$A_2SbB_3O_8$(A = Na, K, Rb) and β-$RbSbB_2O_6$: Two Types of Alkali Boroantimonates with 3D Anionic Architectures Composed of SbO_6 Octahedra and Borate Groups

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Supporting Information

Table S1. The state energies (eV) of the lowest conduction band (L-CB) and the highest valence band (H-VB) of $A_2SbB_3O_8$ (A = Na, K, Rb) and β-$RbSbB_2O_6$.

Compound	k-point	L-CB	H-VB
$Rb_2SbB_3O_8$	Z (0.000, 0.000, 0.500)	4.61253	-0.09080
	G (0.000, 0.000, 0.000)	4.21108	-0.10796
	Y (0.000, 0.500, 0.000)	4.61592	-0.10250
	A (-0.500, 0.500, 0.000)	5.24188	-0.02587
	B (-0.500, 0.000, 0.000)	5.15104	0
	D (-0.500, 0.000, 0.500)	5.27320	-0.01850
	E (-0.500, 0.500, 0.500)	5.31155	-0.04330
	C (0.000, 0.500, 0.500)	4.83354	-0.09262
$K_2SbB_3O_8$	Z (0.000, 0.000, 0.500)	4.55655	-0.04960
	G (0.000, 0.000, 0.000)	4.17492	-0.05144
	Y (0.000, 0.500, 0.000)	4.55703	-0.05208
	A (-0.500, 0.500, 0.000)	5.14115	-0.01278
	B (-0.500, 0.000, 0.000)	5.07518	0
	D (-0.500, 0.000, 0.500)	5.19040	-0.00553
	E (-0.500, 0.500, 0.500)	5.21278	-0.02264
	C (0.000, 0.500, 0.500)	4.76024	-0.03547
$Na_2SbB_3O_8$	Z (0.000, 0.000, 0.500)	4.66769	-0.01897
	G (0.000, 0.000, 0.000)	4.22391	0
	Y (0.000, 0.500, 0.000)	4.67902	-0.02653
	A (-0.500, 0.500, 0.000)	5.26679	-0.03458
	B (-0.500, 0.000, 0.000)	5.21826	-0.01257
	D (-0.500, 0.000, 0.500)	5.27497	-0.04600
	E (-0.500, 0.500, 0.500)	5.31048	-0.05461
	C (0.000, 0.500, 0.500)	4.90486	-0.03907
β-$RbSbB_2O_6$	L (-0.500, 0.000, 0.500)	4.74498	-0.13374
	M (-0.500, -0.500, 0.500)	4.95869	-0.14393
	A (-0.500, 0.000, 0.000)	4.34456	0
	G (0.000, 0.000, 0.000)	3.63938	-0.17664
	Z (0.000, -0.500, 0.500)	4.74498	-0.13374
	V (0.000, 0.000, 0.500)	5.00123	-0.18864

Table S2. The calculated bond orders of the crystal $A_2SbB_3O_8$ (A = Na, K, Rb) and β-$RbSbB_2O_6$.

