

# ***New ceramic bricks based on pretreated MSW bottom ash***

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# Traditional Ceramic Body

Plastic raw materials

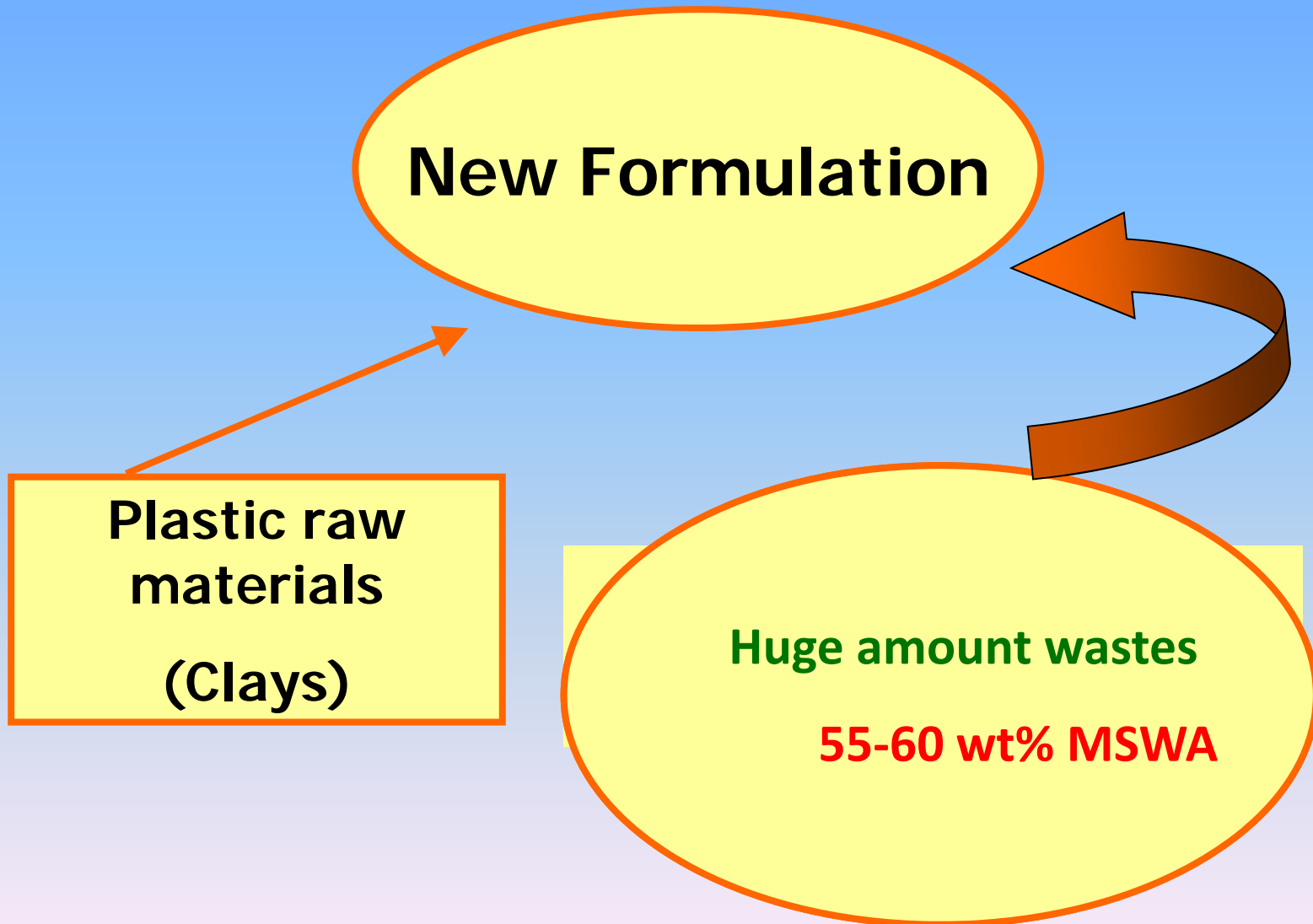
(clays)

Inert

(quartz sand)

Partially substitution of fluxes by cullet glass, CRT glass, volcanic rocks, ect.

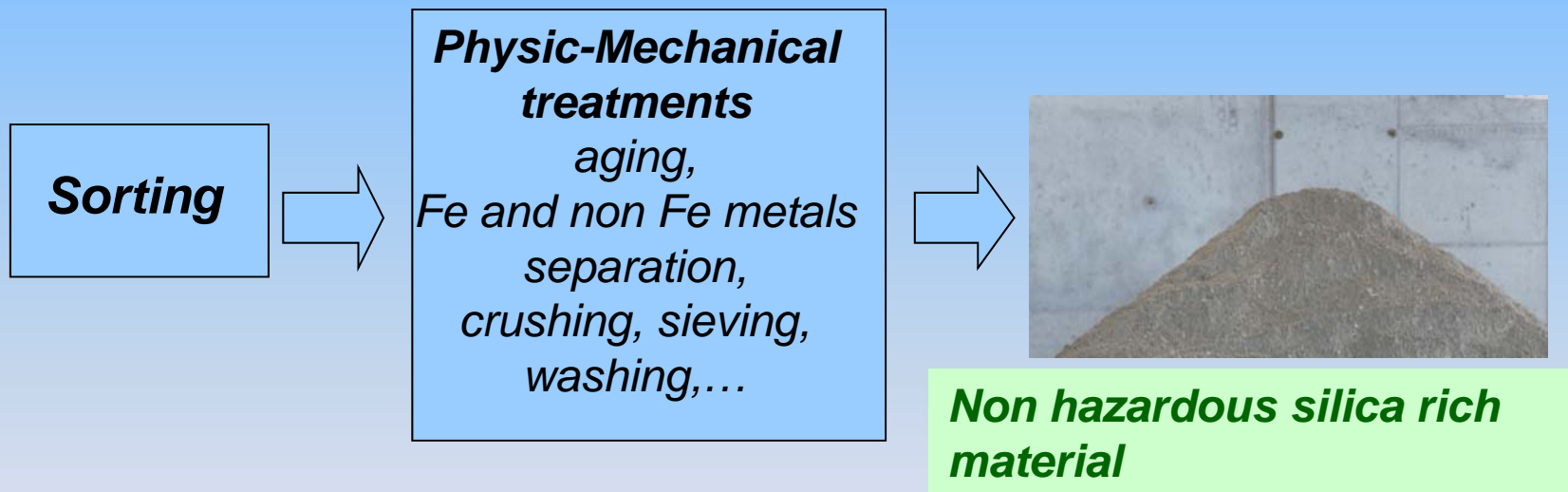
## *AIM OF THE WORK*



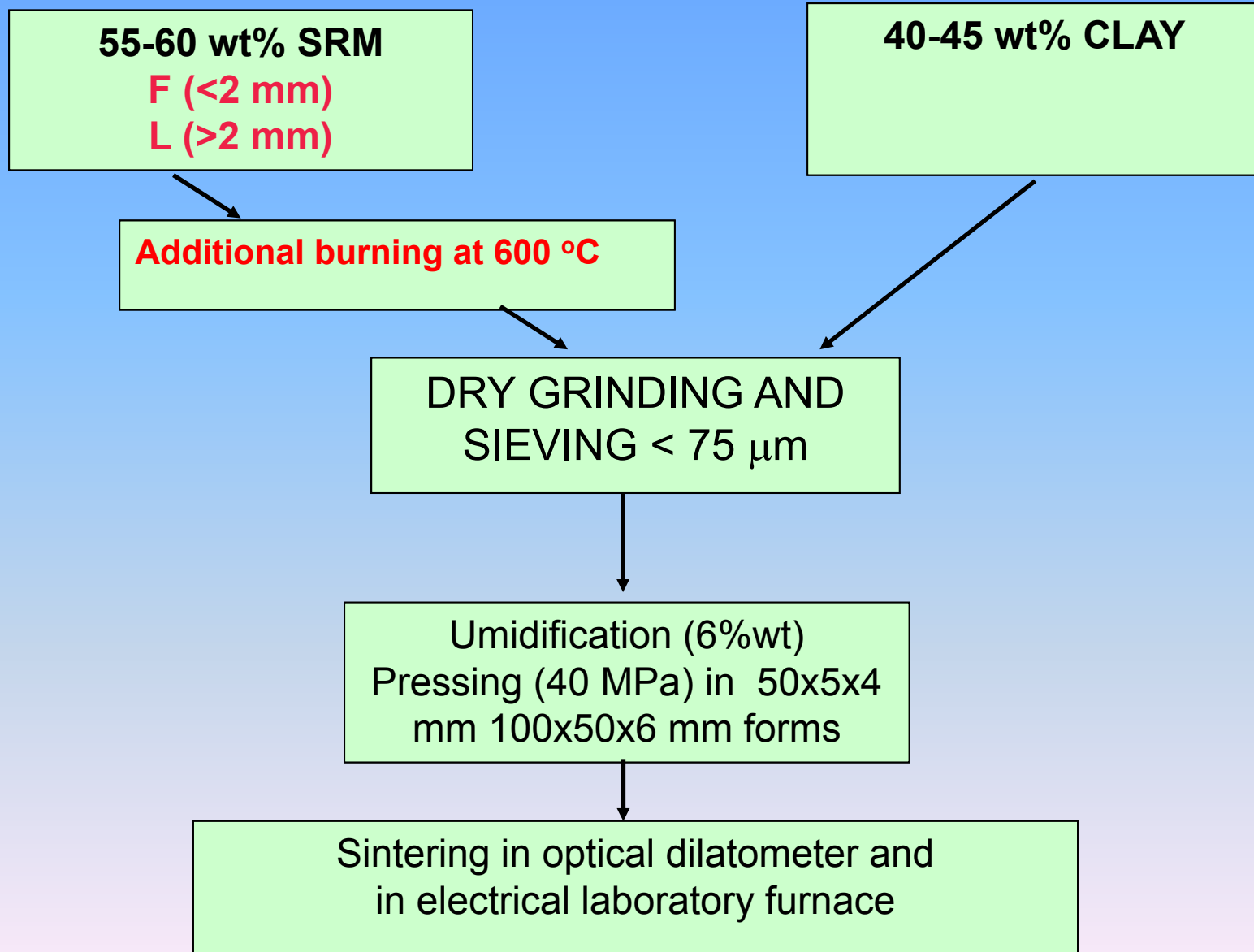
# ***Secondary Raw Material***

***Pre-treated bottom MSW ash***

## ***Technological Recovery Process***



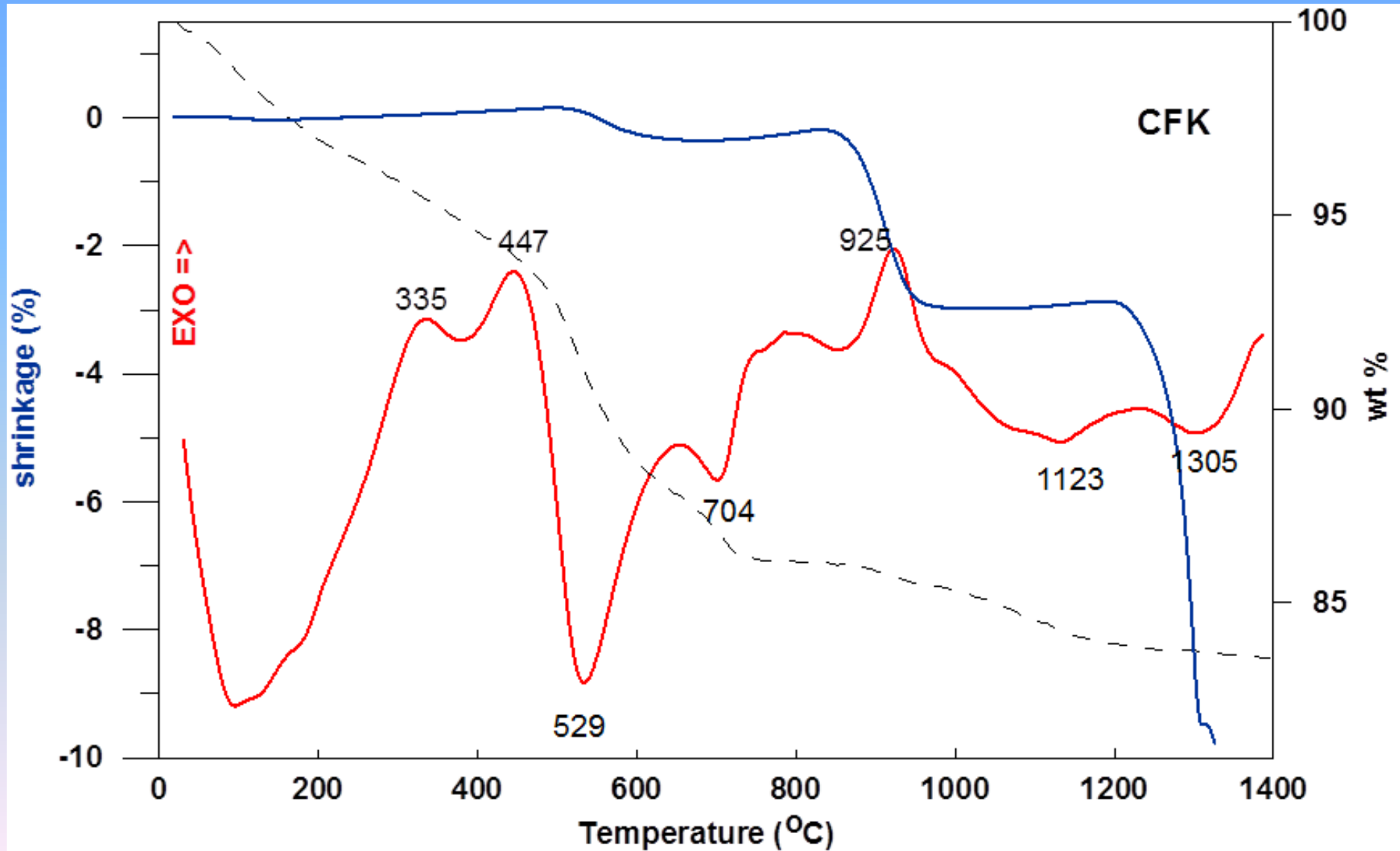
# Experimental procedure



| Chemical compositions of the raw materials (wt%) |      |             |            |
|--|------|-------------|------------|
| OXIDE  | K    | F (<2 mm)   | L (>2 mm)  |
| SiO <sub>2</sub>                                 | 47,1 | 30,3        | 47,4       |
| TiO <sub>2</sub>                                 | 0,2  | 1,1         | 0,8        |
| Al <sub>2</sub> O <sub>3</sub>                   | 36,1 | 13,3        | 10,0       |
| Fe <sub>2</sub> O <sub>3</sub>                   | 1,0  | 10,8        | 4,4        |
| CaO  | 0,4  | 20,8        | 18,8       |
| MgO  | 0,3  | 2,8         | 2,9        |
| K <sub>2</sub> O                                 | 1,1  | 0,9         | 1,0        |
| Na <sub>2</sub> O                                | 0,6  | 1,9         | 4,5        |
| B <sub>2</sub> O <sub>3</sub>                    | 0,0  | 0,3         | 0,6        |
| MnO  | 0,0  | 0,8         | 0,3        |
| ZnO  | 0,0  | 0,8         | 0,3        |
| PbO  | 0,0  | 0,4         | 0,3        |
| SO <sub>3</sub>                                  | 0,0  | 1,7         | 1,0        |
| P <sub>2</sub> O <sub>3</sub>                    | 0,0  | 2,0         | 1,3        |
| CuO  | 0,0  | 0,7         | 0,5        |
| Chloride   | 0,0  | 0,5         | 0,0        |
| Others   | 0,0  | 0,1         | 0,2        |
| L.O.I  | 12,5 | <u>11,7</u> | <u>5,6</u> |
| Total  | 99,3 | 101,0       | 99,8       |

