ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Contemplation of NaA zeolite cubic crystal formation and deformation: Cubes with crystalline core, simultaneous growth of surface and core crystals, and layer-by-layer destruction

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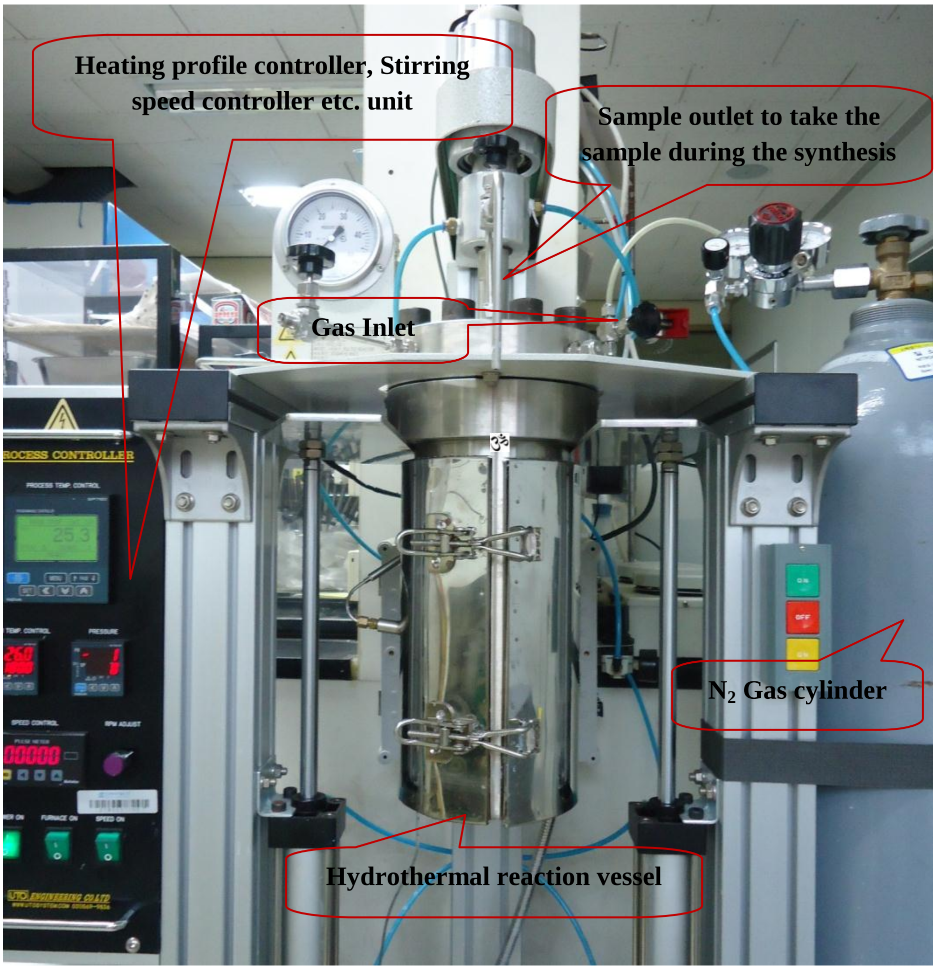
SI1. Specially designed autoclave

It is a specially designed autoclave with inner volume of 2.1 L, manufactured by UTO Engineering Co. Ltd., South Korea. This autoclave has some special features in comparison to other commonly used autoclaves for zeolite material synthesis. It contains heat profile controller, pressure monitor and also mechanical stirrer with controller, which help in highly desirable homogenous heating and mixing of hydrogel throughout the synthesis process. A gas inlet-outlet is also provided in this autoclave to make desirable changes in synthesis environment by introducing the desired gas. Another exciting feature of this autoclave is that an aliquot can be taken from the precursor mixture at any time without stopping the crystallization reaction and changing the synthesis conditions.



SI1. Specially designed autoclave.

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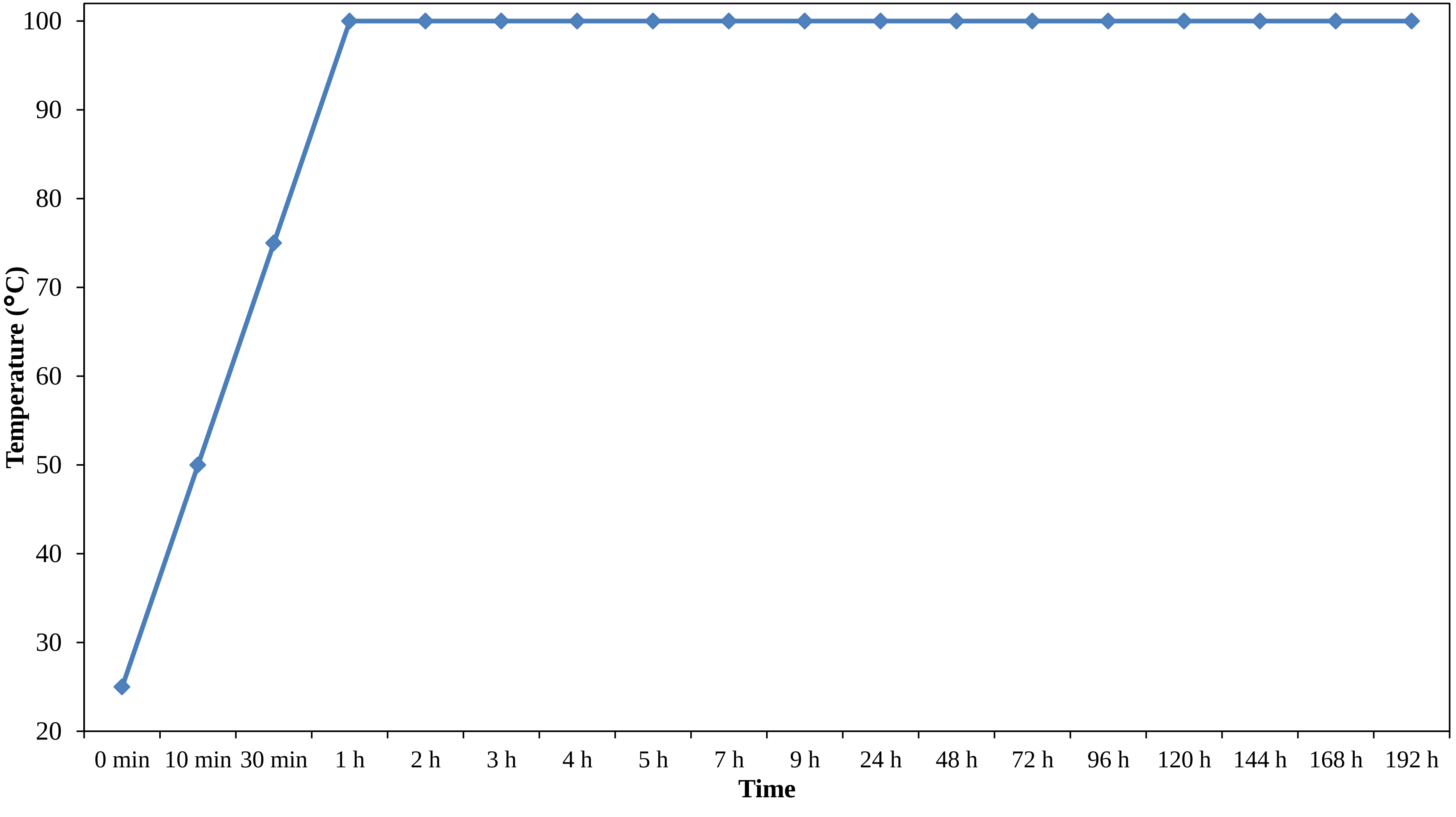
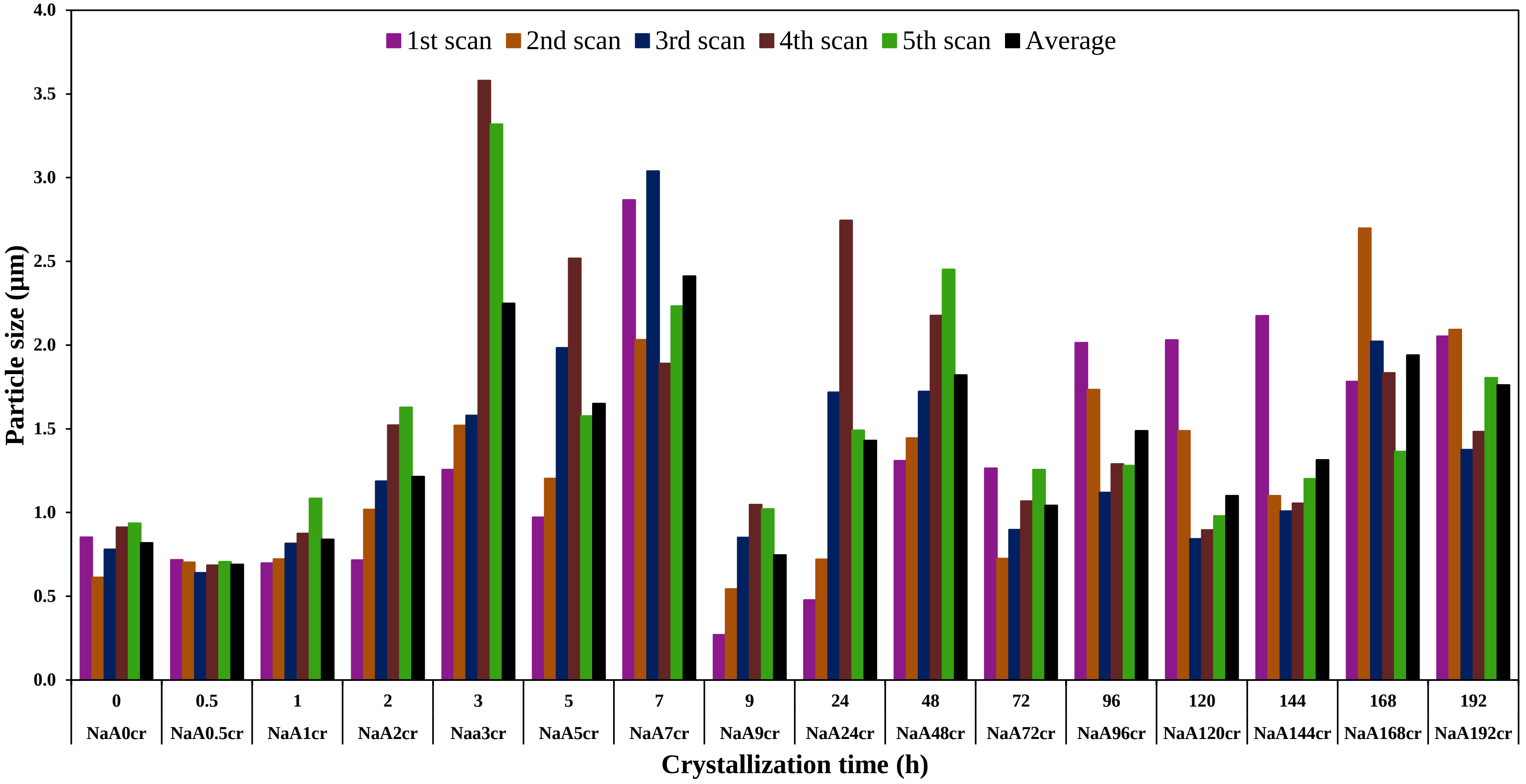
SI2

Heating profile/rate during the crystallization process.



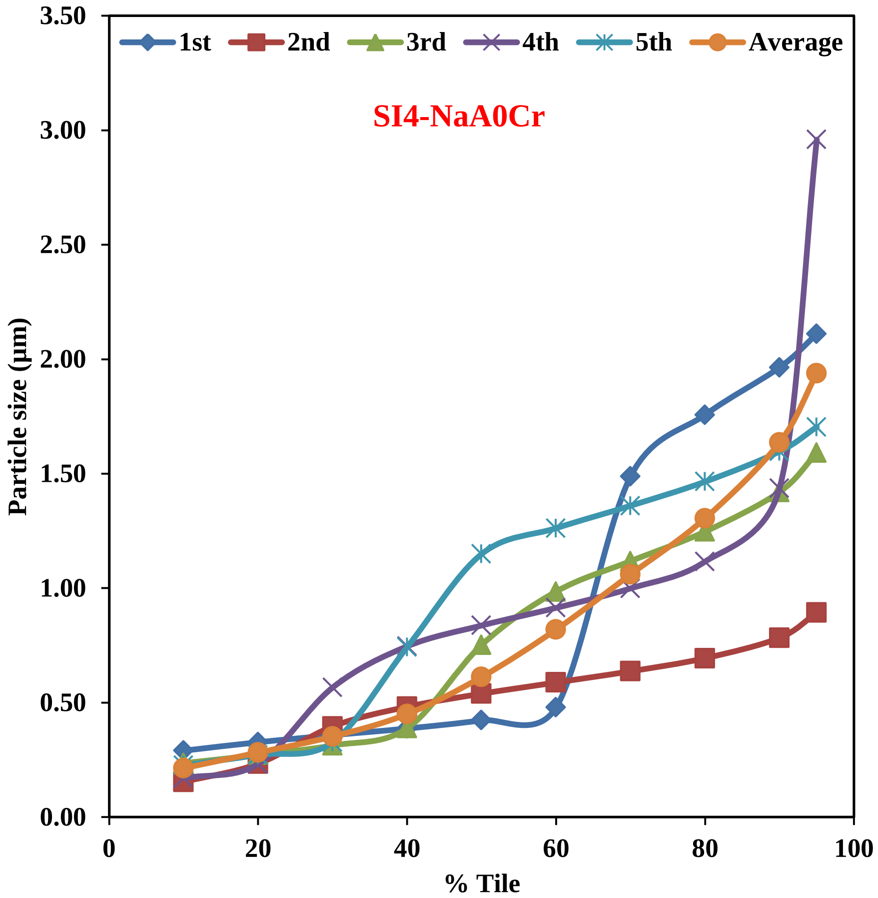
SI3

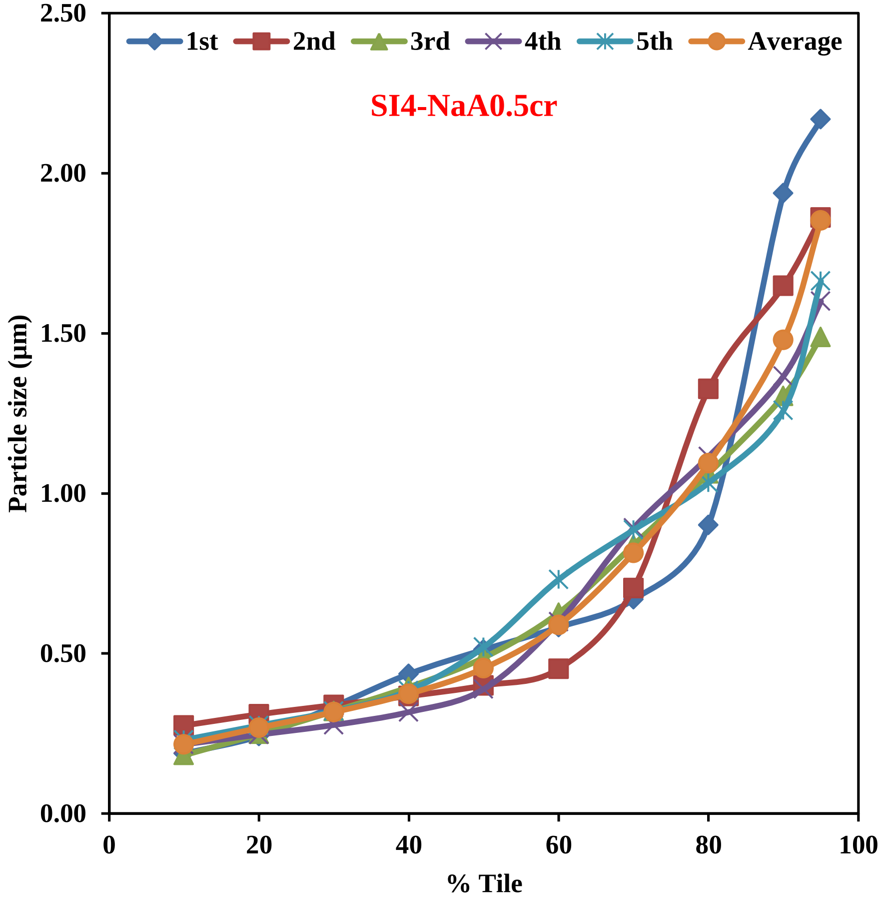
Mean particle size corresponding to 1st scan, 2nd scan, 3rd scan, 4th scan, 5th scan and averge of these scans for the NaA zeolite specimens obtaing at different crystallization time.

