Supporting information

$A_2P_2S_6$ (A=Ba, Pb): A Good Platform to Study Polymorph Effect and Lone Pairs Effect to Form Acentric Structure

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13. **Figure S9.** Tauc plots for allowed direct and indirect transitions of $Pb_2P_2S_6$.

1. Table S1. Refined crystallographic parameters of **α-**$Ba_2P_2S_6$, β-$Ba_2P_2S_6$, and $Pb_2P_2S_6$.

Compound	**α-$Ba_2P_2S_6$**	**β-$Ba_2P_2S_6$**	**$Pb_2P_2S_6$**
Formula weight (g mol-1)	528.98	264.49	668.68
Crystal color	Pink/light orange	white	yellow orange
Temperature	298(2) K		
Radiation, wavelength	Mo-Kα, 0.71073 Å		
Crystal system	Monoclinic		
Space group	*Pn* (no.7)	*P2₁/n* (no. 14)	*Pn* (no.7)
a(Å)	6.7411(2)	6.7459(6)	6.5961(6)
b(Å)	7.5818(2)	7.5871(6)	7.4542(7)
c(Å)	9.9870(3)	9.9983(9)	9.3854(10)
β (°)	91.2005(12)	91.204(3)	91.515(6)
V (Å^3)	510.32(3)	511.62(8)	461.31(8)
Z	2	4	2
D_c (g cm-1)	3.443	3.434	4.814
μ (mm-1)	9.136	9.113	38.071
F(000)	476	476	580
R1, wR2 (I > 2σ(I))	0.0162, 0.0405	0.0276, 0.0881	0.0402, 0.0588
R1, wR2 (all data)	0.0212, 0.0906	0.0384, 0.0939	0.0772, 0.0764

$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, and $w = 1/[\sigma^2F_o^2 + (A \cdot P)^2 + B \cdot P]$, $P = (F_o^2 + 2F_c^2)/3$; *A* and *B* are weight coefficients.

2. Table S2. Atomic coordinate parameters for **α-**$Ba_2P_2S_6$, β-$Ba_2P_2S_6$, and $Pb_2P_2S_6$.

Atoms	Wyckoff	*x*	*y*	*z*	Occupancy	U_{eq} (Å^2)
			α-$Ba_2P_2S_6$			
Ba1	*2a*	0.26582(18)	0.3419(4)	0.97379(10)	1	0.0137(6)
Ba2	*2a*	0.68861(19)	-0.1578(4)	0.97524(13)	1	0.0144(8)
P1	*2a*	0.184(3)	0.863(2)	0.7846(16)	1	0.009(3)
P2	*2a*	-0.225(2)	0.366(2)	1.1624(16)	1	0.012(3)
S1	*2a*	-0.211(2)	0.2753(19)	0.9756(17)	1	0.014(3)
S2	*2a*	0.164(2)	0.777(2)	0.9776(17)	1	0.018(3)
S3	*2a*	0.053(2)	0.457(2)	0.6824(13)	1	0.015(3)
S4	*2a*	0.032(2)	0.452(2)	1.2462(14)	1	0.013(3)
S5	*2a*	0.403(2)	0.044(2)	0.7580(14)	1	0.016(3)

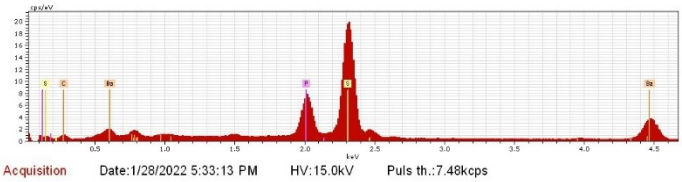
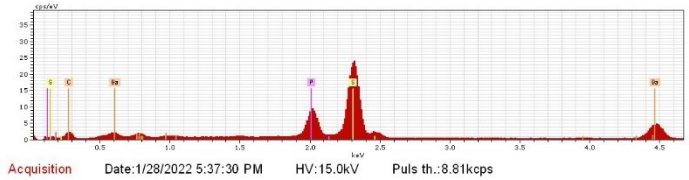
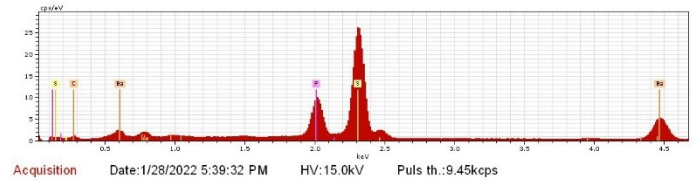
S6	*2a*	0.424(2)	0.0481(19)	1.2039(15)	1	0.014(3)
			β-$Ba_2P_2S_6$			
Ba1	*4e*	0.03858(5)	0.59197(5)	0.74938(3)	1	0.01486(15)
P1	*4e*	-0.0453(2)	0.11437(18)	0.56081(15)	1	0.0112(3)
S1	*4e*	0.1966(2)	0.2980(2)	0.97893(14)	1	0.0144(3)
S2	*4e*	0.1748(2)	0.29313(19)	0.53803(15)	1	0.0150(3)
S4	*4e*	-0.0620(2)	1.0265(2)	0.75068(14)	1	0.0169(3)
			$Pb_2P_2S_6$			
Pb1	*2a*	0.09293(10)	0.1326(4)	0.54137(9)	1	0.0221(7)
Pb2	*2a*	0.67133(10)	-0.3670(4)	0.54250(9)	1	0.0228(7)
P1	*2a*	0.1932(17)	-0.3610(17)	0.7258(12)	1	0.009(2)
P2	*2a*	0.0703(16)	-0.1416(18)	0.8575(14)	1	0.013(2)
S1	*2a*	-0.1875(17)	-0.0556(19)	0.7555(15)	1	0.017(3)
S2	*2a*	-0.469(2)	0.2435(18)	0.5533(15)	1	0.016(3)
S3	*2a*	0.232(2)	-0.2546(18)	0.5299(14)	1	0.016(3)
S4	*2a*	0.9513(16)	-0.5551(17)	0.3261(12)	1	0.011(2)
S5	*2a*	-0.0255(18)	0.4463(17)	0.7370(14)	1	0.015(2)
S6	*2a*	0.2851(17)	0.0521(17)	0.8488(15)	1	0.014(2)

