Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

From $AgTeO_2F$, $Ag_2(TeO_2F_2)$ to $Ag_3F_3(TeF_6)(TeO_2)_{12}$: First Silver Tellurite Oxyfluorides with Linear and Nonlinear Optical Property

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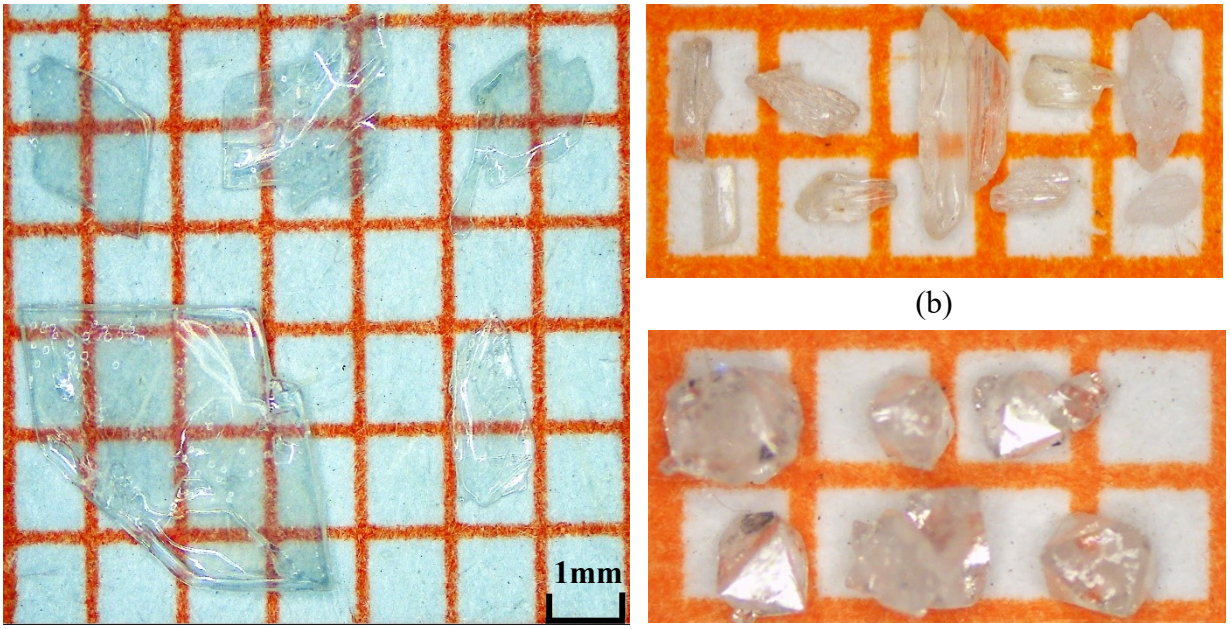
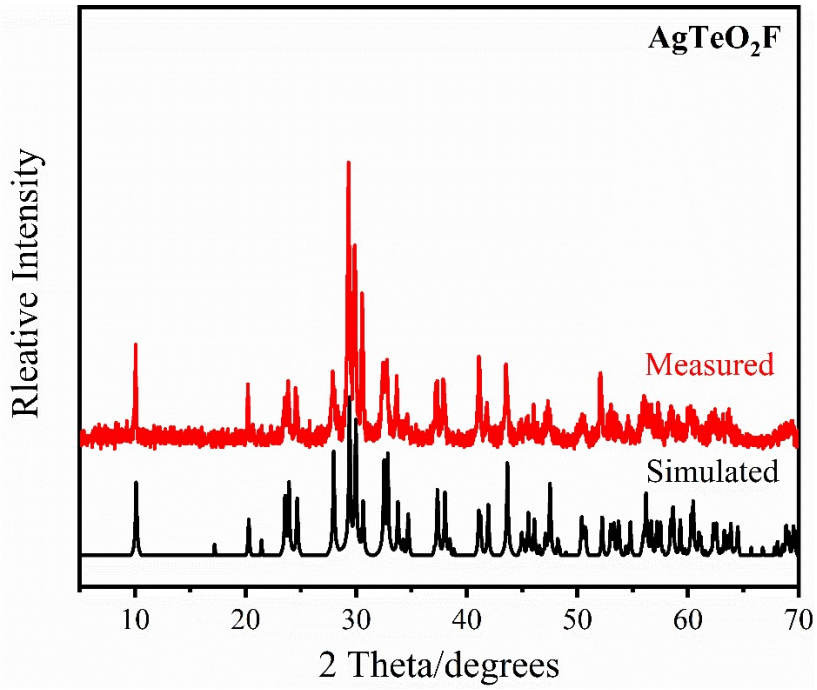
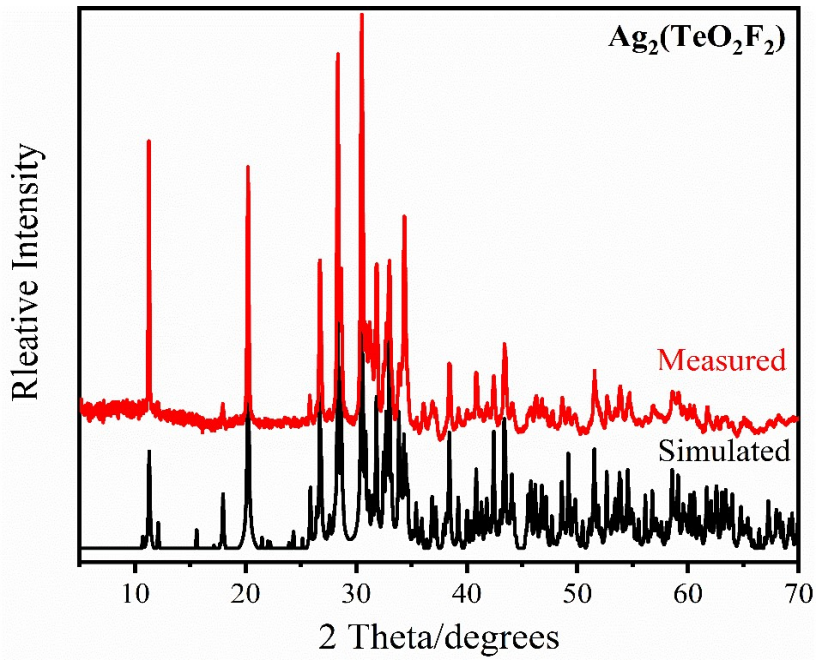


