Electronic Supplementary Material (ESI) for CrystEngComm.

A thermodynamic criterion for the choice of flux and its validity in the $NaBO_2$-fluxed β-BaB_2O_4 crystal growth

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Growth of the β-BaB_2O_4 crystal

BaB_2O_4 polycrystalline raw material was synthesized through a solid-state reaction. Stoichiometric amounts of $BaCO_3$ (99.0%, Aladdin) and H_3BO_3 (99.5%, Sinopharm Chemical Reagent Co. Ltd.) were ground and mixed thoroughly in a mortar and loaded into a corundum crucible. Then, the mixture was heated at 850°C for 48 hours with an intermediate grind. $NaBO_2$ polycrystalline raw material was synthesized following a similar procedure, using Na_2CO_3 (99.8%, Sinopharm Chemical Reagent Co. Ltd.) and H_3BO_3 as the reactants and heating the mixture at 700°C.

BaB_2O_4 and $NaBO_2$ polycrystalline raw materials were mixed with a molar ratio of BaB_2O_4: $NaBO_2$ = 3: 4, heated in a platinum crucible, and eventually melted into a uniform high temperature solution. The solution temperature was carefully adjusted until the saturation point (876 ℃) was reached. After that, a BaB_2O_4 seed crystal was immersed in the saturated solution and started to grow. During the growth process, the cooling rate was kept at 1.0°C/day and the crystal rotation rate was kept at 5 rpm. Finally, transparent single crystals were obtained (Fig. S1a).

The phase of the obtained crystals was identified by the X-ray powder diffraction (XRPD) method. The XRPD patterns were collected on a computer-controlled TTR-III diffractometer equipped with graphite-monochromatized Cu Kα radiation (λ = 1.54056 Å). A typical experimental XRPD pattern is shown in Fig. S1b, which is in good agreement with the standard pattern of β-BaB_2O_4 (JCPDS No. 24−86), indicating that the product is the β-BaB_2O_4 crystal.

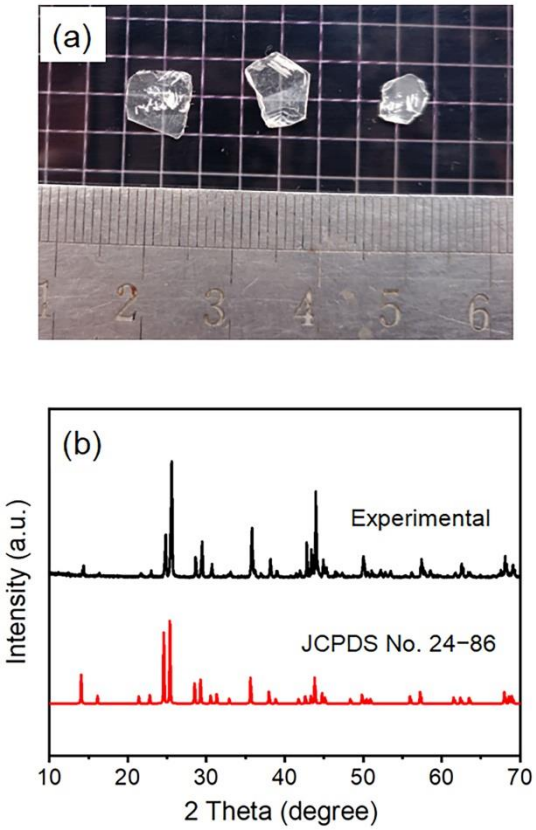
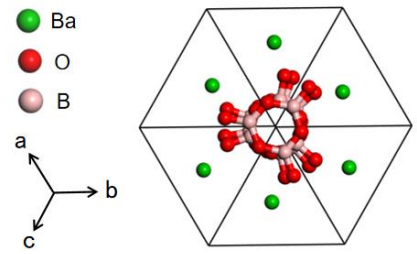


Fig. S1 (a) β-BaB_2O_4 crystals grown by the flux method. (b) A typical experimental XRPD pattern of the obtained crystals and the standard XRPD pattern of β-BaB_2O_4.

