CHAPTER - 10

GROWTH OF ZEOLITE CRYSTALS IN THE SYSTEM

\( \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{H}_2\text{O} \) BY HYDROTHERMAL METHOD

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10.1 Introduction

The word "hydrothermal" has been used for many years by geochemists and mineralogists to describe reactions which take place at high temperature and pressure in the presence of water. By carrying out such reactions in the laboratory many minerals of complicated compositions and inorganic compounds have been prepared. Almost all these reactions take place in situ, however, and the crystal size of the products is usually small, unless some special techniques are adopted to grow large single crystals as in the case of quartz. Thus the word "hydrothermal crystal growth" will be restricted to mean a process in which an aqueous solution is held at high temperature and pressure. This process is usually carried out in sealed vertical autoclaves.

The successful solution of the
problem of growing synthetic quartz crystals has drawn the attention of many investigators to the hydrothermal method of synthesis. Almost all the important minerals have been synthesized, the recrystallization conditions have been found for the great majority of minerals, and the solubility has been determined for many minerals in a wide range of temperatures and pressures and in many solvents. Although much work has already been done, the final target of all these investigations, which is the development of methods which yield crystals suitable for subsequent investigations and applications, has been achieved completely only for quartz and its structural analogue in the form of aluminium phosphate and, purtly, for zinc oxide (zincite).

Zeolites are hydrated aluminosilicates believed to have been formed under hydrothermal conditions. Many attempts have been made to produce these crystalline minerals in the laboratory by methods which were believed to simulate natural process. Growth and characterization of more than 100 different types of synthetic zeolites have been reported. Present chapter deals with the growth and
characterization of hydrothermally grown zeolite crystals in this laboratory in the system
Na$_2$O·Al$_2$O$_3$·SiO$_2$·H$_2$O.

10.2 Summary of Earlier Work of Hydrothermal Growth of Synthetic Zeolites

Most of the natural zeolites are formed under hydrothermal conditions. The term hydrothermal is used in a broad sense and includes the crystallization of zeolites from aqueous systems which contain the necessary chemical components. Attempts to synthesize silicates under hydrothermal conditions began with Schafhautle, who, in 1845 reported the preparation of quartz by heating a "gel" silica with water in an autoclave. In 1862, St. Claire Deville reported the synthesis of "levynite" by heating aqueous solutions of potassium silicate and sodium aluminate in glass tubes at 170°C.

The work published on hydrothermal alteration and synthesis of silicates up to 1937 has been reviewed extensively by Morey and Ingerson. Identification of materials synthesized by hydrothermal method as a crystalline zeolite was not possible
until the advent of X-ray powder diffraction studies. Synthetic materials with a chemical composition corresponding to that of analcime has been claimed by many investigators. A summary of these reports is given by Barrer\(^2\). Barrer and White\(^3\) synthesized analcime-type zeolite, for the first time, substantiated by X-ray diffraction analysis. The formation of synthetic types of analcime and mordenite in the range 250\(^\circ\)C-300\(^\circ\)C was reported by Ames\(^4\). Two synthetic types of "large port\(^*\) and "small port" have been synthesized by Sand\(^5\). Saha\(^6,7\) reported synthesis of analcime-type phases from glasses with difference in chemical compositions. Hydrothermal crystallization of zeolite in the system Na\(_2\)O-Al\(_2\)O\(_3\)-SiO\(_2\)-H\(_2\)O was reported earlier by Litvin and Melnikov\(^8\) at temperatures between 250\(^\circ\) and 550\(^\circ\)C and pressures between 200 and 2000 K bars. Studies on positions of cations and other molecules in hydrothermally grown faujasite-type zeolite were reported by Bennett and Smith\(^9,10\). Chatterjee et al\(^11\) obtained the conditions of synthesis of zeolite A. Mechanism of the crystallization of zeolite at moderate temperatures is
reported by Freund\textsuperscript{12}). Hydrothermal synthesis and characterization of gmelinite and chabazite-type zeolites was studied by Chatterjee et al\textsuperscript{13}). The crystallization of zeolite (species P) from volcanic ash in Southern Kyushu, Japan under the hydrothermal conditions with alkaline solution was investigated by Eiji and Akio\textsuperscript{14}). Astakhov et al\textsuperscript{15)} reported study of the process occurring during the hydrothermal treatment of zeolite NaY. Recently, synthesis and study of the new L-D zeolite by hydrothermal method was reported by Ragimove et al\textsuperscript{16)}.

