

## Supporting Information

### Unidirectional thermal expansion in $\text{KZnB}_3\text{O}_6$ : role of alkali metals

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## Experimental methods

**Samples.** Polycrystalline samples of  $K_{1-x}M_xZnB_3O_6$  ( $M = Na$  and  $Rb$ ) ( $x \leq 0.8$ ) were synthesized by traditional solid-state reaction techniques. The stoichiometric mixtures of A.R.  $Na_2CO_3/K_2CO_3/Rb_2CO_3$ ,  $H_3BO_3$  and  $ZnO$  were ground well and packed into  $Al_2O_3$  crucible. In order to compensate for volatilization of alkali metals, 15% excess of  $Na_2CO_3/K_2CO_3/Rb_2CO_3$  (A.R.) is required. They were preheated at  $500\text{ }^\circ\text{C}$  for 12 h to decompose the carbonate and eliminate the water. Then they were intermediate grindings adequately, and calcined at  $700\text{ }^\circ\text{C}$  for 48 h. The single-phase powder of them was obtained. The purity of the samples was confirmed by powder X-ray diffraction (XRD) analysis. The powder XRD data were carried out with a Panalytical diffractometer (X'Pert PRO MRD) operating in Bragg–Brentano geometry with  $CuK\alpha$  ( $\lambda = 1.5418\text{ \AA}$ ) radiation and a graphite monochromator. The diffraction patterns were taken from  $10^\circ$  to  $80^\circ$  ( $2\theta$ ) with a scan step width of  $0.017^\circ$  at room temperature.

**High temperature XRD measurements.** Temperature-dependent *in situ* X-ray diffractometry was performed on an XPERT-PRO powder diffractometer system ( $CoK\alpha_1$ ;  $1.78901\text{ \AA}$ ) equipped with an Anton Paar HTK-1200N Oven Sample stage. The room-temperature diffraction pattern in the angular range from  $10^\circ$  to  $80^\circ$  with a scanning step width of  $0.017^\circ$  was firstly obtained as a standard, and then the sample was heated from 373 K to 973 K at intervals of 100 K. Each diffraction pattern was obtained 30 min after the required

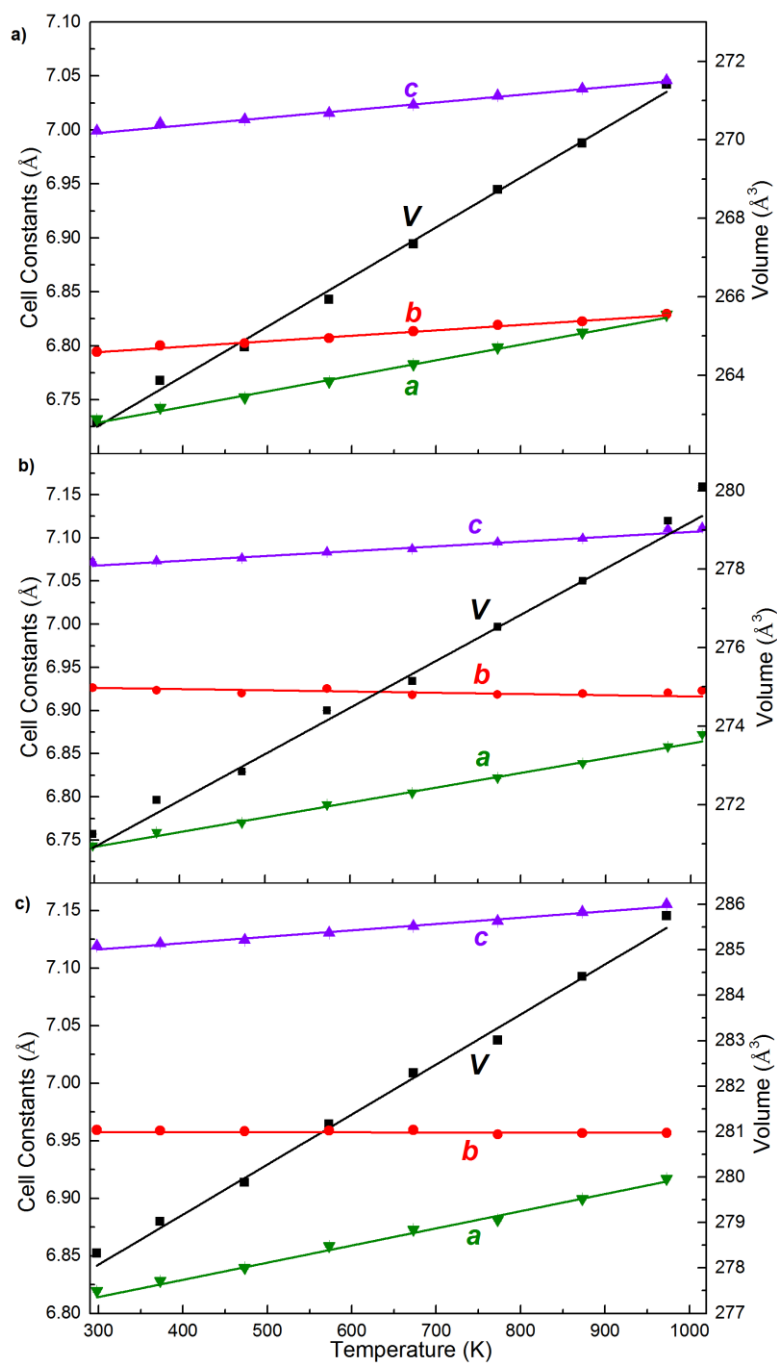
temperature was reached. Unit cell parameters were then calculated by using the pattern indexing software Dicvol06.<sup>1</sup>

