ESRF	**Experiment title:** In situ X-ray diffraction study of the Spark Plasma Sintering process under very high pressure	**Experiment number**: **MA-2752**
Beamline: ID27	**Date of experiment**: from: 06 May 2016 to: 10 May 2016	**Date of report**: 06 April 2020
Shifts: 12	**Local contact(s)**: Mohamed Mézouar	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

LE FLOCH Sylvie*, Institut lumière matière UMR 5306, CNRS & Université Claude Bernard Lyon 1 Campus LyonTech- La Doua, Bât. Kastler, 10 rue Ada Byron, 69622 Villeurbanne Cedex, France

PAILHES Stéphane*, Institut lumière matière UMR 5306, CNRS & Université Claude Bernard Lyon 1 Campus LyonTech- La Doua, Bât. Kastler, 10 rue Ada Byron, 69622 Villeurbanne Cedex, France

LE GODEC Yann*, IMPMC Inst. Minér. et de Physique des Milieux Cond. CNRS & Sorbonne Université, 4 place Jussieu, 75252 PARIS Cedex 05, France

LARGETEAU Alain*, ICMCB Institut de Chimie de la Matière Condensée UMR 5026, CNRS & Université de Bordeaux, 87 avenue du Dr Albert Schweitzer, 33608 PESSAC Cedex, France

Report:

The Spark Plasma Sintering (SPS) is a sintering technique under moderate pressure and at high temperature (up to 2000°C). It allows the production of bulk materials by densification of powders in shorter times and at lower temperatures compared to conventional processes. The originality of this technique is based on the use of a pulsed current of several thousand amperes which goes through the graphite mold containing the sample, or even the sample itself if it is conductive. The heating induced by the Joule effect is therefore very fast (up to 1000 ° C / min). The current SPS technique is limited to a pressure of 150 MPa (or 400 MPa with WC mold). However, it has been shown that increasing the pressure can significantly lower the powder densification temperature. Lowering the processing temperature limits the granular growth and allows the elaboration of nanoceramics. In addition, the performance of the SPS process is recognized, but the mechanisms involved are still poorly understood and subject to controversy. The sintering chamber is inaccessible for *in situ* observation. Thus each optimization process needs numerous blind tests. To overcome these drawbacks, we have adapted a pulsed current heating to a Paris-Edinburgh press which allows reaching pressure as high as 10 GPa and is portable[1].

This experiment MA-2752, allowed us to install our SPS-HP portable device on the ID27 beamline (fig. 1). We followed, by *in situ* X-ray diffraction, the grain growth and the phase transition of a TiO_2 nanopowder (8 nm) during sintering. This type of real-time analysis is not possible on any other SPS device. It is a powerful means of studying the mechanisms involved in SPS process and optimizing the conditions of material sintering. Recently, two teams from Bordeaux and Krakow also produced SPS-HP devices by coupling pulsed current heating to a belt press (6GPa-1800°C) and a toroidal anvil device (8GPa -1800°C). However, these devices do not allow any temperature measurement inside the sintering chamber. During this *in situ* experiment at the ESRF, we obtained a good estimation of the temperature and pressure of the sample using the equation of state of the sample itself and a calibrant (gold) placed on the oven wall. With these first measurements, we highlighted the efficiency of heating by pulsed electrical current compared to direct electrical current (Fig.2 curves A and

C). We also observed that this efficiency is enhanced for a conducting sample (Fig. 2 curves B and D). We are still working on these data to find a physical explanation for these observations. We have also studied the influence the process parameters (P, T, heating rate) on the anatase rutile transition and the grain growth rate. Comparative experiments in the lab are still in progress. However, the process parameters deduced from these *in situ* experiments already allowed us to synthesize in the lab nanostructured Nb doped TiO_2 ceramics with controlled grain size. Their physical study demonstrates that nanostructuration enhances the thermoelectric properties[2].

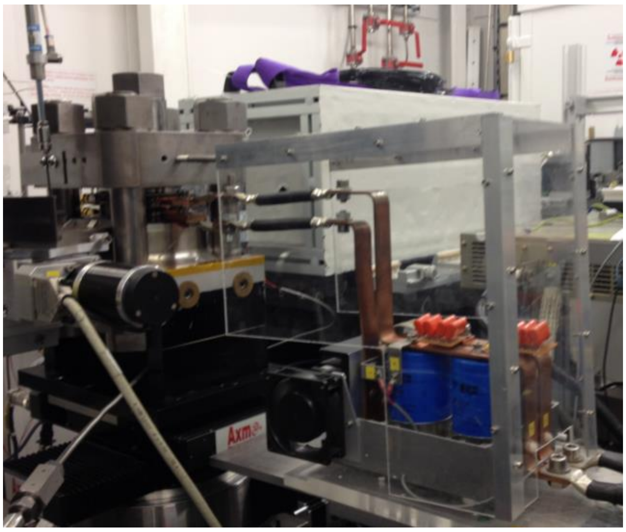

Figure 1 : Our portable high intensity pulsed current generator connected to the ESRF's Paris-edinburg V4 press .

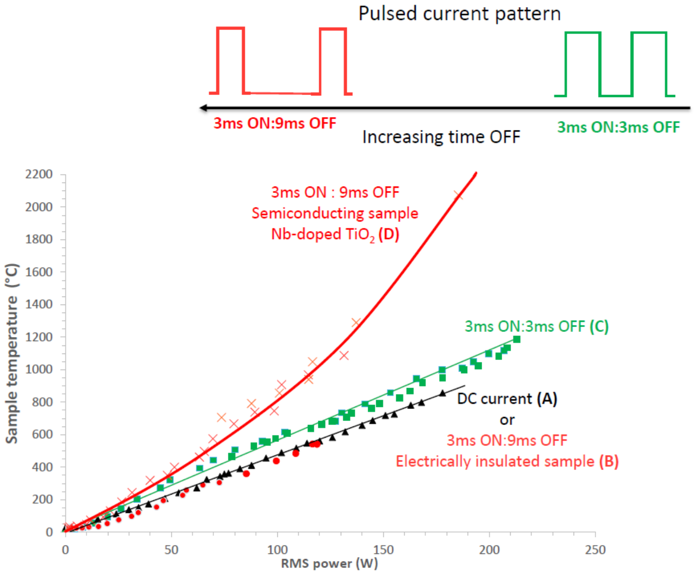

Figure 2 : Temperature of the heart of the sample versus RMS power of the current for different experimental configurations : (A) DC current- pure TiO_2 sample in the graphite heater; (B) Pulsed current- pure TiO_2 sample isolated from the graphite heater with a BN capsule; (C) Pulsed current- pure TiO_2 sample in the graphite heater; (D) Pulsed current- Nb-doped TiO_2 sample in the graphite heater. These four experiments were carried under 1 GPa.

This first in situ X-ray diffraction experiment allowed us to achieve the proof of concept of a real time analysis of a powder during a spark plasma sintering under high pressure. Our portable SPS-HP device coupled with synchrotron radiation is a new powerful tool to optimize the elaboration of nanostructured sintered materials.

[1] Y. Le Godec, S. Le Floch, S. Pailhes, J.-M. Combes, Device for sintering by pulsating current and associated method, WO 2018/083325 A1, 2018.

[2] A. Verchère, S. Pailhès, S. Le Floch, S. Cottrino, R. Debord, G. Fantozzi, S. Daniele, S. Mishra, Optimum in the thermoelectric efficiency of nanostructured Nb-doped TiO2 ceramics: from polarons to Nb-Nb dimers, Physical Chemistry Chemical Physics. (2020) submitted.