ESRF	**Experiment title:** Coupling of diffuse scattering and monoclinic – tetragonal structural phase transition into pure zirconia: an in-situ high-temperature study.	**Experiment number**: 02-02-836
Beamline: BM02	**Date of experiment**: From 2016, June 8 to 2016, June 12	**Date of report**: Fev., 2017
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Report:

Aim

The studied samples were part of large zirconia blocks elaborated through a specific fused cast process developed by the St Gobain company in order to manufacture large bricks (sub-meter scale) used as refractory components in industrial furnaces devoted to the production of glass. During the cooling process, after solidification at high temperature (2700 °C) zirconia is cubic ($Fm\bar{3}m$ space group). Under normal pressure, a cubic–tetragonal transition occurs at lower temperature (2300 °C). The tetragonal phase ($P4_2/nmc$) transforms into the monoclinic one ($P2_1/c$) at 1150 °C. This last structural phase transition (SPT) is accompanied by a spontaneous large volume increase inducing large stresses [1] which strongly modify the temperature of the phase transitions and induces the formation of microcracks. The microstructural characteristics and the thermomechanical properties of the material are strongly related to the successive SPTs and the induced stress states [2, 3]. We had shown during a previous experiment (see the experimental report of the proposal 20150520) that the monoclinic zirconia reciprocal space are characterized by the presence of a large diffuse scattering signal related to the strain state [4]. The aim of this experiment was to determine through in-situ high-temperature XRD measurements the coupling between the monoclinic-tetragonal SPT and this diffuse scattering signal. The experiments were conducted using the new prototype furnace developed in the frame of the QMAX research program (ANR-09-NANO-031-01) and available at the BM02 beamline. 3D reciprocal space mapping was done at 17.9 keV (just before the zirconium absorption edge) using the XPad 3.1 detector allowing a direct 2D collection of diffraction and diffuse scattering signal. The samples are made of large zirconia areas embedded in a glassy phase and made of a very large number of zirconia crystals. We have shown previously that such an area is corresponding to one initial cubic zirconia crystal [2]. The size of the primary x-ray beam was chosen in such a way that roughly only one area was probed during the experiment (see fig. 1). One 2D map recorded at room temperature before the thermal treatment is reported fig. 2. Because to the texture inherited to the successive SPTs, the Debye-Scherrer rings are very spotty. All the experimental work was concentrated on the determination of the evolution of the diffuse scattering signal around the $\bar{1}11_m$, 111_m and 111_t reciprocal space nodes.

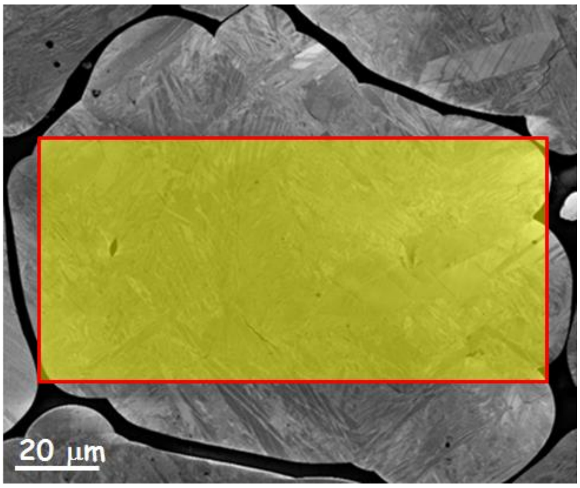


Fig. 1. SEM observation of the sample microstructure. The rectangle is corresponding to the imprint of the primary x-ray beam.

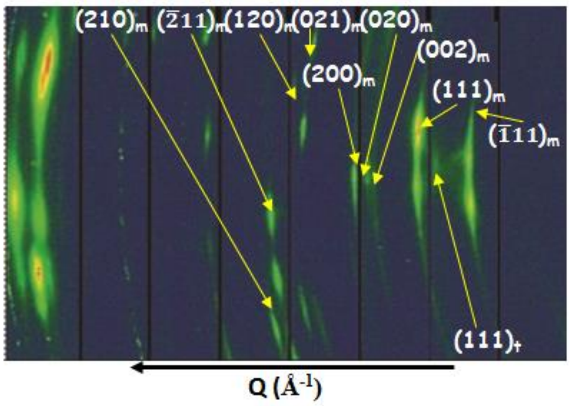


Fig. 2. 2D map recorded at room temperature before the thermal treatment.

