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

Electronic Supplementary Information

First-principles study of the temperature-induced band renormalization in thermoelectric filled skutterudites

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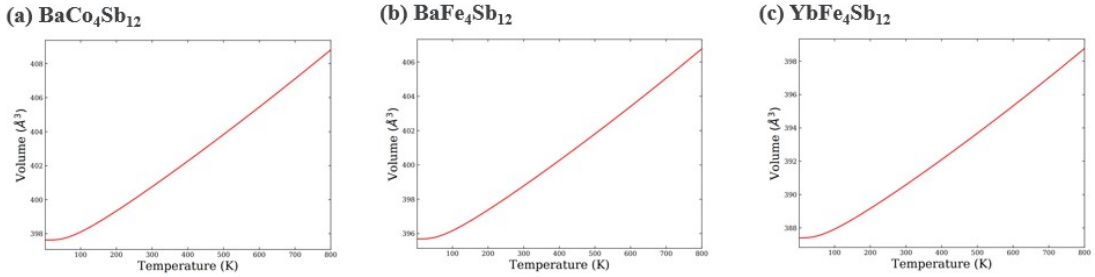

Fig. S1 Volume–temperature relations of (a) $BaCo_4Sb_{12}$, (b) $BaFe_4Sb_{12}$ and (c) $YbFe_4Sb_{12}$, respectively.

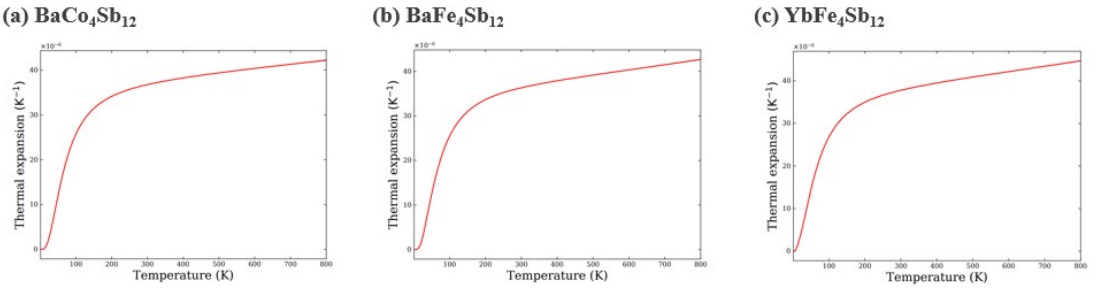

Fig. S2 Volumetric thermal-expansion-coefficient–temperature relations of (a) $BaCo_4Sb_{12}$, (b) $BaFe_4Sb_{12}$ and (c) $YbFe_4Sb_{12}$, respectively.

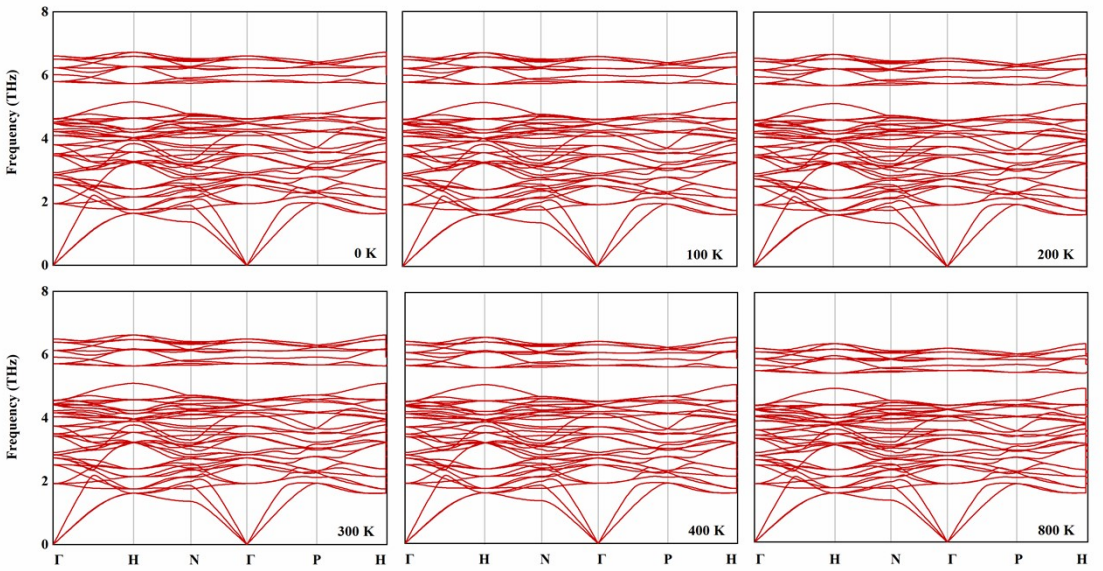

Fig. S3 Phonon spectra with the lattice parameters at different temperatures for $BaCo_4Sb_{12}$.

