Electronic Supplementary Information

Enhancing optical anisotropy of crystals by optimizing bonding electron distribution in anionic groups

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Methods

During the calculation, geometry optimization was performed using the BFGS minimization technique in CASTEP module. The converged criterions for the geometry optimization are that the residual forces on the atoms, the displacements of atoms and the energy change are less than 0.01 eV/Å, 5×10^{-4} Å, 5.0×10^{-6} eV/atom, respectively. The exchange-correlation functional and pseudopotential for BPO_4 and KBBF all are generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional and norm-conserving pseudopotential (NCP). The valence electrons are B-$2s^2 2p^1$, P-$3s^2 3p^3$ and O-$2s^2 2p^4$ respectively. The energy cutoff of plane wave's basis sets of them are all 830 eV. Monkhorst-Pack k-point of them are sampled with a separation of 0.050 $Å^{-1}$, respectively. We kept the default values of the CASTEP code on the aspect of the other calculation parameters and convergent criteria. For WIEN2k, the converged criterions were that the energy change, the force and the charge are less 0.0001 Ry, 1 mRy/au and 0.001 e respectively. The Monkhorst-Pack k-point is 10×10×10.

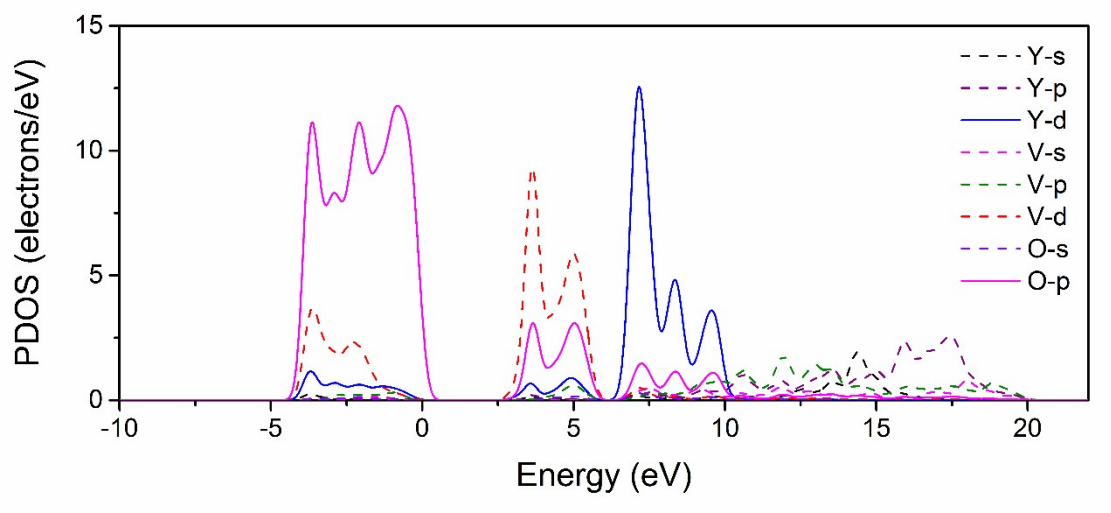

Figure S1. The partial density of states of YVO_4.

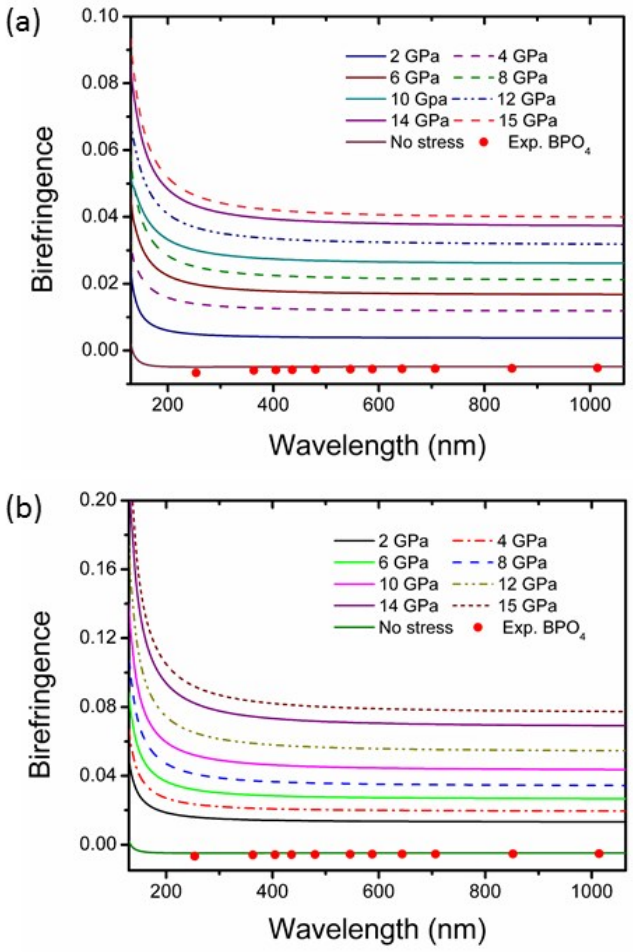

Figure S2. The birefringence of BPO_4 at a series of pressure along x- axis (a) and z- axis (b).