Computations for the band structures and thermodynamic properties of β-BaB_2O_4 and $NaBO_2$

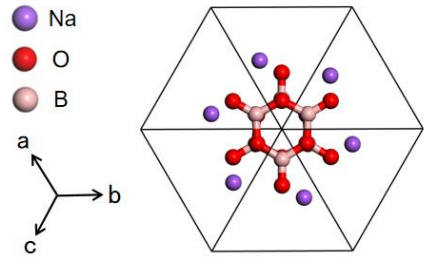
The band structures and thermodynamic properties (*i.e.* the contribution of lattice vibration to the atomic chemical potential in this work) of β-BaB_2O_4 and $NaBO_2$ were performed using density functional theory (DFT) implemented in the Cambridge Sequential Total Energy Package (CASTEP).[1] The reported crystal structures of β-BaB_2O_4 and $NaBO_2$ were adopted as the initial structural models.[2,3] Plane wave basis sets and norm-conserving pseudo-potentials were used in all computations. According to convergence tests, an energy cutoff of 750 eV was employed to expand the plane waves; a 2 × 2 × 2 Monkhorst-Pack *k*-point grid was used to sum over the Brillouin zones. The valence electron configurations were $5s^25p^66s^2$ for barium, $2s^22p^63s^1$ for sodium, $2s^22p^1$ for boron, and $2s^22p^4$ for oxygen. The convergence thresholds between two neighboring optimization cycles for the total energy change, maximum displacement, maximum force, and maximum stress were set as 10^{-6} eV/atom, 0.001 Å, 0.03 eV/Å, and 0.05 GPa, respectively.

The Perdew−Burke−Ernzerhof (PBE) functional of the generalized gradient approximation (GGA) was chosen to describe the exchange−correlation energy in the β-BaB_2O_4/$NaBO_2$ structural optimization and in the thermodynamic property study.[4] On the basis of the GGA-PBE optimized structures (with the benchmark volume at 0 K and different expanded volumes at different temperatures), the Heyd−Scuseria−Ernzerhof 06 (HSE06) screened hybrid functional were employed to get accurate band structures.[5]



Formula: β-BaB_2O_4
Space group: *R*3*c* (No. 161)
Primitive cell parameters:
$a = b = c = 8.5062$ Å
$\alpha = \beta = \gamma = 96.03°$
$Z = 6$

Fig. S2 Optimized structural model and primitive cell parameters of β-BaB_2O_4.



Formula: $NaBO_2$
Space group: *R*$\bar{3}$*c* (No. 167)
Primitive cell parameters:
$a = b = c = 7.2623$ Å
$\alpha = \beta = \gamma = 111.25°$
$Z = 6$

Fig. S3 Optimized structural model and primitive cell parameters of $NaBO_2$.

Estimation of the atomic chemical potentials of β-BaB_2O_4 and $NaBO_2$

In density functional theory, the atomic chemical potential (ACP) of a solid (with the chemical formula of $M_1^{n_1}\ldots M_i^{n_i}\ldots M_n^{n_n}$) is defined as the negative of its electronegativity, and can be estimated through the following formula[6]

$$\mu = -\left[\prod_{i=1}^{n}\left(\chi_{\mathrm{M}_i}^{n_i}\right)\right]^{1/n} \qquad (1)$$

where, μ is the atomic chemical potential of the solid, χ_{Mi} is the electronegativity of the *i*th constituent atom, n is the total number of atoms in the chemical formula ($n = n_1 + n_2 + \cdots + n_n$). As shown in Table 1, the calculated ACPs of β-BaB_2O_4 and $NaBO_2$ are −5.45 eV and −5.14 eV, respectively, and the calculated ACP difference is 0.315 eV.