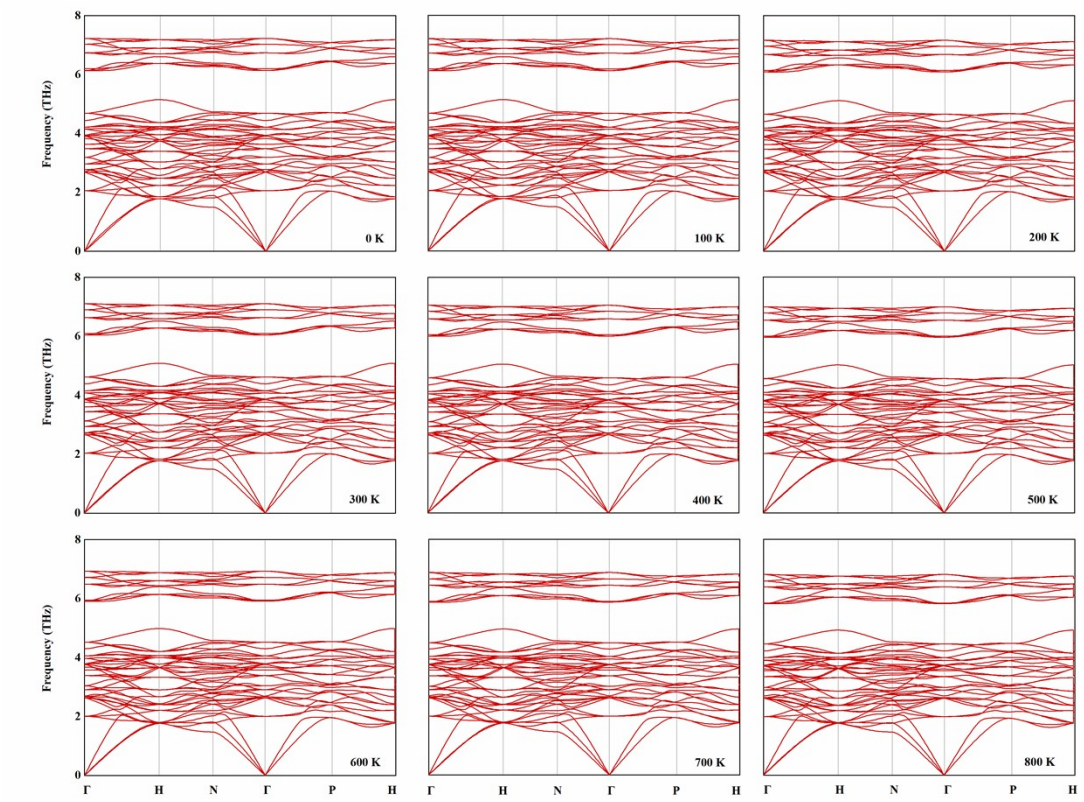

Fig. S4 Phonon spectra with the lattice parameters at different temperatures for $BaFe_4Sb_{12}$.