10.3 Kinetics and Mechanism of Zeolite Crystallization

Many papers containing information concerning kinetics and mechanism of zeolite crystallization have appeared since Zhdanov's review\textsuperscript{17}). Aiellow et al\textsuperscript{18)} showed that crystallization of zeolites from solution proceeds through formation of amorphous solid lamellae which evolve into larger particles after which X-ray crystallinity occurs. Nucleation is heterogeneous. The transition through amorphous gel solid
is consistent with Ostwald's law of successive transformations and Goldsmith's simplexity principle.

McNicol et al.\(^1\) used luminescence and Raman spectroscopy to study structural and chemical aspects of gel growth of zeolite A and faujasite-type crystals. Changes occurred in the solid phase which supported the conclusion that crystal growth takes place in the solid-gel phase by a condensation mechanism. Beard\(^2\) used infrared spectroscopy to determine the size and structure of silicate species in solution in relationship to crystallization.

The thermodynamic stabilization of open aluminosilicate structures by the intracrystalline guest species, water or salts, has been developed by Barrer\(^3\) and should be considered in their formation. The role of water structure in templating open zeolite frameworks was suggested by Belov\(^4\).

There is considerable evidence that the alkali cation is strongly and stoichiometrically associated with the aluminate species.
The alkali-Al ratio in the solid phase of the gel reaches a value near 1 in early stage of crystallization reaction. This suggests that an ion pairing of an associated species of $[\text{Na}^+] [\text{AlOH}_4^-]$ or NaAlO$_2$ is the reacting or diffusing species and is also the precipitating agent.

The aluminosilicate gels are crystallized in a closed hydrothermal system at temperatures varying generally from room temperature to 175°C. In some cases, higher temperatures up to 300°C are also used. The pressure is generally auto-geneous pressure approximately equivalent to the saturated vapour pressure (SVP) of water at temperature designated. The time required for crystallization varies from a few hours to several days.

The ease with which the zeolites crystallize is attributed to the high reactivity of the gel, the concentration of the alkali hydroxide, and the high surface activity due to the small particle size of the solid phase concerned. The gel is probably produced by the copolymerization of the individual silicate and
aluminate species by the condensation polymerization mechanism. The gel composition and the structure appear to be controlled by the size and structure of the polymerization.

The crystallization of highly complex zeolite structures at relatively low temperatures from reactive gels requires that the disordered gel phase be converted to a more ordered but metastable zeolite phase. Zhdanov\(^ {17} \) described a quasi-equilibrium between the solid and the liquid phases in gels and concluded that nuclei form and grow in the liquid phase. The gel material dissolves continuously and the dissolved species from the gel are transported to the nuclei crystals in the liquid phase. This is analogous to the solution mechanism described by Kerr\(^ {23} \).

In solutions of high pH silica exists as silicate ions. The solubility of silica, particularly in amorphous forms, has been extensively studied.\(^ {24} \) Dissolution involves a simultaneous hydration and depolymerization. Dissolution is catalyzed by the presence of a strong base such as
sodium hydroxide and when the pH is above 10.5, silica dissolves extensively. This probably involves depolymerization through hydration to form Si(OH)$_4$, followed by addition of an OH$^-$ ion to form the silicate ion. The dissolution depolymerization reaction can be represented by

$$(\text{SiO}_2)_n + 2n \text{H}_2\text{O} = n \text{Si(OH)}_4$$

$$\text{Si(OH)}_4 + \text{H}_2\text{O} + \text{OH}^- = (\text{H}_2\text{O}) \text{Si(OH)}_5^-$$

