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Supplementary Materials

Regulating Second Harmonic Generation of Telluromolybdate Materials by Atomic Substitution

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S1 Details of the calculation results

Table. S1. The bond length of the optimized stable ATMOs

	A-O(Å)	Te-O(Å)	Mo-O(Å)
MnTeMoO6	2.173	1.925-2.168	1.741-1.898
FeTeMoO6	2.093	1.943-2.102	1.748-1.873
CoTeMoO6	2.146	1.936-2.149	1.738-1.905
NiTeMoO6	2.061	1.951-2.080	1.745-1.869
RuTeMoO6	2.235	1.929-2.182	1.744-1.900
AgTeMoO6	2.252	1.928-2.168	1.745-1.892
CdTeMoO6	2.256	1.193-2.178	1.742-1.894
ZnTeMoO6	2.147	1.935-2.150	1.740-1.899
MgTeMoO6	2.149	1.920-2.162	1.739-1.901

Table. S2. Lattice parameters and magnetic moment in x, y, z direction of optimized ATMOs (A=Mn, Fe, Co, Ni, Ru, Ag, Cd, Zn, Mg） structure($\mu_B = \frac{e\hbar}{2m_e}$)

	a(Å)	b(Å)	c(Å)	mag (x) (μ_B)	mag (y) (μ_B)	mag (z) (μ_B)
MnTeMoO6	5.36	5.36	9.35	5.78	5.77	5.76

FeTeMoO6	5.17	5.17	8.76	4.62	4.63	4.60
CoTeMoO6	5.36	5.36	9.35	3.49	3.49	3.36
NiTeMoO6	5.15	5.15	8.82	5.77	5.77	5.76
RuTeMoO6	5.36	5.36	9.35	4.50	4.04	5.43
AgTeMoO6	5.36	5.36	9.35	1.13	1.13	1.10
CdTeMoO6	5.36	5.36	9.35	0	0	0
ZnTeMoO6	5.36	5.36	9.35	0	0	0
MgTeMoO6	5.36	5.36	9.35	0	0	0

S2 Total and partial density of states of ATMOs (A= Mn, Co, Ni, Cd, Zn, Mg)

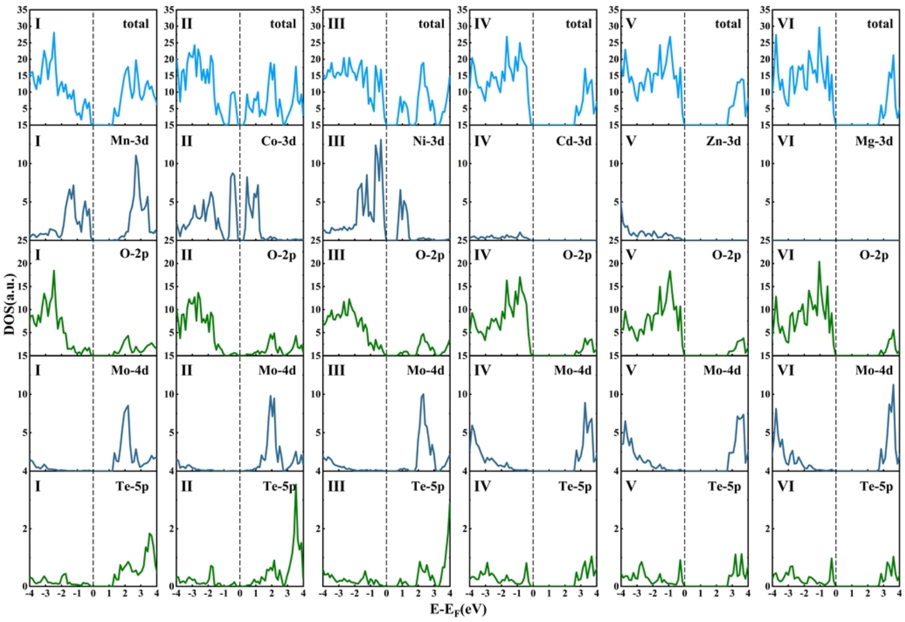

Fig.S1. I-IV: Total and partial density of states of ATMOs (A= Mn, Co, Ni, Cd, Zn, Mg)

