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# Eco-efficient melting of glass frits by concentrated solar energy

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ABSTRACT

This research aims to study the feasibility of applying real concentrated solar radiation to achieve the energy needed for melting glass frits. For this purpose, five glass compositions corresponding to different types of commercial frits were prepared. For comparison, the batches were melted by both in a solar furnace using concentrated solar energy (CSE) and in an electric furnace. The final frits were characterised by means of X-ray Fluorescence, X-ray Diffraction, Differential Thermal Analysis, Field Emission Scanning Electron Microscopy and Fourier Transformed Infrared Spectrometry. Results show that the frits prepared by CSE present short-range order, thermal behaviour and microstructure analogous to frits prepared in electric furnace. Moreover, the use of CSE for manufacturing glass frits reduces the melting time in about 80%, which leads to both lower corrosion of crucible wall and lower boron volatilization.

## 1. Introduction

Glass frits are glassy materials prepared by melting a mixture of raw materials at high temperature. Frits are the main component of nearly all ceramic glazes and they are also present in many compositions of different materials where a glassy phase is needed as binder. Currently, on the market there are many varieties of frits, with different fusibility, brightness, opacity and shading characteristics.

Nowadays, the production of frits is conducted in continuous melting furnaces and common temperatures in furnaces ranging between 1350 and 1550 °C. Once the raw materials batch is melted, it is cooled on water at high cooling rate; thus, the melt solidifies as small pieces of glass. This melting process implies a significant energy consumption and low efficiency and productivity of the process.

Frit manufacture is a highly intensive energy process, requiring high temperature usually provided by burning fossil fuels. The highest energy consumption of the process occurs inside the melting oven; in general, the energy necessary for melting accounts for over 75% of all energy consumed in the frit manufacturing process. The theoretical energy required to convert the raw materials mixture into glass is around 2.7 GJ/t (Trier, 1987; Scalet et al., 2013). This theoretical value takes only into account the chemical heat of reaction and the enthalpy changes associated with heating up the batch from room temperature to the melting temperature. However, from a practical point of view it is required to overcome heat losses linked with upholding the glass melt temperature. The real energy consumption for modern industrial glass melting can vary from 3.5 to 40 GJ/t depending on furnace design and scale (Scalet et al., 2013). Thus, it is of great importance to search new sustainable melting techniques for diminishing the use of non-renewable energy.

In that sense, solar energy is nearly limitless and it can be concentrated to promptly supply high temperature. Important research work has been carried out aimed to use concentrated solar energy (CSE) in different industrial processes, such as the production of lime from limestone (Meier et al., 2005), alumina from boehmite (Padilla et al., 2014) and anhydrite from gypsum (López-Delgado et al., 2014). CSE has also been applied for sintering of alumina (Román et al., 2008) and cordietie-based ceramics (Costa Oliveira et al., 2005) and to metallurgical processes such melting of aluminium from aluminium scrap (Funken et al., 2001), production of titanium foams (García et al., 2016) recovery of zinc from zinc containing materials, (Tzouganatos et al., 2013) tempering of steels (Vázquez et al., 1991), production of titanium nitride (Sierra and Vázquez, 2005) and stainless steel (de Damborenea et al., 1994) coatings, welding of steels and titanium alloys (Romero et al., 2013) and thermal shock tests on intermetallic materials (Morris et al., 2015). However, no research has been previously conducted aiming to use CSE for producing glasses or glassy materials such as glass frits or glass enamels. Recently, the feasibility of using high flux solar simulator to provide a sustainable source of process heat for glass production was investigated (Ahmad et al., 2014). Initial experiments involved melting a ternary common soda–lime–silica (SLS) glass batch, which demonstrated that rapid and full conversion of the crystalline

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raw materials into an X-ray amorphous vitreous state was possible. The possibility of apply CSE to create a light-beam technology for obtaining art objects with a glass enamel coating has been also explored (Otmakhov, 2015). However, it is necessary to point out that the last two works did not use real CSE to achieve the necessary process energy. Instead, a high flux solar simulator consisting of xenon arc lamps, whose radiation spectrum is close to the solar spectrum, was used as sources of heat.

The aim of this research is to study the feasibility of applying real concentrated solar radiation to achieve the energy needed for performing, in only one step, the preparation of glass frits of different typology, from the raw materials. Thus the process includes decarbonation, melting and homogenization of molten fluids. To our knowledge, it is the first time that such a study has been undertaken.

## 2. Experimental

### 2.1. Materials and method

Five glass compositions were formulated with the aim of preparing different types of commercial frits, namely, crystalline (C); white of zirconium (WZr); middle fusibility (MF); fluxing (F) and matte of titanium (MTi). The compositions of the starting frits are shown in Table 1. Moreover, for evaluating the efficacy of concentrated solar radiation (CSE) for melting and homogenisation of molten fluids with different viscosity, the theoretical melting temperature ($T_m$) for the studied compositions, was determined according to the Fluegeĺs Model for predicting the complete viscosity curve of glasses, by using polynomial functions for estimating the temperature-viscosity behaviour of silicate glasses from their chemical composition (Fluegel, 2007). The melting temperature is considered as that at which the viscosity of molten glass is $10^2$ dPa s. Calculated $T_m$ values are also reported in Table 1.

