BNL-113232-2016-JA

**Quantification of Honeycomb
Number-Type Stacking Faults:
Application to Na₃Ni₂BiO₆
Cathodes for Na-Ion Batteries**

**Jue Liu, Liang Yin, Lijun Wu, Jianming Bai, Seong-Min Bak,
Xiqian Yu, Yimei Zhu, Xiao-Qing Yang, Peter G. Khalifah**

Submitted to Inorganic Chemistry

September 2016

Chemistry Department

Brookhaven National Laboratory

**U.S. Department of Energy
USDOE Office of Science (SC),
Basic Energy Sciences (BES) (SC-22)**

Notice: This manuscript has been authored by employees of Brookhaven Science Associates, LLC under Contract No. DE- SC0012704 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Quantification of honeycomb number-type stacking faults: application to $\text{Na}_3\text{Ni}_2\text{BiO}_6$ cathodes for Na-ion batteries

Jue Liu^{§,†}, Liang Yin[§], Lijun Wu[⊥], Jianming Bai[#], Seong-Min Bak[†], Xiqian Yu[†], Yimei Zhu[⊥], Xiao-Qing Yang[†], Peter G. Khalifah^{§,†,*}

[§] Department of Chemistry, State University of New York at Stony Brook, Stony Brook, N.Y., 11794-3400, United States

[†] Chemistry department, Brookhaven National Laboratory, Upton, NY, 11973, United States

[⊥] Condensed Matter Physics and Material Science Department, Brookhaven National Laboratory, Upton, NY 11973, United States

[#] Photon Science Division, Brookhaven National Laboratory, Upton, NY, 11973, United States

KEYWORDS *honeycomb lattice, sodium ion batteries, $\text{Na}_3\text{Ni}_2\text{BiO}_6$, Li_2MnO_3 , stacking faults.*

ABSTRACT: Ordered and disordered samples of honeycomb-lattice $\text{Na}_3\text{Ni}_2\text{BiO}_6$ were investigated as cathodes for Na-ion batteries and it was determined that the ordered sample exhibits better electrochemical performance with a specific capacity of 104 mAh/g delivered at plateaus of 3.5 and 3.2 V (vs. Na^+/Na) with minimal capacity fade during extended cycling. Advanced imaging and diffraction investigations showed that the primary difference between ordered and disordered samples is the amount of number-type stacking faults associated with the three possible centering choices for each honeycomb layer. A labeling scheme for assigning the number position of honeycomb layers is described, and it is shown that the translational shift vectors between layers provide the simplest method for classifying different repeat patterns. It is demonstrated that the number position of honeycomb layers can be directly determined in STEM-HAADF imaging studies. Using fault models derived from STEM studies, it is shown that both the sharp, symmetric subcell peaks and the broad, asymmetric superstructure peaks in powder diffraction patterns can be quantitatively modeled. About 20% of the layers in the ordered monoclinic sample are faulted in a non-random manner, while the disordered sample stacking is not fully random but instead contains about 4% monoclinic order. Furthermore, it is shown that the ordered sample has a series of higher-order superstructure peaks associated with 6-, 9-, 12-, and 15-layer periods whose existence is transiently driven by the presence of long-range strain that is an inherent consequence of the synthesis mechanism revealed through the present diffraction and imaging studies. This strain is closely associated with a monoclinic shear that can be directly calculated from cell lattice parameters and which is strongly correlated with the degree of ordering in samples. The present results are broadly applicable to other honeycomb-lattice systems including Li_2MnO_3 and related Li-excess cathode compositions.

1. Introduction

Both Li^+ and Na^+ ions have been used as charge carriers for electrochemical energy storage since the early 1980s¹⁻³ though Li-ion systems have received more attention in recent decades due to their higher energy density^{4,5}. However, there has been a resurgent interest in sodium-ion batteries due to the lower cost and far greater abundance of sodium relative to lithium, which offers advantages for emerging large-scale applications such as electric vehicles and grid-scale electrical energy storage⁶⁻¹³. A very important structural class for both Na- and Li-ion battery cathodes is the $\alpha\text{-NaFeO}_2$ type structure which has the general formula of ABO_2 and represents an ordered variant of the rock-salt structure type in which both the mobile ions (A) and redox-active transition metals (B) are found in distinct layers. Some of the most industrially relevant Li-ion battery cathodes materials belong to this structure type, most notably LiCoO_2 ^{1,14} and $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ ¹⁵. Good electrochemical behavior has also been observed for many Na-ion battery cathodes with the $\alpha\text{-NaFeO}_2$ type structure type including NaCrO_2 ^{10,16} and NaFeO_2 ¹⁷. Some $\alpha\text{-NaFeO}_2$ type Na-ion battery systems with both high capacity and high initial discharge voltages have been identified, though the steeply-sloping voltage profile of these systems limits their use in applications^{12,18,19}.

A promising approach to further improve the performance of layered battery materials that has been recently pursued is introducing mixed transition metal layers with a honeycomb lattice into $\alpha\text{-NaFeO}_2$ type battery systems, resulting in the general stoichiometry of $\text{A}(\text{B}_{2/3}\text{B}'_{1/3})\text{O}_2$. A comparison of the rock salt, $\alpha\text{-NaFeO}_2$, and honeycomb-ordered structures is shown in Figure 1. The precise crystallographic relationships between the unit cells used to describe these three closely related structure types has been discussed previously²⁰. The interest in these compounds is not limited to their electrochemical performance^{20,21}, but also extends to the ionic conductivity^{22,23} and magnetic investigations of these materials²⁴⁻²⁶.

Figure 1. Structure, unit cell, and stacking sequence of cubic ($Fm\bar{3}m$) rock salt FeO , rhombohedral ($R\bar{3}m$) $\alpha\text{-NaFeO}_2$ with an O3 stacking arrangement, and honeycomb-ordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ with an O3 stacking arrangement drawn in a hypothetical ideal trigonal ($P\bar{3}_1I2$) supercell (blue). The honeycomb lattice of Ni^{2+} ions surrounding central Bi^{5+} ions is indicated with dashed yellow lines. Cation positions are labeled with capital letters, while lower case letters are used for anion positions.

Our group²⁰ and others^{20,21} have demonstrated that honeycomb-ordered Na-ion systems can have well-defined flat plateaus at very high voltages during galvanostatic cycling, providing a substantially improved discharge voltage relative to traditional $\alpha\text{-NaFeO}_2$ systems with sloped voltage profiles. Presently, capacity fade is an issue for Na-ion honeycomb lattice compounds, though evidence to date suggests that the battery performance is improved in samples for which disorder in the honeycomb layers is minimized²⁰. For Li-ion batteries, substantially enhanced specific capacities have been demonstrated in honeycomb compounds derived from the $\text{Li}(\text{Mn}_{2/3}\text{Li}_{1/3})\text{O}_2$ composition²⁷⁻²⁹. These compounds are commonly termed Li-excess compounds and are often reported using the equivalent integer stoichiometry, Li_2MnO_3 ^{30,31}.

However, the discharge profile of Li-excess compounds changes over time in an undesirable manner, a process which is termed voltage fade^{28,32}. Despite extensive efforts to eliminate voltage fade, a good method for doing so has yet to be identified.

It is clear that the structure of these layered battery materials influences their performance. While the stacking sequences and positions (*A/B/C*) associated with the transition metal layers are well known, there is a much more limited understanding of the additional degrees of order associated with the honeycomb lattice of this general class of compounds. Honeycomb ordering within the *ab*-plane results in each *B*-layer (transition metal layer) within a single unit cell having total 3 cation positions for the 2 *B* and 1 *B'* cations, in contrast to the base α -NaFeO₂ unit cell which has only a single cation position for each layer (Figure 1). As a result, it was demonstrated by Brger *et al.* that there are 27 possible honeycomb stacking sequences for honeycomb-lattice compounds such as Li₂MnO₃ or Li[Li_{1/3}Mn_{2/3}]O₂ with a base O3 arrangement.³³ It was also noted that due to the symmetry of the system these 27 stacking variants give rise to only two unique structures, with 1/3 of them producing monoclinic *C2/m* symmetry and 2/3 of producing a structure with trigonal *P3₁12* symmetry. Although a general nomenclature for classifying the 9 combinations (**A₁**, **A₂**, **A₃**, **B₁**, **B₂**, **B₃**, **C₁**, **C₂**, **C₃**) of the 3 different possible honeycomb layer positions (**1**, **2**, and **3**) for each of the three layers (**A**, **B**, and **C**) was proposed in that work, a specific method for explicitly identifying these location of these 9 site positions was not described. More recently, it was demonstrated by our group that both the disordered and ordered polymorphs for NaNi_{2/3}Sb_{1/3}O₂ contain well-developed honeycomb layers which obey the expected **ABC** stacking repeat sequence for O3-type α -NaFeO₂ layered materials, and that the primary difference between these two polymorphs is the degree of order in the number positions of the honeycomb layers. As such, it appears that the *number* faults rather than *letter* faults are most responsible for the structural differences between the ordered and disordered variants of Na₃Ni₂SbO₆ as well as for the corresponding differences in electrochemical performance.

While the formalism for developing letter faults has previously been explored³⁴, the formalism for treating number faults is not well developed. Additionally, methods for experimentally characterizing the pattern of number faults have not been previously described. Methods for both the theoretical and experimental quantification and classification of number faults relevant to both ordered and disordered polytypes will be presented here in the context of an investigation of Na₃Ni₂BiO₆, a known honeycomb compound which has previously been investigated for its magnetic rather than electrochemical properties²⁶. The present results are relevant for both the study of high-voltage Na-ion honeycomb compounds like Na₃Ni₂SbO₆ in which the *B'* cation at the center of the honeycomb lattice has a higher valence (HV) than the surrounding *B* cations, and for the study of high specific capacity Li-ion compounds like Li₂MnO₃ in which central cation has a lower valence (LV) than the surrounding cations.

2. Experimental

The same synthetic method with different starting materials was used to synthesize powder samples of two polymorphs of Na₃Ni₂BiO₆. For the first disordered polymorph, stoichio-

metric amount of anhydrous Na₂CO₃ (EMD, pre-dried), NiO (Sigma-Aldrich, 99.9%) and Bi₂O₃ (Alfa Aesar, >99%) were ball milled in a vibratory mill for 2 hours. A thin layer of the well mixed powder was then placed on an alumina boat. The boat was transferred into a mullite tube inside a horizontal tube furnace (Mellen, SV Series). The sample was heated up to 720 °C with a ramp rate of 200 °C/h, and was held at this temperature for 12 hours before cooling down to room temperature at furnace cooling rate, the whole process was carried out under the flowing of O₂ gas. The obtained dark yellow powder was well ground by using mortar and pestle and then transferred to glass vials and stored in desiccator for further structure and electrochemical characterization. The second ordered polymorph was synthesized at the same conditions as those for the disordered phase, though with the difference that NaBiO₃ (CHEM-IMPLEX) was used instead of Bi₂O₃ as a starting material in the synthesis. The final product for the ordered phase was found to be yellow powder.

Laboratory X-ray diffraction data were collected on a Bruker Advance D8 diffractometer using Cu K_ radiation from a fine focus X-ray tube (K_{1} = 1.54053 , K_{2} = 1.54431), and was used for phase identification. The system was operated at a 217.5 mm working radius utilizing a 1D position-sensitive LynxEye Si detector with 192 channels. Data were collected between 8 and 100 with a step size of 0.02/step and a scan speed of 2 second/step. High resolution 1D synchrotron X-ray diffraction data were collected at 11-BM beamline at Argonne National Laboratory with a wavelength of 0.41398 . Lower resolution synchrotron X-ray powder diffraction data suitable for both Rietveld and PDF analysis were collected at the XPD beamline (NSLS-II, Brookhaven National Laboratory) using a 2D area detector and a wavelength of 0.1878 . For data collection, powder samples were packed into a 0.8 mm diameter Kapton capillary and rotated at a speed of 1 rad/s. The data collection time was 1 s/image and a total of 60 images were collected and averaged for each data set. Powdered Ni was used to calibrate the sample to detector distance, beam center position and tilting angles. Image data were integrated using Fit2D³⁵. Diffraction data was further converted into pair distribution function using PDFgetX³⁶. Routine structure refinements (Le Bail³⁷ and Rietveld³⁸ refinements) were carried out using TOPAS software (Version 4.2), while the explicit and probabilistic modeling of the stacking faults were done using the Faults program³⁹. Fitting of PDF data was carried out in PDFgui software⁴⁰ with the initial crystal structure model obtained from Rietveld refinements using the same diffraction data, and with Q_{broad} and Q_{damp} fixed to the values obtained from refinement of the Ni standard.

