$Na_6Te_4W_6O_{29}$ and $Na_2TeW_2O_9$: Synthesis, structure, crystal growth, morphology and characterization of two d^0 transition metal tellurites with large birefringence

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Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Na_6Te_4W_6O_{29}$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}	BVS
Na(1)	9927(5)	123(1)	7519(3)	29(1)	1.13
Na(2)	4775(4)	2567(1)	2086(3)	16(1)	1.09
Na(3)	4587(9)	10(2)	7112(7)	26(1)	0.83
Na(4)	10168(8)	1440(3)	9837(6)	28(1)	0.91
W(1)	5092(1)	1285(1)	4848(1)	6(1)	6.01
W(2)	10248(1)	1227(1)	4970(1)	6(1)	6.17
W(3)	4992(1)	3712(1)	5012(1)	7(1)	6.17
Te(1)	9579(1)	2555(1)	6899(1)	7(1)	3.98
Te(2)	9592(1)	969(1)	9956(1)	8(1)	3.82
Te(3)	6176(1)	274(1)	8192(1)	7(1)	3.97
O(1)	7629(6)	712(2)	10385(5)	13(1)	2.02
O(2)	10282(6)	2142(2)	5685(5)	11(1)	1.98
O(3)	2874(6)	1552(2)	5108(4)	9(1)	2.08
O(4)	3785(6)	1746(2)	2989(5)	16(1)	2.04
O(5)	7405(6)	2007(2)	6655(5)	11(1)	1.96
O(6)	13118(6)	1097(2)	7593(4)	13(1)	2.03
O(7)	3612(6)	588(2)	3798(5)	15(1)	1.81
O(8)	8100(6)	1045(2)	5311(4)	9(1)	2.07
O(9)	7721(6)	1503(2)	2600(4)	12(1)	1.92
O(10)	7199(6)	826(2)	7454(4)	10(1)	2.18
O(11)	3042(6)	3126(2)	4612(5)	14(1)	2.04
O(12)	7100(6)	3073(2)	4879(4)	12(1)	2.02
O(13)	10446(6)	496(2)	4454(5)	13(1)	2.01
O(14)	6080(7)	-679(2)	9560(5)	20(1)	1.86
O(15)	9485(11)	-106(3)	9680(8)	7(1)	1.75

Table S2. Selected bond distances (Å) and angles (deg) for $Na_6Te_4W_6O_{29}$.

