CHAPTER 13
HYDROTHERMAL GROWTH AND CHARACTERIZATION OF VSZ-3
ZEOLITE CRYSTALS

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CHAPTER 13
HYDROTHERMAL GROWTH AND CHARACTERIZATION OF VSZ-3 ZEOLITE CRYSTALS

13.1 Introduction

Although over a hundred zeolites have been synthesized including synthetic analogues of those occurring naturally, it has been postulated by crystallographers that only ten percent of the possible polymeric configurations have been discovered. If this assumption is true, it follows that inspite of large number of useful molecular sieve zeolites that have been synthesized, the field is in an early stage of development with many opportunities to create new species. The broad base in synthesis and properties established by Professor Barrer and his associates has been extended remarkably by the industrial laboratories. Out of proprietary necessity, much of the data in zeolite synthesis are couched in patent language or remains unpublished. Even so, the volume of information can be overwhelming.

The present chapter includes the results of investigations on the hydrothermal growth and
characterization of an analcime type zeolite, VSZ-3
in the system Na$_2$O - SiO$_2$ - Al$_2$O$_3$ - H$_2$O at around 350°C.

13.2 Hydrothermal method of crystal growth

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. The history of hydrothermal synthesis of crystals is almost a hundred years old, but as a method for growing single crystals it came into use comparatively recently - perhaps several decades ago. The successful utilization of diverse techniques for growing highly perfect large size single crystals of quartz (2-7) has aroused interest in hydrothermal synthesis research on single crystal growth of other compounds. Today, there are known to be different methods and conditions of producing quite a number of crystals of other classes of inorganic substances.

Similar to other crystal growth methods using solvents, hydrothermal crystallization involves
several stages. In a general sense they are: dissolution, formation of the nuclei of the compound under growth, and crystallization. The solubility of most compounds in water is low at temperature higher than 100°C. Hence, usually, mineralizers are added for raising the solubility of the substances in hydrothermal synthesis process. Alkaline solutions are usually used for growing different oxygen compounds (oxides, silicates, and salts of oxygen containing acids) and solutions of different acids are employed for producing crystals of sulfides, selenides etc. The introduction of a mineralizer and the raising of the temperature (pressure) aid in turning the substance into a soluted state to such an amount in order to ensure the required supersaturation at the crystal solution interface and the crystal growth.

When growing crystals by hydrothermal method it is desirable that under growth conditions only this crystalline phase should be stable. The formation of other phases makes the process complicated. In view of this fact the development of a crystal growth method is usually followed by the investigation of the phase equilibria in the system used in crystal growth.

The comparatively mild crystal growth
conditions at hydrothermal synthesis (the growth temperature being much lower than $T_{\text{melt}}$, low growth rate, uniform pressure) allow one to grow rather perfect crystals free from stresses, plastic strains and inclusion of the mother liquor, etc. The most common defects are cracks, lamellar or zone structures arising from nonuniform capture of impurities, non-stoichiometric composition, dislocations and less frequently thermal stresses. Defects in hydrothermal crystals are due to the presence of impurities in the solution and their capture by the crystal, to the stability of growth conditions as well as to the individual features of the medium where the growing of crystal takes place.

Since in hydrothermal synthesis the growth of crystals takes place in the aqueous medium, water and its dissociation products are the main impurities captured by the crystals. The impact of water on the quality and properties of hydrothermal crystals has been discussed by several workers\textsuperscript{11-14}. Several reviews have appeared on the hydrothermal synthesis of crystals and minerals\textsuperscript{12,15,16}.

An epitome of earlier work of hydrothermal growth of synthetic zeolites has been given by Bhoskar\textsuperscript{17}. 
Recently, several crystalline metallic silicates with zeolitic structures (pentasyl type structures similar to ZSM-5) have been synthesized by employing hydrothermal technique\textsuperscript{18-20}.