Ni K-edge X-ray absorption (XAS) spectra were collected at either the X-18A beamline of the NSLS, Brookhaven National Laboratory, or at BL2-2 of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory. Data were collected in transmission mode with the beam intensity detuned to 60% to minimize high-order harmonics. A reference spectrum of Ni foil used as an energy calibrant was collected simultaneous. XANES and EXAFS spectra were first processed using the Athena software package⁴¹. The AUTOBK code was then used to normalize corresponded absorption coefficient. The corresponding EXAFS signal $\chi(k)$ was weighted by k^3 to emphasize the signal character and then Fourier transferred into real space. Fitting of EXAFS data

from 1.0 Å and 3.5 Å were carried out using the Artemis⁴¹ and FEFF6 software packages⁴².

Scanning electron microscopy images of as-prepared $\text{Na}_3\text{Ni}_2\text{BiO}_6$ powders were collected on a JEOL 7600, to minimize charge effects, the data was collected at high vacuum and low voltage (5 kV). High resolution scanning transmission electron microscopy (HRSTEM) imaging, selected-area electron diffraction were performed using the double aberration-corrected JEOL-ARM200CF microscope with a cold-field emission gun and operated at 200 kV. The microscope is equipped with JEOL and Gatan high angle annular dark field (HAADF) detectors for incoherent STEM-HAADF (Z-contrast) imaging. The contrast of the STEM-HAADF image is proportional to $Z^{1.7}$ along the atom column, where Z is the atomic number.

Performances of cathode materials for Na-ion batteries were evaluated in CR2025 type coin cells. The ceramic material was first hand ground for 30 min and then mixed with acetylene black in a mass ratio of 7:2. The mixture was further ground for ~30 min, mixed with polyvinylidene difluoride (PVDF) in a mass ratio of 9:1, and then further ground for ~10 min. An appropriate amount of 1-methyl-2-pyrrolidinone (NMP) was added into the mixture to form a thick slurry, which was then recovered from the mortar and cast onto Al foil using a doctor blade (aperture of 40 µm). The cast electrode film was dried in a vacuum oven at 100 °C for 12 hours. The dried electrode foil was punched into 0.75 inch diameter discs, with a measured active material loading of around 4-5 mg/disc. Metallic sodium was used as the anode while saturated NaClO_4 in 1:1 (volume ratio) EC/DEC was used as the electrolyte. Galvanostatic cycling was carried out at a C/30 rate (calculated using the assumption of only a $\text{Ni}^{3+}/\text{Ni}^{2+}$ redox couple) at 20 °C on Land cycler. Galvanostatic intermediate titration technique (GITT) data for the ordered phase were also collected on a Land cycler. The cell was charged/discharged for one hour and then relaxed for 15 hours with a net charge/discharge rate of about C/320. Cyclic voltammetry (CV) tests were carried out on Biologic VMP 3 spectrometer with a scan rate of 5 mV/s.

3. Results and discussion

3.1 Synthesis of two $\text{Na}_3\text{Ni}_2\text{BiO}_6$ polymorphs. When different Bi sources are used to prepare $\text{Na}_3\text{Ni}_2\text{BiO}_6$, two different polymorphs are produced even when identical reaction conditions are used. Based on a comparison of synchrotron X-ray diffraction patterns (Figure 2), the sample synthesized using Bi_2O_3 (black) as a bismuth source is disordered while that prepared with NaBiO_3 (red) is ordered. While the intensities of the major diffraction peaks (reflecting the periodicity of the $R\bar{3}m$ subcell) are nearly indistinguishable for the two polymorphs, it can be seen that the ordered phase has additional superstructure peaks, most of which can be effectively indexed using either the $C2/m$ or $P3_112$ supercell previously reported for honeycomb-ordered compounds. In contrast, the disordered phase has no substantial peaks at these supercell positions other than two highly asymmetrical peaks with very extended high-angle tails, a Warren-type peak shape that is well-known to occur for many layered compounds with stacking faults⁴³. The most intense peak of this type can be seen around 5° 2θ in Figure 2. Asymmetrical peaks characteristic of stack-

ing faults are also present in the ordered phase, indicating that the ordering is not fully developed in the ordered sample.

It has previously been suggested that the varying degrees of order in honeycomb compounds (such as $\text{Na}_3\text{Ni}_2\text{SbO}_6$ and $\text{Li}_4\text{FeSbO}_6$) may be driven by differences in synthesis temperature or by differing vacancy concentrations at the mobile ion sites^{20,44}. However, the synthesis temperature, time, and atmosphere were the same for both the ordered and disordered samples of $\text{Na}_3\text{Ni}_2\text{BiO}_6$, so only one of these can be the thermodynamic ground state for this composition at the investigated reaction conditions. Similarly, there is no evidence from SEM-EDX studies (Figure S1) nor from Rietveld refinements (discussed later) for different Na-ion concentrations in the two polymorphs. Evidence for different reaction rates using different Bi sources can be seen in SEM studies (Figure 2). The disordered sample synthesized from Bi_2O_3 lacks facets and has particle sizes varying from hundreds of nanometers to several microns. In contrast, the ordered sample synthesized from NaBiO_3 is much more highly crystalline with larger hexagonal shaped platelets that are a few microns in width, and has horizontal striations on these well-developed facets whose separation ranges from tens to hundreds of nanometers, as seen in Figure S1. Also, the disordered sample synthesized from Bi_2O_3 was found to be a darker yellow color than the ordered sample synthesized from NaBiO_3 (ordered), behavior that would be expected if the ordered sample has a larger average grain size and thus scatters light less effectively.

Figure 2. Top: Comparison of synchrotron ($\lambda = 0.41398$ Å) XRD patterns of disordered (black) and ordered (red) $\text{Na}_3\text{Ni}_2\text{BiO}_6$. Bottom: SEM comparison of morphology of hand-ground samples of disordered (left) and ordered (right) $\text{Na}_3\text{Ni}_2\text{BiO}_6$.

For these reasons, the mobility of ions must be much higher in the reaction that produced the ordered phase, presumably due to a low-melting precursor or transient intermediate phase that greatly enhanced diffusion and reaction rates. This indicates that the polymorphism originates from kinetic rather than thermodynamic causes. As such, it is expected that the ordered sample is the closest to being at thermodynamic equilibrium, and the disordered phase reflects a very incomplete reaction in

which the long-range ordering of honeycomb planes along the *c*-axis is not fully developed. This is fully consistent with results previously obtained for single crystals, in which the as-grown crystals exhibited streaking in their diffraction patterns perpendicular to the layers in a manner characteristic of stacking faults.²⁶ It was shown that these streaks could be effectively decreased by annealing crystals at 500 °C.

3.2 Electrochemical performance. The electrochemical performance of both ordered and disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ indicates that Na ions can be reversibly intercalated into these phases with a performance that has many excellent attributes for a rechargeable Na-ion battery (Figure 3). Surprisingly, the performance of ordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ is substantially better than that of disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$, despite the significantly larger particle size of the ordered material. The ordered phase exhibits an initial discharge capacity of 104 mAh/g during galvanostatic cycling against a Na metal anode, which indicates the virtually all of the theoretical capacity (112 mAh/g) should be accessible once device fabrication is fully optimized. More than 100 mAh/g of this capacity can be delivered at voltages of 3.0 V (vs. Na^+/Na) or higher. This is a high voltage for a Na-ion battery, leading to a good calculated ceramic energy density of 325 Wh/Kg when the discharge curve is integrated. The capacity is delivered through three well-defined plateaus with median voltages of 3.45, 3.18, and 3.10 V, each of which delivers about 1/3 of the total specific capacity when cycling is carried out at a C/30 rate. The measured capacity suggests that only the $\text{Ni}^{3+}/\text{Ni}^{2+}$ redox couple is active, an observation which is fully consistent with XANES measurement on this system (Figure S2). Due to the stoichiometry of this system, only 2/3 of the Na ions are removed during charging, and the specific capacity of this system could be increased by 50% if the remaining Na ions were accessed during electrochemical cycling.

A close inspection of galvanostatic cycling data shows that an overpotential of about 0.05 V is required for the initial Na removal during the first charge plateau of the first charge cycle. It is believed that this overpotential is associated with a low intrinsic conductivity (electronic or ionic) of the fully stoichiometric compound which is mitigated by the formation of Na-ion vacancies and/or the partial oxidation of Ni during charging, as this overpotential is not necessary in subsequent cycles. Throughout the remainder of cycling, the polarization remains low (0.1 – 0.2 V), as can be seen in both GITT and CV data (Figure 3). The electrochemistry of this system therefore appears to be very promising. Curiously, the two lower-voltage plateaus seen during discharge are more similar in voltage during GITT studies than during galvanostatic cycling. This suggests that the kinetics for inserting the final Na ions into the structure are substantially slower than for earlier Na ions, hinting that the initial 0.05 V excess overpotential may be associated with poor ionic (rather than electronic) conductivity.

Although good capacity retention is often difficult to achieve for Na-ion cathode systems, it can be seen that the present system has excellent capacity retention. The discharge capacity on the 25th cycle remains above 100 mAh/g when cycled at a C/30 rate, representing a capacity fade of about 0.1% a cycle and a net capacity loss of about 4% over the month-long timescale of the measurements. In contrast to $\text{Na}_3\text{Ni}_2\text{SbO}_6$, which was found to suffer from self-discharge processes, the present data for $\text{Na}_3\text{Ni}_2\text{BiO}_6$ show nearly identical charge and discharge capacities for every cycle, indicating that self-discharge is not a problem and suggesting that the issues with $\text{Na}_3\text{Ni}_2\text{SbO}_6$ were specifically associated with the presence of Sb ions in that phase. The intrinsically high discharge voltages and the exceptionally stable electrochemical performance of the $\text{Na}_3\text{Ni}_2\text{BiO}_6$ system during initial lab measurements suggest that both the structure and chemistry of this phase are very favorable for rechargeable Na-ion battery applications.

Figure 3. (a) Galvanostatic response (first 10 cycles) of ordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ cycled from 2.7 to 3.8 V (vs. Na^+/Na) at a C/30 rate compared to (b) corresponding data for disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$. Capacity retention at a C/30 rate for (c) ordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ and (d) disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$. Detailed evaluation of ordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ by (e) GITT (load applied for 30 min followed by relaxation for 15 hours, with a net rate of C/320) and by (f) cyclic voltammetry with a 5 mV/s scan rate.

While the ordered phase represents an exceptionally stable Na-ion cathode system, the electrochemical behavior of the disordered system is less attractive (Figure 3b). For disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$, the first cycle specific capacity is about 10 mAh/g lower than for the ordered phase, and the capacity loss over the first 10 cycles is seen to be about 50% larger than for the ordered phase (Figure 3d). For the disordered phase, the difference in the measured charge and discharge capacity for every cycle (10 – 20 mAh/g) is larger than for the ordered material. This is tentatively ascribed to self-discharge effects similar to those previously described for the Sb analogue of this system, likely due to higher dissolution rates redox-active cations at the surface of the disordered phase. It is clear that the disordered polymorph of $\text{Na}_3\text{Ni}_2\text{BiO}_6$ has much worse behavior than the ordered polymorph. For this reason, it is important to achieve a quantitative understanding of the nature and amount of disorder in different samples of $\text{Na}_3\text{Ni}_2\text{BiO}_6$, as disorder appears to significantly influence the electrochemical performance of this promising Na-ion cathode system. In particular, the shape of the diffraction peaks of ordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ suggests that this phase is not fully ordered, and that further improvements in electrochemical performance should be achievable if the degree of ordering is enhanced.