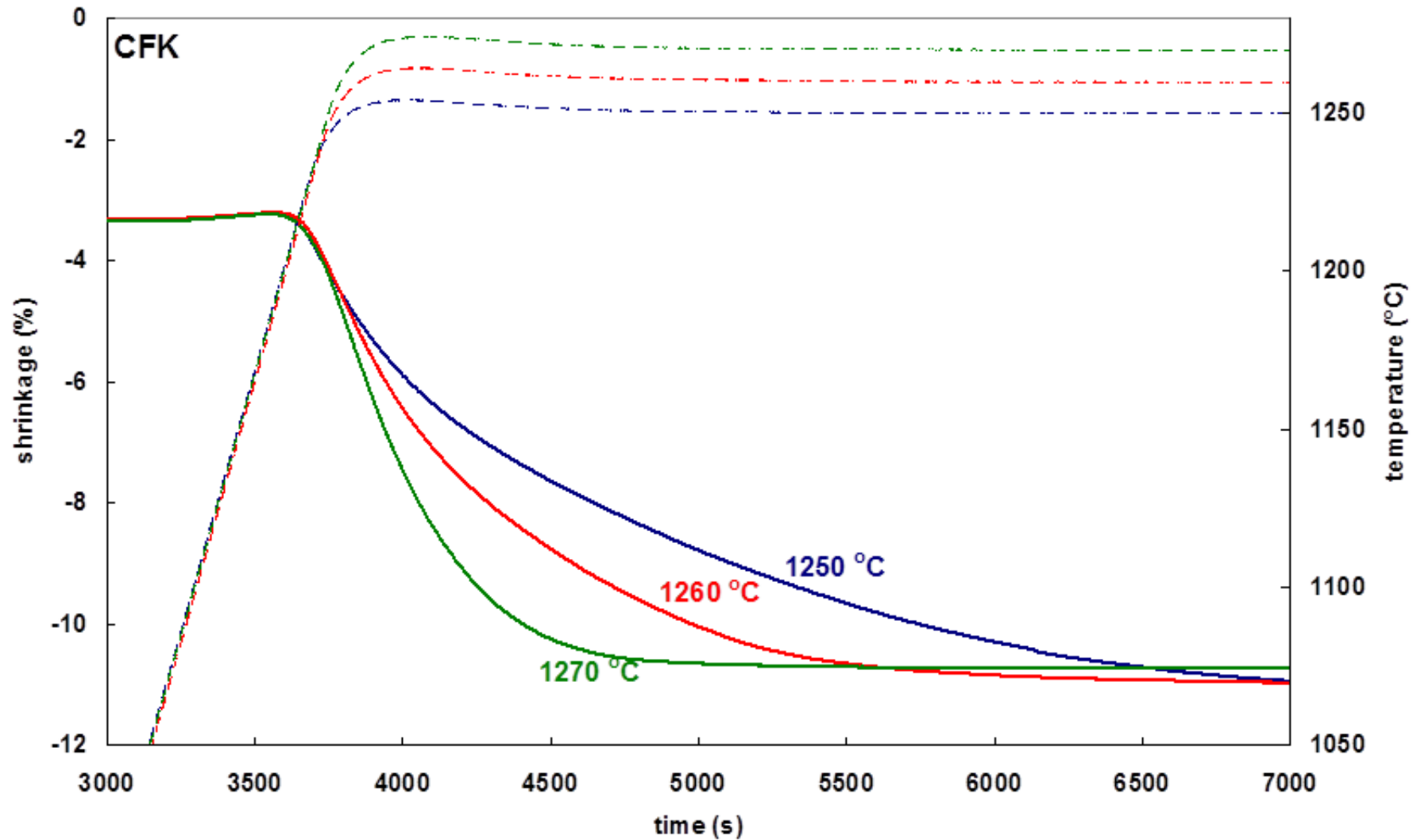
# THERMAL CHARACTERIZATION

Non-isothermal DTA-TG and DIL curves



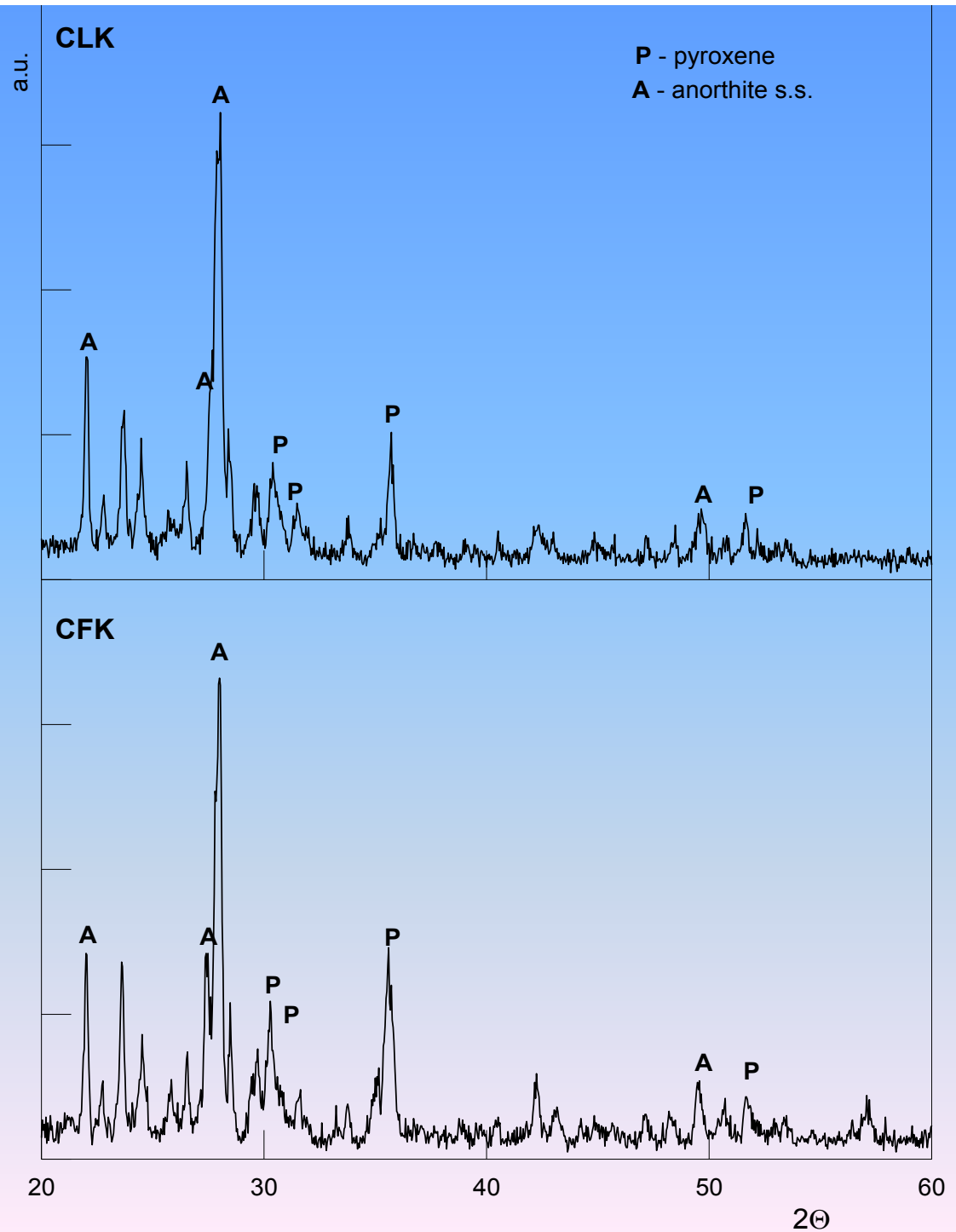
# THERMAL CHARACTERIZATION

*isothermal DTA-TG and DIL curves*





# XRD of final ceramics

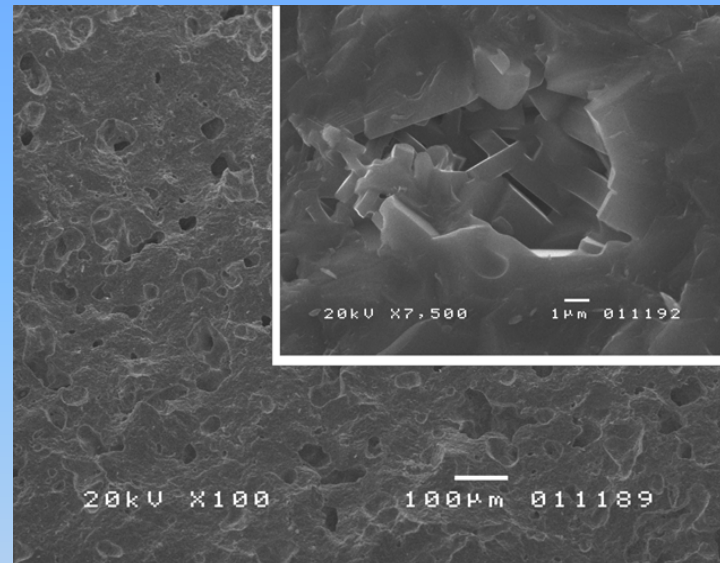
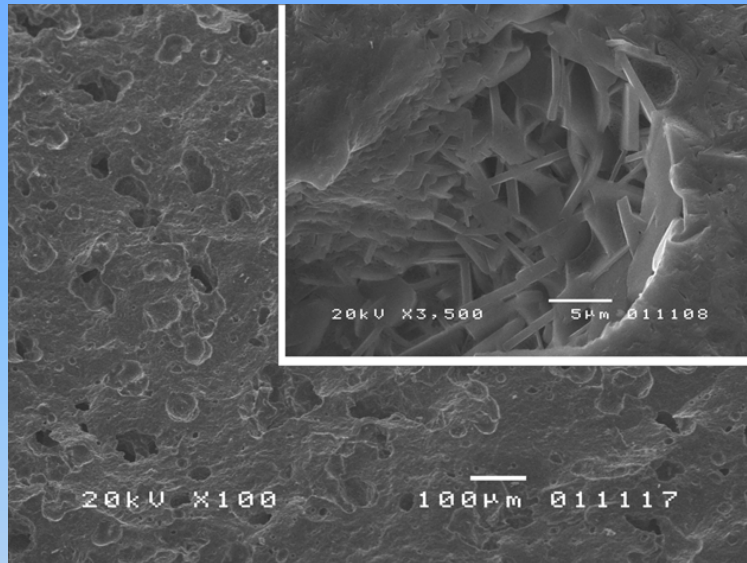


# STRUCTURE OF THE FINAL CERAMICS

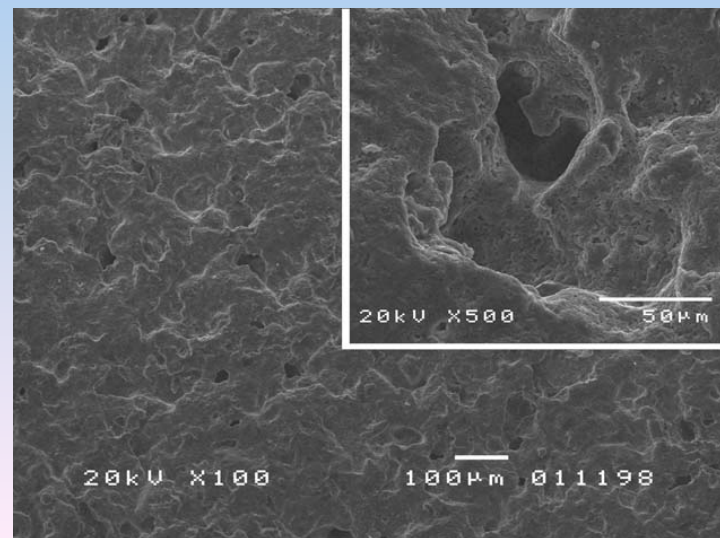
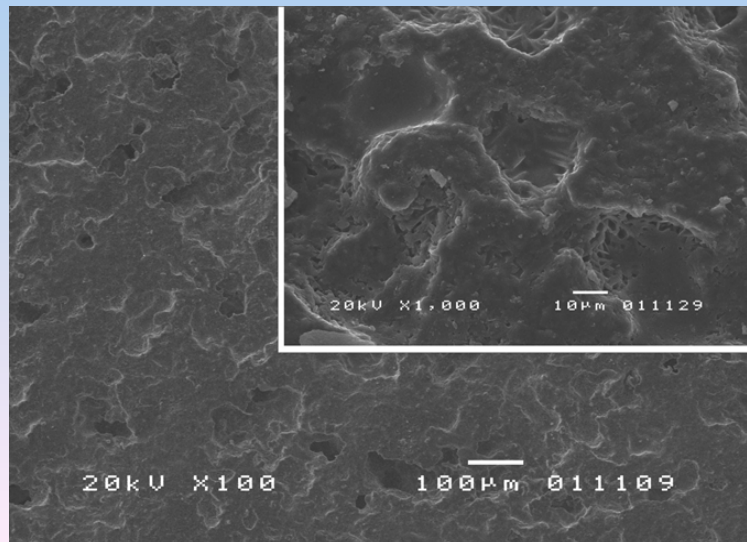
CLK