$Na_2SbB_3O_8$					
Bond	Bond length	Bond order	Bond	Bond length	Bond order
B-O	1.36020	0.87	B-O	1.45040	0.69
B-O	1.36721	0.87	B-O	1.45319	0.70
B-O	1.37001	0.82	B-O	1.48286	0.63
B-O	1.37310	0.86	B-O	1.48776	0.61
B-O	1.38307	0.82	B-O	1.38585	0.81
Sb-O	1.93229	0.53	Sb-O	1.97630	0.44
Sb-O	1.93864	0.45	Sb-O	1.99115	0.41
Sb-O	1.96783	0.41	Sb-O	1.99276	0.45
Na-O	2.36292	0.11	Na-O	2.37490	0.14
Na-O	2.40573	0.07	Na-O	2.45097	0.07
Na-O	2.51490	0.12	Na-O	2.51974	0.04
Na-O	2.60770	0.06	Na-O	2.71505	0.01
Na-O	2.76093	0.04			
$K_2SbB_3O_8$					
Bond	Bond length	Bond order	Bond	Bond length	Bond order
B-O	1.35987	0.83	B-O	1.36042	0.87
B-O	1.37755	0.86	B-O	1.37793	0.86
B-O	1.38732	0.82	B-O	1.38970	0.80
B-O	1.45826	0.69	B-O	1.47706	0.67
B-O	1.48033	0.62	B-O	1.48404	0.63
Sb-O	1.92613	0.49	Sb-O	1.93321	0.52
Sb-O	1.97973	0.44	Sb-O	1.98288	0.46
Sb-O	1.99328	0.41	Sb-O	2.00748	0.42
K-O	2.61467	0.04	K-O	2.63193	0.10
K-O	2.70562	0.05	K-O	2.71370	0.02
K-O	2.78704	0.11	K-O	2.86915	0.06
K-O	2.88053	0.03	K-O	2.93903	0.01
$Rb_2SbB_3O_8$					
Bond	Bond length	Bond order	Bond	Bond length	Bond order
B-O	1.33953	0.89	B-O	1.39261	0.82
B-O	1.35150	0.88	B-O	1.44961	0.70
B-O	1.36728	0.88	B-O	1.46017	0.64
B-O	1.37712	0.81	B-O	1.47051	0.68
B-O	1.37876	0.82	B-O	1.49522	0.60
Sb-O	1.92058	0.52	Sb-O	1.97503	0.45
Sb-O	1.92113	0.51	Sb-O	1.97657	0.42
Sb-O	1.97348	0.46	Sb-O	2.00350	0.44
Rb-O	2.75331	0.07	Rb-O	2.90110	0.06

Rb-O	2.80029	0.02	Rb-O	2.94887	0.11
β-$RbSbB_2O_6$					
Bond	Bond length	Bond order	Bond	Bond length	Bond order
B-O	1.34964	0.90	B-O	1.35174	0.90
B-O	1.35156	0.86	B-O	1.36815	0.76
B-O	1.38964	0.85	B-O	1.40821	0.73
Sb-O	1.92652	0.53	Sb-O	1.95034	0.44
Sb-O	1.95687	0.41	Sb-O	1.98879	0.52
Sb-O	1.97513	0.45	Sb-O	1.98806	0.38
Rb-O	2.78545	0.04			