Table. S1 Atomic chemical potentials (ACPs) of β-BaB_2O_4 and $NaBO_2$

Crystal	Atom	χ_M [a]	ACP (eV)	ACP difference (eV)
β-BaB_2O_4	Ba	2.40	−5.45	0.31 eV
	B	4.29		
	O	7.54		
$NaBO_2$	Na	2.85	−5.14	
	B	4.29		
	O	7.54		

[a] χ_M is the electronegativity of the constituent atom on Mulliken scale.[7]

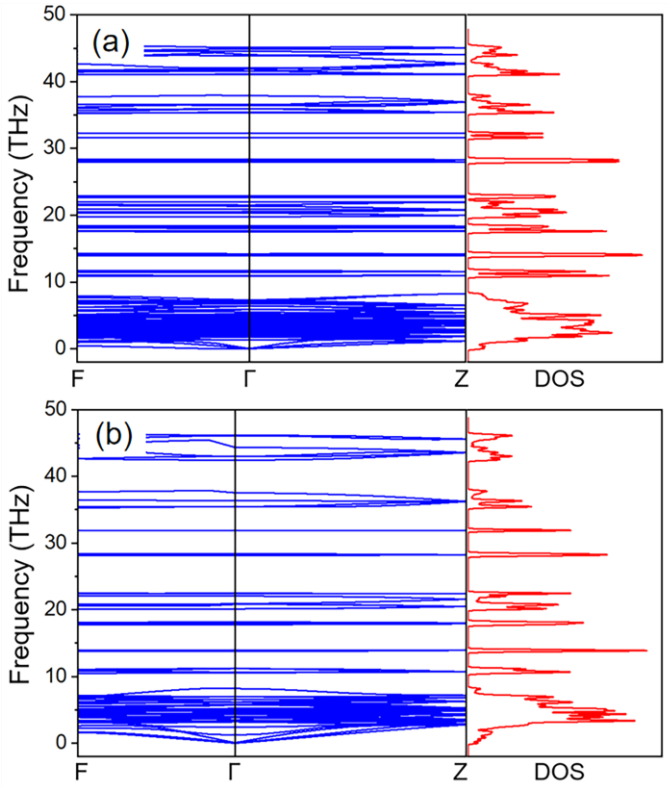


Fig. S4 Computational phonon dispersions (blue lines) and densities of states (red lines) for (a) β-BaB_2O_4 and (b) $NaBO_2$.

Table. S2 Primitive cell parameters of β-BaB_2O_4 and $NaBO_2$ at different volume expansion rates

$\Delta V/V$ (%)	β-BaB_2O_4[a]			$NaBO_2$[a]		
	a (Å)	α (°)	V (Å^3)	a (Å)	α (°)	V (Å^3)
0	8.5062	96.03	604.45	7.2623	111.25	273.68
2	8.5554	95.62	616.54	7.2909	111.08	279.15
4	8.6040	95.18	628.63	7.3174	110.89	284.62
6	8.6524	94.74	640.72	7.3410	110.68	290.10
8	8.7006	94.29	652.81	7.3644	110.47	295.57
10	8.7477	93.75	664.90	7.3865	110.24	301.05

[a] β-BaB_2O_4 and $NaBO_2$ crystallize in the trigonal crystal system; therefore, $a = b = c$, $\alpha = \beta = \gamma$.

Table. S3 Computational valence-band-edge (E_{VB}) and conduction-band-edge (E_{CB}) positions of β-BaB_2O_4 and $NaBO_2$ with different expansion ratios and the corresponding atomic chemical potentials

$\Delta V/V$ (%)	β-BaB_2O_4			$NaBO_2$		
	E_{CB} (eV)	E_{VB} (eV)	ACP (eV)	E_{CB} (eV)	E_{VB} (eV)	ACP (eV)
0	5.728	−0.671	2.528	5.587	−0.0017	2.793
2	5.544	−0.776	2.384	5.387	−0.121	2.633
4	5.367	−0.881	2.243	5.195	−0.234	2.481
6	5.197	−0.981	2.108	5.011	−0.339	2.336
8	5.034	−1.077	1.978	4.834	−0.440	2.197
10	4.873	−1.178	1.847	4.666	−0.535	2.065

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