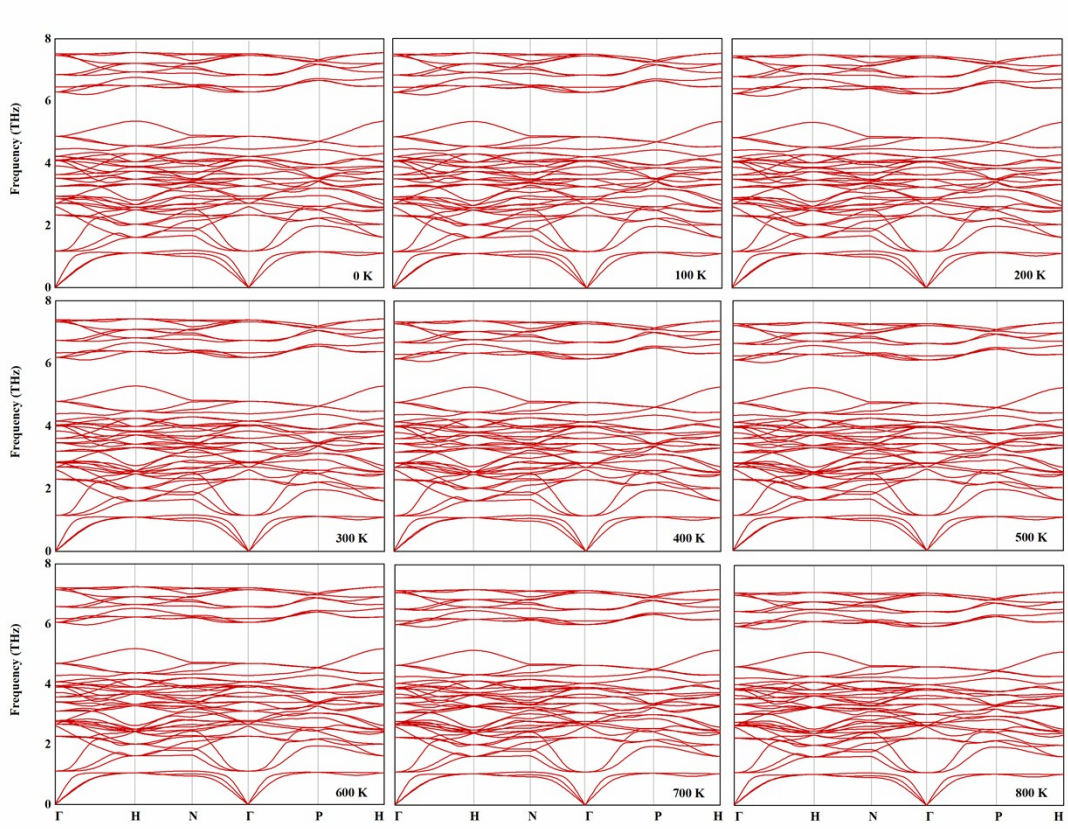

Fig. S5 Phonon spectra with the lattice parameters at different temperatures for $YbFe_4Sb_{12}$.

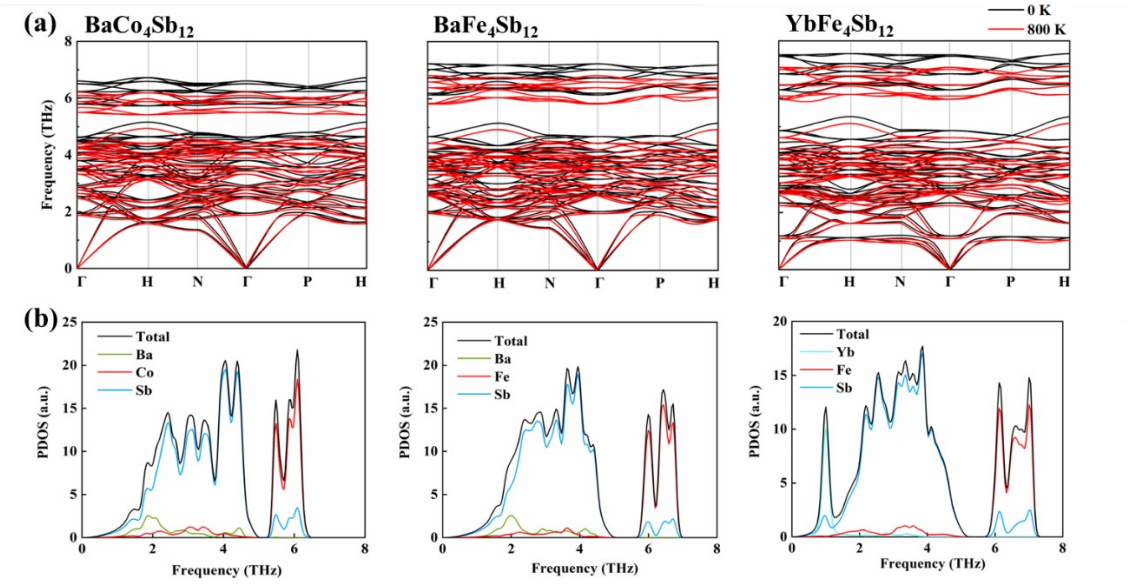

Fig. S6 (a) Phonon spectra with the lattice parameters at 0 K and 800 K for $BaCo_4Sb_{12}$, $BaFe_4Sb_{12}$ and $YbFe_4Sb_{12}$, respectively. (b) Phonon density of states (DOS) with the lattice parameters at 800 K for $BaCo_4Sb_{12}$, $BaFe_4Sb_{12}$ and $YbFe_4Sb_{12}$, respectively.