CFK

fracture



surface



# PROPERTIES

Linear shrinkage (LS%), water absorption (WA%), densities, porosities, bending strength (BS) and Young's modulus (E)

| Properties                    | CFK | CLK |
|-------------------------------|-----|-----|
| LS (%)                        | 7.5 | 4.5 |
| WA (%)                        | 2.1 | 1.6 |
| $\rho_a$ (g/cm <sup>3</sup> ) | 2.3 | 2.1 |
| P <sub>T</sub> (%)            | 23  | 20  |
| BS(MPa)                       | 53  | 42  |
| E (GPa)                       | 49  | 44  |

**Additional burning at 600 °C**

*(work in progress)*

**Chemical composition (wt %) of raw materials**

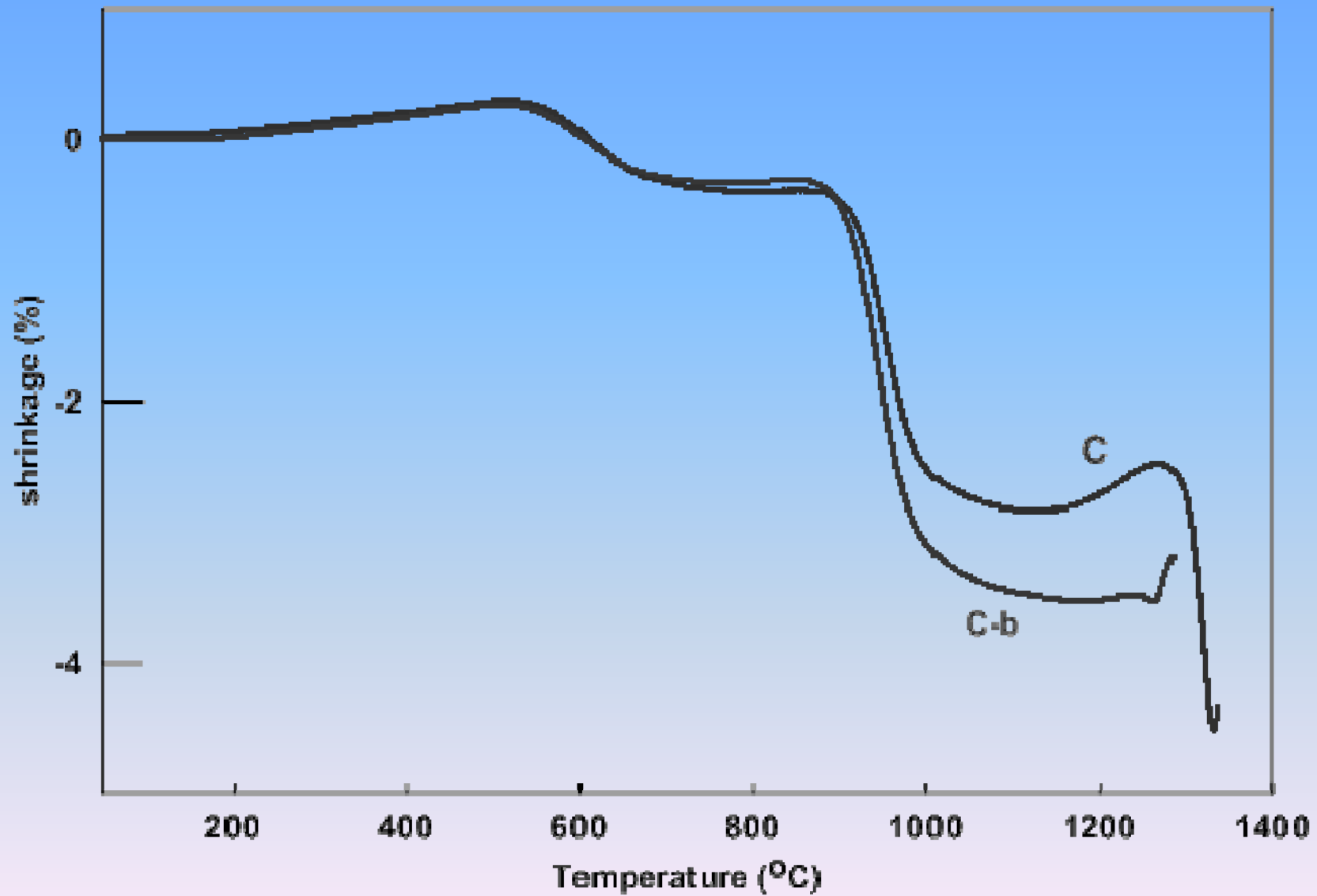
| <b>OXIDE</b>                   | <b>K</b> | <b>SRM</b> | <b>SRM-b</b> |
|--------------------------------|----------|------------|--------------|
| SiO <sub>2</sub>               | 52,5     | 46,8       | 48,7         |
| TiO <sub>2</sub>               | 0,5      | 0,7        | 0,8          |
| Al <sub>2</sub> O <sub>3</sub> | 33,3     | 9,8        | 10,2         |
| Fe <sub>2</sub> O <sub>3</sub> | 0,6      | 4,3        | 4,5          |
| CaO                            | 0,2      | 18,6       | 19,3         |
| MgO                            | 0,4      | 2,9        | 3,0          |
| K <sub>2</sub> O               | 0,9      | 1,0        | 1,0          |
| Na <sub>2</sub> O              | 0,1      | 4,5        | 4,7          |
| B <sub>2</sub> O <sub>3</sub>  | 0,0      | 0,6        | 0,6          |
| MnO                            | 0,0      | 0,3        | 0,3          |
| ZnO                            | 0,0      | 0,3        | 0,3          |
| PbO                            | 0,0      | 0,3        | 0,3          |
| SO <sub>3</sub>                | 0,0      | 1,0        | 1,0          |
| P <sub>2</sub> O <sub>3</sub>  | 0,0      | 1,2        | 1,3          |
| CuO                            | 0,0      | 0,5        | 0,5          |
| Others                         | 0,0      | 0,2        | 0,2          |
| L.O.I                          | 11,7     | <u>7,3</u> | <u>3,1</u>   |

**Chemical composition (wt %) of the studied ceramics**

| <b>OXIDE</b>                   | <b>C</b> | <b>C-b</b> | <b>C-b-Al</b> | <b>C-b-Na</b> |
|--------------------------------|----------|------------|---------------|---------------|
| SiO <sub>2</sub>               | 54,4     | 54,2       | 51,5          | 52,7          |
| TiO <sub>2</sub>               | 0,7      | 0,7        | 0,7           | 0,7           |
| Al <sub>2</sub> O <sub>3</sub> | 22,5     | 22,2       | <b>26,9</b>   | 22,1          |
| Fe <sub>2</sub> O <sub>3</sub> | 2,9      | 3,1        | 2,7           | 2,8           |
| CaO                            | 11,4     | 11,6       | 10,5          | 10,7          |
| MgO                            | 2,0      | 2,0        | 1,8           | 1,8           |
| K <sub>2</sub> O               | 1,1      | 1,0        | 1,0           | 1,0           |
| Na <sub>2</sub> O              | 2,8      | 2,8        | 2,6           | <b>5,9</b>    |
| B <sub>2</sub> O <sub>3</sub>  | 0,4      | 0,4        | 0,3           | 0,3           |
| MnO                            | 0,2      | 0,2        | 0,2           | 0,2           |
| ZnO                            | 0,2      | 0,2        | 0,2           | 0,2           |
| PbO                            | 0,2      | 0,2        | 0,2           | 0,2           |
| SO <sub>3</sub>                | 0,6      | 0,6        | 0,5           | 0,5           |
| P <sub>2</sub> O <sub>3</sub>  | 0,7      | 0,8        | 0,7           | 0,7           |
| CuO                            | 0,3      | 0,3        | 0,3           | 0,3           |

