Supplement

A Chemical, High-Temperature Way to $Ag_{1.9}Te$ via Quasi-Topotactic Reaction of Stuetzite-type $Ag_{1.54}Te$: Structural and Thermoelectrical Properties

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1. Crystal chemistry on stuetzite in literature

Table S1. Literature overview of published compositions and space groups for $Ag_{5-x}Te_3$.

Published composition	Unified composition		Cell parameter		Space group	Year
			a / Å	*c* / Å		
$Ag_{32}Te_{27}$	$Ag_{3.56}Te_3$	$Ag_{1.19}Te$	13.4	8.4	*P*6/*mmm*	1989[1]
$Ag_{4.53}Te_3$	$Ag_{4.53}Te_3$	$Ag_{1.51}Te$	13.38	8.49	-	1961[2]
$Ag_{4.53}Te_3$	$Ag_{4.53}Te_3$	$Ag_{1.51}Te$	13.456(9)	16.917(6)	$P\bar{6}2m$	1996[3]
$Ag_{4.53}Te_3$	$Ag_{4.53}Te_3$	$Ag_{1.51}Te$	13.46	16.9	$P\bar{6}2m$	1996[4]
$Ag_{5.4(2)}Te_{3.49(1)}$	$Ag_{4.63}Te_3$	$Ag_{1.54}Te$	13.4680(5)	8.4701(2)	$P\bar{6}2m$	this publ.
$Ag_{5-x}Te_3$	$Ag_{5-x}Te_3$	$Ag_{1.67-x}Te$	13.49	8.48	*P*6/*mmm*	1962[5]
Ag_5Te_3	Ag_5Te_3	$Ag_{1.67}Te$	13.49	8.48	" *C*6/*mmm* "	1951[6]
Ag_5Te_3	Ag_5Te_3	$Ag_{1.67}Te$	13.46	8.47	-	1956[7]
Ag_5Te_3	Ag_5Te_3	$Ag_{1.67}Te$	13.38	8.45	" *C*6/*mmm* "	1964[8]
$Ag_{12}Te_7$	$Ag_{5.14}Te_3$	$Ag_{1.71}Te$	13.43	8.45	-	1939[9]
Ag_7Te_4	$Ag_{5.25}Te_3$	$Ag_{1.75}Te$	13.48(5)	8.49(5)	*P*6/*mmm*	1966[10]

2. Synthesis of stuetzite

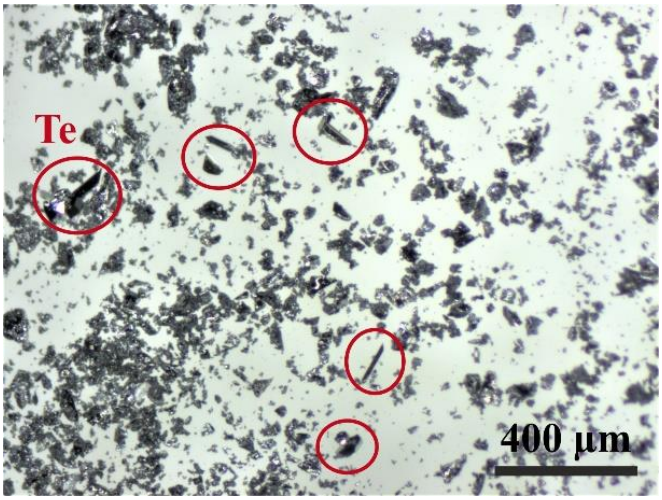

Figure S1. Representative view on the final product after high temperature synthesis of $Ag_{4.63}Te_3$. Even using an excess of silver do not prevent the formation of tellurium as side phase. Tellurium crystals are emphasized in red circles.

