Supporting Information

for

Dual role of lone pair electron and rattling vibration in Zintl phase BaCaPb thermoelectric material

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Section I. Calculation principle of relative regular residual

The standard Taylor series expansion of the function *f*(x) can be expressed in the following equation:

$$f(x)=f(0)+\frac{1}{1!}f'(0)x+\frac{1}{2!}f'(0)x^2+\frac{1}{3!}f'''(0)x^3+\frac{1}{4!}f^4(0)x^4+\cdots \qquad \text{(S1)}$$

where x is a small perturbation near 0. Considering the actual physical problems, the polynomial function $F(x)$ is defined as：

$$F(x)=ax^2-bx^3+cx^4+O(x^5) \qquad \text{(S2)}$$

where a , b and c are the coefficients of the second, third and fourth order terms, respectively. $O(x^5)$ is the sum of the higher order terms, which are typically negligible in Hamiltonian quantities. Under actual physical conditions, the potential well curves typically exhibit a "U" shape in response to small atomic displacements. Second-degree polynomials are fitted by least squares, and the regular normalized residual r_i are calculated using the difference between the observed value $F(x)_i$ and the predicted value $F(x)$:

$$r_i=F(x)_i-F(x) \qquad \text{(S3)}$$

r_i describes the anharmonicity of the potential well curve, and the shape and height of the plotted conventional residual curve can be used to estimate the degree of anharmonicity. When the conventional residual curve resembles a "Z"-like shape, the coefficient of the fourth-order term can be neglected relative to the third-order term. The absolute value of the coefficient for the second-order term does not affect the shape of the residual curve. As the atomic displacement increases, the curve diverges in opposite directions at the left and right ends. Since no criterion exists to judge the necessity of considering the fourth-order coefficient by comparing the magnitudes of the values, the anharmonicity of Zintl phase BaCaPb compound is evaluated based on the shape of the residual curve.

When the conventional residual curve assumes a "W"-like shape, the coefficient of the fourth-order term becomes significant relative to the third-order term, indicating the necessity of computing the 4^{ph} scattering in the BaCaPb compound. During this process, as the atomic displacement increases, the residual curve shows simultaneous divergence in both directions.

To ascertain the magnitude of the atomic displacement threshold, the equilibrium ab initio molecular dynamics (EAIMD) simulations of BaCaPb compound are conducted for 10 ps within the NVT ensemble at 300 K. During this period, the vibrations of each atom are recorded and averaged to determine the effective amplitude of the atomic vibrations. This average value was then employed as the maximum displacement to analyze the residuals.

It important to note that the differences in the shapes of "Z" or "Z" -like and "M" or "W"-like curves merely represents the positive and negative signs of the polynomial coefficients, respectively, and does not influence the magnitude of the anharmonicity of Zintl phase BaCaPb compound.

Section II. Calculation principle of two-channel model

Lattice thermal conductivity of the within the Boltzmann transport equation (BTE) algorithm can be calculated by the following equation:

$$\kappa_l^{\mathrm{BTE}} = \frac{1}{V} C\, v_{\mathrm{g}}^2 \tau \tag{S4}$$

where V, C, v_{g}, τ denote the original cell volume, heat capacity, phonon group velocity and phonon scattering time, respectively. The lattice thermal conductivity within the two-channel model can be calculated from the following equation:

$$\kappa_l^{\text{two-channel}} = \kappa_l^{\mathrm{ph}} + \kappa_l^{\mathrm{diff}} \tag{S5}$$

$$\kappa_l^{\mathrm{ph}} = \sum_{i=1}^{N_{\mathrm{ph}}} C_{\mathrm{s}}(i) D_{\mathrm{ph}}(i) \tag{S6}$$

$$\kappa_l^{\mathrm{diff}} = \sum_{j=1}^{N_{\mathrm{diff}}} C_s(j) D_{\mathrm{diff}}(j) \tag{S7}$$

$$C_s(i;j) = \frac{1}{V} k_B \left(\frac{\hbar\omega(i;j)}{k_B T}\right)^2 \frac{\exp(\hbar\omega(i;j/k_B T)}{[\exp(\hbar\omega(i;j)/k_B T)-1]^2} \tag{S8}$$