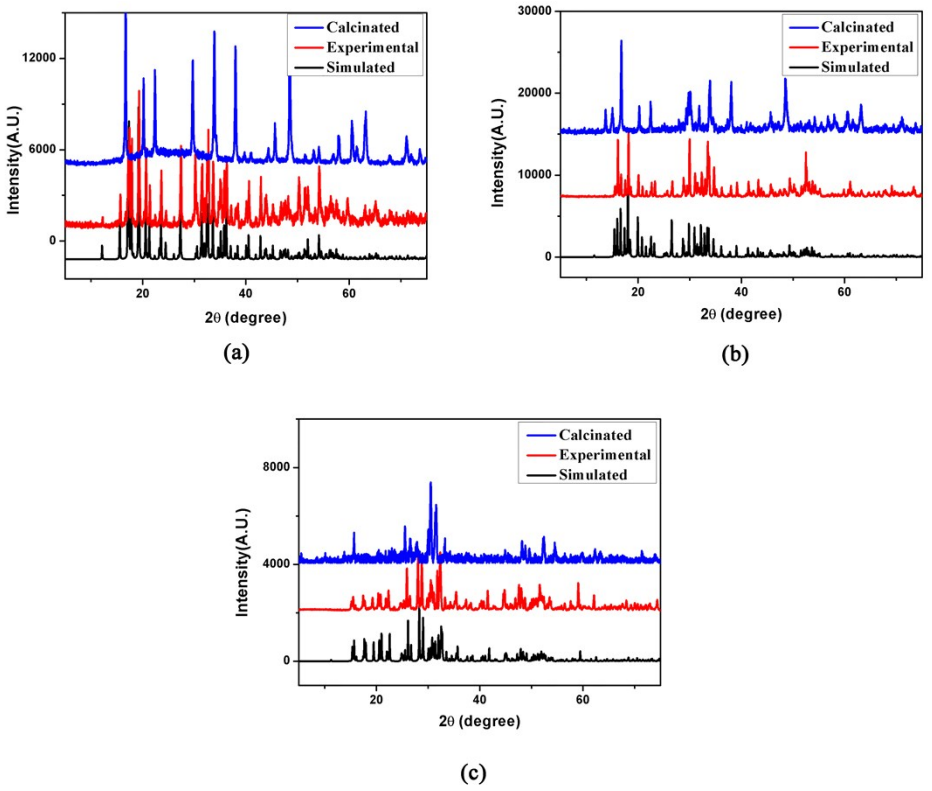

Figure S1. Calcinated, experimental and simulated X-ray powder diffraction patterns for $Na_2SbB_3O_8$ (a), $K_2SbB_3O_8$ (b), and $Rb_2SbB_3O_8$ (c).

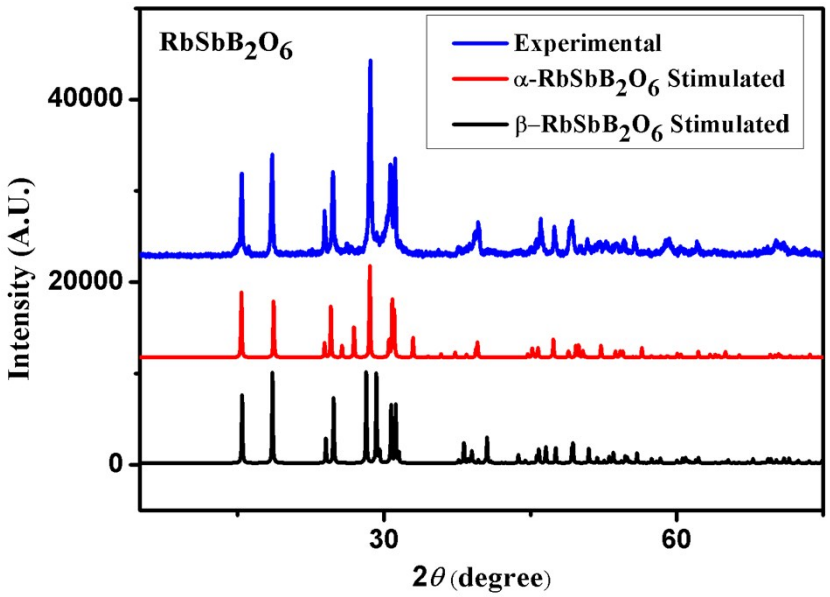

Figure S2. Experiment and simulated X-ray powder diffraction patterns for α-$RbSbB_2O_6$ and β-$RbSbB_2O_6$.