When the solutions of the aluminate and polysilicate anions are mixed to form the hydrous gel, the aluminate anions and silicate anions undergo a polymerization process. The structure thus produced is amorphous and is in a state of high simplicity. The composition and structure of this hydrous gel is controlled by the size and structure of the polymerizing species. Since the silicate may vary in chemical composition and molecular weight distribution, different silicate solutions may lead to differences in the gel structure.
Therefore gelation controls nucleation of the zeolite crystallites. Crystal size and morphology of zeolites grown from gels generally appear to support this. The crystals have almost identical morphology, size (several microns) and composition. The high degree of supersaturation of the ionic species present in the gel must lead to rapid and heterogeneous nucleation and the formation of a large number of nuclei.

Size and charge of the hydrated cation species which serves as a nucleation site for the polyhedral structural unit also influences the nucleation process. The cation is known to have effect on the silicate and probably on the aluminate species in solution. (The more open zeolite structures appear to be crystallized from gels, which contain sodium as the alkali rather than potassium, the later leading to less open zeolite structures in general). During crystallization of the gel, the aluminate and silicate components must undergo rearrangement in order to form the crystalline structure. This occurs by depolymerization and solubilization of the gel.
The crystallization of an amorphous aluminosilicate to a zeolite is shown in Fig. 10.1. The gel structure, represented in two dimensions, is depolymerized by the hydroxyl ions which produce soluble aluminosilicate species that may regroup to form the nuclei of the ordered zeolite structure. Tetrahedra regroup about hydrated sodium ions to form the basic polyhedral units. In this version the hydrated cation act as a template. The representation shown in Fig. 10.1 is for the formation of the zeolite X structure based upon the truncated octahedron unit. A similar scheme could be worked out on the use of other secondary building units such as the double 6-rings.

10.4 Particle Size of Synthetic Zeolites

Zeolite crystals are formed under typical synthesis conditions from reactive hydrogels at low temperatures which contain the various components in high concentrations. Though in several cases, natural zeolite crystals of bigger size are available, in general, particle sizes of synthetic zeolite crystals range from 1 to 10 microns.
The very small particle size of most synthetic zeolites is not suitable for their use in most applications and, as a result, the crystals must be formed into polycrystalline aggregates in order to be packed into columns and beds for use in adsorption or catalytic processes. Although the average particle size of synthetic zeolite crystals is small (1-5 μ), the internal adsorption void space which becomes available after dehydration of the zeolites is far in excess to the integrated external surface area of the particles. For ex. 1 gm. of a zeolite having 1 μ particle size can provide as large as 800 square meter of internal void space. The largest particle size yet observed for single crystals of zeolites appears to be about 0.14 mm (140 μ)\textsuperscript{25}.

10.5 **Zeolite Metastability**

Most of the synthetic zeolites are produced under non-equilibrium conditions and are considered, in a thermodynamic sense, as metastable phases\textsuperscript{26}. The nature of the starting materials, factors governing nucleation and reaction time are important in determining the zeolite species
produced from reaction mixtures.

A mineral zeolite which has existed over long periods of geological time and a synthetic zeolite with a related structure but which is synthesized rapidly in the laboratory may exhibit differences in properties due to the ordering that may occur in the mineral as opposed to the lack of ordering the synthetic structure shows.

Because of the rapid rates of reaction of many of the components, true equilibrium may never be attained. It is probable that many of the synthetic zeolites which do not have mineral relatives are non-equilibrium phases and, do not exist when true equilibrium conditions prevail. Many of the synthetic zeolites are not structurally related to a mineral. This may be due to the metastability of the synthetic zeolite and its ease of conversion to a more stable species.

10.6 Experimental Set Up

Starting materials used in the present investigation for the crystallization of
zeolites were: (i) NaOH pellets (SM) (ii) sodium metasilicate and (iii) sodium aluminate (Riedel).

