

Optical investigation of intergrowth and the accessibility of catalytic sites in etched zeolite SSZ-13 by confocal fluorescence microscopy

Linn Sommer, Stian Svelle, Karl Petter Lillerud, Michael Stöcker, Bert M. Weckhuysen and Unni Olsbye

Supporting Information

Part 1: Morphology predictions using Materials Studio 5.0

Often, the observed morphology of materials with CHA topology is nearly cubic. However, the SEM overview picture (Figure 1) shows crystals with some deviations from this pseudocubic morphology. This can be rationalized by taking into account that the crystal habit is determined by the relative growth rate of the different facets. As a consequence, facets with high growth rates disappear whereas the facets with the smallest growth rates will dominate the crystal habit.

The program Materials Studio 5.0 from Accelrys Software Inc. was used in order to imitate the crystal habits found in Figure 1 (SEM images) and Figure 2 (confocal image of the crystal surface) of this study. The crystal habits presented in Figures S1 and S2 were generated using the Bravais-Friedel Donnay-Harker (BFDH) task of the Morphology Calculation module. The BFDH method is based on cell parameters and symmetry operators only and does not account for the energetics of the system. The generated crystal habit was manipulated manually in order to create different morphologies. The properties of the final crystal habits shown in the Figures S1 and S2 are reported in Tables S1 and S2. Here, the centre-to-facet distances indicate the relative growth rates of the planes.

Figure S1 shows simulated crystal habits compared to crystal morphologies found in SEM (A-C, sections from Figure 1) and a confocal fluorescence micrograph of the crystal surface (D, as presented in Figure 2). Habit A corresponds to the pseudocubic morphology. In habit B, the corners are cut due to the development of the $\{111\}$ and $\{11\bar{1}\}$ facets. When the $\{-110\}$, $\{-10\bar{1}\}$, $\{-101\}$ and $\{-110\}$ facets gradually develop at the expense of the $\{010\}$ facet, habit C is obtained, showing a terrace like feature on top. Full development of these facets at the expense of the $\{010\}$ facet results in the formation of a tetragonal-pyramidal tip (D). In order to keep track

of the development based on the most common pseudocubic morphology, the terrace like feature (C) and the tetragonal-pyramidal tip (D) were simulated on top of one crystal plane only.

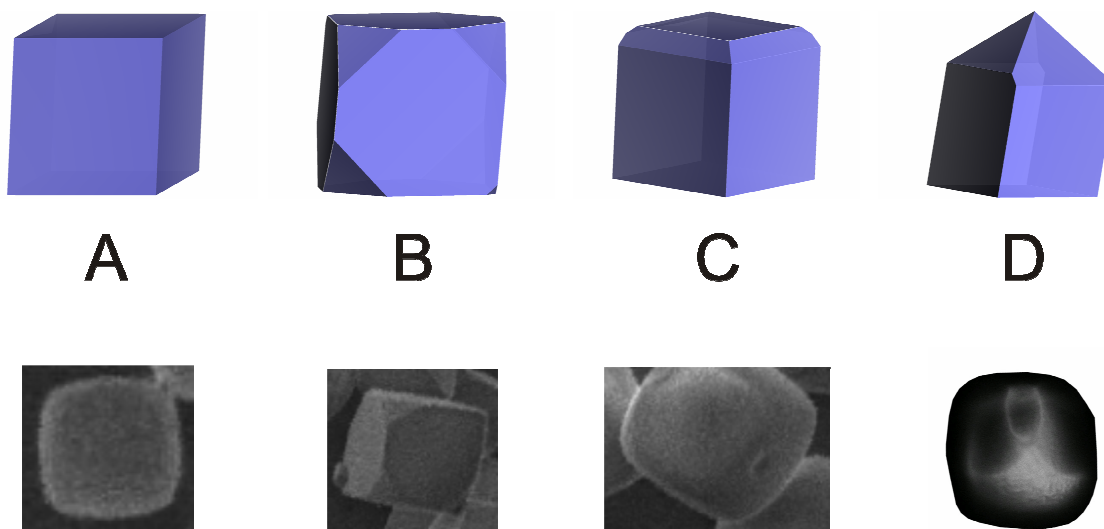


Figure S1: Simulated crystal habits compared to crystal morphologies found in SEM (A-C, snapshots taken from Figure 1) and a confocal fluorescence micrograph of the crystal surface (D, as presented in Figure 2).

