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$Li_3Cs_2M_2B_3P_6O_{24}$ (M = Pb, Sr): Borophosphates with Double 6-member Ring of $[BP_2O_8]^{3-}$

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Table S1. Atomic Coordinates and Equivalent Isotropic Displacement Parameters of $Li_3Cs_2Pb_2B_3P_6O_{24}$.

Atom	Wyckoff	*x*	*y*	*z*	*U(eq)*	S.O.F
Cs(1)	4a	0.64965(3)	0.35055(3)	0.85055(3)	0.0016(1)	1
Cs(2)	4a	0.15382(3)	0.65382(3)	0.84618(3)	0.0023(1)	1
Pb(1)	4a	0.40633(1)	0.09367(1)	0.90633(1)	0.0009(1)	1
Pb(2)	4a	0.43582(2)	0.56418(2)	0.06418(2)	0.0012(1)	1
Li	12b	0.4376(7)	0.5989(7)	0.8034(6)	0.0013(1)	1
B	12b	0.8670(4)	0.6185(4)	0.8527(4)	0.0005(1)	1
P(1)	12b	0.5856(2)	0.31572(9)	0.5545(2)	0.0006(1)	1
P(2)	12b	0.6527(2)	0.6360(2)	0.8781(2)	0.0006(1)	1
O(1)	12b	0.4041(2)	0.7081(2)	0.8998(2)	0.0012(1)	1
O(2)	12b	0.6026(2)	0.3040(2)	0.4338(2)	0.0006(1)	1
O(3)	12b	0.5863(2)	0.6054(2)	0.7847(2)	0.0010(1)	1
O(4)	12b	0.4712(2)	0.3598(2)	0.5604(2)	0.0008(1)	1
O(5)	12b	0.6602(2)	0.3941(2)	0.6023(2)	0.0012(1)	1
O(6)	12b	0.7614(2)	0.5798(2)	0.8668(2)	0.0009(1)	1
O(7)	12b	0.6768(3)	0.7545(2)	0.8806(3)	0.0011(1)	1
O(8)	12b	0.6064(2)	0.6005(3)	0.9814(2)	0.0011(1)	1

[a]U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S2. Selected Bond Lengths (Å) of $Li_3Cs_2Pb_2B_3P_6O_{24}$.

$Li_3Cs_2Pb_2B_3P_6O_{24}$			
Cs(1)-O(5)	3.211(3)	Pb(1)-O(5)	2.680(3)
Cs(1)-O(5)	3.211(3)	Pb(2)-O(8)	2.457(3)
Cs(1)-O(5)	3.211(3)	Pb(2)-O(8)	2.457(3)
Cs(1)-O(6)	3.253(3)	Pb(2)-O(8)	2.457(3)
Cs(1)-O(6)	3.253(3)	Pb(2)-O(2)	3.091(3)
Cs(1)-O(6)	3.253(3)	Pb(2)-O(2)	3.091(3)
Cs(1)-O(3)	3.444(3)	Pb(2)-O(2)	3.091(3)
Cs(1)-O(3)	3.444(3)	Pb(2)-O(1)	2.809(3)
Cs(1)-O(3)	3.444(3)	Pb(2)-O(1)	2.809(3)
Cs(1)-O(8)	3.632(3)	Pb(2)-O(1)	2.809(3)
Cs(1)-O(8)	3.632(3)	Li-O(3)	1.910(9)
Cs(1)-O(8)	3.632(3)	Li-O(8)	1.946(9)
Cs(2)-O(4)	3.161(3)	Li-O(1)	1.902(9)
Cs(2)-O(4)	3.161(3)	Li-O(5)	1.905(9)
Cs(2)-O(4)	3.161(3)	B-O(7)	1.464(6)
Cs(2)-O(1)	3.329(3)	B-O(6)	1.442(6)
Cs(2)-O(1)	3.329(3)	B-O(4)	1.472(6)
Cs(2)-O(1)	3.329(3)	B-O(2)	1.478(6)

