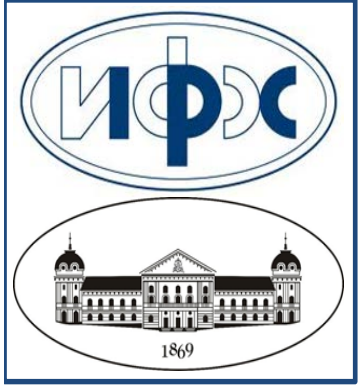

New glass ceramic by Fe Ni wastes with improved structure and properties

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Content :

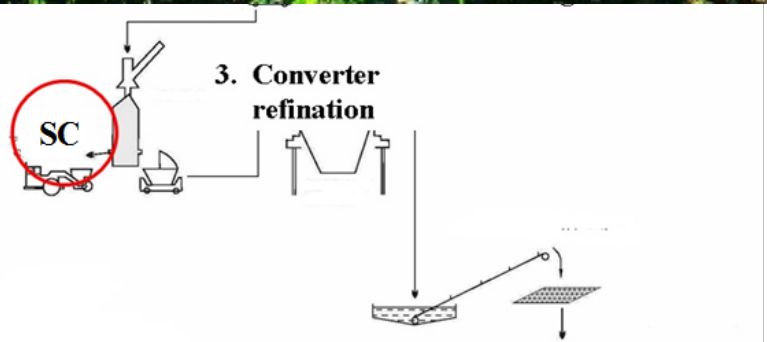
- Basal tiles and petrurgical products
- Used wastes and parent glass
- Evaluation of the crystallization heat-treatment regime
- Morphology and structure by SEM and TEM
- Properties of obtained glass-ceramic

Main techniques and apparatus: **DTA-TG** *(Perkin Elmer Diamond)*, **Density measurements** *(AccuPyc 1330)*, **HSM** *(Misura 1400)*, **XRD** *(PANalytical Empyrean),* **TEM** *(JEOL 200 kV),* **SEM-EDS** *(JEOL JSM 6390) and* **FESEM** *(Zeiss Merlin)*

Basalt road tiles – Roman Empire and Napoli – Italy (today)

Products of the petrurgy - cast basaltic tiles

Analysis of used wastes and parent glass

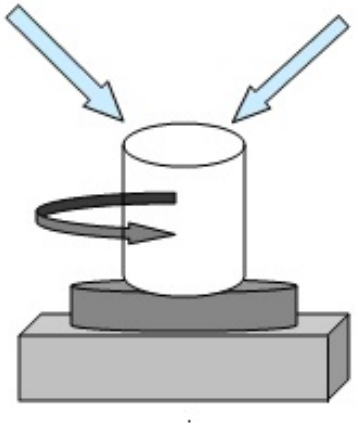


Dust (FD)	102 000
Electro-furnace slag (SEF)	1 135 000
Converter slag (SC)	109 000

Leaching test (TCLP) results for the used wastes (mg/l)

Solid waste

CH_3COOH



- CH_3COOH,
- pH ≤ 5,
- 24 h,
- 30 rpm,
- *s:l* = 1:20

	SEF	FD	SC	Applied limits
Zn	0.29	3.6	0.42	5
Ni	2.7	6.1	19.2	1
As	0.01	1.2	0.18	0.2
Cr	1.1	0.22	2.9	1.0

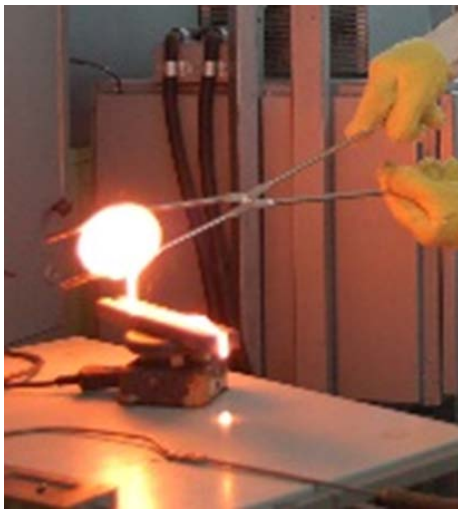
Analysis of used wastes and parent glass

Chemical compositions

	SEF	FD	SC	WM	GC	WG
SiO_2	53	37.5	1.9	47.8	71.4	55
Al_2O_3	2	1.8	0.3	1.9	0.6	1.5
MgO	16.9	14.5	6.2	15.9	3.3	12.1
CaO	2.4	2.3	15.9	3.5	9.8	5.4
Cr_2O_3	2.5	1	0.7	2.2		1.5
CoO	0.1	0.1	0.1	0.1		0.1
NiO	0.1	2.7	0.45	0.3		0.2
Fe_2O_3	14	30	60	19		19.8*
FeO	9		19	8.8		
Na_2O					13.3	4
K_2O					1.3	0.4
Wt %	58	6	6	70	30	100

Melting procedure:

- ~ 0,5 kg glass
- 1400 °C
- 1.5 h

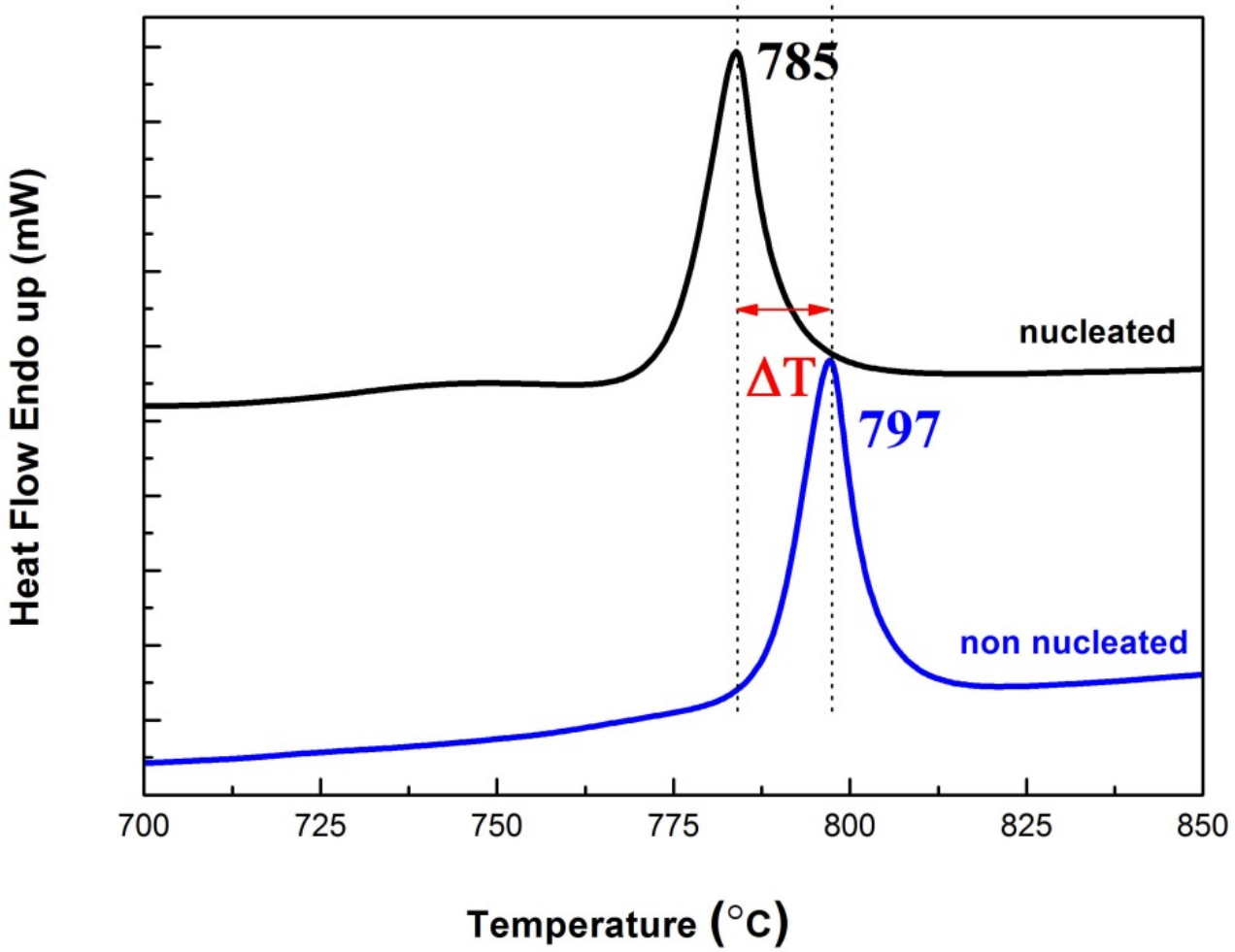


Evaluation of the heat-treatment regime

Evaluation of the optimal nucleation treatment by DTA

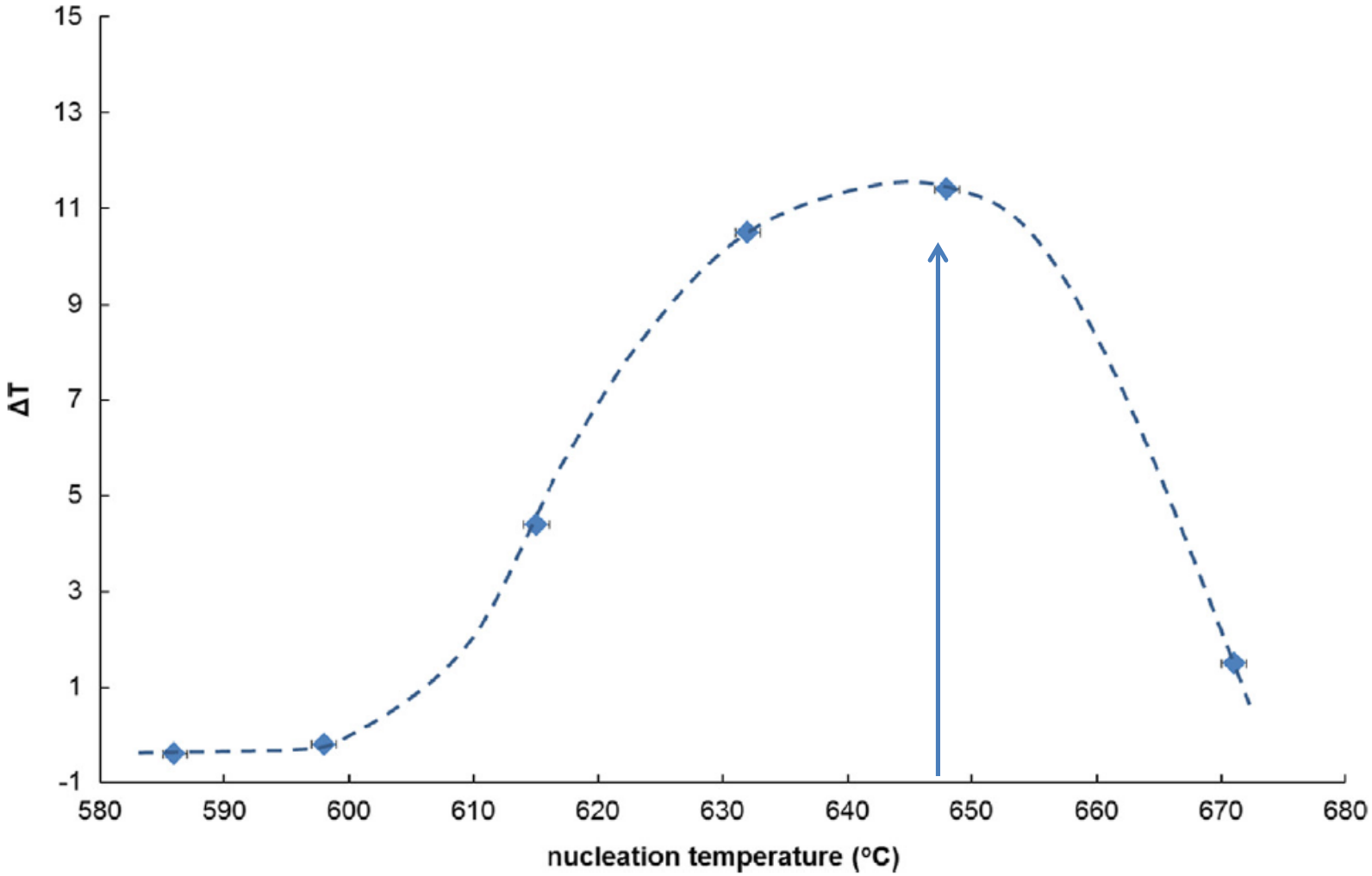
12-15 mg bulk samples, treated at 20 °C/min after various nucleation treatment (temperature and time)

The maximum temperature shift (optimal nucleation) was obtained after ***45-60 min at 650 °C.***



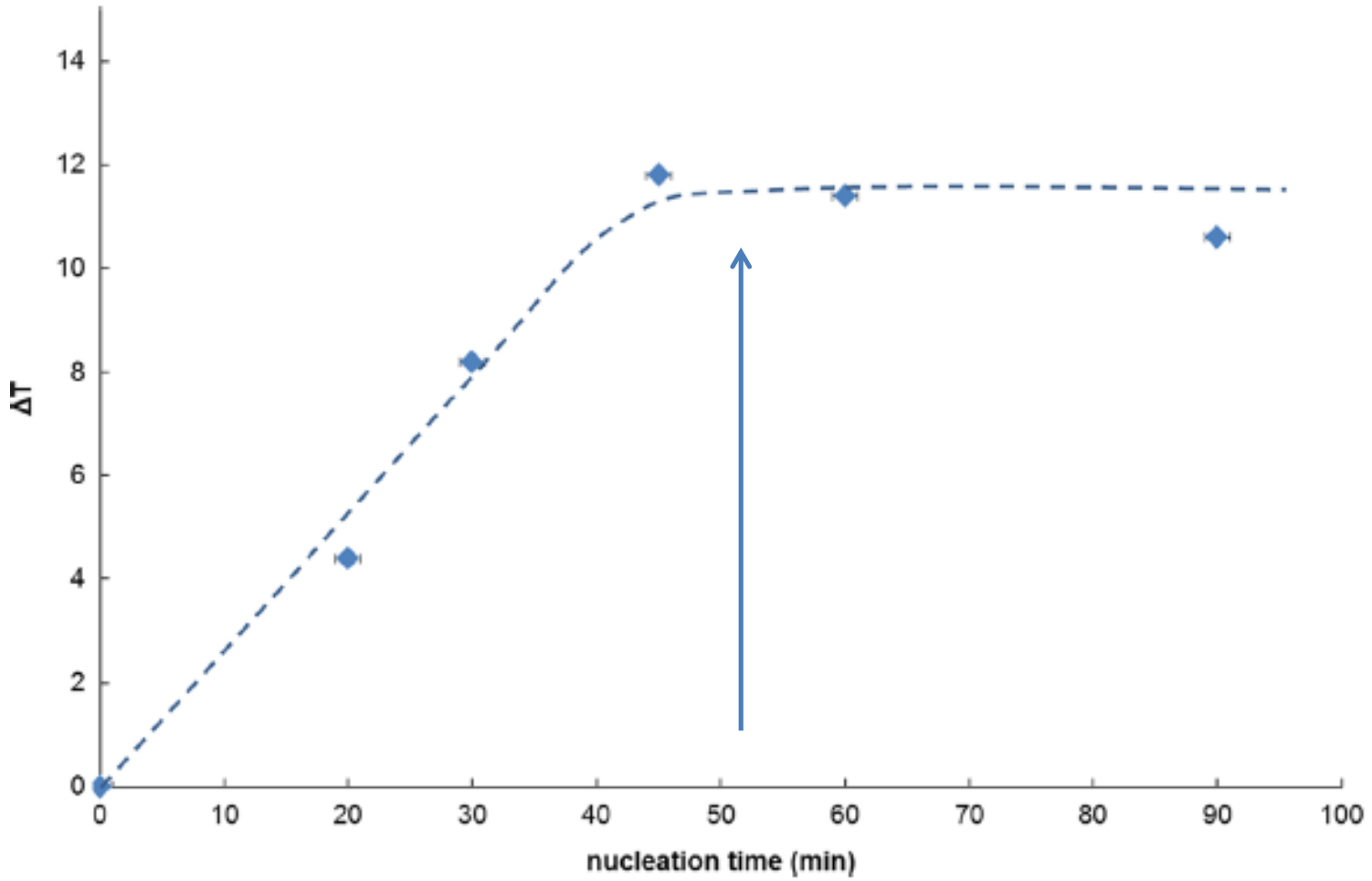
Evaluation of the optimal nucleation treatment by DTA