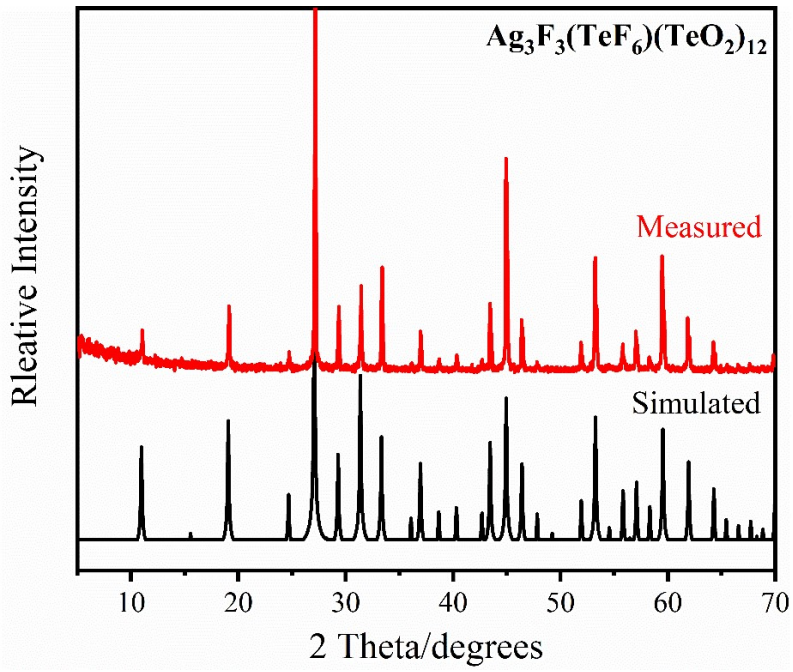
Figure S1. As-grown small crystals of $AgTeO_2F$ (a), $Ag_2(TeO_2F_2)$ (b) and $Ag_3F_3(TeF_6)(TeO_2)_{12}$ (c)


AgTeO2F
Rleative Intensity
Measured
Simulated
10
20
30
40
50
60
70
2 Theta/degrees

(a)


Ag2(TeO2F2)
Rleative Intensity
Measured
Simulated
10
20
30
40
50
60
70
2 Theta/degrees

(b)



(c)

Figure S2. Simulated and experimental XRD powder patterns of $AgTeO_2F$ (a), $Ag_2(TeO_2F_2)$ (b) and $Ag_3F_3(TeF_6)(TeO_2)_{12}$ (c).

