Supporting Information

The impact of anionic group arrangement on the optical properties of the arsenate series.

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Figure S2 Ternary arsenate crystal structures A_3AsO_4(A= Li, Na, K, Rb, Cs)(a-e); $B_3(AsO_4)_2$(B=Be,

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Figure S3 Ternary arsenate calculated band structures: Li_3AsO_4(a), Na_3AsO_4(b), K_3AsO4(c), Rb_3AsO4(d), Cs_3AsO_4(e), $Be_3(AsO_4)_2$(f), $Mg_3(AsO_4)_2$(g), $Ca_3(AsO_4)_2$(h), $Sr_3(AsO_4)_2$(i), $Ba_3(AsO_4)_2$(j), $ScAsO_4$(k), $YAsO_4$(l), $Zn_3(AsO_4)_2$(m), $Cd_3(AsO_4)_2$(n), $Hg_3(AsO_4)_2$(o), Band_sum(p).

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Figure S7 The SHG density of occupied and unoccupied states for $LiAsO_4$(a, b), $NaAsO_4$(c, d), $Mg_3(AsO_4)_2$(e, f) and $Ca_3(AsO_4)_2$(g, h).

Reference

Table S1. Crystal structure information of 14 different metal cation ternary arsenates.

Compounds	Space group	Crystallographic data		ICSD / Materials Project number
		a, *b*, *c*(Å)	α, β, γ(°)	
Li_3AsO_4[1]	$Pmn2_1$	*a*=6.28560, *b*=5.39020, *c*=4.96160	α=β=γ=90	75927-ICSD
Na_3AsO_4	$Pmn2_1$	*a*=7.00636, *b*=6.03650, *c*=5.50106	α=β=γ=90	mp-756044
K_3AsO_4[2]	*Cccm*	*a*=10.6011, *b*=11.3521, *c*=16.9401	α=β=γ=90	412391-ICSD
Rb_3AsO_4[2]	*Pnma*	*a*=11.9959, *b*=8.66185, *c*=6.37123	α=β=γ=90	Atomic substitution
Cs_3AsO_4[2]	*Pnma*	*a*=12.5427, *b*=9.02900, *c*=6.58500	α=β=γ=90	412392-ICSD
$Mg_3(AsO_4)_2$[3]	*I***Error!**	*a*=*b*=6.80820, *c*=18.8271	α=β=γ=90	mp-758196
$Ca_3(AsO_4)_2$[4]	*R*3	*a*=*b*=10.9293, *c*=38.3498	α=β=90, γ=120	mp-530449
$Sr_3(AsO_4)_2$[5]	*R***Error!**m	*a*=*b*=5.66440, *c*=20.1919	α=β=90, γ=120	mp-755082
$Ba_3(AsO_4)_2$[5]	*R***Error!**m	*a*=*b*=5.85300, *c*=21.4717	α=β=90, γ=120	mp-9783
$ScAsO_4$[6]	$I4_1/amd$	*a*=*b*=6.71020, *c*=6.11320	α=β=γ=90	155920-ICSD
$YAsO_4$[7]	$I4_1/amd$	*a*=*b*=6.90400, *c*=6.28200	α=β=γ=90	24513-ICSD
$Zn_3(AsO_4)_2$[8]	$P2_1/c$	*a*=6.30610, *b*=8.65200, *c*=11.3210	α=γ=90, β=92.25	404199-ICSD
$Cd_3(AsO_4)_2$[9]	$P2_1/c$	*a*=9.28500, *b*=11.9360, *c*=6.59900	α=γ=90, β=98.45	14257-ICSD
$Hg_3(AsO_4)_2$[10]	$P2_1/c$	*a*=10.0049, *b*=11.7555, *c*=6.53740	α=γ=90, β=99.6870	72527-ICSD

Table S2. Mulliken population analysis of 14 different metal cation ternary arsenates.

Compounds	Species	s	p	d	Total	Charge(e)	Bond	Population	Length (nm)
Li_3AsO_4	Li	-0.05	-	-	-0.05	1.05	O-As	0.80	1.673
	As	1.62	1.95	-	3.57	1.43	O-Li	0.01	1.977
	O	1.89	5.27	-	7.16	-1.16			
Na_3AsO_4	Na	2.26	6.09	-	8.35	0.65	O-As	0.74	1.681
	As	1.07	2.09	-	3.16	1.84	O-Na	0.04	2.372
	O	1.87	5.08	-	6.95	-0.95			
K_3AsO_4	K	2.20	6.30	-	8.50	0.50	O-As	0.84	1.664
	As	1.14	2.14	-	3.28	1.72	O-K	0.06	2.607
	O	1.87	5.07	-	6.94	-0.94			
Rb_3AsO_4	Rb	2.21	5.98	-	8.19	0.81	O-As	0.77	1.680
	As	1.23	2.12	-	3.35	1.65	O-Rb	0.19	2.732

	O	1.88	5.08	-	6.96	-0.96			
	Cs	2.22	6.02	-	8.24	0.76	O-As	0.74	1.684
Cs_3AsO_4	As	1.10	2.08		3.19	1.81	O-Cs	0.13	2.947
	O	1.89	5.09	-	6.97	-0.97			
	Mg	2.37	6.51	-	8.88	1.12	O-As	0.64	1.662
$Mg_3(AsO_4)_2$	As	0.86	1.98	-	2.84	2.16	O-Mg	0.07	2.643
	O	1.86	5.11	-	6.97	-0.97			
	Ca	2.22	6.00	0.47	8.69	1.31	O-As	0.65	1.641
$Ca_3(AsO_4)_2$	As	1.01	1.92	-	2.93	2.07	O-Ca	0.10	2.509
	O	1.88	5.13	-	7.01	-1.01			
	Sr	2.22	6.00	0.55	8.77	1.23	O-As	0.63	1.676
$Sr_3(AsO_4)_2$	As	0.99	1.96	-	2.94	2.06	O-Sr	0.13	2.864
	O	1.86	5.10	-	6.96	-0.96			
	Ba	2.22	6.00	0.57	8.78	1.22	O-As	0.62	1.665
$Ba_3(AsO_4)_2$	As	0.98	1.95	-	2.93	2.07	O-Ba	0.15	2.594
	O	1.88	5.09	-	6.97	-0.97			
	Sc	0.30	0.23	1.14	1.66	1.34	O-As	0.58	1.666
$ScAsO_4$	As	0.82	1.99	-	2.81	2.19	O-Sc	0.25	2.297
	O	1.86	5.02	-	6.88	-0.88			
	Y	0.27	0.11	1.25	1.63	1.37	O-As	0.58	1.667
$YAsO_4$	As	0.83	1.99	-	2.82	2.18	O-Y	0.33	2.316
	O	1.85	5.03	-	6.89	-0.89			
	Zn	0.39	0.64	9.99	11.02	0.98	O-As	0.69	1.657
$Zn_3(AsO_4)_2$	As	0.93	1.92	-	2.86	2.14	O-Zn	0.35	2.035
	O	1.86	5.04	-	6.90	-0.90			
	Cd	0.35	0.53	9.99	10.88	1.12	O-As	0.62	1.666
$Cd_3(AsO_4)_2$	As	0.95	1.96	-	2.91	2.09	O-Cd	0.34	2.158
	O	1.88	5.06	-	6.94	-0.94			
	Hg	0.78	0.46	9.85	11.10	0.90	O-As	0.72	1.634
$Hg_3(AsO_4)_2$	As	0.87	1.93	-	2.81	2.19	O-Hg	0.48	1.975
	O	1.88	5.00	-	6.88	-0.88			

