Supporting Information

Low Thermal Expansion and High Lattice Thermal Conductivity in β-Sodalite $Co_4B_6O_{13}$: Enhancing the Local Rigidity of Cationic Tetrahedra Cluster

Yuanyuan Li[1a*], Dingfeng Yang[1b*], Wen Jiang[a], Xiangnan Gong[c*], Wenjing Huang[b], Jie Gao[a]

[a]Department of Biological and Chemical Engineering, Chongqing University of Education, Chongqing 400067, People's Republic of China.

[b]College of Chemistry and Chemical Engineering, Chongqing University of Technology, 69 Hongguang Rd., Lijiatuo, Banan District, Chongqing 400054, People's Republic of China.

[c]Analytical and Testing Center of Chongqing University, Chongqing 401331, People's Republic of China.

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Debye Callaway model

In Debye-Callaway model, the lattice thermal conductivity (κ) can be calculated by the following formula[1-2]:

$$\kappa=\kappa_{LA}+\kappa_{TA}+\kappa_{TA`} \qquad (1)$$

Where κ_{LA} and $\kappa_{TA}+\kappa_{TA`}$ stands for the contribution of longitudinal and two transverse acoustic phonon branches. The role of optical phonons to κ is not taken into account in this model. Each of acoustic phonon contribution can be calculated by the formulas:

$$\kappa_{\mathrm{i}}=\frac{1}{3}C_iT^3\left\{\int_0^{\Theta_i/T}\frac{\tau_c^i(x)x^4e^x}{(e^x-1)^2}dx+\frac{[\int_0^{\Theta_i/T}\frac{\tau_c^i(x)x^4e^x}{\tau_N^i(e^x-1)^2}dx]^2}{\int_0^{\Theta_i/T}\frac{\tau_c^i(x)x^4e^x}{\tau_N^i\tau_U^i(e^x-1)^2}dx}\right\} \qquad (2)$$

$$\frac{1}{\tau_N^{LA}(x)}=\frac{k_B^3\gamma_{LA}^2V}{M\mathsf{h}^2\upsilon_{LA}^5}(\frac{k_B}{\mathsf{h}})^2x^2T^5,$$
$$\frac{1}{\tau_N^{TA/TA`}(x)}=\frac{k_B^4\gamma_{TA/TA`}^2V}{M\mathsf{h}^3\upsilon_{TA/TA`}^5}\frac{k_B}{\mathsf{h}}xT^5, \qquad (3)$$

$$\frac{1}{\tau_U^i(x)}=\frac{\mathsf{h}\gamma^2}{M\upsilon_i^2\Theta_i}(\frac{k_B}{\mathsf{h}})^2x^2T^3e^{-\Theta_i/3T} \qquad (4)$$

$$1/\tau_c=1/\tau_N+1/\tau_U \qquad (5)$$

$$x=\frac{\mathsf{h}\omega}{k_BT},C_i=\frac{k_B^4}{2\pi^2\mathsf{h}^3\upsilon_i}, \qquad (6)$$

$$\gamma_i=-\frac{V}{\omega_i}\frac{\partial\omega_i}{\partial V} \qquad (7)$$

$\upsilon,V,M,\gamma,\Theta$ and T is acoustic phonon velocity, volume per atom, average mass of an atom, Grüneisen parameter, Debye temperature and Temperature, respectively. Thus, the κ is affected by $\upsilon,V,M,\gamma,\Theta$ and T. T is the Independent Variable. The Θ and υ are directly obtained from acoustic phonon dispersion at 0 K. The Grüneisen parameters γ is calculated from formula (7), and the isotopically expanded unit cell is adopted by +3%.

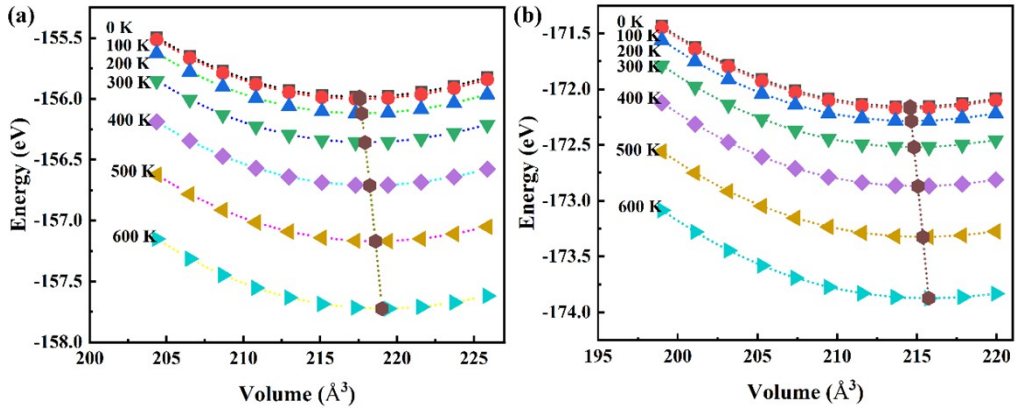

Figure S1. Free energies of (a) $Zn_4B_6O_{13}$ and (b) $Co_4B_6O_{13}$ with respect to volumes at temperatures from 0 K to 600 K.