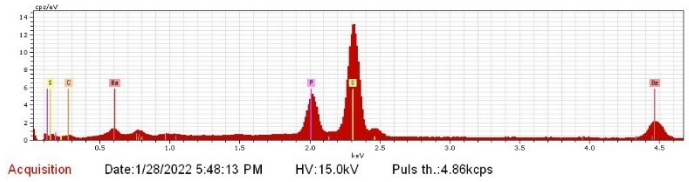
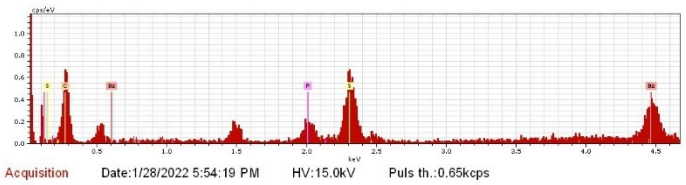
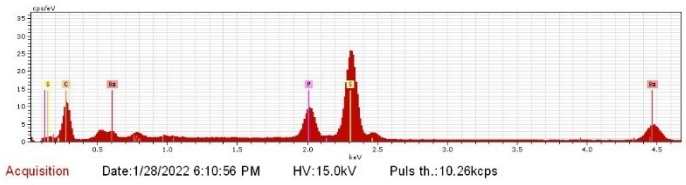
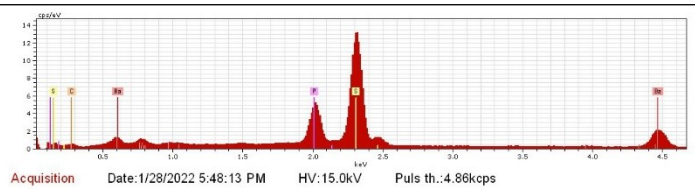
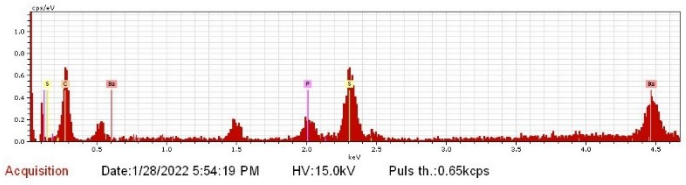
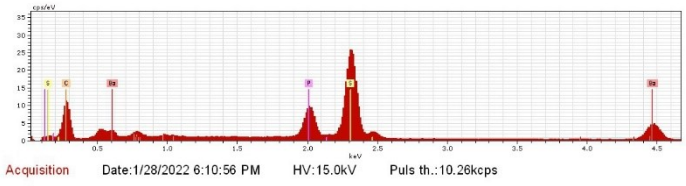
3. Table S3. Selected interatomic distances for **α-**$Ba_2P_2S_6$, β-$Ba_2P_2S_6$, and $Pb_2P_2S_6$.

