

## **Supporting Information**

### **Slow Excitonic Carrier Cooling in Sr-doped PbS Nanocrystals for Hot Carrier Devices: Integrated Experimental and First-principles Approach**

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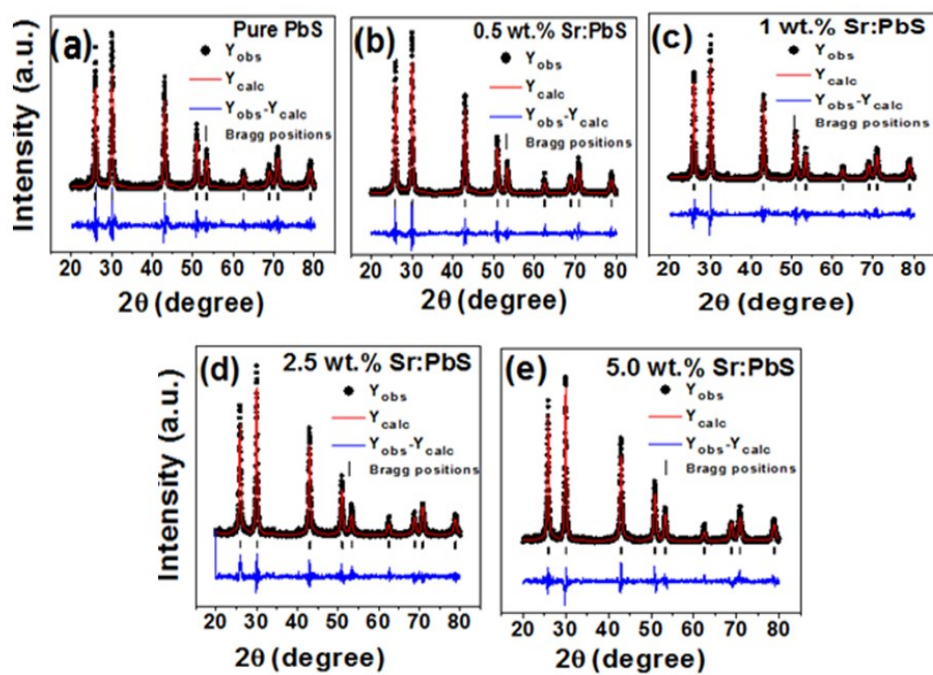


Fig. S1: Rietveld refined XRD data for all samples.

Table S1: Estimated values of crystallite size (D), lattice constants and unit cell volume.

Samples	D (nm)	$a = b = c$ (Å)	V (Å <sup>3</sup> )
Pure PbS	18.82	5.9357	209.1318
0.5 wt.% Sr:PbS	20.42	5.9445	210.0589
1.0 wt.% Sr:PbS	20.35	5.9355	209.1131
2.5 wt.% Sr:PbS	20.47	5.9460	210.2256
5.0 wt.% Sr:PbS	20.44	5.9445	210.0568

Table S2: Rietveld refined parameters for pure and Sr:PbS.

Parameters	PbS Samples with different wt.% of Sr				
	Pure	0.5 wt.%	1.0 wt.%	2.5 wt.%	5.0 wt.%
Chi <sup>2</sup>	1.45	1.59	1.39	1.44	1.47
R <sub>p</sub>	37.8	29.1	25.1	25.2	24.2
R <sub>wp</sub>	39.6	32.9	32.6	31.3	31.0
R <sub>e</sub>	32.9	26.1	27.7	26.1	25.6
R <sub>Brag</sub>	14.1	30.8	8.89	8.74	7.78
R <sub>F</sub>	9.42	26.3	5.52	6.51	6.74

Table S3: Dislocation density ( $\delta$ ), strain ( $\epsilon$ ), x-ray density ( $\rho_{x\text{-ray}}$ ) and specific surface area for pure PbS and Sr:PbS samples.

