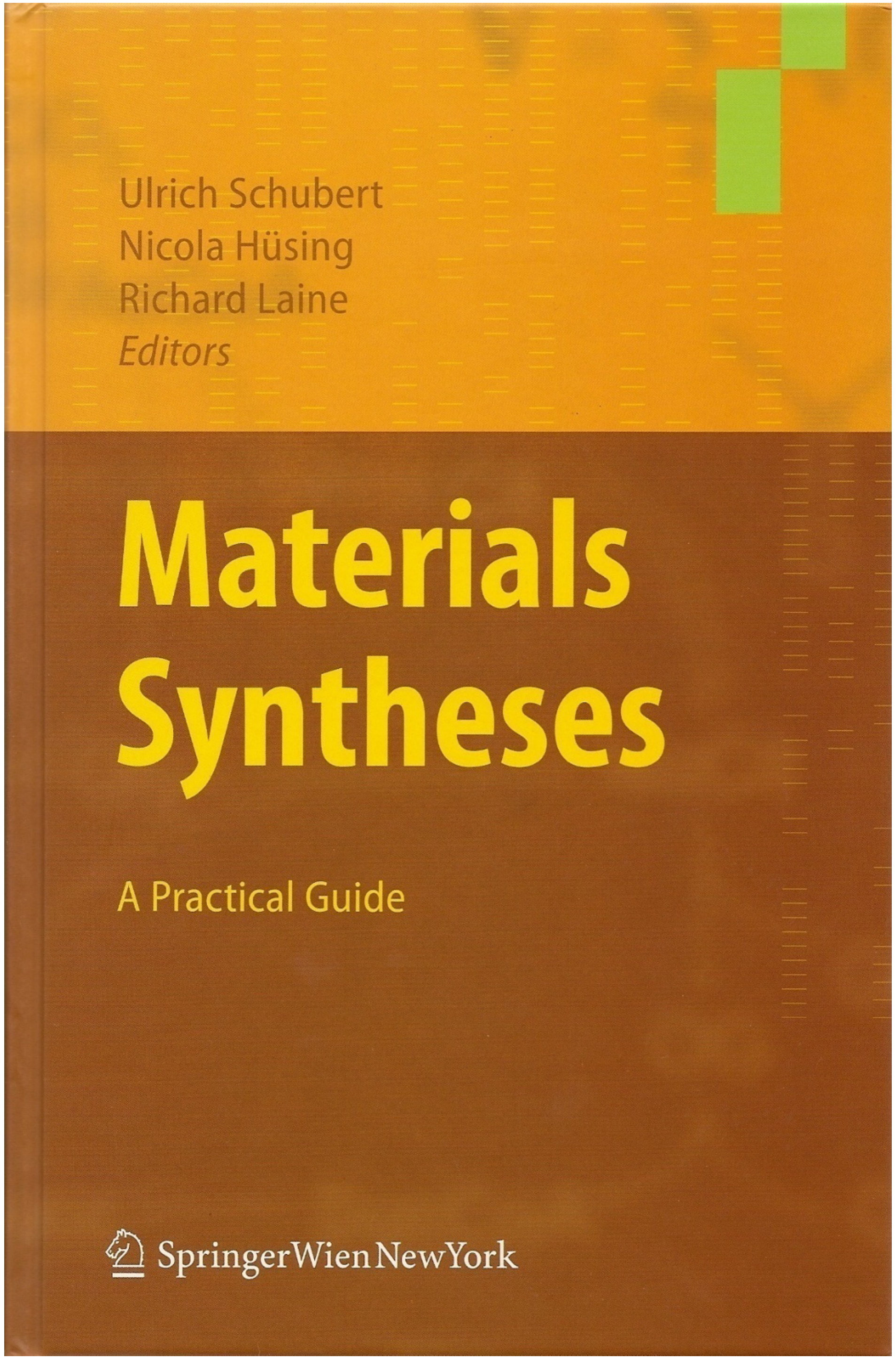

Ulrich Schubert
Nicola Hüsing
Richard Laine
Editors

Materials Syntheses

A Practical Guide

SpringerWienNewYork

Prof. Dr. Ulrich Schubert
Institute of Materials Chemistry, Vienna University of Technology,
Vienna, Austria

