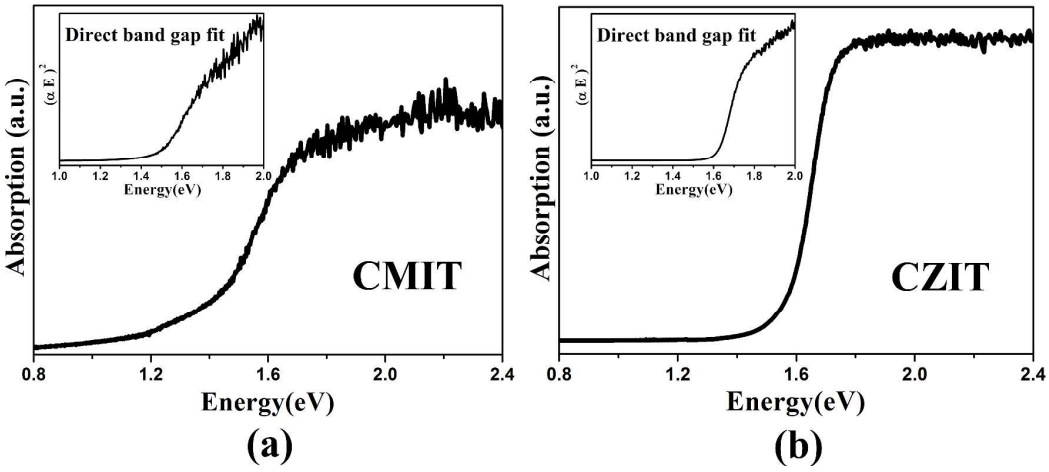

Figure S1. UV-Vis diffuse-reflectance spectrum of (a) **CMIT**, and (b) **CZIT** (inset: direct band gap fit based on the theoretical calculations).

