Pressure-induced phase transitions in $\text{Na}_2\text{B}_{12}\text{H}_{12}$, structural investigation on a candidate for solid-state electrolyte

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closo-Borates, such as $\text{Na}_2\text{B}_{12}\text{H}_{12}$, are an emerging class of ionic conductors that show promising chemical, electrochemical and mechanical properties as electrolytes in all-solid-state batteries. Motivated by theoretical predictions, high-pressure *in situ* powder X-ray diffraction on $\text{Na}_2\text{B}_{12}\text{H}_{12}$ was performed and two high-pressure phases are discovered. The first phase transition occurs at 0.5 GPa and it is persistent to ambient pressure, whereas the second transition takes place between 5.7 and 8.1 GPa and it is fully reversible. The mechanisms of the transitions by means of group theoretical analysis are unveiled. The primary-order parameters are identified and the stability at ambient pressure of the first polymorph is explained by density functional theory calculations. Finally, the parameters relevant to engineer and build an all-solid-state battery, namely, the bulk modulus and the coefficient of the thermal expansion are reported. The relatively low value of the bulk modulus for the first polymorph (14 GPa) indicates a soft material which allows accommodation of the volume change of the cathode during cycling.

1. Introduction

All-solid-state batteries have a promising future for the next generation of batteries as the performance of their solid electrolytes may exceed the thermal and electrochemical stabilities of liquid electrolytes. They also exhibit transference numbers (ratio of electrical current derived by the cation) close to unity which enable higher power and energy density than batteries based on liquid electrolytes. Furthermore, solid-state batteries promise higher operational safety as they overcome the use of a flammable liquid electrolyte and leakages are prevented (Choi & Aurbach, 2016). However solid-state electrolytes usually have low ionic conductivity and reduced contact area with the electrodes, hindering their development in real life applications (Choi & Aurbach, 2016). There is a promising, yet under-investigated, new class of solid-state electrolytes, namely the *closo*-borates and related compounds, that combine high conductivity with electrochemical and thermal stabilities. Up to now, the conduction mechanism in these materials is not known in detail. For the sodium and lithium salts these materials display a common feature: they undergo a structural phase transition, driven by the temperature, to a dense (often close-packed) structure that is highly conductive (Udovic, Matsuo, Unemoto *et al.*, 2014; Tang *et al.*, 2015; Udovic, Matsuo, Tang *et al.*, 2014; Tang,

Matsuo, Wu, Stavila, Zhou *et al.*, 2016). For instance, sodium dodecahydro-*closo*-dodecaborate ($\text{Na}_2\text{B}_{12}\text{H}_{12}$) adopts a body-centered cubic (b.c.c.) packing at 529 K allowing a superionic conductivity of 0.1 S cm^{-1} (Udovic, Matsuo, Unemoto *et al.*, 2014). As this temperature is too high for practical applications, different strategies have been proposed in order to decrease this temperature (He *et al.*, 2015; Sadikin *et al.*, 2015; Tang, Yoshida *et al.*, 2016; Duchene, Kühnel, Rentsch *et al.*, 2017). One of them, anion mixing, led to the discovery of a solid-electrolyte based on a solid-solution of deca- and dodecaborate ($\text{Na}_4[(\text{B}_{12}\text{H}_{12})(\text{B}_{10}\text{H}_{10})]$). This material has a high ionic conductivity of 0.9 mS cm^{-1} at room temperature, exceeding those of its precursors by orders of magnitude (Udovic, Matsuo, Unemoto *et al.*, 2014; Duchene, Kühnel, Rentsch *et al.*, 2017). Combined with an impregnation technique to enhance the contact between electrolyte and cathode material, a stable all-solid-state 3 V battery with excellent capacity and cyclability has been demonstrated (Duchene, Kühnel, Stilp *et al.*, 2017). Furthermore, Moury *et al.* (2017) showed that $\text{Na}_2\text{B}_{12}\text{H}_{12}$ can be prepared in a three-step synthesis starting from the cheapest borohydride, NaBH_4 , decreasing the price of production and making these materials available for further study.