2 gm of sodium metasilicate, 0.5 gm of sodium aluminate and 0.7 gm of sodium hydroxide were mixed together and about 50 ml of distilled water was added to the mixture to form a composite sodium aluminosilicate gel. Most of the runs were carried by preparing a sodium aluminosilicate gel at room temperature, allowing it to age also at room temperature, for about 24 hrs and crystallizing the aged gel at an elevated temperature without stirring. This gel was later transferred to a high pressure vessel.

A steel container (a small autoclave) used for the crystallization is shown in Fig. 10.2. This specially fabricated high pressure vessel (called bomb) consists of a solid steel cylinder, 4.7 cm in diameter, with a cavity of about 3.2 cm in diameter and 9.5 cm in depth. After transferring the gel to this vessel more water is added (if required) until 2/3 of the volume of the cavity of the vessel is filled. This
bomb was closed with the help of a brass cap using one copper washer and one washer of steam packing material. The bomb was then transferred to a thermostatically controlled muffle furnace for the required time and at the required temperature.

A muffle of 10 cm internal diameter and a coil of 18 gauge kanthal wire were used in the design of muffle furnace. Two kanthal wounds were separated by asbestos rope. Muffle furnace was designed to give an accuracy of 10°C and a maximum range of 500°C. The temperatures were registered by a chromul-almul thermocouple incorporated in the furnace and could be read on a calibrated dial. A calibrated temperature recorder of chromul-almul thermocouple was used for recording the temperatures directly. Temperature of crystallization ranged from 120°C to 170°C, whereas duration of runs varied from 3 hours to 6 days.

10.7 Observations

Several runs were undertaken with the same composition of reactants and in the same temperature range, but with different time durations.
It is observed that the growth time plays an important role in regard to the particle size, morphology and system of the crystal. It is observed that up to a particular time duration, Si/Al composition also changes with time. Two types of crystallites resulted: one up to 24 hours (cube-like) and another after 48 hours (rod-like crystals). The first type is named as VHZA, whereas the second one is named as VHZB.

10.8 Characterization

These hydrothermally grown crystals were characterized with the help of X-ray powder analysis, by electron microscopy and by infrared spectral studies.

10.8.1 X-ray powder analysis

X-ray powder photographs of both the varieties of the crystals were taken to ascertain the state of crystallinity and if possible, to find the symmetry of the crystals. d values obtained from the X-ray powder photographs are given in Table 10.1. Since the d values in two cases differ
Table 10.1 X-ray powder data of zeolites
VHZ A and VHZ B

<table>
<thead>
<tr>
<th>d (Å)</th>
<th>d (Å)</th>
<th>d (Å)</th>
<th>d (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.10</td>
<td>6.00</td>
<td>-</td>
<td>2.00</td>
</tr>
<tr>
<td>4.90</td>
<td>5.60</td>
<td>1.90</td>
<td>1.92</td>
</tr>
<tr>
<td>3.85</td>
<td>5.00</td>
<td>1.80</td>
<td>1.85</td>
</tr>
<tr>
<td></td>
<td>4.80</td>
<td>1.74</td>
<td>1.70</td>
</tr>
<tr>
<td></td>
<td>3.75</td>
<td>1.68</td>
<td>1.66</td>
</tr>
<tr>
<td>3.30</td>
<td>3.50</td>
<td>1.58</td>
<td>1.60</td>
</tr>
<tr>
<td>3.05</td>
<td>3.40</td>
<td>1.48</td>
<td>1.48</td>
</tr>
<tr>
<td>2.75</td>
<td>3.00</td>
<td>1.44</td>
<td>1.47</td>
</tr>
<tr>
<td>2.55</td>
<td>2.90</td>
<td>1.34</td>
<td>-</td>
</tr>
<tr>
<td>2.40</td>
<td>2.80</td>
<td>1.32</td>
<td>-</td>
</tr>
<tr>
<td>2.35</td>
<td>-</td>
<td>1.29</td>
<td>-</td>
</tr>
<tr>
<td>2.25</td>
<td>2.65</td>
<td>1.26</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2.50</td>
<td>1.24</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2.40</td>
<td>1.21</td>
<td>-</td>
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<tr>
<td></td>
<td>2.15</td>
<td>1.19</td>
<td>-</td>
</tr>
</tbody>
</table>
appreciably, it can be concluded that VHZ A and VHZ B are two distinct phases of the hydrothermally grown zeolite crystals.