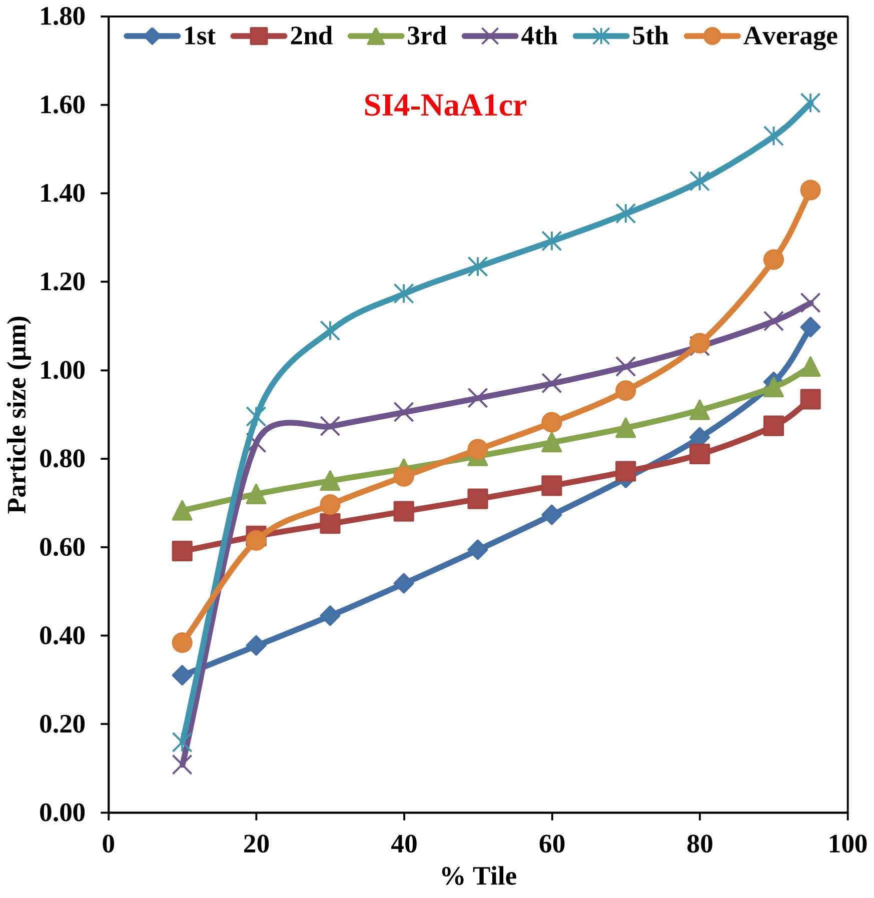


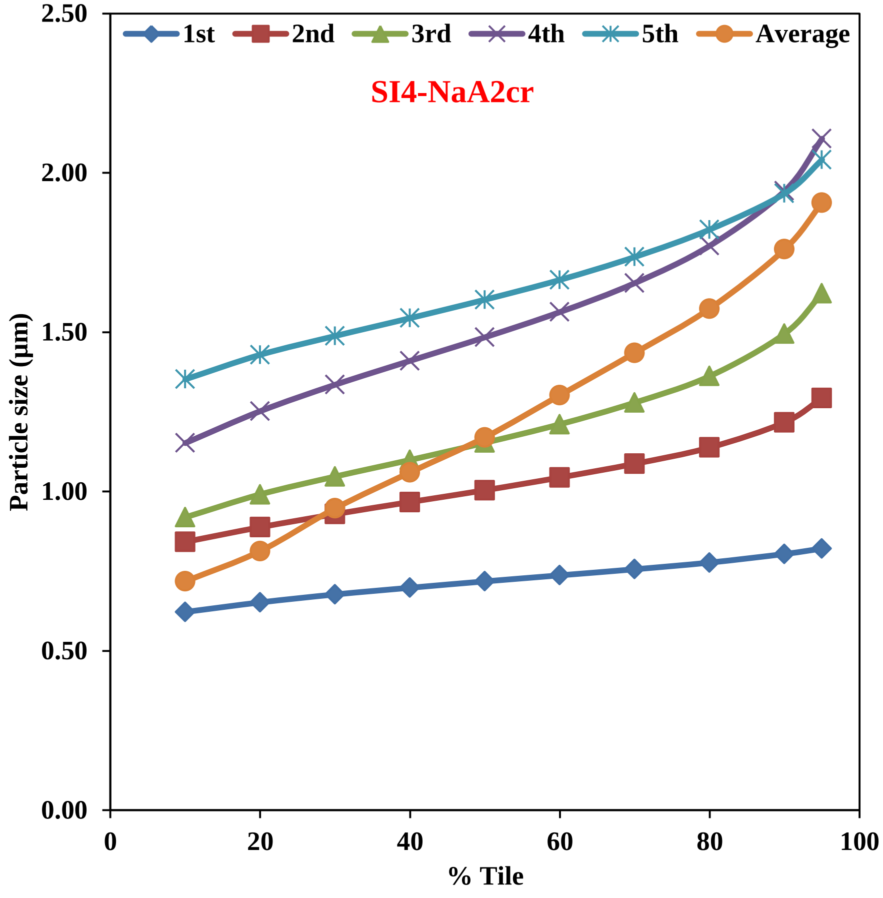
SI4

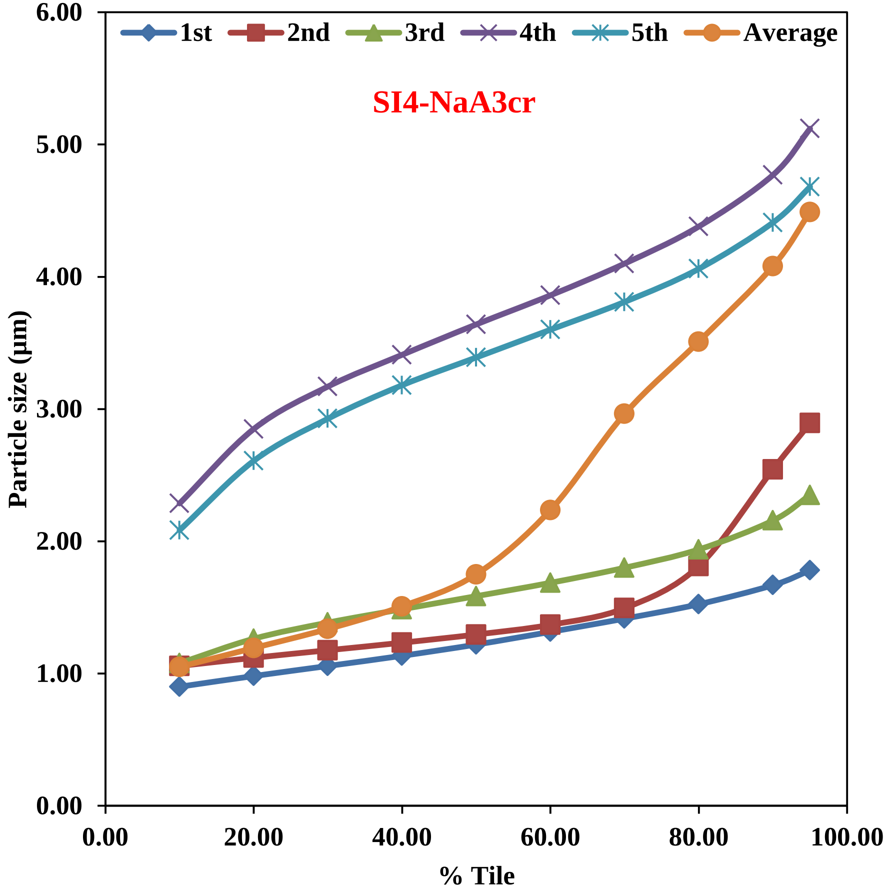
% Tile of particle size corresponding to 1st scan, 2nd scan, 3rd scan, 4th scan, 5th scan and averge of these scans for the specimens obtaing at different crystallization time.

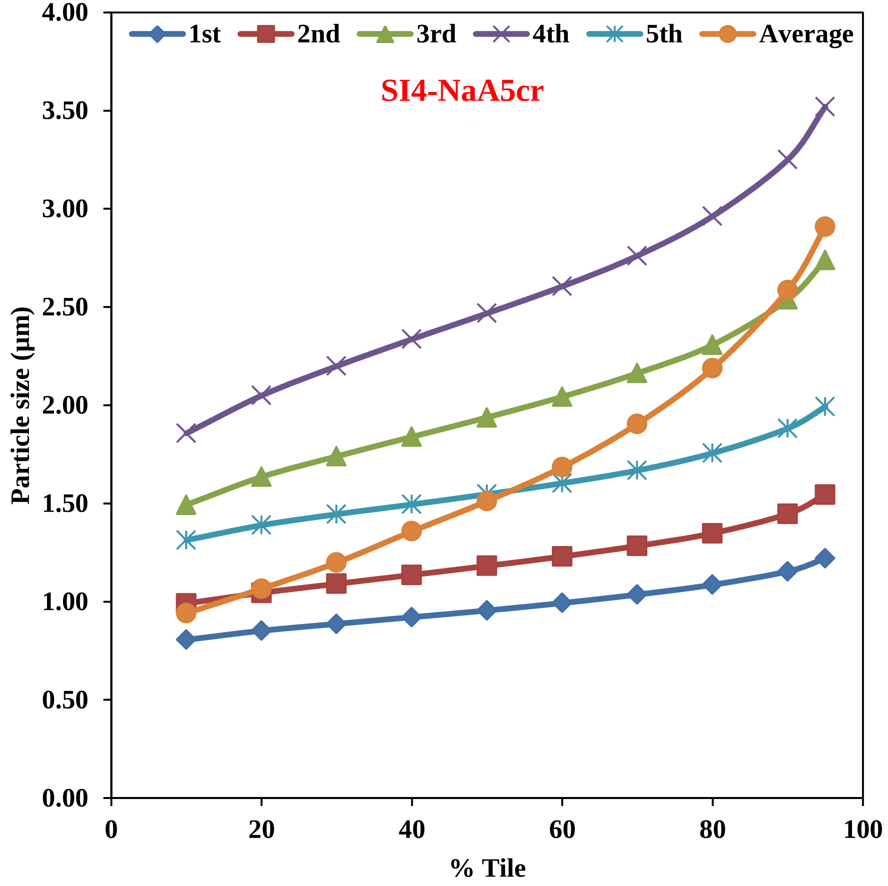


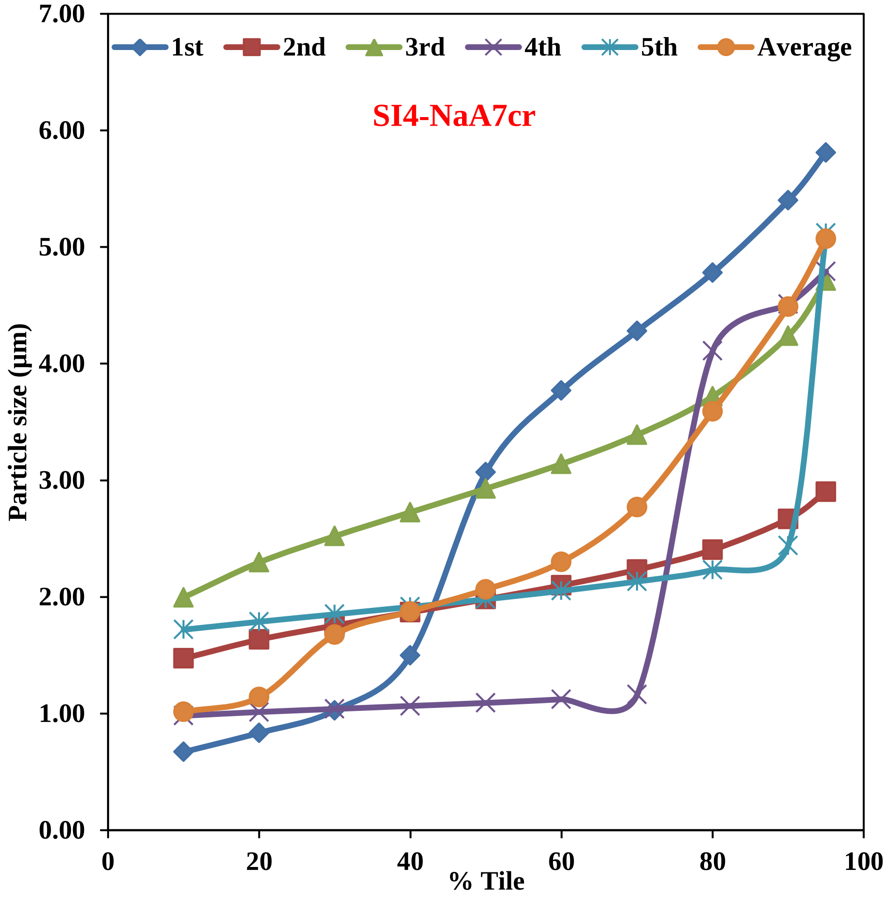


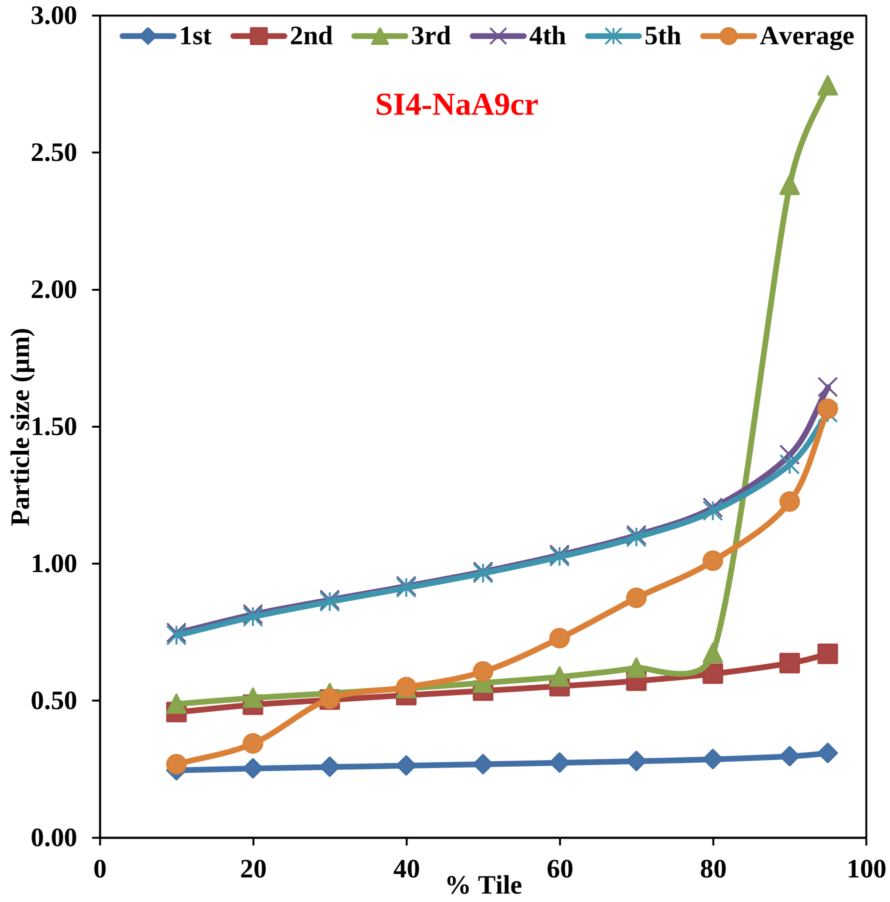

1st
2nd
3rd
4th
5th
Average
SI4-NaA1cr
Particle size (µm)
% Tile
0.00
0.20
0.40
0.60
0.80
1.00
1.20
1.40
1.60
1.80
0
20
40
60
80
100

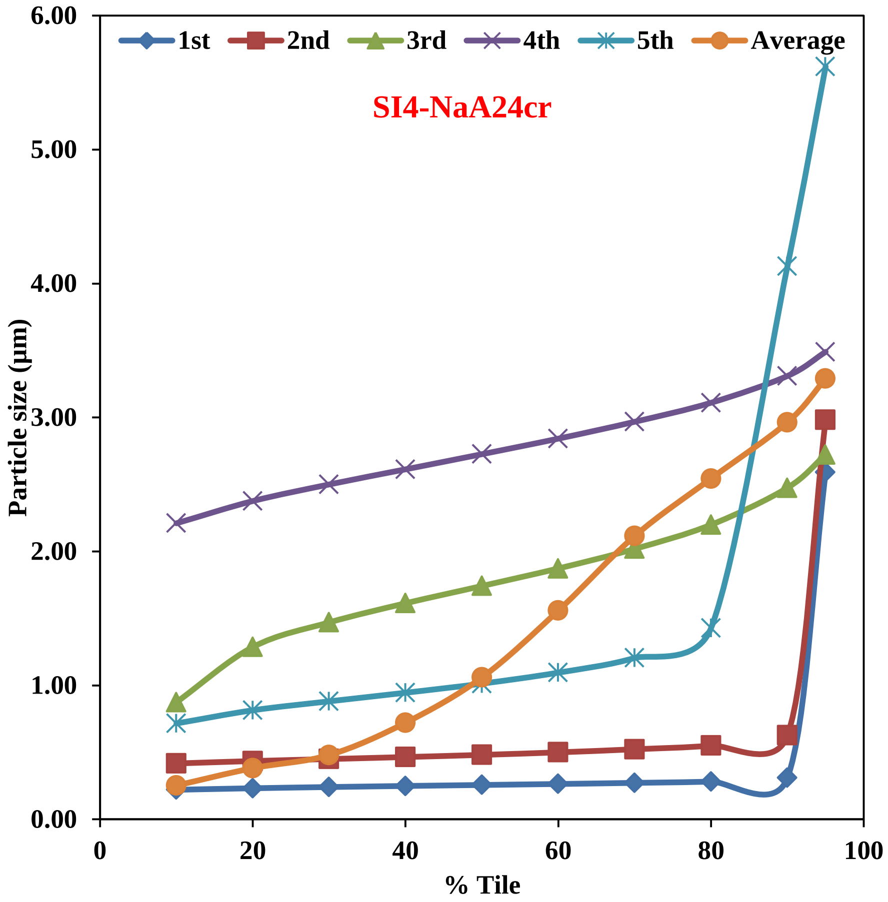

1st
2nd
3rd
4th
5th
Average
SI4-NaA2cr
Particle size (µm)
% Tile
0.00
0.50
1.00
1.50
2.00
2.50
0
20
40
60
80
100