Cs(2)-O(2)	3.489(3)	P(1)-O(1) (T)	1.493(3)
Cs(2)-O(2)	3.489(3)	P(1)-O(5) (T)	1.505(3)
Cs(2)-O(2)	3.489(3)	P(1)-O(4) (B)	1.561(3)
Pb(1)-O(3)	2.437(3)	P(1)-O(2) (B)	1.558(3)
Pb(1)-O(3)	2.437(3)	P(2)-O(3) (T)	1.510(3)
Pb(1)-O(3)	2.437(3)	P(2)-O(8) (T)	1.510(3)
Pb(1)-O(5)	2.680(3)	P(2)-O(7) (B)	1.537(3)
Pb(1)-O(5)	2.680(3)	P(2)-O(6) (B)	1.564(3)

T: Terminal O^{2-} anion. B: Bridging O^{2-} anion.

Table S3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters of $Li_3Cs_2Sr_2B_3P_6O_{24}$.

Atom	Wyckoff	*x*	*y*	*z*	*U(eq)*	S.O.F
Cs(1)	4a	0.64966(2)	0.35034(2)	0.85034(2)	0.0017(1)	1
Cs(2)	4a	0.15527(2)	0.65527(2)	0.84473(2)	0.0021(1)	1
Sr(1)	4a	0.40813(2)	0.09187(2)	0.90813(2)	0.0010(1)	1
Sr(2)	4a	0.42594(2)	0.57406(2)	0.07406(2)	0.0010(1)	1
Li	12b	0.4389(4)	0.5949(4)	0.8040(4)	0.0012(1)	1
B	12b	0.8660(3)	0.6213(2)	0.8529(3)	0.0006(1)	1
P(1)	12b	0.58323(7)	0.31711(6)	0.55520(6)	0.0007(1)	1
P(2)	12b	0.65195(6)	0.63674(6)	0.88068(6)	0.0007(1)	1
O(1)	12b	0.4030(2)	0.7111(2)	0.8953(2)	0.0013(1)	1
O(2)	12b	0.6003(2)	0.2982(2)	0.4338(2)	0.0008(1)	1
O(3)	12b	0.5879(2)	0.6001(2)	0.7877(2)	0.0012(1)	1

O(4)	12b	0.4673(2)	0.3603(2)	0.5593(2)	0.0010(1)	1
O(5)	12b	0.6554(2)	0.4015(2)	0.5977(2)	0.0012(1)	1
O(6)	12b	0.7618(2)	0.5800(2)	0.8749(2)	0.0010(1)	1
O(7)	12b	0.6793(2)	0.7558(2)	0.8746(2)	0.0013(1)	1
O(8)	12b	0.6033(2)	0.6107(2)	0.9858(2)	0.0014(1)	1

[a]U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S4. Selected Bond Lengths (Å) of $Li_3Cs_2Sr_2B_3P_6O_{24}$.

$Li_3Cs_2Sr_2B_3P_6O_{24}$			
Cs(1)-O(5)	3.272(2)	Sr(1)-O(5)	2.547(2)
Cs(1)-O(5)	3.272(2)	Sr(2)-O(8)	2.556(2)
Cs(1)-O(5)	3.272(2)	Sr(2)-O(8)	2.556(2)
Cs(1)-O(6)	3.257(2)	Sr(2)-O(8)	2.556(2)
Cs(1)-O(6)	3.257(2)	Sr(2)-O(2)	2.865(2)
Cs(1)-O(6)	3.257(2)	Sr(2)-O(2)	2.865(2)
Cs(1)-O(3)	3.360(2)	Sr(2)-O(2)	2.865(2)
Cs(1)-O(3)	3.360(2)	Sr(2)-O(1)	2.873(2)
Cs(1)-O(3)	3.360(2)	Sr(2)-O(1)	2.873(2)
Cs(1)-O(1)	3.644(2)	Sr(2)-O(1)	2.873(2)
Cs(1)-O(1)	3.644(2)	Li-O(3)	1.903(6)
Cs(1)-O(1)	3.644(2)	Li-O(8)	1.922(6)
Cs(2)-O(4)	3.141(2)	Li-O(1)	1.929(6)
Cs(2)-O(4)	3.141(2)	Li-O(5)	1.945(6)
Cs(2)-O(4)	3.141(2)	B-O(7)	1.440(4)
Cs(2)-O(1)	3.284(2)	B-O(6)	1.449(4)
Cs(2)-O(1)	3.284(2)	B-O(4)	1.474(4)
Cs(2)-O(1)	3.284(2)	B-O(2)	1.509(4)
Cs(2)-O(2)	3.484(2)	P(1)-O(1) (T)	1.495(2)
Cs(2)-O(2)	3.484(2)	P(1)-O(5) (T)	1.508(2)
Cs(2)-O(2)	3.484(2)	P(1)-O(4) (B)	1.570(2)
Sr(1)-O(3)	2.487(2)	P(1)-O(2) (B)	1.574(2)
Sr(1)-O(3)	2.487(2)	P(2)-O(3) (T)	1.507(2)
Sr(1)-O(3)	2.487(2)	P(2)-O(8) (T)	1.507(2)
Sr(1)-O(5)	2.547(2)	P(2)-O(7) (B)	1.551(2)
Sr(1)-O(5)	2.547(2)	P(2)-O(6) (B)	1.571(2)