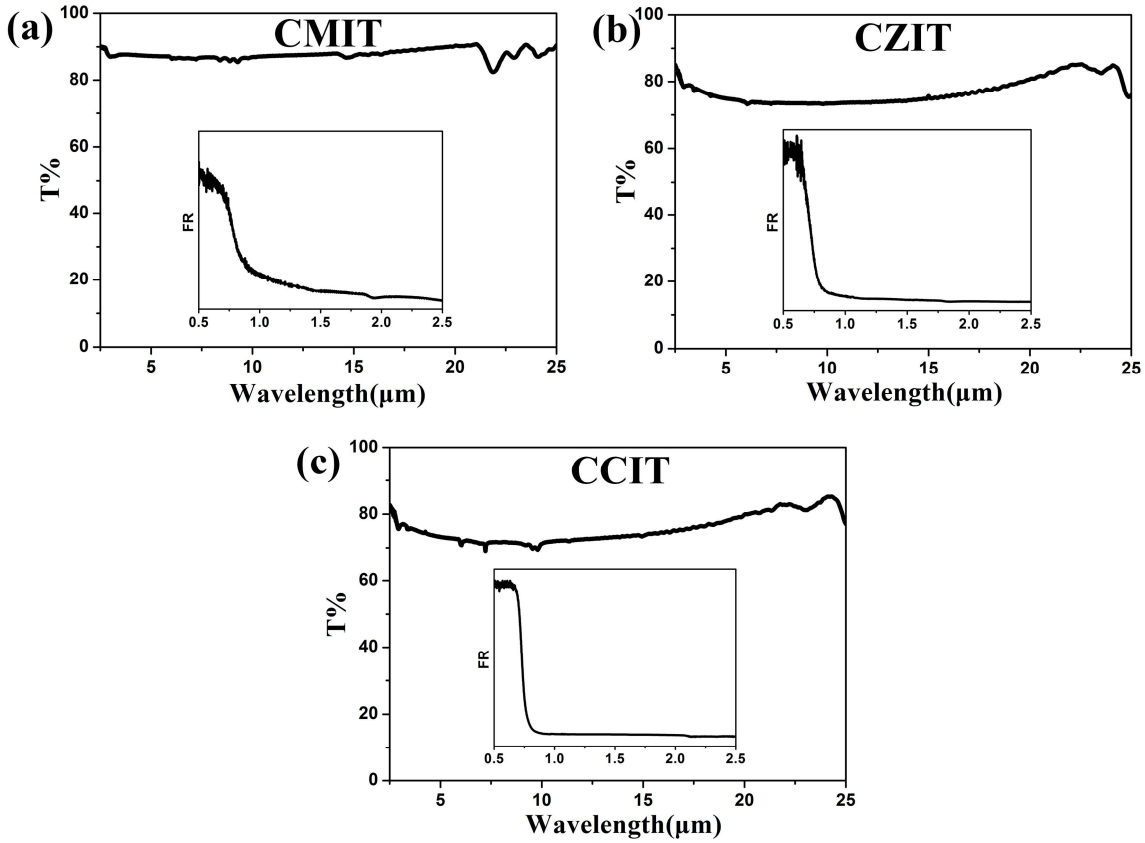

Figure S2. Reflection spectra and FT-IR spectra of (a) **CMIT**, (b) **CZIT** and (c) **CCIT**.

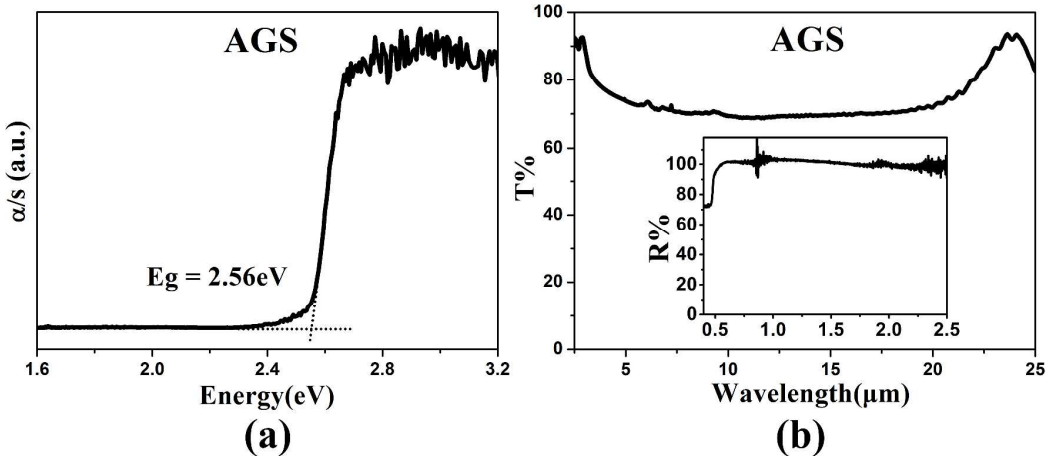

Figure S3. (a) Diffuse reflection spectra and (b) Reflection spectra and FT-IR spectra of $AgGaS_2$ (**AGS**).

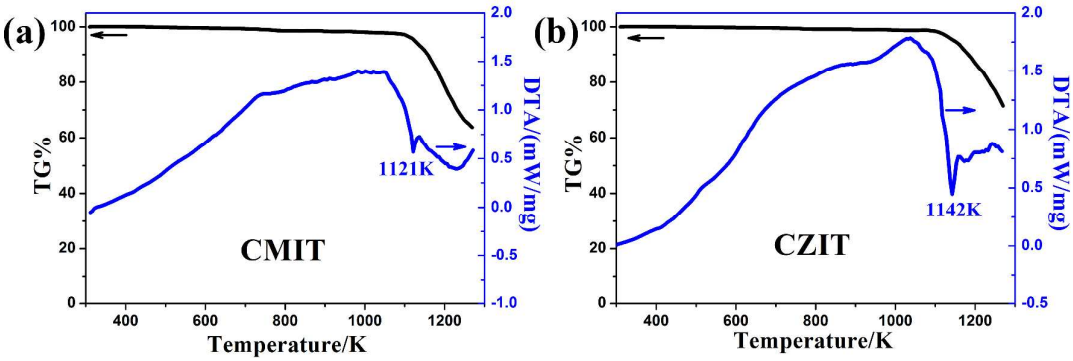

Figure S4. TG (black) and DTA (blue) diagrams of (a) **CMIT**, and (b) **CZIT**.