Optimal nucleation temperature



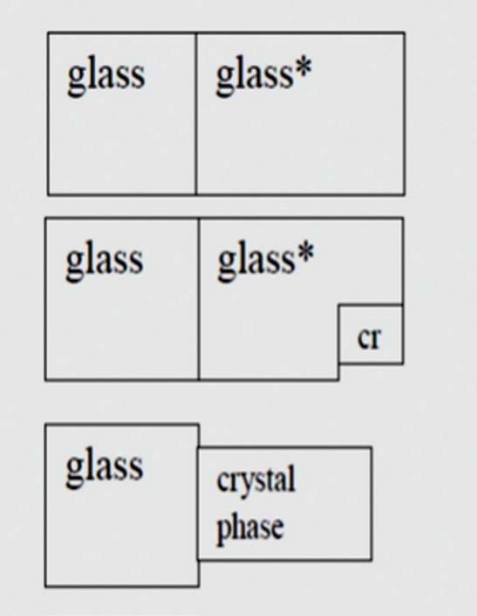
Evaluation of the optimal nucleation treatment by DTA

Optimal nucleation time



Evaluation of the heat-treatment regime

Evaluation of the optimal crystallization treatment by density measurements



$$vol\,\%\ crystal\ \ phase = 100 * \frac{\frac{1}{\rho_{pg}} - \frac{1}{\rho_{gc}}}{k}$$

ρ_{pg} - *parent glass density*

ρ_{gc} - *glass-ceramic density*

$$k = \frac{1}{\rho_{g*}} - \frac{1}{\rho_{cr}}$$

ρ_{cr} - *crystal phase density*

ρ_{g*} - *density of a glass with composition of the formed crystal phase*

In the case of pyroxene crystallization $\rho_{g*}/\rho_{cr} \sim 0.84 \pm 0.1$

In the case of spinel crystallization $\rho_{g*}/\rho_{cr} \sim 0.82 \pm 0.2$

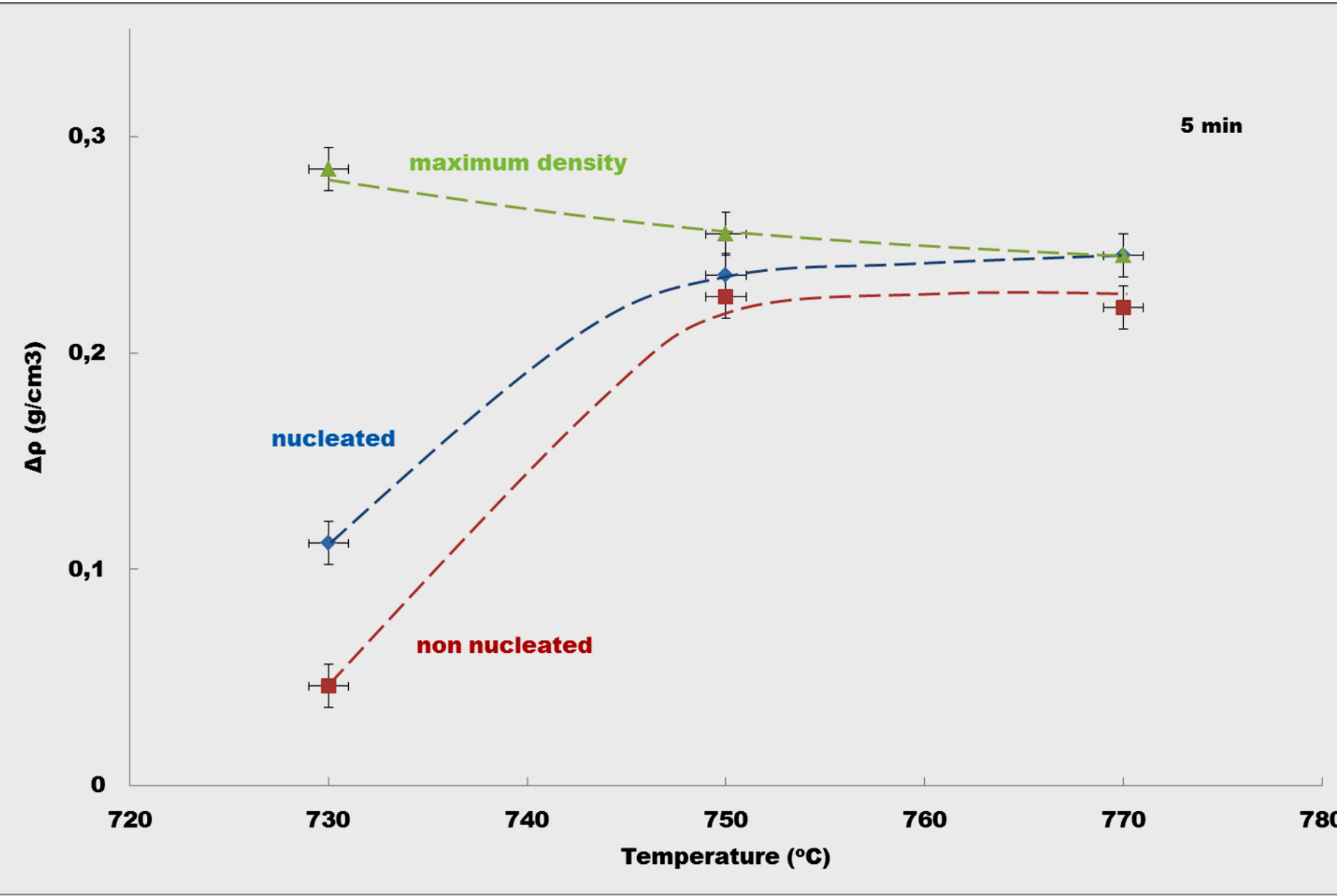
In our experiments:

ρ_{pg} *- 2.91 ± 0.006 g/cm³*

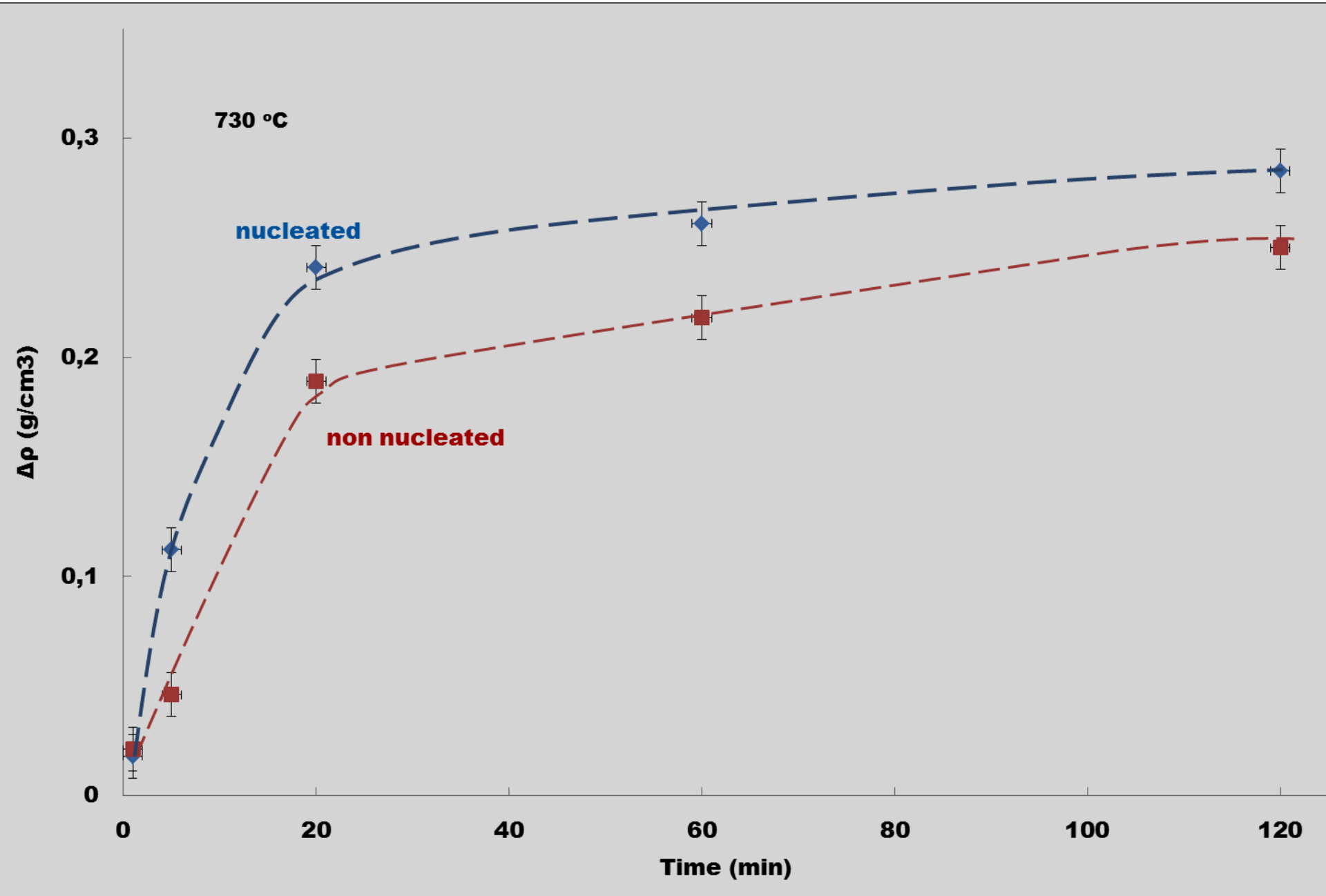
ρ_{gc} *- 3.19 ± 0.004 g/cm³ , reached after* **45-60 min at 730-740 ° C**

(corresponding to total crystallinity of 58 ± 2)