T: Terminal O^{2-} anion. B: Bridging O^{2-} anion.

Table S5. Selected Bond Angles (deg) of $Li_3Cs_2M_2B_3P_6O_{24}$ (M = Pb, Sr).

$Li_3Cs_2Pb_2B_3P_6O_{24}$		$Li_3Cs_2Sr_2B_3P_6O_{24}$	
O(6)-B(1)-O(7)	112.9(4)	O(7)-B(1)-O(6)	114.8(3)
O(6)-B(1)-O(4)	108.2(4)	O(7)-B(1)-O(4)	113.3(2)
O(7)-B(1)-O(4)	111.7(4)	O(6)-B(1)-O(4)	107.4(2)
O(6)-B(1)-O(2)	112.6(4)	O(7)-B(1)-O(2)	102.4(2)
O(7)-B(1)-O(2)	103.1(4)	O(6)-B(1)-O(2)	111.9(2)
O(4)-B(1)-O(2)	108.1(4)	O(4)-B(1)-O(2)	106.9(2)
O(1)-P(1)-O(5)	113.26(2)	O(1)-P(1)-O(5)	114.67(2)
O(1)-P(1)-O(2)	106.48(2)	O(1)-P(1)-O(4)	114.21(2)
O(5)-P(1)-O(2)	111.94(2)	O(5)-P(1)-O(4)	108.00(2)
O(1)-P(1)-O(4)	113.13(2)	O(1)-P(1)-O(2)	104.97(2)
O(5)-P(1)-O(4)	109.33(2)	O(5)-P(1)-O(2)	111.98(2)
O(2)-P(1)-O(4)	102.16(2)	O(4)-P(1)-O(2)	102.36(2)
O(8)-P(2)-O(3)	112.90(2)	O(3)-P(2)-O(8)	113.85(2)
O(8)-P(2)-O(7)	110.69(2)	O(3)-P(2)-O(7)	112.47(2)
O(3)-P(2)-O(7)	112.44(2)	O(8)-P(2)-O(7)	110.45(2)
O(8)-P(2)-O(6)	106.70(2)	O(3)-P(2)-O(6)	107.52(2)
O(3)-P(2)-O(6)	107.68(2)	O(8)-P(2)-O(6)	107.71(2)
O(7)-P(2)-O(6)	105.97(2)	O(7)-P(2)-O(6)	104.23(2)

Figure S1. Photo of the as-synthesized $Li_3Cs_2Pb_2B_3P_6O_{24}$ (a) and $Li_3Cs_2Sr_2B_3P_6O_{24}$ (b) crystals.