10.8.2 **Electron microscopy**

Electron microscopy has been used extensively to study the habit and surface topography of synthetic zeolites. Intergrowth and different forms in the case of synthetic zeolites L, O and T were studied by electron microscopy\(^{27,28}\). Ciric\(^{29}\) studied the particle size of zeolite A, whereas the size distributions of three different batches of zeolite CaA crystals was measured by Loughlin et al\(^{30}\). Changes in the solid phase of the aluminosilicate gels during the crystallization of the zeolite have been studied by means of electron microscopy\(^{27}\). Recently, Weeks and Passoja\(^{31}\) by electron microprobe analysis of synthetic X type zeolite, showed that the silica to alumina molar ratio increases from the crystal centre to exterior. In the present investigation electron microscope was used for the (a) electron microprobe analysis, (b) for the TEM work and (c) for the SEM work.
(a) **Electron microprobe analysis**

Electron microprobe analysis of the samples of different hydrothermal runs was carried out and the presence of different constituent elements (Na, Si, Al) was confirmed. Si/Al ratio was computed in each case. The results are given in Table 10.2. It is observed that aluminium percentage in the crystals increases with time and, as expected, this is accompanied by an increase in Na percentage. Si/Al ratio for amorphous gel is 3.34, whereas it is around 3 for VHZ A and less than 1.5 for VHZ B. This shows that Si/Al ratio conclusively decides the morphology and symmetry of the crystal. Both the phases occur in the system Na$_2$O.Al$_2$O$_3$.SiO$_2$.H$_2$O.

(b) **Transmission electron microscopy**

TEM photomicrographs of amorphous gel, zeolite VHZ A and VHZ B are presented in Figs. 10.3(a), 10.3(b) and 10.3(c) respectively. Amorphous nature of the starting aluminosilicate gel and the crystallinity of A and B phases were confirmed by electron diffraction method. However,
### Table 10.2 Silicon-aluminium composition in the hydrothermally grown zeolite crystals

<table>
<thead>
<tr>
<th>Growth time (hrs)</th>
<th>Phase</th>
<th>Si/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Amorphous alumino-silicate gel</td>
<td>3.34</td>
</tr>
<tr>
<td>3</td>
<td>VHZA</td>
<td>3.02</td>
</tr>
<tr>
<td>12</td>
<td>VHZA</td>
<td>2.06</td>
</tr>
<tr>
<td>24</td>
<td>VHZA</td>
<td>2.05</td>
</tr>
<tr>
<td>48</td>
<td>VHZB</td>
<td>1.47</td>
</tr>
</tbody>
</table>
well defined electron diffraction patterns could not be obtained because the crystals were too thick and, on account of their very small size they could not be thinned. Fig. 10.3(d) shows the presence of phase B along with phase A after 36 hours. The average particle size obtained from TEM photographs is about 10 \( \mu \) for VHZ A and about 20 \( \mu \) for VHZ B. Morphology of the crystals, cube-like of VHZ A and rod-like of VHZ B, is evident from the TEM photomicrographs.

