Structural study of zeolites utilizing novel electron crystallographic methods – A voyage into the world of zeolite structures

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Structural study of zeolites utilizing novel electron crystallographic methods

A voyage into the world of zeolite structures

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Doctoral Thesis 2013

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Cover:
HRTEM image of zeolite beta on top of the reconstructed 3D reciprocal lattice of zeolite beta.

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Printed in Sweden by US-AB, Stockholm 2013
Distributor: Department of Materials and Environmental Chemistry, Stockholm University
Abstract

Electron crystallography has evolved as a powerful method for structural characterization of a wide range of materials. It has two significant advantages over other methods for structure determination, e.g. X-ray diffraction. Electrons interact much more strongly with matter compared to X-rays and they can be focused by electromagnetic lenses to form images with atomic resolution. These advantages make electron crystallography a unique tool for characterization of crystalline materials suffering from small crystal size and complex or disordered structures.

Zeolites are a class of microporous materials with significance in several applications. They often possess complex and disordered structures, which demand large efforts in the structure determination.

Over the last years, two new electron crystallographic methods have been developed; the rotation electron diffraction (RED) and the structure projection reconstruction from a through-focus series of high resolution transmission electron microscopy (HRTEM) images. In this thesis, they will be applied for structure determination of four new zeolite structures; EMM-25 and EMM-23 with two ordered structures, and ITQ-39 and ITQ-38 with disordered structures. Each of the structures have different challenges to overcome. The high silica borosilicate EMM-25 was solved by the RED method. The aluminosilicate EMM-23 was solved by a combination of HRTEM and RED. The structure solution of the two materials with disordered structures, ITQ-39 and ITQ-38, was possible by combining HRTEM and RED. For materials containing disorders, structure projection images are of utmost importance.

Furthermore, the mesoporosity inside hierarchically porous ZSM-5 crystals was studied by a combination of focused ion beam (FIB) and HRTEM imaging. The last part of this thesis explores STEM imaging for use in structure determination from 3D reconstruction.

Keywords: Electron crystallography, zeolites, structure determination, disorder, electron microscopy
This thesis is based on the following papers:

**PAPER I:** Stacking disorders in zeolites and open-frameworks - structure elucidation and analysis by electron crystallography and X-ray diffraction  
Tom Willhammar, Xiaodong Zou  
Zeitschrift für Kristallographie, **228**, 11-27 (2013)  
DOI: 10.1524/zkri.2012.1564  
**My contribution:** I did a major part of the literature survey as well as wrote a large part of this review paper.

**PAPER II:** Structural Determination of Ordered Porous Solids by Electron Crystallography  
Tom Willhammar, Yifeng Yun, Xiaodong Zou  
Advanced Functional Materials, (2013) Published online  
DOI: 10.1002/adfm.201301949  
**My contribution:** I performed a considerable portion of the literature survey and did major contribution to the writing of this review paper.

**PAPER III:** Synthesis and characterization of pure silica zeolite beta obtained by an aging-drying method  
Farlán Taborda, Tom Willhammar, Zhenyang Wang, Consuelo Montes, Xiaodong Zou  
Microporous and Mesoporous Materials, **143**, 196-205 (2011)  
DOI: 10.1016/j.micromeso.2011.02.030  
**My contribution:** I performed the TEM analysis of the synthesised materials as well as the analysis regarding the disorder. I also contributed to the analysis of the disorder from the X-ray diffraction patterns and wrote the section about TEM analysis.
PAPER IV: Rational synthesis and structure of a borosilicate zeolite with intersecting 10- and 11-ring channels
Yifeng Yun, Tom Willhammar, Junliang Sun, Wei Wan, Allen Burton, Karl G. Strohmaier, Gene Terefenko, Hilda Vroman, Mobae Afeworki, Guang Cao, Xiaodong Zou
In Manuscript
My contribution: I collected the HRTEM image as well as contributed to the structure analysis of the material.

PAPER V: The first stable high silica zeolite with extra-large 24-ring channels
Tom Willhammar, Yifeng Yun, Junliang Sun, Allen Burton, Mobae Afeworki, Karl G. Strohmaier, Hilda Vroman, Jane Cheng, Xiaodong Zou
In Manuscript
My contribution: I collected the initial RED data as well as the HRTEM images. Based on this data, I obtained the structure model of the material. I made major contributions towards writing the manuscript.

PAPER VI: A New Aluminosilicate Molecular Sieve with a System of Pores between those of ZSM-5 and Beta Zeolite
Manuel Moliner, Jorge González, M. Teresa Portilla, Tom Willhammar, Fernando Rey, Francisco J. Llopis, Xiaodong Zou, Avelino Corma
Journal of the American chemical society, 133, 9497-9505 (2011) DOI: 10.1021/ja2015394
My contribution: I contributed to the structural analysis of the material by acquisition and analysis of electron diffraction data. I also wrote the section about electron diffraction.
PAPER VII: **Structure and catalytic properties of the most complex intergrown zeolite ITQ-39 determined by electron crystallography**
Tom Willhammar, Junliang Sun, Wei Wan, Peter Oleynikov, Daliang Zhang, Xiaodong Zou, Manuel Moliner, Jorge González, Christina Martinez, Fernando Rey, Avelino Corma
DOI: 10.1038/nchem.1253
**My contribution:** I collected high resolution transmission electron microscopy images, performed the analysis of all data, solved the structure and did major contribution to verifying the structure. I made major contributions towards writing the paper.

PAPER VIII: **Synthesis Design and Structure of a new Multipore Zeolite with Interconnected 12- and 10-MR Channels**
Manuel Moliner, Tom Willhammar, Wei Wan, Jorge González, Fernando Rey, Jose L. Jorda, Xiaodong Zou, Avelino Corma
DOI: 10.1021/ja301082n
**My contribution:** I collected electron diffraction patterns and HRTEM images and performed the electron crystallographic analysis. Based on the data, I built the structure model and verified the structure. I contributed to writing the paper.

PAPER IX: **ZSM-5 Zeolite Single Crystals with b-Axis-Aligned Meso-porous Channels as an Efficient Catalyst for Conversion of Bulky Organic Molecules**
Fujian Liu, Tom Willhammar, Liang Wang, Longfeng Zhu, Qi Sun, Xiangju Meng, Wilder Carrillo-Cabrera, Xiaodong Zou, Feng-Shou Xiao
*Journal of the American chemical society, 134*, 4557-4560 (2012)
DOI: 10.1021/ja300078q
**My contribution:** I carried out the electron microscopic analysis of the material as well as the analysis of the orientation of the mesopores. I wrote the section about electron microscopy in the paper.
PAPER X: 3D reconstruction of atomic structures from HAADF STEM images
Tom Willhammar, Alvaro Mayoral, Xiaodong Zou

In Manuscript

My contribution: I designed the experiments, collected the HRTEM images and performed the crystallographic analysis of the data. Major contribution towards writing the manuscript.

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Papers VI, VIII and IX are reprinted with permission from American Chemical Society (2011, 2012 and 2012)

Papers not included in this thesis:

PAPER XI: Synthesis of Al-Si-beta and Ti-Si-beta by the aging-drying method
Farlán Taborda, Zhenyang Wang, Tom Willhammar, Consuelo Montes, Xiaodong Zou
Microporous and Mesoporous Materials, 150, 38-64 (2011)
DOI: 10.1016/j.micromeso.2011.09.015

PAPER XII: A Stacking Faults-Containing Silicogermanate with 24-Ring Channels and Unbranched Zweier Silica Double Chains
Liqiu Tang, Xiaoyan Ren, A. Ken Inge, Tom Willhammar, Daniel Grüner, Jihong Yu, Xiaodong Zou
Crystal growth and design, 12, 3714-3719 (2012)
DOI: 10.1021/cg300519t

PAPER XIII: Solving Complex Open-Framekwork Structures from X-ray Powder Diffraction by Direct-Space Methods using Composite Building Units
A. Ken Inge, Henrik Fahlquist, Tom Willhammar, Yining Huang, Lynne B. McCusker, Xiaodong Zou
DOI: 10.1107/S0021889813013101
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1. Introduction

Structure characterization is essential for the understanding of Nature. Knowledge about the atomic structure of a material is the key to understand its properties and to develop possible applications. The same holds for proteins and our understanding of the basis of life. The desire to understand the details of how things around us are built up has haunted mankind over thousands of years. Over the last century the understanding of the chemical essence has evolved rapidly. A decisive moment was when the first atomic structures were brought to light using single crystal X-ray diffraction by W. H. Bragg and W. L. Bragg in 1913.[1,2]

The first method used for structure determination was single crystal X-ray diffraction, SXRD, which has been developed into a standard method for structure solution. It is today fast and very accurate, but with some drawbacks and limitations. In order to obtain X-ray diffraction data from one single crystal, the crystal has to be larger than a few micrometers in each dimension. Many materials rarely grow that large. The second drawback is that the diffraction data is an average over the whole crystal which makes it difficult to obtain information about the local structure when the structure is not perfectly ordered. An alternative to SXRD, when the crystals are too small, is to collect data on a large number of crystals with random orientations. In this way the problem of crystals being too small is overcome. However the data loses its 3 dimensional information. This makes it difficult to interpret the data.

By replacing X-rays by electrons, single crystal diffraction data can by acquired from crystals several orders of magnitudes smaller than SXRD. This is possible since electrons are charged particles and interact much more strongly with matter than X-rays. The first structural analysis from electron diffraction data was performed in the end of the 1940s.[3,4] The strong interaction between electrons and matter is a great asset for electron diffraction but it has also become its greatest problem. The intensities from electron diffraction are often not directly proportional to the structure factors. This has scared scientists from using and developing methods for electron diffraction.

Porous materials include a wide variety of different materials with one thing in common. They refuse to obey the basic principle in Nature about close packing. Instead, they contain voids of different kinds, often forming channels inside the material. This gives porous materials unique properties
and applications. Porous materials are often classified into three groups based on the size of the pores. Materials with pores smaller than 2 nm are called microporous materials. If the pores are between 2 and 50 nm, the material is referred to as mesoporous materials. If the pores are larger than 50 nm they are called macroporous materials, see Figure 1.1. Micropores are in the size range of small molecules, which gives them interesting properties for many applications. Materials with larger pores can be utilized for incorporating larger species, for example drug molecules or enzymes. This thesis will focus on one class of porous materials with porosity mostly in the microporous range; zeolites. Zeolites are naturally occurring as well as synthetic porous aluminosilicates with applications in the chemical industry for catalysts, for separation of molecules of different sizes, for removal of unwanted species from various systems to mention some examples, see section 2.1 for a more thorough description.

Figure 1.1: A visual comparison between size ranges for the wavelengths of electromagnetic radiation and electrons, with energy common in transmission electron microscopes. The size of pores in different ranges as well as suitable crystal sizes for characterization by different methods are shown.
The unique properties of zeolite materials, for example shape selectivity, ion-exchange properties and sorption capacity, are to a large extent determined by their structures. In order to understand the properties, to predict possible applications and to design new synthesis routes it is hence of greatest importance to explore and determine the essence of their structures. Features such as pore opening, void volume, channel dimensionality and distribution of cations in the pores are of crucial importance for their properties.

Zeolites have a large structural variety. The structure may contain large voids limited by smaller windows or channels with uniform size. The pores can be as small as the smallest ions or as large as ~2 nm. The pores can be extended along one or several directions to form 1 - 3 dimensional intersecting networks. Today more than 200 different zeolite frameworks have been reported.[5]

The fact that electrons are charged particles also makes it possible to focus them by electromagnetic lenses; to create a microscope. Images acquired by a transmission electron microscope can have atomic resolution. If the image has a contrast related to the atomic arrangement in the specimen, it is called a high resolution transmission electron microscopy (HRTEM) image. The first HRTEM image of a zeolite was presented in 1958 by Menter.[6] The images show lattice information of the zeolite faujasite. During the 1970s several groups acquired HRTEM images of zeolites[7–9] and zeolite related materials[10]. Zeolites are sensitive to irradiation by electron beams. If an electron beam with too strong intensity is used, the atomic structure of the material will degrade. This makes imaging of zeolites a challenging task. The beam sensitivity depends on several factors, such as composition of the framework, the structure, the energy of the electrons and the guest species inside the pores.[7; 11; 12]

Structure determination of zeolites is often a challenging task, for several reasons. The first is that the crystals rarely grow large enough for measurements by SXRD, so for structure determination we have to use other more demanding methods. Zeolite structures are also often rather complex with large unit cells, which makes structure solution from PXRD difficult. Many zeolites contain disorder which is difficult to elucidate by diffraction techniques. Electron crystallography has the power to overcome all these problems.

HRTEM images bring great benefits to structural studies. Since the images show the locations of the atoms they can be used to overcome a problem in structure solution, the phase problem. From HRTEM images of crystalline materials both the structure factor amplitudes and phases can be extracted by a mathematical operation, the Fourier transform. This was first shown by Klug and De Rosier in 1968.[13] This has shown to be crucial in structure determination of complex structures from HRTEM images. HRTEM images are ideal
for studies of disordered materials since the local information is recorded.

Electron crystallography has shown over the years to be a powerful method for structure determination of a wide range of materials. Yet it has not become a widespread standard method, but rather a method that a few specialized experts use. Two electron crystallographic methods developed over the last few years aim to change this. The rotation electron diffraction (RED) method offers the possibility of automated collection of a 3 dimensional single crystal electron diffraction data. The structure projection reconstruction from a through-focus series facilitates the acquisition and interpretation of HRTEM images. The aim of this thesis is to utilize the power of electron crystallography to characterize zeolites, for cases where other methods are not sufficient. I aim at applying the two recently developed methods, mentioned above, for structure solution of new zeolite structures. A common theme in my work has been that all projects have included electron microscopy imaging in some form.

The first three chapters, Chapters 2-4, will give a background in the fields of zeolites, electron crystallography and methods for structure determination respectively. Chapter 5 will show the structure determination of four new zeolite structures, among them some of the most complex zeolite structures solved up to date. I will also show how HRTEM imaging can be used for structural characterization of zeolites with hierarchical pore system. In the last chapter I will explore the possibility to utilize a different imaging technique, scanning transmission electron microscopy (STEM) for applications in electron crystallography.
2. Zeolites

2.1 General introduction to zeolites

2.1.1 Early history of natural zeolites

In the year of 1756 the Swedish mineralogist Axel Fredrik Cronstedt made an excursion to the mountainous Swedish province Jämtland. A few years earlier he discovered the new element nickel from an ore found in Losgruvan in Hälsingland. Now his aim was to study the possible resources of silver ores in Jämtland. Instead he made a very different discovery. When he analyzed a mineral acquired from Åreskutan, he observed an unexpected behavior. He found that upon heating the rock in the flame of a blowpipe, a large amount of water vapor was formed, as if the rock started to boil. This was a behavior not observed earlier. Cronstedt decided to name the mineral after the two Greek words zeo (to boil) and lithos (stone). This was the beginning of the zeolite era. Today we know that the water vapor Cronstedt saw in his experiment originates from water molecules trapped inside the small, well defined pores that give zeolites their unique and valuable properties. The channels of zeolites are in the range of small molecules and hence the zeolites can act as molecular sieves. The size and shape of the channels determine which molecules are able to enter the channels.

Starting from the 1790s, the number of reported naturally occurring zeolite minerals started to increase. By the mid 19th century ∼20 zeolites were reported, including faujasite and chabazite, materials of which the synthetic analogue today have significant industrial importance. A recently published book on natural zeolites describes 67 naturally occurring zeolites.

2.1.2 Definition and properties

The traditional definition of a zeolite is a material that fulfills the following set of rules. It should be a crystalline aluminosilicate built by tetrahedrally coordinated silicon/aluminium atoms which are linked by oxygen atoms forming a three dimensional framework. The framework should contain porosity which allows guest species, for example water or counter ions, to move freely in and through the material, see Figure for an example of a typical zeolite. As
the number of discovered zeolite materials increased, the definition has now changed slightly allowing not only silicon and aluminium in the tetrahedral sites (T-sites) but also other elements, such as P, Ge, B, Ga, Be, Zn. Materials containing \( \text{TO}_4 \) tetrahedra without full coordination to other \( \text{TO}_4 \) tetrahedrons leaving one or more free terminal hydroxide group are today also referred to as zeolites. These frameworks are referred to as interrupted frameworks.\[23\]

**Figure 2.1:** Zeolites are 3D frameworks built from alternating Si and O atoms. (a) The zeolite A is shown with Si (yellow) and O (red) and (b) drawn with tilings, showing the open porosity with an inorganic cation in the channel.