At ambient pressure and room temperature, $\text{Na}_2\text{B}_{12}\text{H}_{12}$ crystallizes in monoclinic space group $P2_1/c$, replacing the $[\text{B}_{12}\text{H}_{12}]^{2-}$ anion by the smaller $[\text{B}_{10}\text{H}_{10}]^{2-}$ anion to get solid-solution $\text{Na}_4[(\text{B}_{12}\text{H}_{12})(\text{B}_{10}\text{H}_{10})]$, resulting in face-centered cubic packing (Duchene, Kühnel, Rentsch *et al.*, 2017), which can be interpreted as adding chemical pressure within the structure of $\text{Na}_2\text{B}_{12}\text{H}_{12}$. Furthermore, Aniya (1992) presented a criterion about super ionic conductor materials that should undergo a structural phase transition at low pressure, and several reports have shown that some superionic conductors do undergo to a structural phase transition at relatively low pressure. This criterion was confirmed in several reports [see Hull (2004) and references therein]. Motivated by these, we studied the structural evolution of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ with pressure, in order to verify this behavior in the class of *closo*-borates.

Interestingly, we observed a rich phase diagram and report two new high-pressure polymorphs for $\text{Na}_2\text{B}_{12}\text{H}_{12}$ with the following transition sequence: $P2_1/c$ (α -polymorph) $\rightarrow$ $Pbca$ (ε -polymorph) $\rightarrow$ $Pnnm$ (ζ -polymorph). The first transition was indeed recorded at relatively low pressures: between 0.3 and 0.5 GPa, confirming the criteria proposed by Aniya (1992). The second transition occurs at higher pressure between 5.7 and 8.1 GPa. We discuss and compare the structure in detail. By means of group theoretical analysis we identify the primary order parameters for the transitions. We perform density functional theory (DFT) calculations on $\text{Na}_2\text{B}_{12}\text{H}_{12}$ which reveal that the $Pbca$ symmetry is the most stable compound over a broad range of pressures which is experimentally observed by the irreversibility of the first transition [$P2_1/c$ (α -polymorph) $\rightarrow$ $Pbca$ (ε -polymorph)]. Finally, using experimental data combined with DFT calculations we extract the bulk and shear modulus and the coefficient of the thermal expansion (CTE) for $\text{Na}_2\text{B}_{12}\text{H}_{12}$, which are important parameters for the design of an all-solid-state battery.

2. Experimental

2.1. Powder X-ray diffraction

Sodium dodecahydro-*closo*-dodecaborate ($\text{Na}_2\text{B}_{12}\text{H}_{12}$) powder was purchased from Katchem company. The sample was measured at the Swiss–Norwegian Beam Lines of the European Synchrotron Radiation Facility in Grenoble, France. The wavelength was $0.71414 \text{ \AA}$. A 2D image plate detector Pilatus 2M pixel area detector was used placed at 411 mm from the sample. The 2D diffraction patterns were integrated with *Bubble* (Dyadkin *et al.*, 2016) software. The sample detector geometry was calibrated with an LaB_6 NIST standard. The diamond anvil cell, with flat culet of diameter $600 \text{ }\mu\text{m}$, was loaded in an MBraun argon-filled glove box ($\text{O}_2 < 0.1 \text{ p.p.m.}$, $\text{H}_2\text{O} < 0.1 \text{ p.p.m.}$). The sample was loaded together with ruby crystals, for pressure calibration, into a hole of $250 \text{ }\mu\text{m}$ drilled in a stainless-steel gasket. No pressure transmitting medium was used owing to the low bulk modulus of this family of materials.

For the first transition, indexing of the diffraction pattern was performed using the *N-TREOR* (Altomare *et al.*, 2000) algorithm in the *EXPO* (Altomare *et al.*, 2013) program. The space group was verified with *Addsym* program in the *PLATON* (Spek, 2009) package. The crystal structure of the ε -phase was solved by the direct space method with a parallel tempering algorithm implemented in the *FOX* (Favre-Nicolin & Cerný, 2002) program; the refinement was made using the Rietveld method (Rietveld, 1969) in the *TOPAS* (Coelho, 2000) program. A comparison between calculated and experimental diffraction patterns is displayed in Fig. S1a. After the refinement, the following agreement factors were obtained, $R_{\text{wp}} = 0.066$, $R_p = 0.096$ (background corrected), and $\text{GOF} = 2.9$. The final positions for boron and hydrogen were optimized using DFT calculations (see below for details).

For ζ - $\text{Na}_2\text{B}_{12}\text{H}_{12}$, the structure was found by DFT calculations (see below for details) with space group $Pnnm$ (No. 58) and unit-cell parameters $a = 6.3039 (6)$, $b = 8.6652 (16)$ and $c = 7.0161 (19) \text{ \AA}$. Using the Rietveld method with *TOPAS*, we compared the theoretical pattern with the experimental one in order to validate the structure, during refinement only the sodium positions were refined to get a better agreement. A comparison between calculated and experimental patterns is shown in Fig. S1b. The following agreement factors were obtained after refinement $R_{\text{wp}} = 0.069$, $R_p = 0.08$ (background corrected) and $\text{GOF} = 2.3$.