### **Computational methods**

The first-principles calculations presented in our work were performed with the CASTEP program code with the plane-wave pseudopotential method.<sup>2</sup> We adopted the generalized gradient approximation (GGA) in the form of the Perdew-Burke-Ernzerhof for the exchange-correlation potentials.<sup>3</sup> The ultrasoft pseudopotential with a plane-wave energy cutoff of 410 eV and a 4×4×4 Monkhorst Pack k-point mesh in the reciprocal space were used for all the calculations.<sup>4</sup> The self-consistent field was set as  $5 \times 10^{-7}$  eV/atom. Based on the experimental lattice parameters, all independent internal atomic coordinates were optimized (Broyden Fletcher Goldfarb Shanno algorithm) with the convergence standard given as follows: energy change less than  $5 \times 10^{-6}$  eV/atom, residual force less than 0.01 eV/Å, stress less than 0.02 GPa, and displacement of atom less than  $5 \times 10^{-4}$  Å. The phonon frequencies and phonon density of states (PHDOS) were obtained with the finite displacement method based on the optimized structures.

**Table S1.** The lattice constants for  $K_{0.5}M_{0.5}ZnB_3O_6$  ( $M = Na, K^5$  and Rb) at 298K.

	$K_{0.5}Na_{0.5}ZnB_3O_6$	$KZnB_3O_6^5$	$K_{0.5}Rb_{0.5}ZnB_3O_6$
a (Å)	6.716(1)	6.742(1)	6.803(2)
b (Å)	6.785(1)	6.921(1)	6.949(1)
c (Å)	6.986(1)	7.068(1)	7.106(1)
$\alpha$ (°)	63.40(1)	63.13(1)	63.18(1)
$\beta$ (°)	71.73(1)	72.40(1)	73.19(1)
$\gamma$ (°)	69.02(1)	69.08(1)	69.08(1)
V (Å <sup>3</sup> )	261.26	270.89	276.73



**Figure S1.** The variation of lattice constants with temperatures for

$K_{0.5}M_{0.5}ZnB_3O_6$  ( $M = Na, K^5$  and Rb).

a)  $K_{0.5}Na_{0.5}ZnB_3O_6$ ; b)  $KZnB_3O_6$ ;<sup>5</sup> c)  $K_{0.5}Rb_{0.5}ZnB_3O_6$ .