The properties of zeolites can be assigned to a number of features. The first and obvious ones are the size and shape of the pores, which limit certain molecules from entering the pores. Whether the channels extend in one, two or three dimensions is also of significance. The chemical composition of a zeolite plays an important role for its properties. The valence of the T-atoms will affect the charge of the framework, for example a pure silicate framework has a neutral charge whereas an aluminosilicate framework will have a negative charge. In a similar manner, the composition will affect the affinity for different molecules by changing the hydrophobicity and hydrophilicity of the material. The composition is also crucial for the stability of the framework. As a rule of thumb, pure silicates have higher thermal and chemical stability. Zeolites with high content of aluminium or germanium have significantly lower stability. The guest species inside the channels of the zeolite are also important. In the case of a charged framework they are needed to balance the charge. In this case it is common with inorganic or organic cations. As Cronstedt realized, water is also a common guest molecule. The acidity of the zeolite is of importance for catalytic applications. Acidity is introduced by protonating the oxygen bound to an aluminium atom of the framework, a fully siliceous framework is not charged and can hence not be made acidic.
2.1.3 Synthetic zeolites

Zeolites can be synthesized by mimicking the conditions where the natural zeolites were formed, under high pressure in the presence of some structure directing agent (SDA) and water. The first hydrothermal synthesis of a zeolite was the preparation of leyynite reported already in 1862 by St. Claire Deville. [24] During the 1940s Richard Barrer made large contributions to zeolite synthesis. In 1948 he managed to synthesize the first zeolite without natural equivalent, the zeolite ZK-5 [25]. In the following years a large number of synthetic zeolites emerged from Barrer’s group, including synthetic analogues of faujasite and zeolite A. In the early 1960s he was the first one to use organic SDA. This extended the variety of possible SDAs greatly and led to the discovery of a number of new zeolites and compositions, including high silica ZSM-5 and zeolite Beta. [26] [27]

2.1.4 Applications

Zeolites have today found applications in a wide variety of fields. A majority of them can be classified into one of the three main fields; gas separation, ion exchange and catalysis.

Gas separation is today an important application for zeolites where molecules of different size or affinity for the zeolite materials can be separated from each other. The separation can be based on steric exclusion where one molecule is too large to enter the channels and the other can be adsorbed. If the rate of diffusion for two species is different inside the channels due to steric effects, the materials are said to have kinetic selectivity. Two species can also be separated based on the affinity to be adsorbed inside the channels, thermodynamic selectivity. [23] There are numerous applications where zeolites are used, including separation of n-alkanes from iso-alkanes and cyclic alkanes from aromatic. Zeolites are also used to separate oxygen and nitrogen in various applications, including enhancement of oxygen levels for pilots flying at high altitude and production of oxygen. Zeolites are also used to clean various gases from contaminants. [28] The most commonly used zeolites for gas separation is zeolite A, zeolite X, mordenite and chabazite. [23]

The possibility of ion exchange creates a number of important applications. The largest market is in detergents where the harder Ca$^{2+}$ and Mg$^{2+}$ ions can be exchanged with the softer Na$^{+}$ ion in zeolite Na-A. This process replaced the previous use of phosphates which caused environmental problems. [26] Zeolites can be used to remove radioactive species, e.g. $^{137}$Cs and $^{90}$Sr, from nuclear wastes. [29] Zeolites have also been tested for distributing contrast agents, Gd$^{3+}$ ions, in diagnostic magnetic resonance imaging (MRI). [30]
Catalysis has evolved into a very important application for zeolites. The most important property used for catalytic applications is the surface acidity. By protonation of the linking oxygen atom bound to an aluminium atom of the framework, a Brönsted acidic site is created at the internal surface of the channel. These acidic sites are ideal for catalyzing various chemical reactions with, for example organic molecules. This has led to large scale applications in the petrochemical industry. Rare earth stabilized ultra stable zeolite Y and H-ZSM-5 are used in the fluid catalytic cracking process to reduce the length of the hydrocarbon chains in crude oil. Zeolites are also used in various other processes such as hydrocracking, isomerization and disproportionation.\cite{26}

Recently silicoaluminophosphates have been applied at a large scale in the methanol to olefin (MTO) conversion processes.\cite{31} Zeolites can also be used as catalysts for several organic reactions, by adding active metal sites to the framework. One example is the Sn doped zeolite Beta which can be used for shape selective oxidation. It has recently gained a lot of interest for the use in turning biomass into fuels.\cite{32,33}

2.1.5 Strong research fields

Among recent strong research topics some stand out. The diffusion rates inside zeolites have long been a limiting factor in applications. By creating hierarchical porosity into zeolite crystals this issue can be overcome. Several different approaches have been used, one of them is to introduce mesopores into the zeolite materials.\cite{34,35} Another approach has been to grow zeolite crystals with extremely anisotropic morphologies, such as sheets, that can intergrow and create larger pores between the sheets.\cite{36,38} When it comes to the synthesis of new zeolite materials, a few trends have been strong in recent years. One has been to create materials with larger and larger channels in order to expand the range of molecules that can enter the channels. This has been done both by designing specific organic SDAs\cite{39} to direct the channel size and by changing the composition of the materials. Addition of germanium to the synthesis favours formation of larger channels. The discovery of aluminophosphates has also led to findings of zeolites with extra-large channels.\cite{40,41}

To find zeolites with different channel sizes has been of importance and even more to find materials with intersecting channels of different sizes. This can enable molecules of different sizes to diffuse in different channels and interact at specific sites of the channel system.

At last I would like to mention the dream in the zeolite community: to create a material with enantio-pure channels systems. So far there are just a few examples of zeolites with chiral channel systems.\cite{42,44}
2.2 Zeolite structures

Although zeolites were known as minerals for nearly two centuries, it was not until 1930 when Taylor and Pauling used X-ray diffraction to solve the atomic structures of four different zeolites (analcime, sodalite, cancrinite and natrolite) that we finally got the first detailed view about how zeolites are built at the atomic scale. A significant part of zeolite properties as described in Section 2.1 can be attributed to and derived from its framework structure. Here concepts related to the structure of zeolites will be described, starting from the basic building units to the complete three dimensional structure.

2.2.1 The tetrahedron

The TO₄ tetrahedron is the basic building unit which by definition entirely builds up every zeolite framework, see Figure 2.2. At the center of each tetrahedron is an atom with a moderate electronegativity. Most commonly it is a Si or Al atom, but it can also be a metalloid (e.g. Ge, B), a metal (e.g. Ga, Sn, Zn) or a non-metal (P). In order to generalize, the term T-atom is used in the meaning: any tetrahedrally coordinated atom. At each of the four corners of the tetrahedron is an oxygen atom. The tetrahedron is rather rigid and the oxygen-T-atom-oxygen (O-T-O) angle is close to the ideal tetrahedral angle. In reported high silica structures, the O-T-O angles rarely deviate with more than a few degrees from the theoretical value of 109.28°. The T-O bond

![Figure 2.2:](image)

*Figure 2.2:*, The basic building unit of all zeolites is a tetrahedron with a T-atom in the center and one oxygen atom in each corner. Two angles are important in the zeolite structure, the O-T-O and T-O-T.
distance is however highly dependent on the element occupying the tetrahedral site (T-site). Reported bond distances range from 1.44Å for B to 1.96Å for Li.\cite{23} The framework structure is built by two neighboring tetrahedra sharing a common oxygen atom. The T-O-T angle created by linking two tetrahedra can be in the range between 134°-180° with an average of 154°.\cite{23} The considerable flexibility of the T-O-T angle is the key to the large diversity of zeolite structures. The element at the T-site can be different but some sequences are not allowed. For example, there are no reported zeolites with an Al-O-Al connectivities due to unfavorable charge interaction. This is known as Löwensteins rule.\cite{49}

2.2.2 The building units

By linking the tetrahedra, composite building units (CBU) can be created. The simplest CBUs are the rings. The most common rings in zeolites contain 4, 5, 6, 8, 10 and 12 T-atoms, see Figure 2.3 for some examples. Rings with odd number of T-atoms other than 5 are rare but there are examples of structures with 3, 7, 9 and 11 T-atoms. Rings with more than 12 T-atoms do occur and the largest ring reported in a zeolite up to date contains 30 T-atoms.\cite{42} The rings can be flat or bent. Rings with 6 T-atoms or less are considered to be impenetrable by guest species. By linking several rings, three dimensional units are created. These units are called cages if they enclose a void that cannot be accessed by guest species. There is a large variety of cages. One of the most basic building units is the sodalite cage. The sodalite cage is built entirely from 4-, and 6-rings and hence leaves an inaccessible void in the center. The cage consists of six 4-rings and eight 6-rings. Following the number of rings, it can also be called a \([4^66^8]\) cage. It can also be described as a truncated octahedron.

\textbf{Figure 2.3:} Some common building units in zeolites, the 4-ring (a), 5-ring (b), 6-ring (c), double 4-ring (d) and a \(4^35^4\) (e).
The cage can be used to build entire structures and is in that case called a secondary building unit (SBU).

A different type of CBU are the chains. The chains extend along one dimension and can also be used to build up entire structures. One example is the double crankshaft chain which is a folded chain of 4-rings. Different packing of this chain can entirely build 6 different known zeolite structures, APC, GIS, GME, MER, PHI and SIV. Many structures are too complex to be described by only one type of building unit. Then it is necessary to combine several different CBUs. The occurrence of different rings and building units are to some extent related to the composition of the framework. For example 5-rings are common in high silica zeolites, 3-rings are common in zinco-, beryllo- and germanosilicates, and double 4-rings are common in germanosilicates. The double crankshaft chain is common in aluminosilicates. Narsarsukite chain are more common in aluminophosphates. If the material has a strict alternation of T-atoms, such as aluminosilicates with Si/Al ratio of 1 or aluminophosphates, all rings of the structure must have an even number of T-atoms.\[26\]

The most important features defining the properties of zeolites are the size, shape and dimensionality of the void space that are created by the framework. The pores can be in the form of a channel, a void that extends in at least one dimension. The channel is described by the smallest ring that limits the diffusion along the channel. The channel is called an n-ring channel if it is limited by n T-atoms. It is also important to describe the shape of the channel, which can e.g. be straight, zigzag or gyroidal. A structure can have channels extending in one, two or three dimensions. The channels can either intersect with each other or run independently. The void space of some structures is better described as cavities. Cavities are normally larger voids inside the structure with windows of smaller rings limiting the diffusion into and out of the cavity.

An 8-ring channel is called a small ring channel. An undistorted 8-ring channel has a free diameter of $\sim$4Å. This is calculated as the distance between oxygen atoms at opposite sides of the ring, subtracted by two oxygen radii (2×1.35Å). 8-ring channels allow small molecules and ions to pass through. Rings with 10 T-atoms are referred to as medium pores. They have a free diameter of approx. 5.5Å allowing some larger molecules such as branched alkanes to pass through. Channels limited by a 12-ring have a free diameter of $\sim$7 Å and are called large ring channels. They permit larger molecules such as some benzene derivatives to pass through. If the structure has a channel limited by more than 12 T-atoms it is called an extra-large pore structure.
2.2.3 The Framework

The sodalite cage (sod) can alone be utilized to construct four different known zeolite frameworks, just by changing the connectivity between them, see Figure 2.4. If the sod cages are connected to six neighboring sod cages by sharing the 4-rings, the cubic sodalite structure is formed. The sodalite structure can be considered as a close packing of sod cages since the voids between the cages themselves are also sod cages. If the sod cages are connected through the 4-rings but not sharing the 4-rings between the sod cages, the structure of zeolite A is formed. This extends the cage between the sod cages and creates a large 8-ring window which now makes the structure accessible for guest species. By connecting each of the sod cages to four other sod cages through the 6-rings, two other structures can be created, faujasite and EMC-2. The two structures are highly related and both contains 12-ring channels.

Every zeolite material is classified by the framework type it belongs to. The framework type does not take into account the element in each T-site, just the connectivity, topology, of the framework. All new zeolite materials with new framework topologies are examined by the Structure Commission of the International Zeolite Association and collected in the Database of Zeolite Structures. Each new zeolite with a novel topology is assigned a three letter code that will be used to classify the framework.

One parameter representing the porosity of the structure is the framework density (FD). It is defined as the number of T atoms/1000Å³. Typically zeolites have a framework density of 11-20 T/1000Å³. As a comparison dense quartz has a framework density of 22.6 T/1000Å³.

A zeolite material should not be considered as having a rigid structure with very well defined pore opening. The exact pore opening is dependent on several factors, e.g. the composition of the framework. If the material has guest species coordinating to specific sites inside the framework, it will alter the available diffusion aperture. Thermal vibrations also affect the actual window size, especially at elevated temperatures.
Figure 2.4: The sodalite (sod) cage (a), here drawn with only T-T connections for simplicity, is the main building unit for four different zeolite structures. Sodalite is formed when the sod cages are connected by sharing 4-rings (b). Zeolite A is formed when the sod cages are connected via two 4-rings (c). The faujasite (d) and EMT (e) frameworks are formed when the sod cages are connected via 6-rings.
2.3 Disordered zeolite structures

Disorder is a common feature in zeolite materials. As already mentioned, zeolites are built from basic building units. In many cases these building units, such as layers or tubes, can connect in different ways without significantly increasing the energy of the system. In these cases a disordered material may be formed. In the case of a structure built from layers or tubes with two or more possible connectivities. An introduction to topological disorders in zeolites is given below. More details can be found in Paper I.

2.3.1 Order and disorder in layered structures

A common form of disorder is when a layer, extending in two dimensions, has the possibility to connect to the adjacent layer in several ways. Disorder of this kind is called stacking disorder. It can be defined by stating the sequence of shift vectors relating the consecutive layers to each other. Stacking disorder can be described in the same way as common brick walls, if we limit the example into two dimensions. The bricklayer first decides how to construct the layer. Let us assume that the layer contains only of bricks with the long edge facing out from the wall. After placing the first layer he has different ways to place the second layer. He can either place the bricks of the second layer strictly on top of the first bricks (with a shift of $0 \times$ the repeat distance along the layer), see Figure 2.5a, or put it half way in between two bricks of the first layer (with a shift of $1/2 \times$ repeat distance), as in Figure 2.5b. He can also chose any other arbitrary shift ($\pm x \times$ repeat distance), as shown in Figure 2.5c and d. After choosing a desired shift for the second layer, the bricklayer can now choose how he would like to place the third layer with respect to the second layer and the first layer. Let us consider the case where the bricklayer choose a shift other than 0 or 1/2 of the repeat distance along the layer. In the case he used a shift to the right between the first and second layer, he can now choose to shift the third layer to the right again, as in Figure 2.5d. He can also change the direction and shift it to the left, as in Figure 2.5c, with the result that the third layer now is straight above the first layer. These two cases create sequences of either alternating right and left stacking or consecutive stacking in one or the other direction. These stacking sequences are the two end members of the stacking sequence with one defined shift. In the case of consecutive shifts to the right or left, only one layer is needed to define the structure. For the wall with alternating shifts, two layers are needed to define the pattern. Of course the bricklayer is not restricted to one or the other of the end members but can create more complex sequences. Figure 2.5e shows a case where 4 layers are needed to complete the sequence (+1/4, +1/2, -1/4, 26
Figure 2.5: The stacking of layers in many zeolite structures is similar to the stacking of bricks in walls. A stacking sequence with zero shift is shown (a), alternating shifts (c) and same shift (d). These patterns are similar to the sequences in polymorphs C, A and B of zeolite beta respectively. The Fourier transform of each wall is inset for comparison.
As the complexity of the pattern increases, the number of layers needed to describe the stacking grows. If the pattern cannot be completely described by extending the number of layers, the structure is disordered, see Figure 2.5 for a pattern of two alternating type of layers stacked without obvious ordering. A disordered structure can be described as an intergrowth between several ordered structures, called end-members. The ordered end-members are said to belong to a disordered family.

Many zeolites have disorder similar to that of the example given above. Among them are zeolite beta (with framework code *BEA), the family of materials SSZ-26/33 (CON)\[^{[50, 52]}\] and the large family of materials called the ABC-6 family. Among microporous materials with mixed coordinations, ETS-10\[^{[53, 54]}\] is a prominent example of similar type of stacking disorder.

### 2.3.2 Order and disorder in zeolite beta

Zeolite beta is known to have a notoriously complex disordered structure. The material was first synthesized by Wadlinger et. al. \[^{[55]}\] in 1967 but the structure was not known until 1988 when Newsam et. al. \[^{[56, 57]}\] and Higgins et. al. \[^{[58]}\] independently reported models of the structure. The structure is built by epitaxial stacking of topologically identical layers, forming a 3-dimensional interconnected 12-ring channel system. Each layer contains a 12-ring opening and is related by a rotation of 90° around the normal to the layer in relation to the previous layer, see Figure 2.6a. Each layer has a number of connection sites along the surface of the layer. Depending on how these sites are combined, the structure can possess different stacking sequences. The beta layer has three possible connection sites per repeat unit in the plane of the layer. This means that the shift between consecutive layers will always be a multiple of 1/3 of the repeat distance ($n \times 1/3$ of the repeat distance), see Figure 2.6b and c. This generates three basic end members of the zeolite beta structure, Figure 2.6d-f. The end member with alternating stacking of +1/3 and -1/3, also referred to as ABA... stacking, has been given the name polymorph A. Consecutive stacking of either +1/3 or -1/3, ABCA... or ACBA..., is called polymorph B and the structure with no shift, AA..., is called polymorph C. The term polymorph has been used for the different stacking sequences of zeolite beta and other related structures. Since the end members are stacking sequences of identical layers with the freedom to shift only in one plane, they can be considered to be polytypes by a more strict definition. The names polymorph A, B and C are used to refer to the three end members by tradition. The most common form of zeolite beta is as an intergrowth between polymorph A and B, with almost equal probability. Since both the two polytypes are built from layer shifts with $\pm 1/3$ shifts and only differ when the second and third nearest neighbors are taken...
The structure of zeolite beta is built from a layer containing a 12-ring opening perpendicular to the layer (a). Two consecutive layers are related by a 90° rotation, viewed along the \(a\)- and \(b\)-axes (b and c respectively). The possible sites for connectivity are marked in red. It is possible to shift the layers along \(a\) and \(b\) and maintain connectivity. The three end members of zeolite beta, polymorphs A, B and C are shown in d, e and f, respectively.

