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Unidirectional thermal expansion in $KZnB_3O_6$: role of alkali metals†

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The driving force of the unidirectional thermal expansion in $KZnB_3O_6$ has been studied experimentally and theoretically. Our results show that the low-energy vibrational modes of alkali metals play a crucial role in this unusual thermal behavior.

Thermal expansion is a common phenomenon occurring in solids, which arises from anharmonic lattice dynamics. Exceptions, however, are not very rare. Negative thermal expansion (NTE) is observed in a variety of solids from elements[1-4] to oxides,[5-11] halides,[12] nitrides[13] and metal organic frameworks[14-18] recently. Moreover, some solids[19-22] even exhibit zero thermal expansion (ZTE) over certain temperature ranges. The mechanisms behind these uncommon thermal responses have been recognized to be diverse,[23-27] such as transverse motion of atoms, rotation of rigid polyhedron, phase transitions and *etc.* For instance, the NTE in ZrW_2O_8[6] can be ascribed to be from the cooperative rotations of rigid units of WO_4 and ZrO_6. A combination of rigid units with loosely pack group in structures often leads to a balance of NTE and normal positive thermal expansion, resulting in ZTE as in cubic $Fe[Co(CN_6)]$,[20] a Prussian Blue analogue. More often, such a combination can give large anisotropic expansions in non-cubic crystals, like area NTE in $LiBeBO_3$[11] and area ZTE in $KZnB_3O_6$.[22]

The latter compound is the first and the only borate that contains edge-sharing BO_4 tetrahedra synthesized under ambient pressure up to now.[28, 29] It possesses a novel property: an area ZTE plane from room temperature up to 1013K.[22] This means the expansion along the direction perpendicular to the ZTE plane can account for the total volume expansion, i.e. the unidirectional expansion. It was thought that this unusual thermal behavior arises from cooperative rotations of rigid groups B_6O_{12} and Zn_2O_6, and very asymmetrical elongation of K-O bonds upon heating.[22] In particular, the alkali metal ion is weakly bonded in an oversized atomic cage formed by oxygen atoms. A similar presence of rare earths has been shown to cause low-energy vibrational modes in filled skutterudites.[30] It is known that the NTE phenomenon typically originates from the presence of low-energy anharmonic vibrations.[6, 20] Here we report the effect of partial substitutions for K site on the thermal expansion behavior of $KZnB_3O_6$. The Rb partial substitution decreases the volume thermal expansion and leads to area NTE in $KZnB_3O_6$, whereas Na partial substitution has opposite effects. The difference in roles of alkali metals is then understood from their phonon modes at low-energies.

Polycrystalline samples of $K_{1-x}M_xZnB_3O_6$ (M = Na and Rb) were synthesized by solid-state reactions of the stoichiometric mixtures of A.R. Na_2CO_3/K_2CO_3/Rb_2CO_3, H_3BO_3 and ZnO. The preparing details can be consulted elsewhere[22] or in the electronic supplementary information (ESI†). It is found that solid solutions $K_{1-x}M_xZnB_3O_6$ with $x \leq 0.8$ exist for both Na and Rb substitutions for K. Fig. 1 shows the X-ray diffraction patterns of $K_{0.5}M_{0.5}ZnB_3O_6$ (M = Na, K[22] and Rb). A closer view of the enlargement of 2θ = 21° ~ 30° portion indicates that all peaks shift unevenly towards low-angles for $K_{0.5}Rb_{0.5}ZnB_3O_6$, while toward high-angles for $K_{0.5}Na_{0.5}ZnB_3O_6$, compared to peaks of $KZnB_3O_6$. All peaks can be indexed based on triclinic cells with high

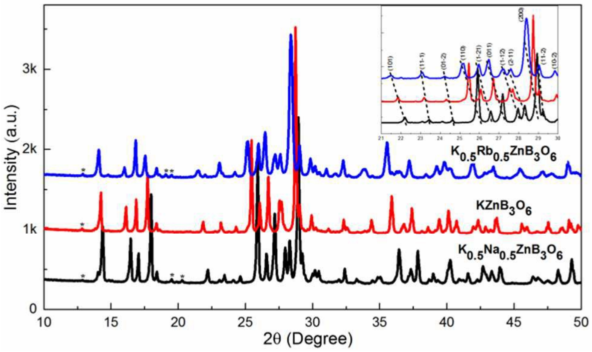

Fig. 1 The X-ray diffraction patterns of $K_{0.5}M_{0.5}ZnB_3O_6$ (M = Na, K[22] and Rb), the inset is the enlargement of 2θ = 21° ~ 30° portion, which shows that all peaks shift unevenly towards low-angles from $K_{0.5}Na_{0.5}ZnB_3O_6$ to $KZnB_3O_6$, and then to $K_{0.5}Rb_{0.5}ZnB_3O_6$, reflecting the K in $KZnB_3O_6$ has been partly replaced by Na and Rb. The stars show the impurity peaks.