Table S3. Optical principal axes of ternary arsenates calculated through Efield.

Compounds	**Optical spindle**		
	x	**y**	**z**
Li_3AsO_4	(0, 0.19, 0)	(0.16, 0, 0)	(0, 0, 0.20)
Na_3AsO_4	(0, 0.16, 0)	(0.14, 0, 0)	(0, 0, 0.18)
K_3AsO_4	(0, 0, 0.06)	(0.09, 0, 0)	(0, 0.08, 0)
Rb_3AsO_4	(0, 0, 0.16)	(0, 0.16, 0)	(0.08, 0, 0)
Cs_3AsO_4	(0, 0, 0.15)	(0, 0.11, 0)	(0.08, 0, 0)
$Mg_3(AsO_4)_2$	(0, 0, 0.05)	(0, 0.15, 0)	(0.15, 0, 0)
$Ca_3(AsO_4)_2$	(0.03, 0.03, 0.03)	(-0.10, 0.08, 0.02)	(-0.03, -0.07, 0.10)
$Sr_3(AsO_4)_2$	(0.21, 0.10, 0)	(0, 0.18, 0)	(0, 0, 0.05)
$Ba_3(AsO_4)_2$	(0.20, 0.10, 0)	(0, 0.17, 0)	(0, 0, 0.05)
$ScAsO_4$	(0.15, 0, 0)	(0, 0.15, 0)	(0, 0, 016)
$YAsO_4$	(0, -0.11, 0)	(0.01, 0, -0.09)	(0.15, 0, 0.01)
$Zn_3(AsO_4)_2$	(0, -0.11, 0)	(0.01, 0, -0.09)	(0.15, 0, 0.01)

$Cd_3(AsO_4)_2$	(0, 0.08, 0)	(-0.09, 0, -0.11)	(-0.06, 0, 0.11)
$Hg_3(AsO_4)_2$	(-0.10, 0, -0.05)	(0, 0.09, 0)	(-0.01, 0, 0.15)

Table S4. Optical static dielectric constants of 14 arsenates in different directions.

Compounds	Optical Permittivity			
	ε_1	ε_2	ε_3	$\Delta\varepsilon$
Li_3AsO_4	2.921	2.912	2.930	0.018
Na_3AsO_4	2.606	2.603	2.591	0.015
K_3AsO_4	2.797	2.793	2.808	0.015
Rb_3AsO_4	2.882	2.867	2.867	0.015
Cs_3AsO_4	3.080	3.071	3.079	0.009
$Mg_3(AsO_4)_2$	3.145	3.268	3.268	0.123
$Ca_3(AsO_4)_2$	3.214	3.223	3.223	0.009
$Sr_3(AsO_4)_2$	3.447	3.447	3.489	0.042
$Ba_3(AsO_4)_2$	3.620	3.620	3.662	0.042
$ScAsO_4$	3.819	3.819	4.479	0.660
$YAsO_4$	3.370	3.852	3.370	0.482
$Zn_3(AsO_4)_2$	3.747	3.674	3.732	0.073
$Cd_3(AsO_4)_2$	3.571	3.596	3.680	0.109
$Hg_3(AsO_4)_2$	4.203	4.349	4.463	0.260

Table S5. The calculated band gaps, birefringence, and Δε of 14 arsenates.

Compounds	Band gap (eV)		Δn (@ 1064 nm)	Δε
	GGA	LDA		
Li_3AsO_4	4.702	4.749	0.005	0.018
Na_3AsO_4	3.348	3.404	0.005	0.015
K_3AsO_4	3.417	3.417	0.005	0.015
Rb_3AsO_4	3.324	3.548	0.004	0.015
Cs_3AsO_4	3.413	3.644	0.003	0.009
$Mg_3(AsO_4)_2$	3.575	3.814	0.035	0.123
$Ca_3(AsO_4)_2$	4.256	4.369	0.003	0.009
$Sr_3(AsO_4)_2$	4.476	4.775	0.011	0.042
$Ba_3(AsO_4)_2$	4.366	4.729	0.011	0.042
$ScAsO_4$	4.229	4.443	0.170	0.660
$YAsO_4$	4.532	4.611	0.130	0.482
$Zn_3(AsO_4)_2$	2.287	2.135	0.017	0.073
$Cd_3(AsO_4)_2$	2.260	2.082	0.030	0.109
$Hg_3(AsO_4)_2$	1.591	1.500	0.066	0.260

Table S6. Using REDA calculations to determine the contributions of [AsO_4] and metal cations X

(X=Zn, Cd, Hg) to the birefringence in $Zn_3(AsO_4)_2$, $Cd_3(AsO_4)_2$, and $Hg_3(AsO_4)_2$.

Compounds	ξ-AsO_4	ξ-*X*	AsO_4- contribute	X- contribute
$Zn_3(AsO_4)_2$	0.0068	0.0144	32.14%	67.86%
$Cd_3(AsO_4)_2$	0.0039	0.0042	48.09%	51.91%
$Hg_3(AsO_4)_2$	0.0087	0.0252	25.75%	74.25%

Table S7. Calculated SHG for $LiAsO_4$, $NaAsO_4$, $Mg_3(AsO_4)_2$, and $Ca_3(AsO_4)_2$.