where N_{ph} and N_{diff} represent the number of normal phonons and diffusive-like phonons in the Zintl phase BaCaPb compound, respectively. D_{ph} and D_{diff} denote the thermal diffusivities of normal phonons and diffusive-like phonons, respectively. k_B is Boltzmann constant, $\hbar$ is the reduced Planck constant, T is the absolute temperature, ω is the phonon vibrational angular frequency, and V is the unit cell volume. D_{ph} and D_{diff} can be calculated by the following formulas:

$$D_{\mathrm{ph}}(i) = \frac{1}{3} V_g(i) l(i) \tag{S9}$$

$$D_{\mathrm{diff}}(j) = \frac{1}{3} \frac{n^{-2/3}\omega(j)}{\pi} \tag{S10}$$

$$l(i) = V_{\mathrm{g}}(i)\tau(i) \tag{S11}$$

where V_{g}, l, n, and τ are the phonon group velocity, mean free path, unit cell atomic number density, and scattering time, respectively.

Section III. Details for the definition of diffusion phonon under the three criteria within the two-channel model

To distinguish the differences between normal phonons and diffusive-like phonons, three criteria within the two-channel model have been proposed. The first two criteria originated from the Ioffe-Regel limit, distinguish the normal and diffusive-like phonons based on the phonon wavelength (I. l-λ criterion) and minimum interatomic distance (II. l-a_{min} criterion), while the third criterion (III. D_{Ph}-D_{diff} criterion) differentiates these two types of phonons by comparing the magnitude of the thermal diffusivity.

Under the Crit. I, normal phonons are identified when the phonon mean free path exceeds the phonon wavelength, whereas the diffusive-like phonons are defined when the phonon mean free path is less than the phonon wavelength. Crit. II uses the minimum atomic spacing a_{min} as the boundary, and the normal phonons are identified when the phonon mean free path is greater than a_{min}, and diffusive-like phonons are defined when the phonon mean free path is less than a_{min}. The Crit. III posits that the thermal diffusivity of normal phonons (D_{ph}) should exceed that of diffusive-like phonons (D_{diff}), i.e., a diffusion-like phonon is defined when $D_{\mathrm{ph}} < D_{\mathrm{diff}}$.

Section IV. Crystal and electronic structure properties

Table S1. Elastic constant (C_{ij}, GPa), Bulk modulus (B, GPa), shear modulus (G, GPa), and Young's modulus (E, GPa) for BaCaPb compound.

	C_{11}	C_{12}	C_{13}	C_{22}	C_{23}	C_{33}	C_{44}	C_{55}	C_{66}	B	G	E
BaCaPb	46.39	14.37	18.36	43.59	15.00	39.20	14.74	21.91	20.91	26.37	17.86	39.75

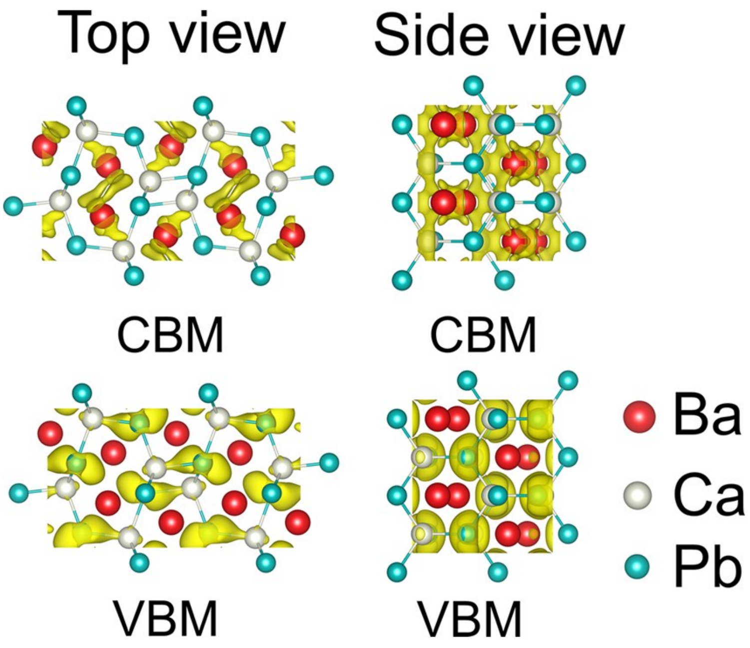

Fig. S1. The top and side views of the space charge density at CBM and VBM of BaCaPb compound.