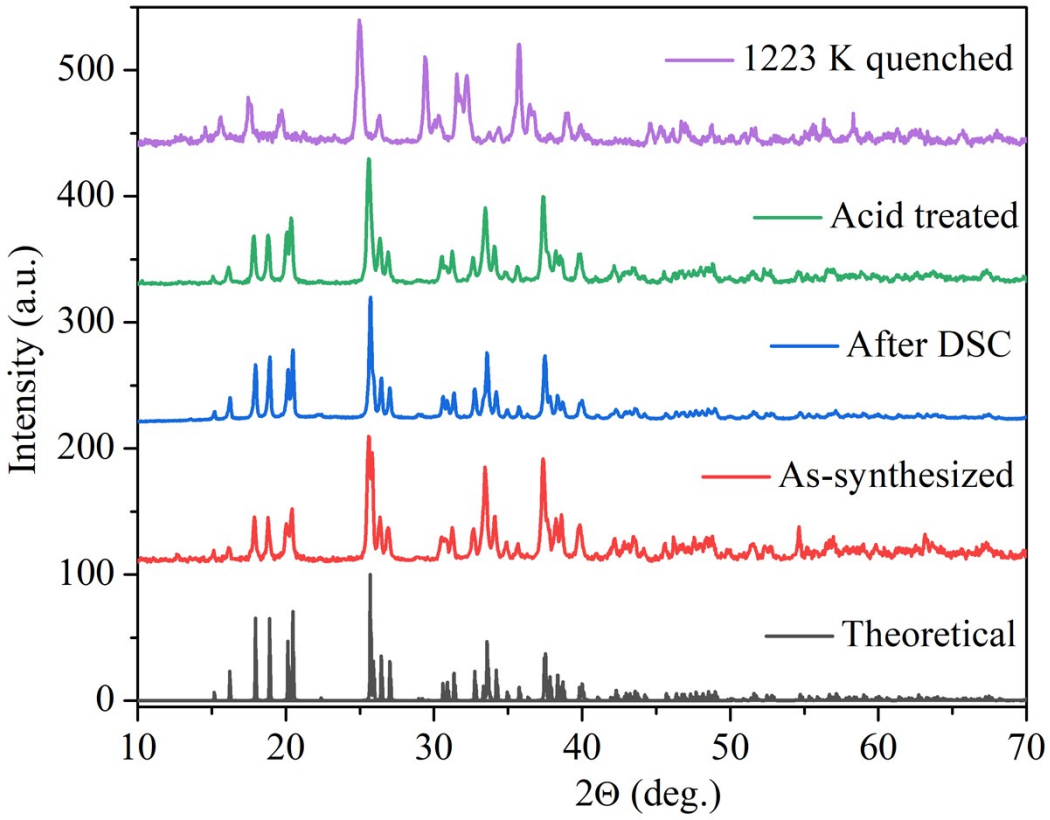
Atom Pairs		Distances (Å)	Atom Pairs		Distances (Å)
			α-$Ba_2P_2S_6$		
Ba1	S1	3.254(17)	Ba2	S1	3.353(15)
	S1	3.562(14)		S2	3.568(17)
	S2	3.373(16)		S2	3.244(17)
	S3	3.200(16)		S3	3.218(16)
	S3	3.334(15)		S4	3.360(14)
	S4	3.283(14)		S5	3.253(17)
	S4	3.313(15)		S5	3.261(16)
	S5	3.267(16)		S6	3.277(15)
	S6	3.359(15)		S6	3.316(15)
P1	S2	2.04(2)	P2	S1	1.99(2)
	S5	2.04(2)		S3	2.02(2)
	S6	2.03(2)		S4	2.02(3)
P1	P2	2.216(5)			
			β-$Ba_2P_2S_6$		
Ba1	S1	3.2825(15)	P1	S1	2.021(2)

	S1	3.3190(15)		S2	2.028(2)
	S1	3.3581(16)		S4	2.017(2)
	S2	3.2268(15)	P1	P1	2.213(3)
	S2	3.2453(16)			
	S2	3.3040(15)			
	S4	3.2530(16)			
	S4	3.3662(18)			
	S4	3.5658(16)			
		$Pb_2P_2S_6$			
Pb1	S1	3.102(14)	Pb2	S1	3.192(12)
	S1	3.142(13)		S2	3.050(13)
	S2	3.004(13)		S3	3.014(13)
	S3	3.032(14)		S4	3.114(12)
	S4	3.214(13)		S4	3.120(12)
	S5	3.086(14)		S5	3.013(12)
	S6	3.015(12)		S5	3.165(12)
	S6	3.184(13)		S6	3.068(13)
P1	S3	2.025(18)	P2	S1	2.033(16)
	S4	2.023(15)		S2	2.011(19)
	S5	2.040(18)		S6	2.026(17)
P1	P2	2.216(6)			