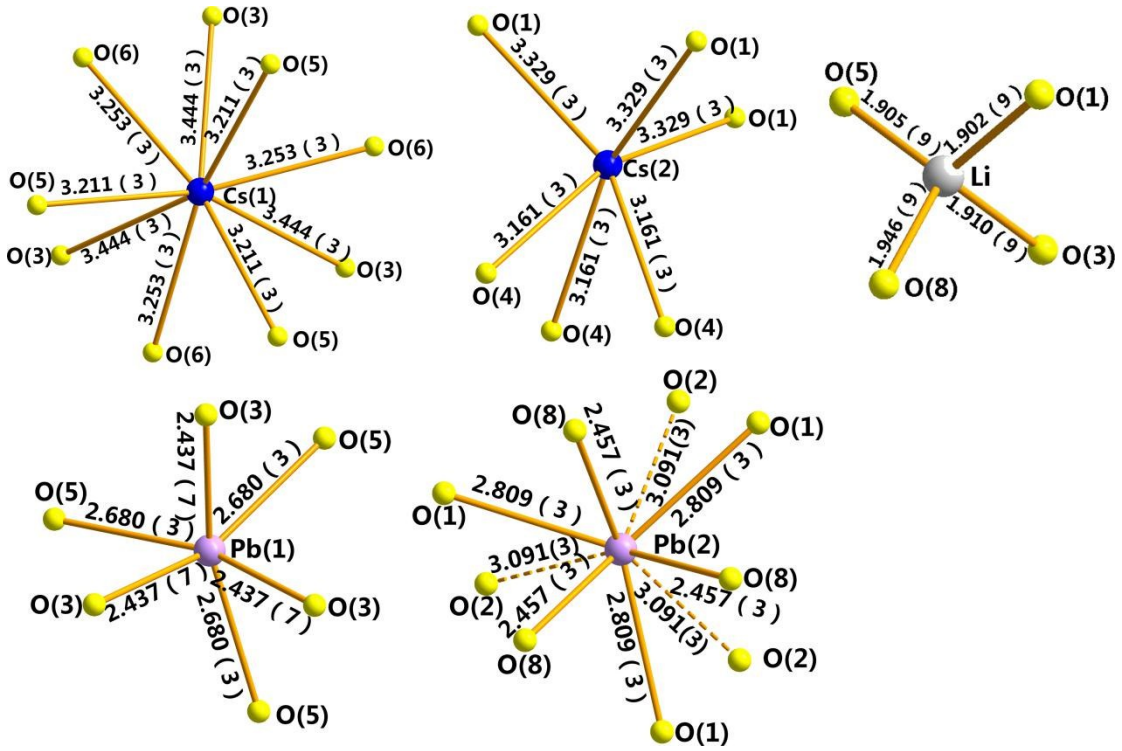


Figure S2a. Coordination environments for Cs, Li and Pb atoms in the structure of $Li_3Cs_2Pb_2B_3P_6O_{24}$.