Prof. Dr. Nicola Hüsing
Inorganic Chemistry I, Ulm University, Ulm, Germany

Prof. Dr. Richard M. Laine
Departments of Chemistry, and Materials Science and Engineering,
University of Michigan, Ann Arbor, MI, USA

Printed in Germany

SpringerWienNewYork is part of
Springer Science+Business Media
springer.at

Typesetting: Camera ready by the editors
Printing: Strauss GmbH, 69509 Mörlenbach, Germany

Printed on acid-free and chlorine-free bleached paper
SPIN: 12123858

With numerous Figures

Library of Congress Control Number: 2008926905

ISBN 978-3-211-75124-4 SpringerWienNewYork

Zeolite A and ZK-4

C. Leiggener, A. Currao and G. Calzaferri

Abstract The synthesis of zeolite A and ZK-4 crystals of high purity and well-defined morphology is described. Three procedures are detailed, leading to cubic crystals of zeolite A with chamfered edges (average size 3–5 μm), cubic crystals of ZK-4 with sharp edges (average size 1–2 μm), and nano-sized cubic crystals of zeolite A with slightly rounded edges (size ≤ 1 μm).

Classification

form:	crystalline powder
function:	molecular sieve, host material for supramolecular organization of quantum dots
preparation:	hydrothermal synthesis
composition:	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot 27H_2O$ (zeolite A), $Na_9[(AlO_2)_9(SiO_2)_{15}]\cdot nH_2O$ (ZK-4)

Introduction

Classical zeolites are crystalline aluminosilicates, consisting of an anionic framework and charge-compensating cations.[1,2] The primary building units of the framework are SiO4 and AlO4 tetrahedra. The framework is build from corner-sharing TO4 tetrahedra (T = Si, Al) leading to microporous materials featuring defined channels and cavities. The presence of aluminum results in a negatively charged framework, which is compensated by protons or cations inside the cavities. Additional water molecules can also be present in the cavities under ambient conditions. Zeolites are used in a broad range of applications. Due to their ion exchange capability they can act as water softeners or be used for the removal of pollutants, and their well defined cavities allow size-selective reactions, for example in catalysis.[3] Being transparent in the UV/Vis/NIR makes zeolites ideal host materials for supramolecular organization of different kinds of molecules, clusters, and metal complexes.[4]

The procedures described here allow the convenient synthesis of zeolite A and ZK-4. Both zeolites have the same structure with a 3-dimensional channel system and a channel opening around 4.1 Å (Fig. 1). The main difference between zeolite A and ZK-4 is the chemical composition, i.e. a different Si/Al ratio (see below), and therefore they have a different number of charge compensating cations. As materials with the same structure but with a different chemical composition they belong to the same framework type (framework code LTA, see Ref. 1 for more details). Two kinds of structural subunits are formed.[1] The smaller consists of 24 T-atoms and is commonly denoted as β-cage, sodalite cage, or pseudo-unit cell. Eight β-cages are linked by four-membered rings giving rise to a larger cavity called α-cage with 48 T-atoms and a diameter around 11.4 Å. Consequently, the framework can also be build from face-sharing α-cages connected by eight-membered rings. The resulting 3-dimensional channel system in zeolite A and ZK-4 turned out to be convenient for hosting small ions and semiconductor clusters.[5,6]

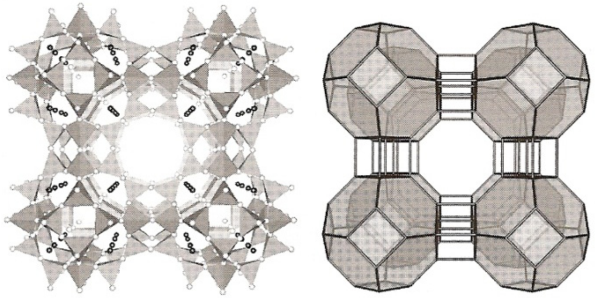

Fig. 1. Left: View of the structure of zeolite A and ZK-4. Oxygen: white spheres; T-positions (Si, Al): center of tetrahedra; cation (Na): black spheres. Right: Framework of zeolite A and ZK-4 (framework code LTA). In framework representations, the bridging oxygen atoms are usually omitted and a straight line is drawn between T-atoms. Gray polyhedra: β-cage.

