UCCS
UNITÉ DE CATALYSE
ET CHIMIE DU SOLIDE

Atelier USTV “Recyclage du verre”
September 22, 2021 (Nancy)

Union
pour la Science
et la Technologie
Verrières

From waste CRT glasses to foam glass: a case of study to re-use electric and electronic end of life materials

François O. MEAR & Ronan LEBULLENGER

Université de Lille
cnrs
UNIVERSITÉ D'ARTOIS
CENTRALE LILLE
Chimie Lille
ÉCOLE NATIONALE SUPÉRIEURE DE CHIMIE
Chevreul Fédération Michel Eugène
Communauté d'Universités et d'Établissements
Lille Nord de France

CRT composition

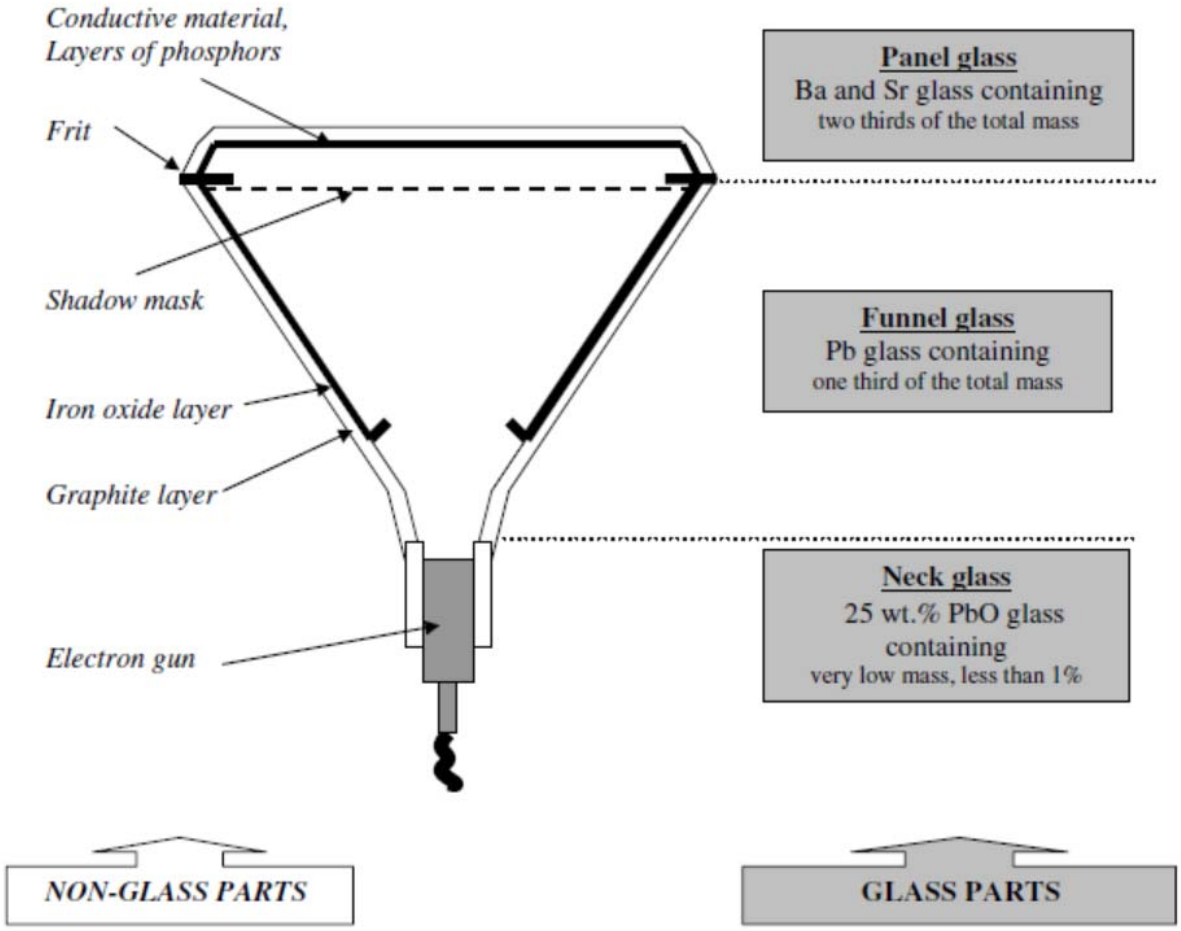


Fig. 1. Schematic view of the CRT components, showing the non-glass and glass parts (left and right side of the figure, respectively).

CRT glass composition

Table 1
Chemical composition ranges (in oxide weight percent) of the CRT glass types found in the literature

Oxide	Black and white		Color panel		Color funnel	
	Range	Standard content	Range	Standard content	Range	Standard content
Network formers						
SiO_2	64–66	65	60–63	62	52–56	52
Sb_2O_3	0.3–0.6	0.45	0.25–0.5	0.35	0.1–0.3	0.25
As_2O_3	0–0.3	0.01	0–0.2	0.02	0–0.1	0.01
Network intermediates						
Al_2O_3	3–5	3	2–3.5	2.2	3.5–5	4
PbO	2.8–4.4	4	0–3	–	19–23	22
ZnO	0–0.1	0.05	0–0.6	0.3	0–0.1	–
TiO_2	0.1–0.2	0.15	0.4–0.6	0.5	0–0.1	0.05
Network modifiers						
Na_2O	6.5–8	7	7.8–9	8	6–8	6.8
K_2O	6–7.5	7	6–7.5	7.5	7.5–8.5	7.8
Li_2O	0–0.6	0.3	0–0.5	0.2	0–0.1	–
CaO	0–1	0.5	0–2	0.5	2–4	3.8
MgO	–	–	0–1	0.2	1.2–2	1.8
Fe_2O_3	0.05–0.2	0.12	0.07–0.12	0.08	0.05–0.07	0.06
SrO	0–2	1	6–10	8.5	0–1	0.5
BaO	9–12	11	9–11	10	0–2	1
CeO_2	0.1–0.2	0.18	0.2–0.3	0.25	–	–
ZrO_2	0–0.5	0.25	0–2.5	1.5	–	–

State of the art different loop of recycling

- ✓ SAINT-GOBAIN process 1935
- ✓ ISOVER - SAINT-GOBAIN process 1981
- ✓ CERNIX process 1995 / 1998
- ✓ MISAPOR SA. process 1988

How to prepare a foam glass ?

➢ Elaboration

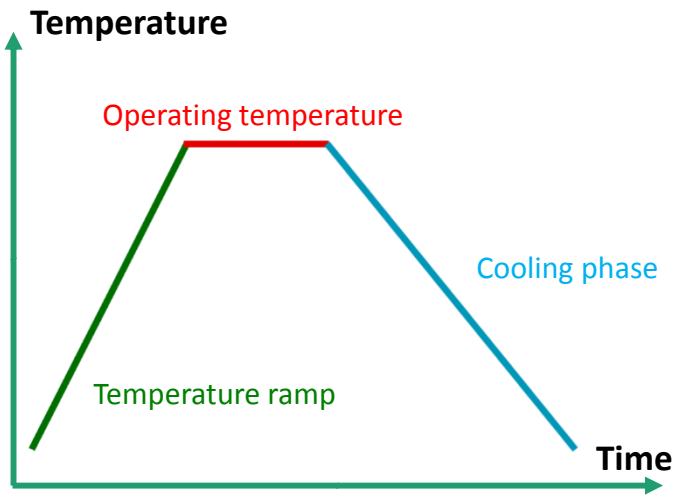
Glass waste + Foaming agent —Heat treatment→ Formation of gas bubbles (CO_2 or N_2) —Expansion→ Glass foam

➢ Glass waste

- **CRT**: Cathode Ray Tube glass
- **SLS**: Soda-Lime Silicate glass

➢ Foaming agent

AlN, **$CaCO_3$**, **SiC** or **C**



Furnace temperature vs. time

How to prepare a foam glass ?

