Supporting Information

A defect pyrochlore−like acentric cubic lead titanium−tellurate crystal exhibiting strong second harmonic generation activity and an extended transparent window

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morphology. (c−f) Ti, Te, Pb, and O mapping results, respectively.

9. **Fig. S3** SHG intensity comparation of PTTO with the $AgGaS_2$ reference at 2 μm.

1. Flexibility Index (*F*) of Computational Methods.

F associated with the bonding electrons can be defined as the follows:

$$F = \frac{\exp\left[\left(R_0 - R_a\right) / B\right]}{\left(\sqrt{C_a} + \sqrt{C_b}\right)^2 / R_a^2}$$

the numerator represents the bond valence electron charge, while the denominator denotes the binding force between the bond electron and the nucleus. The term R_a represents the average bond length of the target group. R_0 denotes the standard bond length when an atom contributes precisely one unit of valence to the central atom of the group. The value of *B* is an empirical constant, typically 0.37 Å. The C_a (and C_b) of Ti, O and Zr are 4, 6 and 4, respectively.

Table S1 Crystallographic data and structural refinement for $Pb_4Ti_3TeO_{13}$.

empirical formula	$Pb_4Ti_3TeO_{13}$
formula weight	654.04
Crystal system	Cubic
Space group	$F\bar{4}3m$
a (Å)	10.3488(2)
b (Å)	10.3488(2)
c (Å)	10.3488(2)
Volume (Å^3)	1108.33(6)
Z	8
density (g/cm^3)	7.839
F (000)	2200
R (int)	0.05
completeness	100.0 %
GOF on (F^2)	1.177
final *R* indices [$F_o^2 > 2\sigma(F_o^2)$][a]	$R_1 = 0.0190$, $wR_2 = 0.0496$
R indices (all data)	$R_1 = 0.0191$, $wR_2 = 0.0501$
Flack factor	0.20(5)
CCDC number	2374242

[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 Selected bond lengths (Å) and angles (deg.) for $Pb_4Ti_3TeO_{13}$.

Pb(1)-O(1)	2.283(2)	Ti(1)-O(2)#10	1.948(5)
Pb(1)-O(3)#1	2.631(5)	Ti(1)-O(2)#11	1.948(5)
Pb(1)-O(3)#2	2.631(5)	Ti(1)-O(2)#12	1.948(5)
Pb(1)-O(3)#3	2.631(5)	Ti(1)-O(3)#13	1.961(4)
Pb(1)-O(2)#4	2.644(6)	Ti(1)-O(3)#14	1.961(4)
Pb(1)-O(2)#5	2.644(6)	Ti(1)-O(3)	1.961(4)
Pb(1)-O(2)#6	2.644(6)	Te(1)-O(3)#13	1.961(4)
Te(1)-O(2)#10	1.948(5)	Te(1)-O(3)#14	1.961(4)
Te(1)-O(2)#11	1.948(5)	Te(1)-O(3)	1.961(4)
Te(1)-O(2)#12	1.948(5)	O(2)#11-Te(1)-O(3)#13	179.0(4)
O(1)-Pb(1)-O(3)#1	80.15(13)	O(2)#12-Te(1)-O(3)#13	88.41(18)
O(1)-Pb(1)-O(3)#2	80.15(13)	O(2)#10-Te(1)-O(3)#14	88.41(18)
O(3)#1-Pb(1)-O(3)#2	117.14(7)	O(2)#11-Te(1)-O(3)#14	88.41(18)
O(1)-Pb(1)-O(3)#3	80.15(13)	O(2)#12-Te(1)-O(3)#14	179.0(4)
O(3)#1-Pb(1)-O(3)#3	117.14(7)	O(3)#13-Te(1)-O(3)#14	92.3(4)
O(3)#2-Pb(1)-O(3)#3	117.14(7)	O(2)#10-Te(1)-O(3)	179.0(4)
O(1)-Pb(1)-O(2)#4	97.48(12)	O(2)#11-Te(1)-O(3)	88.41(18)
O(3)#1-Pb(1)-O(2)#4	62.21(4)	O(2)#12-Te(1)-O(3)	88.41(18)
O(3)#2-Pb(1)-O(2)#4	62.21(4)	O(3)#13-Te(1)-O(3)	92.3(4)
O(3)#3-Pb(1)-O(2)#4	177.6(2)	O(3)#14-Te(1)-O(3)	92.3(4)
O(1)-Pb(1)-O(2)#5	97.48(12)	O(2)#10-Ti(1)-O(2)#11	90.9(3)
O(3)#1-Pb(1)-O(2)#5	62.21(4)	O(2)#10-Ti(1)-O(2)#12	90.9(3)
O(3)#2-Pb(1)-O(2)#5	177.6(2)	O(2)#11-Ti(1)-O(2)#12	90.9(3)
O(3)#3-Pb(1)-O(2)#5	62.21(4)	O(2)#10-Ti(1)-O(3)#13	88.41(18)
O(2)#4-Pb(1)-O(2)#5	118.33(5)	O(2)#11-Ti(1)-O(3)#13	179.0(4)
O(1)-Pb(1)-O(2)#6	97.48(12)	O(2)#12-Ti(1)-O(3)#13	88.41(18)
O(3)#1-Pb(1)-O(2)#6	177.6(2)	O(2)#10-Ti(1)-O(3)#14	88.41(18)
O(3)#2-Pb(1)-O(2)#6	62.21(4)	O(2)#11-Ti(1)-O(3)#14	88.41(18)