13.3 Experimental

The reactants used in the present study are silica gel (6 - 20 mesh), aluminium hydroxide and sodium hydroxide. These reactants are mixed in the ratio 4 : 1 : 1 with excess of double-distilled water. The mixture is stirred well to get a homogeneous gel. This aluminosilicate gel is transferred to the stainless steel line\textsuperscript{2} of length 20 cm and of diameter slightly smaller than 2.5 cm (- for easy insertion of the line\textsuperscript{2} into the below mentioned autoclave) which is inserted in an autoclave.

The autoclave used in the present work (outer diameter = 7.5 cm and the chamber size = 2.5 cm x 25 cm) is fabricated from stainless steel type 304, which works on the principle of cone-seal. The sealing of the cone with autoclave aperture is done with six thick hexagonal nuts (1.25 cm diameter) made up of stainless steel. The nuts are utilized for tightly
pressing the cone against the autoclave aperture. The whole pressure of the nuts is applied on a flat mild steel washer plate. The washer on both sides is polished to mirror finish, which transmits the pressure on the large flat upper surface of the cone which is also polished.

The autoclave with the liner is heated in a kanthal wound vertical muffle furnace. The temperature is measured by chromel-alumel thermocouple with the thermocouple junction placed inside a 0.3 cm deep bore made on the outer wall of the autoclave at a suitable height.

Crystallization is carried out at around 350°C and autogeneous pressure (~ 2500 psi) for 24-96 hours. Quite transparent crystals are obtained in the 48 hours runs. After each run the product is washed several times with distilled water to remove the gel particles. The crystals are then dried in an oven.

Morphological and topographical studies of these crystals named here as VSZ-3 are carried out with the help of SEM and the results will be illustrated and discussed in chapter 15. These crystals are also characterized by chemical analysis, EDAX, X-ray
diffraction, infrared spectroscopy, thermogravimetric analysis (TGA) and differential thermal analysis (DTA). All these are included in relevant sections of this thesis.

13.4 Observations

13.4.1 Chemical analysis

Results of chemical analysis of the synthesized VSZ-3 crystals are given in Table 13.1. On the basis of this chemical analysis, the chemical formula of VSZ-3 zeolite (in its oxide form) can be written as 0.86 Na₂O. Al₂O₃. 9.96 SiO₂. 0.26 H₂O.

13.4.2 EDAX

To check the composition obtained by the chemical analysis, EDAX analysis of the VSZ-3 crystals is carried out. Figure 13.1 depicts the characteristic X-ray spectrum and Figs. 13.2 and 13.3 show the At % and Wt % of the elements and the corresponding oxides as obtained from EDAX analysis. The ratios calculated from these observations are

\[ \frac{\text{SiO}_2}{\text{Al}_2\text{O}_3} = 5.98 \quad \text{and} \quad \frac{\text{Si}}{\text{Al}} \approx 5\]
### Table 13.1 Chemical analysis for VSZ-3

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Weight percent</th>
</tr>
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<tbody>
<tr>
<td>SiO₂</td>
<td>79.405</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>13.524</td>
</tr>
<tr>
<td>Na₂O</td>
<td>07.071</td>
</tr>
<tr>
<td>H₂O</td>
<td>00.610</td>
</tr>
</tbody>
</table>

**Total**: 100.610
13.4.3 X-ray powder analysis

X-ray powder diffraction analysis of VSZ-3 zeolite crystals is carried out using the X-ray diffractometer (HZG 3 DDR). The peaks are scanned with a counter speed of 5'/min. The d spacings computed are given in Table 13.2. The diffraction peaks are indexed and the crystal is found to belong to face centred cubic system. The unit cell constant is calculated as $a = 13.12 \text{Å}$.

13.4.4 Infrared spectral studies

Infrared spectrum of VSZ-3 in the region 400 - 4000 cm$^{-1}$ obtained using KBr wafer technique is shown in Fig. 13.4. It shows the characteristic absorption bands of zeolite family crystals. The assignment of the absorption peaks to different types of vibrations, according to Flanigen et al$^{21}$, is given in Table 13.3.