3.3 Framework for describing number faults. Prior to experimentally investigating the structure and faulting of $\text{Na}_3\text{Ni}_2\text{BiO}_6$ in detail, it is important to establish an explicit framework for labelling (1) the *positions* of the central honeycomb B' cations (Bi^{5+} in the case of $\text{Na}_3\text{Ni}_2\text{BiO}_6$), (2) the translational *shift vectors* that describe the differences in position of the B' cation in a pair of successive layers, and (3) the *local environment* of any individual layer, which requires information about both the previous and successive layer. These quantities contain knowledge about interactions 0, 1, and 2 layers beyond the layer of interest, respectively, and are illustrated in Figures 4 and 5. All three of these quantities have relevance to both the energy scale and the symmetry of different layer stacking schemes. It should be noted that the present schemes are defined under the assumption of ideal three-fold rotational symmetry within each layer, an assumption which is only very weakly violated in compounds with monoclinic distortions such as $\text{Na}_3\text{Ni}_2\text{SbO}_6$ and $\text{Na}_3\text{Ni}_2\text{BiO}_6$.

In all rock-salt derived compounds for which the transition metal cations occupy vacancies within a close-packed anion lattice, and these cations are found at either the **A**, **B**, or **C** site positions, labels defined relative to the anion lattice of the $R\text{-}3m$ subcell of the $\alpha\text{-NaFeO}_2$ structure type. While the in-plane coordinates of the atomic sites at the **A**, **B**, and **C** positions are (0,0), (1/3, 2/3), and (2/3, 1/3), respectively in the $R\text{-}3m$ subcell, these sites are split three ways in the triple-volume honeycomb-lattice supercell ($\sqrt{3}a \times \sqrt{3}a \times c$ in the ideal $P3_1I2$ trigonal setting), as illustrated in Figure 4a. The explicit fractional coordinates of the nine resulting sites (**A**₁, **A**₂, **A**₃, **B**₁, **B**₂, **B**₃, **C**₁, **C**₂, **C**₃) are given in Table S1. The position of each honeycomb layer can therefore be uniquely

specified by the position of the B' cation at the center of the honeycomb hexagons. These definitions were chosen so that all atomic sites within a layer with the same numerical index (e.g., **A**₁, **B**₁, **C**₁) will project onto a single point when viewed along the vectors of **a**, **b**, or **u**, where **u** = **-a** – **b**. These three vectors are related by a rotation of 120° normal to the layer plane, as shown in Figure 4a. Within this convention, it will be possible to directly image the number position of each layer through scanning transmission electron microscopy with high angle annular dark field detector (STEM-HAADF) imaging techniques, a result which will be demonstrated later. The present convention differs from that previously proposed by Ma *et al.*,²⁰ and should supersede it.

Figure 4. (a) In-plane transition metal site positions of the A, B, and C layers (at $z = 0, 1/3$, and $2/3$, respectively) relative to the ideal trigonal $P3_112$ superlattice associated with a honeycomb lattice. Honeycomb center positions (e.g., for Bi^{5+}) are shown in blue, while the honeycomb hexagon positions (e.g., for Ni^{2+}) are shown in yellow. (b) The three possible shift vectors relating all possible translations between the position of the honeycomb center in one layer and the subsequent layer. If only one type of shift is present, ordered arrangements will lead to monoclinic $C2/m$ symmetry for a 3-layered repeat, while any cyclical permutation of all three translations will lead to trigonal $P3_112$ symmetry. (c) Superimposed view of the three sets of layer positions for one $C2/m$ (left) and one $P3_112$ (right) structure. The preserved symmetry element from the $R\bar{3}m$ subcell is indicated, as are the sequence of shift vectors associated with these structures.

Although there are a total of 9 possible positions for the B' cation (Bi^{5+}) with respect to the O3 structure of $\text{NaNi}_{2/3}\text{Bi}_{1/3}\text{O}_2$, only 3 different shift vectors are required to describe the 27 possible lateral shifts between pairs of successive layers. The net shift for a honeycomb translation (e.g., $A_1 \rightarrow B_2$) is the sum of the letter shift ($A \rightarrow B$) and a number shift ($1 \rightarrow 2$). A complete list of the shift vectors for the letter, number, and honeycomb translations is provided in Table S2, while a graphical illustration is shown in Figure 4b. In all cases, the honeycomb shift vector has a value of $t_a = (1/3, 0, 1/3)$, $t_b = (0, 1/3, 1/3)$, or $t_u = (-1/3, -1/3, 1/3)$, where the labels reflect that the lateral component of the honeycomb translation vectors has a value of $1/3a$, $1/3b$, or $1/3u$.

In order to have a translational symmetry with a 3-layered repeat period, it is necessary that the in-plane components of the translational shift vectors associated with each of the three layers will sum to an integer value. This is only mathematically possible if the three honeycomb shift vectors are all equal

(in which case the symmetry will be monoclinic) or if the three honeycomb shift vectors are all different (in which case the symmetry will be trigonal), as is graphically illustrated in Figure 4b. Since each honeycomb layer has three possible positions, there are 27 possible layer arrangements in a 3-layered unit cell, which are listed in Table 1. However, it can also be seen in Table 1 that only 9 different combinations of honeycomb shift vectors which are possible, leading to a simplification when describing structures using translational vectors instead of absolute positions. When these 9 honeycomb shift vector patterns are standardized, it can be easily seen that only two possible space groups ($C2/m$ or $P3_112$) are possible for O3-layered compounds, as was previously been reported.³³ The use of honeycomb shift vectors can be generally used to simplify the description of any experimental or hypothetical structure containing honeycomb layers and not just those with an O3 stacking pattern. Figure 5 shows the pattern of shift vectors and layer positions that occur for honeycomb-lattice structures with increasing complexity of their basic repeat unit:

the experimentally determined 3-layered stacking of monoclinic Li_2MnO_3 (t_a only, $C2/m$ symmetry), the 6-layered stacking sequence experimentally determined for Li_2SnO_3 (repeating $t_a t_b$, $C2/c$ symmetry), and a hypothetical 3-layered trigonal structure of $\text{Na}_3\text{Ni}_2\text{BiO}_6$ ($t_a t_b t_u$, $P3_1I2$ symmetry). A simple pattern of shift vectors generates these complex structures.

Figure 5. Stacking patterns for honeycomb-lattice compounds, including experimentally determined 3L $C2/m$ Li_2MnO_3 (t_a), experimentally determined 6L $C2/c$ Li_2SnO_3 ($t_a t_b$), and hypothetical 3L $P3_1I2$ trigonal $\text{Na}_3\text{Ni}_2\text{BiO}_6$ ($t_a t_b t_u$). The Na and Li atom positions are omitted for clarity. Unit cells are shown in red.

Table 1. The 27 possible O3 stacking patterns*.

$C2/m$		
$t_a t_a (t_a)$	$A_1 B_1 C_1$	$A_2 B_2 C_2$ $A_3 B_3 C_3$
$t_b t_b (t_b)$	$A_1 B_2 C_3$	$A_1 B_3 C_2$ $A_2 B_1 C_3$
$t_u t_u (t_u)$	$A_2 B_3 C_1$	$A_3 B_1 C_2$ $A_3 B_2 C_1$
$P3_1I2$		
$t_a t_b (t_u)$	$A_1 B_1 C_2$	$A_2 B_2 C_3$ $A_3 B_3 C_1$
$t_a t_u (t_b)$	$A_1 B_1 C_3$	$A_2 B_2 C_1$ $A_3 B_3 C_2$
$t_b t_a (t_u)$	$A_1 B_2 C_2$	$A_2 B_3 C_3$ $A_3 B_1 C_1$
$t_b t_u (t_a)$	$A_1 B_2 C_3$	$A_2 B_3 C_1$ $A_3 B_1 C_2$
$t_u t_a (t_b)$	$A_1 B_3 C_3$	$A_2 B_1 C_1$ $A_2 B_1 C_1$
$t_u t_b (t_a)$	$A_1 B_3 C_1$	$A_2 B_1 C_2$ $A_2 B_1 C_2$

*The 9 possible pairs of translation vectors (left column) and 27 possible absolute layer number positions (right column) for compounds with an O3 letter stacking sequence (ABC). The third translation vector (in parenthesis) will necessarily follow for periodic compounds with a 3-layer repeat, but not in compounds lacking translational symmetry in the c -axis direction.

In addition to describing the repeat patterns of periodic solids, the shift vector approach can also be applied to understand solids in which the stacking of layers is aperiodic, as is the case for compounds with stacking faults. For aperiodic structures, it is suggested that each individual honeycomb layer be designated as either monoclinic (m) or trigonal (t), in

analogy to the conventional letter stacking sequences for close-packed layers where the each individual layer can be classified as hexagonal (h) or cubic (c) based on the character of its neighboring layers listed in Table 1. The assignment of a layer as monoclinic or trigonal is independent of its absolute position, and only depends on its position relative to the previous and successive layer, information which is specified by two shift vectors. If the translations shifts relative to the layer above and below are the same (e.g., $t_a t_a$), the local environment will be monoclinic. Otherwise, the layer will be locally trigonal. When long range order is present, all pairs of shift vectors that give rise to monoclinic (3 pairs) or to trigonal cells (6 pairs) will be indistinguishable from each other. However, if translational symmetry perpendicular to the planes is lost, there will be three distinguishable types of monoclinic shifts (m_a , m_b , and m_u) which differ in the plane of their local mirror symmetry (ac -plane, bc -plane, or uc -plane, with the three possibilities related by rotations of 120°). Similarly, there will be two distinguishable types of trigonal symmetry (t_1 and t_2) depending on the nature of the shift-generated screw axis (3_1 or 3_2) relative to the positive c -axis. The honeycomb layer number position (1, 2 or 3) can be directly extracted when a crystal structure is viewed along the a , b , or u direction (Figure 5, dashed red lines). Once the hexagon center positions are known, the sequence of shift vectors can be determined using Table 1. It is important to note that if structures are viewed from a different direction or if arbitrary permutations of the labels of the number positions are applied, the apparent number sequence may change. However, the classification of individual layers as either monoclinic or trigonal will always be robust against these arbitrary symmetry-equivalent labelling conventions.

3.4 In-plane honeycomb lattice exists in disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$. The XRD pattern of disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ does not exhibit any well-defined honeycomb superlattice diffraction peaks. However, it exhibits very broad asymmetrical diffraction peaks at the positions where the most intense superstructure peaks (010_p and 020_p) are seen for ordered honeycomb compounds. For the analogous compound $\text{Na}_3\text{Ni}_2\text{SbO}_6$, it was previously found that these Warren-type peaks corresponded to the presence of well-developed honeycomb order within individual planes, but the absence of c -axis coherence between lateral positioning of these honeycomb planes.

Based on PDF data (Figure S3) and Ni K -edge EXAFS data (Figure S4), it can clearly be seen that in-plane honeycomb ordering is also well-developed for the present disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ sample. The disordered α - NaFeO_2 structural model ($R-3m$) without honeycomb order gives a R_{wp} of 25.1% when PDF data are fit from 1.8 – 16.0 Å, a much poorer quality of fit than is obtained when using honeycomb-ordered models with either trigonal ($P3_1I2$, 14.6%) or monoclinic ($C2/m$, 13.5%) symmetry. Complementary EXAFS data were tested over a more limited range ($d_{\text{max}} \sim 4$ Å), but also were much more effectively fit with honeycomb-lattice models, and again exhibit slightly a better fit to the monoclinic model than the trigonal model. In both cases, the fit of the disordered model is clearly very inferior at the specific distance of 5.3 Å that corresponds to the in-plane distance between the central atoms of hexagons within the honeycomb-ordered lattice (Figures S3, S5). When PDF fits are carried out over longer distances (16

– 30 Å), a much smaller improvement in fit quality is obtained when using ordered monoclinic ($R_{wp} = 16.7\%$) or trigonal ($R_{wp} = 17.5\%$) models instead of a disordered model ($R_{wp} = 20.3\%$). These longer distances correspond to interactions over a length scale of 3 – 6 honeycomb layers, and the fitting results suggest that the interlayer coherence is weak at this length scale for disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$.

Figure 6. Image (a) and SAED of “disordered” $\text{Na}_3\text{Ni}_2\text{BiO}_6$ along the (b,c) $[001]_p$ and (d) $[100]_p$ zone axis direction.