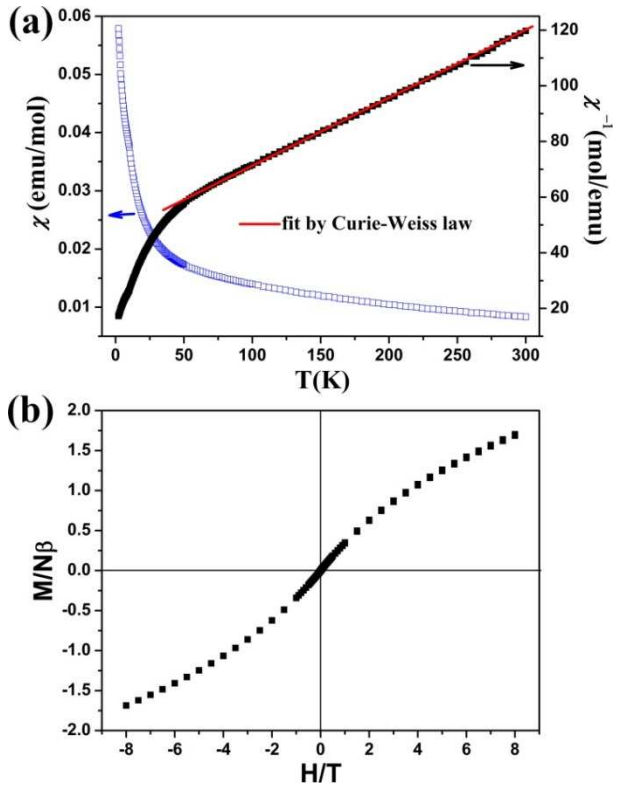

Figure S5. (a) Temperature dependence of the molar magnetic susceptibility (χ; blue) and the inverse molar magnetic susceptibility (χ^{-1}; black) for **CMIT** in a magnetic field of 1000 Oe. The Curie–Weiss fit of the data above 50 K gives C = 4.28 emu K/mol and θ= – 196.42 K. The effective magnetic moment ($\mu_{eff} \approx 5.85\ \mu_B$ /Mn^{II} for **CMIT**) obtained according to the equation $\mu_{eff} = (7.997C)^{1/2}\mu_B$ deviates slightly from the theoretical value for a high-spin Mn^{2+} spin (5.92 μ_B /Mn^{II}). (b) Field dependence of magnetization of **CMIT** measured by cycling the field between +8 and −8 T at 2 K. A nonlinear behavior of M–H curve is observed and the magnetization increases to 1.75 Nβ without a saturation up to 8 T, which is much less than the common value of 20 Nβ for four Mn^{II} centers. Thus, **CMIT** suggests a spin-canted antiferromagnetic interaction between the magnetic ions below 50K.