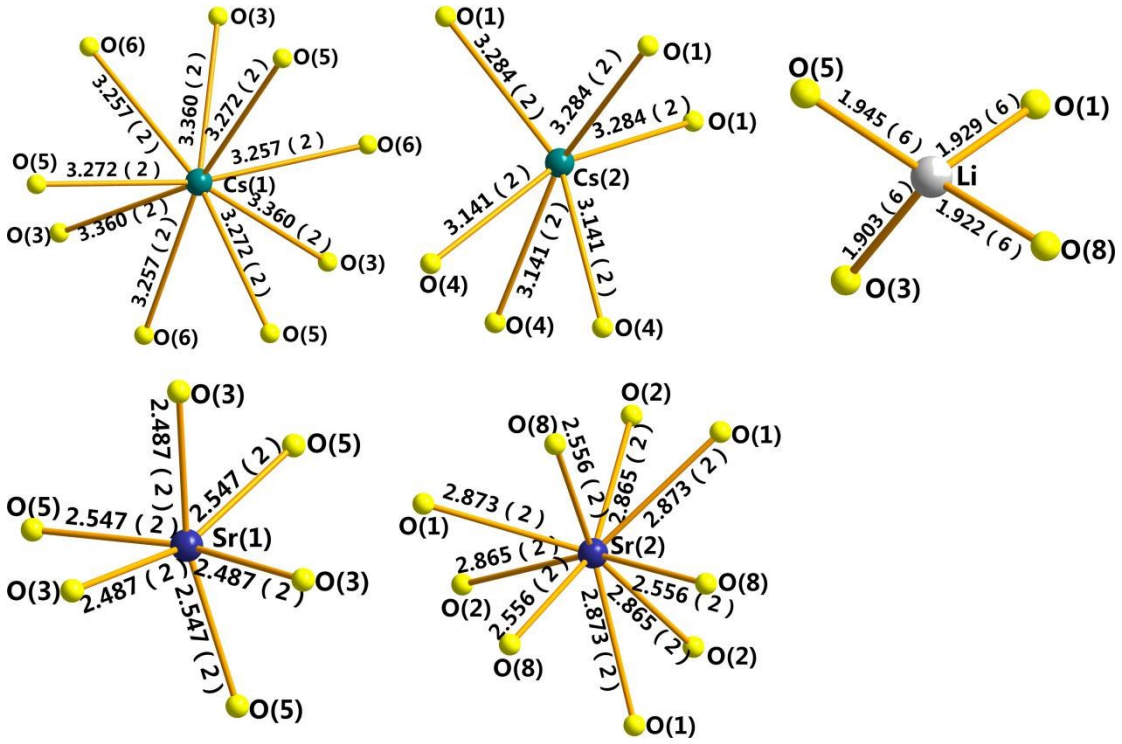


Figure S2b. Coordination environments for Cs, Li and Sr atoms in the structure of $Li_3Cs_2Sr_2B_3P_6O_{24}$.