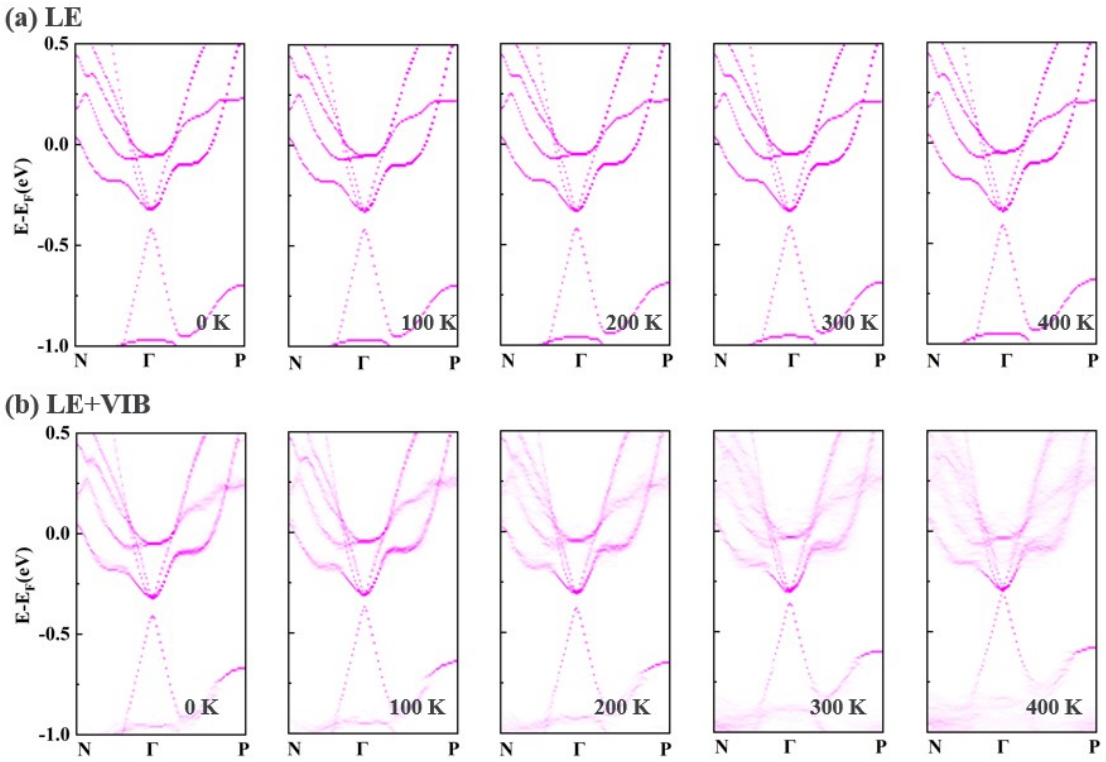

Fig. S7 Effective band structures (EBSs) of $BaCo_4Sb_{12}$ at different temperatures. (a) The effect of lattice expansion (LE) is only included. (b) The effects of lattice expansion and phonon-induced atomic vibrations are both included (LE + VIB). The high-symmetry **k**-points are **Γ** (0 0 0), **N** (0 0 0.5) and **P** (0.25 0.25 0.25).