3. X-ray powder diffraction

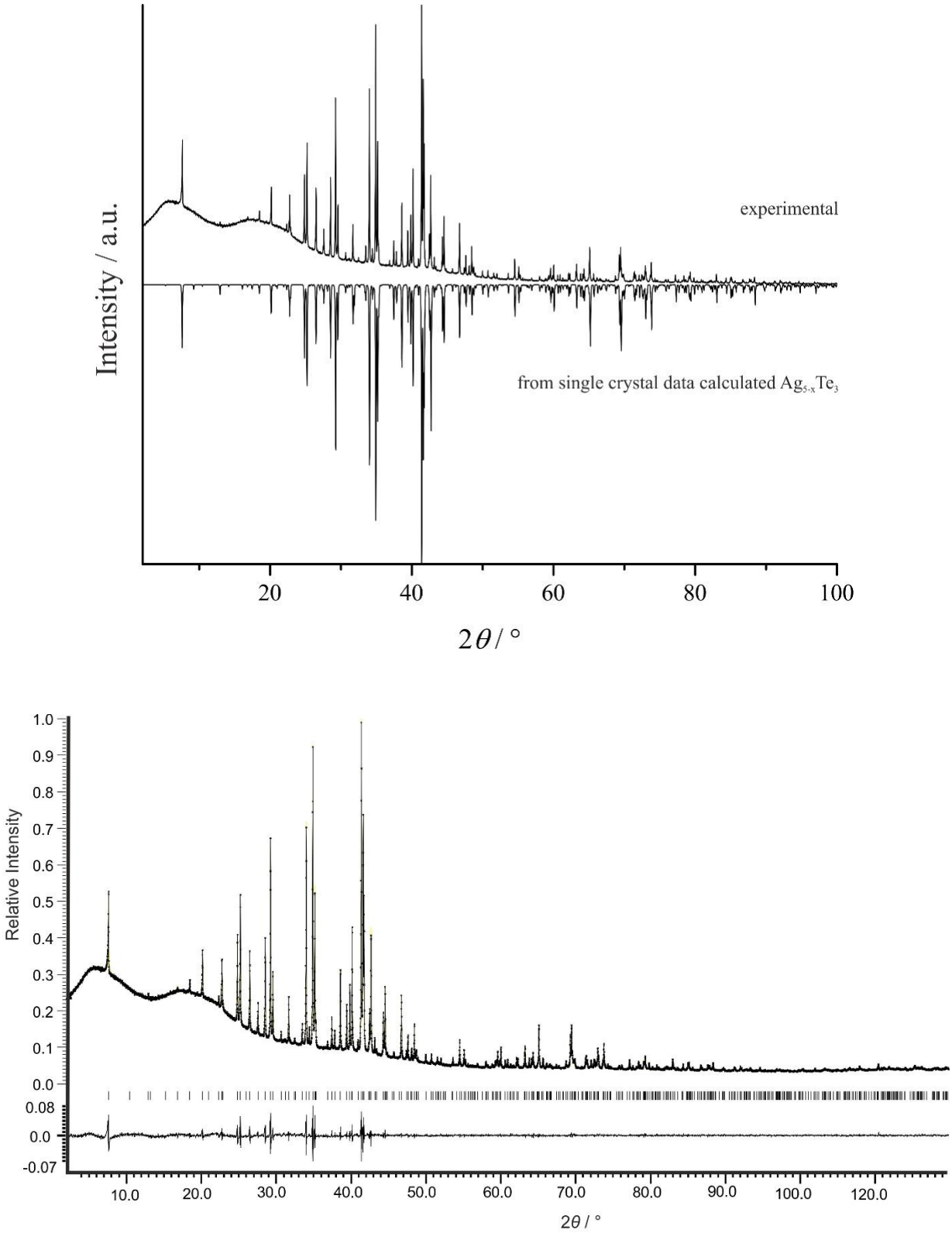

Figure S2. Top: X-ray powder diffractogram (Cu-Kα_1 radiation) of a phase pure sample of $Ag_{4.63}Te_3$ after removing tellurium as side phase. Bottom: Rietveld refinement of $Ag_{4.63}Te_3$ (GOF on F^2 = 1.98; R_p = 2.29; wR_p = 3.18; $R1$(all data) = 6.08; $wR2$ (all data) = 5.30) substantiating the phase purity of the title compound.

