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Dynamic Atomic-scale Imaging of Cluster-ion Anti-perovskites Using Low-dose Cryogenic HRTEM

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Cluster-ion anti-perovskites have gained recent interest as potential electrolytes for next-generation, solid-state batteries due to their high ionic conductivity and structural diversity [1, 2]. In cluster-ion anti-perovskites, the conductivity stems from correlated ion motion that is highly dependent on local structural features, such as atomic composition and lattice distortion, as well as external factors, such as temperature and pressure [2, 3]. An in-depth understanding of ionic motion is essential to the design of electrolytes for solid-state batteries that are safer, cheaper, and have higher performance than their liquid counterparts [2].

While a dynamic understanding of ion motion in cluster-ion anti-perovskites is of paramount importance, it also represents a significant characterization challenge. Each anti-perovskite has diverse ion interactions, making identification of a dominant structural motif difficult [2-4]. Furthermore, few experimental studies exist to probe the ion mobility and conduction pathways dynamically on the atomic scale, meaning theoretical predictions have yet to be experimentally verified [2]. In principle, in-situ transmission electron microscopy (TEM) in combination with direct electron detection can address this challenge, providing local, high-resolution structural determination as a function of temperature in real-time. Yet few atomic-scale TEM studies of these materials have been reported, likely due to the combined challenges of air and beam sensitivity. Here we use cryogenic, high-resolution TEM (cryo-HRTEM) at 300 kV to dynamically investigate the air-free, atomic-scale structure of cluster-ion anti-perovskites.

We investigate disodium amide borohydride ($Na_2NH_2BH_4$) (NNB) (Figure 1), a cluster-ion anti-perovskite of interest due to its high sodium ionic conductivity and electrochemical stability [5]. We prepare NNB in an argon glove box, dipping the TEM grid in the as-synthesized powder and then sealing in an air-tight container. Once we remove the sealed grid from the glove box, we immediately plunge it in liquid nitrogen. Plunge freezing and imaging at cryogenic temperatures provides essential benefits for TEM studies of cluster-ion anti-perovskites, including preservation of the air-free structure and up to 6x improvement in critical dose. Figure 1 shows an energy-filtered, summed, cryo-HRTEM image of an NNB crystal acquired using a K2 direct electron detector. By measuring the cryogenic critical dose of NNB to be ~60 $e^-/Å^2$ for the {001} spots, we are able to capture the atomic-scale structure with information transfer up to 2.2 Å (Figure 1c). Via careful calibration of the {001} spots, we measure an effective doubling of the 4.7 Å NNB lattice constant to 9.4 Å. This indicates the NNB crystal is likely disordered, as disordered phases are known to contain clustering and short-range order [6].

Using dynamic, atomic-scale cryo-HRTEM we also observe electron-beam-driven structural transformations in NNB. Figure 2 shows a time series of energy-filtered, cryo-HRTEM images where the crystal visibly expands under electron beam irradiation. By tracking the change in d-spacing with accumulated dose, we observe a unidirectional expansion of 7.5% within 21.5 $e^{-}/Å^2$ (Figure 2b). While further investigation into the origins of this large volume change is needed, possibilities include a beam-induced strain, local charge imbalance, change in elemental composition, chemical reaction, or phase transition. Overall, we have developed a robust, cryo-transfer protocol to preserve the air-free structure of cluster-ion anti-perovskites. We quantify the beam sensitivity of NNB and dynamically image the atomic-scale structure, observing short-range structural disorder and an electron-beam-driven lattice expansion. Our results demonstrate the potential of using cryo-HRTEM imaging to study the atomic-scale structure of cluster-ion anti-perovskites and highlight the importance of further investigation into the phase structure and stability of these systems.

