Supporting Information:

On the Local Structure in Ordered and Disordered *Closo*-hydroborate Solid Electrolytes

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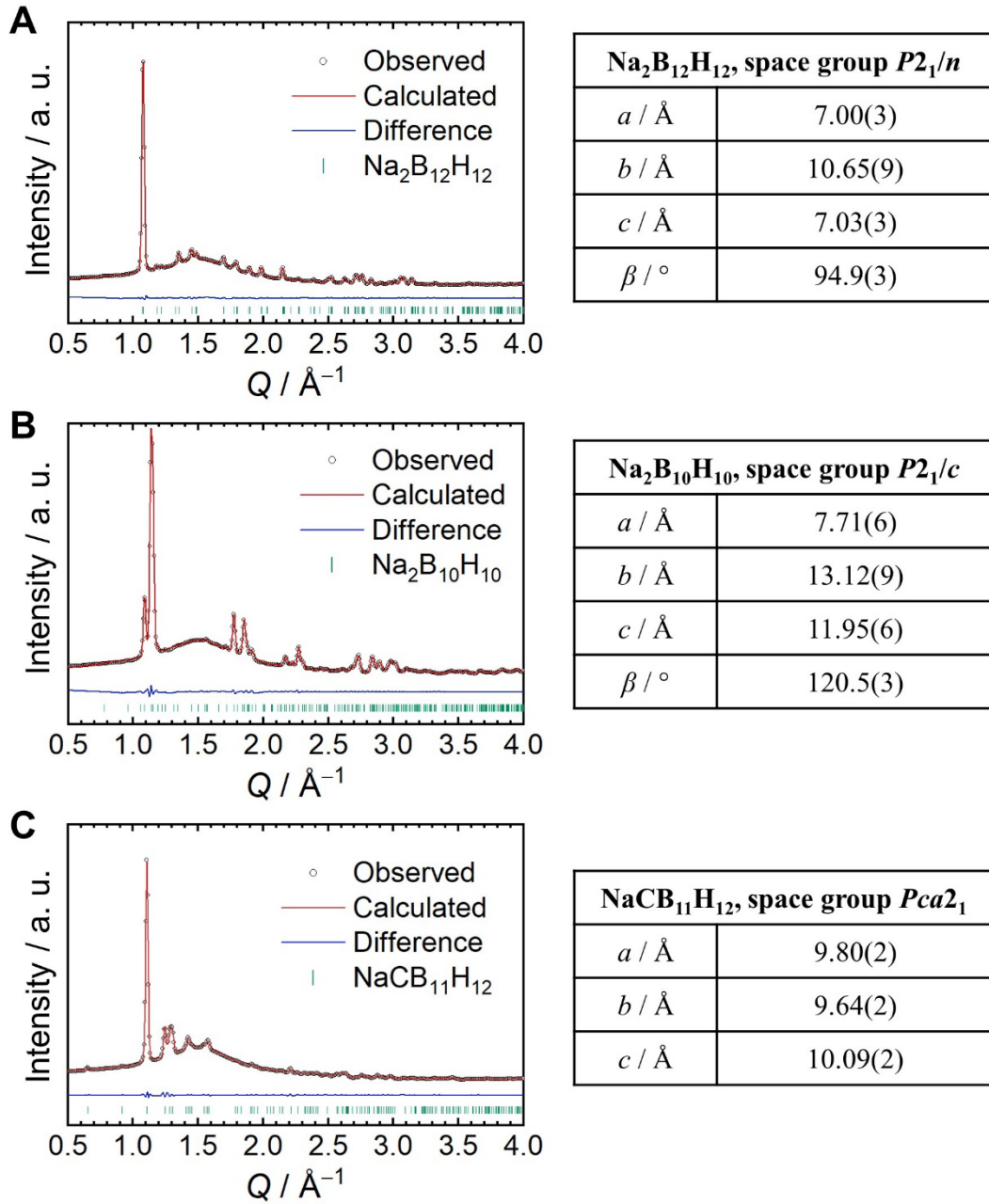
Pawley fitting

A

Na$_2$B$_{12}$H$_{12}$, space group $P2_1/n$	
a / Å	7.00(3)
b / Å	10.65(9)
c / Å	7.03(3)
β / °	94.9(3)

