Supplementary information

Table S1: Quantification of the size of ice crystals

Concentration	Non-seeded samples		Seeded samples		Ice spheres	
	Samples	Ice crystals	Samples	Ice crystals	Samples	Ice crystals
0.005 M	3	28 (9, 11, 8)	3	22 (8, 5, 9)	1	8
0.05 M	5	50 (15, 8, 8, 11, 8)	2	14 (7, 7)	1	10
0.5 M	1	13	3	38 (12, 13, 13)	2	27 (12, 15)

Table S1: The number of independent samples and ice crystals used to calculate the average sizes of the crystals. Number of analysed crystals in each independent sample is given in brackets. Two perpendicular dimensions of each crystal were evaluated.

Table S2: Number of samples used for the analysis of the grooves width

Concentration	Non-seeded samples		Seeded samples		Ice spheres	
	Samples	Grooves	Samples	Grooves	Samples	Grooves
0.005 M	3	15 (5, 5, 5)	3	15 (5, 5, 5)	2	10 (5, 5)
0.05 M	4	25 (10, 5, 5, 5)	3	13 (5, 5, 3)	2	20 (10, 10)
0.5 M	0	0	3	30 (10, 10, 10)	2	20 (10, 10)

Table S2: Number of independent samples and grain boundary grooves used to calculate the average width of the grooves. Number of analysed grooves in each independent sample is given in brackets.

Table S3: Quantification of the surface coverage

	Individual samples					Mean ± SE
Non-seeded samples	33.5	11.0	12.5	17.8	16.1	18.2 ± 4.0
Seeded samples	2.7	3.0	16.7	8.5	13.8	9.0 ± 2.8
Ice spheres	9.2	3.5	5.5	1.0	1.2	4.1 ± 1.5

Table S3: Surface coverage of the frozen samples with CsCl brine in the beginning of the microscopic observations. The frozen samples were prepared from 0.05 M CsCl solution. The uncertainties express standard errors of the means (SE).

Movie S1. Surface coverage with brine as a function of temperature for the seeded 0.005 M sample. The temperature was first stepwise increased from −23.4 °C to −12.4 °C and then decreased to −27 °C. The temperature is stated in the upper left corner. The whole sequence took 30 minutes (Figure 3). The air pressure in the microscope chamber was 500 Pa during whole sequence. The movie can be seen and downloaded from https://doi.org/10.5446/39404.

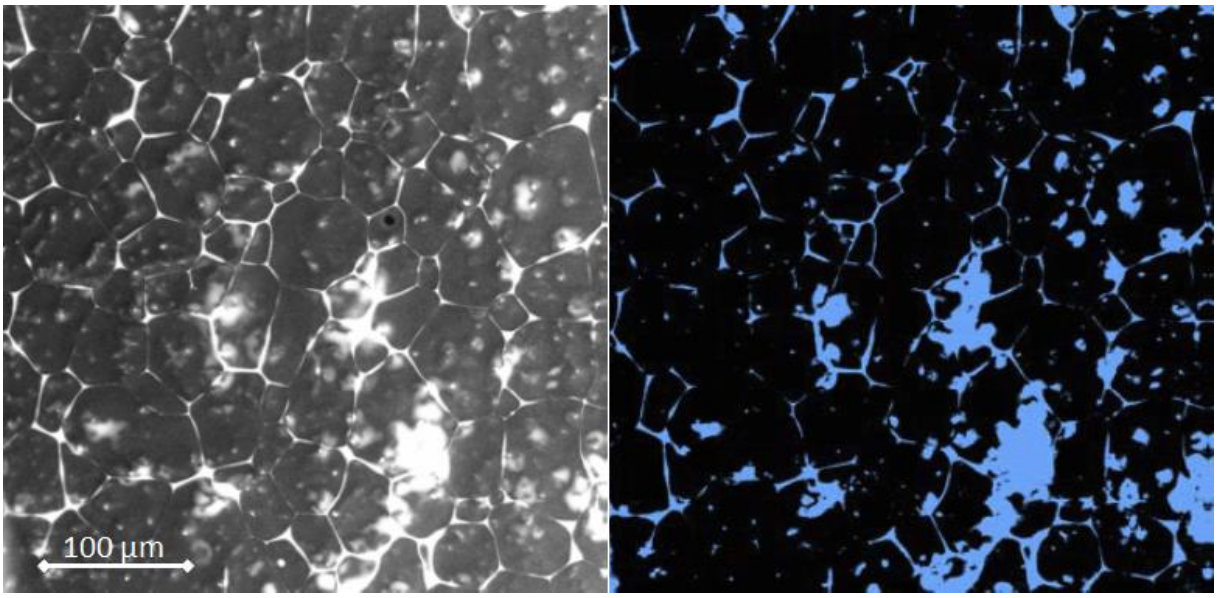

Figure S1. An example of estimation of the surface ratio covered with CsCl brine. The ESEM image of the frozen sample (left) was processed in Mountains® Software (right), brine-containing areas on the sample surface were selected (they are highlighted in blue) and their relative surface area was calculated by the software.