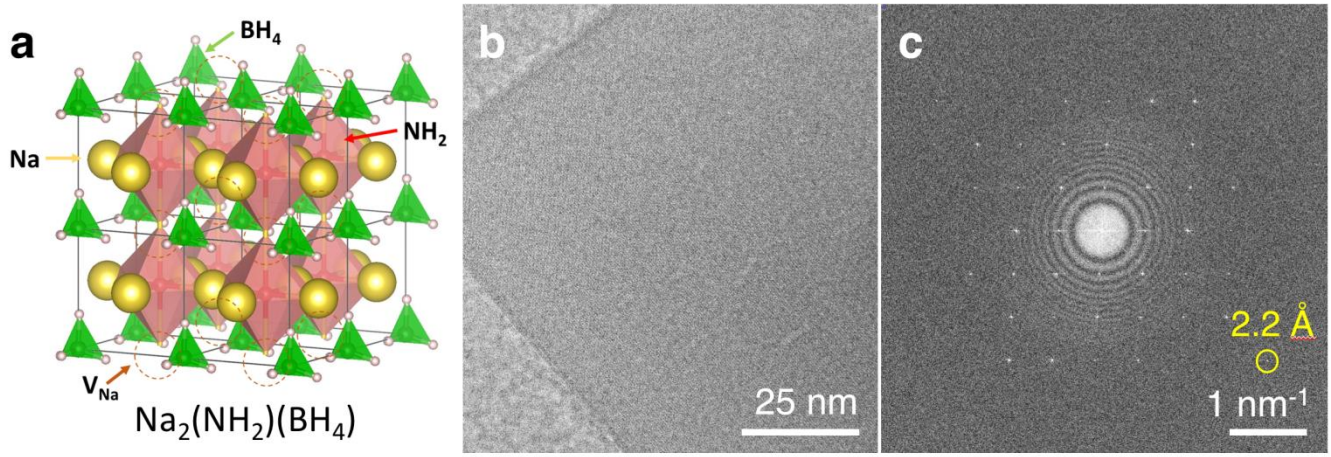

Figure 1. Structure and cryo-HRTEM imaging of the disodium amide borohydride ($Na_2NH_2BH_4$) (NNB). (a) Theoretically predicted structure of NNB. (b) Energy-filtered, summed, cryo-HRTEM image acquired with a K2 direct electron detector at 300 kV. The image is a motion-corrected sum of 40 frames, with a total electron exposure of 38.5 $e^{-}/Å^2$. (c) FFT of the image in (b), showing information transfer up to 2.2 Å. The d-spacing of the {001} spots is 9.4 Å, an effective doubling of the 4.7 Å NNB lattice constant.

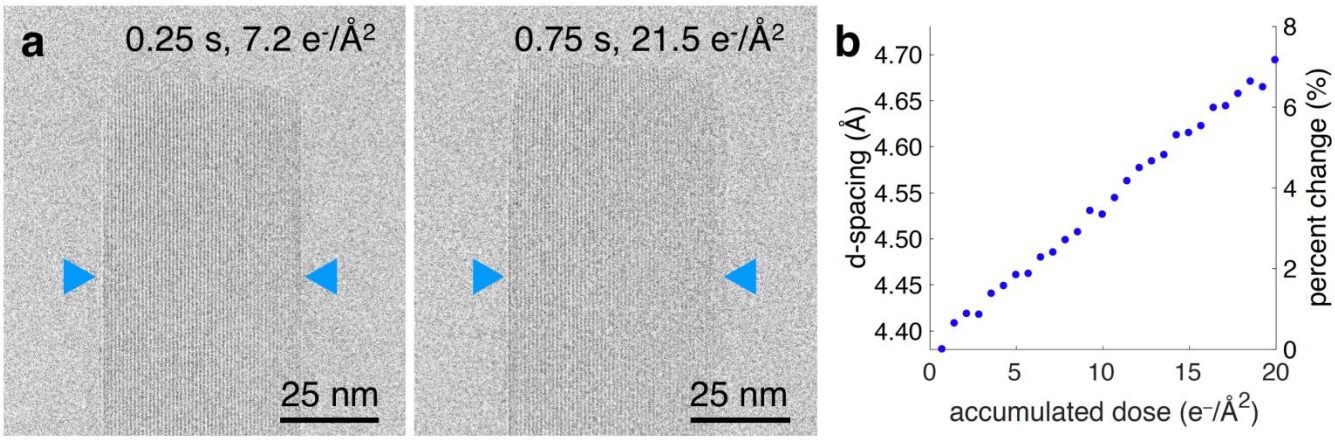

Figure 2. Cryo-HRTEM observation of an electron-beam-driven structural transformation in NNB. (a) Energy-filtered, cryo-HRTEM time series acquired with a K2 direct electron detector at 300 kV. Each

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image is a motion-corrected sum of 10 frames, with the total dose and time since the initial exposure reported. The crystal is visibly wider in the second panel, as indicated by the blue arrows. (b) Plot of the lattice expansion of the crystal in (a) as a function of accumulated dose, calculated by tracking the position of the ~4.5 Å d-spacing spots in the FFT of each individual frame. The data are plotted over a 30-frame series. During 21.5 $e^{-}/Å^{2}$ of beam exposure the lattice expands by 7.5%.

References:

[1] Z Zhang, *et al.*, Energy & Environ. Sci. **11** (2018), p. 1945.
[2] J Dawson, *et al.*, J. Mater. Chem. A, **9** (2021), p. 18746.
[3] K Kim and D Siegel, J Mater. Chem. A, **7** (2019), p. 3216.
[4] Y. Sun, *et al.*, JACS **141** (2019), p. 5640.
[5] M. Matsuo, *et al.*, Appl. Phys. Lett. **100** (2012), p. 203904.
[6] A. Navrotsky,. ECS Trans. **45** (2012), p. 11.
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