(c) **Scanning electron microscopy**

SEM photomicrographs of amorphous gel, VHZ A and VHZ B are shown in Figs. 10.4(a), 10.4(b) and 10.4(c) respectively. Observations of TEM regarding particle size and morphology of the crystals in both the phases are further confirmed by SEM photomicrographs. Average particle size measured from SEM photomicrographs is around 10 \( \mu \) in the case of VHZ A and 20 \( \mu \) in the case of VHZ B, which is almost same as from TEM photomicrographs. Occasionally VHZ B crystals of as large as 100 \( \mu \) were also obtained. One such case is shown in Fig. 10.4(d).
10.8.3 **Infrared spectral studies**

Infrared spectrum in the region 200-4000 cm\(^{-1}\) is a sensitive tool indicating structural features of the zeolite framework (Chapter 7). Using the KBr wafer technique infrared transmission of the VHZ A and VHZ B were recorded and are shown in Fig. 10.5. All the bands characteristic of zeolite framework structure are present in both the phases. Spectral frequencies of these bands are given in Table 10.3. It is evident from the table that not only the bands which correspond to external linkages (double rings, pore opening etc.) are affected, but even those which correspond to internal tetrahedra are also affected. This is evident from the fact that Si/Al composition of these two forms is different. Appearance of two bands of 215 cm\(^{-1}\) and 235 cm\(^{-1}\) may correspond to pore openings in VHZ A indicating that the structure becomes more open as the growth of VHZ B crystals proceeds.

10.9 **Discussion**

From the results obtained by X-ray
Table 10.3  Infrared spectral data of zeolites VHZ A and VHZ B

<table>
<thead>
<tr>
<th>Characteristic bands of zeolite framework</th>
<th>VHZ A</th>
<th>VHZ B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore opening (200 - 420 cm(^{-1}))</td>
<td>-</td>
<td>215</td>
</tr>
<tr>
<td>T - O bend (420 - 500 cm(^{-1}))</td>
<td>435</td>
<td>455</td>
</tr>
<tr>
<td>Double rings (500 - 650 cm(^{-1}))</td>
<td>580</td>
<td>-</td>
</tr>
<tr>
<td>Symmetric stretch (650 - 820 cm(^{-1}))</td>
<td>680</td>
<td>670</td>
</tr>
<tr>
<td>Asymmetric stretch (950 - 1250 cm(^{-1}))</td>
<td>960</td>
<td>1000</td>
</tr>
<tr>
<td>Water bands</td>
<td>1450</td>
<td>1640</td>
</tr>
<tr>
<td></td>
<td>3520</td>
<td>3600</td>
</tr>
</tbody>
</table>
powder analysis, electron microscopy work and IR spectral studies, it is confirmed that the crystals grown (VHZ A and VHZ B) under hydrothermal conditions are a kind of zeolite. Both the forms have grown in the system Na₂O·Al₂O₃·SiO₂·H₂O. It seems that, during the synthesis, first the amorphous gel crystallizes to the form VHZ A and, if, under identical conditions, growth time is increased it changes to VHZ B. Crystals of A form start appearing within couple of hours whereas crystals of B form appear only after 36 hours of growth period. Except time all other conditions of growth are the same, in both the cases. Thus it can be inferred that amorphous aluminosilicate gel first crystallizes as phase A which seems to be unstable phase but as time proceeds it changes completely to a more stable phase VHZ B after 48 hours. In other words VHZ A is a metastable phase having the tendency, with the increasing time to change to a more stable phase VHZ B. Such a metastable phase formation in the case of synthetic zeolites is reported earlier.

Existence of two different phases
VHZ A and VHZ B was confirmed by X-ray powder diffraction studies. Both the phases seem to have non cubic symmetry.

Si/Al composition plays an important role in the crystallization of these crystals. For the amorphous gel this value is greater than 3. For metastable phase VHZ A its value lies between 2 and 3, whereas when it is less than 1.5, more stable phase VHZ B results. This is stable phase since no further change occurs either in composition, morphology or symmetry of the crystals on further increase in the growth time. Zeolitic nature of VHZ A and VHZ B was further confirmed by studying their dehydration behaviour (recording DTA and TGA) and ion-exchange property qualitatively.

