Supporting Information

$Te_3O_3(PO_4)_2$: a Phosphate Crystal With Large Birefringence Activated by Highly Distorted [TeO_5] Group and Antiparallel [PO_4] Pseudo-layer

Weimin Dong,[†] Yingjie Sun,[‡] Qian Yao,[†] Lintao Liu,[†] Qingbo Wang,[†] Hang Wen,[†] Jing Li,*[,†] Xinguang Xu,[†] and Jiyang Wang[†]

[†]State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, P. R. China

[‡]School of Materials Science and Engineering, Yunnan University, Kunming 650091, P. R. China

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Czochralski method
（P_2O_5=20% mol）

flux method
（P_2O_5=22% mol）

flux method
（P_2O_5=25% mol）

Fig. S1. As-growth $Te_3O_3(PO_4)_2$ crystals by the Czochralski method and flux method.

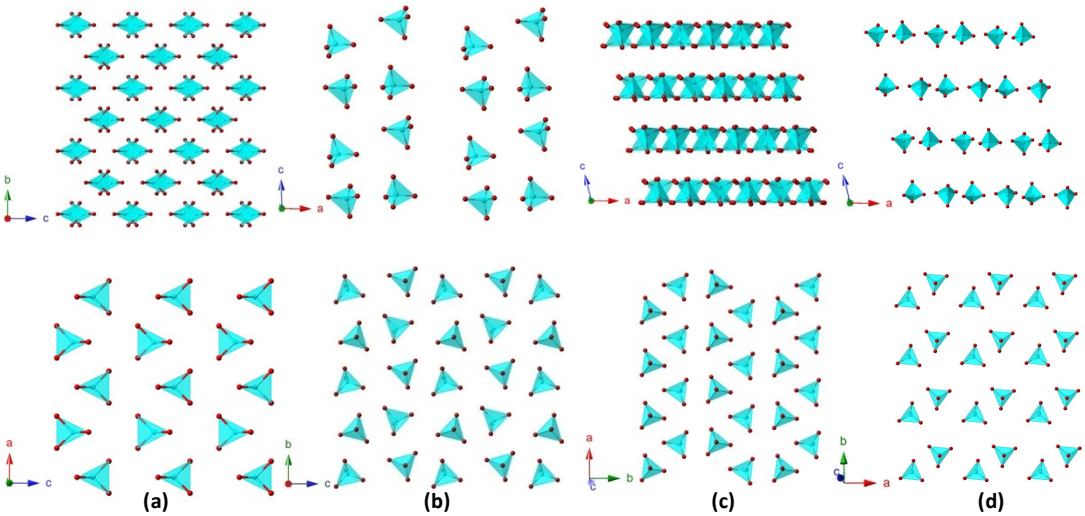

Fig. S2. Antiparallel [PO_4] pseudo-layer structure in (a) YPO_4, (b) $BaSn_2(PO_4)_2$, (c) $Te_2O(PO_4)_2$, and $Pb_2(IO_3)(PO_4)$.

Table S1. Crystallographic parameters and details of the structure refinement for $Te_3O_3(PO_4)_2$.

Empirical formula	$Te_3O_3(PO_4)_2$
Formula mass	620.74
Temperature/K	273(2)
Wavelength/nm	0.71073
color, habit	colorless block
Crystal system	Monoclinic
space group	$P2_1/c$
a/Å	12.371(8)
b/Å	7.325(5)
c/Å	9.836(6)
β/º	98.002(7)
Volume/Å^3	882.6(10)
Z	4
density/g/cm^3	4.671
Absorption coefficient/mm^{-1}	10.268
F(000)	1906
Crystal size/mm^3	0.21×0.20×0.20
GOF on F^2	1.035
Final R indices [I>2σ(I)]	R_1=0.0412, wR_2=0.1324
R indices (all data)	R_1=0.0505, wR_2=0.1464
Extinction coefficient	0.0026(4)

Table S2. Selected bond angles (deg.) in $Te_3O_3(PO_4)_2$.

