Pergamon

Prog. Solid St. Chem. Vol. 27, pp. 29–73, 1999
©2000 Elsevier Science Ltd. All rights reserved
Printed in Great Britain
0079-6780/00/$ - see front matter

PII: S0079-6786(00)00002-9

Zeolites — from kitchen to space

H. Ghobarkar [1], O. Schäf [2,*] and U. Guth [3]

[1] *Free University of Berlin, Institute for Mineralogy, Berlin, Germany*
[2] *University of Greifswald, Institute for Chemistry and Biochemistry, Greifswald, Germany*
[3] *Technische Universität Dresden, Institut for Physical Chemistry und Electrochemistry*

Abstract

Zeolites have been synthesized by a new concept of in-situ conversion of artificial glasses of zeolite composition with water as reaction medium under the influence of temperature and pressure. These synthesis conditions, which lead to a direct correlation between the educt and zeolite product, give the possibility of zeolite preparation under conditions comparable to nature. Natural zeolites phases can be synthesized with this method which are, until now, not accessible for synthesis by conventional sol-gel processing or other methods. The specific synthesis acts as key for new applications in all fields of human life, as zeolite properties can now be trimmed to particular applications and special application conditions. Some of these approaches will be presented in this article.

Keywords: Zeolite synthesis; High pressure; Zeolite synthesis from glass; Glass conversion to zeolite; Future zeolite applications

1. Introduction

The unique physicochemical properties of zeolites have made them the most interesting class of minerals for scientists since their first known description [1]. The Greek name of zeolite, "ζειν", to boil, and "λιϑος", stone, describes the zeolite behavior under fast heating conditions, when the zeolite minerals seem to boil because of the fast water loss.

Older systematic groupings of zeolites classified them as framework alumosilicates. Without acting external energy, a pure silicate framework consisting of [SiO_4] tetrahedra will be uncharged. In an alumosilicate framework however, [AlO_4] tetrahedra are negatively charged with respect to [SiO_4] tetrahedra because of the trivalent state of Al. The charge of the whole framework is normally compensated by mono and/or divalent cations within the cavities,

---

*Corresponding author: e-mail: schaef@mail.uni-greifswald.de

while additional water molecules are present in the framework cavities. The general chemical formula unit of zeolites is given in Eq. (1):

$$Me^{z+}_{(\frac{m}{z})}\left[Al_m \cdot Si_n \cdot O_{2(n+m)}\right] \cdot qH_2O \tag{1}$$

with Me as extraframework cations (e.g. Li^+, Na^+, K^+..., Ca^{2+}, Sr^{2+}...), z the charge of cations, framework ions in brackets, m as the number of Al per formula unit, n the number of Si per formula unit and q the number of water molecules in the cavity system. The molar ratio of Si to Al is always bigger or equal to one and no direct link between [AlO_4] tetrahedra is observed (Loewenstein rule [2]). Al is charged with respect to the framework. The compensation of the negatively charged framework by extraframework cations Me^{z+} can be written according to the Kröger-Vink notation [3] as follows:

$$Al'_{Si} = \frac{1}{z} Me^{z+} \tag{2}$$

The first known classification properties of zeolites were their exchange capability of extraframework cations and the possibility of reversible water absorption [4]. Figure 1 shows a common zeolite typically applied in kitchen for calcium removal from water by ion exchange during the cleaning process.

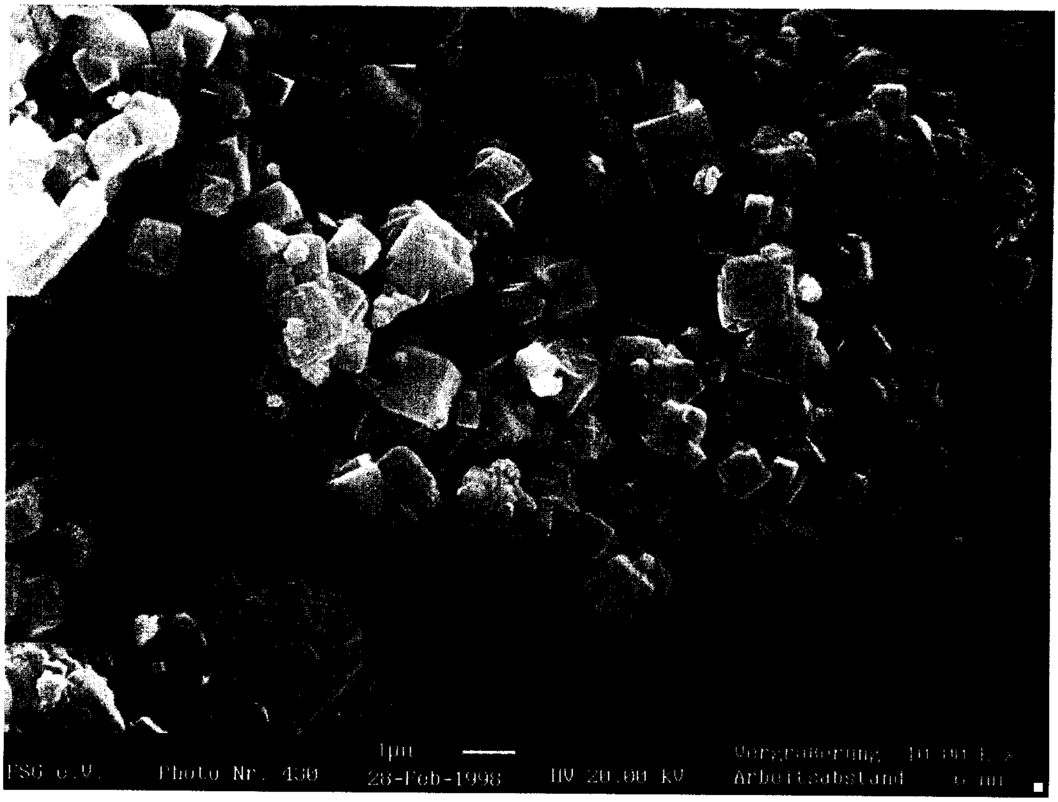


Fig. 1: Zeolite applied in kitchen: soap powder zeolite Na-LTA for water softening.

Within the zeolite structure, water molecules are present in the cavities (channels and cages) of the framework structure. Between polar water molecules and the framework system dipole forces act the one hand side. On the other hand side water molecules on well defined crystallographic places act as solvent for the present extraframework cations dependent on charge distribution of the zeolite framework caused by (Si, Al)-distribution together with the charge distribution within in the void system. This binding state of water in zeolites is typical for this class of solid state materials, therefore the term "zeolitic" water is used [4]. The desorption of the zeolitic water is time- and temperature-dependent. Some natural zeolites stored for many years under environmental conditions loose most of their water and only a residual equilibrium water content remains in the channel system. The same behavior is observed under vacuum conditions. Dependent on temperature, water is desorbed and the temperature dependent water loss under dynamic conditions shows the different crystallographic positions of water molecules in between the zeolite framework [5]. A fast water removal, however, destroys the channel and cage system irreversibly.

Four different positions of extraframework cations of zeolites are possible according to Gottardi and Galli [5]. At the first position the cation is only coordinated by framework oxygens. At the second, the cation is coordinated by framework oxygens at two nearly opposite sides together with some water molecules. At a third possible position, the cation is bound one sided to framework oxygen and on the other side by water molecules. A fourth possible position is the completely surrounding of the cation by water molecules.

Besides of zeolites with alumosilicate frameworks, alumophosphates based on alternating [AlO4] and [PO4] tetrahedra are also classified as zeolites because of their tetrahedral building units and their channel systems [6]. In contrast to alumosilicate zeolites, alumophosphate frameworks are uncharged if P and Al is not substituted for other framework cations (BPH, SAPOs [6,7]). Therefore, no additional cations are necessary to compensate the framework charge and only absorbed molecules like H_2O are present in the channel system. The framework system of some alumophosphates are isostructural with zeolites based on alumosilicate frameworks, others are completely different [6].

The chemical composition strongly influences the physicochemical properties of zeolites. Alumosilicate zeolites are very stable under humid conditions. Barrer et al. [8,9] showed that the unique ion exchange properties of zeolites are very specifically dependent on the different crystallographic building principles. Natural zeolites are stable at pH values > 6, but not under extreme pH-values. Especially under acidic conditions the framework is destroyed. In general it was found that the higher the Si/Al ratio better the stability under acidic conditions. Al in normally synthesized zeolites can be exchanged against Si by dealumination [7,10], and thus made stable against acids. At $Si/Al \geq 10$ a zeolite is named high silica zeolite. Even zeolite frameworks without any Al can be achieved (all silica zeolites, $Si/Al = \infty$). On the other hand, the dealumination leads to a successive removal of cations from the cavity system as the charge of the framework gets canceled. This leads to a successive passivation of the cavity system as the removal of cations diminishes the possibility of interaction with other species in the cavity system as well as the ion exchange capability, which means that basic zeolite specific properties get lost.

Normal Alumophosphate zeolites are much less stable in aqueous solutions compared to alumosilicates [7, 11].

The physico-chemical properties of zeolites and related porous materials can be trimmed by cation substitution in the cavity system in general. Another possibility is the substitution of framework cations e.g. trivalent Ga, Be, Fe, Cr, Ni for Al^{3+} and P^{5+} and tetravalent Ge for Si^{4+}, but also e.g. Si^{4+} and others for P^{5+} and Be^{2+} for Al^{3+} in alumophosphates (BPH, SAPOs), in order to get special properties. In general this can only be done by synthesis and leads to isostructural but also completely new structures, with the disadvantage that some of these zeolite like materials still contain big templating molecules in the cavity system (see GaGe-FAU, SOD, CoAl-FAU etc. [6]).

The separation of zeolites from other structure types is rather complicated. An important characteristic of zeolites is the four coordination of framework cations forming a tetrahedron. The linkage to other tetrahedra is performed via bridging anions like oxygen which are two-coordinated. Another specific property of zeolites is the kind of water, or, in general: polar molecule binding in the microporous cavity system. Water in zeolites is always adsorbed in a zeolitic way as described above, but in some specific cases (RON, SOD, ANA-type etc. [5,6]) also binding of (OH) is found.

In general, zeolites fulfill the following classification rules:

framework cations tetrahedrally coordinated,

channel and cage system in the range of 0.2Å to 20Å,

zeolitically bound water (or in general: polar molecules) if these molecules are present in the cavity system and

cation exchange properties if cations are present in the cavity system.

Rule 3 and 4 is exclusively fulfilled by true zeolites, while rule 1 and 2 is a necessary condition for a structure type to be a zeolite. The number of zeolites would grow extremely if the existence of a cavity system would be the only condition for a structure type to be a zeolite. Some of the structure types classified as zeolites in [6], synthetic and natural, are no true zeolites as they do not have original water present in the channel system (zeolitic water) and no cation exchange capability.

Zeolite materials known today do have maximum diameters of pore openings (window size) of 7.4Å in case of alumosilicate-type zeolites (faujasite, FAU-type) and 12.1Å in case of alumophosphate-type zeolites (VPI-5, VFI-type [6]). It is characteristic for true zeolites, that the channel and cage systems do have crystalline properties (e.g. periodicity, crystallographically defined places for ions and molecules).

Mesoporous materials are, in contrast, substances with pore diameters larger than 20Å, up to 500Å (2-50nm), while macroporous materials have pore diameters bigger than 50nm. No mesoporous zeolite with zeolite inherent crystalline properties of cavity system exists until now. Mesoporous materials known today do have a broad pore size distribution, and a distribution of physicochemical and crystallographic properties within, in detail not comparable to zeolites. Based on different building principles, with crystalline (e.g. pillard clays) or amorphous frameworks (e.g. MCMs), mesoporous materials are produced by treatment of precursor materials to obtain the specific mesoporous properties [7].

2. Classification of zeolites

The extraordinary properties of zeolites are caused by their crystal lattice. Therefore, a proper classification starts from the 3-dimensional bonding of the tetrahedrally coordinated framework cations. Today about 800 different zeolites are known [7] which can be classified by 119 different zeolite structure types [6]. These structure types are described by a three letter code and listed in the "Atlas of zeolite structure types", revised version 10/97, [6]. Only about 1/4 of them are naturally occurring, the others are synthetic.

Instead of using the unit cell of the respective zeolite for description, which is only specific for the zeolite type, secondary building units (SBU's) consisting of different arrangements of tetrahedra (primary building units) are used [5]. The SBUs are, however, only building elements of the zeolite unit cell. Different SBUs can be used for the classification of a zeolite. In order to facilitate the zeolite structure description, the central atoms of framework tetrahedra (T) are drawn as balls, while the binding between two T-atoms via oxygen (O) are drawn as stick (T-O-T-model). Meanwhile a SBU graphic rendition with only sticks is also used (see Fig. 2). Figure 3 shows the different SBUs used for zeolite structure type classification.

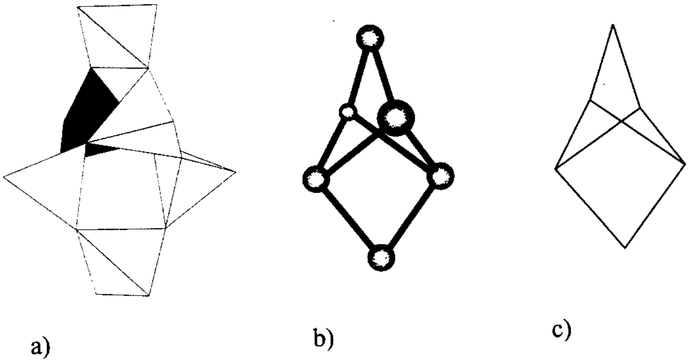


Fig. 2: (Si,Al)O$_4$-tetrahedra forming two 3-dimensional 4=1 units of NAT-type zeolite chains in three different presentations: a) tetrahedral model, b) ball and spoke model with centers of (Si, Al) as balls and T-O-T bond as stick, c) stick-model.

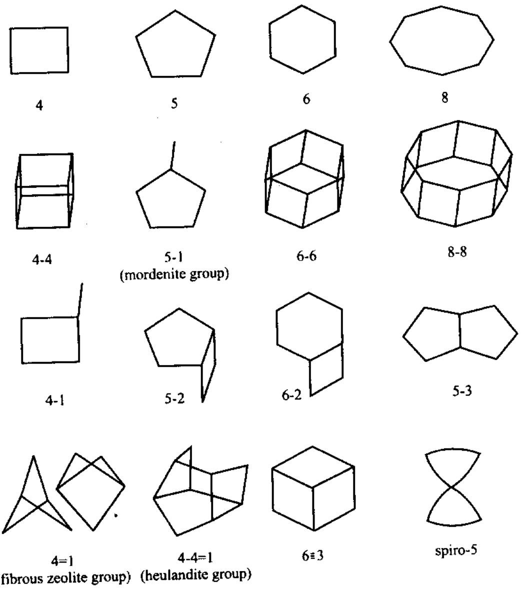


Fig. 3: The different Secondary Building Units (SBUs) of today known zeolite structure types.

Zeolites can also be distinguished from non zeolite framework structures like tectosilicates by their framework density (FD), defined as number of T atoms per 1000Å3 which is always lower than the FD for normal tetrahedral framework structures. This is caused by the channel and cage system [6]. A characteristic gap between zeolite structure types and nonporous framework structure types exists between under 20 to over 21 T-atoms per 1000Å3 (see Fig. 4). This fact can be used for the independent control of a structure type to be classified as zeolite, although no correlation between framework density and cavity (channel or cage) diameter exists.

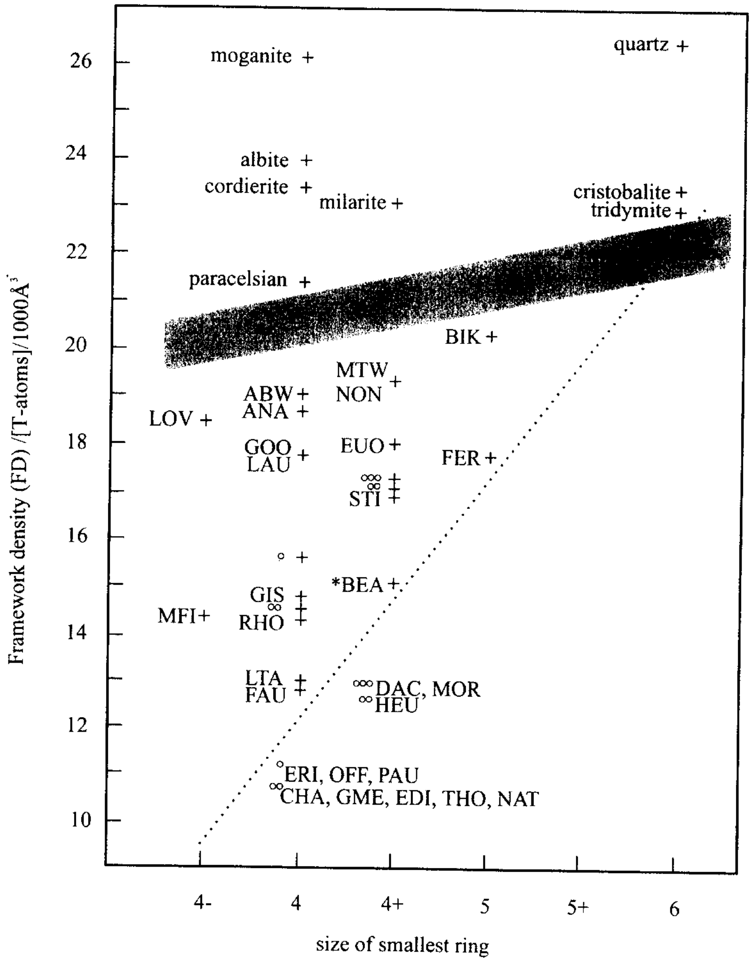


Fig. 4: Framework density of selected zeolites in respect to normal tectosilicates. Data from Atlas of Zeolite Structure Types (6).

The main crystallographic characteristics of zeolites are the channel and cage systems. Zeolite channels are classified according to the number of oxygen or T-atoms forming the window together with the geometrical dimensions of the two dimensional channel opening. Per definition the minimum T atoms necessary to build up a channel is six [6] but even a four membered ring is actually a gateway to a channel. Up to 20 membered rings exist as channel openings (in case of the cloverite (-CLO) structure type see [6]). The cross-section of the opening however must not necessarily be ring-shaped, also elliptical, drop-shaped or asymmetrically shaped openings exist. One-, two- and three- dimensional channel systems are directed to main crystallographic directions of zeolite structures. They are distinguished by their connectivity. Different kinds of arrangements of 3-dimensional channel systems exist, e.g. tetrahedrally (FAU), octahedrally (PHI), hexahedrally (ANA), trigonal, hexagonal etc. Even channel systems set in each other do exist. Table 1 shows the dimensions of window openings of alumosilicate based zeolite channels dependent on T-atoms forming the opening in different crystallographic directions based on the notation defined in [6]. Phosphate based zeolites are omitted in this table. Actually the sizes of the channel openings are dependent on water content and/or cation species present in the channel system. In general the zeolite structures are quite flexible as the unit cell dimensions are dependent on water content of the cavity system. The change in crystal habit and structure caused by the change of water content in the channel system might be big enough to be observed macroscopically like in case of laumontite, where the dehydrated phase is described as leonhardite. For certain zeolites like laumontite dehydration can lead to a collapse of the channel system [5].

Zeolite cages are as important for the zeolite specific properties as the channel systems are. A proper definition of cages has to include the fact that the channels themselves are also cages of infinite length. Cages can be defined as voids bigger in diameter than normal channel systems. They are only accessible through the channel system. The most simple cages are formed at the crossing of two channel systems. Molecules bigger than those accessible to the channel system (formed within the cages or remaining from the synthesis process) fit into these cages. In some zeolites like in FAU, supercages exist at the crossing of the channel systems. In FAU-type zeolites they are formed by the tetrahedral crossing of channel systems.