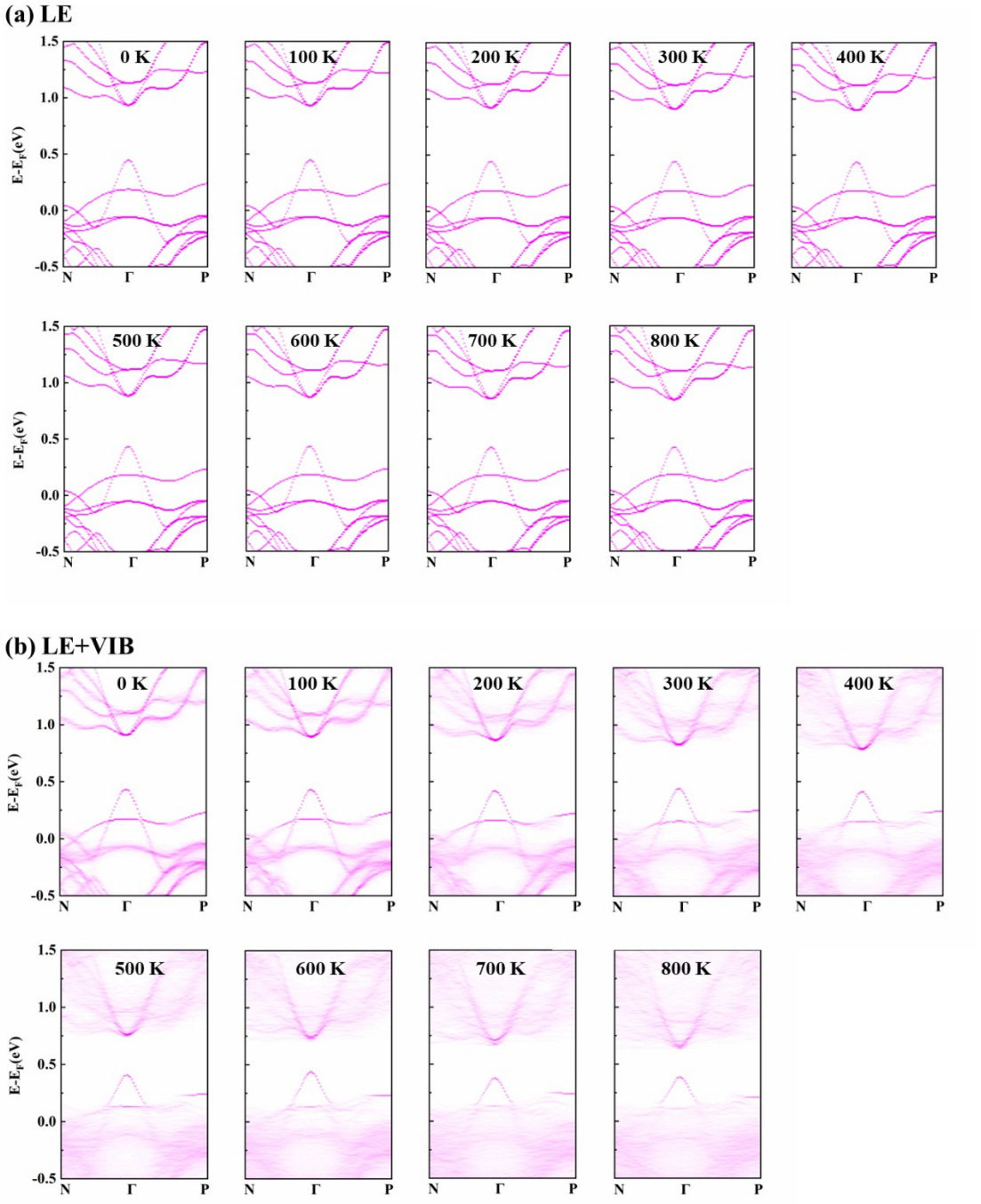

Fig. S8 Effective band structures (EBSs) of $BaFe_4Sb_{12}$ at different temperatures. (a) The effect of lattice expansion is only included (LE). (b) The effects of lattice expansion and phonon-induced atomic vibrations are both included (LE + VIB). The high-symmetry **k**-points are **Γ** (0 0 0), **N** (0 0 0.5) and **P** (0.25 0.25 0.25).

