

# The Morphology of Hydrothermally Synthesized Stilbite Type Zeolites

H. Ghobarkar,\* O. Schäf,†‡ and U. Guth†‡

\*Institute for Mineralogy, Free University of Berlin, Germany; †Sensor Research Center Greifswald, Germany; and ‡Institute of Chemistry and Biochemistry, Ernst-Moritz-Arndt-Universität Greifswald, Germany

Received June 4, 1998; in revised form October 14, 1998; accepted October 19, 1998

Stilbite, stellerite, and barrerite—zeolites having the stilbite framework—were synthesized in a temperature range between 200 and 250°C by hydrothermal conversion of artificial water-free precursor glasses of the respective same composition at 1 kbar H<sub>2</sub>O pressure. No template materials and no sol–gel-like preparation technique was applied. Stilbite was formed from glass of the composition 1Na<sub>2</sub>O–8CaO–9Al<sub>2</sub>O<sub>3</sub>–54SiO<sub>2</sub> with monoclinic symmetry (*C2/m*,  $a = 13.61 \text{ \AA}$ ,  $b = 18.24 \text{ \AA}$ ,  $c = 11.27 \text{ \AA}$ ,  $\beta = 127.85^\circ$ , or: *F2/m*,  $a = 13.61 \text{ \AA}$ ,  $b = 18.24 \text{ \AA}$ ,  $c = 17.8 \text{ \AA}$ ,  $\beta = 90.75^\circ$  in pseudoorthorhombic setting). These preparation conditions could be successfully applied to the synthesis of zeolites stellerite (glass composition 4CaO–4Al<sub>2</sub>O<sub>3</sub>–28SiO<sub>2</sub>, symmetry *Fmmm*,  $a = 13.60 \text{ \AA}$ ,  $b = 18.22 \text{ \AA}$ ,  $c = 17.84 \text{ \AA}$ ) and barrerite (glass composition 4Na<sub>2</sub>O–4Al<sub>2</sub>O<sub>3</sub>–28SiO<sub>2</sub>, symmetry *Amma*,  $a = 13.64 \text{ \AA}$ ,  $b = 18.20 \text{ \AA}$ ,  $c = 17.84 \text{ \AA}$ ). The investigations showed, that the formation of these zeolites with the same type of crystal lattice was dependent only on the chemical composition of the starting material in general while the sodium and/or calcium content of the precursor glass was responsible for the formation of the respective zeolite phase in particular. Therefore it could be concluded that stellerite, stilbite, and barrerite are members of the same solid–solution series.

© 1999 Academic Press

**Key Words:** stilbite; stellerite; barrerite; hydrothermal synthesis; preparation of STI-type zeolites; morphology of STI-type zeolites; preparation from glass.

## INTRODUCTION

Stilbite, stellerite, and barrerite belong to the zeolite group with 4–4–1 building units (see Table 1). These building units are linked together to build up the three-dimensional framework by sharing the same (Si, Al) or the same oxygen (1). There are two main zeolite channels present in the stilbite structure type, in *a* ([100]) and *c* ([001]) direction containing H<sub>2</sub>O, Na, and Ca, dependent on the crystal phase (2, 3). The channels are linked together holding the monoclinic angle  $\beta$  (127.85° in case of stilbite, 90° in case of stellerite and barrerite, respectively) and form a two-

dimensional system (see Fig. 1). No channels exist in the [010] direction and the two-dimensional channel-system perpendicular to this direction leads to a weakening in the structure and causes the easy cleaving as well as the leafy morphology of common natural crystals. According to Gottardi and Galli (1), stilbite is always twinned but without a definite contact plane, while stellerite is untwinned and natural barrerite is mostly lamellar. No (Si, Al) ordering could be found in the tetrahedral framework of natural stilbite type zeolites (1, 3, 4).

The temperature dependent dehydration shows the different crystallographic positions of the zeolitic water. In stilbite and stellerite in dried air three main steps of water loss during the heating process can be observed: the smallest at 70°C, the largest at 175°C, and one at 250°C (1, 5), while barrerite steps of water loss are shifted to lower temperatures values of 50, 150, and 200 ((1); Table 1).