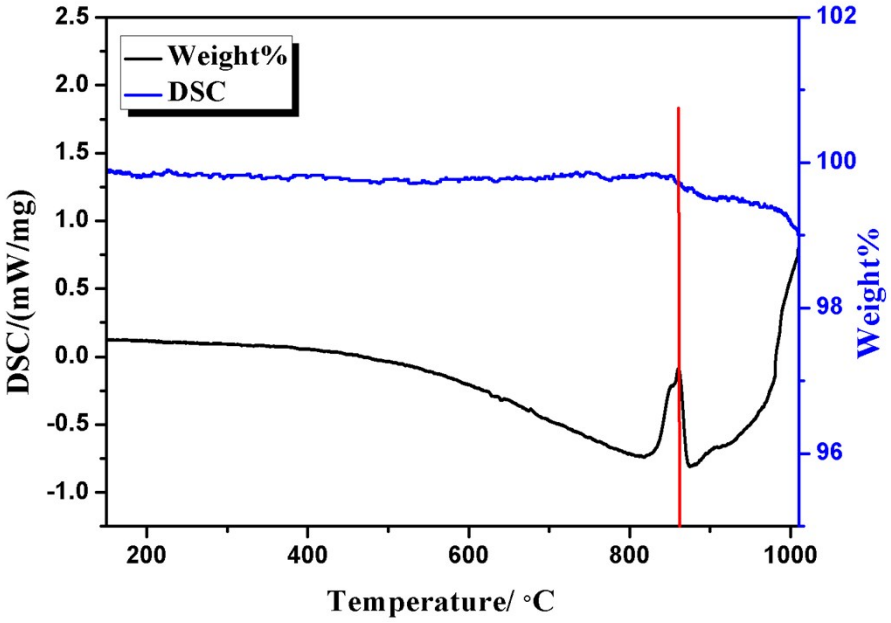

Figure S3. TGA and DSC curves for α-$RbSbB_2O_6$.

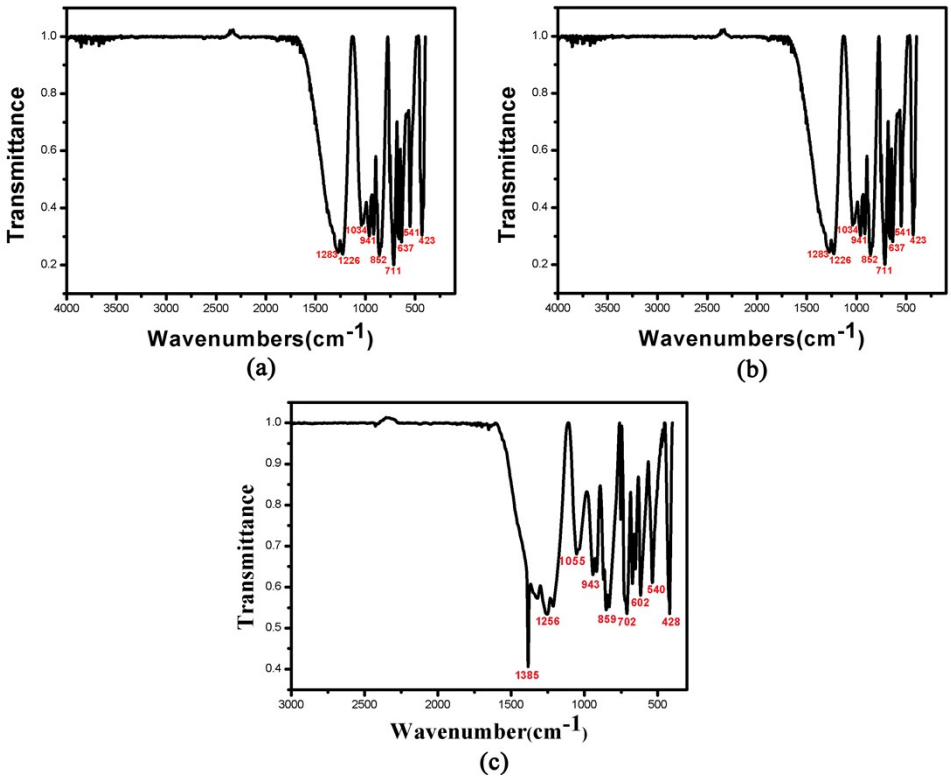

Figure S4. The IR spectra of $Na_2SbB_3O_8$ (a), $K_2SbB_3O_8$ (b), and $Rb_2SbB_3O_8$.