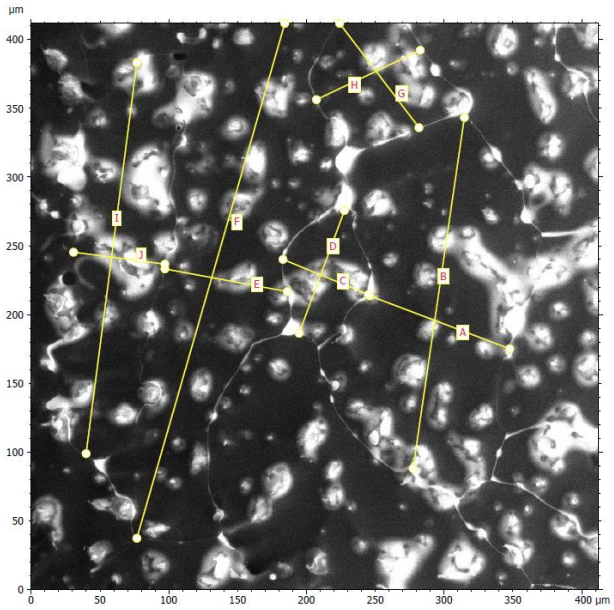

Figure S2. An example of estimation of the average size of the ice crystals in a frozen sample. This ESEM image was recorded for the seeded sample of 0.005 M CsCl at −23.5 °C. The lengths and widths of the ice crystals were manually selected in Mountains® Software and their sizes were automatically calculated by the software. In few cases (0.005 M and 0.005 M seeded sample), selected crystals overreached the image; then, the distance from the end of the crystal towards the edge of the image was evaluated. Therefore, the calculated values for these samples might be biased towards smaller values.

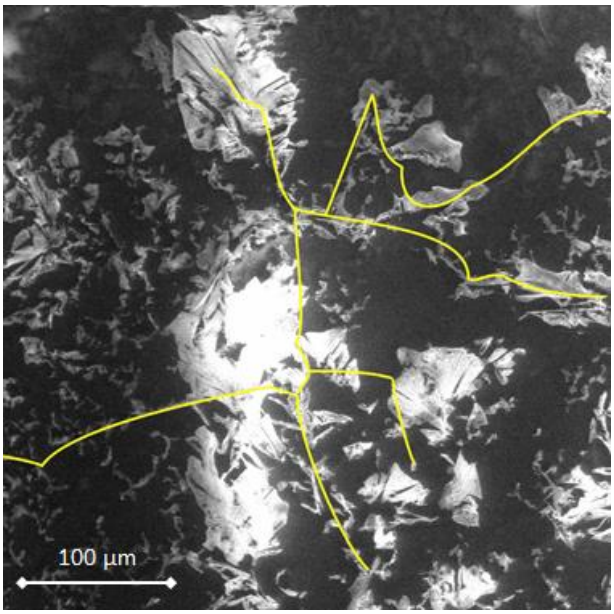

Figure S3. The surface of the frozen sample (0.005 M CsCl solution, seeded droplet) after crystallization of CsCl. This figure was made as a combination of the panels h and i of Figure 2; the grain boundaries before the crystallization of the brine are highlighted in yellow, so the crystallization of the salt along the grain boundaries is indicated.