Category	Foaming agent	Mechanism
Metal carbonates /-sulfates	Na_2CO_3 $CaCO_3$ $MgCa(CO_3)_2$ (Dolomite) Na_2SO_4 $CaSO_4$	Reactive- / Thermal decomposition
Metal oxides	Mn_xO_y Fe_xO_y Cr_xO_y PbO	Redox reaction in melt
Nitrides	AlN TiN Si_3N_4	Redox reaction
Carbonaceous	SiC Carbon	Surface reaction Solid-Gas reaction
	Water glass	
	Virgin glass	Redox

Gas production

$$2\ AlN\ (s) \rightarrow Al_2O_3\ (s) + N_2\ (g)$$

$$4\ AlN(s) + 3\ TiO_2\ (s) \rightarrow 2\ Al_2O_3\ (s) + 3\ TiN\ (s) + ½\ N_2\ (g)$$

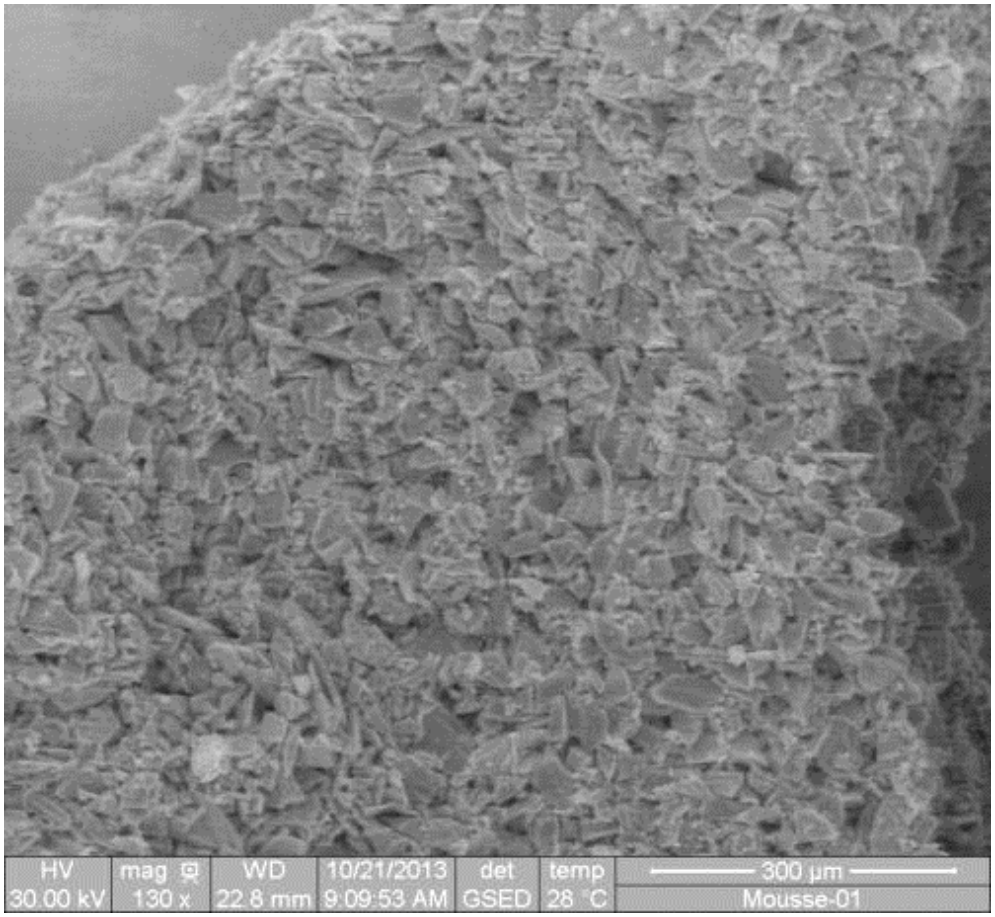
$$TiN\ (s) \rightarrow TiO_2\ (s) + ½\ N_2\ (g)$$

$$SiC\ (s) \rightarrow SiO_2\ (s) + CO, CO_2\ (g)$$

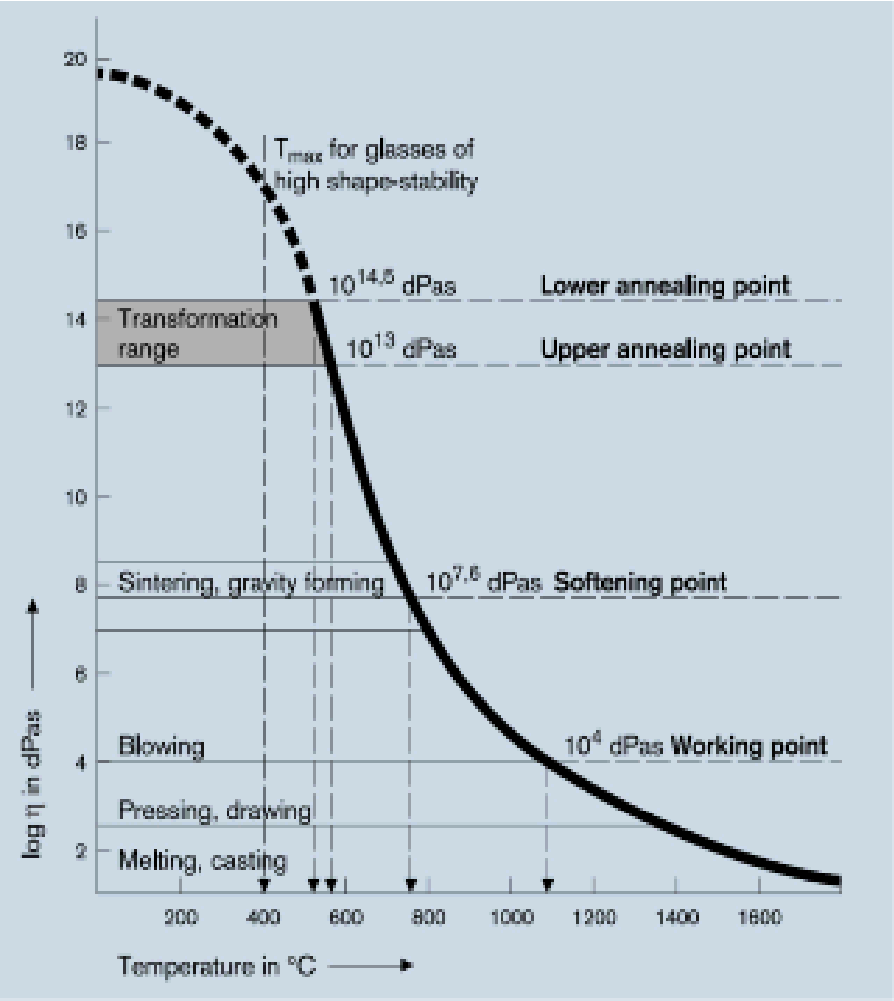
$$CaCO_3\ (s) \rightarrow CaO\ (s) + CO, CO_2\ (g)$$