A classification of some well known zeolite cage types is given in Fig. 5.

Another sub-classification of porous tectosilicates and related compounds was done by Liebau et al. [12] based on geometrical and chemical considerations. They claimed porous all silica phases "zeosils" and "clathrasils" as "porosils". According to this definition "clatra" compounds contain cages with guest species (mainly caused by the synthesis process) which are too big to pass the linked channel system while "zeo" materials are claimed as materials with a cavity containing framework topology. According to this classification "porolites" contain the group of commonly known zeolites and also "clatra-lites" (see definition above), while all aluminum phases "poroals" consist of the groups "clatrals" and "zeoals", all tetrahedrally arranged aluminum oxide phases which do not exist at present. Alumophosphate materials are classified as "poroalpos" which again consist of "clatralpos" and "zeoalpos".

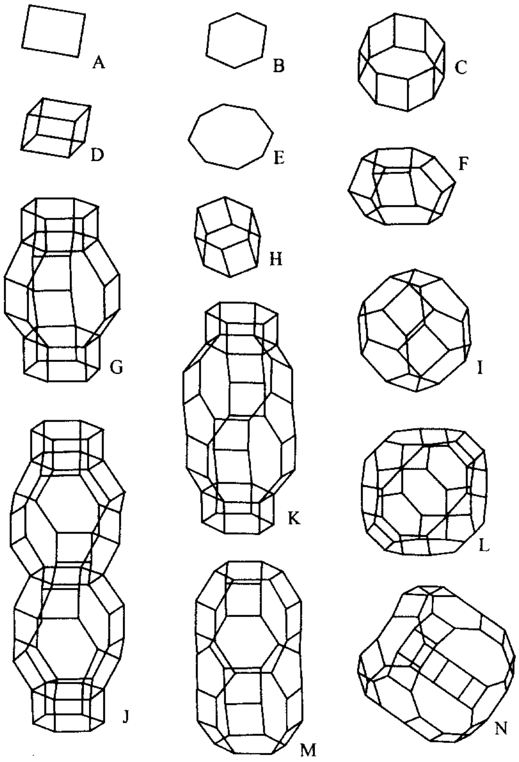


Fig. 5: Selected zeolite cages: A = 4-ring (window opening to cage of infinite length); B = 6-ring (window opening to cage of infinite length); C = 8-8-cage (δ-cage); D = 4-4-cage; E = 8-ring (window opening to cage of infinite length); F = cancrinite cage (ε-cage); G = gmelinite cage (γ-cage); H = 6-6-cage; I = sodalite cage (β-cage); J = levyne cage; K = chabazite cage; L = α-cage; M = erionite cage; N = faujasite supercage.

3. Zeolite synthesis

3.1 Conventional hydrothermal sol-gel synthesis

Systematic synthesis of zeolites started with the pioneering works of Barrer and coworkers in the 1950's (see Refs. [4,13,14] and references given there). These zeolites synthesis have been performed by the sol-gel method in aqueous solutions under mainly autogenous pressures, the vapor pressures of the mixture itself, in a temperature range between room temperature up to about 300°C. In this process, which was firstly developed for alumosilicate zeolite synthesis, a silica source is used, mostly a colloidal suspension of silica-acid, an alumina source and a cation source - alkali or alkaline earth cations in conventional syntheses - as starting materials. The highly reactive precursor materials are mixed together, while the pH value has to be kept higher than 7, because most zeolites are only formed in a caustic environment. Hundreds of patents for zeolite synthesis and many more publications about synthesis exist today [7,13–18].

A general problem of this kind of synthesis is, however, that different components constituting the later zeolite product have to react in such a way that a certain zeolite with the desired stoichiometry and crystal structure is formed. This means that the educt stoichiometry and the stoichiometry of the later product are different. In most cases of sol-gel hydrothermal synthesis the relation between educt and zeolite product stoichiometry is only empirical [19]. Although some natural zeolites could be synthesized by this low temperature - low pressure synthesis process and the very most synthetic zeolites have been synthesized in this way, some natural zeolites were not accessible for synthesis as the product stoichiometry as well as the structure is not predictable without empirical processes. Although about 1/3 of the periodic table can be introduced in the framework system of alumosilicate zeolites by direct synthesis or framework modification, only partial substitution of Al and/or Si can be achieved by the conventional synthesis route. Furthermore, only a few examples of full framework cation substituted zeolites are known in literature [6, 20–23].

In contrast to the high pressure hydrothermal synthesis process, a non-empirical synthesis route for tailored framework ion substitution is not known.

The sol-gel method has been developed further by using structure directing agents which act as templates for the zeolite cavities to be formed. One of the most commonly used agent is tetramethyl-ammonium, TMA. Many zeolite synthesis could be successfully performed by using these matrix molecules, especially the class of clatrasils, the all silica compounds with cages.

Most alumosilicate zeolites for application purposes with high Si/Al ratios are prepared by direct synthesis using templates [7]. Afterwards template removal has to be done by thermal and oxidative decomposition or a combined process (see Ref. [23] and references therein). A few zeolite frameworks like e.g. that of mordenite with higher silica contents however can be dealuminated up to a certain degree using acids without destruction of the framework [23].

Steaming/acid treatment processes at elevated temperatures and Si-halide treatments are reported as further processes of dealumination at different stages of Si/Al ratios in the framework proved only for a very few zeolite structure types [23].

Until now, certain problems arose during the template removal from the cavity systems, therefore the clathra-compounds still contain the template materials. Some templates could not be removed without destruction of the zeolite, others are fractionated during the removal process. Most template materials are toxic or the fraction products of remaining templates are disturbing the application process in case of release during application, which limits the application fields of these kinds of zeolite like compounds.

Another problem is the substitution of framework cations in known alumosilicate structures or to create new kind of structures on the basis of theoretical considerations with tetrahedrally coordinated cations different from Al or Si and anions different from P and O. Although some progress has been achieved in this field, the recent state of the art is far from a tailored synthesis of these zeolite analogous or in general: tectosilicate analogous compounds (e.g. Zn, Be, transition metals etc.: see Ref. [6] and references therein).

It is assumed that the lower the zeolite framework density, the lower the stability of the respective zeolite [24]. Nevertheless, it is possible to synthesize zeolites with low framework density without structure directing agents in an equilibrium like synthesis process described in the following chapter. The low stability of investigated zeolites seems, therefore, be caused by the sol-gel-synthesis process itself. Size and shape of zeolite crystals synthesized by these two different processes (Fig. 6) confirm the hypothesis that the sol-gel synthesis process is responsible for some negative properties of hitherto applied synthetic zeolites. Furthermore, zoning of zeolite crystals is never observed in crystals synthesized by the high pressure hydrothermal synthesis process, where usually glass of the respective zeolite composition is used as starting material. Here, the crystal growth process continues until the physico-chemical conditions are altered (see following chapter). The formation of a second crystal generation (of a natural zeolite never been synthesized under sol-gel conditions, Fig. 7) the same structure type and chemical composition is, under these high pressure hydrothermal

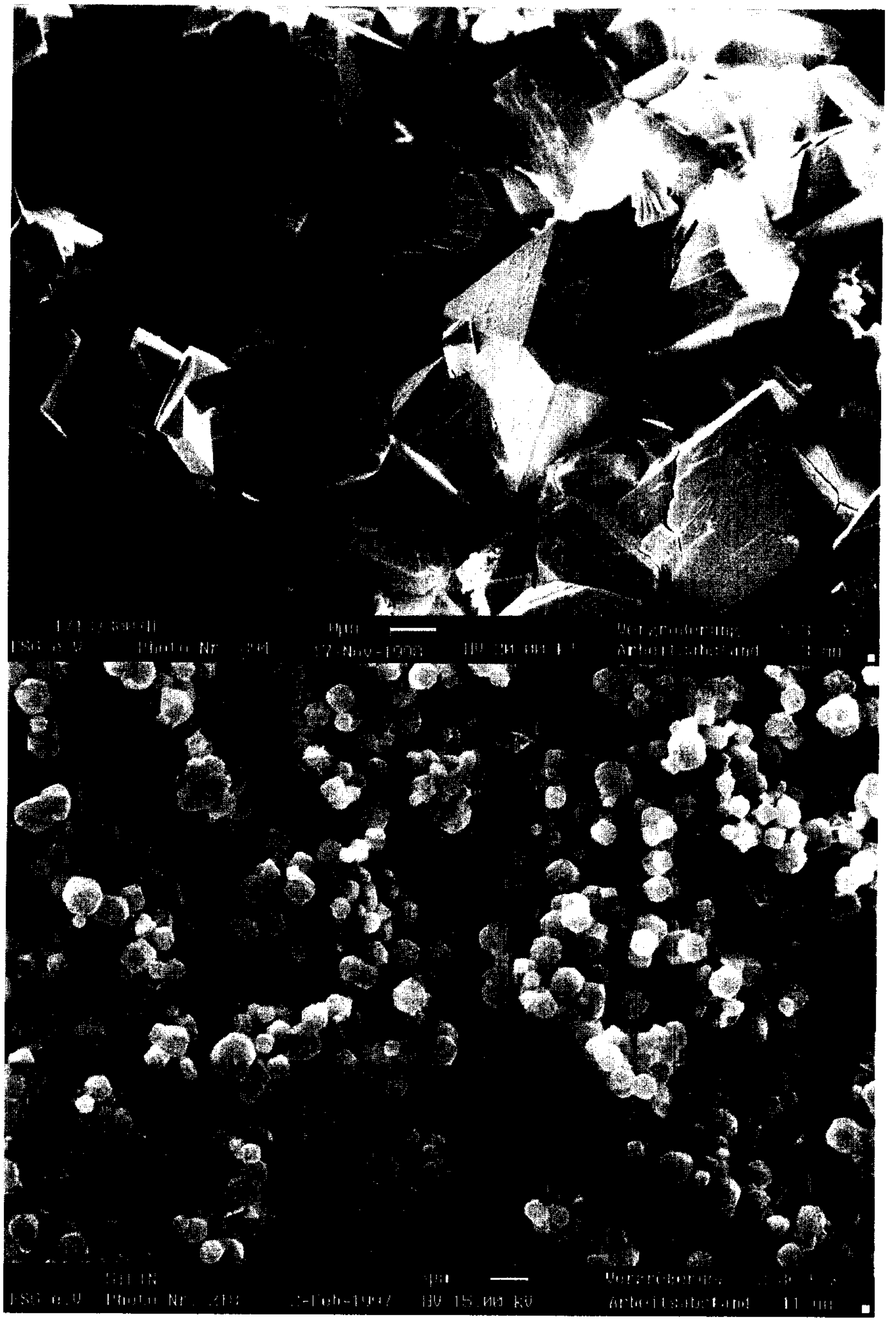


Fig. 6: Comparison of morphology of high-pressure hydrothermally synthesized GIS-type zeolite Ca-gismondine (glass powder of gismondine composition as starting material treated for 13 days at 1kbar water pressure at 300°C) and sol-gel derived GIS-type zeolite Na-gismondine (mixture of aqueous colloid silica, sodiumaluminate- and NaOH-solution, treated at 80°C for 9 days).

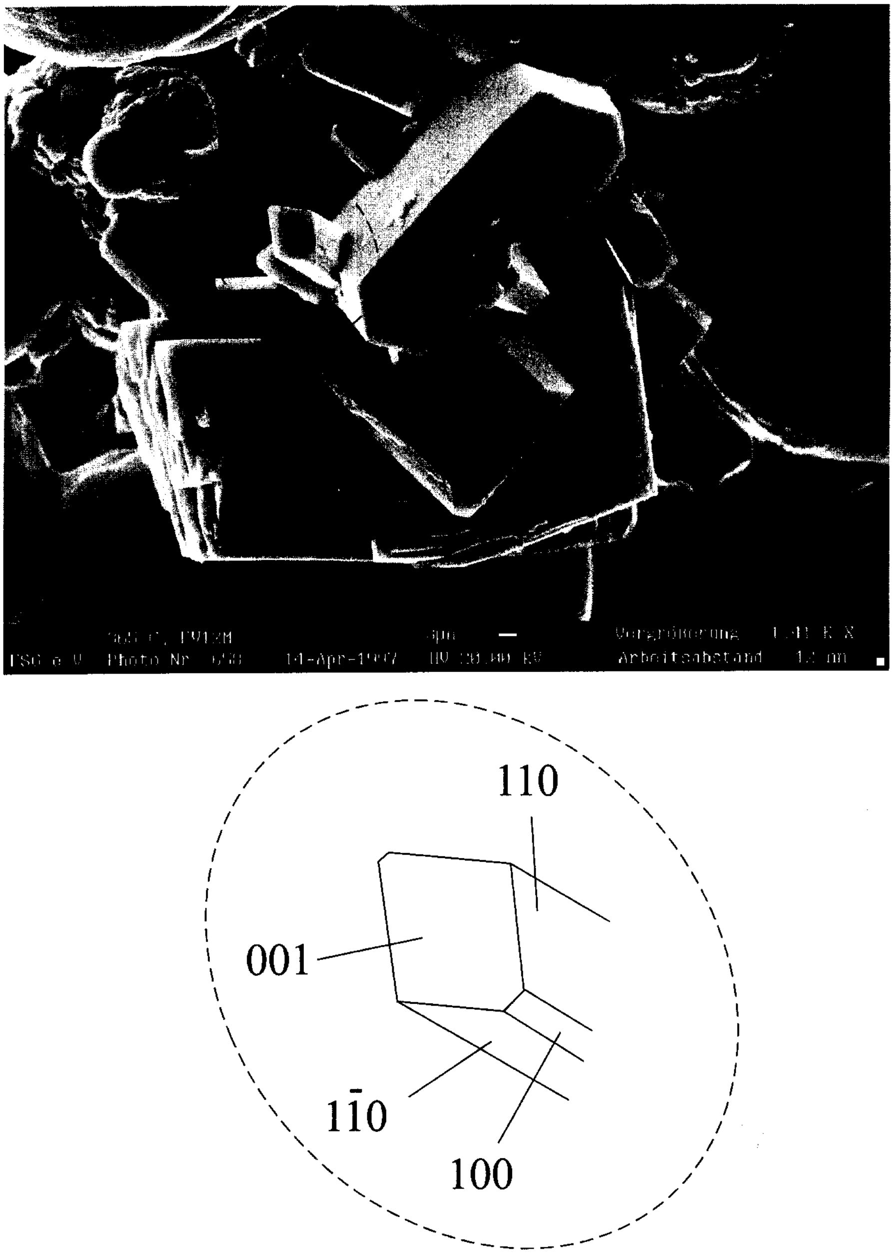


Fig. 7: The formation of second generation of zeolite laumontite under high pressure hydrothermally synthesis conditions at 1kbar from the water containing fluid phase and glass of LAU composition as starting material (no seed crytals, no templates).

conditions, a sure hint for the phase stability. The solubility of the glassy starting phase is, if still present, under almost all circumstances higher than that of the crystallized zeolite phase. This is one of the major differences between the "low pressure" sol-gel process and the high pressure hydrothermal process.

High pressure synthesis processes have already been successfully performed in the field of solid state chemical syntheses using other media than water as the fluid phase [25]. This gives additional, alternative, synthesis methods for zeolite like compounds in the future. Although the conventional zeolite synthesis is also possible in other media than water (Ref. [26] and references therein), the process of complete dissolution-recrystallization under high pressure conditions will be a much more powerful process, described here for zeolite synthesis processes in the hydrothermal medium.

Zeolites synthesized by the sol-gel method show different properties which have already been applied, but no effectiveness with respect to basic low temperature long term stability in aqueous media could be achieved. Our concept of zeolite synthesis is therefore different. We did not follow this pathway as nature itself did not follow this pathway of zeolite formation.

3.2 High pressure hydrothermal synthesis

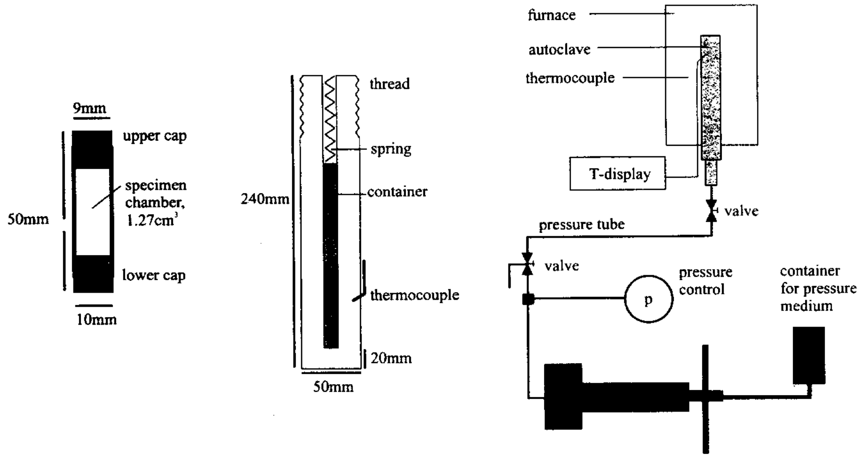
Natural zeolites are mostly found in regions of former or present magmatic activity which means that high temperature and the presence of water influenced the formation. During the cooling process of a magmatic intrusion, the dissolved reminding ions, water-vapor, carbon dioxide and other volatile compounds are separated trying to reach the earth surface. This volatile phase also called fluid phase crystallizes during the cooling process loosing its high pressure. Different stages of crystallization can be observed during the loss of temperature and pressure [27]. Only at the lowest stage of pressure and temperature, at the mildest conditions called the hydrothermal state, the formation conditions for alumosilicate zeolite phases are reached. This can be achieved in nature not only by crystallization of the volatile phase itself in cavities, but also by intrusion into neighboring alumosilicate beds transforming the material partially to zeolites. Even at the lowest pressures, like e.g. in hot springs (a phenomenon which is also related to magmatism) the formation of zeolites can be observed [5].

Natural zeolites are not only formed in the last stage of postmagmatic activity but also in the earliest stage of metamorphosis, the rock forming process, from alumosilicate bearing sediments. Older metamorphic classifications used the term "laumontite facies" and also "zeolite facies" for the first step of metamorphosis, as zeolites, especially laumontite (Ca-zeolite), were the first new phases formed. At higher pressures and temperatures, zeolites are destroyed and denser alumosilicate phases without zeolite properties are formed [28].

Low temperature and low pressure formation conditions in the sense of rock formation under the influence of water is the reason for the low density framework structure with characteristic channels and cages. Water molecules are an active element during this formation process, as they are the solvent for the ionic species forming the later zeolite and part of the zeolite structure under very special, "zeolitic" binding conditions. Therefore, the properties of water in zeolites have to be examined more carefully in the future [29,30].

Our approach was the simulation of these natural formation conditions of zeolites, therefore our new alternative synthesis method was first tested by the reconstruction of natural zeolites. Nature itself does neither use sol-gel processing, template molecules nor solutions containing high pH values for zeolite formation. In nature the formation process of zeolites is a process of dissolution of alumosilicate or other, analogous, framework ion bearing oxide materials with water as dissolution and reaction medium under the influence of - essentially - temperature, pressure and time. Two different states of high pressure hydrothermal conditions can be distinguished. An autogenous pressure synthesis, which means that the equilibrium pressure of water containing fluid dependent on temperature was used at values normally higher than 100oC. A high pressure hydrothermal synthesis (hp-hydrothermal synthesis) means a pressure higher than the vapor pressure of the fluid phase was used. Both autogenous and high pressure formation conditions can be observed in nature but high pressure experiments have been performed in general during these investigations.