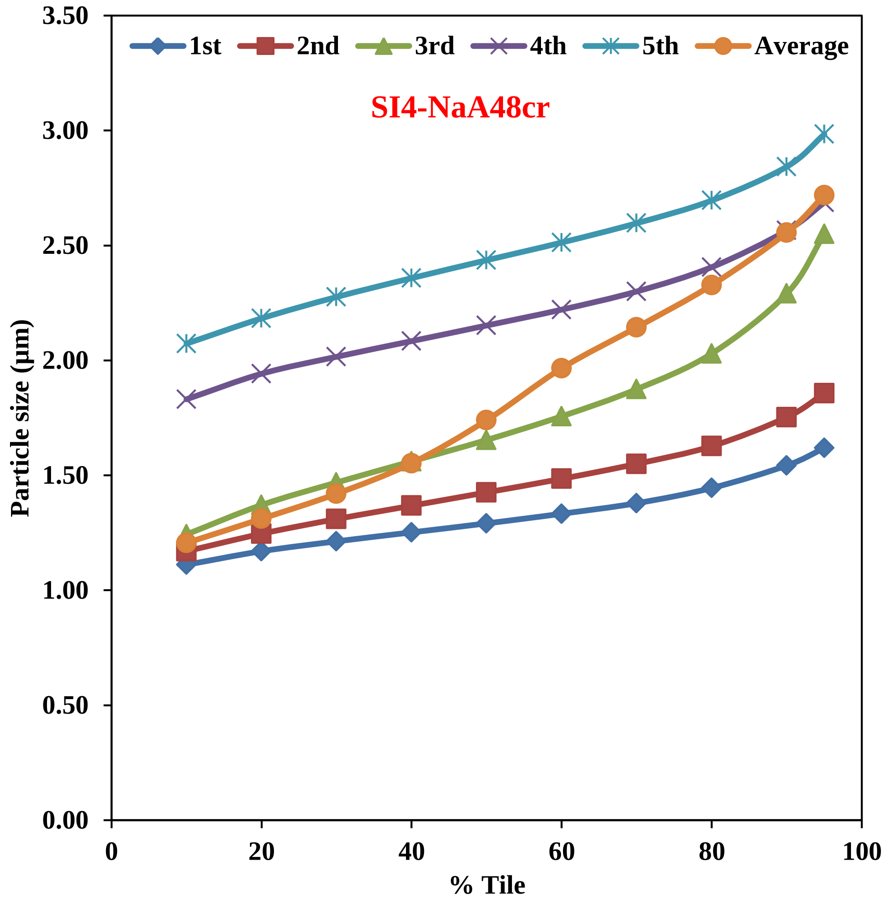

SI4-NaA3cr
1st
2nd
3rd
4th
5th
Average
Particle size (µm)
% Tile
0.00
1.00
2.00
3.00
4.00
5.00
6.00
0.00
20.00
40.00
60.00
80.00
100.00

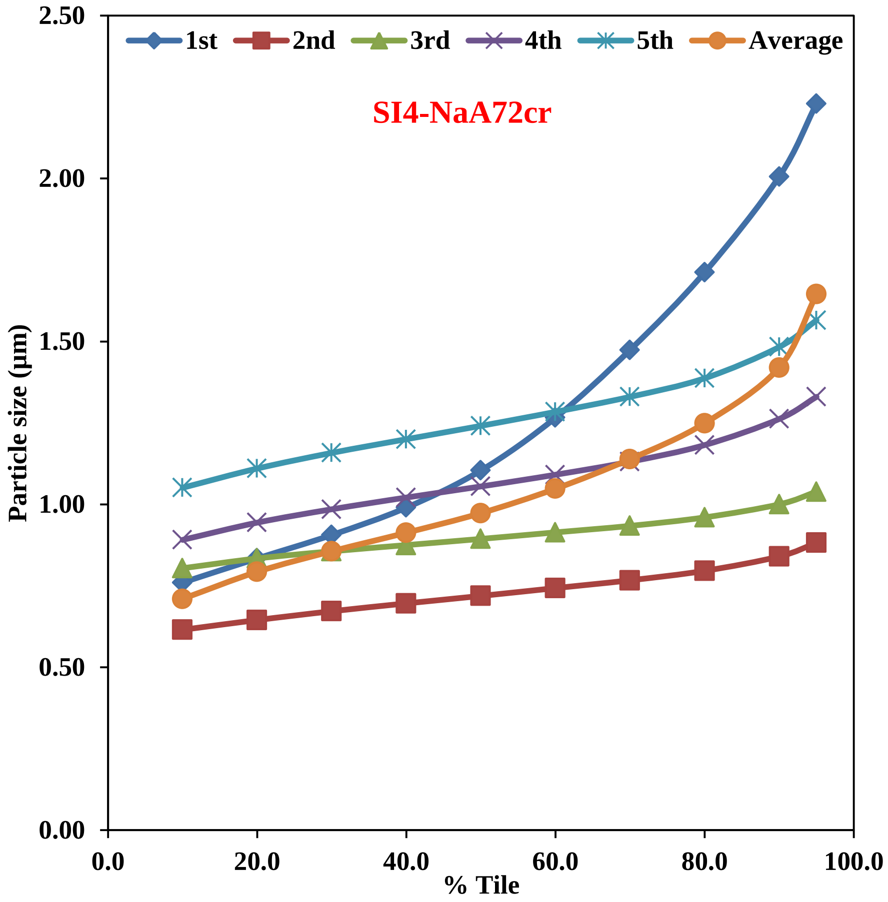

SI4-NaA5cr
1st
2nd
3rd
4th
5th
Average
Particle size (µm)
% Tile
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
0
20
40
60
80
100

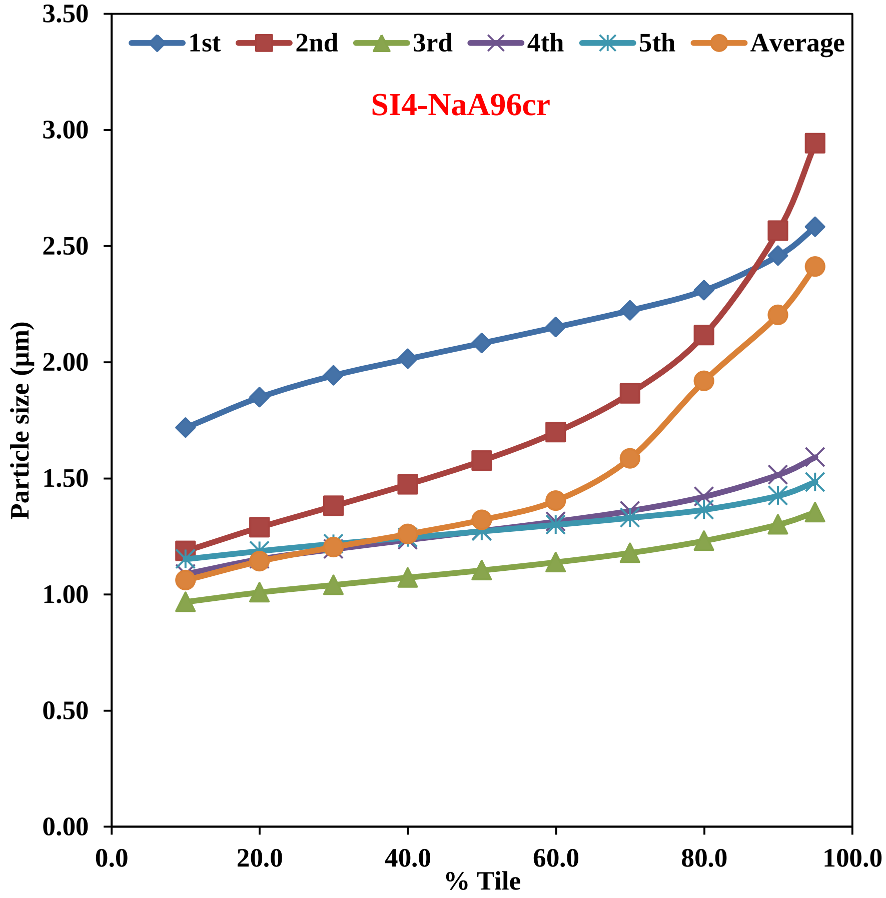

SI4-NaA7cr
1st
2nd
3rd
4th
5th
Average
Particle size (µm)
% Tile
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
0
20
40
60
80
100

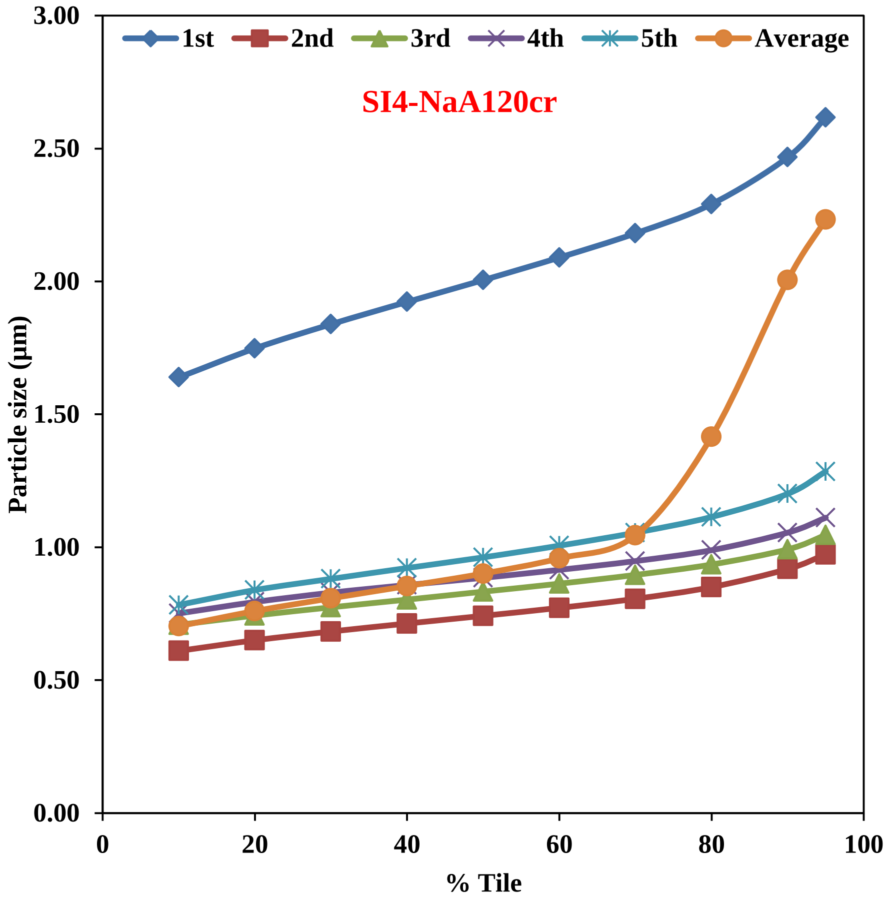

SI4-NaA9cr
1st
2nd
3rd
4th
5th
Average
Particle size (µm)
% Tile
0.00
0.50
1.00
1.50
2.00
2.50
3.00
0
20
40
60
80
100

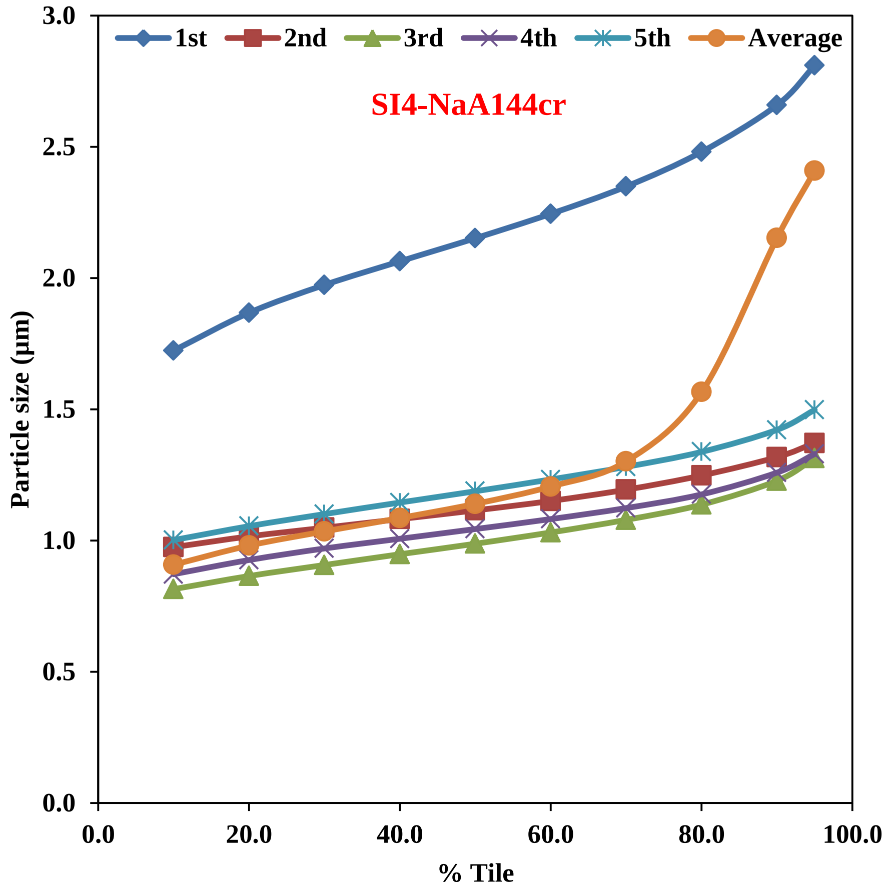

SI4-NaA24cr
1st
2nd
3rd
4th
5th
Average
Particle size (µm)
% Tile
0.00
1.00
2.00
3.00
4.00
5.00
6.00
0
20
40
60
80
100

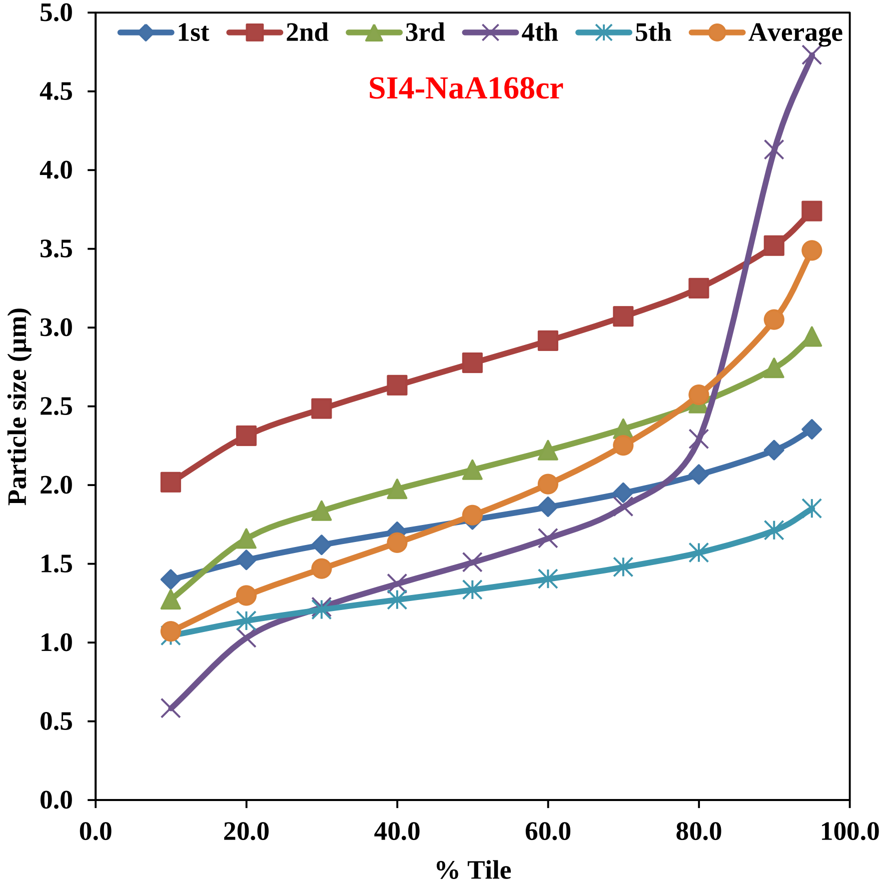

SI4-NaA48cr
1st
2nd
3rd
4th
5th
Average
Particle size (µm)
% Tile
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
0
20
40
60
80
100

