Electron crystallography has two main advantages in structure solution compared to X-ray diffraction: 1) crystals millions times smaller than what is needed for X-ray diffraction can be studied and 2) the crystallographic structure factor phases are present in high resolution transmission electron microscopy (HRTEM) images [1]. In order to make electron crystallography more feasible for non-TEM experts, we have developed two methods; 1) rotation electron diffraction (RED) [2] for collecting complete 3D electron diffraction data that transforms a TEM into a single nano-crystal diffractometer and 2) structure projection reconstruction [3] that determines the defocus values from a through-focus series of HRTEM images. Each image in the series is corrected for the effects of contrast transfer function and then combined into a structure projection image. The method works for both crystalline and non-crystalline objects. Here we show how these two methods are used to solve the structures of complex intergrown zeolites ITQ-39 [4]. The structure was confirmed by simulations of powder X-ray diffraction from the disordered model. The methods are general and can be applied to any crystalline materials, where the crystals are too small or the structures too complicated to be solved by X-ray powder diffraction alone, especially for those crystals containing defects.

![Figure 1](a-b) Reconstructed electron diffraction patterns and (c-d) reconstructed structure projection from a series of 20 HRTEM images of ITQ-39.

Keywords: ab-initio structure solution; rotation electron diffraction; zeolites

--

Nano-sized zeolites which have high external surface area are easy to be disordered and they are not suitable to be studied by the single crystal/powder X-ray diffraction technique. Structure solution for this kind of materials raised a lot of interests, not only for X-ray crystallographers, but also for electron microscopists. Some new methods in determining this kinds of materials such as 2D-charge-flipping [1] and automated electron diffraction tomography (ADT) [2] are vigorously developed in recent years, and they are successfully used in difficult structure solutions especially in zeolites. Recently, our group developed rotation electron diffraction (RED) data collection and reduction software based on JEOL TEM microscopes, which can tilt the nano-crystal from -70° to 70° with the high angle tilt holder [3]. This high angle tilt data can not only be successfully used in unit cell determination, but also have high completeness and accuracy for structure determination of various materials such as zeolites, aluminum borates, metal organic frameworks (MOF), etc. Here we present the results on two nano-sized zeolites whose structures were solved from the data collected and extracted through the software RED developed by Wan et al. [4]. The dataset for the zeolite PIR was collected on a crystal with a size of 800 nm × 700 nm × 400 nm with the tilt angle range from -60° to 70°. The dataset has the R_{int} = 24.6%. The crystal structure can be solved by direct methods with SHELX [5] in the space group Immm and all the silicon atoms and most of the oxygen atoms were directly located. The least square refinement by SHELX converged with R_{l} about 0.15. For the MTW zeolite, the R_{int} for this dataset is 22.5%, the structure can also be solved with the space group of C2/c and all the temperature factors can be refined in an acceptable range. Based on RED data, plenty of nano-sized crystals even with lower symmetry and beam sensitive characteristics can be solved and refined successfully. These results shows that rotation electron diffraction has the potential to produce single crystal like dataset that is comparable with X-ray diffraction.


Keywords: Electron diffraction; High resolution transmission electron microscopy; Zeolite