

## Electronic Supplementary Information for:

# Unparalleled Lithium and Sodium Superionic Conduction in Solid Electrolytes with Large Monovalent Cage-like Anions

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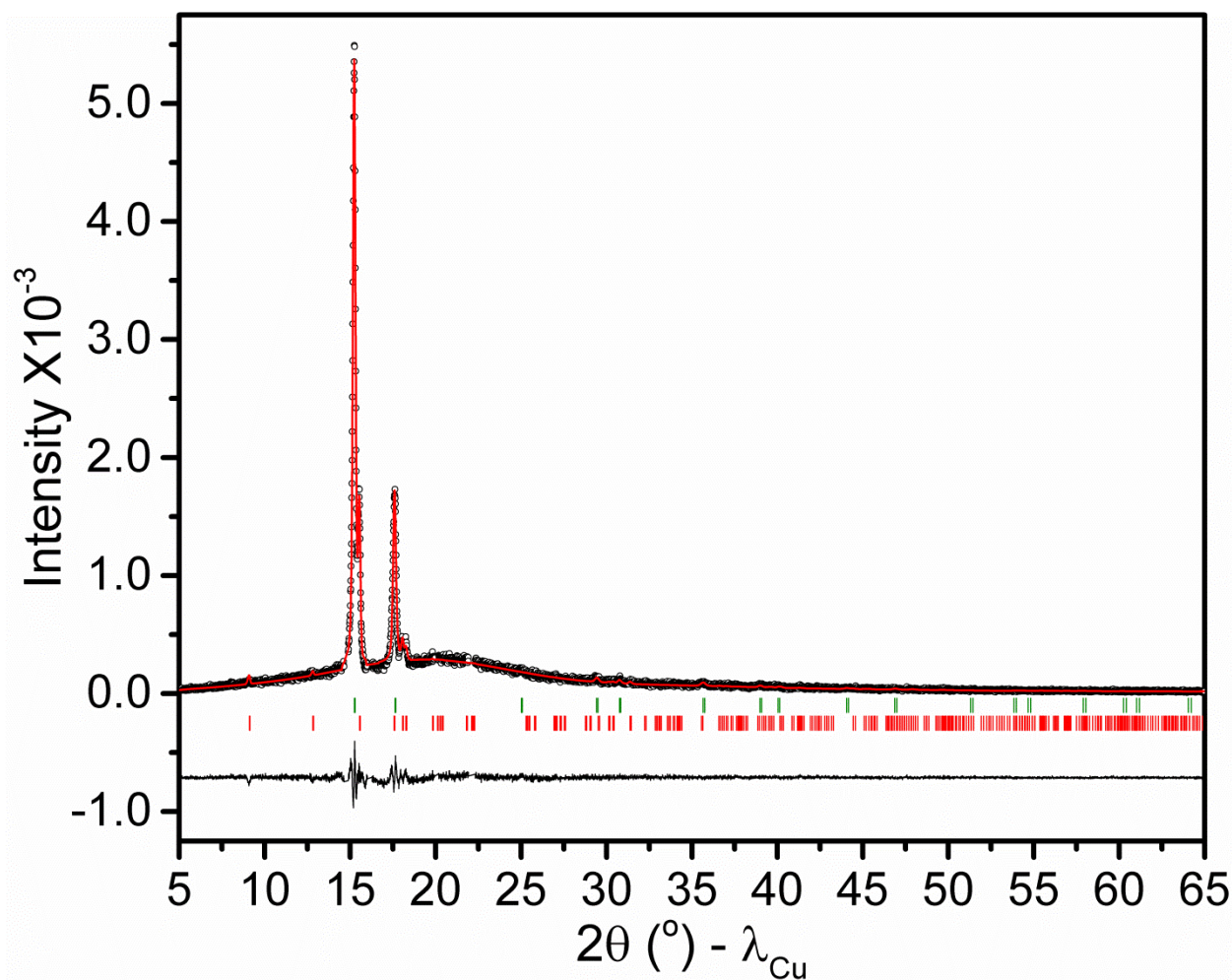
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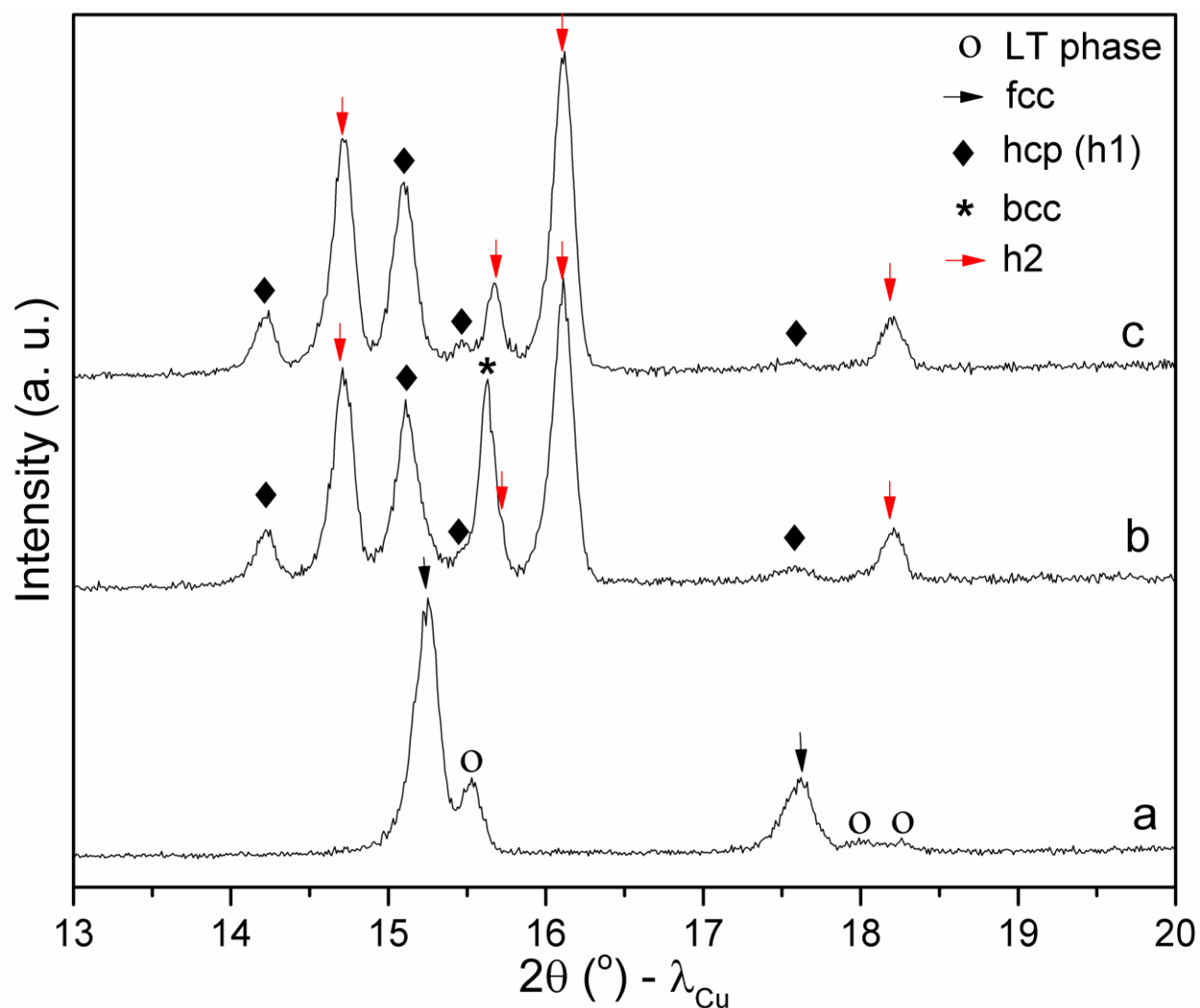
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**Fig. S1.** Experimental (circles), fitted (line), and difference (line below observed and calculated patterns) XRPD profiles for  $\text{NaCB}_{11}\text{H}_{12}$  at 356 K ( $\text{CuK}\alpha$  radiation). Vertical bars indicate the calculated positions of Bragg peaks for the high-temperature fcc (77.8(1) wt. %) and the low-temperature orthorhombic phases (22.2(2) wt. %) of  $\text{NaCB}_{11}\text{H}_{12}$ , respectively (from the top).  $R_{\text{wp}}=0.0782$ ,  $R_p=0.0678$ ,  $\chi^2=1.444$ . The refined lattice parameter of the high-temperature fcc phase is  $10.066(3) \text{ \AA}$ ; and  $a= 9.818(3) \text{ \AA}$ ,  $b= 9.712(4) \text{ \AA}$ , and  $c= 10.101(3) \text{ \AA}$  for the low-temperature orthorhombic phase. As for  $\text{LiCB}_{11}\text{H}_{12}$  in Fig. 5, the refinement model for the fcc phase ignored the cations and H atoms and employed multiple B/C positions to mimic a spherical shell of B/C scatterers due to the isotropically orientationally disordered anions.



**Fig. S2.** The high-temperature phase evolution in NaCB<sub>11</sub>H<sub>12</sub>: (a) 356 K XRPD pattern (CuK $\alpha$  radiation) with the presence of high-temperature fcc phase and a small amount of low-temperature (LT) orthorhombic phase. (b) 428 K XRPD pattern indicating the formation of body-centered-cubic (bcc) phase and two hexagonal phases, (hexagonal-close-packed (hcp)) h1 and hexagonal h2. (c) 428 K XRD pattern with extended time showing only the two hexagonal phases (h1 and h2). The tentative lattice parameters of these phases at 428 K can be indexed as  $a=8.011$  Å for the bcc phase,  $a=7.185$  Å and  $c=17.19$  Å for the hcp (h1) phase, and  $a=6.945$  Å and  $c=16.49$  Å for the h2 phase. These phases all revert back to the ordered orthorhombic phase upon cooling.