NB: These reactions for gas production are dependent of redox equilibria

In situ foaming observation by HT-ESEM vs. time @ 750°C



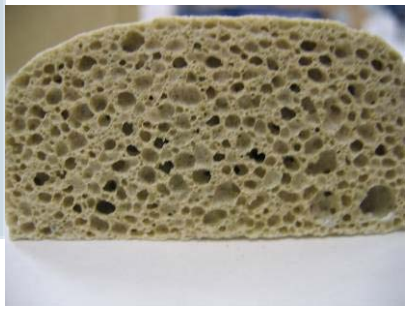
Viscous window



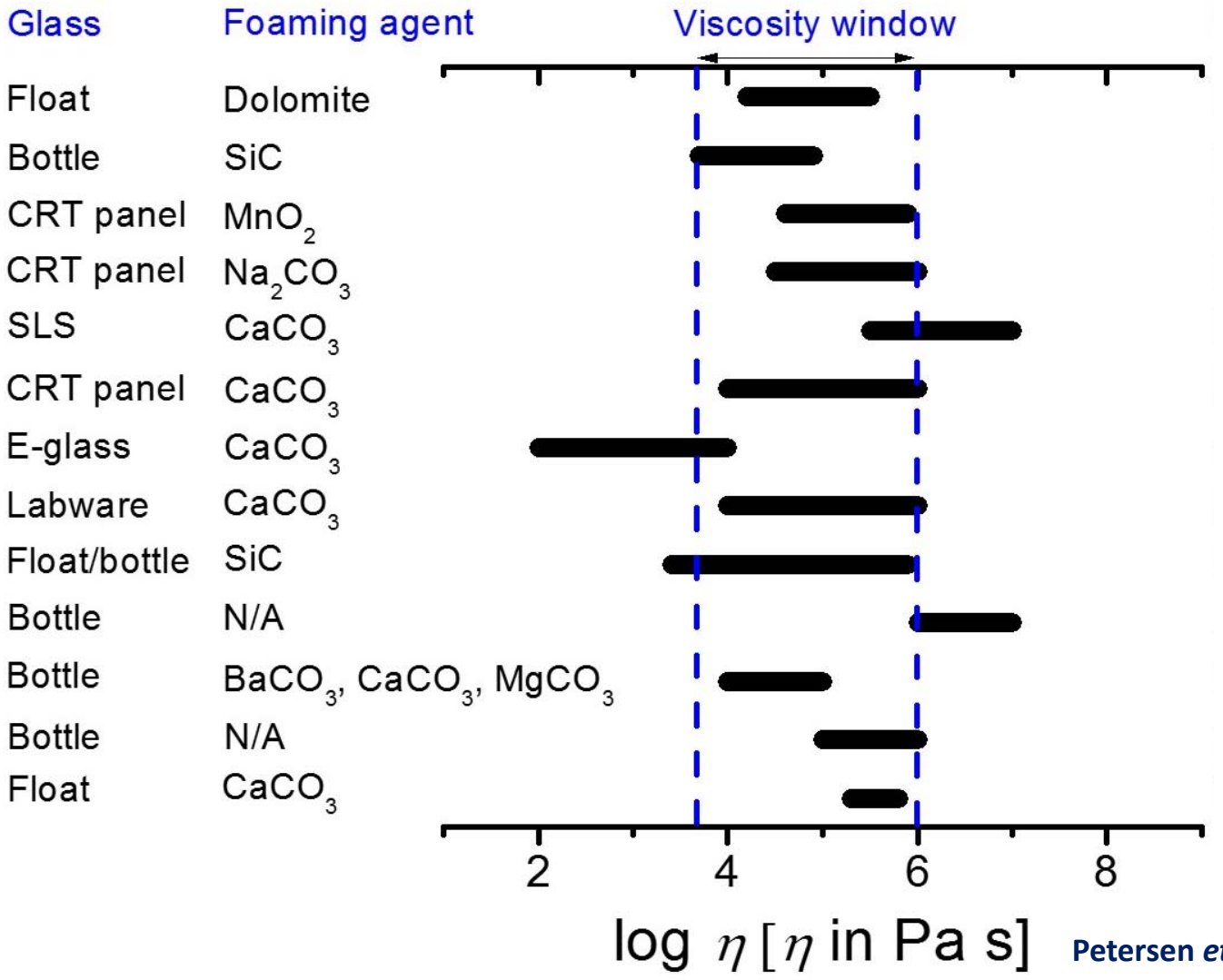
viscosity curve

Gas bubbles prisoners of the viscous melt

→ Expanded glass



Viscous window

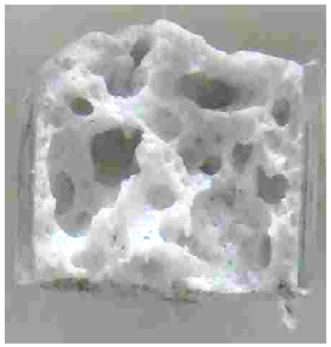


Petersen *et al*, JNCS, 2017

Tunning apparent density