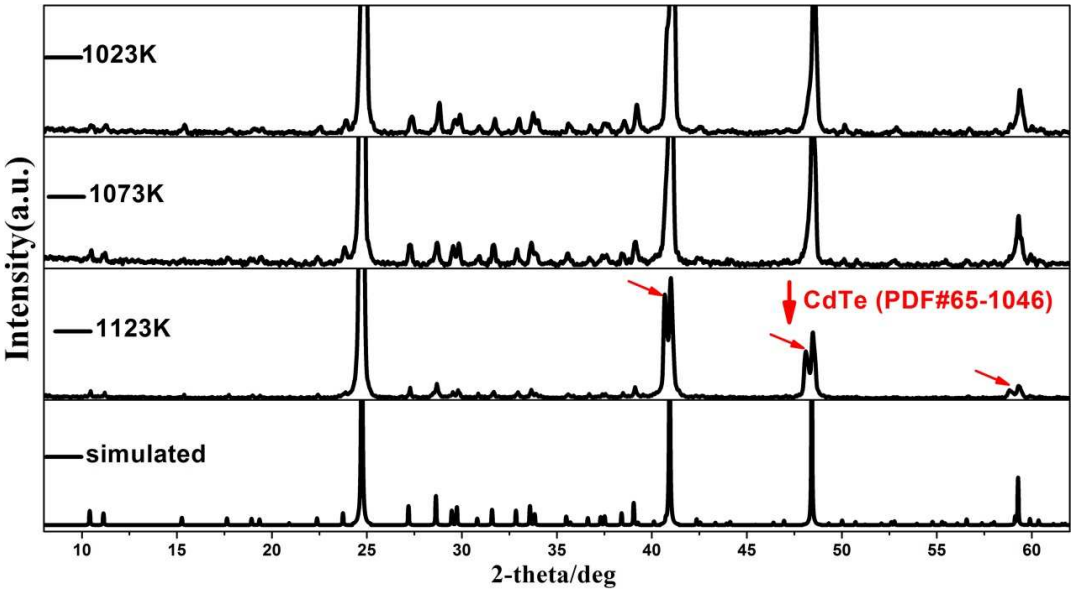

Figure S6. The PXRD patterns of sample of **CCIT** heated at various temperatures and the simulated one (special symbols indicate the decomposed product). The samples heated at 1023 and 1073K were still single phased **CCIT**; that heated at 1123K contained minor binary CdTe (↓) as impurities.

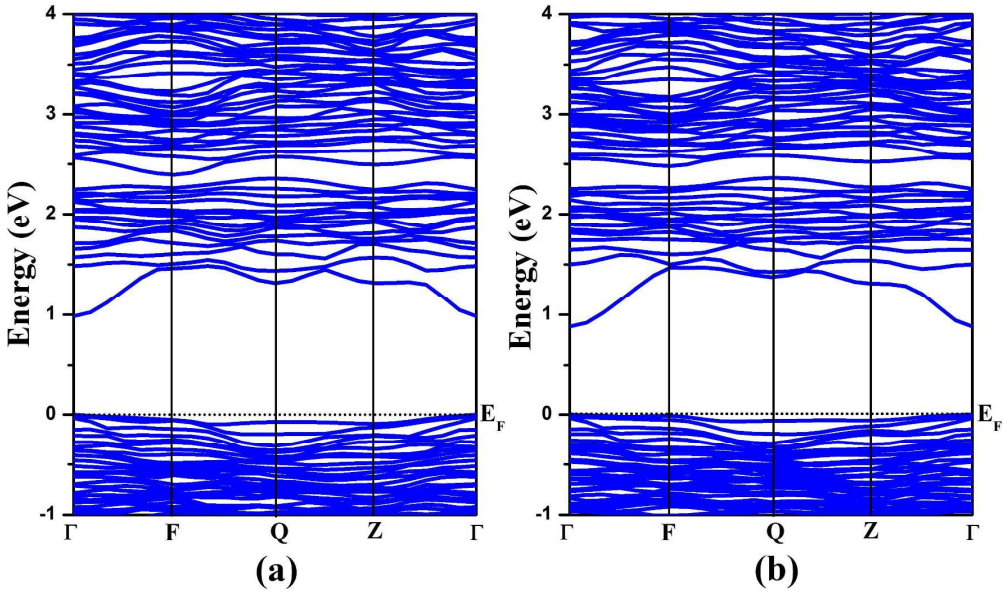

Figure S7. Calculated band structure of (a) **CZIT** and (b) **CCIT** (Γ (0, 0, 0); F (0, 1/2, 0); Q (0, 1/2, 1/2) and Z (0, 0, 1/2)), the Fermi level is set at 0.0 eV.