Evaluation of the optimal crystallization treatment

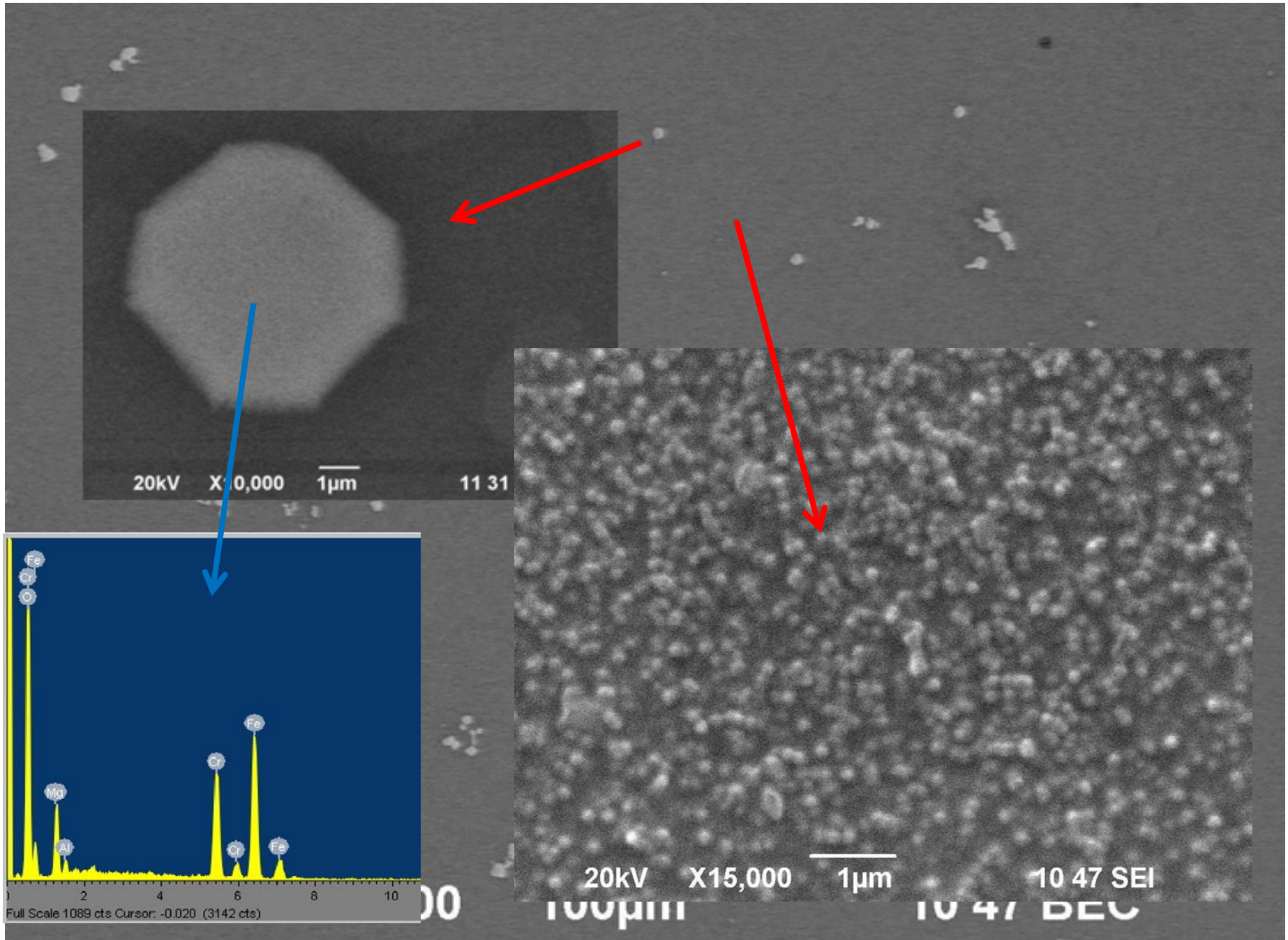


Evaluation of the optimal crystallization treatment



Morphology and structure

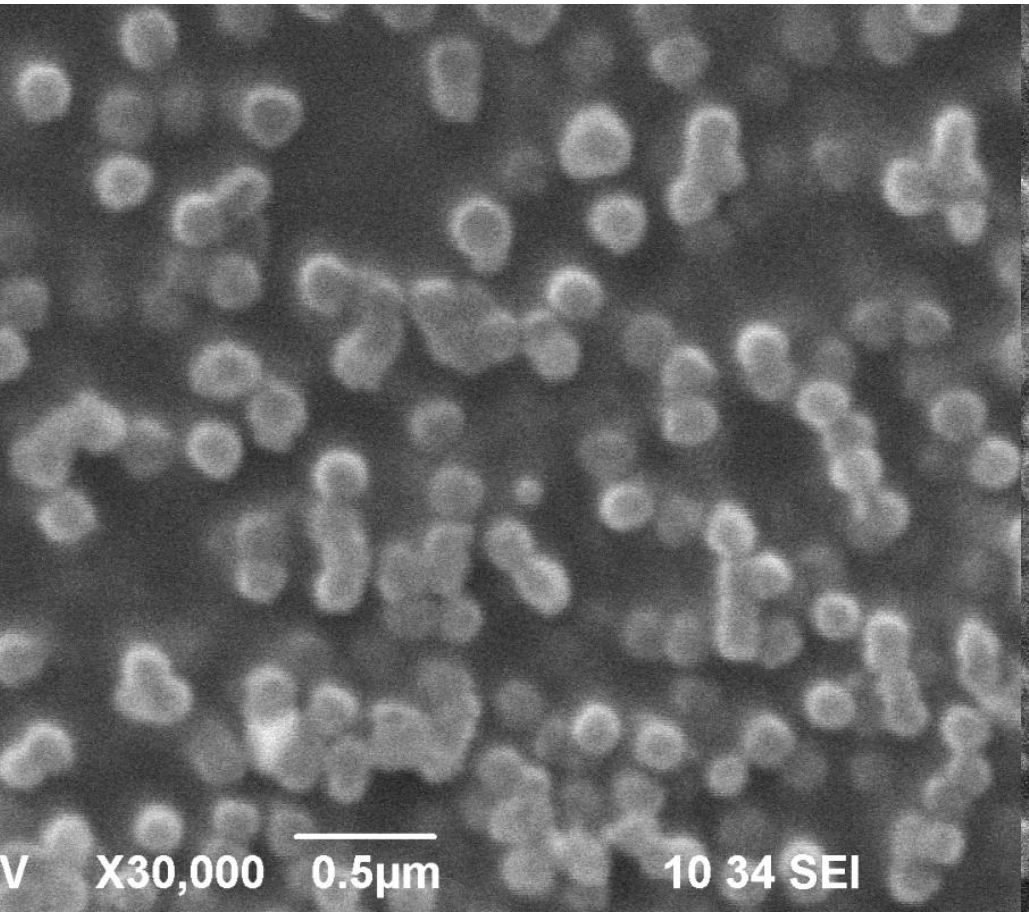
SEM - *1 min at 730 °C*



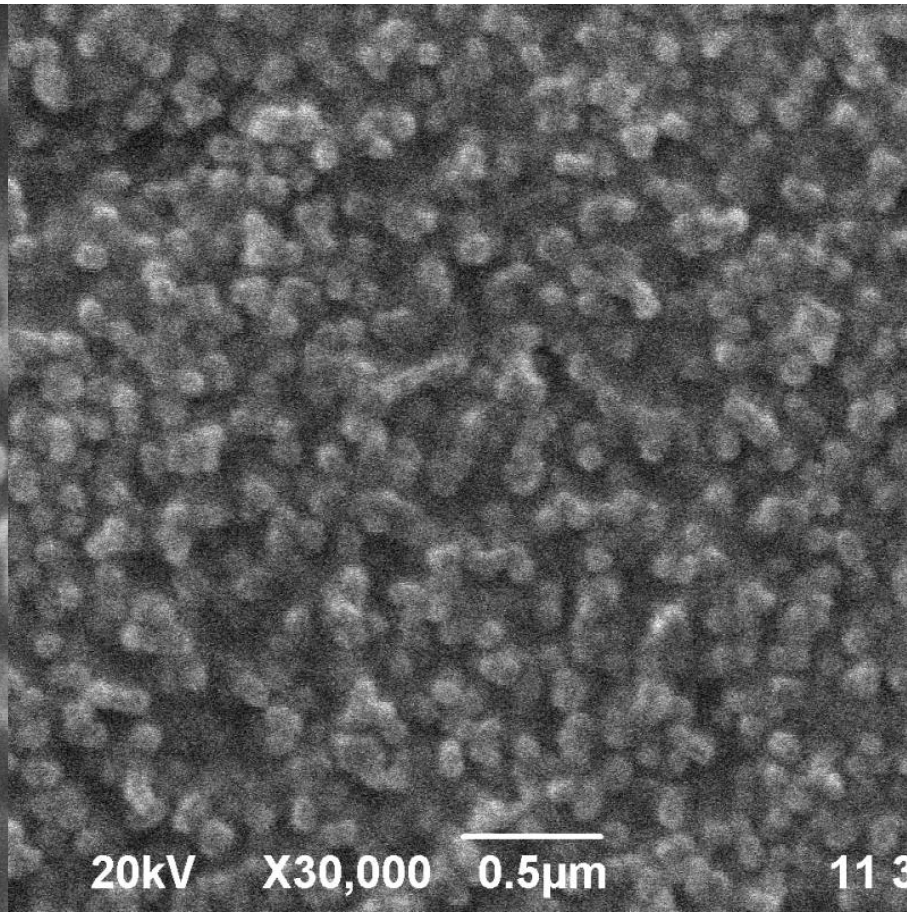