CRT + $CaCO_3$

@ 850°C



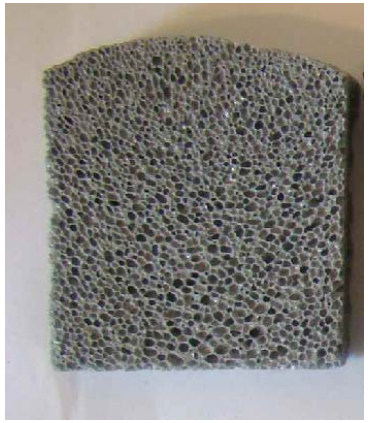
@ 800°C

@ 760°C

CRT + AlN @ 850°C

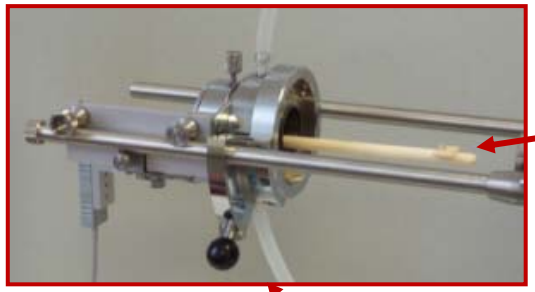
- d_{app} : 0.33 ± 0.06

CRT + SiC @ 850°C

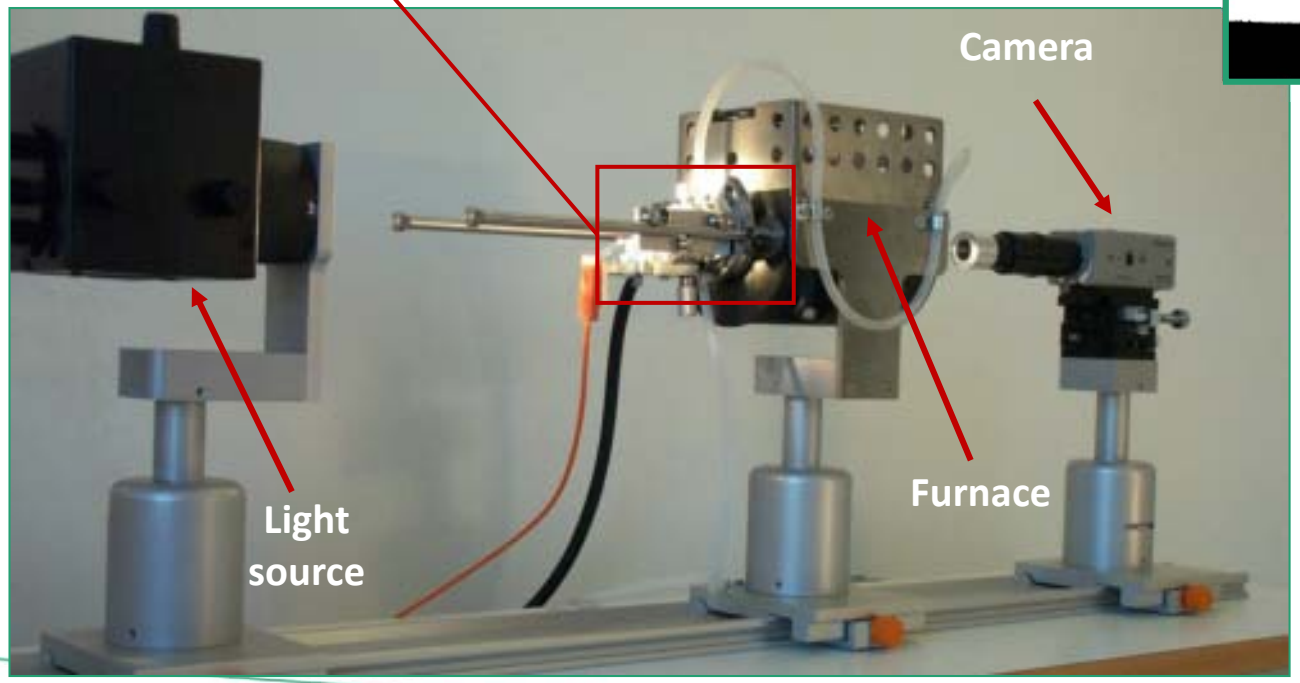


- d_{app} : 0.32 ± 0.01

Heating stage microscope (HSM)



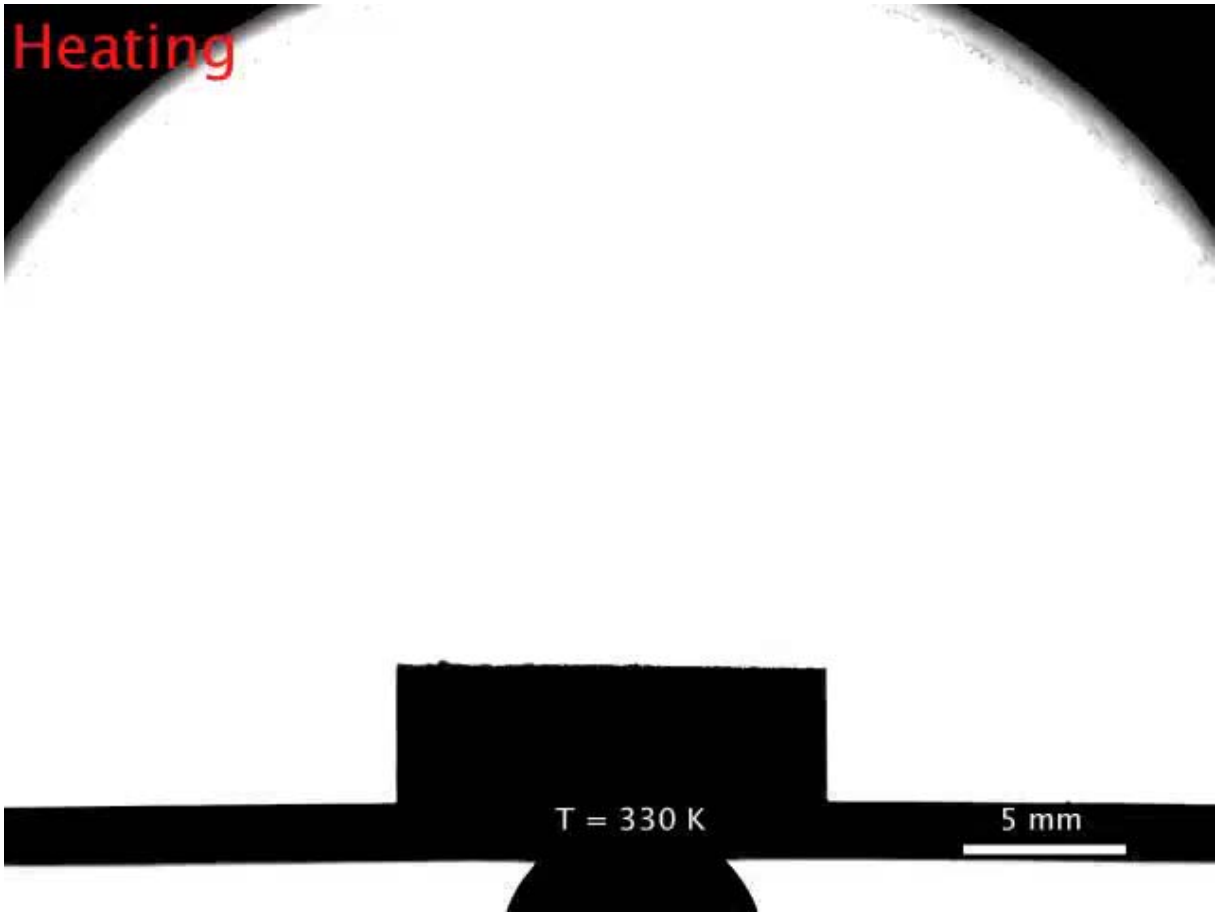
Support sample
/ thermocouple



Characterization of sample evolution:

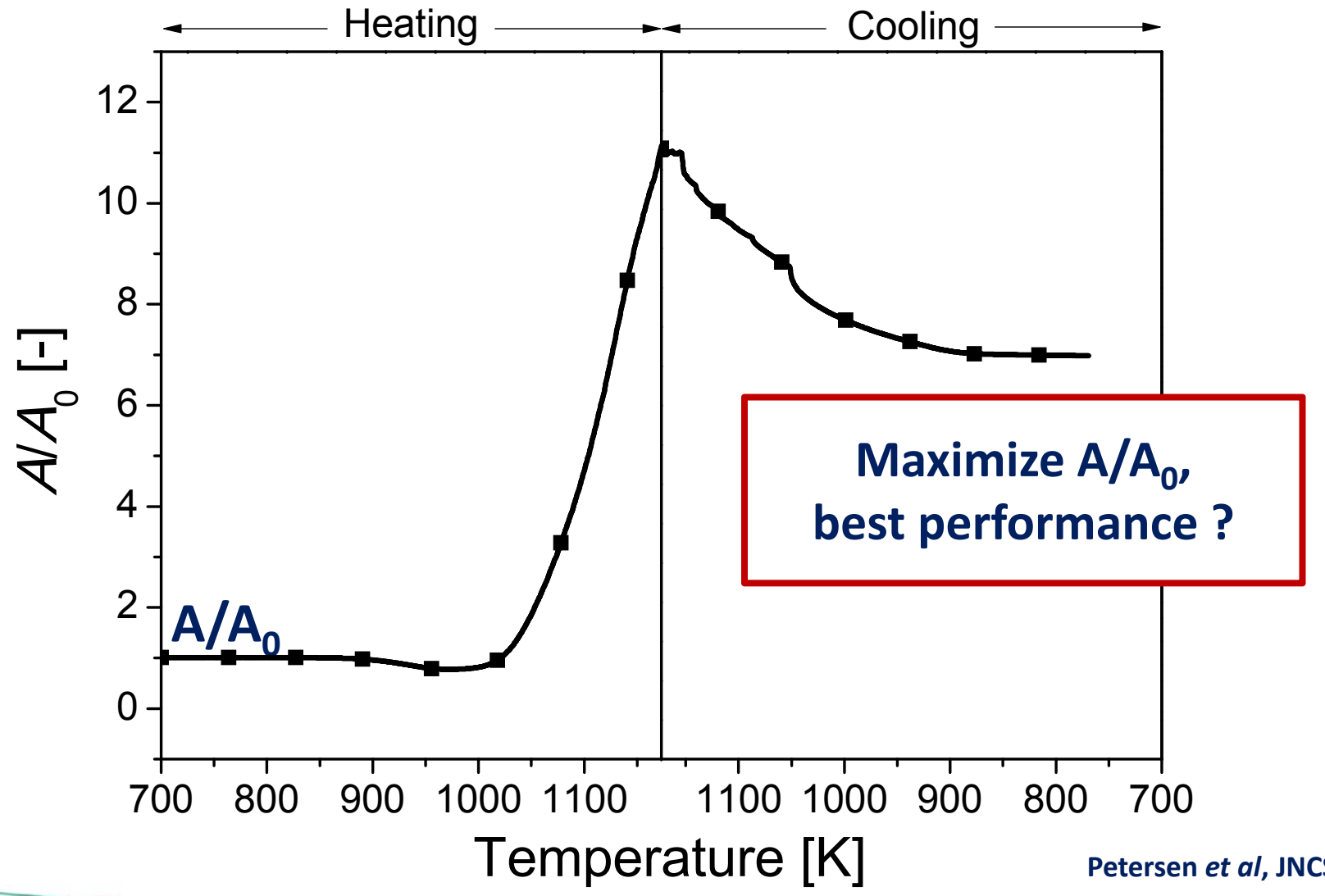
→ area (S/S_0)
→ shape factor
→ wetting

Heating stage microscope (HSM)



Foaming ability

CRT panel + MnO_2

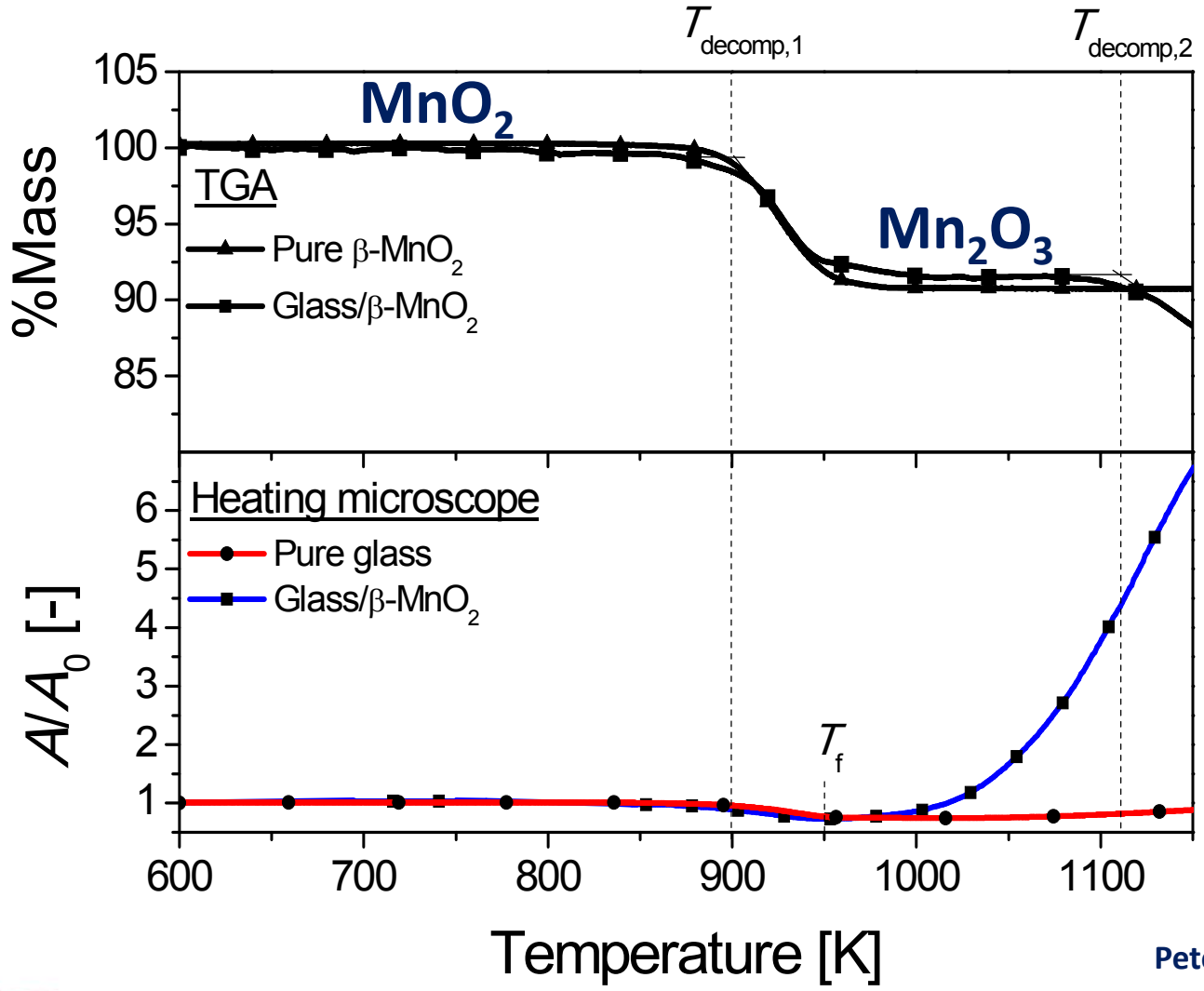


Maximize A/A_0, best performance ?

