Electronic Supplementary Information

$AX^{II}_4X^{III}_5Te_{12}$ (A = Rb, Cs; X^{II} = Mn, Zn, Cd; X^{III} = Ga, In): quaternary semiconducting tellurides with very low thermal conductivities

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Experimental

Syntheses

All operations were carried out under an argon-filled glovebox. Reaction mixtures of X (X = Mn or Cd, 5N), Ga (5N), Te (5N) and ACl (A = Rb or Cs, 3N) in the molar ratio of 4/5/12/2 into fused-silica tubes under vacuum. These tubes were placed into the computer–controlled furnace and then heated to 1273K in 50h, kept at this temperature for 4 days, followed by slowly cooled at 4 K/h to 473K and then turned off the furnace. The raw products were washed with distilled water and then dried with ethanol. Title compounds were stable for more than six months in air. Analyses of title compounds by SEM/EDX (JSM6700F, FESEM) showed the presence of A, X, Ga and Te in the approximate ratio of 1:4:5:12, but no other element. The homogeneous target products were checked by the powder X-ray diffraction (PXRD) data using a

Rigaku DMAX 2500 diffractometer with Cu-K_α radiation (see Figure S1 in ESI).

The resulting pure phases of title compounds were ground into a fine powder and subsequently hot pressed around 773 K under a pressure of 100 MPa for 1 h. The obtained pellets had relative densities no less than 98% of the theoretical value.

Property Characterization

The solid-state optical absorption spectrum was performed at room temperature using a Perkin-Elmer Lambda 950 UV–Vis spectrophotometer. The thermal conductivity were measured by laser flash techniques with a Netzsch LFA 457 system and calculated using the formula $\kappa = D \times C_p \times d$, where D was the measured thermal diffusivity, C_p was the heat capacity estimated using the Dulong-Petit model ($C_p = 3nR$, where n is the number of atoms per formula unit and R is the gas constant) and d was the sample density.[1] The uncertainty of the thermal conductivity k is estimated to be within 5%, considering the uncertainties for D, C_p and d.

Single-Crystal X-ray diffraction (XRD)

Single-crystal XRD at room temperature was collected on a Mercury 70 CCD diffractometer with Mo Kα radiation. The absorption correction was done,[2] and structures were solved by direct methods and refined using the SHELX-97 software.[3] The structural refinement was performed in similar method as the $AX^{II}_4X^{III}_5Q_{12}$ compounds,[4] the three tetrahedral position are randomly

occupied by the X (X = Mn or Cd) and Ga atoms with refined occupancy of X:Ga = 4:5, which is consistent with the EDX analysis. The refinement data are listed in Tables S1–4.