2.2. Raman spectroscopy

Raman spectra were collected in a diamond anvil cell on a Renishaw 1000 spectrometer with a 633 nm excitation laser. The pressure was monitored using an internal ruby standard. The spectra were recorded between 500 cm^{-1} and 2700 cm^{-1} .

2.3. DFT calculations

DFT calculations were performed in order to resolve the structure of the ζ -polymorph; to refine the crystal structure of the high-pressure ε -polymorph and to determine their ther-

Table 1

Summary of the different polymorphs known for $\text{Na}_2\text{B}_{12}\text{H}_{12}$ up to now with their temperature and pressure stability range.

Polymorph	α	β	γ	δ	ε	ζ
Space group	$P2_1/c$	$Pm\bar{3}n$	$Im\bar{3}m$	$Fm\bar{3}m$	$Pbca$	$Pnnm$
a (Å)	7.083915	8.05511	8.134716	10.3950	9.71959	6.30201
b (Å)	10.747533	8.05511	8.134716	10.3950	10.8522	8.67046
c (Å)	9.714884	8.05511	8.134716	10.3950	9.22670	7.01125
β (°)	133.10928	—	—	—	—	—
T (K) range†	RT–540	511–587	587–700	587–700	—	—
P (GPa) range‡	0–0.5	—	—	—	0.5–5.7	>8.1

† At ambient pressure. ‡ At room temperature.

modynamic properties. The electronic ground state energy was calculated with plane wave formulation of the DFT method implemented in *Vienna Ab initio Simulation Package* (VASP) (Kresse & Furthmüller, 1996). The electronic configurations of $1s^1$ for H, $2s^22p^1$ for B, and $2p^63s^1$ for Na were represented by projected augmented wave potentials (Kresse & Joubert, 1999). The gradient-corrected exchange-correlation functional and the non-local correction accounting for weak dispersive interactions were applied. Both exchange and correlation electron density was based on revPBE functional (Perdew *et al.*, 1996; Dion *et al.*, 2004).

All considered crystal structures were optimized with respect to the internal atomic positions as well as the unit-cell parameters. For the highest pressure phase, an extensive structure search was performed considering the candidate structures with ion packing based on cubic-closed packing (c.c.p.), body-centered cubic (b.c.c.) packing, hexagonal-closed packing (h.c.p.), as well as structures based on Ag_2S (ICSD No. 262634), Co_2Si (ICSD No. 44858); Cu_2O (ICSD No. 190598). For each candidate structure the initial specific volume per formula unit was 200 Å^3 . Each structure was optimized with respect to: (i) the orientation of anions, (ii) cation positions within the unit cell and (iii) the shape of the unit cell. Each optimized structure was subjected to simulated annealing (heating to 350 K at a rate of 100 K ps^{-1} , cooling at a rate of 50 K ps^{-1}); and final re-optimization of the internal degrees of freedom. The symmetry was analyzed for the final

structures (Stokes & Hatch, 2005). When new symmetry was found, the structures were re-optimized with the symmetry constraints.

The charge of ions was analyzed with the Bader method (Henkelman *et al.*, 2006), the normal modes and the elastic properties were calculated with the finite displacement method (Hector *et al.*, 2007). The bulk modulus was calculated as the average of Voigt and Reuss moduli (Hill, 1952).

3. Results and discussion

3.1. High-pressure crystal structures

The polymorphs of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ will be named with Greek letters, as given in Table 1, in the following discussion. The ambient polymorph is denoted α , the three high-temperature polymorphs described therein (Verdal *et al.*, 2014) are denoted β , γ and δ . Temperature-induced-phase transitions will be discussed in the last section.

In this section, we report two pressure-induced phase transitions for the α - $\text{Na}_2\text{B}_{12}\text{H}_{12}$ measured at room temperature. The first pressure-induced transition occurs between 0.3 and 0.5 GPa. The second transition is observed between 5.4 and 8.1 GPa [Fig. 1(a)]. The crystal structure of this phase was determined by a simulated-annealing, global energy minimum search to have orthorhombic $Pnnm$ (ζ -phase) symmetry, as shown in Fig. S2. As it can be inferred from Fig. 1(b), the transition $\varepsilon \rightarrow \zeta$ is fully reversible and it has a hysteresis. In contrast, the transition $\alpha \rightarrow \varepsilon$ is irreversible or has a large hysteresis as it can be seen in Fig. 1(b), the ε -phase remains at ambient pressure.