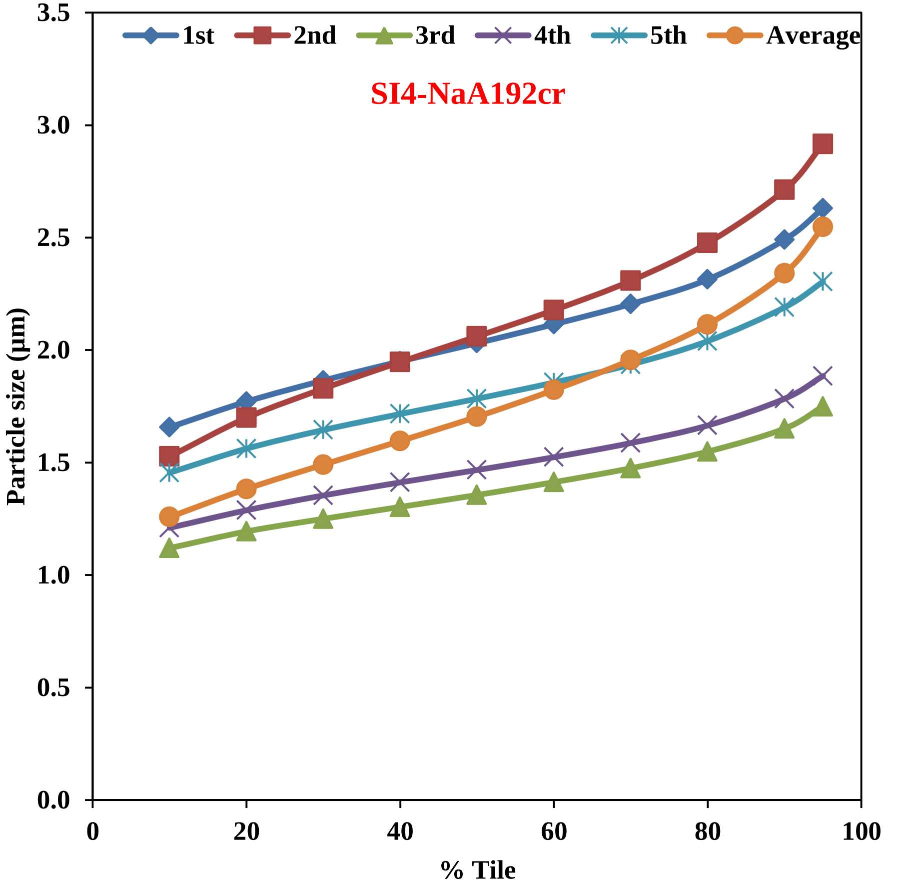

SI4-NaA72cr
1st
2nd
3rd
4th
5th
Average
Particle size (µm)
% Tile
0.00
0.50
1.00
1.50
2.00
2.50
0.0
20.0
40.0
60.0
80.0
100.0


SI4-NaA96cr
1st
2nd
3rd
4th
5th
Average
Particle size (µm)
% Tile
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
0.0
20.0
40.0
60.0
80.0
100.0

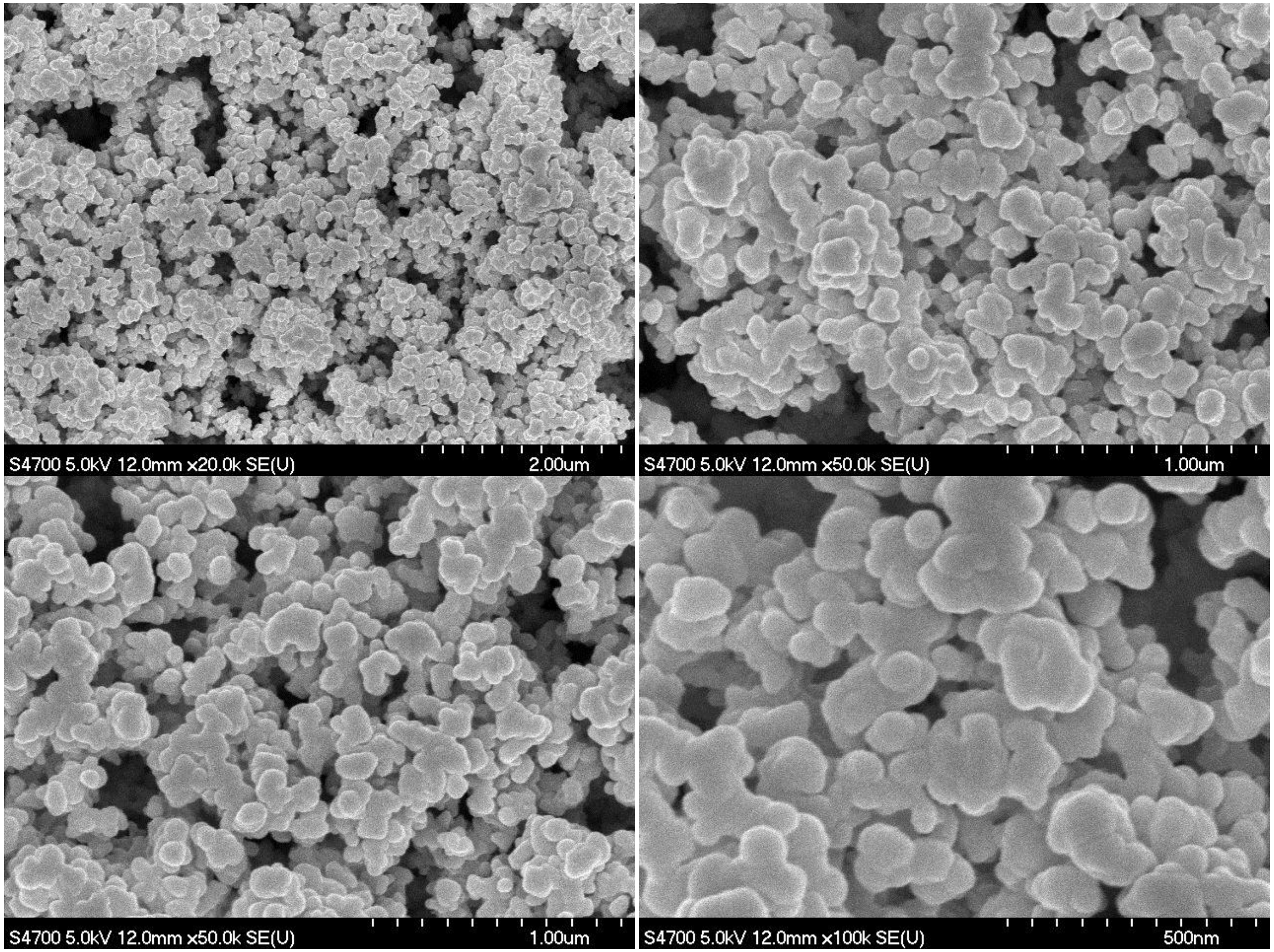

SI4-NaA120cr
1st
2nd
3rd
4th
5th
Average
Particle size (µm)
% Tile
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
20
40
60
80
100


SI4-NaA144cr
1st
2nd
3rd
4th
5th
Average
Particle size (µm)
% Tile
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.0
20.0
40.0
60.0
80.0
100.0

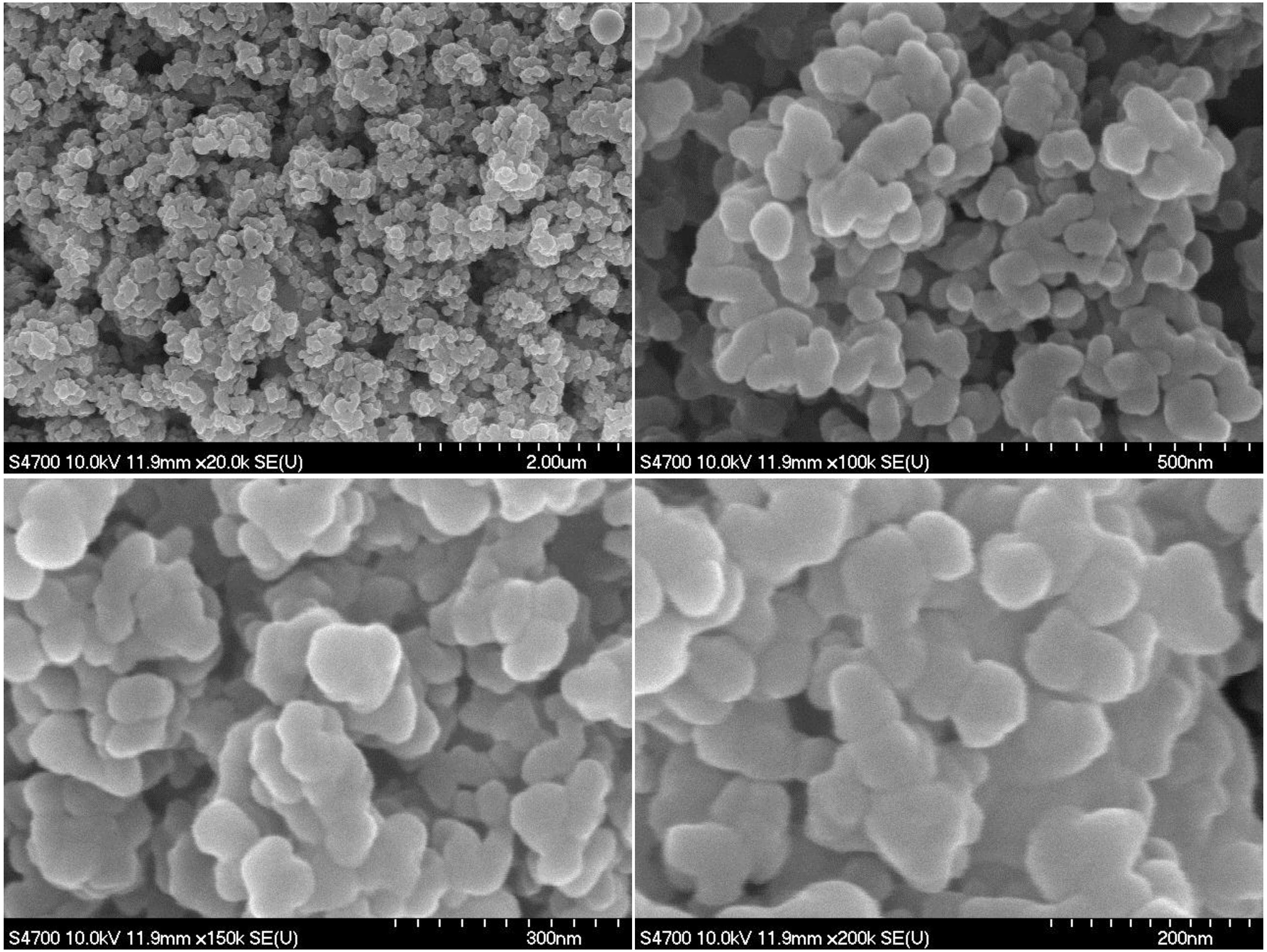

SI4-NaA168cr
1st
2nd
3rd
4th
5th
Average
Particle size (µm)
% Tile
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.0
20.0
40.0
60.0
80.0
100.0


SI4-NaA192cr
1st
2nd
3rd
4th
5th
Average
Particle size (µm)
% Tile
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
20
40
60
80
100

SI5. SEM micrographs of the different specimens obtained during the growth process of NaA zeolite crystals at different magnifications. In these microgahs the corresponding specimen code is written on page bottom center.



SI5-NaA22ag


S4700 10.0kV 11.9mm x20.0k SE(U)
2.00um
S4700 10.0kV 11.9mm x100k SE(U)
500nm
S4700 10.0kV 11.9mm x150k SE(U)
300nm
S4700 10.0kV 11.9mm x200k SE(U)
200nm

SI5-NaA0cr

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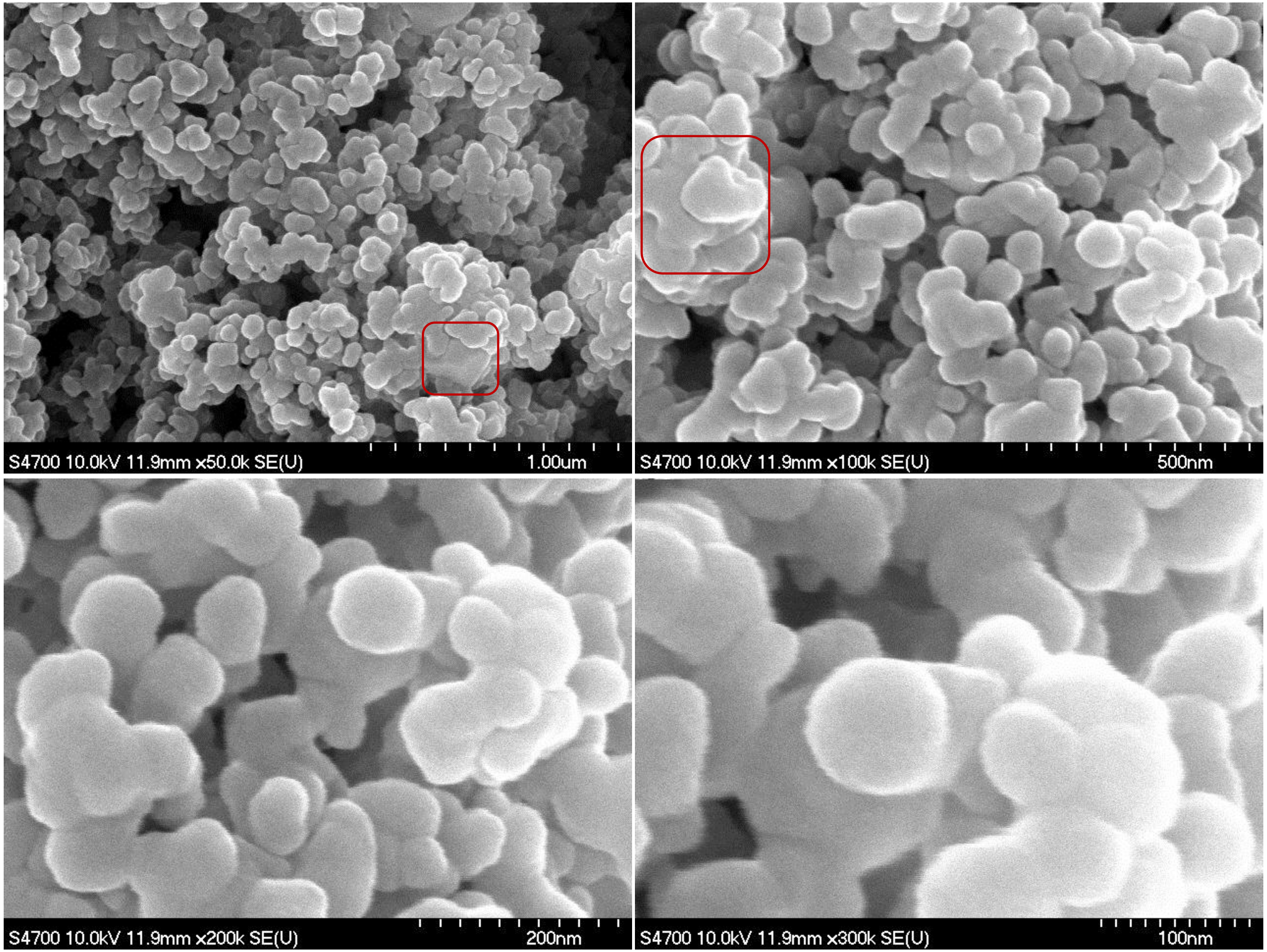
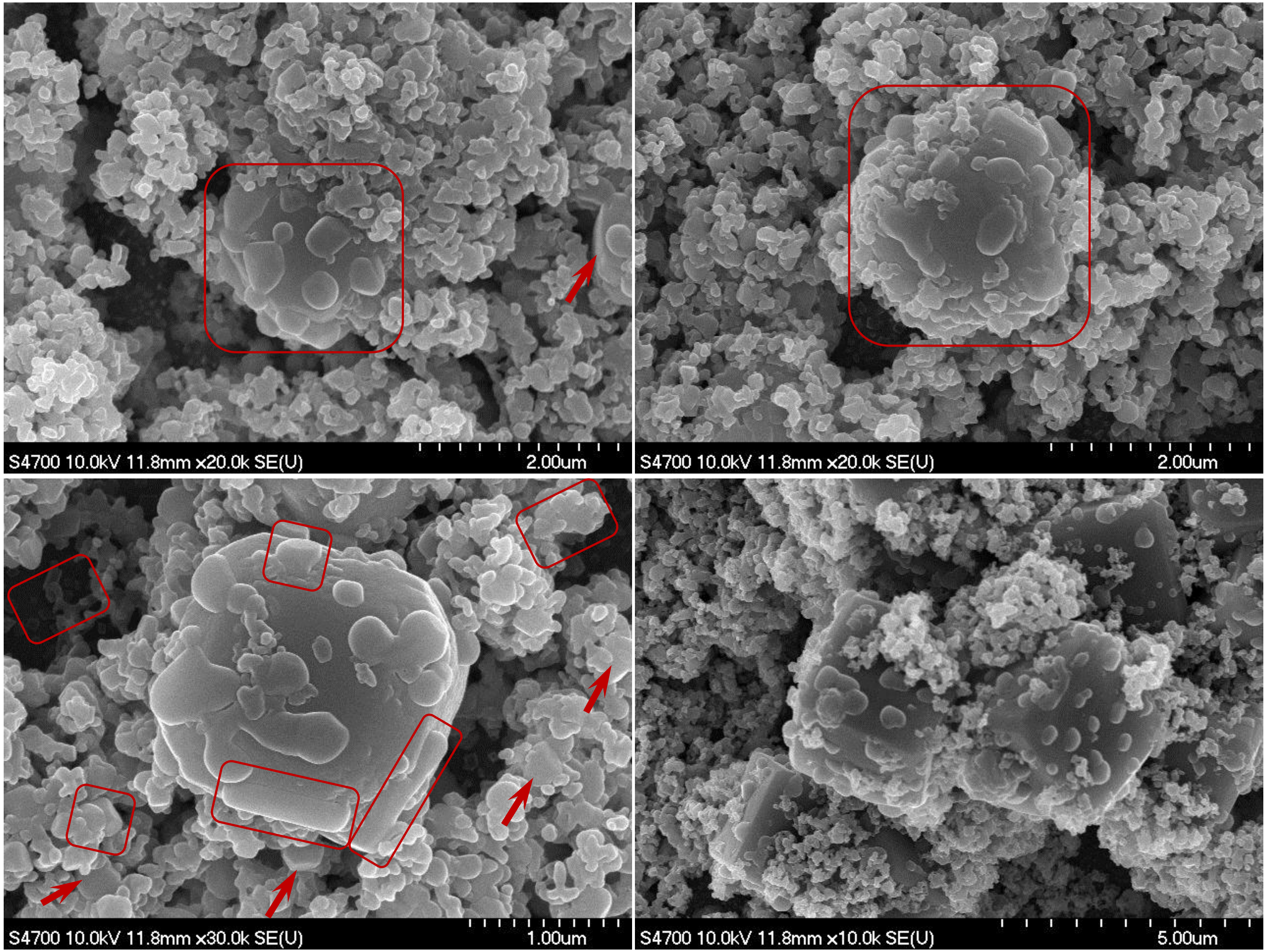
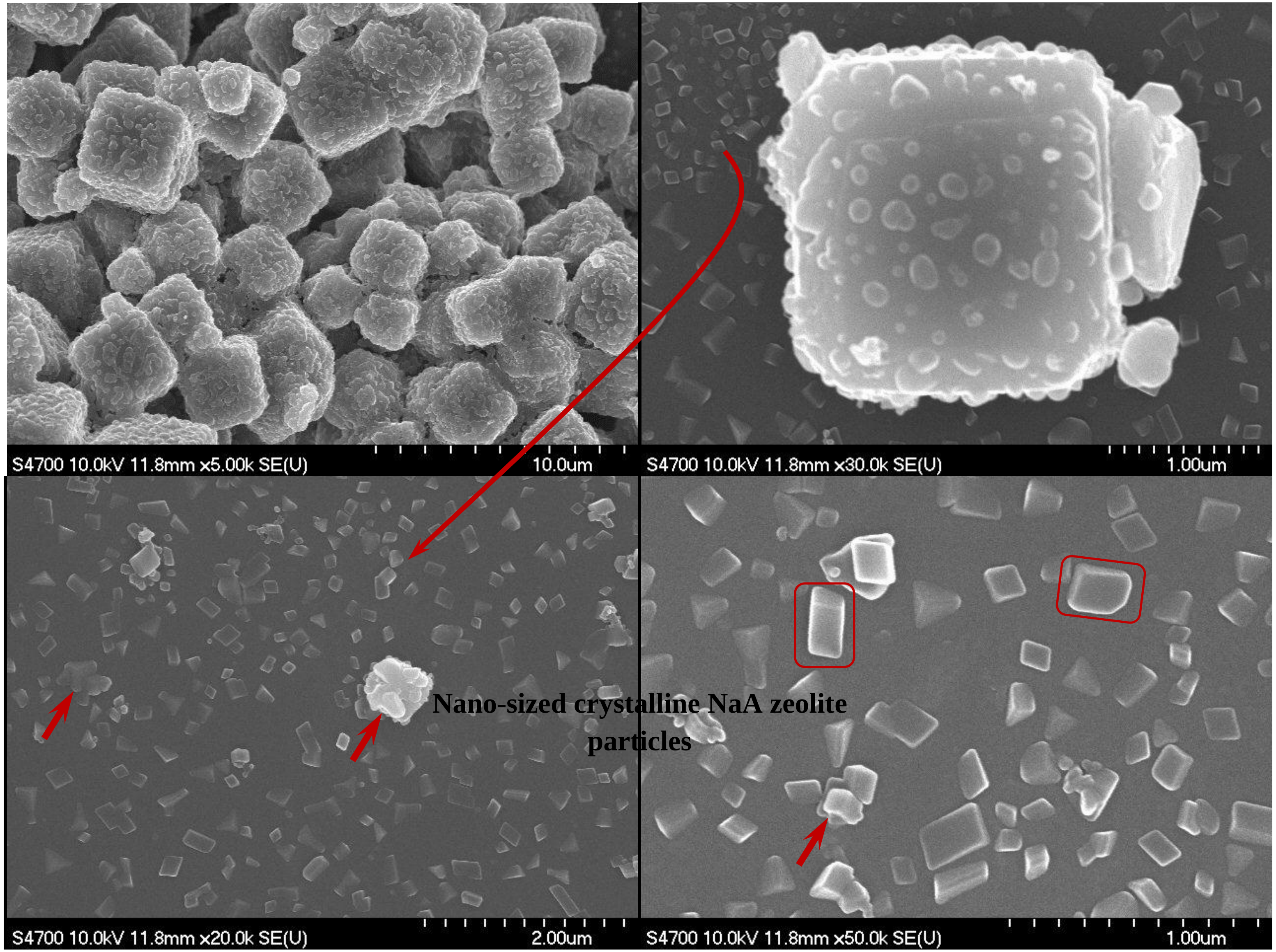


