Supporting Information

Crystal Growth and Optical Properties of a Noncentrosymmetric Molybdenum Tellurite, $Na_2Te_3Mo_3O_{16}$

Table S1 Crystallographic Data for $Na_2Te_3Mo_3O_{16}$

formula	$Na_2Te_3Mo_3O_{16}$
formula weight	972.6
crystal sizes (mm^3)	0.29×0.22×0.21
color, habit	yellow, block
crystal system	monoclinic
space group	I2 (No. 5)
a (Å)	7.3130(15)
b (Å)	11.236(2)
c (Å)	8.2171(16)
β (deg)	97.26(3)
V ($Å^3$)	669.8(2)
Z	2
T (°C)	153(2)
λ (Å)	0.71073
ρ_{calcd} (g cm^{-3})	4.823
μ (mm^{-1})	9.326
$2\theta_{max}$ (deg)	65.12
reflection collected/unique	4261/2129
Absorption correction	Psi-scan
R(int)	0.0458
GOF	1.073
Extinction coefficient	0.00347(13)
R1, wR2 [I >2σ(I)]a	0.0292, 0.0641
R1, wR2 (all data)	0.0307, 0.0646

$^aR1=\sum ||F_o| - |F_c||/ \sum|F_o|$, $wR2=\{\sum w[(F_o)^2- (Fc)^2]^2/\sum w(F_o^2)^2\}^{1/2}$.

Structure Description:

$Na_2Te_3Mo_3O_{16}$ crystallizes in the noncentrosymmetric monoclinic space group $I2$ with cell parameters a = 7.3130(15) Å, b = 11.236(2) Å, c = 8.2171(16) Å, β = 97.26(3)° and Z = 2. Structure of $Na_2Te_3Mo_3O_{16}$ is illustrated along the c axis in Fig. S1 The compound has a one-dimensional structure composed of $[Te_3Mo_3O_{16}]^{2-}$ anionic chain and Na^+ cations for charge balance. In the $Na_2Te_3Mo_3O_{16}$ structure, three $[MoO_6]^{6-}$ octahedra share their edges to form a $[Mo_3O_{14}]^{10-}$ trimer. Two $[TeO_3]^{2-}$ and one $[TeO_4]^{4-}$, are connected via corner-sharing oxygen atoms to form a $[Te_3O_8]^{4-}$ cluster. And the $[Mo_3O_{14}]^{10-}$ (see Fig. S2a) and $[Te_3O_8]^{4-}$ (see Fig. S2b) are corner-sharing each other to form infinitely long $[Te_3Mo_3O_{16}]^{2-}$ anionic chain (see Fig. S3c). Both Mo^{6+} and Te^{4+} cations are in asymmetric coordination environments owing to SOJT effects. The Mo^{6+} cations in octahedral coordination environments are distorted toward an edge, with Mo–O bond distances ranging from 1.711(6) to 2.194(5) Å. The value of the distortion (Δ*d*) was calculated to be 0.929 and 0.988 Å^2 for Mo(1) and Mo(2), respectively.[S1] The Te(1)$^{4+}$ cation is bound to four oxygen atoms to form trigonal-bipyramidal $[TeO_4]^{4-}$, while the Te(2)$^{4+}$ cation is bound to three oxygen atoms to form pyramidal $[TeO_3]^{2-}$. The Te–O distances vary from 1.852(5) to 2.050(5) Å. The bond valence sums (BVS) are calculated to be values of 6.022, 5.972, 4.084 and 3.852 for Mo(1)$^{6+}$, Mo(2)$^{6+}$, Te(1)$^{4+}$ and Te(2)$^{4+}$, respectively,[S2–S4] which is consistent with the structure reported previously.[S5]

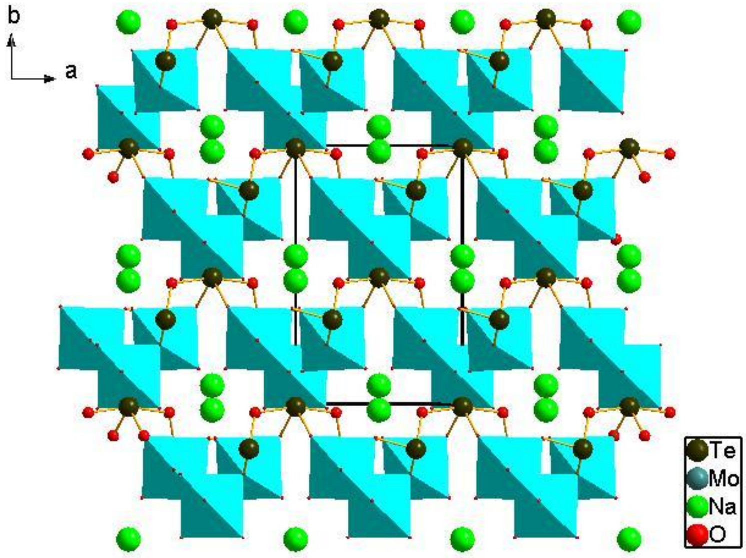

Fig. S1 One-dimensional crystal structure of $Na_2Te_3Mo_3O_{16}$ viewed down c axis with Na–O bonds omitted for clarity. The MoO_6 octahedra are shaded in turquoise.