The variation of volume as a function of pressure is shown in Fig. 2. Considering the volume per formula unit, we estimate the volume collapses by 4.8% during the transition $\alpha \rightarrow \varepsilon$. For the transition $Pbca \rightarrow Pnnm$, the volume decreases by 2.1%, smaller than the first transition but high enough to classify the transition as first order. The Murnaghan equation-

Figure 1
High-pressure *in situ* PXD patterns of $\text{Na}_2\text{B}_{12}\text{H}_{12}$. (a) During compression: blue diffraction pattern $P2_1/c$ (0 GPa, α -polymorph), red diffraction pattern $Pbca$ (0.5 GPa, ε -polymorph) and black diffraction pattern $Pnnm$ (8.1 GPa, ζ -polymorph). (b) During decompression: black diffraction pattern $Pnnm$ (8.1 GPa, ζ -polymorph), red diffraction pattern $Pbca$ (1.1 GPa, ε -polymorph) and blue diffraction pattern corresponds to the $Pbca$ (0 GPa, ε -polymorph) at ambient pressure (showing the irreversibility).

Figure 2
Variation of volume per formula unit as a function of pressure for α -, ε - and ζ - $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and for ε - $\text{Na}_2\text{B}_{12}\text{H}_{12}$ with the fit using Murnaghan equation-of-state [equation (1)].

of-state [equation (1)] was used to fit the volume change of the ε -polymorph (Murnaghan, 1944):

$$V(P) = V_0 \left(1 + B'_0 \frac{P}{B_0} \right)^{-1/B'_0}, \quad (1)$$

where V_0 is the volume at 0 pressure, B_0 the bulk modulus, and B'_0 is the first-pressure derivative of B_0 . The result is represented in Fig. 2. We determined that $V_0 = 250.7 \pm 0.4 \text{ \AA}^3$ per formula unit, $B_0 = 14.0 \pm 0.5 \text{ GPa}$ and $B'_0 = 6.1 \pm 0.2$. The bulk modulus for $\varepsilon\text{-Na}_2\text{B}_{12}\text{H}_{12}$ is lower than NaBH_4 revealing a higher compressibility (Kumar & Cornelius, 2005). It is noteworthy that, as for NaBH_4 , no pressure-transmitting medium was used leading to non-hydrostatic conditions, which could tend to overestimate the bulk modulus (Duffy *et al.*, 1999). In fact, inelastic X-ray scattering has been demonstrated to give more accurate values for the bulk modulus in the case of light borohydride compounds (Chernyshov *et al.*, 2008).

In view of potential applications, the high compressibility of $\varepsilon\text{-Na}_2\text{B}_{12}\text{H}_{12}$ is useful for absorbing volume changes of electrode materials during cycles.

The elastic properties were also calculated for each of the high-pressure phases at the equilibrium volume, similar to measurements presented above. For $\zeta\text{-Na}_2\text{B}_{12}\text{H}_{12}$, the B_0 value is calculated to be 14.0 GPa; $B_0 = 15.4 \text{ GPa}$ for $\varepsilon\text{-Na}_2\text{B}_{12}\text{H}_{12}$ and for the low-temperature phase with $P2_1/c$ symmetry $B_0 = 17.3 \text{ GPa}$. The shear modulus $G = 3.7, 6.9$ and 3.3 GPa for ζ -, ε - and α -polymorphs, respectively. The shear modulus is small for all compounds. Taking into account the polycrystalline nature of the powder sample, agreement with the experimental data for $\varepsilon\text{-Na}_2\text{B}_{12}\text{H}_{12}$ is good (14.0 GPa versus 15.4 GPa), validating the methodology used for DFT calculations. Previous calculations report $B_0 = 10.52 \text{ GPa}$ for $\alpha\text{-Na}_2\text{B}_{12}\text{H}_{12}$ (Lu & Ciucci, 2017). This is a lower value than the present calculations, however, different methodology was used in this work. Discrepancies of a similar order are noticed for the bulk modulus for NaBH_4 reported to vary between 16.27 GPa and 19.27 GPa (Lu & Ciucci, 2017).

Elastic properties close to normal conditions are of practical interest and extrapolation to V_0 presented above refers to such a situation. With increasing pressure, the bulk modulus increases due to the smaller interatomic distances. Thus, the high-pressure ζ -polymorph has the lowest B_0 value at the calculated equilibrium volume $V_0 = 259.9 \text{ \AA}^3$ per formula unit. With increasing volume, B_0 increases reaching values above 30 GPa for volumes $\sim 200 \text{ \AA}^3$ per formula unit that corresponds to the pressures above transition to $Pnmm$ symmetry.