13.4.5 Thermal analysis

The TGA and DTA curves for the VSZ-3 crystals (heating rate 10°C/min) are shown in Fig. 13.5. The TGA curve shows two steps, one at about 120°C and the other at about 250°C, each of which corresponds to
<table>
<thead>
<tr>
<th>I</th>
<th>d(Å)</th>
<th>hkl</th>
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<tbody>
<tr>
<td>33</td>
<td>6.3436</td>
<td>200</td>
</tr>
<tr>
<td>17</td>
<td>4.2342</td>
<td>220</td>
</tr>
<tr>
<td>18</td>
<td>4.0185</td>
<td>311</td>
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<tr>
<td>25</td>
<td>3.7323</td>
<td>222</td>
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<tr>
<td>14</td>
<td>3.6303</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>3.3362</td>
<td>400</td>
</tr>
<tr>
<td>100</td>
<td>3.2045</td>
<td>331</td>
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<tr>
<td>8</td>
<td>3.0178</td>
<td>420</td>
</tr>
<tr>
<td>7</td>
<td>2.6367</td>
<td>422</td>
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<td>2.1270</td>
<td>442</td>
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<tr>
<td>6</td>
<td>1.8173</td>
<td>533</td>
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</table>
Table 13.3 IR spectral data for VSZ-3

<table>
<thead>
<tr>
<th>Mode of vibrations</th>
<th>Frequency cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyl bond</td>
<td>3440 (ms)</td>
</tr>
<tr>
<td>(H_2)O bend</td>
<td>1620 (vw)</td>
</tr>
<tr>
<td>Asym. stretch</td>
<td>1125 (wsh), 1010 (s)</td>
</tr>
<tr>
<td>Sym. stretch</td>
<td>795 (wsh), 790 (ms)</td>
</tr>
<tr>
<td></td>
<td>745 (sh), 645 (ms)</td>
</tr>
<tr>
<td>(S(\bar{\text{BU}}))Dbl. Rings</td>
<td>580 (w), 550 (vw)</td>
</tr>
<tr>
<td>T-O bend</td>
<td>435 (ms)</td>
</tr>
<tr>
<td>Pore—opening</td>
<td>395 (ms)</td>
</tr>
</tbody>
</table>

* s - strong, ms - medium strong
* w - weak, vw - very weak
* sh - shoulder
the dehydration of VSZ-3 zeolite. The total weight loss is 0.6% which agrees quite well with the water content obtained by chemical analysis. The DTA curve shows no sharp peaks indicating the thermal stability of VSZ-3 zeolite crystals up to 1000°C.

**Induction period and crystal size**

During the hydrothermal synthesis of VSZ-3 crystals, it is observed that the time of hydrothermal run plays an important role. No crystallization is observed for the runs under 24 hours. For the 24 hours run in the range 340-360°C, the crystals obtained are small in size and are not quite transparent. Only for the runs of about 48 hours, in the temperature range 340 - 360°C, quite transparent crystals are obtained. These results indicate existence of some critical or induction period for the crystallization of VSZ-3 zeolite to begin.

Average size of the crystals at these optimum conditions (T = 360°C, p = 2700 psi, time = 48 hours) is 180 - 200 microns. This size is certainly much bigger than the largest size of synthetic zeolite crystals ever reported.
13.5 Discussion

Most of the sodium zeolites crystallize from sodium aluminosilicate gels below 200°C \(^{22-27}\). Based on the phase rule, in the system \(\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}\), two tectosilicates may co-exist in equilibrium with the aqueous solution at a given temperature and pressure. In the presence of silica as a separate phase, only one zeolite can theoretically co-exist with the aqueous solution. However, two zeolites have been formed in this system at temperatures above 200°C \(^{28}\). These are synthetic types of analcime and mordenite. Of these, analcime is the more stable and was one of the first zeolites reported to be synthesized by early investigators. A sodium form of mordenite was first synthesized by Barrer in 1948\(^{22}\), which has been designated as Na-D.