The indirect determination of in-plane honeycomb order and out-of-plane stacking disorder from powder diffraction data was confirmed through direct TEM studies of disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ samples. While the most intense electron diffraction peaks can be indexed using the $R\bar{3}m$ subcell, there are many additional reflections that can only be indexed as superstructure peaks, such as the 100_p and 200_p reflections visible in the $[001]_p$ zone axis (where the “P” subscript indicates indexing relative to an ideal trigonal $P\bar{3}12$ superstructure rather than the true $C2/m$ monoclinic superstructure). The stacking disorder of the present cell is most clearly seen in electron diffraction patterns for the orthogonal $[100]_p$ zone axis, which reveals the rods of scattering along the c -axis direction that are expected when stacking faults are present. These rods were also seen in prior single crystal diffraction experiments in which the $hk0$ reciprocal lattice planes were reconstructed from the diffraction data²⁶.

3.5 Signatures of stacking faults in disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$. The ability of STEM-HAADF imaging to resolve individual atomic columns allows the number stacking sequence of honeycomb layers in disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ samples to be directly resolved (Figure 8), something that has never previously been reported. The number position (1, 2, or 3) of layers in the image can be determined from their lateral position when viewed along the $[100]_p$ zone axis, as was schematically illustrated in Figures 5 and 6. The bright spots in the STEM-HAADF image of Figure 7 correspond to Bi positions (the heaviest atom with $Z = 83$), and the dashed yellow

line indicates the expected positions of bright spots when Bi atoms are at the 1 position of layers. It should be noted that the octahedral layers intersect the viewing plane as vertical (and not horizontal) lines in this image. The simulated electron diffraction pattern (inset) of this specific image is similar to the diffraction pattern experimentally measured for the entire particle (Figure 6d).

Figure 7. HRTEM images of disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ viewed along the $[100]_p$ zone axis, where honeycomb layers are stacked in the horizontal direction (instead of the vertical direction of Figure 5). Bi atoms appear as bright spots. The number stacking sequence, transitions vectors, and layer designations for this sample are overlaid. Inset shows the simulated electron diffraction pattern obtained from the image through a FFT.

From the positions of the 27 layers in the image, the 26 interlayer transitions are assigned as either t_a , t_b , or t_u . Furthermore, it is possible to assign monoclinic (m) or trigonal (t) character to the 25 interior layers, as knowledge about two transitions (to the prior and successive layer) is required to make this assignment. For simplicity, the subscripts indicating the subtype of monoclinic (m_a , m_b , m_u) or trigonal (t_1 , t_2) layer are omitted. The layer sequences for 3 additional regions of the disordered sample determined from STEM-HAADF studies are provided in the Figure S6, and show a similar distribution of layer transitions. It should be noted that the indistinguishable nature of the layers means that the labels of 1, 2, and 3 will be arbitrarily permuted across different imaging regions and therefore cannot be directly compared. Across all images, it is found that 36.1% of the layers are monoclinic and 63.9% are trigonal, indicating that there might be a slight enhancement in the degree of order relative to that expected for purely random stacking, which would have 33.3 % monoclinic layers.

The degree of disorder will influence the lattice parameters of $\text{Na}_3\text{Ni}_2\text{BiO}_6$ samples, which are expected to best be described by a trigonal lattice in the case of a fully disordered sample and by a monoclinic lattice for a fully ordered sample. For a fully random structure, the t_a , t_b , and t_u translations between layers will occur with equal probability and thus the

average structure will retain 3-fold symmetry even when these vectors individually cause a local in-plane shear distortion away from the c -axis orthogonality of a trigonal lattice. For a fully ordered monoclinic sample, every layer will have its in-plane shear distortion occur in the same direction (*e.g.*, $\mathbf{t}_a$) and the lattice will have the largest possible monoclinic distortion away from the trigonal ideal. For intermediate degrees of order, it is expected that the magnitude of the monoclinic distortion away from trigonal symmetry will vary continuously, with partially ordered samples having a lesser degree of monoclinic shear than the fully ordered end member.

For a perfectly ordered trigonal (T) structure, each **A** layer position must fall exactly above the **A** layer positions in lower layers and the β_T angle for the trigonal cell must be exactly 90° . In an ideal $C2/m$ monoclinic (M) ordered structure in the conventional setting, when the **A** layer positions are perfectly stacked in vertical columns the ideal β_M angle is not 90° but is instead $[180^\circ - \cos^{-1}(a/c)]$ – a quantity which evaluates to 109.47° when the a and c lengths are equal – due to the built-in lateral offset between successive layers (Figure 8). However, a trigonal-equivalent β'_M angle can be defined even for non-ideal cells if the conventional single-layer monoclinic cell is transformed to a nearly-trigonal 3-layer unit cell ($\mathbf{a}' = 0.5\mathbf{a}_M - 0.5\mathbf{b}_M$, $\mathbf{b}' = 0.5\mathbf{a}_M + 0.5\mathbf{b}_M$, $\mathbf{c}' = 3\mathbf{c}_M + \mathbf{a}_M$), as is shown in Figure S7. The ideal β'_M angle is 90° , though it is expected that the β' angle for actual monoclinic structures will always deviate from 90° since there is no symmetry constraint for orthogonality. The deviation of β' from 90° can be thought of as occurring due to the lateral displacement of successive close-packed layers with the same letter designation (*e.g.*, two **A** layers). The magnitude of this can be described using a shear angle, ϕ , defined as $\phi = \beta' - 90^\circ$.

Figure 8. Relationship between the conventional monoclinic cell (black solid lines) and the transformed trigonal-equivalent monoclinic cell (blue dashed lines). Circles indicate relative positions of atoms in **A** (blue), **B** (green), and **C** (red) close-packed layers. In an ideal monoclinic unit cell (left), there is no shear distortion and atoms in successive **A** layers have no lateral offset, as is also the case for trigonal lattices, so $\beta' = 90^\circ$. In an actual monoclinic cell (right), there is typically a small shear between successive **A** layers causing the β' angle of the monoclinic-equivalent cell to deviate from 90° by an amount defined as the shear angle, ϕ .

The angle β' can be directly calculated from a conventional monoclinic unit cell through the relationship $\beta' = \tan^{-1}(3c_M \sin \beta / [3c_M \cos \beta + a_M])$ when the $\tan^{-1}$ function operates on a positive number and $\beta' = 180^\circ - \tan^{-1}(3c_M \sin \beta / [3c_M \cos \beta + a_M])$ for a negative input, with the derivation of this relationship provided in the Supporting Information. When refined in a conventional monoclinic $C2/m$ unit cell, the lattice parameters of disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ are: $a = 5.3990(1)$, $b = 9.3513(1)$, $c = 5.6770(1)$, and $\beta = 108.486(1)$. These give a β' angle of 90.004° and shear angle of $\phi = 0.004^\circ$, showing that disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ has a negligible distortion away from an ideal trigonal lattice. Single crystals of ordered monoclinic $\text{Na}_3\text{Ni}_2\text{BiO}_6$ were found to have monoclinic $C2/m$ symmetry in prior diffraction studies,²⁶ and the calculated angles based on that literature unit cell are $\beta' = 90.087^\circ$ and $\phi = 0.087^\circ$, reflecting a monoclinic shear which is much larger than is observed for the present disordered sample of $\text{Na}_3\text{Ni}_2\text{BiO}_6$.

3.6 Fault models for fitting diffraction data from disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ – imperfect disorder. While the subcell diffraction peaks of disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ can be effectively fit using $R-3m$, $P3_1I2$, and $C2/m$ structural models (Figure 9, top), none of these three models are able to effectively fit the 100_p Warren-type^{43,45,46} diffraction peaks with an extended high-angle tail associated with the superstructure introduced by honeycomb ordering, as illustrated in the bottom portion of Figure 9. The intensity of this peak is severely underestimated by both ordered structural models ($C2/m$ and $P3_1I2$) and this peak is necessarily absent in the $R-3m$ subcell model. In addition to this 100_p peak, there is a series of additional superstructure diffraction peaks with higher orders in l (101_p , 102_p , 103_p , *etc.*) whose maximum intensities are overestimated by the two ordered structural models. It is therefore clear that the observed diffraction behavior cannot be accurately fit using a “small box” average structural model, and that more complex structural models which properly account for the loss of translational symmetry in the c -axis direction are needed to fit bulk diffraction data and to quantify the disorder in this system.

In the present study, a variety of aperiodic modeling methods were utilized to obtain a quantitative understanding of the stacking faults in $\text{Na}_3\text{Ni}_2\text{BiO}_6$ samples. The first method was the evaluation of explicitly specified stacking sequences, in particular, using stacking sequences obtained from the sample using STEM-HAADF imaging techniques. This was not previously possible since experimentally measured number stacking sequences were not described prior to the present imaging studies. The second method is through refinements using the recursive method of DIFFAX,⁴⁷ in which a long stacking sequence of $\sim 10^4$ layers is generated through the repeated application of a simple 3×3 matrix of transition probabilities (giving rise to 9 total parameters that can be refined) and the diffraction pattern is calculated in a simplified manner from the layer form factors. The transition probability matrix was either fixed to specific values, refined with symmetry constraints, or refined in an unconstrained manner. This was accomplished using the FAULTS program³⁹, which incorporates the original methodology of DIFFAX into the FullProf suite⁴⁸ for fitting powder diffraction data, allowing conventional parameters such as peak shape, instrument aberrations, and atomic site position information to be refined in a manner that was impossible in the original DIFFAX software. The present

work therefore goes beyond prior comparative studies which relied purely on simulation without refinement³³. We note that refinements in FAULTS have been recently carried out

for another honeycomb compound $\text{Li}_4\text{FeSbO}_6$ ⁴⁴, though the goal of those refinements was to investigate the average structure rather than to quantify stacking faults.

Figure 9. “Small box” fits to synchrotron data ($\lambda = 0.24877 \text{ \AA}$) for disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ using disordered ($R\bar{3}m$) and honeycomb-ordered ($P3_1I2$ and $C2/m$) models. Zoom shows fit to honeycomb superstructure peaks with $l = 0$ (100_p) or $l \neq 0$ (101_p , 102_p , 103_p).

The results of the different aperiodic modeling methods applied to disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ are compared in Figure 10. The top pattern shows the fit of a model based on a stacking sequence of 93 honeycomb layers (resulting in a c-axis length of $\sim 50 \text{ nm}$). It can be seen that this local sequence measured within the sample does an excellent job capturing the essential features of the both the sharp Bragg peaks associated with the subcell and the extended Warren-type peak associated with the supercell. The intensity of the 100_p reflection at 3.05° is accurately reproduced, and extra intensity above the tail is observed at the positions of the higher order 101_p (3.18°) and 102_p (3.52°) reflections. The major error in these fits is the ripples associated with the use of one specific local configuration to model the diffraction data rather than averaging over the many possible local configurations which are represented in the actual sample. It should in theory be possible to suppress these ripples by either using longer stacking sequences as input, by artificially disrupting the periodicity of the experimental sequence, or by applying statistical filtering and smoothing algorithms, though such approaches were not evaluated in this initial study.

In order to approach this problem in a more general fashion, the probability matrix approach of DIFFAX was next tested. The simplest model is one in which the stacking of layers is purely random, as is shown in Figure 10b. The purely random model clearly provides a worse description of the diffraction from the sample than the explicit stacking sequence extracted locally from STEM-HAADF imaging, as can be seen in the substantial overestimation of the intensity of the Warren-type 100_p peak. This indicates that the stacking of disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ is not purely random, but instead has a small degree of partial ordering.