Structures (light-blue: total-orbital, red: s-orbital, green: p-orbital, dark-blue: d-orbital)

S3 The SHG polarization response of ATMO(A=Cd, Zn, Mg)

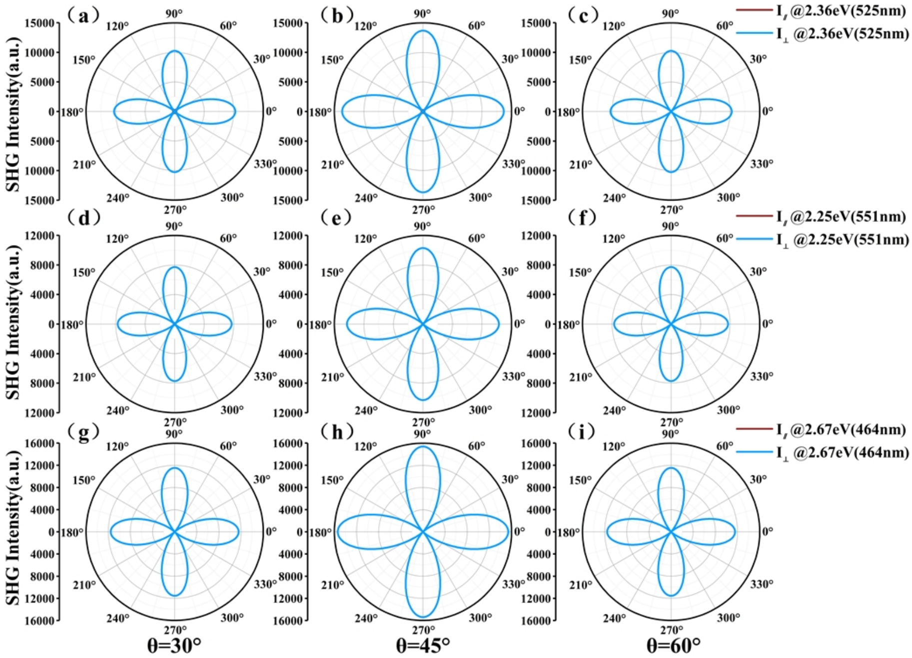

Fig.S2. The SHG polarization response of ATMOs (A=Cd, Zn, Mg) at incidence angles of 30°,45°,60°. (a-c)CdTeMoO6 (d-f) ZnTeMoO6 (g-i) MgTeMoO6. Red line represents parallel components and blue line represents perpendicular components.

S4.SHG Calculation Methods

The SHG generation process can be simply described as two incident photons of equal frequency, under the action of a medium, producing a photon of double frequency[1,2]. The interaction between light and the medium can be described by the polarization response $P_i(2\omega)$ of the medium to the light field $E(\omega)$:

$$\mathrm{P_i}(2\omega) = \sum_{\mathrm{j,k}} \chi^{(2)}_{\mathrm{ijk}} \mathrm{E_j}(\omega) \mathrm{E_i}(\omega) \#(1)$$

where $\chi^{(2)}_{ijk}$ represents the second-order susceptibility tensor, with subscript *i* denoting the polarization variable of the emitted photon and subscripts *j, k* representing the polarization variables of the incident photons. Under the independent particle approximation[3,4], $\chi^{(2)}_{ijk}(2\omega,\omega,\omega)$ consists of the following three components: the contribution of the inter-band transition, the contribution of the in-band transition, and the modulation of the inter-band transition to the in-band transition, which can be expressed as the sum of three terms[4]:

$$\chi^{(2)}_{ijk}(2\omega,\omega,\omega) = \chi^{ijk}_{inter}(2\omega,\omega,\omega) + \chi^{ijk}_{intra}(2\omega,\omega,\omega) + \chi^{ijk}_{mod}(2\omega,\omega,\omega) \#(2)$$