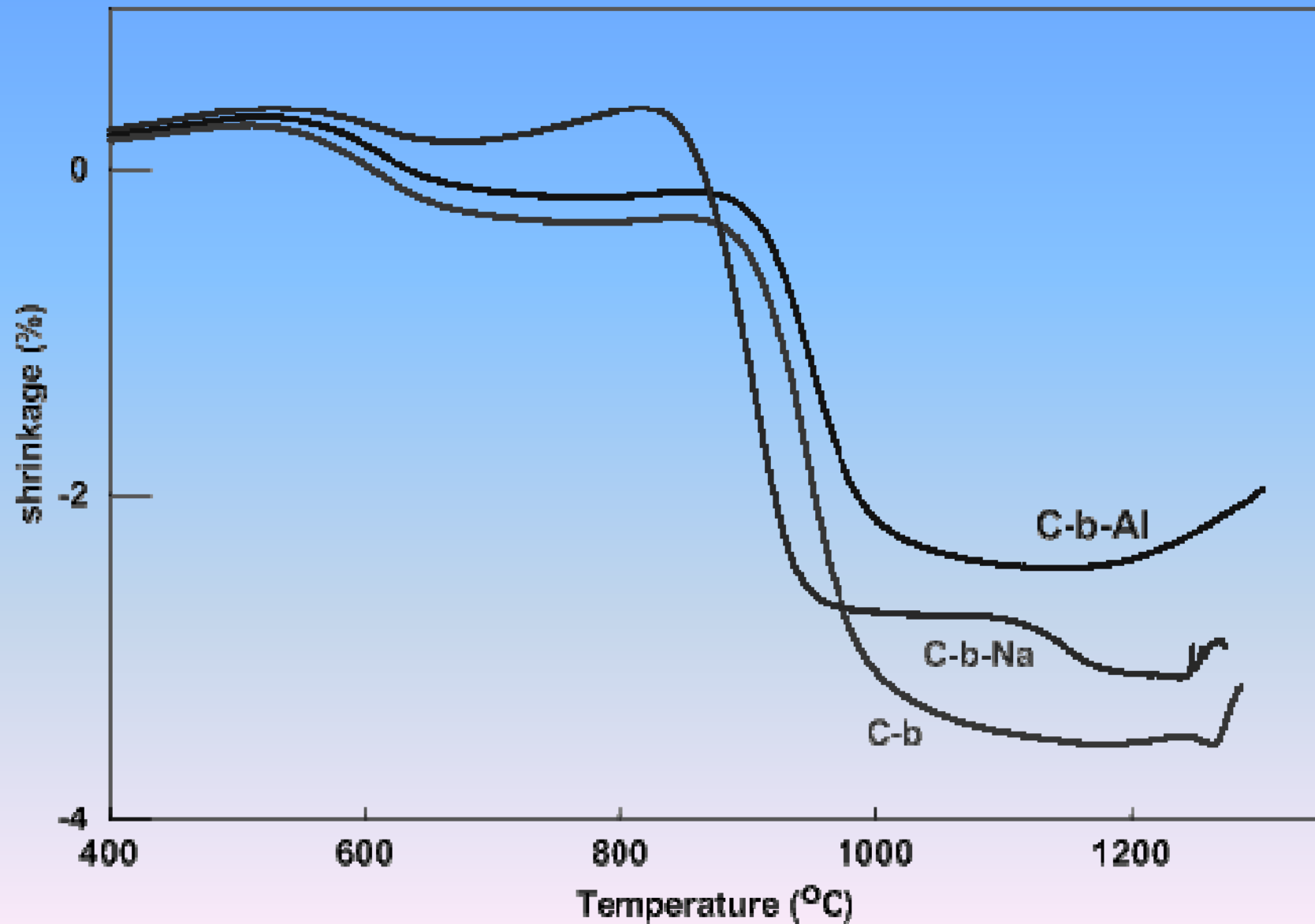
# THERMAL CHARACTERIZATION

Non-isothermal dilatometric results of compositions C and C-b



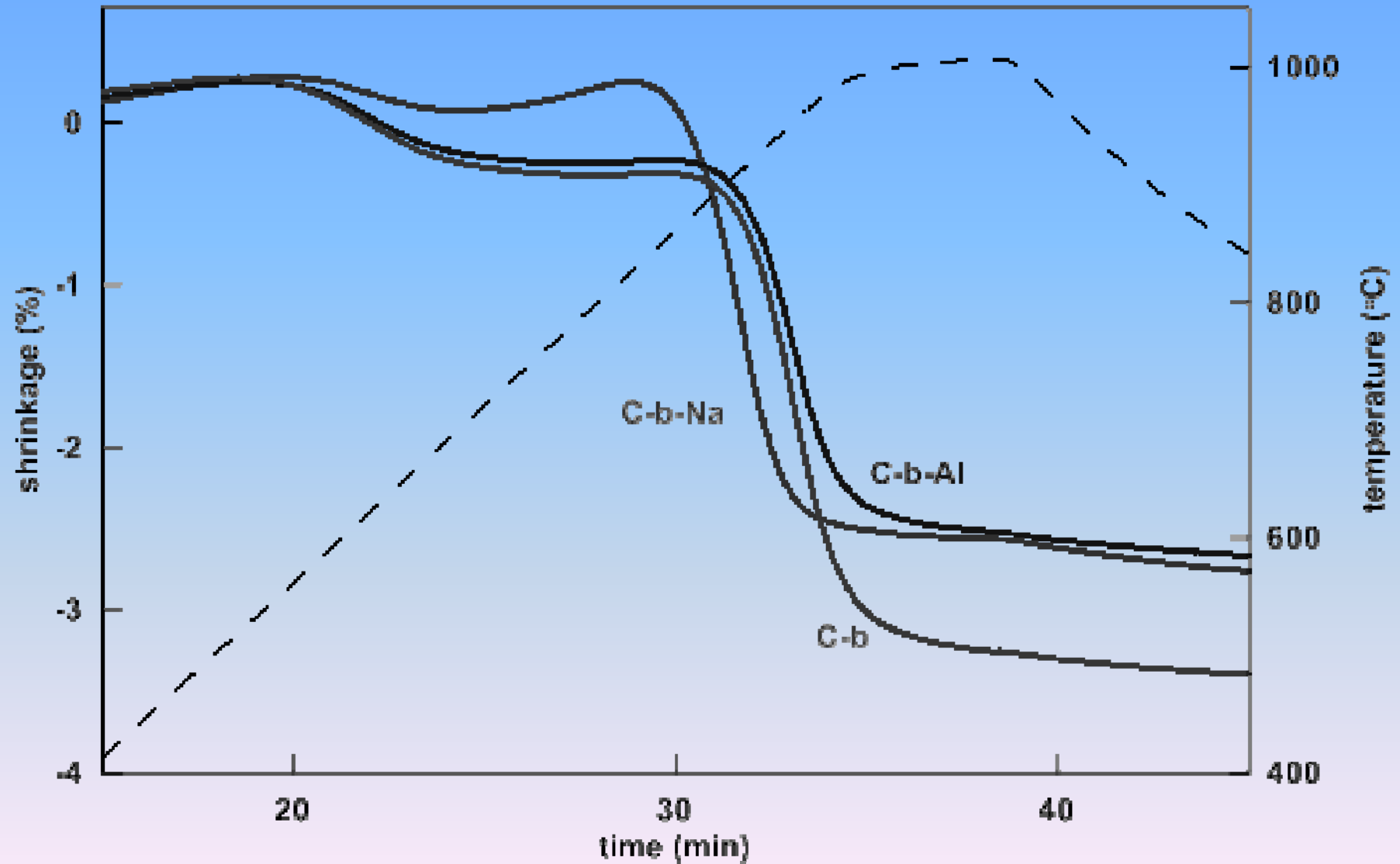
# THERMAL CHARACTERIZATION

Non-isothermal dilatometric results of compositions C-b, C-b-Al and C-b-Na



# THERMAL CHARACTERIZATION

Isothermal dilatometric results of compositions C-b, C-b-Al and C-b-Na



Density (g/cm<sup>3</sup>), porosity (vol %) and water absorption of the final samples **obtained for 5 min at 1000°C**

|  | <b>C-b</b>         | <b>C-b-Al</b>      | <b>C-b-Na</b>      |
|--|--------------------|--------------------|--------------------|
| <b>apparent density<br/>(g/cm<sup>3</sup>)</b> | <b>1.86 ± 0.02</b> | <b>1.95 ± 0.03</b> | <b>1.92 ± 0.02</b> |
| <b>water absorption<br/>(%)</b>                | <b>14.5 ± 0.5</b>  | <b>13.0 ± 0.5</b>  | <b>11.5 ± 0.5</b>  |
| <b>total porosity<br/>(%)</b>                  | <b>31±1</b>        | <b>29±1</b>        | <b>27±1</b>        |

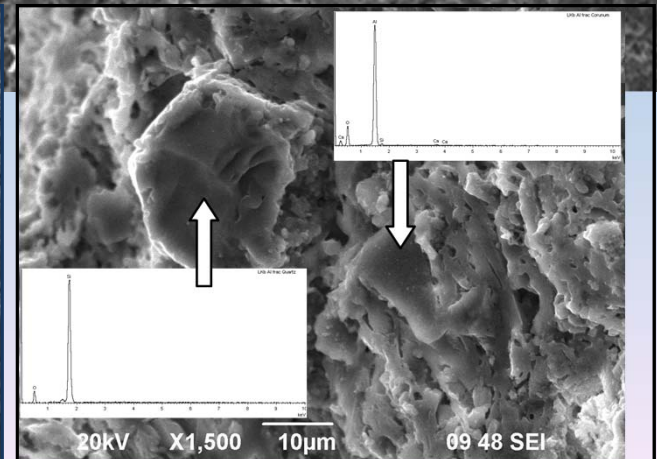
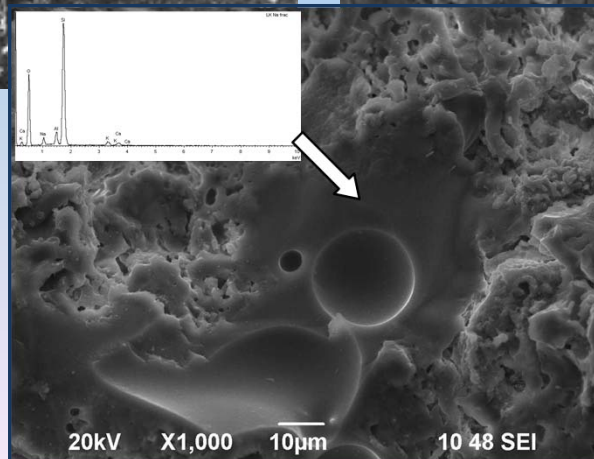
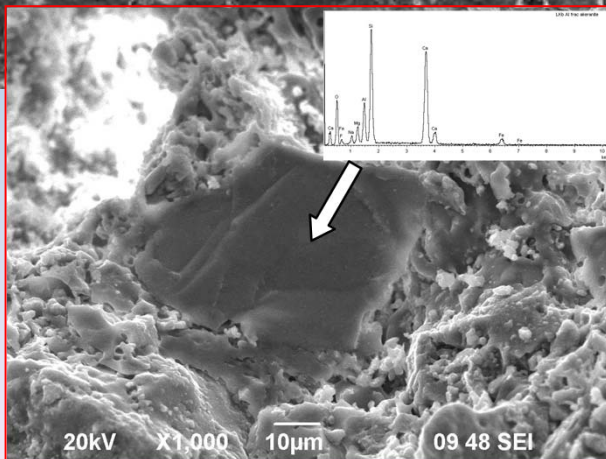
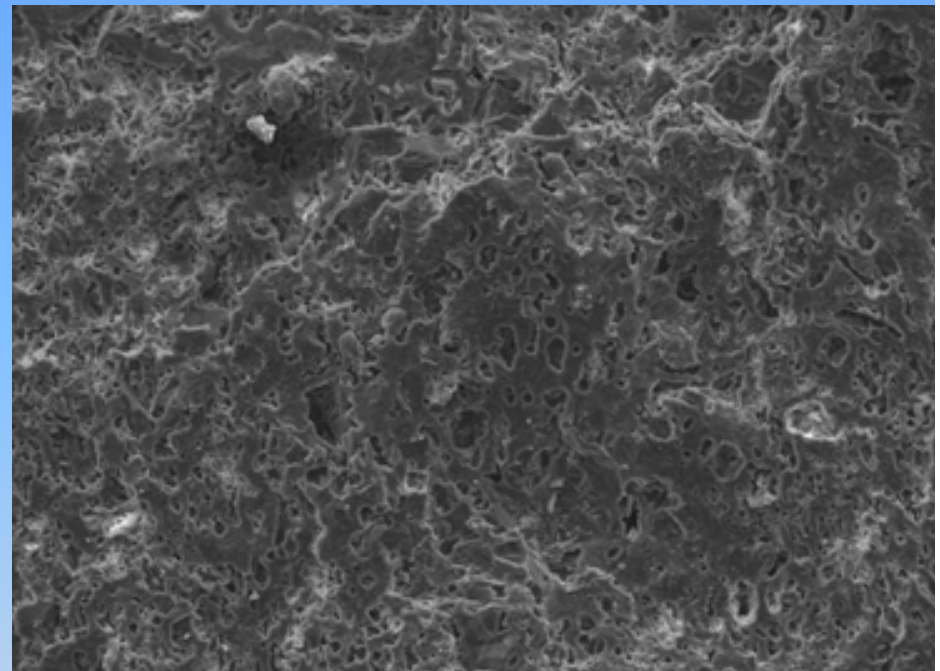
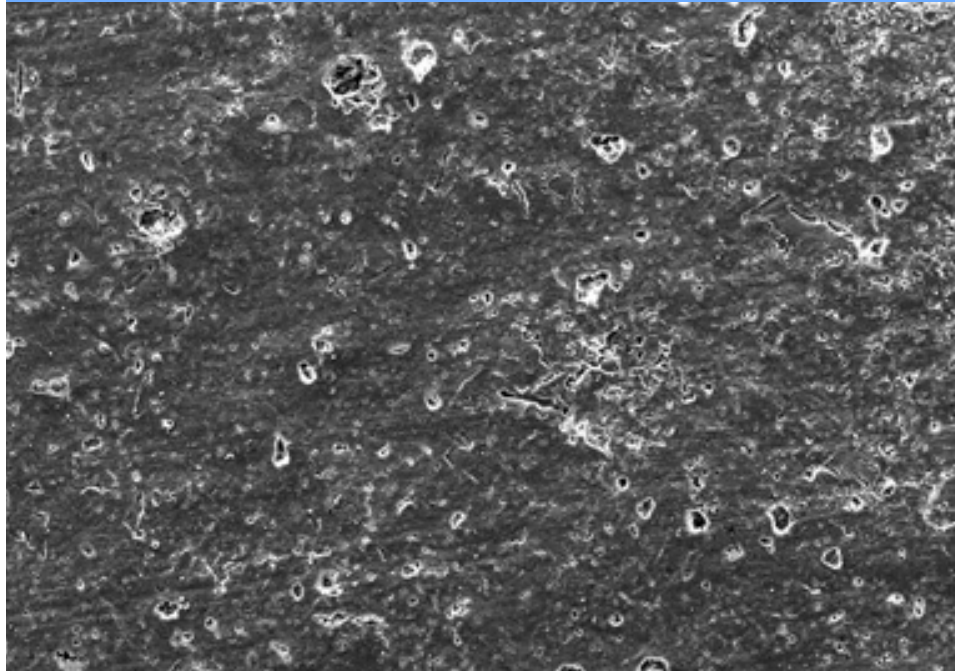


# STRUCTURE OF THE FINAL CERAMICS

surface

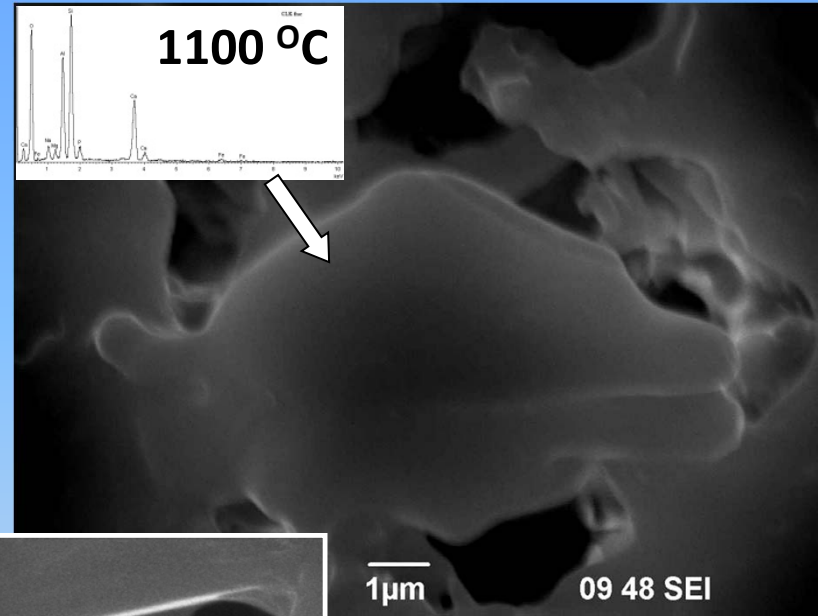
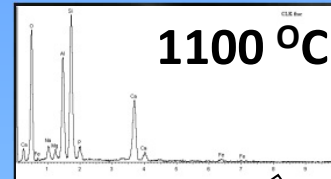
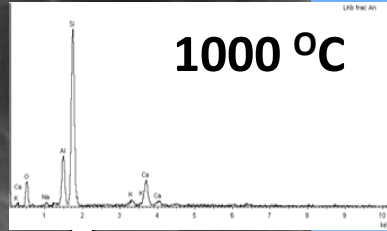
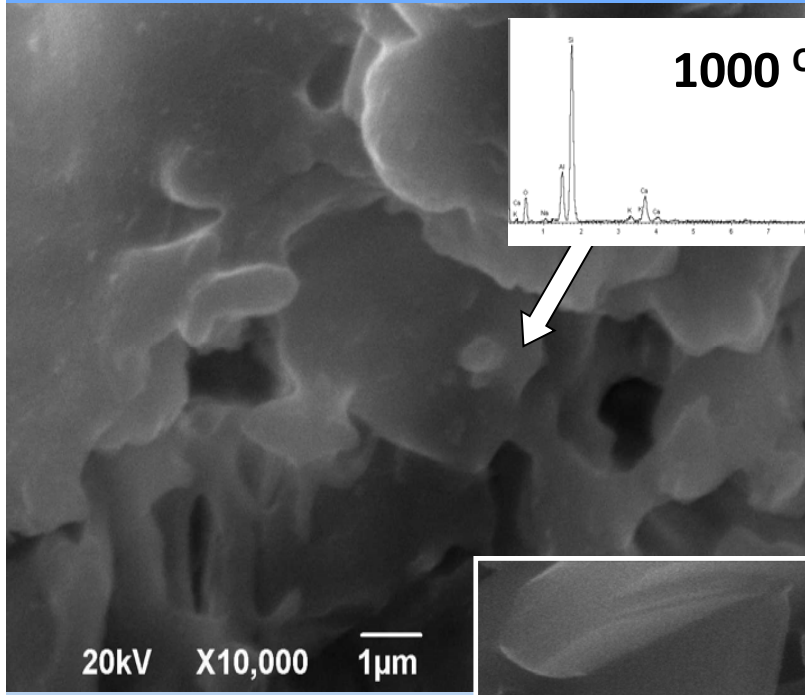
1000 °C

