

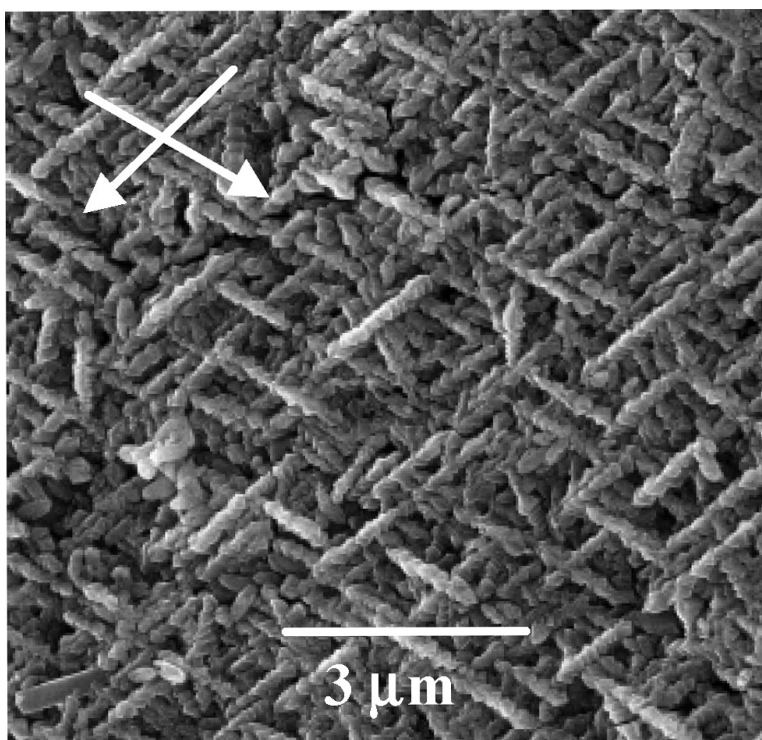
Communication

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Heteroepitaxial Growth of a Zeolite Film with a Patterned Surface-Texture

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Zeolites contain molecular-sized voids within their crystal structures.^{1,2} Recently, research on zeolites for novel applications of their unique structures as host frameworks for molecules, ions, and clusters has been reported.³ For these potential uses, we focus on the preparation of oriented films of zeolites by heteroepitaxial growth. The ability to connect heterogeneous zeolite structures also enables the construction of multidimensional, nanospatial networks. Such nanospatial networks may serve as hosts to integrate molecular electronics and other molecular devices within their structures.

To control both in-plane and out-of-plane orientations of a crystalline film, epitaxial growth is a direct approach. As for zeolite, intergrowth or overgrowth phenomena have been well known,⁴ although the intended epitaxy, such as FAU/EMT,^{5,6} MAZ/EMT,⁷ ETS-10/ETS-4,⁸ and CAN/SOD,^{5,9} has been reported very recently. In our previous work, heteroepitaxial growth of hexagonal cancrinite on a millimeter-sized cubic sodalite single crystal^{9,10} has been shown. Sodalite and cancrinite have structural similarities, because their aluminosilicate layers of six-membered rings are identical to each other. The differences in the structures originate from the stacking sequences of the six-membered rings.² Sodalite along [111] is constructed by an “abc” stacking sequence, while cancrinite along [0001] is constructed by “ab”. In our previous study, cancrinite layers consisting of columnar crystals were successfully grown heteroepitaxially, but the grains among the crystals could not be removed.

In this study, we focus on the heteroepitaxial growth of trigonal chabazite with voids of three-dimensional intersection structures. Chabazite is also constructed from six-membered ring layers with a stacking sequence of “aabcc” along [111]. Therefore, chabazite can grow heteroepitaxially on a sodalite substrate while keeping the relation of chabazite (111)/sodalite {111}, as shown in Figure 1. In this Communication, we report on the first success of the heteroepitaxial growth of a continuous zeolite film on a millimeter-sized sodalite single crystal. Because of twin formation of chabazite, a unique patterned surface-texture is obtained on the millimeter-scale.