Samples	$\delta_{\text{ave}} \times 10^{-3} \text{ (nm}^{-2}\text{)}$	$\epsilon_{\text{ave}} \times 10^{-3}$	$\rho_{x\text{-ray}} \text{ (g/cm}^3\text{)}$	S (m <sup>2</sup> /g)
Pure PbS	2.82	6.81	7.60	41.95
0.5 wt.% Sr:PbS	2.41	6.22	7.57	38.82
1.0 wt.% Sr:PbS	2.44	6.30	7.60	38.79
2.5 wt.% Sr:PbS	2.40	6.26	7.56	38.77
5.0 wt.% Sr:PbS	2.41	6.24	7.57	38.78

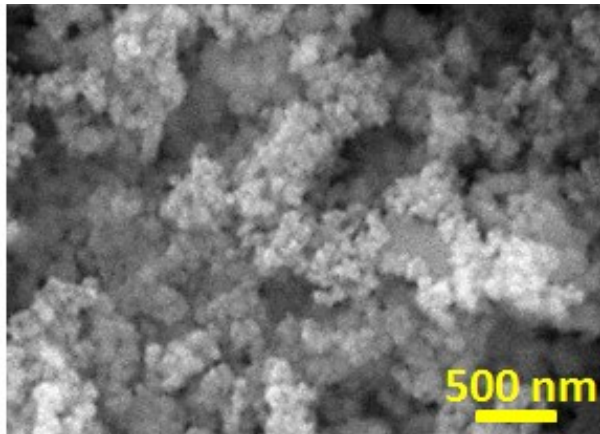


Fig. S2: SEM image of 2.5 wt. Sr:PbS.

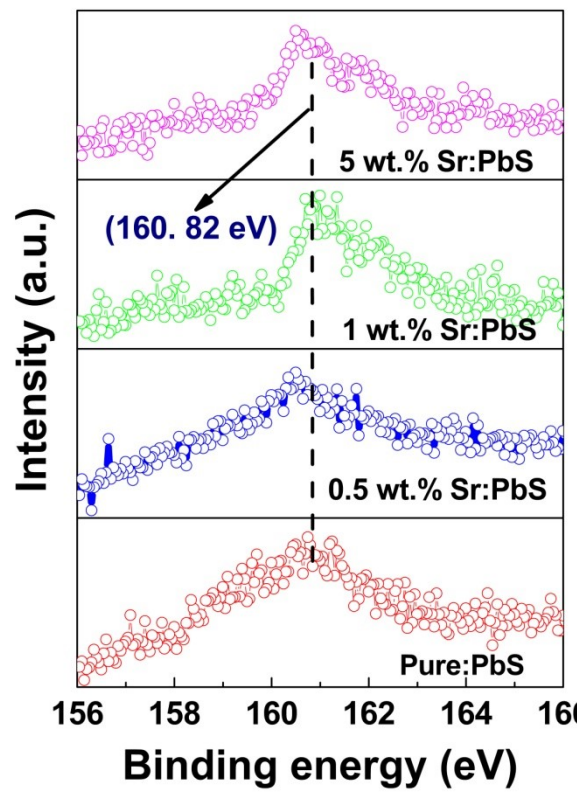


Fig: S3: Binding energy spectra of S  $P_{3/2}$  state in pure PbS, 0.5, 1, and 5 wt.% Sr:PbS nanocrystals, respectively.

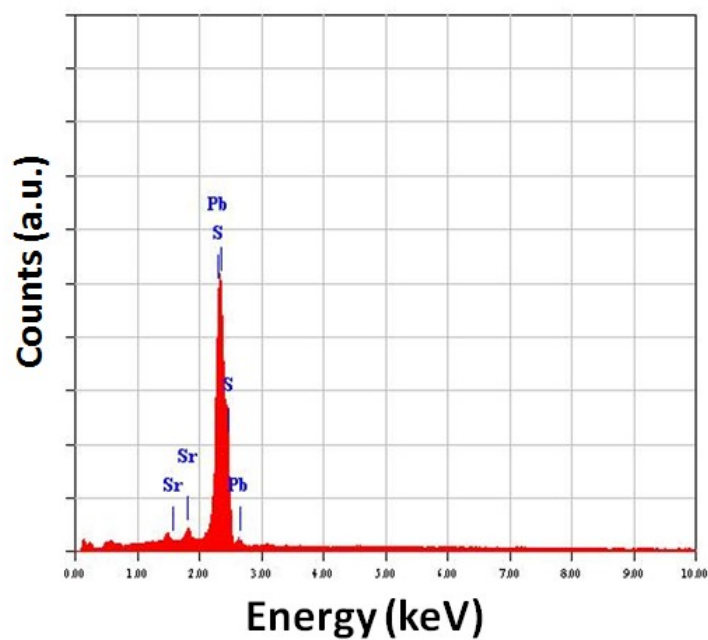


Fig. S4: Energy dispersive X-ray analysis spectra of 0.5 wt.% Sr:PbS.