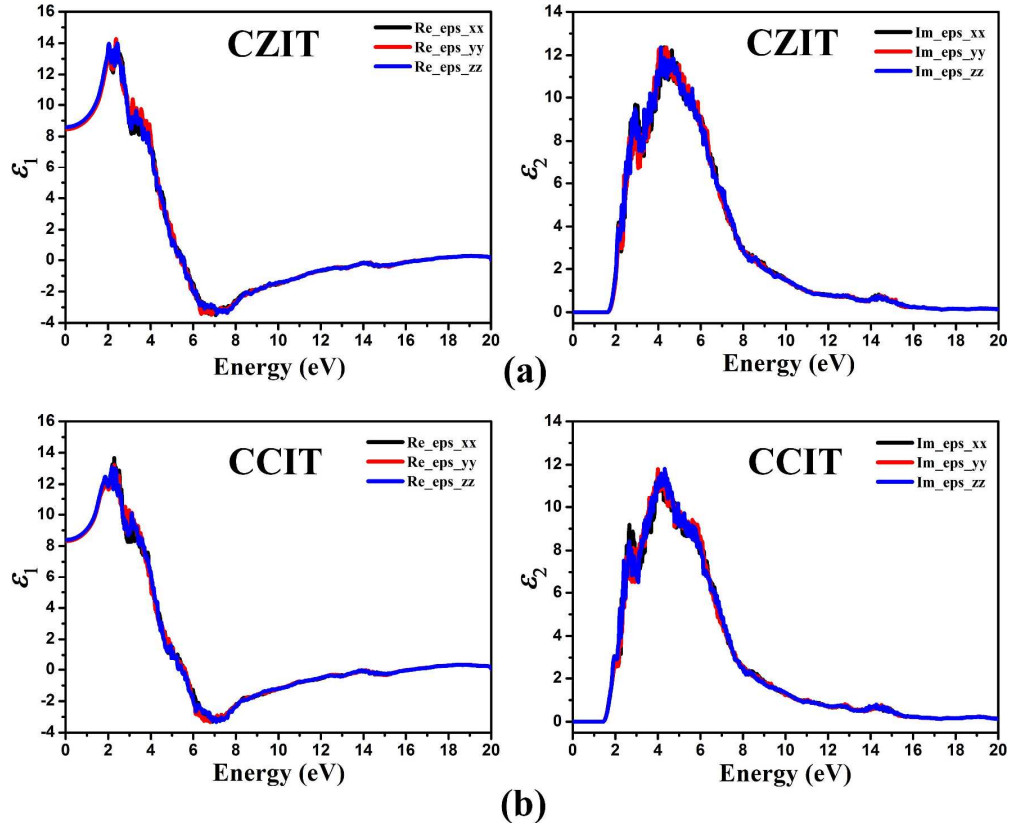

Figure S8. Energy dependences of the real part ε_1 and imaginary part ε_2 of (a) **CZIT** and (b) **CCIT**.

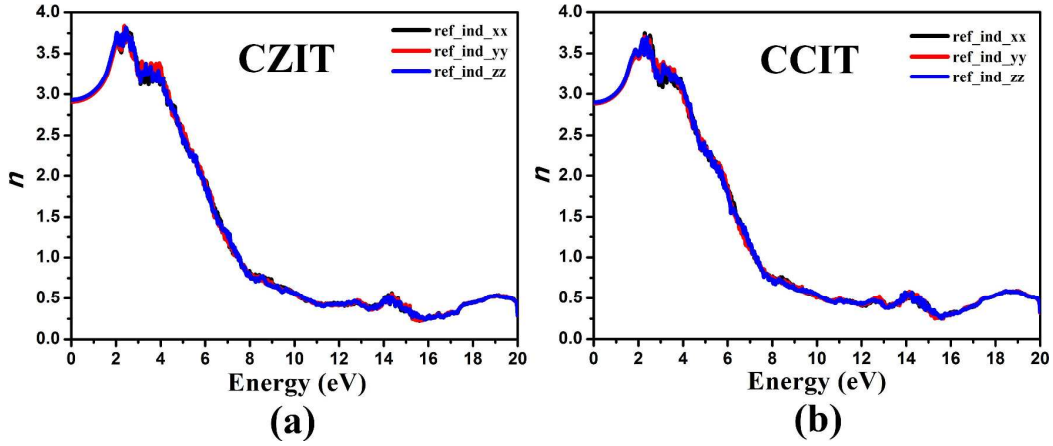

Figure S9. The calculated refractive index *n* of (a) **CZIT** and (b) **CCIT**.