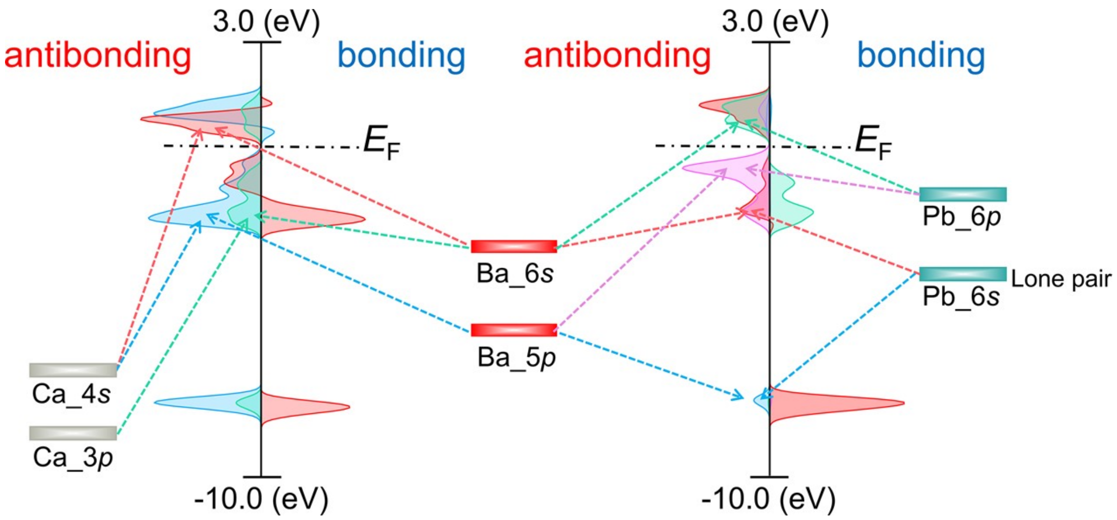

Fig. S2. Schematic diagram for orbital interactions in the Ba-Ca and Ba-Pb bonds.

Section V. Thermal transfer properties

Table S2. The second-order force constants for BaCaPb compound.

System	Bonds	second-order force (eV Å^{-2})
BaCaPb	Ba-Ba	0.488
	Ba-Pb	0.253
	Ba-Ca	0.791
	Ca-Pb	1.030

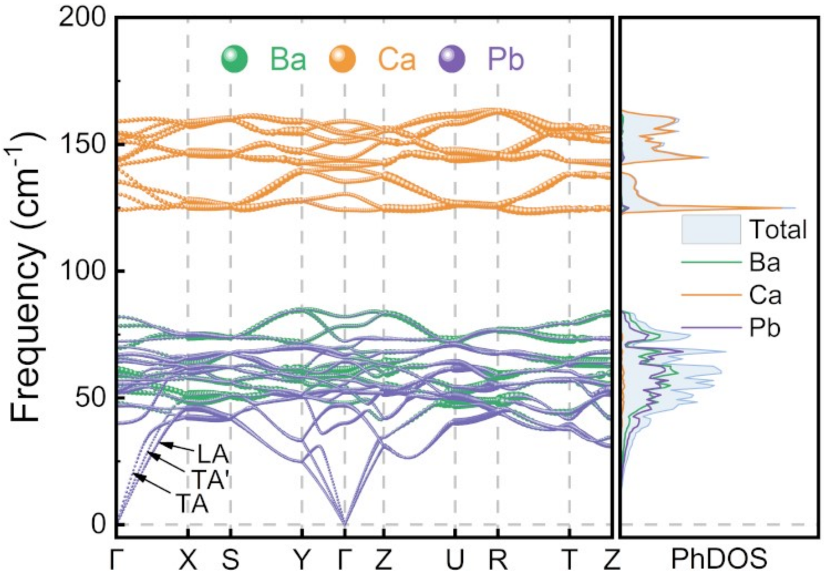

Fig. S3. Projected phonon dispersion curves and density of states (PhDOS) for BaCaPb compound.