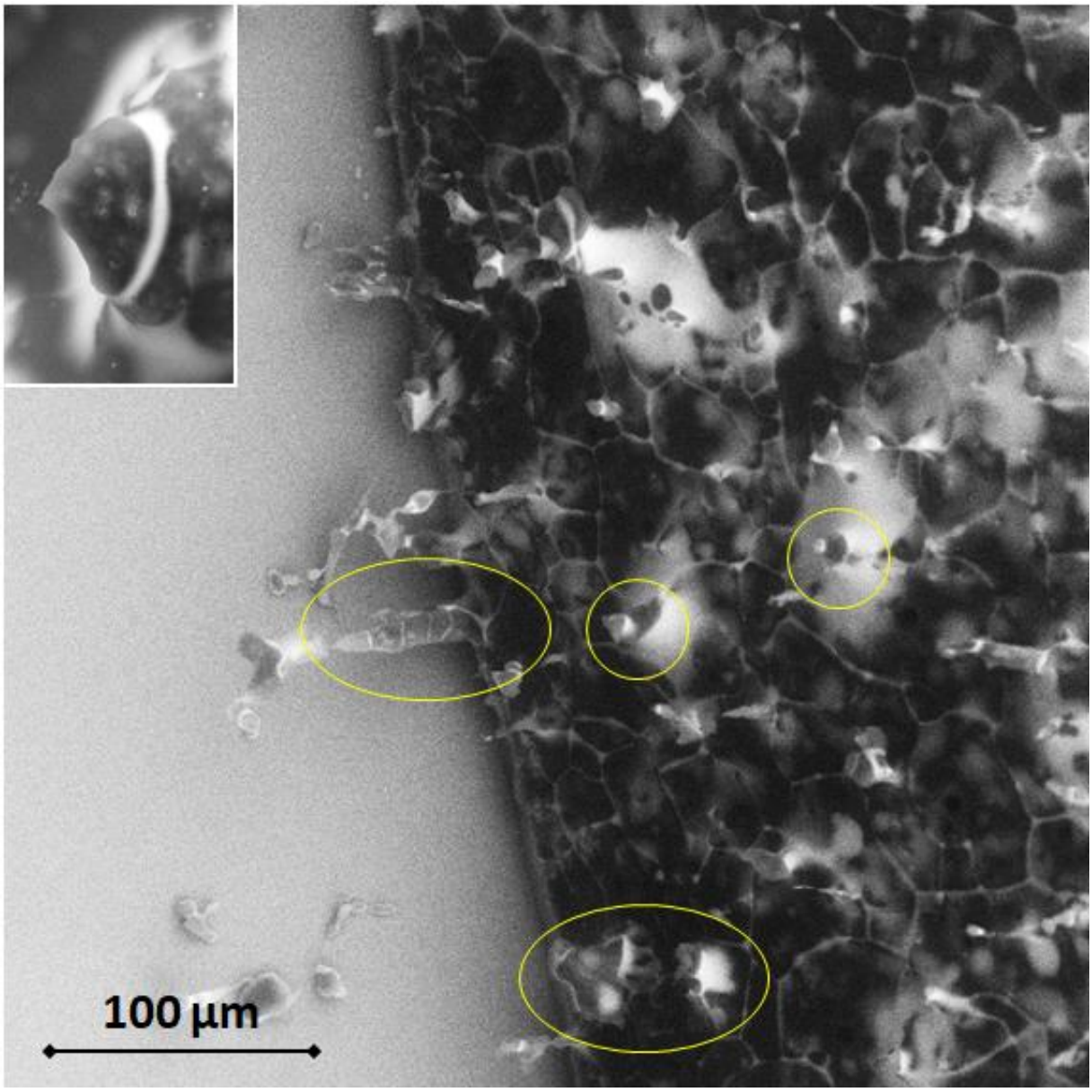

Figure S4: Partially sublimed non-seeded sample prepared from 0.05 M CsCl solution. An edge of the sample is imaged in the ESEM. A few humps on the surface of the sample are highlighted. Shapes of the humps are well visible from this view. The brine is accumulated at the bases of the humps, not on the tips. One magnified hump is imaged in the upper left corner. The image was recorded at −21 °C. The dark-grey area represents ice surface, white area represents the CsCl brine, and the light area in the left side of the image represents the sample holder of the ESEM. A few particles that broke off the frozen sample are visible on the holder.

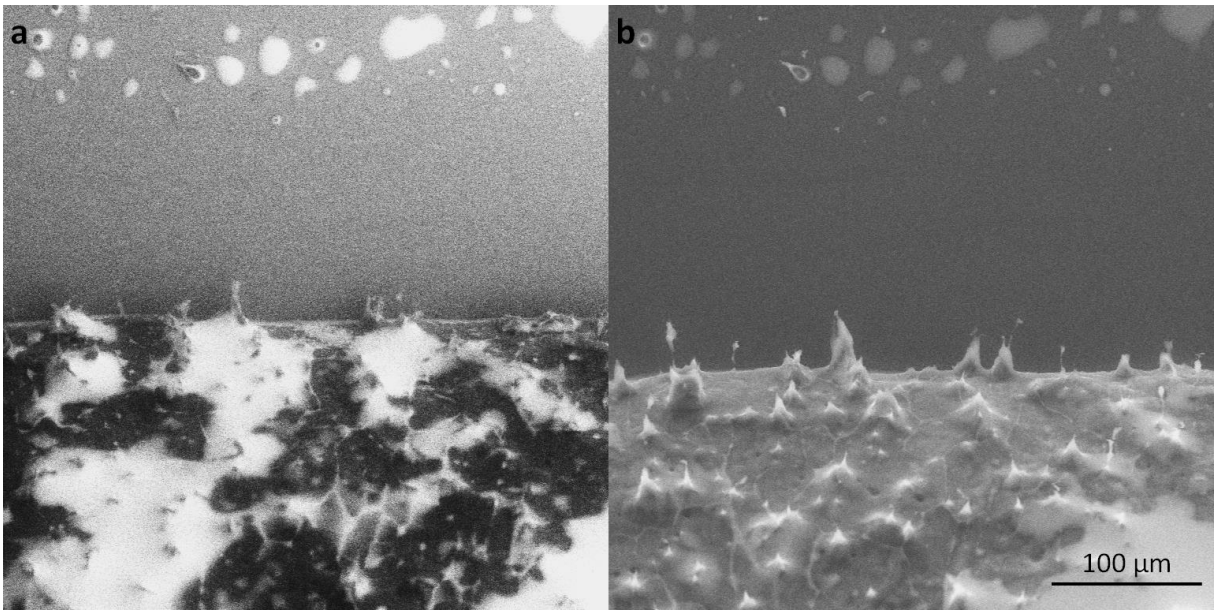

Figure S5: Partially sublimed non-seeded sample prepared from 0.05 M CsCl solution. An edge of the sample is imaged in the ESEM by the BSE detector sensitive to atoms with large atomic number (a) and ionization detector more sensitive to the surface topology (b). The images was recorded at −22.6 °C. The image from the ionization detector was recorded 30 s after the image from the BSE detector on the same spot of the sample.