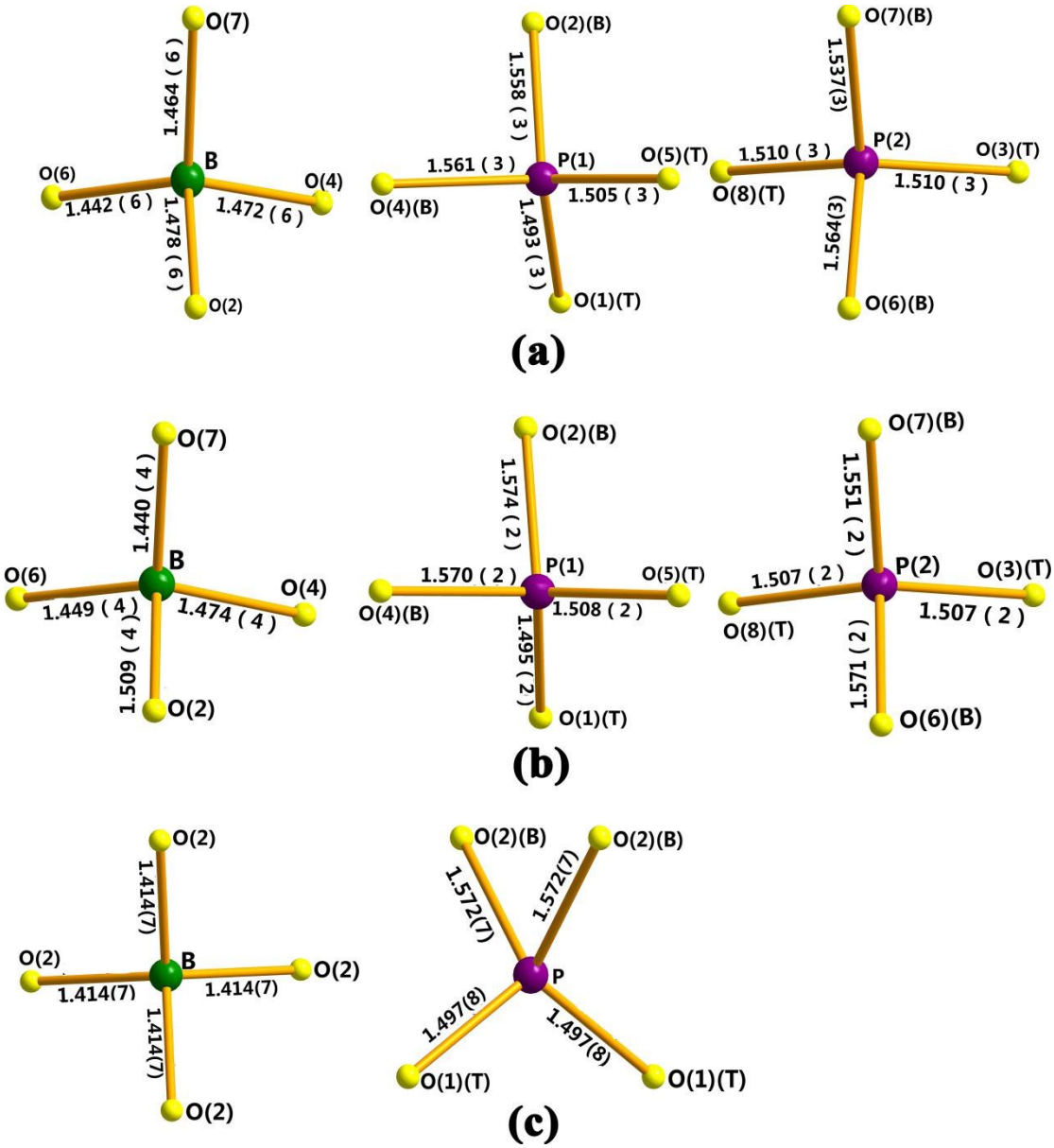


Figure S3. The bond-lengths of B−O and P−O in the compound of $Li_3Cs_2Pb_2B_3P_6O_{24}$ (a), $Li_3Cs_2Sr_2B_3P_6O_{24}$ (b) and $KPbBP_2O_8$ (c).

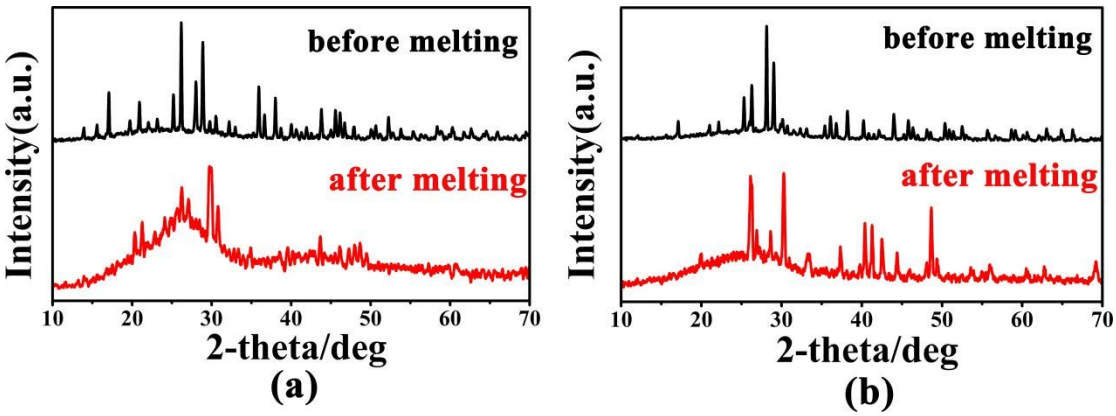
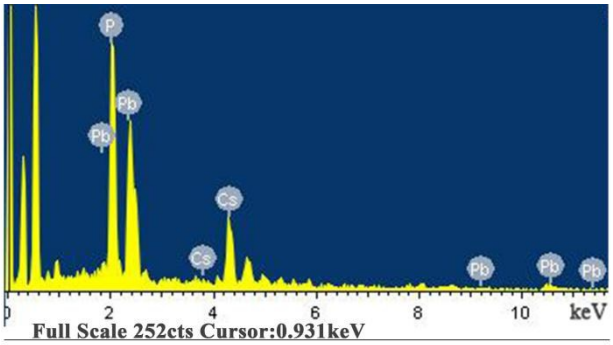
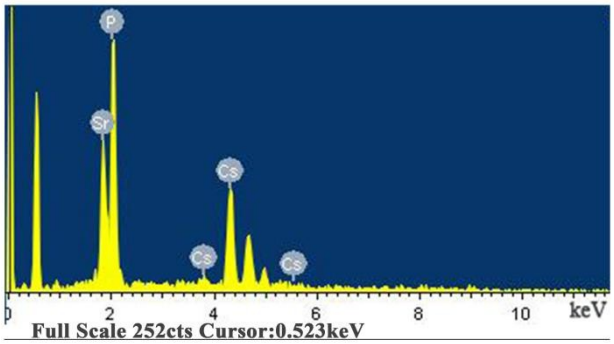


Figure S4. XRD patterns of $Li_3Cs_2Pb_2B_3P_6O_{24}$ (a) and $Li_3Cs_2Sr_2B_3P_6O_{24}$ (b) before melting and after melting.