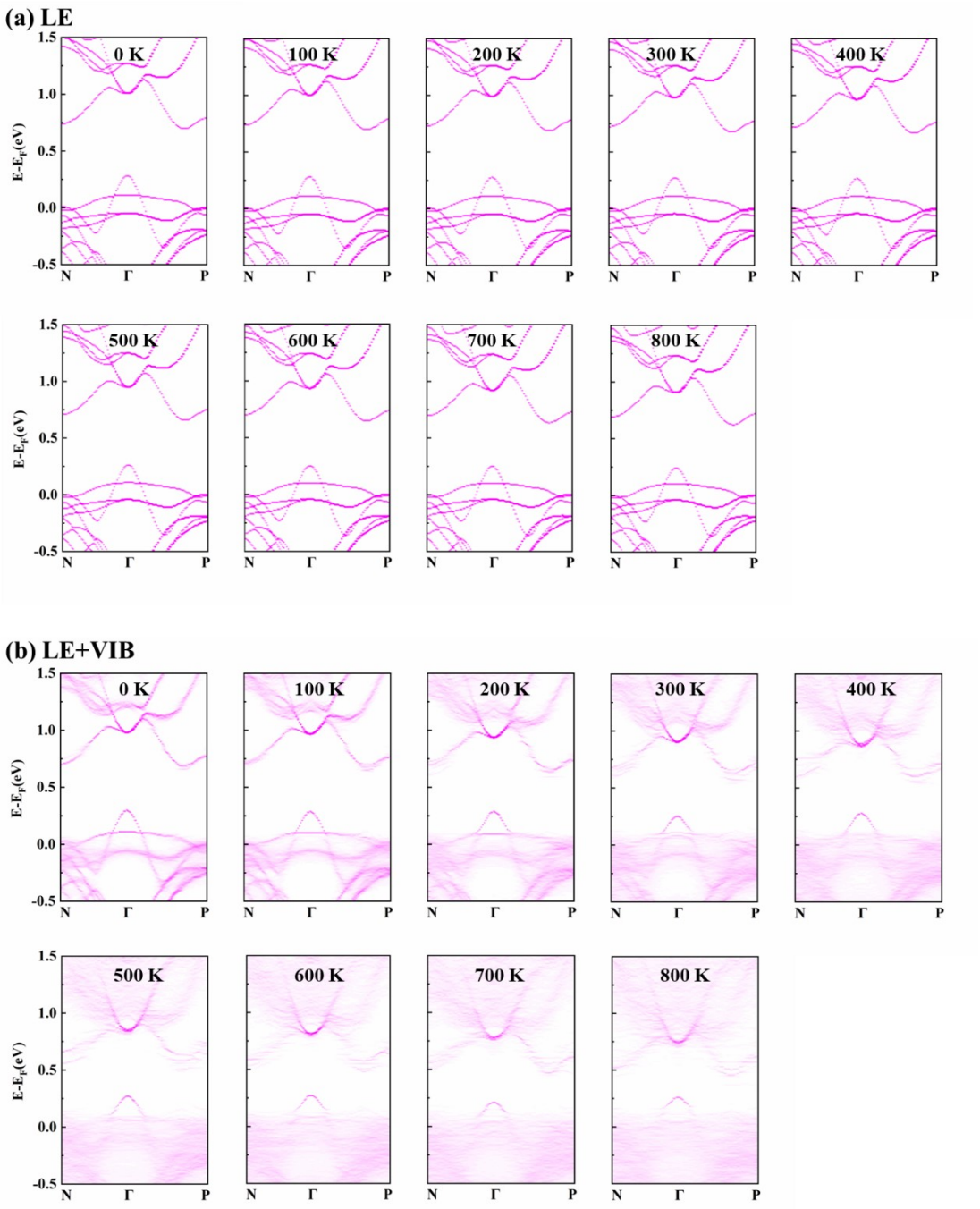

Fig. S9 Effective band structures (EBSs) of $YbFe_4Sb_{12}$ at different temperatures. (a) The effect of lattice expansion is only included (LE). (b) The effects of lattice expansion and phonon-induced atomic vibrations are both included (LE + VIB). The high-symmetry **k**-points are **Γ** (0 0 0), **N** (0 0 0.5) and **P** (0.25 0.25 0.25).

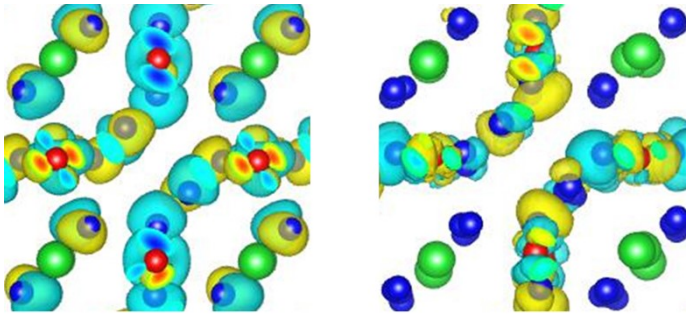

Fig. S10 (a) and (b) are the wave functions of CBM in $BaFe_4Sb_{12}$ at 0 K and 400 K, respectively. The green, red and blue balls represent the Ba, Fe, and Sb atoms, respectively.