Convenient synthesis procedures for pure zeolite A and ZK-4 by sol-gel methods were developed to obtain chloride-free microcrystals of high chemical quality, very good crystallinity and size homogeneity.[7] Modification of the composition of the starting gel, especially the Si/Al ratio and the Na^+ content, results in different morphologies of the crystals or alteration in the size distribution (Fig. 2). A lower Na^+ content in the gel generally leads to smaller crystals, while an excess of Si leads to ZK-4. The synthesis procedures presented here typically yield crystals with the chemical composition $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot 27H_2O$ for zeolite A and $Na_9[(AlO_2)_9(SiO_2)_{15}]\cdot nH_2O$ for ZK-4, respectively. The number n of water molecules per pseudo-unit cell depends on the cation. The water content in ZK-4 was not determined. The Na^+ can be replaced by other monovalent or divalent cations by means of ion exchange.[6] For zeolite A the Si/Al ratio is around 1. For ZK-4 the ratios is around 1.7. This increased silicon content in ZK-4 results in a small contraction of the unit cell parameters.[1,2] In procedure A, tetraethoxysilane ($Si(OEt)_4$), aluminium, and sodium hydroxide (NaOH) were used. In procedure B and C a certain amount of NaOH was replaced by tetramethylammoniumhydoxide (TMAOH) in order to reduce the Na^+ content. Very fine SiO_2 powder was used as silicon source. The TMA-ions were removed by calcination after the synthesis. Afterwards, full sodium loading can be obtained by ion exchange of protons with Na^+ from sodium nitrate ($NaNO_3$) solution.

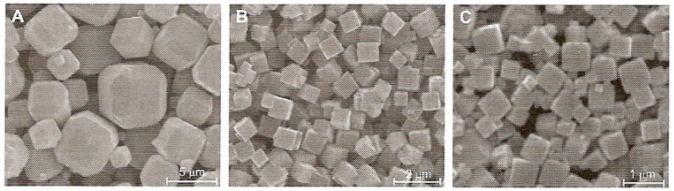

Fig. 2. SEM images of the products obtained by synthesis procedure A (cubic crystals of zeolite A with chamfered edges, average size 3–5 µm), procedure B (cubic crystals of ZK-4 with sharp edges, average size 1–2 µm), and procedure C (nano-sized cubic crystals of zeolite A with slightly rounded edges, size ≤ 1 µm).

Materials

- Tetraethoxysilane, $Si(OEt)_4$, purchased from Aldrich, purity >99 %, used as received.
- Diisopropylamine purchased from Merck, used as received.
- Aluminium wire (1 mm) purchased from Balzers, purity 99.999 %.
- Sodium hydroxide (NaOH) pellets purchased from Merck, purity >99 %, used as received.
- Tetramethylammoniumhydroxide (TMAOH) purchased from Aldrich, used as received.
- Doubly distilled water (used throughout the synthesis).
- Ethanol absolute (99.8 %).
- Sodium nitrate ($NaNO_3$) purchased from Merck, purity p.a., used as received.
- Pressure-tight polytetrafluoroethylene (PTFE) vessel (see Ref. 8 for details).
- For the application of dynamic crystallization conditions in procedure C, a drying oven equipped with a device was used enabling rotation of the PTFE vessels at various speeds (see Ref. 8 for details).

Safety and Disposal

Safety and handling instructions for the chemicals are found in the corresponding materials safety data sheets (MSDS). The pressure-tight PTFE vessel should be designed to well withstand the vapor pressure of water at the employed temperatures (at least 175°C, which corresponds to approximately 890 kPa or 9 bar).

Procedures

In all procedures, two solutions, solution 1 and 2, are prepared separately in Teflon flasks. Solution 1 contains the Si precursor and solution 2 the Al precursor. The two solutions are combined forming a gel. Heating the gel for several hours leads to zeolite crystal formation. Size, morphology, and final composition of the crystals depend mainly on the composition and ageing of the starting gels. The silicon source in procedure A is tetraethoxysilane, while in procedures B and C SiO_2 is used (see Fig. 3 and 4).