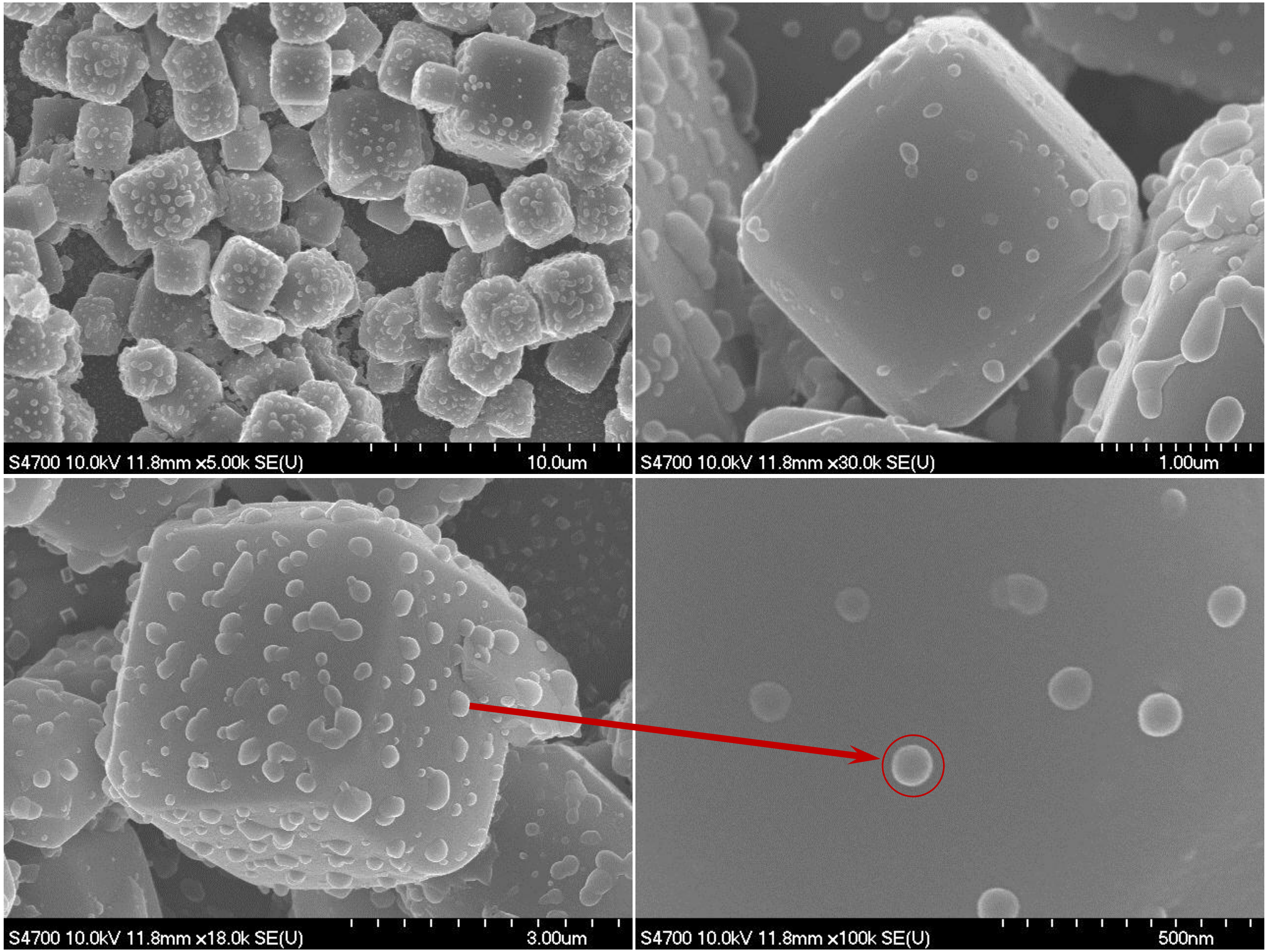
SI5-NaA0.5cr


S4700 10.0kV 11.8mm x20.0k SE(U)
2.00um
S4700 10.0kV 11.8mm x20.0k SE(U)
2.00um
S4700 10.0kV 11.8mm x30.0k SE(U)
1.00um
S4700 10.0kV 11.8mm x10.0k SE(U)
5.00um

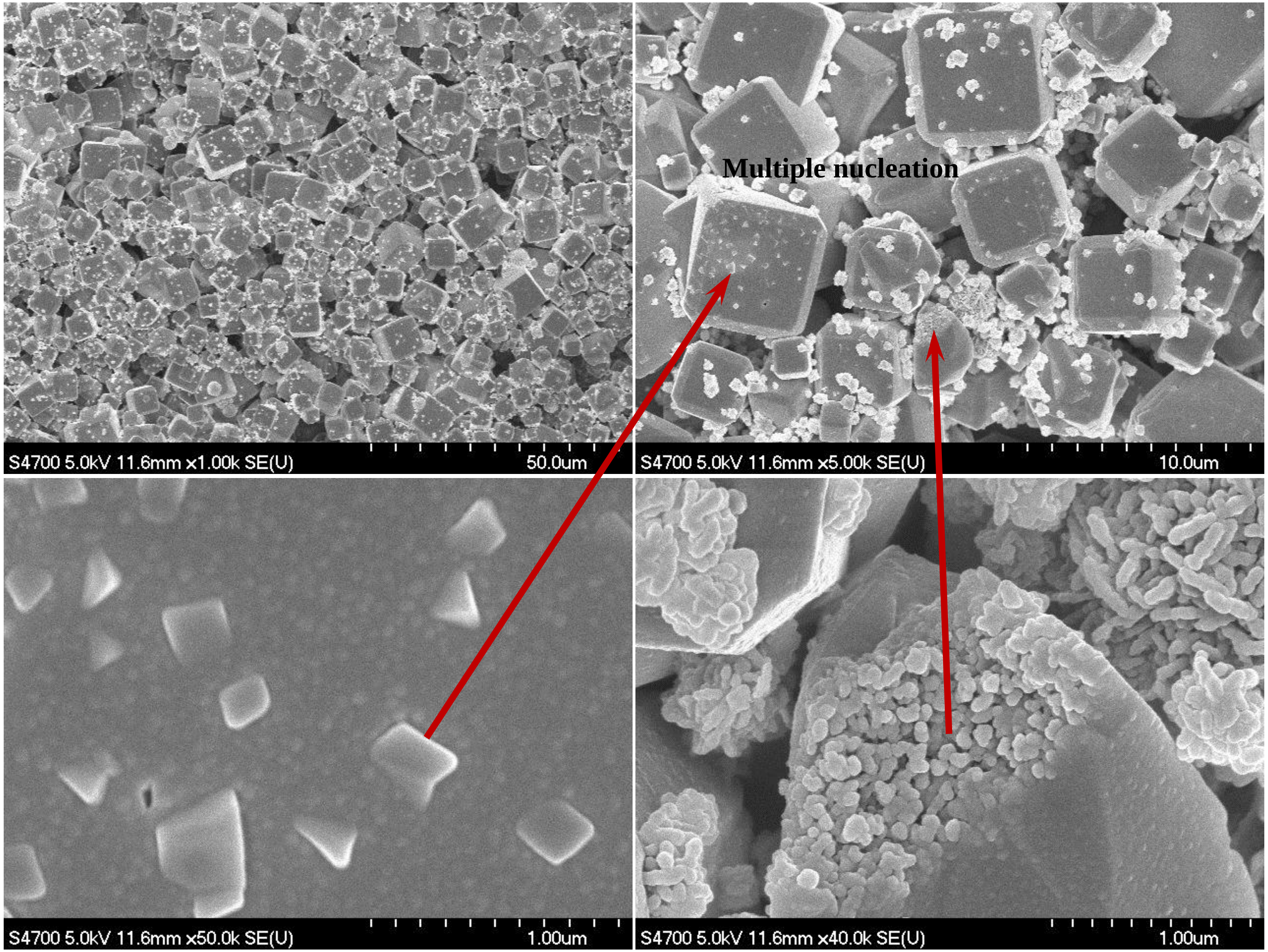
SI5-NaA1cr


S4700 10.0kV 11.8mm x5.00k SE(U)
10.0um
S4700 10.0kV 11.8mm x30.0k SE(U)
1.00um
S4700 10.0kV 11.8mm x20.0k SE(U)
2.00um
S4700 10.0kV 11.8mm x50.0k SE(U)
1.00um
Nano-sized crystalline NaA zeolite particles

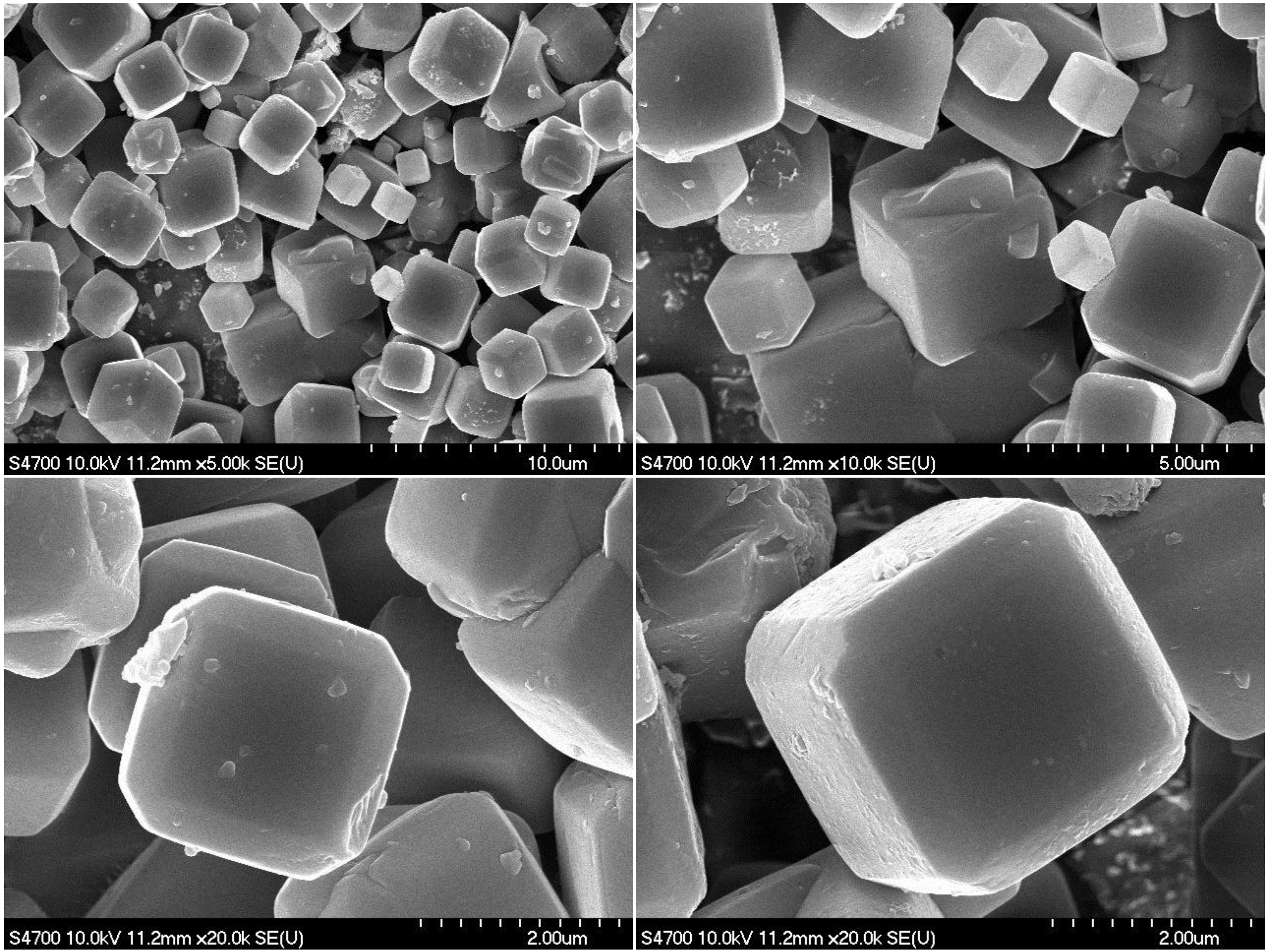
SI5-NaA2cr


S4700 10.0kV 11.8mm x5.00k SE(U)
10.0um
S4700 10.0kV 11.8mm x30.0k SE(U)
1.00um
S4700 10.0kV 11.8mm x18.0k SE(U)
3.00um
S4700 10.0kV 11.8mm x100k SE(U)
500nm