O(3)#3-Pb(1)-O(2)#6	62.21(4)	O(2)#12-Ti(1)-O(3)#14	179.0(4)
O(2)#4-Pb(1)-O(2)#6	118.33(5)	O(3)#13-Ti(1)-O(3)#14	92.3(4)
O(2)#5-Pb(1)-O(2)#6	118.33(5)	O(2)#10-Ti(1)-O(3)	179.0(4)
O(2)#10-Te(1)-O(2)#11	90.9(3)	O(2)#11-Ti(1)-O(3)	88.41(18)
O(2)#10-Te(1)-O(2)#12	90.9(3)	O(2)#12-Ti(1)-O(3)	88.41(18)
O(2)#11-Te(1)-O(2)#12	90.9(3)	O(3)#13-Ti(1)-O(3)	92.3(4)
O(2)#10-Te(1)-O(3)#13	88.41(18)	O(3)#14-Ti(1)-O(3)	92.3(4)

Symmetry transformations used to generate equivalent atoms:

#1 -y-1/2,z-5/2,-x+2 #2 z-5/2,-x,-y+3/2 #3 -x,-y-1/2,z-1/2

#4 -y-1,z-2,-x+2 #5 -x,-y-1,z #6 z-2,-x,-y+1

#7 -x-1/2,-y-1/2,z #8 x,-y-1/2,-z+7/2 #9 -x-1/2,y,-z+7/2

#10 y+1/2,z-2,x+3/2 #11 z-3/2,-x,-y+3/2 #12 -x+1/2,-y-1/2,z

#13 -y,z-2,-x+2 #14 z-2,-x,-y+2 #15 x,-y-1,-z+3

#16 -x-1,y,-z+3 #17 -x-1,-y-1,z #18 x+1/2,-y-1,-z+7/2

#19 x,-y,-z+4 #20 -x,-y-1/2,z+1/2 #21 -x,y+1/2,-z+7/2

Table S3 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) as well as atomic occupancy factors for $Pb_4Ti_3TeO_{13}$. U_{eq} is defined as one−third of the trace of the orthogonalized U_{ij} tensor, and the bond valence sum for each atom in asymmetric unit.

	x	y	z	*U(eq)*	BVS	OCC
Pb(1)	-3726(1)	-3726(1)	16274(1)	19(1)	2.079	1
Te(1)	1250(3)	-1250(3)	18750(3)	6(1)	4.442	0.25
Ti(1)	1250(3)	-1250(3)	18750(3)	6(1)		0.75
O(1)	-5000	-5000	15000	17(4)	2.519	1
O(2)	2500	-4397(7)	17500	8(1)	1.87	1
O(3)	1932(7)	0	20000	7(1)	1.84	1

Table S4 Anisotropic displacement parameters (Å^2 × 10^3) for $Pb_4Ti_3TeO_{13}$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pb(1)	19(1)	19(1)	19(1)	-3(1)	-3(1)	-3(1)
Te(1)	6(1)	6(1)	6(1)	0(1)	0(1)	0(1)
Ti(1)	6(1)	6(1)	6(1)	0(1)	0(1)	0(1)
O(1)	17(4)	17(4)	17(4)	0	0	0
O(2)	8(1)	7(2)	8(1)	0	-1(1)	0
O(3)	7(2)	7(1)	7(1)	0(1)	0	0

Table S5 The calculated "flexibility index" F of $Pb_4Ti_3TeO_{13}$ and Li_2ZrTeO_6.

	M-O (R_0)	M-O (R_a)	$exp[(R_0-R_a)/B]$	C_a (M)	C_b (O)	$\frac{\left(\sqrt{C_a}+\sqrt{C_b}\right)^2}{R_a^2}$	F
PTTO	1.815 (Ti-O)	1.955	0.686	4	6	5.182	0.132
Li_2ZrTeO_6	1.937 (Zr-O)	2.090	0.661	4	6	4.532	0.146