Experimental conditions are shown in Supporting Information 1 and 2. The morphology of chabazite on a sodalite surface is observed with a field-emission scanning electron microscope (FE-SEM: Hitachi, S-900). The cross section is also observed with a transmission electron microscope (TEM: JEOL, JEM 2010F), and the orientation of chabazite is determined. For the TEM observation, the sample is processed using a focused ion beam (FIB: Micrion, JFIB-2100), similar to the previous case of cancrinite.⁹

An FE-SEM image of the unique patterned surface-texture obtained is shown in Figure 2. Chabazite film, which is ca. 1 μm thick, is composed of “rodlike” structures facing two directions. As shown later, such a texture is formed by the heteroepitaxial

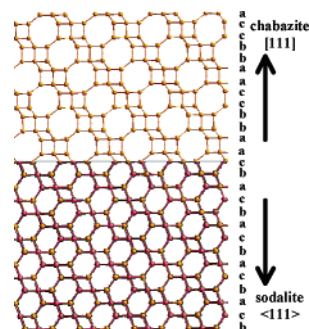


Figure 1. A model of heteroepitaxial growth of chabazite on sodalite. The stacking sequence along the chabazite [111] is “aabcc” (top), and that along the sodalite $\langle 111 \rangle$ direction is “abc” (bottom). Chabazite can grow heteroepitaxially on a sodalite substrate while keeping the relation of chabazite (111)/sodalite {111}.

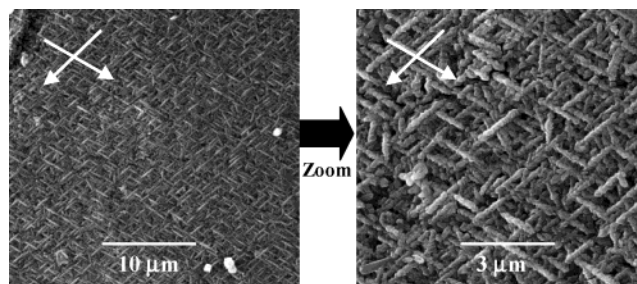


Figure 2. An FE-SEM image of a patterned surface-texture of chabazite on a sodalite surface. “Rodlike” structures are observed in two directions as marked in the image.

growth of chabazite on a sodalite surface and the subsequent twin formation of chabazite.

In the early stages of chabazite growth, disk-shaped products facing two different directions are observed, as shown in Figure 3a. From a morphological point of view, the top surface of the chabazite disk is assigned as (111). The as-grown sodalite is surrounded by {110} planes, and there are two kinds of accessible six-membered rings facing two different directions on the sodalite (110) surface, as shown in Figure 3b. Two possible overgrowth directions are represented by sodalite $[11\bar{1}]$ and sodalite $[1\bar{1}1]$ in Figure 3b. The angle between sodalite $[110]$ and sodalite $[11\bar{1}]$, as well as that between sodalite $[110]$ and sodalite $[1\bar{1}1]$, is about 35°. Therefore, Figure 3a supports the claim that chabazite grows heteroepitaxially toward two different directions while keeping the relation of chabazite (111)/sodalite {111}, as shown in Figure 3c. Selected area electron diffraction (SAED) patterns of the interface between sodalite and chabazite regions are shown in Figure 3d. This pattern is taken along with the sodalite $[\bar{1}11]$ zone axis. The outer six spots in Figure 3d are identified as those due to the sodalite {110} plane, and the inner four spots are due to the chabazite $\{1\bar{1}0\}$ plane. From the SAED patterns, it is demonstrated that chabazite

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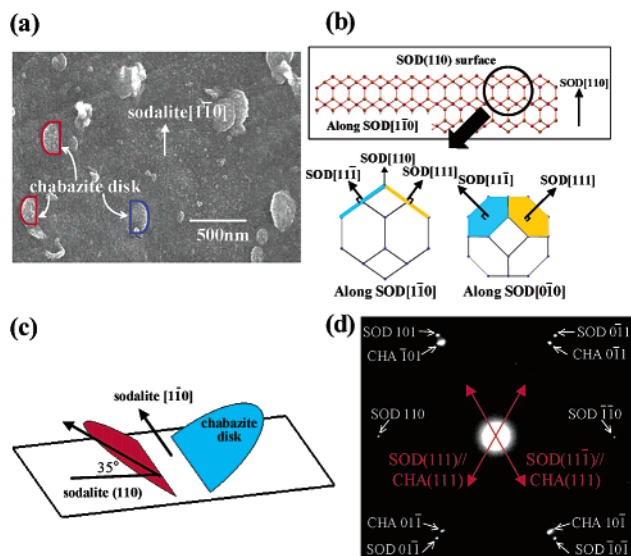