4. Refinement details for $Ag_{4.63}Te_3$ at 293 K

Table S2. Anisotropic displacement parameters / Å^2 of $Ag_{4.63}Te_3$ at 293 K.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Te1	0.0232(6)	0.0226(6)	0.0257(5)	0.0122(5)	0	0
Te2	0.0348(6)	0.0348(6)	0.0271(7)	0.0174(3)	0	0
Te3	0.0228(6)	0.0331(11)	0.0497(12)	0.0166(6)	0	0
Te4	0.0341(8)	0.0429(13)	0.0314(11)	0.0215(6)	0	0
Te5	0.0298(7)	0.0250(9)	0.0267(10)	0.0125(5)	0	0
Te6	0.0236(9)	0.0236(9)	0.0241(13)	0.0118(4)	0	0
Te7	0.021(16)	0.021(16)	0.001(19)	0.010(8)	0	0
Ag1	0.15(4)	0.17(4)	0.24(3)	0.13(3)	−0.14(3)	−0.15(3)
Ag2	0.074(3)	0.0435(13)	0.053(4)	0.0349(16)	0.015(3)	0.0007(14)
Ag3	0.273(16)	0.087(9)	0.027(4)	0.101(10)	0.038(6)	0.006(4)
Ag4	0.0348(9)	0.0370(9)	0.0500(11)	0.0175(8)	0	0
Ag5	0.041(2)	0.042(2)	0.059(3)	0.0192(19)	0	0
Ag6	0.095(8)	0.065(4)	0.056(5)	0.033(2)	−0.044(6)	0
Ag7	0.0425(10)	0.0696(19)	0.0396(12)	0.0348(9)	0.0002(7)	0
Ag8	0.20(4)	0.13(5)	0.013(14)	0.07(2)	0	0

Table S3. Non-harmonic refinement of third order of $Ag_{4.63}Te_3$ at 293 K.

Atom	C_{111}	C_{112}	C_{113}	C_{122}	C_{123}	C_{133}	C_{222}	C_{223}	C_{233}	C_{333}
Ag1	0.03(2)	0.04(2)	−0.09(4)	0.04(2)	−0.10(4)	0.24(7)	0.04(3)	−0.10(4)	0.27(7)	−0.6(1)
Ag2	0.004(1)	0.0013(7)	0.004(1)	−0.0009(5)	−0.0003(7)	0.007(2)	−0.0015(6)	−0.0032(5)	0.0039(9)	−0.001(3)
Ag3	−0.39(8)	−0.13(3)	−0.09(2)	−0.06(2)	−0.029(7)	0.012(6)	−0.04(1)	−0.021(5)	0.009(3)	0.028(4)
Ag5	0.002(1)	0.0007(7)	0	0.0021(7)	0	−0.001(1)	0.001(1)	0	−0.002(1)	0
Ag6	0.003(3)	−0.001(1)	−0.006(3)	−0.001(1)	−0.0008(8)	0.007(3)	0	−0.002(2)	0	0.000(5)
Ag7	−0.0001(4)	0.0004(3)	−0.0008(4)	0.0004(3)	−0.0025(3)	0.0003(5)	0	−0.0050(6)	0	0.001(1)
Ag8	−0.3(1)	−0.08(5)	0	−0.08(5)	0	0.05(2)	0	0	0	0

5. Refinement details for $Ag_{1.9}Te$ at 660 K

Table S4. Anisotropic displacement parameters / Å^2 of $Ag_{1.9}Te$ at 660 K.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Te1	0.119(4)	0.119(4)	0.129(8)	0.060(2)	0	0
Te2	0.110(9)	0.110(9)	0.37(5)	0.055(5)	0	0
Ag1	0.26(4)	0.26(4)	0.19(5)	0.13(3)	0	0
Ag2	0.40(3)	0.40(3)	0.47(5)	0.20(2)	0	0
Ag3	0.22(3)	0.22(3)	0.38(3)	0.11(1)	0	0
Ag4	0.084(8)	0.084(8)	0.20(4)	0.041(4)	0	0
Ag5	0.17(2)	0.17(2)	0.21(4)	0.083(8)	0	0

Table S5. Non-harmonic refinement of third order of $Ag_{1.9}Te$ at 660 K.

Atom	U_{111}	U_{112}	U_{113}	U_{122}	U_{123}	U_{133}	U_{222}	U_{223}	U_{233}	U_{333}
Ag1	4.0(14)	2.0(9)	0	−2.0(9)	0	0.14(5)	−4.0(14)	0	−0.14(5)	0
Ag2	2(4)	1.1(2)	3.7(8)	−1.1(2)	1.8(4)	0	−2(4)	3.7(8)	0	0.7(3)
Ag3	−1.1(4)	−0.6(2)	0.5(2)	0.6(2)	0.25(9)	0	1.1(4)	0.6(2)	0	0.8(2)
Ag4	0.1(1)	0.07(6)	0.11(3)	−0.07(6)	0.06(2)	0	−0.1(1)	0.11(3)	0	−0.11(5)
Ag5	0.1(1)	0.07(7)	−0.33(7)	−0.07(7)	−0.17(3)	0	−0.1(1)	−0.33(7)	0	−0.08(4)