Figure 8 shows the experimental setup for this high pressure hydrothermal synthesis process under laboratory conditions. For this synthesis procedure the educt material is placed in a specimen container of pure copper with caps on both sides (Fig. 8a)). The container is constructed in such a way, that the external pressure can acess the specimen chamber but the solid materials can not leave the container. For special purposes containers are used which can be completely closed on both sides. Inexpensive copper is used for its high stability against the hydrothermal fluid phase under neutral or weakly caustic synthesis conditions. Three to four containers fixed by a spring are put into a high temperature - high pressure vessel (MRA/112R type, fig 8b)) and placed in a temperature controlled furnace as shown in figure 8c). After reaching the chosen temperature the fluid pressure is adjusted for the desired value. Synthesis times laid between 12 hours and 72 days, pressures between 100bar and 4kbar and temperatures between room temperature and 700°C. Four to eight autoclaves with characteristic temperature gradients were always running in parallel while every experiment was repeated between one and two times.



a) b) c)

Fig. 8a) - c): Facilities for high pressure hydrothermal synthesis of zeolites (Autoclave type MRA/112R type, manufacturer: TEM-PRESS Research Div., The Carborundum Company, 1401 South Atherton-Str., State College, Pennsylvania 16801, USA)

In the developed hp-hydrothermal synthesis process glasses of the respective zeolite composition were used as starting materials. The greatest advantages of using glasses as educts are the higher solubility compared to crystalline materials and the reduced effect of nuclei formation by epitaxy. It was also our aim to avoid further components in the synthesis process, therefore always glasses of approximately the same chemical composition as zeolites to be synthesized were used. In natural formation processes of zeolites linked with volcanism glasses also play an important role as they have higher solubilities under hydrothermal conditions than respective crystalline phases.

During the synthesis process of zeolites the glassy educt is dissolved in a dynamic process under isothermal conditions (see Fig. 9). The initial solution at point I consists of pure destilled water. Dependent on time, the concentration of the solution grows by continuous dissolution of the starting glass. Spontaneous crystallization occurs at point II when the region of supersaturated solution is passed and nuclei of the equilibrium phase are formed, at the surface of the dissolving glass or the copper container. In figure 10 the process of nucleation and growth of a zeolite phase at the surface of the educt glass can be seen. The nucleation leads to a lowering of concentration in the medium which means that no more nuclei formation can take place but only a more or less continuous growth of the crystalline phase in a time dependent dynamic process (Fig. 9, point II to III), while by the glass dissolution the components for zeolite synthesis are always delivered in the proportion needed. This process of oscillating dissolution-recrystallization is easy explainable by the higher solubility of the glass phases compared to the recrystallized zeolite products. Dissolution and recrystallization, however, are in general processes with different time constants. In the field of supersaturated solution either the dissolution of the precursor glass is faster than the zeolite crystallization

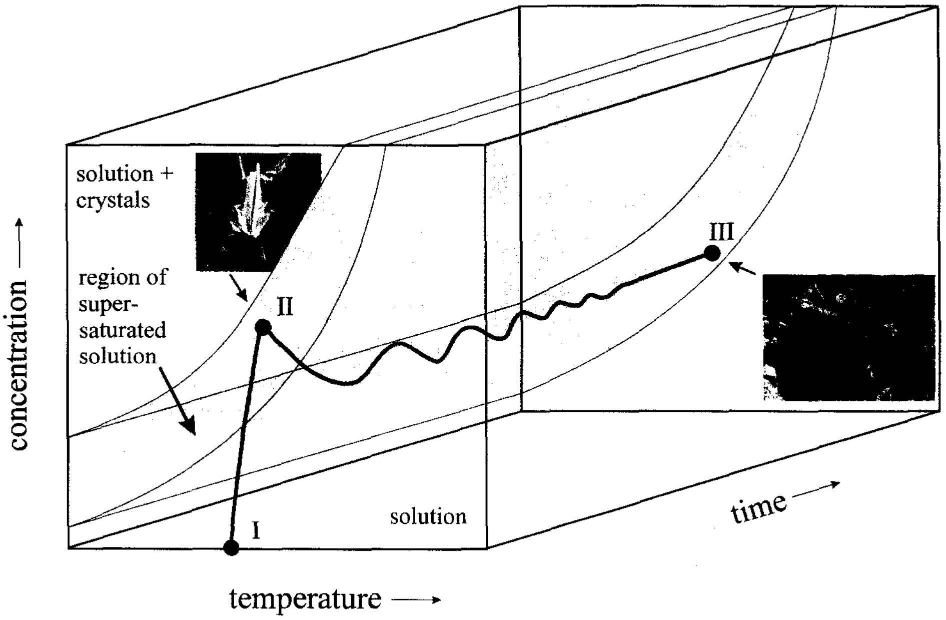


Fig. 9: Crystallization process during the high-pressure hydrothermal synthesis.

Fig. 10: First state of zeolite crystal formation by growth of nuclei on glass surface.

Fig. 11: Simultaneous dissolution of glass (right hand side) and recrystallization to zeolite (left hand side) under hp-hydrothermal conditions.

process - which means the supersaturation grows, or the zeolite crystallization is faster than the precursor glass dissolution, which means the supersaturation is reduced. Therefore, under dynamic equilibrium conditions an oscillation of concentration will be observed. Only if the supersaturation gets too high new spontaneous crystallization occurs. This leads to a second crystal generation as can be seen in figure 7. If, in opposite to this, for any reason during the process the lower supersaturation border is arrived, the crystal is again dissolved.

The solving medium water is not inert with respect to the formed zeolite phase, it takes part in the synthesis process and is built into the cavity systems. In the end, dependent on synthesis time, temperature and pressure, microscopic crystals of the desired zeolite phase are formed (Fig. 9, point III). The scanning electron microscopy image in figure 11 shows the dissolution process of an educt glass while the zeolite phase is formed at the same time.

Two main methods for zeolite characterization synthesized by this method are used. The first, X-ray diffraction (XRD) has however, some disadvantages. First of all, if several phases are present which superimpose, it becomes rather difficult to determine the desired zeolite phase. Secondly if only very less material of the desired phases is formed by synthesis, it can not be distinguished by XRD, because of the low detection limit of approximately 5% for the respective phase by this method.

An alternative and supplementary method of microcrystal examination is applicable caused by the special synthesis conditions. The hp-hydrothermal synthesis leads to idiomorphous crystal formation with equilibrium faces. This means that the morphology of the crystals and, therefore, the face angles of crystals reflect the inner lattice geometry [31]. Microcrystals can, therefore, be examined by the stereo-comparator method [32, 33]. With this method, the direction of a face normal vector of a microcrystal can be determined by means of stereo-images taken by SEM and evaluated by a special fabricated stereo-comparator (ZEISS-JENA). The normal vectors of all different crystal faces of a respective crystal can be determined in this way and be related to each other. With these results a crystallographic indexing of crystal faces as well as the determination of the crystal system of a microcrystal is possible [32]. This method is very often applied in examination of the hp-hydrothermal synthesis products.

Systematic investigations on the reconstruction of the natural formation conditions of zeolites showed a change of crystal habit dependent on temperature of synthesis. The special growth conditions are responsible for this behavior, which can also be observed for other, non zeolite crystals in general. The temperature range of hp-hydrothermal synthesis can be seen during the synthesis of zeolite laumontite (LAU-type), from glass of laumontite composition, which was formed under 1kbar water pressure in a temperature range between 30°C and 450°C, the maximum temperature of synthesis, during 42 days (Fig. 12, [29]). As crystallization is a dynamic process, the field of existence of a specific zeolite is limited in time, temperature and pressure as can be seen for zeolite stilbite in figure 13, [34]. Stilbite is formed from glass of stilbite composition at one kbar water pressure, within synthesis times of 42 days in the temperature range 155°C to 365°C. These long synthesis times were chosen to obtain crystalline phases under almost equilibrium conditions. Above 240°C stilbite is successively substituted by sodium bearing wairakite, a zeolite of ANA type framework with similar chemical composition but a higher framework density and a narrow sized channel system. The field of existence at a given synthesis pressure is however not only dependent on temperature. After longer synthesis times kinetic effects will lead in case of stilbite to wairakite transformation by a complete dissolution - recrystallization process which can be

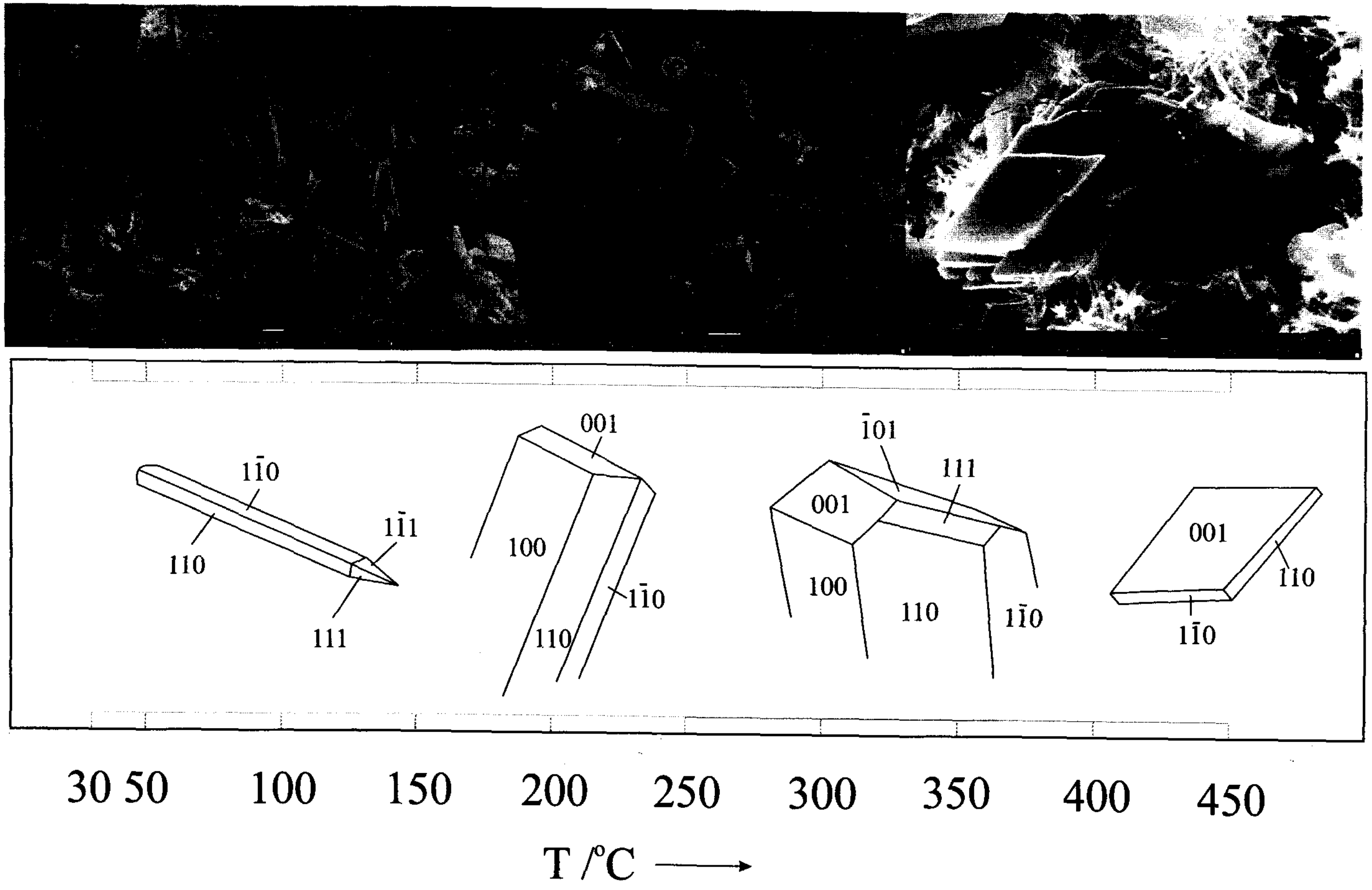


Fig. 12: Synthesis of zeolite laumontite (LAU) from glass of LAU composition in a temperature range between 30 and 450°C (note: only morphological change, phase angles and symmetry keeps constant (monoclinic), 1kbar water pressure, 42 days).

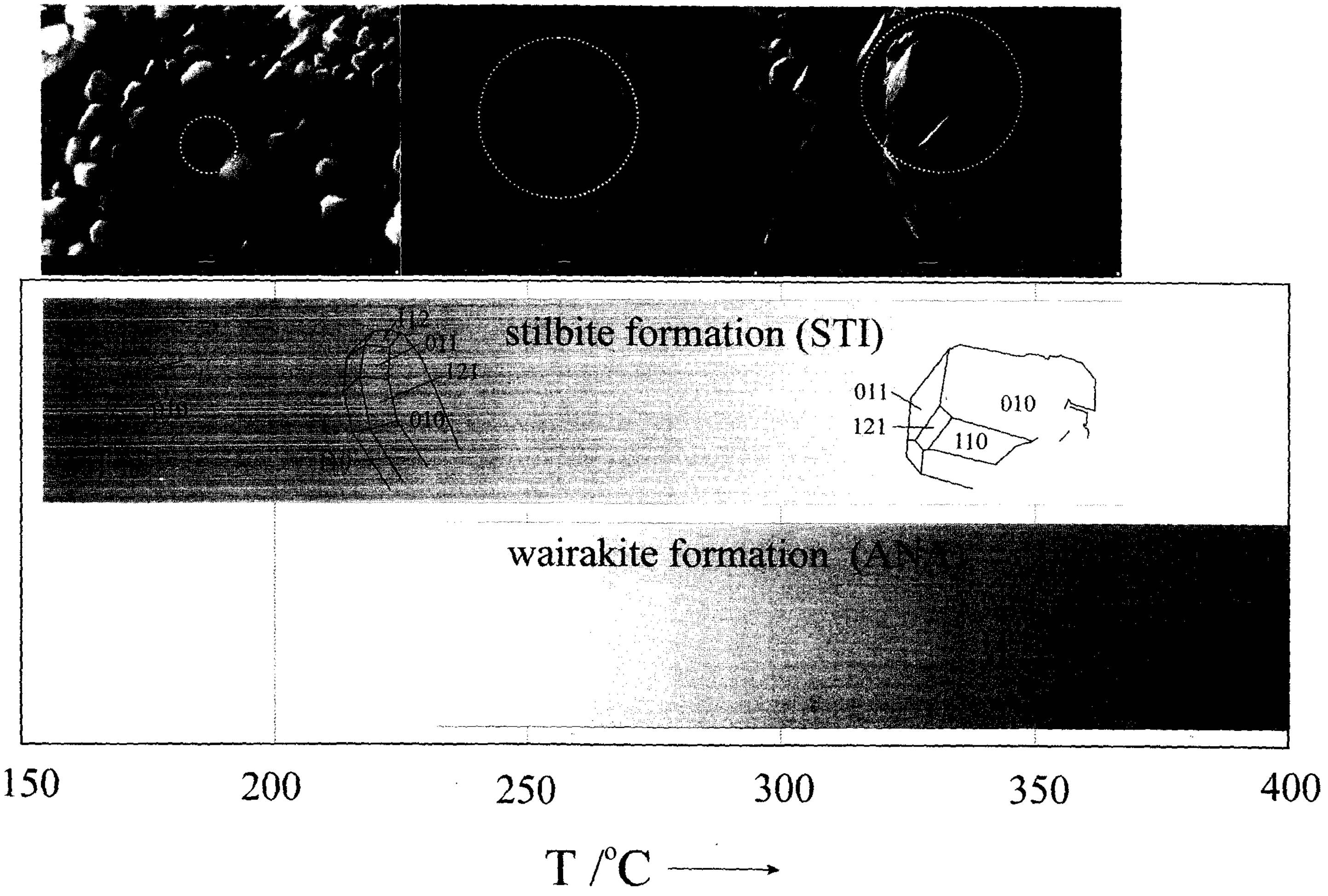


Fig. 13: Effect of temperature on the synthesis of stilbite (STI) from glass of STI-composition (note: only morphological change, phase angles and symmetry keeps constant (monoclinic)), and phase transformation effect to a zeolite with similar stoichiometry but higher density (1kbar water pressure, 42 days).

seen by the lack of intergrowth of stilbite and wairakite and the formation of hopper crystals of stilbite at the highest synthesis temperature (365°C, see Fig. 14). Therefore it must be concluded, that zeolites like stilbite are only existing as kinetically favored metastable phases as the thermodynamic stability of wairakite is a little higher - although starting STI dissolution was not observed. In ihis case, after very long synthesis times (which are not relevant for practical purposes), thermodynamically more stable denser phases (zeolite or non zeolite tectosilicate) are formed.

Zeolites synthesized by the high pressure hydrothermal process are, however, in a certain time-temperature window, formed under equilibrium like conditions as the nuleation is performed without seeds and the crystal growth process continues until the physico-chemical conditions are altered.

The use of synthetic glasses of the respective zeolite composition as staring material is also a useful tool for zeolite synthesis with tailored channel size. The hp-hydrothermal synthesis method makes it possible to synthesize the whole spectrum of alumosilicate zeolites known today of channel diameters between maximum known values of 7.4Å for zeolite faujasite (FAU-type) and wairakite (ANA-type) with small irregular channels of about 1.6 x 4.2Å diameter (see table 1). A cross section of synthesis examples is shown in Fig. 15a) and 15b). Some of these selected zeolites like stilbite and laumontite have never been synthesized by other methods before [29,34–42].