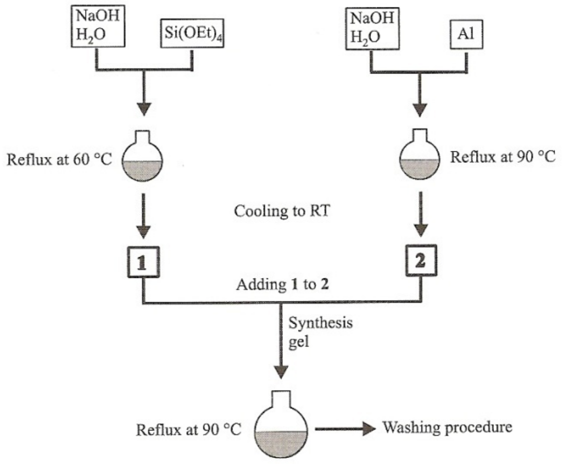

Fig. 3. Scheme of the synthesis procedure for zeolite A with NaOH (procedure A).

Very fine SiO_2 powder is obtained as follows: 72.86 g of diisopropylamine is diluted in 75 ml doubly distilled water and stirred for 1 h until the solution is clear. An amount of 150 g of tetraethoxysilane is added under vigorous stirring, and the mixture is stirred for 48 h. The product is centrifuged (4500 rpm, 20 min) and the white sediment suspended in 400 ml of ethanol. The suspension is stirred for 1 h and then filtrated (glass frit, pore size 4). The product is washed twice with ethanol and dried in vacuum at 100°C for 2 – 3 h. Thermogravimetric analysis gives a loss of 20 % at 800°C.

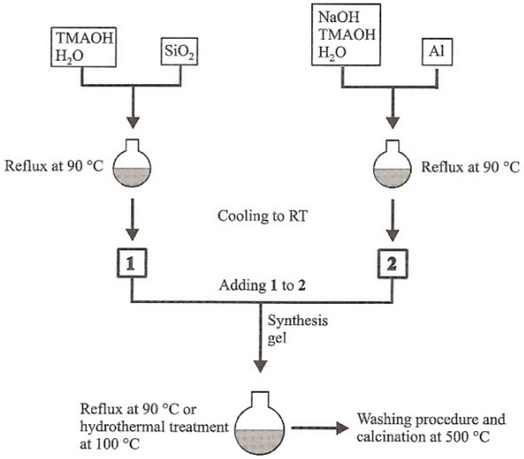

Fig. 4. Scheme of the synthesis procedure for ZK-4 and nano-sized zeolite A with NaOH/TMAOH (procedures B and C).

A. Zeolite A Crystals (Fig. 3)

Solution 1: 5.93 g of NaOH is dissolved in 150 ml of doubly distilled water and 7.721 g of $Si(OEt)_4$ is added. The mixture is refluxed under nitrogen atmosphere at 60 °C for 3 h under stirring. *Solution 2:* 5.93 g of NaOH is dissolved in 150 ml doubly distilled water and 2 g of Al-wire is added. The mixture is refluxed under nitrogen atmosphere at 90 °C for 3 h under stirring.

The two clear solutions are cooled to room temperature before solution 1 is added to solution 2 under stirring. The gel is stirred for 15 min at room temperature and then for 16 h under reflux at 90°C. The mixture is transferred into a beaker for sedimentation of the product. The supernatant liquid is carefully removed, and the zeolite crystals are washed three times with 250 ml of boiling doubly distilled water each time. Separation is done by centrifugation (4500 rpm, 15 min). The product is washed with ethanol, filtrated (glass frit, pore size 4) and dried at 80°C in an oven.

Characterization

The product was analyzed by X-ray powder diffraction, XRD, for phase identification (STOE STADI P, transmission mode, CuK$_{\alpha 1}$ radiation) (Fig. 5). The pattern was compared to a standard pattern of commercial zeolite A (Union Carbide). A reference XRD pattern for zeolite A is also available from Ref. 9. The morphology of the crystals (Fig. 2) was examined by means of scanning electron microscopy, SEM, (JOEL JSM 840 and Hitachi S-3000N). Cubic crystals of zeolite A with chamfered edges and nearly no intergrowth are obtained (average size 3–5 μm). The composition determined by means of energy dispersive X-ray spectroscopy, EDX, is $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]$.