The raw materials used to prepare the glasses were: silica sand with low contents of iron oxide and reagent grade oxide such as $Al_2O_3$, $B_2O_3$, ZnO, PbO and $ZrO_2$. To complete the glasses composition alkali and alkaline earth elements were introduced as reagent grade carbonates. Mixtures were homogenised in a planetary ball mill (TURBULA) for 15 min. In order to compare the properties of frits obtained by melting in a solar furnace using concentrated thermal radiation, the same experiments were carried out using a conventional electric furnace. In both cases, experiments were performed using tabular alumina crucibles and 35 g of the mixture of raw materials. After the required time to complete the decarbonation, melting and homogenization stages, the glass frits were obtained by pouring the low-viscosity melts into cool water.

For experiments carried out by CSE, a Medium Size Solar Furnace (MSSF) of CNRS-PROMESS Solar facilities (Font Romeu-Odeillo, France) was used. The solar furnace of 0.9 kW equipped with a vertical axis parabolic reflector of 1.5 m diameter produces a focal spot, ca. 15 mm in diameter, with a very high power density (1000 W/m$^2$). To control the incident solar radiation a shutter is positioned between the parabolic concentrator (placed in a 6th floor level) and the heliostat (placed on first floor level). Temperature was measured by a type K thermocouple, which was positioned at half height of crucible. This vertical configuration is the only one that allows the heat treatment of powdered materials. Fig. 1 shows the crucible receiving the solar radiation concentrated by the parabolic reflector.

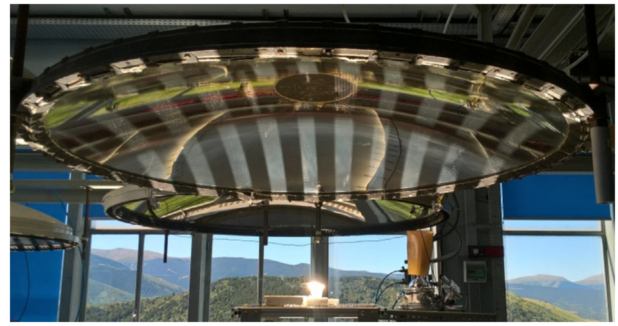

**Fig. 1.** Parabolic solar concentrator.

The temperature-time register followed for the experiment to produce glass frits in both the electric furnace and the solar furnace are shown in Fig. 2. In the case of the experiments with CSE, the temperature was registered by a thermocouple placed outside in the crucible bottom.

**Table 1**
Starting chemical composition (wt. %) of the investigated glasses.

| | C | WZr | MF | F | MTi |
|---|---|---|---|---|---|
| $SiO_2$ | 50 | 50 | 40 | 50 | 40 |
| $B_2O_3$ | 15 | 15 | 10 | 20 | 20 |
| $Al_2O_3$ | 4 | 4 | 2 | – | 2 |
| $Na_2O$ | 3 | – | 4 | 10 | 2 |
| $K_2O$ | – | – | – | 10 | – |
| $Li_2O$ | 3 | 7 | 3 | – | 2 |
| CaO | 8 | 4 | 6 | 10 | 2 |
| BaO | 2 | 2 | 2 | – | 25 |
| ZnO | 5 | 8 | 3 | – | 7 |
| PbO | 10 | – | 30 | – | – |
| $ZrO_2$ | – | 10 | – | – | – |
| $T_m$ (°C) | 993 | 1079 | 822 | 880 | 885 |

### 2.2. Characterization techniques

Glass frits were characterised for determining if the type of energy, power density and thermal schedule used in their preparation lead to materials with the same physical-chemical characteristics. The chemical analysis of frits was determined by X-ray fluorescence (XRF) using a Bruker S8 Tiger spectrometer. The analysis was performed on pressed pellets of powder glass samples (< 63 µm). $B_2O_3$ and $Li_2O$ were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) in a Varian 725-ES equipment. The evaluation of the amorphous nature of the frits after melting was performed by X-ray diffraction (XRD) using Bruker D8 Advance equipment with Ni-filtered Cu Kα radiation operating at 30 mA and 40 kV. Data were recorded in the 5–60° 2θ range (step size 0.019732° and 0.5 s counting time for each step).

The thermal stability of the glass frits was analysed by differential thermal analysis (DTA) on both powder (< 63 µm) and bulk or

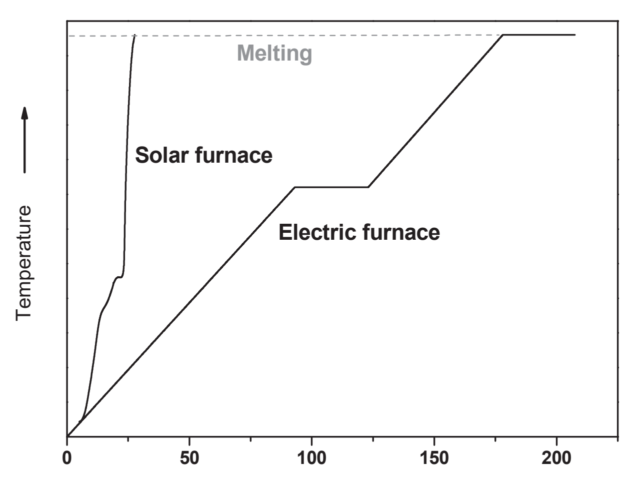


**Fig. 2.** Temperature-time schedule used for raw materials melting in both solar and electric furnace.