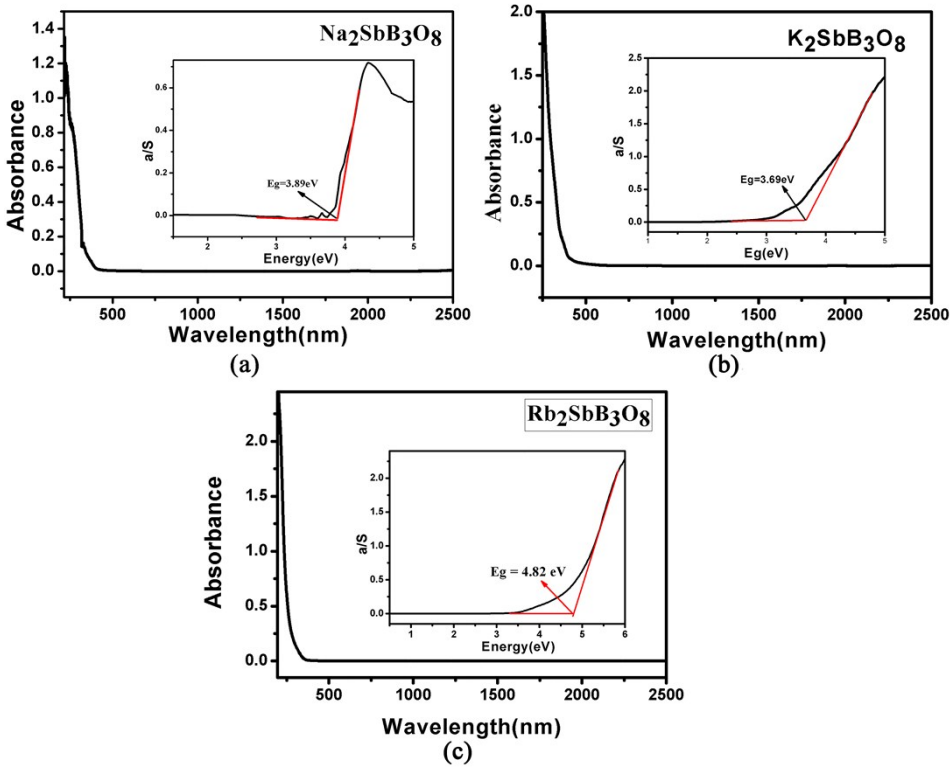

Figure S5. UV-vis optical diffuse reflectance spectra of $Na_2SbB_3O_8$ (a), $K_2SbB_3O_8$ (b), and $Rb_2SbB_3O_8$.