The crystal structures of the ε - and ζ -polymorphs are reported in Figs. 3(a) and 3(b), respectively. A distorted f.c.c.-fashion packing is adopted by the $\text{B}_{12}\text{H}_{12}^{2-}$ anions in all three polymorphs. The transition $\alpha \rightarrow \varepsilon$ is a first-order displacive phase transition, with a direct group-subgroup relationship $Pbca \rightarrow P2_1/c$. For structure comparison, we have transformed the α -phase into a cell with f.c.c.-based packing and $P2_1/c$ symmetry using the following transformation matrix: $\mathbf{a}_{\text{fcc,mono}} = 2\mathbf{a}_{\text{mono}} + \mathbf{c}_{\text{mono}}$, $\mathbf{b}_{\text{fcc,mono}} = -\mathbf{b}_{\text{mono}}$ and $\mathbf{c}_{\text{fcc,mono}} = -\mathbf{c}_{\text{mono}}$ (Fig. S3a). For the second transition, there is no direct group-

subgroup relationship between $Pbca$ and $Pnmm$. However, for comparison, one can build a distorted f.c.c.-based cell using the following transformation matrix: $\mathbf{a}_{\text{fcc,mono}} = \mathbf{a}_{\text{bcc,ortho}} + \mathbf{c}_{\text{bcc,ortho}}$, $\mathbf{b}_{\text{fcc,mono}} = \mathbf{b}_{\text{bcc,ortho}}$ and $\mathbf{c}_{\text{fcc,mono}} = \mathbf{a}_{\text{bcc,mono}} - \mathbf{c}_{\text{bcc,ortho}}$ with a splitting of the Wyckoff positions 4g into the two positions 4e give an apparent $P2_1/c$ symmetry within this new cell, which is a subgroup of the $Pbca$ (Fig. S3b). Hence, the second transition can be described as a first-order displacive phase transition. It is noteworthy that the symmetry for the analogs of alkali dodecahydro-*closo*-dodecaborates with cations with higher radii, namely K, Rb and Cs, is $Fm\bar{3}$ (202) (Tiritiris & Schleid, 2003; Tiritiris *et al.*, 2000) whereas the symmetry is $Pa\bar{3}$ (205) in $\text{Li}_2\text{B}_{12}\text{H}_{12}$ (Her *et al.*, 2008). Interestingly, there is a chain of maximal subgroups from $Fm\bar{3}$ to $P2_1/c$ containing all the mentioned symmetries, which is $Fm\bar{3} \rightarrow Pa\bar{3} \rightarrow Pbca \rightarrow P2_1/c$ with f.c.c.-based packing. The $Pbca$ symmetry is connected to the higher space groups adopted by the analog alkali dodecahydro-*closo*-dodecaborates at room temperature.

In order to describe the mechanisms of the transitions, we performed a group theoretical analysis using *AMPLIMODES* (Orobengoa *et al.*, 2009; Perez-Mato *et al.*, 2010) on the Bilbao Crystallographic Server (Aroyo *et al.*, 2011; Aroyo, Perez-Mato *et al.*, 2006; Aroyo, Kirov *et al.*, 2006). Both transitions combine a diffusionless (martensitic-like) transformation and a displacement of sodium. Regarding the diffusionless transformation, in the first transition, the monoclinic lattice is brought into the orthorhombic one, as shown in Figs. 4(a), 4(b) and 4(c). The second transition has an orthorhombic lattice transformed into a monoclinic one [Figs. 4(d), 4(e) and 4(f)], combining shrinking and shearing for both transitions. The components of the strain tensor induced by the distortion of the lattice, in $\alpha \rightarrow \varepsilon$ transition, are rather small: $e_{11} = -0.0514$, $e_{22} = 0.0208$, $e_{33} = -0.0126$ and $e_{13} = e_{31} = 0.0093$. Therefore, we can conclude that the strains do not play an important role. The deformation of the orthorhombic lattice has a biaxial behavior in the second transition, and the diagonal components of the strain tensor are: $e_{22} = -0.1477$ and $e_{33} = 0.1342$, which are twice as high as the component $e_{11} = -0.0681$. Hence, spontaneous strains cannot be neglected in the order parameter for this transition. The second mechanism is the

Figure 3
Graphical representation of the crystal structure for (a) ε -polymorph ($Pbca$) and (b) ζ -polymorph ($Pnmm$): boron (green), hydrogen (white) and sodium (yellow).