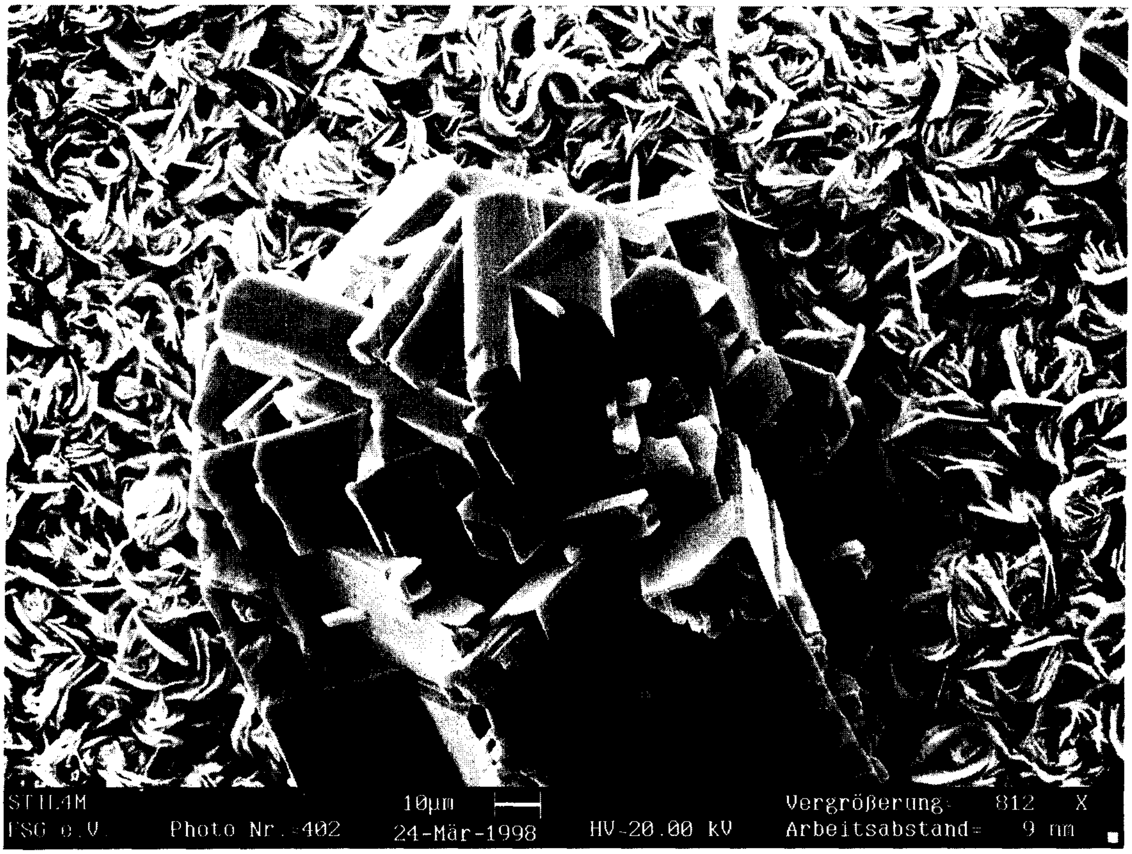


Fig. 14: The formation of hopper crystals by dissolution of STI (365°C, 42d of synthesis)

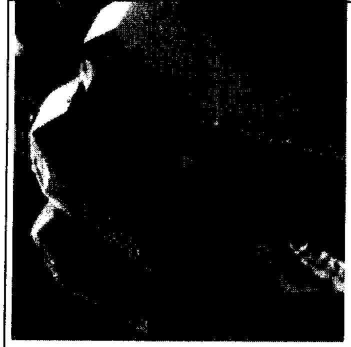
	**FAU** faujasite, cubic <111> **12** 7.4*** glass composition = zeolite composition: $Na_{20}Ca_{12}Mg_8(Al_{60}Si_{132}O_{384}) \cdot 235\ H_2O$ $Fd\bar{3}m$, z = 1 $a_o = 24.60Å$ magnification: 141x, (111)-faces of crystal
	**GME** gmelinite, hexagonal [001] **12** 7.0* ↔ ⊥[001] **8** 3.6 x 3.9** glass composition = zeolite composition: $Na_8(Al_8Si_{16}O_{48}) \cdot 22\ H_2O$ $P6_3/mmc$, z = 1 $a_o = 13.75Å$ $c_o = 10.06Å$ magnification: 454x, pyramid faces of crystal in anti-clockwise order (3 of 6) starting with darkest face in front: $(2\bar{1}\bar{1}2)$, $(10\bar{1}1)$, $(\bar{1}2\bar{1}1)$, etc.
	**OFF** offretite, hexagonal [001] **12** 6.7* ↔ ⊥[001] **8** 3.6 x 4.9** glass composition = zeolite composition: $KCaMg(Al_5Si_{13}O_{36}) \cdot 15\ H_2O$ $P\bar{6}m2$, z = 1 $a_o = 13.29Å$ $c_o = 7.58Å$ magnification: 2070x, up: (0001)-face, prism faces in anti-clockwise order (3 of 6) starting with darkest face in front: $(1\bar{1}00)$, $(01\bar{1}0)$, $(01\bar{1}0)$, etc.
	**STI** stilbite, monoclinic [100] **10** 4.9 x 6.1 ↔ [101] **8** 2.7 x 5.6* - IZA setting glass composition = zeolite composition: $NaCa_4(Al_9Si_{27}O_{72}) \cdot 30\ H_2O$ C2/m, z = 1 $a_o = 13.61$ $b_o = 18.24$ $c_o = 11.27$ (Å) β = 127° 51′ magnification: 2000x, top: (010)-face, upper side faces in clockwise order starting with face in front: (110), (121), (011), $(\bar{1}12)$.

Fig. 15a): Tailored synthesis of Zeolites of different channel size (IZA = International zeolite association).

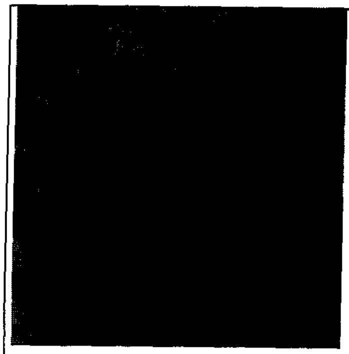
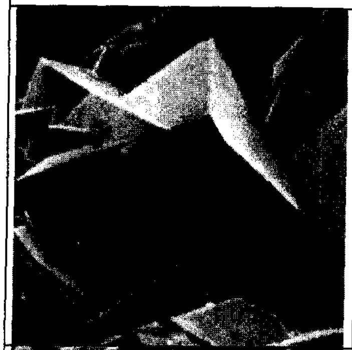
	**LAU** laumontite (leonhardite), monoclinic [100] **10** 4.0 x 5.3* glass composition = zeolite composition: $Ca_4(Al_8Si_{16}O_{48}) \cdot 16\ H_2O$ C2/m, z = 1 a_o= 15.04Å b_o= 13.17Å c_o= 7.71Å β = 113° 12′ magnification: 4640x, top: (001)-face, side faces in anticlockwise order starting with face on the left: (100), (110), $(\bar{1}10)$.
	**GIS** gismondine, monoclinic {[100] **8** 3.1 x 4.5* ↔ [010] **8** 2.8 x 4.8}* glass composition = zeolite composition: $Ca_4(Al_8Si_8O_{32}) \cdot 16\ H_2O$ $P2_1/c$, z = 1 a_o = 10.02Å b_o = 10.62Å c_o = 9.84Å β = 92° 25′ magnification: 69x, pyramid faces (110), (101), etc.
	**THO** thomsonite, orthorhombic [101] **8** 2.3 x 3.9* ↔ [010] **8** 2.2 x 4.0* ↔ [001] **8** variable - IZA setting glass composition = zeolite composition: $Na_4Ca_8(Al_{20}Si_{20}O_{80}) \cdot 24\ H_2O$ Pcnn, z = 1 a_o = 13.05Å b_o = 13.09Å c_o = 13.22Å magnification: 2000x, top: (001)-face, front faces in anticlockwise order starting with face in front: (010), $(\bar{1}10)$.
	**ANA** wairakite, cubic [110] **8** 1.6 x 4.2*** irregular - IZA setting glass composition = zeolite composition: $Ca_8(Al_{16}Si_{32}O_{96}) \cdot 16H_2O$ Ia3d, z = 1 a_o= 13.64Å magnification: 1470x, central face: (111), central to down left: (211), (100), etc.

Fig. 15b): Tailored synthesis of Zeolites of different channel size (IZA = International zeolite association).

Not only the tailored synthesis of zeolites of different SBU groups having different channel and cage systems is possible, but also the hp-hydrothermal synthesis of zeolites of the same group, with the same kind of building units [43] and also the same kind of cavity systems [44, 45]. Two examples are shown, the synthesis of GIS-type zeolites gismondine, amicite, garronite and gobbinsite and the synthesis of STI-type zeolites stilbite, stellerite and barrerite (see Fig. 16 and Fig. 17, [44, 45]. These zeolites of respectively the same group belong to the same framework and differ mainly in chemical composition. By the presented synthesis method it could therefore be shown that these zeolites form solid solution series.

Table 2 shows ideal chemical compositions of some alumosilicate based zeolites (data from Gottardi and Galli [5] and Gmelin inorganic crystal structure database, here: zeolites [21]). All zeolites of these given compositions but even more, can be synthesized by hp-hydrothermal synthesis method in principal using a precursor glass of the given stoichiometry.

Synthesis temperature however does not only influence the crystal habit of hp-hydrothermally synthesized zeolites but also the (Si, Al)-order of the framework. Gottardi and Galli [5] found different symmetries of natural zeolite analcime (ANA type framework) and also, correlated with symmetry, gradually different (Si, Al) ordering within the framework. Triclinic analcime was completely odered, while the (Si, Al) order was lowered with rising symmetry: orthorhombic, tetragonal and cubic. Cubic analcime crystals were found to have a completely disordered (Si, Al) distribution. Our results of synthesis showed that (Si, Al) ordering, and therefore, crystal symmetry is effected by temperature (see Fig. 18). At lowest synthesis temperatures the lowest symmetries and therefore a maximum order of framework cations can be found, while the disorder proceeds gradually with rising synthesis temperature under isobaric synthesis conditions [41,46–48]. These effects are possible as the synthesis process takes place under, sometimes even metastable, equilibrium conditions. Changes in crystal symmetry of alumosilicate zeolites are therefore mostly correlated with order-disorder effects in the framework, but sometimes cation distribution in the channel and cage system as well as present water content also plays an important role (Ref. [5] and references therein, [44]).

Disadvantages of the high pressure hydrothermal synthesis process compared to conventional sol-gel processes like e.g. the necessity of precursor glass preparation, long reaction times or the use of high pressure autoclaves are always overcome in industrial sized synthesis where the whole process is, of course, technically and economically optimized. This can be seen in the production of quartz resonators by a similar hydrothermal process, the production of ammonia from air, etc., etc.

4. Application of zeolites

4.1 Common zeolite applications

Zeolites have basically become interesting because of their applicability in almost all fields of human life where chemical, biochemical, and physicochemical processes are taking place. They can be used for purification of gaseous as well as liquid mixtures and solutions by sorption, sieving and filtering, for storing of molecules, for ion exchange purposes and catalysis under non oxidizing and oxidizing environments. All these zeolite applications using natural and synthetic zeolites show certain advantages but also certain disadvantages of the

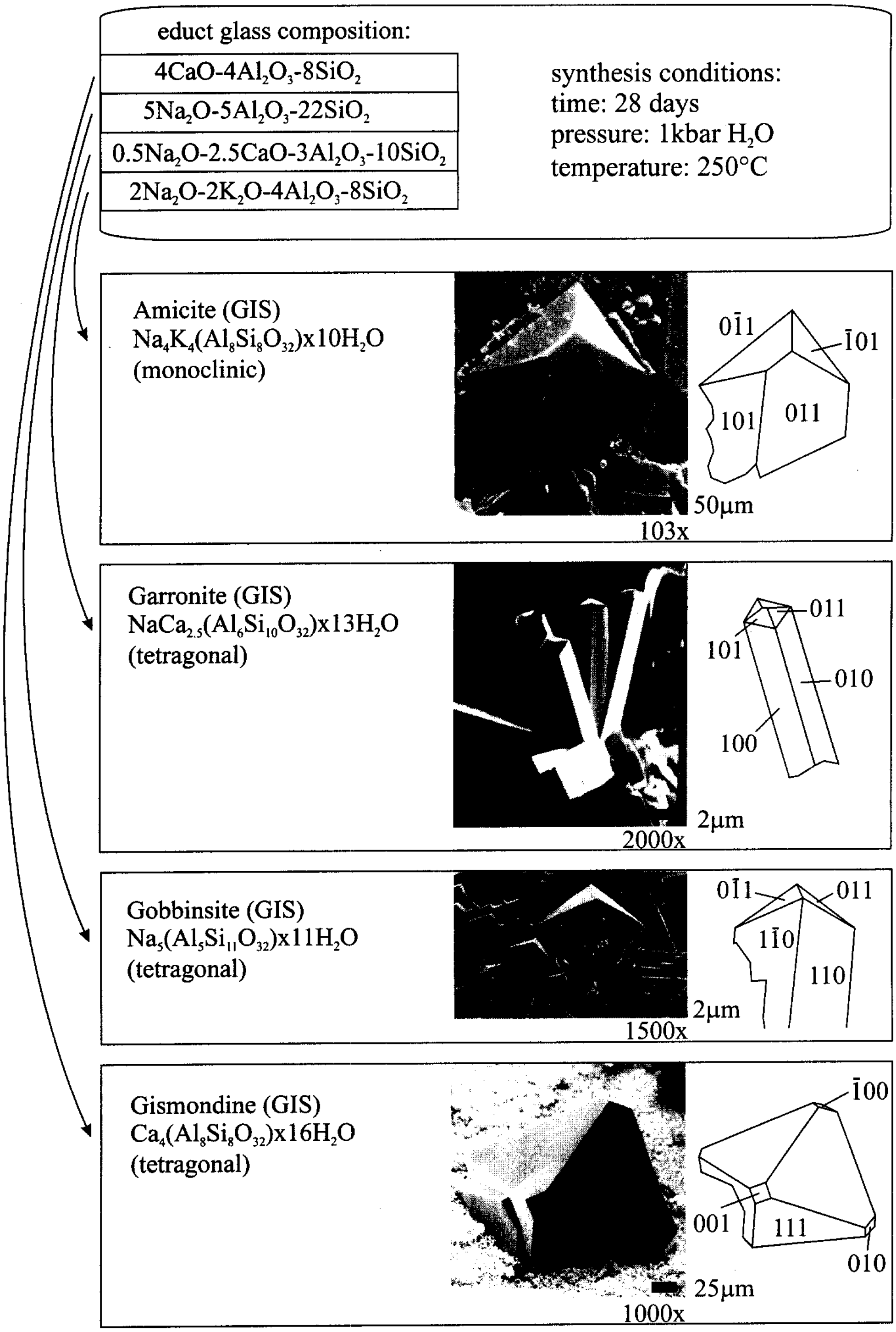


Fig. 16: Effect of chemical composition on gismondine (GIS) type zeolite synthesis by hp-hydrothermal conversion of the respective educt glass (44).
]

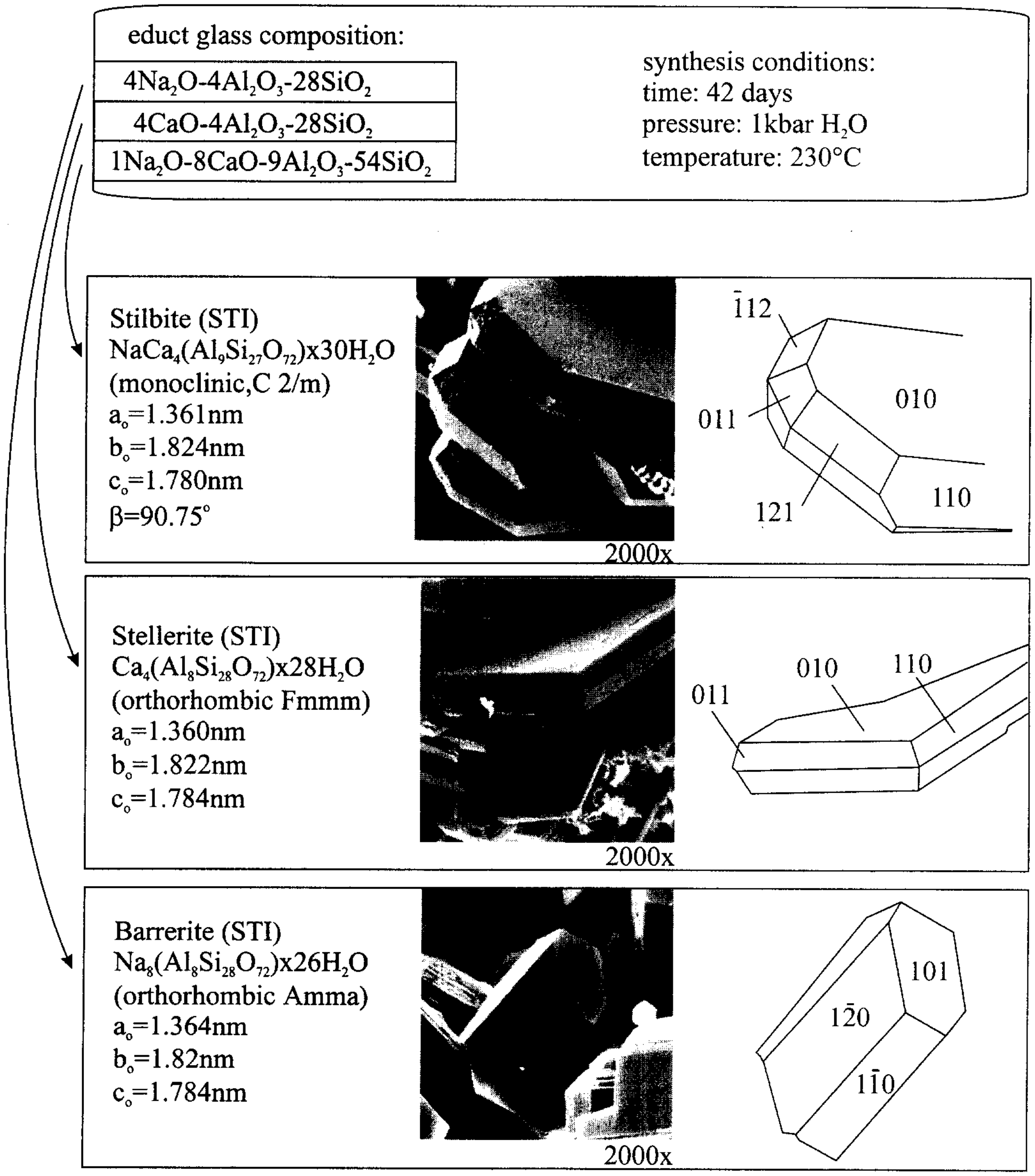


Fig. 17: Stilbite (STI) type zeolite hp-hydrothermal synthesis by change of educt glass composition (45).

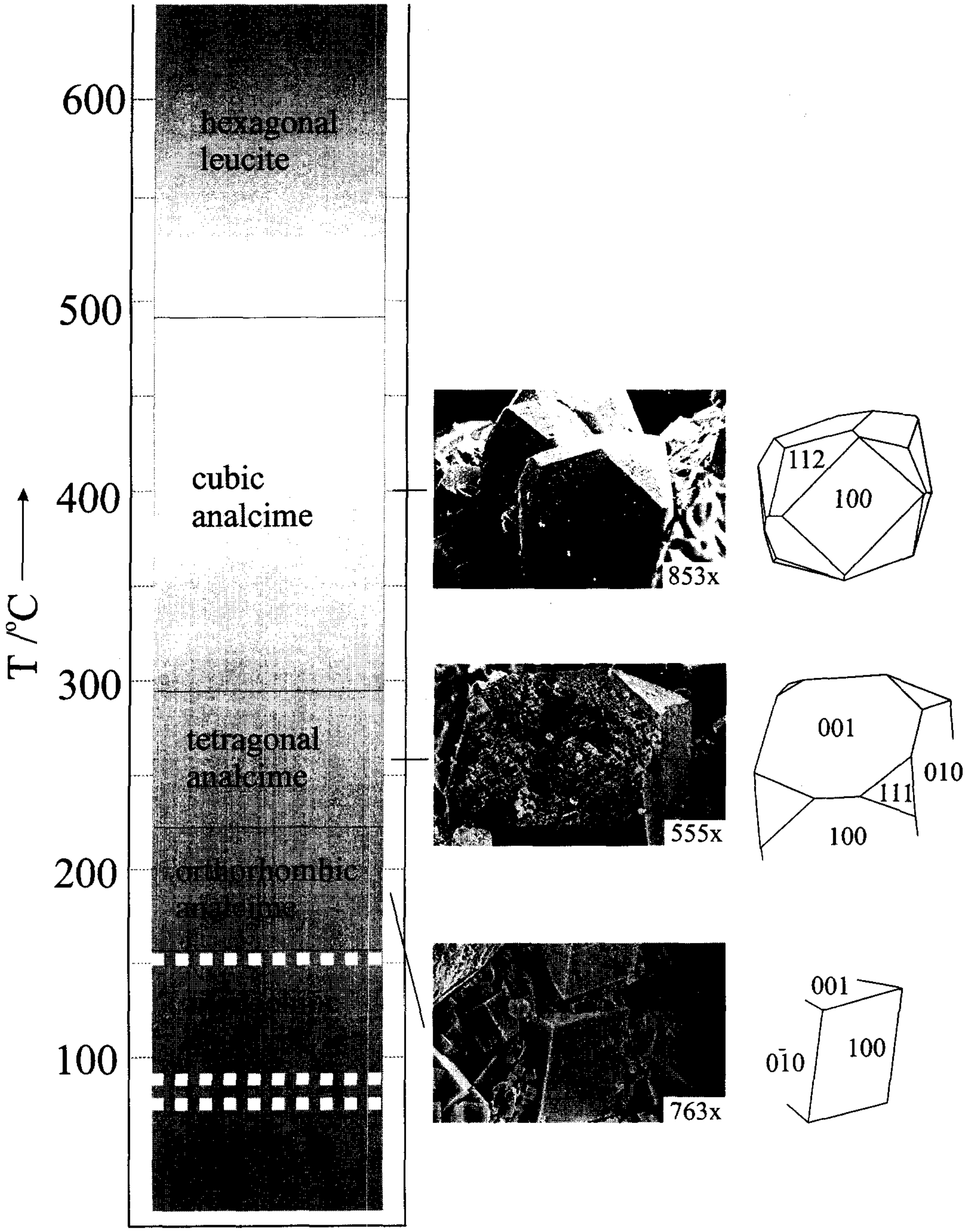


Fig. 18: Temperature effect under isobaric hp-hydrothermal synthesis conditions on crystal symmetry of analcime (48).