fracture

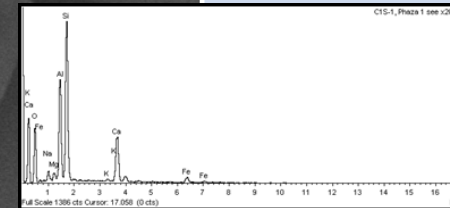
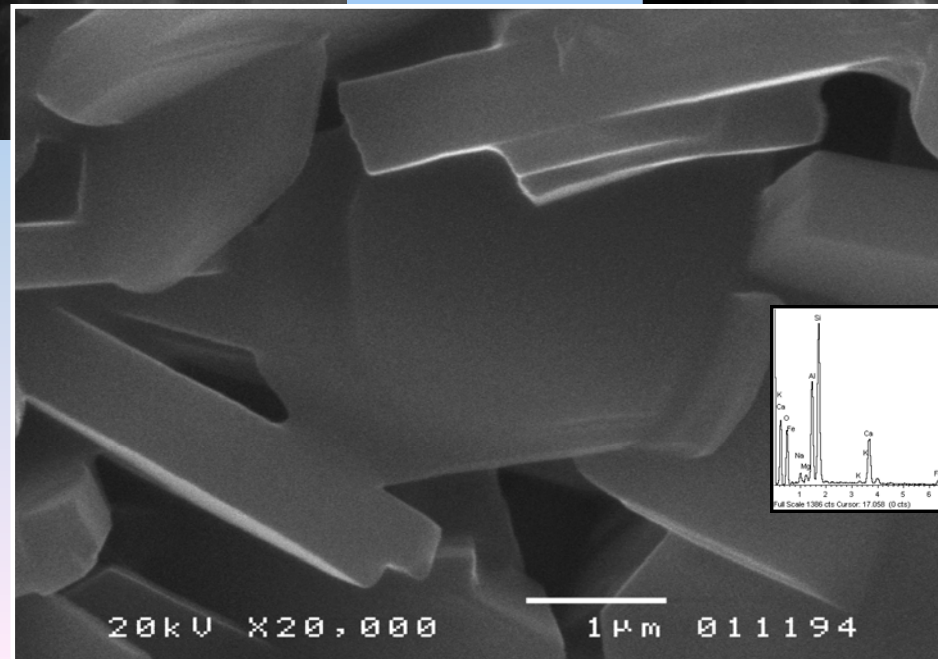


# MICROSTRUCTURAL ANALYSIS

Development of main anorthite phase



1260°C



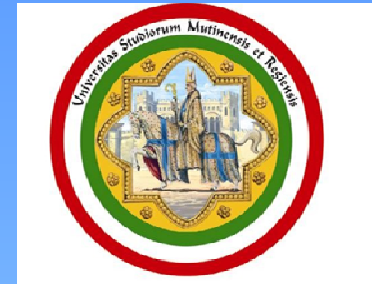
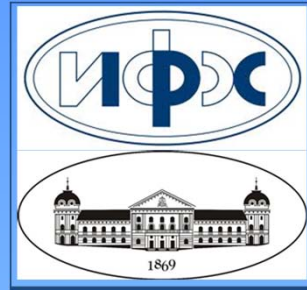
## **CONCLUSIONS**

- **New cheap ceramics, based on huge amount of industrial wastes, were synthesized at sintering temperatures of 1200-1250 °C and holding times of 10-30 min.**
- **The new compositions are characterized by an elevated crystallinity, resulting in improved mechanical properties.**
- **The possibility to obtain samples with bricks structure after very short thermal treatment at low temperature is also demonstrated.**



**Thank You for the attention**





# *Sintered glass-ceramic from iron-rich MSWA*

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***•The vitrification is considered as an ultimate method for immobilization of hazardous and non-inert industrial wastes because during glass melting the harmful elements are chemically bonded in the durable amorphous network.***

***• However this procedure is economically favoured only if materials with commercial value are obtained.***

***•From this point of view, the synthesis of quality glass-ceramics seems to be one of the most promising solutions.***

***•A significant part of the hazardous and non-inert industrial wastes industrial residues are iron-rich.***

## Slagsital Production

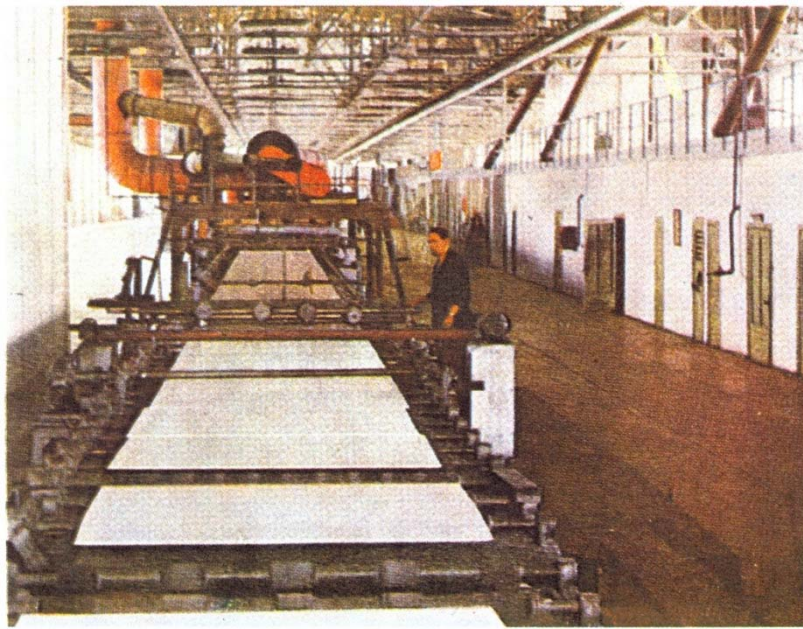


Fig. 4-8 The end of a crystallization, continuous roll furnace for production of Slagsital

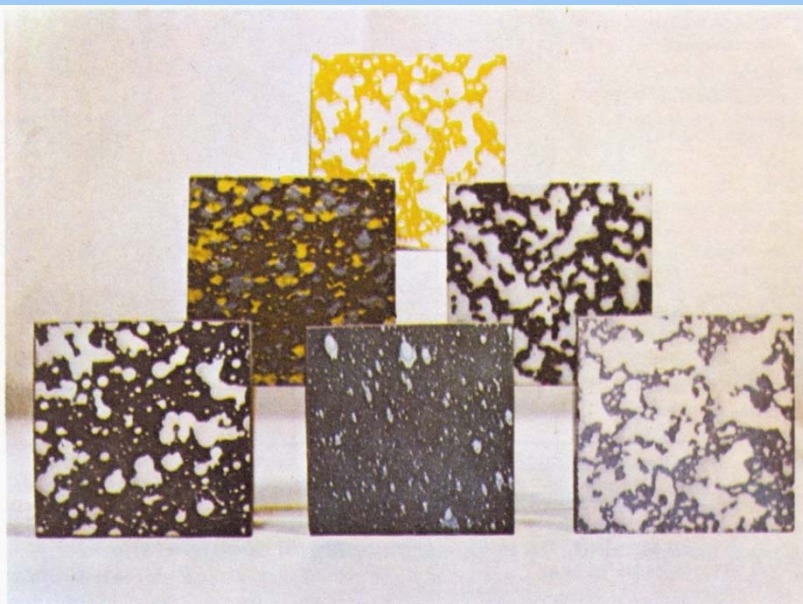
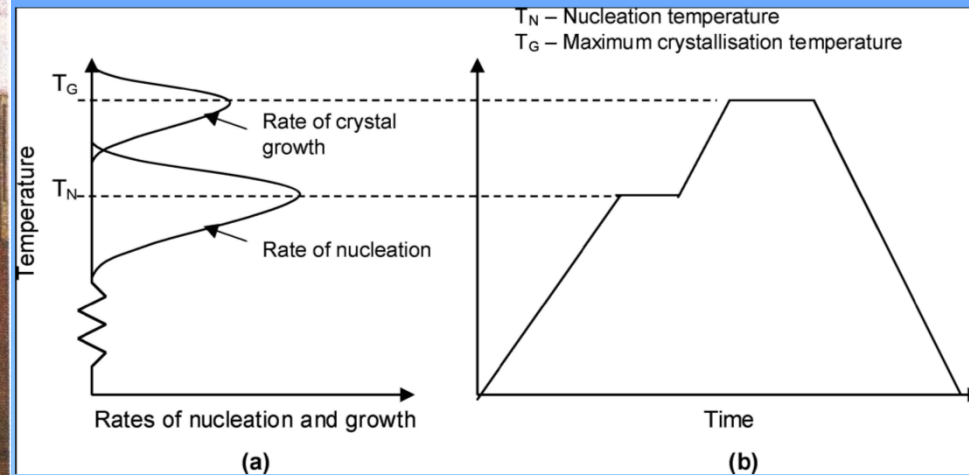


Fig. 7-38 Slagsital tiles

- Cheap batch composition, based on 50-60 wt % blast furnace slags;
- Melting at 1450-1500 °C;
- Rolling
- Crystallization treatment
  - 1-1.5 h nucleation at 800-850 °C
  - 1-2 h crystal growth at 950-1000°C



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**2007**





**Inter-crystallization of glass powders or grains (i.e. frits) is an alternative prospective technique for glass-ceramic production.**



**Advantages:**

*Inter-crystallization of nucleants and no nucleation treatment are needed.  
Glasses with lower degree of homogenisation can be used.  
Components with complicated shapes and various sizes can be produced.*

**Disadvantages:**

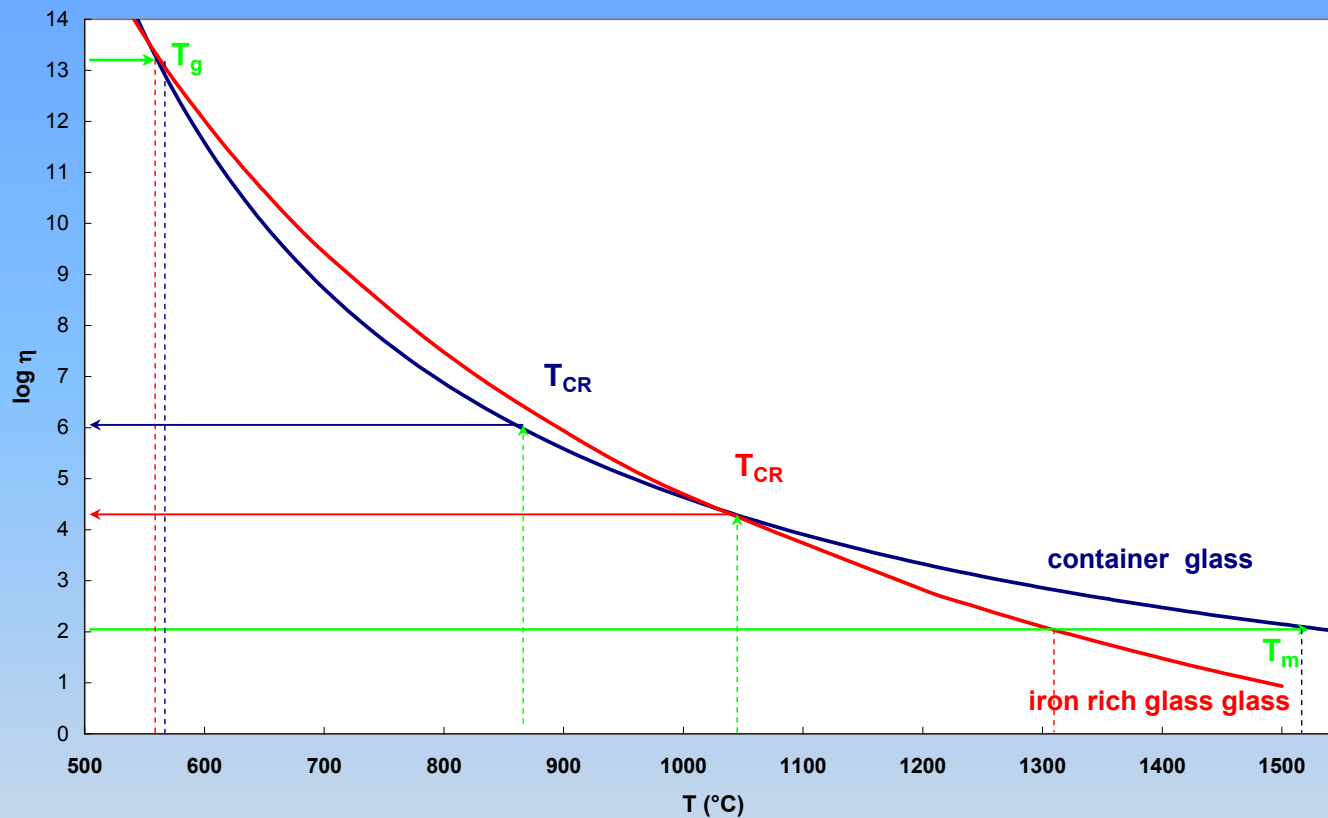
## ***specific features of the iron-rich glasses***

***in the glasses is presented in  $Fe^{2+}$  and  $Fe^{3+}$  forms and the  $Fe^{2+}/Fe^{3+}$  ratio depends on the temperature, the melting conditions and parent glass composition.***

***iron oxides have limited solubility in silicate melts, resulting in a homogeneous liquid-liquid immiscibility which leads to high crystallization trend.***

***heating the glasses above the glass transformation range surface oxidation of  $Fe^{2+}$  to yield  $Fe^{3+}$  takes place. However this oxidation process can be avoided in an inert atmosphere.***