Compounds	d_{ij} **(pm/V)**							
	d_{11}	d_{14}	d_{15}	d_{22}	d_{24}	d_{33}	d_{eff}	×**KDP**
Li_3AsO_4	--	--	0.414	--	0.581	0.911	0.721	1.849
Na_3AsO_4	--	--	0.602	--	0.707	1.622	0.985	2.526
$Mg_3(AsO_4)_2$	--	0.424	0.267	--	--	--	0.398	1.021
$Ca_3(AsO_4)_2$	0.007	--	0.224	0.144	--	1.053	0.518	1.328

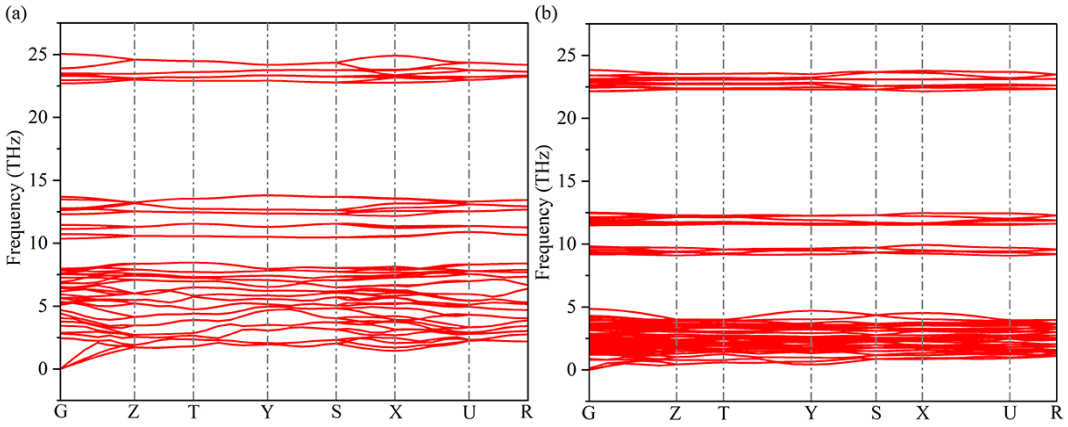
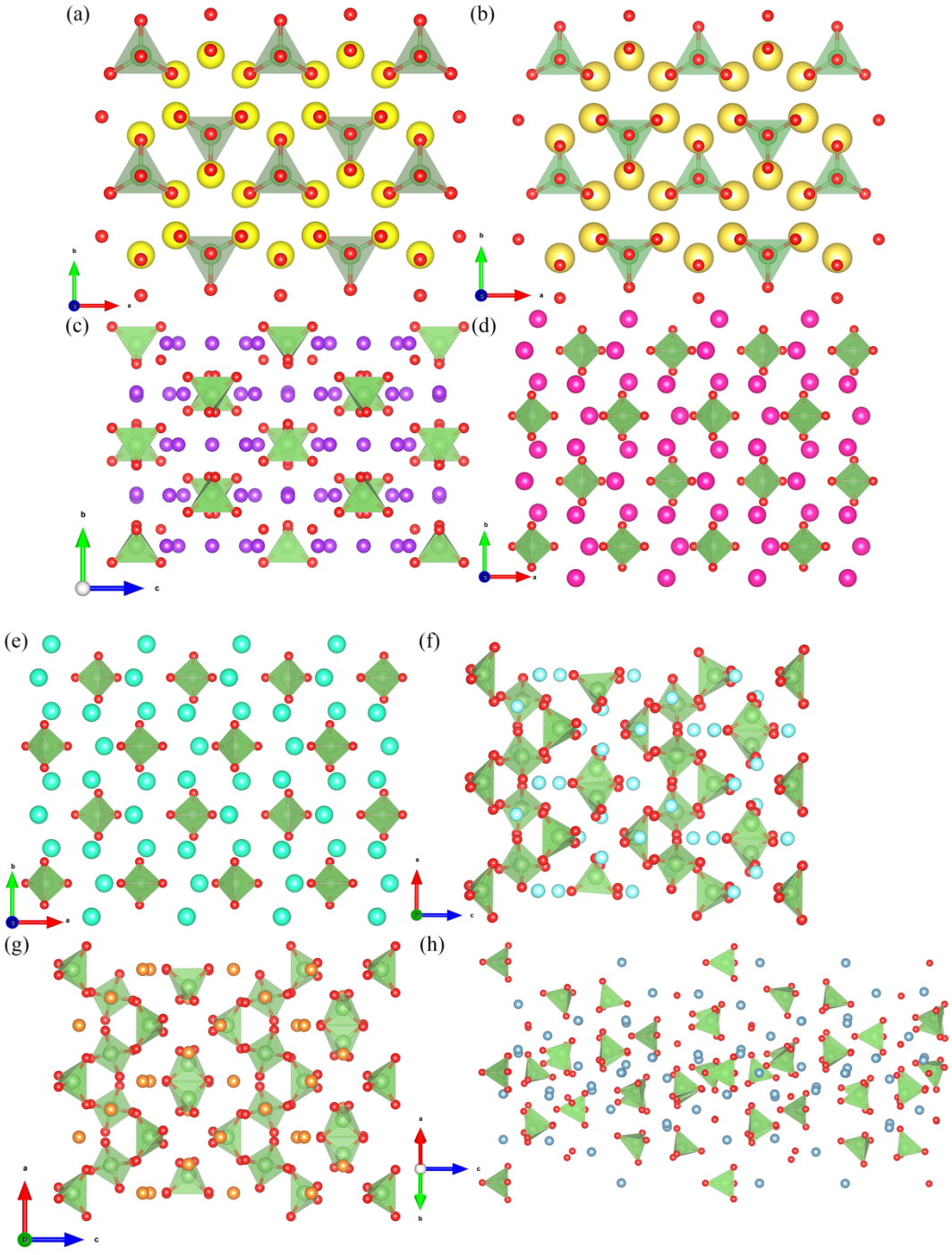


Figure S1 Phonon dispersion curves of Na_3AsO_4 (a) and Rb_3AsO_4 (b).


