Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplement Information

1. Energy band structures of BP calculated using different exchange and/or correlation functionals

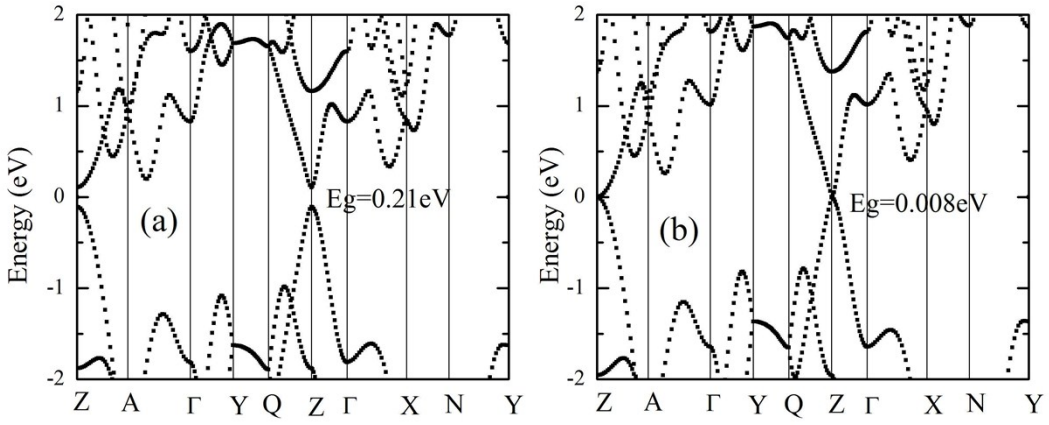

Figure S1 Energy band structures of BP calculated using different exchange and/or correlation functionals: (a) DFT-D2 and mBJ, (b) optB86b-vdW and mBJ. The corresponding band gaps are indicated.

2. The carrier relaxation time of BP

The relaxation time τ can be derived from the experimentally measured carrier mobility (μ) and effective mass (m^*) in the temperature range of 50 ~ 200 K [1, 2]. The obtained τ can be generalized to higher temperatures by using an exponential fitting [3]. Table S1 lists all the fitted relaxation time of BP.

Table S1 The fitted relaxation time of BP along three directions at different temperature.

carrier type	direction	300K (10^{-13}s)	400K (10^{-13}s)	500K (10^{-13}s)	600K (10^{-13}s)	700K (10^{-13}s)	800K (10^{-13}s)
p-type	*x*	5.83	5.78	5.78	5.78	5.78	5.78
	y	0.90	0.89	0.89	0.89	0.89	0.89
	z	1.57	1.55	1.55	1.55	1.55	1.55

n-type	*x*	2.38	2.35	2.35	2.35	2.35	2.35
	y	0.27	0.27	0.27	0.27	0.27	0.27
	z	1.14	1.13	1.13	1.13	1.13	1.13

3. The Lorenz number of BP as a function of carrier concentration

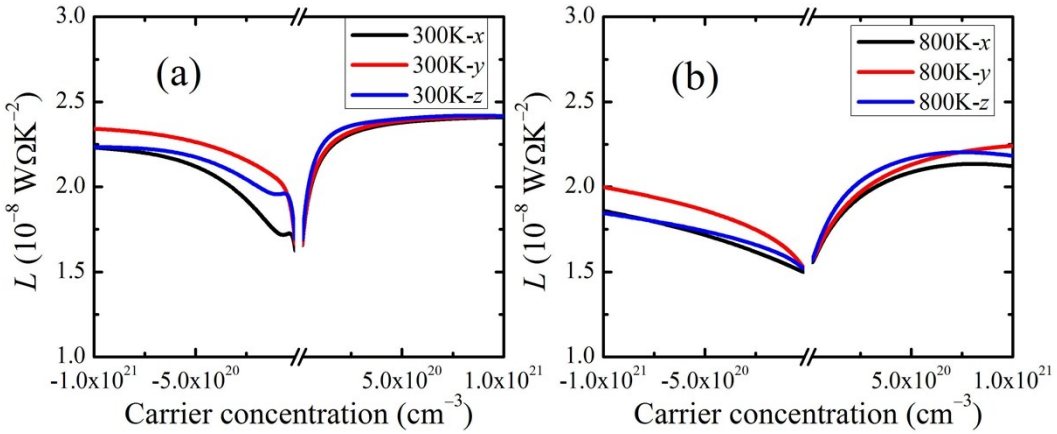

Figure S2 The calculated Lorenz number of BP as a function of carrier concentration at (a) 300 K and (b) 800 K. Negative and positive carrier concentrations represent *n*- and *p*- type carriers, respectively.

4. The phonon dispersion relations of Sb-substituted BP

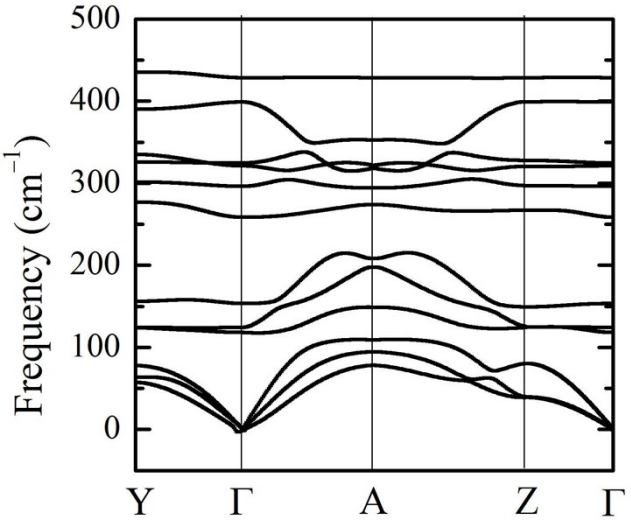

Figure S3 The phonon dispersion relations of $P_{0.75}Sb_{0.25}$.

Reference

[1] Y. Akahama, S. Endo, and S. Narita, J. Phys. Soc. Jpn. **52**, 2148 (1983).

[2] A. Morita, Appl. Phys. A **39**, 227 (1986).

[3] J. Zhang, H. J. Liu, L. Cheng, J. Wei, J. Shi, X. F. Tang, and C. Uher, J. Appl. Phys. **116**, 023706 (2014).