Figure 2.6: The structure of zeolite beta is built from a layer containing a 12-ring opening perpendicular to the layer (a). Two consecutive layers are related by a 90° rotation, viewed along the \(a\)- and \(b\)-axes (b and c respectively). The possible sites for connectivity are marked in red. It is possible to shift the layers along \(a\) and \(b\) and maintain connectivity. The three end members of zeolite beta, polymorphs A, B and C are shown in d, e and f, respectively.

into account, their formation energies are very close. It is hence very difficult to control the growth. A material highly enriched in polymorph B has been synthesized under controlled conditions.\[17\] Despite a lot of efforts, a pure or highly enriched form of polymorph A has not yet been reported. Such a material is highly desirable since one of its channels is chiral. The connectivity between the layers in the structure of polymorph C is different compared to polymorph A and B and hence the energy of formation differs. Polymorph C contains double 4-ring units, which can be promoted by incorporating germanium into the structure. Materials with pure polymorph C type stacking have been reported first as a germanate\[59\], then germanosilicate\[60\] and later as a pure silicate\[61\].

The layers of zeolite beta are related by a rotation of 90°. This means that the stacking disorder is present along two perpendicular directions. This leads to the possibility of combining the three end-members to construct three additional frameworks. By using the earlier allegory of the stacking of bricks, it is possible to think of a house where one wall is built with alternating left and right stacking and the wall around the corner has a stacking sequence without any shifts. If ABA type stacking along one direction is combined with ABCA type stacking in the perpendicular direction. These structure is called polymorph \(C_H\). Polymorph C type stacking can be combined with either poly-
morphs A or B along the perpendicular direction the structure is now called polymorphs D and E, respectively.\cite{62} These polymorphs might seem far-fetched but recently a material with intergrowth between polymorphs D and E was reported.\cite{63} The channel size and dimensionality are not affected by the stacking disorder. It will remain a 3 dimensional 12-ring channel system. The only difference to the channel system is the shape of the channels.

2.3.3 Other disordered zeolite families

A very rich family of disordered zeolite structures is the ABC-6 family. It contains more than 15 different structures, several of them, e.g. chabazite, with industrial importance. Their structures can be regarded as stacking of layers containing individual planar 6-rings. The 6-rings in one layer can be connected to the next layer of 6-rings in two different ways. The three different possible locations for the 6-rings can be denoted as A, B and C, see Figure 2.7. Materials with a large number of different stacking sequences have been found. The simplest one is cancrinite\cite{47} containing only 2 layers, ABA..., and the longest sequence reported contains 28 layers, in the sequence ABCABACACABACBACBACABACABCA...\cite{64}. Different sequences will result in structures with completely different channel system ranging from 3-dimensional 8-ring channels to 1-dimensional 12-ring channels. Some of the materials do not contain any pores. Intergrowth between structures with different stacking sequences are common. One example is the intergrowth between errionite and offretite, as confirmed and studied by electron microscopy.\cite{65} Recently a new member to the ABC-6 family built from 18 layers was reported, SSZ-52.\cite{66} The structure is related to the chabazite framework but has cavities twice as large. The materials was found to contain some intergrowth.
Figure 2.7: The structures of the materials in the ABC-6 family are built from layers of single 6-rings that can have three different positions, seen perpendicular to the $ab$-plane (a) and $ac^*$-plane (b) of a hexagonal unit cell. Depending on the stacking sequence a large number of different structures can be built. Two examples of related structures are errionite and offretite which can be found intergrown in materials, see structure model in (c).
ZSM-48 (*MRE)\cite{67,68}, SSZ-31 (*STO)\cite{69,70} and UTD-1 (DON)\cite{69,71} are three examples of zeolites with one dimensional channels of 10-, 12- and 14-rings, respectively. The disorder in these materials can be divided into two categories. The channels can be considered as tubes with a single wall of tetrahedrons. The tubes can be combined with each other with different shifts along the channel direction to form layers. These layers can then be stacked in a manner similar to the polymorph A and B discussed for zeolite beta above.

A third common type of disorder in zeolites is the intergrowth between layers that are not solely related by translation but also by a symmetry operation. Two well studied families with this type of disorder are the intergrowth between faujasite (FAU) and EMC-2 (EMT) and the intergrowth between ZSM-5 (MFI) and ZSM-11 (MEL). The MFI and MEL structures are built from the same topological layer. The consecutive layers can be related either by a mirror plane (MEL) or by an inversion center (MFI) creating two different topologies, see Figure 2.8. The two structures can be synthesized as pure structures but materials with intergrowth between the two have also been observed.\cite{72}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{zeolite_diagram.png}
\caption{The two framework structures MFI and MEL are built from the same building layer, in red. The only difference is that in the MFI structure the layers are related by an inversion center (i) and in the MEL structure the layers are related by a mirror plane (m).}
\end{figure}

The zeolite community has been haunted for decades by these disordered materials. Now it can be shown experimentally on an atomic scale how these materials are built up. This is achieved by a combination of the structure projection reconstruction from a through-focus series of HRTEM images and the RED method.
3. Basic electron crystallography

3.1 Transmission electron microscopy

A microscope is a tool used to magnify objects too small to be seen by our naked eyes. In the early days the microscope was synonymous with a light microscope. Today we have a variety of different microscopes, one of them is transmission electron microscope. Louie de Broglie proposed the wave-particle duality of electrons in his PhD thesis in 1924, which was confirmed by Davdsson and Germer through electron diffraction experiments a few years later.[73] In the early 1930s the German scientists Knoll and Ruska constructed the first electron microscope, utilizing the fact that electrons can be focused by electromagnetic lenses.

A transmission electron microscope (TEM) contains a number of different components each with its specific tasks. The microscope can be divided into three basic parts, the illumination system, the image formation system and the projector system, as can be seen in Figure 3.1. The illumination system serves the purpose to create a suitable beam. Firstly the electrons are emitted from a filament. The performance of the microscope is dependent on the coherence of the electrons. This depends on the energy spread and the size of the point source. The electrons are accelerated by the high tension to gain energy corresponding to the chosen accelerating voltage. The speed of electrons in a TEM is approaching the speed of light at typical accelerating voltages such as 200 kV. The last part of the illumination system is condenser lenses with the purpose of further improving the coherency of the electron beam and to provide a suitable beam, parallel or convergent depending on the application.

The second part of the microscope is the image formation system in which the electrons interact with the specimen. The specimen should be thin enough so that the electrons can pass through. After interaction with the specimen, the electron is focused by the objective lens. This is the most important lens of the microscope. The performance of the objective lens determines to a large extent the performance of the entire microscope. After the objective lens, two apertures, one in the back focal plane (objective aperture) and one in the first image plane (selected area aperture), are used to select the desired electrons. By adjusting the focus of the intermediate lens, either an image
Electrons are charged particles. As such, they interact with the charges in the sample, formed by the nuclei and electrons of the atoms, through Coulombic forces. This means that the electrons, after passing through the specimen, carry information about a combination of both the electrons and the nuclei of the atoms. X-rays on the other hand interact with the electrons in the specimen. The fact that electrons are charged has two important consequences. The first is that the electrons can be focused by electromagnetic lenses, in a manner similar to that of light focused by a glass prism. This provides the possibility of image formation. The second feature is that the interaction with matter is much stronger for electron than that for X-rays. This has the major advantage that electrons can be used to study samples much smaller than what X-rays can. However it has the drawback that multiple scattering may occur. The multiple scattering makes the interpretation of the data more difficult.

When electrons pass through the sample, the interaction can be divided into two major groups. If the electrons interact with the specimen without losing any energy, the interaction is elastic. If any portion of the energy of the electrons is lost, the interaction is inelastic. In the elastic interaction between
electrons and specimen, the speed and hence the wavelength of the electron beam are preserved. This is a prerequisite for Bragg diffraction and image formation by phase contrast. Inelastic interaction between electrons and matter is as common as the elastic interaction. The electron can lose energy through several different events. The incident electron may interact with an electron of the core shell of the specimen and transfer a part of its energy. If enough energy is transferred, an electron of the specimen may be kicked out and a characteristic X-ray will be formed as an electron from an outer shell takes its place. It is also possible that the X-ray is reabsorbed by an electron causing the ejection of yet another electron; this electron is called Auger electron. If the electron beam interacts with the nuclei, it may lose energy in the form of X-rays, brehmsstrahlung. If the incoming electron loses energy by kicking out an electron of the valence shell, a secondary electron is formed. If the incident electron causes oscillations of either the electrons or the atoms of the specimen, it loses energy in the form of plasmons or phonons respectively.

3.1.1 High resolution transmission electron microscopy

As electrons pass through the specimen they will be scattered by atoms in the specimen. The electron beam will be diffracted by the lattice plane of a crystalline sample. The interference between the diffracted beams forms a high resolution transmission electron microscopy (HRTEM) image. If the crystal is thin enough to fulfill the weak phase object approximation, the contrast of this image is related to the projected electrostatic potential of the specimen.

Since the electron beam passes through a series of apertures and lenses with aberrations, it undergoes further phase modifications. The phase modification can be described by the contrast transfer function (CTF) here called $T(u)$, see Equation 3.1. The CTF is composed of two parts. $D(u)$ is a damping function. It contains contributions from the objective aperture ($A(u)$), the energy spread of the beam ($E^\Delta(u)$) and the beam convergence ($E^\alpha(u)$), see Equation 3.2. One effect of all three functions is a damping of high resolution information. $\chi(u)$ is a function highly dependent on the defocus condition of the objective lens, see Equation 3.3.

\[
T(u) = D(u) \sin \chi(u) \tag{3.1}
\]
\[
D(u) = A(u) E^\Delta(u) E^\alpha(u) \tag{3.2}
\]
\[
\chi(u) = \pi \Delta f \lambda u^2 + \frac{\pi C_s \lambda^3 u^4}{2} \tag{3.3}
\]
where $\lambda$ is the electron wavelength, $\Delta f$ is the defocus condition of the objective lens and $C_s$ is the spherical aberration coefficient of the objective lens. The most important parameter that can be adjusted during data collection is the defocus value. It is often desirable to choose a defocus value by which the $\sin \chi(u)$ term of the CTF has a uniform sign in the resolution range of the image, see Figure 3.2. The largest range of uniform sign for $\sin \chi(u)$ is obtained at the Scherzer focus condition, $\Delta f_{\text{Sch}}$, which can be calculated from Equation 3.4:

$$\Delta f_{\text{Sch}} = \sqrt{\frac{4C_s\lambda}{3}}$$  \hspace{1cm} (3.4)

The position of the first crossover at Scherzer focus condition can be determined by setting $\sin \chi(u) = 0$ which gives Equation 3.5:

$$u_{\text{Sch}} = 1.5C_s^{-1/4}\lambda^{-3/4}$$  \hspace{1cm} (3.5)

**Figure 3.2:** The contrast transfer function, $T(u)$, shown for a focus condition close to the Scherzer focus ($\Delta f=\text{-}40 \text{ nm}$). The envelope functions $E^\Delta(u)$ and $E^\alpha(u)$ are shown as well as the product of them $D(u)$. $u_{\text{Sch}}$ is the first crossover of the CTF. The CTF was calculated by CTFExplorer$^{[74]}$ for acc. voltage of 200 kV, $C_s$ 1.2mm, energy spread 1.6 eV and beam convergence 0.6 mrad.
3.1.2 Scanning transmission electron microscopy

The basic principle of scanning transmission electron microscopy (STEM) imaging is that the electron beam is focused onto the specimen, forming a small probe. The probe is scanned in a raster over the sample by coils above the specimen. The distance between each raster point defines the magnification. The resolution of a STEM image is determined by the size of the probe. Modern aberration corrected microscopes have pushed the limit of the probe size into a new era, allowing resolution in the sub Ångström range. As the electron beam passes through the sample, it interacts with the atoms and the transmitted beam will be scattered. There are a number of different detectors available detecting electrons scattered at different angles, see Figure 3.3. A bright field detector will detect the intensity of the unscattered electrons and electrons scattered at low angles. An annular dark field (ADF) detector will detect the scattered electrons at higher angles. If an ADF detector is designed to collect electrons at high scattering angles, it is called a high angle annular dark field (HAADF) detector. The electrons detected by the HAADF detector are generally inelastically scattered by the atomic nuclei. Hence the contrast formed by such events is proportional to the atomic number and therefore called Z contrast. The contrast of a STEM image is not altered by any CTF and is normally more easily interpreted as the projection of the specimen.

![Figure 3.3](image.png)

**Figure 3.3:** A schematic ray path for STEM imaging showing the positions and differences in scattering angles for the bright field (BF) annular dark field (ADF) and high angle annular dark field (HAADF) detectors.

A second advantage of STEM imaging is that it allows collection of spectroscopic data from each of the raster points. This gives the possibility to construct a 2D map containing information about for example the composition. This is especially powerful in combination with atomic resolution imaging.
3.2 Crystallography

Crystalline materials surround us everywhere. The early studies of crystals were based on examining the geometry of their surfaces. Already in the early days it was believed that the ordered geometry of the surfaces reflected an ordered arrangement of some kind of inner building unit. Not until von Laue showed that crystals can diffract an X-ray beam and father and son Bragg solved the structure of some basic salts in 1913[1], the first evidence of an ordered arrangement of atoms was proven.

So what makes a crystal a crystal? As stated in the previous paragraph there should be some kind of ordered arrangement of the atoms, but that is not enough. A simplified definition would be that a crystal is built from an ordered arrangement of atoms, repeating on a lattice extending in three dimensions. However, this definition does not include some special cases of crystals, for example quasicrystals, so the International Union of Crystallography has extended the definition to:

A material is a crystal if it has essentially a sharp diffraction pattern. The word essentially means that most of the intensity of the diffraction is concentrated in relatively sharp Bragg peaks, besides the always present diffuse scattering.

In the next chapters, some materials which possess disorder as an intrinsic feature of its nature will be described. This disorder will give rise to diffuse scattering.

3.2.1 The unit cell and symmetry

Let us here consider the basic definition of a crystal. The most basic feature of a crystal is the unit cell. The unit cell can be thought of as a box with a certain shape, filled with a specified arrangement of atoms. The box is defined by three basic vectors called the crystallographic axes and is specified by their lengths (a, b and c) and the angles between them (α, β and γ). The unit cells are stacked face to face related by pure translation.

The next concept describing a crystal is the symmetry. Since the crystal possesses translation of the unit cell in three dimensions it is enough to use the symmetry of the unit cell to describe the symmetry of the entire crystal structure. The translational nature of crystals also limits the symmetry elements that are possible in a unit cell. The possible symmetry elements are mirror planes, inversion center and rotation axes (only 2-, 3-, 4- and 6-fold). These symmetry elements can then be combined with each other or with translation.
to form three additional elements; rotoinversion (combination of center of in-
version and rotation axis), screw axis (rotation axis plus translation) and glide
plane (mirror plus translation). The symmetry of the unit cell will enforce re-
strictions to the shape of the unit cell, and will divide crystalline structures into
seven basic classes called crystal systems, see Table 3.1. Several symmetry el-
ements can be combined in different orientations of the unit cell. In total 230
different combinations of symmetries, called space groups, exist. When the
shape and content of the unit cell are defined, the entire chemical structure of
the material can be built by pure translation of the unit cell.

Table 3.1: The seven crystal systems and their characteristic symmetries, unit
cell restrictions and point groups.

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Characteristic symmetry</th>
<th>Unit cell restrictions</th>
<th>Point groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>1 or ̅1</td>
<td>none</td>
<td>1, ̅1</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>2, m or g along/</td>
<td>α = γ = 90°</td>
<td>2, m, 2/m</td>
</tr>
<tr>
<td></td>
<td>perpendicular to one axis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Orthorombic</td>
<td>three perpendicular elements (2, m or g)</td>
<td>α = β = γ = 90°</td>
<td>222, mm2, mmm</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>4 or ̅4</td>
<td>α = β = γ = 90° a ≠ c</td>
<td>4, 4, 4/m, 422, 4mm, 4̅2m, 4/mmm</td>
</tr>
<tr>
<td>Trigonal</td>
<td>One 3 or ̅3</td>
<td>α = β = 90° γ = 120° a ≠ c</td>
<td>3, 3</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>6 or ̅6</td>
<td>α = β = 90° γ = 120° a ≠ c</td>
<td>6, 6, 6/m, 622, 6mm, 6̅2, 6/mmm</td>
</tr>
<tr>
<td>Cubic</td>
<td>4 equivalent 3-fold axes</td>
<td>α = β = γ = 90° a = b = c</td>
<td>23, m3, 432, 43m, 4̅3m, m3̅m</td>
</tr>
</tbody>
</table>

3.2.2 The reciprocal lattice

A crystal can be described in reciprocal space just as well as in real space.
A crystalline material will have a reciprocal lattice. Just as in real space, a
unit cell can be used to describe a crystal in reciprocal space. A lattice point
in reciprocal space corresponds to a set of parallel planes in real space. The
orientation of the series of parallel planes and the distance between them, $d_{hkl}$, are defined by the Miller indices for a given lattice. The Miller indices, $hkl$, are defined as the number of interceptions of the unit cell vectors, $a$, $b$ and $c$, for the given plane. An index of zero corresponds to a plane whose normal is parallel to the specified axis, see Figure 3.4.