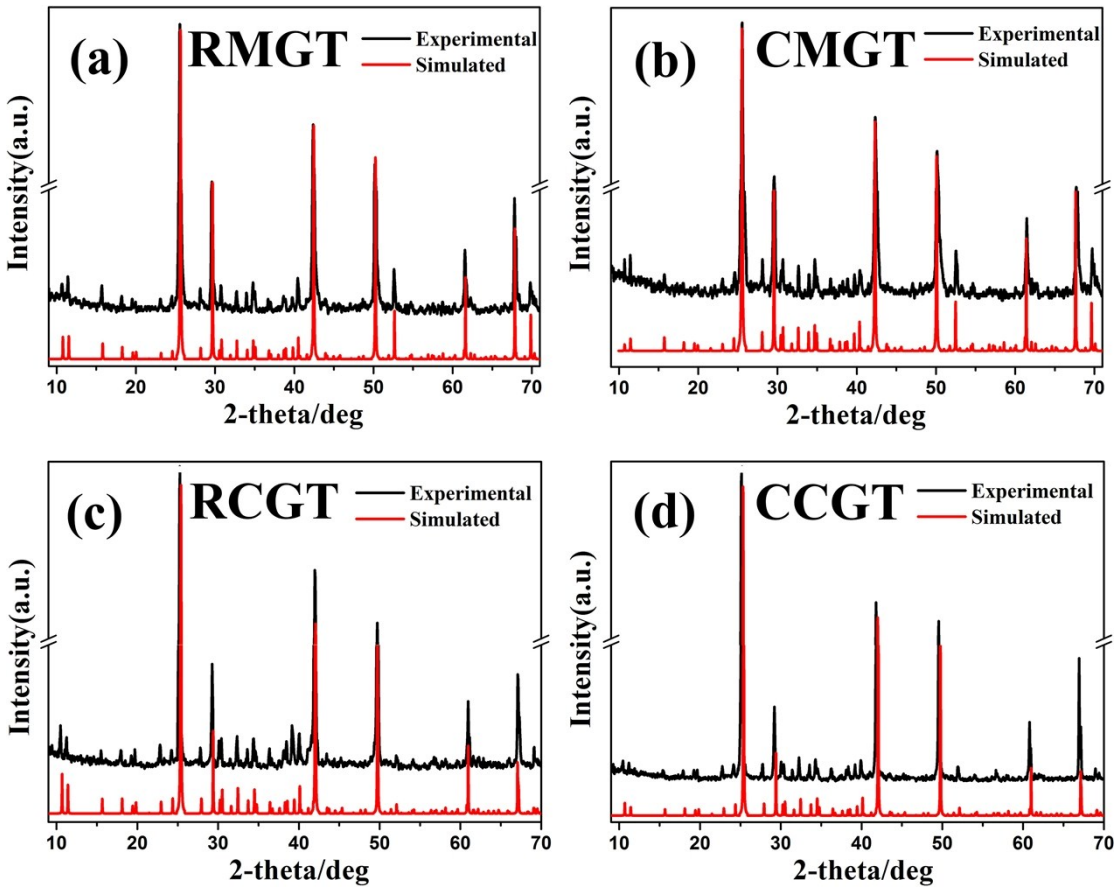

Figure S1. Experimental (black) and simulated (red) X-ray powder diffraction patterns for (a) **RMGT**, (b) **CMGT**, (c) **RCGT**, and (d) **CCGT**.

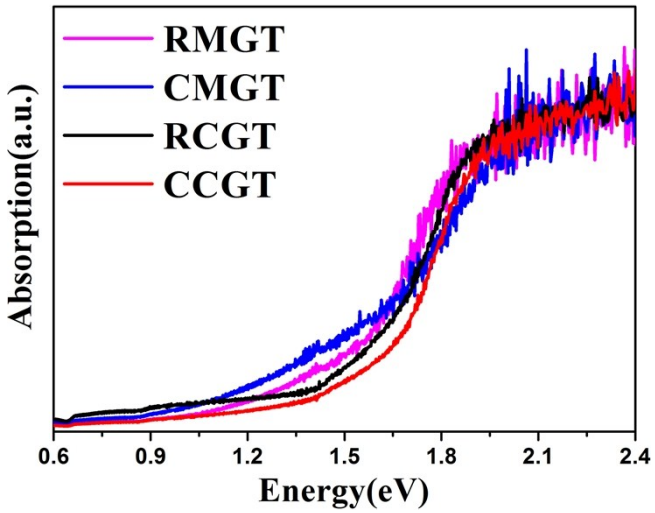

Figure S2. Diffuse reflection spectra of $AX_4Ga_5Te_{12}$ (A = Rb, Cs; X = Mn, Cd).