Natural stilbite is normally formed under hydrothermal conditions, but in some cases low grade metamorphic formation conditions are assumed (1). Stellerite is formed under postmagmatic hydrothermal and also metamorphic conditions while barrerite is known to be formed only under postmagmatic hydrothermal conditions (1).

Synthetic crystals with stilbite structure were obtained from laumontite under hydrothermal conditions at 170–180°C and 2–6 kbar using stilbite nuclei (6). Juan and Lo (7) investigated the behavior of stilbite under hydrothermal conditions of 0.7–2.5 kbar pressure. According to their investigations stilbite is stable between 175 and 222°C and decomposes above 222°C to an analcime type zeolite, quartz, and water. Joshi *et al.* (8) investigated the synthesis of analcime type zeolites from natural stilbites at autogenous pressures at 180°C.

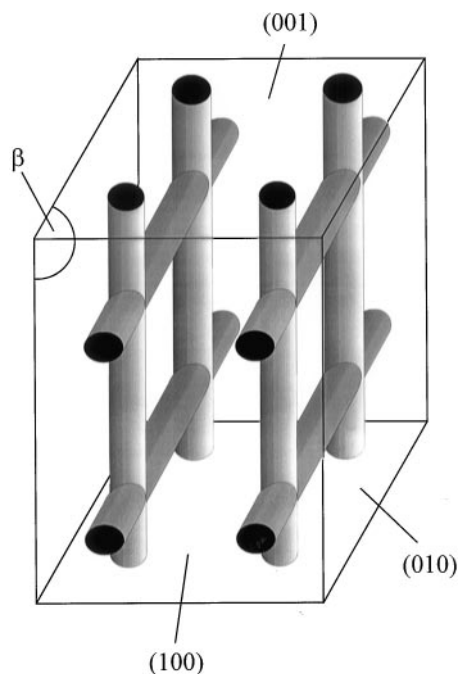
According to the knowledge of the authors no direct syntheses of stilbite have been reported up to now in literature and no stellerite and barrerite syntheses are known. The aim of the present examinations was, therefore, to investigate the formation conditions of stilbite type zeolites systematically.

**TABLE 1**  
General Crystallographic Data of the Investigated STI-Type Zeolites (1)

	Stilbite	Stellerite	Barrerite
Chemical formula	$(\text{NaCa}_4(\text{Al}_9\text{Si}_{27}\text{O}_{72})_x \cdot 30\text{H}_2\text{O})$	$(\text{Ca}_4(\text{Al}_8\text{Si}_{28}\text{O}_{72})_x \cdot 28\text{H}_2\text{O})$	$(\text{Na}_8(\text{Al}_8\text{Si}_{28}\text{O}_{72})_x \cdot 26\text{H}_2\text{O})$
Symmetry	$C2/m$ ( $F2/m$ , in pseudorthorhombic setting)	Fmmm	Amma
Unit cell parameters	$a = 13.61 \text{ \AA}$ $b = 18.24 \text{ \AA}$ $c = 11.27 \text{ \AA}$ $\beta = 127.85^\circ$ ( $a = 13.61 \text{ \AA}$ $b = 18.24 \text{ \AA}$ $c = 17.8 \text{ \AA}$ $\beta = 90.75^\circ$ )	$a = 13.60 \text{ \AA}$ $b = 18.22 \text{ \AA}$ $c = 17.84 \text{ \AA}$	$a = 13.64 \text{ \AA}$ $b = 18.20 \text{ \AA}$ $c = 17.84 \text{ \AA}$
Water positions	3(4)	3(4)	3(4)

### EXPERIMENTAL

Glasses of stilbite composition ( $1\text{Na}_2\text{O}-8\text{CaO}-9\text{Al}_2\text{O}_3-54\text{SiO}_2$ ), stellerite composition ( $4\text{CaO}-4\text{Al}_2\text{O}_3-28\text{SiO}_2$ ) and barrerite composition ( $4\text{Na}_2\text{O}-4\text{Al}_2\text{O}_3-28\text{SiO}_2$ ) were molten in a high frequency furnace in open carbon crucibles in air. Water free alkali- and/or alkaline earth carbonate,  $\gamma$ -alumina, and silicon dioxide (quartz) blended in the desired amount were used as starting materials. Visually



**FIG. 1.** Tubular sketch of the two-dimensional channel system in the stilbite structure directed in the main crystallographic directions.