Further modeling was therefore done by allowing the 9 elements of the 3×3 transition matrix elements to vary away from the ideal random values of $1/3$ during the course of a refinement in FAULTS. This was carried out in both constrained and unconstrained refinements. If an assumption is

made that the **1**, **2**, and **3** type layers are indistinguishable and therefore occur with equal probability, it also follows that the two types of transitions to layers of a different type (e.g., **1** $\rightarrow$ **2** and **1** $\rightarrow$ **3**) must be equal in probability. The result of this will be that the all elements of the 3×3 matrix depend on a single independent parameter, giving it the form specified in Equation (1), and a constrained refinement of this type is therefore labeled as a 1-parameter fit.

$$(1) \quad \begin{pmatrix} x & (1-x)/2 & (1-x)/2 \\ (1-x)/2 & x & (1-x)/2 \\ (1-x)/2 & (1-x)/2 & x \end{pmatrix}$$

When this type of constrained 1-parameter refinement is carried out, a very good fit to the Warren tail of the 100_p peak is obtained, though no insufficient intensity is assigned to the integer order superstructure reflections which are higher order in l (101 , 102 , etc.) resulting in a discrepancy with the experimental data at positions marked with red arrows. The refined value of $x = 0.465(1)$ is larger than the value of $x = 0.333$ expected for purely random stacking, and provides a quantitative (but indirect) measure of the degree of ordering in this sample. The relative probabilities of monoclinic and trigonal transitions can be directly calculated from this matrix, and it is found that monoclinic transitions occur more often (36.0%) than would be expected for a purely random system (33.3%). This again suggests that the disordered sample is not fully random. It is possible to define a monoclinic order parameter η_m for this system which varies linearly from $\eta_m = 0$ for a fully random stacking sequence (where the probability of a monoclinic transition is 33.3%) to $\eta_m = 1$ (when 100% of the layer transitions are monoclinic). For the constrained matrix, it can be analytically derived that $\eta_m = (9/4)(x - 1/3)^2$, or conversely, $x = (1 + 2\eta_m)/3$. Using this constrained refinement, it is calculated that the present disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ sample contains about 4% monoclinic order.

Figure 10. Refinements for disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ using synchrotron data ($\lambda = 0.24877 \text{ \AA}$) using the translation vector probability model implemented within the Faults software. Inset shows fits to the large 100_p superstructure peak and smaller peaks associated with the 101_p , 102_p , and 103_p reflections. (a) Explicit model using the sequence determined from STEM as input. (b) Fully random model. (c) 1-parameter model. (d) 6-parameter model.

One limitation of the single-parameter fit method is that it implicitly assumes three-fold rotational symmetry and forces the average abundance of monoclinic domains with shear in the **a**, **b**, and **u** directions to be equal. This assumption must break down as the degree of ordering increases since a fully ordered monoclinic sample will have only one type of monoclinic domain rather than an equal mixture of all three. It is therefore worthwhile to explore unconstrained refinements in which all 9 matrix elements are allowed to refine, and this is found to result in a noticeable improvement in the quality of the fit. Since the sum of the translation probabilities away from any layer must sum to 1, this unconstrained refinement only investigates 6 independent parameters, and is labeled as a 6-parameter fit. It can be seen that discrete intensity is added at the position of the higher order 101_p and 102_p reflections, though there are still errors in the calculated intensities of some of these peaks. In the unconstrained 6-parameter matrix,

the refined layer probabilities are 42.6 % (layer 1), 31.6 % (layer 2), and 25.8 % (layer 3). Similarly, the refined probability of t_a (26.8 %), t_b (39.9%), and t_u (33.2 %) are no longer equal. It should be noted that identical fits can be obtained using a variety of permutations of the probability matrix as the **a**, **b**, and **u** directions and the 1, 2, and 3 positions are fundamentally indistinguishable due to the symmetry relationships of this system. The unequal abundances of layer types and translation vectors again provide evidence for the partial development of monoclinic order within the disordered sample.

While the unconstrained probability matrix approach improves the fit to the 101_p and higher order reflections, it does not perfectly model their intensities. It is believed that this is due to a fundamental limitation of the probability matrix approach, which implicitly assumes that the energy of the system is exclusively determined by the nearest neighbor layer interactions. This hypothesis is supported by the analysis of the ordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ diffraction data which shows that long range strain plays an important role in the observed stacking patterns, as will be discussed in the next section. These long range interactions can never be captured in purely local models for stacking fault transition probabilities.

3.7 Imperfect order in $\text{Na}_3\text{Ni}_2\text{BiO}_6$. The synchrotron diffraction pattern of ordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ contains two classes of superstructure peaks that were not present in the disordered phase. The first class of superstructure peaks are those associated with the in-plane honeycomb ordering, which is known in general to produce either a trigonal $P3_112 \sqrt{3} \times \sqrt{3} \times 1$ supercell of the basic $\alpha\text{-NaFeO}_2 R\text{-}3m$ subcell or a closely related monoclinic $C2/m$ supercell. Both Le Bail (Figures S8 and S9) and Rietveld (Figure 11) refinements show the monoclinic $C2/m$ space group to be most appropriate superstructure for the present ordered sample, consistent with prior single crystal and powder diffraction investigations of this phase.²⁶ The monoclinic distortion away from trigonal symmetry is small but significant, as reflected in the shear angle of $\phi = 0.108^\circ$ and the β' angle of 89.892° . However, it should be noted that the peak corresponding to the 010_p reflection (where P indicates the indexing is relative to the ideal $P3_112$ trigonal unit cell) found at 3.1° in the synchrotron data still has a clearly visible high-angle tail extending to the right of the sharp Bragg peak associated with this honeycomb superstructure reflection, indicating that the $C2/m$ ordering is dominant but not perfect in the present sample.

Another signature of the imperfect monoclinic ordering can be found in refined site occupancies during Rietveld refinements (Table S3). Even within the ordered monoclinic superstructure, the best fits are obtained only when partial anti-site disordering across the two transition metal sites is included. The best fit is obtained when 12.6% of the Ni and 25.1% Bi atoms are placed at minority sites (corresponding to 20.9% of the total number of transition metal sites). This observation does not indicate actual cation mixing, but instead reflects an indirect mechanism for describing the influence of stacking faults, which violate the translational symmetry expected for the average structure^{26,49}. The refined site mixing was found to be about 50% (relative) higher in a prior $\text{Na}_3\text{Ni}_2\text{BiO}_6$ study²⁶, suggesting that different preparations have different degrees of order as is expected for a kinetically limited process. Based on these results, it is clear that sharp superstructure peaks can be observed even when $\text{Na}_3\text{Ni}_2\text{BiO}_6$ is relatively far away from having perfect monoclinic ordering (80% vs. 100%).

Figure 11. Top: Rietveld refinement of synchrotron data ($\lambda = 0.41398 \text{ \AA}$) for ordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ sample using a $C2/m$ model. Bottom: Zoom showing three classes of superstructure peaks near the 100_p peak that are not indexed by the $R\bar{3}m$ subcell. Although all peaks marked 3L can be indexed when a $C2/m$ or $P3_1I2$ honeycomb-ordered supercell is used, reflections with a 6L, 9L, and 12L period remain unindexed. The detailed indexing of these peaks is provided in the Supporting Information (Figure S10).

A second class of superstructure reflections associated with longer period c -axis superstructures can also be observed for the ordered sample, as shown in Figure 11. These reflections have been previously observed for other honeycomb lattice compounds^{20,50} but the specific nature of the ordering giving rise to these reflections has not previously been understood. A detailed indexing and whole-pattern fitting study of these reflections (Figure S10) shows there are two curious aspects of these superstructure peaks. First, when indexed using ideal primitive trigonal honeycomb-ordered unit cells (where the basic cell has a height of 3 layers, denoted 3L), the c -axis period is always a multiple of three with the intensity of the superstructure peaks always decreasing for larger superstructures. Periods of 6L, 9L, and 12L are labeled, and even weaker peaks associated with a 15L period can also be resolved if the data are inspected closely. Second, the superstructure peak widths remain narrow even as the peak intensities decrease. If the non-instrumental peak broadening is fit to a model where the only contribution to the peak width is size broadening, the refined coherence length is at least 200 nm for all of the clearly resolved superstructures (Figure S10).

Taken together, these results indicate that the superstructures represent neither the random generation of ordered domains by stacking faults (inconsistent with narrow peak widths) nor a specific long range ordering that is more thermodynamically stable than the base 3L period of the fundamental $O3$ honeycomb lattice (inconsistent with the multiple phases, and with the intensities which scale inversely with the c -axis period). We instead propose that these superstructure peaks represent a macroscopic strain-relief mechanism. We earlier defined a shear angle ϕ such that ϕ is equal to the deviation from orthogonality of the angle between these two crystallographic directions with the convention that $\phi = 0$ in the presence of ideal trigonal symmetry. When a 100% or-

dered monoclinic distortion occurs, a layer shear will be generated and the shear angle will be $\phi = \mu$, where the maximum shear possible is μ . However, if short range monoclinic domains with each of these three possible shear vectors are present in equal abundances, as will be the case in the limit of high randomness, then it is expected that the overall lattice symmetry of the average unit cell will retain three-fold symmetry and thus have $\phi = 0$ due to the coherence between layers with the three types of monoclinic symmetry. This is an example of the local symmetry differing from the average symmetry, as has been previously observed for other types of crystal structures⁵¹.

At the limit of no randomness, it is expected that the ideal monoclinic shear of $\phi = \mu$ will only occur for honeycomb samples with fully developed long range order. Near this limit samples with partial monoclinic order will have $\phi < \mu$. Conversely, if for a sample the shear ϕ is fixed at a value less than the ideal monoclinic μ (for example, by the kinetics of an incomplete reaction), a fully ordered monoclinic stacking sequence (e.g., $t_a t_a t_a$) that maximizes the shear **cannot** be the lowest energy arrangement of layers. In the presence of such partial shear, a lower energy stacking sequence will be one in which the average layer shear some fraction of μ . For a 6L period, the stacking sequence $t_a t_a t_a t_b t_b t_a$ (**111311**) should give a value of $\phi = \mu/2$ since the first three layers will produce the maximum shear for 3 layers while the last three layers will produce no net shear. Similarly, it is easy to construct periodic stacking sequences with shears of $2\mu/3$ (9L), $3\mu/4$ (12L), and $4\mu/5$ (15L) if larger period stacking sequences are utilized. These nearly-monoclinic stacking sequences will represent **transiently** thermodynamically stable stacking arrangements as the average shear of a sample evolves from $\phi = 0$ to $\phi = \mu$ as the layer sequence evolves from random to fully ordered.

The large-period superstructure peaks should represent a general signature of nearly-completely developed monoclinic ordering. Although the complex c -axis superstructure peaks for monoclinic $\text{Na}_3\text{Ni}_2\text{SbO}_6$ were previously indexed using a mixture of 4L and 9L superstructures²⁰, the incorrectly indexed 4L peaks instead represent a partial indexing of the 12L peaks and do not contradict the model proposed in the previous paragraph. In fact, the same pattern of intensities (continuously decreasing with increasing period length) are observed when the previously published “ordered” $\text{Na}_3\text{Ni}_2\text{SbO}_6$ pattern is re-indexed with 6L, 9L, and 12L superstructure peaks. Another implication of this shear analysis is that the monoclinic β' angles provide a good measure of the degree of ordering. A fully-ordered monoclinic sample is expected to have a higher degree of shear than was observed in the present sample as well as a β' angle that is further distorted from 90° , in both cases exceeding the values refined for the present sample of $\text{Na}_3\text{Ni}_2\text{BiO}_6$ ($\phi = -0.108^\circ$, $\beta' = 89.892^\circ$).

While some conclusions about the nature of the stacking can be indirectly inferred from X-ray diffraction patterns, it is now possible to use stacking sequences from STEM-HAADF images collected in the $[100]_p$ zone to evaluate these hypotheses. Images for two regions of the present ordered sample are shown in Figure 12, together with the sequences extracted from these images. Complementary electron images and diffraction patterns for the sample are provided in Figure S11. Many regions of the ordered sample are found to be perfectly ordered with every honeycomb layer at the same number position, as can be seen for the $20 \times 10 \text{ nm}$ region in Figure 12a in

which the highlighted **1111** sequence corresponds to a $t_a t_a t_a$ monoclinic shift sequence, which is present everywhere in the field of view. In contrast, some other regions can be clearly seen to have occasional trigonal faults, as can be seen in the **1311** region highlighted in Figure 12b, which corresponds to a cyclical $t_u t_b t_a$ shift sequence with no net monoclinic shear.

