Oral Contributions

[MS18-05] New TEM techniques for solving 3D structures of nanosized and/or intergrown zeolites and minerals

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X-ray crystallography has beeen the main technique for routine structure determination but is limited to micrometer-sized crystals. Many zeolites and minerals form only powders, too small for single crystal X-ray diffraction. Powder X-ray diffraction (PXRD) has beeen successfully used for solving structures of such crystals. However, structure solution by PXRD becomes difficult for complex structures with severe reflection overlap and for disordered structures. Electron crystallography is an important technique complement too X-ray crystalography for studying such structures and disorders. There are two main advantages of structure determination by electron crystallography compared to X-ray diffraction : 1) crystals millions times smaller than what is needed for X-ray diffraction can be studied and 2) thee phases of the crystallographic structure factors, which are lost in X-ray diffraction, are present in high resolution transmission electron microscopy (HRTEM) images.[1] We and others have demonstrated that complex zeolite structures can be solved by electron crystalography alone or combined with powder X-ray diffraction[2-3]. However, examples of structures solved by electron crystallography alone are still very rare, due too the high demands for TEM data collection and data analysis. In order to make electron crystalography more feasible for non-TEM experts, we have developed two methods; 1) rotaation electron diffraction (RED) [4] for collecting complete 3D electron diffraction data that transforms a TEM into a single nano-crystal diffractometer and 2) structure projection reconstruction [5] 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. Figure 1 illustrates a complete structure solution of silicalite-1 by RED. 1427 ED frames were collected with a tilt step of 0.1°. A 3D reciprocal lattice of silicalite-1 was reconstructed, from which the unit cell parrameters were determined. It was possible to cut the 3D reciprocal lattice perpendicular to any directions andd study the reflection conditions, from which the possible space groups were deduced. The reflection intensities could be extracted. The structure was solved by direct methods using SHELX-97. All Si and O atoms could be located and refined to an accuracy better than 0.08 Å.

We will present structures of several zeolites and minerals solved from the RED data [6]. We will also demonstrate thee structure solution of an aluminosilicate zeolite family ITQ-399 solved by electron crystallography [7]. ITQ-39 is an intergrowth of three different polytypes, built from the same layer but with different stacking sequences. It contains stacking faults and twinning witth nano-sized domains, being the most complex zeolite ever solved. The methods are generall andd can be applied to any crystalline materials, where thee crystals are too small or the structures too complicated to bee solved by X-ray powder diffraction alone, especially for those crystals containing defects.

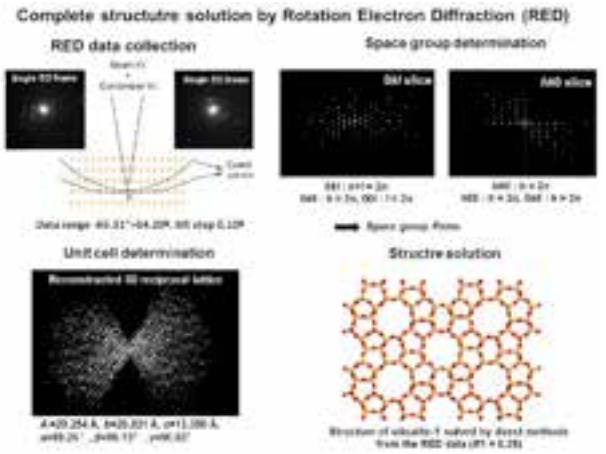

Fig. 1. Illustration of a complete structure solution from RED data.

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