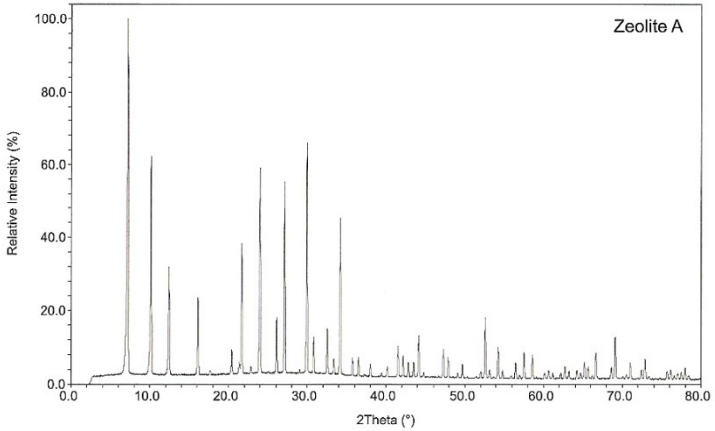

Fig. 5. X-ray powder diffraction diagram of zeolite A synthesized according to the procedures above.

B. ZK-4 Crystals (Fig. 4)

Solution 1: 4.34 g of SiO_2 and 25.74 g of TMAOH are dissolved in 57 ml of doubly distilled water. The mixture is refluxed under nitrogen atmosphere at 90 °C for 2 h under stirring. *Solution 2:* 0.962 g of Al-wire, 2 g of NaOH, and 6.435 g of TMAOH are dissolved in 50 ml doubly distilled water. The mixture is refluxed under nitrogen atmosphere at 90°C for 3 h under stirring.

The two clear solutions are cooled to room temperature before solution 1 is added to solution 2 under stirring. The gel is stirred for 15 min at room temperature and then for 24 h under reflux at 90°C. The product is separated by centrifugation (4500 rpm, 15 min). The white sediment is washed by suspending it three times in boiling doubly distilled water (250 ml) and each time centrifuged. After washing with ethanol the product is first dried at 80°C in an oven. The TMA ions are removed by calcination at 500°C for 16 h in air. Afterward, full sodium loading is obtained by ion exchange of protons with Na^+ by suspending the zeolites three times for 15 min in 0.1 M $NaNO_3$ solution.

Characterization

Characterization was performed as described for zeolite A. Cubic crystals of ZK-4 with sharp edges (average size 1–2 μm). Composition determined by EDX: $Na_9[(AlO_2)_9(SiO_2)_{15}]$ (Fig. 2). The X-ray diffractogram is shown in Fig. 6.

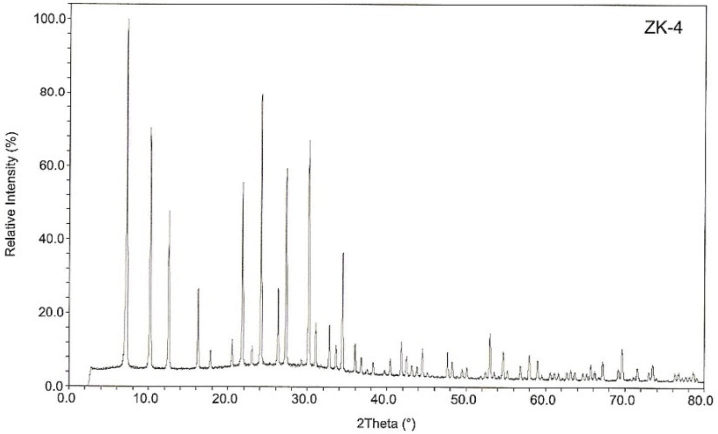

Fig. 6. X-ray powder diffraction diagram of zeolite ZK-4 synthesized according to the procedures above.

C. Nano-sized Zeolite A Crystals (Fig. 4)

Solution 1: 0.6225 g of SiO_2 and 4.47 g of TMAOH are dissolved in 57 ml of doubly distilled water. The mixture is refluxed under nitrogen atmosphere at 90 °C for 2 h under stirring. *Solution 2:* 0.5 g of Al-wire, 0.6 g of NaOH, and 5.328 g of TMAOH are dissolved in 50 ml of doubly distilled water. The mixture is refluxed under nitrogen atmosphere at 90°C for 4 h under stirring.