## Viscosity curves of *container glass* and a typical *iron-rich glass* from industrial wastes



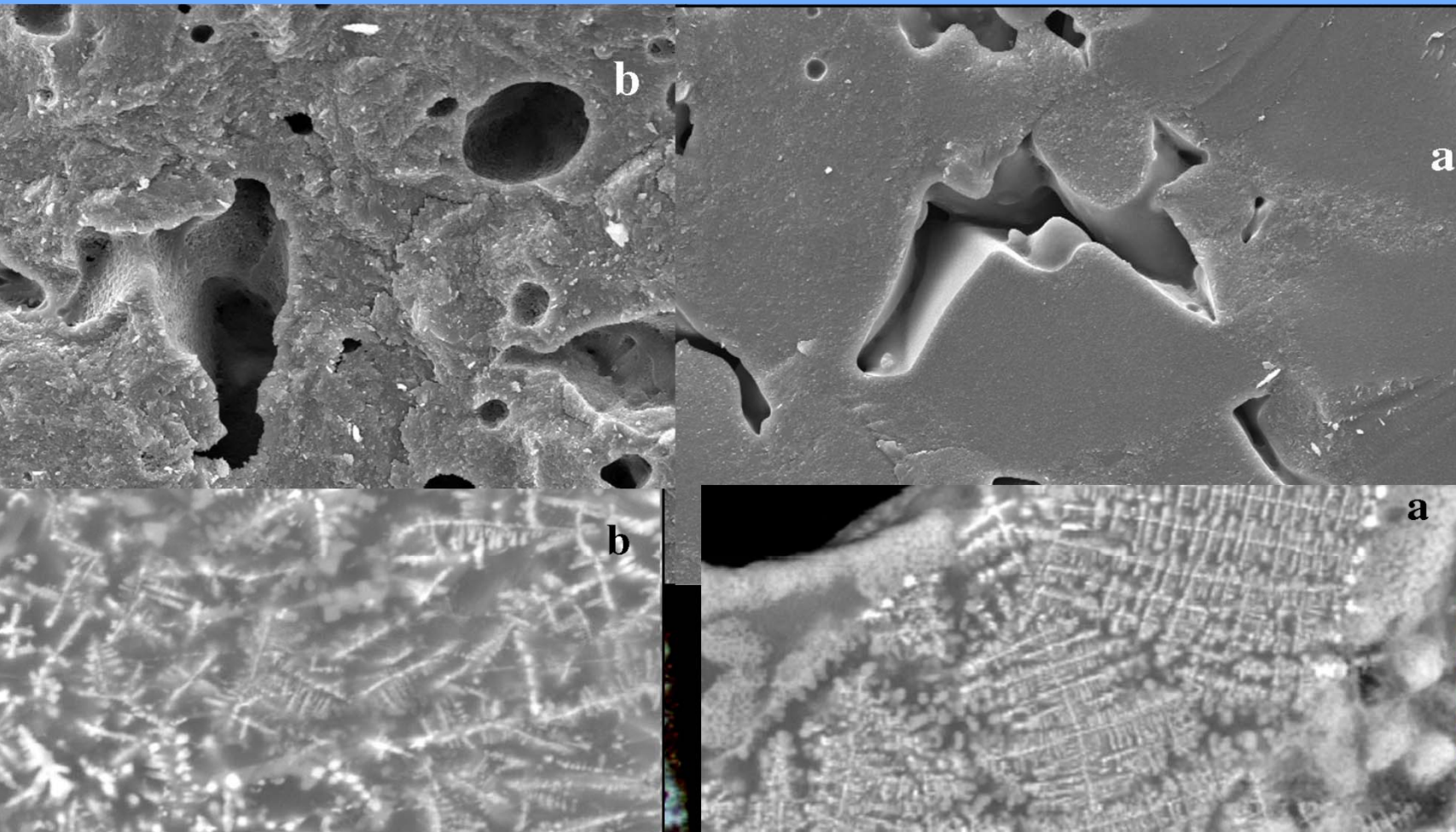
age:

er price of the vitrification procedure;

er tendency for evaporation of heavy metals during the glass melting.

antages:

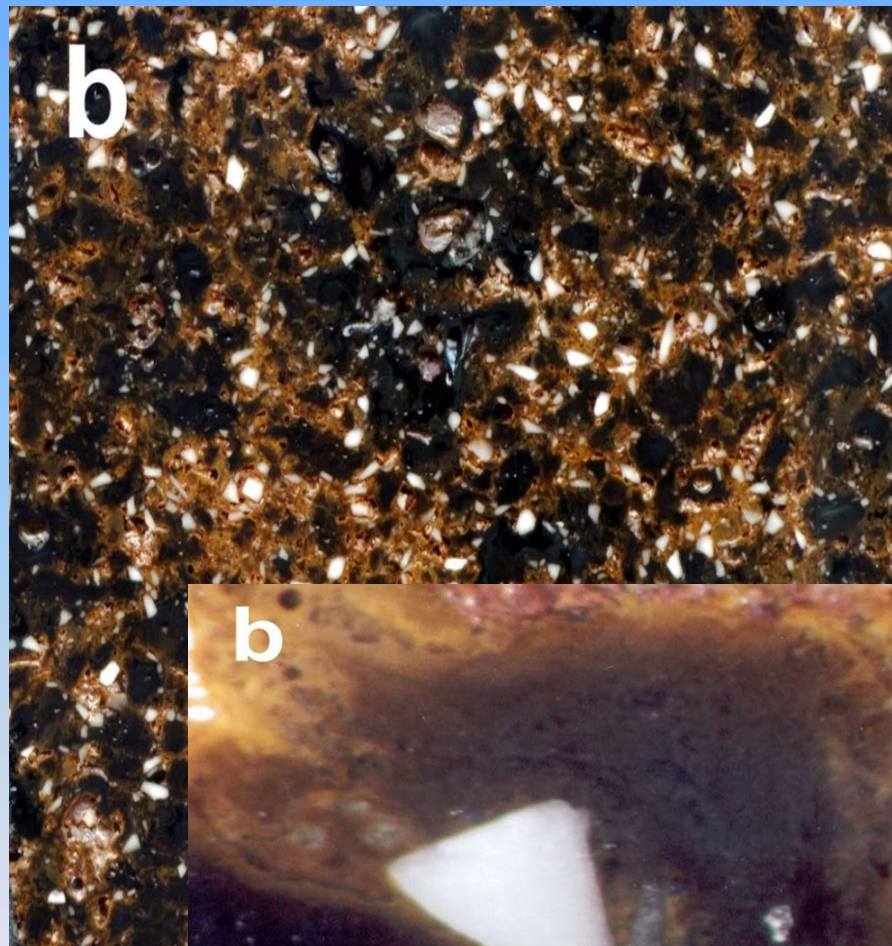
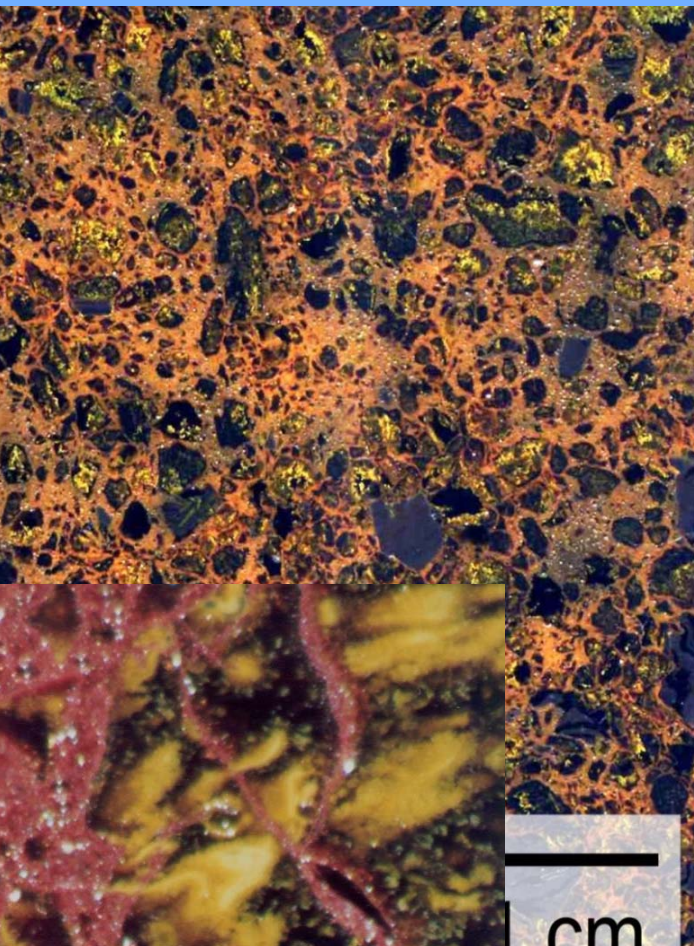
*Structure of sintered Jar iron-rich glass-ceramic  
sintered in nitrogen and **in air** and atmospheres*



***Properties of sintered iron rich glass-ceramic in  
air and in nitrogen atmosphere  
(1 h step)***

|  | <b><i>in air</i></b>   | <b><i>In N<sub>2</sub></i></b> |
|--|------------------------|--------------------------------|
| <b><i>Sintering temperature (°C)</i></b> | <b><i>1050</i></b>     | <b><i>970</i></b>              |
| <b><i>Linear shrinkage (%)</i></b>       | <b><i>11.5±0.2</i></b> | <b><i>12.2±0.3</i></b>         |
| <b><i>Flexural strength (MPa)</i></b>    | <b><i>84±8</i></b>     | <b><i>126±6</i></b>            |
| <b><i>Young's Modulus (GPa)</i></b>      | <b><i>78±4</i></b>     | <b><i>81±4</i></b>             |

***G-Goe glass-ceramic (a) and G-Flo composite (b)***  
***(sintering 30-60 min at 1010-1030 °C)***



**Properties of sintered iron rich glass-ceramic from frits  
(G-Jar) , Neoparies (N) and granites (G)**

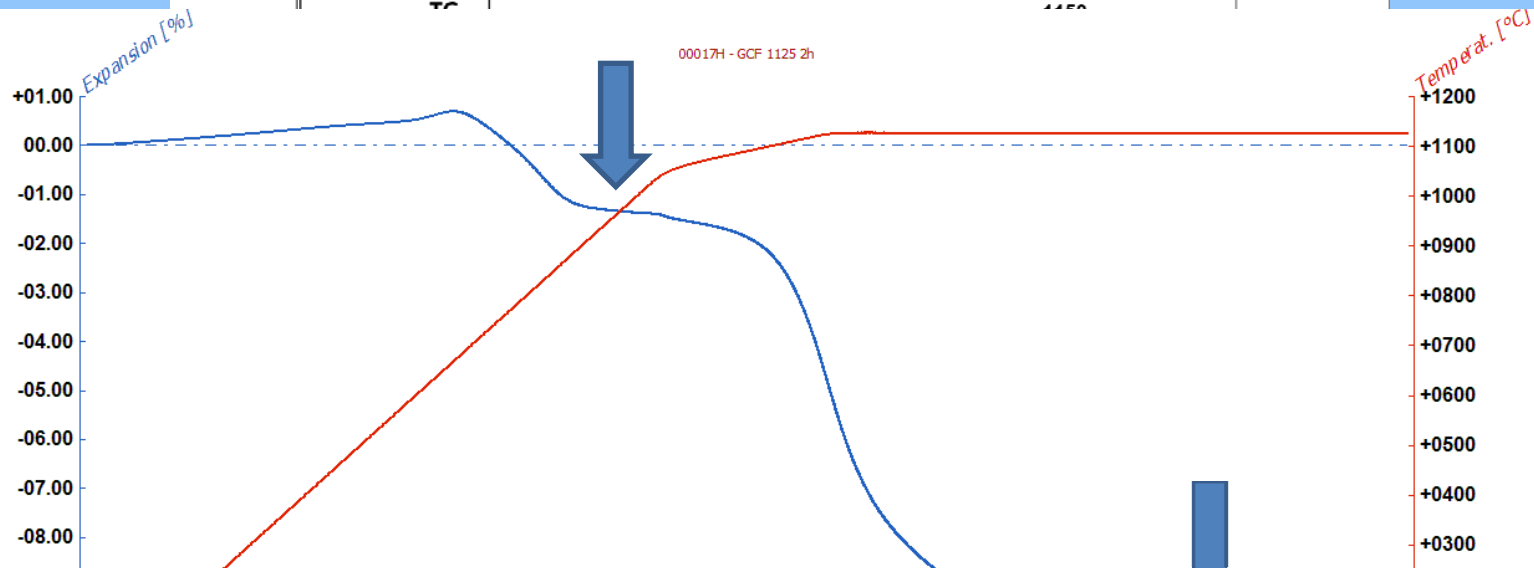
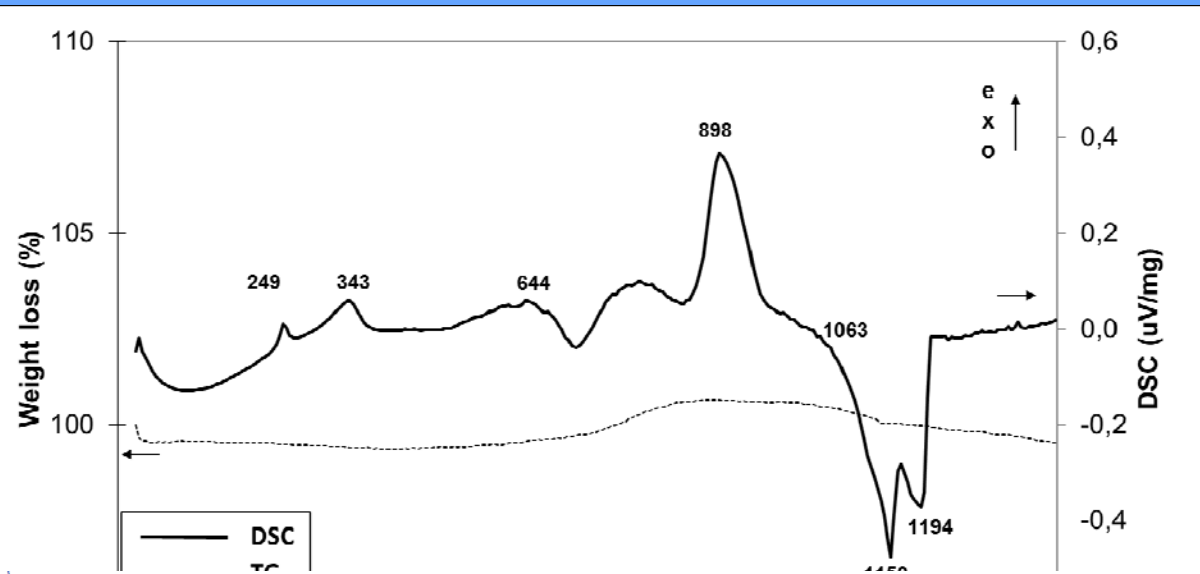
| <b>Properties</b>  | <b>G-Jar</b>   | <b>N</b>   | <b>G</b>       |
|--|----------------|------------|----------------|
| <b>Density<br/>(g/cm<sup>3</sup>)</b>                      | <b>2.8-2.9</b> | <b>2.7</b> | <b>2.6-2.8</b> |
| <b>Compressive strength (Mpa)</b>                          | <b>72±7</b>    | <b>55</b>  | <b>12-20</b>   |
| <b>Modulus of Elasticity (GPa)</b>                         | <b>48±4</b>    | <b>85</b>  | <b>35-55</b>   |
| <b>Mooh's hardness</b>                                     | <b>6</b>       | <b>6.5</b> | <b>4.5-6.5</b> |
| <b>Thermal expansion (*10<sup>-7</sup> K<sup>-1</sup>)</b> | <b>65-70</b>   | <b>65</b>  | <b>65-90</b>   |

