

Hg₂(SeO₃)(TeO₃): A novel tellurite-selenite birefringent crystal achieved by assembling multiple functional groups

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S1. Experimental Section

Reagents and Instruments

SeO₂ (Adamas-beta, 99.99%), TeO₂ (Adamas-beta, 99.99%) and HgO (J&K Scientific, 99.9%) were obtained from commercial sources and used without further purification.

Powder X-ray diffraction (PXRD) patterns of Hg₂(SeO₃)(TeO₃) was collected on the Miniflex 600 powder X-ray diffractometer using Cu K α radiation ($\lambda = 1.54186 \text{ \AA}$) at room temperature in the angular range of $2\theta = 10\text{-}70^\circ$ with a scan step size of 0.02° .

Microprobe elemental analyses was carried out with the aid of a field-emission scanning electron microscope (FESEM, JSM6700F) equipped with an energy-dispersive X-ray spectroscope (EDS, Oxford INCA).

IR spectra was carried out on a Magna 750 FT-IR spectrometer using air as background in the range of $4000\text{-}400 \text{ cm}^{-1}$ with a resolution of 2 cm^{-1} at room temperature.

The UV-vis-NIR spectra was obtained at $2000\text{-}200 \text{ nm}$ by a PerkinElmer Lambda 900 spectrophotometer using BaSO₄ as the reference, and the reflection spectra was converted into an absorption spectrum using the Kubelka-Munk function. Absorption data was calculated from the diffuse reflection data by the Kubelka-Munk function: $\alpha/S = (1-R)^2/2R$, where α and S represent the absorption coefficient and the scattering coefficient, respectively. The band gap value can be given by extrapolating the absorption edge to the baseline in the α/S vs. energy graph[1].

Thermogravimetric analyses (TGA) were measured by Netzsch STA 499C installation. The samples about 3.0-5.0 mg were placed in alumina crucibles and heated in 20-1000 °C at a rate of 15 K/min under N₂ atmosphere.

Single-crystal X-ray diffraction

Single crystal X-ray diffraction data of Hg₂(SeO₃)(TeO₃) was obtained on Agilent Technologies SuperNova dual-wavelength CCD diffractometer with a graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. Data reduction and cell refinement and were performed with *CrysAlisPro*. The structure was solved by the direct methods and refined by full-matrix least-squares fitting on F^2 using *Olex2-1.5* crystallographic software package[2, 3]. All of the atoms were refined with anisotropic thermal parameters and finally converged for $F_0^2 \geq 2\sigma(F_0^2)$. The structural data was also checked for possible missing symmetry with the program *PLATON*, and no higher symmetry was found[4, 5]. The detailed crystallographic data for Hg₂(SeO₃)(TeO₃) was given in Table S1. The bond lengths were listed in Table S2.

Syntheses

Single crystals of Hg₂(SeO₃)(TeO₃) were successfully obtained by high-temperature hydrothermal reaction. A mixture of SeO₂ (111.1 mg, 1 mmol), TeO₂ (159.6 mg, 1 mmol) and HgO (325 mg, 1.5 mmol) was sealed in an autoclave containing PPL liner equipped (23 ml), heated at 270 °C for 5760 minutes, and then slowly cooled to room temperature in 4320 minutes. The products were separated by vacuum filtration, washed with alcohol and dried in air at room temperature. The transparent Hg₂(SeO₃)(TeO₃) crystal was obtained. Its purity has been verified through X-ray diffraction (XRD) studies (Figure S1). (*Note: PPL lining is renowned*

for its high-temperature resistance and strong corrosion resistance, maintaining its integrity and sealing even under conditions of 280 °C.)

S2. Computational Method

Single-crystal structural data of $\text{Hg}_2(\text{SeO}_3)(\text{TeO}_3)$ was used for the theoretical calculations. The electronic structures were performed using a plane-wave basis set and pseudo-potentials within density functional theory (DFT) implemented in the total-energy code CASTEP[6]. For the exchange and correlation functional, we chose Perdew–Burke–Ernzerhof (PBE) in the generalized gradient approximation (GGA)[7]. The interactions between the ionic cores and the electrons were described by the Norm conserving pseudopotential[8]. The following valence-electron configurations were considered in the computation: Se-4s²4p⁴, Te-5s²5p⁴, Hg-5d¹⁰5p⁶6s² and O-2s²2p⁴. The numbers of plane waves included in the basis sets were determined by cutoff energy of 750 eV for $\text{Hg}_2(\text{SeO}_3)(\text{TeO}_3)$. The numerical integration of the Brillouin zone was performed using Monkhorst-Pack k-point sampling of $3 \times 2 \times 3$ for $\text{Hg}_2(\text{SeO}_3)(\text{TeO}_3)$. The other parameters and convergent criteria were the default values of CASTEP code.