Petersen *et al*, JNCS, 2017

Foaming reaction

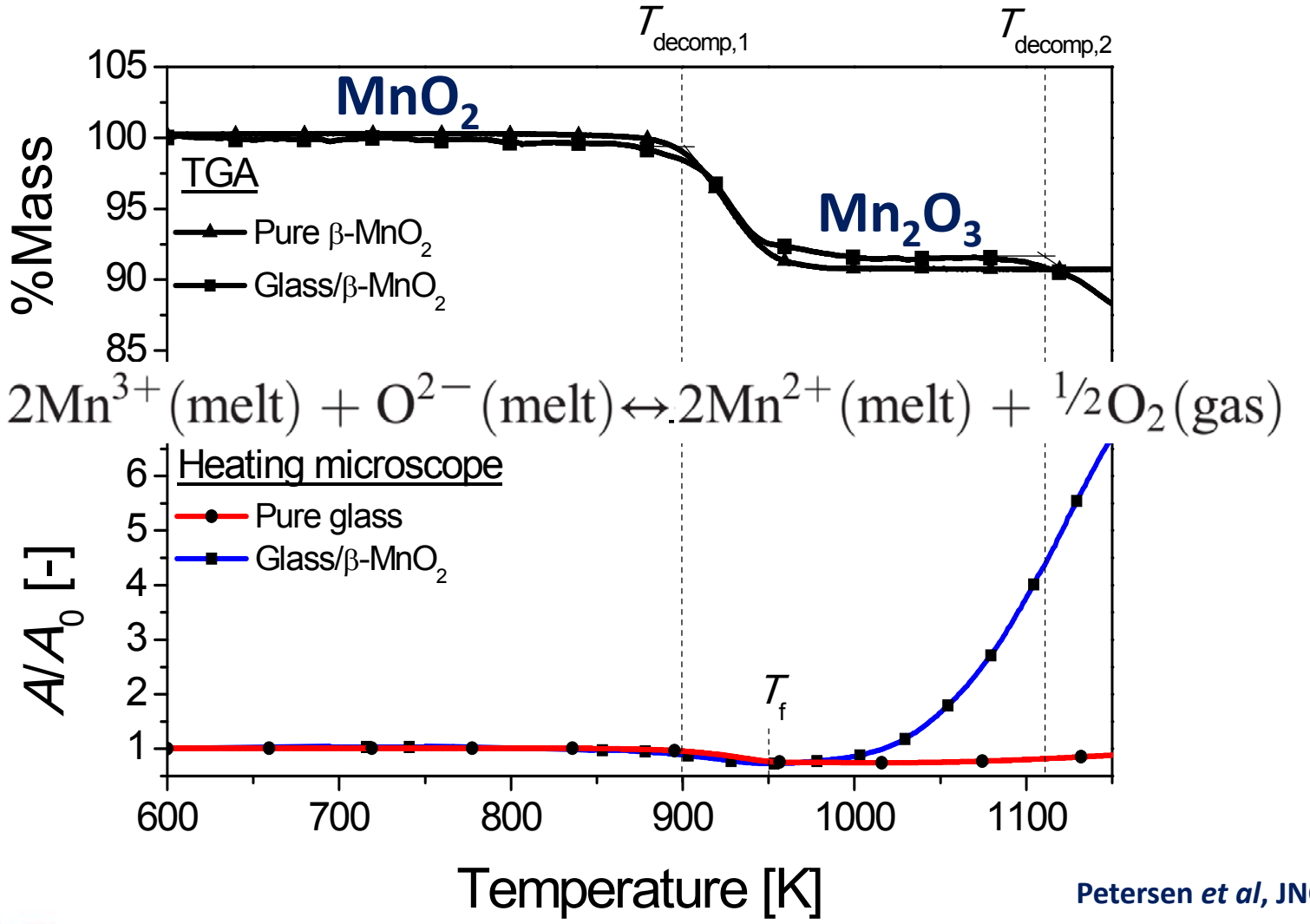
CRT panel + MnO_2



Petersen *et al*, JNCS, 2015

Foaming reaction

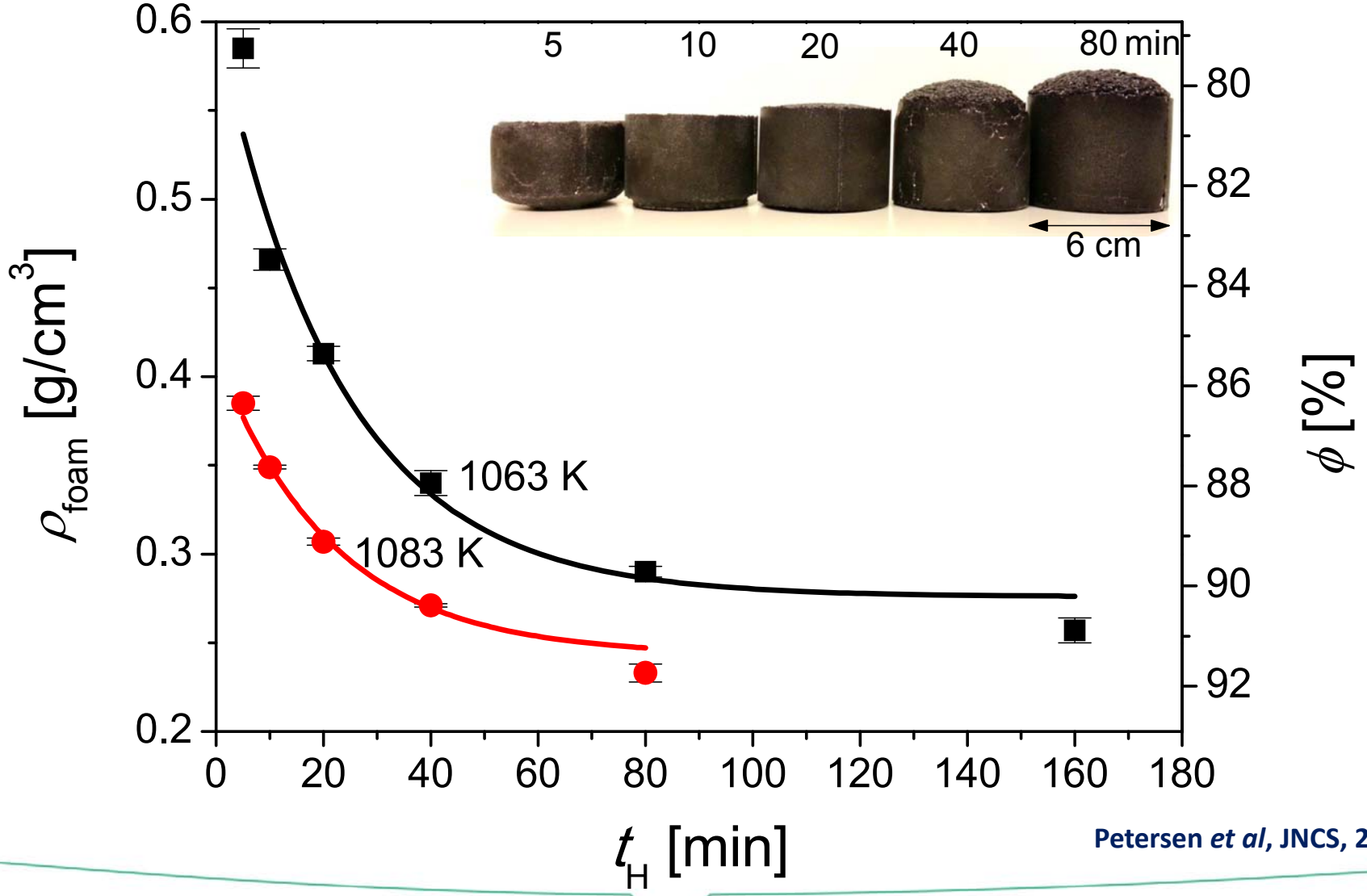
CRT panel + MnO_2



Petersen *et al*, JNCS, 2015

Volume expansion

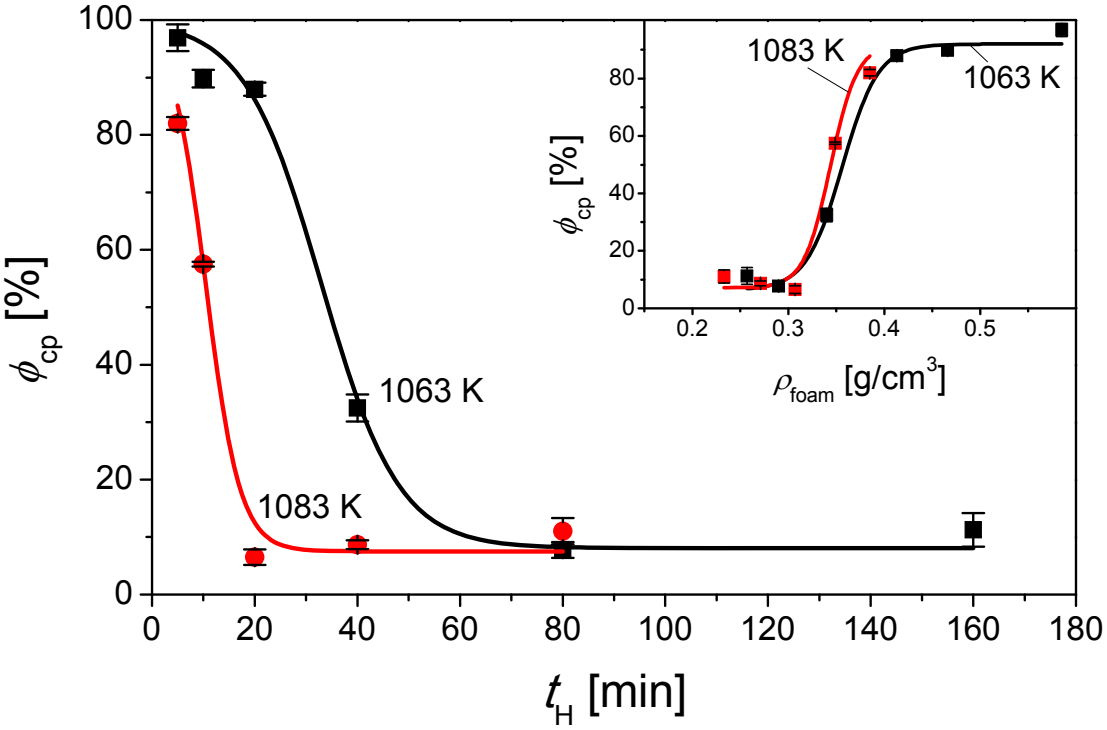
CRT panel + MnO_2

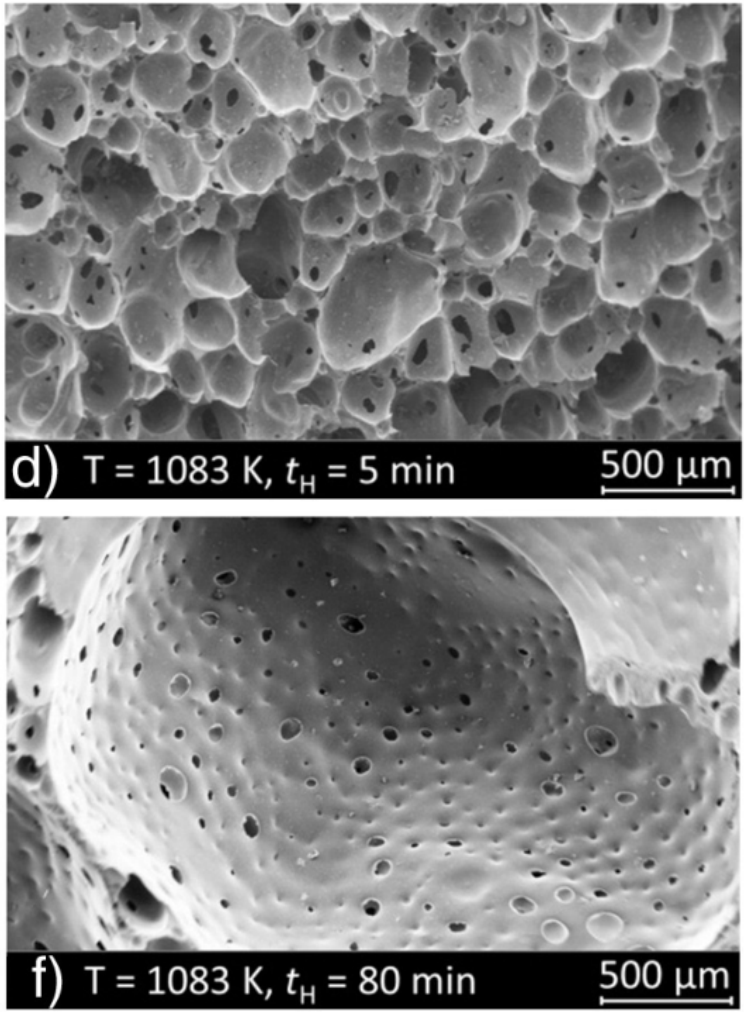