diffusion of Na within the structure. The stability of the distorted structure could be rationalized by identifying the primary distortion modes: unstable modes in the high-symmetry structure. The analysis is made for the transitions $Pbca \rightarrow P2_1/c$ ($\alpha \leftarrow \varepsilon \rightarrow \zeta$). The group theoretical analysis allowed us to identify two modes, characterized by Γ^{1+} and Γ^{4+} for $\varepsilon \rightarrow \alpha$ [Figs. 5(a) and 5(b)], and by Γ^{1+} and Γ^{3+} for $\varepsilon \rightarrow \zeta$ [Figs. 5(c) and 5(d)] irreducible representations (irreps) at the Brillouin zone center. The primary modes breaking the symmetry, with $P2_1/c$ as the isotropy subgroup, are the Γ^{4+} and Γ^{3+} for the transitions $\varepsilon \rightarrow \alpha$ and $\varepsilon \rightarrow \zeta$, respectively. Hence, the primary mode responsible for the stabilization of the distorted structure at ambient pressure is Γ^{4+} . However, the amplitude of this mode is fairly high at 2.4 Å, which could explain the non-reversibility of the transition. This result agrees with DFT calculations revealing that $Pbca$ symmetry is the most thermodynamically stable compound over a broad range of pressure at 0 K (Fig. S2). Then, $P2_1/c$ symmetry found at RT and ambient pressure could be a metastable phase formed kinetically. It would be interesting to study the influence of the temperature on the $\varepsilon \rightarrow \alpha$ reversibility.

According to the present DFT calculation, octahedral interstitials are unstable for sodium in α - and ε - $\text{Na}_2\text{B}_{12}\text{H}_{12}$ but they are stable in the ζ -polymorph, the most stable sites being trigonal voids for the former polymorphs. These results are in agreement with the experiments. In fact, sodium is in a trigonal environment slightly out of the plane with improper torsion angles of 11.2° and 12.4° toward the tetrahedral sites in the α -polymorph and with improper torsion angles of 15.5° and 21.1° toward the octahedral sites in the ε -polymorph. During this transition, sodium is pushed in the direction of the octahedral voids (Figs. S4a and S4b), increasing the closest Na–Na distance from 4.46 to 4.57 Å. Regarding the ζ -polymorph, sodium cations get into the octahedral interstitials with improper torsion angles in the range of 23–34.3° out of the octahedral facets. Consequently, they tend to form dimers with Na–Na distances of 3.38 and 3.87 Å (Fig. S4c). The $\text{B}_{12}\text{H}_{12}^{2-}$

anions are in distorted octahedron for the three polymorphs, the ε -polymorph is the least distorted (Fig. S5). The angles between vertices are in the range of: 65.1–114.9° for α -, 86.3–93.7° for ε -, and 50.4–129.6° for ζ - $\text{Na}_2\text{B}_{12}\text{H}_{12}$. The length of the edges is in the range of 4.85–7.03 Å, 5.56–6.52 Å and 3.30–7.01 Å for α -, ε - and ζ - $\text{Na}_2\text{B}_{12}\text{H}_{12}$, respectively. In the ε -phase, four sodium cations are coordinated to the edges formed by two hydrogen cations in $\text{B}_{12}\text{H}_{12}^{2-}$ and two sodium cations are coordinated through the face formed by three H on the $\text{B}_{12}\text{H}_{12}^{2-}$ unit (Fig. S6b). The ζ -polymorph has four sodium cations coordinated to the faces and two sodium cations coordinated to the edges (Fig. S6c). The α -polymorph has two sodium cations coordinated through the faces and the other four are in between, tilted from the plane formed by the H–B–B–H edges by about 30° (Fig. S6a). A perfect octahedron would be obtained if the six sodium cations were coordinated to the edges of the $\text{B}_{12}\text{H}_{12}^{2-}$ unit.

Due to some large changes in the local ion environment between high-pressure phases, we performed analysis of the charges through the Bader space partitioning method. All three analyzed phases are strongly ionic with a calculated charge on sodium larger than +0.86 e. With increasing pressure (decreasing specific volume), the charge on ions reduces by about 2% in the range of specific volumes corresponding to our experiments. Interestingly, in ζ - $\text{Na}_2\text{B}_{12}\text{H}_{12}$ due to Na dimer formation the charge on sodium is larger than for other phases at similar volumes. Thus, migration of Na toward the octahedral void and formation of the Na–Na dimer allows the ionic character of the compound to be preserved.