Now, the appropriateness of these simulations must be discussed. All crystal habits shown here are generated from a model that is based on the ideal, defect free crystal structure. In contrast, the confocal fluorescence measurement shown in Figure 2 of this article as well as results from Karwacki et al.¹ strongly suggest that the crystals possess a tetragonal-pyramidal intergrowth structure. Hence, the fact that the observed crystal habits can be imitated without taking into account intergrowth demonstrates the result of simulations might be misleading. From these simulations, the orientation of the micropore system can be deduced, but such deductions should be supported by experimental crystallographic data from for example electron backscatter diffraction (EBSD) measurements².

However, the tetragonal-pyramidal feature in the simulated crystal habits, namely the tetragonal-pyramidal tip in habit D, can be used as starting point for further speculations about the crystal growth and the observed intergrowth features. The intergrowth structure for the CHA topology consists of six tetragonal pyramids. In Figure S2, habit D is modified further by shrinking the underlying pseudocubic, resulting in a nearly tetragonal pyramid (E). Thus, it can be suggested

that the crystal growth starts from the tip of six pyramids like shown in Figure S2, resulting in the experimentally observed intergrowth. A set of EBSD measurements, which are beyond the scope of the present study, might help to verify this hypothesis experimentally.

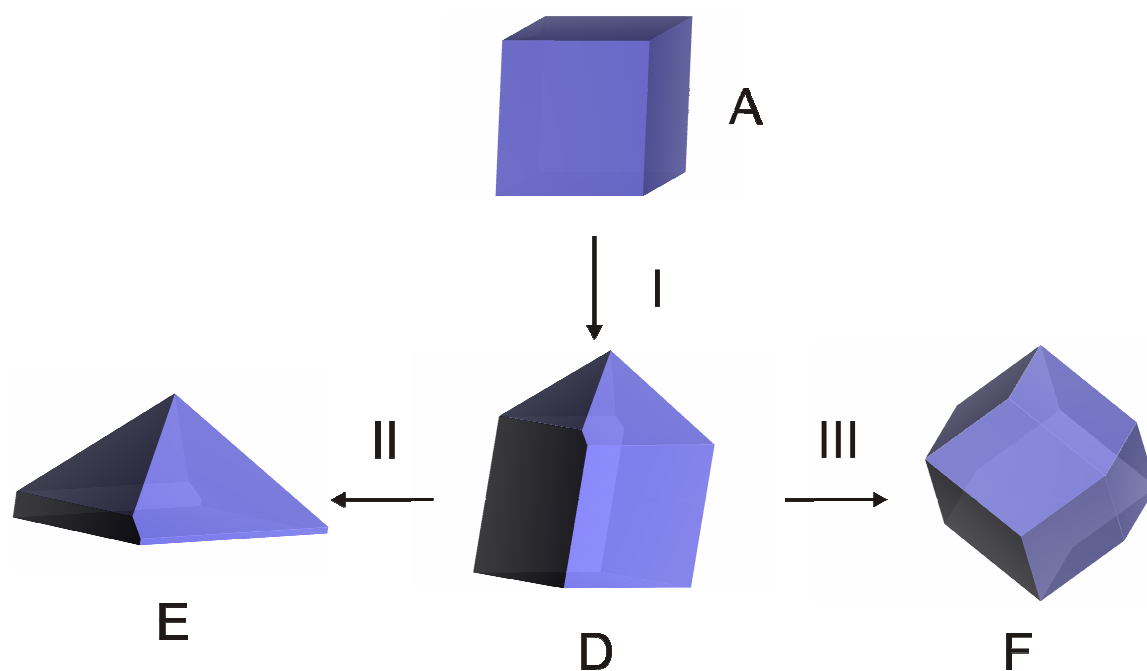


Figure S2: Generation of a pyramidal crystal habit starting from a cubic habit (E). Consequent development of pyramids in all directions results in habit F.

