The microstructural changes and phase transitions taking place during the charge/discharge cycles critically influence battery performance and lifetime. Recently, NaFePO$_4$ has attracted a great attention as the one of promising materials for sodium ion batteries. The formation of superstructures in Na$_x$FePO$_4$ ($x\approx0.7$) during FePO$_4$ to NaFePO$_4$ transformation was reported by several groups, however no direct imaging of sodium/vacancy ordering has been provided yet. Here we report the observation of Na atoms/vacancies ordering in Na$_x$FePO$_4$ ($x\approx0.7$) nanoparticles as revealed by electron diffraction (ED), high resolution (scanning) transmission electron microscopy (HR(S)TEM), atomic modeling and HRSTEM image simulations.

An intermediate Na$_x$FePO$_4$ ($x\approx0.7$) phase, as a powder, was prepared both chemically and electrochemically. The superstructure formation was confirmed for particles obtained for both synthesis methods. Electron diffraction patterns (Figure 1 a-c) collected from main zone axes and accompanied with local Energy Dispersive X-ray (EDX) analysis revealed the presence of several phases with the same elemental composition but different Na/vacancy ordering. Different superstructures were found in different particles as well as coexistence of differently oriented domains with superstructure was demonstrated within one nanoparticle (Figure 1 d-f). It was also observed that electron beam strongly influenced on the structure of Na$_x$FePO$_4$ phase causing redistribution of Na atoms. This process was found to be extremely fast, however the use of cooling specimen holder allowed reducing significantly the beam influence and tracing the structural transformations. Thus, it has been discovered that FePO$_4$ to NaFePO$_4$ transformation proceeds through the formation of different commensurate and incommensurate phases.

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Fig. 1: (a)-(c) ED pattern along [100], [010] and [001] directions, respectively; (d) low magnification HAADF image of Na$_x$FePO$_4$ particle; (e) and (f) HRSTEM images from area 1 and area 2 (Fig.1d), respectively. Atomic models are shown in insets.