Morphology and structure

SEM

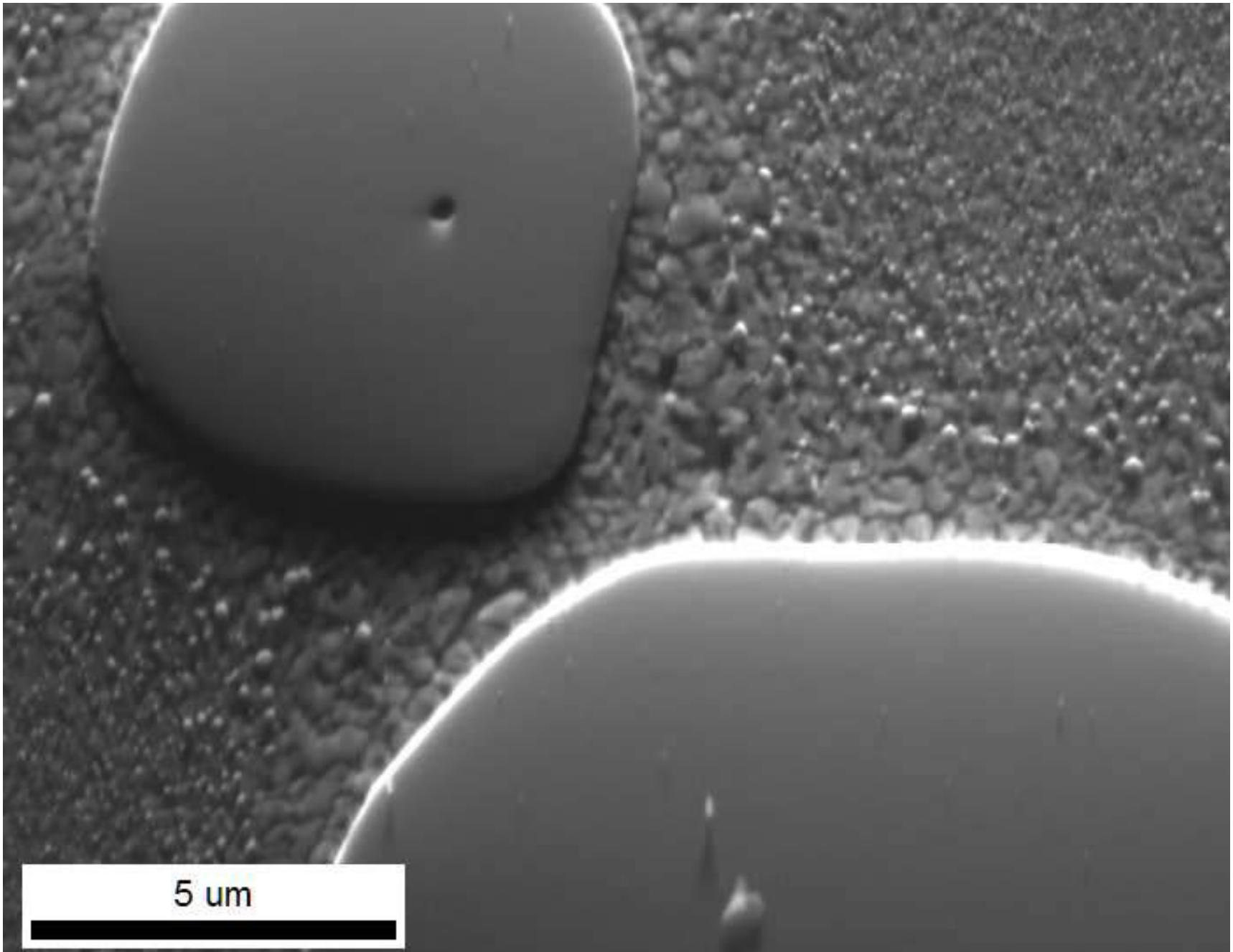
1 min at 730 °C



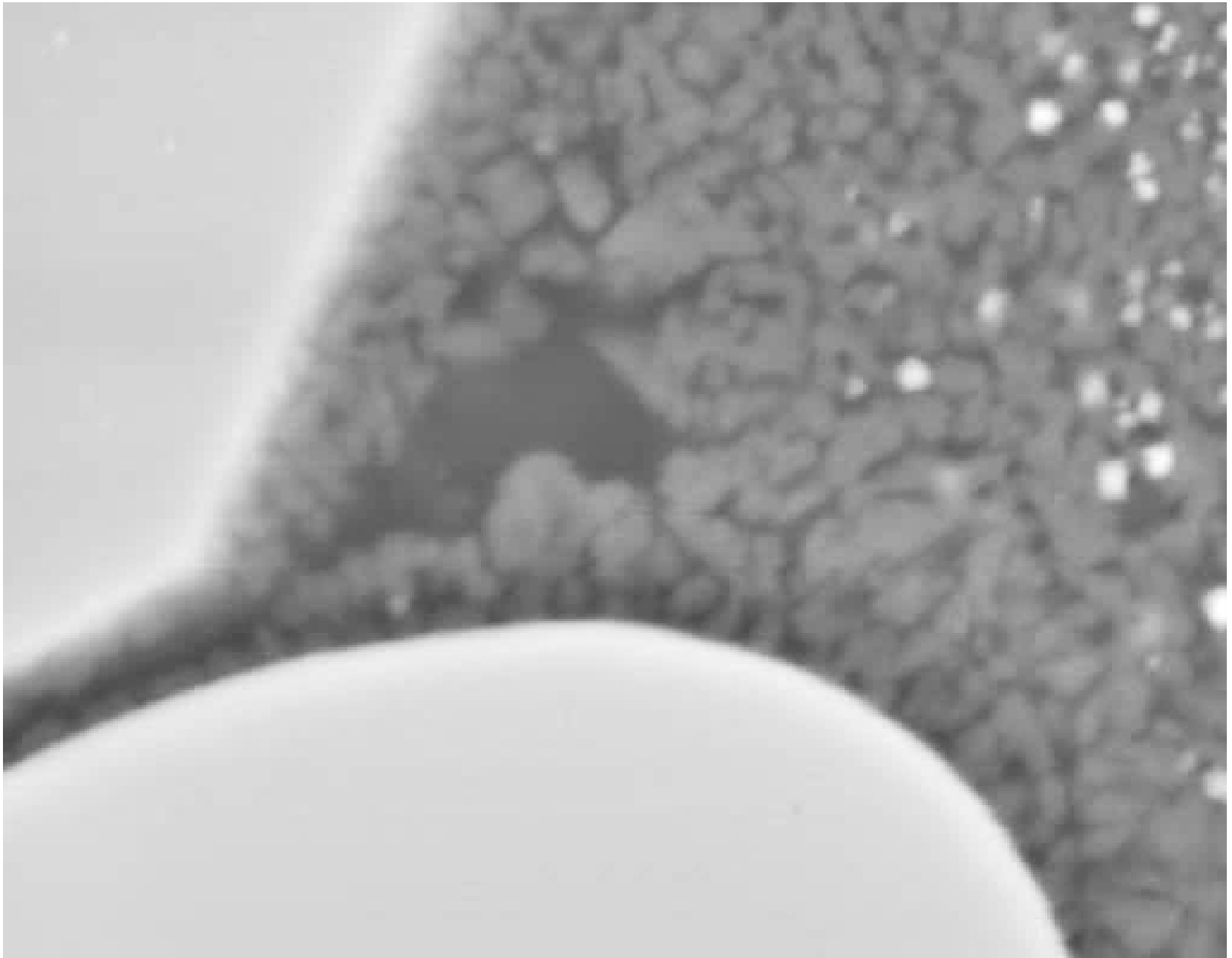
60 min at 650 °C and 1 min at 730 °C



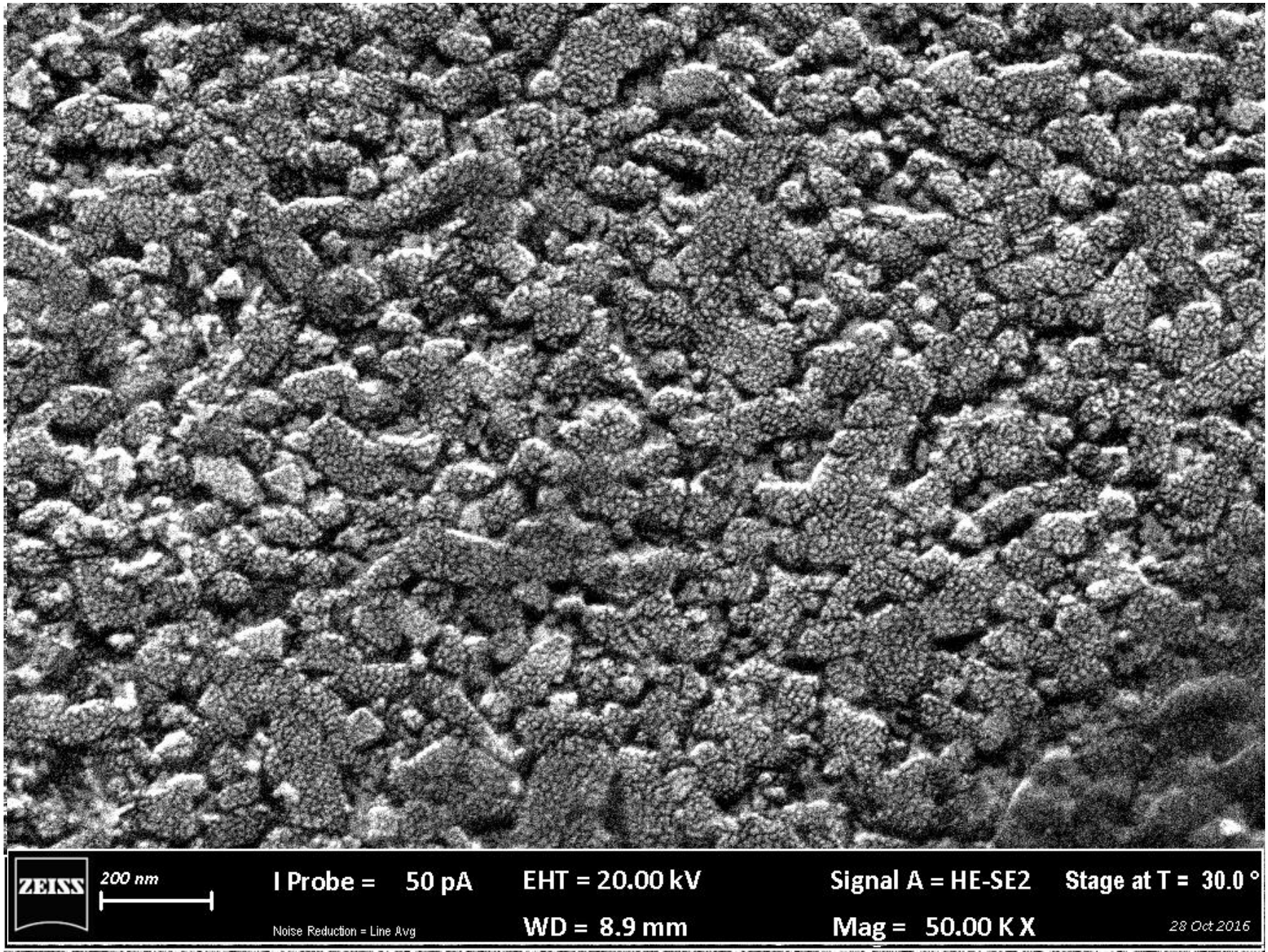
FESEM - *60 min at 650 °C and 60 min at 730 °C*