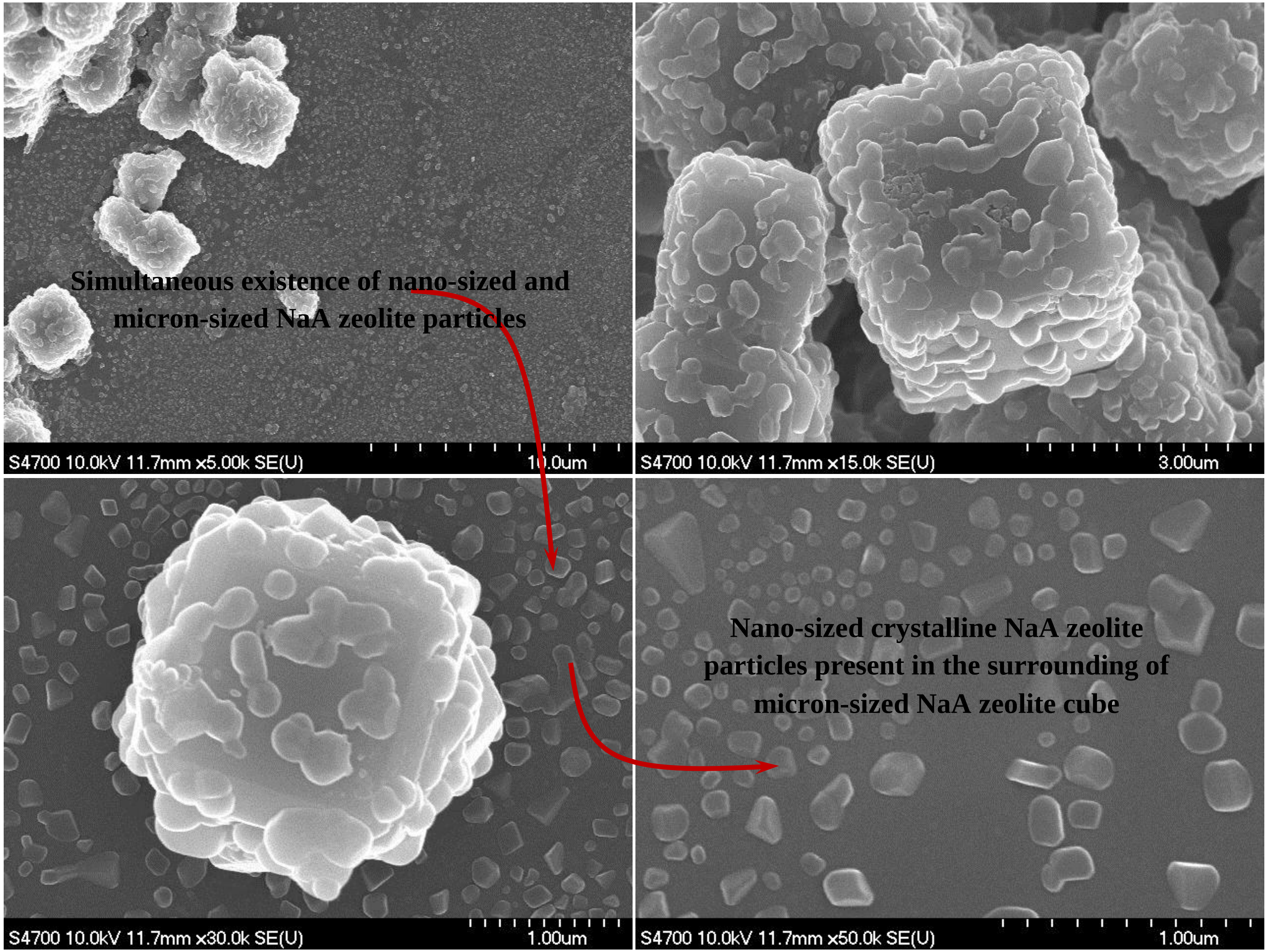
SI5-NaA3cr


Multiple nucleation
S4700 5.0kV 11.6mm x1.00k SE(U)
50.0um
S4700 5.0kV 11.6mm x5.00k SE(U)
10.0um
S4700 5.0kV 11.6mm x50.0k SE(U)
1.00um
S4700 5.0kV 11.6mm x40.0k SE(U)
1.00um

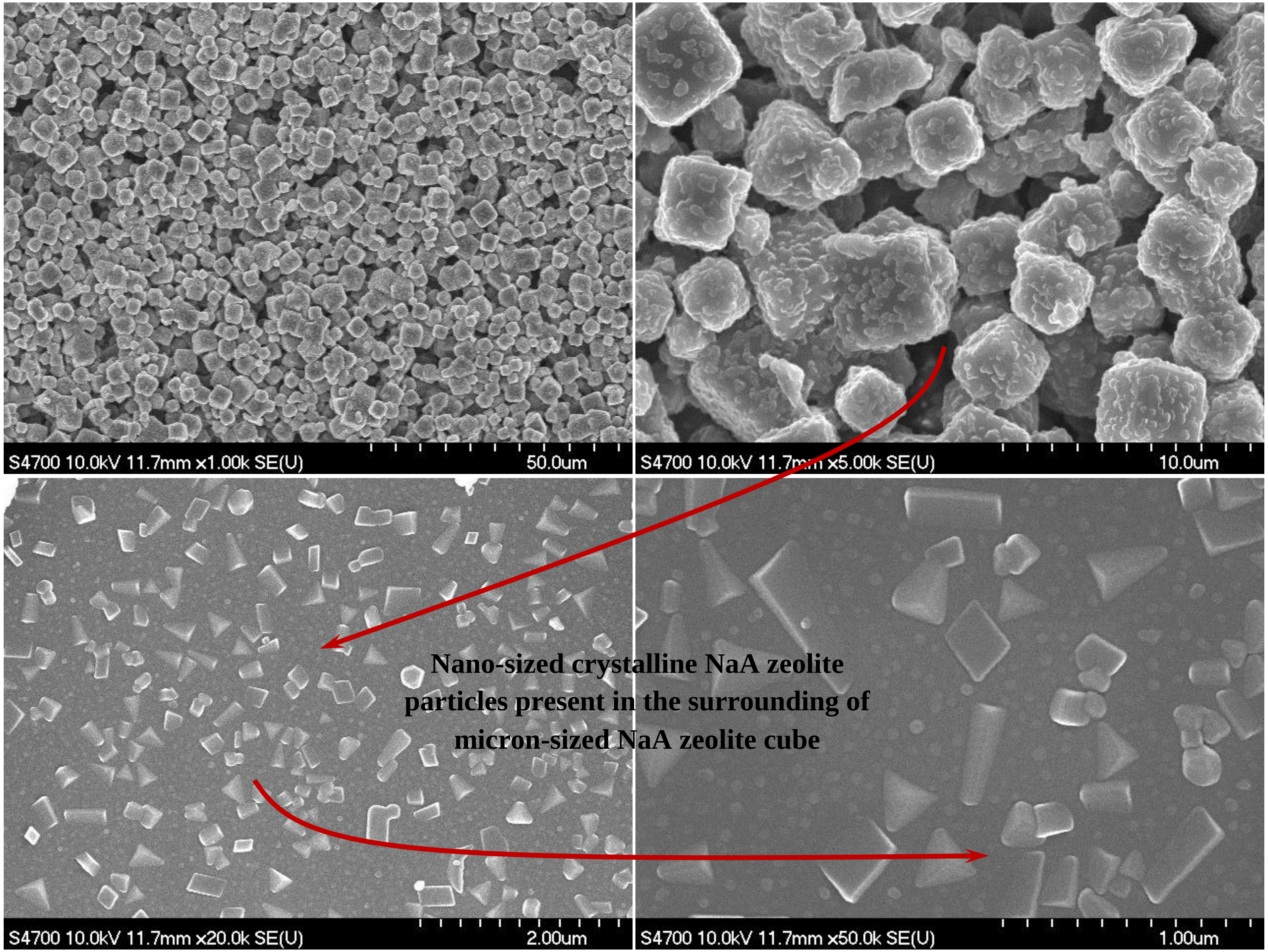
SI5-NaA4cr


S4700 10.0kV 11.2mm x5.00k SE(U)
10.0um
S4700 10.0kV 11.2mm x10.0k SE(U)
5.00um
S4700 10.0kV 11.2mm x20.0k SE(U)
2.00um
S4700 10.0kV 11.2mm x20.0k SE(U)
2.00um

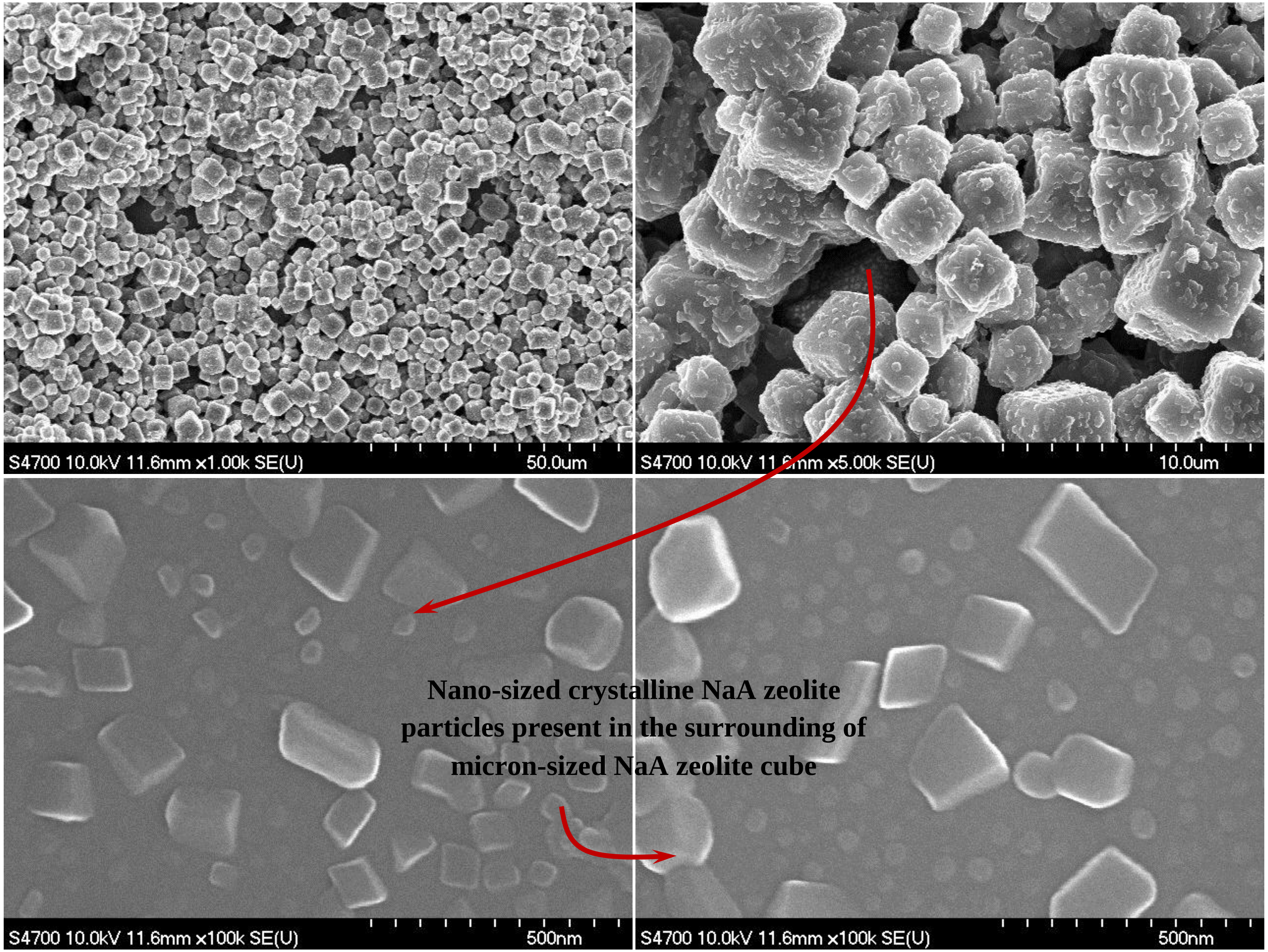
SI5-NaA5cr


Simultaneous existence of nano-sized and micron-sized NaA zeolite particles
S4700 10.0kV 11.7mm x5.00k SE(U)
10.0um
S4700 10.0kV 11.7mm x15.0k SE(U)
3.00um
S4700 10.0kV 11.7mm x30.0k SE(U)
1.00um
Nano-sized crystalline NaA zeolite particles present in the surrounding of micron-sized NaA zeolite cube
S4700 10.0kV 11.7mm x50.0k SE(U)
1.00um

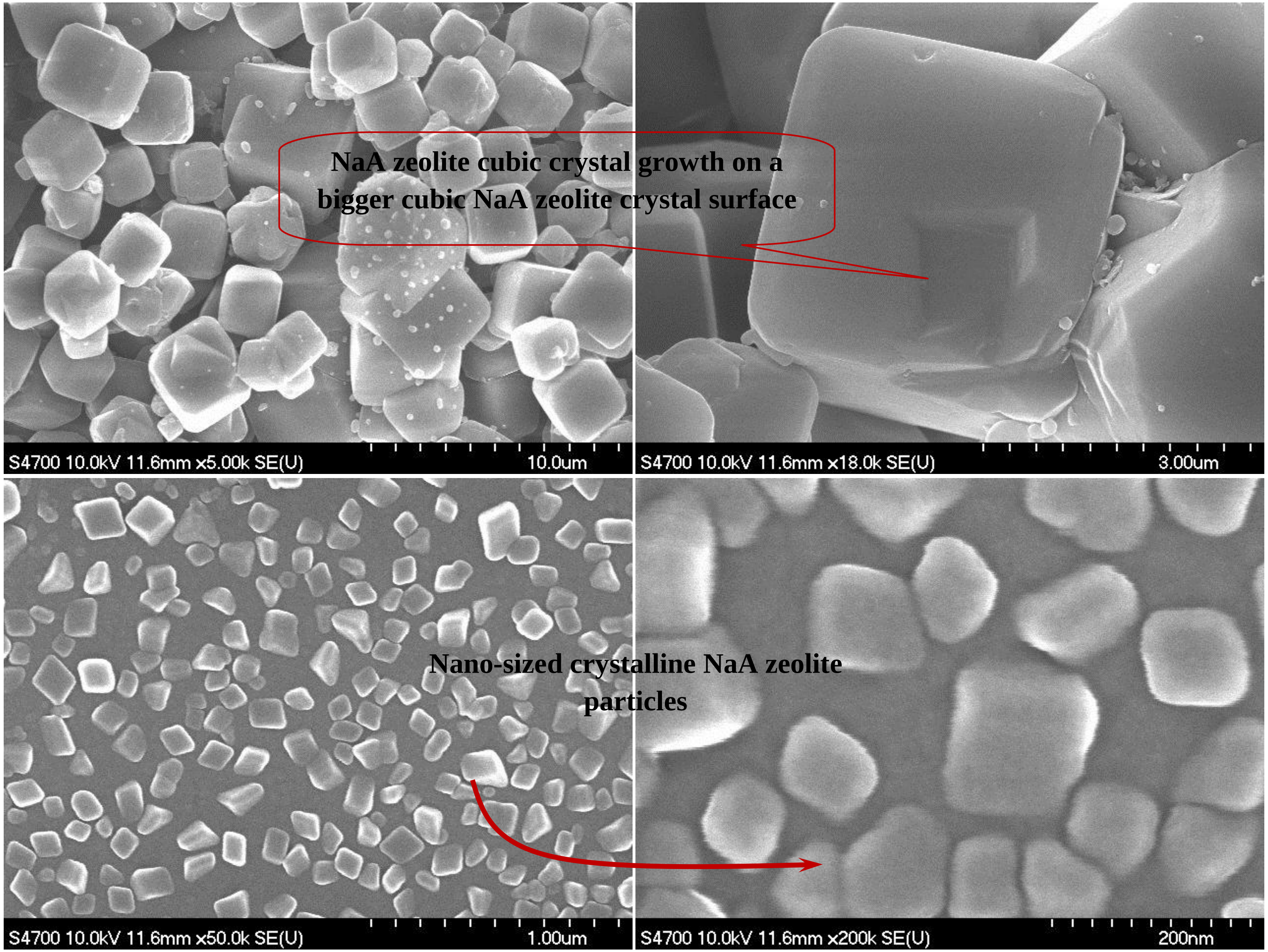
SI5-NaA7cr


S4700 10.0kV 11.7mm x1.00k SE(U)
50.0um
S4700 10.0kV 11.7mm x5.00k SE(U)
10.0um
Nano-sized crystalline NaA zeolite particles present in the surrounding of micron-sized NaA zeolite cube
S4700 10.0kV 11.7mm x20.0k SE(U)
2.00um
S4700 10.0kV 11.7mm x50.0k SE(U)
1.00um