(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)

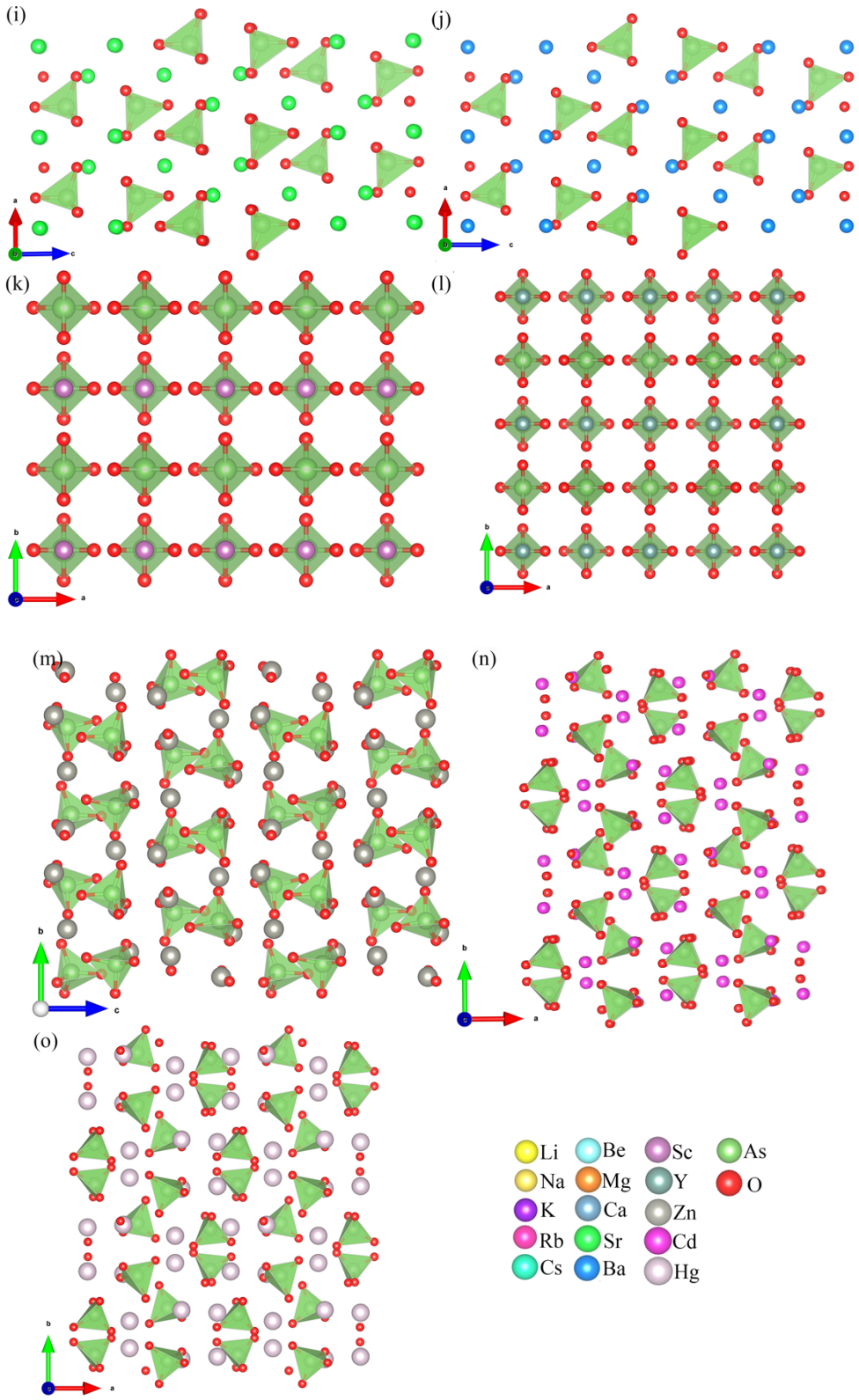
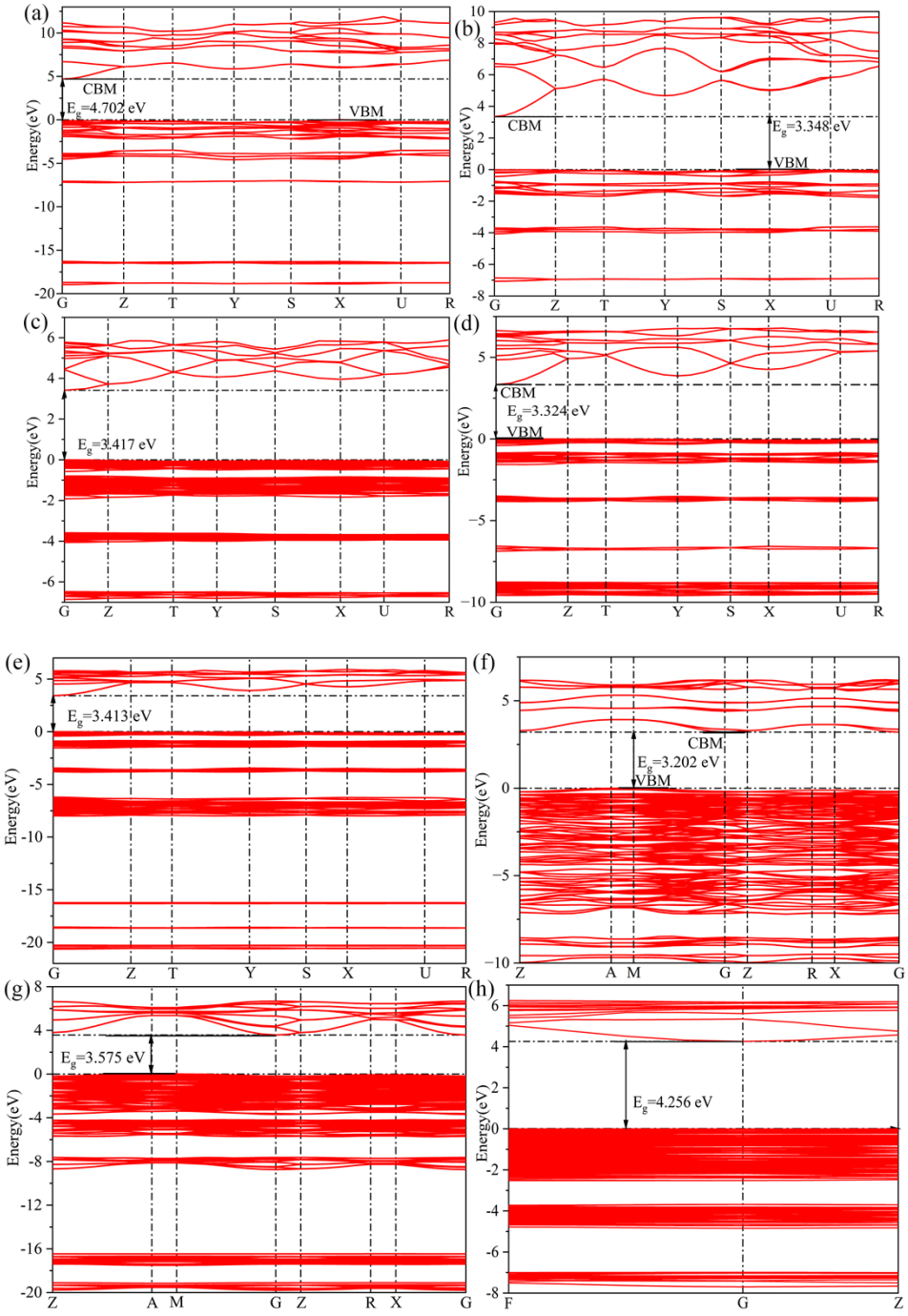