Barrer and White have investigated the hydrothermal crystallization of aluminosilicate gels of composition \(\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - n\text{SiO}_2 - \text{H}_2\text{O}\)\(^{29}\). The analcime-type Na-B crystallized in high yields for \(n = 4\) or \(5\). The formation of synthetic types of analcime and mordenite in this system at 250 - 300°C has been reported by Ames\(^{30}\). Recent studies of the synthesis of analcime type phases include those of Saha\(^{31}\), who
prepared synthetic types from glasses ranging in chemical composition from \( \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2-6 \text{SiO}_2 \). Guyer et al.\(^{32}\) have also prepared synthetic types of analcime at 300°C. The Si/Al ratio has been reported to vary from 1 to 5.

In the present study hydrothermal synthesis of VSZ-3 is carried out at a comparatively higher temperature (\( \sim 350^\circ\text{C} \)). This high temperature in the alkaline medium should cause higher solubility of silica and accordingly silica content in VSZ-3 crystals (as obtained by EDAX and chemical analysis) is higher. Such substantial changes in the ratio \( \text{SiO}_2 : \text{Al}_2\text{O}_3 \) in the crystallized phase, as compared with that in the parent gel, can occur during crystallization. Examples of such behaviour have been illustrated for several sodium and potassium aluminosilicates\(^{23}\).

The value of unit cell constant obtained by X-ray diffraction studies shows that VSZ-3 crystals belong to analcime type zeolite. The thermal stability, as observed by DTA, supports the above proposition. The weak absorption bands in the region 500 - 650 cm\(^{-1}\) show absence of the double 4- and double 6-rings in the secondary building units (SBU).
This observation once again favours the opinion that VSZ-3 is an analcime-type zeolite.

In the formation of VSZ-3 zeolite, there is a pre-nucleation stage, and then after an induction period, these germ-nuclei begin to exceed a critical size, after which they grow spontaneously.

The mode of growth of complex aluminosilicate crystals from alkaline media, in which alumina and silica are at least partially dissolved, is of great interest. In the pre-nucleation stage the number of potentially competing species could be considerable. Hence it may be a matter of delicate balance, which germ-nuclei begin to cross the critical size barrier and grow spontaneously into crystals, or merely disappear as a result of the continuous fluctuations to which all are subjected. From a gel as the mother substance, the solution formed may be highly supersaturated with respect to the species (here VSZ-3) precipitated. This, after the induction period (≈ 24 hours in the present case) favours a high nucleation rate as compared with the growth rate of the crystals, and results in a shower of tiny crystals. Reaction ceases when one or more of a limited number of chemical 'nutrients' becomes exhausted.
Growth of large single crystals of zeolites in small yield for crystal structure determinations and for basic studies of diffusion and separation mechanisms is very important. Although large crystals of mineral analcime have been found, synthetic analcime-type zeolite crystals have not exceeded 100 microns in size. In this respect, the present studies attain superiority since the VSZ-3 crystals synthesized in the present experiments (of size 180-200 microns) are about 60 microns larger in size than the largest synthetic zeolites reported so far.

Summary and conclusions

A high-silica variety of analcime type zeolites, VSZ-3 (Si/Al ≈ 5) has been synthesized hydrothermally in the system Na$_2$O – Al$_2$O$_3$ – SiO$_2$ – H$_2$O at about 350°C and autogenous pressure. The X-ray, infrared and thermal analyses confirm that these crystals are in fact zeolites belonging to analcime-type.

In the growth of VSZ-3 zeolite crystals, reaction time plays an important role. Following the pre-nucleation stage, there exists an induction period.
of 24 hours after which the spontaneous crystallization begins and a shower of tiny VSZ-3 crystals result. The VSZ-3 crystals synthesized in the present investigation are 180–200 microns in size, which is about 60 microns larger than the largest ever reported. This is indeed a significant advance, since growth of large single crystals in small yield is one of the important areas of current interest in zeolite synthesis.
References