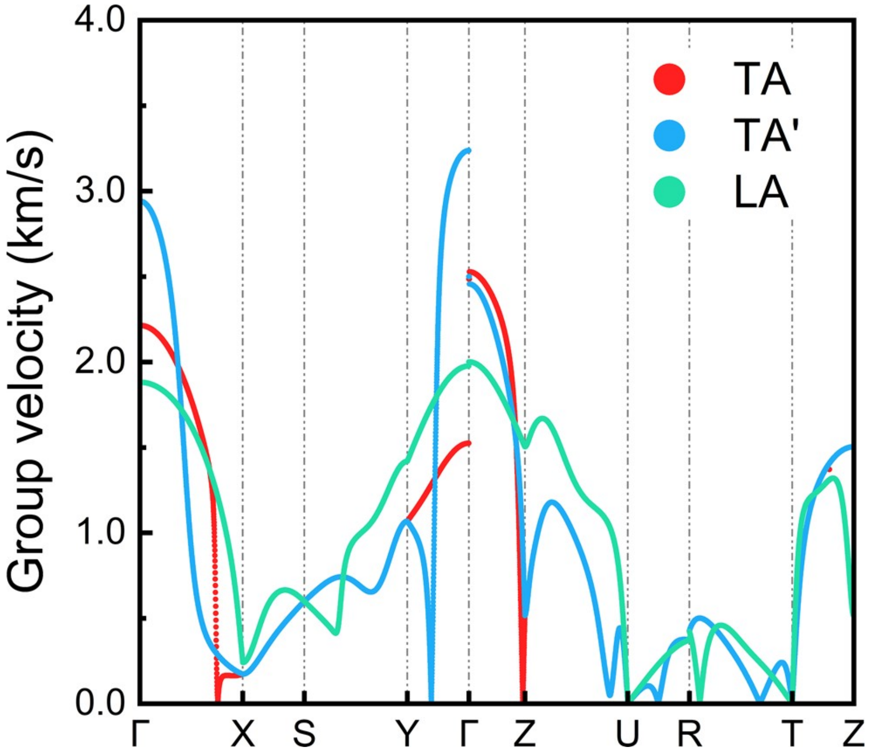

Fig. S4. The phonon group velocity along various paths within the Brillouin zone for BaCaPb compound.

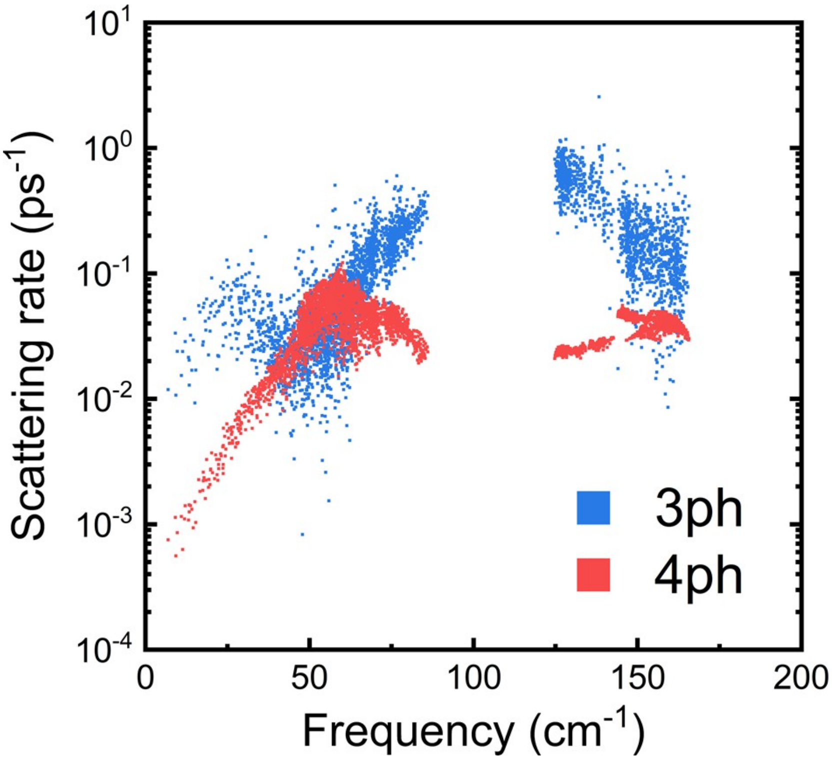

Fig. S5. Comparison of three-phonon and four-phonon scattering rates in BaCaPb compound.