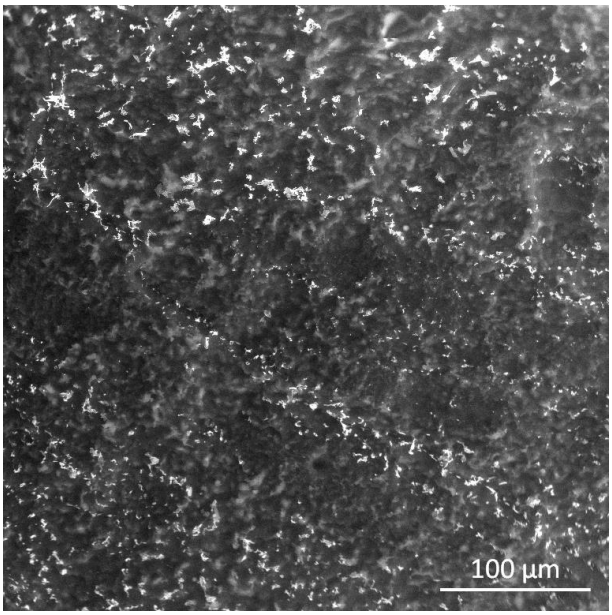

Figure S6: Surface of a macroscopic LN-frozen sample (c_{CsCl} = 0.05 M) at −25 °C observed in the ESEM. Preparation method: a droplet (diameter ~ 5 mm) of the solution was put on a piece of aluminium foil and immersed into LN. The aluminium foil was used to ensure a flat bottom of the sample for a better thermal contact with a cold sample holder of the ESEM. In comparison with the interior of the LN-frozen sample revealed by sample fragmentation (Figures 7, S15), no parallel lines of the brine were visible on the surface of the macroscopic LN-frozen droplet.

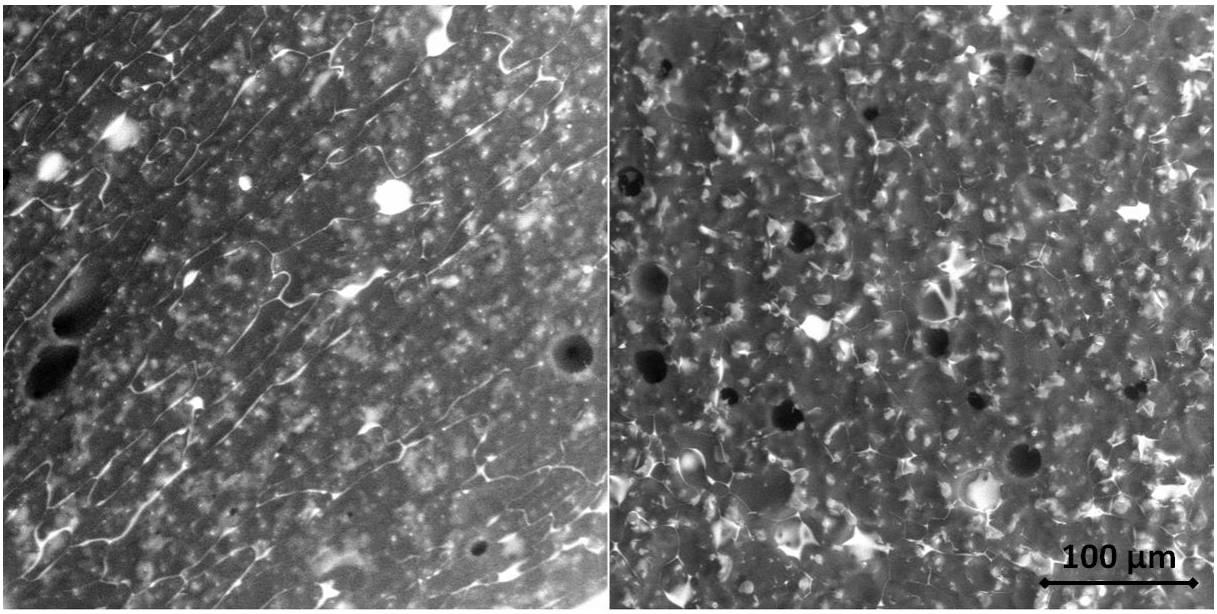

Figure S7: ESEM images of two independent frozen samples prepared from 0.005 M CsCl solution by spontaneous freezing of supercooled (non-seeded) droplets. The images were recorded in the very beginning of the observations at −25 °C. Grey areas represent ice, white colour represents CsCl brine. Numerous humps and hollows are visible on the surface of the samples.