Petersen *et al*, JNCS, 2015

Closed porosity

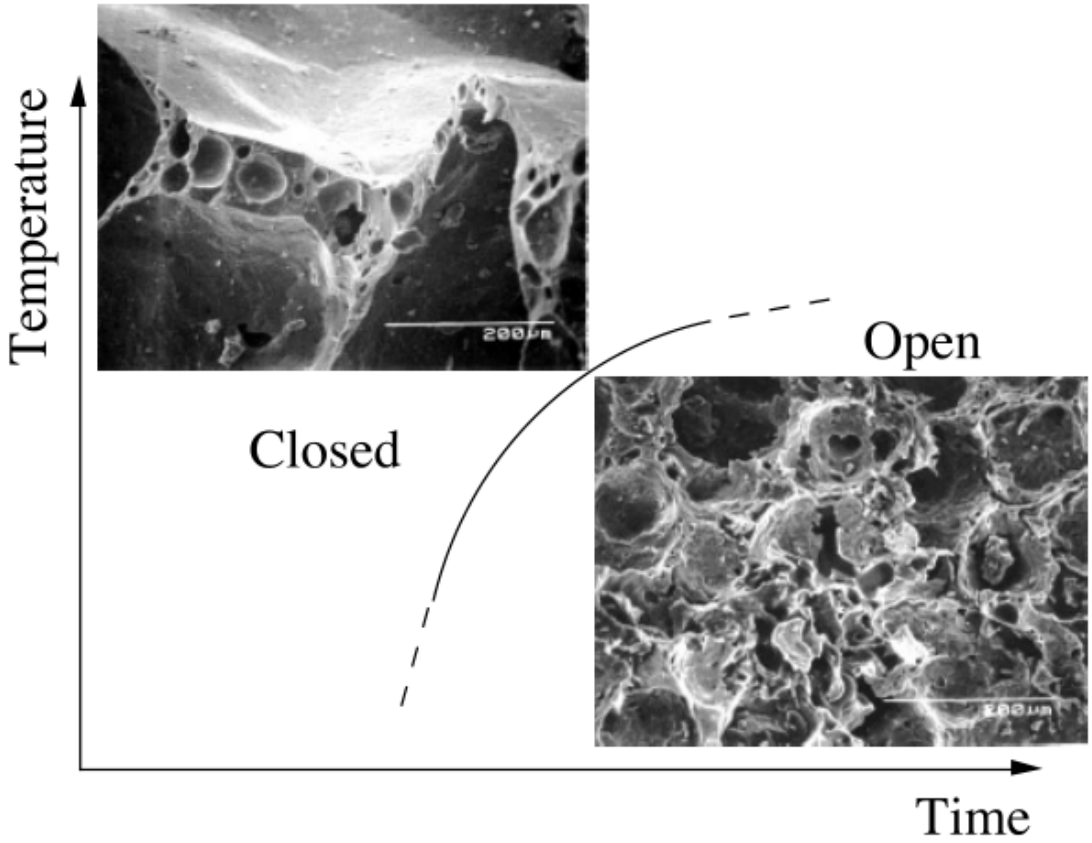
CRT panel + MnO_2





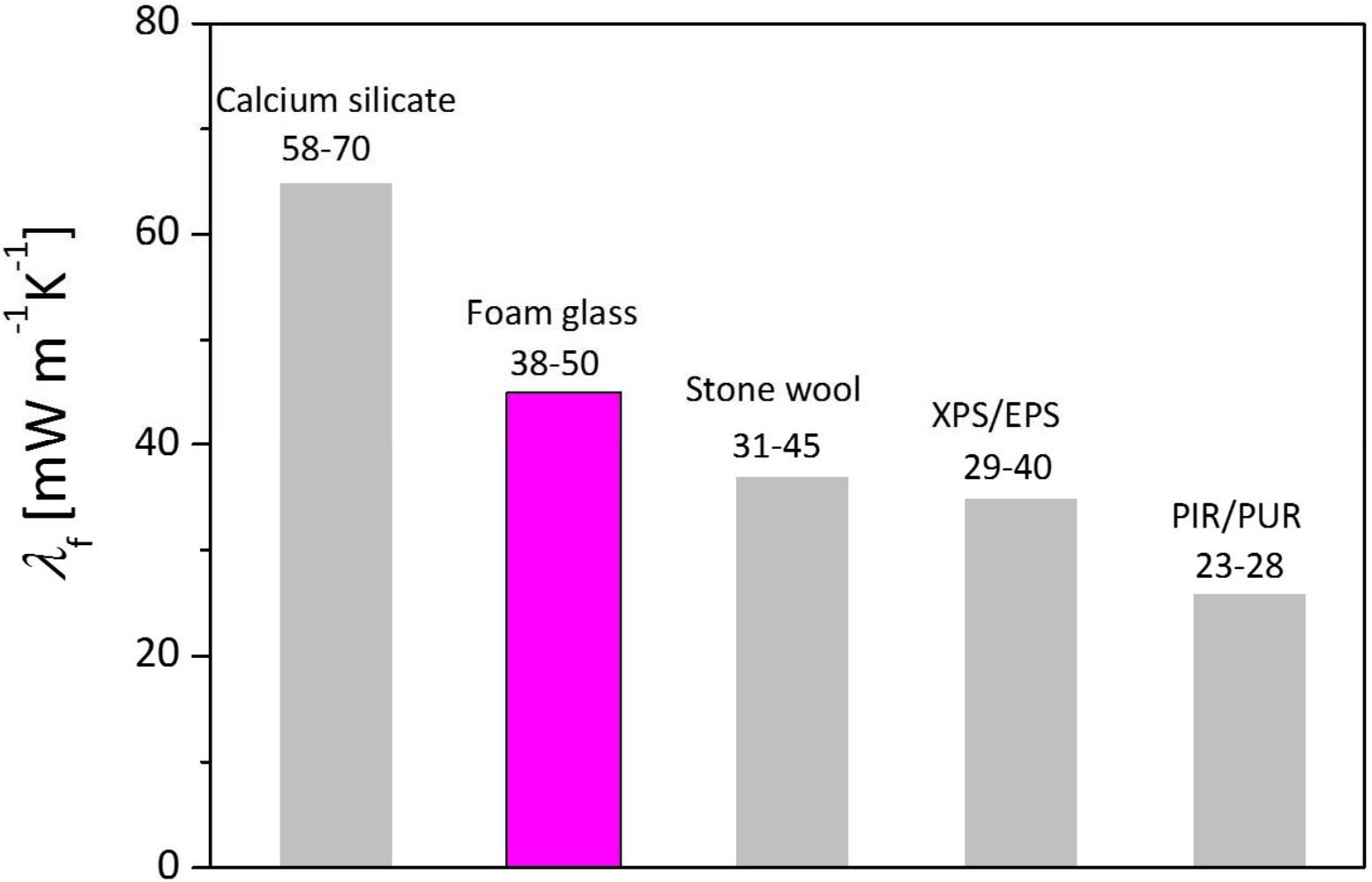
Petersen *et al*, JNCS, 2015

Porosity limit



Pittet 1999, JP_A_MathGen

Insulating conductivity



Application

Granulates

Sheets

Glass beads synthesis

Granulator: rotary plate