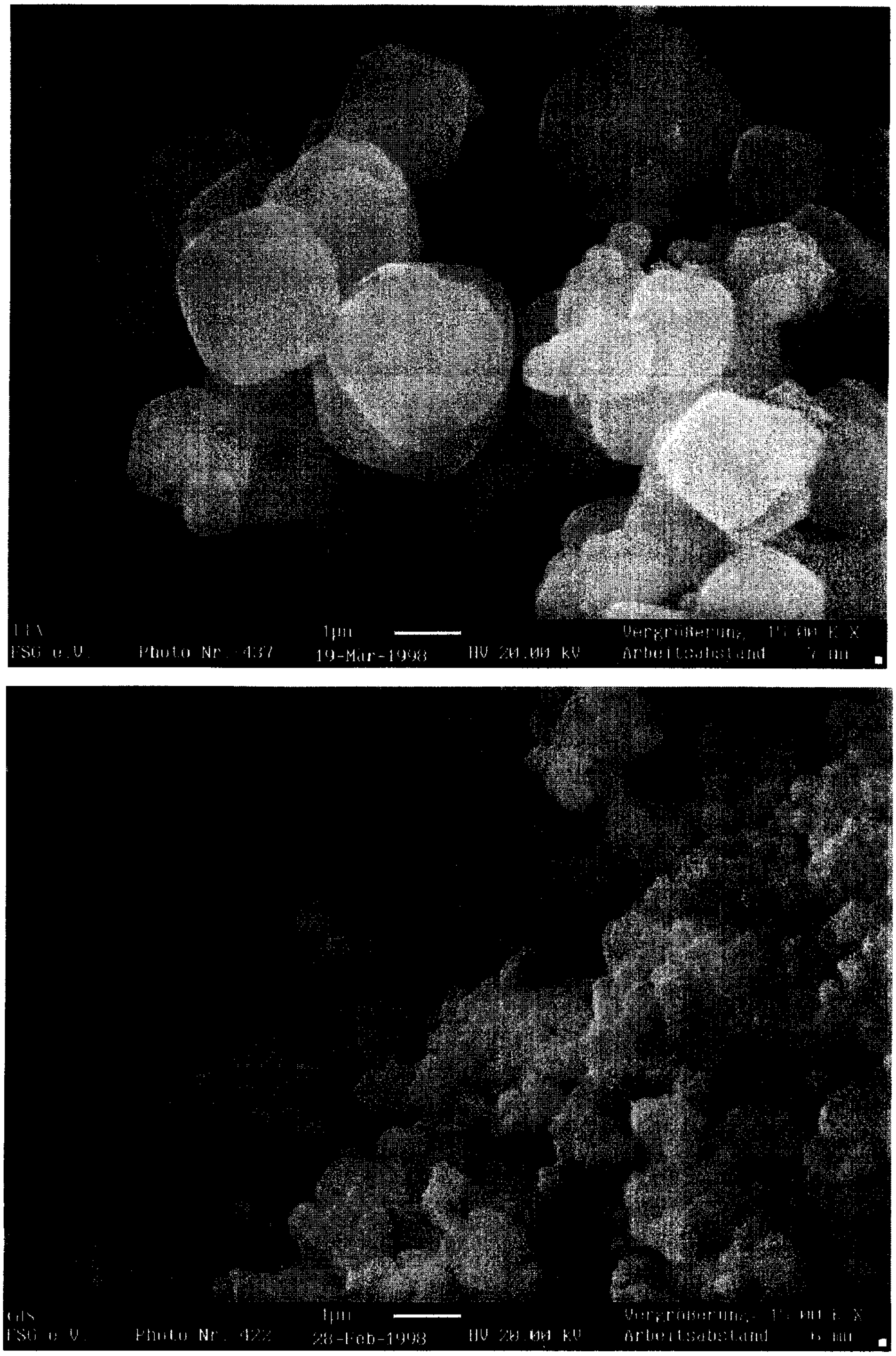


Fig. 19a), b): Soap powder zeolite LTA (above), soap powder zeolite Na-gismondine (below)

respective materials applied. Therefore the tailored synthesis of zeolites allows modifications, optimizations and extensions of hitherto existing zeolite application fields.

Today nearly everybody in highly industrialized countries is in touch with zeolites as their application fields already start in kitchen where zeolites have almost completely substituted polyphosphates in softening water for washing purposes. Nowadays not only the alkaline earth ion Ca but also Mg, both mainly responsible for the deactivation of soap powder, can be removed from washing water by ion exchange. In soap powders mainly synthetic alumosilicate zeolites Linde Type A (Na -LTA) and Na-gismondine (GIS) have been applied for these purposes. The zeolite materials are removed from the laundry by the washing process itself and are insensitive to environment (Fig. 19 a), b)). Na-LTA can be found in softening powders for dishwashers, immobilized by titanium-silicate fibers to avoid acess to the dishwashing chamber (see Fig. 19 c)). LTA is also applied in water treatment for households and in water treatment plants for the removal of heavy metal ions from solution by ion exchange. Also other zeolites with medium sized windows like synthetic zeolites ABW (Zeolite A-Barrer-White), gismondine (GIS), natrolite-type (NAT) and natural and synthetic phillipsite (PHI) are applied in this field. Zeolites have also been applied for sweetening of ocean water but until now only in small quantities. These medium window sized zeolites can also be applied for the removal of ammonia from drinking water and municipal wastewater to a quite safe level, removal of heavy metal ions in mine wastewater and for the removal of radioactive fission products cesium and strontium as ions during the treatment of radioactive waste water [13,49,50]. In this respect, zeolites are selective, radiation stable and show a high cation exchange capacity.

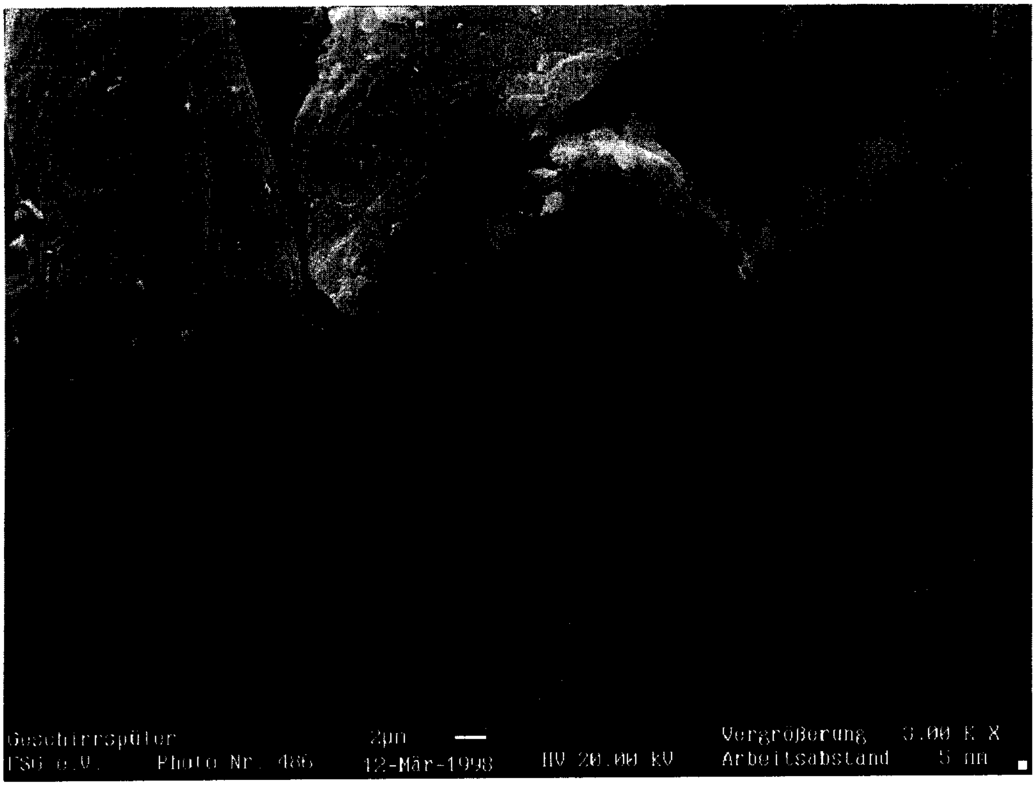


Fig. 19c): Dishwasher zeolite LTA (poorly crystallized, remaining gel phase) with Ti-silicate fibers to inhibit migration.

Activation of zeolites for sorption purposes is commonly done by evacuation by heating or in a combined process. The high and reversible sorption capacity of activated zeolites for water, which is up to 25% of weight, is also applied in many fields of everyday life. It can be used for considerate drying of food in households and for conservation purposes of food by drying in general. Not only water is absorbed and built into the structure of these medium sized zeolites, they can also remove odors in households, bureaus and in industrial processes by absorption. Zeolites can therefore specifically remove indoor pollutants like formaldehyde, chloroform and ammonia. Recently zeolites have been modified in industries in order to absorb especially organic compounds. They can be fixed on polymers in order to absorb odors and tastes. All of these processes are reversible and make zeolites a powerful tool in everyday life.

Natural zeolites sometimes occur in huge masses and are cheaper and than sol-gel derived synthetic but there is often the problem of impurities - sometimes also toxic ions like Ba are present in the channel system. Until now some of the natural zeolites could not be synthesized in large quantities necessary for application but some application fields have opened yet. Natural zeolites like clinoptilolite (HEU), scolecite (NAT) and others have been applied for soil fertilizing purposes. In general, soils can be improved in this way as theses zeolites are able to submit ions of potassium and ammonium in small necessary quantities and constant rates. Phosphate ions can also be released in a controllable way under influence of zeolites, while the high water absorption ability reduces the need to water frequently [51].

Further advantages are, that these processes are reversible and the use of solvable fertilizers polluting water is avoided while soil intoxication by sodium containing zeolites can be avoided using potassium or calcium zeolites as starting materials.

Synthetic sodium alumosilicate zeolites have also been applied in the nutrification of animals where it improves health and yield of cattle, pigs, sheeps and birds [50]. Fed zeolites are completely non toxic while it is assumed that they store sugars during the digestion process in a positive way. All of theses application fields are directly or indirectly bound to human households.

Zeolites are commercially applied for air-purification purposes - separation of CO_2 and H_2O from the air gas mixture but the main purpose of zeolite application in this field is the separation of O_2 and N_2 [52,53].

In chemical industries zeolites have become extremely important in the field of separation of azeotropic solutions [13], solutions with one boiling point consisting of different compounds.

They are also used for highly effective gas separation of organic gas mixtures by specific adsorption [13], main industrial application fields however are catalytic processes.

Under oxidizing conditions involving O_2, ZSM-5 type zeolites (MFI) have been applied in the field of NO_x abatement [54–56].

In catalyst application in petrochemical industries, zeolites have become indispensable as today almost all gasoline is produced with the help of zeolites [13,57–61].

Only some zeolites of mainly a few zeolite structure types have been applied for these purposes yet. Mordenite-type zeolites (MOR), Linde X- and Y-type (FAU), ZSM-5-type (MFI), ZSM-57-type (MFS), ZSM-20-type (FAU/EMT-intermediate), beta-type (BEA), ferrierite-type (FER), gismondine-type (GIS), A-zeolite-type (ABW) and Linde type A (LTA) are the most commonly used zeolites for catalysis in the field of conversion of organic molecules (liquid and gaseous hydrocarbons). For these purposes the zeolites are specially treated [62] in order to maximize the proton content in the cavity system and regarded as "solid acids". Partial substitution of framework Si and the exchange of cations in the void system are sometimes combined with these properties [63]. Using the respective zeolites "shape selectivity" in different aspects [63], they are in general applied at process temperatures mostly higher than 150°C. Zeolitic water is almost completely missing under these conditions.

As usually gaseous and fluid hydrocarbons without OH groups are non polar, the interaction with hydrophilic zeolites like those based on high Al containing alumosilicates is inhibited caused by their high cavity polarity. In addition, high alumina zeolites are quite unstable in the protonated form. Therefore, these processes are optimized reducing the zeolite hydrophility by tuning the of Si/Al ratio and the development of low-alumina (high silica, all silica) zeolites. In this field, non alumosilicate materials mainly based on phosphates play their dominant role in application.

In petrochemical industries two main fields can be distinguished. Fuel production is the commercially most important part and here, in oil refining, zeolite catalysts are used in order to obtain the maximum conversion of crude oil residue after distillation to fuel with specific properties. In chemical industries based on oil, zeolites catalysts have substituted non zeolitic materials since the 1960´s for the manufacturing of educts, pre-products, components for further processes and special chemicals itself. A few thousand publications and more than 6800 patents scattered over the world deal with these topics of zeolite application.

As mentioned above, the oil refining industry is the bigger part and the number of catalytic processes here is restricted compared to the rest of petrochemical industry (see also Refs. [63,64].

In principal, zeolites are used in oil refining industries for:

- Hydrocracking
- catalytic cracking
- dewaxing
- hydrotreating dewaxing
- hydrotreating reforming
- isomerization
- oligomerization
- aromatization of olefins

The zeolite catalyst lifetime in these processes lies between a few months and several years. Depending on the special process and the zeolite species applied, deactivation is basically caused by sintering and thermal deactivation, poisoning (mainly coking), fouling, phase transformations and vapor transport. Only in some cases a zeolite reactivation is possible.

4.2 Application in science

4.2.1 Fields of previous investigations

The experience of presently known research and application shows the potential and the frontiers of what has been done with zeolites yet based on the zeolite materials available.

The main fields of basic research on zeolites today are directed to the understanding of structure related properties. Structure analysis is done by X-ray and neutron diffraction (powders and single crystals [56]], additional information on water positions in the structure and on sorption properties are obtained by Thermal Analysis Methods [66]. Information on the chemical environment of cationic species in the framework are obtained by Nuclear Magnetic Resonance (NMR), in case of some cations also information about the chemical configuration within the channel system could be obtained by this method. Infrared spectroscopy delivers further information on this topic. Scanning electron microscopy (SEM) gives information about morphology, intergrowth and, by stereo comparator evaluation, also about the crystal symmetry. Atomic force microscopy (AFM) is able to visualize crystal surface properties with window openings in zeolites under in situ conditions. Transmission electron microscopy (TEM) can show window openings even with higher resolutions. Additional information on the sorption properties are obtained by BET method. Chemical analysis are done directly by Energy Disperse X-ray analysis (EDX) or similar methods, while methods like Atomic Absorption Spectroscopy (AAS) deliver batch chemical compositions with higher accuracy but no local resolution.

The main applied research on zeolites has been done in the existing application fields already described: ion storage and exchange for many purposes, absorption, storage and exchange of small molecules in gaseous or liquid environment and catalysis under reducing and oxidizing conditions. These are the main topics for zeolite application in industry and, therefore, also in zeolite research today.

Further investigations have basically to keep in mind under which physico-chemical conditions which species (ion or molecule) can be put into the zeolite structure and which species should be moved out of the structure. Based on this, the potentials and frontiers of application of today existing zeolites have to be evaluated. There are many new corners and niches for industrial applications of zeolites that have not been covered yet because the scientific community was not interested in yet. We hope that the proposed application fields will cause interest by research and industry in the future. A tailored synthesis of zeolites for a respective application has to start at this point.

4.2.2 New investigations in the field of zeolite research

The most important step in the specific application of zeolites is the clarification of the fundamental processes and basic interactions taking place in the channel and cage systems related to ions and molecules accessing the zeolite cavity system. If these processes are understood, new application fields will be possible and existing fields will be deepened and widened if zeolites with the properties needed are available.

Because of their high water sorption properties zeolites are applied in science for drying purposes of organic liquids. Polarity, shape selectivity and stability of the respective zeolite and its cavity system with respect to chemical influences make them very suitable for these purposes. By the modification of these absorption properties for specific absorption of polar aliphates like ethanol, zeolites are applicable for the removal of alcohol in drinks. Research in this field would be an important step for a ´softening´ of drinks as it is assumed that alcohol e.g. in wine and beer does not influence the taste of these products if the ethanol component is only removed without any further process like heating etc.

Another new research fields based on hp-hydrothermally tailored synthesized zeolites is the storage and cracking of in vivo components like e.g. sugars as additives for food (optimized gain of food). New research on zeolite application must be done in the field of organ substitution in medicine for:

self controlled artificial liver (storage and conversion of hydrocarbons)

artificial lung ("breathing" behavior of zeolites: reversible selective adsorption of CO_2)

artificial heart (use of piezoelectric zeolites)

artificial blood (transport of hydrocarbons, body supply with O_2 and removal of CO_2 with much higher effectiveness than hemoglobin.)

artificial kidney (in vivo membranes which allow the separation of blood and metabolic products like urea)

Zeolites are until now only applied to regenerate artificial dialysis solutions [67].

The removal of urea in a recycling process of water under in vitro conditions is also interesting for specific applications (see below).

Another approach is the application of zeolites as catalysts in multiphase reactions in liquid media to prepare fine chemicals and biochemicals [68,69]. The substitution of enzymes by zeolites in the field of biochemical catalysis of molecules small sized with respect to zeolite window size can widen the application fields to higher temperatures with better performances (sterilizability, bio-inertness, etc.).

Further investigations should be performed in the improvement of functionalization of zeolites in respect to other substances.

Optical applications have yet been only of minor interest in zeolite research. The ion exchange capability for ions however, combined with their charge distribution within the void system and the optical transmittivity of the alumosilicate framework makes them very interesting as tunable luminescent materials [70–72] and materials with non linear optical properties [73].

First attempts have been made using the zeolite void system to incorporate dye molecules [71].

Only few has been done yet in the field of zeolites/zeolite host-guest systems as laser active materials [74-76] or proposed [77] as the specific properties of zeolites can be used for the trimming of the optical properties of the laser active component by changing the charge density and distribution in the void system in principal.

Optical transmittivity combined with their piezoelectricity makes zeolites especially used as small single crystals promising materials for optical switches. Again, zeolite specific properties like ion exchange capability and sorptivity allow the trimming of the switching behavior.

First steps have been performed using the optical absorption of modified zeolites dependent on cavity absorbed molecule species for sensing purposes [78]. Conductivity sensors based on polycrystalline zeolites have also been built for applications in the range of 300°C [79-81] and they have been applied for modified electrodes in aqueous solutions [70]. Sensors have also been built using the change in capacity during the adsorption process of zeolites [82, 83] and they have also been applied as microballance sensor component [84]. The piezoelectric properties of some zeolites however have not been applied yet.

The high pressure-hydrothermal synthesis method allows the acess to zeolite compositions and therefore zeolite properties not available by sol-gel processes. With the hp-hydrothermal synthesis Al and Si can be substituted in the alumosilicate framework by transition metals in such a way, that semiconducting zeolites with similar stability in aqueous solutions are formed [85]. It will also be possible to substitute alkali and alkaline earth ions in the cavity system for transition metal ions in order to obtain a coupled semiconductivity, from the framework as well as from the channel system [70,85]. These new kinds of zeolites can be applied as electrode materials in electrochemically enhanced catalysis/biocatalysis as well as for sensor elements for gas sensing selectivity by molecule polarity and shape) as for liquid sensing (selective ion-sensitivity caused by the cavity system). They can be used as electrochemically activable membranes, electrode materials and as sensor elements which is electrochemically trimable in selectivity. Together with specified conventional alumosilicate zeolites they can be used for electrochemically determination of component concentrations or as sensor element itself. The enrichment of harmful ions like arsenic and other heavy metals, for the trapment of insecticide residues and organic compounds (like DDT, benzene, etc.) with zeolite electrodes in aqueous media and also drinks (milk, wine etc.) is also possible.