Figure S2 Ternary arsenate crystal structures A_3AsO_4(A= Li, Na, K, Rb, Cs)(a-e); $B_3(AsO_4)_2$(B=Be, Mg, Ca, Sr, Ba)(f-j); D^0AsO_4(D^0=Sc, Y)(k-l); $D^{10}{}_3$ $(AsO_4)_2$(D^{10}=Zn, Cd, Hg)(m-o).


(a)
CBM
E_g=4.702 eV
VBM
Energy(eV)
G Z T Y S X U R
(b)
CBM
E_g=3.348 eV
VBM
Energy(eV)
G Z T Y S X U R
(c)
E_g=3.417 eV
Energy(eV)
G Z T Y S X U R
(d)
CBM
E_g=3.324 eV
VBM
Energy(eV)
G Z T Y S X U R
(e)
E_g=3.413 eV
Energy(eV)
G Z T Y S X U R
(f)
CBM
E_g=3.202 eV
VBM
Energy(eV)
Z A M G Z R X G
(g)
E_g=3.575 eV
Energy(eV)
Z A M G Z R X G
(h)
E_g=4.256 eV
Energy(eV)
F G Z

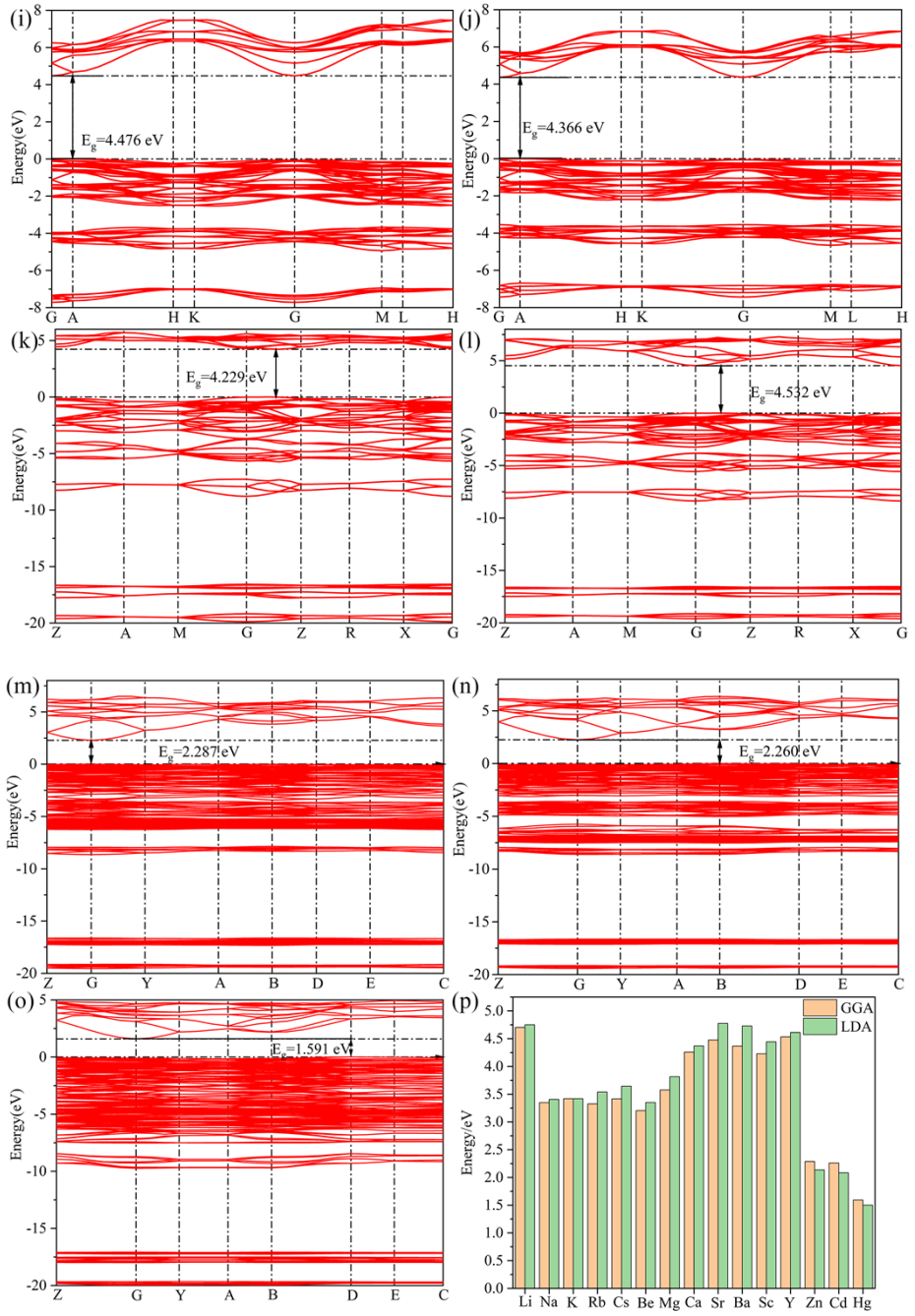
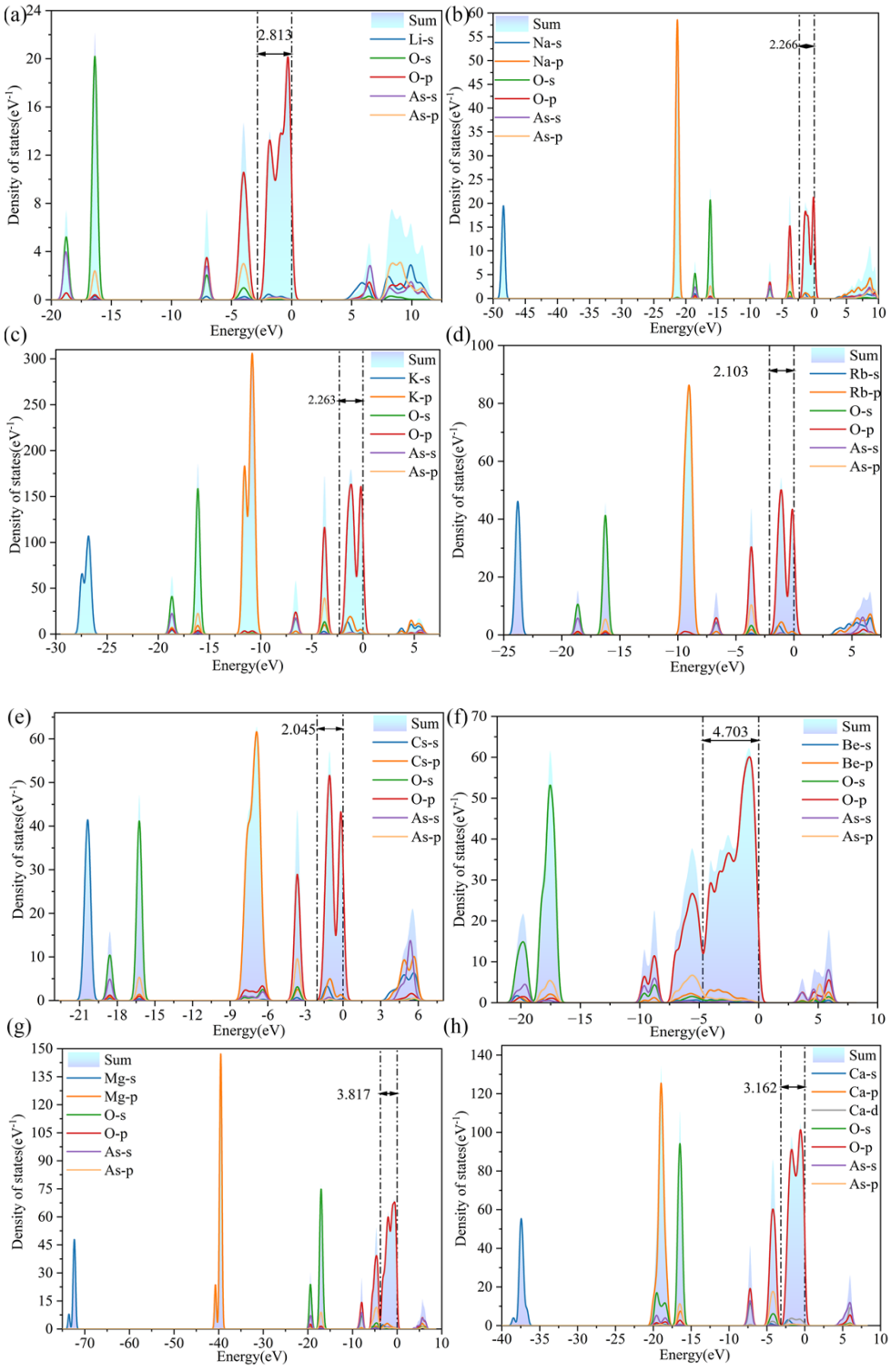


Figure S3 Ternary arsenate calculated band structures: Li_3AsO_4(a), Na_3AsO_4(b), K_3AsO4(c), Rb_3AsO4(d), Cs_3AsO_4(e), $Be_3(AsO_4)_2$(f), $Mg_3(AsO_4)_2$(g), $Ca_3(AsO_4)_2$(h), $Sr_3(AsO_4)_2$(i), $Ba_3(AsO_4)_2$(j), $ScAsO_4$(k), $YAsO_4$(l), $Zn_3(AsO_4)_2$(m), $Cd_3(AsO_4)_2$(n), $Hg_3(AsO_4)_2$(o), Band_sum(p).


(a)
Sum
Li-s
O-s
O-p
As-s
As-p
2.813
Density of states(eV⁻¹)
Energy(eV)
(b)
Sum
Na-s
Na-p
O-s
O-p
As-s
As-p
2.266
Density of states(eV⁻¹)
Energy(eV)
(c)
Sum
K-s
K-p
O-s
O-p
As-s
As-p
2.263
Density of states(eV⁻¹)
Energy(eV)
(d)
Sum
Rb-s
Rb-p
O-s
O-p
As-s
As-p
2.103
Density of states(eV⁻¹)
Energy(eV)
(e)
Sum
Cs-s
Cs-p
O-s
O-p
As-s
As-p
2.045
Density of states(eV⁻¹)
Energy(eV)
(f)
Sum
Be-s
Be-p
O-s
O-p
As-s
As-p
4.703
Density of states(eV⁻¹)
Energy(eV)
(g)
Sum
Mg-s
Mg-p
O-s
O-p
As-s
As-p
3.817
Density of states(eV⁻¹)
Energy(eV)
(h)
Sum
Ca-s
Ca-p
Ca-d
O-s
O-p
As-s
As-p
3.162
Density of states(eV⁻¹)
Energy(eV)