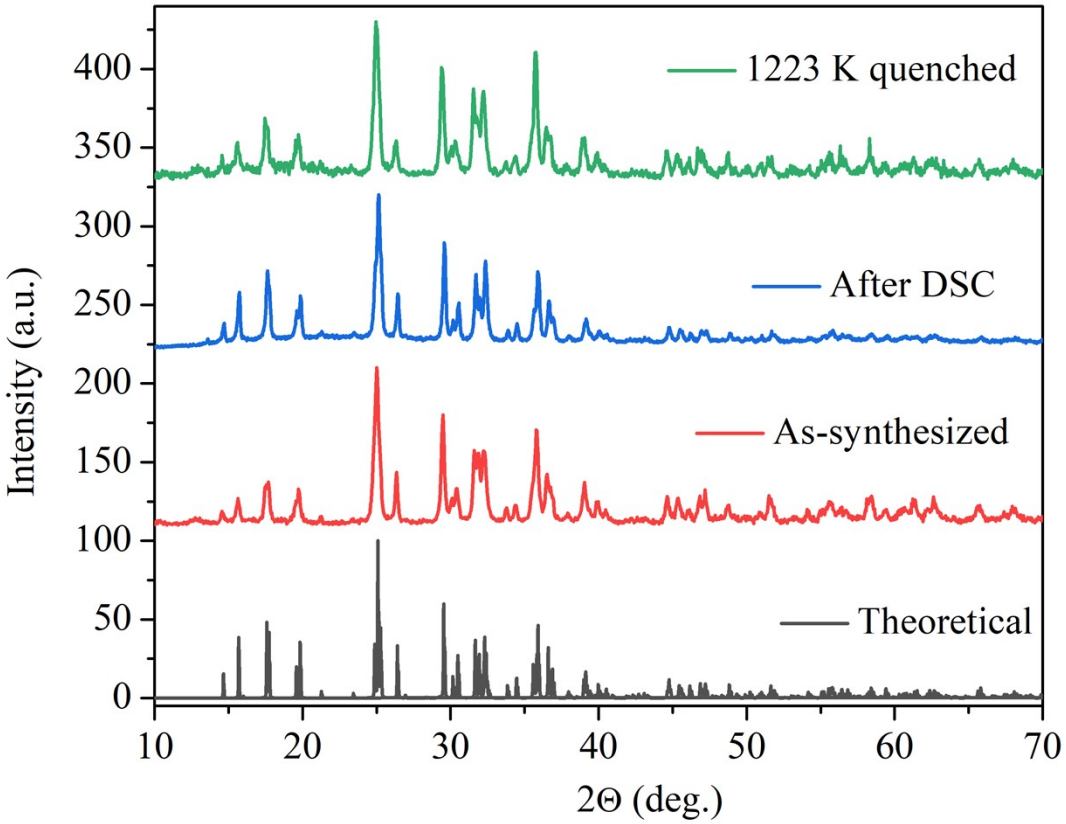
4. Table S4. Results of EDX analysis of selected crystals of **α**-$Ba_2P_2S_6$, β-$Ba_2P_2S_6$, and $Pb_2P_2S_6$.

Spectrum	Measured results	Normalized Composition
α-Ba_2P_2S		
	(Atomic.%) C 47.40 Ba 10.90 P 10.12 S 31.58	$Ba_{2.15}P_2S_{6.24}$
	(Atomic.%) C 59.91 Ba 8.13 P 7.68 S 24.27	$Ba_{2.11}P_2S_{6.32}$
	(Atomic.%) C 42.16 Ba 12.38 P 10.89 S 34.56	$Ba_{2.27}P_2S_{6.34}$

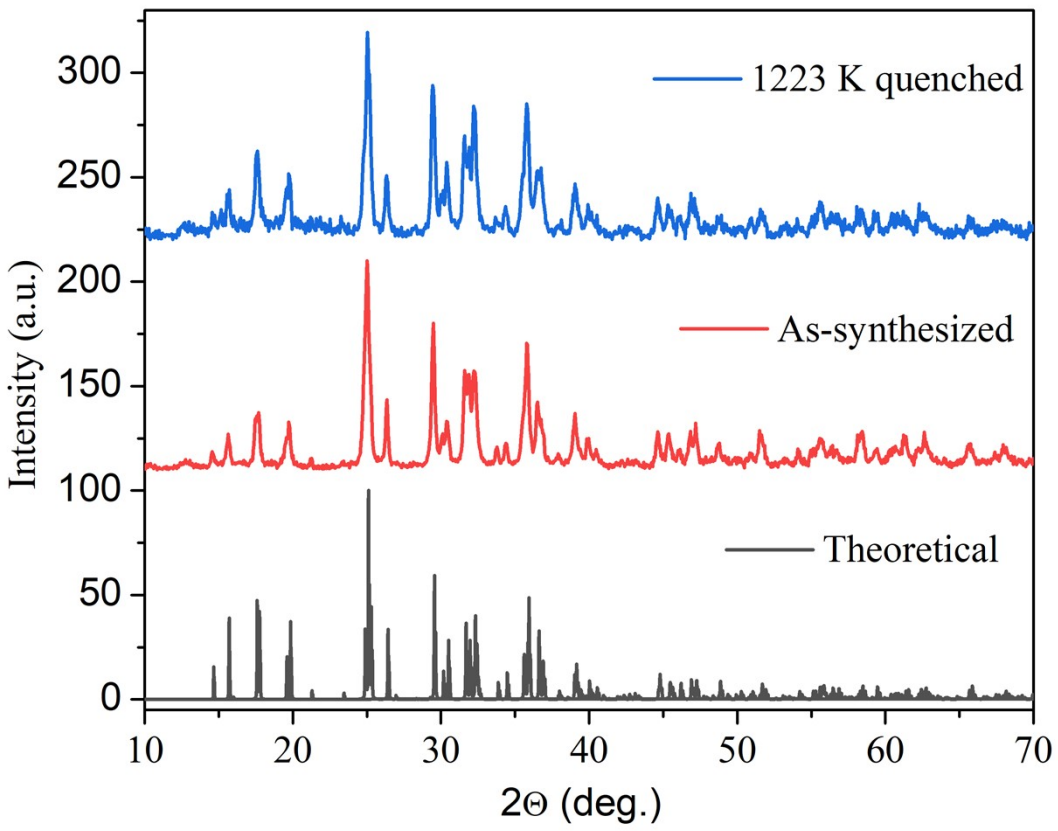
	Averaged	**$Ba_{2.18}P_2S_{6.30}$**
β-$Ba_2P_2S_6$		
	(Atomic.%) C 45.23 Ba 9.18 P 11.70 S 33.90	$Ba_{1.57}P_2S_{5.79}$
	(Atomic.%) C 76.40 Ba 4.27 P 4.17 S 15.16	$Ba_{2.05}P_2S_{7.27}$
	(Atomic.%) C 82.49 Ba 3.21 P 3.56 S 10.75	$Ba_{1.80}P_2S_{6.04}$
	Averaged	**$Ba_{1.81}P_2S_{6.37}$**
$Pb_2P_2S_6$		
	(Atomic.%) C 33.47 Pb 17.03 P 14.31 S 35.19 I 0.0	$Pb_{2.38}P_2S_{4.91}$
	(Atomic.%) C 35.82 Pb 16.52 P 13.91 S 33.62 I 0.13	$Pb_{2.37}P_2S_{4.83}$
	(Atomic.%) C 32.86 Pb 17.32 P 14.21 S 35.38 I 0.23	$Pb_{2.43}P_2S_{5.00}$
	Averaged	**$Pb_{2.39}P_2S_{4.91}$**
Notes: the large deviation of S is due to the overlap between Pb and S		