Na(1)-O(13)#1	2.296(4)	O(7)-W(1)-O(3)	97.32(15)
Na(1)-O(1)#2	2.426(4)	O(4)-W(1)-O(3)	95.63(15)
Na(1)-O(7)#3	2.480(4)	O(7)-W(1)-O(8)	91.76(15)
Na(1)-O(10)	2.489(4)	O(4)-W(1)-O(8)	95.58(15)
Na(1)-O(15)	2.508(8)	O(3)-W(1)-O(8)	163.97(14)
Na(1)-O(15)#2	2.604(7)	O(7)-W(1)-O(5)	166.96(15)
Na(1)-O(8)	2.616(4)	O(4)-W(1)-O(5)	91.91(15)
Na(1)-O(14)#2	2.641(5)	O(3)-W(1)-O(5)	83.91(13)
Na(2)-O(4)	2.356(4)	O(8)-W(1)-O(5)	84.31(13)
Na(2)-O(12)	2.377(4)	O(7)-W(1)-O(10)	88.31(15)
Na(2)-O(3)#4	2.430(4)	O(4)-W(1)-O(10)	170.53(15)
Na(2)-O(11)#4	2.438(4)	O(3)-W(1)-O(10)	85.46(13)
Na(2)-O(5)#4	2.441(4)	O(8)-W(1)-O(10)	81.62(13)
Na(2)-O(2)#5	2.607(4)	O(5)-W(1)-O(10)	78.83(13)
Na(2)-O(9)	2.967(4)	O(13)-W(2)-O(8)	96.83(15)
Na(3)-O(14)	2.455(6)	O(13)-W(2)-O(9)	96.65(16)
Na(3)-O(7)#3	2.456(6)	O(8)-W(2)-O(9)	96.11(14)
Na(3)-O(10)	2.461(6)	O(13)-W(2)-O(3)#11	94.14(15)
Na(3)-O(13)#7	2.529(6)	O(8)-W(2)-O(3)#11	166.05(14)
Na(3)-O(15)	2.623(8)	O(9)-W(2)-O(3)#11	91.13(14)
Na(3)-O(6)#7	2.794(6)	O(13)-W(2)-O(6)	92.83(15)
Na(3)-O(1)	2.888(6)	O(8)-W(2)-O(6)	87.49(14)
Na(3)-O(8)#3	2.946(6)	O(9)-W(2)-O(6)	169.37(14)
Na(4)-O(10)	2.282(6)	O(3)#11-W(2)-O(6)	83.38(14)
Na(4)-O(11)#8	2.464(6)	O(13)-W(2)-O(2)	175.63(14)
Na(4)-O(4)#9	2.482(6)	O(8)-W(2)-O(2)	87.00(13)
Na(4)-O(12)#10	2.516(6)	O(9)-W(2)-O(2)	84.99(14)
Na(4)-O(5)	2.690(6)	O(3)#11-W(2)-O(2)	81.76(13)
Na(4)-O(1)	2.788(6)	O(6)-W(2)-O(2)	85.22(14)
Na(4)-O(14)#2	2.894(6)	O(11)-W(3)-O(14)#12	100.60(18)
Na(4)-O(15)#2	2.945(9)	O(11)-W(3)-O(6)#5	96.76(15)
W(1)-O(7)	1.751(3)	O(14)#12-W(3)-O(6)#5	96.76(17)
W(1)-O(4)	1.753(4)	O(11)-W(3)-O(9)#10	92.73(15)
W(1)-O(3)	1.911(3)	O(14)#12-W(3)-O(9)#10	93.15(16)
W(1)-O(8)	1.980(3)	O(6)#5-W(3)-O(9)#10	164.78(15)
W(1)-O(5)	2.119(3)	O(11)-W(3)-O(1)#4	168.71(15)
W(1)-O(10)	2.210(3)	O(14)#12-W(3)-O(1)#4	90.69(16)
W(2)-O(13)	1.725(3)	O(6)#5-W(3)-O(1)#4	81.44(14)
W(2)-O(8)	1.877(3)	O(9)#10-W(3)-O(1)#4	86.93(14)
W(2)-O(9)	1.877(3)	O(11)-W(3)-O(12)	90.78(16)
W(2)-O(3)#11	1.963(3)	O(14)#12-W(3)-O(12)	167.07(15)
W(2)-O(6)	1.994(3)	O(6)#5-W(3)-O(12)	87.88(14)
W(2)-O(2)	2.130(3)	O(9)#10-W(3)-O(12)	80.09(13)

W(3)-O(11)	1.747(3)	O(1)#4-W(3)-O(12)	78.04(14)
W(3)-O(14)#12	1.751(4)	O(5)-Te(1)-O(2)	101.55(14)
W(3)-O(6)#5	1.884(3)	O(5)-Te(1)-O(12)	98.60(15)
W(3)-O(9)#10	1.995(3)	O(2)-Te(1)-O(12)	93.07(15)
W(3)-O(1)#4	2.110(3)	O(1)-Te(2)-O(10)	97.40(15)
W(3)-O(12)	2.157(3)	O(1)-Te(2)-O(15)#2	83.4(2)
Te(1)-O(5)	1.869(3)	O(10)-Te(2)-O(15)#2	88.6(2)
Te(1)-O(2)	1.878(3)	O(1)-Te(2)-O(15)	76.1(2)
Te(1)-O(12)	1.926(3)	O(10)-Te(2)-O(15)	75.49(19)
Te(2)-O(1)	1.859(4)	O(15)#2-Te(2)-O(15)	16.2(3)
Te(2)-O(10)	1.893(3)	O(10)-Te(3)-O(1)	95.71(15)
Te(2)-O(15)#2	1.955(7)	O(15)-Te(3)-O(1)	84.8(2)
Te(3)-O(10)	1.841(3)	O(10)-Te(3)-O(15)#2	79.1(2)
Te(3)-O(15)	1.952(7)	O(15)-Te(3)-O(15)#2	16.8(3)
Te(3)-O(1)	1.959(4)	O(1)-Te(3)-O(15)#2	71.79(19)
O(7)-W(1)-O(4)	100.85(17)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z+1 #2 -x+2,-y,-z+2 #3 -x+1,-y,-z+1 #4 x,-y+1/2,z-1/2 #5 x-1,-y+1/2,z-1/2 #6 x-1,y,z-1 #7 x-1,y,z #8 x+1,-y+1/2,z+1/2 #9 x+1,y,z+1 #10 x,-y+1/2,z+1/2 #11 x+1,y,z #12 -x+1,y+1/2,-z+3/2 #13 -x+1,y-1/2,-z+3/2