Only some effort has been done to characterize the ionic conductivity behavior on single crystals and compressed powdered samples (Refs. [86–88] and references therein, [89–92]], but basic insight in the processes taking place is only possible using single crystal zeolites with the respective necessary specimen dimension. Polycrystallinity of "non ceramic" zeolites influences the conductivity paths as sorption and/or temperature influence the grain dimensions. Even the application of A.C. methods in conductivity research under these conditions can not guaranty the separation of grain surface conduction from grain and grain-boundary effects [93].

Basic measurements on conductivity under in situ conditions using single crystalline alumosilicate materials are quite difficult because of the permanent water loss. Figure 20 shows the desorption of water in different natural alumosilicate zeolites indicating the different crystallographic water positions within the cavity system. Under these dynamic conditions water loss of certain zeolites starts even at 50 °C. Not all zeolites do have conductivites high enough to be measured by methods available like impedance spectroscopy. Conductivity measurements on single crystals using impedance spectroscopy are however very sensitive to alterations of the system [30,94–97]. They show, that if water is present in the measuring chamber (in situ conditions), reproducible results can be obtained for these selected zeolites of different building principles and cage systems up to 110 °C (see Fig. 21). In general, a strong dependence of impedance of single crystalline zeolites on water partial pressure is observed (Fig. 22) while in contrast to other materials, for certain zeolites a growth of impedance with growing water partial pressure can be seen. Under equilibrium water partial pressures (in situ conditions), zeolite conductivity is not only sensitive to water but also to different other polar and non polar substances (see Fig. 23). This figure shows however, that zeolite conductivity is not only dependent on concentration of polar substances but also on the geometrical dimensions with respect to the zeolite channel system. The results of our

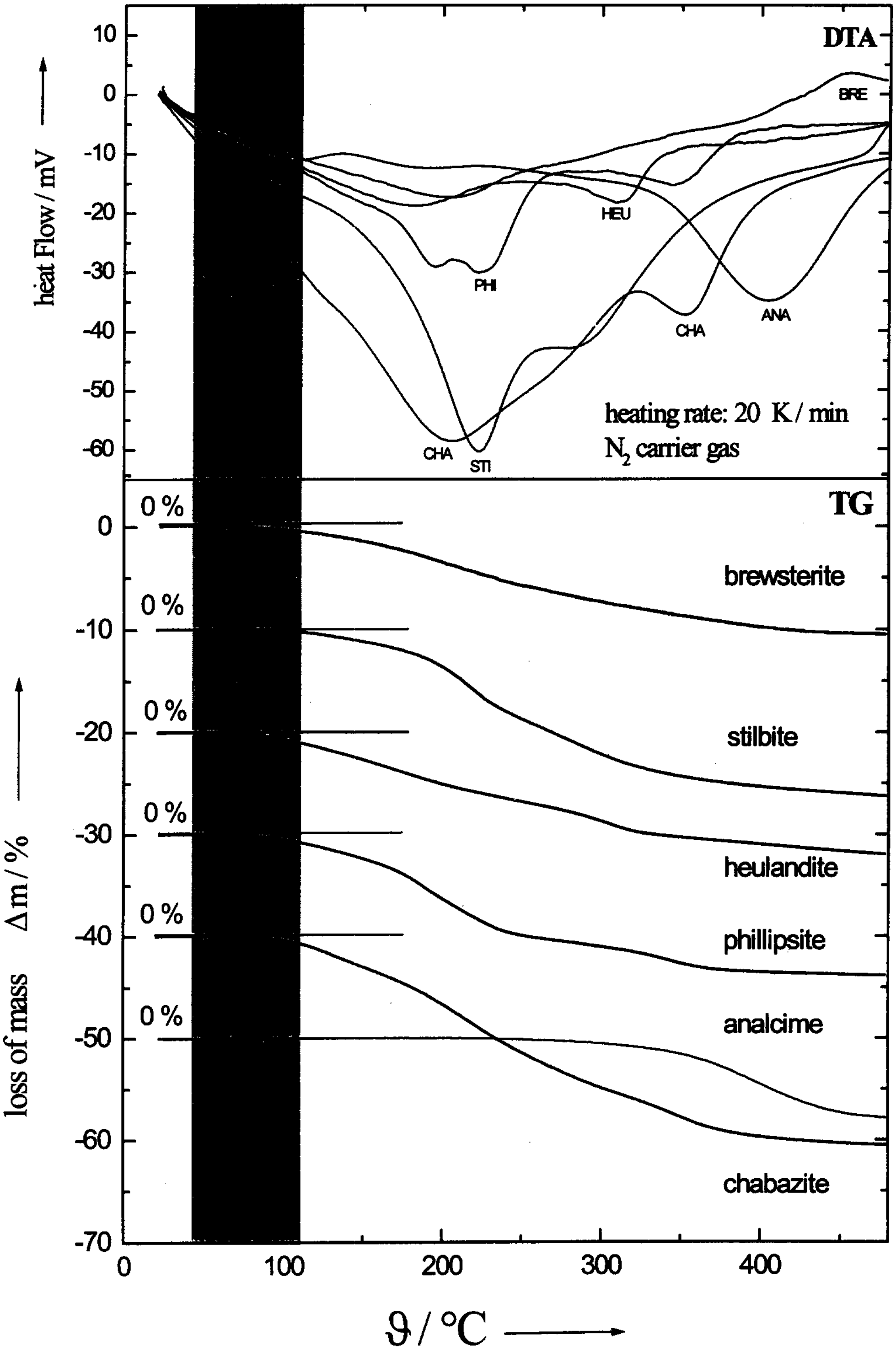


Fig. 20: DTA analysis of different zeolites, heating rate 20K/min, in nitrogen.

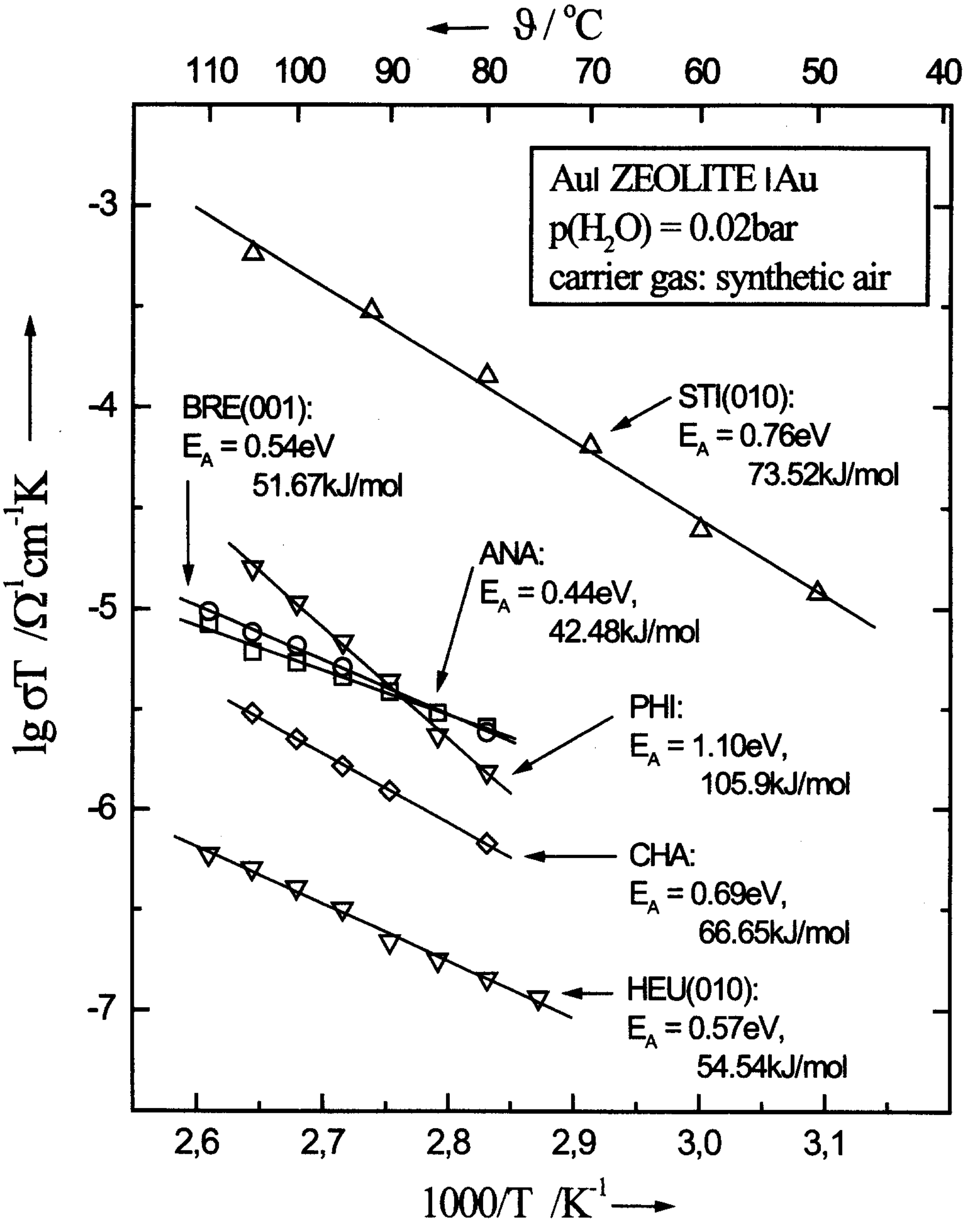


Fig. 21: The conductivity of zeolites of different channel size and systems under in-situ conditions

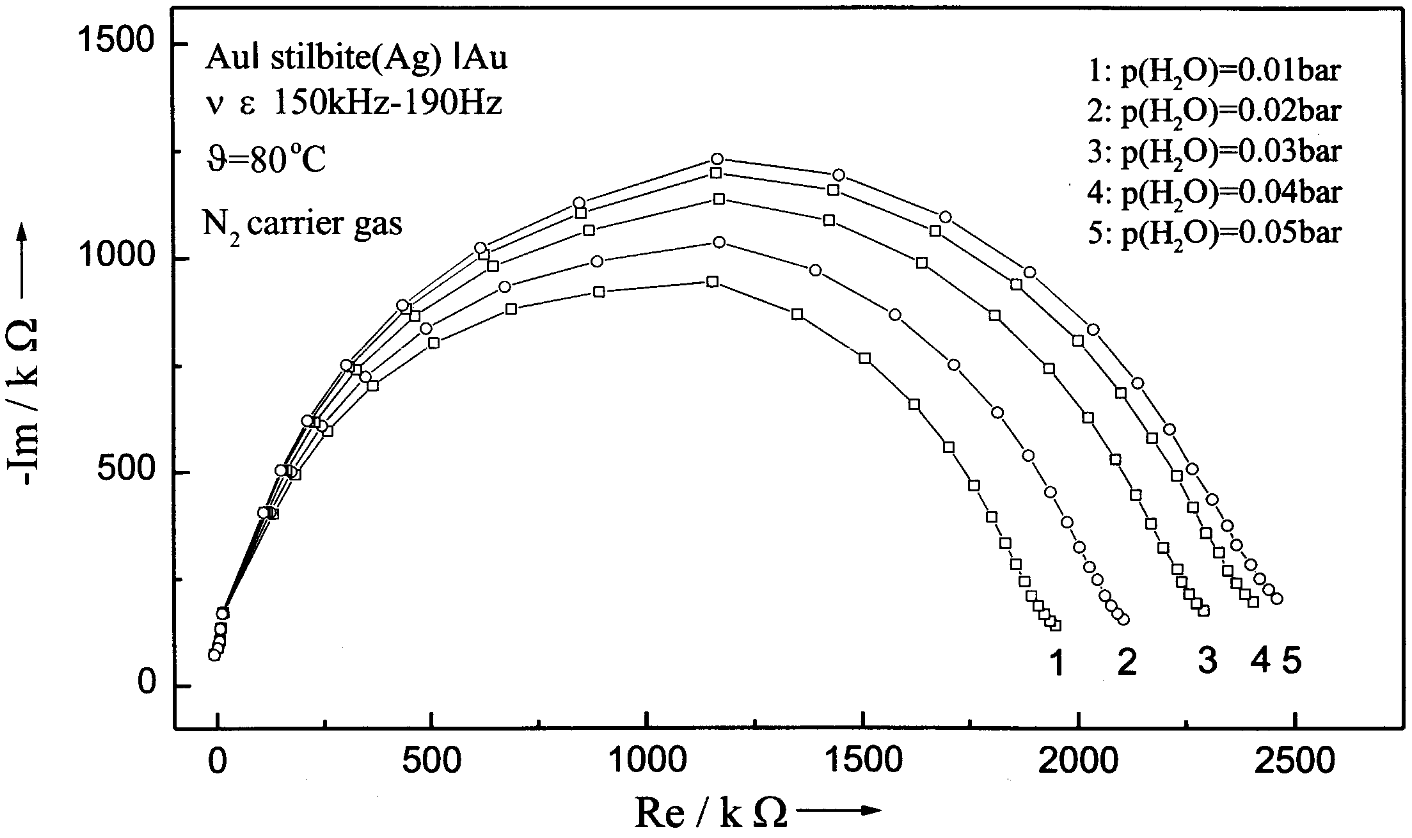


Fig. 22: Dependence of impedance of single crystal stilbite (Ag-exchanged) on water partial pressure.

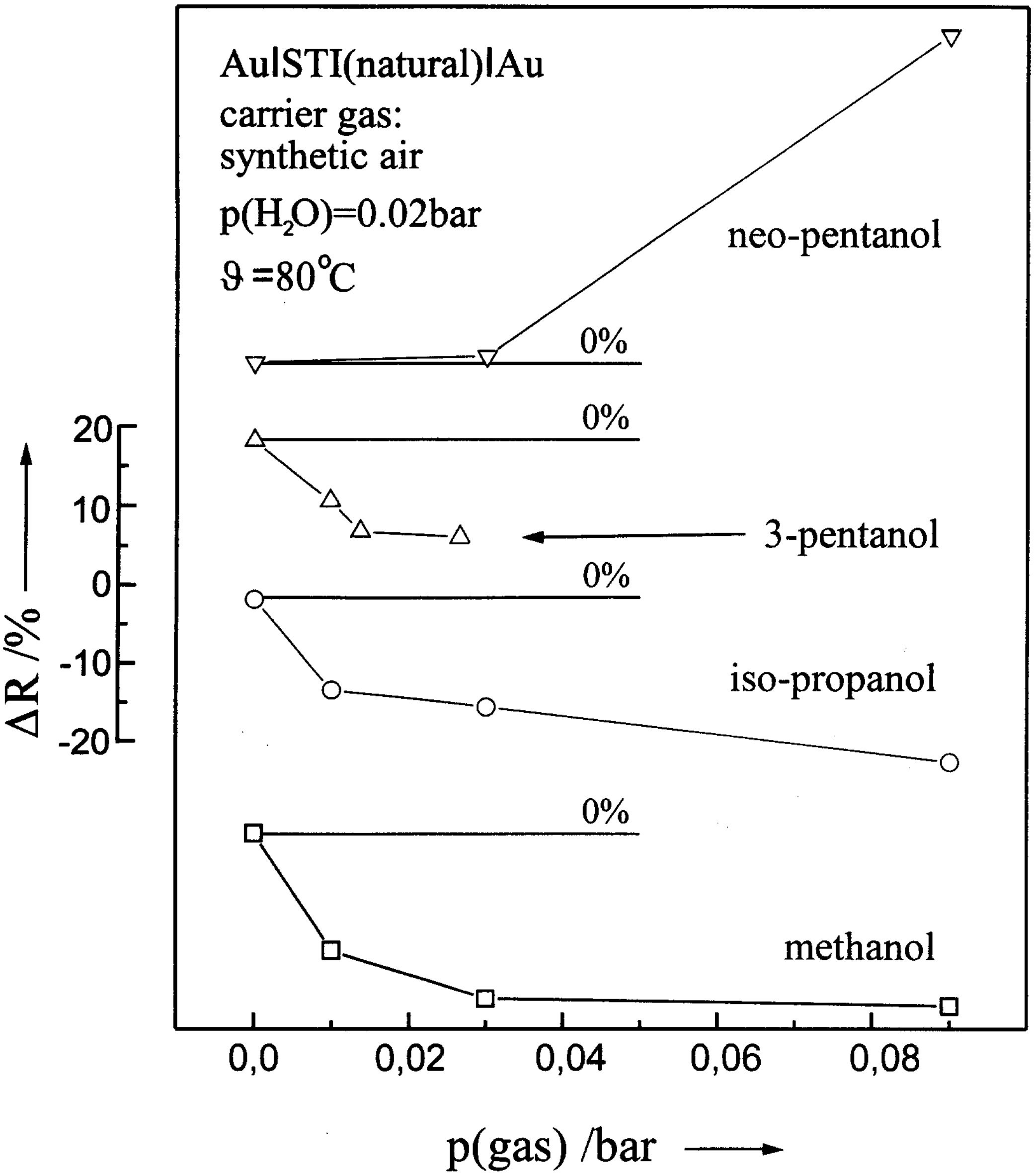


Fig. 23: Effect of guest molecules on stilbite single crystal conductivity under in situ conditions.

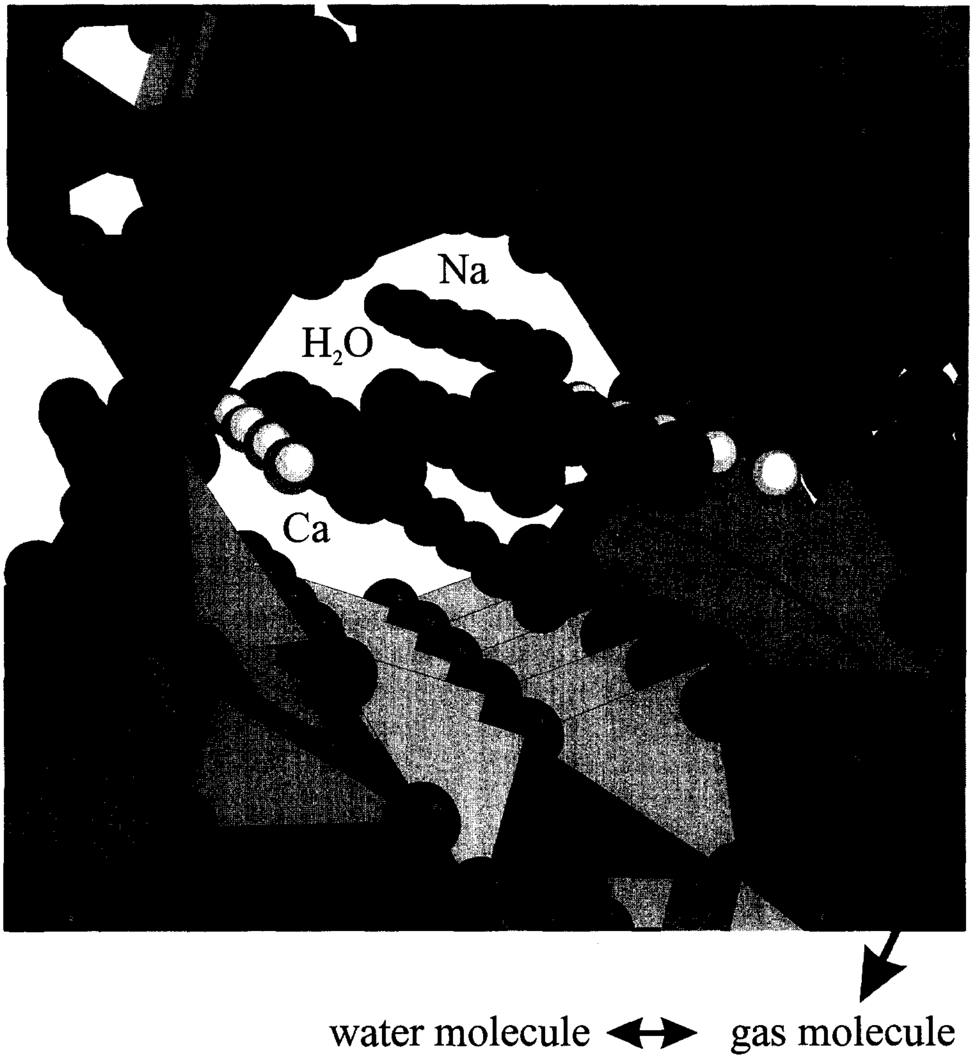


Fig. 24: Model for ionic and molecular interaction in the channel system of zeolites ([001] direction of stilbite structure).

investigations give, therefore, new basic insight in the processes taking place within the zeolite cavity system. As shown in Fig. 24, small polar molecules can substitute water in the cavity system of a zeolite. The mechanisms of the conduction process itself are still under investigation, but first hints could be obtained based on these results, showing that the population of the channel system plays an important role but also the polarity of substances involved in the process [30,94–97].