It is interesting to specify that a similar phase sequence has been reported previously for ZrO_2 both as a function of temperature and as a function of pressure. These transitions have been discussed in detail using Landau theory and first-principles calculations (Fadda *et al.*, 2002; Wang *et al.*, 2015).

Figure 4

Representation of the transformation of the monoclinic lattice (α -polymorph $P2_1/c$, purple) into the orthorhombic lattice (ε -polymorph $Pbca$, red) along (a) a axis, (b) b axis and (c) c axis. Representation of the transformation of the orthorhombic lattice (ε -polymorph $Pbca$, red) into the monoclinic lattice (ζ -polymorph $Pnnm$) green) along (d) a axis, (e) b axis and (f) c axis. For the sake of clarity, sodium have been removed and the $\text{B}_{12}\text{H}_{12}^{2-}$ replaced by spheres.

Figure 5

Representation of the symmetry-adapted displacive modes described by the irreps (a) Γ^{1+} and (b) Γ^{4+} for the transition $\varepsilon \rightarrow \alpha$, and (c) Γ^{1+} and (d) Γ^{3+} for the transition $\varepsilon \rightarrow \zeta$. The $\text{B}_{12}\text{H}_{12}^{2-}$ anions are represented by purple spheres and sodium are in yellow.

3.2. High-pressure vibrational spectra

For isolated $\text{B}_{12}\text{H}_{12}^{2-}$, six Raman active modes are expected and observed in aqueous solution at 584 (H_g), 743 (A_g), 770 (H_g), 949 (H_g), 2475 (H_g) and 2518 (A_g) cm^{-1} (Sethio *et al.*, 2016, 2017). At room temperature and ambient pressure the site symmetry of the *closo*-borate anion is lowered to C_{2v} in the monoclinic $\text{Na}_2\text{B}_{12}\text{H}_{12}$ structure. Thus, the fivefold degenerate modes H_g are split into five components. Experimentally, at ambient pressure, the H_g normal mode around 584 cm^{-1} (Nogi & Tanaka, 2006) is split into two components (579 and 590 cm^{-1}). Two signals are observed at 751 and 768 cm^{-1} (A_g and H_g normal mode, respectively), as well as some weaker features. The band expected around 949 cm^{-1} is split into several weak peaks. The B–H stretching mode of the $\text{B}_{12}\text{H}_{12}^{2-}$ ion shows several components with maxima at 2484, 2503 and 2527 cm^{-1} (corresponding to H_g and A_g stretching modes), see Fig. 6.

With increasing pressure, all bands are shifted to higher frequencies owing to the contraction of B–H bonds. It should be emphasized that the magnitude of the pressure shift of the B–H stretching modes (*ca* 19 $\text{cm}^{-1} \text{GPa}^{-1}$) is similar to the one observed in $\text{Cs}_2\text{B}_{12}\text{H}_{12}$ up to 1 GPa (between 16 and 23 $\text{cm}^{-1} \text{GPa}^{-1}$) (Benham *et al.*, 1987). According to our theoretical calculations, this would correspond to a contraction of the B–H bond of 0.002 Å GPa^{-1} (Hagemann *et al.*, 2018). In agreement with X-ray data, the Raman measurements also reveal two phase transitions. The first transition appears around 0.5 GPa, while the second one appears between 5.4 and 8.1 GPa. Fig. 6 also shows the effect of pressure release. While the ζ -phase reverts to the ε -phase, the α -polymorph is not recovered upon pressure release as shown by the differences in the spectra at 0 GPa before compression and after decompression.

Figure 6
High-pressure Raman spectra during compression (black, red and blue lines) and after pressure release (green and black lines).

3.3. High-temperature crystal properties

Temperature-induced phase transitions in $\text{Na}_2\text{B}_{12}\text{H}_{12}$ have already been studied (Verdal *et al.*, 2014; Sadikin *et al.*, 2017). Nevertheless, no CTE for the low- and high-temperature (β -polymorph $Pm\bar{3}n$ and γ -polymorph $Im\bar{3}m$) phases of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ was determined. The CTE is an important parameter to design all-solid-state batteries to minimize detrimental stress at the interface of materials. Hence, we have performed high-temperature *in-situ* powder X-ray diffraction (HT-PXD) to get the CTE. Fig. 7 shows the patterns from the HT-PXD experiments. The result is consistent with the reports made by Verdal *et al.* (2014) and Sadikin *et al.* (2017). $\text{Na}_2\text{B}_{12}\text{H}_{12}$ undergoes to two successive order–disorder phase transitions starting at 511 K, where the $P2_1/c$ phase transforms into the cubic $Pm\bar{3}n$ phase and both phases coexist until 540 K. The primitive cubic phase is transformed into the more disordered $Im\bar{3}m$ phase at 587 K. Simultaneously, another minor transition into the δ -phase $Fm\bar{3}m$ takes place (see Fig. S7 for the attribution of the different phases).