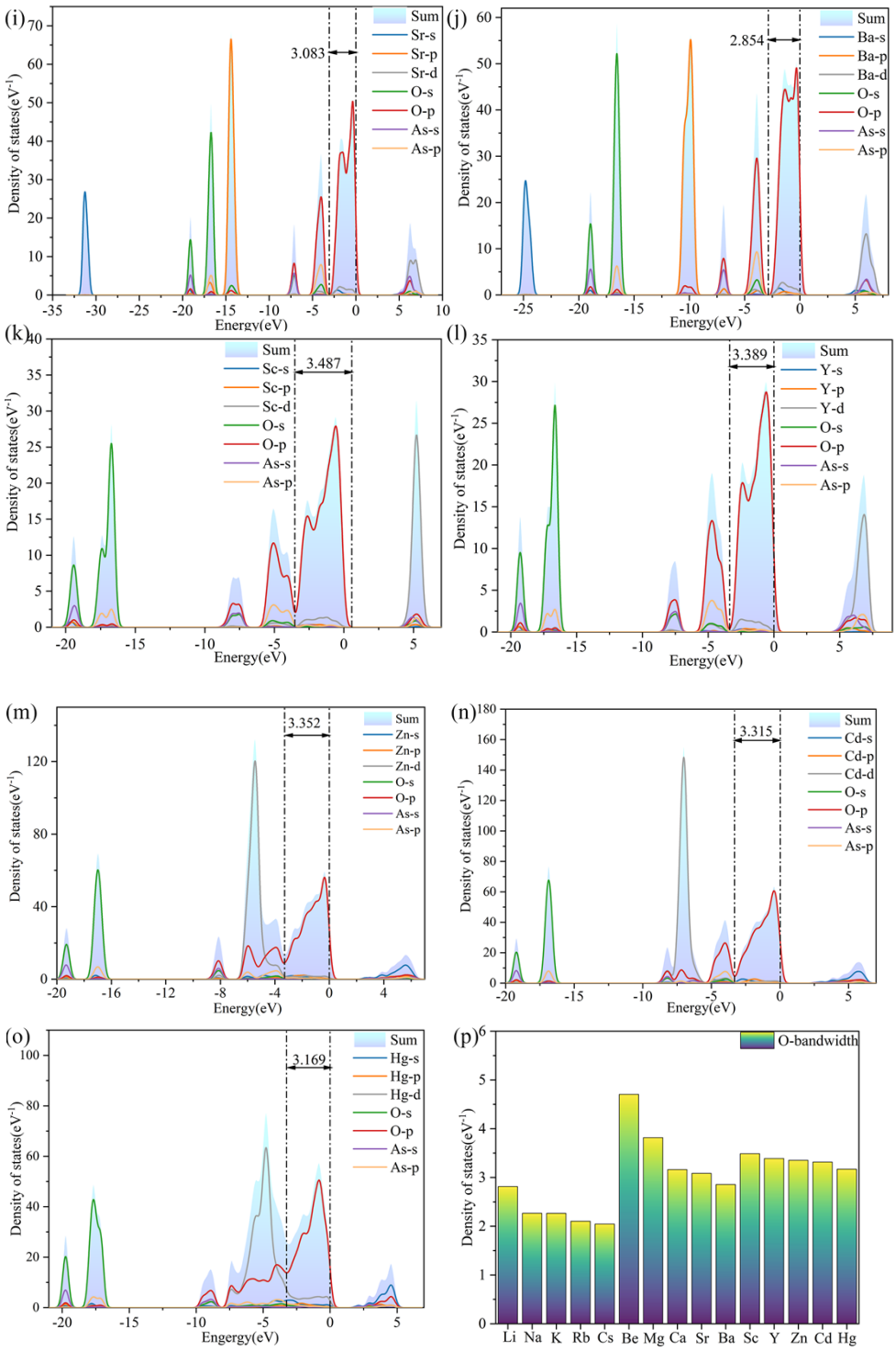


Figure S4 Ternary arsenates calculated density of states: Li_3AsO_4(a), Na_3AsO_4(b), K_3AsO4(c), Rb_3AsO4(d), Cs_3AsO_4(e), $Be_3(AsO_4)_2$(f), $Mg_3(AsO_4)_2$(g), $Ca_3(AsO_4)_2$(h), $Sr_3(AsO_4)_2$(i), $Ba_3(AsO_4)_2$(j), $ScAsO_4$(k), $YAsO_4$(l), $Zn_3(AsO_4)_2$(m), $Cd_3(AsO_4)_2$(n), $Hg_3(AsO_4)_2$(o), DOS broadening(p).

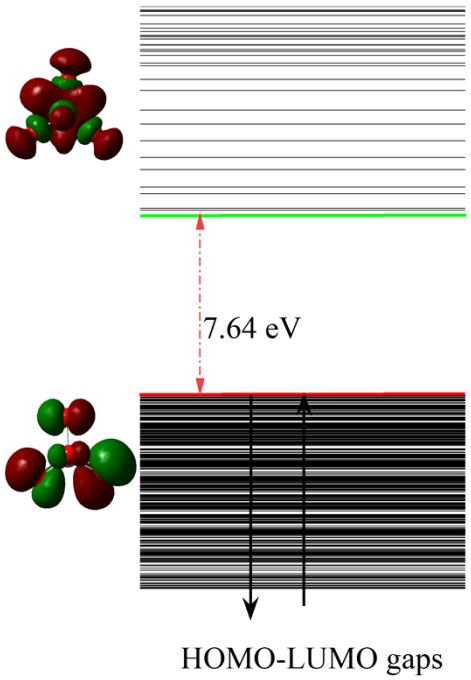


Figure S5 The HOMO-LUMO gaps of the [AsO_4] group.

