# Effect of the oxidation stage on the foaming performance of Iron-rich sintered glass-ceramics

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## Introduction

In the proposed research we aim to introduce the necessary utilization of a preliminary programmed isothermal oxidation stage to maintain higher oxidation state of the ions governing the bloating process in the synthesis of new glass-ceramic materials from waste [1, 2]. At higher temperatures an intensive autocatalytic foaming initiates. This bloating process is related to oxidation of the iron and manganese oxides, presented in the slag. This process carries out in the glass transition region (*Tg*). It may be noted however, that the subsequent oxygen release at higher temperatures is due to their reverse partial thermal reduction. The use of higher constant linear heating rates is technologically worthy to obtain new glass-ceramics. However this is a condition at which no sufficient initial significant oxidation is possible. The reported experiments with new materials consist of in-situ synthesis and measurements of the sintering and expansion curves and optical analysis of the volume change due to the thermal treatment.

## Materials and methods

The investigations were carried out with a thermal-optical measuring and imaging system ESS HSM-1400 ExpertLabService (Italy, USA). An iron and manganese containing slag from the steel and iron company Helwan in Cairo, Eqypt was used for the in-situ synthesis of the studied glass-ceramic foams. 30% wt. industrial quartz sand were added to 70% wt. slag. The mixed batch was melted in an electric furnace. After 2 h of holding at 1450 $^{o}$C, the melt was finally quenched in water. The obtained glassy frit was crushed, ground in a mechanical mill FRITSCH (Germany) and additionally sieved below 75 μm with a digital sieving machine CISA (Spain).The resulting glassy frit was characterized with the following chemical composition in % wt. determined by XRF analysis: 49.2 $SiO_2$; 5.1 $Al_2O_3$; 5.5 $Fe_2O_3$; 18.6 CaO; 1.1 MgO; 5.8 MnO; 10.9 BaO; 0.7 $TiO_2$; 0.7 $K_2O$ [1]. The measurements were performed with holding times of 30 minutes at a temperature of 720 °C to promote oxidation and a subsequent linear heating up to 1400 $^{o}$C with scan rates between 5 and 40 $^{o}$C min$^{-1}$. For the first time we analyze thermal curves recorded with a linear heat rate of 40 $^{o}$C min$^{-1}$.
The structural units of the newly obtained recycled glass-ceramic foams were revealed by FT-IR spectroscopy of pressed ground samples as KBr-matrix pellets. Infrared spectra were recorded with a JASCO 4X (Japan) FT-IR spectrometer with resolution of 4 cm$^{-1}$and 64 scans.

## Results and discussion

In Fig. 1a is presented the complete thermal treatment curve of the synthesis of glass-ceramic foam starting from the initial glass-frit. The sample is firstly subject to an isothermal oxidation treatment then via a linear heating the sample is being sintered and further at higher temperatures bloated (by autocatalytic bloating). This is due to the reverse thermal reduction, releasing oxygen bubbles in the bulk of the softened material thus promoting the obtaining of partially crystalline glass-ceramic foam. The foam reveals a fire-resisting feature at temperatures of about 1000 $^{o}$C and its crystalline structure is stabilized at that temperature. A freezed at the temperature of formation glass-ceramic foam is presented in color in Fig. 1b.
The temperature evolution of the synthesis of a recycled glass-ceramic foam sample is presented in red color on the right ordinate in Fig. 1a. For the first time we propose high-rate non-isothermal synthesis with a linear heating scan rate of 40 $^{o}$C min$^{-1}$. The areas of interest are shaded on the graph (sintering interval and foaming interval). The bloating process is characterized with intensive expansion of the volume of the material by more than 90 %, compared to the sintered compacted material.
The true-color photograph in Fig. 1b represents a real HSM sample subject to thermal expansion and cooled down after maximum structural bloating (c.f. the maximum point of the expansion curve in Fig. 1a corresponding to the photograph in Fig. 1b).

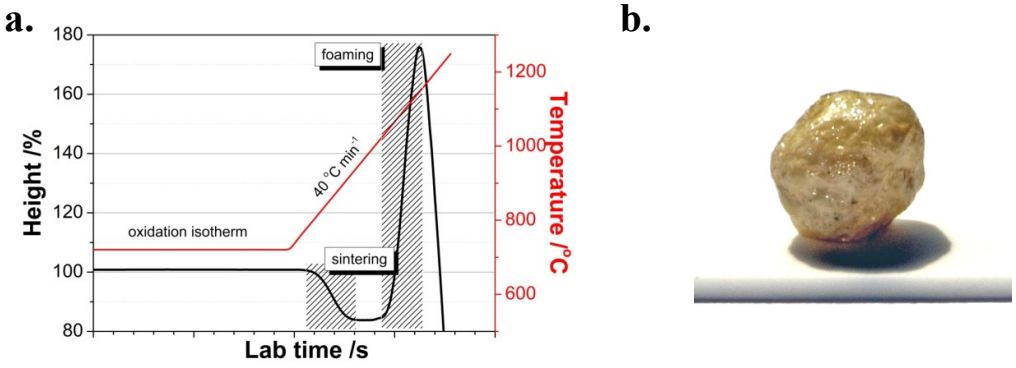


**Figure 1. a.** Thermal behavior curve of in-situ sintering and auto-catalytic foaming of a glass-ceramic sample with a programmed isothermal oxidation stage;
**b.** True-color digital photograph of glass-ceramic foam on an alumina substrate (as prepared).