As seen from Table S1, the generation of the terrace like habit C and the pyramidal habit E is accompanied by a severe loss of symmetry. The symmetry equivalence of the $\{100\}$ family of facets is broken, the multiplicity decreases from 6 to 1. The question arises how likely such a severe loss of symmetry is. However, recalling that zeolite growth is dominated by kinetics rather than thermodynamics, a growth model as suggested here, might occur and should be subject of further experimental verification.

References

- (1) Karwacki, L.; Stavitski, E.; Kox, M. H. F.; Kornatowski, J.; Weckhuysen, B. M., *Angew. Chem., Int. Ed.* **2007**, 46, 38, 7228-7231.
- (2) Karwacki, L.; Kox, M. H. F.; de Winter, D. A. M.; Drury, M. R.; Meeldijk, J. D.; Stavitski, E.; Schmidt, W.; Mertens, M.; Cubillas, P.; John, N.; Chan, A.; Kahn, N.; Bare, S. R.; Anderson, M.; Kornatowski, J.; Weckhuysen, B. M., *Nature Materials* **2009**, 8, 12, 959-965.

Table S1: Habit properties: summary.

Habit	A	B	C	D	E	F
Aspect ratio:	1.78	1.55	2.04	3.09	1.48	0
Relative surface / volume ratio:	1.24	1.18	1.21	1.20	1.11	1.46
Crystal structure document:	CHA	CHA	CHA	CHA	CHA	CHA
Space group:	R-3M	R-3M	P1	P1	R-3M	P1
Point group:			1	1		1
Unique number of facets:	1	3	10	9	2	9

Table S2: Habit properties: facets.

Habit	hkl	Multiplicity	Centre-to-facet distance*	% Area	% Total area	Vertices
A	{ 1 0 0}	6	6.6	16.7	100	4
B	{ 1 0 0}	6	12.9	14.8	89.0	8
	{ 1 1 -1}	6	17.6	1.8	10.9	3
	{ 1 1 1}	2	19.9	0.1	0.1	3
C	{ 0 0 -1}	1	4.4	16.0	16.0	5
	{ 0 -1 0}	1	4.4	15.8	15.8	4
	{ -1 0 0}	1	4.5	15.9	15.9	4
	{ 0 0 1}	1	5.3	17.2	17.1	5
	{ 1 0 0}	1	5.3	17.1	17.1	5
	{ 0 1 0}	1	6.7	10.4	10.4	4
	{ -1 1 0}	1	7.2	2.7	2.7	6
	{ 0 1 -1}	1	7.2	2.7	2.7	5
	{ 0 1 1}	1	7.8	1.1	1.1	4
	{ 1 1 0}	1	7.8	1.1	1.1	4
D	{ 1 0 0}	1	3.4	16.2	16.2	4
	{ 0 1 0}	1	4.4	14.7	14.7	5
	{ 0 0 1}	1	4.5	14.5	14.5	4
	{ 0 -1 0}	1	5.3	16.0	16.0	6
	{ 0 0 -1}	1	5.3	15.8	15.8	5
	{ -1 1 0}	1	7.2	6.4	6.4	5
	{ -1 0 1}	1	7.3	6.4	6.4	5
	{ -1 0 -1}	1	7.8	5.0	5.0	4
	{ -1 -1 0}	1	7.8	5.0	5.0	4
E	{ 0 1 0}	1	4.4	1.1	1.1	5
	{ 0 0 1}	1	4.5	1.0	1.0	4
	{ 1 0 0}	1	5.1	37.3	37.3	4
	{ 0 -1 0}	1	5.3	4.2	4.2	6
	{ 0 0 -1}	1	5.3	4.0	4.0	5
	{ -1 1 0}	1	7.2	14.7	14.7	5
	{ -1 0 1}	1	7.3	14.7	14.7	5
	{ -1 0 -1}	1	7.8	11.6	11.6	4
	{ -1 -1 0}	1	7.8	11.4	11.4	4
F	{ 1 -1 0}	6	14.5	9.2	55.4	4
	{ 1 1 0}	6	15.7	7.4	44.6	4