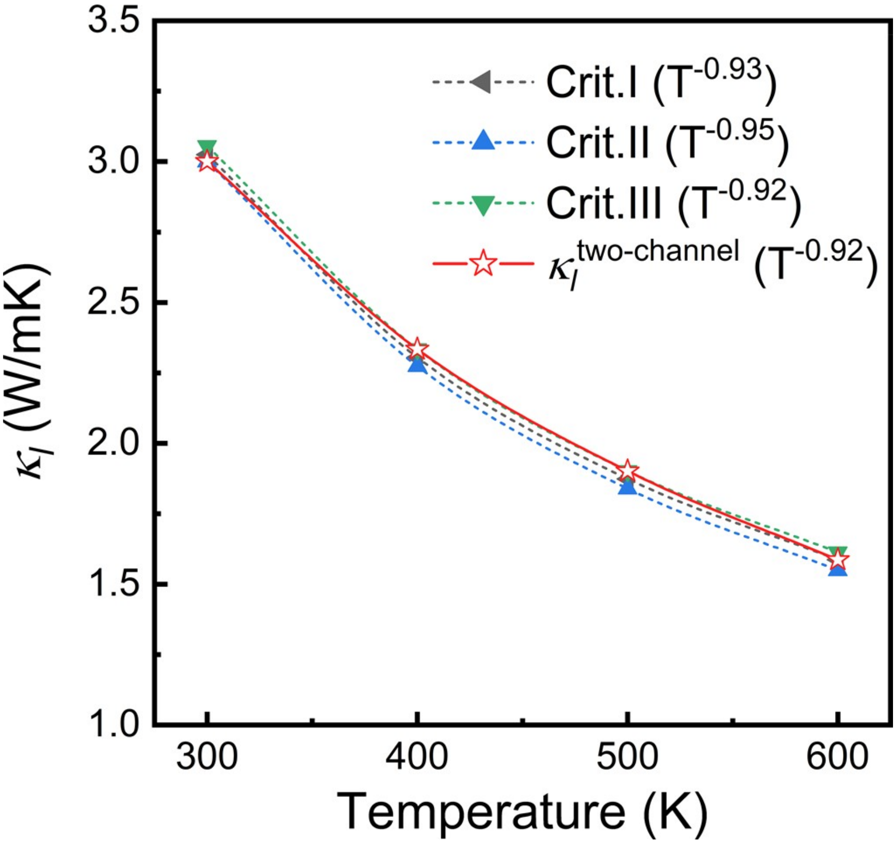

Fig. S6. The lattice thermal conductivity (κ_l) of BaCaPb compound in consideration of three-phonon scattering mechanism.