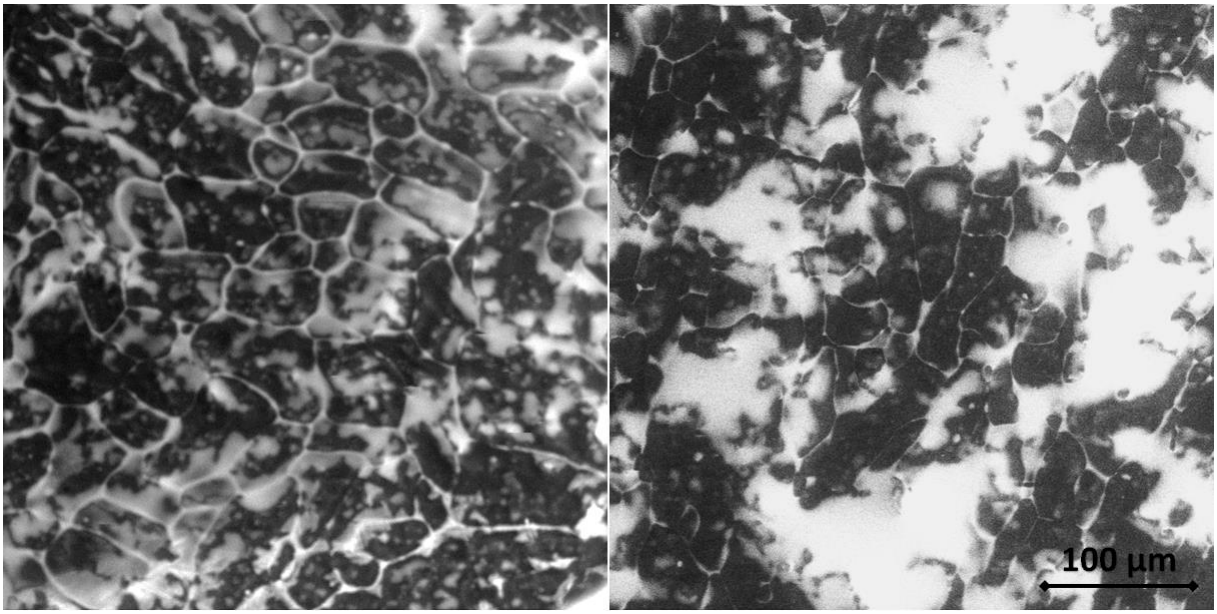

Figure S8: ESEM images of two independent frozen samples prepared from 0.05 M CsCl solution by spontaneous freezing of supercooled (non-seeded) droplets. The images were recorded in the very beginning of the observations at −25 °C (left) or −22.6 °C (right). Grey areas represent ice, white colour represents CsCl brine.

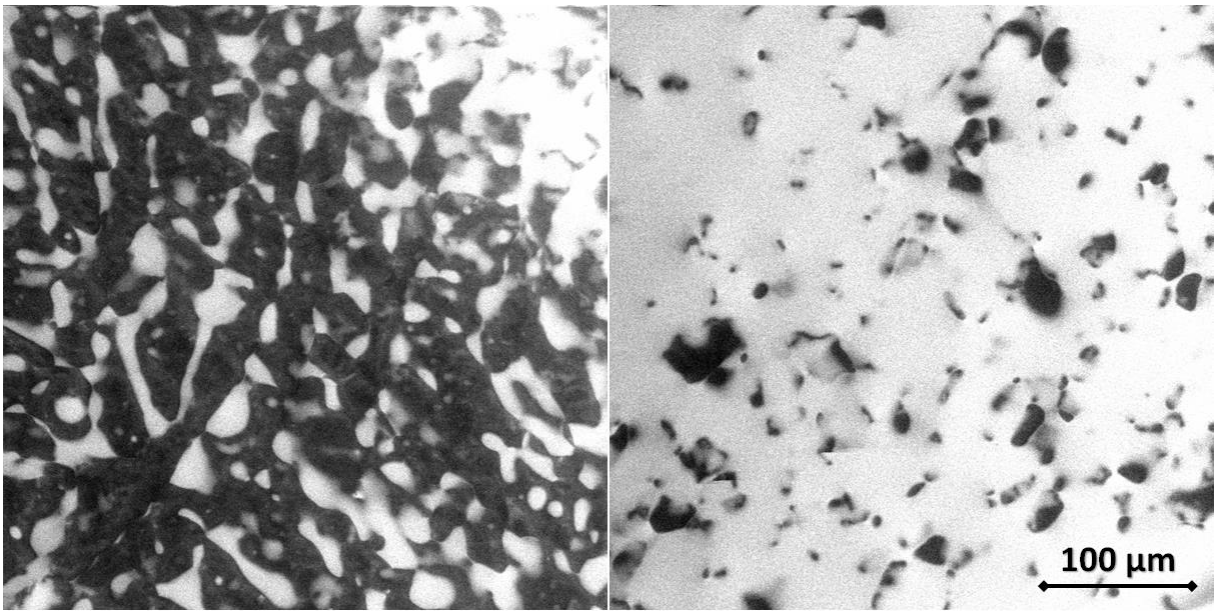

Figure S9: ESEM images of two independent frozen samples prepared from 0.5 M CsCl solution by spontaneous freezing of supercooled (non-seeded) droplets. The images were recorded in the very beginning of the observations at −22 °C (left) or −25 °C (right). Grey areas represent ice, white colour represents CsCl brine. Numerous humps and hollows are visible on the surface of the samples.