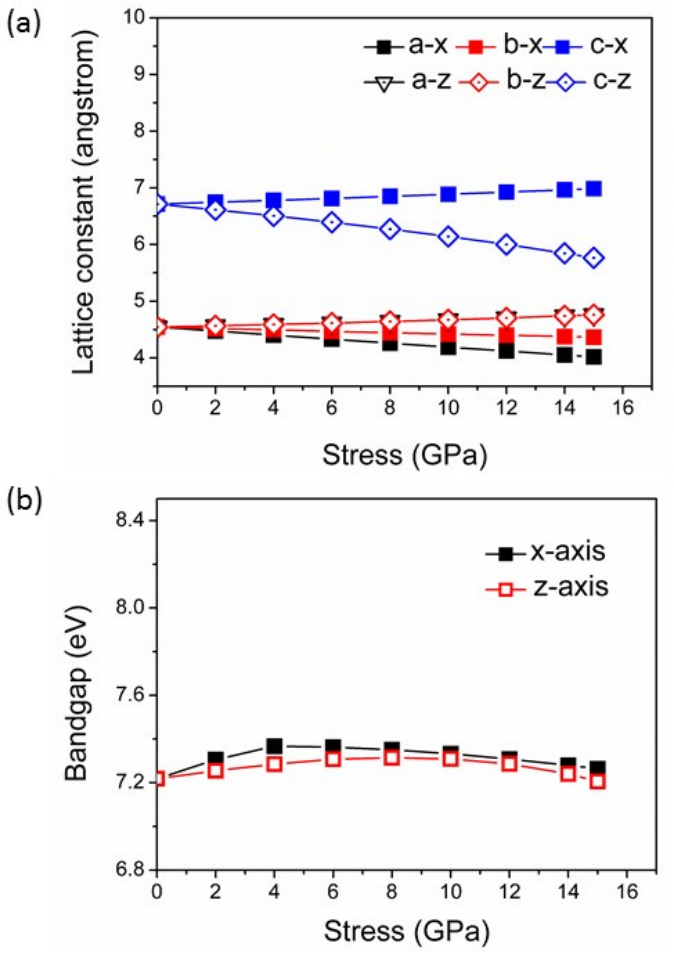

Figure S3. Change of (a) lattice and (b) bandgap as the increasing stress along x-axis and z-axis.

Table S1. The larger rotation angle θ and bond angle φ of BO_4 and PO_4 in BPO_4 under pressure along z-axis.

Groups	BO_4			PO_4		
Function	cos θ	cos φ	$\Delta\rho^c$	cos θ	cos φ	$\Delta\rho^c$
No stress	0.915	0.565	-0.066	0.921	0.557	-0.072
2 Gpa	0.915	0.557	-0.030	0.921	0.550	-0.014
4 Gpa	0.913	0.548	0.010	0.919	0.541	0.047
6 Gpa	0.921	0.538	0.038	0.926	0.532	0.091
8 Gpa	0.911	0.528	0.098	0.917	0.522	0.187
10 Gpa	0.910	0.517	0.147	0.916	0.512	0.266
12 Gpa	0.908	0.505	0.198	0.915	0.500	0.352
14 Gpa	0.907	0.492	0.255	0.914	0.487	0.443
15 Gpa	0.907	0.485	0.284	0.914	0.480	0.492

Table S2. The B-O and P-O bond length (Å) of BPO_4 under pressure along x-axis.

BPO_4	B-O(1)	B-O(2)	β_{zzz}	P-O(1)	P-O(2)	β_{zzz}
No stress	1.472	1.472	0.00	1.517	1.517	0.00
2 Gpa	1.471	1.471	0.00	1.517	1.517	0.00
4 Gpa	1.475	1.465	-2.96	1.518	1.515	5.01
6 Gpa	1.476	1.463	-4.57	1.518	1.515	7.50
8 Gpa	1.478	1.461	-6.18	1.519	1.515	9.85
10 Gpa	1.479	1.459	-7.89	1.519	1.514	12.24
12 Gpa	1.480	1.458	-9.22	1.519	1.514	14.44
14 Gpa	1.481	1.458	-10.93	1.520	1.515	16.63
15 Gpa	1.482	1.457	-11.64	1.520	1.515	17.75

Table S3. The hyperpolarizabilities (a.u.) of BO_4 and PO_4 groups (Gr.) under pressure along z-axis and x-axis.