Calculated method of linear optical response properties

The calculations of linear optical properties in terms of the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ were made. The imaginary part of the dielectric function ε_2 was given in the following equation:

$$\varepsilon_{ij_2}(\omega) = \frac{8\pi^2 \hbar^2 e^2}{(m^2 V)} \sum_k \sum_{cv} (f_c - f_v) \frac{p_{cv}^i(k) p_{cv}^j(k)}{E_{vc}^2} \delta[E_c(k) - E_v(k) - \hbar\omega]$$

The f_c and f_v represent the fermi distribution functions of the conduction and valence band. The term $p_{cv}^i(k)$ denotes the momentum matrix element transition from the energy level c of the conduction band to the level v of the valence band at the k th

point in the Brillouin zone (BZ), and V is the volume of the unit cell.

The real part $\varepsilon_1(\omega)$ of the dielectric function $\varepsilon(\omega)$ follows from the Kramer–Kronig relationship. All the other optical constants may be derived from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$. For example, the refractive index $n(\omega)$ can be calculated using the following expression[7]:

$$n(\omega) = \frac{1}{\sqrt{2}} \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} + \varepsilon_1(\omega) \right]^{1/2}$$

Table S1. Summary of crystal data and structural refinements for Hg₂(SeO₃)(TeO₃).

molecular formula	Hg₂(SeO₃)(TeO₃)
Formula Weight	703.74
crystal system	monoclinic
space group	<i>P2₁/c</i>
Temperature(K)	286.15
F(000)	1176.0
a/Å	7.4108(3)
b/Å	12.2602(6)
c/Å	6.9718(4)
α(deg)	90
β(deg)	96.634(4)
γ(deg)	90
V/Å ³	629.20(5)
Z	4
Dc(g.cm ⁻³)	7.429
GOF on F ²	1.037
R ₁ , wR ₂ [I > 2σ(I)] ^a	R ₁ = 0.0290, wR ₂ = 0.0695
R ₁ , wR ₂ (all data) ^a	R ₁ = 0.0309, wR ₂ = 0.0704
^a R ₁ = $\sum F_o - F_c /\sum F_o $, wR ₂ = $\{\sum w[(F_o)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$	

Table S2. Calculated bond valences for Hg₂(SeO₃)(TeO₃).

Compound	Bond	Bond	Bond-valence	BVS
		lengths		
Hg ₂ (SeO ₃)(TeO ₃)	Se(1)-O(1)	1.720(8)	1.28	3.98
	Se(1)-O(3)	1.711(9)	1.31	
	Se(1)-O(4)	1.690(9)	1.39	
	Te(1)-O(2)	1.846(9)	1.42	4.15
	Te(1)-O(5)	1.854(9)	1.39	
	Te(1)-O(6)	1.869(9)	1.34	
	Hg(1)-O(1)	2.126(8)	0.59	1.78
	Hg(1)-O(3)#1	2.480(9)	0.23	
	Hg(1)-O(4)#2	2.451(9)	0.24	
	Hg(1)-O(4)#3	2.627(9)	0.15	
	Hg(1)-O(6)	2.139(9)	0.57	
	Hg(2)-O(2)#2	2.458(10)	0.24	
	Hg(2)-O(2)#4	2.154(10)	0.55	1.71 1.81
	Hg(2)-O(3)	2.306(9)	0.36	
	Hg(2)-O(5)	2.143(10)	0.56	
	Hg(2)-O(4)	2.780	0.10	

Green font: Longer Hg-O bonds are considered.

Symmetry transformations used to generate equivalent atoms:

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

Table S3. State energies (eV) of the lowest conduction band (L-CB) and the highest valence band (H-VB) of Hg₂(SeO₃)(TeO₃).

k-point	L-CB	H-VB
Z (0.000, 0.000, 0.500)	2.968588	-0.01797
G (0.000, 0.000, 0.000)	2.774069	-0.11617
Y (0.000, 0.500, 0.000)	2.857683	-0.18739
A (-0.500, 0.500, 0.000)	2.789223	-0.1695
B (-0.500, 0.000, 0.000)	2.467077	-0.09258
D (-0.500, 0.000, 0.500)	2.835134	-0.10066
E (-0.500, 0.500, 0.500)	2.908111	-0.17195
C (0.000, 0.500, 0.500)	3.059388	-0.08067

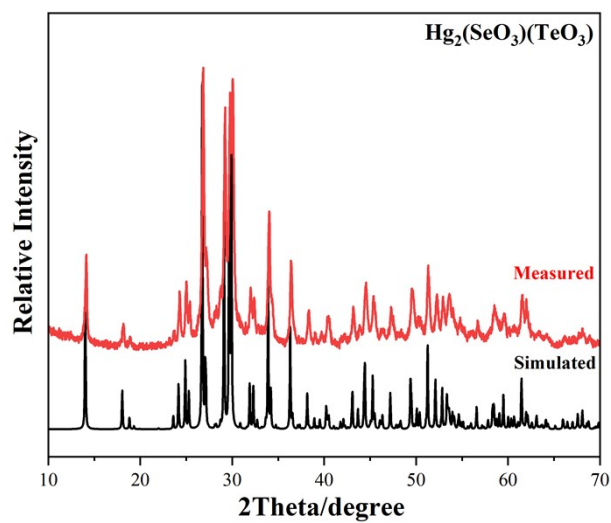


Figure S1. Simulated and experimental powder X-ray diffractometer patterns of $\text{Hg}_2(\text{SeO}_3)(\text{TeO}_3)$.