1. L. B. Sand
   Pure and Appl. Chem. 52 (1980) 2105

2. E. Buehler
   Bell. Lab. Rec. 31 (1953) 241

3. E. Buehler and A. Walker
   Sci. Monthly 69 (1949) 148

4. V. P. Butuzov and L. V. Bryatov
   "Growth of Crystals" Vol. 1 Moskva (1958)
   P. 305

5. R. A. Laudise and R. A. Sullivan
   Chem. Engg. Prog. 55 (1959) 55

6. A. A. Ballman and R. A. Laudise
   "The Art & Science of Crystal Growth"
   Ed. J. J. Gilman, Wiley, New York
   (1963) P. 231

7. K. B. Saraf
   Ph. D. Thesis, Sardar Patel University
   (1981)

8. Y. Fujiki, T. Milsushaki and Y. Suzuki
   J. Amer. Ceram. Soc. 55 (1972) 223

9. F. Kiren and H. Liedeneeser
   J. Cryst. Growth 2 (1968) 111

10. D. F. Weirauch and R. Kung
    J. Cryst. Growth 10 (1973) 139

11. E. D. Kolb, D. L. Wood, E. G. S. Spener,
    and R. A. Laudise
    J. Appl. Phys. 28 (1967) 1027
<table>
<thead>
<tr>
<th>No.</th>
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</tr>
</thead>
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<tr>
<td>12</td>
<td>R. A. Laudise</td>
<td>&quot;Crystal Growth and Introduction &quot; Ed. P. Hartman, North Holland (1973) P. 162</td>
</tr>
<tr>
<td>13</td>
<td>V. A. Kuznetsov and A. N. Lobachev</td>
<td>Kristallografia 17 (1972) 878</td>
</tr>
<tr>
<td>15</td>
<td>L. N. Demianets and A. N. Lobachev</td>
<td>Kristall und Technik 14 (1979) 509</td>
</tr>
<tr>
<td>16</td>
<td>R. M. Barrer</td>
<td>Trans. British Ceram. Soc. 56 (1957) 155</td>
</tr>
<tr>
<td>22</td>
<td>R. M. Barrer</td>
<td>J. Chem. Soc. (1948) 2158</td>
</tr>
</tbody>
</table>
23 R. M. Barrer, J. W. Baynham, F. W. Bultitude and W. M. Meier

24 D. W. Breck and E. M. Flanigen
London (1968) 47

25 L. B. Sand
(1968) 71

26 K. E. Senderov and N. I. Khitarov

27 S. Ueda and M. Koizumi
Amer. Mineral. 64 (1979) 1172

28 D. S. Coombs, A. J. Ellis, W. F. Fyfe, and A. M. Taylor

29 R. M. Barrer and E. A. D. White
J. Chem. Soc. (1952) 1561

30 L. L. Ames Jr.
Amer. Mineral. 48 (1963) 1374

31 P. Saha
Amer. Mineral. 46 (1961) 859

32 A. Guyer, M. Ineichen and P. Guyer
Captions of the figures

Fig. 13.1 Characteristic X-ray spectrum of VSZ-3 zeolite crystals

Fig. 13.2 Elemental analysis (At %) of VSZ-3 zeolite

Fig. 13.3 Elemental analysis (WT %) of VSZ-3 zeolite

Fig. 13.4 Infrared spectrum of VSZ-3 zeolite

Fig. 13.5 TGA and DTA of VSZ-3 zeolite
Fig. 13.1

ENTER OXIDE RATIOS:

ELEM NA RATIO 0.5
ELEM AL RATIO 1.5
ELEM SI RATIO 2

ELEM K
NA K 26.344 6.366 0.561
AL K 70.267 7.917 14.771
SI K 406.135 39.020 77.894

Fig. 13.2

ENTER OXIDE RATIOS:

ELEM NA RATIO 0.5
ELEM AL RATIO 1.5
ELEM SI RATIO 2

ELEM K
NA K 26.344 5.575 8.362
AL K 70.267 5.033 14.504
SI K 406.135 25.685 77.054

Fig. 13.3
Fig. 13.4

Fig. 13.5