Figure 12. STEM-HAADF images of two different regions of ordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$. Perfect 1111 ($t_a t_a t_a$) monoclinic layer sequences are seen in many regions, including over the entire 20 nm block imaged in (a). However, other regions have 1311 defects ($t_u t_b t_a$) that correspond to a local block of 3 trigonal layers with zero net shear, as shown in (b). Axes labels and indexing are relative to the ideal primitive trigonal supercell.

The probability matrix used to model bulk X-ray diffraction patterns of disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ was also applied to study ordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$, and supports the key conclusion that the predominant local arrangement is one in which two types of layer number positions co-exist, rather than having only a single layer position (as would be expected for a fully ordered monoclinic sample) or having all three number positions present in equal amounts (as would be expected in the presence of random stacking faults). The results for a 6-parameter fit to the ordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ data is shown in Figure S12. An analysis of the 3×3 probability matrix (given in Figure S12) shows that the probabilities of the three layer positions are 77.1%, 22.9%, and 0.0%, and suggests that individual layers have a 48.3% chance of being monoclinic and a 51.7% chance of being trigonal. While these results are in qualitative agreement with the other data for the ordered phase (STEM, Rietveld refinements), they exhibit quantitative differences which reflect the limitations of the probability matrix approach. In particular, the net faulting probability deduced from the Ni/Bi site mixing refined using Rietveld methods was much lower (20%), and much more consistent with direct STEM counting statistics (15.3%). In STEM observations, it could be clearly seen that the trigonal stacking defects typically occurred in groups of 3 or more, and this tendency for clustering cannot be captured in the simple probability matrix approach, which ignores long range interactions. If a model that more closely reproduces the actual experimental stacking arrangements is used, it is expected that quantitative agreement between the different methods will be achieved, though this is beyond the scope of the present work.

4. Discussion

By explicitly determining the stacking sequences, it is possible to use the observed stacking patterns to gain insights into the synthetic mechanism by which the initial disordered ar-

range of honeycomb layers develops long range order. A compilation of the stacking sequences measured for six different regions of the ordered sample is presented in Figure 13. Again, it must be remembered that the layer number positions are determined in a relative and not absolute manner, so values of the numbers assigned to different images cannot be directly compared. Still, it can be clearly seen that the residual disorder is distinctly non-random. In particular, although a number of images contained multiple layers that deviated from the dominant monoclinic stacking domain, no image contained layers at more than two of the three possible types of honeycomb layer positions. This confirms that stacking faults do not occur randomly throughout the sample, but are arranged in a specific pattern which reflects the history of the sample.

Figure 13. Non-random faulting of layer positions in ordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ determined from STEM images. No more than two layer types occur in any region of the ordered sample.

From a comparison of the stacking patterns for the disordered and ordered sample, a mechanism for the development of order can be deduced. Layers initially form with well-developed honeycomb order, but with a nearly random distribution across the 1, 2, and 3 positions. Since a purely monoclinic arrangement of layers has a lower free energy than a purely trigonal arrangement, layers locally begin to develop monoclinic order. At first, all three monoclinic variants (m_a , m_b , and m_c) will be present in approximately equal amounts. Even if these three variants are present globally in exactly equal amounts, the distribution locally will favor an excess of one type of monoclinic distortion over the other two as this represents a lower strain and lower energy configuration. All three types of monoclinic domains will grow over in size over time, though this growth will be subject to constraints. First, the three types of domains will compete with each other in a competitive process similar to Ostwald ripening, and one of the three monoclinic domains will come to dominate in each particle. This ripening process will be driven by coherency strain within the lattice which is tied to the amount of shear that occurs on average between successive layers. Because of the long range nature of the strain associated with shear, the energy of the dominant monoclinic domain will be continuously lowered relative to the other two types of monoclinic domains, with the stabilization of the majority domain becoming more pronounced as the domain grows in relative abundance. However, the ripening process is slow and the same strain-mediated interactions will transiently stabilize the presence of higher-order superstructures (6L, 9L, 12L, etc.) during the ripening process, as these superstructures have an average shear in their periodic cell which is more closely matched to the average shear of the particle than that of a purely monoclinic (or purely trigonal cell).

While it is expected that the thermodynamic equilibrium state for $\text{Na}_3\text{Ni}_2\text{BiO}_6$ is one in which monoclinic order is fully developed within the sample, the timescale for achieving full

order is extremely slow under normal synthetic conditions. For this reason, honeycomb compounds should not be considered to have two distinct polymorphs (fully ordered, fully disordered), but instead should be recognized as having a continuum of history-dependent intermediate structures that sample a broad spectrum of possible structural arrangements. As such, both the structure and properties of partially ordered polymorphs will vary with the degree of order, leading to day-to-day and lab-to-lab variation between the structure and properties of different synthetic batches due to the strong history-dependence of structure. However, the tools that have been developed here for quantifying the degree of order should represent an effective tool for properly measuring the position along this spectrum where any particular sample exists.

The methods and mechanisms that have been described here are expected to be generally applicable for all honeycomb compounds which have a monoclinic ground state, and therefore should be directly applicable to Li_2MnO_3 and other closely related Li-excess compounds. Any honeycomb-lattice compound whose ground state is trigonal rather than monoclinic is expected to behave in a somewhat different fashion since the thermodynamic ground state is one in which shear distortions are absent ($\phi = 0$), and such compounds are expected to have a different mechanism for fully developing long range order due to the absence of long range strain effects. However, we have found no robust literature evidence that any known honeycomb-lattice compound has a trigonal $P3_12$ ground state, perhaps reflecting the higher complexity of the fundamental repeat unit of this cell (3 layers) relative to a $C2/m$ (1 layer) and the $C2/c$ (2 layers) symmetry stacking arrangements, as was illustrated in Figure 5.

5. Conclusions

It has been demonstrated that $\text{Na}_3\text{Ni}_2\text{BiO}_6$ has many promising characteristics desirable for a cathode in Na-ion batteries, including its low capacity fade ($\sim 0.1\%$ / cycle) and high voltage discharge plateaus. It was observed that ordered samples of $\text{Na}_3\text{Ni}_2\text{BiO}_6$ have substantially better performance than disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$, so general methods for characterizing and quantifying the degree of ordering in honeycomb-lattice compounds have been developed. It was shown for the first time that number stacking sequences can be directly resolved on the atomic scale using STEM-HAADF imaging techniques, and average fault probabilities can be determined through the quantitative fitting of bulk diffraction data. These fits were accomplished through the use of explicit superstructure models, which were far more effective at describing the observed diffraction peaks than previously proposed two-phase refinements of trigonal and monoclinic phases (due to the inability of two-phase models to capture lattice coherence effects). Through these studies, it is found that there is imperfect order in an ordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ sample ($\sim 20\%$ faults) and imperfect disorder in a disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ sample ($\sim 5\%$ monoclinic ordering), suggesting that further improvements in electrochemical performance may be achievable with more highly ordered samples. The first complete indexing of higher-order stacking superstructure peaks is demonstrated, and it is shown the existence of these superstructures is driven by the influence of long-range strain effects. A proposed mechanism for the gradual development of long-range through Oswald ripening like processes is consistent with all experimental observations in both ordered and disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$. It is expected that the proposed structure and crystal growth model

will be generally applicable for other important honeycomb ordered layered oxide systems.

ASSOCIATED CONTENT

Supporting Information. Additional fits, SEM images, STEM-HAADF images, schematic illustration of 9 layers and 3 layers model, cycling of disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$, *ex situ* Ni K-edge XANES of ordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ during charge/discharge

AUTHOR INFORMATION

Corresponding Author

kpete@bnl.gov

ACKNOWLEDGMENT

Research of J.L. was supported as part of the NorthEast Center for Chemical Energy Storage (NECCES), an Energy Frontier Research Center funded by the U. S. Department of Energy, Office of Basic Energy Sciences under Award #DE-SC0012583, including matching support from NYSTAR-NYSERDA. L.Y. was supported by the National Science Foundation Grant No. DMR-0955646. S.B., X.Y., and X.-Q.Y. at BNL were supported by the U.S. Department of Energy, the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies, under Contract No. DE-SC0012704. L.W. and Y.Z. were supported by the U.S. Department of Energy, Office of Basic Energy Science, Division of Materials Science and Engineering, under Contract No. DE-SC0012704. Research was in part carried out at Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-SC0012704. This research utilized the facilities at the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-SC0012704. Use of the National Synchrotron Light Source (beamlines X18A and XPD), Brookhaven National Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-SC0012704. J.L. would also like to thank technical supports by the beamline scientists from BL2-2 of SSRL, SLAC, supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences under contractor No. DE-AC02-76SF00515.