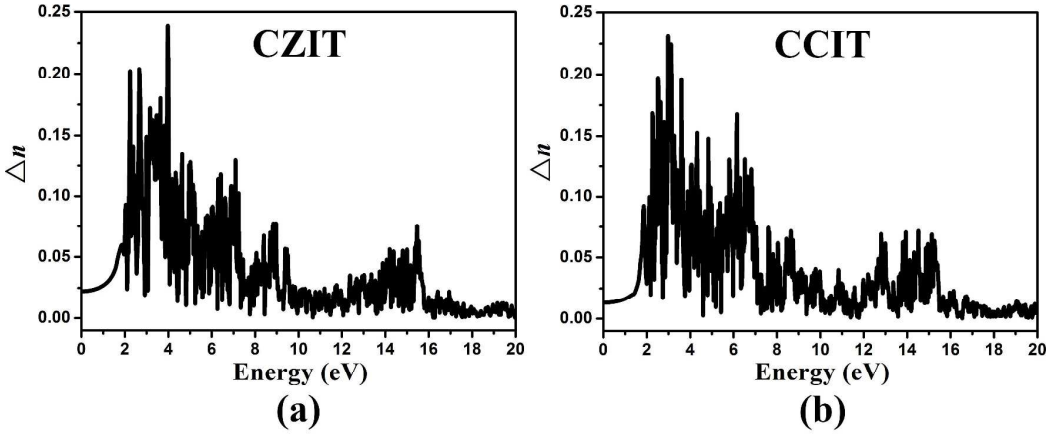

Figure S10. The calculated birefringence (△*n*) of (a) **CZIT** and (b) **CCIT**.

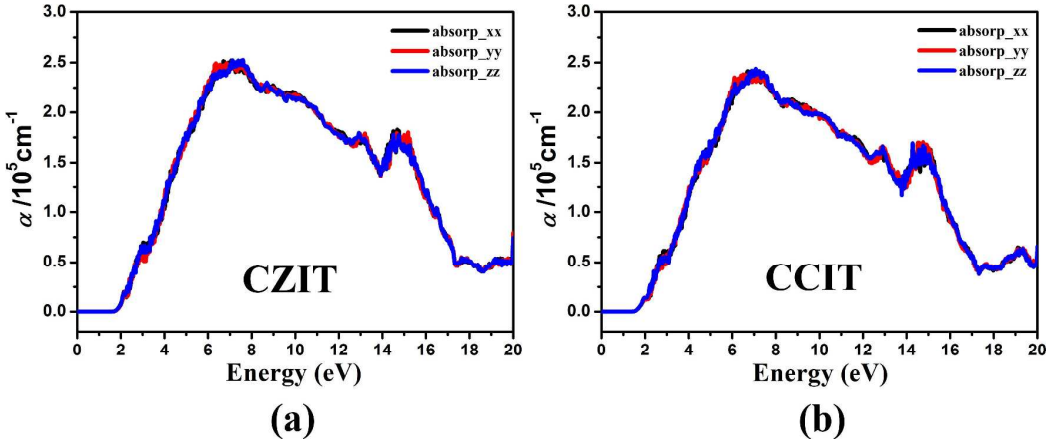

Figure S11. The calculated absorption coefficient α of (a) **CZIT** and (b) **CCIT**.

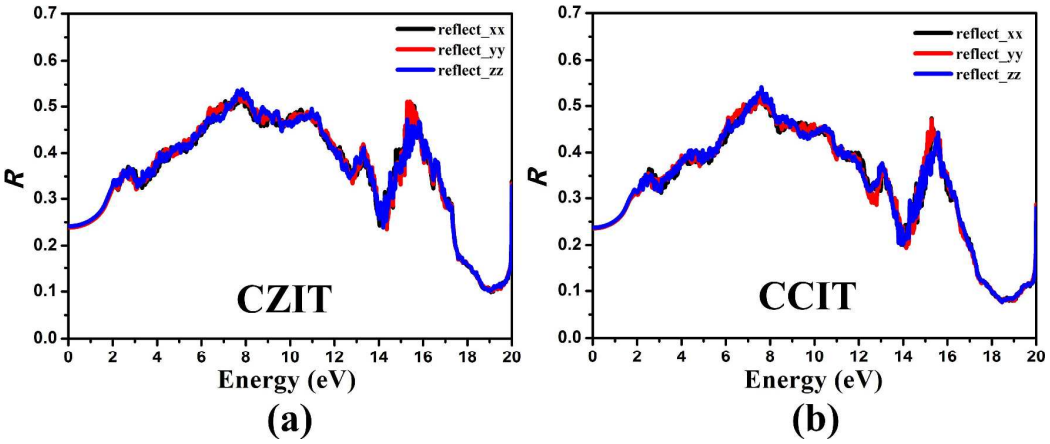

Figure S12. The calculated reflectivity *R* of (a) **CZIT** and (b) **CCIT**.

