Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Revisiting Thiophosphate $Pb_3P_2S_8$: A Multifunctional Material Combining a Nonlinear Optical Response and Photocurrent Response

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Supporting information

Single Crystal X-ray Diffraction: Data collections were performed at room temperature for $Pb_3P_2S_8$ using a Bruker Kappa APEX II diffractometer with graphite monochromated Mo-*K*α radiation (λ = 0.71073 Å). Data reduction and integration, together with global unit cell refinements, were performed in the APEX2 software.[1] Multi-scan absorption corrections were applied.[1] The structures were solved by direct methods and refined by full matrix least-squares methods on F^2 using the SHELX package with anisotropic displacement parameters for all atoms.[2] In the last refinement cycles, the atomic positions for the three compounds were standardized using the program Structure TIDY.[2-3]

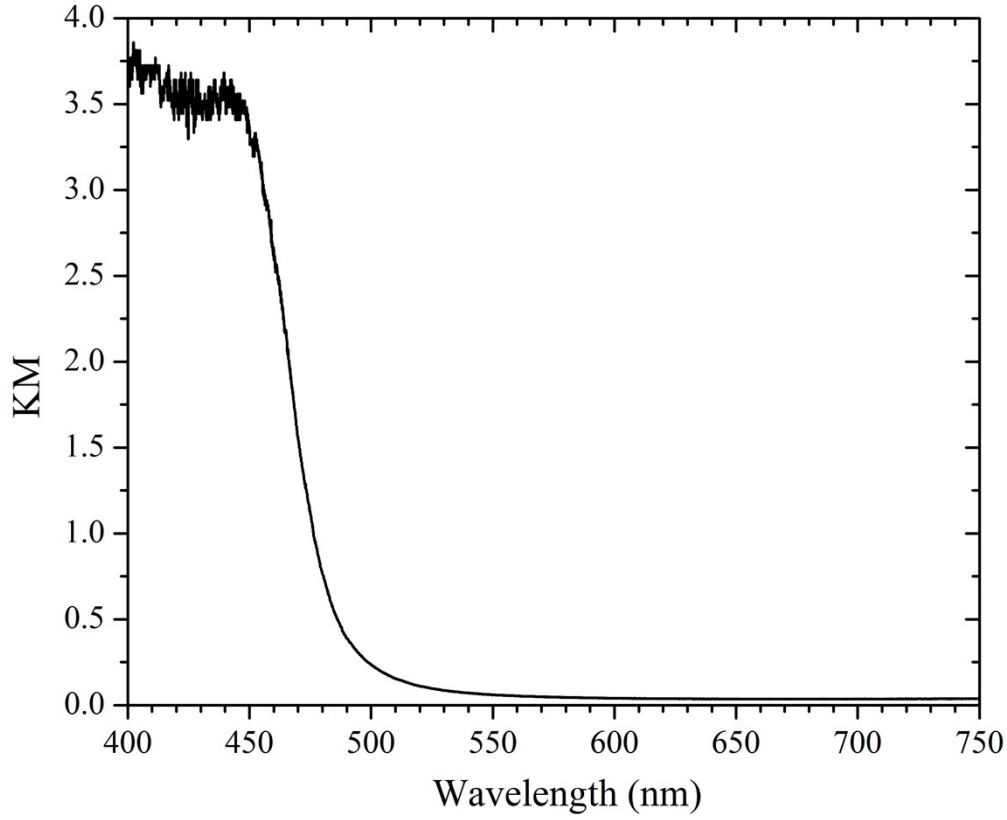

Figure S1. Kubelka-Munk Diffuse reflectance solid-state UV-Vis spectra of $Pb_3P_2S_8$.

Table S1. Selected crystal data and structure refinement parameters for $Pb_3P_2S_8$ at 300 K

Empirical formula		$Pb_3P_2S_8$	
Formula weight	939.99 g/mol	Unit cell volume	1304.1(4)Å^3
Temperature	300(2) K	*Z*	4
Radiation, wavelength	Mo-Kα, 0.71073 Å	Density (*calc.*)	4.788 g/cm^3
Crystal system	Cubic	Absorption coefficient	40.133 mm^{-1}
Space group	*P2$_1$3*(No.198)		
Unit cell dimensions	*a* =10.9253(10) Å	Final R indices [a] [I>2σ$_{(I)}$]	R_1 = 0.0451 wR_2 = 0.1066
		Final R indices [a] [all data]	R_1 = 0.0891 wR_2 = 0.1841
		G.O.F	1.116

$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, 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

Table S2. The measured LDT of $Pb_3P_2S_8$ compared with AGS.