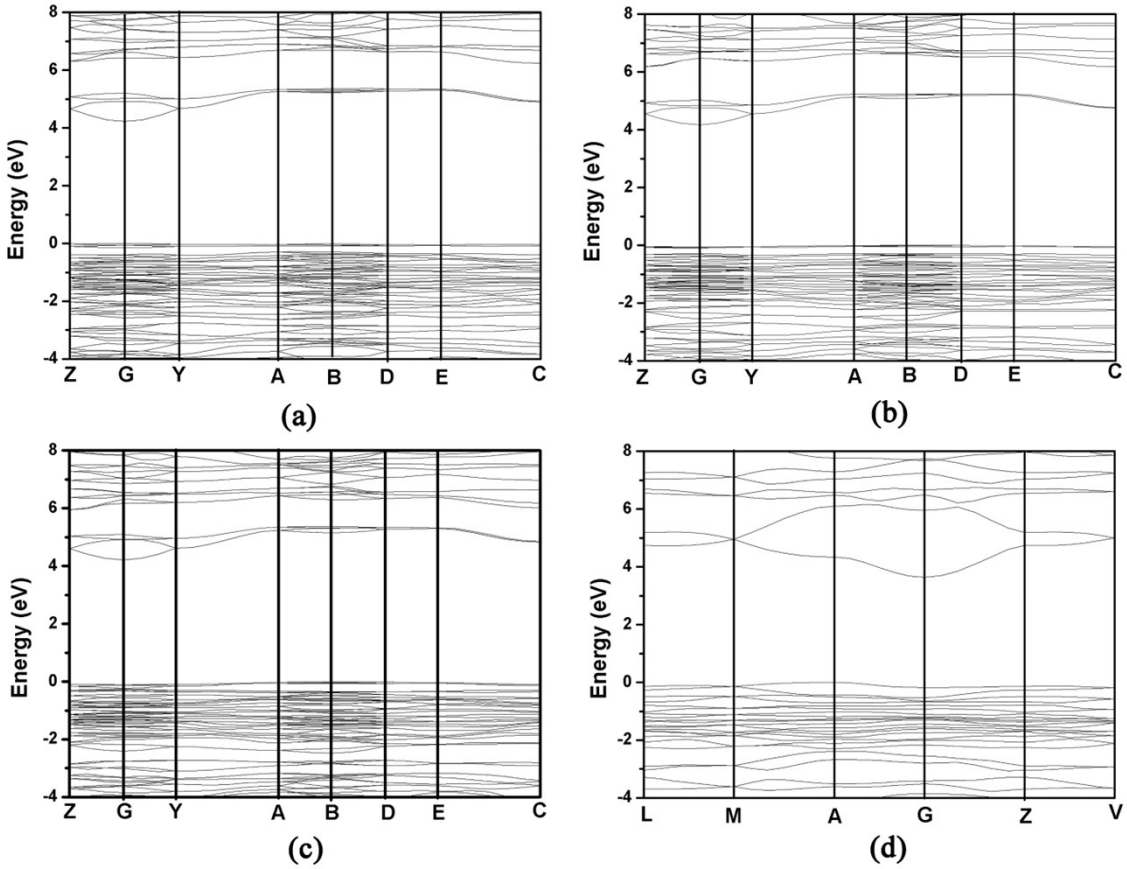

Figure S6. Band structures for $Na_2SbB_3O_8$ (a), $K_2SbB_3O_8$ (b), $Rb_2SbB_3O_8$ (c), and $RbSbB_2O_6$ (d).

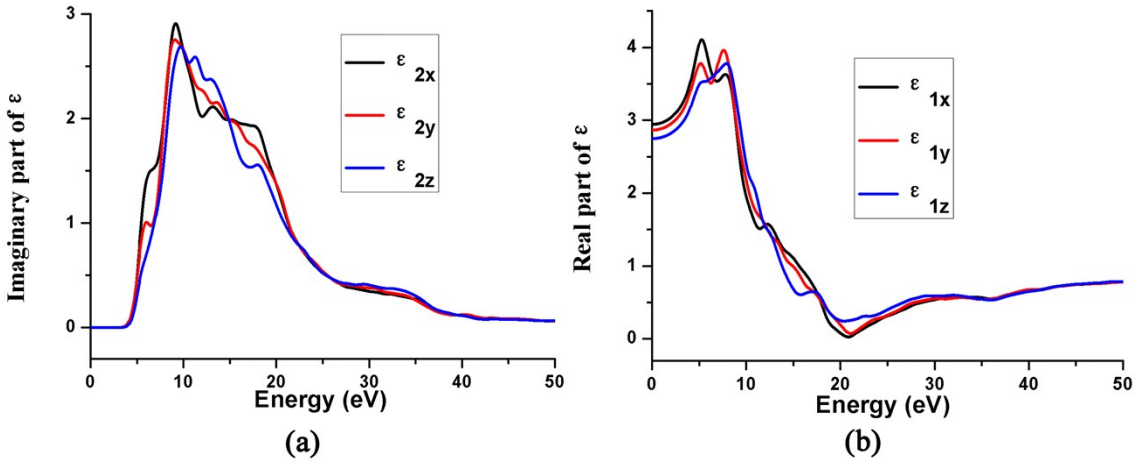

Figure S7. The calculated imaginary part (a) and the real part (b) of the dielectric function polarized along three directions for $Na_2SbB_3O_8$.