Zeolite applications in space have basically to consider the limitation of resources of human beings under these conditions. Therefore important application fields of zeolites are the CO_2 removal in breathing atmosphere in space and the recycling of wastewater. An alternative approach of CO_2 removal is to use specifically loaded zeolites together with minerals with additional properties as planting substrates and artificial soil (see Ref. [51]) in extraterrestrial stations to grow plants absorbing CO_2 and delivering additional fresh food. Future applications of zeolites in space could also be the use as catalysts for sugar and carbohydrate fractionating as an effective energy conditioning medium for food in space.

Latest zeolite application in space by NASA is the removal of gas components under ultra clean room conditions in satellite systems and the Hubbell telescope, where zeolites of faujasite-type reduce the outgasing rate inside instruments and absorb molecules without producing additional particles by themselves.

5. Future expectations for zeolites

Zeolites do have a very bright future as application can now be extended based on the additional method of tailored synthesis of highly stable physicochemically active materials of desired properties.

Application of zeolites can be performed in respect to known zeolites and with tailored new zeolites with specific new properties. Ion conductivity, semiconductivity, piezoelectricity, as well as special optical properties in combination with already known and new zeolite properties to be developed will widen the existing application fields and open new fields for zeolite application in medicine, technical medicine, pharmacy, biochemistry, etc., etc.

Zeolites of desired purity and stability will be able to substitute hitherto passive materials like plastics and polymers — but also crystalline materials which look like zeolites — in the future.

Table 1: The channel sizes of alumosilicate-based zeolites in descending order. Data and notation from Ref [6].

Code	**Zeolite phase**	**Channel system in 1st crystallographic direction**	**2nd crystallographic direction**	**3rd crystallographic direction**
FAU	Faujasite	<111> **12** 7.4***		
MAZ	Mazzite	[001] **12** 7.4* |	[001] **8** 3.4 x 5.6*	
LTL	Linde Type L	[001] **12** 7.1*		
EMT	EMC-2	[001] **12** 7.1* ↔	⊥[001] **12** 7.4 x 6.5**	
BOG	Boggsite	[100] **12** 7.0 x 7.0* ↔	[010] **10** 5.2 x 5.8*	
GME	Gmelinite	[001] **12** 7.0* ↔	⊥[001] **8** 3.6 x 3.9**	
MEI	ZSM-18	[001] **12** 6.9* ↔	⊥[001] **7** 3.2 x 3.5**	
OFF	Offretite	[001] **12** 6.7* ↔	⊥[001] **8** 3.6 x 4.9**	
MOR	Mordenite	[001] **12** 6.5 x 7.0* ↔	[010] **8** 2.6 x 5.7*	
BEA	Beta	[001] **12** 5.5 x 5.5* ↔	<100> **12** 7.6 x 6.4**	
CON	CIT-1	[001] **12** 6.4 x 7.0* ↔	[100] **12** 6.8* ↔	[010] **10** 5.1 x 5.1*
CAN	Cancrinite	[001] **12** 5.9*		
VET	VPI-8	[001] **12** 5.9*		
MTW	ZSM-12	[010] **12** 5.5 x 5.9*		
MEL	ZSM-11	<100> **10** 5.3 x 5.4***		
MFI	ZSM-5	{[010] **10** 5.3 x 5.6 ↔	[100] **10** 5.1 x 5.5}***	
MFS	ZSM-57	[100] **10** 5.1 x 5.4* ↔	[010] **8** 3.3 x 4.8*	
TER	Terranovaite	[100] **10** 5.0 x 5.5* ↔	[001] **10** 4.2 x 7.0*	
STI	Stilbite	[100] **10** 4.9 x 6.1 ↔	[101] **8** 2.7 x 5.6*	
NES	NU-87	[100] **10** 4.7 x 6.0**		
MTT	ZSM-23	[001] **10** 4.5 x 5.2*		
TON	Theta-1	[001] **10** 4.4 x 5.5*		
FER	Ferrierite	[001] **10** 4.2 x 5.4* ↔	[010] **8** 3.5 x 4.8*	
RON	Roggianite	[001] **12** 4.2*		
EUO	EU-1	[100] **10** 4.1 x 5.7* with large side pockets		
LTA	Linde Type A	<100> **8** 4.1***		
LAU	Laumontite	[100] **10** 4.0 x 5.3*		
CHI	Chiavennite	[001] 9 3.9 x 4.3*		
KFI	ZK-5	<100> **8** 3.9*** |	<100> **8** 3.9***	
RTH	RUB-13	[100] **8** 3.8 x 4.1* ↔	[001] **8** 2.5 x 5.6*	
CHA	Chabazite	⊥[001] **8** 3.8 x 3.8***		
PAU	Paulingite	<100> **8** 3.8*** |	<100> **8** 3.8***	
EPI	Epistilbite	[100] **10** 3.4 x 5.6*↔	[001] **8** 3.7 x 5.2*	
EAB	TMA-E	⊥[001] **8** 3.7 x 5.1**		
JBW	NaJ	[100] **8** 3.7 x 4.8*		
DAC	Dachiardite	[010] **10** 3.4 x 5.3* ↔	[001] **8** 3.7 x 4.8*	
RTE	RUB-3	[001] **8** 3.7 x 4.4*		
VSV	VPI-7	[011] 9 3.3 x 4.5* ↔	$[01\bar{1}]$ 9 3.3 x 4.5* ↔	$[10\bar{1}]$ **8** 3.7 x 3.7*
ERI	Erionite	⊥[001] **8** 3.6 x 5.1***		
LEV	Levyne	⊥[001] **8** 3.6 x 4.8**		
DDR	Deca-dodecasil 3R	⊥[001] **8** 3.6 x 4.4**		
LOV	Lovdarite	[010] 9 3.2 x 4.4* ↔	[001] 9 3.2 x 3.7* ↔	[100] **8** 3.6 x 3.7*
PHI	Phillipsite	[100] **8** 3.6* ↔	[010] **8** 3.0 x 4.3* ↔	[001] **8** 3.2 x 3.3*
RHO	Rho	<100> **8** 3.6*** |	<100> **8** 3.6***	
MON	Montesommaite	[100] **8** 3.2 x 4.4* ↔	[001] **8** 3.6 x 3.6*	
PAR	Partheite	[001] **10** 3.5 x 6.9*		
VNI	VPI-9	⊥[001] {<110> **8** 3.5 x 4.0 ↔	[001] **8** 3.5 x .3.5 }**	
MER	Merlinoite	[100] **8** 3.1 x 3.5* ↔	[010] **8** 2.7 x 3.6* ↔	[001]{**8** 3.4 x 5.1* + **8** 3.3 x 3.3*}
RSN	RUB-17	[100] 9 3.3 x 4.4* ↔	[001] 9 3.1 x 4.3* ↔	[010] **8** 3.4 x 4.1*
ABW	Li-A	[001] **8** 3.4 x 3.8*		
HEU	Heulandite	{[001] **10** 3.0 x 7.6* + **8** 3.3 x 4.6*} ↔	[100] **8** 2.6 x 4.7*	
YUG	Yugawaralite	[100] **8** 2.8 x 3.6* ↔	[001] **8** 3.1 x 5.0*	
GIS	Gismondine	{[100] **8** 3.1 x 4.5* ↔	[010] **8** 2.8 x 4.8}*	
BRE	Brewsterite	[100] **8** 2.3 x 5.0* ↔	[001] **8** 2.8 x 4.1*	
GOO	Goosecreekite	[100] **8** 2.8 x 4.0* ↔	[010] **8** 2.7 x 4.1* ↔	[001] **8** 2.9 x 4.7*
EDI	Edingtonite	[110] **8** 2.8 x 3.8** ↔	[001] **8** variable*	
BIK	Bikitaite	[001] **8** 2.8 x 3.7*		
WEN	Wenkite	<100> **10** 2.6 x 4.9** ↔	[001] **8** 2.2 x 2.7*	
NAT	Natrolite	<100> **8** 2.6 x 3.9** ↔	[001] **8** variable*	
THO	Thomsonite	[101] **8** 2.3 x 3.9* ↔	[010] **8** 2.2 x 4.0* ↔	[001] **8** variable
CAS	Cs Aluminosilicate	[100] **8** 2.2 x 4.7*		
ANA	Analcime	[110] **8** 1.6 x 4.2*** irregular		

Table 2: The chemical compositions of some important alumosilicate zeolites. Data from Refs. [5,21]

Ca- zeolites

Zeolite code	**Zeolite phase**	**Zeolite structural units**	**Molar ratio Ca:Al:Si**	**Idealized chemical formula**	**Z***
SOD	bicculite	4 & 6	1:1:0.5	$Ca[Al_2SiO_6]$ x 2(OH)	4
RON	roggianite	4-ring	1:1:2	$Ca_{16}[Al_{16}Si_{32}O_{88}]$ x 16(OH) x $16H_2O$	1
LTA	linde type A	4 & 4-4	1:2:2	$Ca_6[Al_{12}Si_{12}O_{48}]$ x $21H_2O$	1
PAR	Parthéite	4-ring	1:2:2	$Ca_2[Al_4Si_4O_{15}]$ x 2(OH) x $4H_2O$	4
GIS	Gismondine	4-ring	1:2:2	$Ca[Al_2Si_2O_8]$ x $4H_2O$	4
LIO	Liottite	6-ring	1:2:2	$Ca_9[Al_{18}Si_{18}O_{72}]$ x $2H_2O$	1
NAT	Scolecite	4=1	1:2:3	$Ca[Al_2Si_3O_{10}]$ x $3H_2O$	4
GIS	Ca-garronite	4-ring	1:2:3.33	$Ca_3[Al_6Si_{10}O_{32}]$ x $12.5H_2O$	1
FAU	Ca-zeolite X	6-6	1:2:3.84	$Ca_{40}[Al_{80}Si_{112}O_{384}]$ x $4H_2O$	1
ANA	Wairakite	4 & 6	1:2:4	$Ca_8[Al_{16}Si_{32}O_{96}]$ x $16H_2O$	1
LAU	Laumontite	4 & 6	1:2:4	$Ca[Al_2Si_4O_{12}]$ x $3H_2O$	4
CHA	Chabazite	6-ring	1:2:4	$Ca_2[Al_4Si_8O24]$ x $13H_2O$	1
LEV	Levyne	6-ring	1:2:4	$Ca_9[Al_{18}Si_{36}O_{108}]$ x $50H_2O$	3
PHI	Ca-harmotome	4-ring	1:2:4.4	$Ca_9[Al_{18}Si_{36}O_{108}]$ x $50H_2O$	1
STI	Stellerite	4-4=1	1:2:5.2	$Ca_{2.5}[Al_5Si_{11}O_{32}]$ x $12H_2O$	1
YUG	Yugawaralite	4 & 8	1:2:6	$Ca[Al_2Si_6O_{16}]$ x $4H_2O$	2
GOO	Goosecreekite	6-2	1:2:6	$Ca[Al_2Si_6O_{16}]$ x $5H_2O$	2
EPI	Epistilbite	5-1	1:2:6	$Ca_3[Al_6Si_{18}O_{48}]$ x $15H_2O$	1
HEU	Heulandite	4-4=1	1:2:7	$Ca[Al_2Si_7O_{18}]$ x $6H_2O$	4
MOR	Ca-mordenite	5-1	1:2:10	$Ca_4[Al_8Si_{40}O_{96}]$ x $31H_2O$	1

Ba- zeolites

Zeolite code	**Zeolite phase**	**Zeolite structural units**	**Molar ratio Ba:Al:Si**	**Idealized chemical formula**	**Z**
BRE	Ba-brewsterite	4-ring	1:2:3	$Ba[Al_2Si_6O_{16}]$ x $5H_2O$	2
EDI	Edingtonite	4=1	1:2:3	$Ba_2[Al_4Si_6O_{20}]$ x $8H_2O$	1
GME	Ba-gmelinite	6-ring	1:2:4	$Ba_4[Al_8Si_{16}O_{48}]$ x $19.12H_2O$	1
CHA	Ba-chabazite	6-ring	1:2:4.45	$Ba_{1.86}[Al_{3.72}Si_{8.28}O24]$ x $7.4H_2O$	1
PHI	Harmotome	4-ring	1:2:6	$Ba_2[Al_4Si_{12}O_{32}]$ x 12H2O	1

Sr- zeolites

Zeolite code	**Zeolite phase**	**Zeolite structural units**	**Molar ratio Sr:Al:Si**	**Idealized chemical formula**	**Z**
BRE	Brewsterite	4-ring	1:2:3	$Ba[Al_2Si_6O_{16}]$ x $5H_2O$	2

Na- zeolites

Zeolite code	**Zeolite phase**	**Zeolite structural units**	**Molar ratio Na:Al:Si**	**Idealized chemical formula**	**Z**
CAN	Cancrinite	4 & 6	1:0.75:0.75	$Na_8[Al_6Si_6O_{24}]$ x 2(OH) x $2.66H_2O$	1
SOD	hydroxy-sodalite	4 & 6	1:0.75:0.75	$Na8[Al_6Si_6O_{24}]$ x 2(OH)x $2H_2O$	1
LTA	zeolite LTA	4 & 4-4	1:1:1	$Na_{12}[Al_{12}Si_{12}O_{48}]$ x $27H_2O$	8
EDI	zeolite F	4=1	1:1:1	$Na_5[Al_5Si_5O_{20}]$ x $9H_2O$	1
LTN	zeolite N, NaZ 21	4 & 6	1:1:1	$Na[AlSiO_4]$ x $1.1H_2O$	384
FAU	Na-zeolite X	6-6	1:1:1.4	$Na_5[Al_5Si_7O_{24}]$ x $9H_2O$	16
NAT	Natrolite	4=1	1:1:1.5	$Na_{16}[Al_{16}Si_{24}O_{80}]$ x $16H_2O$	1
GIS	Gobbinsite	4-ring	1:1:2.2	$Na_5[Al_5Si_{11}O_{32}]$ x $11H_2O$	1
GME	Gmelinite	6 & 6-6	1:1:2	$Na_2[Al_2Si_4O_{12}]$ x $5H_2O$	4
ANA	Analcime	4 & 6	1:1:2	$Na_{16}[Al_{16}Si_{32}O_{96}]$ x $16H_2O$	1
KFI	zeolite ZK 5	4 & 6-6	1:1:2.2	$Na_{30}[Al_{30}Si_{66}O_{192}]$ x $98H_2O$	1
CHA	Na-chabazite	6-ring	1:1:2.22	$Na_{3.72}[Al_{3.72}Si_{8.28}O_{24}]$ x $9.7H_2O$	1
FAU	Na-zeolite Y	6-6	1:1:2.76	$Na_{51}[Al_{51}Si_{141}O_{348}]$ x $7.83H_2O$	1
EAB	zeolite TMA	4 & 6	1:1:2.83	$Na_{9.4}[Al_{9.4}Si_{26.6}O_{72}]$ x $36.8H_2O$	1
ERI	Erionite	4 & 6	1:1:3	$Na_9[Al_9Si_{27}O_{72}]$ x $27H_2O$	1
HEU	Na-heulandite	4-4=1	1:1:3.04	$Na_{8.9}[Al_{8.9}Si_{27.1}O_{72}]$ x $26H_2O$	1
STI	Barrerite	4-4=1	1:1:3.5	$Na_8[Al_8Si_{28}O_{72}]$ x $26H_2O$	2
MOR	Na-mordenite	5-1	1:1:5	$Na_8[Al_8Si_{40}O_{96}]$ x $24H_2O$	1
MEL	zeolite ZSM 11	5-1	1:1:11	$Na_8[Al_8Si_{88}O_{192}]$ x $16H_2O$	1
MFI	zeolite ZSM 5	5-1	1:1:86.27	$Na_{1.1}[Al_{1.1}Si_{94.9}O_{192}]$ x $2.36H_2O$	1

Li- zeolites

Zeolite code	**Zeolite phase**	**Zeolite structural units**	**Molar ratio Li:Al:Si**	**Idealized chemical formula**	**Z**
EDI	zeolite Li-F	4=1	1:1:1	$Li_5[Al_5Si_5O_{20}]$ x $8H_2O$	1
NAT	Natrolite	4=1	1:1:1	$Li_2[Al_2Si_3O_{10}]$ x $2H_2O$	1
ABW	zeolite Li-A(BW)	4 & 6 & 8	1:1:1.2	$Li_{0.91}[Al_{0.91}Si_{1.09}O_4]$ x $1H_2O$	4
BIK	Bikitaite	5-1	1:1:2	$Li[AlSi_2O_6]$ x $1H_2O$	2

K- zeolites

zeolite code	Zeolite phase	zeolite structural units	molar ratio K:Al:Si	idealized chemical formula	Z
EDI	zeolite K-F	4=1	1:0.77:0.77	$K_{13}[Al_{10}Si_{10}O_{40}]$ x 3(OH) x $13H_2O$	2
ABW	zeolite K-A(BW)	4 & 6 & 8	1:1:1	$K_{12}[Al_{12}Si_{12}O_{48}]$ x $20H_2O$	1
NAT	K-gonnardite	4=1	1:1:1.22	$K_9[Al_9Si_{11}O_{40}]$ x $20.5H_2O$	1
NAT	K-natrolite	4=1	1:1:1.5	$K_2[Al_2Si_3O_{10}]$ x $2H_2O$	8
CHA	zeolite K-ZK 14	6-ring	1:1:2.24	$K_{11.1}[A_{111.1}Si_{24.9}O_{72}]$ x $8H_2O$	1
FAU	K-zeolite X, Y	6-ring	1:1:2.51	$K_{6.84}[Al_{6.84}Si_{17.16}O_{48}]$ x $2H_2O$	8
HEU	K-heulandite	4-4=1	1:1:3	$K_9[Al_9Si_{27}O_{72}]$ x $18H_2O$	1
DAC	K-dachiardite	5-1	1:1:3.8	$K_5[Al_5Si_{19}O_{48}]$ x $12H_2O$	1
LTL	K-zeolite L	6-ring	1:1:3.83	$K_{7.32}[Al_{7.32}Si_{28.08}O_{72}]$ x $25.5H_2O$	1

Rb- zeolites

zeolite code	Zeolite phase	zeolite structural units	molar ratio Rb:Al:Si	idealized chemical formula	Z
EDI	zeolite Rb-F	4=1	1:1:1	$Rb_{10}[Al_{10}Si_{10}O_{40}]$ x $13H_2O$	1