![Figure 3.4: Three lattice planes with the Miller indices (010), (110) and (111).](image)

X-rays, electron and neutrons will be scattered by atoms. Since the atoms in a crystal are ordered, the scattered wave from one lattice plane will interfere with the wave from another plane. This gives rise to constructive or destructive interference. When the difference in ray path is equal to an integer of the wavelength, the interference will be constructive and the Bragg condition is fulfilled, see Fig 3.5. The relationship between the wavelength ($\lambda$), the interplanar spacing ($d$) and the scattering angle ($2\theta$) is defined by Bragg's law, Equation 3.6.

$$n\lambda = 2d \sin \theta$$  \hspace{1cm} (3.6)

While the positions of the reflections are determined only by the unit cell, their intensities are determined by how well the corresponding lattice plane coincides with the atomic arrangement in the unit cell. The reciprocal lattice is measured through the scattered intensities. The reciprocal lattice carries all information about the atomic arrangement in real space and is suitable to describe crystalline materials.

One way to describe the diffraction geometry is to use the Ewald sphere, see Figure 3.6. The Bragg condition is fulfilled when the scattering vector is equal to the lattice vector in reciprocal space. The incident wave vector, $k_0$, with the length of $1/\lambda$ will point at the origin of the reciprocal lattice, $O$. Considering an elastically scattered event the wave vector of the scattered beam, $k_s$, has the same length as $k_0$ and is scattered by the angle $2\theta$ from the incident wave vector. Since the two vectors have the same length they
Figure 3.5: Two parallel beams scattered by equivalent atomic planes will interfere constructively when the difference in path lengths, $2d \sin \theta$, is equal to an integer multiple of the wavelength.

will always fall on a sphere with a radius of $1/\lambda$, this sphere is called the Ewald sphere. If the difference between the incident and the scattered wave vectors, called the scattering vector, is equal to a reciprocal lattice vector the corresponding reflection will fulfill the Bragg condition, see Equations 3.7 and 3.8.

$$\mathbf{k}_s - \mathbf{k}_0 = 2\lambda^{-1} \sin \theta \quad (3.7)$$

$$\mathbf{g}_{hkl} = d_{hkl}^{-1} = 2\lambda^{-1} \sin \theta \quad (3.8)$$

The radius of the Ewald sphere is proportional to $1/\lambda$, the wavelength of the incident beam, so the geometry of the diffracted reflections for a given incident beam direction will be different for electrons and X-rays. For X-ray diffraction the wavelength is in the range of 0.5-1.6Å, for example 1.5418Å for Cu Kα radiation. In a transmission electron microscope, the electrons are typically accelerated by a voltage of a few hundreds of kV, which results in a much shorter wavelength. For 200 kV, the wavelength of electrons is 0.0251Å. The effect of this is that the radius of the Ewald sphere will be much larger for electron diffraction. In relation to the dimensions of a typical reciprocal lattice, it will be essentially flat.

When a crystal is illuminated with an electron beam along a specific direction, [uvw], in real space, all reflections on the Ewald sphere will diffract. Those reflections will fulfill the Laue equation, Equation 3.9.
Figure 3.6: A 2 dimensional illustration of the Ewald sphere. When $g_{hkl}$ is equal to $1/d_{hkl}$, the Bragg condition is satisfied.

$$uh + vk + wl = n$$  \hspace{1cm} (3.9)

where $n$ is an integer number. Because of the large radius of the Ewald sphere in electron diffraction, most of the excited reflections will belong to the group where $n=0$, called zero order Laue zone.

3.2.3 The electrostatic potential

The electrostatic potential of a crystalline sample can be described as the sum of the contributions from each of the atoms of the unit cell.

$$\varphi(r) = \sum_{j=1}^{N} \varphi_j(r - r_j)$$  \hspace{1cm} (3.10)

Since the atomic arrangement, and hence the electrostatic potential in a crystal is periodic, $\varphi(u)$ can be described as a summation of Fourier components, also called structure factors. The structure factor is defined as:

$$F(hkl) = \sum_{j=1}^{N} f_j(hkl)e^{2\pi i(hx + ky + lz)}$$  \hspace{1cm} (3.11)

where $f(hkl)$ is the atomic scattering factor. This describes the scattering power of a given atom type as a function of the scattering angle. The Fourier transform of $\varphi(r)$ is related to the structure factor by a constant.
\[ FT[\varphi(r)] = \Phi(u) = \frac{h^2}{2\pi me\Omega} F(u) \] (3.12)

where \( h \) is the Planck constant, \( m \) and \( e \) are the relativistic mass and charge of the electron, respectively and \( \Omega \) is the volume of the unit cell. For a crystalline material the potential distribution can be described as a summation of the crystallographic structure factors.

\[ \varphi(xyz) = \frac{\lambda}{\sigma\Omega} \left[ \sum_{hkl} |F(hkl)| \cos[2\pi(hx + ky + lz) - \varphi(hkl)] \right] \] (3.13)

### 3.2.4 The phase problem

The crystallographic structure factors contain an amplitude part \( |F(hkl)| \) and a phase part \( \varphi(hkl) \). They must both be known in order to calculate the potential distribution of the crystal. In a diffraction experiment only the amplitude part is obtained by measuring the scattered intensity but the phase information is lost, this is called the phase problem in crystallography. In order to construct the potential of the structure, the phase information has to be recovered. Several methods have been developed over the years for this purpose; the Patterson method, Direct methods and Charge flipping are examples of powerful methods to mathematically recover the phase information. There is however an experimental way to record the phase information together with the amplitudes, it is called HRTEM imaging. Under the condition that the HRTEM image is acquired at such conditions that the contrast is proportional to the projected potential of the specimen, a Fourier transform of the image will contain both the amplitude and the phase part of the crystallographic structure factors for the reflections in the reciprocal plane corresponding to the projection imaged. If the HRTEM image is acquired along the [001] direction in real space, the crystallographic structure factors in the \( hk0 \) plane can be determined as in Equation 3.14.

\[ \phi(xy) = \int_0^t \phi(xyz)dz = \frac{\lambda t}{\sigma\Omega} \left[ \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} |F(hk0)| \cos[2\pi(hx + ky) - \varphi(hk0)] \right] \] (3.14)

The information obtained from one HRTEM image is limited to the projection of the three dimensional potential onto a two dimensional plane. In order to recover the full three dimensional information, HRTEM images acquired along several projections of the structure must be combined. The reconstruction is made in reciprocal space by merging the structure factors extracted...
from HRTEM images along several projections of the structure into one data set. The three dimensional potential distribution is then calculated by an inverse Fourier transform of the set of structure factors. The structure factors extracted along different directions of the structure have to be scaled to each other before merging. This can be done by utilizing the amplitudes of the common reflections along the line that the two planes have in common in reciprocal space.

3.2.5 Symmetry determination

An important step of determining the structure of a material is to deduce its symmetry. For this purpose HRTEM has an important advantage over diffraction techniques such as X-ray diffraction. Symmetry determination from diffraction data normally involves evaluation of systematic absences and comparison of the scattered intensities to confirm the point group of the structure. The structure factor phase information from HRTEM images also gives the possibility to evaluate the phase relationship between symmetry dependent reflections. By comparing the structure factor phases it is possible to distinguish between symmetry element with and without translational components, such as rotation axis and screw axis or mirror plane and glide plane. By combining information from the above mentioned sources it is often possible to reduce the possible number of space groups down to one or two.

3.3 New electron crystallographic methods

3.3.1 Rotation electron diffraction (RED)

Collection of electron diffraction data has long been a manual and tedious work. The first step towards the use of a different geometry was when Vincent and Midgley in 1992 introduced the precession electron diffraction (PED) technique. [75] In PED the electron beam is not static but precesses around the optical axis with an angle of typically, 1°-2°. The speed of the precession is in the range of hundreds to thousands Hz and hence the acquired pattern will be an average of off-axis patterns. Inspired by PED and earlier work in X-ray diffraction, together with the possibility of computer controlled TEMs, new methods were developed to take electron diffraction into 3 dimensions. In parallel two different methods were developed for collection of 3 dimensional electron diffraction, automated diffraction tomography (ADT)[76,77] and rotation electron diffraction (RED)[78,79]. They both have the same aims, to make an automated routine for collection of electron diffraction data in 3 dimensions and to develop a method to process the data and extract diffraction
intensities for structural analysis. Both methods have proven to be very pow-
erful for structural analysis over the last years. For the rest of the thesis I
will focus on the RED method since that is the method we are developing and
applying.

The RED data collection combines physical tilting of the specimen, go-
niometer tilt, with a fine electron beam tilt, see Figure 3.7. This combination
allows collection of electron diffraction patterns with a very fine sampling of
reciprocal space. The two tilt procedures are synchronized to tilt around the
same axis. A typical data collection, in this work, combines a beam tilt step of
0.1°-0.2° with a goniometer tilt of 2°. The electron diffraction patterns used
in this work have been acquired in selected area (SAED) mode, but nano-beam
mode can also be used. In the case of a beam tilt step of 0.1° and a goniometer
step of 2°, 21 separate SAED frames are collected for each goniometer tilt.
Because of a limited space for the sample holder in the TEM a normal RED
data set covers an angular range of ~130°-150°, leaving a missing wedge in
reciprocal space. For a crystalline material the missing wedge can often be
filled in by applying the symmetry of the structure. It is also possible to collect
several datasets from different crystals and merge them after proper scaling.
A normal dataset contains ~1500 SAED frames. In order to combine them
into a 3 dimensional data set, a proper data processing is needed. The data
processing contains several steps including alignment of the ED frames and
extraction of position and intensity for each reflection in the ED frames. The
positions of the reflections in the 2 dimensional ED frames are then combined
with the tilt angles to reconstruct the 3 dimensional reciprocal lattice. After
the reciprocal lattice is reconstructed, the unit cell can be determined. The
reflections can be indexed and the intensity of each reflection extracted. The
RED method turns the TEM into a single crystal electron diffractometer. The
above mentioned procedure of data collection and processing can be done us-
ing the software package RED developed in our group.[79] The collection of
RED data does not involve any crystal alignment as conventional TEM meth-
ods. The fact that the data is collected under conditions with fewer reflections
excited simultaneously reduces the multiple scattering significantly compared
to zone axis SAED patterns.

For crystalline materials, the intensities extracted from the RED data have
been shown to be useful for solving structures using direct methods, e.g. im-
plemented in the software SHELX[80] and SIR[81]. Although intensities ex-
tracted from RED data are closer to kinematical than conventional electron
diffraction, multiple scattering is still present. This is reflected by both the
intensity agreement of symmetry related reflections, $R_{int}$, and the agreement
between experimental and calculated amplitudes from the deduced structure
model, $R_1$, which are significantly higher for RED data compared to X-ray
Rotation electron diffraction combines beam tilt with goniometer tilt in order to collect complete three dimensional electron diffraction data.

Figure 3.7: Rotation electron diffraction combines beam tilt with goniometer tilt in order to collect complete three dimensional electron diffraction data.

diffraction. The structure models determined from RED have however been confirmed to be correct. This is proven by the fact that the structure models can be refined by Rietveld refinement of the PXRD patterns, with good agreement for the atomic coordinates.\textsuperscript{[41],[82]}

RED is a very helpful method also for characterization of materials containing severe disorder. Severe disorder will give rise to diffuse scattering in reciprocal space. The diffuse scattering is present between the reciprocal lattice points and can be difficult to understand from single 2D SAED patterns. Studying the diffuse scattering in 3D greatly facilitates the interpretation and can give crucial information about the disorder of the material.
3.3.2 Structure projection reconstruction from through-focus series of HRTEM images

An issue with HRTEM imaging is that the contrast is very sensitive to the optical condition used for the acquisition. In order to obtain an image with contrast representative for the projected potential of the specimen some conditions have to be fulfilled. First the specimen has to be thin enough to let the weak phase object be valid. Secondly the focus condition has to be controlled. Over the years several methods have been developed to solve this problem. One of them is the exit wave reconstruction [83][84], where the electron wave function at the exit surface of the specimen is reconstructed. Another method is the CTF correction based on crystallographic image processing and the analysis of the Thon rings.[85][86] The structure projection reconstruction is a development of the CTF correction approach in order to create a more general method.

The relationship between the contrast of the image and the projected potential is described by the CTF, see section 4.2. The idea behind the structure projection reconstruction is quite simple. If the defocus condition of an image is known, the CTF function can be accurately calculated and the effect of the CTF can be compensated for, following Equation 3.15.

\[
F(u) = \frac{I(u)}{kT(u)}
\]

(3.15)

where \(F(u)\) is the structure factor, \(I(u)\) the Fourier transform of the image, \(k\) a constant and \(T(u)\) the CTF. The inverse Fourier transform of the structure factor \(F(u)\) will be a true representation of the projected potential of the specimen. The method can be applied on periodic as well as non-periodic specimens and is suitable for studying disordered and beam sensitive materials.

The structure projection reconstruction utilizes the fact that although the exact focus condition for a single image may not be known, the defocus step between two images can be accurately determined with high reproducibility. A through-focus series of 20 images with a constant focus step is acquired. Given an absolute defocus value for the first image, the CTF can be calculated for each of the images in the series and then be compensated for in each of the images individually. If the assumed defocus value for the first image is correct, the phase of \(F(u)\) obtained from each image, via Equation 3.15 will be the same for all images. If the starting defocus value was incorrect, the phases will be different in the different corrected images. A figure of phase similarity describing how well the phases agree for a given starting defocus value is calculated. By comparing the phase similarity for a series of different starting defocus values, the correct starting defocus value can be identified. After the correct focus condition has been found, the calculated CTF can be used to
produce a CTF-corrected image. The last step is to sum all the CTF-corrected images in the series to produce an image corresponding to the projected potential of the specimen, see Figure 3.8. This method was developed in our group and is available in the software QFocus. [87]

Figure 3.8: Structure projection reconstruction by QFocus from a through-focus series of HRTEM images acquired under different defocus values to compensate for the contrast transfer function and create an image representing the projected potential of the specimen.

The structure projection reconstruction is a useful tool in HRTEM imaging since the interpretation of the contrast of the images is facilitated. A major advantage of the structure projection reconstruction is the transfer of the high resolution information to the final image. The information in the high resolution range will be in the oscillating region of the CTF and will be scrambled in an HRTEM image. With the structure projection reconstruction, however, the information will be transferred without distortions and hence contribute to the useful contrast of the image. The work of this thesis focuses on studies of zeolites which are beam sensitive and have a rather limited resolution compared to for example dense inorganic oxides and alloys. This means that most of the information related to the atomic structure of the zeolite will be present in the band where the CTF has the same sign and any amplitude above this band will, for most zeolites, be very weak. This would be an argument that the structure projection reconstruction is not as important for zeolites. The method however has important advantages when imaging beam sensitive materials. It is not necessary to find the correct defocus value before acquiring the HRTEM images. This is very useful when working in low dose conditions. Furthermore the signal to noise ratio is enhanced by the summation of images, which is important especially for disordered materials where it is not possible to perform lattice averaging over large areas.
This chapter aims at giving an overview of various methods and combinations used for structure determination of zeolite materials. Focus will be on methods that are related to electron crystallography. The example in this chapter comes from the field of zeolites, but the methods as such are feasible for structure determination of other crystalline materials as well. This chapter will give an overview, more details can be found in Paper II.

The standard technique for structure determination is single crystal X-ray diffraction, SXRD. The complete 3 dimensional reciprocal lattice of a crystal can be collected from a crystal using either an in-house diffractometer or a synchrotron light source. The SXRD intensities are often kinematical and can be used to solve unknown structures of a large variety of complexity by a number of different methods. If the structure is not too complex, the structure solution is straightforward and can be done in a few hours. There are two major limitations for structure determination by SXRD. The first one is the crystal size. The crystal needs to be at least a few micrometers even using the brightest synchrotron light sources. The second limitation is that it is difficult to determine structures of crystals suffering from severe disorder. Unfortunately many zeolite materials are difficult to grow as large single crystals so SXRD is often not a possibility.

For samples with crystals too small for SXRD, powder X-ray diffraction (PXRD) has been an obvious choice. PXRD data is collected from millions of randomly oriented crystals in order to obtain strong enough diffraction intensities. The collection of PXRD data is very simple on in-house or synchrotron sources. The drawback of PXRD data is that since intensities from differently oriented crystals are measured simultaneously, the 3 dimensional information of the reciprocal lattice is lost and projected onto one single dimension. This results in overlap of reflections with similar d-spacings in PXRD patterns. Then the intensity of each reflection cannot be determined unambiguously. This makes the structure determination by PXRD much more difficult than that by SXRD. Even so, PXRD has been a very important technique for structure determination of zeolites in recent years.

Although structure solution by powder diffraction has been more and more
powerful with new methods emerging, structures of many porous materials can still not be solved by PXRD alone. Among these complex structures with large unit cells that cause severe reflection overlapping, and crystals containing defects such as intergrowth and stacking disorders.

Every new material has its own unique properties, which gives both problems and opportunities. The structure solution route has to be chosen in order to overcome its unique challenges. Some common obstacles are small crystal size, low beam stability causing degradation in the electron beam, high complexity of the crystal structure, presence of elements interrupting the translational symmetry such as twinning, stacking disorder or other kinds of disorder.