B

Na$_2$B$_{10}$H$_{10}$, space group $P2_1/c$	
a / Å	7.71(6)
b / Å	13.12(9)
c / Å	11.95(6)
β / °	120.5(3)

C

NaCB$_{11}$H$_{12}$, space group $Pca2_1$	
a / Å	9.80(2)
b / Å	9.64(2)
c / Å	10.09(2)

Figure S1: Plots of Pawley refinements and obtained lattice parameters for samples with only one cage type, namely a) Na$_2$B$_{12}$H$_{12}$, b) Na$_2$B$_{10}$H$_{10}$ and c) NaCB$_{11}$H$_{12}$.

$Na_4(B_{12}H_{12})(B_{10}H_{10})$ Space group $Fm\overline{3}m$	
a / Å	10.037(3)

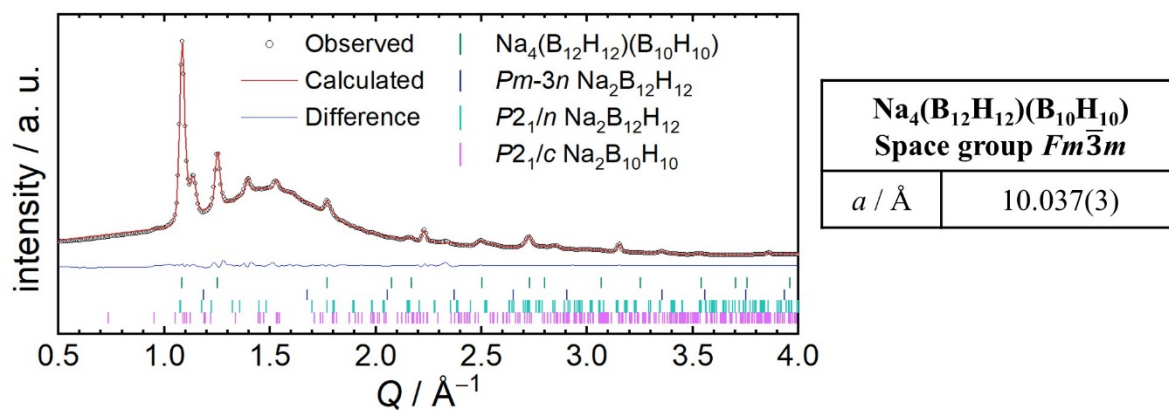*Figure S2: Plot of the Pawley refinement and obtained lattice parameters for $Na_4(B_{12}H_{12})(B_{10}H_{10})$. A reliable Pawley refinement against $Na_3(CB_{11}H_{12})(B_{12}H_{12})$ Bragg diffraction data was not possible, due to the broad reflections.*

Simulated pair distribution functions of specific atom-atom distances in $Na_2B_{10}H_{10}$