6. Thermoanalytic measurements

Figure S3 shows two cycles of a DSC measurement with the thermal effects caused by the α- to β–$Ag_{4.63}Te_3$ phase transition and the decomposition afterwards to $Ag_{1.9}Te$. The signal at 625 K matches with a peritectic effect which is mentioned in literature but not described in detail.[11]

The DSC measurements were performed in a temperature range where $Ag_{1.9}Te$ is stable. It therefore could be possible that $Ag_{1.9}Te$ reacts again with the decomposed tellurium to form $Ag_{1.54}Te$ in a kind of reversible reaction. With a heating and cooling rate of 10 K min^{-1} combined with the observed tellurium depositions during the high temperature single crystal X-ray measurements this explanation is probable.

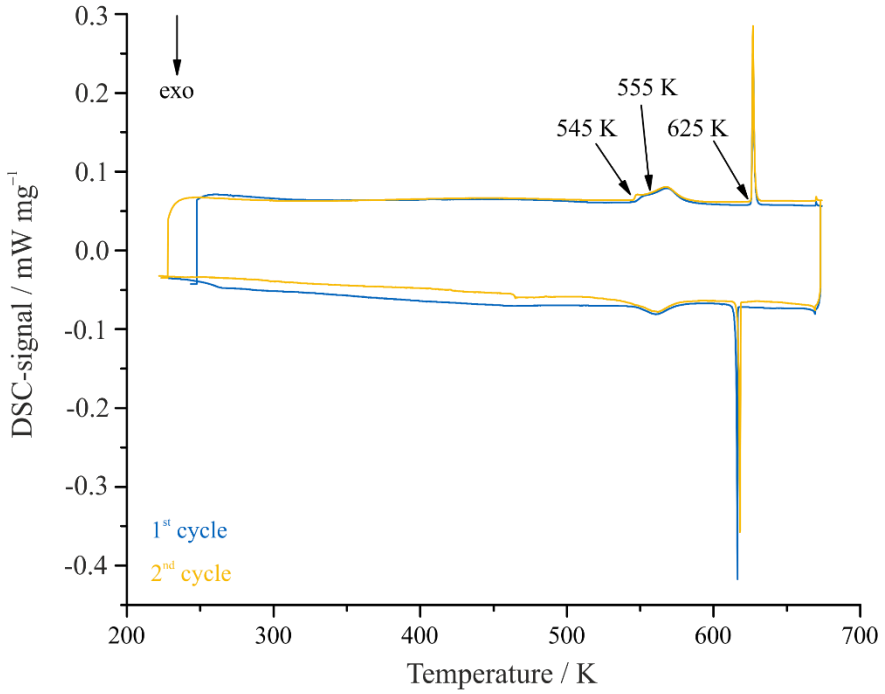

Figure S3. DSC measurement of $Ag_{4.63}Te_3$ between 213 and 675 K. The α- to β-$Ag_{4.63}Te_3$ phase transition starts at 545 K. The quasi-topotactic reaction to $Ag_{1.9}Te$ can be observed at 625 K. The slow decomposition pretends a reversible phase transition at 625 K.