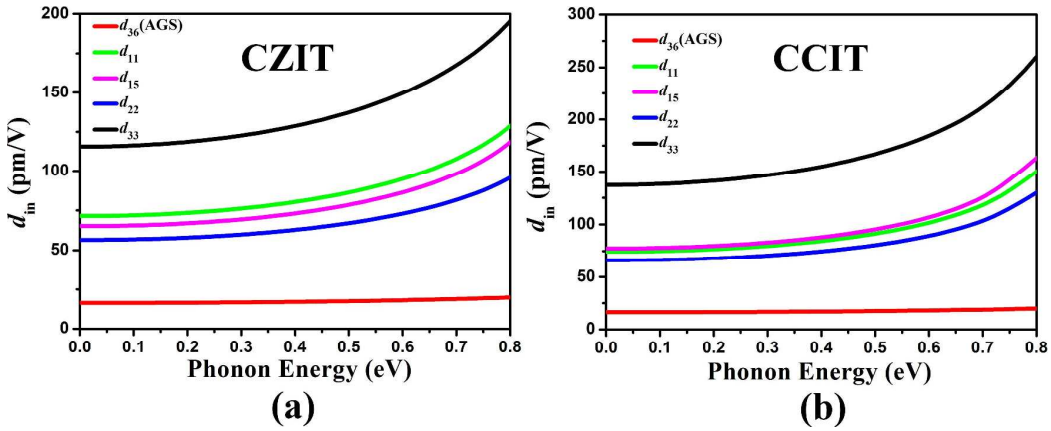

Figure S13. Calculated frequency-dependent SHG coefficients for (a) **CZIT** and (b) **CCIT**.

Supporting Information

Table S1. EDX results for **CCIT**.

Point-1				Point-2			
Element	Weight%	Atomic%	Formula	Element	Weight%	Atomic%	Formula
Cd L	16.93	18.39	4.10	Cd L	15.73	17.15	3.80
In L	21.66	23.04	5.13	In L	20.61	22.00	4.87
Te L	56.29	53.87	12	Te L	56.41	54.17	12
Cs L	5.12	4.70	1.05	Cs L	7.25	6.68	1.48
Total	100.00			Total	100.00		
Point-3				Point-4			
Element	Weight%	Atomic%	Formula	Element	Weight%	Atomic%	Formula
Cd L	17.35	18.83	4.21	Cd L	16.12	17.53	3.92
In L	21.69	23.05	5.15	In L	21.77	23.18	5.18
Te L	56.15	53.70	12	Te L	56.09	53.75	12
Cs L	4.81	4.42	0.99	Cs L	6.02	5.54	1.24
Total	100.00			Total	100.00		
Point-5							
Element	Weight%	Atomic%	Formula	Average formula: $Cs_{1.1(2)}Cd_{4.0(3)}In_{5.1(1)}Te_{12}$			
Cd L	16.99	18.45	4.10				
In L	21.97	23.35	5.19				
Te L	56.41	53.95	12				
Cs L	4.63	4.25	0.95				
Total	100.00						

Table S2. Atomic coordinates and equivalent isotropic displacement parameters of $CsX^{II}_4In_5Te_{12}$ (X^{II} = Mn, Zn and Cd).