(a)



(b)

Figure S5. EDX spectrum of $Li_3Cs_2Pb_2B_3P_6O_{24}$ (a) and $Li_3Cs_2Sr_2B_3P_6O_{24}$ (b).

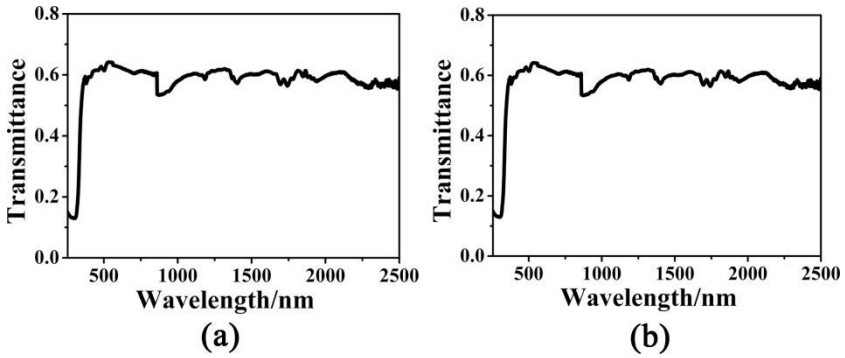


Figure S6. Transmittance of the polycrystalline samples of $Li_3Cs_2Pb_2B_3P_6O_{24}$ (a) and $Li_3Cs_2Sr_2B_3P_6O_{24}$ (b) in UV−Vis−NIR regions.

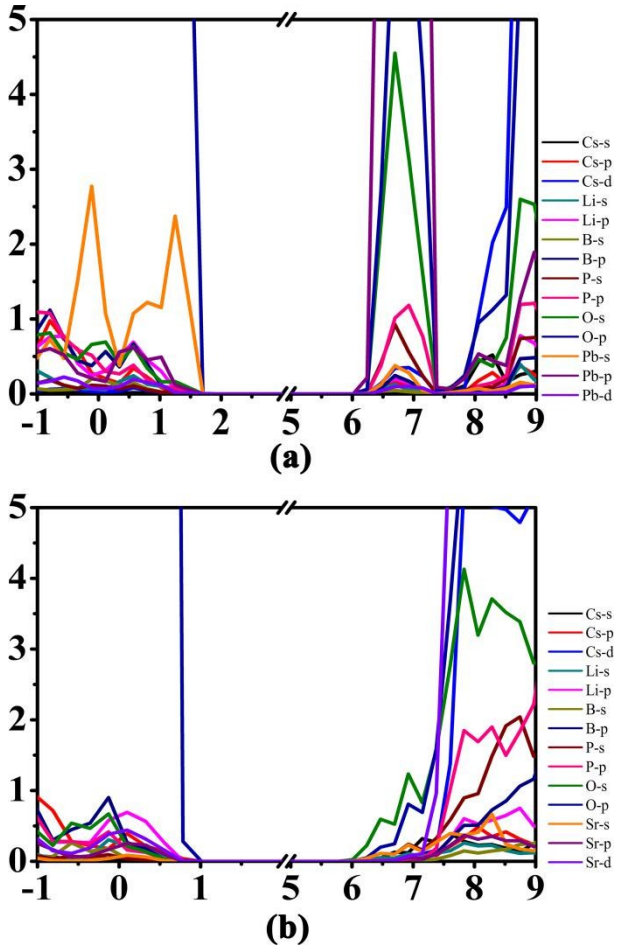


Figure S7. The region from -1 to 9 eV in density of states of $Li_3Cs_2Pb_2B_3P_6O_{24}$ (a) and $Li_3Cs_2Sr_2B_3P_6O_{24}$ (b).

Table S6a. EDX Results for $Li_3Cs_2Pb_2B_3P_6O_{24}$.