REFERENCES

- (1) Mizushima, K.; Jones, P. C.; Wiseman, P. J.; Goodenough, J. B. *Mater. Res. Bull.* **1980**, *15*, 783.
- (2) Braconnier, J. J.; Delmas, C.; Fouassier, C.; Hagenmuller, P. *Mater. Res. Bull.* **1980**, *15*, 1797.
- (3) Whittingham, M. S. *Prog. Solid State Chem.* **1978**, *12*, 41.
- (4) Tarascon, J.-M.; Armand, M. *Nature* **2001**, *414*, 359.
- (5) Ozawa, K. *Solid State Ionics* **1994**, *69*, 212.
- (6) Billaud, J.; Clément, R. J.; Armstrong, A. R.; Canales-Vázquez, J. s.; Rozier, P.; Grey, C. P.; Bruce, P. G. *J. Am. Chem. Soc.* **2014**, *136*, 17243.
- (7) Park, Y.-U.; Seo, D.-H.; Kwon, H.-S.; Kim, B.; Kim, J.; Kim, H.; Kim, I.; Yoo, H.-I.; Kang, K. *J. Am. Chem. Soc.* **2013**, *135*, 13870.
- (8) Slater, M. D.; Kim, D.; Lee, E.; Johnson, C. S. *Adv. Funct. Mater.* **2013**, *23*, 947.
- (9) Pan, H. L.; Hu, Y. S.; Chen, L. Q. *Energy & Environmental Science* **2013**, *6*, 2338.
- (10) Zhou, Y. N.; Ding, J. J.; Nam, K. W.; Yu, X. Q.; Bak, S. M.; Hu, E. Y.; Liu, J.; Bai, J. M.; Li, H.; Fu, Z. W.; Yang, X. Q. *Journal of Materials Chemistry A* **2013**, *1*, 11130.
- (11) Kim, S. W.; Seo, D. H.; Ma, X.; Ceder, G.; Kang, K. *Advanced Energy Materials* **2012**, *2*, 710.
- (12) Yabuuchi, N.; Kubota, K.; Dahbi, M.; Komaba, S. *Chem. Rev. (Washington, DC, U. S.)* **2014**, *114*, 11636.
- (13) Song, J.; Wang, L.; Lu, Y.; Liu, J.; Guo, B.; Xiao, P.; Lee, J.-J.; Yang, X.-Q.; Henkelman, G.; Goodenough, J. B. *J. Am. Chem. Soc.* **2015**, *137*, 2658.
- (14) Mizushima, K.; Jones, P. C.; Wiseman, P. J.; Goodenough, J. B. *Solid State Ionics* **1981**, *3-4*, 171.
- (15) Ohzuku, T.; Makimura, Y. *Chem. Lett.* **2001**, *7*, 642.
- (16) Komaba, S.; Takei, C.; Nakayama, T.; Ogata, A.; Yabuuchi, N. *Electrochem. Commun.* **2010**, *12*, 355.
- (17) Takeda, Y.; Nakahara, K.; Nishijima, M.; Imanishi, N.; Yamamoto, O.; Takano, M.; Kanno, R. *Mater. Res. Bull.* **1994**, *29*, 659.
- (18) Delmas, C.; Braconnier, J.-J.; Fouassier, C.; Hagenmuller, P. *Solid State Ionics* **1981**, *3*, 165.
- (19) Komaba, S.; Yabuuchi, N.; Nakayama, T.; Ogata, A.; Ishikawa, T.; Nakai, I. *Inorg. Chem.* **2012**, *51*, 6211.
- (20) Ma, J.; Bo, S. H.; Wu, L. J.; Zhu, Y. M.; Grey, C. P.; Khalifah, P. G. *Chem. Mater.* **2015**, *27*, 2387.
- (21) Yuan, D. D.; Liang, X. M.; Wu, L.; Cao, Y. L.; Ai, X. P.; Feng, J. W.; Yang, H. X. *Adv. Mater. (Weinheim, Ger.)* **2014**, *26*, 6301.
- (22) Evstigneeva, M. A.; Nalbandyan, V. B.; Petrenko, A. A.; Medvedev, B. S.; Kataev, A. A. *Chem. Mater.* **2011**, *23*, 1174.
- (23) Smaha, R. W.; Roudebush, J. H.; Herb, J. T.; Seibel, E. M.; Krizan, J. W.; Fox, G. M.; Huang, Q.; Arnold, C. B.; Cava, R. J. *Inorg. Chem.* **2015**, *54*, 7985.
- (24) Zvereva, E. A.; Evstigneeva, M. A.; Nalbandyan, V. B.; Savelieva, O. A.; Ibragimov, S. A.; Volkova, O. S.; Medvedeva, L. I.; Vasiliev, A. N.; Klingeler, R.; Buechner, B. *Dalton Trans.* **2012**, *41*, 572.
- (25) Seibel, E. M.; Roudebush, J. H.; Ali, M. N.; Ross, K. A.; Cava, R. J. *Inorg. Chem.* **2014**, *53*, 10989.
- (26) Seibel, E. M.; Roudebush, J. H.; Wu, H.; Huang, Q. Z.; Ali, M. N.; Ji, H. W.; Cava, R. J. *Inorg. Chem.* **2013**, *52*, 13605.
- (27) Johnson, C.; Kim, J.; Lefief, C.; Li, N.; Vaughey, J.; Thackeray, M. *Electrochem. Commun.* **2004**, *6*, 1085.
- (28) Yabuuchi, N.; Yoshii, K.; Myung, S.-T.; Nakai, I.; Komaba, S. *J. Am. Chem. Soc.* **2011**, *133*, 4404.
- (29) Thackeray, M. M.; Johnson, C. S.; Vaughey, J. T.; Li, N.; Hackney, S. A. *J. Mater. Chem.* **2005**, *15*, 2257.
- (30) Strobel, P.; Lambertandron, B. *J. Solid State Chem.* **1988**, *75*, 90.
- (31) Massarotti, V.; Bini, M.; Capsoni, D.; Altomare, A.; Moliterni, A. G. G. *J. Appl. Crystallogr.* **1997**, *30*, 123.
- (32) Armstrong, A. R.; Holzapfel, M.; Novák, P.; Johnson, C. S.; Kang, S.-H.; Thackeray, M. M.; Bruce, P. G. *J. Am. Chem. Soc.* **2006**, *128*, 8694.
- (33) Breger, J.; Jiang, M.; Dupre, N.; Meng, Y. S.; Shao-Horn, Y.; Ceder, G.; Grey, C. P. *J. Solid State Chem.* **2005**, *178*, 2575.
- (34) Croguennec, L.; Poullerie, C.; Mansour, A. N.; Delmas, C. *J. Mater. Chem.* **2001**, *11*, 131.
- (35) Hammersley, A. P.; Svensson, S. O.; Hanfland, M.; Fitch, A. N.; Hausermann, D. *High Pressure Research* **1996**, *14*, 235.
- (36) Juhas, P.; Davis, T.; Farrow, C. L.; Billinge, S. J. L. *J. Appl. Crystallogr.* **2013**, *46*, 560.
- (37) Le Bail, A.; Duroy, H.; Fourquet, J. L. *Mater. Res. Bull.* **1988**, *23*, 447.
- (38) Rietveld, H. M. *J. Appl. Crystallogr.* **1969**, *2*, 65.
- (39) Casas-Cabanas, M.; Rodriguez-Carvajal, J.; Palacin, M. R. *Z. Kristallogr.* **2006**, 243.
- (40) Farrow, C. L.; Juhas, P.; Liu, J. W.; Bryndin, D.; Bozin, E. S.; Bloch, J.; Proffen, T.; Billinge, S. J. L. *Journal of Physics-Condensed Matter* **2007**, *19*.
- (41) Ravel, B.; Newville, M. *J. Synchrotron Radiat* **2005**, *12*, 537.
- (42) Zabinsky, S. I.; Rehr, J. J.; Ankudinov, A.; Albers, R. C.; Eller, M. J. *Physical Review B* **1995**, *52*, 2995.
- (43) Biscoe, J.; Warren, B. E. *J. Appl. Phys.* **1942**, *13*, 364.
- (44) McCalla, E.; Abakumov, A.; Rousse, G.; Reynaud, M.; Sougrati, M. T.; Budic, B.; Mahmoud, A.; Dominko, R.; Van Tendeloo, G.; Hermann, R. P.; Tarascon, J. M. *Chem. Mater.* **2015**, *27*, 1699.
- (45) Warren, B. E. *X-ray Diffraction*; Courier Corporation, 1969.
- (46) Warren, B. E. *Physical Review* **1941**, *59*, 693.
- (47) Treacy, M. M. J.; Newsam, J. M.; Deem, M. W. *Proceedings of the Royal Society of London Series a-Mathematical Physical and Engineering Sciences* **1991**, *433*, 499.
- (48) Rodriguez-Carvajal, J. *Physica B* **1993**, *192*, 55.
- (49) Roudebush, J. H.; Andersen, N. H.; Ramlau, R.; Garlea, V. O.; Toft-Petersen, R.; Norby, P.; Schneider, R.; Hay, J. N.; Cava, R. J. *Inorg. Chem.* **2013**, *52*, 6083.
- (50) Politaev, V. V.; Nalbandyan, V. B.; Petrenko, A. A.; Shukaev, I. L.; Volotchaev, V. A.; Medvedev, B. S. *J. Solid State Chem.* **2010**, *183*, 684.
- (51) Page, K.; Kolodiazny, T.; Proffen, T.; Cheetham, A. K.; Seshadri, R. *Phys. Rev. Lett.* **2008**, *101*, 205502.

For Table of Contents Only:

Indexing of multiple strain-stabilized superstructures for $\text{Na}_3\text{Ni}_2\text{BiO}_6$ using synchrotron diffraction data.

Supporting information

Quantification of honeycomb number-type stacking faults: application to $\text{Na}_3\text{Ni}_2\text{BiO}_6$ cathodes for Na-ion batteries

Jue Liu^{§,†}, Liang Yin[§], Lijun Wu[⊥], Jianming Bai[#], Seong-Min Bak[†], Xiqian Yu[†], Yimei Zhu[⊥], Xiao-Qing Yang[†], Peter G. Khalifah^{§,†}

§ Department of Chemistry, State University of New York at Stony Brook, Stony Brook, N.Y., 11794-3400, United States

† Chemistry department, Brookhaven National Laboratory, Upton, NY, 11973, United States

⊥ Condensed Matter Physics and Material Science Department, Brookhaven National Laboratory, Upton, NY 11973, United States

Photon Science Division, Brookhaven National Laboratory, Uptown, NY, 11973, United States

Figure S1. (Top) SEM images and EDX spectra of disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$. (Bottom) SEM images and EDX spectra of ordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$, which clearly showed the striations on these hexagonal platelets.

Figure S2. Top: Ni K-edge XANES spectra of pristine $\text{Na}_3\text{Ni}_2\text{BiO}_6$ (black), sample charged to 3.3 V (blue) and 3.6 V (red). Bottom: Ni K-edge XANES spectra of sample discharged to 3.4 V (cyan) and 3.1 V (brown).

Figure S3. Fits of local (1.8 – 16.0 Å, top) and non-local (16 – 30 Å, bottom) PDF data for disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ to structural models without honeycomb order ($R-3m$) or with honeycomb order ($P3_112$ and $C2/m$). The highlighted peak at $r \sim 5.3$ Å corresponds to the primary periodicity of the honeycomb order, as illustrated in Figure S5, and provides the most direct insights about the presence or absence of honeycomb order.

Figure S4. Fits to Ni K-edge EXAFS data of “disordered” $\text{Na}_3\text{Ni}_2\text{BiO}_6$ with Ni/Bi randomly distributed $R-3m$ model, Ni/Bi honeycomb ordered $P3_112$ and $C2/m$ models. Only the ordered $P3_112$ and $C2/m$ models adequately fit the second and third coordination shells.

Figure S5. Schematic illustration of Ni/Bi arrangements in randomly distributed $R\bar{3}m$ and honeycomb lattice $C2/m$ and $P3_1I2$ models. For the $R\bar{3}m$ model, there is a probability of 1/9 for Bi-Bi pairs, 4/9 for Ni-Ni pairs and 4/9 for Ni-Bi pairs between transition metal sites at $r \sim 5.3$ Å, whereas at this distance in layers with a fully ordered honeycomb lattice there are only Bi-Bi (3/9) and Ni-Ni (6/9) pairs.

X-rays have good sensitivity to the degree of Ni/Bi disorder due to the large difference in their atomic scatter factors. Thus, high quality X-ray PDF data of disordered sample was collected at XPD beam line at NSLS-II. Three different structure models were used to fit the PDF pattern up to 16 Å (the approximate c -axis length of one trigonal unit cell), as can be seen in Figure S3. It clearly shows that $C2/m$ and $P3_1I2$ with honeycomb ordered Ni/Bi layer provides better fit than that of $R\bar{3}m$ with randomly distributed Ni/Bi. Interestingly, it can be seen the biggest difference among these fits arises from the peak at about 5.3 Å. The $C2/m$ and $P3_1I2$ models with in-plane honeycomb ordered Ni/Bi can fit this peak well, whereas the $R\bar{3}m$ model fails to capture the full intensity of this peak. This ~ 5.3 Å peak is associated with the second nearest metal-metal pairs (Ni-Bi or Na-Na) within the ab -plane. This distance is also equal to the in-plane unit cell parameters ($a = b = 5.3$ Å) of the $\sqrt{3}a \times \sqrt{3}a$ supercell in the trigonal setting. For PDF modeling, we used the following equation to calculate the *reduced pair distribution function* ($G(r)$) from an initial structural model¹:

$$G(r) = \frac{1}{r} \sum_m \sum_n \frac{f_m f_n}{\langle f \rangle^2} \delta(r - r_{mn}) - 4\pi r \rho_0$$

Here, f_m and f_n are the X-ray form factors of the m^{th} and n^{th} atom, $\langle f \rangle$ is the average X-ray scattering factor of all atoms in the formula, r_{mn} is the distance between the m^{th} and n^{th} atom, ρ_0 is the number density of atoms and δ is the Dirac delta function. For the specific case here, all atom pairs not at the transition metal site should contribute almost identically in all three cases ($R\bar{3}m$, $C2/m$ and $P3_1I2$), so only the different behavior of Ni-Bi pairs in these different structural models will be considered. Therefore for the pairs of interest, f_m and f_n are taken to be f_{Bi} and f_{Ni} , respectively, while r_{mn} is taken to be the distance for second nearest Ni-Bi pairs. The X-ray scattering factor of Bi (f_{Bi}) is much (~ 3 times) larger than that of Ni (f_{Ni}). For this reason, the total $f_m f_n$ term in the ordered honeycomb layer configuration should be proportional to $(1/3 f_{\text{Bi}}^2 + 2/3 f_{\text{Ni}}^2)$, which should be much larger than that of a randomly distributed $R\bar{3}m$ model $(1/9 f_{\text{Bi}}^2 + 4/9 f_{\text{Ni}}^2 + 4/9 f_{\text{Ni}} f_{\text{Bi}})$. Therefore, this ~ 5.3 Å peak for a random $R\bar{3}m$ model should be much weaker than that from honeycomb ordered $C2/m$ or $P3_1I2$ model. Indeed, the random model underestimates the intensity of the 5.3 Å peak in the experimental data, a result which confirms Ni/Bi still adopt honeycomb ordered within individual layers of disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$.

Figure S6. Four different STEM-HAADF images of disordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ viewed along the $[100]_p$ zone axis. Bi atoms appear as bright spots. The number stacking sequence, transitions vectors, and layer designations for this sample are overlaid on these images.