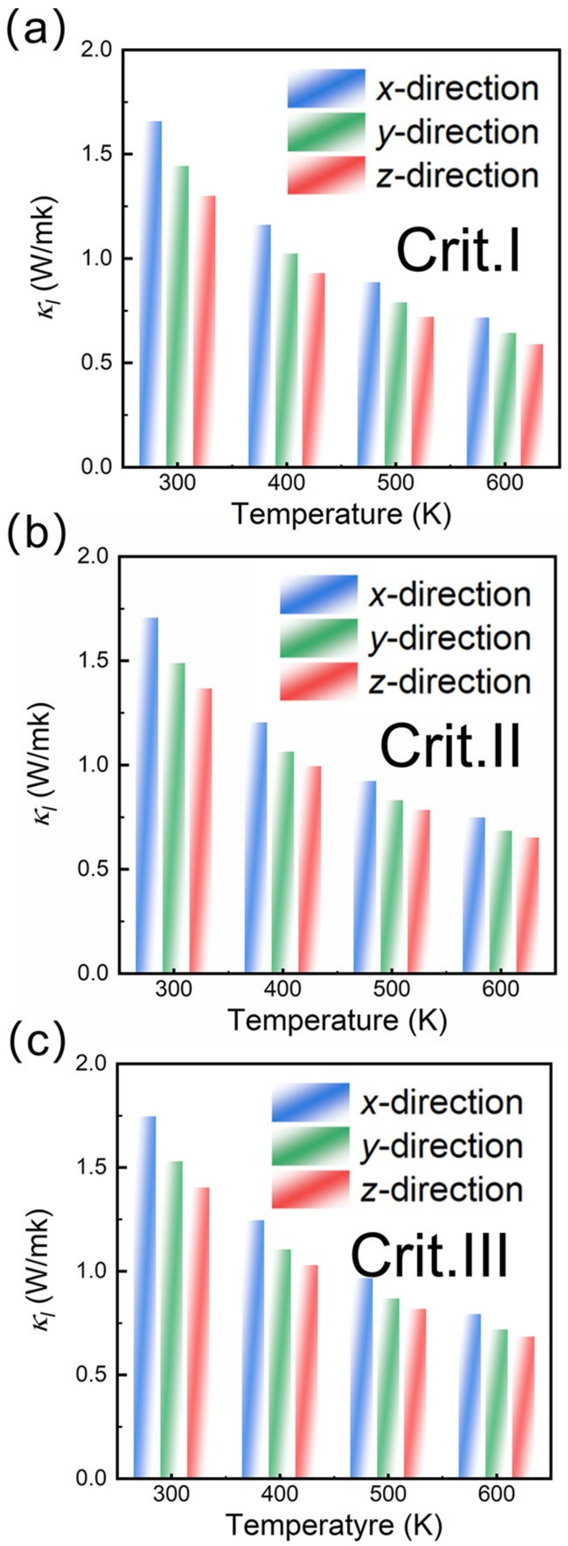

Fig. S7. (a-c) The temperature-dependent lattice thermal conductivity (κ_l) of BaCaPb compound along different directions under the three criteria (Crit. I, II, and III) within the two-channel model.

Section VI. Carrier transport properties

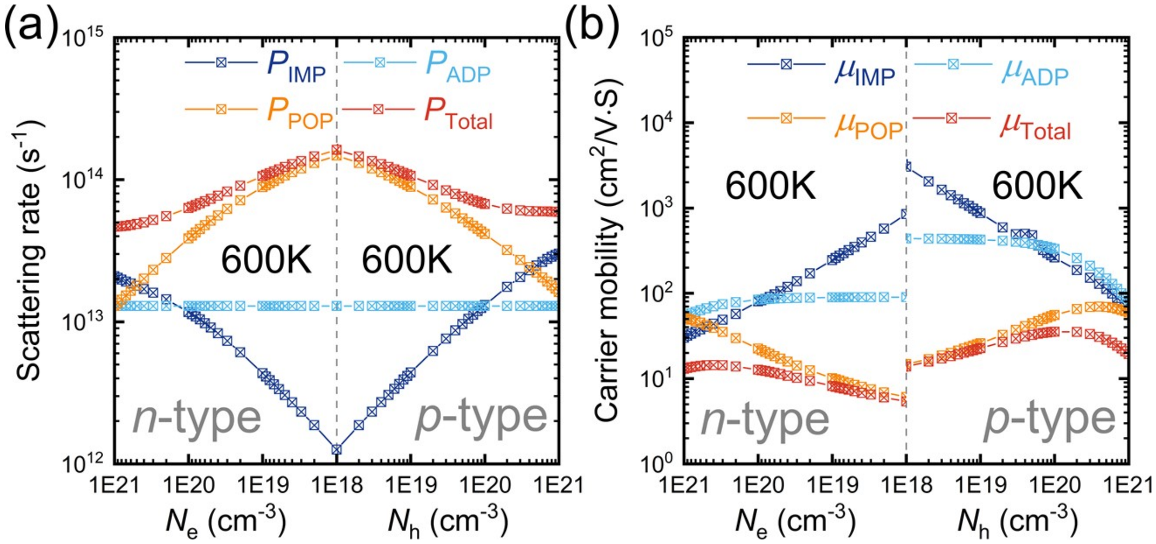

Fig. S8. The carrier scattering rates and carrier mobility of BaCaPb compound at 600 K.