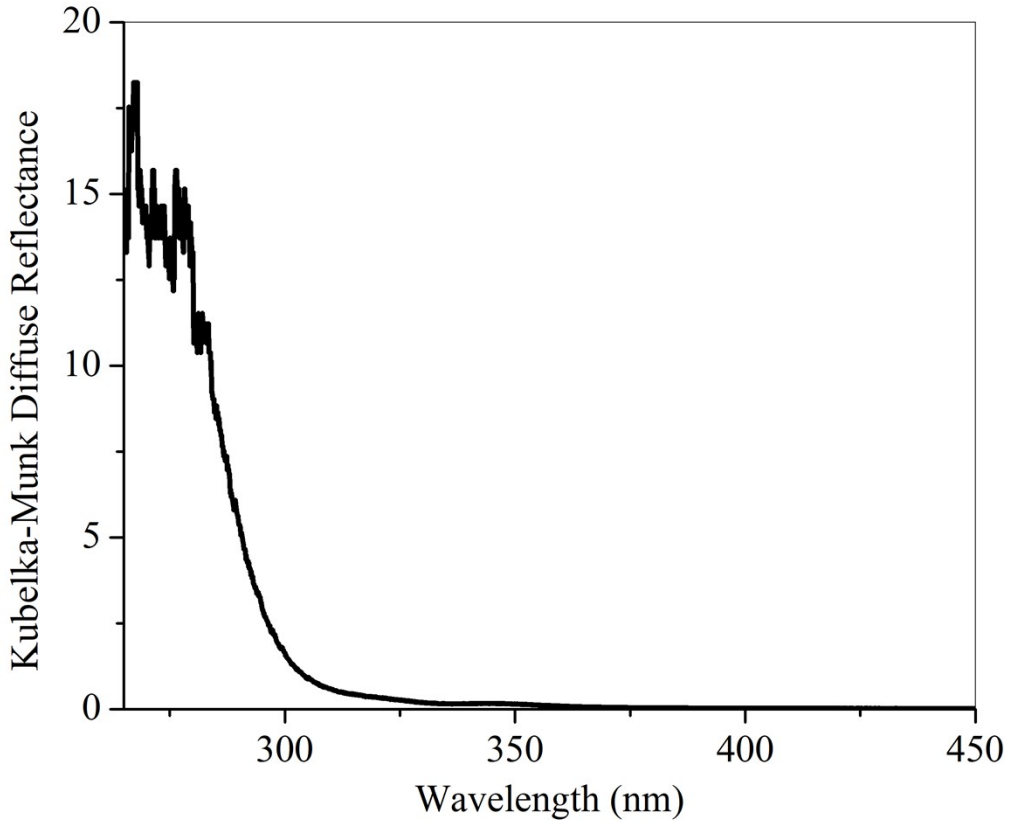
5. Figure S1. Powder X-ray diffraction results of theoretical, as-synthesized (stored in air for around 240 days), after DSC measurement, acid treated, and 1223 K quenched $Pb_2P_2S_6$.