As elaborated in the main text, partial pair distribution functions, which only consider specific atom-atom distances, were calculated to obtain a better understanding of the measured $D(r)$. The same conclusions can be drawn for $Na_2B_{10}H_{10}$ and $Na_2B_{12}H_{12}$. While the results obtained for $Na_2B_{12}H_{12}$ are discussed exemplarily in the main text, discussion of the simulated partial pair distribution functions of $Na_2B_{10}H_{10}$ is added here for completeness.
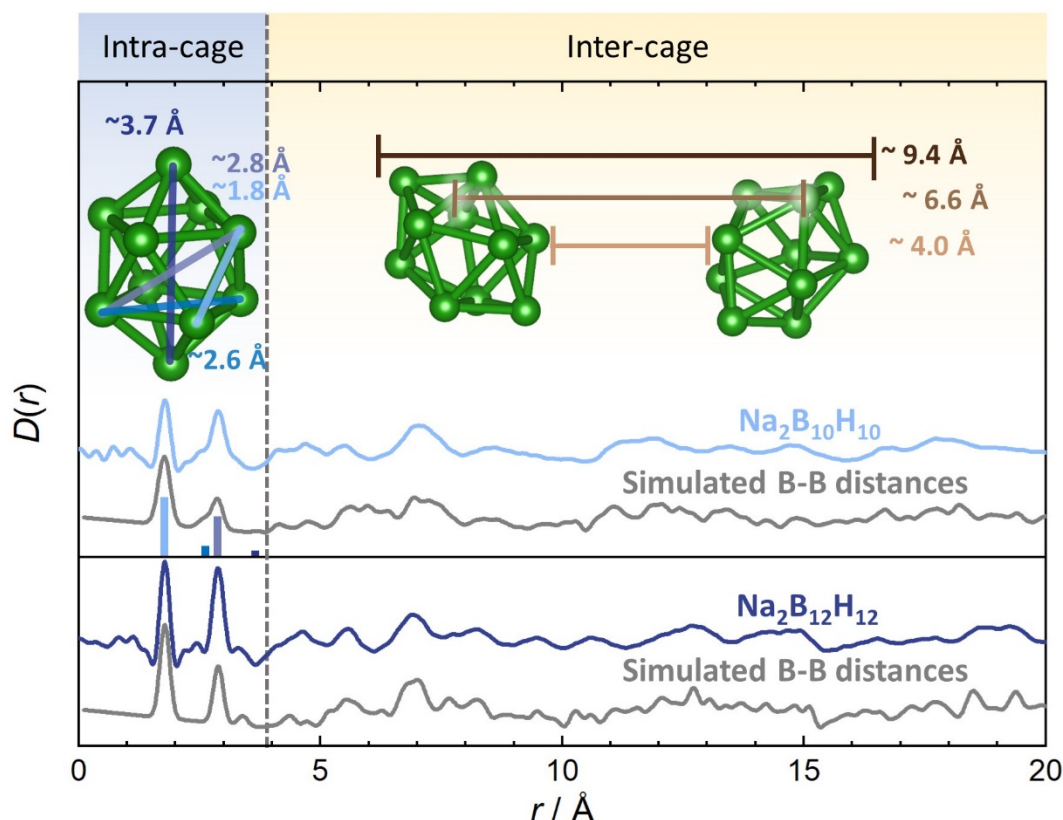

Figure S3: Measured D(r) of $Na_2B_{10}H_{10}$ and the simulated partial D(r) that arises from B-B distances only. The published structure from reference 1 with adjusted lattice parameters was used for the simulation. In the low r region, D(r) peaks correspond to intra-cage B-B distances. For r > 4 Å, inter-cage B-B distances are observed. Since various inter-cage B-B distances are found, the D(r) is broad. The center of mass distances of $B_{10}H_{10}^{2-}$ anions do not fully correspond to the higher intensity feature around 7 Å. This however, may be due to the ellipsoidal shape of the $B_{10}H_{10}^{2-}$ anions. The largest B-B distances of neighboring cages are found around ~9.4 Å. The measured and simulated partial D(r) of $Na_2B_{12}H_{12}$ are added for comparison. In both compounds measured and simulated D(r) are similar up to ~ 10 Å and become increasingly different with higher r.

As shown in Figure S3 the simulated partial B-B pair distribution functions and measured $D(r)$ for $Na_2B_{12}H_{12}$ and $Na_2B_{10}H_{10}$ are similar up to 10 Å, and the simulated partial $D(r)$ contributes significantly to the measured $D(r)$ in both compounds. Noteworthy, in $Na_2B_{12}H_{12}$ the intense feature around ~7 Å was found to coincide with the center of mass distance of the $B_{12}H_{12}^{2-}$ anions. In $Na_2B_{10}H_{10}$ the anion centers are closer to one another (~6.6 Å), so that the center-to-

center distance does not coincide with the broad peak around 7 Å. This difference may be due to the ellipsoidal shape of the $B_{10}H_{10}^{2-}$ cages. The different cage sizes and shapes may ultimately also be the reason for the increasing disparity between measured as well as simulated $D(r)$ of $Na_2B_{12}H_{12}$ and $Na_2B_{10}H_{10}$ for $r > 10$ Å. Overall, the simulated partial $D(r)$ of both compounds in comparison to the measured $D(r)$ shows that the earlier described intensity decay occurs once atom-atom distances in the inter-cage region are considered.