## MSWA iron- rich glass (as it is melting for 1 h at 1400 °C)

|                                | GF   | GF-ox |
|--------------------------------|------|-------|
| SiO <sub>2</sub>               | 38.2 | 39.9  |
| TiO <sub>2</sub>               | 1.4  | 1.5   |
| Al <sub>2</sub> O <sub>3</sub> | 8.7  | 9.1   |
| Fe <sub>2</sub> O <sub>3</sub> | 0.8  | 5.4   |
| FeO                            | 8.8  | -     |
| CaO                            | 30.3 | 31.7  |
| MgO                            | 6.0  | 6.3   |
| CuO                            | 0.7  | 0.7   |
| MnO                            | 0.2  | 0.2   |
| ZnO                            | 0.4  | 0.4   |
| PbO                            | 0.1  | 0.1   |

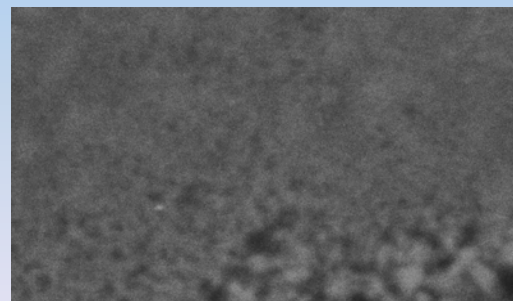
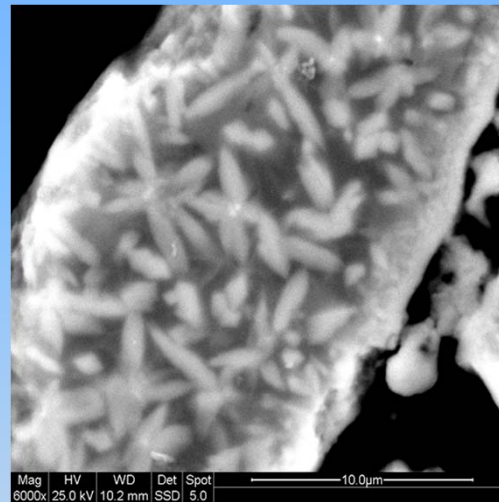
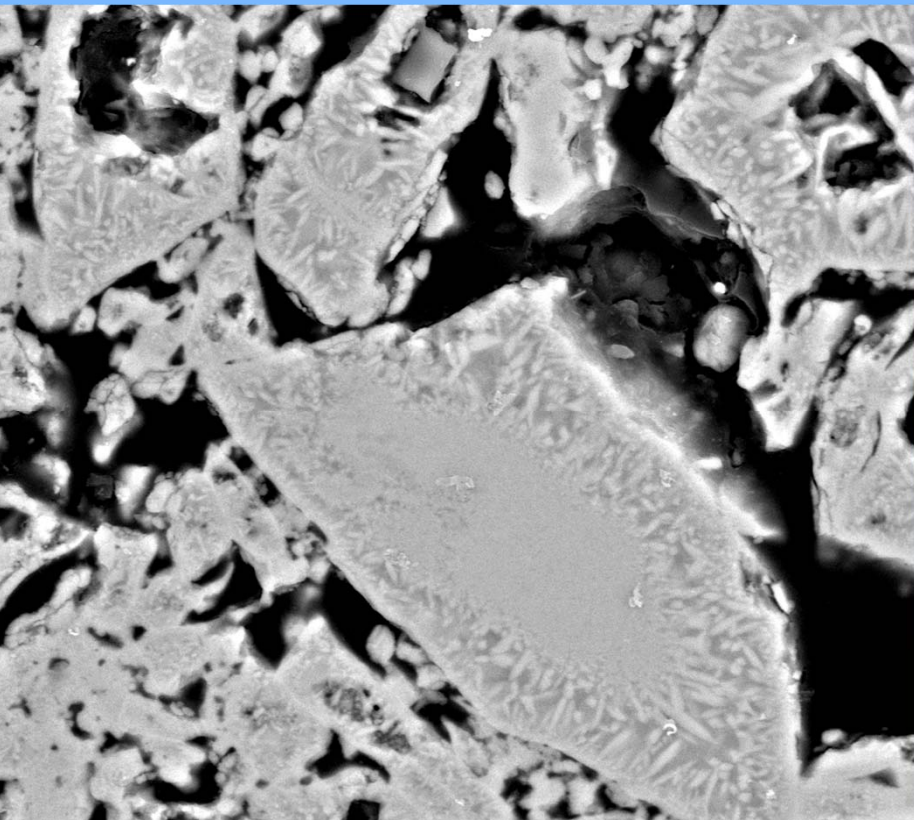


## Sinter-crystallization of sintered MSWA glass-ceramic

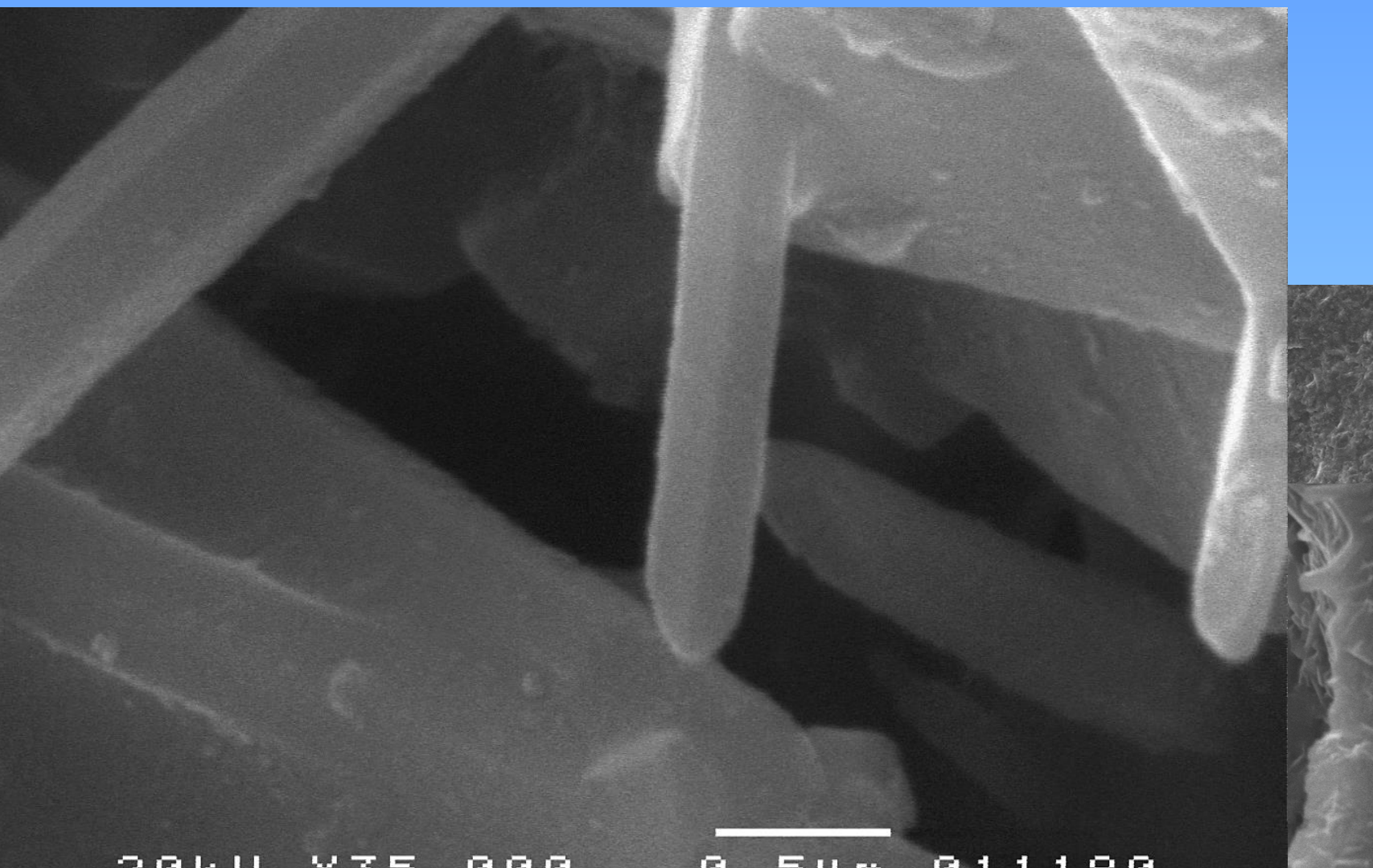


***Structure of sintered G-MSWA glass-ceramic***

***(1 h at 950 °C)***



*Structure of sintered MSWA glass-ceramic*



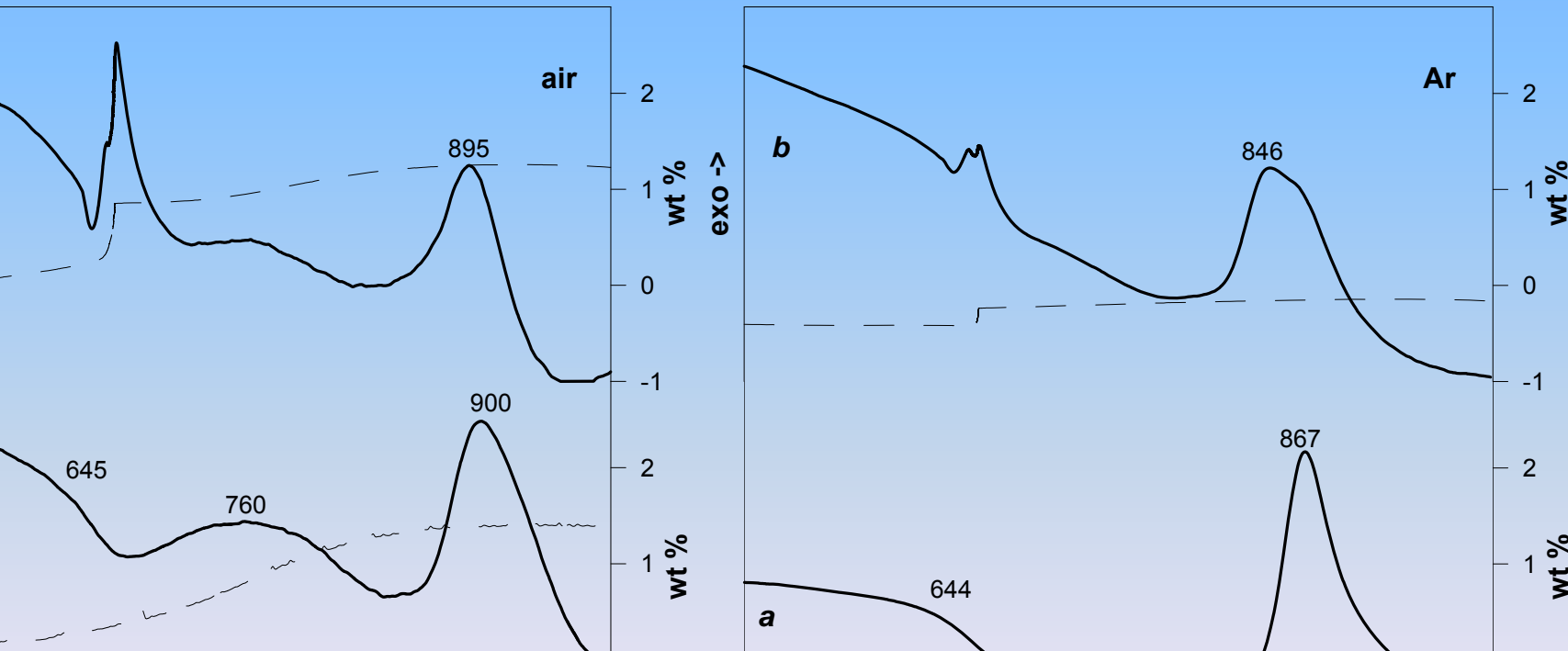
**DTA traces without (a) and with (b) nucleation step**