A comparative representation of the effect of structural expansion due to reverse thermal reduction with or without a promoted oxidation isothermal stage in the HSM instrument is presented in Fig. 2a. The intentionally oxidized species is revealing a shift in the temperature of onset of foaming in the direction of lower temperatures (i.e. the foaming starts earlier) of approx. 15 degrees, which is more or less a desired technological advantage.
The effect of heating rate on the bloating process is graphically illustrated in Fig. 2b as a comparison between the temperature evolution curves of expansion with the used two extremal temperatures of linear heat treatment of 5 and 40 $^{o}$C min$^{-1}$ of a preliminary oxidized sample in a single thermal treatment run. The maximum of foaming is shifted to higher temperatures with the high rate of heating of about 25 degrees.

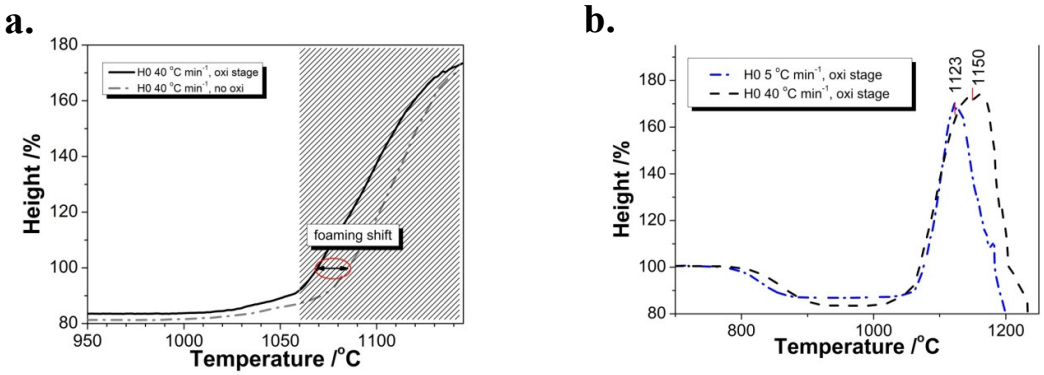


**Figure 2. a.** Effect of the oxidation stage on the foaming trend;
**b.** Effect of the oxidation stage on foaming peak performance.

The obtained infrared transmission spectrum is relatively pure and simple, and highlights the presence of silica ($SiO_2$) and calcium oxide (CaO), both constituting the composition of the thermally synthesized material, as it is presented graphically in Fig. 3. Here are evaluated the main peaks constituting the infrared spectrum of the final foam material.

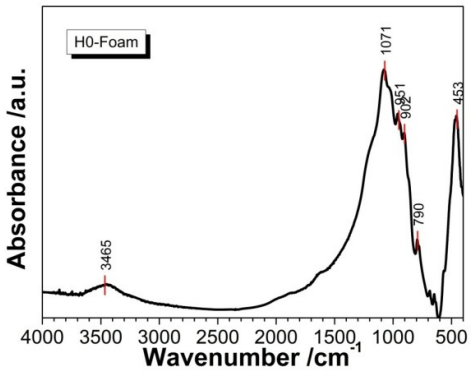


**Figure 3.** Infrared spectrum of a recycled sintered glass-ceramic foam sample.

The analyzed and assigned frequencies of normal infrared vibrations are summarized in Tab. 1 and have been subject to reference with literature data.

**Table 1**. IR frequencies of normal vibrations of identified species.

| Species | Band measured, $\nu_m$ /cm$^{-1}$ | Band reference, $\nu_r$ /cm$^{-1}$ |
|---|---|---|
| Si-OH, $H_2O$ | 3465 | 3425 [3] |
| Si-O-Si (siloxane) sym., asym str. | 1071, 951 | 1087 [4], 1040 [5] |
| CaO | 902 | 875 [4] |
| Si-O bending | 790 | 802 [3], 820 [5] |
| Si-O rocking | 453 | 455 [3], 450 [5] |

**Conclusions**

The study shows that by proper engineering of a single heat treatment run, a recycled glass-ceramic material with fire-resisting features up to 1100°C can be successfully obtained in-situ in a laboratory HSM instrument. This could be considered as a very satisfactory result as it is previously discussed in [1].

The foaming performance of the sample obtained with higher rate of 40 oC min-1 is higher compared to lower heating rates. It is worthy to use a programmed preliminary oxidation stage when working with higher linear heating rates.

We have observed the typical chemical bonds in the IR spectrum of the recycled foam. The obtained spectrum is similar to those of the initial glass.

In presented investigation the authors have shown the possibilities for carrying out successful synthesis of well densified materials with the option of a subsequent structural expansion if desired by the industry.

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