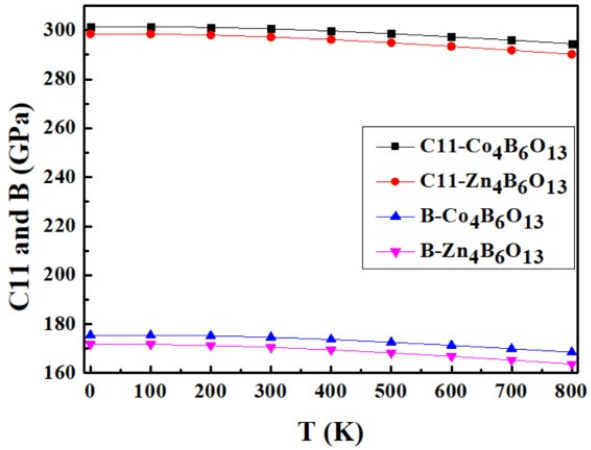

Figure S2 The temperature dependent C11 and B for $Zn_4B_6O_{13}$ and $Co_4B_6O_{13}$

Table S1. The calculated vibration frequencies for zero wave vector for $Co_4B_6O_{13}$. The symbols R and IR indicates Raman and infrared activity, respectively. "-" of T1 modes are inactive in both Raman and IR spectroscopy.

Mode	Frequency(cm^{-1})	Activity	Mode	Frequency(cm^{-1})	Activity
T2	0	R, IR	T2	629.6	R, IR
T1	145.5	-	T1	634.6	-
T2	173.7	R, IR	T2	688.4	R, IR
E	178.8	R	E	698.3	R
T2	202.6	R, IR	A1	706.4	R
T2	264.2	R, IR	T1	771.9	-

A1	272.1	R	E	804.9	R
T1	276.9	-	A2	881.5	-
A2	400.2	-	T2	898.4	R, IR
E	401.7	R	T1	903.7	-
A1	409.9	R	T2	981.9	R, IR
T1	428.4	-	T2	1,008.3	R, IR
T2	447.2	R, IR	T1	1,029.2	-
T2	470.3	R, IR	E	1,039.4	R

Table S2 The experimental and reported thermal physical parameters at room temperature of $Co_4B_6O_{13}$ and other state-of-art borates.

	Thermal expansion ($\times 10^{-6}$ K^{-1})			Lattice thermal conductivity (W/m-K)		
[t]$Co_4B_6O_{13}$	9.7			125.1		
$Zn_4B_6O_{13}$	[t]12.4/[e,3]1.0			[t]55.7/[e,3]30.5		
	a	*b*	*c*	*a*	*b*	*c*
[e,4-5]β-BaB_2O_4(BBO)	3.74	3.74	40.37	1.20	1.20	1.60
[e,6]LiB_3O_5(LBO)	59.73	-49.43	23.94	3.49	4.00	5.20

t: Simulated results; e: experimental results.

Table S3. The temperature dependent elastic modulus of $Co_4B_6O_{13}$.

T(K)	V(Å^3)	C11(GPa)	C12(GPa)	C44(GPa)	B	G
0	214.574	301.445	112.451	88.184	175.449	90.709
100	214.577	301.434	112.439	88.184	175.437	90.709
200	214.643	301.189	112.209	88.199	175.202	90.715
300	214.810	300.625	111.624	88.235	174.625	90.741
400	215.062	299.713	110.714	88.281	173.714	90.769
500	215.374	298.613	109.538	88.357	172.563	90.829
600	215.731	297.329	108.342	88.382	171.338	90.827

Table S4. The temperature dependent elastic modulus of $Zn_4B_6O_{13}$.

T(K)	V(Å^3)	C11(GPa)	C12(GPa)	C44(GPa)	B(GPa)	G(GPa)
0	217.565	298.550	108.337	91.040	171.742	92.667
100	217.585	298.480	108.301	91.034	171.694	92.656
200	217.697	298.069	107.890	91.038	171.283	92.658
300	217.917	297.287	107.174	91.030	170.545	92.641
400	218.228	296.212	106.097	91.047	169.469	92.651
500	218.603	294.928	104.876	91.054	168.226	92.643
600	219.026	293.444	103.487	91.040	166.806	92.616

Table S5. Linear fitting of C11 and B versus temperature for $Zn_4B_6O_{13}$ and $Co_4B_6O_{13}$

	C11/T	B/T
$Zn_4B_6O_{13}$	-0.01421 K^{-1}	-0.01378 K^{-1}
$Co_4B_6O_{13}$	-0.0123 K^{-1}	-0.01231 K^{-1}

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