In-situ synchrotron microtomography reveals multiple reaction pathways during soda-lime glass synthesis

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Ultrafast synchrotron microtomography has been used to study in-situ and in real time the initial stages of silicate glass melt formation from crystalline granular raw materials. Significant and unexpected rearrangements of grains occur below the nominal eutectic temperature, and several drastically different solid-state reactions are observed to take place at different types of intergranular contacts. These reactions have a profound influence on the formation and the composition of the liquids produced, and control the formation of defects.

I. INTRODUCTION

Many commonplace materials are manufactured from a loose packing of coarse reactive grains. Among such materials, window-glass production relies on synthesis from a mixture of quartz sand, sodium carbonate, and calcium carbonate. Industrial synthesis of good-quality soda-lime glass is generally carried out at 1400 – 1500°C, despite the fact that typical compositions are completely molten at 1050°C. Such high temperatures are required to eliminate defects (gas bubbles and unmolten sand grains), and to homogenize the melt. Parameters such as the grain size of raw materials are known to influence the quality of glasses [1-4]. However, little direct information is available concerning the complex interplay between the geometry of the system and the rate of chemical reactions taking place during the earliest stages of melting.

In this respect, in-situ high-temperature tomographic X-ray imaging [5] is a potentially powerful technique as it provides the possibility to: a) quantitatively describe the distribution of grains and the nature of solid-solid contacts in the initial pile; b) identify where and at what temperature reactions between grains occur; c) quantify the extent to which these reactions occur. This technique has been employed in the past to study the evolution of powder compacts during the sintering of glass beads [6] or metallic powders [7]. However, no tomographic data have been acquired concerning a high temperature system involving chemical reactions between grains and the irreversible formation of a liquid.

II. EXPERIMENTAL PROCEDURE

An in-situ microtomography experiment has been performed on the ID15A beamline at the European Synchrotron Radiation Facility (ESRF). We used white X-ray radiation with a peak photon energy of 40 keV. The spatial resolution was 1.6µm. A mixture of Roncevaux silica sand, Solvay® sodium carbonate and Saint-Germain calcium carbonate was poured into a 2-mm-diameter silica crucible. Weight percentages of these three materials were 64, 19 and 17 respectively, and each material had a characteristic grain-size of: 160 – 200 µm, 250 – 320 µm, and 80 – 100 µm for sand, sodium carbonate and calcium carbonate respectively (see Fig. 1a and Supplementary Materials). All of the 175 grains in the analyzed volume at room temperature have been identified and segmented (see Supplementary Movie). In order to obtain quantitative information, 3-D volumes have been processed and segmented (see Supplementary Materials). All of the 175 grains in the analyzed volume at room temperature have been identified (see Fig. 1a). Sodium carbonate grains are characterized by their large internal porosity (red grains in Fig. 1a).

III. RESULTS AND DISCUSSION

Our data reveal the importance of solid-state reactions before the first appearance of melts. Between room temperature and 750°C, many sodium carbonate grains have unexpectedly broken up (Fig. 1b). This dramatic change in morphology continues with increasing temperature, as illustrated in Fig. 2 for the reaction between a sodium carbonate grain (in red), and two sand grains (in yellow and blue). As temperature increases, the original sodium
that the occurrence of such solid-state reactions is conditioned by the proximity of sand and calcium carbonate to sodium carbonate. Consideration of the statistics of contact types demonstrates that in the initial packing, 28 sand grains (out of 108) and 18 calcium carbonate grains (out of 56) did not have any contact with a sodium carbonate grain. The volumes of 47 individual silica grains have been compared at room temperature and at 760 °C (Fig. 4). These grains are a mixture of grains with and without contacts with sodium carbonate. We find that a little over 30 of these grains show a volume increase of 0.05 of the fraction \( c \) of solid sodium carbonate and silicate phase incorporated into its larger neighbor, suggesting the formation of a double carbonate. At 825 °C, the eutectic melting of sodium carbonate and the double carbonate produces a carbonate liquid, as shown by the absence of porosity on the right part of the grain.

![FIG. 1.](image1)

FIG. 1. (a) Slice through the reconstructed 3-D volume of the pile of raw materials at room temperature. The segmented volumes of sand, sodium carbonate and calcium carbonate grains have been coloured in yellow, red and green respectively. The top-right quarter has been left uncolored to show the original slice. (b-d) Slice through the same plane as in (a), at 760 °C, 860 °C, and 905 °C. Fragmented sodium carbonate grains react with sand to produce porous crystalline silicates (panel b), and rare liquid bridges (white arrow in panel b). Further increase in temperature leads to formation of a significant proportion of liquid (panel c), finally reaching a state in which the granular packing is transformed into a viscous melt with bubbles and grain inclusions (d).

![FIG. 2.](image2)

FIG. 2. Top- and side-view of one sodium carbonate grain (red) and two sand grains (yellow and blue) at four different temperatures, that react together to form silicates (white). For the sake of clarity, neighboring grains have not been represented.

![FIG. 3.](image3)

FIG. 3. (a-c) Evolution of two neighboring grains of sodium carbonate (large grain at the center) and calcium carbonate (small grain on the right) at room temperature, 760 °C, and 825 °C. The calcium carbonate grain (delineated in yellow in (b) and indicated by the presence of additional facets) is incorporated into its larger neighbor, suggesting the formation of a double carbonate. At 825 °C, the eutectic melting of sodium carbonate and the double carbonate produces a carbonate liquid, as shown by the absence of porosity on the right part of the grain.