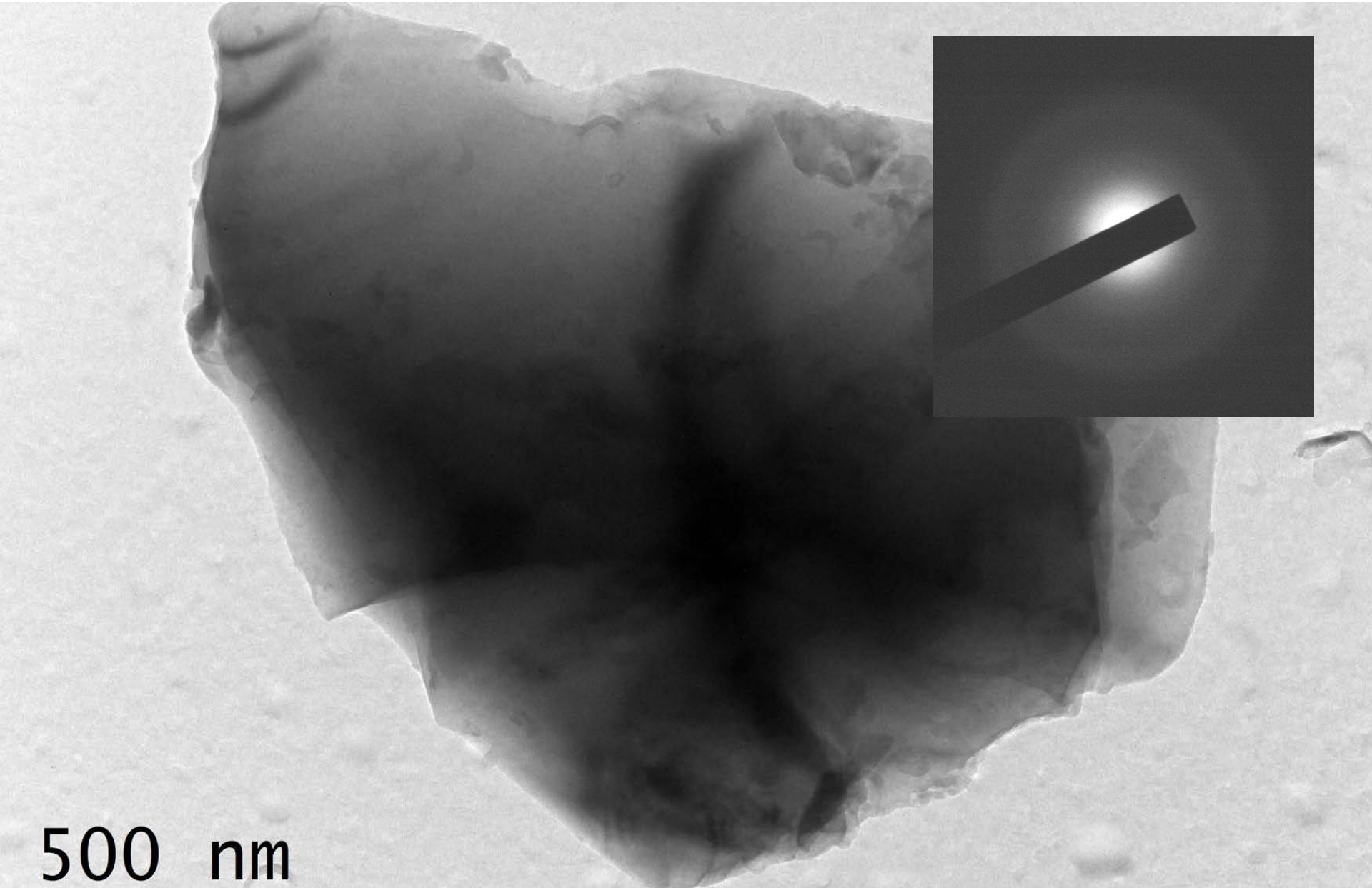
FESEM - *60 min at 650 °C and 60 min at 730 °C*



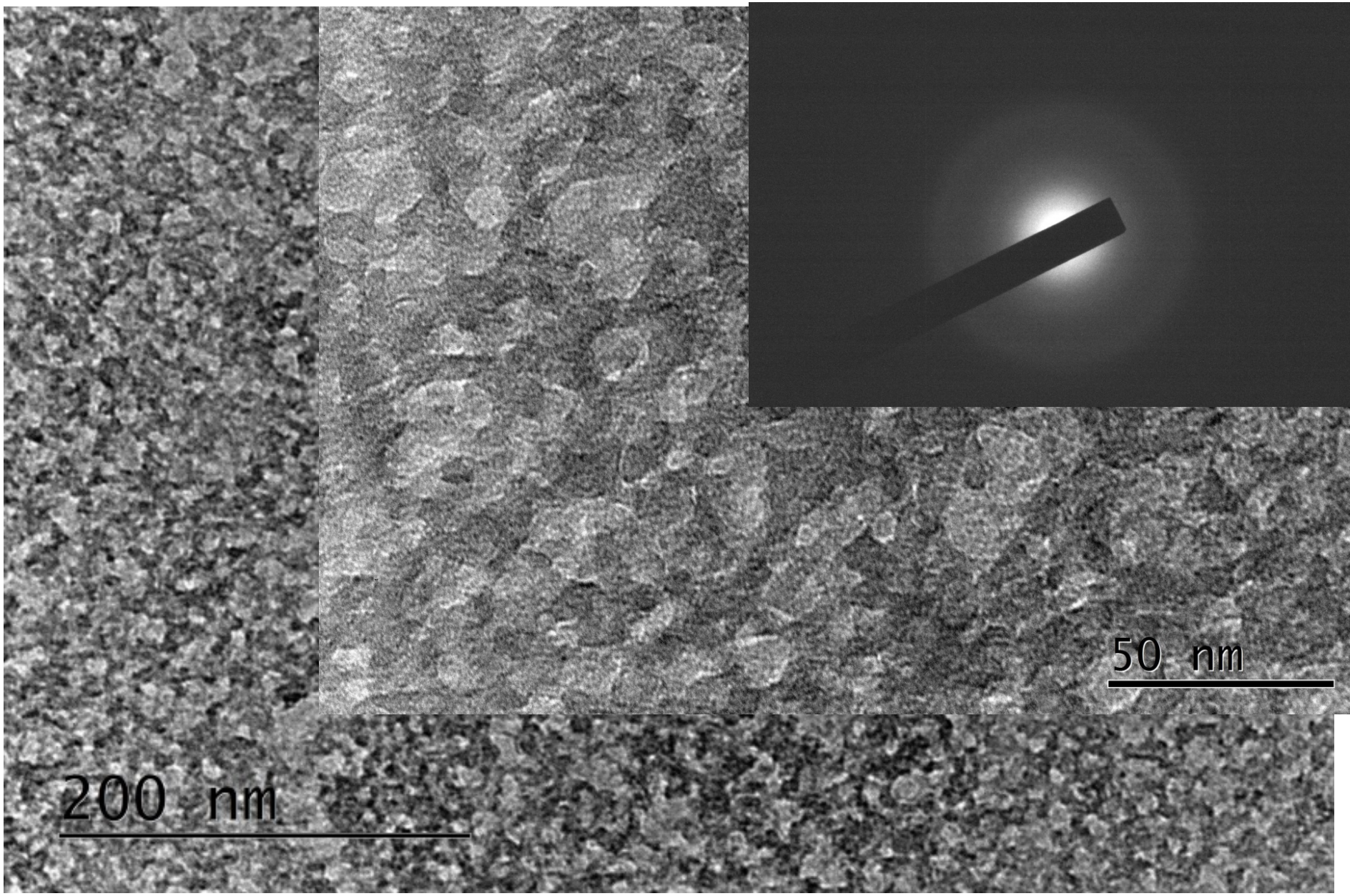
Morphology and structure FESEM - *60 min at 650 °C and 60 min at 730 °C*