Among them, the three parts of the above formula are respectively represented by the following three formulas:

$$\chi^{ijk}_{inter}(2\omega,\omega,\omega) = \frac{e^3}{\hbar^2}\sum_{nml}{}^{'}\int \frac{d\vec{k}\, r^a_{nm}\left\{r^b_{ml}r^c_{ln}\right\}}{4\pi^3(\omega_{ln}-\omega_{ml})}\left\{\frac{2f_{nm}}{(\omega_{mn}-2\omega)}+\frac{f_{ml}}{(\omega_{ml}-\omega)}+\frac{f_{ln}}{(\omega_{ln}-\omega)}\right\}\#(3)$$

$$\chi^{ijk}_{intra}(2\omega,\omega,\omega) = \frac{e^3}{\hbar^2}\int\frac{d\vec{k}}{4\pi^3}\left[\sum_{nml}{}^{'}\omega_{mn}r^a_{nm}\left\{r^b_{ml}r^c_{ln}\right\}\left\{\frac{f_{nl}}{\omega^2_{ln}(\omega_{ln}-\omega)}-\frac{f_{lm}}{\omega^2_{ml}(\omega_{ml}-\omega)}\right\}-8i\sum_{nm}{}^{'}\frac{f_{nm}r^a_{nm}\left\{\Delta^b_{mn}r^c_{mn}\right\}}{\omega^2_{mn}(\omega_{mn}-2\omega)}+2\sum_{nml}{}^{'}\frac{f_{nm}r^a_{nm}\left\{\mathrm{r}^b_{ml}r^c_{ln}\right\}(\omega_{ml}-\omega_{ln}}{\omega^2_{mn}(\omega_{mn}-2\omega)}\right]\#(4)$$

$$\chi^{ijk}_{mod}(2\omega,\omega,\omega) = \frac{e^3}{2\hbar^2}\int\frac{d\vec{k}}{4\pi^3}\left[\sum_{nml}{}^{'}\frac{f_{nm}}{\omega^2_{mn}(\omega_{mn}-\omega)}\left\{\omega_{nl}r^a_{lm}\left\{r^b_{mn}-r^c_{nl}\right\}-\omega_{lm}r^a_{nl}\left\{r^b_{lm}-r^c_{mn}\right\}\right\}-i\sum_{nm}{}^{'}\frac{f_{nm}r^a_{nm}\left\{r^b_{mn}\Delta^c_{mn}\right\}}{\omega^2_{mn}(\omega_{mn}-\omega)}\right]\#(5)$$

The symbol Δ is defined as:

$$\Delta^b_{mn}(\vec{k}) = \mathrm{v}^b_{mm}(\vec{k})-\mathrm{v}^b_{nn}(\vec{k})\#(6)$$

v^b_{mn} represents the b component of a given electron velocity:

$$\mathrm{v}^b_{mn}(\vec{k}) = \mathrm{i}\omega_{mn}(\vec{k}) * r^b_{mn}(\vec{k})\#(7)$$

$r^b_{mn}(\vec{k})$ represents the position matrix element between the states m and n, which can be obtained from the momentum matrix,

$$r^b_{mn}(\vec{k}) = \frac{p^b_{mn}(\vec{k})}{\mathrm{i}m\omega_{mn}(\vec{k})}\#(8)$$

And,

$$r^b_{ml}(\vec{k})r^c_{ln}(\vec{k}) = \frac{1}{2}\left[r^b_{ml}(\vec{k})r^c_{ln}(\vec{k}) + r^c_{ml}(\vec{k})r^b_{ln}(\vec{k})\right]\#(9)$$

The incident pump light frequency ω contains a small imaginary smearing factor δ: ω→ ω + iδ, where δ = 0.05 eV in this work to avoid divergence problem.