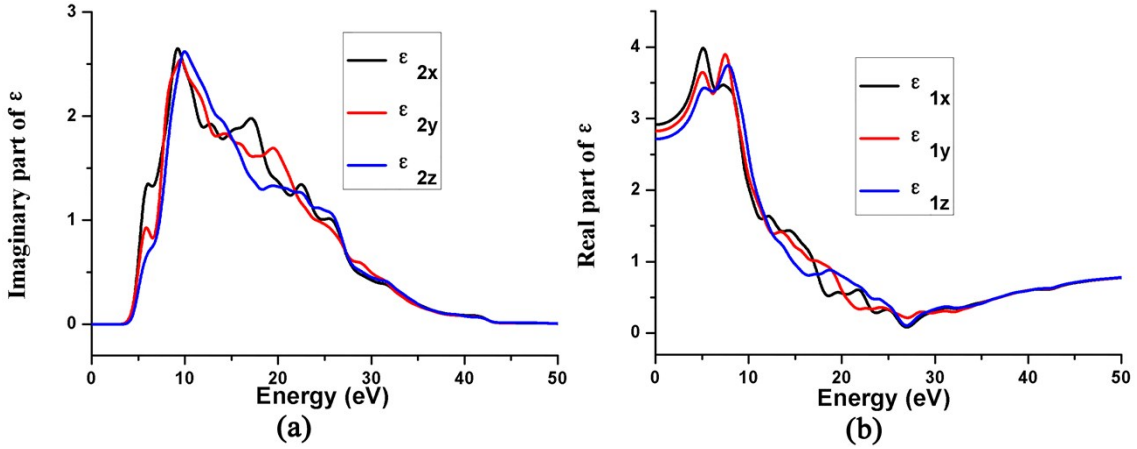

Figure S8. The calculated imaginary part (a) and the real part (b) of the dielectric function polarized along three directions for $K_2SbB_3O_8$.

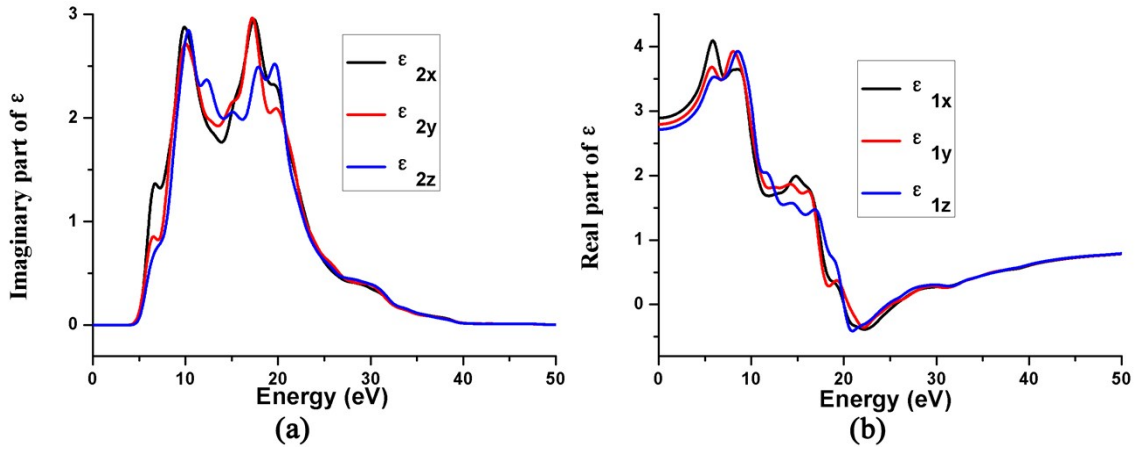

Figure S9. The calculated imaginary part (a) and the real part (b) of the dielectric function polarized along three directions for $Rb_2SbB_3O_8$.