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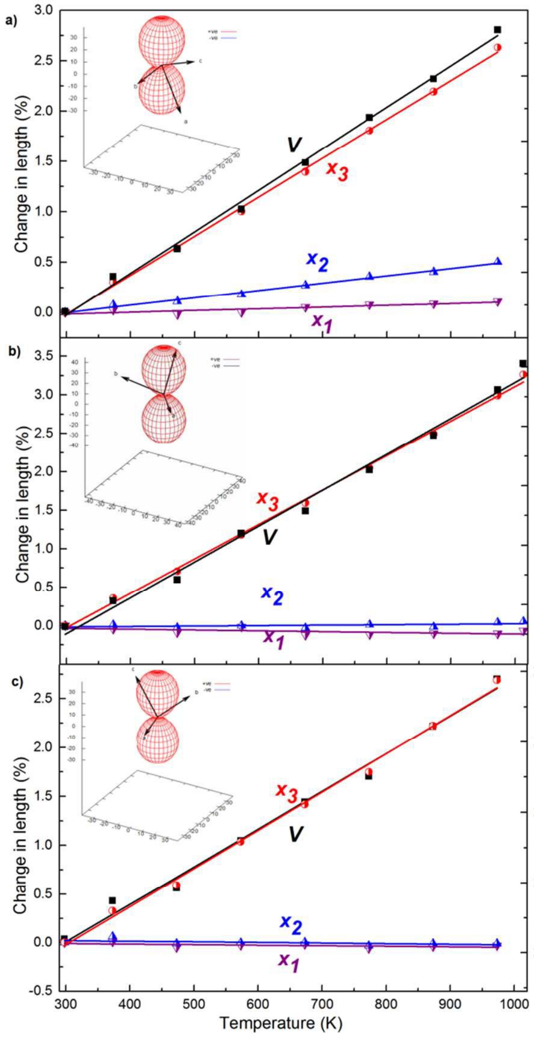

Fig. 2 Thermal expansion behavior of $K_{0.5}M_{0.5}ZnB_3O_6$ (M = Na, K[22] and Rb). The solid squares, half-filled circles, half-filled triangles stand for experimental data, the lines are fitting results. Inset: The thermal expansivity indicatrix, which describes the expansion rate in all directions in the set of orthogonal axes. a) $K_{0.5}Na_{0.5}ZnB_3O_6$; b) $KZnB_3O_6$[22]; c) $K_{0.5}Rb_{0.5}ZnB_3O_6$. x_1 and x_2 become more parallel to each other from upper to lower.

Table 1 The expansivity α from room temperature to 973 K for $K_{0.5}M_{0.5}ZnB_3O_6$ (M = Na and Rb). The data for $KZnB_3O_6$[22] are included here for comparison.

	α(MK^{-1})		
Axes	$K_{0.5}Na_{0.5}ZnB_3O_6$	$KZnB_3O_6$[22]	$K_{0.5}Rb_{0.5}ZnB_3O_6$
x_1	1.73(26)	-1.05(41)	-0.55(26)
x_2	7.29(23)	0.56(31)	-0.62(36)
x_3	38.65(48)	44.80(78)	39.10(89)
V	48(1)	44(1)	38(1)