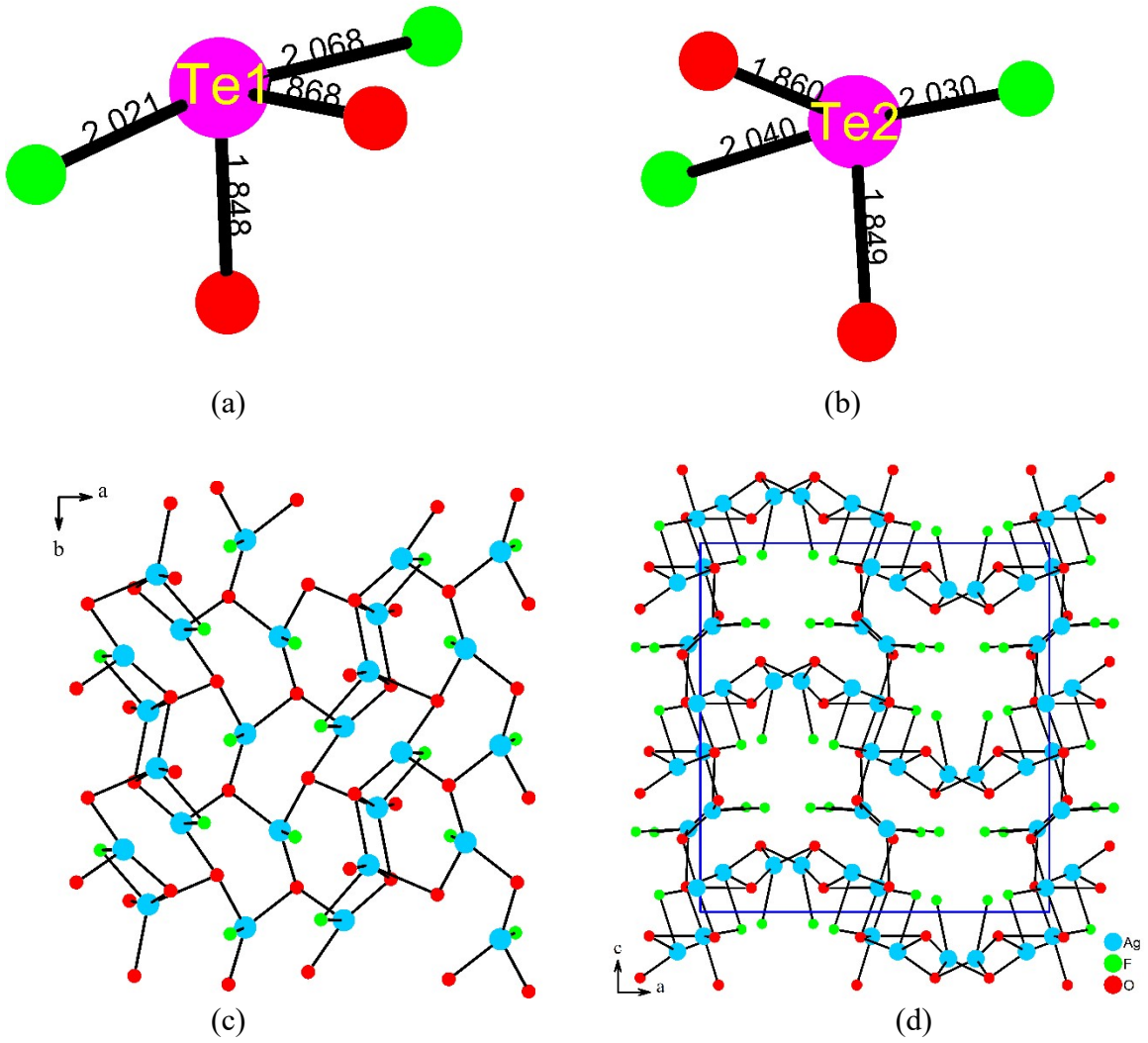
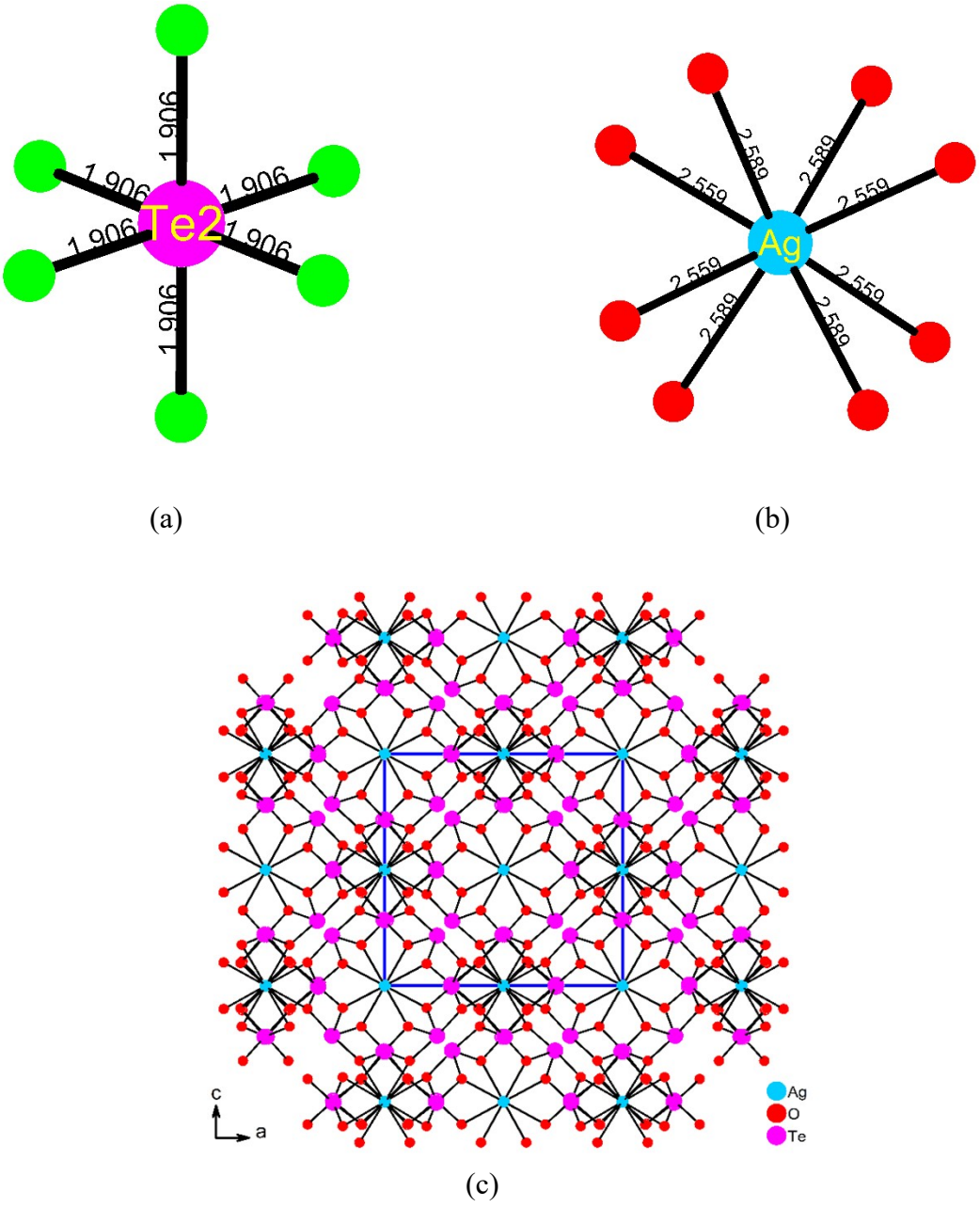