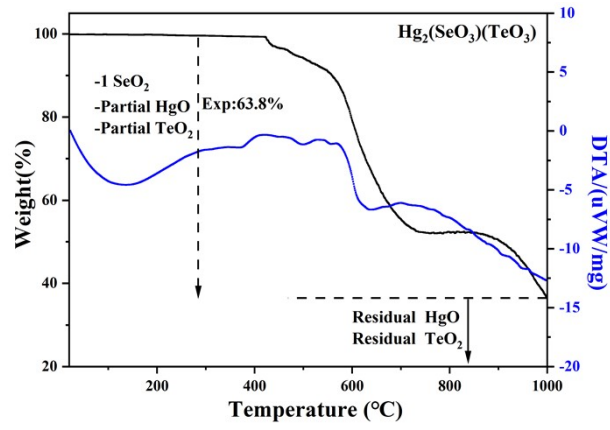


Figure S2. TGA and DTA results of $\text{Hg}_2(\text{SeO}_3)(\text{TeO}_3)$.



Figure S3. IR spectra of $\text{Hg}_2(\text{SeO}_3)(\text{TeO}_3)$.

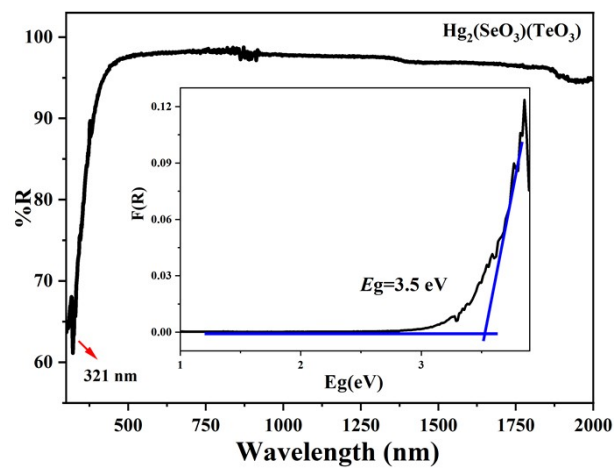


Figure S4. UV–vis–NIR diffuse-reflectance spectra of $\text{Hg}_2(\text{SeO}_3)(\text{TeO}_3)$.

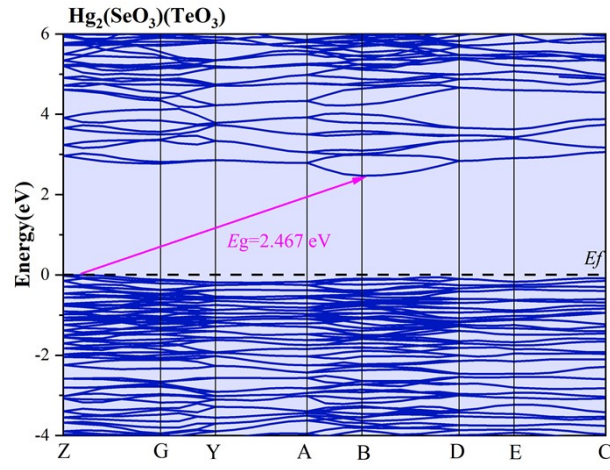


Figure S5. Band structures of $\text{Hg}_2(\text{SeO}_3)(\text{TeO}_3)$.

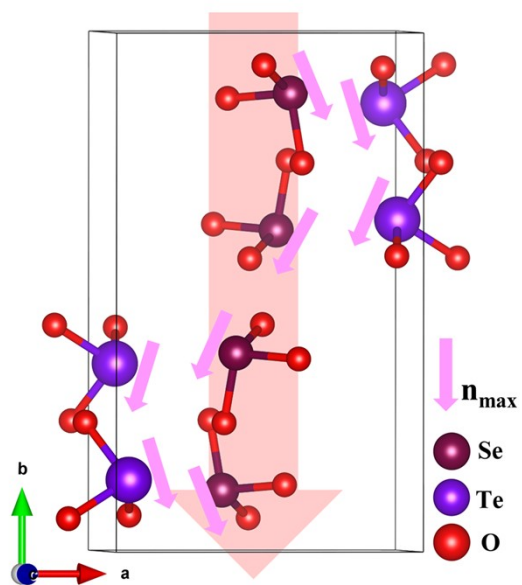


Figure S6. Arrangement of SeO₃ and TeO₃ groups in the structure of Hg₂(SeO₃)(TeO₃).

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