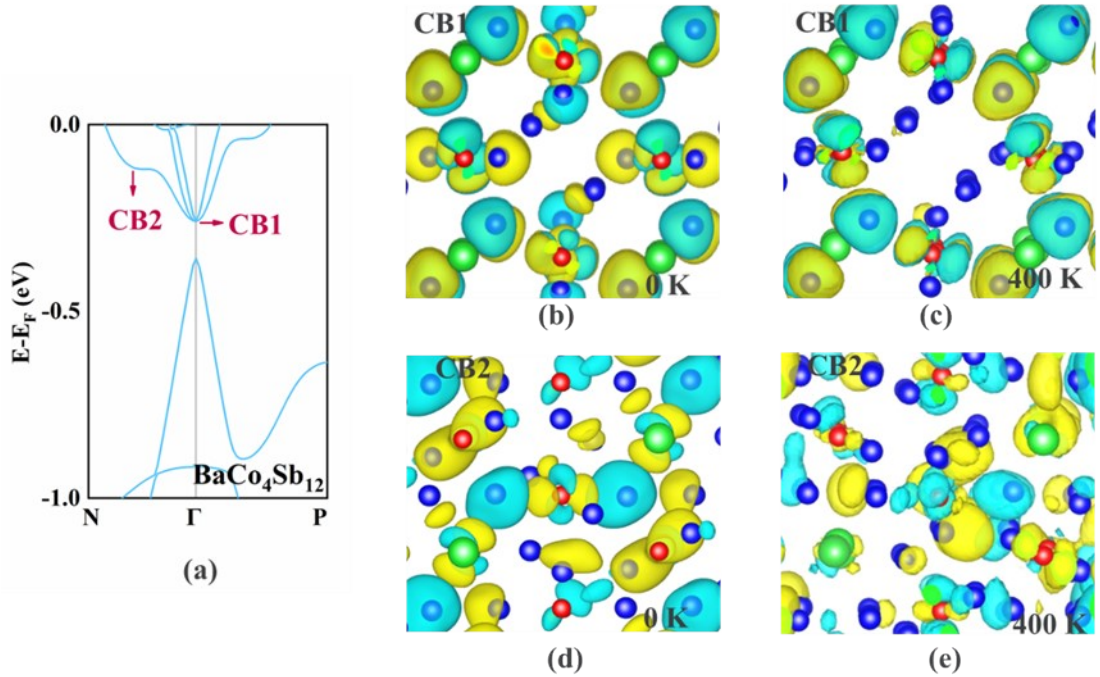

Fig. S11 (a) Band structure of primitive cell of $BaCo_4Sb_{12}$. (b) and (c) are the wave functions of CB1 at 0 K and 400 K, respectively. (d) and (e) are the wave functions of CB2 at 0 K and 400 K, respectively. The green, red and blue balls represent the Ba, Co, and Sb atoms, respectively.