Glass beads synthesis

Granulator: rotary plate

Rotary furnace: direct heating

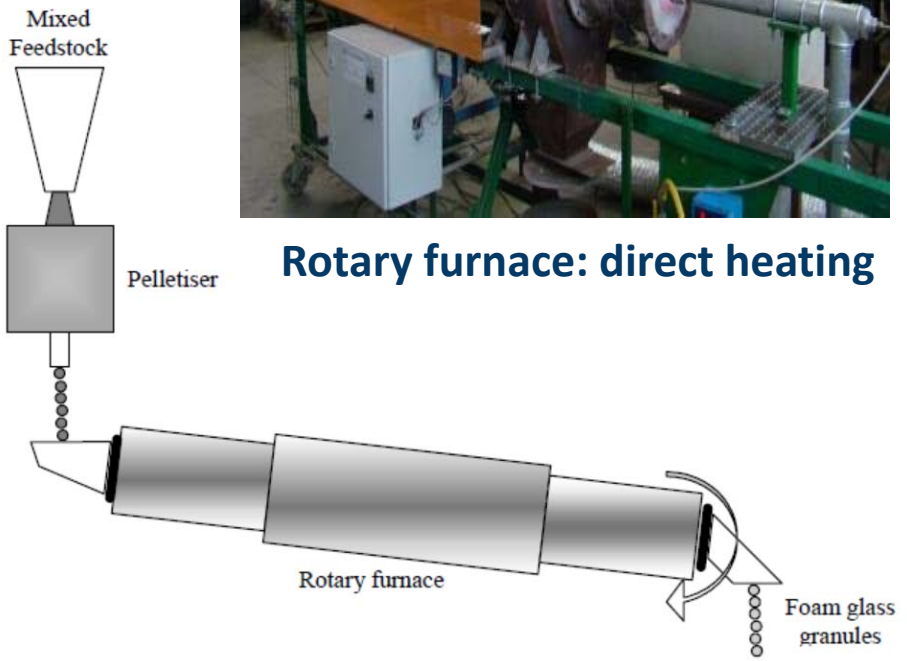
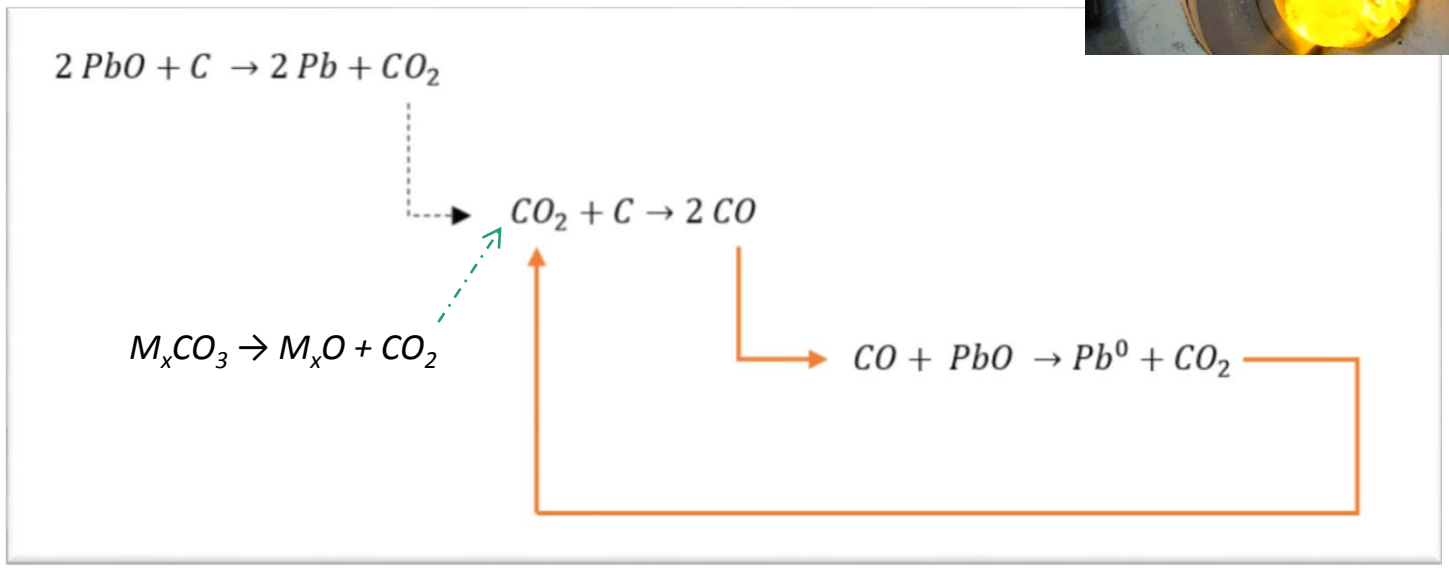


Figure 4 - Continuous production of foam glass granules using a rotary furnace.

Lead reduction from CRT funnel glass

CRT + Na_2CO_3 (wt%) + carbon (wt%) 3h@1250°C



Lead reduction from CRT funnel glass