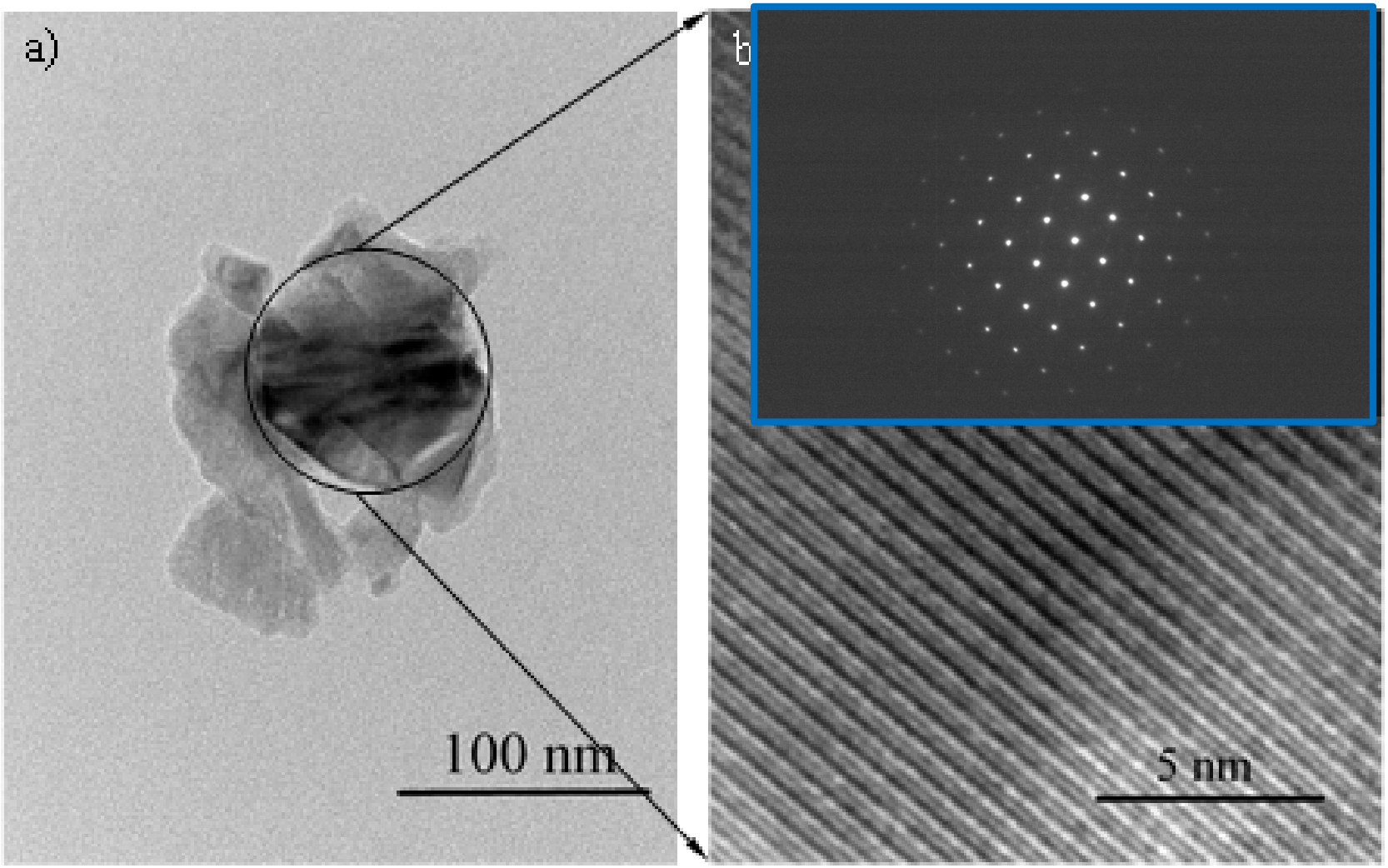
TEM – initial glass



TEM - *60 min at 650 °C and 1 min at 730 °C*



TEM - *60 min at 650 °C and 60 min at 730 °C*



Leaching test (TCLP) results of the used wastes and obtained glass and glass-ceramic (mg/l)

	SEF	FD	SC	G	GC	Applied limits
Zn	0.29	3.6	0.42	<0.005	<0.005	5
Ni	2.7	6.1	19.2	0.311	0.098	1
As	0.01	1.2	0.18	0.009	0.003	0.2
Cr	1.1	0.22	2.9	<0.005	<0.005	1.0

properties of obtained glass-ceramic

Properties	Slag Sitalls	FeNi GC
Density (g/cm^3)	2.7-2.9	3.1
Coefficient of linear thermal expansion 20-400°C (10^{-7}/C)	75-90	71
Bending strength (MPa)	80-110	120
Compressive strength (MPa)	250-350	280
Vickers Hardness (GPa)	7.5-9	9
Fracture toughness (MPa•m1/2)	1.2-1.5	1.6
Main technological parameters		
Melting Temperature (°C)	1450-1550	1350-1400
Nucleation step	1-2 h at 750-800 °C	0.5-1h at 650 °C
Crystallization step	2-3 h at 850-950 °C	0.5-1h at 750-760 °C

Conclusions:

- The parent glass is obtained using huge amount of hazardou… from ferronickel production at moderate melting temper…
- The optimal low temperature crystallization regi… …eation at about 650 °C and 30-45 min crystallization at… , was estimated by alternative fast methods: the nucleati… …ted by DTA analysis, while the crystallization step – by pyr… …nents.
- The phase formation starts du… …ng with the precipitation of preliminary Fe-Mg-Cr spin… …ese crystals act as centers for epitaxial growth of pyr… …s is formed a part of the glass-ceramic arrangement.
- The main st… 60-85 vol %) is a result of the tendency for binodal liquid-li… …. It leads to the formation of secondary magnetite spi… …0-70 nm size and to crystallization of main phase in glass- …ed by a new pyroxene with crystal size of 200-300 nm.

…lass-ceramic is characterized by a high chemical durability and …d mechanical characteristics.

Thank You for the attention !