Figure 3. (a) An FE-SEM image of chabazite disks in the early stages of growth. (b) A model of the top surface structure of a sodalite (110) surface. Sodalite and chabazite are mentioned as “SOD” and “CHA”, respectively. There are two kinds of accessible six-membered rings in two different directions (SOD [11 $\bar{1}$] and SOD [111]) on the sodalite (110) surface. (c) A model of heteroepitaxial growth of chabazite on sodalite (110) surface. (d) Selected area electron diffraction (SAED) patterns of the interface between the sodalite and chabazite regions.

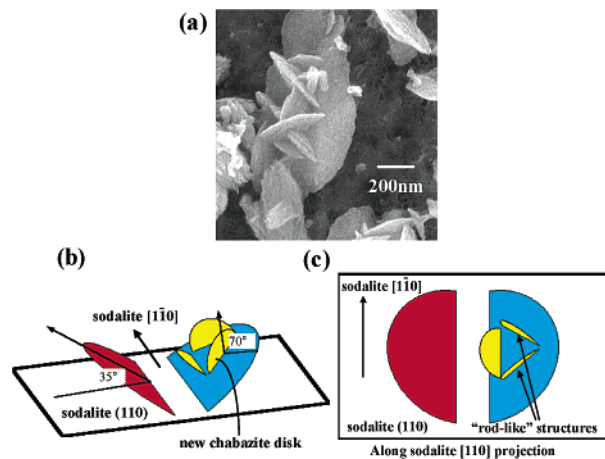


Figure 4. (a) An FE-SEM image of twin formation of chabazite in the early stages of heteroepitaxial growth. (b) A model of twin formation of chabazite. (c) A projection image of (b) along sodalite [110]. Two of the three chabazite disks are seen as “rod-like” structures.

grows toward two different directions on a sodalite surface. Spots are assigned as sodalite (0 $\bar{1}$ 1)//chabazite (0 $\bar{1}$ 1) and sodalite (101)//chabazite ($\bar{1}$ 01). Therefore, the relations of the planes are determined as follows: (1) sodalite (111)//chabazite (111), and sodalite (0 $\bar{1}$ 1)//chabazite (0 $\bar{1}$ 1), and (2) sodalite (11 $\bar{1}$)//chabazite (111), and sodalite(101)//chabazite (101).

The unit-cell orientation relationships correspond to the heteroepitaxial growth of chabazite on the sodalite substrate, as shown in Figure 1.

Figure 4a shows an FE-SEM image of twin formation of chabazite on a chabazite disk in the early stages of heteroepitaxial growth (Supporting Information 3). From a morphological point of view, the twin formation originates from the stacking fault of

the six-membered rings¹¹ (Supporting Information 4). New chabazite disks can overgrow at an angle of about 70° on chabazite disks, and there are three equivalent directions that the twin formation can occur in, as shown in Figure 4b. Figure 4c shows a model of a projection image of chabazite disks perpendicular to sodalite {110}. Two of the three chabazite disks are seen as “rodlike” structures. Therefore, the “rodlike” structures observed in Figure 2 are composed of edges of the disk-shaped products, as shown in Figure 4c. Thus, heteroepitaxial growth of chabazite on sodalite and the subsequent twin formation of chabazite continue to form unique patterned surface-textures of chabazite.

In conclusion, the heteroepitaxial growth of a continuous chabazite film has been accomplished on a millimeter-sized sodalite crystal for the first time. The unique patterned surface-texture of chabazite films is rationalized by the heteroepitaxial growth of chabazite on sodalite and the subsequent twin formation of chabazite. Further studies on the fabrication of multidimensional, nanospacial networks using the zeolites will be published elsewhere.