Compounds	Damage energy (mJ)	Spot diameter (mm)	LDT (MV/cm^2)	LDT (×AGS)
$AgGaS_2$	0.58	0.5	29.6	1
$Pb_3P_2S_8$	1.42	0.5	77.2	2.6

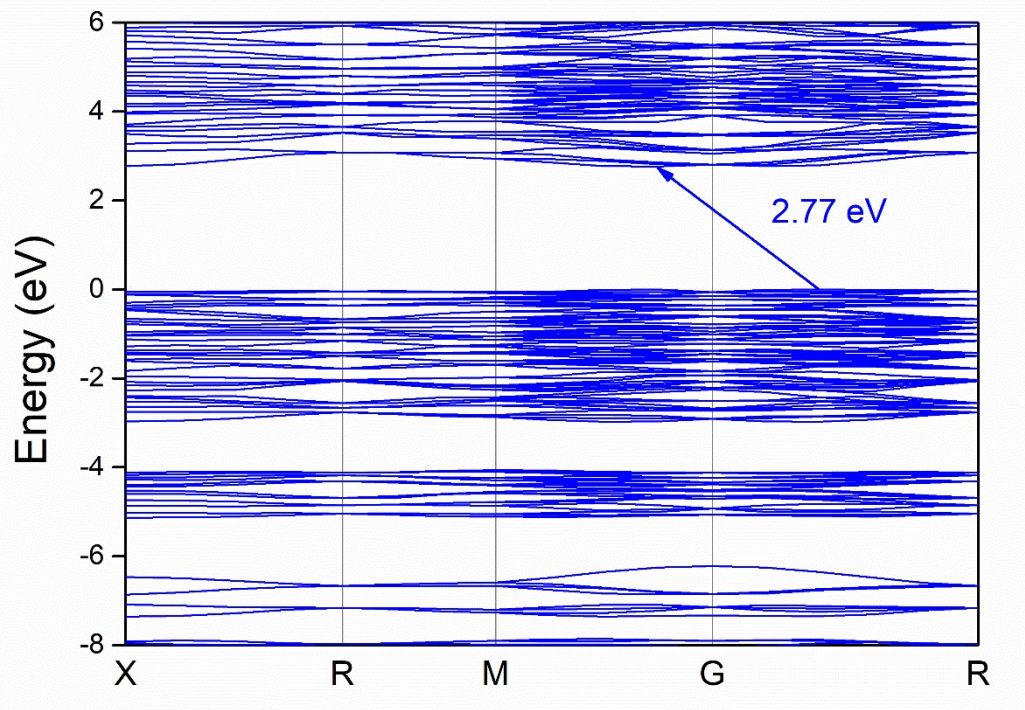

Figure S2. Calculated HSE bandgap of $Pb_3P_2S_8$.

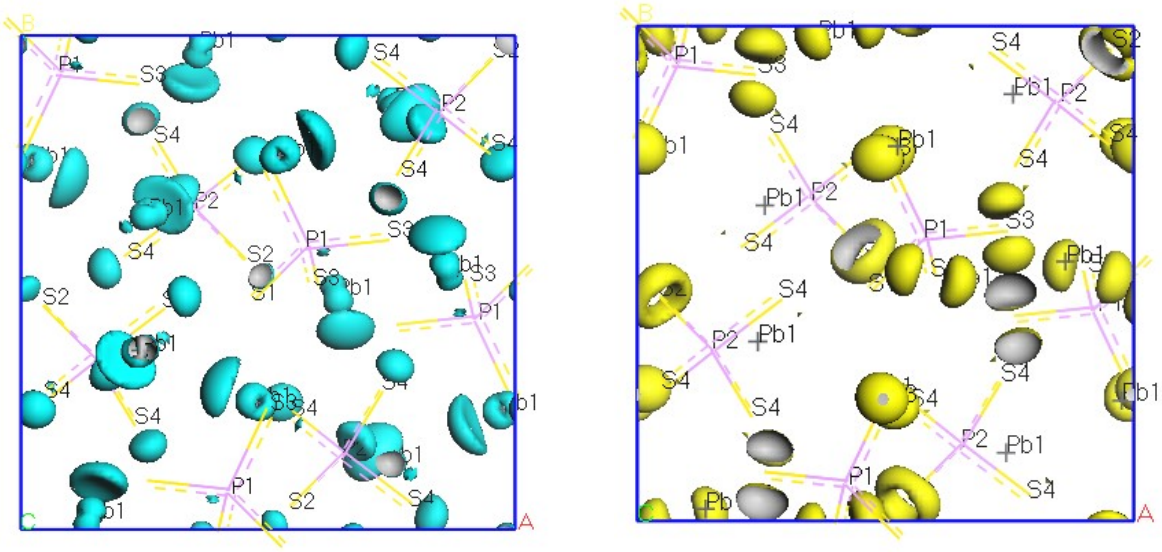

Figure S3. Calculated charge density of the bottom of conduction band (left) and the top of the valance band (right).

References

1. Bruker APEX2; Bruker AXS Inc.: Madison, WI, 2005.
2. G. M. Sheldrick, A short history of *SHELX*, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.
3. E. Parthé and L. M. Gelato, The standardization of inorganic crystal-structure data, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1984, **40**, 169–183.