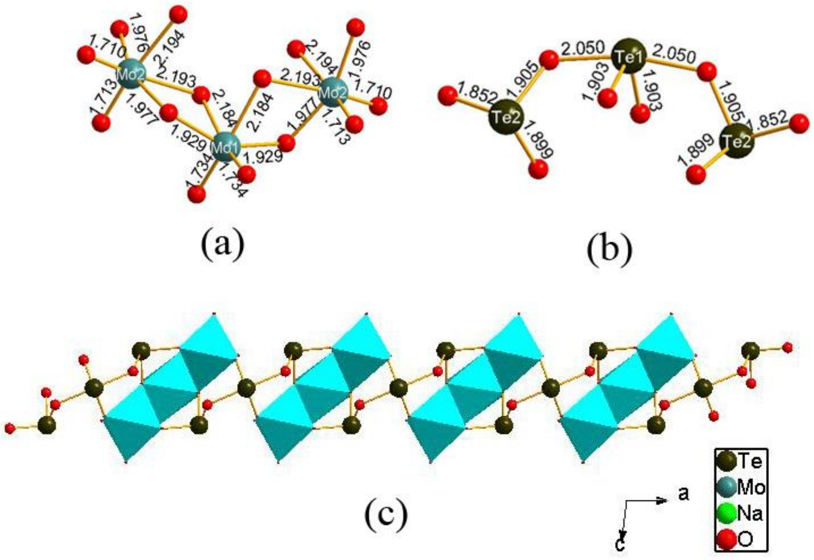

Fig. S2 The coordinations of Mo atoms (a) and Te atoms (b), 1D $[Te_3Mo_3O_{16}]^{2-}$ anionic chain (c) in $Na_2Te_3Mo_3O_{16}$. The MoO_6 octahedra are shaded in turquoise.

Table S2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for $Na_2Te_3Mo_3O_{16}$. Ueq is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	U(eq)
Te(1)	0	0.9896(1)	0.5000	0.004(1)
Te(2)	0.2789(1)	0.8268(1)	0.2811(1)	0.005(1)
Mo(1)	0.5000	0.5790(1)	0.5000	0.005(1)
Mo(2)	0.2536(1)	0.7403(1)	0.7275(1)	0.005(1)
Na(1)	0.5000	0.10718(7)	0.5000	0.026(2)
Na(2)	0.5000	0.9771(5)	0	0.011(1)
O(1)	0.0919(7)	0.8779(4)	0.6643(6)	0.008(1)
O(2)	0.2421(7)	0.9675(5)	0.4021(7)	0.008(1)
O(3)	0.3111(7)	0.7303(5)	0.4723(6)	0.007(1)
O(4)	0.5200(7)	0.8693(4)	0.2625(6)	0.007(1)
O(5)	0.4582(7)	0.6265(4)	0.7178(6)	0.006(1)
O(6)	0.1859(7)	0.9843(5)	0.0494(6)	0.009(1)
O(7)	0.2718(8)	0.7464(5)	0.9369(7)	0.014(1)
O(8)	0.0802(8)	0.6375(5)	0.6914(7)	0.013(1)

Table S3. Bond distances (Å) for $Na_2Te_3Mo_3O_{16}$.

Te(1)-O(1)	1.903(5)	Na(1)-O(2)	2.279(7)
Te(1)-O(1)#1	1.903(5)	Na(1)-O(2)#6	2.279(7)
Te(1)-O(2)	2.050(5)	Na(1)-O(8)#2	2.774(6)
Te(1)-O(2)#1	2.050(5)	Na(1)-O(8)#7	2.774(6)
Te(2)-O(4)	1.852(5)	Na(1)-O(7)#7	2.886(8)
Te(2)-O(3)	1.899(5)	Na(1)-O(7)#2	2.886(8)
Te(2)-O(2)	1.905(5)	Na(1)-O(4)#6	3.013(8)
Mo(1)-O(6)#4	1.734(5)	Na(1)-O(4)	3.013(8)
Mo(1)-O(6)#5	1.734(5)	Na(2)-O(6)	2.384(5)
Mo(1)-O(5)	1.929(5)	Na(2)-O(6)#8	2.384(5)
Mo(1)-O(5)#6	1.929(5)	Na(2)-O(8)#7	2.415(7)
Mo(1)-O(3)#6	2.184(5)	Na(2)-O(8)#9	2.415(7)
Mo(1)-O(3)	2.184(5)	Na(2)-O(4)#8	2.462(6)
Mo(2)-O(7)	1.711(6)	Na(2)-O(4)	2.462(6)
Mo(2)-O(8)	1.713(6)	O(4)-Mo(2)#6	2.194(5)
Mo(2)-O(1)	1.976(5)	O(6)-Mo(1)#3	1.734(5)
Mo(2)-O(5)	1.977(5)	O(7)-Na(1)#10	2.886(8)
Mo(2)-O(3)	2.193(5)	O(8)-Na(2)#10	2.415(7)
Mo(2)-O(4)#6	2.194(5)	O(8)-Na(1)#10	2.774(6)

Symmetry transformations used to generate equivalent atoms:

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

References

S1. P. S. Halasyamani, Chem. Mater., 2004, **16**, 3586–3592.

S2. D. Brown, D. Altermatt, Acta Crystallogr., Sect. B: Struct. Sci., 1985, **41**, 244–247.

S3. N. E. Brese, M. O’Keeffe, Acta Crystallogr., Sect. B: Struct. Sci., 1991, **47**, 192–197.

S4. Bond valences calculated with the program Bond Valence Calculator Version 2.00, Hormillosa, C., Healy, S., Stephen, T. McMaster University (1993).

S5. E. O. Chi, K. M. Ok, Y. Porter, P. S. Halasyamani, Chem. Mater., 2006, **18**, 2070–2074.