figure of merits by using Dicvol06[31] except a few impurity peaks with intensities less than 3%. The lattice constants for $K_{0.5}M_{0.5}ZnB_3O_6$ (M = Na, K[22] and Rb) are deposited in Table S1 (see ESI†). The variation of lattice constants a, b, c and V with temperatures for $K_{0.5}M_{0.5}ZnB_3O_6$ (M = Na, K[22] and Rb) are shown in Fig. S1 (see ESI†). We can clearly see that the thermal expansions of these three compounds exhibit strong anisotropic behavior with increasing temperatures. Since the crystallographic axes of the present triclinic unit cell are chosen by convention, the variations in the lattice constants will not always reflect the fundamental thermal response of the compounds. Meanwhile, for any system there exists a unique set of orthogonal axes (the principal axes) along which the material responds in a purely linear fashion, either expanding or contracting, with the response along other directions involving nonzero shear components. To this end, we applied software PASCal[32] to find the set of orthogonal axes x_1, x_2 and x_3 by transforming the unit cell data at all measured temperatures. (see Fig. 2). The linear thermal expansivity along x_1 and x_2 axes are 1.73(26) MK^{-1} and 7.29(23) MK^{-1} for $K_{0.5}Na_{0.5}ZnB_3O_6$, -1.05(41) MK^{-1} and 0.56(31) MK^{-1} for $KZnB_3O_6$,[22] -0.55(26) MK^{-1} and -0.62(36) MK^{-1} for $K_{0.5}Rb_{0.5}ZnB_3O_6$, and the area thermal expansivity in the x_1-x_2 plane is 9.02(49) MK^{-1} for $K_{0.5}Na_{0.5}ZnB_3O_6$, -0.49(72) MK^{-1} for $KZnB_3O_6$,[22] -1.18(62) MK^{-1} for $K_{0.5}Rb_{0.5}ZnB_3O_6$, respectively (see Table 1). The results show that the area ZTE plane in $KZnB_3O_6$ becomes normal positive expansion in $K_{0.5}Na_{0.5}ZnB_3O_6$, while becomes area NTE in $K_{0.5}Rb_{0.5}ZnB_3O_6$. Moreover, x_1 and x_2 become more parallel to each other from $K_{0.5}Na_{0.5}ZnB_3O_6$ (Fig. 2a) to $KZnB_3O_6$[22] (Fig. 2b), and then to $K_{0.5}Rb_{0.5}ZnB_3O_6$ (Fig. 2c), indicating that the thermal expansivity become more isotropic in the planes. The unusual thermal expansions imply that distinct vibrational modes may exist in these materials, which are usual in low-energies as in the case with ZrW_2O_8.[6]

To investigate further the distinct vibrational modes of the compounds $K_{0.5}M_{0.5}ZnB_3O_6$ (M = Na, K and Rb), we measured their specific heat (C_p) from 2 to 45 K. The results illustrate the significant differences in the low-temperature behavior of the three compounds (see inset of Fig. 3), i.e., the C_p values increased monotonically from $K_{0.5}Na_{0.5}ZnB_3O_6$ to $KZnB_3O_6$ and then to $K_{0.5}Rb_{0.5}ZnB_3O_6$, especially at higher temperature range. We find that the C_p deviates somewhat from simple Debye behavior, the addition of a quantized harmonic oscillator (Einstein oscillator) is required in order to model the C_p of the three compounds (see Fig. S2, ESI†). Fig. 3 shows the fitted results along the experimental data for comparison for $KZnB_3O_6$ as an example. As illustrated in Fig. 3, the black line represents the fit result for $KZnB_3O_6$ to the equation[30]:

$$C_p = a\left[9R\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{x^4e^x}{(e^x-1)^2}dx\right] + b\left[3R\frac{(\theta_E/T)^2e^{\theta_E/T}}{(e^{\theta_E/T}-1)^2}\right]$$

Where the first term is Debye model, the second is Einstein model, a and b are their weight respectively. θ_D is Debye temperature and θ_E is Einstein temperature, R is gas constant. The obtained b are 0.051 for $K_{0.5}Na_{0.5}ZnB_3O_6$, 0.055 for $KZnB_3O_6$ and 0.073 for $K_{0.5}Rb_{0.5}ZnB_3O_6$. Those values are approaching but still less than 1/11 = 0.091, a value obtained by treating the alkali metals as pure

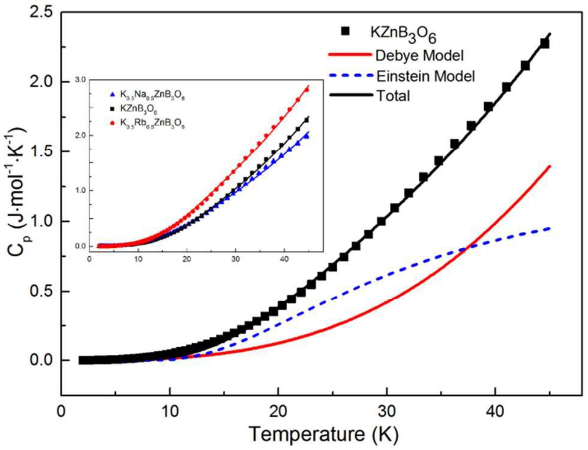

Fig. 3 The specific heat of $KZnB_3O_6$ (symbols) and the fitting result. The red line stands for Debye model; the blue short dash stands for Einstein model; the black line stands for the sum fitting result of Debye and Einstein model. Inset: the specific heat of $K_{0.5}M_{0.5}ZnB_3O_6$ (M = Na, K and Rb) and their sum fitting results of Debye and Einstein model.