**TABLE 2**  
Dihedral Angles of Investigated Stilbites

Plane I ( $h k l$ )	Plane II ( $h k l$ )	Angle ( $^\circ$ )
0 1 0	1 1 0	59
0 1 0	1 2 1	59
0 1 0	0 1 1	64
0 1 0	$\bar{1}$ 1 2	73
1 1 0	1 2 1	25
1 1 0	0 1 1	46
1 1 0	$\bar{1}$ 1 2	70

homogeneous glasses were amorphous according to powder X-ray-diffraction investigations ((XRD),  $\text{CuK}\alpha$ -radiation, Bragg-Brentano geometry). The glasses were placed in high pressure autoclaves using open copper capsules under the attach of distilled  $\text{H}_2\text{O}$  (water:glass ratio ca. 10:1). The whole system was set under pressure by using only distilled water as pressure medium.

The hydrothermal experiments were performed at 200, 220, and 250 $^\circ\text{C}$ , up to three times, at 1 kbar  $\text{H}_2\text{O}$  pressure for 6 weeks. The crystalline phases formed at the surface of the precursor glasses were subsequently investigated by XRD, energy-disperse X-ray analysis for chemical composition (EDX), and the crystal-morphology finally by scanning electron microscope images (SEM) which were evaluated with the stereocomparator for crystal indexing and crystallographic analysis (9).

### RESULTS

The evaluation of the hydrothermal experiments established that under the chosen conditions the zeolite phases stilbite, stellerite, and barrerite were formed from the respective precursor glass in the whole temperature range of investigations (confirmed by JCPDS-file 44-1479 (stilbite), 11-0125 (stellerite), and 29-1185 (barrerite), chemical analysis, and the dihedral angles of stereocomparator measurements; see Tables 2 to 4). Figures 2 to 4 show the formed crystals of the respective phase and the crystal planes. The determined dihedral angles between neighboring crystal planes are given in Tables 2 to 4. The values were within the experimental error of 3% according to the accuracy of the method.

**TABLE 3**  
Dihedral Angles of Investigated Stellerites

Plane I ( $h k l$ )	Plane II ( $h k l$ )	Angle ( $^\circ$ )
0 1 0	1 1 0	52
0 1 0	0 1 1	46
1 1 0	0 1 1	65

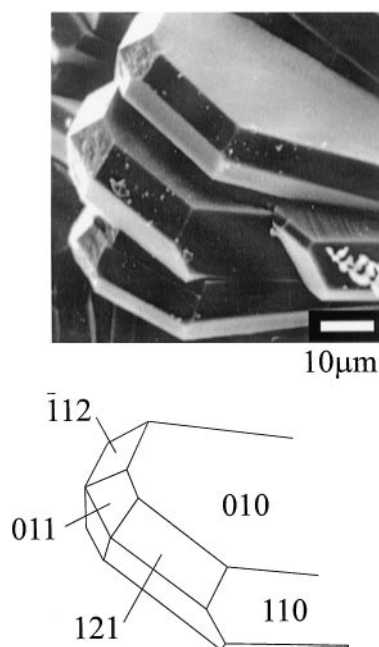
**TABLE 4**  
**Dihedral Angles of Investigated Barrerites**

Plane I ( <i>h k l</i> )	Plane II ( <i>h k l</i> )	Angle (°)
1 0 1	1 $\bar{2}$ 0	64
1 $\bar{1}$ 0	1 0 1	50
1 $\bar{1}$ 0	1 $\bar{2}$ 0	20