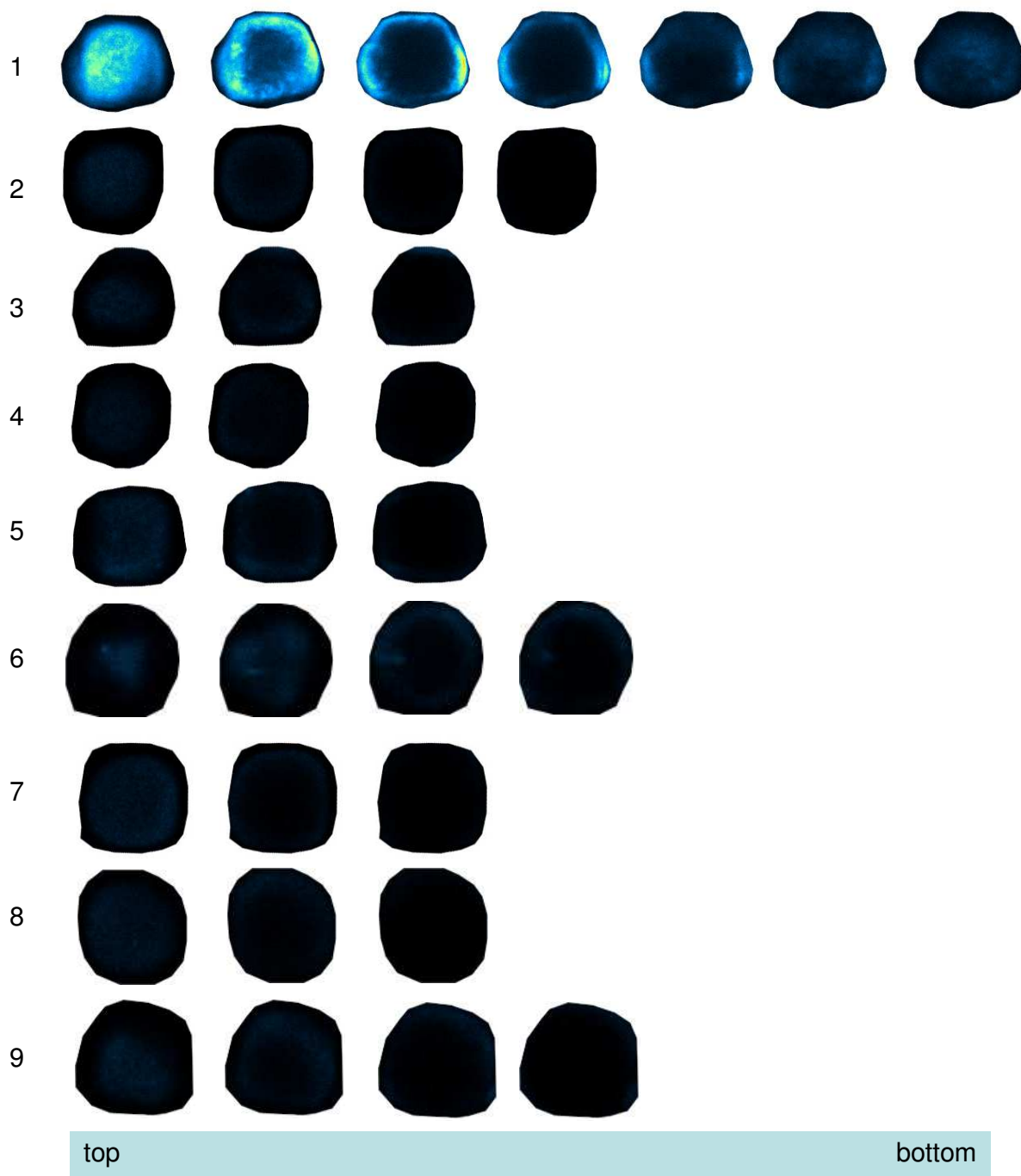
* The centre-to-facet distance reflects the growth rate of the respective facet.