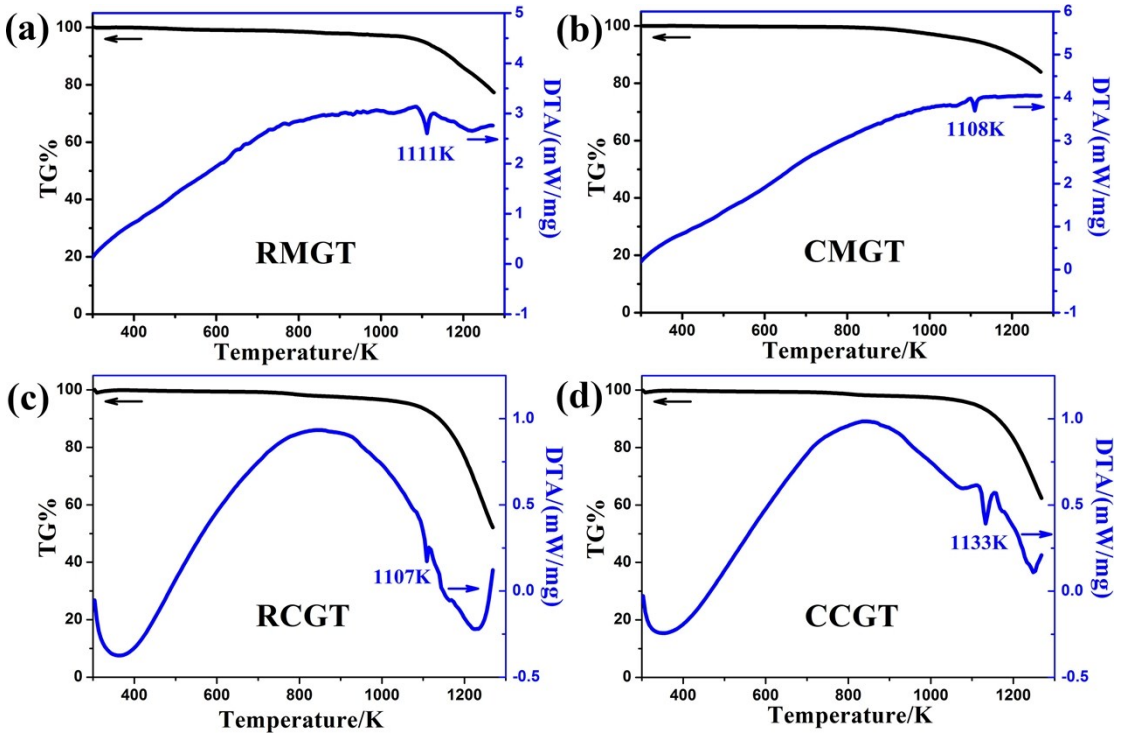

Figure S3. TG (black) and DTA (blue) diagrams of (a) **RMGT**, (b) **CMGT**, (c) **RCGT**, and (d) **CCGT**.

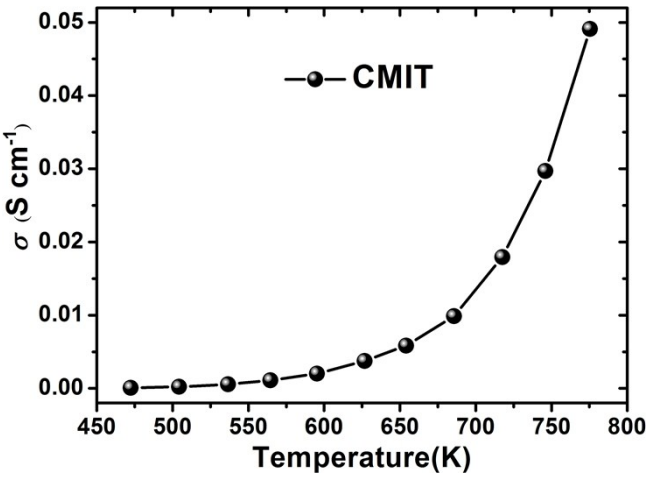

Figure S4. Electrical conductivity (σ) as a function of temperature for **CMIT** using a ULVAC-RIKO ZEM-3 instrument system at 473–773K.

Electronic Supplementary Information

Table S1. Crystallographic data and refinement details for $AX_4Ga_5Te_{12}$ (A = Rb, Cs; X = Mn, Cd).