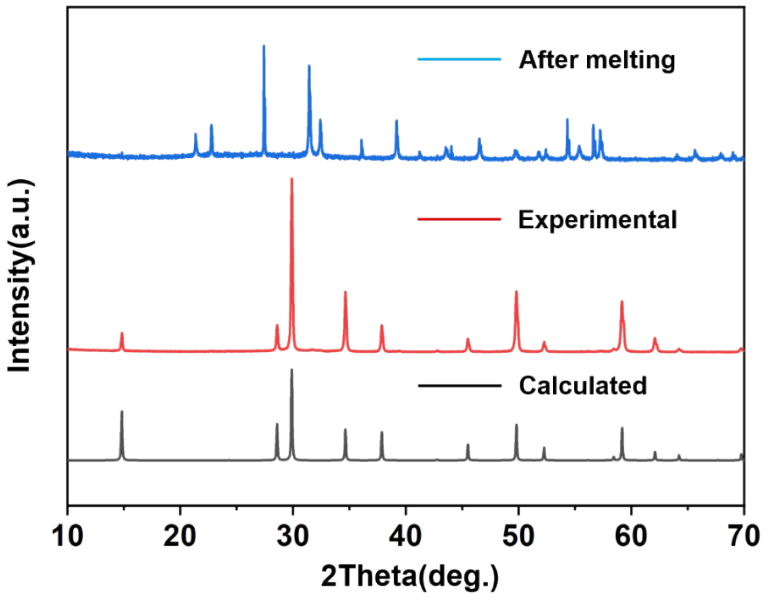

Fig. S1 PXRD curves of the initial and melted $Pb_4Ti_3TeO_{13}$ compound compared with the corresponding calculated data.

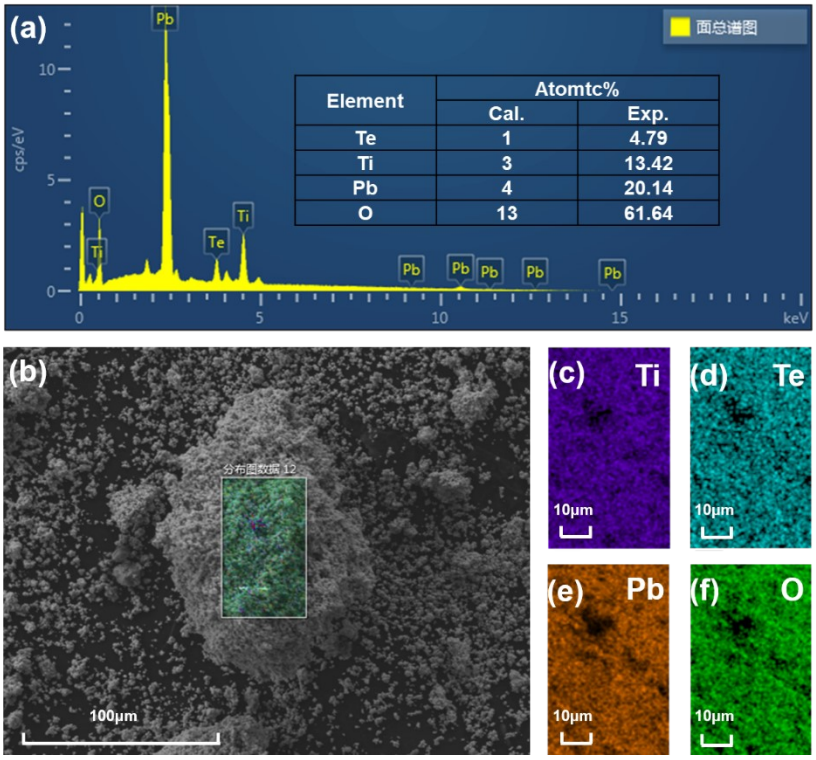

Fig. S2 EDS of $Pb_4Ti_3TeO_{13}$ (a) Atomic ratio of various elements, (b) Surface morphology, (c−f) Ti, Te, Pb and O mapping results, respectively.

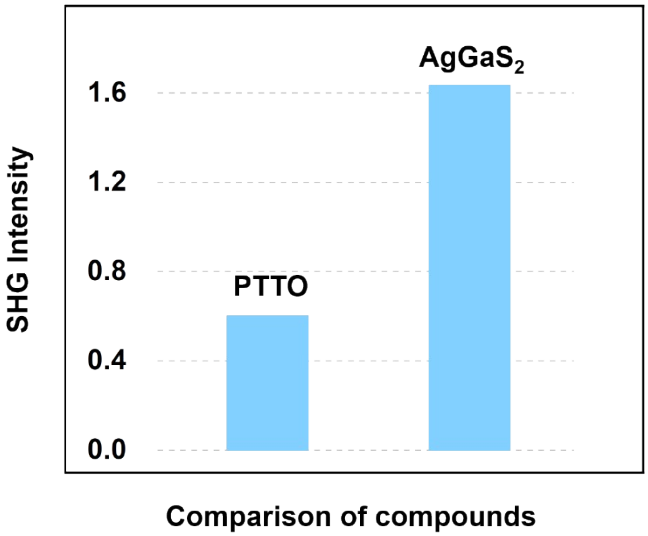

Fig. S3 SHG intensity comparation of $Pb_4Ti_3TeO_{13}$ with the $AgGaS_2$ reference at 2 μm.