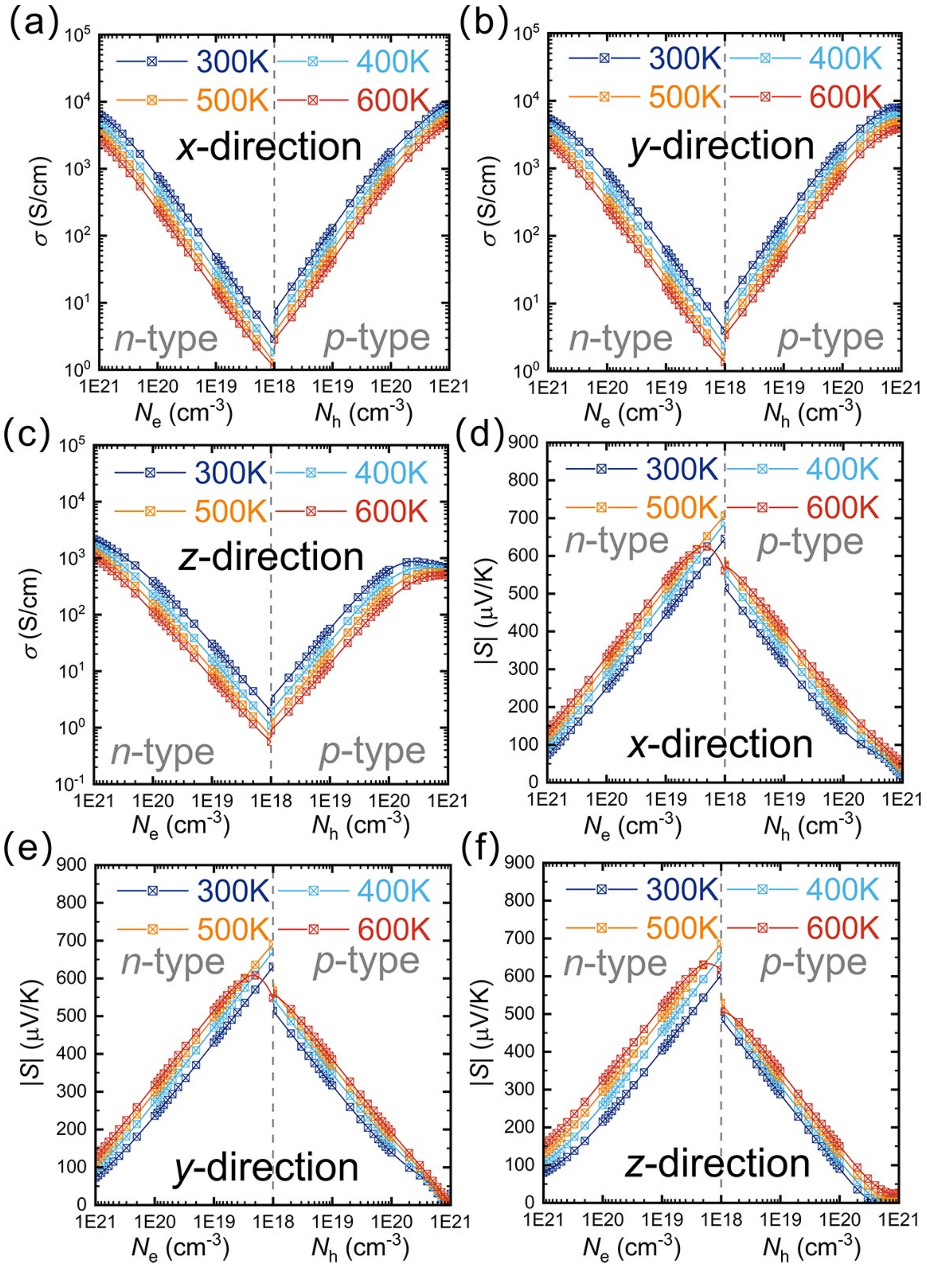

Fig. S9. (a-c) Electrical conductivity (σ) and (d-f) Seebeck coefficient ($|S|$) as a function of carrier concentration for the *n*-type and *p*-type BaCaPb compounds along different directions.