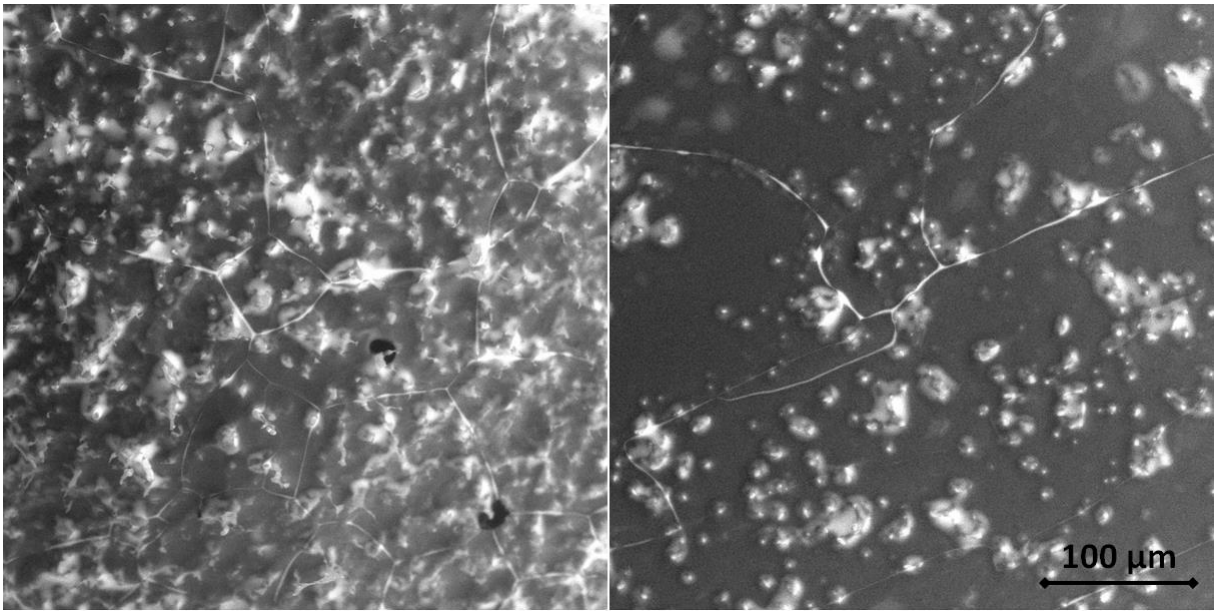

Figure S10: ESEM images of two independent frozen samples prepared from 0.005 M CsCl solution by freezing of droplets seeded with ice crystals. The images were recorded in the very beginning of the observations at −25 °C (left) or −20 °C (right). Grey areas represent ice, white colour represents CsCl brine. Numerous humps are visible on the surface of the samples. Two hollows are visible in the surface of the sample in the left panel.

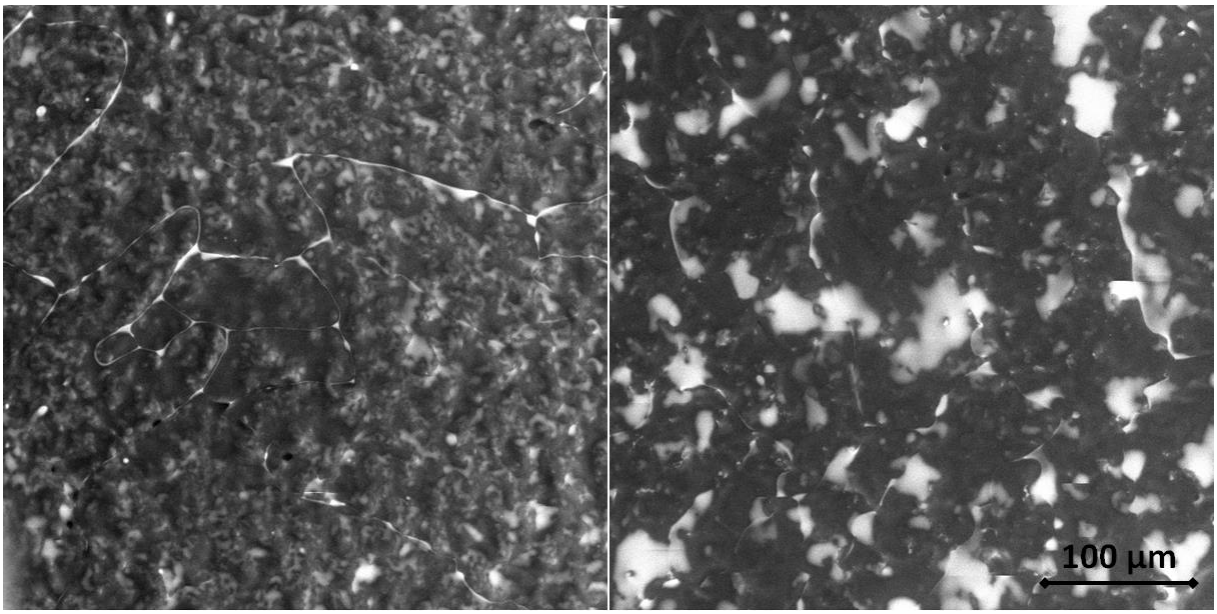

Figure S11: ESEM images of two independent frozen samples prepared from 0.05 M CsCl solution by freezing of droplets seeded with ice crystals. The images were recorded in the very beginning of the observations at −21 °C (left) or −25 °C (right). Grey areas represent ice, white colour represents CsCl brine. Numerous humps are visible on the surface of the left sample.