Considering the sample shedding by the linearly polarized pump light with an incident angle θ, the electric field of the pump light can be given as follows[5]:

$$\begin{bmatrix}E_x\\E_y\\E_z\end{bmatrix} = \begin{bmatrix}E_0\cos(\theta)\\0\\E_0\sin(\theta)\end{bmatrix}\#(10)$$

The relationship between the second order nonlinear susceptibility $\chi^{(2)}_{ijk}$ and the second-order nonlinear coefficient $d_{\mu L}$ can be described as:

$$d_{\mu L} = \frac{1}{2}\chi^{(2)}_{ijk} = \begin{bmatrix}d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16}\\d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26}\\d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36}\end{bmatrix}\#(11)$$

Where, μ = i(1,2,3correspond to the x, y, z directions, respectively); L=jk, corresponding to the following:

Table S3.Correspondence between μL and ijk

jk	11(xx)	22(yy)	33(zz)	23=32(yz=zy)	31=13(zx=xz)	12=21(xy=yz)
L	1	2	3	4	5	6

By the use of rotation operation $\mathrm{T}(\varphi)$, we can obtain the transformed tensor containing azimuthal angle:

$$d_{ijk}^{(2)} = \sum_{f=1}^{3} T_{i,f} \times \sum_{g=1}^{3} T_{j,g} \times \sum_{\mathrm{h}=1}^{3} T_{k,\mathrm{h}} \times d_{fgh}^{(2)} \#(12)$$

$$\mathrm{T}(\varphi) = \begin{bmatrix} \cos(\varphi) & \sin(\varphi) & 0 \\ -\sin(\varphi) & \cos(\varphi) & 0 \\ 0 & 0 & 1 \end{bmatrix} \#(13)$$

Here φ is the azimuthal angle between the mirror plane in the crystal structure and the polarization of the pump beam. $T_{i,f}, T_{j,g}, T_{k,\mathrm{h}}$ are components in $\mathrm{T}(\varphi)$. Thus the SHG elements can be expressed as:

$$\begin{bmatrix} p_x(2\omega) \\ p_y(2\omega) \\ p_z(2\omega) \end{bmatrix} = 2\varepsilon_0 d_{\mu L}(\varphi) \begin{bmatrix} E_x^2(\omega,\theta) \\ E_y^2(\omega,\theta) \\ E_z^2(\omega,\theta) \\ 2E_y(\omega,\theta)E_z(\omega,\theta) \\ 2E_z(\omega,\theta)E_x(\omega,\theta) \\ 2E_x(\omega,\theta)E_y(\omega,\theta) \end{bmatrix} \#(14)$$

where ε_0 represents the permittivity of the space.

Thus, the two polarization components (parallel and perpendicular) of SHG intensity as a function of azimuthal and incident angle can be described as[5]:

$$I_{\parallel} \propto \left[-P_x\left(d_{\mu l},\varphi\right)\cos[\theta] + P_z\left(d_{\mu l},\varphi\right)\sin[\theta]\right]^2 \#(15)$$

$$I_{\perp} \propto P_y^2\left(d_{\mu l},\varphi\right) \#(16)$$

For an ATMOs with point group D_{2d}, bring in the elements that its symmetry allows. Lastly, the $I_{\parallel}$ and $I_{\perp}$ can be expressed as:

$$I_{\parallel} = 64E_0^4\epsilon_0^2\left(-\chi_{xyz} + \frac{1}{2}\chi_{zxy}\right)^2\sin^2(\varphi)\sin^2(\theta)\cos^2(\varphi)\cos^4(\theta) \#(17)$$

$$I_{\perp} = 16E_0^4\epsilon_0^2\left(-2\chi_{xyz}\sin^2(\varphi) + \chi_{zxy}\right)^2\sin^2(\theta)\cos^2(\theta) \#(18)$$

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