Figure S3. Te(1)O_2F_2 group (a), Te(2)O_2F_2 unit (b), the 2D Ag-O-F layer in the ab plane (c) and the 3D silver oxyfluoride open framework of $Ag_2(TeO_2F_2)$ (d)



(a) (b)

(c)

Figure S4. Te(2)F_6 octahedron (a), AgO_8 polyhedron (b) and the 3D cationic framework of $[Ag_3(TeO_2)_{12}]^{3+}$ (c) in $Ag_3F_3(TeF_6)(TeO_2)_{12}$

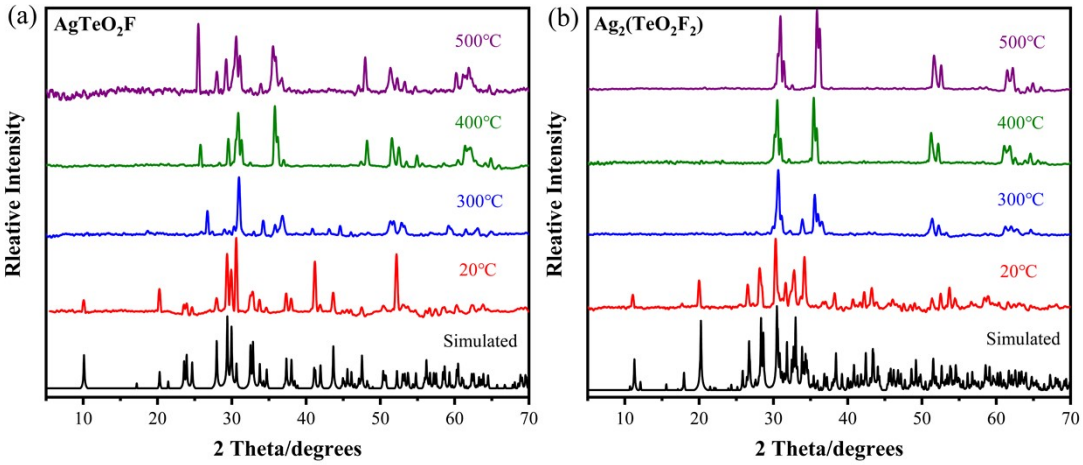
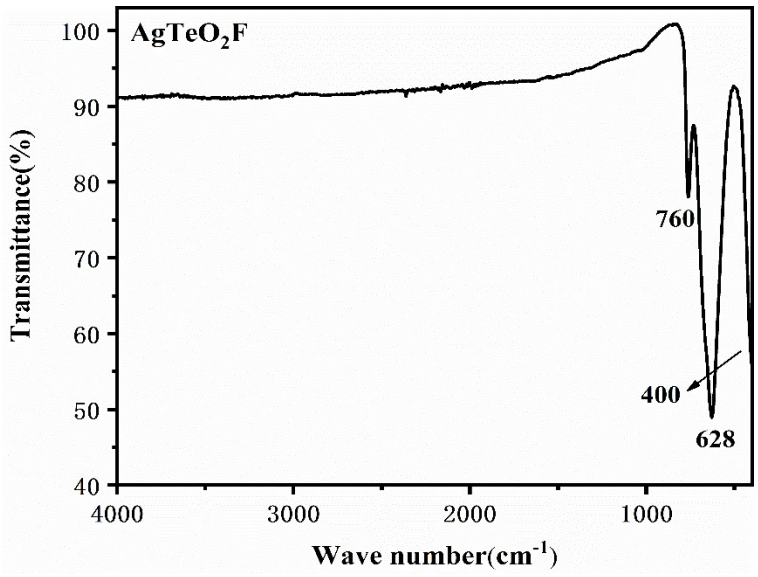
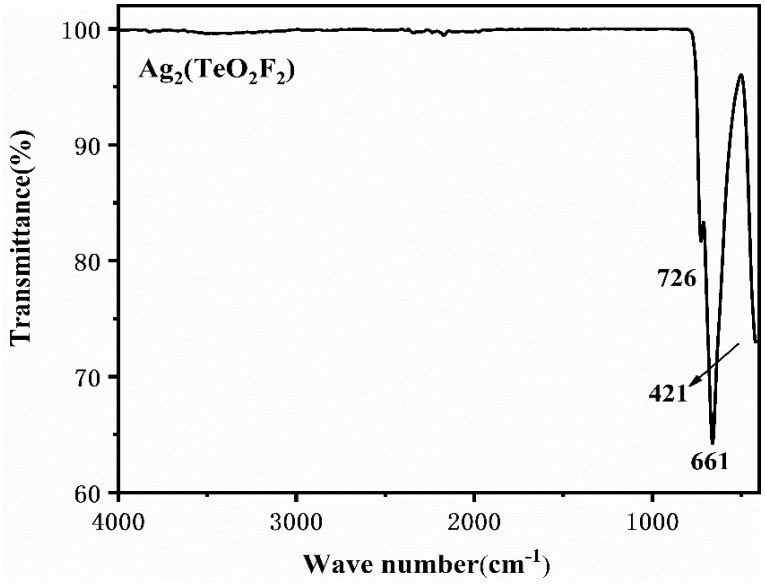