The expansion of cell parameters as a function of temperature for the RT α -phase may be expressed as a third-order polynomial function (Fig. S8). The choice of the third order was made by comparing the residual of the fit with different orders until no trend in the residual was observed (Fig. S10). With regards to the β - and γ -polymorphs, the volumes V vary linearly with temperature (Fig. S9). Table S1 summarizes the obtained temperature-dependent equations for the three polymorphs. As a result, we could determine the CTE α value using equation (2):

$$\alpha = \frac{1}{V} \times \frac{dV}{dT}, \quad (2)$$

where V is the volume and T is the temperature.

Fig. 8 shows the evolution of the CTE as a function of temperature of the α -, β - and γ -polymorphs. The average CTE for the α -polymorph is $130.10^{-6} \text{K}^{-1}$ over the range 273–

Figure 7
Evolution of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ diffraction patterns with temperature increase.

Figure 8
CTE evolution as a function of temperature for LT- and HT- $\text{Na}_2\text{B}_{12}\text{H}_{12}$.

540 K, for $\beta\text{-Na}_2\text{B}_{12}\text{H}_{12}$ it is $230.10^{-6} \text{ K}^{-1}$ over the range 540–580 K and it is equal to $180.10^{-6} \text{ K}^{-1}$ for the γ -phase between 580 and 700 K. For the α -phase, the CTE first decreases with temperature until 340 K reaching its minimum value of $111.10^{-6} \text{ K}^{-1}$. Then, the CTE increases smoothly with temperature to come up to $186.10^{-6} \text{ K}^{-1}$ at 813 K. Such anomalous evolution of the CTE reveals a lattice anharmonicity at temperatures below the phase transition. At this stage, the α -phase transforms into the β -phase, where the CTE jumps by 22% to $228.10^{-6} \text{ K}^{-1}$ and it goes down linearly with temperature to $226.10^{-6} \text{ K}^{-1}$ at 580 K, the temperature at which the last transition takes place and the CTE drops by 19% to $183.10^{-6} \text{ K}^{-1}$ and linearly decreases with temperature to $178.10^{-6} \text{ K}^{-1}$. In Table S2, we summarize the different physical properties of all the polymorphs studied herein.

4. Conclusion

We investigated the high-pressure phase diagram of $\text{Na}_2\text{B}_{12}\text{H}_{12}$, a novel, boron-based sodium superionic conductor. In this study we highlight that $\text{Na}_2\text{B}_{12}\text{H}_{12}$ has a rich phase diagram and a transition at a relatively low pressure. Indeed, we found two successive phase transitions: the first to $\varepsilon\text{-Na}_2\text{B}_{12}\text{H}_{12}$ (*Pbca*) at 0.5 GPa and the second to $\zeta\text{-Na}_2\text{B}_{12}\text{H}_{12}$ (*Pnnm*) between 5.7 and 8.1 GPa. The relatively low pressure for the first transition confirms the criterion proposed by Aniya (1992) and several experimental reports (reviewed by Hull, 2004, and references therein) that superionic materials should undergo pressure-induced phase transition at low pressure. Moreover, our *in-situ* XRD data allowed us to determine the bulk modulus, $B_0 = 14$ GPa, for the α -polymorph with a striking agreement with the calculated one, $B_0 = 15.4$ GPa, validating the strategy used for the DFT calculation. The elastic properties of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ reveal a high compressibility for this material which is beneficial to accommodate the volume changes during charge and discharge of the battery.

The mechanism of the transition revealed an interesting formation of an Na–Na dimer by displacement of the sodium from the tetrahedral sites, in the f.c.c.-like cell, to the octa-

hedral void in order to preserve the ionic character of the material.

Interestingly, we observed that the ε -polymorph persists to ambient pressure; we explained this phenomenon using group theoretical analysis and DFT calculations. Indeed, we determined the amplitude of the primary order parameter for the transition $\varepsilon \rightarrow \alpha$ to be 2.4 Å, which is fairly high. Furthermore, the stability of the orthorhombic phase was calculated by DFT and revealed that this symmetry is the most stable symmetry over a broad range of pressure.

Finally through the evolution of the cell parameters as a function of the temperature we determined the CTE for this compound which should be of use in the design of an all-solid-state battery.

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