Supporting Information

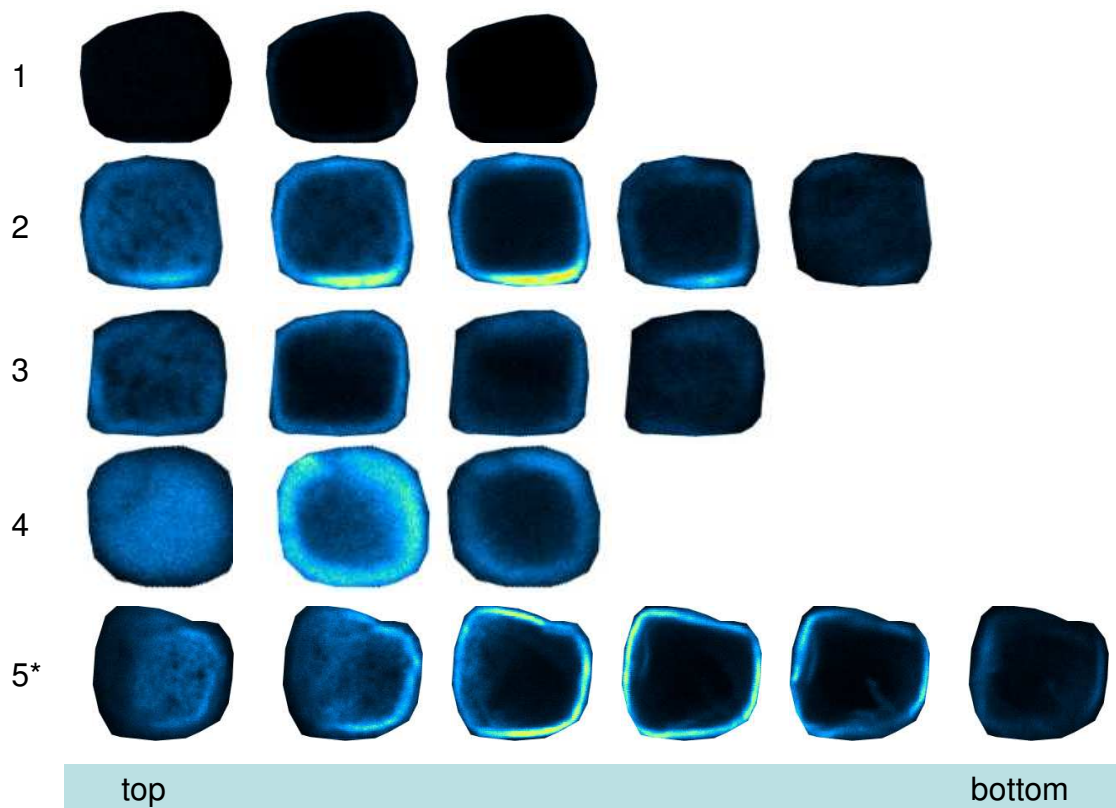
Part II: Catalogue of investigated H-SSZ-13 crystals after the oligomerization of 4-methoxystyrene and 4-ethoxystyrene.

The following figures give a broader overview over the investigated samples than could be presented in the article. Crystals that were subjected to neutron irradiation prior to this study are marked with an asterisk (*). The crystals are presented starting with confocal fluorescence images from the top layer (left) and gradually going deeper to the bottom (right). In Table S3 and S4, the dimensions as obtained from the confocal microscopy measurements are listed. The dimension for the depth (z) was left out because the fluorescence signal lost intensity when coming closer to the bottom layer. This is due to the optical properties of the individual crystals, making it difficult to define the bottom layer of the crystals confidently.