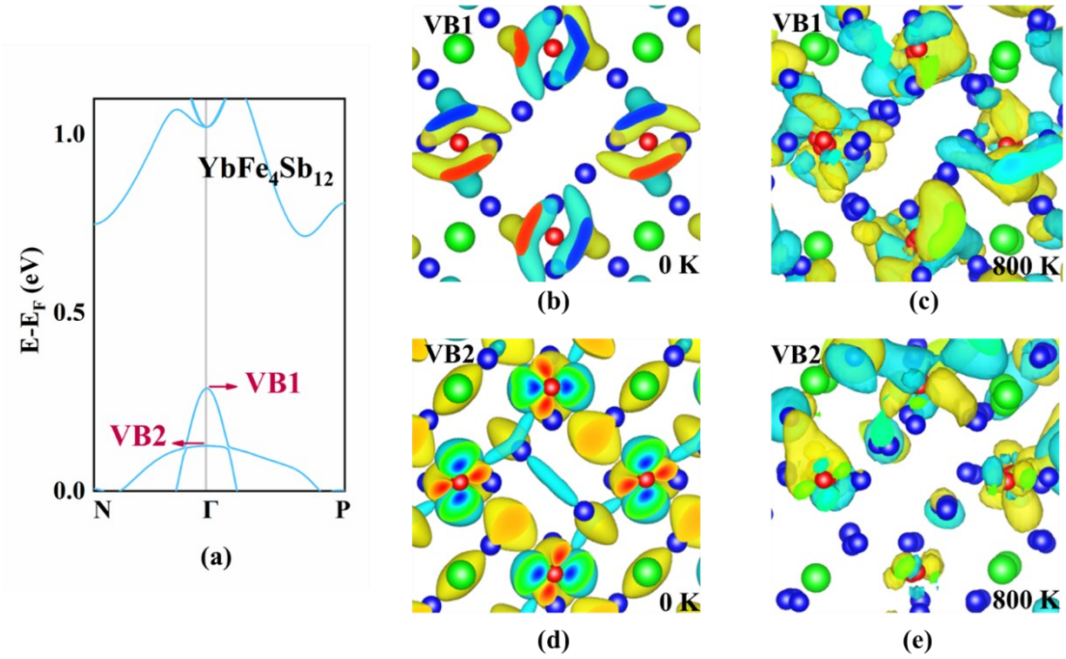

Fig. S12 (a) Band structure of primitive cell of $YbFe_4Sb_{12}$. (b) and (c) are the wave functions of VB1 at 0 K and 800 K, respectively. (d) and (e) are the wave functions of VB2 at 0 K and 800 K, respectively. The green, red and blue balls represent the Yb, Fe, and Sb atoms, respectively.

Table S1 Bond length (in Å) of Sb–Sb and Fe/Co–Sb and volume (in Å^3) for these three skutterudites in optimized primitive cells. The variation (in Å) and the rate of change compared with $CoSb_3$ are also presented. Bond length of Sb–Sb and Co–Sb in $CoSb_3$ is 2.9716 Å and 2.5377 Å, respectively, the volume of $CoSb_3$ is 377.86 Å^3, from Chem. Mater., 2021, 33, 1046.

	Sb–Sb	Variation	Rate	Fe/Co–Sb	Variation	Rate	Volume	Rate
$BaCo_4Sb_{12}$	3.0014	0.0298	1.00%	2.5817	0.0440	1.73%	395.69	4.72%
$BaFe_4Sb_{12}$	3.0194	0.0478	1.61%	2.5711	0.0334	1.32%	393.98	4.27%
$YbFe_4Sb_{12}$	3.0149	0.0433	1.46%	2.5479	0.0102	0.40%	385.76	2.09%

Table S2 Bond length (in Å) of Sb–Sb and Fe/Co–Sb for the four skutterudites' supercells at 0 K, and 800 K with only lattice expansion considered. The variation (in Å) and the rate of change are also presented. The corresponding data of $CoSb_3$ are from Chem. Mater., 2021, 33, 1046.

	Sb–Sb				Fe/Co–Sb			
	0 K	800 K	Variation	Rate	0 K	800 K	Variation	Rate
$CoSb_3$	2.9728	2.9983	0.0255	0.86%	2.5396	2.5627	0.0231	0.91%
$BaCo_4Sb_{12}$	3.0067	3.0363	0.0296	0.98%	2.5858	2.6093	0.0235	0.91%
$BaFe_4Sb_{12}$	3.0232	3.0539	0.0307	1.02%	2.5750	2.5980	0.023	0.89%
$YbFe_4Sb_{12}$	3.0195	3.0530	0.0335	1.11%	2.5515	2.5749	0.0234	0.92%

Table S3 Band gaps (in eV) of $BaCo_4Sb_{12}$, $BaFe_4Sb_{12}$ and $YbFe_4Sb_{12}$ at different temperatures, respectively. These values are extracted from the EBSs. LE means the EPR effect including only lattice expansion, and LE + VIB means the EPR effect including both lattice expansion and vibrations. The values of ZPR for $BaCo_4Sb_{12}$, $BaFe_4Sb_{12}$ and $YbFe_4Sb_{12}$ are 0.008 eV, 0.013 eV and 0.011 eV, respectively.

Temperature	$BaCo_4Sb_{12}$		$BaFe_4Sb_{12}$		$YbFe_4Sb_{12}$	
(K)	LE	LE+VIB	LE	LE+VIB	LE	LE+VIB
0	0.106	0.098	0.489	0.476	0.407	0.396
100	0.097	0.062	0.487	0.464	0.412	0.361
200	0.089	0.069	0.480	0.443	0.409	0.343
300	0.078	0.057	0.465	0.379	0.407	0.322
400	-	-	0.451	0.373	0.406	0.272
500	-	-	0.446	0.351	0.391	0.239
600	-	-	0.439	0.299	0.389	0.231
700	-	-	0.428	0.296	0.387	0.248
800	-	-	0.406	0.254	0.381	0.195