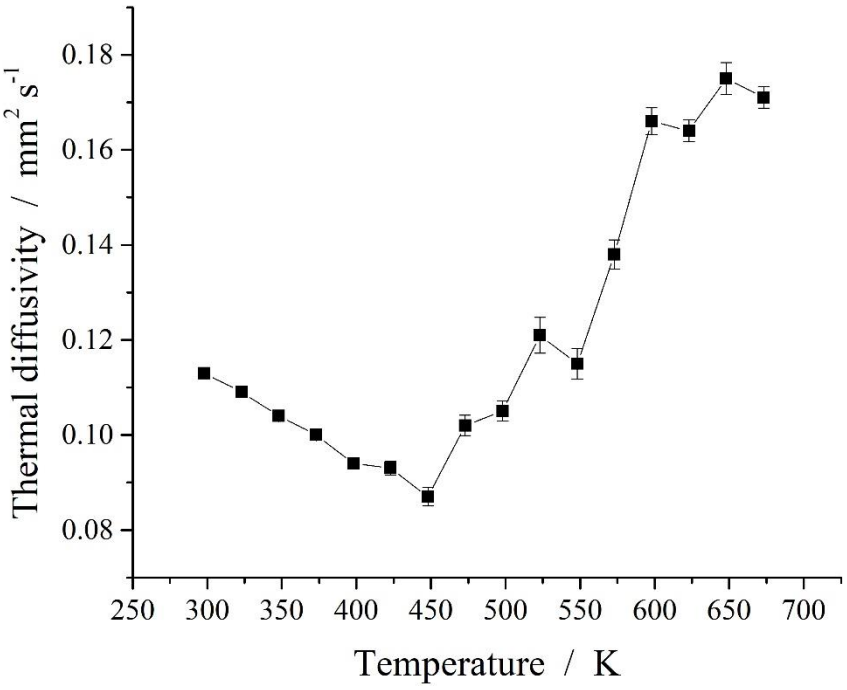

Figure S4. Thermal diffusivity of $Ag_{4.63}Te_3$ between 300 and 675 K.

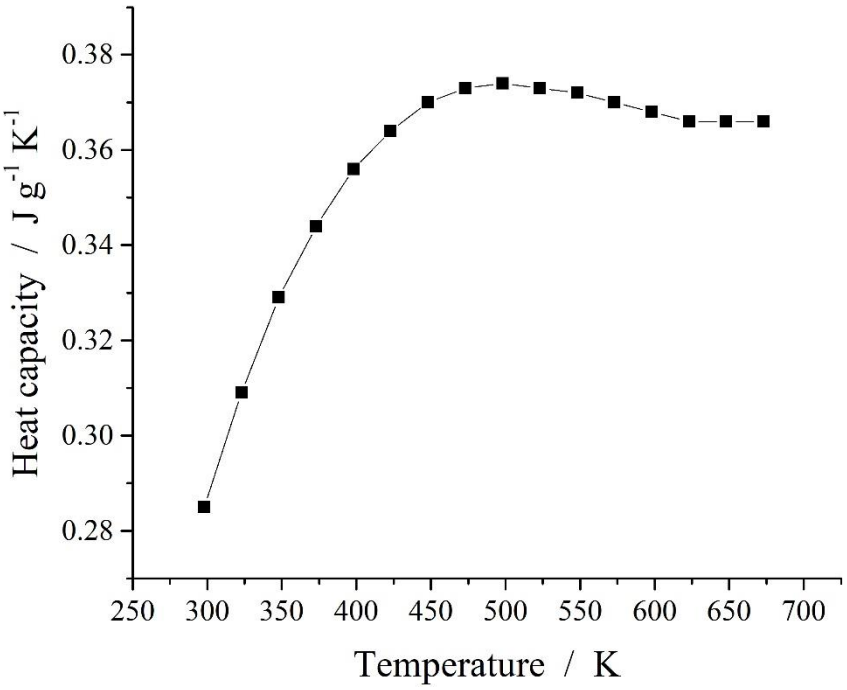

Figure S5. Heat capacity of $Ag_{4.63}Te_3$ between 300 and 675 K.

7. Crystal structure determination of $Ag_{1.9}Te$

Due to a difference of only five electrons an explicit atom assignment to the atom site is not easy. A structure model based on the structure of $Cu_{2-x}Te$ was used as a starting one for $Ag_{1.9}Te$ at 660 K.[12–18] However, this model assumes an extraordinarily four-coordinated tellurium and was therefore rejected due to crystal chemical considerations.

Table S6. Selected crystallographic data of $Ag_{1.9}Te$ at 660 K analogous to the $Cu_{2-x}Te$ structure model.

Refined composition	$Ag_{5.0(5)}Te_{3.2(1)}$
Temperature / K	660
Space group	$P\bar{6}m2$
a / Å	4.693(3)
c / Å	11.486(7)
V / Å³	219.1(2)
Z	1
Molar mass / g mol^{-1}	943.3
Calculated density / g cm^{-3}	7.15
θ-range / °	1.8-29.3
F(000)	400
Total number of reflection	5603
Independent reflections; R_{int}	278; 0.542
Reflections with $I \geq 3\sigma(I)$	1144
Data / parameter	278 / 40
Goodness of fit on F²	1.10
*R*1 / *wR*2 [$I \geq 3\sigma(I)$]	0.0396; 0.0824
*R*1 / *wR*2 (all data)	0.0994; 0.2545
Largest diff. peak and hole / e Å^{-3}	1.00; −1.44

Table S7. Coordinates and isotropic displacement parameters of $Ag_{1.9}Te$ at 660 K analogous to the $Cu_{2-x}Te$ structure model.