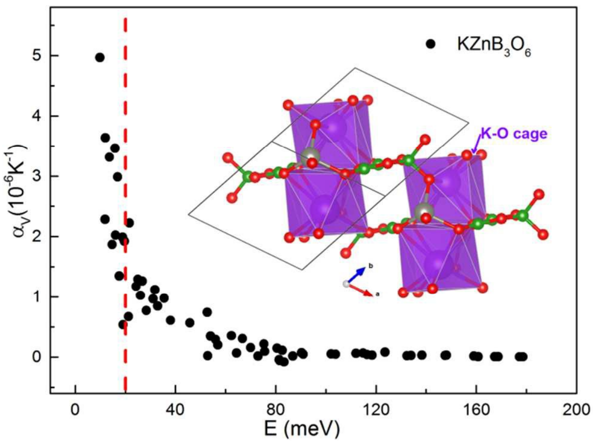

Fig. 4 Each mode of energy *E(q,j)* contributes to the volume thermal expansion coefficient α_V as a function of *E(q,j)* at 298K in $KZnB_3O_6$. Inset: The crystal structure of $KZnB_3O_6$. The purple polyhedra are KO_9 cages, gray balls stand for Zn atoms, green balls for B atoms, and red balls for O atoms.

harmonic oscillators. The results suggest that the coupling between the alkali metals with the cage oxygens decreased continually from Na to K, and then to Rb. The obtained θ_E are 90 K for $K_{0.5}Na_{0.5}ZnB_3O_6$, 97 K for $KZnB_3O_6$ and 90 K for $K_{0.5}Rb_{0.5}ZnB_3O_6$, corresponding to mode energies 7.76 meV, 8.36 meV and 7.76 meV. The fact that an Einstein oscillator is required to model each data indicates that the distinct localized modes may exist in these compounds, which are consistent with the results of the thermal expansions.

In order to investigate the role of different modes of phonons in thermal expansion, we first calculated the phonon dispersions and phonon density of states based on the experimental lattice parameters of $KZnB_3O_6$ at 298 K for $MZnB_3O_6$ (M = Na, K[22] and Rb), the computational methods and details are archived in the electronic supplementary information (ESI†). Each mode of energy *E(q,j)* contributes to the volume thermal expansion coefficient α_V[10,33,34] equals to $(1/BV)\,\Gamma\,(q,j)C_V\,(q,j,T)$, where V is the unit cell volume, B is the bulk modulus; $\Gamma(q,j) = -\,\partial ln\omega(q,j)/\partial lnV$ is the mode Grüneisen parameters, which define the relative change of mode frequency with volume V; $C_V\,(q,j,T) = \partial E(q,j)/\partial T$ is the contribution of the *j*th phonon mode to the specific heat; $E(q,j) = (n+1/2)\hbar\omega(\mathrm{q,j})$, $n = [\exp(\hbar\omega(\mathrm{q,j})/\mathrm{kT}) - 1]^{-1}$. The calculated contribution of phonons of energy *E(q,j)* to the volume thermal expansion coefficient α_V as a function of *E(q,j)* at 298 K (see Fig. 4) for $KZnB_3O_6$ shows that the main contribution to α_V is from phonons below 20 meV. This means that overall thermal expansions in $KZnB_3O_6$ are mainly contributed from the low-energy vibrational modes. Examination of the structure reveals that the alkali metal is weakly bonded in the oversized atomic cage of nine oxygen atoms (see inset of Fig. 4). The bondlengths within the cage are nonuniform, being more striking on going from Rb, to K and then to Na (see Table S2, ESI†). It is then anticipated that the vibrational modes become more diffuse accordingly.

Now we get down to the size effect of alkali metals on the phonon modes. The phonon dispersion of $MZnB_3O_6$ (M = Na, K[22] and Rb) (see Fig. S3, ESI†) are similar, but with low-energy modes downshifting on going from Na to K, and then to Rb. The partial density of phonon states contributed by alkali metals in $MZnB_3O_6$ (M = Na, K[22] and Rb) are shown in Fig. 5, showing that the most densities of phonon states of alkali metals lie below 20 meV, except an obvious peak located between 20 and 30 meV for Na. The distribution of the density of phonon states becomes more local upon the substitution of Rb for K, while more diffuse with the appearance of additional vibrational modes upon the substitution of Na for K, which confirms our anticipation.