Structure solution is a creative process where everything is allowed; any method by which a suitable structure model can be obtained is fine. Ab-initio structure solution by well established methods is just as good as model building, with just general information about the specimen as a base. This means that for structure solution it is important to have a broad knowledge about different available methods for structure solution as well as deep understanding of the type of materials investigated. In the case of zeolites, many structures are built from the same building units, assembled in different ways. In the extreme cases, a new structure could be solved based only on knowledge about the unit cell and comparison with known structures. The second step of the structure determination process, to verify the structure, is on the other hand a process that has to be done with great care and perfection. For ordered structures the structure verification is done mainly by a least squares refinement, which should converge to reasonable levels according to conventions. For heavily disordered materials the structure verification involves obtaining as much information as possible from different sources in order to confirm the proposed model.

The rest of this chapter will give some examples of structure solution of zeolites by different methods and combinations. Some of the possible routes to obtain a structure model are shown in Figure 4.1.

4.1 Electron diffraction

For ordered materials electron diffraction is often a method of choice. It requires a lower electron dose compared to HRTEM imaging and is hence also suitable for beam sensitive materials. Because of the dynamical effects, care has to be taken during data collection to achieve intensities as kinematical as possible. This can be done by choosing thin crystals. Dynamical effects can be further reduced by using either PED or a 3 dimensional electron diffraction technique such as RED or ADT. Ab-initio structure solution based on intensities extracted from electron diffraction has been successful by a variety of
Figure 4.1: Map over some possible routes for structure solution. Routes marked by black lines are suitable for ordered structures and red routes for disordered structures. Blue routes indicate additional symmetry information.
different methods. The first unknown zeolite structure solved ab-initio from electron diffraction data was the high silica zeolite SSZ-48\cite{88}. The structure was obtained by direct methods using intensities from 326 symmetry independent reflections extracted from SAED patterns acquired along 11 different zone axes. The structure has rather low symmetry, \(P_2_1\), and medium complexity, 7 unique T-sites. Another example is the structure solution of the germanosilicate ITQ-40\cite{89}. In this case only 98 unique reflections from SAED patterns of two main zone axes, [001] and [100], were extracted. The structure model was obtained using maximum entropy and likelihood method in the program MICE\cite{90}. The structure of ITQ-40 has high symmetry, \(P6_3/mmc\) and 5 unique T-sites. PED data has been applied for structure solution of several known zeolite structures.\cite{91}

Over the last few years the development of 3 dimensional electron diffraction techniques has simplified the data collection and enabled collection of more complete data. Structure solution from RED, ADT and related methods has shown to be very powerful and is now a robust method for structure solution of zeolites, as long as the material is stable enough for data collection. Two recent examples of ab-initio structure solution are ITQ-51 and ITQ-43. ITQ-51 is a silicoaluminophosphate with space group \(P2_1/n\) and contains 8 independent T-atom sites. All T-sites as well as most of the O atoms could be obtained using direct methods in SHELX\cite{41}. The structure model was further refined by Rietveld refinement against the PXRD data. The atomic positions obtained from the RED data deviated on average by 0.11 Å for T-sites and 0.13 Å for O from those obtained by the Rietveld refinement. ITQ-43 was solved from ADT data using direct methods in the software SIR2008.\cite{92} All T-atoms and most of the O could be found. The residual values after refinement against the electron diffraction data are high for reasons not fully understood. The structure still needs to be confirmed by Rietveld refinement against PXRD data.

It is also possible to use electron diffraction data to complement structure solution by other methods, often PXRD. From electron diffraction, the unit cell is easy to determine. Together with the unit cell, systematic absences as well as point group symmetry can be deduced. This information is often of crucial importance since it can be very difficult to obtain such information from PXRD data. Electron diffraction can also be used to pre-partition the intensities of the PXRD peaks. Let us consider the case where three peaks completely overlap in the PXRD pattern. If it is possible to see from electron diffraction that two of them are much stronger than the third, the intensities can be set to 50:50:0 instead of 33:33:33 as would be the case without pre-knowledge from electron diffraction. These methods were applied for the structure solution of ITQ-37, with space group \(P4_1\overline{3}2\) and 10 unique T-atoms.\cite{42} In this case the space
group could be determined from electron diffraction data and the intensities of overlapping reflections could be pre-partitioned before structure solution was performed using charge flipping from the PXRD data. The material is very beam sensitive and the electron diffraction data did not have enough resolution for ab-initio structure solution.

Recently a new approach to use electron diffraction data has been shown. By applying the charge flipping algorithm on intensities extracted from a 2 dimensional PED pattern, the projected potential of the crystal can be determined. [93] This means that the structure factor phases of reflections in one reciprocal lattice plane can be determined. These phases can be used either as starting phases for a structure solution by charge flipping or to produce an envelope function that can be used in for example the zeolite specific software FOCUS[94]. An envelope function is a function defining the boundary between voids and matter inside the porous structure and can be used as a form of pre-knowledge in the structure solution process.

4.2 HRTEM imaging

Taking good HRTEM images are more demanding than electron diffraction, but it is often more rewarding. HRTEM images have several benefits over diffraction techniques. Firstly the structure factor phases can be extracted, which is of outermost importance during structure determination. Secondly HRTEM images give local information, whereas diffraction techniques always average over a whole crystal or even a large number of crystals. The local information is crucial when studying disordered materials.

The occurrence of disorder in crystals will create diffuse scattering which in many cases obstruct structure solution ab-initio from the diffraction data. One common form of disorder in zeolite structures is the stacking of layers. This will generate diffuse streaks perpendicular to the layer in reciprocal space, see Figure 4.2. One zeolite with this kind of disorder is zeolite beta, which is built from layers with an allowed shift of n × 1/3 of the repeat distance of the layer, see Section 2.3 for more details. The reciprocal lattice of zeolite beta exhibits sharp intensities for reflections with index 3n, 3n, l, all other reflections form streaks along the c*-axis. A more detailed description of the diffraction behavior from zeolite beta can be found in Papers I and III. Important information about e.g. the stacking vector can be determined, by examining the sharp spots and diffuse streaks of the reciprocal lattice.

Structure solution from HRTEM images mainly follow two routes, either model building or 3D reconstruction. Model building utilizes HRTEM images along one or more projections and is sometimes combined with additional information from NMR, adsorption, electron diffraction and other methods,
From all the available information a feasible model is built. Model building is a technique that needs knowledge and experience in the type of materials studied. It has shown to work well for structure solution of numerous zeolite structures over the years. Some prominent examples are the disordered materials zeolite Beta, SSZ-26/33, SSZ-31, ZSM-48, UTD-1, and the zeolite related material ETS-10. It has also been applied to solve the ordered zeolite structure MCM-22. A more general route is to use 3D reconstruction, described in section 3.2. This method has been used to characterize two zeolite structures, both polytypes of zeolite Beta. The first case was a material with pillars of polytype C growing on top of intergrown Beta crystal. In the HRTEM images along two projections of the pillars, pure polytype C of Beta could be found. The second case was zeolite Beta highly enriched in polytype B (ratio B/A 85/15). A 3D reconstruction of HRTEM images shows that the structure in the large ordered regions are polytype B of Beta. 3D reconstruction is a more general method than model building for structure determination.

The structure factor phase information extracted from HRTEM images has played a crucial role in the structure solution of several of the most complex zeolite structures. The phase information can be used as prior knowledge for ab-initio structure solution from PXRD data. In the structure solution of IM-5, HRTEM images from the three main zone axes were acquired and 95 independent reflections were extracted. The phases of these reflections were used as staring phases for a run of the powder charge flipping algorithm implemented in the software SUPERFLIP. The obtained structure model with 24 symmetry independent T atoms could be refined against the PXRD data. Structure factor phase information has been utilized in a similar way to solve two other very complex zeolite structures, TNU-9 and SSZ-74.
5. Structure determination of new zeolite materials

5.1 Ordered materials

5.1.1 EMM-25 (Paper IV)

Zeolites with different channel sizes can be used for different applications due to their shape selectivity. However, most zeolite structures have pore openings defined by even number of TO$_4$ tetrahedra (T=Si, Al, Ge, P, B...). While some zeolites containing 9-ring pore openings are reported, zeolites with larger odd-numbered rings (≥11) are very rare. Among the reported zeolite structures, there are only two germanates that contain large odd-numbered rings; a germanosilicate ITQ-40[92] with 15x15x16-ring channels and a gallogermanate zeolite JU-64 with 11-ring[100]. None of them are stable in air after calcination. In this section the structure solution of the first high silica zeolite with 11-ring channels, EMM-25, will be described, for more details see Paper IV. EMM-25 is a new borosilicate synthesized using the C4 diquat of N-methyldihexylamine as the structure directing agent. The structure was solved from sub-micrometer-sized single crystals using the rotation electron diffraction (RED) method. 1242 ED frames were collected within a tilt range of 108.3° with a tilt step of 0.10°.

3D reciprocal space was reconstructed from the RED data, as shown in Figure 5.1. The 3D reciprocal lattice of EMM-25 was determined to be orthorhombic, unit cell parameters $a = 11.055$ Å, $b = 22.912$ Å and $c = 24.914$ Å, as refined against PXRD. The possible space groups are $Cmc2_1$ (No. 36), $C2cm$ (No. 40) and $Cmcm$ (No. 63), as deduced from the systematic absences. An HRTEM image of the material along the [100] direction shows 10-ring channels running along the $a$-axis which are surrounded by 4-, 5- and 6-rings, see Figure 5.2. The plane group symmetry in the HRTEM image is $pmg$ which is consistent only with the space groups $C2cm$ (No. 40) and $Cmcm$ (No. 63). A reasonable structure model of EMM-25 was obtained from the RED dataset by direct methods using $Cmcm$ symmetry. All ten symmetry-independent T-atoms (Si/B) and 16 out of 20 symmetry-independent oxygen atoms were directly located. Three of the remaining oxygen atoms were located in the refinement.
against the RED data and the last oxygen atom could be identified and added manually. The structure model obtained from the RED data was further refined by Rietveld refinement against synchrotron powder X-ray diffraction, with \( R_F = 6.4\% \) and \( R_{wp} = 10.4\% \).

Figure 5.1: (a) 3D reciprocal lattice of EMM-25 reconstructed from the RED dataset. Inset is the crystal from which the RED data was collected. (b-d) 2D cuts of the (b) \( h0l \) slice, (c) \( h0l \) slice and (d) \( 0kl \) slice from the 3D reciprocal lattice in (a). The reflection conditions can be deduced from the 3D reciprocal lattice as \( hkl: h+k = 2n \), \( hk0: h+k = 2n \), \( h0l: h = 2n \) and \( l = 2n \), \( 0kl: k = 2n \), \( h00: h = 2n \), and \( 00l: l = 2n \). The possible space groups deduced from the reflection conditions are \( Cmc2_1 \), \( C2cm \) and \( Cmcm \).

The 3D framework of EMM-25 contains 10 symmetry-independent T-atoms and 20 symmetry-independent oxygen atoms. All the T-atoms are tetrahedrally coordinated. As shown in Figure 5.3, the structure of EMM-25 contains straight 10-ring channels along the \( a \)-axis (Figure 5.3a) and zig-zag 11-ring channels along the \( c \)-axis (Figure 5.3b). The structure is in good agreement with the HRTEM image along the \( a \)-axis, see Figure 5.2. The 10-ring and 11-rings intersect with each other.
**Figure 5.2:** HRTEM image of EMM-25 along the $a$-axis showing the 10-ring channels. The inset is the symmetry averaged projected potential map after imposing $pmg$ symmetry.

**Figure 5.3:** (a) The structure model of EMM-25 viewed along the $a$-axis showing the straight 10-ring channels. (b) A 2D slice cut perpendicular to the $c$-axis showing the 11-ring windows in EMM-25.
During the recent years, great interest has been in synthesizing zeolites with extra-large channels, i.e. channels limited by rings containing more than 12 TO$_4$ tetrahedra. Zeolites with extra-large channels have been made by introducing elements other than Al and Si, such as Ge, B, P, Ga, Be etc. However, pure and high silica zeolites with extra-large channels are rare. For practical applications of a zeolite such as catalysis, the material has to be stable not only after removal of the guest molecules in the pores but also under harsh conditions, e.g. high temperatures. The introduction of heteroatoms, for example Ge, to the frameworks can create extra-large channels, for example ITQ-33[101], ITQ-37[42], ITQ-40[92], ITQ-43[92], ITQ-44[89] and IM-12[102]. Unfortunately the incorporation of Ge in the framework often causes a decrease in stability of the framework. Over the years, zeolite frameworks with extra-large pores have been discovered in a number of phosphates, e.g. VPI-5[40], AlPO-8[103] and cloverite[104].

In some cases, not all the TO$_4$ tetrahedra in a zeolite framework are four-connected. This leads to an interrupted framework. There is only one example of a high silica zeolite material with an interrupted structure, SSZ-74[99]. In the structure of SSZ-74, one T-site is left unoccupied in order to create an energetically favorable framework. There are a few examples of extra-large pore zeolites with terminals pointing towards the extra-large channels, for example the silicogermanates ITQ-37[42] and ITQ-43[92] and the gallophosphate cloverite[104]. These terminals give a geometrical freedom to the framework to create the large channels. All reported zeolites with pores larger than 18-rings have interrupted structures; cloverite, ITQ-37 and ITQ-43.

EMM-23 can be synthesized in a range of silicon to aluminium ratios including a pure silica form. The structure has an interrupted framework and contains a three dimensional 24 x 10 x 10 channel system. EMM-23 is the first stable high silica zeolite with extra-large 3D channel system. In this section, the structure solution of a new extra-large pore zeolite, EMM-23 is described, more details can be found in Paper V.

The synthesis of EMM-23 is described in a patent[105]. The crystals of EMM-23 have a hexagonal prismatic morphology, see Figure 5.4. The PXRD pattern of EMM-23 shows sharp peaks, which can be indexed by a hexagonal unit cell with $a = 19.95$ Å and $c = 13.94$ Å (Figure 5.5). Upon calcination at $540^\circ$C, some intensity decrease and significant peak shifts are observed, see Figure 5.5. However, the PXRD pattern could still be successfully indexed by a hexagonal cell, although with shortened unit cell parameters ($a = 19.64$ Å, $c = 13.22$ Å). The PXRD pattern of the calcined sample can also be indexed in a hexagonal cell. Compared to the PXRD pattern of the as-made EMM-23, the
Figure 5.4: SEM images showing the hexagonal prismatic morphology of the EMM-23 crystals.

Figure 5.5: PXRD patterns of as-made (bottom), calcined (middle) and ozone treated (top) EMM-23.
PXRD pattern of the calcined sample shows only minor shifts for the (100) and (110) peak positions, but a substantial shift to higher angle for the (101) peak. The shifts in peak positions corresponds to a contraction of the \( c \)-parameter of 5.2% and smaller change in the \( a \) and \( b \) parameters of 1.6%. Minor changes in unit cell dimensions of zeolites upon calcination are often observed with the removal of occluded organic or water molecules. However the changes rarely exceed 3% for high-silica zeolites. The large decrease of the \( c \)-parameter in EMM-23 might be due to condensation of possible silanol groups in the structure.

In order to remove the OSDAs while still preserving the original framework, a different approach with ozone treatment was used. This will remove the OSDAs without introducing silanol condensation. All the OSDAs could be removed after this treatment, as confirmed by TGA of the ozone treated material. The changes in the PXRD pattern of the ozone-treated sample, particularly the increases of the relative intensities for the low angle reflections, are consistent with removal of extra-framework material. However the shifts in the peak positions are minor when compared to those of the as-made material. The refined unit cell dimensions for the ozone-treated sample are \( a = 19.68 \text{ Å} \) and \( c =13.73 \text{ Å} \). There is only a minor contraction of the unit cell dimensions when compared to those of EMM-23 calcined at 540°C.

From TGA/MS measurements of the as-made material the OSDA comprise about 24% of the as-made product. This is an unusually large OSDA content for zeolites prepared in hydroxide media. \(^{29}\text{Si}\) NMR spectrum of an aluminosilicate EMM-23 prepared from a gel with Si/Al ratio of 75 shows that there are at least five different components that can be resolved. The \(^{29}\text{Si}\) NMR spectrum contains peaks that may be assigned to Q2 and Q3 Si species, the Q2 and Q3 peaks account for 6.5% and 24.2% of the total \(^{29}\text{Si}\) signal intensity respectively.

Ab-initio structure solution of EMM-23 from the PXRD data was not successful. In order to solve the structure of EMM-23 both RED and structure projection reconstruction from through-focus HRTEM image series were applied. From the RED data, the unit cell determined from PXRD data could be confirmed. From the 2D slices cut from the 3D reciprocal lattice reconstructed from the RED data (Figure 5.6), the following systematic reflection conditions were obtained: \( 00l : l = 2n \) and \( hhl : l = 2n \). Five possible space groups could then be identified: \( P6_3mc \) (No. 186), \( P-6_2c \) (No. 190), \( P6_3/mmc \) (No. 194), \( P31c \) (No. 159) and \( P-31c \) (No. 163).