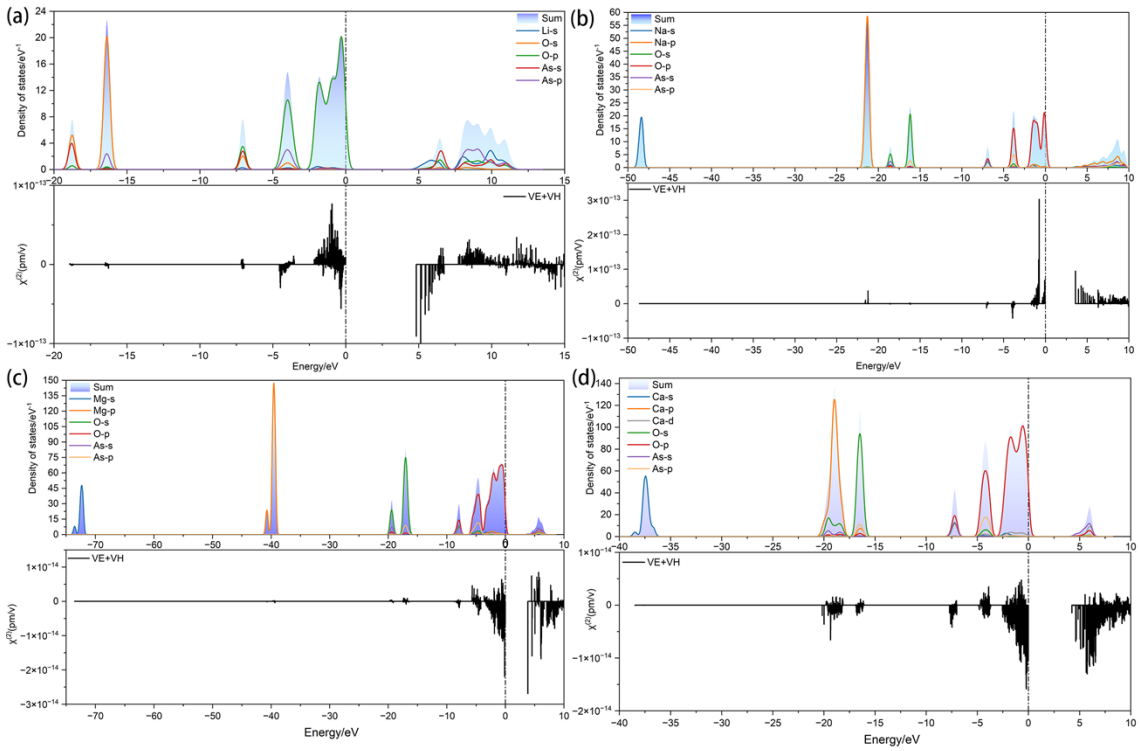


Figure S6 Comparison between the PDOS (top) and band-resolved $\chi^{(2)}$(pm/V) (bottom) of $LiAsO_4$(a), $NaAsO_4$(b), $Mg_3(AsO_4)_2$(c) and $Ca_3(AsO_4)_2$(d).

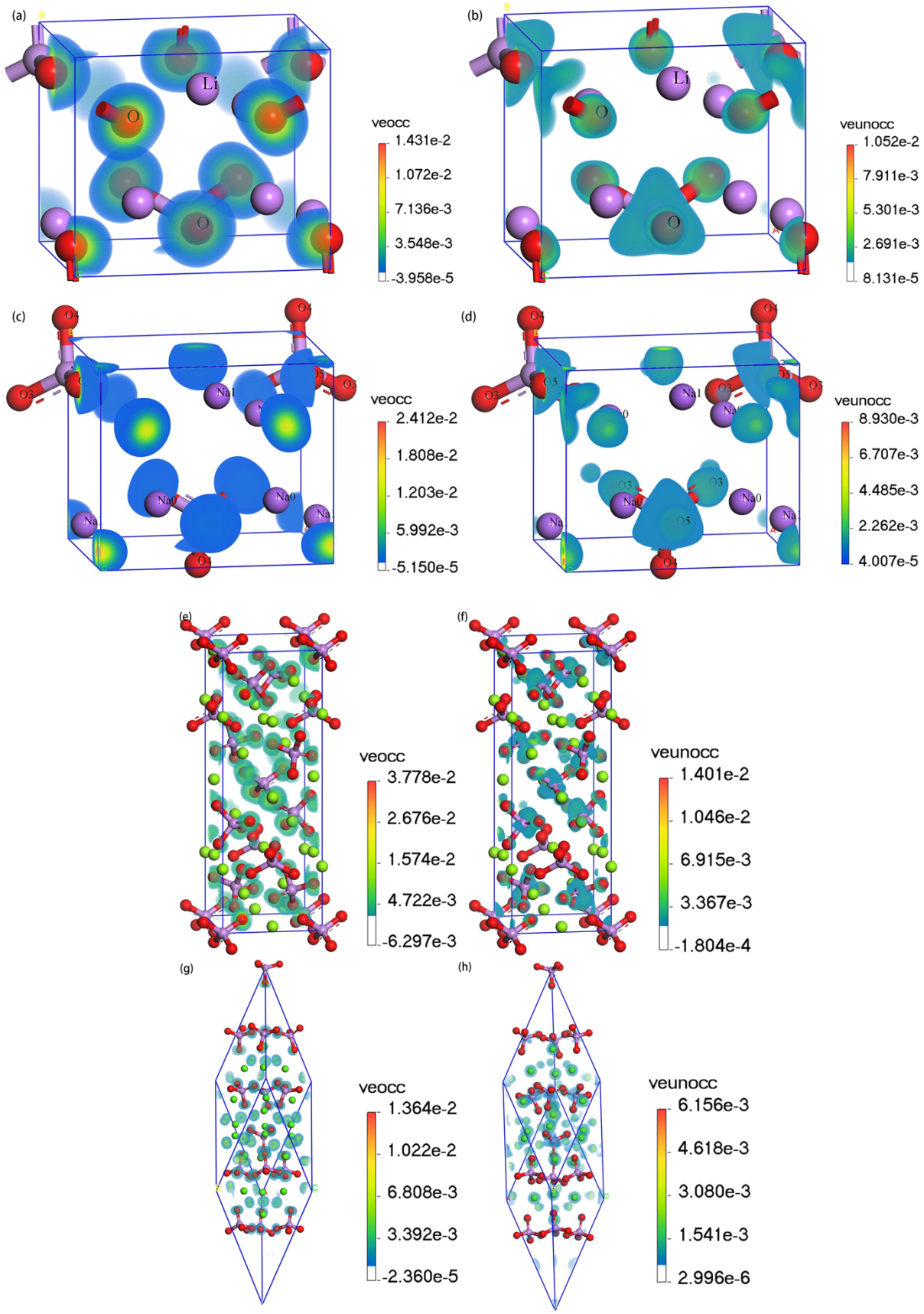


Figure S7 The SHG density of occupied and unoccupied states for $LiAsO_4$(a, b), $NaAsO_4$(c, d), $Mg_3(AsO_4)_2$(e, f) and $Ca_3(AsO_4)_2$(g, h).

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