If we simply model the alkali metals as localized harmonic oscillators, then the vibrational frequency ω equals to $(1/2\pi)\sqrt{k/m}$, where m is the mass of the harmonic oscillator and k the Hooke coefficient. There is

$$\omega_{\mathrm{Na}} : \omega_{\mathrm{K}} : \omega_{\mathrm{Rb}} = 21\sqrt{k_{Na}} : 16\sqrt{k_K} : 11\sqrt{k_{Rb}}\ .$$

Meanwhile, we note from Fig. 5 that the highest frequency of the three alkali metals $\omega_{Na(max)}$: $\omega_{K(max)}$: $\omega_{Rb(max)}$ = 180 cm^{-1} (22 meV) : 135 cm^{-1} (17 meV) : 90 cm^{-1} (11 meV) = 22 : 17 : 11, suggesting that the simple harmonic oscillator model is valid considering the chemical environments around those alkali metals are similar, i.e., $k_{Na} \approx k_K \approx k_{Rb}$. Beside those localized harmonic oscillator models, the more diffuse phonon states at lower frequencies should be from anharmonic vibrations, which become more confined from Na, K to Rb and indicating the decreased coupling with the cage oxygens in these compounds. The result agrees well with the heat capacity measurements and explained the decreased volume expansivities, 48 (1) MK^{-1} for $K_{0.5}Na_{0.5}ZnB_3O_6$, 44 (1) MK^{-1} for $KZnB_3O_6$,[22] 38 (1) MK^{-1} for $K_{0.5}Rb_{0.5}ZnB_3O_6$ (see Table 1). Thus, the size and mass of alkali metals have a substantial effect on these low-energy modes and subsequently alter the unusual thermal behavior.

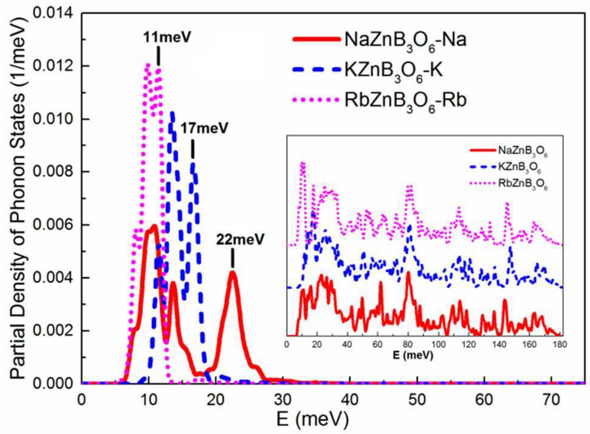

Fig. 5 The partial density of phonon states of alkali metals in $M\text{ZnB}_3\text{O}_6$ (M = Na, K[22] and Rb). It shows that the densities of phonon states of alkali metals become more diffuse from Rb to K, then to Na. The peaks of 11 meV, 17meV and 22 meV are their harmonic terms, respectively, and the others are anharmonic terms. Inset: The density of phonon states of $M\text{ZnB}_3\text{O}_6$ (M = Na, K[22] and Rb).

In conclusion, the driving force for the unidirectional thermal expansion of KZnB_3O_6 has been investigated by the alkali metals substitution and first-principles calculations. Partial substitution of K by Na and Rb changed the observed thermal expansion behavior, i.e., the thermal expansion behavior of the title compound can be continually tuned from common thermal expansion to area ZTE and then to area NTE, which imply that distinct vibrational modes may exist in these materials. The fitting results of the experimental specific heat further confirm the existence of distinct localized vibrational modes. The calculated results show that the main contribution to the volume thermal expansion coefficient is from phonon modes below 20 meV, which are mainly from the alkali metals. The partial density of phonon states of alkali metals in $M\text{ZnB}_3\text{O}_6$ (M = Na, K and Rb) become more local from KZnB_3O_6 to RbZnB_3O_6, while more diffuse to NaZnB_3O_6, indicating the broadening of the low-energy peaks leads to an increase in volume thermal expansion. Above all, this work reveals that the size and mass of alkali metals have profound effects on the unusual thermal behavior of *es*-KZnB_3O_6, which probably provide useful helps in designing novel materials of ZTE property.

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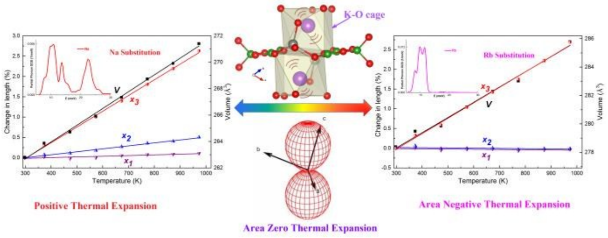

The size and mass of alkali metals have profound effects on the area zero thermal expansion behavior of edge-sharing $KZnB_3O_6$.