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Supporting Information Available: Detailed experimental procedure and explanation of twin formation (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Breck, D. W. *Zeolite Molecular Sieves*; Wiley: New York, 1974. (b) Cundy, C. S.; Cox, P. A. *Chem. Rev.* **2003**, *103*, 663–701.
- (2) Barrer, R. M. *Hydrothermal Chemistry of Zeolites*; Academic Press: London, 1982.
- (3) (a) Davis, M. E. *Nature* **2002**, *417*, 813–821. (b) Nozue, Y.; Kodaira, T.; Goto, T. *Phys. Rev. Lett.* **1992**, *68*, 3789–3792. (c) Nozue, Y.; Kodaira, T.; Ohwashi, S.; Goto, T.; Terasaki, T. *Phys. Rev. B* **1993**, *48*, 12253–12261. (d) Vietze, U.; Krauss, O.; Laeri, F.; Ihlein, G.; Schüth, F.; Limberg, B.; Abraham, M. *Phys. Rev. Lett.* **1998**, *21*, 4628–4631. (e) Ihlein, G.; Schüth, F.; Krauss, O.; Vietze, U.; Laeri, F. *Adv. Mater.* **1998**, *10*, 1117–1119. (f) Yang, P.; Wirnsberger, G.; Huang, H. C.; Cordero, S. R.; McGhee, M. D.; Scott, B.; Deng, T.; Whitesides, G. M.; Chmelka, B. F.; Buratto, S. K.; Stucky, G. D. *Science* **2000**, *287*, 465–467. (g) Wada, Y.; Okubo, T.; Ryo, M.; Nakazawa, T.; Hasegawa, Y.; Yanagida, S. *J. Am. Chem. Soc.* **2000**, *122*, 8583–8584. (h) Ryo, M.; Wada, Y.; Okubo, T.; Nakazawa, T.; Hasegawa, Y.; Yanagida, S. *J. Mater. Chem.* **2002**, *12*, 1748–1753.
- (4) For example: (a) Lillerud, K. P.; Raeder, J. H. *Zeolites* **1986**, *6*, 474–483. (b) Thomas, J. M.; Millward, G. R. *J. Chem. Soc., Chem. Commun.* **1982**, *24*, 1380–1383. (c) Feijen, E. J. P.; Devadder, K.; Bosschaerts, M. H.; Lievens, J. L.; Martens, J. A.; Grobet, P. J.; Jacobs, P. A. *J. Am. Chem. Soc.* **1994**, *116*, 2950–2957. (d) Nair, S.; Villaescusa, L. A.; Cambor, M. A.; Tsapatsis, M. *Chem. Commun.* **1999**, *10*, 921–922.
- (5) Martens, J. A.; Jacobs, P. A. *Adv. Funct. Mater.* **2001**, *11*, 337–338.
- (6) (a) Goossens, A. M.; Wouters, B. M.; Buschmann, V.; Martens, J. A. *Adv. Mater.* **1999**, *11*, 561–564. (b) Goossens, A. M.; Wouters, B. H.; Grobet, P. J.; Buschmann, V.; Fiermans, Lucien; Martens, J. A. *Eur. J. Inorg. Chem.* **2001**, *5*, 1167–1181. (c) Yonkeu, A. L.; Buschmann, V.; Miede, G.; Fuess, H.; Goossens, A. M.; Martens, J. A. *Cryst. Eng.* **2001**, *4*, 253–267.
- (7) Goossens, A. M.; Buschmann, V.; Martens, J. A. *Stud. Surf. Sci. Catal.* **2001**, *135*, 176–183.
- (8) Jeong, H.; Krohn, J.; Sujaoti, K.; Tsapatsis, M. *J. Am. Chem. Soc.* **2002**, *124*, 12966–12968.
- (9) (a) Okubo, T.; Wakihara, T.; Plévert, J.; Nair, S.; Tsapatsis, M.; Ogawa, Y.; Komiyama, H.; Yoshimura, M.; Davis, M. E. *Angew. Chem., Int. Ed.* **2001**, *40*, 1069–1071. (b) Wakihara, T.; Plévert, J.; Nair, S.; Tsapatsis, M.; Yamakita, S.; Ogawa, Y.; Komiyama, H.; Sadakata, M.; Davis, M. E.; Okubo, T. *Stud. Surf. Sci. Catal.* **2001**, *135*, 350–357.
- (10) Shiraki, T.; Wakihara, T.; Sadakata, M.; Yoshimura, M.; Okubo, T. *Microporous Mesoporous Mater.* **2001**, *42*, 229–234.
- (11) Cartledge, S.; Wessicken, R.; Nissen, H.-U. *Phys. Chem. Miner.* **1983**, *9*, 139–145.

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