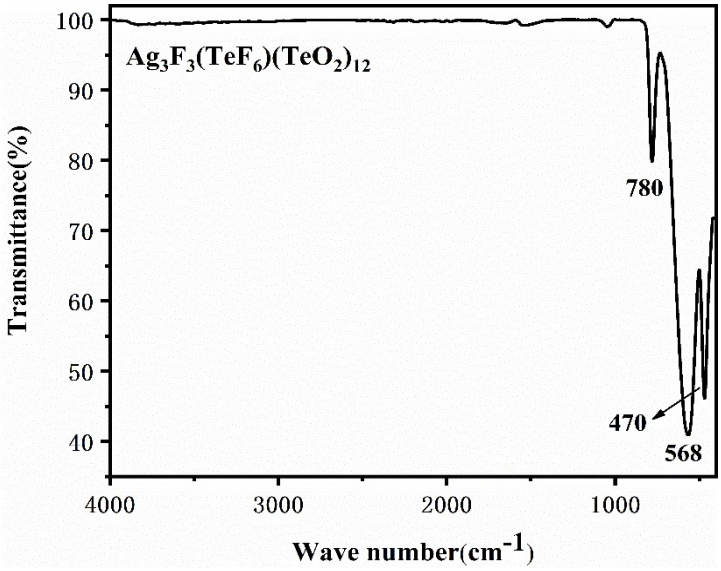
Figure S5. Simulated and experimental PXRD patterns of $AgTeO_2F$ (a), $Ag_2(TeO_2F_2)$ (b) at different temperatures.


AgTeO2F
Transmittance(%)
100
90
80
70
60
50
40
760
400
628
4000
3000
2000
1000
Wave number(cm-1)

(a)


Ag2(TeO2F2)
Transmittance(%)
100
90
80
70
60
726
421
661
4000
3000
2000
1000
Wave number(cm-1)

(b)



(c)

Figure S6. Infrared spectrum of $AgTeO_2F$ (a), $Ag_2(TeO_2F_2)$ (b) and $Ag_3F_3(TeF_6)(TeO_2)_{12}$ (c)

Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $AgTeO_2F$, $Ag_2(TeO_2F_2)$ and $Ag_3F_3(TeF_6)(TeO_2)_{12}$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

	Atom	x	y	z	U(eq)
$AgTeO_2F$	Ag(1)	5883.1(7)	9397.7(8)	2239.9(10)	24.3(2)
	F(1)	8930(5)	6729(5)	4845(7)	26.7(9)
	O(1)	6435(5)	5872(6)	1709(8)	17.4(10)
	Te(1)	8239.0(5)	4510.4(6)	2389.4(7)	12.84(19)
	O(2)	7433(6)	3004(6)	5032(8)	22.6(11)
$Ag_2(TeO_2F_2)$	Ag(1)	2893.2(8)	4695.3(13)	1261.7(5)	45.7(3)
	F(1)	3154(4)	10614(9)	2824(3)	30.8(12)
	O(1)	3275(4)	7631(10)	1787(4)	23.6(14)
	Te(1)	3334.0(4)	7645.5(8)	2903.5(3)	14.37(17)
	Ag(2)	5345.3(6)	6638.3(13)	2252.5(6)	39.2(3)
	F(2)	3689(4)	4828(9)	2838(3)	31.9(13)
	O(2)	4482(4)	8325(9)	3022(4)	21.9(14)
	Te(2)	6536.1(4)	7131.0(8)	5463.9(3)	15.99(18)
	Ag(3)	4902.0(6)	8520.7(13)	4347.8(5)	39.8(3)
	F(3)	6765(4)	10027(9)	5321(4)	31.9(14)
	O(3)	5410(4)	7805(10)	5684(4)	26.9(16)
	Ag(4)	5655.4(6)	4327.2(13)	3927.6(5)	35.7(2)
	F(4)	6177(4)	4298(9)	5468(4)	37.5(14)
	O(4)	6465(5)	6999(10)	4349(4)	28.2(16)
$Ag_3F_3(TeF_6)(TeO_2)_{12}$	Ag(1)	0	-5000	-10000	20.5(4)
	Te(1)	-2162.9(5)	-5044.5(7)	-7797.3(5)	13.1(2)
	O(1)	-1761(6)	-3946(7)	-9027(7)	18.1(16)
	O(2)	-959(7)	-6006(7)	-8237(6)	18.1(16)
	F(1)	0	-8328(15)	-10000	108(5)
	Te(2)	0	-10000	-10000	41.6(7)
	F(2)	-1836(17)	-1836(17)	-8164(17)	96(10)

Table S2. The bond lengths (Å) and calculated bond valences for $AgTeO_2F$, $Ag_2TeO_2F_2$ and $Ag_3F_3(TeF_6)(TeO_2)_{12}$.