	RMGT	**CMGT**	**RCGT**	**CCGT**
formula	$RbMn_4Ga_5Te_{12}$	$CsMn_4Ga_5Te_{12}$	$RbCd_4Ga_5Te_{12}$	$CsCd_4Ga_5Te_{12}$
fw	2185.03	2232.47	2414.87	2462.31
crystal system	trigonal	trigonal	trigonal	trigonal
crystal color	black	black	black	black
space group	*R*3（no.146）	*R*3（no.146）	*R*3（no.146）	*R*3（no.146）
a (Å)	15.3432(6)	15.376(4)	15.439(8)	15.485(8)
c (Å)	10.4161(8)	10.441(4)	10.477(8)	10.507(14)
V (Å^3)	2123.6(2)	2138(3)	2163(2)	2182(3)
Z	3	3	3	3
D_c (g/cm^3)	5.13	5.20	5.56	5.62
μ (mm^{-1})	20.1	19.6	21.0	20.4
GOOF on F^2	1.036	1.034	1.042	1.012
R_1, wR_2 ($I > 2\sigma(I)$) [a]	0.0285,0.0665	0.0232,0.0489	0.0199,0.0497	0.0255,0.0641
R_1, wR_2 (all data)	0.0294,0.0669	0.0237,0.0491	0.0201,0.0498	0.0282,0.0648
largest diff. peak and hole(e/ Å^3)	2.79, -1.31	1.48, -1.23	0.82, -0.90	0.81, -1.06

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2. Atomic coordinates and equivalent isotropic displacement parameters of $AMn_4Ga_5Te_{12}$ (A = Rb and Cs).

Atom	Wyck.	x	y	z	$U_{(eq)}$(Å^2)*	Occu.
			$RbMn_{4.0(3)}Ga_{5.0(3)}Te_{12}$			
Rb1	3*a*	0	0	0.5001(3)	0.0472(4)	1
M1=Mn1/Ga1	9*b*	0.17909(7)	0.12852(6)	0.9197(2)	0.0215(2)	0.60(4)/0.40(4)
M2= Mn2/Ga2	9*b*	0.31233(7)	0.08005(7)	0.2491(2)	0.0208(3)	0.53(3)/0.47(3)
M3= Mn3/Ga3	9*b*	0.23347(6)	0.30630(7)	0.2441 (2)	0.0184(2)	0.20(3)/0.80(3)
Te1	9*b*	0.16781(5)	0.11876(4)	0.17699(6)	0.0198(2)	1
Te2	9*b*	0.21851(4)	0.29737(3)	0.49955(5)	0.0190(2)	1
Te3	9*b*	0.29718(4)	0.07228(5)	0.50495(4)	0.0206(2)	1
Te4	9*b*	0.05032(4)	0.17669(5)	0.81289(7)	0.0219(2)	1
			$CsMn_{4.0(3)}Ga_{5.0(3)}Te_{12}$			
Cs1	3*a*	0	0	0.5004(2)	0.0305(2)	1
M1=Mn1/Ga1	9*b*	0.17896(6)	0.12867(5)	0.91948(8)	0.0173(2)	0.62(4)/0.38(4)
M2= Mn2/Ga2	9*b*	0.31216(6)	0.08002(6)	0.24946(8)	0.0174(3)	0.50(3)/0.50(3)
M3= Mn3/Ga3	9*b*	0.23363(5)	0.30638(6)	0.24412(9)	0.0155(2)	0.21(3)/0.79(3)
Te1	9*b*	0.17896(6)	0.12867(5)	0.91948(8)	0.0173(2)	1
Te2	9*b*	0.31216(6)	0.08002(6)	0.24946(8)	0.0174(3)	1
Te3	9*b*	0.23363(5)	0.30638(6)	0.24412(9)	0.0155(2)	1
Te4	9*b*	0.16807(4)	0.11908(3)	0.17643(5)	0.0174(2)	1

*$U_{(eq)}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S3. Atomic coordinates and equivalent isotropic displacement parameters of $ACd_4Ga_5Te_{12}$ (A = Rb and Cs).