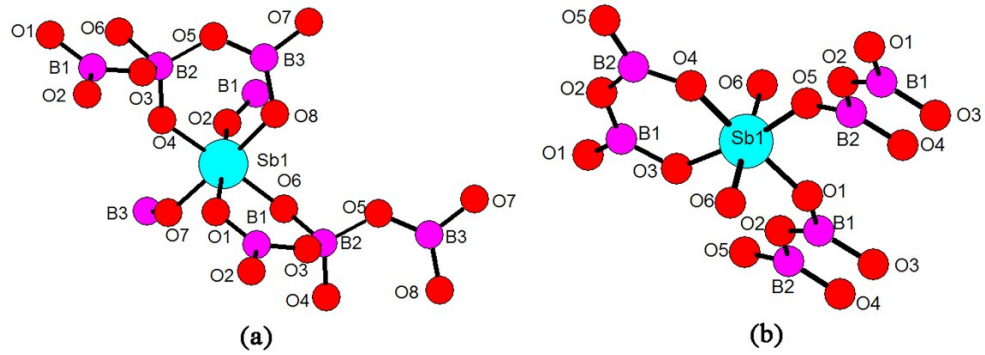

Figure S10. The coordination geometries around the Sb atoms in $A_2SbB_3O_8$ (A = Na, K, Rb) (a) and β-$RbSbB_2O_6$ (b).

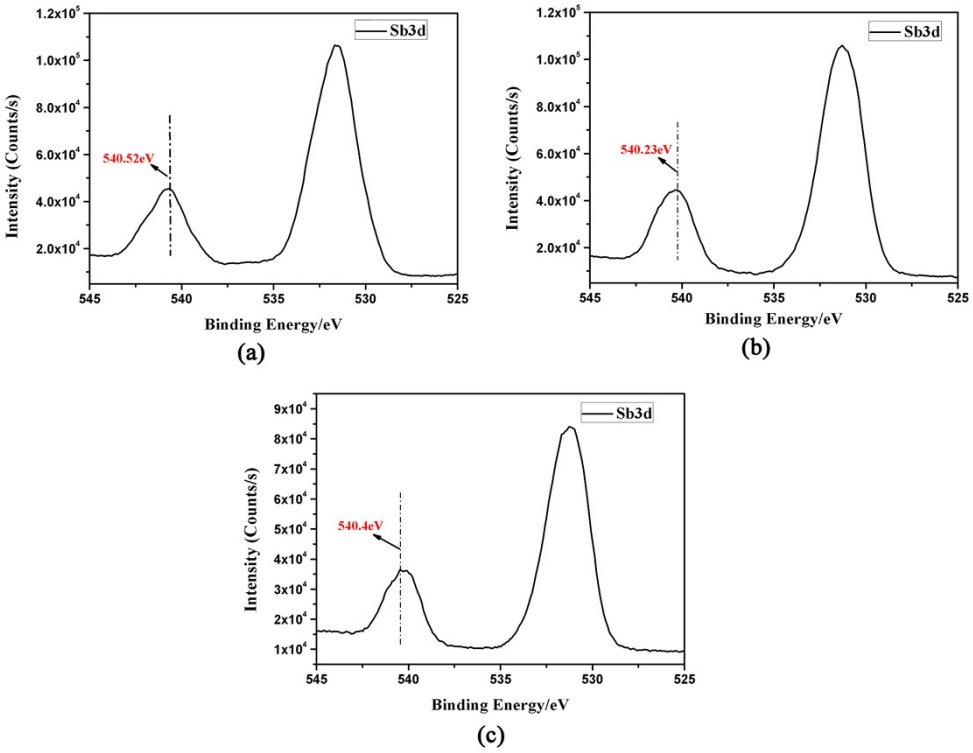

Figure S11. The Sb 3d XPS spectra of $Na_2SbB_3O_8$ (a), $K_2SbB_3O_8$ (b), and $Rb_2SbB_3O_8$ (c).