**(>125  $\mu\text{m}$ )**

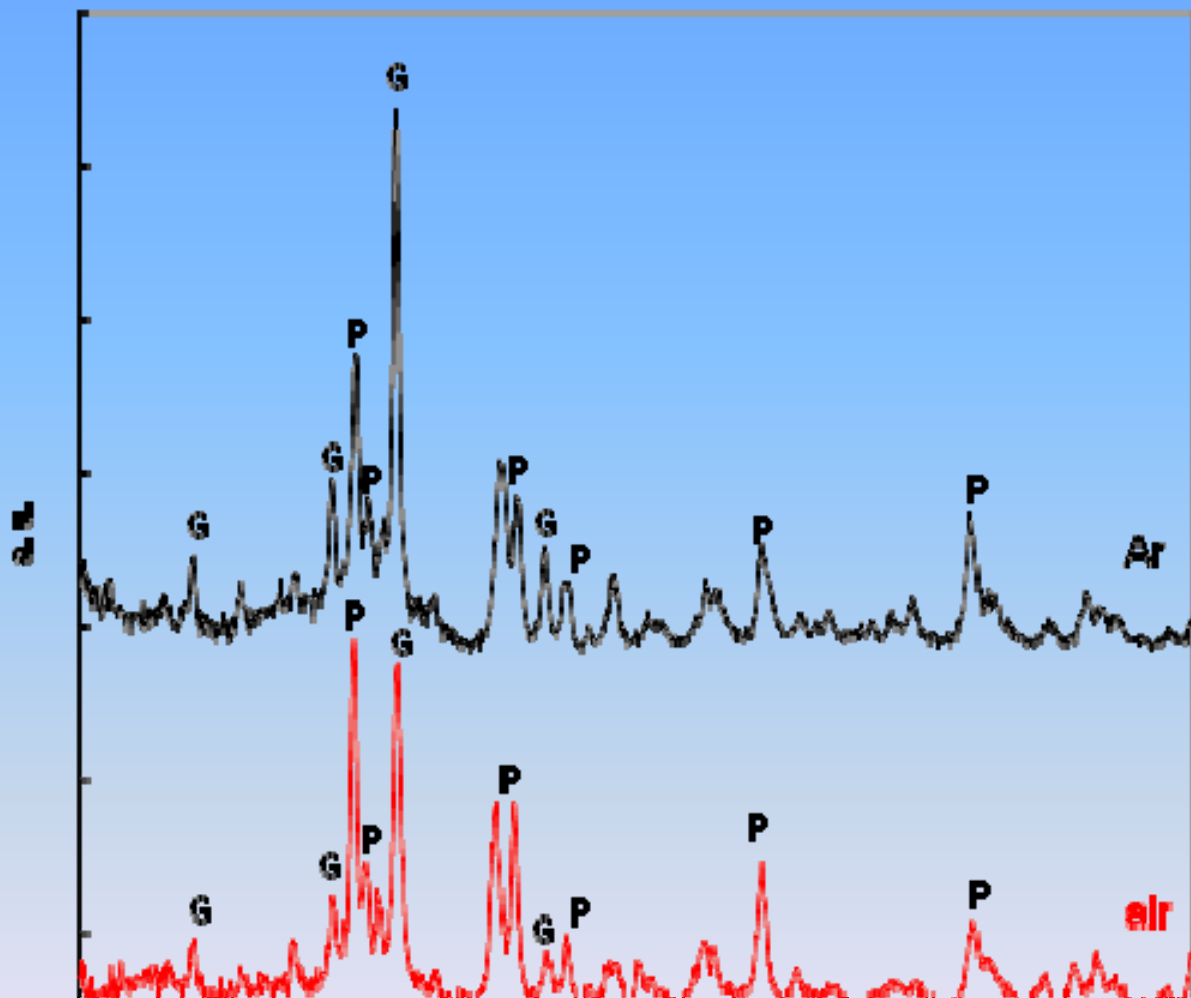
**in**

**air**

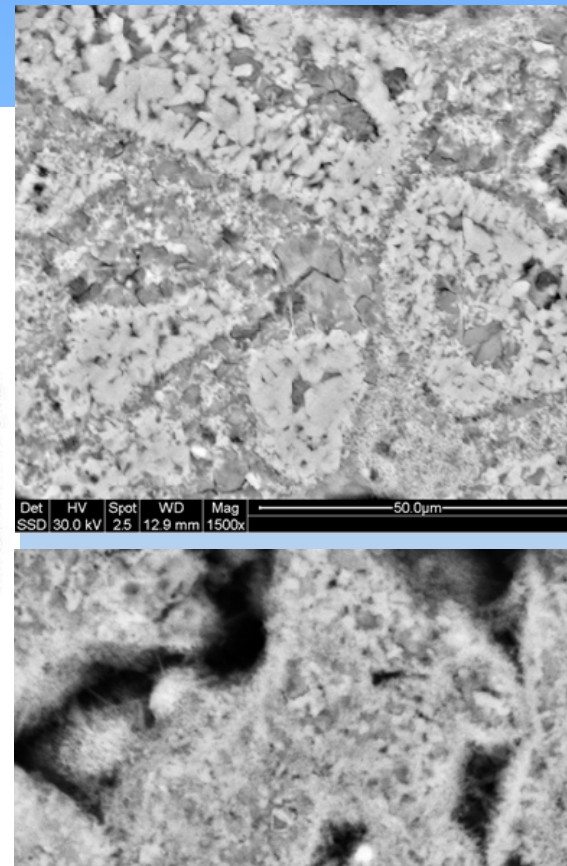
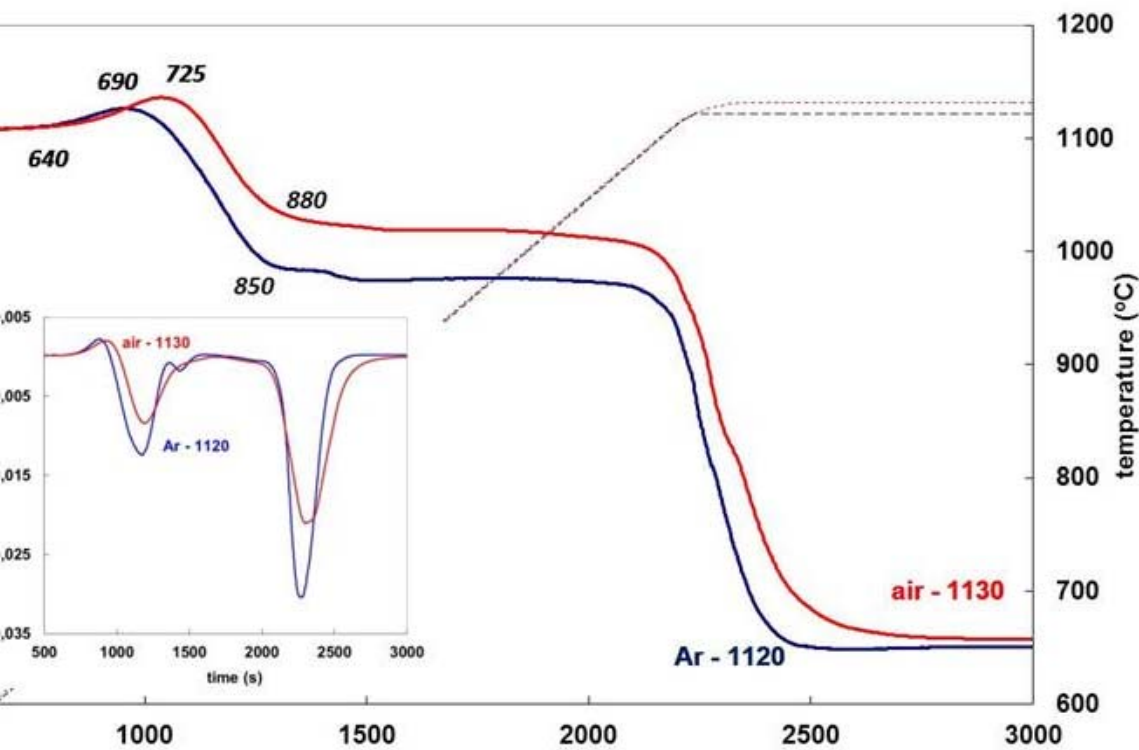
**argon**



*D results for MSWA glass-ceramics in air and argon atmospheres after*



**ification results and structure for samples, obtained in *air* (1 h holding at 1130°C) and in *argon flux* (1 h holding at 1120°C).**

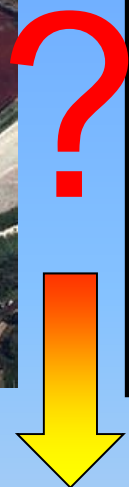
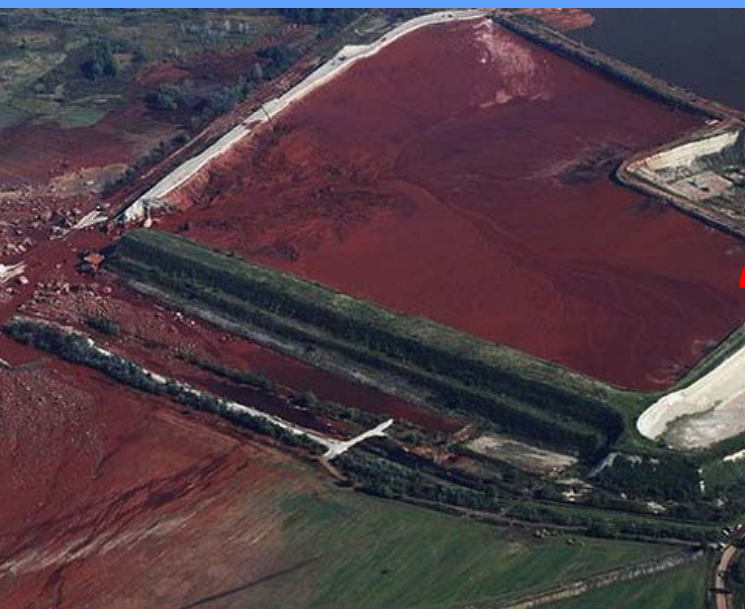


## Conclusions

The possibility to use “as it is” vitrified MSWA for synthesis of cheap sintered material with very fine crystalline structure and short thermal cycle near the eutectic temperature is demonstrated.

The investigated glass powders are characterized with high crystallization trend and formation of pyroxene and melilite solid solutions at 850-900°C. In air atmosphere, after  $\text{Fe}^{2+}$  oxidation, the phase formation leads to pyroxene/melilite ratio of about 2, while in inert atmosphere no oxidation takes place and the ratio pyroxene/melilite notably decreases.

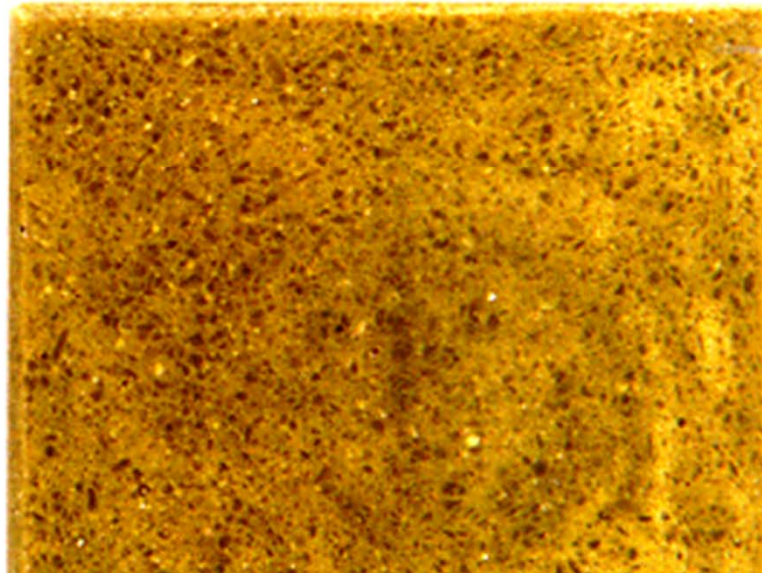
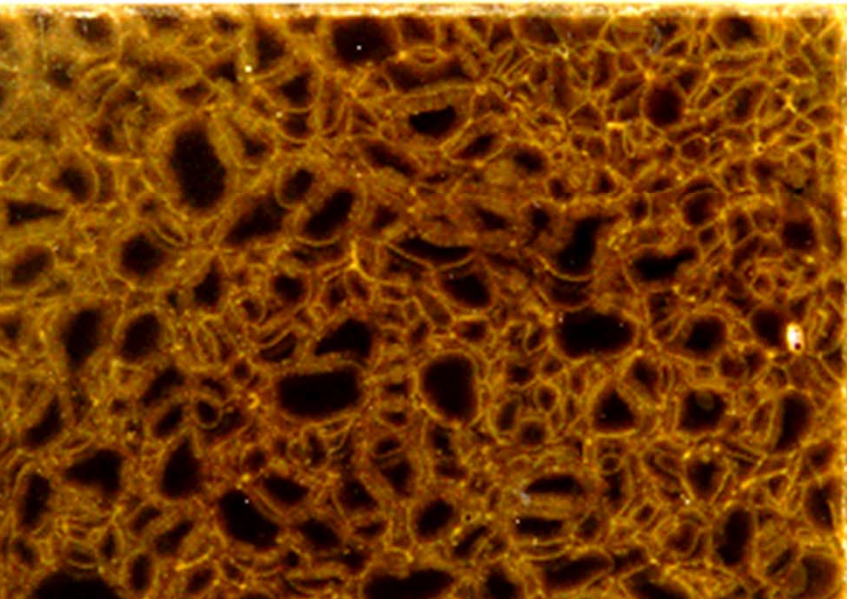
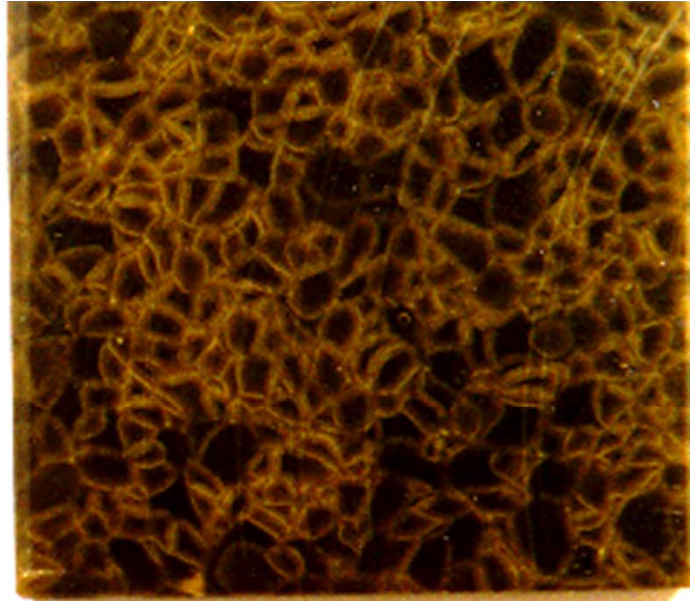
Intensive phase formation inhibits the densification at low temperatures in both atmospheres. However, after increasing of the sintering temperature up to 1050-1130°C secondary densification carries out, resulting in material with zero water absorption, low closed porosity and high crystallinity.







Sintered glass-ceramic G-60 MSA



## Sintered glass-ceramics from MSW fly ash

### STRUCTURE OF SINTERED GRANITE-LIKE GLASS-CERAMIC (G-60)