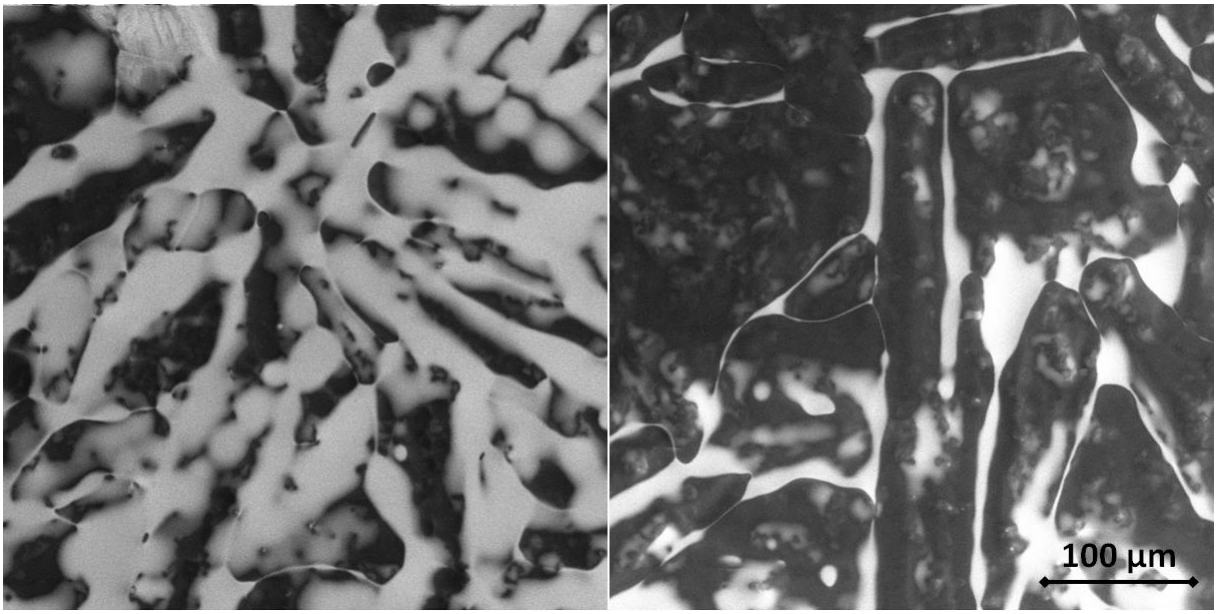

Figure S12: ESEM images of two independent frozen samples prepared from 0.5 M CsCl solution by freezing of droplets seeded with ice crystals. The images were recorded in the very beginning of the observations at −22.5 °C (left) or −20 °C (right). Grey areas represent ice, white colour represents CsCl brine.

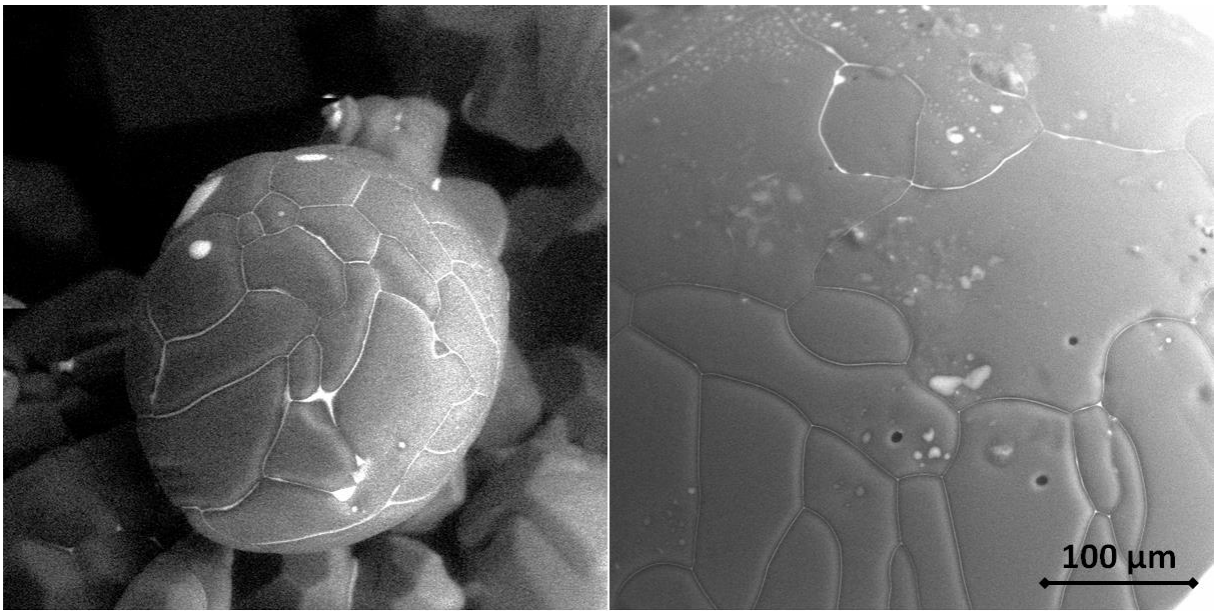

Figure S13. ESEM images of the frozen samples prepared from 0.005 M CsCl solution by spraying the solution into LN. The images were recorded in the very beginning of the observations at −23.4 °C (left) or −21.8 °C (right). Grey areas represent ice, white colour represents CsCl brine.