At this stage, the structure could not be solved ab-initio from the RED data. A through-focus series of 20 HRTEM images was acquired along the \( c \)-axis with a constant focus step of 103 Å. In the structure projection image reconstructed from the through-focus series, an extra-large triangular shaped
Figure 5.6: 2D slices cut from the reconstructed 3D reciprocal lattices obtained from the RED data of EMM-23 showing (a) $hk0$ plane, (b) $h0l$ plane and (c) $hhl$ plane. The reflection conditions can be deduced as $hhl: l = 2n$ and $00l: l = 2n$. A few reflections in (c) violate the reflection conditions, due to double diffraction, which are obvious by examining the individual ED frames with those reflections.

channel can be seen, see Figure [5.7]a. The extra-large channel is surrounded by small rings. The structure factor phases and amplitudes were extracted from the reconstructed images. By examining the phase and amplitude relationships, the plane group symmetry was determined to be $p31m$. In the structure projection image along the $a$-axis, a smaller channel can be observed, see Figure [5.7]b. The plane group symmetry along the $a$-axis was determined to be either $pmg$ or $pg$. This confirms that the reflection conditions determined from the RED data were correct. By combining the symmetry information from the HRTEM images with the aforementioned possible plane groups, only two candidates remain, $P-62c$ and $P31c$. The structure factor amplitudes and phases

Figure 5.7: HRTEM images along the (a) $c$-axis and (b) $a$-axis of the as-made EMM-23. The symmetry averaged potential maps with (a) $p31m$ and (b) $pmg$ symmetry are inserted with the structure model overlayed. The extra-large channels can be seen in (a) and the 10-ring channels can be recognized in (b).
extracted from the reconstructed structure projection images along the c- and α-axes were merged into a 3D data set. The scale factor was determined by using the common reflections from the two projections. From this data set, a 3D potential map was constructed, see Figure 5.8. From the 3D potential map and the individual structure projection images, a structure model was built, assuming the higher symmetry space group P-62c. The model contains seven symmetry-independent T-sites; three of them are four-connected, three are three-connected and one is two-connected.

Figure 5.8: 3D electrostatic potential map of EMM-23 (in blue) generated from the structure factors extracted from the two HRTEM images, with the corresponding structure model (in yellow) overlaid.

In order to further confirm the structure model, RED data with higher resolution and less beam damage was collected using a lower electron dose than the previous RED data. A structure model of EMM-23 was obtained using direct methods using the space group P-62c. The model was in good agreement with that built from the HRTEM images, except that one additional T-site was found. By examining the structure model, one possible T-atom site was added to complete the framework. The final model after the structure solution contains 8 four connected and one three connected T-site.

The structure model obtained from HRTEM and RED was refined against the synchrotron PXRD data. The PXRD data from the ozone treated sample was used to refine the framework. During the refinement, it was clear that in order to obtain a proper geometry of the framework, a lower symmetry space group P31c had to be chosen. The refinement converged with good agreement factors, \( R_{wp} = 11.55\% \), \( R_p = 8.84\% \) and \( R_{exp} = 8.14\% \). The refined model contains two partially occupied T-sites. The ratios between four- (Q4), three- (Q3)
and two connected (Q2) T-sites, in the structure will be dependent on the occupancy of these two atoms. The total ratios can be calculated statistically from the four different models produced by altering the presence of the two atoms and weighted by the occupancies achieved from the Rietveld refinement. The ratio calculated from the refined model is 71 : 23 : 6 for Q4 : Q3 : Q2 which is in good agreement with the results from $^{29}$Si NMR; 67 : 26 : 7.

The refined structure of EMM-23 in $P\overline{3}1c$ contains 13 symmetry independent Si atoms, out of which two are partially occupied. The framework formed by the fully-occupied T-atoms, contains 24-rings along the c-axis, which intersect with zig-zag 10-ring channels perpendicular to the c-axis to form a 3D channels system. The presence of partially occupied terminal tetrahedra, however, reduces the size of the 24-ring channels. With full occupation of the terminal tetrahedra, the 24-ring channel is reduced to 21-ring channel. In practice, the extra-large channel will be limited by a ring between 21- and 24-ring. The 10-ring channels are not affected by the partially occupied terminal tetrahedra. The framework density is 11.27 T/1000Å$^3$, the model with all sites fully occupied would have a framework density of 15.17 T/1000Å$^3$. The framework density of the final structure is inbetween the two. Further details about the EMM-23 structure can be found in Paper V.

5.2 Disordered materials

5.2.1 ITQ-39 (Papers VI & VII)

Introduction
The new zeolite material ITQ-39 was synthesized using 1,1-dipropyl-4-(1-propylpirroldine-1-yl)piperidinium as the OSDA. ITQ-39 can be synthesized in a high silica form as well as aluminosilicates and titanosilicates[106]. It shows promising catalytic properties, see Paper VII. The crystals of the high silica materials are needle-like with a diameter of only $\sim$30 nm. The needles grows together in bundles, see the inset in Figure 5.9. The PXRD pattern of ITQ-39 shows severe peak broadening with some peaks broader than others, see Figure 5.9. This is characteristic for a disordered structure. For details about ITQ-39 see Papers VI and VII.

There exists no standard ab-initio structure determination method for heavily disordered materials. Structure determination of disordered structures has been a great challenge, involving combining information obtained from several techniques such as powder diffraction, HRTEM imaging, electron diffraction, NMR, adsorption etc. In addition, successful structure solutions often require model building and extensive knowledge about the type of zeolite structures. In this section a new method that makes structure determination of materials
with disordered structures much more straight forward will be presented. The two new electron crystallographic methods, RED and structure projection reconstruction from a through-focus series are combined.

An initial study of ITQ-39, see Paper VI, showed that the material might have a structure related to zeolite beta. SAED diffraction patterns show diffuse streaks along one direction, only every third line exhibits sharp spots. The ratio between the two lattice vectors are however slightly different from those in zeolite beta.

Since there are no existing ab-initio structure solution methods for these kind of structures, the following route was used to obtain a structure model of ITQ-39:

1. Collect RED data in order to reconstruct the 3D reciprocal lattice, from which to determine possible unit cells and get information about the disorder.

2. Acquire a series of through-focus HRTEM images from selected projections and reconstruct the structure projections from the through-focus series.

3. Perform a 3D reconstruction of the structure factors extracted from ordered regions of the HRTEM images, in order to determine the 3D atomic structure.

**Figure 5.9:** PXRD pattern of ITQ-39 ($\lambda=1.54\text{Å}$). Inset is an SEM image showing the needle like morphology of the crystals.
4. Refine the geometry of the structure model using distance least squares refinement.

5. Verify the structure model using different methods to confirm that the structure is correct.

**Rotation electron diffraction**

A RED data set of 880 single ED frames was collected with a step of 0.15°. The scan covered 116° (~63% of the complete reciprocal lattice). From the RED data, the three dimensional reciprocal lattice was reconstructed. Both sharp spots and diffuse streaks could be seen. The diffuse streaks indicate a layered building unit with stacking disorders. The building layers are oriented perpendicular to the diffuse streaks. When viewing along the diffuse streaks, the 3D reciprocal lattice shows only discrete diffraction spots. Two perpendicular 2D slices were cut out from the 3D reciprocal lattice, see Figures 5.10b and c. These two slices show the two dimensional reciprocal lattice along two of the main zone axes. Figure 5.10b shows only sharp spots. It is perpendicular to the \( b \)-axis, i.e. corresponding to the \( h0l \) plane. Twinning is observed in 5.10b, which can be indexed with two oblique lattices related by a mirror perpendicular to the \( c^* \)-axis. Figure 5.10c is perpendicular to the \( a \)-axis, i.e. corresponding to the \( 0kl \) plane. It shows diffuse streaks running along the \( c^* \)-axis. All reflections with index \( k=3n \) appear as sharp spots, while other reflections form only diffuse streaks. This indicates that the stacking of the layers perpendicular to the \( c^* \)-axis has a defined shift of 1/3 of the repeat distance along the \( b \)-axis.

![Figure 5.10](image)

**Figure 5.10**: (a) 3D reciprocal lattice reconstructed from the RED data acquired from a sub micrometer sized ITQ-39 crystal. Two perpendicular slices cut from the reconstructed 3D reciprocal lattice show (b) the \( h0l \) plane and (c) the \( 0kl \) plane.

The behavior of diffuse streaks in disordered zeolite structures were extensively studied in zeolite Beta, see Chapter 4.2. The \( 0kl \) plane of ITQ-39 shows some similarity with that of Beta. In both cases, every third line contains sharp
spots whereas the others contain diffuse streaks. Because of this similarity the 0kl plane was indexed by two different lattices from two different structures. In analogy with the notation for different polytypes in zeolite Beta, they are named polymorph A and polymorph B, see Figure 5.10c. The lattice for polymorph A is rectangular with the $b^*$-axis perpendicular to the $c^*$-axis and the length of the $c^*$-axis half of the distance between the discrete spots along the $c^*$-axis. The lattice of polymorph B is oblique with the common $c^*$-axis as that of polymorph A but the length of the $c^*$-axis equal to the distance between the sharp spots. The $b^*$-axis is 70° from the $c^*$-axis. These result in a monoclinic unit cell for polymorph A and a triclinic unit cell for polymorph B.

HRTEM imaging

Once the unit cells and the possible disorders have been identified, the next step is to acquire HRTEM images along different directions and reconstruct the projected potential of the ITQ-39 material. From the projected potential, more details about the disorder can be revealed and the crystallographic structure factor amplitudes and phases can be extracted. Because of the disorder in the crystal, most of the projections are not easily interpretable. They will show averaged projections. Only when the structure is viewed along the [100] or [010] the projection is more easily interpretable. Thus through-focus series of HRTEM images were acquired along the [010] and [100] directions, with the characteristic SAED patterns identified from Figure 5.10b and c, respectively. Each through-focus series contained 20 HRTEM images acquired with a constant focus step. The series passed through the Scherzer focus and hence contained at least one image close to the Scherzer focus. The focus step was 53.3 Å for the series along [010] and 106.6 Å for the series along [100]. The effect of the CTF was compensated for in each of the images and then the 20 images were summed together. The resolution of the HRTEM images is ∼2.2 Å. Since the ideal neighboring Si-Si distance in zeolites is ∼3.16 Å, this resolution is enough to resolve most of the Si atoms, see Figure 5.11.

Both large channels and smaller rings can be seen in the two reconstructed structure projection images in Figure 5.11. In the [100] projection, both 10-ring channels and rings containing 5 and 6 T-atoms are identified. The 5- and 6-rings for a layer perpendicular to the $c^*$-axis, with the repeating sequence 5, 5, 6... In between these layers, large 10-ring channels can be seen running along the [100] direction. Some overlapping atoms can be found between the channels, but the channels are most likely limited by 10 T-atoms. The [100] image further confirms the stacking disorder predicted from the 0kl electron diffraction pattern. The structure of ITQ-39 is built up by layers perpendicular to the $c^*$-axis. These layers can be connected with a translation of either $+1/3 b$ or $-1/3 b$ between them. Alternating positive and negative translations results
in polymorph A. Continuous positive or negative translations results in polymorph B. In addition a third polymorph was found, with no translation between two connecting layers, Figure 5.11b. This polymorph is named polymorph C in agreement with the notation from zeolite Beta.

In the HRTEM image along the [010] direction, large channels as well as small rings containing 4, 5 and 6 T-atoms can be seen. The large channels contain 12 T-atoms, which appear in pairs separated only by one bridging T-atom, in projection. Twin domains can be identified, related by a mirror perpendicular to the a-axis. This is in agreement with the results from the analysis of the RED data.

**Structure determination of ITQ-39**

In order to obtain a structure model for ITQ-39, structure factor phases and amplitudes were extracted from the reconstructed structure projection images. For this purpose, ordered areas in the thin part of the crystal were selected. In the image along the [010] projection, a domain close to the edge (∼3 × 10 nm) was used. In the projection along the [100] projection a region of pure polymorph B type stacking (∼5 × 10 nm) was used. Crystallographic image processing was made using the software CRISP. Since the chosen regions are ordered, the Fourier transforms (FTs) of those ordered regions exhibits only sharp spots and no diffuse streaks. The phase residuals for the symmetry related reflections in each of the structure projection images were examined in order to identify the correct plane group symmetry. For both images the plane group $p2$ was found to be the best one with phase residuals of 14.2 %
and 20.0 % for the [100] and [010] projections respectively. Since the unit cell is triclinic for polymorph B the plane group symmetry is consistent with the space group $P\bar{1}$. A common origin was chosen for the two projections in order to ensure that the phases of the common 00$l$ reflections agree to each other. The structure factors from the two projections were merged into one three-dimensional data set using the amplitudes of the common reflections for scaling. From the list of the 53 strongest structure factors, the three dimensional electrostatic potential map was constructed by an inverse Fourier transformation. The potential map revealed the positions of 28 unique T-atoms in the space group $P\bar{1}$, see Figure 5.12. The oxygen atoms of the framework could not be located from the potential map due to low resolution. They were added manually half way in between the nearest neighboring T-atoms of the framework.

**Figure 5.12:** The three dimensional electrostatic potential map of ITQ-39 (blue) reconstructed from the structure factors extracted from the two structure projection images. The framework structure of polymorph B of ITQ-39 determined from the potential map is superimposed (yellow). Below, the structure of ITQ-39 seen along the $a$-axis (left) and $b$-axis (right). The building layer is marked in grey.
The structure model obtained from the three dimensional reconstruction based on the structure projection images was refined geometrically in order to get a more accurate model. For this purpose, a geometrical distance least squares (DLS) refinement in the program DLS76 was used. All Si-O distances, the Si-Si between neighboring Si atoms, as well as the distances between the O atoms within the same tetrahedron were refined towards their optimal lengths, 1.610 Å, 3.052 Å and 2.613 Å respectively. In total the refinement used 334 distances to optimize the 252 xyz-coordinates of the 84 atoms in the asymmetric unit. In the first step, only the atomic coordinates were refined. In the next step also the six unit cell parameters were refined together with the new atomic coordinates. After refinement the tetrahedrally coordinated Si atoms moved by less than 0.35 Å and the oxygen atoms by less than 0.71 Å compared to the positions in the initial structure model. The refined unit cell parameters deviated by less than 3.6% from the unit cell determined from the RED data. The O-T-O angles range from 108.4° to 110.7° and the T-O-T angles range from 136.3° to 169.3°.

The obtained structure model is polymorph B of ITQ-39. In the images along [100] two other types of stackings could be found. With the structure model of polymorph B as a base, structure models of polymorph A, with alternating stacking of +1/3 b and -1/3 b, and polymorph C, with zero shift between the layers, were built in the space groups \( P2_1/c \) and \( P2_1/m \) respectively, see Figure 5.12. The models were geometrically refined in the same way as the model of polymorph B, see Table 5.1 for the refined unit cells, space groups and number of unique T-atoms. All three structure models can be used to explain the twinning behavior without any additional strain to the framework or creation of additional terminals, see Figure A1 in Appendix. The structure models of polymorph A and B have 28 unique T-atoms each. This make these structures two of the most complex zeolite structures solved.

**Table 5.1:** Geometrically refined unit cells, space groups and number of unique T-atoms for the three polytypes of ITQ-39.

<table>
<thead>
<tr>
<th>Space group</th>
<th>( a (\text{Å}) )</th>
<th>( b (\text{Å}) )</th>
<th>( c (\text{Å}) )</th>
<th>( \alpha (\degree) )</th>
<th>( \beta (\degree) )</th>
<th>( \gamma (\degree) )</th>
<th>( N_T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A ( P2_1/c )</td>
<td>24.15</td>
<td>12.48</td>
<td>26.98</td>
<td>90</td>
<td>125.14</td>
<td>90</td>
<td>28</td>
</tr>
<tr>
<td>B ( P-1 )</td>
<td>24.09</td>
<td>12.46</td>
<td>14.18</td>
<td>72.60</td>
<td>123.21</td>
<td>90.10</td>
<td>28</td>
</tr>
<tr>
<td>C ( P2_1/m )</td>
<td>23.97</td>
<td>12.55</td>
<td>13.63</td>
<td>90</td>
<td>124.91</td>
<td>90</td>
<td>16</td>
</tr>
</tbody>
</table>

**Structure verification**

Verifying the structure model is an important step in all structure determinations. The most common way to confirm a structure model is to minimize the
difference between experimental and calculated PXRD patterns using a least squares approach, Rietveld refinement. Since the structure of ITQ-39 contains severe stacking disorder it is not possible to perform Rietveld refinement. Instead, the structure was verified by comparing simulated diffraction from the disordered model with experimental PXRD data.

The simulations were carried out using the software DIFFaX.[108] This is designed for simulating diffraction patterns from structures that can be described as layers stacked on top of each other and related by a translation vector. For the simulations of ITQ-39, the disorder of the model was divided into two parts. One describing the stacking disorder as can be seen along the [100] direction and one describing the twinning seen along the [010] direction.