bonds	bond angles	bonds	bond angles
O2-P1-O4	112.99(2)	O6-Te1-O2	84.46(2)
O2-P1-O3	107.01(9)	O11-Te2-O10	94.58(7)
O2-P1-O1	110.88(7)	O11-Te2-O5	89.36(8)
O4-P1-O3	111.50(3)	O11-Te2-O8	80.19(2)
O4-P1-O1	106.49(9)	O11-Te2-O6	84.20(4)
O3-P1-O1	107.87(0)	O10-Te2-O5	79.73(1)
O8-P2-O7	110.99(0)	O10-Te2-O8	81.45(7)
O8-P2-O9	112.65(9)	O10-Te2-O6	146.28(9)
O8-P2-O10	106.58(8)	O5-Te2-O8	157.64(6)
O7-P2-O9	110.18(0)	O5-Te2-O6	66.58(2)
O7-P2-O10	111.71(4)	O8-Te2-O6	130.96(5)
O9-P2-O10	104.50(4)	O6-Te3-O1	83.12(6)
O5-Te1-O11	88.26(0)	O6-Te3-O3	85.40(6)
O5-Te1-O4	78.19(5)	O6-Te3-O7	83.92(7)
O5-Te1-O6	76.68(9)	O6-Te3-O9	78.87(7)
O5-Te1-O2	84.03(8)	O1-Te3-O3	82.21(9)
O11-Te1-O4	91.51(9)	O1-Te3-O7	92.74(9)
O11-Te1-O6	88.4708	O1-Te3-O9	161.85(7)

O11-Te1-O2	170.56(3)	O3-Te3-O7	168.68(3)
O4-Te1-O6	154.87(3)	O3-Te3-O9	94.00(0)
O4-Te1-O2	92.2319	O7-Te3-O9	87.64(5)

Table S3. Bond length (Å) and Mulliken bond population in $Te_3O_3(PO_4)_2$.

bonds	length	population	bonds	length	population
Te1-O2	2.196(7)	0.13	Te3-O6	1.889(7)	0.32
Te1-O4	2.086(1)	0.11	Te3-O7	2.145 (6)	0.16
Te1-O5	1.908(1)	0.40	Te3-O9	2.149(3)	0.14
Te1-O6	2.088(5)	0.23	P1-O1	1.556(2)	0.56
Te1-O11	1.980(9)	0.17	P1-O2	1.519(4)	0.66
Te2-O5	1.976(6)	0.24	P1-O3	1.525(0)	0.61
Te2-O6	2.482(0)	0.04	P1-O4	1.521(1)	0.61
Te2-O8	2.284(6)	0.09	P2-O7	1.527(4)	0.62
Te2-O10	1.965(9)	0.22	P2-O8	1.513(5)	0.70
Te2-O11	1.825(7)	0.45	P2-O9	1.542(3)	0.60
Te3-O1	2.091(1)	0.17	P2-O10	1.570(3)	0.51
Te3-O3	2.125(7)	0.16			

Table S4. The UV and IR cutoff edge for the reported inorganic phosphate crystals.

compounds	UV cutoff edge (nm)	IR cutoff edge (nm)
KDP[1]	175	1500
ADP[2]	190	1500
DKDP[1]	175	1800
$CsLa(PO_3)_4$[3]	167	4000
$Kla(PO_3)_4$[4]	162	4000
$KGd(PO_3)_4$[5]	180	4000
$K_4Mg_4(P_2O_7)_3$[6]	170	4210
BPO_4[7]	134	4230
Ga_3PO_7[8]	250	4300
$LiFeP_2O_7$[9]	480	4300
RTP[10]	350	4500
KTP[10]	350	4500
$YSr_3(PO_4)_3$[11]	190	4500
$YBa_3(PO_4)_3$[11]	190	4500
$Te_2O(PO_4)_2$[12]	290	4700
$Te_3O_3(PO_4)_2$	290	4760

Table S5. Birefringence at 1064 nm of $Te_3O_3(PO_4)_2$ and some known phosphate crystals.

compound	birefringence	refs.
$RbNaMgP_2O_7$	0.0034	[13]
BPO_4	0.005	[7]
$K_4Mg_4(P_2O_7)_3$	0.007	[6]
$LiCs_2PO_4$	0.008	[14]
$KLa(PO_3)_4$	0.0084	[4]
$Ba_5P_6O_{20}$	0.009	[14]
$RbPb_4(PO_4)_3$	0.014	[15]
$LiPbPO_4$	0.021	[16]
$KPb_2(PO_3)_5$	0.021	[17]
$Ba_3P_3O_{10}Cl$	0.028	[6]
KDP	0.034	[18]
$Ba_3(ZnB_5O_{10})PO_4$	0.040	[19]
$Pb_3Mg_3TeP_2O_{14}$	0.050	[20]
$Pb_2(IO_3)(PO_4)$	0.060	[21]
$LiHgPO_4$	0.068	[16]
$BaSn_2(PO_4)_2$	0.071	[14]
KTP	0.09	[22]
YPO_4	0.101	[23]
$Te_2O(PO_4)_2$	0.103	[12]
$ScPO_4$	0.112	[23]
$Te_3O_3(PO_4)_2$	0.148	this work

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