The two clear solutions are cooled to room temperature before solution 1 is added to solution 2 under stirring. The gel is stirred for 2 d at room temperature. For crystallization, the gel is filled into a PTFE vessel and placed in an oven equipped with a device enabling rotation(rotation at 40 rpm) for 3 d at 100°C. The pressure vessel is then cooled in ice for 1 h before opening. The product is separated by centrifugation (5000 rpm, 30 min) and washed three times with boiling doubly distilled water, centrifuging each time. After washing with ethanol the product is first dried at 80°C in an oven. The TMA ions are removed by calcination at 500°C for 16 h in air. Afterward, full sodium loading is obtained by ion exchange of protons with Na^+ by suspending the zeolites three times for 15 min in 0.1 M $NaNO_3$ solution.

Characterization

Characterization was performed as described above (Figs. 2 and 5). Nano-sized cubic crystals of zeolite A with slightly rounded edges (size ≤ 1 µm). Composition determined by EDX: $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]$

References

[1] C. Baerlocher, W. M. Meier, D. H. Olson, Atlas of Zeolite Framework Types, Fifth Revised Edition, Elsevier, Amsterdam, 2001, and references therein (see also: www.iza-structure.org).

[2] H. Robson, K. P. Lillerud, Verified Syntheses of Zeolitic Materials, 2nd Ed., Elsevier, Amsterdam, 2001 (see also: www.iza-synthesis.org).

[3] S. T. King, J. Catal. 1996, **161**, 530. M. Anpo, M. Matsuoka, K. Hanou, H. Mishima, H. Yamashita, H. H. Patterson, Coord. Chem., Rev. 1998, **171**, 175. S. M. Kanan, C. P. Tripp, R. N. Austin, H. H. Patterson, J. Phys. Chem. B 2001, **105**, 9441. J. Weitkamp, A. Raichle, Y. Traa, Appl. Cat. A 2001, **222**, 277.

[4] G. Schulz-Ekloff, D. Wöhrle, B. van Duffel, R. A. Schoonheydt, Microporous Mesoporous Mater. 2002, **51**, 91. D. Brühwiler, G. Calzaferri, Microporous Mesoporous Mater. 2004, **72**, 1.

[5] W. Sachtler, Acc. Chem. Res., 1993, **26**, 383. M. Wark, G. Schulz-Ekloff, N. I. Jaeger, Bulg. Chem. Comm. 1998, **30**, 129. A. A. Demkov, O. F. Sankey, J. Phys.: Cond. Matter 2001, **13**, 10433; d) K. Kuge, G. Calzaferri, Microporous Mesoporous Mater. 2003, **66**, 15.

[6] D. Brühwiler, R. Seifert, G. Calzaferri, J. Phys. Chem. B 1999, **103**, 6397. D. Brühwiler, C. Leiggener, S. Glaus, G. Calzaferri, J. Phys. Chem. B 2002, **106**, 3770. C. Leiggener, D. Brühwiler, G. Calzaferri, J. Mater. Chem. 2003, **13**, 1969. C. Leiggener, G. Calzaferri, ChemPhysChem 2004, **5**, 1593. M. Meyer, C. Leiggener, G. Calzaferri, ChemPhysChem 2005, **6**, 1071. M. Meyer, A. Currao, G. Calzaferri, ChemPhysChem 2005, **6**, 2167. C. Leiggener, G. Calzaferri, Chem. Eur. J. 2005, **11**, 7191.

[7] P. Lainé, R. Seifert, R. Giovanoli, G. Calzaferri, New J. Chem. 1997, **21**, 453. R. Seifert, R. Rytz, G. Calzaferri, J. Phys. Chem. A 2000, **104**, 7473.

[8] A. Zabala Ruiz, D. Brühwiler, T. Ban, G. Calzaferri, Monatsh. Chem. 2005, **136**, 77.

[9] M. M. J. Treacy, J. B. Higgins, Collection of Simulated XRD Powder Patterns for Zeolites, 4th Ed., Elsevier, Amsterdam, 2001 (see also: www.iza-structure.org).