The program DIFFaX has two major parts. In the first part one or more type of layers are defined by defining the content of the layers. In the second part details are specified for how the layers are combined and by which probability. Here I will describe how to construct a sequence for the intergrowth of polymorphs A and B. First we need to think about the characteristics of the two structures. In polymorph A the stacking sequence is alternating, $+1/3b$, $-1/3b$, $+1/3b$, while polymorph B the sequence is either $+1/3b$, $+1/3b$ or $-1/3b$, $-1/3b$. The only allowed translations in polymorphs A and B are $\pm 1/3b$. The important parameter to define is whether the next translation vector is identical or opposite to the previous one. If we define the probability of one shift to be the same as the previous one as $\alpha_{\text{same}}$, the probability for the different shift will be $\alpha_{\text{different}}=1-\alpha_{\text{same}}$. This sequence can be achieved by creating four identical layers, see Figure 5.13. The incoming translation vectors to each of

![Figure 5.13](image_url)

*Figure 5.13:* An example of a scheme creating an intergrowth between two polytypes A and B in DIFFaX. In this case all 4 layers are identical, the shift associated with each transition is specified by the arrow. The blue arrows creates a polytype A stacking, $\alpha_{\text{same}}$, and the red arrows polytype B, $\alpha_{\text{different}}$.
the layers are always the same. To Layer 1 two transitions comes in, both with a shift of \(-1/3b\) etc. From each layer, two transitions are possible; one with each of the possible translations. If the translation vector is the same for the outgoing vector as the incoming vector, it gives the probability \(\alpha_{\text{same}}\). If it is different, it will be assigned as \(\alpha_{\text{different}}\). The sequence created by \(\alpha_{\text{same}}\) will correspond to polymorph B type stacking and \(\alpha_{\text{different}}\) to Polymorph A. They are marked in red and blue respectively, in Figure 5.13. The complete stacking schedule used for the simulation of ITQ-39 including all three polytypes A, B and C as well as the twinning is given in Table A1 in Appendix. A rough content of the three polytypes could be quantified from images obtained along the [100] projection. The ratio was estimated to 45:45:10 for polymorphs A, B and C respectively. In the images along the [010] projection, the sizes of the twin domains differ greatly. On average the domains are \(\sim 4\) layers thick. These quantitative measures were included as probabilities in the simulation. The simulated PXRD pattern shows great similarity to the experimental PXRD pattern in terms of peak positions as well as intensities, see Figure 5.14. The structure model is also in good agreement with the NMR data. Adsorption and catalytic test further confirmed the structure model.

**Figure 5.14:** Experimental PXRD pattern of ITQ-39 (top) and a PXRD pattern simulated with a model including stacking disorders and twinning using DIFFaX (bottom).
All three polytypes of ITQ-39 have 3 dimensional channel systems, with intersecting channels limited by 12 T-atoms running along the $b$-direction and 10 T-atoms in the perpendicular directions. The intergrowth between the three polytypes and the twinning do not interrupt the channels.

**Details about the disorder**
The needle like crystals of ITQ-39 grow together in bundles, see Figure 5.9. Figure 5.15 shows the magnified cross section of one such bundle of needles. All crystallites are aligned along the [010] direction. Some domains are large and well ordered, whereas other regions are severely disordered. Larger cavities are formed inbetween the different domains. These might introduce a mesoporosity to the material.

![HRTEM image of ITQ-39 along the [010] direction of a sample cut by ultramicrotome. Inbetween the different domains, empty space in the mesoporous range is created.](image)

**Figure 5.15:** HRTEM image of ITQ-39 along the [010] direction of a sample cut by ultramicrotome. Inbetween the different domains, empty space in the mesoporous range is created.
In addition to the disorder described above, some other kinds of disorder and defects can be observed. A second version of the stacking disorder can be seen in Figure 5.16b, where the channels are no longer straight along the \(a\)-axis and the projected potential looks like a grid instead of channels. This can be thought of as a stacking disorder within the layer, see Figure A2 in Appendix. This kind of disorder can be created by deleting the terminal T-atom inbetween the two 12-ring channels and shift only a part of the layer by \(\pm 1/3\) of \(b\). This kind of disorder will not create any additional geometrical strain to the framework but instead increase the number of terminals from 2 to 4 per unit cell in polymorph B. In Figure 5.16b taken along the [100] direction, a transition within the same layer from straight channels to overlapping channels can be seen. This kind of disorder can not be created without generating a large number of terminals or large geometrical strain. In the image along the [010] direction, see Figure 5.16a some point defects can be seen. These defects create single 12-ring channels instead of pairwise 12-rings. These single 12-ring channels arise from the fact that the same building layer contains different twin components. These point defects cannot be created with an intact geometry and connectivity. Thus they may inhibit further crystal growth. This kind of defect often occur close to the edge of the crystals. The possibility for this type of defects is one plausible reason to why the crystals do not extend in the \(ac\)-plane but form only very thin needles along the \(b\)-axis. A collection of the different types of disorders found in ITQ-39 can be seen in Table 5.2.

**Figure 5.16:** (a) HRTEM images of ITQ-39 along the [010] direction showing single 12-ring channels as marked by red arrows. The defects are created when two different twins (green) meet in one layer (horizontal). (b) In the structure projection image along [100] the contrast within one layer (marked in red) can change from straight channels to non-straight.
Table 5.2: Five different types of disorder have been found in ITQ-39. The first three are geometrically reasonable and are described by structure model.

<table>
<thead>
<tr>
<th>Description</th>
<th>Geometrically reasonable</th>
<th>Additional terminals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stacking disorder between layers along $c^*$</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Twinning</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Stacking disorder within layers</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Transition from perfect layer to disordered</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Single 12 ring channels</td>
<td>No</td>
<td>-</td>
</tr>
</tbody>
</table>

This shows that the material is severely disordered. ITQ-39 has a rather large degree of freedom, allowing twinning and stacking disorder between and within the building layer. However, the presence of other defects including point defects, together with the very small crystal sizes indicate that the conditions to form this material might not be ideal. Hopefully more perfect crystals of ITQ-39 can be synthesized if more efforts are spent on optimizing the synthesis conditions. This would be very important both for the more detailed characterization of the material as well as from the applications point of view. If the unique channel system of ITQ-39 is to be utilized for applications, a material with fewer defects is beneficial.

5.2.2 ITQ-38 (Paper VIII)

The new zeolite material ITQ-38 was synthesized as a silicogermanate using 1,1-dimethyl-4-(1-methylpyrrolidine-1-yl)piperidinium as OSDA, a similar template as that used for ITQ-39. The result is a more ordered material than ITQ-39. The introduction of germanium to the framework is known to promote the formation of double 4-rings. It was attempted to direct the synthesis towards a material with the structure of pure polymorph C of ITQ-39. In this section the structure determination of ITQ-38 will be described. The structure of ITQ-38 is related to that of ITQ-39 polymorph C, but it is not the same. For details please see Paper VIII.

SAED patterns were used to confirm the monoclinic unit cell of ITQ-38, with $a = 13.02 \, \text{Å}$, $b = 12.70 \, \text{Å}$, $c = 21.25 \, \text{Å}$, $\beta = 96.87^\circ$. In order to determine the structure, a through-focus series of HRTEM images was collected along the [010] direction, see Figure 5.17a. In the reconstructed projected potential, large channels of 12 and 10 rings as well as smaller rings of 4, 5 and 6 T-atoms can be seen. The unit cell of ITQ-38 was found to have major similarities with the unit cell of the known zeolite ITQ-22. The unit cells of the two structures share one common plane, see Table 5.3. However, the unit cell of ITQ-22 is
doubled perpendicular to the plane compared to that of ITQ-38. The structure of ITQ-22 is built from a layer, which is identical to the projected potential of the images of ITQ-38. By rotating every second layer of the structure of ITQ-22 by $180^\circ$ around the normal to the layer, a new structure model can be created, see Figure 5.18.

Table 5.3: Comparison of the unit cells of ITQ-22 and ITQ-38. The common unit cell parameters are marked in bold.

<table>
<thead>
<tr>
<th></th>
<th>ITQ-22</th>
<th>ITQ-38</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>41.71</td>
<td>13.02</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>12.71</td>
<td>12.70</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>12.71</td>
<td>21.25</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>90</td>
<td>96.87</td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
<td>90</td>
<td>90</td>
</tr>
</tbody>
</table>

The framework of ITQ-38 contains straight 10- and 12-ring channels along [010]. These intersect with zigzag 10-ring channels along [100] and [101]. The structure was refined geometrically with a distance least-squares refinement, obtaining a $R_{DLS}$ value of 0.0027. This confirms that the structure is geometrically reasonable. The unit cell parameters of the refined structure model are $a = 12.87$ Å, $b = 12.85$ Å, $c = 21.22$ Å, $\beta = 96.23^\circ$. The structure model was further confirmed at this stage by simulations of PXRD pattern.
In some structure HRTEM images viewed along the $b$-axis the crystals are perfect, see Figure 5.17a. In other HRTEM images the crystals contain disorder, see Figure 5.17b. The disorder can be described as an intergrowth between the ITQ-22 and ITQ-38, where ITQ-38 is the dominant phase. The layer containing the 12-ring channels can connect in two ways: either by creating a series of 8-rings resulting in the ITQ-22 structure or by creating alternating 10- and 6-rings in the ITQ-38 structure.

Despite the fact that disorder is observed in ITQ-38, the peaks in the PXRD pattern are rather sharp, see Figure 5.19. The TEM study indicates that the ordered phase is dominating. A Rietveld refinement was performed in order to confirm the structure model. The as-made material was used since it has

Figure 5.19: Observed (blue), calculated (red) and difference (black) PXRD profiles for the Rietveld refinement of ITQ-38, which converged successfully. The PXRD data was collected with $\lambda=0.5198$ Å.
higher crystallinity. The refinement was performed in TOPAS. Out of the 16 unique T-sites, ten were refined with mixed occupancies of Ge and Si. The other six were occupied only by Si. The refinement converged successfully with $R_{exp} = 0.078\%$, $R_{wp} = 7.30\%$ and $R_p = 5.65\%$, see Figure 5.19. The geometry of the refined framework is reasonable, with T-O distances in the range 1.59Å - 1.68Å depending on the Si/Ge occupancy. The O-T-O angles are all in the range of 105°-115°. The Rietveld refinement further confirms that the structure of ITQ-38 is correct and that the material is mainly ordered with only minor disorder.

The structures ITQ-38 and ITQ-39C are related. Both of them have 16 unique T-atoms in the unit cell and crystallize in space group $P2_1/m$. The framework densities for the two materials are similar. ITQ-39 polymorph C contains one three coordinated T-atom to the framework. In ITQ-38, all T-atoms are four coordinated. The [101] projection of ITQ-38 (Figure 5.20a) is very

![Figure 5.20](https://example.com/figure520.png)

Figure 5.20: The structure of ITQ-38 and polymorph C of ITQ-39 are highly related. (a) The structure of ITQ-38 viewed along the [101] direction and (b) that of ITQ-39 polymorph C viewed along the [100] direction are very similar. The difference between the two structures can be seen when viewed along the [010] directions (c) ITQ-38 and (d) ITQ-39C. Both structures are built from the same building unit (in green) but with connections through different units as seen in (e).
similar to the [100] projection of ITQ-39C (Figure 5.20b). Both contain layers of 10-ring channels separated by layers of 4- and 6-rings, in the sequence 6, 6, 4 ... The differences between the two structures become evident when viewed along the [010] direction (Figures 5.20c and d). ITQ-38 contains alternating 10- and 12-ring channels (Figure 5.20c) whereas ITQ-39 has pair-wise 12-ring channels (Figure 5.20d). However, the two structures are built from a topologically identical unit, marked in green in Figure 5.20c-e. The building unit is connected along the a-direction of ITQ-39 and a+c direction of ITQ-38 via different connecting units, shown in yellow in Figure 5.20e, to form the 3D frameworks, Figure 5.20e. The connecting unit in ITQ-39 polymorph C contains two bridging three connected T-atoms whereas in ITQ-38 all atoms are fully connected. This is the only difference between the two frameworks. The initial hypothesis that ITQ-38 is identical to ITQ-39 polymorph C is not correct but indeed the two structures are closely related.
6. Characterization of Mesoporous ZSM-5 (Paper IX)

The micropores in zeolites are crucial for many applications. However, the diffusion rate for guest species in the pores can be limited because of the small pore size. A low rate of mass transfer will limit the reaction rates in catalysis. Large attention has been made in solving this problem by introducing mesoporosity into zeolite materials. This has been done in various approaches, for example by introducing mesostructured carbon into the zeolite synthesis, which resulted in mesoporosity surrounded by aggregates of small zeolite crystals.[34] Another approach has been to synthesize highly anisotropic crystals, e.g. sheets.[36; 37] A disordered assembly of the sheets will introduce mesoporosity to the material. Mesoporosity in zeolites has been studied with success using electron tomography.[109]

In this section, the characterization of single crystals of the widely used zeolite ZSM-5 with oriented mesoporosity, preferentially aligned along the straight 10-ring channels will be described. The material was characterized by combining focused ion beam (FIB) and HRTEM imaging. For more details see Paper IX.

Zeolite ZSM-5 is normally synthesized using the OSDA tetrapropyl ammonium hydroxide (TPAOH). By introducing a copolymer between polystyrene and poly (4-vinylpyridine) into the synthesis, zeolite crystals with mesoporosity are formed. The crystals have the typical shape of ZSM-5, a distorted hexagonal prism. An initial TEM study confirmed that the entire particle is a single crystal, since the SAED pattern of one particle shows only one lattice, see Figure[6.1]
Figure 6.1: TEM image (a) and the corresponding selected area electron diffraction pattern (b) from one ZSM-5 particle showing that the entire particle is one single crystal.

In order to check if the mesopores are present not only close to the surface of the crystals but also inside the crystals, an approach using focused ion beam (FIB) to prepare TEM samples was used. Slices with a thickness of \( \sim 70 \text{ nm} \) of the crystals were cut by the FIB. In order to study the size, shape and orientations of the mesopores, the slices were cut perpendicular to the three main crystallographic directions, [010], [100] and [001], see Figure 6.2.

Figure 6.2: The crystals of ZSM-5 were cut by FIB perpendicular to the three main zone axes. The blue line indicates the cut perpendicular to the \( a \)-axis, the green line perpendicular to the \( b \)-axis and the red line perpendicular to the \( c \)-axis.
In the slice perpendicular to the \( b \)-axis the micropores of the ZSM-5 framework as well as circular mesopores could be seen, Figure 6.3. The size of the mesopores are in the range of 10-50 nm and they can be observed in the center as well as closer to the edge of the crystals. The HRTEM image confirms the previous conclusion that the particles are single crystals, since the microporous structure of ZSM-5 extends throughout the entire crystal and no domains are observed. In the HRTEM images acquired along the \( a \)- and \( c \)-axes mesoporous regions can be observed. They are elongated along the \( b \)-direction. The observations of circular channels perpendicular to the \( b \)-axis together with the elongation of the mesopores along the \( b \)-axis in the HRTEM images indicates that the mesoporous channels have a preference to run along the \( b \)-direction of the crystals, which is the direction of the straight 10-ring channels in ZSM-5. However the mesoporous channels are not perfectly straight and the channel diameter them varies, see Figure 6.4.

\[ \text{Figure 6.3: (a) Low and (b) high magnification image of a ZSM-5 crystal viewed along the [010] direction. Circular mesopores with sizes in the range 10-50 nm can be seen.} \]
Figure 6.4: HRTEM images taken along (a-b) [001] and (c) [100] directions. The mesoporosity is seen extend roughly along the b-axis in all three images.

In this chapter mesoporous ZSM-5 zeolite single crystals are characterized by a combination of FIB and HRTEM imaging. The material contains mesopores which are in preferably aligned along the b-axis. The advantage of this approach over electron tomography is that larger crystals can be studied and both the micro- and mesopores can be visualized simultaneously in the same image.
HRTEM imaging has shown to be an important tool for structure determination over the past years. Structure determination by 3D reconstruction from HRTEM images has been successful both for zeolites [16; 60] [Paper VII], as well as for other materials [14; 15]. Structure factors extracted from HRTEM images have also been used as a complement to other diffraction methods such as PXRD with great success. Recent developments of electron microscopes, including aberration correctors, have pushed the resolution of Scanning Transmission Electron Microscopy (STEM) images into atomic and even sub atomic length scales. Recently STEM imaging has been used to study zeolites with success [110–113]. So far no examples of 3D reconstruction from STEM images has been reported. There are two main aims in this chapter; 1) to evaluate the feasibility of STEM images for 3D reconstruction and 2) to compare the results with those from HRTEM images. The details of the study can be found in Paper X.

STEM has some advantages over HRTEM. The contrast of STEM images are not altered by any transfer function. This means that the contrast of STEM images can be directly interpreted in terms of the projected structure. Furthermore, the contrast of STEM images is related to the atomic number of the atoms, so called Z contrast. This means that it is possible to distinguish between elements of different atomic number. A third advantage is that it is possible to combine STEM imaging with various spectroscopic methods, for example EELS and EDS, in order to perform elemental mapping. The fundamentals of the two methods were described in section 3.1.1 and 3.1.2. Here high angle annular dark field (HAADF)-STEM imaging is applied to 3D reconstruction with the aim to determine the three-dimensional structure.

For this study, the known high silica zeolite silicalite-1 is used as a test sample. The as-prepared silicalite-1 has an orthorhombic structure with the space group \( \text{Pnma} \), \( a=20.09\text{Å} \), \( b=19.738\text{Å} \), \( c=13.142\text{Å} \) [5]. Both HAADF-
STEM images and HRTEM images were acquired along the three main zone axes [010], [001] and [100], see Figure 7.1. The HAADF-STEM images were collected on a FEI Titan equipped with a CEOS CETOR C₃s-probe corrector and a monochromator, at an accelerating voltage of 300 kV. The HRTEM images were collected at 200 kV using a JEOL JEM 2100F equipped with a field emission gun and ultra resolution polepices (C₃s=0.5 mm).