Compound	Bond	Bond-length	Bond-valence	BVS
$AgTeO_2F$	Ag(1)-O(1)	2.319(4)	0.249	0.825
	Ag(1)-O(1)#1	2.320(5)	0.249	
	Ag(1)-O(1)#2	2.478(5)	0.162	
	Ag(1)-O(2)#3	2.472(4)	0.165	
	Te(1)-F(1)	2.029(4)	0.651	4.031
	Te(1)-O(1)	1.832(4)	1.480	
	Te(1)-O(2)	1.882(4)	1.293	
	Te(1)-O(2)#4	2.162(4）	0.607	
$Ag_2(TeO_2F_2)$	Ag(1)-O(1)	2.281(7)	0.276	0.769
	Ag(1)-O(1)#1	2.475(7)	0.164	
	Ag(1)-F(3)#2	2.680(6)	0.093	
	Ag(1)-O(4)#2	2.340(7)	0.236	
	Ag(2)-O(2)	2.190(6)	0.353	0.961
	Ag(2)-O(2)#2	2.342(7)	0.234	
	Ag(2)-O(3)#3	2.623(7)	0.110	
	Ag(2)#4-F(1)	2.458(6)	0.169	
	Ag(2)#4-F(2)	2.671(7)	0.095	
	Ag(3)-O(3)#5	2.578(7)	0.124	0.711
	Ag(3)-O(3)	2.399(7)	0.201	
	Ag(3)-O(2)	2.292(6)	0.268	
	Ag(3)-O(4)	2.663(8)	0.098	
	Ag(3)-F(4)#6	2.591(7)	0.118	
	Ag(4)#6-O(3)	2.313(7)	0.253	0.809
	Ag(4)-F(4)	2.674(6)	0.095	
	Ag(4)-O(4)	2.341(7)	0.235	
	Ag(4)#4-O(1)	2.359(7)	0.224	
	Te(1)-F(2)	2.021(6)	0.665	4.007
	Te(1)-O(2)	1.869(7)	1.339	
	Te(1)-F(1)	2.068(6)	0.586	
	Te(1)-O(1)	1.848(7)	1.417	
	Te(2)-F(3)	2.040(6)	0.632	4.066
	Te(2)-O(3)	1.860(7)	1.372	
	Te(2)-F(4)	2.030(6)	0.649	
	Te(2)-O(4)	1.849(6)	1.413	
$Ag_3F_3(TeF_6)(TeO_2)_{12}$	Ag(1)-O(2)#1	2.559(7)	0.130	1.000
	Ag(1)-O(2)#2	2.559(7)	0.130	
	Ag(1)-O(2)#3	2.559(7)	0.130	
	Ag(1)-O(2)	2.559(7)	0.130	

	Ag(1)-O(1)#2	2.590(7)	0.120	
	Ag(1)-O(1)#1	2.590(7)	0.120	
	Ag(1)-O(1)	2.590 (7)	0.120	
	Ag(1)-O(1)#3	2.590(7)	0.120	
	Te(1)-O(2)	1.827(7)	1.500	4.078
	Te(1)-O(2)#4	2.107(7)	0.704	
	Te(1)-O(1)#5	2.083(7)	0.751	
	Te(1)-O(1)	1.934(7)	1.123	
	Te(2)-F(1)	1.906(17)	1.030	6.180
	Te(2)-F(1)#1	1.906(17)	1.030	
	Te(2)-F(1)#2	1.906(17)	1.030	
	Te(2)-F(1)#3	1.906(17)	1.030	
	Te(2)-F(1)#4	1.906(17)	1.030	
	Te(2)-F(1)#5	1.906(17)	1.030	

Symmetry transformations used to generate equivalent atoms:

For $AgTeO_2F$:
#1 1-X,1/2+Y,1/2-Z; #2 +X,3/2-Y,1/2+Z; #3 +X,3/2-Y,-1/2+Z; #4 +X,1/2-Y,-1/2+Z

For $Ag_2(TeO_2F_2)$:
#1 1/2-X,-1/2+Y,+Z; #2 1-X,-1/2+Y,1/2-Z; #3 +X,3/2-Y,-1/2+Z; #4 1-X,1/2+Y,1/2-Z; #5 1-X,2-Y,1-Z; #6 1-X,1-Y,1-Z

For $Ag_3F_3(TeF_6)(TeO_2)_{12}$:
#1 -X,-1-Y,+Z; #2 +X,-1-Y,-2-Z; #3 -X,+Y,-2-Z; #4 1/2+Y,-1/2-X,-3/2-Z; #5 -1/2-X,-3/2-Z,-1/2+Y

Table S3. The bond angles (deg.) for $AgTeO_2F$, $Ag_2(TeO_2F_2)$ and $Ag_3F_3(TeF_6)(TeO_2)_{12}$ (c)

