In-situ synchrotron high resolution powder diffraction: the mullite formation and the role of quartz grain size in traditional ceramic

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Ceramic manufacturing is one of the key industries within the global market, with the sanitary-ware subsector representing about 6% of European ceramic production [1]. During this process, a blend of raw materials (clay, fluxes and filler) reacts during a high temperature process to form the fired body, which consists of a glassy phase (up to 65 wt.%), residual quartz, and mullite. This specific mineralogical composition provides the required technological properties to the final products. For our research, we exploited synchrotron high resolution powder diffraction technique at the ID22 beamline (ESRF, Grenoble [2]) to investigate two cases of interest.

The first case is represented by the kinetic mechanisms of mullite formation by in-situ isothermal analysis. Specifically, 'dried' samples were heated from room temperature (RT) to the target temperatures (1080 °C, 1090 °C, and 1100 °C) by an induction furnace. At each temperature, high-resolution diffraction patterns were collected continuously with a time resolution of 5 minutes, starting from t_0 (prior to mullite formation) until the completion of the crystallization process. For each diffraction pattern, the integrated intensities of the (110) and (121) mullite Bragg reflections were determined. The evolution of these integrated areas was used to calculate the reaction rate (α) as a function of time. To describe the kinetic mullitisation, the Avrami model [3] was applied, allowing us to determine the apparent activation energy, which resulted in the 166.2-310.3 kJ/mol range. The high resolution was essential to discern and resolve peak overlapping, which is critical in such complex multi-phase systems.

The second case of interest is focused on the thermal expansion behavior of quartz in the fired body, especially when raw quartz particle size distribution is different. To do this, high resolution patterns were collected on fired body with coarse (V_0) and with fine (V_{0_f}) quartz. Measurements were performed from 22 °C up to 500 °C, every 100 °C and from 520 °C to 600 °C, every 10 °C, and back at RT, using a hot air blower heating system. The presence of two different types of quartz was pointed out: a regular one and a strained one, as evidence by Rietveld refinement with Topas [4]. In both V_0 and V_{0_f} samples, the $\alpha_{L,quartz}$ and unit cell volume values for regular quartz were consistent with those reported by Carpenter et al. [5]. In contrast, the strained quartz exhibited a lower $\alpha_{L,quartz}$ in the range 22-600 °C, in particular it resulted 21.9 x 10^{-6} C^{-1} in V_0 and 20.9 x 10^{-6} C^{-1} in V_{0_f}, indicating the presence of internal lattice distortions. This was related to larger unit cell volume at RT in both V_0 and V_{0_f} samples (113.839 Å³ in V_{0_f} and 113.744 Å³ in V_0), compared to the regular type (113.036 Å³). These results partially agree with previous studies, as they did not explain the larger linear thermal expansion coefficient of the body (α_{BODY}) measured by dilatometer for V_{0_f} fired body compared to V_0 [6], indicating that the ceramic body thermal expansion is complex. Another aspect is that unit cell volume differences between strained and regular quartz decrease near the α-β transition as peaks become sharper and the strained component reduces (see Figure 1.)

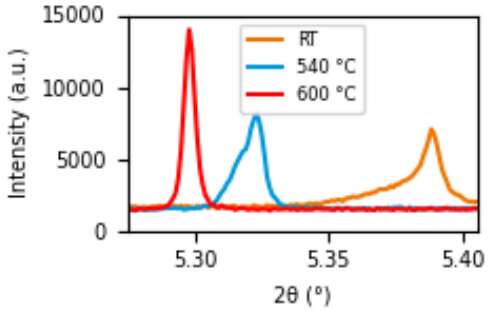


***Figure 1**. Evolution of the (101) quartz peak during heating at RT, 540 °C and 600°C in the sample V_0.*

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[5] Carpenter, M. A., et al., (1998). 83(1-2), 2-22. 33.
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