Table S4: Elemental composition percentage of different atoms in 0.5 wt.% Sr:PbS.

Elements	Spot one				Spot two		
	Energy (keV)	Error (%)	Mass %	At. %	Error (%)	Mass %	At. %
Pb	2.342	0.74	73.00	30.65	1.13	70.81	28.37
S	2.307	0.16	24.73	67.10	0.25	26.80	69.37
Sr	1.806	0.54	2.27	2.25	0.83	2.39	2.26
Total			100	100		100	100

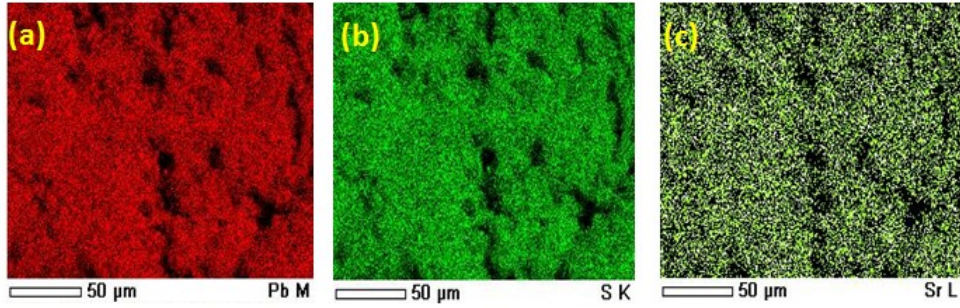


Fig. S5: EDS elemental mapping of 0.5 wt.% Sr:PbS.

### Energy levels of conduction and valence band:

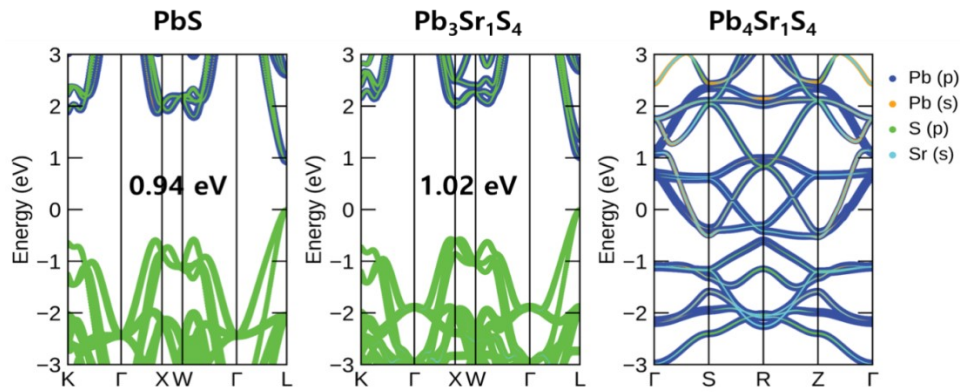


Fig. S6: Energy levels of conduction and valence band calculated by HSE functional approach.

To understand the influence of Sr dopants on the electronic properties of PbS, the electronic band structures were calculated using HSE06 functional (Fig. S6). It can be noticed that the conduction band minimum (CBM) and valence band maximum (VBM) in the pristine PbS are mainly governed by *p*-orbital of Pb and S, respectively. Interestingly, Sr dopant in substitutional site did not have much influence on both CBM and VBM except a small increase in electronic energy band gap (from 0.94 to 1.02 eV). The substituted Sr atom provides excess charge to the nearby S atoms, which rather weakens the interaction between Pb and S. On the other hand, the interstitial Sr hybridizes the orbitals, especially between *p*-orbital of Pb and *s*-orbital itself, and alters the structure to be metallic. This drastic change is mainly because of the highly theoretical doping concentration, which inevitably causes strong

overlap between the orbitals. Yet, the results show that the experimental observations on the band gap fluctuations and differences in the optical properties depending on the doping concentration, which are closely related to the location of Sr atoms.