Atom	sof	site	*x*	*y*	*z*	U_{eq}
Te1	1	2i	2/3	1/3	0.3833(12)	0.128(5)
Te2	0.58(5)	2g	0	0	0.265(2)	0.117(12)
Ag1	0.26(4)	3k	0.21(3)	0.79(3)	1/2	0.31(6)
Ag2	0.42(5)	2i	2/3	1/3	0.171(3)	0.45(3)
Ag3	0.67(7)	2h	1/3	2/3	0.092(5)	0.25(2)
Ag4	0.52(8)	2h	1/3	2/3	0.280(11)	0.13(3)
Ag5	1	1a	0	0	0	0.169(13)

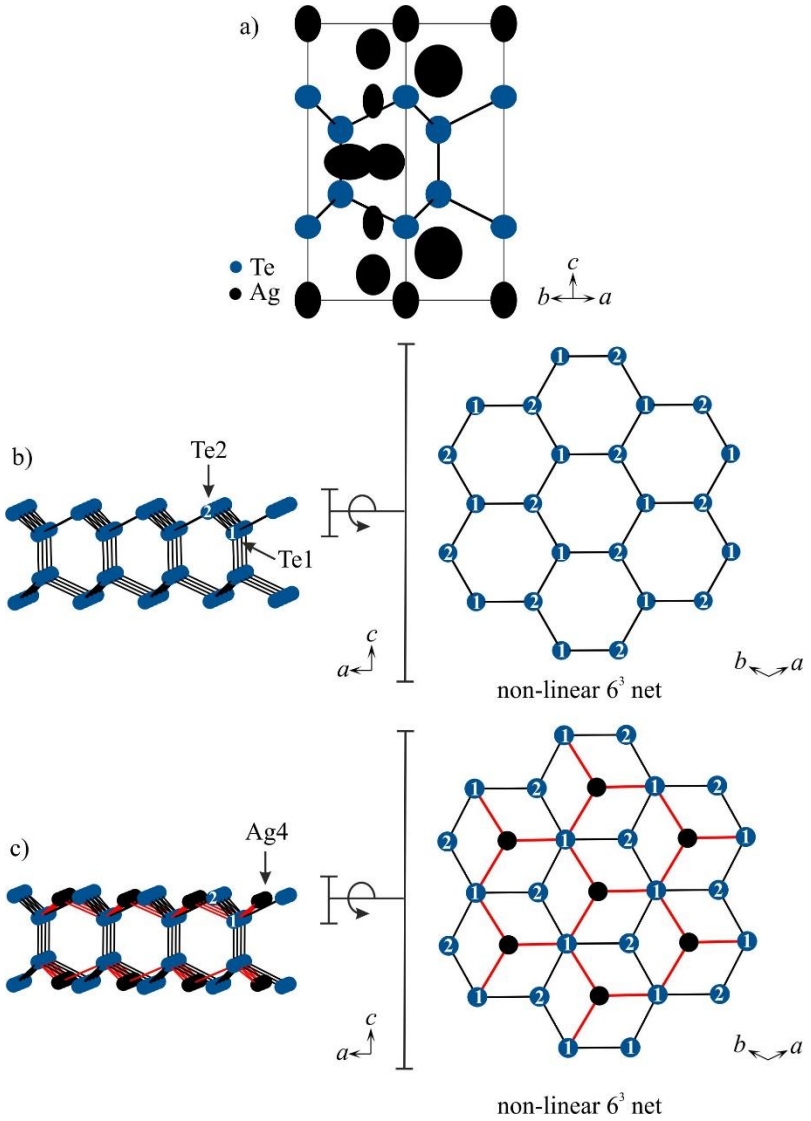

Figure S6. Crystal structure model for $Ag_{1.9}Te$ based on the $Cu_{1.75}Te$ structure model.[12–18] Due to four-coordinated tellurium this model was rejected.

References

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