Atom	Wyck.	x	y	z	U(eq)(Å^2)*	Occu.
			$CsMn_{4.0(3)}In_{5.0(3)}Te_{12}$			
Cs1	3*a*	0	0	0.9997(2)	0.0420(3)	1
M1=Mn1/In1	9*b*	0.17797(7)	0.12704(6)	0.4197(2)	0.0202(3)	0.60(2)/0.40(2)
M2=Mn2/In2	9*b*	0.43352(7)	0.02059(7)	0.07984(9)	0.0190(3)	0.48(3)/0.52(3)
M3=Mn3/In3	9*b*	0.36018(6)	0.25966(6)	0.07968(8)	0.0190(2)	0.25(3)/0.75(3)
Te1	9*b*	0.61688(5)	0.16877(5)	0.00954(7)	0.0183(2)	1
Te2	9*b*	0.21384(5)	0.29661(4)	0.00575(6)	0.0173(2)	1
Te3	9*b*	0.29281(5)	0.06761(5)	0.00279(6)	0.0171(2)	1
Te4	9*b*	0.05071(4)	0.17554(5)	0.31037(6)	0.0187(2)	1
			$CsZn_{4.0(3)}In_{5.0(3)}Te_{12}$			
Cs1	3*a*	0	0	0.0001(3)	0.0378(5)	1
M1=Zn1/In1	9*b*	0.17833(9)	0.12769(8)	0.4203(2)	0.0184(4)	0.53(2)/0.47(2)
M2=Zn2/In2	9*b*	0.4330(2)	0.0205(2)	0.0793(2)	0.0184(5)	0.48(3)/0.52(3)
M3=Zn3/In3	9*b*	0.3600(2)	0.25969(9)	0.0798(2)	0.0168(3)	0.32(3)/0.68(3)
Te1	9*b*	0.61586(8)	0.16689(8)	0.0085(2)	0.0191(3)	1
Te2	9*b*	0.21554(9)	0.29851(7)	0.0055(2)	0.0176(2)	1
Te3	9*b*	0.29443(8)	0.06821(8)	0.0016(2)	0.0179(3)	1
Te4	9*b*	0.05024(7)	0.17558(9)	0.31277(9)	0.0183(3)	1
			$CsCd_{4.0(3)}In_{5.0(3)}Te_{12}$			
Cs1	3*a*	0	0	0.0000(2)	0.0442(5)	1
M1=Cd1/In1	9*b*	0.17881(7)	0.12741(6)	0.4195(2)	0.0234(2)	0.36(2)/0.64(2)
M2=Cd2/In2	9*b*	0.43375(7)	0.02076(7)	0.08000(9)	0.0220(3)	0.49(3)/0.51(3)
M3=Cd3/In3	9*b*	0.36018(7)	0.26006(7)	0.0799(2)	0.0203(2)	0.48(3)/0.52(3)
Te1	9*b*	0.61835(6)	0.17120(7)	0.01067(8)	0.0191(2)	1
Te2	9*b*	0.21253(7)	0.29440(6)	0.00609(8)	0.0188(2)	1
Te3	9*b*	0.29146(7)	0.06718(6)	0.00432(8)	0.0185(2)	1
Te4	9*b*	0.05137(6)	0.17687(6)	0.30613(9)	0.0192(2)	1

*U(eq) is defined as one-third of the trace of the orthogonalized Uij tensor.

Table S3. Selected bond lengths (Å) of $CsX^{II}_4In_5Te_{12}$ (X^{II} = Mn, Zn and Cd).

	CMIT	**CZIT**	**CCIT**
M1–Te4	2.742(2)	2.707(2)	2.793(2)
M1–Te4	2.754(2)	2.716(2)	2.806(2)
M1–Te1	2.758(2)	2.706(2)	2.794(2)
M1–Te2	2.796(2)	2.738(2)	2.832(2)
M2–Te4	2.746(2)	2.700(2)	2.771(2)
M2–Te3	2.761(2)	2.719(2)	2.796(2)
M2–Te1	2.763(2)	2.718(2)	2.804(2)
M2–Te3	2.793(2)	2.739(2)	2.826(2)
M3–Te1	2.759(2)	2.724(2)	2.783(2)
M3–Te2	2.764(2)	2.724(2)	2.777(2)
M3–Te3	2.786(2)	2.754(2)	2.810(2)
M3–Te2	2.793(2)	2.753(2)	2.816(2)
Cs1–Te4×3	4.146(2)	4.114(3)	4.145(2)
Cs1–Te1×3	4.164(2)	4.140(3)	4.168(2)
Cs1–Te2×3	4.181(2)	4.160(2)	4.181(8)
Cs1–Te3×3	4.188(2)	4.161(2)	4.199(2)