The simulated Na^+-B partial pair distribution function of $Na_2B_{10}H_{10}$ is compared to the measured $D(r)$ in Figure S4a. Similar to $Na_2B_{12}H_{12}$, Na^+ is surrounded by four *closo*-hydroborate cages in an approximately tetrahedral configuration and Na^+ is located closer to one of the triangular faces. The first peak of the partial Na^+-B $D(r)$ consequently arises from distances of Na^+ and B atoms of these three cages, as shown in Figure S4a. Due to the spatial extension of the *closo*-hydroborate cages, peaks arising from Na^+-B distances of these first three cages overlap with Na^+-B peaks from cages located further away from Na^+, so that a continuum of peaks is observed.
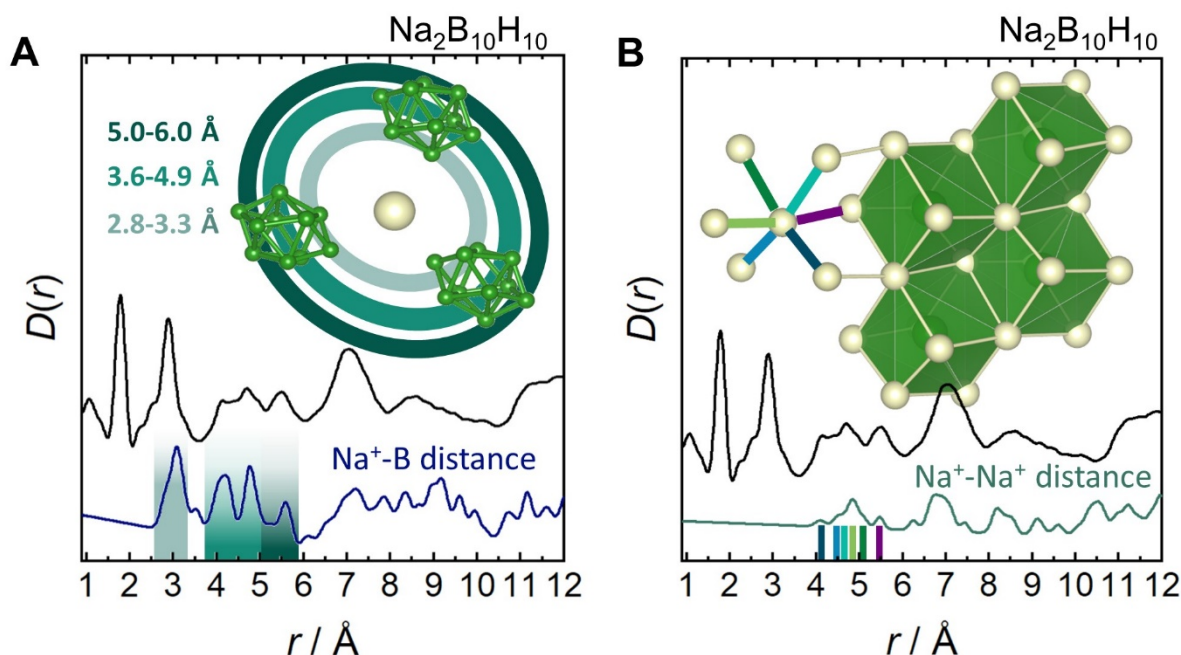

Figure S4: a) Measured D(r) of Na₂B₁₀H₁₀ compared to the simulated partial D(r) of Na⁺-B distances. The most intense peak around 3 Å arises from the first B coordination sphere. Na⁺-B distances of these nearest B cages extend up to 6 Å. Within this distance, further hydroborate cages are found, which also contribute to the D(r) so that a continuum of Na⁺-B peaks is observed. b) Measured D(r) of Na₂B₁₀H₁₀ compared to the simulated partial D(r) of Na⁺-Na⁺ distances. Na⁺ surrounds the B₁₀H₁₀²⁻ cages in a distorted, cube like configuration. For better visibility, closo-hydroborate cages are represented by spheres. Na⁺ is surrounded by 6 other Na⁺ in the shape of a distorted octahedron.