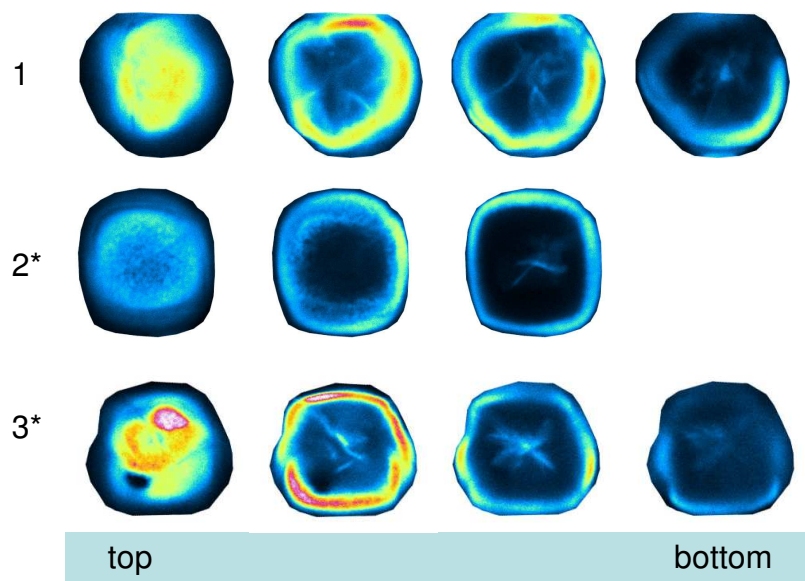
H-SSZ-13 untreated / 4-methoxystyrene



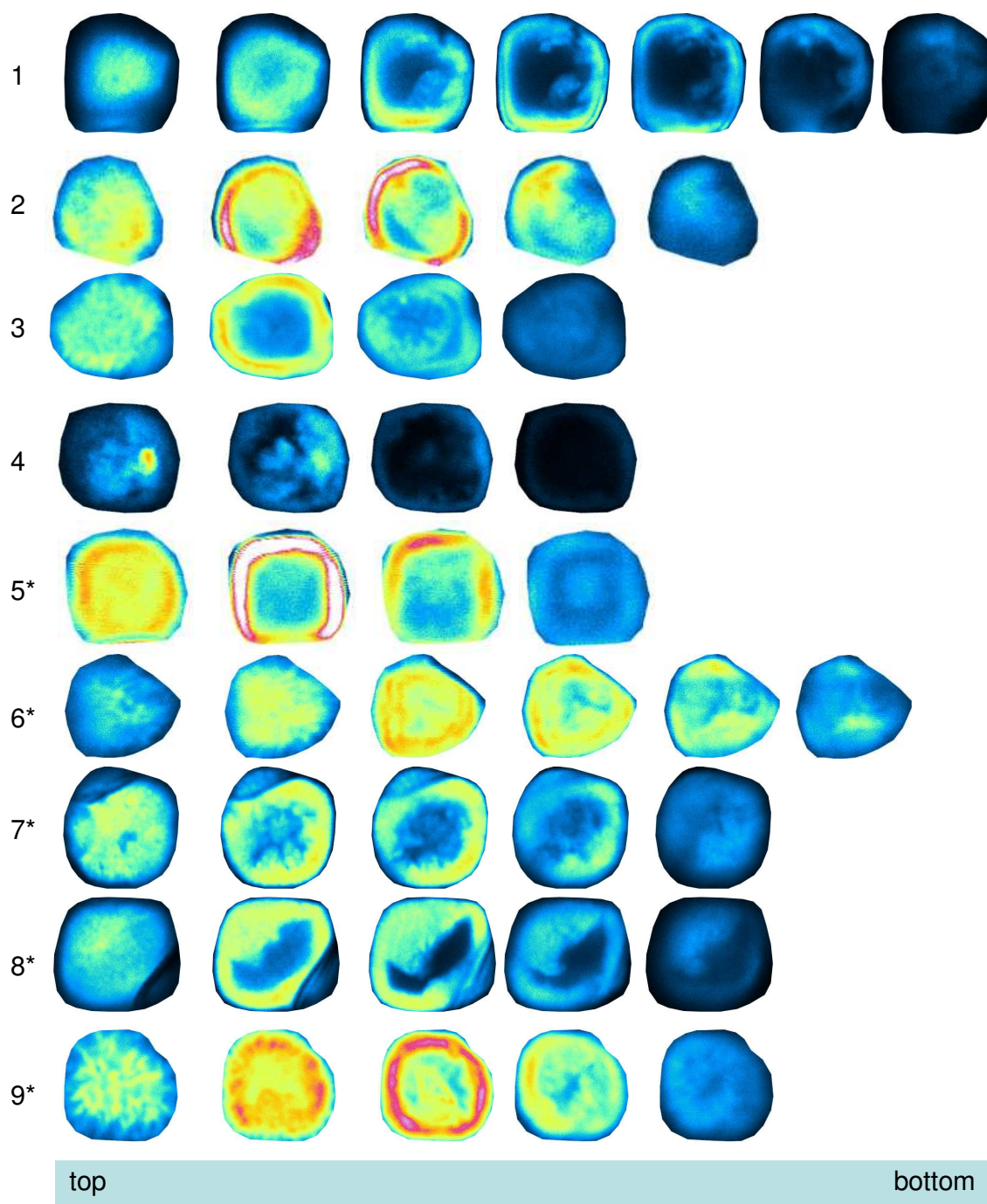
H-SSZ-13 etched / 4-methoxystyrene / type 1