$AgTeO_2F$			
O(1)-Ag(1)-O(1)#3	91.10(14)	F(1)-Te(1)-O(2)#6	175.15(16)
O(1)-Ag(1)-O(1)#1	127.55(13)	O(1)-Te(1)-F1	92.56(17)
O(1)#1-Ag(1)-O(1)#3	86.33(16)	O(1)-Te(1)-O(2)	93.4(2)
O(1)#1-Ag(1)-O(1)#4	110.02(15)	O(1)-Te(1)-O(2)#6	87.94(19)
O(1)-Ag(1)-O(2)#4	118.06(15)	O(2)-Te(1)-F(1)	87.81(18)
O(2)4-Ag(1)-O(1)#3	115.40(15)	O(2)-Te1-O(2)#6	87.34(10)

$Ag_2(TeO_2F_2)$			
O(1)-Ag(1)-O(1)#1	124.7(3)	F(1)#2-Ag(2)-O(3)#5	87.4(2)
O(1)-Ag(1)-F(1)#2	104.1(2)	O(2)#2-Ag(2)-F(1)#2	66.4(2)
O(1)#1-Ag(1)-F(3)#2	122.6(2)	O(2)-Ag(2)-F(1)#2	140.6(2)
O(1)-Ag(1)-O(4)#2	139.0(3)	O(2)-Ag(2)-O(2)#2	134.48(19)
O(4)#2-Ag(1)-O(1)#1	90.8(2)	O(2)#2-Ag(2)-O(3)#5	86.9(2)
O(4)#2-Ag(1)-F(3)#2	63.9(2)	O(2)-Ag(2)-O(3)#5	121.4(2)
O(2)-Ag(3)-O(3)#6	89.1(2)	O(1)#2-Ag(4)-F(4)	104.9(2)
O(2)-Ag(3)-O(3)	164.5(2)	O(3)#7-Ag(4)-O(1)#2	109.7(2)
O(2)-Ag(3)-F(4)#7	83.2(2)	O(3)#7-Ag(4)-F(4)	87.2(2)
O(3)-Ag(3)-O(3)#6	106.46(19)	O(3)#7-Ag(4)-O(4)	143.8(2)
O(3)-Ag(3)-F(4)#7	87.4(2)	O(4)-Ag(4)-O(1)#2	98.8(2)
O(3)#6-Ag(3)-F(4)#7	127.9(2)	O(4)-Ag(4)-F(4)	63.7(2)
O(1)-Te(1)-F(1)	86.3(3)	O(3)-Te(2)-F(3)	86.9(3)
O(1)-Te(1)-F(2)	87.5(3)	O(3)-Te(2)-F(4)	88.6(3)
O(1)-Te(1)-O(2)	98.9(3)	F(4)-Te(2)-F(3)	171.2(2)
F(2)-Te(1)-F(1)	169.5(2)	O(4)-Te(2)-F(3)	86.7(3)
O(2)-Te(1)-F(1)	83.7(3)	O(4)-Te(2)-O(3)	98.6(3)
O(2)-Te(1)-F(2)	88.9(3)	O(4)-Te(2)-F(4)	86.5(3)

$Ag_3F_3(TeF_6)(TeO_2)_{12}$			
O(1)-Ag(1)-O(1)#2	124.7(3)	O(1)-Te(1)-O(1)#5	90.7(5)
O(1)#1-Ag(1)-O(1)#3	124.7(3)	O(1)-Te(1)-O(2)#6	84.6(3)
O(1)-Ag(1)-O(1) #3	129.3(3)	O(1)#5-Te(1)-O(2)#6	175.1(3)
O(1)#2-Ag(1)-O(1)#3	78.3(4)	O(2)-Te(1)-O(1)#5	88.0(3)
O(2)-Ag(1)-O(1)#3	77.7(2)	O(2)-Te(1)-O(1)	90.7(3)
O(2)#2-Ag(1)-O(1)#2	62.6(2)	O(2)-Te(1)-O(2)#6	90.5(5)
O(2)#2-Ag(1)-O(1)#1	77.7(2)	O(1)-Te(1)-O(1)#5	90.7(5)
O(2)#3-Ag(1)-O(1)#1	151.1(2)	O(1)-Te(1)-O(2)#6	84.6(3)
O(2)#2-Ag(1)-O(1)	151.1(2)	O(1)#5-Te(1)-O(2)#6	175.1(3)
O(2)#1-Ag(1)-O(1)#1	62.6(2)	O(2)-Te(1)-O(1)#5	88.0(3)
O(2)#1-Ag(1)-O(1)#2	77.7(2)	O(2)-Te(1)-O(1)	90.7(3)
O(2)#3-Ag(1)-O(1)	77.7(2)	O(2)-Te(1)-O(2)#6	90.5(5)
O(2)#3-Ag(1)-O(1)#3	62.6(2)	F(1)#8-Te(2)-F(1)#9	90.000(4)
O(2)#3-Ag(1)-O(1)#2	78.3(3)	F(1)#10-Te(2)-F(1)#8	180
O(2)#2-Ag(1)-O(1)#3	78.3(2)	F(1)#11-Te(2)-F(1)#9	90.000(1)
O(2)#1-Ag(1)-O(1)#3	151.1(2)	F(1)-Te(2)-F(1)#12	90.000(2)
O(2)-Ag(1)-O(1)#1	78.3(3)	F(1)-Te(2)-F(1)#9	90.000(2)
O(2)#1-Ag(1)-O(1)	78.3(2)	F(1)-Te(2)-F(1)#11	180