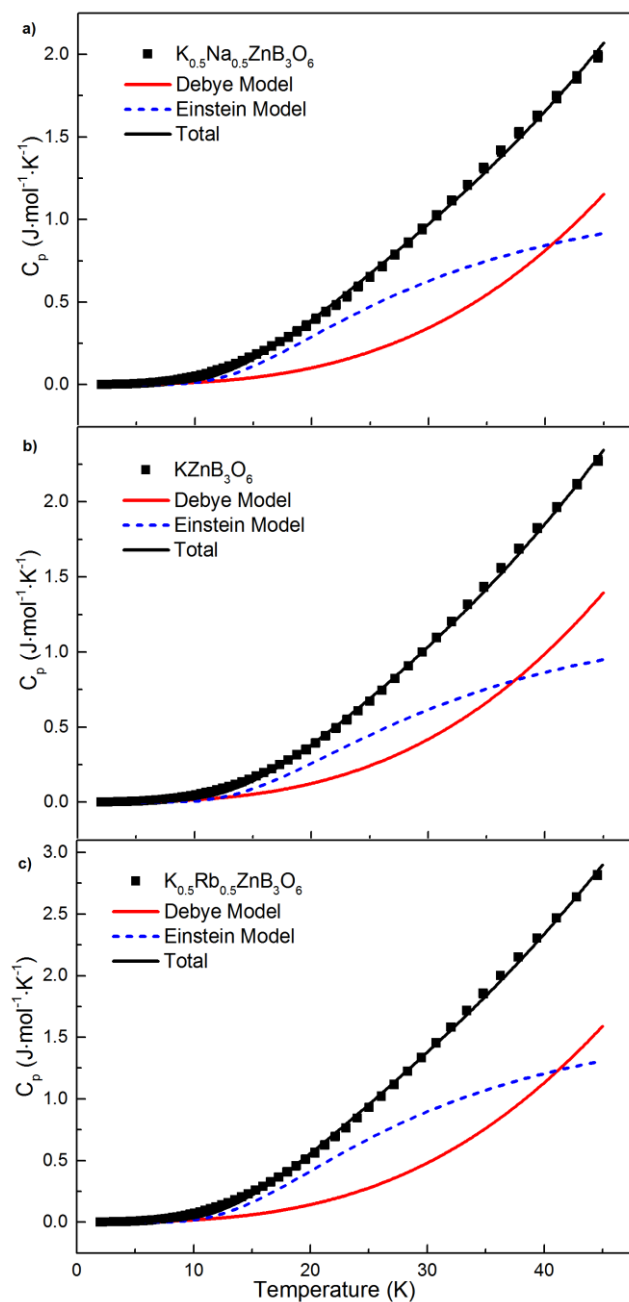
**Table S2.** The calculated bondlengths of *M*-O in *MZnB<sub>3</sub>O<sub>6</sub>* (*M* = Na, K<sup>5</sup> and Rb)

at ground states.

Bonds	<i>M</i> = Na	<i>M</i> = K <sup>5</sup>	<i>M</i> = Rb
M-O1	2.493	2.863	3.062
M-O2	3.433	3.228	3.255
M-O2	2.340	2.665	2.820
M-O3	2.997	3.115	3.286
M-O4	2.655	2.852	2.943
M-O5	3.307	3.276	3.268
M-O5	2.595	2.871	3.016
M-O6	2.631	2.884	2.992
M-O6	2.882	2.885	2.958
Δ%*	31.8%	18.7%	14.2%