The structure of the Na^+ sublattice and the partial $D(r)$ arising from Na^+-Na^+ distances is shown in Figure S4b. Each Na^+ is surrounded by six other Na^+ with six distinct distances in a distorted octahedral arrangement. This octahedral motif is also observed in the Na^+ sublattice of $Na_2B_{12}H_{12}$ but in that compound one Na^+-Na^+ distance is significantly larger than the other distances, while in $Na_2B_{10}H_{10}$ the spread of Na^+-Na^+ distances in the octahedral motif is comparably smaller. Each hydroborate cage in $Na_2B_{10}H_{10}$ is surrounded by eight Na^+ ions in a distorted, cube-like arrangement. These distorted cubes are edge sharing, as shown in the inset of Figure S4b.
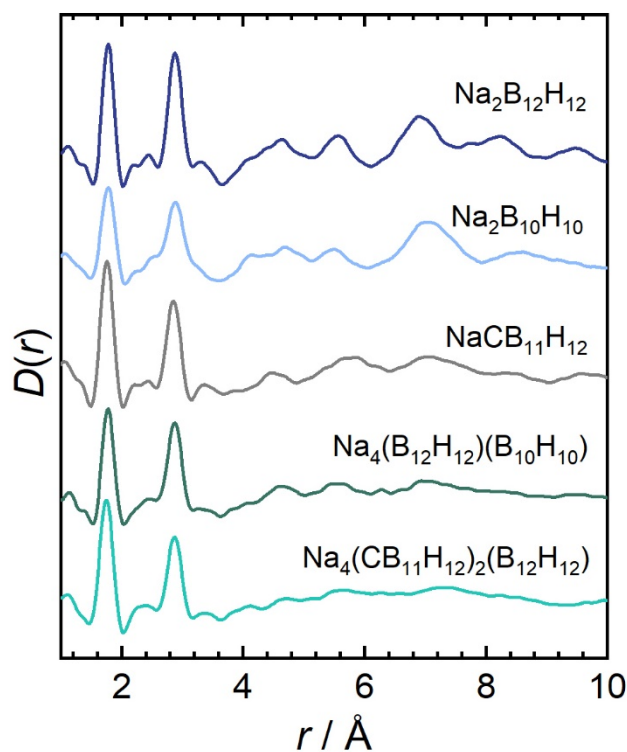
Comparison of all five compounds in the low *r* range

Figure S5: Comparison of all five measured D(r). All D(r) show a similar pattern at low r. Samples with higher orientation disorder have an almost flat and featureless D(r) for r > 5 Å.

Comparison of all simulated contributions to the pair distribution functions

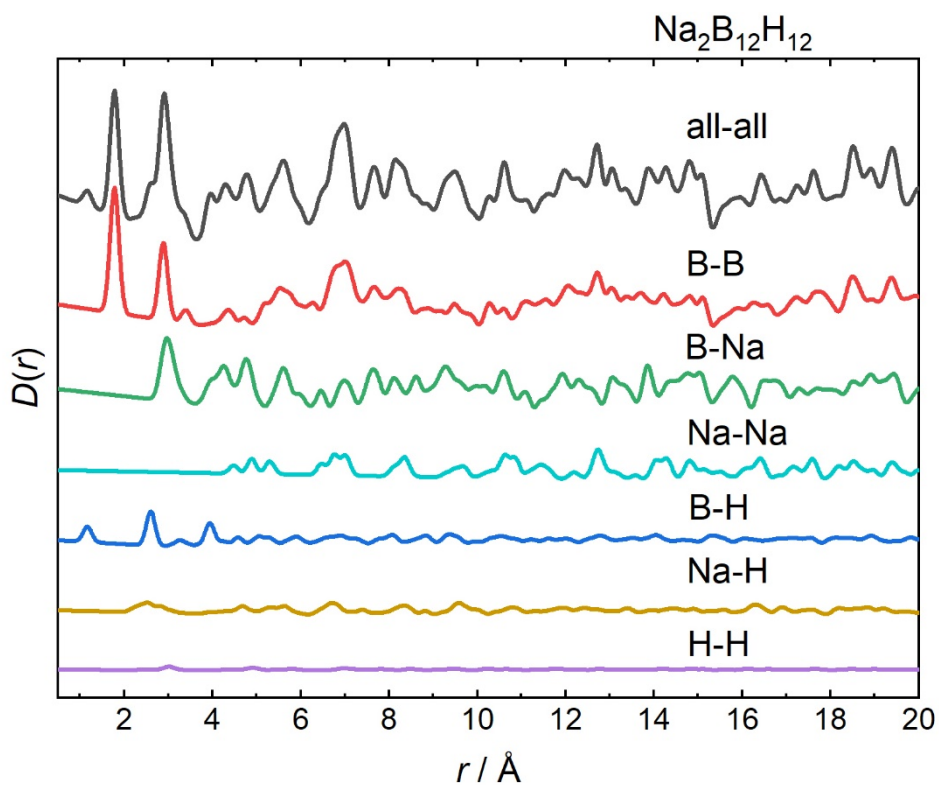*Figure S6: Simulated D(r) of Na₂B₁₂H₁₂ based on the structure reported by Her and co-workers.[2] Peaks arising from B-B distances have the largest intensity contribution to the D(r), compared to contributions from other atom-atom pair interactions.*