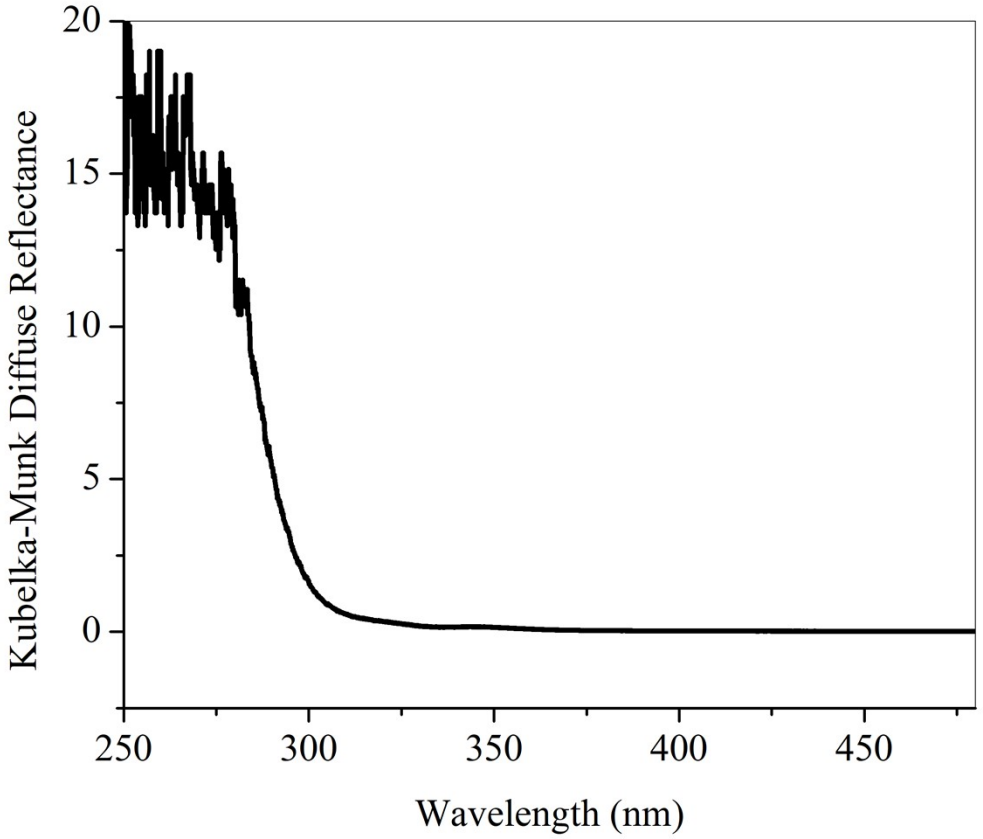
6. Figure S2. Powder X-ray diffraction results of theoretical, as-synthesized, after DSC measurement, and 1223 K quenched α-$Ba_2P_2S_6$.



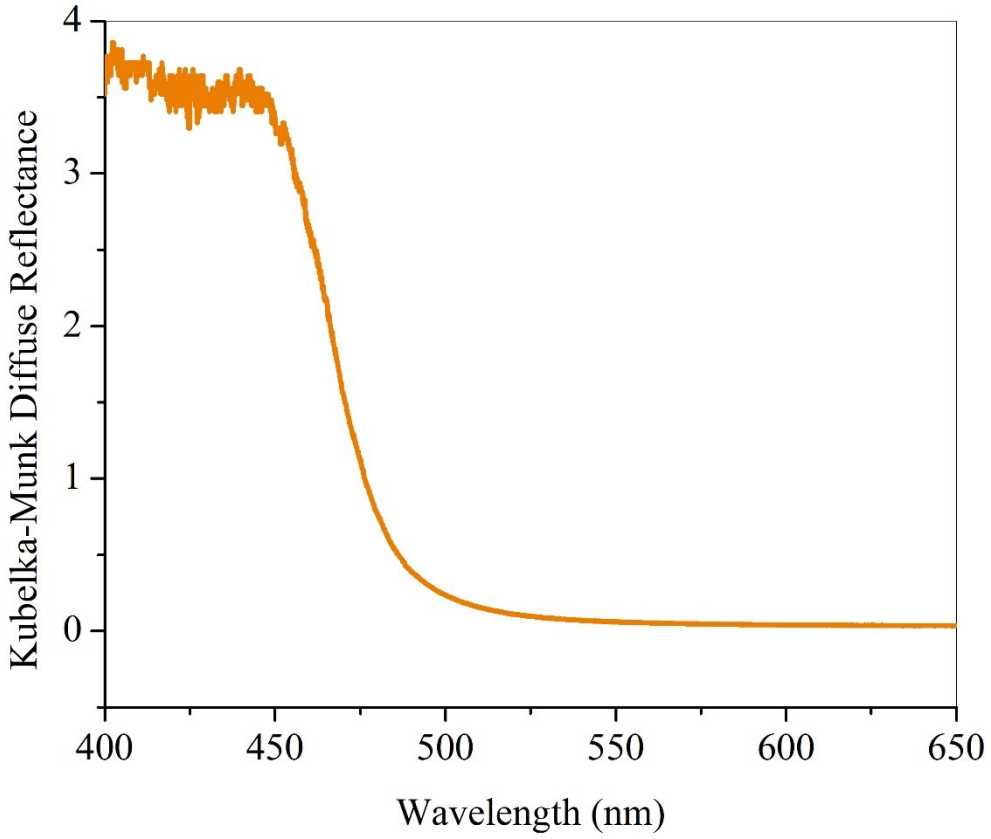
7. Figure S3. Powder X-ray diffraction results of theoretical, as-synthesized, and 1223 K quenched β-$Ba_2P_2S_6$.