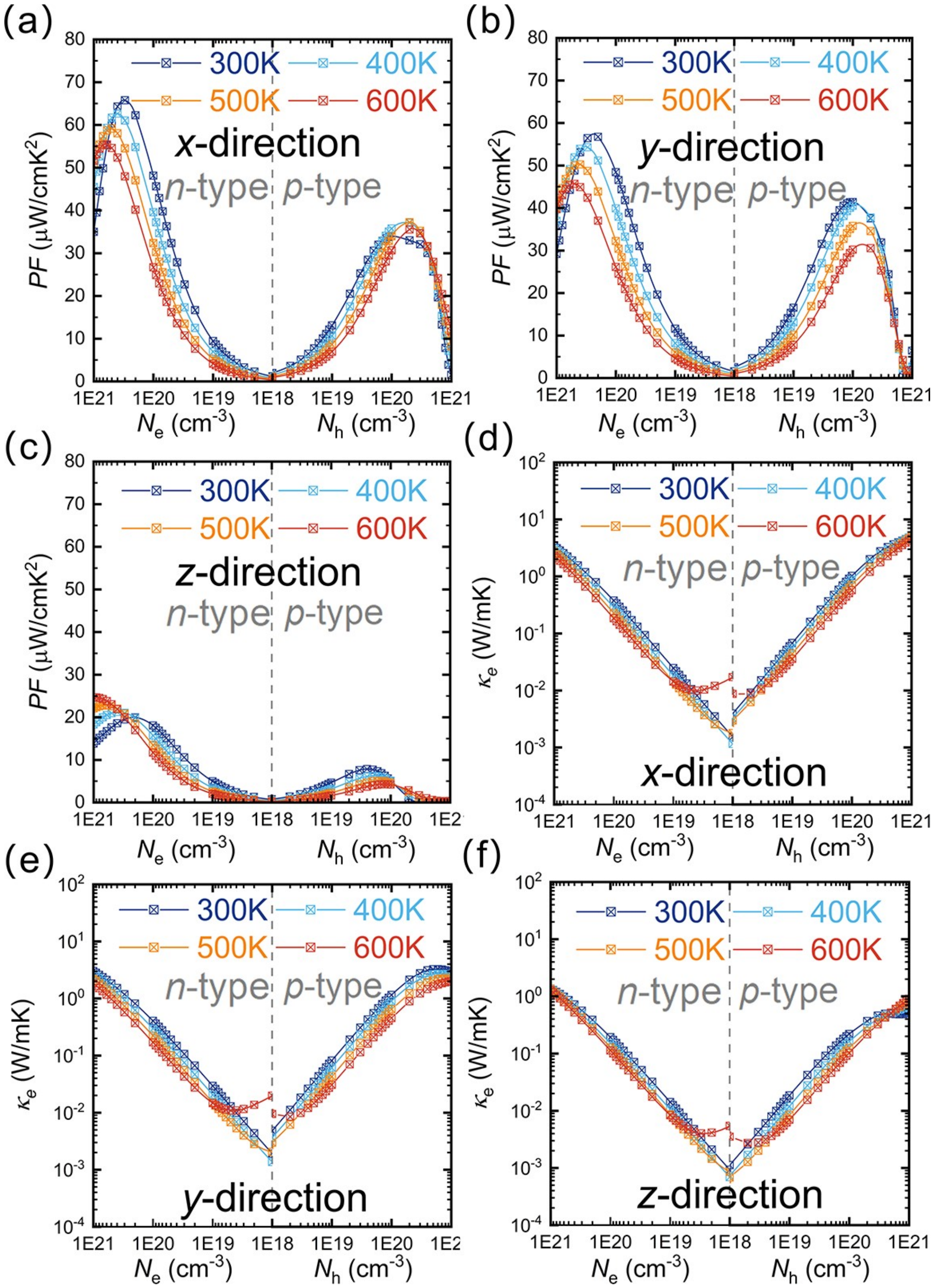

Fig. S10. (a-c) Power factor (*PF*) and (d-f) electronic thermal conductivity (κ_e) as a function of carrier concentration for the *n*-type and *p*-type BaCaPb compound along different directions.