Figure S7: Simulated D(r) of Na₂B₁₀H₁₀ based on the structure reported by Wu and co-workers.[1] Peaks arising from B-B distances have the largest intensity contribution to the D(r), compared to contributions from other atom-atom pair interactions.
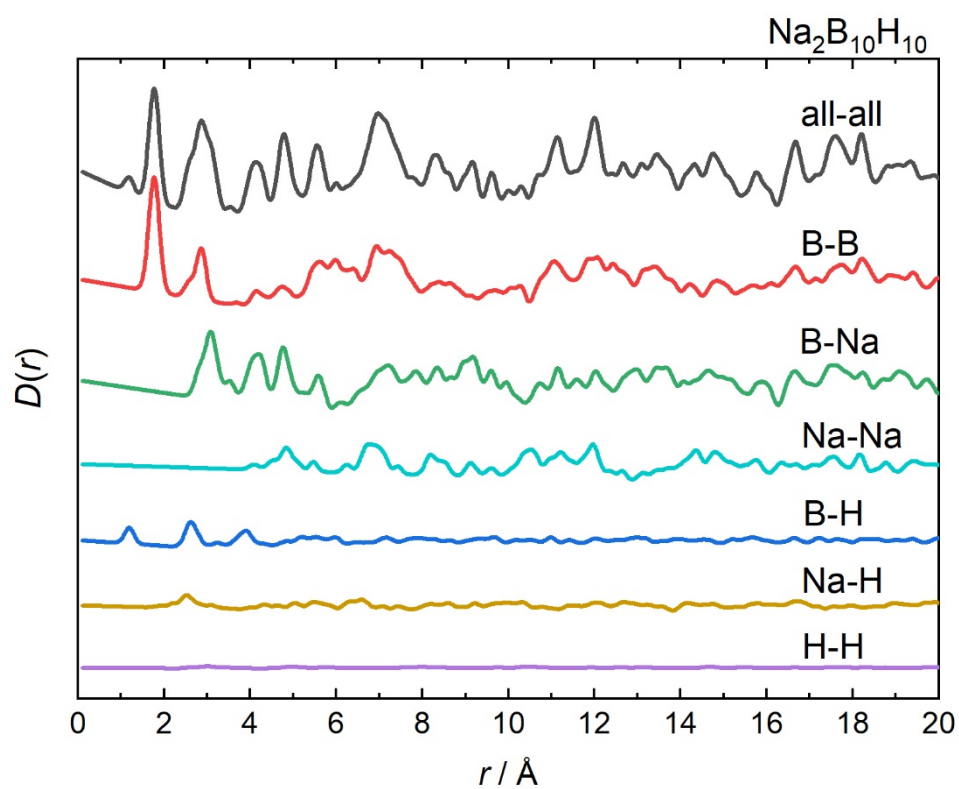
References

(1)   Wu, H.; Tang, W. S.; Zhou, W.; Stavila, V.; Rush, J. J.; Udovic, T. J. The Structure of Monoclinic $Na_2B_{10}H_{10}$: A Combined Diffraction, Spectroscopy, and Theoretical Approach. *CrystEngComm* **2015**, *17* (18), 3533–3540. https://doi.org/10.1039/c5ce00369e.

(2)   Her, J.-H.; Zhou, W.; Stavila, V.; Brown, C. M.; Udovic, T. J. Role of Cation Size on the Structural Behavior of the Alkali-Metal Dodecahydro- Closo - Dodecaborates. *J. Phys. Chem. C* **2009**, *113* (26), 11187–11189. https://doi.org/10.1021/jp904980m.