O(2)-Ag(1)-O(1)#2	151.1(2)	F(1)#12-Te(2)-F(1)#11	90.000(4)
O(2)-Ag(1)-O(1)	62.6(2)	F(1)#10-Te(2)-F(1)#9	90.000(3)
O(2)#3-Ag(1)-O(2)#1	126.7(3)	F(1)-Te(2)-F(1)#8	90.000(8)
O(2)#1-Ag(1)-O(2)#2	76.5(3)	F(1)#12-Te(2)-F(1)#9	180
O(2)#3-Ag(1)-O(2)#2	129.4(3)	F(1)#10-Te(2)-F(1)	90.000(3)
O(2)#1-Ag(1)-O(2)	129.4(3)	F(1)#10-Te(2)-F(1)#11	90.000(7)
O(2)#2-Ag(1)-O(2)	126.7(3)	F(1)#10-Te(2)-F(1)#12	90.000(3)
O(2)#3-Ag(1)-O(2)	76.5(4)	F(1)#8-Te(2)-F(1)#11	90.000(4)
		F(1)#12-Te(2)-F(1)#8	90

Symmetry transformations used to generate equivalent atoms:

For $AgTeO_2F$:

#1 1-X,1/2+Y,1/2-Z; #2 1-X,2-Y,-Z; #3 +X,3/2-Y,1/2+Z; #4 +X,3/2-Y,-1/2+Z; #5 1-X,-1/2+Y,1/2-Z; #6 +X,1/2-Y,-1/2+Z; #7 +X,1/2-Y,1/2+Z

For $Ag_2TeO_2F_2$:
#1 1/2-X,-1/2+Y,+Z; #2 1-X,-1/2+Y,1/2-Z; #3 1-X,1/2+Y,1/2-Z; #4 1/2-X,1/2+Y,+Z; #5 +X,3/2-Y,-1/2+Z; #6 1-X,2-Y,1-Z; #7 1-X,1-Y,1-Z

For $Ag_3F_3(TeF_6)(TeO_2)_{12}$:
#1 +X,-1-Y,-2-Z; #2 -X,+Y,-2-Z; #3 -X,-1-Y,+Z; #4 -1/2-X,1/2+Z,-3/2-Y; #5 -1/2-X,-3/2-Z,-1/2+Y; #6 1/2+Y,-1/2-X,-3/2-Z; #7 -1/2-Y,-1/2+X,-3/2-Z; #8 1+Y,+Z,-1+X; #9 1+Z,-1+X,+Y; #10 -1-Y,-2-Z,-1+X; #11 -X,-2-Y,+Z; #12 -1-Z,-1+X,-2-Y

Table S4. State energies (eV) of the highest valence band (H-VB) and the lowest conduction band (H-CB) of $AgTeO_2F$ and $Ag_2(TeO_2F_2)$.

Compound	K-point	H-VB	L-CB
$AgTeO_2F$	Z(0.000, 0.000, 0.500)	-0.00778	3.21377
	G(0.000, 0.000, 0.000)	-0.12896	2.28288
	Y(0.000, 0.500, 0.000)	-0.2482	3.09269
	A(-0.500,0.500, 0.000)	-0.24597	2.95289
	B(-0.500, 0.000, 0.000)	-0.20134	2.28718
	D(-0.500,0.000, 0.500)	-0.00981	3.1081
	E(-0.500, 0.500, 0.500)	-0.0261	3.50632
	C(0.000, 0.500, 0.500)	-0.01677	3.48323
$Ag_2(TeO_2F_2)$	G(0.000, 0.000, 0.000)	-0.05844	1.63577
	Z(0.000, 0.000, 0.500)	-0.07541	1.79551
	T(-0.500, 0.000, 0.500)	-0.1152	1.90439
	Y(-0.500, 0.000, 0.000)	-0.06226	1.78815
	S(-0.500, 0.500, 0.000)	-0.02199	2.53857
	X(0.000, 0.500, 0.000)	0	2.41571
	U(0.000, 0.500, 0.500)	-0.0204	2.53774
	R(-0.500, 0.500, 0.500)	-0.039	2.60582

Computational Methods.

Single-crystal structural data of $AgTeO_2F$ and $Ag_2(TeO_2F_2)$ were directly used for the theoretical calculations. The electronic structures and optical properties were calculated by using a plane-wave pseudopotentials method within density functional theory (DFT) implemented in the total energy code of CASTEP [1]. For the exchange-correlation functional, we chose Perdew−Burke−Ernzerhof (PBE) in the generalized gradient approximation (GGA) [2]. The interactions between the ionic cores and the electrons were described by the norm-conserving pseudopotential [3]. The following valence-electron configurations were considered in the computation: O-$2s^2 2p^4$, F-$2s^2 2p^5$, Te-$5s^2 5p^4$, and Ag-$4s^2 4p^6 4d^{10} 5s^1$. The number of plane waves included in the basis sets was determined by a cutoff energy of 850 eV. Monkhorst−Pack k-point sampling of 3 × 4 × 5 and 2 × 4 × 2 were used to perform numerical integration of the Brillouin zone for the two compounds.

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