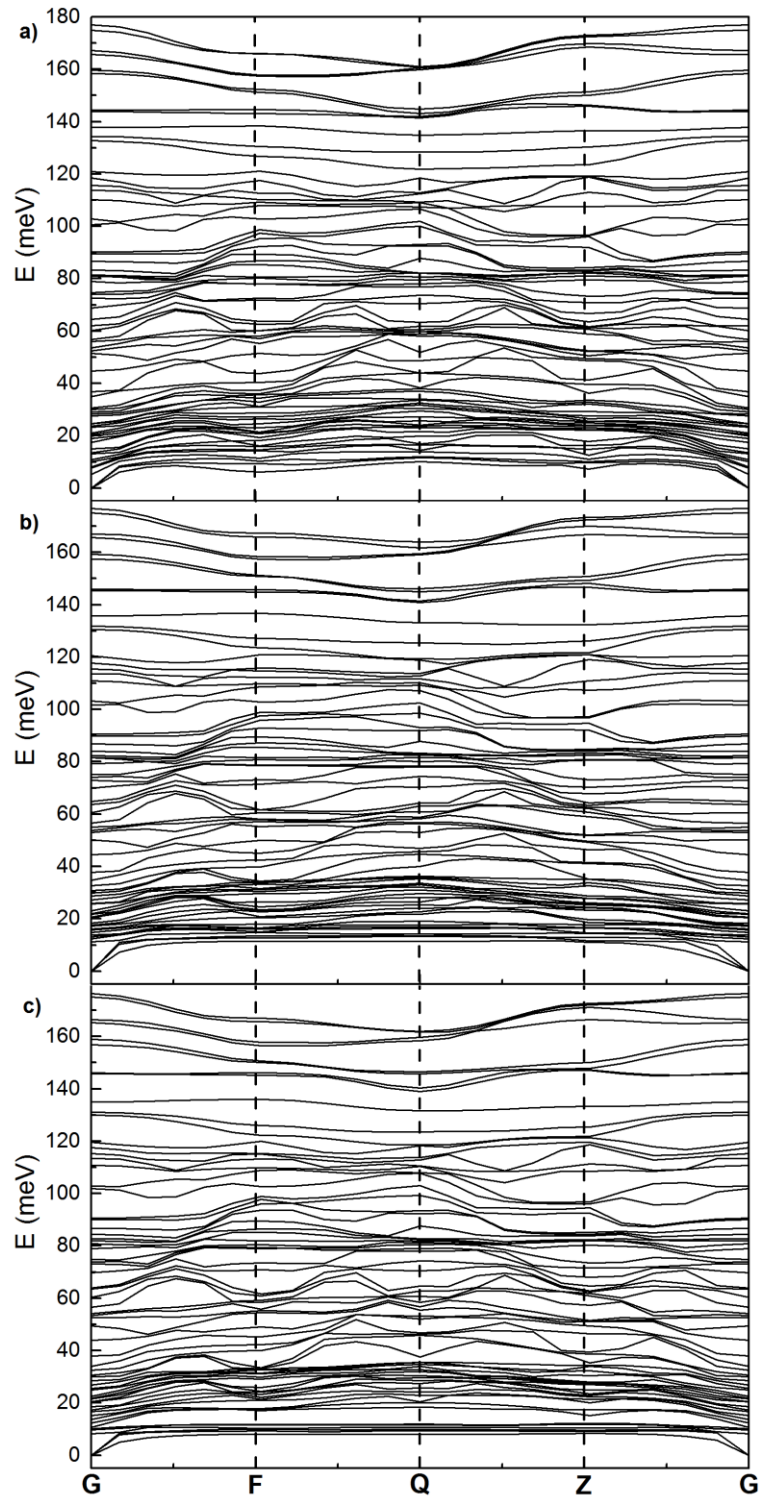
\*Δ%: Nonuniformity of the bond lengths

$$\Delta\% = [(\text{bond length})_{\max} - (\text{bond length})_{\min}] / (\text{bond length})_{\max}$$



**Figure S2.** Specific heat of  $K_{0.5}M_{0.5}ZnB_3O_6$  ( $M = Na, K$  and  $Rb$ ) and their fitting results. a)  $K_{0.5}Na_{0.5}ZnB_3O_6$ ; b)  $KZnB_3O_6$ ; c)  $K_{0.5}Rb_{0.5}ZnB_3O_6$ . The symbols stand for experimental data; the red lines are the fitting results of the fraction of the Debye model; the blue short dashes are the fitting results of the fraction of the Einstein model; the black lines are the sum fitting results of Debye and Einstein model.





**Figure S3.** The phonon dispersion of  $M\text{ZnB}_3\text{O}_6$  ( $M = \text{Na}, \text{K}^5$  and  $\text{Rb}$ ). a)  $\text{NaZnB}_3\text{O}_6$ ; b)  $\text{KZnB}_3\text{O}_6$ ;<sup>5</sup> c)  $\text{RbZnB}_3\text{O}_6$ . It shows that the phonon dispersions above 20meV are similar, but downshifting on going from Na to K, and then to Rb below 20meV.

## References

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