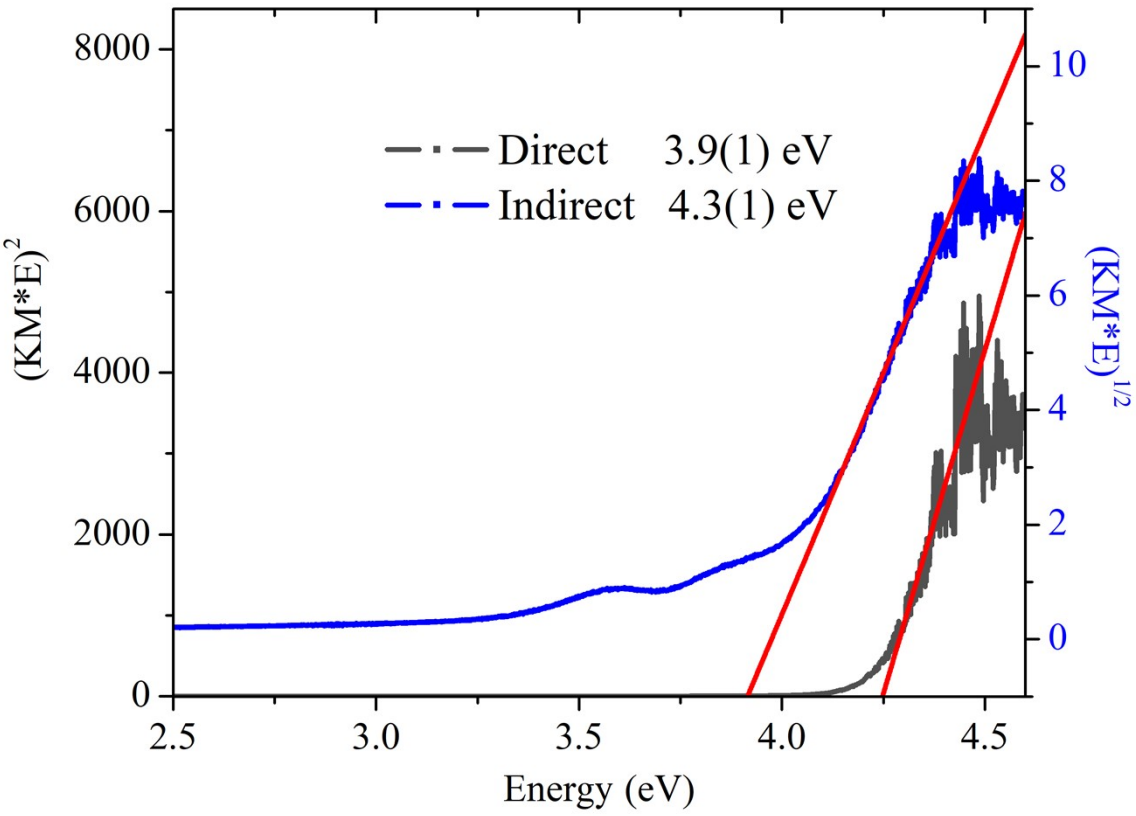
8. Figure S4. Kubelka-Munk Diffuse reflectance solid-state UV–Vis spectra of α-$Ba_2P_2S_6$.



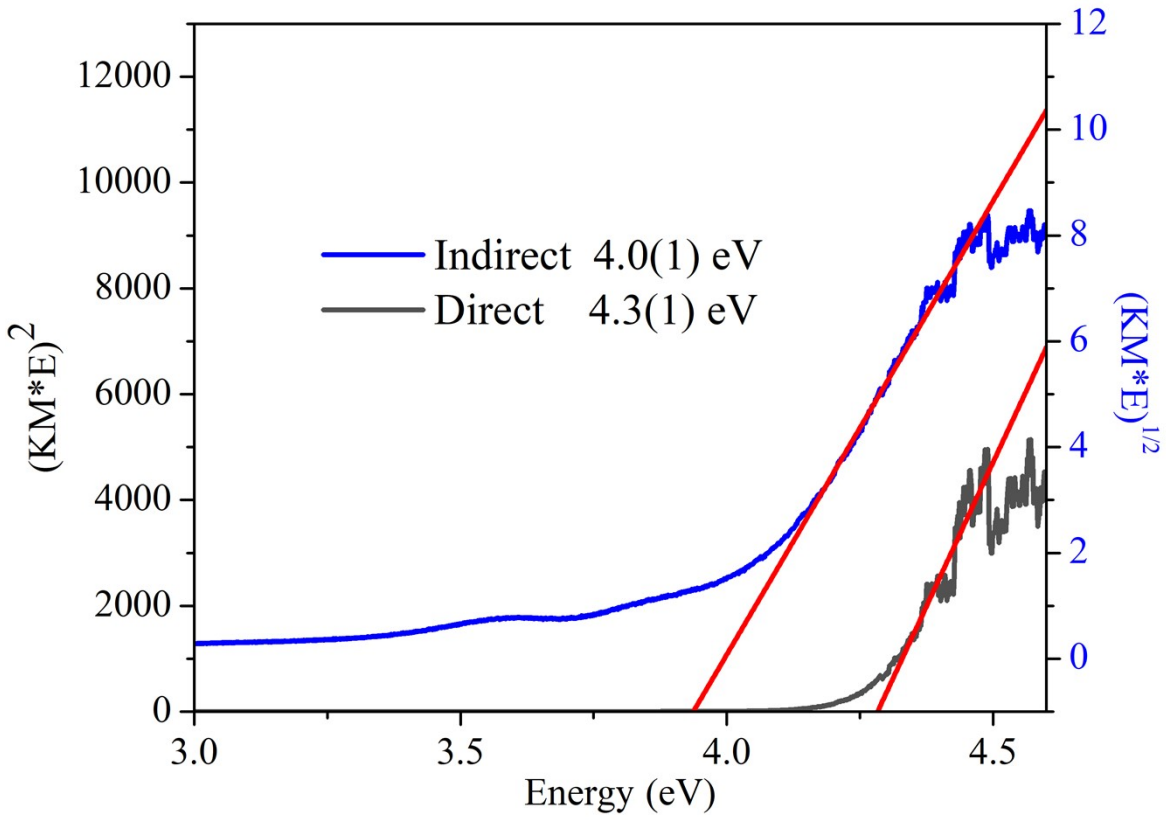
9. Figure S5. Kubelka-Munk Diffuse reflectance solid-state UV–Vis spectra of β-$Ba_2P_2S_6$.