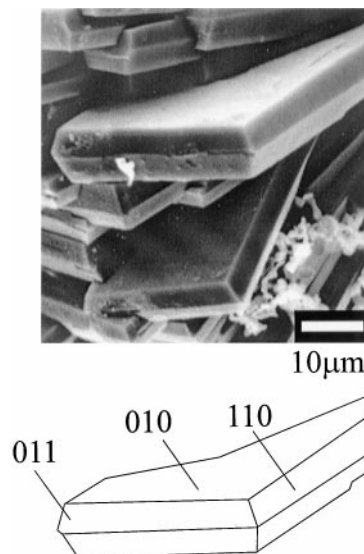
Up to 50% of the former glass was hydrothermally converted to crystalline products. All zeolite phases show a chemical composition close to that given in literature (1): 74.5 mol% SiO<sub>2</sub>-13 mol% Al<sub>2</sub>O<sub>3</sub>-11 mol% CaO-1 mol% Na<sub>2</sub>O (stilbite) 78 mol% SiO<sub>2</sub>-11 mol% Al<sub>2</sub>O<sub>3</sub>-12 mol% CaO (stellerite), 77 mol% SiO<sub>2</sub>-12 mol% Al<sub>2</sub>O<sub>3</sub>, 11 mol% Na<sub>2</sub>O (barrerite, accuracy of the measurements: 10%, water content not regarded).

### DISCUSSION

Contrary to the assumption of Gottardi and Galli (1) stilbite was found to be formed under equilibrium conditions in the temperature range between 200 and 250°C by using synthetic water-free glass of the same composition as starting material at 1 kbar water pressure. Under the same conditions stellerite and barrerite are formed by changing the respective stoichiometry of the precursor glasses. All three zeolites have the same lattice type and the formation



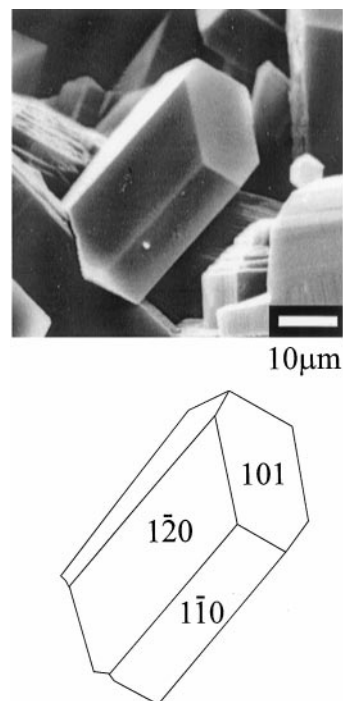
**FIG. 2.** SEM photograph of monoclinic stilbite crystals at 250°C (bottom, design of crystal habit; 1 kbar H<sub>2</sub>O pressure, after 6 weeks).



**FIG. 3.** SEM photograph of orthorhombic stellerite crystals 220°C and design of crystal habit (1 kbar H<sub>2</sub>O pressure, after 6 weeks).

of the respective phase is mainly dependent on the Na and Ca content of the starting material. Therefore it is concluded that they form a solid solution series.

Based on the experimental results, the isothermal solution-crystallization process can be explained in principle as shown in Fig. 5 (Point I, initial solution, pure distilled water and glass; point II, supersaturated solution, spontaneous



**FIG. 4.** SEM photograph of orthorhombic barrerite crystals at 220°C and design of crystal habit (1 kbar H<sub>2</sub>O pressure, after 6 weeks).