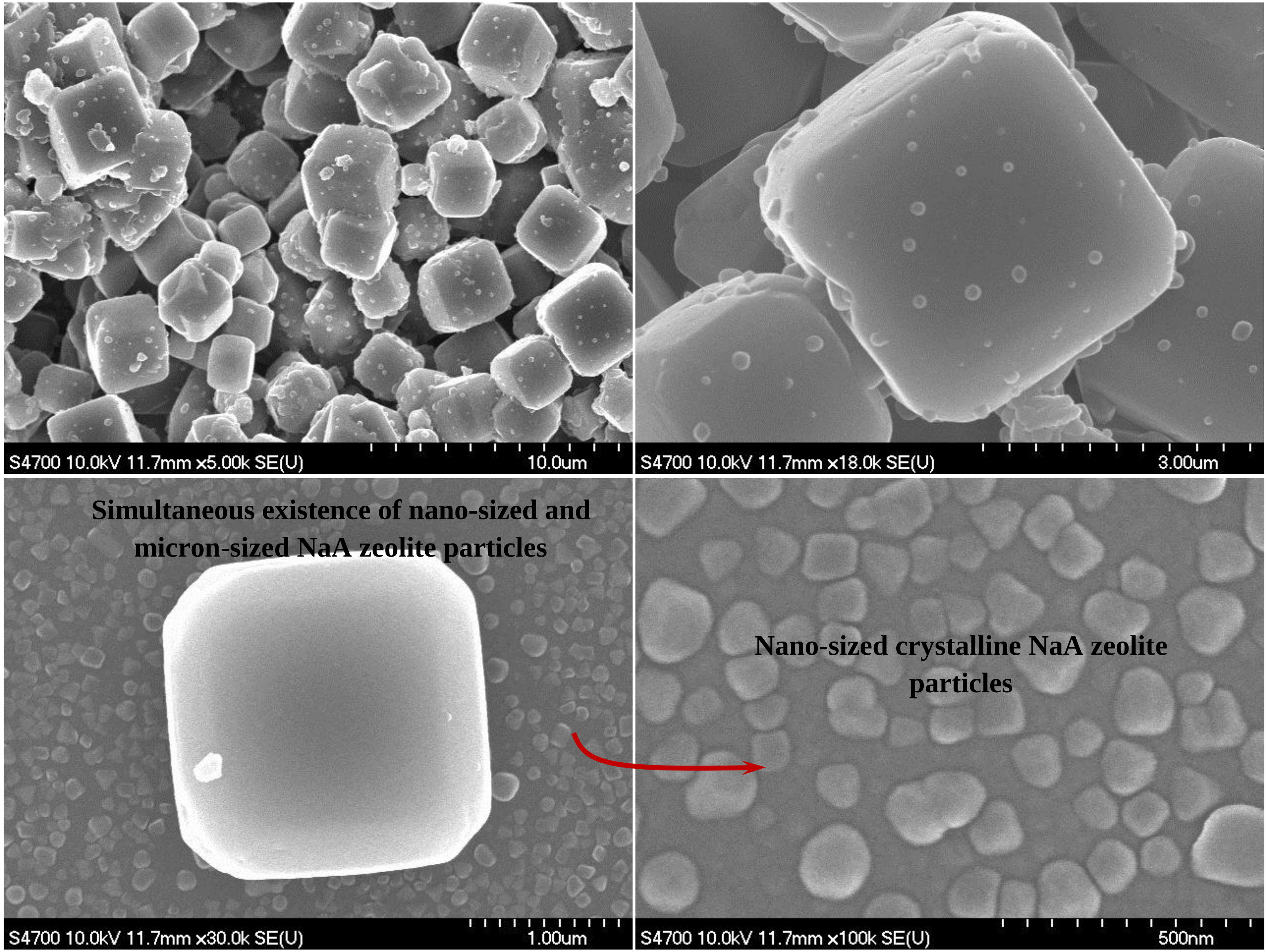
SI5-NaA9cr


S4700 10.0kV 11.6mm x1.00k SE(U)
50.0um
S4700 10.0kV 11.6mm x5.00k SE(U)
10.0um
Nano-sized crystalline NaA zeolite particles present in the surrounding of micron-sized NaA zeolite cube
S4700 10.0kV 11.6mm x100k SE(U)
500nm
S4700 10.0kV 11.6mm x100k SE(U)
500nm

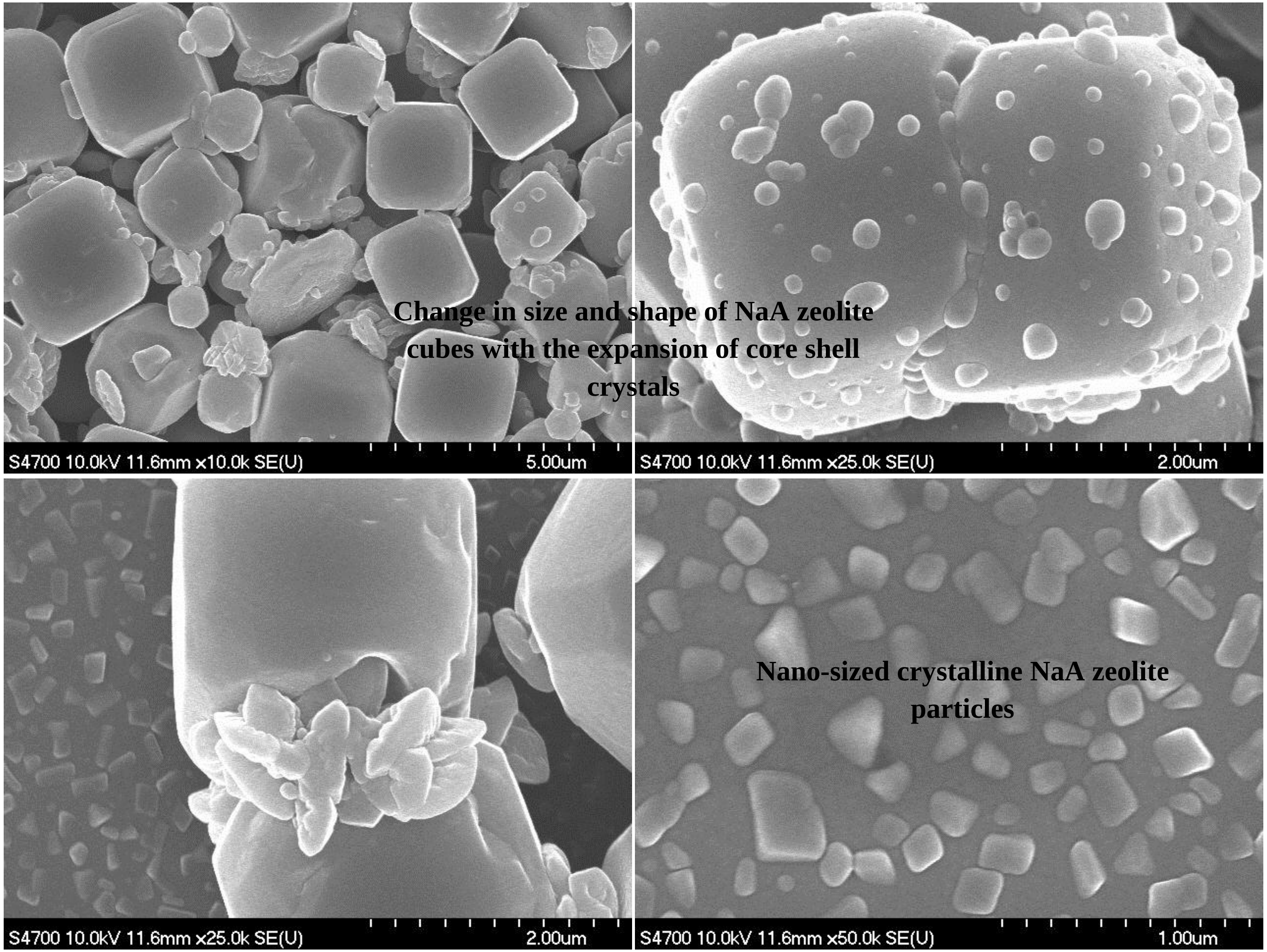
SI5-NaA24cr


NaA zeolite cubic crystal growth on a bigger cubic NaA zeolite crystal surface
S4700 10.0kV 11.6mm x5.00k SE(U)
10.0um
S4700 10.0kV 11.6mm x18.0k SE(U)
3.00um
Nano-sized crystalline NaA zeolite particles
S4700 10.0kV 11.6mm x50.0k SE(U)
1.00um
S4700 10.0kV 11.6mm x200k SE(U)
200nm

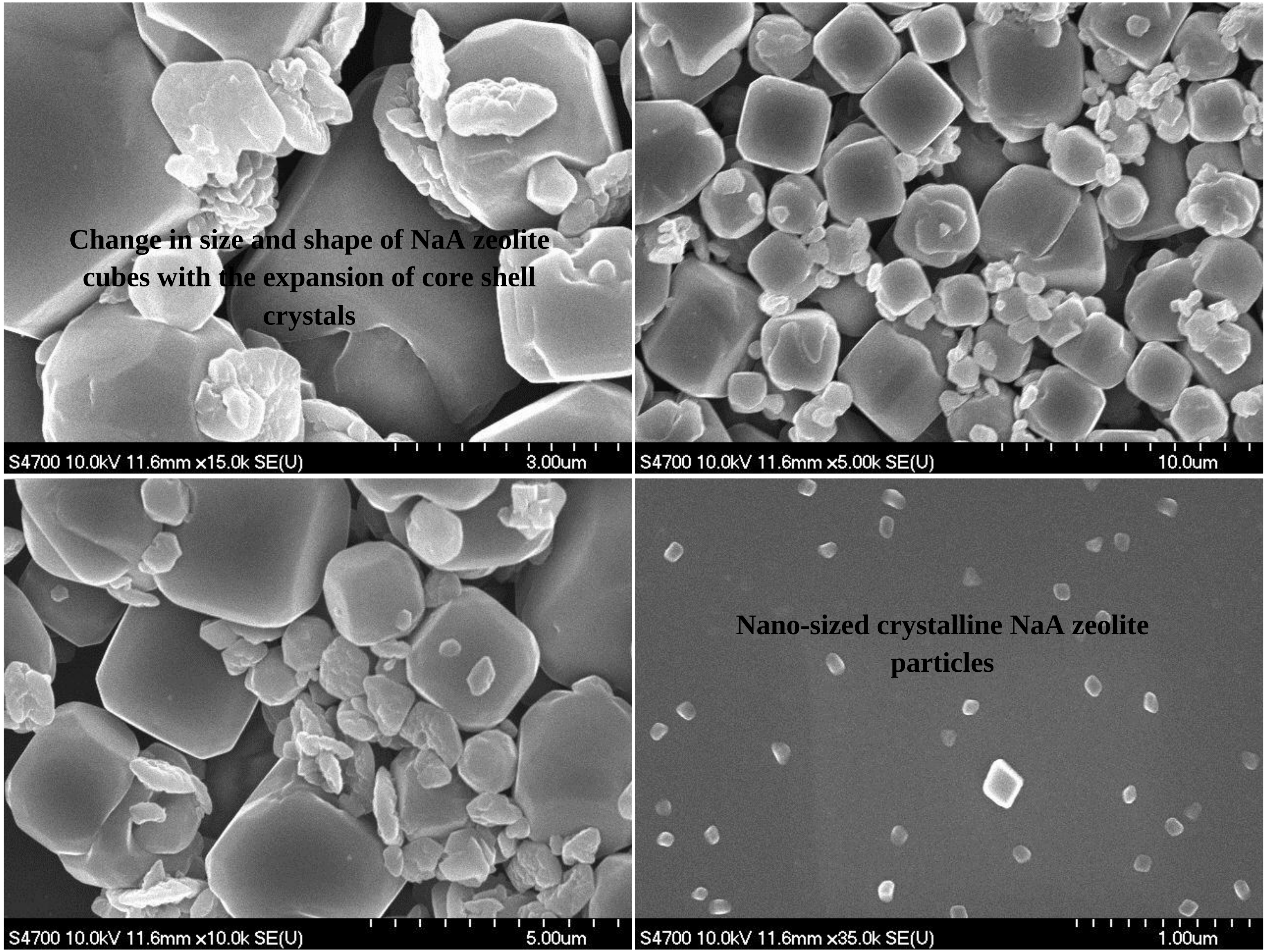
SI5-NaA48cr


S4700 10.0kV 11.7mm x5.00k SE(U)
10.0um
S4700 10.0kV 11.7mm x18.0k SE(U)
3.00um
Simultaneous existence of nano-sized and micron-sized NaA zeolite particles
S4700 10.0kV 11.7mm x30.0k SE(U)
1.00um
Nano-sized crystalline NaA zeolite particles
S4700 10.0kV 11.7mm x100k SE(U)
500nm

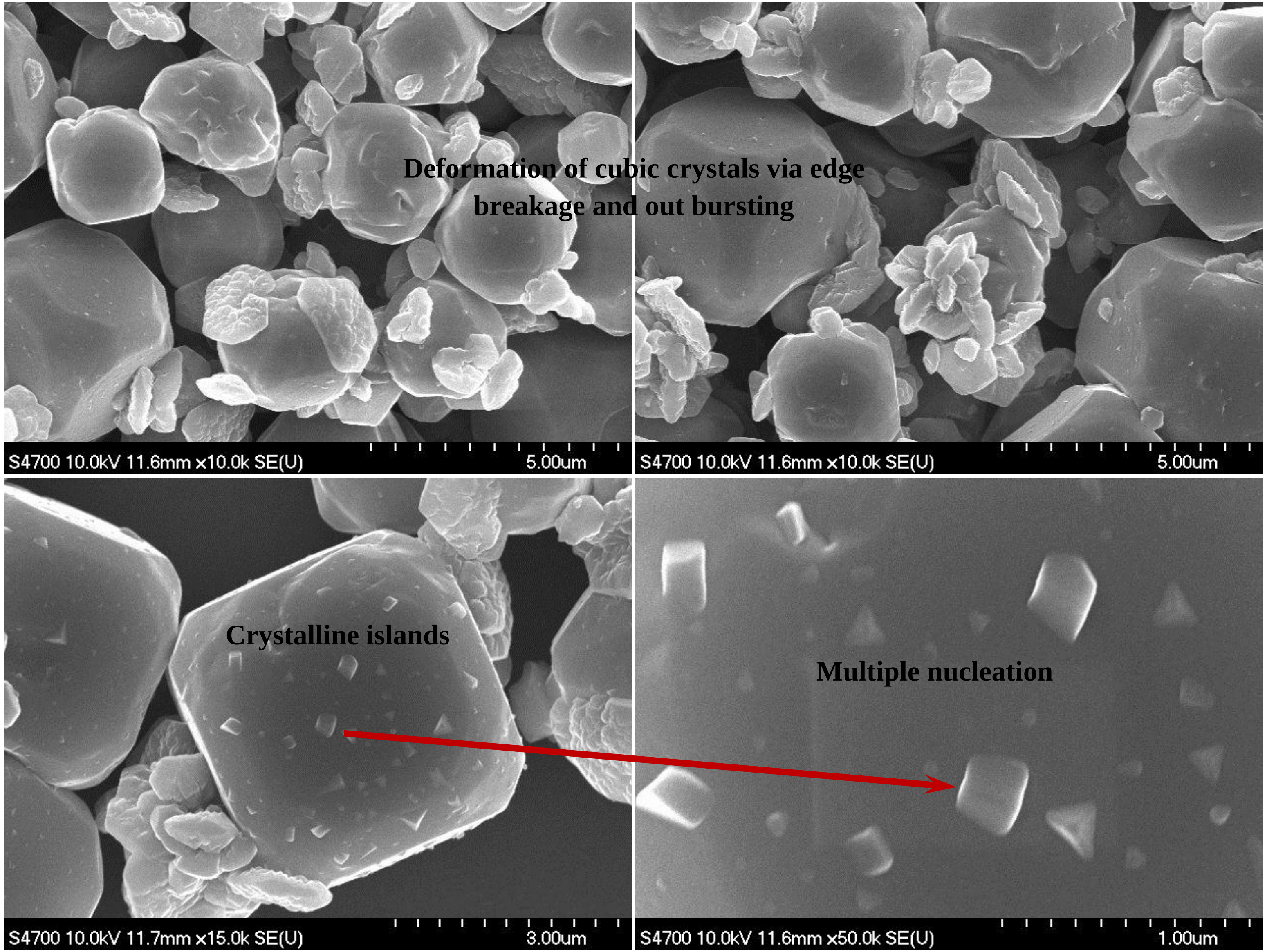
SI5-NaA72cr


Change in size and shape of NaA zeolite cubes with the expansion of core shell crystals
S4700 10.0kV 11.6mm x10.0k SE(U)
5.00um
S4700 10.0kV 11.6mm x25.0k SE(U)
2.00um
S4700 10.0kV 11.6mm x25.0k SE(U)
2.00um
Nano-sized crystalline NaA zeolite particles
S4700 10.0kV 11.6mm x50.0k SE(U)
1.00um