10.10 Conclusions

It is possible to crystallize zeolite phases in the system Na₂O·Al₂O₃·SiO₂·H₂O at comparatively low temperatures, moderate pressures and with the simple experimental set up. Similar to natural processes, synthetic zeolites
first acquire a metastable phase which, later changes to a more stable phase. Considering the influence of Si/Al composition on the structure, symmetry and morphology of the crystals it is possible to crystallize zeolites with predetermined composition. Electron microscopy can be used rigorously to study particle size, morphology, crystallinity, stages of growth and, if possible, symmetry of the crystals in the case of synthetic zeolites. Openness and thus the zeolitic nature (of VHZ B phase) can be studied with the help of their infrared spectral studies.

10.11 References

1. Morey G.W. and Ingerson E. Econ. M Geol., 32 (1937) 607


5. Sand L. E.
Molecular Sieves, Society of Chemical Industry, London (1968)

6. Shah P.
Am. Mineral., 46 (1961) 859

7. Shah P.
Am. Mineral., 44 (1959) 300

8. Litvin B. N. and Melnikov O. K.
Kristallografiya (USSR), 14(1) (1969) 101 (In Russian)
English Translation in Sov. Phys. Cryst. (USA)

9. Bennett J. M. and Smith J. V.
Materials Res. Bull. (USA), 2 (1968) 865

10. Bennett J. M. and Smith J. V.
Materials Res. Bull. (USA), 4 (1969) 77

11. Chatterjee Minati, Ganguli Dibyendu, De Ashok and Saha P.

12. Freund E. F.
J. Crystal Growth, 34 (1976) 11

13. Chatterjee Minati, Ganguli Dibyendu and Shah P.
Trans. Indian Ceramic Society, 35 (1976) 99
14. Eiji Sakamoto and Akio Yamada
   Yogyo Kyokai Shi., 85 (1977) 367 (Japan)

15. Astakhov V.A., Meerson L.A., Mikhailova
    M.V. and Klyushkova G.S.

16. Ragimov N.G., Ganbarov D.M., Aminrov
    S.T. and Mamedov Kh. S.
    14(7) (1978) 1338 (Russ.)

17. Zhdanov S.P.
    Advanc. Chem. Ser., American Chemical
    Society, Washington 101 (1971) 20

    Advanc. Chem. Ser., American Chemical
    Society, Washington 101 (1971) 44

    J. Phys. Chem., 76 (1972) 3388

20. Beard W. C.
    Advanc. Chem. Ser., American Chemical
    Society, Washington 121 (1973) 200

21. Barrer R. M.
    Molecular Sieves, Society of Chemical
    Industry, London (1968)

22. Belov N. V.
    "Crystal Chemistry of Large-Cation
    Silicates", Academy of Science Press,
    Moscow (1961) 34

23. Kerr G. T.

25. Charnell J.F.
    J. Crystal Growth 8 (1971) 291

    Econ. Geol., 52 (1957) 169

27. Breck D.W. and Flanigen E. M.
    Molecular Sieves, Society of Chemical Industry London (1968)

    and Galabova I.M.

29. Ciric J.
    J. Colloid Interface Sci., 23 (1968) 315

30. Loughlin K.F., Derrah R.I. and Ruthven D.M.

31. Weeks T.J. (Jr) and Passoja D.E.
    Clays Clay Miner., 25 (1977) 211
Fig. 10.5
Captions of the figures

Fig. 10.1 Crystallization of an amorphous aluminosilicate to a zeolite.

Fig. 10.2 Steel vessel used for crystallization.

Fig. 10.3(a) TEM photomicrograph of the amorphous gel.

Fig. 10.3(b) TEM photomicrograph of VHZ A.

Fig. 10.3(c) TEM photomicrograph of VHZ B.

Fig. 10.3(d) TEM photomicrograph of mixed phases (VHZ A and VHZ B).

Fig. 10.4(a) SEM photomicrograph of amorphous gel.

Fig. 10.4(b) SEM photomicrograph of VHZ A.

Fig. 10.4(c) SEM photomicrograph of VHZ B.

Fig. 10.4(d) SEM photomicrograph of a large (100 μ) VHZ B crystal.

Fig. 10.5 Infrared spectra of VHZ A and VHZ B.