![FIG. 4.](image4)

FIG. 4. (a) Relative volume growth of sand grains between room temperature and 760 °C, sorted by increasing volume loss. Full (resp. hollow) circles correspond to sand grains with (resp. without) sodium carbonate neighbors. (b) Evolution of the fraction \( c \) of solid sodium carbonate and silicate phase with increasing temperature. Two major drops occur around the eutectic temperatures between sodium metasilicate (NS) and sodium disilicate (NS\(_2\)), and the melting temperature of sodium carbonate.
8% ± 2% (dotted line in Fig. 3b) corresponding to that expected from the α to β transition of quartz. On the other hand, approximately one third of the original sand grains have experienced a volume increase smaller than 8%, or even a significant volume decrease. The grains concerned are found to be systematically surrounded by the fine grained phase produced from sodium carbonate. It is found that at least one sodium carbonate neighbor at room temperature is a necessary but not sufficient condition for a sand grain to have decreased in size at 760°C. Only about one half of the original sand-sodium carbonate contacts are concerned by a loss in volume of the sand grain at 760°C, probably because some of the contacts are lost when sodium carbonate starts reacting and moving, as illustrated in Fig. 2. Concerning calcium carbonate, given the large fraction of sand and the reaction-induced elimination of sodium carbonate (Fig. 2), the majority of calcium carbonate grains are not in contact with sodium carbonate. Such grains isolated from Na$_2$CO$_3$ are observed to simply lose their CO$_2$, producing refractory grains of CaO (Fig. 3b), in contrast to the reactive pathway shown in Fig. 3.

The appearance of the first melts appears to be determined by the solid-state reactions. Even at 760°C certain sand grains show textural evidence for the presence of a small amount of liquid (highlighted by the arrows in Fig. 1b), despite the fact that the lowest stable eutectic in the Na$_2$O – SiO$_2$ system is at 790°C.[11, 12]. The presence of liquid at such low temperature may be explained by the existence of a metastable eutectic between sodium metasilicate and silica (see Supplementary materials). Quantification of the amount of liquid is not possible directly, but may be estimated indirectly from the evolution of the amount of texturally distinctive sodium carbonate and associated secondary phases (e.g. Fig. 1b). The proportion of these porous phases increases up to 820°C (Fig. 3), interpreted to reflect the conversion of sand grains to sodium silicates. From 760 to 820°C, we observe in places a scarce production of liquid between some of the sand grains; nevertheless, the production of crystalline phases is much more important than the production of liquid, as shown by Fig. 4b. Despite the large fraction of silica in the final glass composition (75%), we do not observe any significant formation of melts around 790°C, the eutectic temperature between silica and sodium disilicate. However, at 820°C there is a sharp drop in the proportion of porus phases, and clear appearance of a significant amount of liquid around sand grains previously covered by a layer of fine-grained porous phase (Fig. 1b). This temperature corresponds to the equilibrium eutectic between sodium metasilicate and sodium disilicate. The formation of this sodium-rich liquid is less favorable for glass melting than formation of the silica-sodium disilicate eutectic, which contains more silica, thus resulting in greater consumption of crystalline silica. These observations therefore provide strong indirect evidence in favor of the low temperature formation of both crystalline Na$_2$SiO$_3$ and Na$_2$Si$_2$O$_5$. An even more abrupt decrease in the fraction of the fine grained porous phase is observed at 865°C (Fig. 4b), corresponding to the melting of sodium carbonate. The proportion of porous solids drops rapidly to zero afterwards. Also, visual inspection reveals that at 825°C, the porosity of the few sodium carbonate grains that have cemented to neighboring calcium carbonate grains (Fig. 3b) is suddenly invaded by the presence of a liquid (Fig. 3c). This temperature agrees well with the incongruent melting temperature of the Na-Ca double carbonate at 820°C.[10, 13].

Finally, our data offer insights into the generation of defects. Quartz grains not surrounded by porous sodium carbonate or silicates below 820°C are found to have approximately the same size at 950°C as at room temperature. It is undoubtedly this population of grains that will remain as high temperature solid defects because of slow local diffusion. In the same way, enhancing the formation of Na-Ca double carbonate will act to eliminate the generation of CaO.

In summary, these in-situ observations combined with quantitative image processing reveal unprecedented processes of glass melting. From a physical point of view, the importance of direct observation is exemplified by the unexpected and dramatic effect of solid-state reactions on the spatial distribution of sodium carbonate, changes in microstructure that in turn lead to accelerated reactions compared to a fixed geometry. From a chemical point of view, many excursions from overall thermodynamic equilibrium are observed. Short range packing arrangements have a profound influence on local reaction pathways, as most eloquently illustrated by the divergent fates of different calcium carbonate grains. The occurrence of different reactions at different places strongly encourages the use of a spatially-resolved technique such as tomographic imaging in order to study glass melting. Other metastable phenomena include the generation of liquids well below those predicted by the equilibrium phase diagram, and the observation of a eutectic transition in the Na$_2$O-SiO$_2$ phase diagram, which is not the closest eutectic to the mean composition.

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