Atom	Wyck.	x	y	z	$U_{(eq)}$(Å^2)*	Occu.
			$RbCd_{4.0(3)}Ga_{5.0(3)}Te_{12}$			
Rb1	3*a*	0	0	0.9991(2)	0.0531(3)	1
M1=Cd1/Ga1	9*b*	0.20485(3)	0.48696(3)	0.08603(6)	0.0225(2)	0.58 (4)/0.42(4)
M2=Cd2/Ga2	9*b*	0.58685(4)	0.02033(4)	0.08078(5)	0.0230(2)	0.49(2)/0.51(2)
M3=Cd3/Ga3	9*b*	0.36018(5)	0.09965(4)	0.07753(6)	0.0196(2)	0.26(2)/0.74(2)
Te1	9*b*	0.54896(3)	0.16804(3)	0.01093(4)	0.0229(2)	1
Te2	9*b*	0.07825(3)	0.29519(3)	0.99962(4)	0.0240(2)	1
Te3	9*b*	0.29580(3)	0.22404(4)	0.00529(4)	0.0262(2)	1
Te4	9*b*	0.38424(3)	0.53989(3)	0.97468(5)	0.0269(2)	1
			$CsCd_{4.0(3)}Ga_{5.0(3)}Te_{12}$			
Cs1	3*a*	0	0	0.9995(2)	0.0363(2)	1
M1=Cd1/Ga1	9*b*	0.20479(4)	0.48712(5)	0.08534(7)	0.0241(2)	0.58 (4)/0.42(4)
M2=Cd2/Ga2	9*b*	0.58686(6)	0.02089(6)	0.08156(7)	0.0248(2)	0.50(2)/0.50(2)
M3=Cd3/Ga3	9*b*	0.36013(7)	0.09961(6)	0.07728(8)	0.0223(2)	0.25(2)/0.75(2)
Te1	9*b*	0.54864(4)	0.16734(4)	0.01008(5)	0.0245(2)	1
Te2	9*b*	0.07838(4)	0.29603(4)	0.99930(5)	0.0261(2)	1
Te3	9*b*	0.29665(4)	0.22466(6)	0.00551(5)	0.0276(2)	1
Te4	9*b*	0.38406(4)	0.53945(5)	0.97549(6)	0.0279(2)	1

*$U_{(eq)}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S4. Selected bond lengths (Å) of $AX_4Ga_5Te_{12}$ (A = Rb, Cs; X = Mn, Cd).

	RMGT	**CMGT**	**RCGT**	**CCGT**
M1–Te4	2.674(2)	2.676(2)	2.721(2)	2.724(2)
M1–Te4	2.684(2)	2.687(2)	2.727(2)	2.729(2)
M1–Te1	2.685(2)	2.687(2)	2.713(2)	2.718(4)
M1–Te2	2.726(2)	2.729(2)	2.760(2)	2.759(2)
M2–Te4	2.658(2)	2.661(2)	2.670(2)	2.680(2)
M2–Te3	2.672(2)	2.678(2)	2.711(2)	2.712(4)
M2–Te1	2.674(2)	2.680(2)	2.723(2)	2.720(2)
M2–Te3	2.713(2)	2.716(2)	2.732(2)	2.734(2)
M3–Te1	2.6239(9)	2.628(2)	2.649(2)	2.657(2)
M3–Te2	2.6357(9)	2.641(2)	2.651(2)	2.656(2)
M3–Te3	2.6553(9)	2.659(2)	2.676(2)	2.681(2)
M3–Te2	2.668(2)	2.668(2)	2.686(2)	2.692(4)
A1–Te4×3	4.058(3)	4.072(2)	4.057(3)	4.075(4)
A1–Te1×3	4.073(3)	4.092(2)	4.065(3)	4.093(4)
A1–Te2×3	4.0940(5)	4.108(2)	4.090(2)	4.114(2)
A1–Te3×3	4.1190(6)	4.132(2)	4.127(2)	4.151(2)

References

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3 G. M. Sheldrick, *SHELXTL*, version 5.1; Bruker-AXS: Madison, WI, 1998.

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