Point 1				**Point 2**			
Element	Weight %	Atomic %	Formula	Element	Weight %	Atomic %	Formula
P	24.47	63.67	6.8	P	20.80	59.84	5.8
Cs	32.02	19.41	2.1	Cs	25.36	17.00	1.7
Pb	43.51	16.92	1.8	Pb	53.84	23.16	2.3
Totals	100.00			Totals	100.00		
Point 3				**Point 4**			
Element	Weight %	Atomic %	Formula	Element	Weight %	Atomic %	Formula
P	22.29	61.29	6.2	P	20.15	58.98	5.6
Cs	29.43	18.86	1.9	Cs	24.87	16.96	1.6
Pb	48.28	19.84	2.0	Pb	54.98	24.06	2.3
Totals	100.00			Totals	100.00		
Point 5							
Element	Weight %	Atomic %	Formula				
P	20.35	58.94	5.7				
Cs	27.13	18.31	1.8				
Pb	52.52	22.74	2.2				
Totals	100.00						

Average ratio

$Cs_{1.8(8)}Pb_{2.1(8)}P_{6.0(20)}$

Table S6b. EDX Results for $Li_3Cs_2Sr_2B_3P_6O_{24}$.

Point 1				**Point 2**			
Element	Weight %	Atomic %	Formula	Element	Weight %	Atomic %	Formula
P	31.43	61.97	6.4	P	31.30	62.06	6.3
Cs	41.09	18.88	1.9	Cs	42.82	19.79	2.0
Sr	27.48	19.15	2.0	Sr	25.88	18.15	1.9
Totals	100.00			Totals	100.00		
Point 3				**Point 4**			
Element	Weight %	Atomic %	Formula	Element	Weight %	Atomic %	Formula
P	29.83	60.85	6.0	P	31.68	62.54	6.4
Cs	46.60	17.00	2.2	Cs	42.92	19.75	2.0
Sr	23.57	22.15	1.7	Sr	25.39	17.72	1.8
Totals	100.00			Totals	100.00		
Point 5							

Element	Weight %	Atomic %	Formula	Average ratio
P	32.20	63.07	6.5	$Cs_{2.0(4)}Sr_{1.8(4)}P_{6.3(7)}$
Cs	42.50	19.40	2.0	
Sr	25.31	17.53	1.8	
Totals	100.00			

Table S7. The conclusion of the refinement the valence bond sums (VBS) around the atoms are list.

$Li_3Cs_2Pb_2B_3P_6O_{24}$		VB	$Li_3Cs_2Sr_2B_3P_6O_{24}$		VB
Pb(1)-O(3)×3	2.437(3)	1.89	Sr(1)-O(3)×3	2.487(2)	2.05
Pb(1)-O(5)×3	2.680(3)		Sr(1)-O(5)×3	2.547(2)	
Pb(2)-O(8)×3	2.457(3)	1.85	Sr(2)-O(8)×3	2.556(2)	1.70
Pb(2)-O(2)×3	3.091(3)		Sr(2)-O(2)×3	2.865(2)	
Pb(2)-O(1)×3	2.809(3)		Sr(2)-O(1)×3	2.873(2)	
Li-O(3)	1.910(9)	1.19	Li-O(3)	1.903(6)	1.16
Li-O(8)	1.946(9)		Li-O(8)	1.922(6)	
Li-O(1)	1.902(9)		Li-O(1)	1.929(6)	
Li-O(5)	1.905(9)		Li-O(5)	1.945(6)	
B-O(7)	1.464(6)	3.11	B-O(7)	1.440(4)	3.09
B-O(6)	1.442(6)		B-O(6)	1.449(4)	
B-O(4)	1.472(6)		B-O(4)	1.474(4)	
B-O(2)	1.478(6)		B-O(2)	1.509(4)	
P(1)-O(1)	1.493(3)	5.09	P(1)-O(1)	1.495(2)	4.99
P(1)-O(5)	1.505(3)		P(1)-O(5)	1.508(2)	
P(1)-O(4)	1.561(3)		P(1)-O(4)	1.570(2)	
P(1)-O(2)	1.558(3)		P(1)-O(2)	1.574(2)	
P(2)-O(3)	1.510(3)	5.07	P(2)-O(3)	1.507(2)	5.02
P(2)-O(8)	1.510(3)		P(2)-O(8)	1.507(2)	
P(2)-O(7)	1.537(3)		P(2)-O(7)	1.551(2)	
P(2)-O(6)	1.564(3)		P(2)-O(6)	1.571(2)	