H-SSZ-13 etched / 4-methoxystyrene / type 2



H-SSZ-13 etched / 4-methoxystyrene / type 3



H-SSZ-13 etched / 4-methoxystyrene / type 4

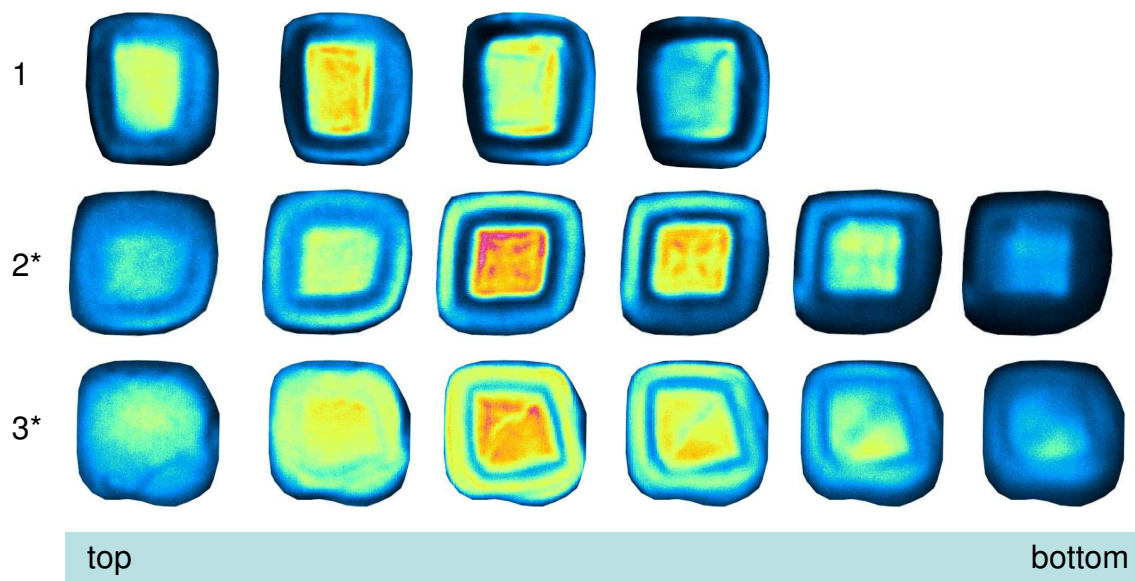


Table S3: Dimensions of the presented crystals after 4-methoxystyrene oligomerization.

	type 1		type 2		type 3		type 4		untreated	
Nr.	size [μm]		size [μm]		size [μm]		size [μm]		size [μm]	
	x	y	x	y	x	y	x	y	x	y
1	8	8	12	12	12	13	7	7.5	14	13
2	7	6.5	17	18	6	6	7	7	14	14
3	6	6	15	15	7	7	7.5	7.5	11	10
4	8	8			10	10			13	11
5	11	10			6.5	6.5			9	9
6					6	6			8.5	7.5
7					12	12			13	13
8					10	10			10	10
9					8	8			14	14