Table S3. The calculated linear density of the valence electrons in $Na_6Te_4W_6O_{29}$ and $Na_2TeW_2O_9$ (The following orbital electrons were treated as valence electrons: Na $2s^2p^63s^1$, W $4f^{14}5d^46s^2$, Te $5s^25p^4$ and O $2s^22p^4$, and they were projected in crystallographic axis, respectively)

$Na_6W_6Te_4O_{29}$	**x (//b)**	**y (37.0° to *z*)**	**z (6.5° to *a*)**
$\rho_{(Na)}$	5.117	3.76	4.74
$\rho_{(Te)}$	4.54	5.29	7.31
$\rho_{(W)}$	8.86	10.39	10.06
$\rho_{(O)}$	12.98	13.22	17.60
ρ for unit cell	31.45	32.66	39.72
Unit cell/V	0.0262	0.0272	0.0331
$Na_2TeW_2O_9$	**x (46.5° to *z*)**	**y (41.5° to *a*)**	**z (//b)**
$\rho_{(Na)}$	5.32	5.76	9.78
$\rho_{(Te)}$	4.83	5.44	6.53
$\rho_{(W)}$	11.70	14.47	19.62
$\rho_{(O)}$	15.20	20.04	30.16
Unit cell	37.06	45.71031	66.08484
Unit cell/V	0.0123	0.0152	0.0219

Figure S1. Experimental and calculated X-ray powder diffraction patterns (* marks the $Na_2TeW_2O_9$ phase in the solid product after melting $Na_6Te_4W_6O_{29}$).

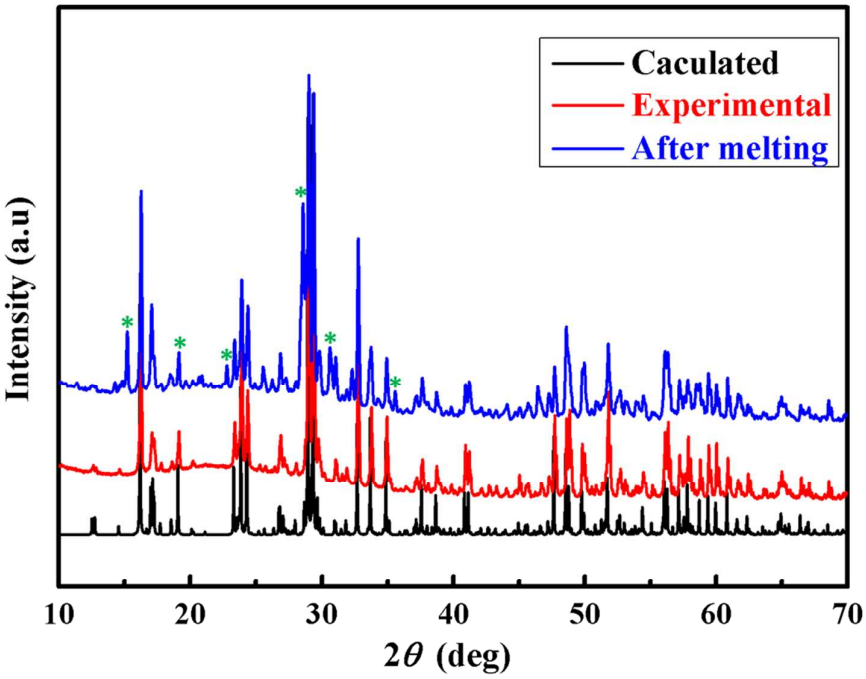

Figure S2. The schematic diagram for the measurement of the refractive index.