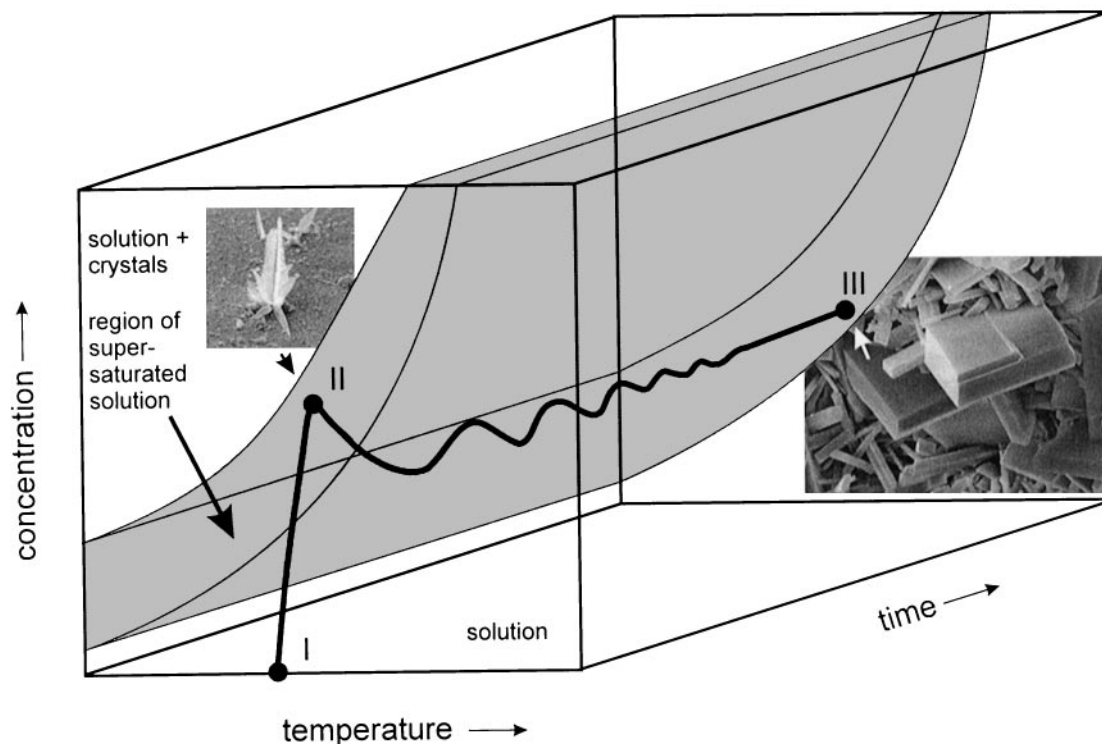


FIG. 5. Scheme of solution-crystallization process during zeolite formation at the glass surface.

crystallization in the region of supersaturated solution; between points II and III; oscillating concentration changes in the field of supersaturated solution leading to the final conditions of point III, continuous crystal growth in the field of supersaturated solution).

### CONCLUSIONS

Previous works exhibited the principal difficulties of stilbite synthesis, while stellerite and barrerite have never been synthesized. The present investigations show the possibility of stilbite type zeolite synthesis by hydrothermal methods. The use of glass of the respective stoichiometry as starting material for synthesis using only water under supercritical conditions as pressure medium only is a very successful method to obtain zeolite phases with similar or even identical chemical composition as the precursor glasses (if water

content is not regarded). A complete solution-recrystallization process occurs during stilbite type zeolite formation at the surface of the glass.

### REFERENCES

1. G. Gottardi and E. Galli, "Natural Zeolites." Springer Verlag, Heidelberg, New York, Tokyo, 1985.
2. W. M. Meier, D. H. Olson and CH. Baerlocher, "Atlas of Zeolite Structure Types," 4th revised ed. Elsevier, London, Boston, Singapore, Sydney, Toronto, Wellington, 1996.
3. E. Galli, *Acta Crystallogr. B* **27**, 833 (1971).
4. S. Quartieri and G. Vezzalini, *Zeolites* **7**, 163 (1987).
5. O. Schäf, H. Ghobarkar, and U. Guth, *Ionics* **3**, 282 (1997).
6. J. G. Liou, *Contrib. Miner. Petrol.* **31**, 171 (1971).
7. V. C. Juan and H. J. Lo, *Proc. Geol. Soc. China (Formosa)* **16**, 37 (1973).
8. M. S. Joshi, A. L. Choudhari, and R. Kanitkar, *Cryst. Res. Technol.* **18**, 1347 (1983).
9. H. Ghobarkar, *Krist. Tech.* **12**, K49 (1977).