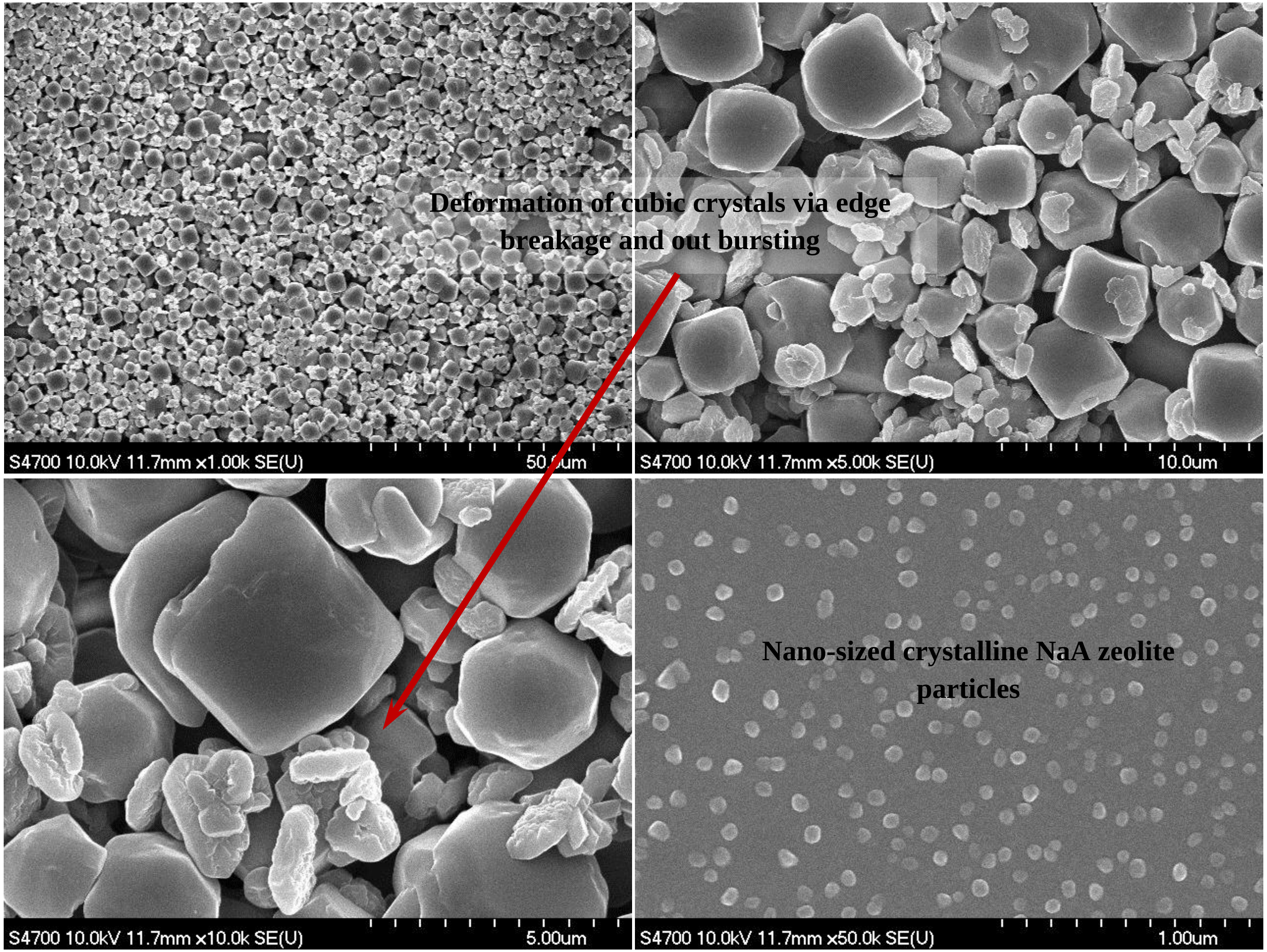
SI5-NaA96cr



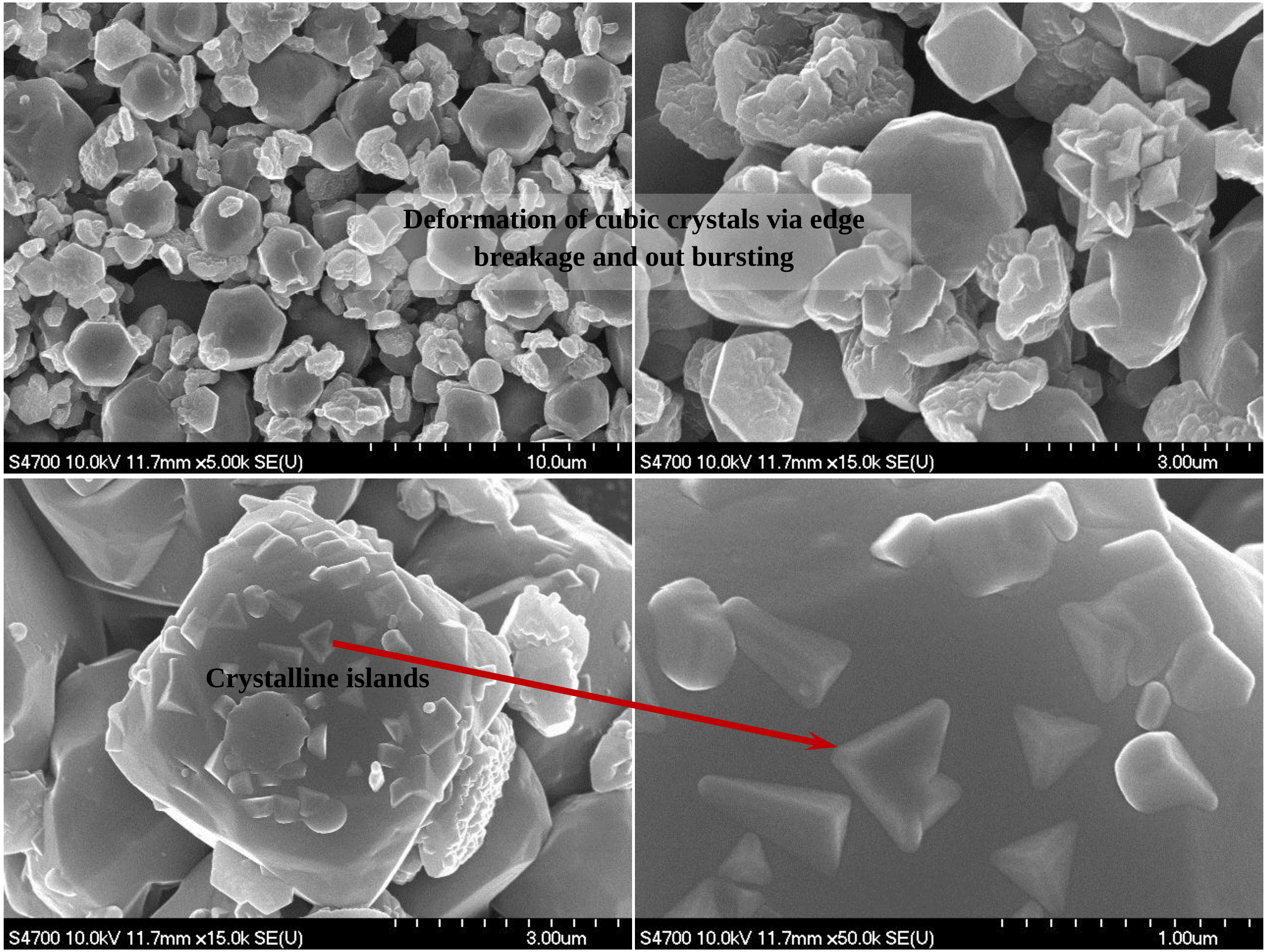
SI5-NaA120cr



SI5-NaA144cr



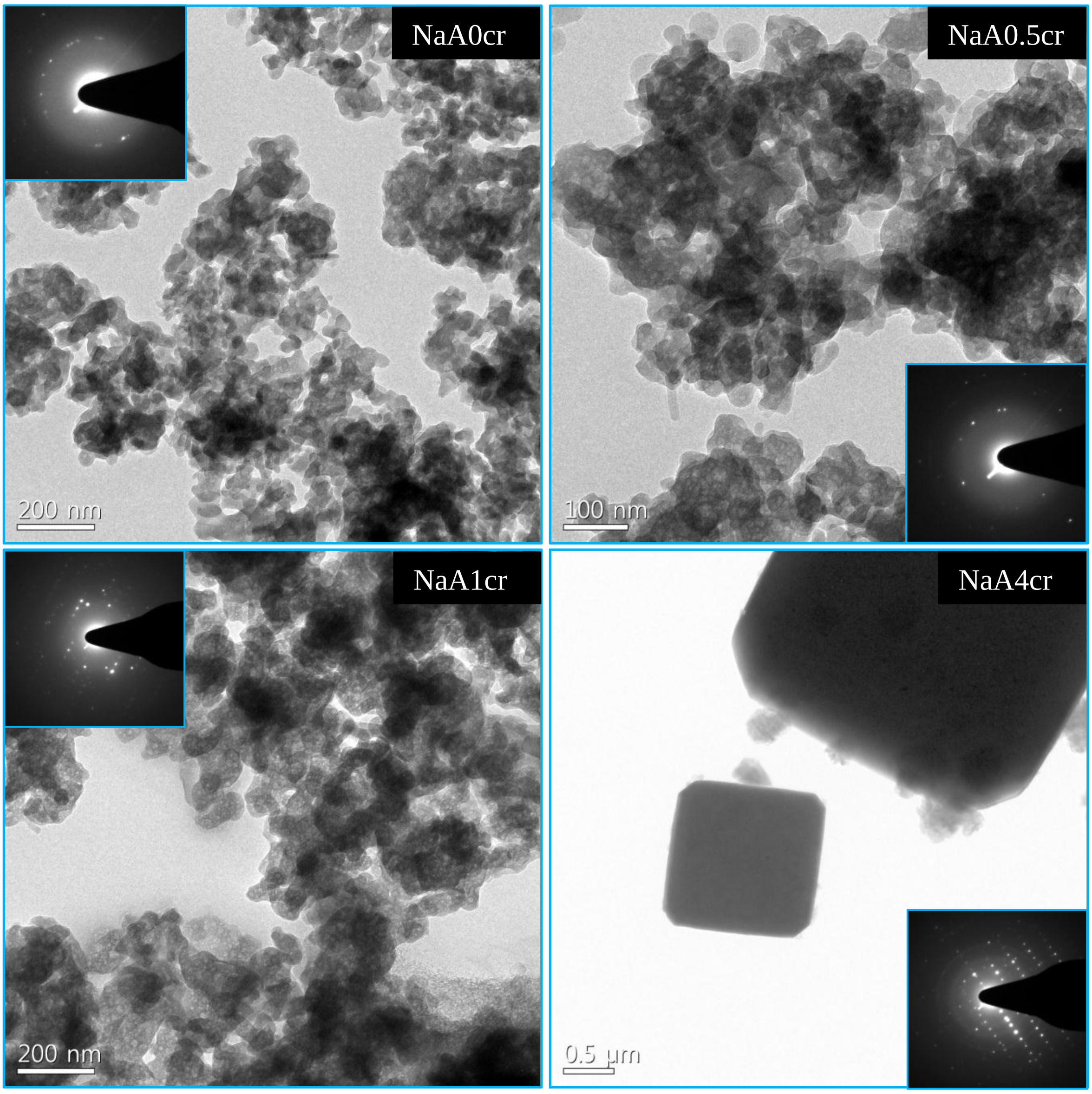
SI5-NaA168cr



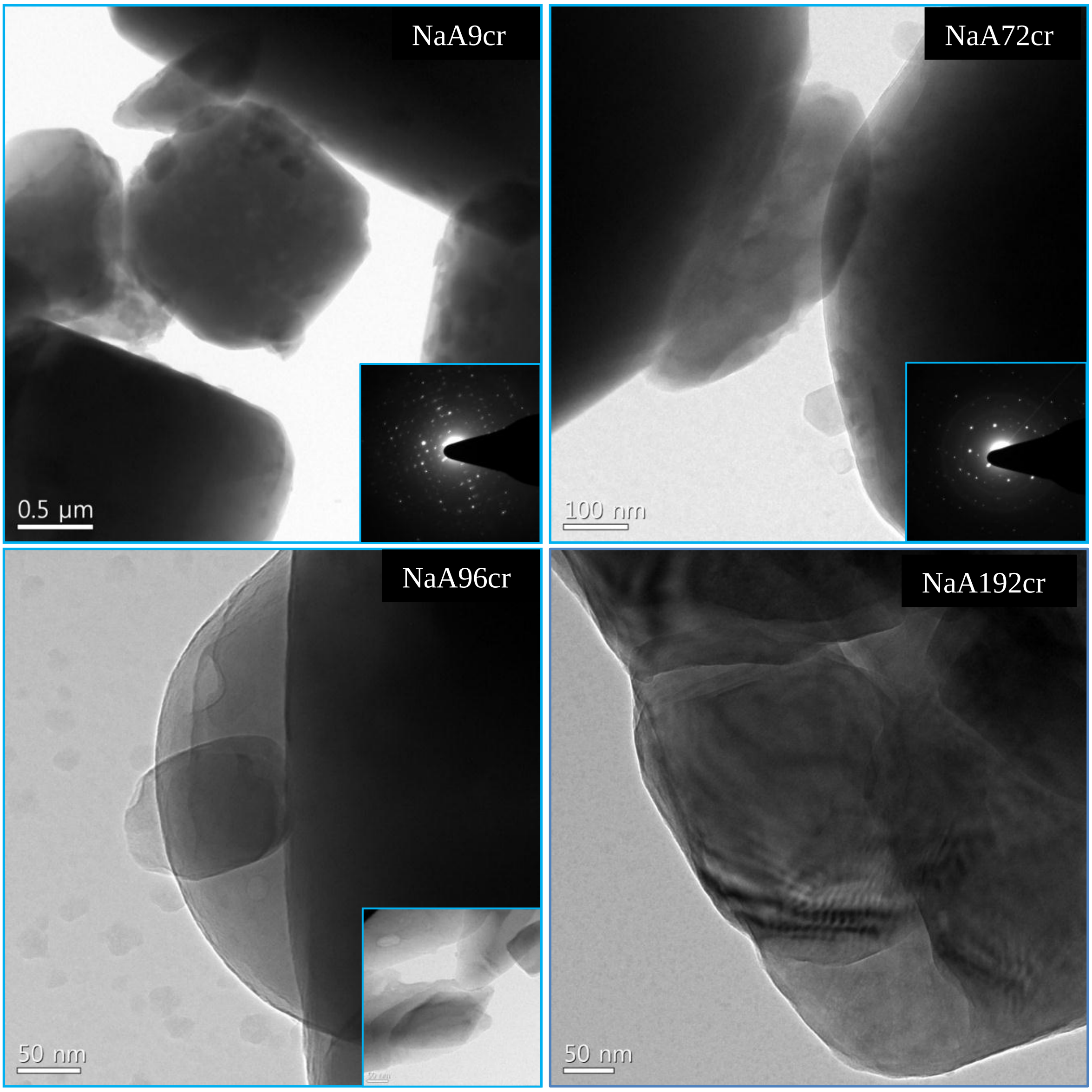
SI5-NaA192cr

SI6

TEM micrographs of the specimens collected at 0 h (NaA0cr), 0.5 h (NaA0cr), 1 h (NaA1cr), 4 h (NaA4cr), 9 h (NaA9cr), 72 h (NaA72cr) and 96 h (NaA96cr) of crystallization showing the micron-size cubes equipped with nano-size crystals (also showing surface grown crystals). As an inset in NaA0cr, NaA0.5cr, NaA1cr, NaA4cr, NaA7cr and NaA72cr SAED patterns reveals the crystalline/polycrystalline nature of PCIP and cubic crystals. The other inset in NaA96cr, a HRTEM image demonstrates the intimately inter-grown NaA zeolite crystals.



SI6 (continued)



SI7

Physical properties of NaA zeolite crystals obtained from N_2 adsorption/desorption studies.

Physical parameters	NaA1cr	NaA2cr	NaA48cr	NaA192cr
BET surface area (m^2 g^{-1})	15.89	1.12	0.79	1.81
Langmuir surface area (m^2 g^{-1})	23.02	0.39	1.31	2.55
Single point surface area(m^2 g^{-1}) (P/P_o= 0.10)	15.04	1.28	1.05	1.79
BET average pore diameter (nm)	8.10	-	4.86	6.11
BJH adsorption average pore diameter (nm)	19.37	4.60	55.17	21.71
BJH desorption average pore diameter (nm)	10.85	42.47	46.88	6.49
t-plot				
Total pore volume (cm^3 g^{-1}) (P/P_o= 0.97)	0.032	-	0.001	0.003
Mesopore volume (cm^3 g^{-1})	0.030	-	0.0001	0.0027
Micropore area (m^2 g^{-1})	3.83	3.41	1.38	0.76
External surface area (m^2 g^{-1})	12.06	-	-	1.05
HK method				
Maximum pore volume (cm^3 g^{-1}) (P/P_o= 0.99)	0.059	0.001	0.002	0.005
Median pore diameter (nm)	84.13	229.36	138.98	88.64
DA method				
Limiting micropore capacity (cm^3 g^{-1} S.T.P.)	11.46	0.19	0.17	1.16
Limiting micropore volume (cm^3 g^{-1})	0.018	0.0003	0.0003	0.002
Equivalent surface area (m^2 g^{-1})	24.41	0.50	0.42	2.40
Mean equivalent pore diameter (nm)	2.91	2.33	2.56	3.00