Cs- zeolites

zeolite code	Zeolite phase	zeolite structural units	molar ratio Cs:Al:Si	idealized chemical formula	Z
ABW	Cs-zeolite A(BW)	4 & 6 & 8	1:1:1	$Cs_{12}[Al_{12}Si_{12}O_{48}]$ x $1H_2O$	1
MFI	zeolite Cs-ZSM 5	5-1	1:1:25.66	$Cs_{0.9}[Al_{0.9}Si_{23.1}O_{48}]$ x $2.4H_2O$	4

mixed cation zeolites

zeolite code	zeolite phase	zeolite structural units	molar ratio* (A+1+B+2)=Me Me:Al:Si	Idealized chemical formula	Z
ANA	Hsianghualite	4 & 6	1:0.375:0.375	$Li_{16}Ca_{24}[Be_{24}Si_{24}O_{96}]$ x 6F	1
ANA	viséite+	4 & 6	1:1.1:0.727	$Na_2Ca_{10}[Al_{20}Si_6P_{10}O_{60}]$ x 36(OH) x $16H_2O$	1
THO	Thomsonite	4=1	1:1:1	$Na_2Ca_4[Al_{10}Si_{10}O_{40}]$ x $12H_2O$	2
GIS	Amicite	4 ring	1.1.1	$Na_4K_4[Al_8Si_8O_{32}]$ x $10H_2O$	1
CHA	Willhendersonite	6-ring	1:1:1	$K_2Ca_2[Al_6Si_6O_{24}]$ x $10H_2O$	1
NAT	Gonnardite	4=1	1:1:1.22	$Na_5Ca_2[Al_9Si_{11}O_{40}]$ x $12H_2O$	1
NAT	Mesolite	4=1	1:1:1.5	$Na_{16}Ca_{16}[Al_{48}Si_{72}O_{240}]$ x $64H_2O$	1
GIS	Garronite	4-ring	1:1:1.66	$NaCa_{2.5}[Al_6Si_{10}O_{32})$ x $13H_2O$	1
PHI	Phillipsite	4-ring	1:1:1.66	$K_2(Ca_{0.5}, Na)_4[Al_6Si_{10}O_{32}$ x $12H_2O$	2
LEV	Levyne	6-ring	1:1:2	$NaCa_{2.5}[Al_6Si_{12}O_{36}]$ x $18H_2O$	3
PHI	Harmotome	4-ring	1:1:2.2	$Ba_2(Ca_{0.5}, Na)[Al_5Si_{11}O_{32}]$ x $12H_2O$	1
FAU	Faujasite	6-6	1:1:2.2	$Na_{20}Ca_{12}Mg_8[Al_{60}Si_{132}O_{384}]$ x $235H_2O$	1
MER	Merlinoite	4 & 8-8	1:1:2.55	$(K,Na)_5(Ba,Ca)_2[Al_9Si_{23}O_{64}]$ x $24H_2O$	1
MAZ	Mazzite	4 & 5-1	1:1:2.6	$K_3Ca_{1.5}Mg_2[Al_{10}Si_{26}O_{72}]$ x $28H_2O$	1
OFF	Offretite	6-ring	1:1:2.6	$KCaMg[Al_5Si_{13}O_{36}]$ x 15 H_2O	1
HEU	Heulandite	4-4=1	1.1:3	$(Na,K)Ca_4[Al_9Si_{27}O_{72}]$ x $24H_2O$	1
STI	Stilbite	4-4=1	1:1:3	$NaCa_4[Al_9Si_{27}O_{72}]$ x $30H_2O$	1
PAU	Paulingite	4-ring	1:1:3.08	$Na_{12}K_{68}Ca_{41}[Al_{162}Si_{500}O_{1344}]$ x $705H_2O$	1
ERI	Erionite	4 & 6	1:1:3.5	$NaK_2MgCa_{1.5}[Al_8Si_{28}O_{72}]$ x $28H_2O$	1
MOR	Mordenite	5-1	1:1:5	$Na_3KCa_2[Al_8Si_{40}O_{96}]$ x 28 H_2O	1
DAC	Dachiardite	5-1	1:1:5	$(Na,K,Ca_{0.5})_4[Al_4Si_{20}O_{48}]$ x $18H_2O$	1
HEU	Clinoptilolite	4-4=1	1:1:5	$(Na,K)_6[Al_6Si_{30}O_{72}]$ x $20H_2O$	1
FER	Ferrierite	5-1	1:1:6	$(Na,K)Mg_2Ca_{0.5}[Al_6Si_{30}O_{72}]$ x $20H_2O$	1

*Z= number of formula units per unit cell

(Al3+,Be2+) as Al, (P5+,Si4+) as Si;

+ status as zeolite questionable

References

[1] A.F. Cronstedt, Kongl. Vetenskaps, Acad. Handl. Stockh. **17** 120 (1756)

[2] E.M. Flanigen, in Zeolites: Science and Technology, p. 3, F. Ramôa Ribeiro, A.E. Rodrigues, L.D. Rollmann, C. Naccache, Eds., NATO ASI series, The Hague, Boston, Lancester, 1984

[3] P. Kovstad, Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides. Wiley, New York 1972

[4] W. Eitel, Silicate Science Vol. IV Hydrothermal Systems, Academic Press, N.Y., London, 1966

[5] G. Gottardi, E. Galli, Natural Zeolites, Springer Verlag, Berlin, Heidelberg, N.Y. 1985

[6] W.M. Meier, D.H. Olson and Ch. Baerlocher, Eds., Atlas of Zeolite Structure Types, 4th revised edition, Elsevier, London, Boston, Singapore, Sidney, Toronto, Wellington 1996

[7] H.G. Karge, J. Weitkamp, Eds., Molecular Sieves, Science and Technology Vol. 1, Synthesis, Springer, Berlin, Heidelberg, N.Y., 1998

[8] R.M. Barrer, L. Hinds, J. Chem. Soc. 1879 (1953)

[9] R.M. Barrer, Proc. Chem. Soc. 99 (1958)

[10] D. Barthomeuf, E.G. Derouane, W.H. Folderich, Guidelines for Mastering the Properties of Molecular Sieves, Plenum Press, N.Y. 1990

[11] A. Tißler, U. Müller, K.K. Unger, Nachr. Chem. Tech. Lab. **36(6)** 624 (1988)

[12] F. Liebau, H. Gies, R.P. Gunawardane, B. Marler, Zeolites **6** 373 (1986)

[13] O. Grubner, P. Jíru and M. Rálek, Molekularsiebe, VEB Verlag der Wissenschaft, Berlin, 1968

[14] R.M. Barrer, The Hydrothermal Chemistry of Zeolites, 1st edn., Academic Press, London, 1982

[15] S.P. Zhdanov, S.S. Khvoshchev, N.N. Feoktistova, Synthetic Zeolites: Crystallization, Structural and Chemical Modification of Crystals, Vol. 1, Gordon and Breach Science Pubs., N.Y., 1990

[16] M.L. Occelli, H.E. Robson, Synthesis of Microporous Materials Vol. 1, Chapman and Hall, London, Amsterdam, 1992

[17] M.L. Occelli, H.E. Robson, Synthesis of Microporous Materials Vol. 2, Chapman and Hall, London, Amsterdam, 1992

[18] E.G. Derouane, Ed., Zeolite Microporous Solids: Synthesis, Structure, and Reactivity, NATO ASI series, series C, Mathematical and Physical Sciences, Vol. 352, Kluwer Academic Pub., Dordrecht, 1991

[19] F. Schwochow, L. Puppe, Angew. Chemie **87(18)** 659 (1975)

[20] J.K. Van Der Waal, Synthesis, Characterization and Catalytic Application of Zeolite Titanium Beta, Coronet Books, Philadelphia, Pennsilvania,1998

[21] Gmelin Institute and FIZ Karlsruhe, Inorganic Crystal Structure Database, 1997

[22] C. Naccache, Y. Ben Taarit in: Zeolites: Science and Technology, p. 373, F. Ramôa Ribeiro, A.E. Rodrigues, L.D. Rollmann, C. Naccache, Eds., NATO ASI series, The Hague, Boston, Lancester, 1984

[23] G.H. Kühl in: Catalysis and Zeolites, Fundamentals and Application, p. 81 and references given there, J. Weitkamp, L. Puppe, Eds., Springer Verlag, Berlin, Heidelberg, N.Y., London, Paris, Tokyo 1999

[24] F. Liebau, Structural Chemistry of Silicates, Springer Verlag, Berlin, Heidelberg, N.Y., Tokyo, 1985

[25] F. Cansell, B. Chevalier, A. Demourgues, J. Etourneau, C. Even, Y. Garrabos, V. Pessey, S. Petit, A. Tressaud and F. Weill, J. Mater. Chem. **8** (1998) published in Proceedings 1st Materials Chemistry Discussion, Solid State Chemistry: Novel Syntheses and New Materials. D1/1, ICMCB, University of Bordeaux, France, 24-26. 9. 1998

[26] J.L. Guth, H. Kessler in: Catalysis and Zeolites, Fundamentals and Application, p. 1, J. Weitkamp, L. Puppe, Eds., Springer Verlag, Berlin, Heidelberg, N.Y., London, Paris, Tokyo 1999

[27] S. Matthes, Mineralogie, Springer, Berlin, Heidelberg, N.Y., Tokyo, 1983

[28] H.G.F. Winkler, Petrogenesis of Metamorphic Rocks, 5th edn., Springer, N.Y. Heidelberg, Berlin, 1979

[29] H. Ghobarkar, O. Schäf, Microporous and Mesoporous Materials **23(106)** (1998) 55-60

[30] O. Schäf, H. Ghobarkar and U. Guth, Ionics **5(1&2)** (1999), in press

[31] W. Kleber, Einführung in die Kristallographie, VEB Verlag Technik, Berlin, 1983

[32] H. Ghobarkar, PH.D. Thesis, Free University of Berlin 1976

[33] H. Ghobarkar, Kristall und Technik **12** K49 (1977)

[34] H. Ghobarkar, O. Schäf, Journal of Physics D: Applied Physics **31** 3172 (1998)

[35] H. Ghobarkar, O. Schäf, Verfahren zur Synthese von Zeolithen mit definierter Stöchiometrie und Struktur. Deutsches Patent, AZ 198 24 184.4-41, Offenlegung 2. 12. 1999

[36] H. Ghobarkar, O. Schäf, Cryst. Res. Technol. **31(3)**, K29 (1996)

[37] H. Ghobarkar, O. Schäf, Cryst. Res. Technol. **31(5)**, K54 (1996)

[38] H. Ghobarkar, O. Schäf, Cryst. Res. Technol. **31(6)**, K67 (1996)

[39] H. Ghobarkar, O. Schäf, Cryst. Res. Technol. **31(6)**, K70 (1996)

[40] H. Ghobarkar, O. Schäf, Cryst. Res. Technol. **32(5)**, 653 (1997)

[41] H. Ghobarkar, Cryst. Res. Technol. **20(9)** K90 (1985)

[42] H. Ghobarkar, W. Franke, Cryst. Res. Technol. **21(8)**, 1071 (1986)

[43] H. Ghobarkar, O. Schäf and U. Guth: The Use of the High Pressure Hydrothermal Method for Tailored Synthesis of Zeolites without Structure Directing Agents. Instance: Synthesis of Natural Zeolites with 5-1 Building Units. 3rd Int. Conf. on Solvothermal Reactions ICSTR-3, Bordeaux, France 19.-23.7. 1999

[44] H. Ghobarkar, O. Schäf, Materials Research Bulletin **34(4)** 517 (1999)

[45] H. Ghobarkar, O. Schäf and U. Guth, Journal of Solid State Chemistry **142** 451 (1999)

[46] H. Ghobarkar, O. Schäf, Zeolites **19** 259 (1997)

[47] H. Ghobarkar, O. Schäf and P. Knauth, Annales de Chimie, Science des Matériaux **24** 209 (1999)

[48] H. Ghobarkar, O. Schäf, Materials Science and Engineering B, Solid State Materials for Advanced Technology **60(3)** 163 (1999)

[49] S.P. Zhdanov, S.S. Khvoshchev, N.N. Feoktistova, Synthetic Zeolites: Absorption & Molecular Properties of Zeolites, Vol. 2, Gordon and Breach Science Pubs., N.Y., 1990

[50] Zeolites: Markets and Opportunities, Business Communications Co., 1997

[51] F.A. Mumpton, W.G. Pond, eds., Zeo-Agriculture: The Use of Natural Zeolites in Agriculture and Aquaculture, Westview Press, Boulder, Colorado, 1994

[52] C.G. Coe, in: Gas Separation Technology, E.F. Vansant and R. Dewolfs eds., p. 149, Elsevier 1990

[53] C.G. Coe, S.M. Kuznicki, U.S. Patent 4,481,018 (1984)

[54] R.L. Keiski, H. Raeisaenen, M. Haerkoenen, T. Maunula, Catal. Today **27(1-2)** 85 (1996)

[55] M. Mitchell, M. White, D. Bruce, E. Gatimu, Proc. NOBCChE **21** 285 (1994)

[56] Z.S. Rak, H.J. Veringa, React. Kinet. Catal. Lett. **60(2)** 303 (1997)

[57] P.A. Jacobs, R.A. van Santen, Zeolites, Facts, Figures, Future, Elsevier, London, N.Y., Tokyo,1990

[58] Y. Isakov, Chemistry Reviews: New Catalytic Applications of Alumosilicate Zeolites & Related Molecular Sieves, Vol 17, Gordon & Breach, N.Y., 1992

[59] P. B. Venuto, Fluid Catalytic Cracking with Zeolite Catalysts, Marcel Dekker Inc., N.Y., 1979

[60] N.Y. Chen, F.G. Dwyer, W. E. Garwood, Shape Selective Catalysis in Industrial Applications, Marcel Dekker Inc., N.Y., 1996

[61] S. Bhatia, Zeolite Catalysts: Principles and Applications, Franklin Book Company Inc., 1990

[62] G.H. Kühl in: Catalysis and Zeolites, Fundamentals and Application, p. 81, J. Weitkamp, L. Puppe, Eds., Springer Verlag, Berlin, Heidelberg, N.Y., London, Paris, Tokyo 1999

[63] P. Espeel, R. Parton, H. Toufar, J. Martens, W. Hölderich and P. Jakobs in: Catalysis and Zeolites, Fundamentals and Application, p. 377, J. Weitkamp, L. Puppe, Eds., Springer Verlag, Berlin, Heidelberg, N.Y., London, Paris, Tokyo 1999

[64] P.M.M. Blauwhoff, J.W. Gosselink, E.P. Kieffer, S.T. Sie, W.H.J. Stork in: Catalysis and Zeolites, Fundamentals and Application, p. 437, J. Weitkamp, L. Puppe, Eds., Springer Verlag, Berlin, Heidelberg, N.Y., London, Paris, Tokyo 1999

[65] M.M. Treacy, J.B. Higgins, R. von Ballmoos, Eds., Collection of simulated X-Ray Diffraction Patterns, 3rd revised edition, Elsevier, London, Boston, Singapore, Sidney, Toronto, Wellington 1996
[66] F. Rouquerol, J. Rouquerol and K. Sing, Adsorption by Powders and Porous Solids. Principles, Methology and Applications, Academic Press, San Diego, London, Boston, N.Y., Sydney, Tokyo, Toronto 1999
[67] J.D. Sherman, in: Zeolites: Science and Technology, p. 583, F. Ramôa Ribeiro, A.E. Rodrigues, L.D. Rollmann, C. Naccache, Eds., NATO ASI series, The Hague, Boston, Lancester, 1984
[68] J.M.S. Cabral, M.R. Aires-Barros, Chimia **50(9)** 420 (1996)
[69] M.M. Sharma, Polytechn Tijdschr.: Procestech. **45(5)** 68 (1990)
[70] G.A. Ozin, A. Kuperman and A. Stein, Angewandte Chemie **101(3)** 373 (1989)
[71] V. Ramamurthy, N.J. Turro, J. Inclusion Phenom. Mol. Recognit. Chem **21(1-4)** 239 (1995)
[72] S.L. Suib, Photochem. Photophys **3** 1 (1991)
[73] S.D. Cox, T.E. Gier, G.D. Stucky, J. Am Chem. Soc **110** 2986 (1988)
[74] U. Vietze, O. Krauß, F. Laeri, G. Ihlein, F. Schüth, B. Limburg, M. Abraham: Lasing, Two-Photon Fluorescence, and Second Harmonic Generation in a Zeolite-Dye Host-Guest System, 10th German Zeolite Meeting, Abstracts KV 11, Bremen, 9.-11.3. 1998
[75] G. Ihlein, F. Schüth, O. Krauss, U. Vietze, F. Laeri, B. Limburg and M. Abraham: Laser Action from a Zeolite Based Host-Guest Composite, 12th International Zeolite Conference Abstracts A46, Baltimore, USA, 6.-11. 7. 1998
[76] U. Vietze, F. Laeri, G. Ihlein, F. Schüth, I. Braun, G. Schulz-Ekloff, D. Wöhrle: Laser Action in $AlPO_4$-5 Molecular Sieve Composites, 11th German Zeolite Meeting, Abstracts KV 18, Stuttgart, 3.-5.3. 1999
[77] V. F. Zolin, Proc. 21st Int. Conf. Lasers 191 (1999)
[78] M. Warnken, M. Wark, G. Grubert and N. Jaeger in: 3rd Dresdener Sensor-Symposium, 8.-10.12. 1997, Dresden-Radebeul, Dresdner Beiträge zur Sensorik Bd. 5, p. 39, Dresden University Press, Dresden, 1998
[79] K. Alberti, F. Fetting, Sensors and Actuators **B21** 39 (1994)
[80] P. Kurzweil, W. Maunz, C. Plog, Sensors and Actuators **B24-25** 653 (1995)
[81] C. Plog, W. Maunz, P. Kurzweil, E. Obermeier, C. Scheibe, Sensors and Actuators **B24-25** 403 (1995)
[82] Y. Yang and T. Bein, Mic. Mat. **1** 401(1993)
[83] H. Tsuchiya, I. Sasaki, A. Harano, T. Okubo and M. Sadakata, Mat. Res. Soc. Symp. Proc. **454** 297 (1997)
[84] T. Bein, S. Feng, J. Meinershagen, S. Mintova, S. Mo, J.H. Visser and K. Yasuda, Synthesis of zeolite Thin Films - Applications in Chemical Sensors, PV2 Paper presented at the 10th German Zeolite Conference, Bremen 9.-11. 3. 1998
[85] H. Ghobarkar, O. Schäf, unpublished results (1999)
[86] I.R. Beattie and A. Dyer, Trans. Faraday Soc. **53** 61(1957)
[87] M. Lal, C.M. Johnson, A.T. Howe, Solid State Ionics **5** 451(1981)
[88] E. Krogh Andersen, I.G. Krogh Andersen and E. Skou in: Proton Conductors, p. 210, P. Columban (ed.), Cambridge University Press, Cambridge 1992
[89] U. Simon, U. Flesch, W. Maunz, R. Muller, C. Plog, Mic. Mes. Mat. **21(1-3)** 111 (1998)
[90] P. Qiu, Y. Huang, R.A. Secco, P. Balog, S. Paul, Solid State Ionics **118** 281(1999)
[91] U. Simon, U. Flesch, J. Porous Mater. **6(1)** 33 (1999)
[92] M.E. Franke, U. Simon, Solid State Ionics **118** 31 (1999)
[93] O. Schäf, H. Ghobarkar, unpublished results (1999)
[94] O. Schäf, H. Ghobarkar and U. Guth, Ionics **3** 282 (1997)
[95] O. Schäf, H. Ghobarkar und U. Guth in: 3rd Dresdener Sensor-Symposium, 8.-10.12. 1997, Dresden-Radebeul, Dresdner Beiträge zur Sensorik Bd. 5, p. 43, Dresden University Press, Dresden, 1998
[96] O. Schäf, H. Ghobarkar and U. Guth: Polycrystalline Zeolite Layers for Low Temperature Gas Sensor Applications. KV6, Paper presented at the 10th German Zeolite Conference, Bremen 9.-11. 3. 1998

[97] O. Schäf, H. Ghobarkar and W.F. Zhang, U. Guth: Influence of Ions and Molecules on Single Crystal Zeolite Conductivity, Paper presented at the 12th Int. Conf. on Solid State Ionics, Sani Beach, Thessaloniki, Greece, 6.-12.6. 1999