H-SSZ-13 etched / 4-ethoxystyrene

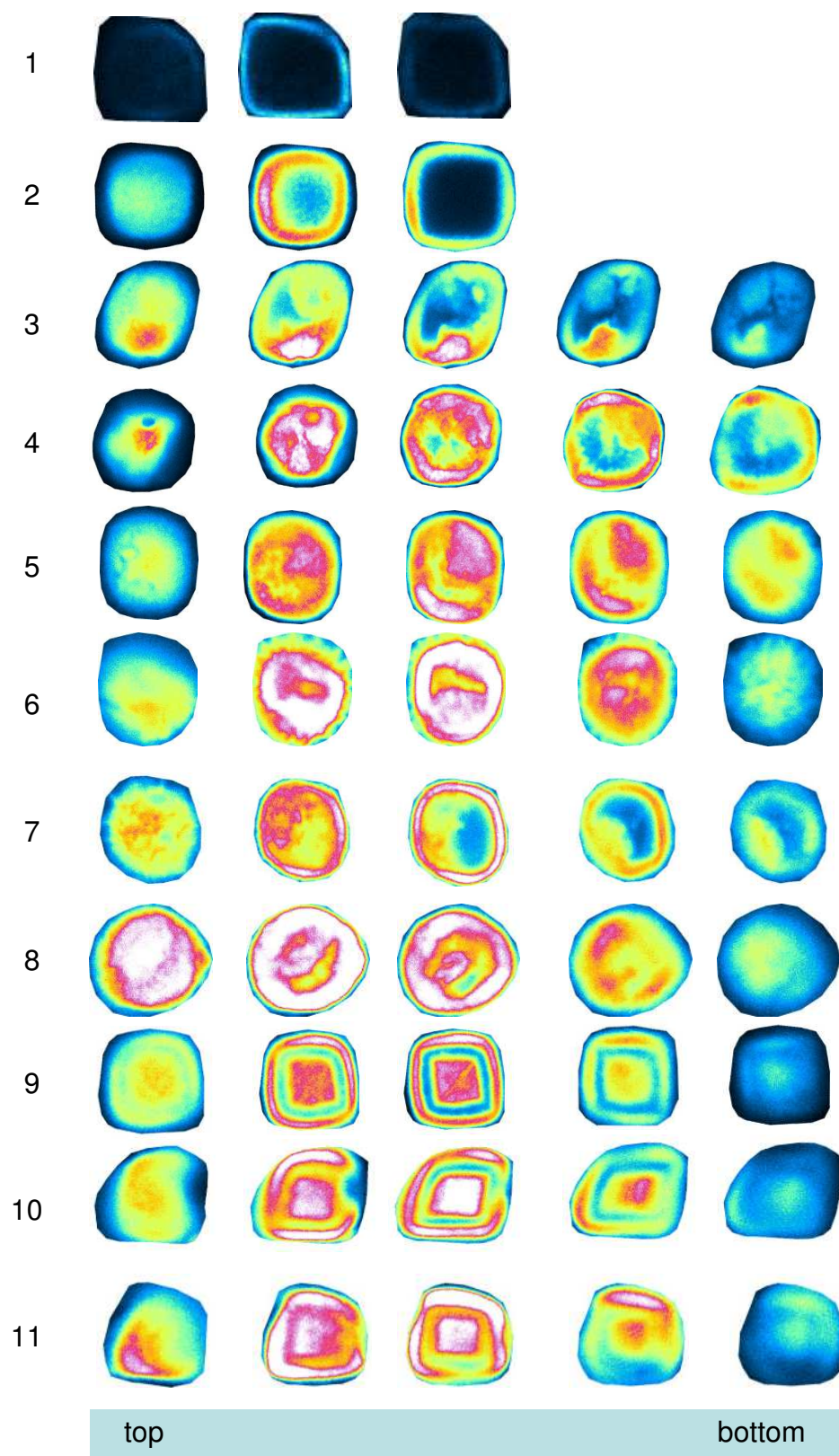


Table S4: Dimensions of the presented crystals after 4-ethoxystyrene oligomeriaztion.

Nr.	size [μm]	
	x	y
1	6	6
2	13	14
3	11	11
4	15	16
5	11	11
6	7	7
7	7.5	7.5
8	8	8
9	7	7
10	7	7
11	5.5	5.5