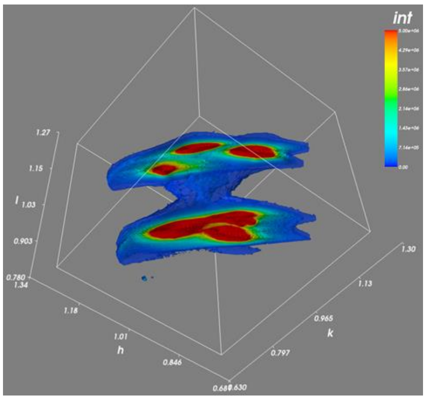
Experiment

The measurements were realized onto as elaborated samples, i.e. without any post elaboration thermal treatment. Because of the strong texture, we were able to define an orientation matrix of a probed volume similar to that one showed fig.1. In all the cases the measurements were centered on the 111_t node. At each considered temperature two hundred 2D maps were recorded in roughly 1 hour during isothermal treatment. The 3D maps were reconstructed using a python routine developed on the beamline.

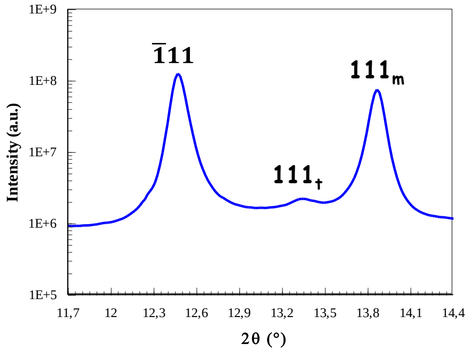
The 3D reciprocal space map around the 111 nodes recorded at 500°C during the heating of the sample is reported fig. 3a. First of all, a 3-fold picture clearly appears both for the 111_m and the $\bar{1}11_m$ nodes. Such observation is illustrating the loss of the 3 fold axis of the initial cubic <111> directions[1]. The split of the 111_t node into the $\bar{1}11_m$ and 111_m nodes result on a clear twinning process. The diffuse scattering signal clearly is spread continuously between the opposite monoclinic nodes and cut the tetragonal 111 node.

Because the spreading of diffuse scattering is quite large the contributions associated with each split nodes are clearly partially superimposed each other's. We thus integrated the whole signal along the 2θ angle (see fig. 3b). Large diffuse signal joining the three nodes is observed, it illustrates the distribution of the 111 d-spacing.

We recorded a number of 3D maps both during the heating and the cooling process. Some of those maps are reported fig.4. At high temperature, the signal is dominated by the tetragonal contribution and the diffuse scattering has disappeared. The interesting point is that it didn't reappear after the cooling to the room temperature. We interpret this observation by a stress relaxation process during the M→T phase transition.



(a) The whole 3D map around the 111 nodes



(b) 1D scan of the whole intensity observed in the 3D map and integrated along the 2θ angle.

Fig. 3. 3D reciprocal space map recorded around the 111 nodes at 500°C during the heating. The map is centered onto the location of the 111_t node.

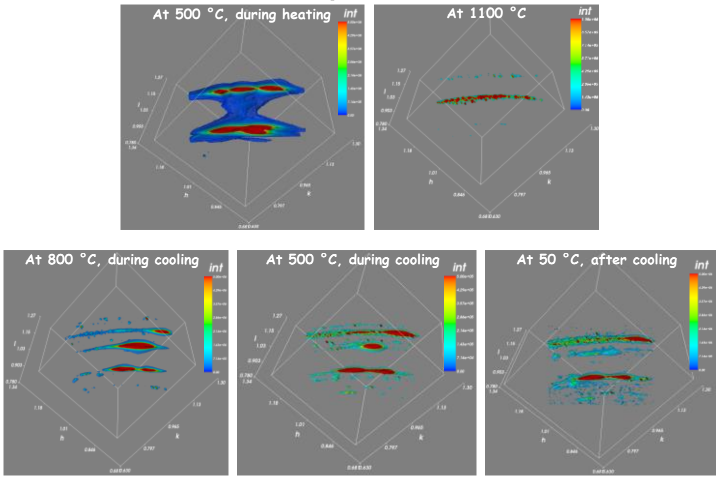


Fig. 4. Some of the 3D maps recorded in-situ during the heating and the cooling process.

References

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[1] It is important to note that, in order to describe the phase transitions, all along this report all the zirconia crystals are indexed respect the cubic setting.