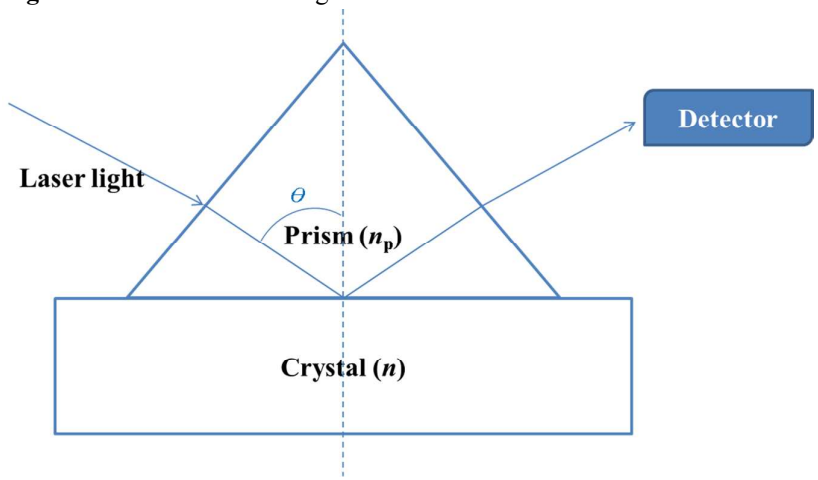

Figure S3. The As-grown $Na_6Te_4W_6O_{29}$ crystal with [010]-orientation seed

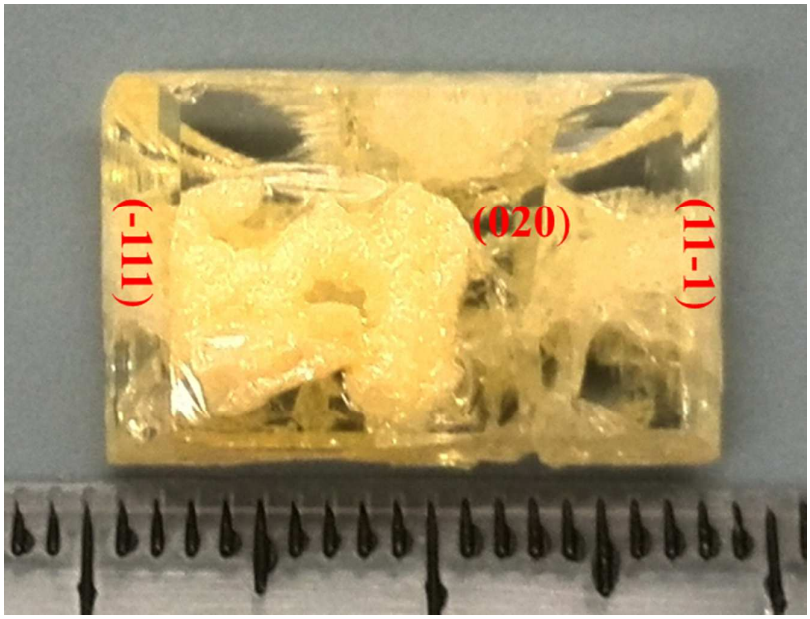
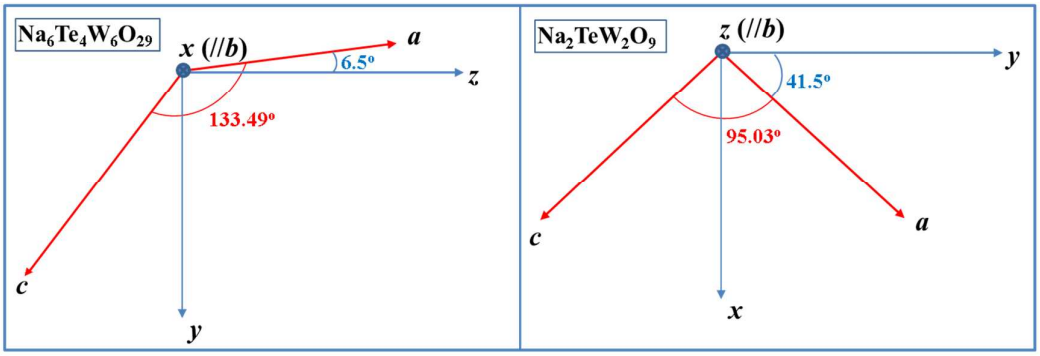
Figure S4. The relationships of the optical axes (*x*, y, and *z*) and crystallographic axes (*a*, *b*, and *c*) in $Na_6Te_4W_6O_{29}$ and $Na_2TeW_2O_9$.