Gr.	z	β_{xxx}	β_{xxy}	β_{xyy}	β_{yyy}	β_{xxz}	β_{xyz}	β_{yyz}	β_{xzz}	β_{yzz}	β_{zzz}
	0	0.00	0.00	0.00	0.00	-7.90	-8.62	7.90	0.00	0.00	0.00
	2	0.00	0.00	0.00	0.00	-7.95	-8.75	7.93	0.00	0.00	-0.03
	4	-0.00	0.00	-0.00	-0.01	-7.95	-8.85	7.95	-0.00	0.00	-0.00
	6	-0.02	0.01	-0.00	0.03	-7.92	-8.93	7.90	-0.00	0.01	-0.03
BO_4	8	-0.03	0.00	-0.01	-0.02	-7.85	-8.96	7.88	-0.01	0.00	0.03
	10	0.02	0.00	0.00	0.00	-7.77	-8.96	7.74	0.00	0.00	-0.03
	12	0.00	-0.00	0.00	-0.02	-7.58	-8.89	7.60	0.00	0.00	0.03
	14	-0.02	0.00	-0.00	-0.00	-7.37	-8.73	7.37	0.00	0.00	0.00
	15	0.00	0.00	0.00	0.00	-7.23	-8.62	7.23	0.00	0.00	0.00
	0	0.00	0.00	0.00	0.00	15.60	-15.96	-15.62	0.00	0.00	-0.02
	2	0.00	0.00	0.00	0.00	15.51	-16.00	-15.51	0.00	0.00	0.00
	4	0.00	0.00	0.00	-0.02	15.38	-16.02	-15.38	0.00	0.00	0.00
	6	0.01	0.00	0.00	0.02	15.18	-16.02	-15.17	0.00	0.00	-0.02
PO_4	8	0.00	0.00	0.00	0.00	14.98	-15.95	-14.97	0.00	0.00	-0.02
	10	0.02	0.00	0.00	0.01	14.70	-15.85	-14.68	0.00	0.00	-0.02
	12	-0.01	0.00	0.00	-0.01	14.35	-15.67	-14.37	0.00	0.00	-0.02
	14	-0.01	0.00	0.00	0.00	13.99	-15.42	-13.99	-0.00	0.00	0.00
	15	0.00	0.00	0.00	0.00	13.77	-15.27	-13.77	0.00	0.00	0.00
Gr.	x	β_{xxx}	β_{xxy}	β_{xyy}	β_{yyy}	β_{xxz}	β_{xyz}	β_{yyz}	β_{xzz}	β_{yzz}	β_{zzz}
	0	0.00	0.00	0.00	0.00	-7.90	-8.62	7.90	0.00	0.00	0.00
	2	0.00	-0.02	0.00	0.04	-7.65	-8.97	7.65	0.04	0.00	0.00
	4	0.01	-0.00	0.00	-0.01	-8.08	-9.31	6.65	0.00	0.00	-2.96
	6	0.03	-0.00	0.01	0.00	-8.21	-9.62	5.94	0.01	0.00	-4.57
BO_4	8	-0.03	0.01	-0.01	0.03	-8.36	-9.90	5.23	-0.01	0.01	-6.18
	10	0.03	-0.00	0.01	0.00	-8.54	-10.15	4.46	0.01	0.00	-7.89
	12	0.01	0.01	0.00	0.03	-8.65	-10.36	3.84	0.00	0.01	-9.22
	14	0.02	0.00	0.00	0.00	-8.83	-10.55	3.05	0.00	0.00	-10.93
	15	0.00	0.00	0.00	0.00	-8.89	-10.63	2.69	0.00	0.00	-11.64

	0	0.00	0.00	0.00	0.00	15.60	-15.96	-15.62	0.00	0.00	0.00
	2	0.03	-0.02	-0.05	-0.06	15.05	-16.53	-15.05	0.00	0.06	0.00
	4	-0.02	-0.00	-0.00	0.00	15.62	-17.03	-13.43	0.00	0.00	5.01
	6	0.00	0.00	0.00	0.02	15.59	-17.53	-12.33	0.00	0.00	7.50
PO_4	8	0.00	0.00	0.00	0.02	15.54	-17.96	-11.29	0.00	0.00	9.85
	10	-0.02	0.00	0.00	0.01	15.50	-18.36	-10.24	0.00	0.00	12.24
	12	0.00	0.00	0.00	0.02	15.47	-18.69	-9.30	0.00	0.00	14.44
	14	0.01	0.00	0.00	0.02	15.37	-19.02	-8.30	0.00	0.00	16.63
	15	0.01	0.00	0.00	-0.00	15.34	-19.16	-7.80	0.00	0.00	17.75

Table S4. The calculated nonzero SHG coefficients (pm/V) of BPO_4 under pressure along x-axis and z-axis.

BPO_4	d_{14}		d_{16}	d_{22}	d_{25}	d_{15}	
	x-axis	*z-axis*				*x-axis*	*z-axis*
No stress	0.803	0.830	0.000	0.000	0.000	-0.026	-0.026
2 Gpa	0.825	0.807	0.000	0.000	0.000	-0.028	-0.027
4 Gpa	0.842	0.810	0.034	-0.041	0.029	0.000	-0.030
6 Gpa	0.845	0.814	0.035	-0.063	0.029	0.000	-0.035
8 Gpa	0.846	0.814	0.035	-0.084	0.028	0.000	-0.040
10 Gpa	0.845	0.812	0.035	-0.105	0.027	0.000	-0.046
12 Gpa	0.842	0.806	0.033	-0.126	0.025	0.000	-0.054
14 Gpa	0.841	0.797	0.031	-0.146	0.024	0.000	-0.060
15 Gpa	0.839	0.789	0.03	-0.157	0.023	0.000	-0.064