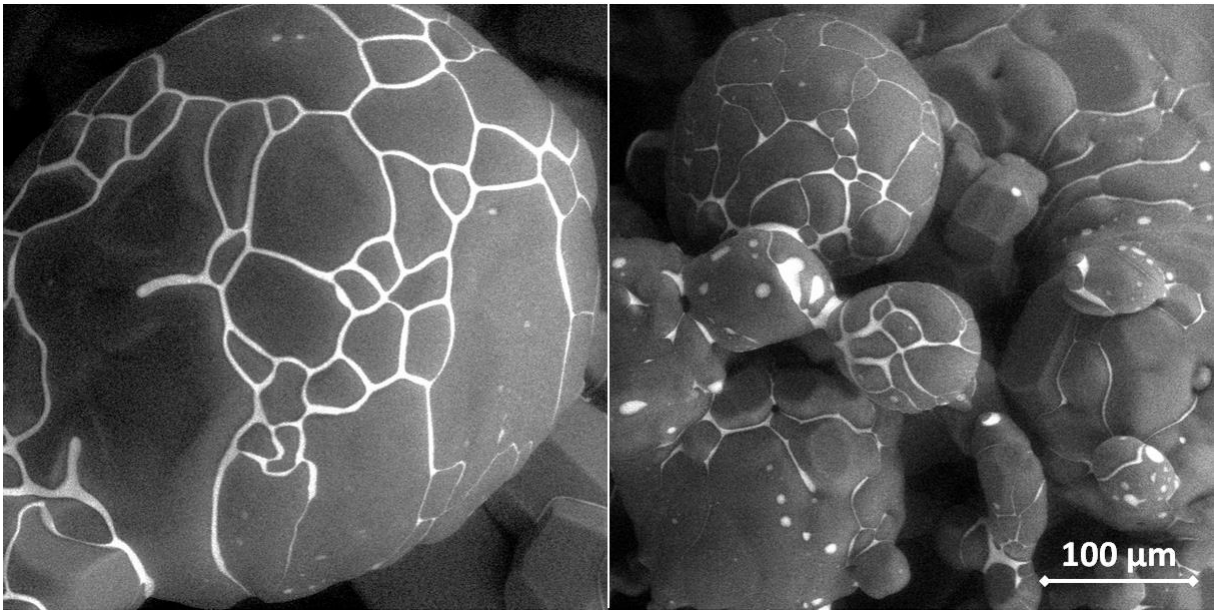

Figure S14. ESEM images of the frozen samples prepared from 0.05 M CsCl solution by spraying the solution into LN. The images were recorded in the very beginning of the observations at −22 °C (left) or −22.5 °C (right). Grey areas represent ice, white colour represents CsCl brine.

Figure S15. ESEM images of the frozen samples prepared from 0.5 M CsCl solution by spraying the solution into LN. The images were recorded in the very beginning of the observations at −23.5 °C. Grey areas represent ice, white colour represents CsCl brine.

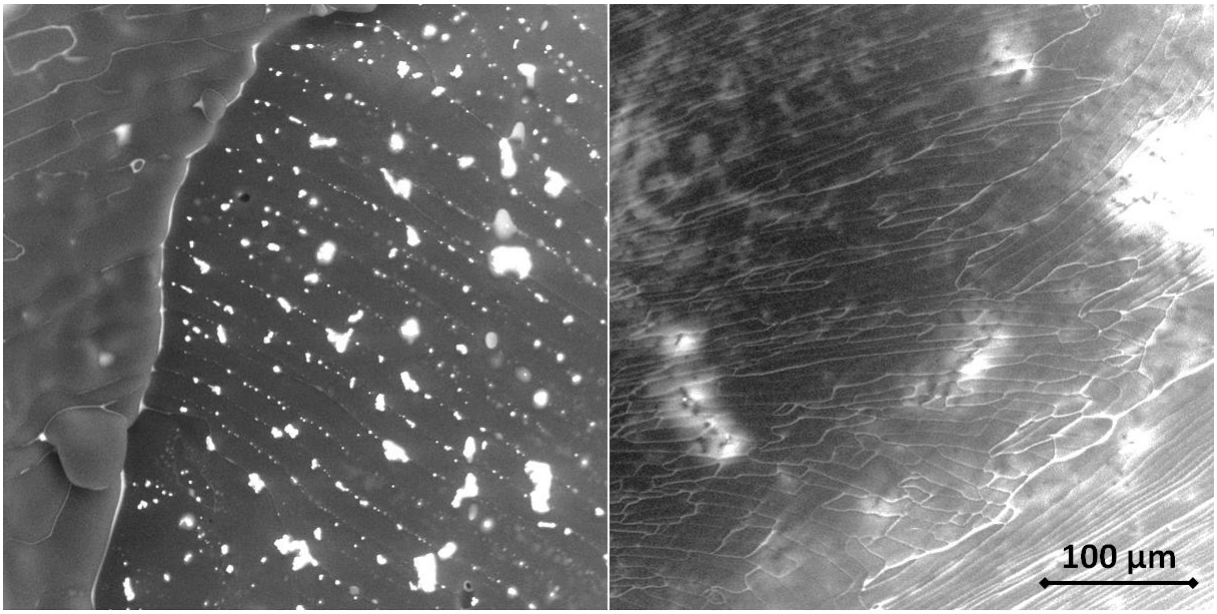

Figure S16: ESEM images of the interior of the fragmentised LN-frozen samples of 0.05 M (left) and 0.005 M (right) CsCl. The images were recorded in the very beginning of the observations at −25 °C (left) or −22.5 °C (right). Grey areas represent ice, white colour represents CsCl brine.

Figure S17 (enclosed as independent document)**:** ESEM images utilized for the measurements of the thicknesses of the grain boundary grooves. The average values can be found in the Table 2.