Figure 7.1: Cs-corrected HAADF-STEM images, left, and HRTEM images, right from the three main zone axes of silicalite-1. The scale bars corresponds to 2 nm. Note that the contrast of the two methods are opposite. Atoms are white in HAADF-STEM but appear black in HRTEM.
The resolutions of the HAADF-STEM and HRTEM images can be determined from the Fourier transform of the images, see Figure 7.2. The resolution is similar in the HAADF-STEM and HRTEM images, in the range of 2.0-1.8 Å for the images along different zone axes. This can be explained by the fact that the image resolution of zeolites is mainly limited by the sample itself, and not by the performance of the microscope. The 2D lattice parameters of the images can be determined from the positions of the reflections in the Fourier transforms (FTs), of the images. The geometrical distortion is larger in the HAADF-STEM images compared to that in the HRTEM images. This can be attributed to sample shift during the scanning of the electron beam in the STEM mode.

Figure 7.2: Fourier transforms calculated from the HAADF-STEM (left) and HRTEM images (right) collected from the three main zone axes of silicalite-1. The unique reflections with amplitudes larger than 2% of the strongest reflection are marked by circles. Yellow circles indicate correct phase and red circles wrong phase, i.e. a phase shift of 180° of the extracted crystallographic structure factor.
A visual comparison of the FTs, in Figure 7.2, shows that the overall intensity distribution is similar for the HAADF-STEM and HRTEM images. In order to perform a 3D reconstruction the amplitudes and phases of the Fourier components at the lattice points were extracted. For HRTEM images these can be considered to be the amplitudes and phases of the structure factors. Out of

**Figure 7.3:** Projected electrostatic potential maps calculated from the inverse Fourier transforms from the HAADF-STEM (left) and HRTEM images (right) for the three main zone axes. The plane group symmetries determined from the images are applied. The symmetries are $pgg$, $pmg$ and $cmm$ for the [010], [001] and [100] respectively.
the 15 reflections with largest amplitudes, 12, 13 and 12 are common between the HAADF-STEM and HRTEM images for the projections along [010], [001] and [100] respectively. In order to compare the phases extracted from the HAADF-STEM and HRTEM images, structure factors were calculated based on the reported structure[5]. Since the structure is centrosymmetric, all structure factor phases are either 0° or 180°. This makes it easy to count the number of wrong phases.

A potential map can be constructed by an inverse FT of the extracted and symmetry averaged amplitudes and phases. Projected potential maps along each of the main zone axes can be seen in Figure 7.3. All the potential maps clearly show a contrast that resembles the projected structure.

The 3D reconstruction was performed by first merging the 2D sets of amplitudes and phases into a 3D data set. The data sets were scaled based on the calculated amplitudes. The three dimensional potential maps constructed from the HAADF-STEM and HRTEM images show good resemblance with the structure model of silicalite-1, see Figure 7.4. The framework T-atoms can be identified from the potential maps. This shows that 3D reconstruction from HAADF-STEM images is successful.

![Figure 7.4: 3D reconstructions from the HAADF-STEM (left) and HRTEM (right) images. Both methods results in potential maps showing the essential features of the structure, but the HAADF-STEM is of higher quality.](image)

Our study shows that HAADF-STEM is better than HRTEM for 3D reconstruction from several viewpoints. The phases extracted from the HAADF-STEM images are closer to the theoretical phases of the structure factors. Correct phases important for structure determination from 3D reconstruction. In the HAADF-STEM images 78 out of 87 phases are correct (90%), while in the HRTEM images 69 out of 89 are correct (78%). Accurate phases are also important in order to determine the projected symmetry. The significantly lower phase residuals between symmetry related reflection in the HAADF-STEM
Table 7.1: Comparison of the unit cell parameters determined from the HAADF-STEM and HRTEM images along the three main zone axes. Those from the zeolite database are also given for comparison. The unit cell dimensions are scaled to have one unit cell dimension (indicated by *) to be the same as the one in the zeolite database.

<table>
<thead>
<tr>
<th></th>
<th>HAADF-STEM</th>
<th>HRTEM</th>
<th>Published</th>
<th>Δ_{HAADF−STEM} (%)</th>
<th>Δ_{HRTEM} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[010]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>*a (Å)</td>
<td>20.09</td>
<td>20.09</td>
<td>20.09</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>c (Å)</td>
<td>13.85</td>
<td>13.48</td>
<td>13.14</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>β (°)</td>
<td>93.4</td>
<td>90.6</td>
<td>90.0</td>
<td>3.8</td>
</tr>
<tr>
<td>[001]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>*a (Å)</td>
<td>20.09</td>
<td>20.09</td>
<td>20.09</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>b (Å)</td>
<td>20.17</td>
<td>20.40</td>
<td>19.74</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>γ (°)</td>
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<td>90.3</td>
<td>90.0</td>
<td>2.1</td>
</tr>
<tr>
<td>[100]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>*b (Å)</td>
<td>19.74</td>
<td>19.74</td>
<td>19.74</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>c (Å)</td>
<td>12.47</td>
<td>13.36</td>
<td>13.14</td>
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</tr>
<tr>
<td></td>
<td>α (°)</td>
<td>91.1</td>
<td>90.8</td>
<td>90.0</td>
<td>1.2</td>
</tr>
</tbody>
</table>

images show that most of the phases obtained from HAADF-STEM images are the same as the structure factor phases. The contrast of the HAADF-STEM images is better defined around the atomic positions. In the 3D reconstruction from the HAADF-STEM images, 10 out of 12 unique T-sites can be clearly resolved and the two remaining T-sites can be located by specifying a larger threshold for the potential. In the 3D reconstruction from the HRTEM images, the individual T-sites are not well resolved but the 4-, 5- and 6-rings of the structure can be identified, from which the framework can be identified. The only drawback of the HAADF-STEM imaging is the large lattice distortion. This was evaluated by determining the angle and ratio between the two lattice vectors in each image, see Table 7.1. HAADF-STEM imaging has the advantage that only the studied area is illuminated at each time and may be damaged, the rest of the crystal still remains untouched. If care is taken to minimize the electron beam dose, HAADF-STEM imaging is well suited to study beam sensitive materials. Based on this study, HAADF-STEM images can be considered better suited for electron crystallographic studies then conventional HRTEM images, even though the difference is not very large.
8. Conclusions

Electron crystallography has shown to be very important for structural characterization of zeolite materials. In cases where other methods, notably SXRD and PXRD, have limitations, e.g. for materials with very complex structures or disordered structures and small crystal sizes, electron crystallography is the only possibility.

The two recently developed electron crystallographic methods, RED and structure projection reconstruction from a series of through-focus HRTEM images, have proven extremely useful for structural studies of zeolite materials. The RED method can be used to solve structures ab-initio from diffraction intensities of ordered materials and give crucial information about the unit cell and disorder in disordered materials. The structure projection reconstruction method facilitates collection and interpretation of HRTEM images. This is particularly important for beam sensitive materials, where it is more challenging to accurately adjust the conditions during data collection. Together they form a powerful toolbox for structure determination of zeolites. The methods can of course equally well be applied to other crystalline materials, but that is outside of the scope of this study.

The structure determination of four new zeolites is presented. Different methods were applied to solve each of the four structures. The approaches were designed to overcome the specific challenges of each material.

EMM-25 has an ordered structure. The diffraction intensities from the RED method were used for the structure determination, assisted by the symmetry information from HRTEM images. EMM-23 also has an ordered structure but contains a considerable amount of non-fully connected T-sites. The structure determination was made by first utilizing structure projection images to get a model and later confirming the structure by ab-initio structure solution from RED data. The obtained structure model has to match the quantitative analysis of the coordination from solid state $^{29}$Si NMR. The new material ITQ-39 suffers from severe disorder. In the structure determination process, structure projection images played a crucial role. From the structure projection images, the details about the disorders can be observed. A 3D reconstruction revealed the atomic structure of one of the polymorphs. By further analyzing the structure projection images it was found that the material is an intergrowth between three different polymorphs. The structure of ITQ-38 was solved by
model building, based on structure projection images. The structure contains disorder, but not as severe as in ITQ-39, as shown by the Rietveld refinement.

A method was developed to characterize the mesoporosity inside large single crystals of the zeolite ZSM-5. The crystals were first cut by focused ion beam (FIB) and studied by HRTEM imaging in order to reveal the micro- and mesopores in the material. It was found that the mesopores inside the crystals have a preference to align along the crystallographic \( b \)-axis.

HRTEM images have been used for a long time for crystallographic image processing and 3D reconstruction in order to determine the structure of materials. Recent developments of STEM imaging have improved the resolution significantly. Here we present for the first time that STEM images also can be used for 3D reconstruction. HAADF-STEM images are well suited for structure determination from 3D reconstruction, as demonstrated by a study of silicalite-1. The HAADF-STEM images show some advantages over conventional HRTEM images. The contrast in STEM images is easier to interpret and the phases extracted are more accurate.
The RED method and the structure projection reconstruction from a through-focus HRTEM series have great advantages for characterization of materials with ordered and disordered structures. Structure determination by 3D reconstruction from structure projection images is an extremely powerful method for studying disordered structures. It however has one drawback; we use two dimensional projections of the material and average over several unit cells. It has been shown, for some simple structures, that electron tomography using STEM images can reach atomic resolution. Atomic resolution image tomography may be the ultimate tool for studying disordered structures in three dimensions. This thesis shows that HAADF-STEM images can be used for 3D reconstruction of zeolite structures. The next step would be to see if STEM images can be used for atomic resolution image tomography of zeolites with disordered structures.

The new zeolite structures presented in this thesis are very interesting, both for their interesting structures and for their promising properties. Two of them are worth a special mention. ITQ-39, with its elaborate way of combining several different types of disorder and EMM-23, with its high content of terminals and an extra-large channel. Both of them have the potential of becoming important materials in the future, and a more thorough investigation of their structures is desired.

It would be interesting to use electron diffraction, and more specifically the RED method, to quantify the disorder in a material, for example the stacking disorder in zeolite beta. It should be much more informative to use the three dimensional diffuse scattering from a single crystal for quantification, rather than using one dimensional PXRD data, as has been the conventional method.
10. Populärvetenskaplig sammanfattning

Att förstå hur naturen är uppbygd ner till minsta beståndsdel har gåckt mänskligheten i årtusenden. Genom att ta reda på hur material, proteiner, läkemedel m.m. är uppbyggda på atomnivå kan vi förstå och skräddarsy dess egenskaper. Vi kan utveckla metoder för att, på syntetisk väg, framställa ämnen som vi sedan kan använda för olika tillämpningar.

Zeoliter är en typ av material som först upptäcktes som ett naturligt mineral av den svenska minerologen Axel Fredrik Cronstedt, år 1756. De har den mycket speciella egenheten att de innehåller små hålrum. Dessa hålrum är så små att enskilda molekyler och joner nätt och jämnt kan få plats. Man kan säga att zeoliterna kan fungera som en sil där de minsta molekylerna kan ta sig genom medan de större stängs ute. Idag kan vi syntetiskt framställa zeoliter med en rad olika egenskaper, så som varierande storlek och form på hålrummen.

Zeoliter används idag för en rad olika ändamål. De används bl.a. för att separera olika gaser från varandra, för att göra tvättmedel mer effektivt och för att rena radioaktiva utsläpp. En av de största tillämpningarna för zeoliter är för att omforma den olja som vi utvinner till de bränslen som vi i slutändan använder som drivmedel i t.ex. bilar och flyg.

Jag har studerat ett antal nya och modifierade zeoliter. Till min hjälp har jag mestadels använt ett instrument som kallas transmissions elektronmikroskop (TEM). Ett TEM fungerar i princip som ett vanligt ljusmikroskop, med den skillnaden att ljusstrålen är utbytt mot en elektronstråle. Eftersom elektronstrålen har en mycket kortare våglängd än ljus, kan vi ta bilder med mycket högre upplösning. I bilderna kan vi se enskilda atomer och hur de bygger upp materialet. Det är t.ex. möjligt att se om ett material har hålrum omgivna av 10 eller 12 kiselatomer.

Genom att ta bilder av atomstrukturen hos en zeolit från flera olika riktningar kan man konstruera en tre-dimensionell model av atomerna i materialet. Detta ger en unik bild av hur materialet är uppbyggt.

11. Acknowledgements

My first and grandest thank goes to Xiaodong Zou, my supervisor. Thanks for giving me the chance to work for five years in this very stimulating project, for sharing your knowledge and great ambition. Thank you for providing an inspiring environment and introducing me to scientific research through numerous collaborations. Without all of this, the present thesis would not be anywhere near what it is.

I also want to thank Junliang Sun, my assistant supervisor. Your knowledge in crystallography and zeolites is immense. Your guidance and advises have been crucial for me.

I am very thankful to Sven Hovmöller for tirelessly putting science into perspective through plentiful stories. I am also very grateful to Osamu Terasaki, you always gave me inspiration through your curiosity and constant desire to learn. I feel very grateful to both of you for all the work you have done over the decades, building up an accumulated knowledge base in electron crystallography/microscopy that has been of great help for me.

I am in dept to Daliang Zhang, for giving me the first guidance into studying zeolites by TEM. Thank you for all your advice during the first year of my PhD study, for setting a landmark of what is achievable and for your thoughts about the importance of never losing faith.

I am deeply grateful to Cheuk-Wai Tai and Kjell Jansson for always keeping our microscopes in the best possible condition. You make a big difference.

I would like to thank my long time roommate Wei Wan for discussions and for solving various issues, besides of course developing the methods and software I have been using.

I want to thank all of you working in the administration for taking care of all kinds of issues. Thank you: Ann-Britt, Daniel, Anna-Karin, Hanna, Karin, Ann, Anna, Eva, Anita, Tatiana, Pia and Camilla. Furthermore I would like to thank Rolf for managing various computer issues and Hans-Erik and Per for being helpful in the workshop.

Farlán Taborda is gratefully acknowledged as collaborator and friend during my early days with disorders in zeolites.

I want to thank all collaborators over the years for providing many interesting samples. Avelino Corma, Manuel Moliner and co-workers in Valencia as well as the group of Feng-Shou Xiao are thanked. I am grateful to ExxonMobil.
for our prosperous joint project. Especially I would like to thank Guang Cao, Allen Burton and Karl G. Strohmaier for interesting discussions. Furthermore I want to thank Alvaro Mayoral in Zaragoza for being a skilled microscopist and hospitable host. ESTEEM is thanked for financial support.

Gunnel Karlsson in Lund and Wilder Carrillo-Cabrera in Dresden are thanked for providing beautifully sliced samples by ultramicrotome and focused ion beam respectively.

Sven Hovmöller and Fabian Carson, your help proof reading this thesis is greatly appreciated.

I would like to thank Lars Eriksson, Ulrich Häussermann, Cheuk-Wai, Kjell and Junliang for being supportive during teaching. Fellow teaching assistant Guido Todde, Wei, Daliang, Yifeng Yun and Peter Oleynikov are also thanked.

The work in the PhD Council has been important. Thank you Amber Mace, Jon Kapla, Henrik Fahlquist, Cecilia Frostne, Henrik Carlsson, Wenming Hao and Neda Keshavarzi.

Being a part of the group interviewing new PhD candidates was stimulating. Thank you Jozef Kowalewski, Lennart Bergström, Margareta Törnqvist, James Shen, Mats Johnsson and Sven.

I would like to thank present and past director of PhD studies Mats Johnsson and Gunnar Svensson as well as director of studies Arnold Maliniak for support.

I would like to thank present and past roommates for nice company and very valuable discussions: Yifeng, Peng, Peter, Tuping, Elina, Yunchen and Devinder. Moreover I like to thank the group members over the years, including Ken, Fabian, Mikaela, Leifeng, Ana, Hong, Jie, Max, Shiliang, Louise, Haoquan, Changhong, Ilich, Alexandra, Feifei, Qingxia, Xin, Yunxiang, Hani, Liang, Mattias.

Besides that there are so many people that have made my time at MMK really enjoyable: Samrand, Daniel, Zoltan, Sumit, Verina, Yanhang, Miia, Niklas, Jekabs, German, Iwan, Henrik S, Margareta S, Dickson, Kristina. And many many more...

At last I want to give my greatest thank to my family and friends for all support and for providing necessary inspiration outside science.
12. Appendix

Table A1: The stacking sequence used for simulation of PXRD pattern for ITQ-39 by the software DIFFaX. Layers 1-6 are identical, layers 7-12 are related by a mirror plane perpendicular to the $a$-axis. In this example the probabilities for polymorphs A, B and C are 45:45:10 respectively and the average twin domain contains 4 layers.
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<td>0.0</td>
</tr>
<tr>
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<td>3 (B)</td>
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<tr>
<td>4 (C)</td>
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</tr>
<tr>
<td>5</td>
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<td>0.0</td>
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<tr>
<td>7</td>
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<tr>
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Figure A1: The structure model shows how the twin boundary can arise in ITQ-39, without any additional geometrical strain or creation of additional terminals.
Figure A2: A schematic drawing of a building layer, marked in grey, of ITQ-39 with faulting along the $a$-axis. This generates a shift of $1/3b$ of the 10-rings within the same layer. This disorder leads to zig-zag 10 ring channels along the $a$-axis.
References