Figure S7. Left: transformation matrix and spatial relationship between the monoclinic $C2/m$ (black) and the trigonal $P3_12$ supercells (blue). Right: Relationships between conventional (solid black line) and transformed trigonal-equivalent (dashed blue line) monoclinic unit cells.

$$(1) z = 3c \sin \beta$$

$$(2) x = y - |a_M|$$

$$(3) y = -3|c_M| \cos \beta$$

$$(4) x = -3|c_M| \cos \beta - |a_M|$$

$$(5) \tan(180^\circ - \beta') = z/x = (3c \sin \beta) / (-3c \cos \beta - |a_M|)$$

$$(6) \tan \beta' = (3c \sin \beta) / (3c \cos \beta + |a_M|)$$

$$(7) \beta' = \tan^{-1} \left[(3c \sin \beta) / (3c \cos \beta + |a_M|) \right] \quad \text{or} \quad \beta' = 180^\circ - \tan^{-1} \left[(3c \sin \beta) / (3c \cos \beta + |a_M|) \right]$$

$$(8) \phi = \beta' - 90^\circ$$

1: Note that x may have a positive or negative value, depending on the value of β .

2: Note that $\tan^{-1}$ can only return a value between $\pi/2$ and $-\pi/2$. The left term applies if the quantity in square brackets is positive ($\beta' < 90^\circ$), and the right if negative ($\beta' > 90^\circ$). The computational atan2 function can be used to avoid this ambiguity as its range is larger (π and $-\pi$).

Figure S8. Le Bail fit of synchrotron XRD data ($\lambda = 0.41398 \text{ \AA}$) of ordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ with $C2/m$ model.

Figure S9. Le Bail fit of synchrotron XRD data ($\lambda = 0.41398 \text{ \AA}$) of ordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ with $P3_112$ model.

Figure S10. Top: Indexing ($P3_1I2$ space group) of region of synchrotron XRD pattern ($\lambda = 0.41398 \text{ \AA}$) most associated with the superstructure reflections of ordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$. Bottom: Le Bail fit of 6L, 9L, and 12L superlattice peaks labelled with the size broadening parameters obtained when assuming that all-non instrumental broadening is due to size and not strain effects. This provides a minimum estimate of the X-ray coherence length for the superstructure peaks.

Figure S11. SAED of “ordered” Na₃Ni₂BiO₆, electron diffraction taken along the [100]_p and the [001]_p zone axis direction, where the “P” subscript indicates indexing in the idealized $P3_1I2$ space group.

$$\begin{pmatrix} 0.781(2) & 0.001(6) & 0.219(2) \\ 1.000(0) & 0.000(0) & 0.000(0) \\ 0.761(3) & 0.000(1) & 0.239(3) \end{pmatrix}$$

Figure S12. Fit to synchrotron XRD data ($\lambda = 0.41398 \text{ \AA}$) for ordered $\text{Na}_3\text{Ni}_2\text{BiO}_6$ using FAULTS with a γ -parameter transition probability model. Refined probability matrix is shown. The transition probabilities away from the middle row (**2** position) were not refined since the probability for a **2** layer occurring ($< 0.1 \%$) is indistinguishable from zero.

Figure S13 (continued).

*No defects were observed at line level, so labels are omitted from this image.

Figure S13 (continued).

Figure S14. Simulated XRD patterns ($\lambda = 1.5418 \text{ \AA}$) as a function of the degree of long-range honeycomb disordering simulated using a 1-parameter model. This simulation makes the assumption that faulting is random and that honeycomb layer correlations are purely local, in contrast with the actual behavior for this phase observed in TEM studies of both ordered and disordered phases.

Constraints in the transition probability matrix of DIFFAX/FAULTS

The transition probability matrix is a 3×3 matrix in which the term P_{ij} gives the probability that the layer after a layer of type i will be a layer of type j . As shown on the right, the constraints that the probabilities of transitions away from a layer of type i must sum to 1 ($P_{i1} + P_{i2} + P_{i3} = 1$), so there are at most 6 independent variables. If these six parameters are freely refined, there is no constraint on the relative probabilities of layers, P_j , where P_j represents the occurrence probability that a layer of type j within the overall structure. Fits of this type are referred to as “6-parameter” fits.

If the system is constrained so that all layers must occur with equal probabilities ($P_1 + P_2 + P_3 = 1$), then the entire system can be described by only one independent variable, denoted x , using the relationships on the left side of the figure. Fits of this type are referred to as “1-parameter” fits.

The recursive nature of the probability relationships are utilized by DIFFAX/FAULTS to simplify calculations, as schematically illustrated at the top of the figure. The relationship between the layer number positions (1, 2, 3), the translational shift vector (t_a , t_b , t_u), and the transition probability matrix elements (P_{ij}) are indicated in this figure.

It should be noted that the entire probability matrix approach assumes that layer transition probabilities only depend on the local environment of layers, an assumption which the present study demonstrates is clearly incorrect by showing that long-range c -axis superstructures form due to strain effects..

Table S1. Fractional coordinates of 9 possible central atom (B') positions ordered $\text{Ni}_{2/3}\text{Bi}_{1/3}$ layers in an ideal P3_112 -symmetry $\sqrt{3}a \times \sqrt{3}a \times c$ honeycomb-lattice superstructure ($a = b \sim 5.2 \text{ \AA}$, $c \sim 16 \text{ \AA}$).

Honeycomb position	Atom type	x	y	z
$\mathbf{A}_1$	$B' = \text{Bi}$	0	0	0
$\mathbf{A}_2$	$B' = \text{Bi}$	2/3	1/3	0
$\mathbf{A}_3$	$B' = \text{Bi}$	1/3	2/3	0
$\mathbf{B}_1$	$B' = \text{Bi}$	1/3	0	1/3
$\mathbf{B}_2$	$B' = \text{Bi}$	0	1/3	1/3
$\mathbf{B}_3$	$B' = \text{Bi}$	2/3	2/3	1/3
$\mathbf{C}_1$	$B' = \text{Bi}$	2/3	0	2/3
$\mathbf{C}_2$	$B' = \text{Bi}$	1/3	1/3	2/3
$\mathbf{C}_3$	$B' = \text{Bi}$	0	2/3	2/3

Note that this table explicitly specifies B' cation (*e.g.*, Bi^{5+}) coordinates but also allows B cation coordinates to be deduced. If the B' cation in an $\mathbf{A}$ layer is for example on the $\mathbf{A}_1$ site, then the B cations (*e.g.*, Ni^{2+}) in this layer will necessarily be found at the other two sites within this layer ($\mathbf{A}_2$ and $\mathbf{A}_3$).

Table S2. Explicit coordinates of all possible letter, number, and honeycomb shift vectors.

<u>Letter</u> shift vectors between successive layers			
$\mathbf{L}^+ = (1/3, 2/3, 1/3)$	$\mathbf{A} \rightarrow \mathbf{B}$	$\mathbf{B} \rightarrow \mathbf{C}$	$\mathbf{C} \rightarrow \mathbf{A}$
$\mathbf{L}^- = (2/3, 1/3, 1/3)^*$	$\mathbf{A} \rightarrow \mathbf{C}$	$\mathbf{B} \rightarrow \mathbf{A}$	$\mathbf{C} \rightarrow \mathbf{B}$
$\mathbf{L}^0 = (0, 0, 1/3)^*$	$\mathbf{A} \rightarrow \mathbf{A}$	$\mathbf{B} \rightarrow \mathbf{B}$	$\mathbf{C} \rightarrow \mathbf{C}$
<u>Number</u> shift vectors within a layer			
$\mathbf{N}^+ = (2/3, 1/3, 0)$	$\mathbf{1} \rightarrow \mathbf{2}$	$\mathbf{2} \rightarrow \mathbf{3}$	$\mathbf{3} \rightarrow \mathbf{1}$
$\mathbf{N}^- = (1/3, 2/3, 0)$	$\mathbf{1} \rightarrow \mathbf{3}$	$\mathbf{2} \rightarrow \mathbf{1}$	$\mathbf{3} \rightarrow \mathbf{2}$
$\mathbf{N}^0 = (0, 0, 0)$	$\mathbf{1} \rightarrow \mathbf{1}$	$\mathbf{2} \rightarrow \mathbf{2}$	$\mathbf{3} \rightarrow \mathbf{3}$
<u>Honeycomb</u> shift vectors between successive layers			
$\mathbf{t}_a = (1/3, 0, 1/3)$	$\mathbf{A}_1 \rightarrow \mathbf{B}_1$	$\mathbf{B}_1 \rightarrow \mathbf{C}_1$	$\mathbf{C}_1 \rightarrow \mathbf{A}_1$
	$\mathbf{A}_2 \rightarrow \mathbf{B}_2$	$\mathbf{B}_2 \rightarrow \mathbf{C}_2$	$\mathbf{C}_2 \rightarrow \mathbf{A}_2$
	$\mathbf{A}_3 \rightarrow \mathbf{B}_3$	$\mathbf{B}_3 \rightarrow \mathbf{C}_3$	$\mathbf{C}_3 \rightarrow \mathbf{A}_3$
$\mathbf{t}_b = (0, 1/3, 1/3)$	$\mathbf{A}_1 \rightarrow \mathbf{B}_2$	$\mathbf{B}_1 \rightarrow \mathbf{C}_2$	$\mathbf{C}_1 \rightarrow \mathbf{A}_2$
	$\mathbf{A}_2 \rightarrow \mathbf{B}_3$	$\mathbf{B}_2 \rightarrow \mathbf{C}_3$	$\mathbf{C}_2 \rightarrow \mathbf{A}_3$
	$\mathbf{A}_3 \rightarrow \mathbf{B}_1$	$\mathbf{B}_3 \rightarrow \mathbf{C}_1$	$\mathbf{C}_3 \rightarrow \mathbf{A}_1$
$\mathbf{t}_b = (-1/3, -1/3, 1/3)$	$\mathbf{A}_1 \rightarrow \mathbf{B}_3$	$\mathbf{B}_1 \rightarrow \mathbf{C}_3$	$\mathbf{C}_1 \rightarrow \mathbf{A}_3$
$= (2/3, 2/3, 1/3)$	$\mathbf{A}_2 \rightarrow \mathbf{B}_1$	$\mathbf{B}_2 \rightarrow \mathbf{C}_1$	$\mathbf{C}_2 \rightarrow \mathbf{A}_1$
	$\mathbf{A}_3 \rightarrow \mathbf{B}_2$	$\mathbf{B}_3 \rightarrow \mathbf{C}_2$	$\mathbf{C}_3 \rightarrow \mathbf{A}_2$

All coordinates are given relative to the unit cell of an ideal trigonal honeycomb lattice superstructure, whose unit cell dimensions have a $\sqrt{3}a \times \sqrt{3}a \times c$ relationship to the $R\text{-}3m$ $\alpha\text{-NaFeO}_2$ subcell, and whose orientation is rotated by 60° relative to the subcell. The site positions related by these shift vectors are specified in Table S1.

*In perfectly ordered O3-layered compounds (such as ideal trigonal $\text{Na}_3\text{Ni}_2\text{BiO}_6$), the $\mathbf{L}^-$ and $\mathbf{L}^0$ letter shifts will never occur as they violate the layer stacking sequence.

Table S3. Average structure of ordered Na₃Ni₂BiO₆ refined from synchrotron XRD data ($\lambda = 0.41398 \text{ \AA}$).

<i>S.G. C2/m a = 5.3989(1) Å b = 9.3525(1) Å c = 5.6751(1) Å β = 108.380(1)°</i>						
Atom	Wyck.	<i>x</i>	<i>y</i>	<i>z</i>	Occ.	<i>B</i> _{iso} (Å ²)
Bi1	2a	0	0.5	0	0.749(1)	0.3
Ni1	2a	0	0.5	0	0.251(1)	0.3
Bi2	4g	0	0.1656(1)	0	0.126(1)	0.3
Ni2	4g	0	0.1656(1)	0	0.874(1)	0.3
Na1	2d	0	0	0.5	1	0.25(5)
Na2	4h	0	0.6674(4)	0.5	1	1.30(4)
O1	4i	0.2324(9)	0	0.2088(7)	1	0.28(7)
O2	8j	0.2379(7)	0.3328(4)	0.2036(4)	1	0.20(4)

(1) Egami, T.; Billinge, S. J. L., *Underneath the Bragg-Peaks: Structural Analysis of Complex Materials*, Plenum, Oxford, 2003.