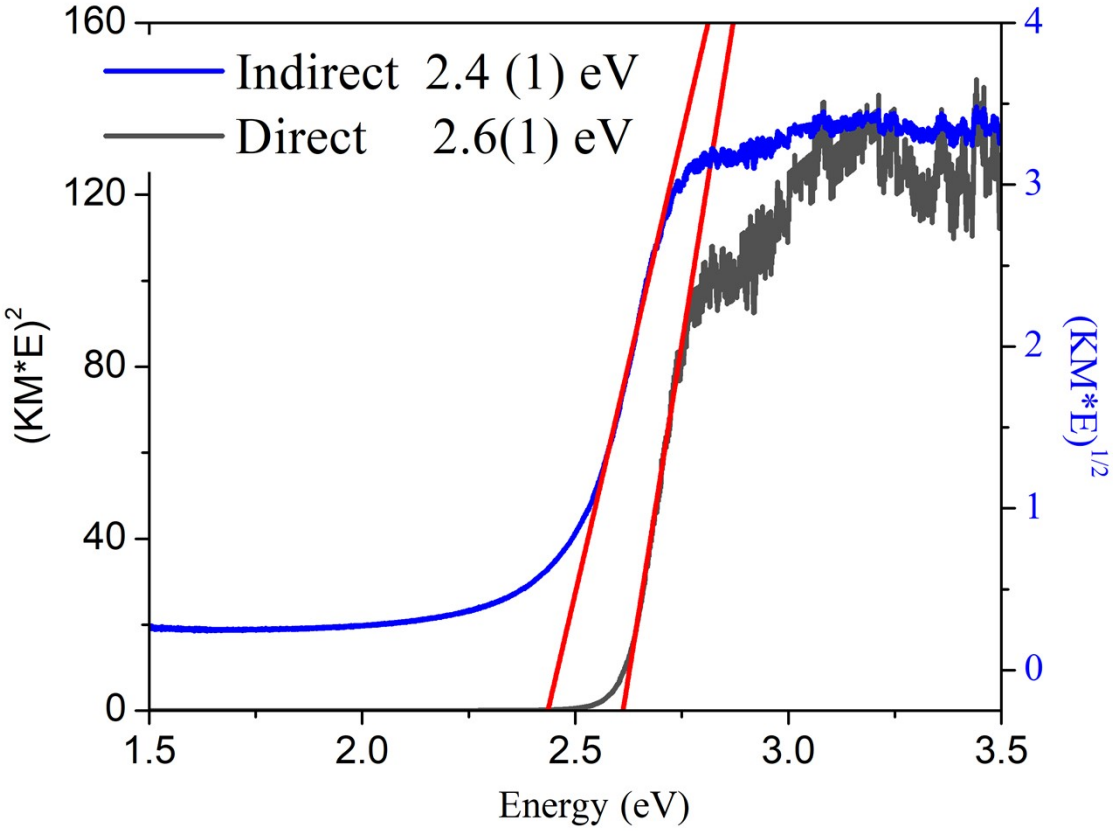
10. Figure S6. Kubelka-Munk Diffuse reflectance solid-state UV–Vis spectra of $Pb_2P_2S_6$.



11. Figure S7. Tauc plots for allowed direct and indirect transitions of α-$Ba_2P_2S_6$.



12. Figure S8. Tauc plots for allowed direct and indirect transitions of β-$Ba_2P_2S_6$.



13. Figure S9. Tauc plots for allowed direct and indirect transitions of $Pb_2P_2S_6$.