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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Peculiarity of the antiferrodistortive phase transition in nano- and micro-ceramics of strontium titanate	**Experiment number**: HC-653
Beamline: ID31	**Date of experiment**: from: 12/06/2013 to: 15/06/2013	**Date of report**: 12/02/2014
Shifts: 9	**Local contact(s)**: Caroline Curfs	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Hehlen Bernard, Laboratoire Charles Coulomb, University Montepllier 2
Maryam Al-Majzoub, Laboratoire Charles Coulomb, University Montepllier 2
J-M. Kiat, Ecole centrale Paris
Ali Al-Zein, ESRF

Report:

Four ceramics of $SrTiO_3$ (STO) with controlled grain size have been investigated. The first one corresponds to the commercial micrograin powder which has been sintered, and the three others have been obtained by ball-milling the aforementioned commercial material, either in ZrO_2 or WC (tungsten carbide) bowl, to reduce the grain size down to nanometers [Ref 1]. The obtained nano powders are then compacted under moderate pressure and sintered with different temperature cycles providing their final grain size. Two ceramics with grain size of 1-2 µm synthesized with slightly different routes (STOµm(ZrO) and STOµm(WC)) have been prepared. The third sample has a grain size of about 30 nm and is called STOnm(ZrO). The ceramics are then crushed into powder to use the 1mm diameter capillary at ID31. All experiments were performed at incident wavelength λ=0.4 Å.

Diffraction patterns were collected between 2θ=5° and 90° at five temperatures between 10 K and 300 K. In addition [400], [440], and [222] Bragg peaks, as well as [3/2 1/2 1/2] and [5/2 3/2 1/2] super-structure peaks, were recorded at more than 10 intermediate temperatures with special attention between 10 K and 150 K.

The lattice parameter of the two micrograin ceramics are shown in figure 1 (before instrumental corrections). One clearly observes a splitting on cooling, attributed in the bulk material to the well known cubic-to-tetragonal transition.

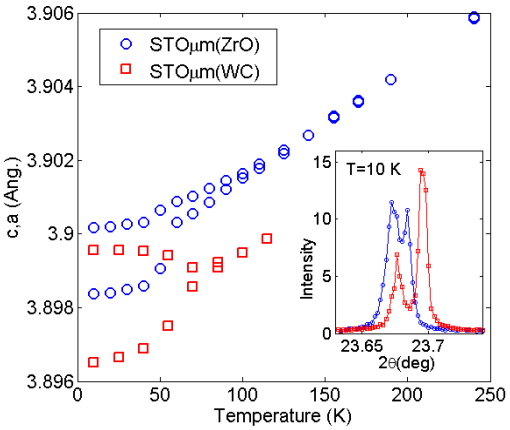

Figure 1: Lattice parameters and [400] Bragg peak at 10 K (inset) in two STO ceramics with same grain size.

However, it seems that the splitting occurs at ~140 K in STOμm(ZrO) and ~90 K in STOμm(WC), values which should be compared to T_c=105 K in the single crystal. This and the different temperature dependences point-out different structural properties between the two prepared ceramics.

These differences can also be observed in a plot of the tetragonal distortion c/a-1 presented in Fig. 2. The latter is compared to the square of the primary order parameter Φ corresponding to the tilting angle of the TiO_6 octahedra below T_c, and proportional to the area of the superstructure peaks. c/a-1 and Φ^2 overlap in STOμm(WC), and profile matching followed by a Rietveld refinement of the full diffraction pattern at 10 K is compatible with the tetragonal I4/mcm space group of a $SrTiO_3$ single crystal. On the contrary c/a-1 and Φ^2 do not match at all in STOμm(ZrO) suggesting a different crystalline structure in that sample.

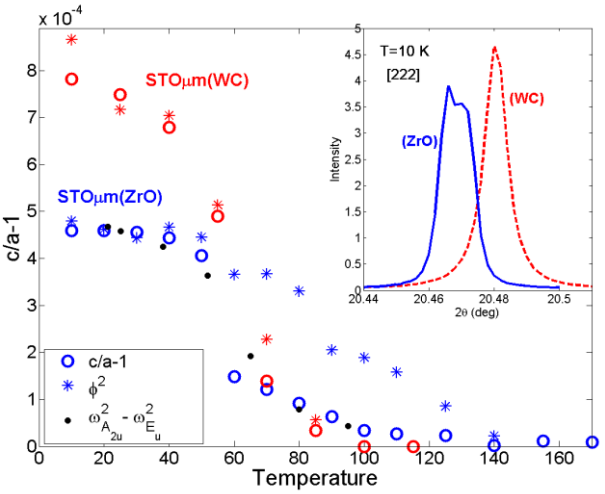

Figure 2: c/a-1 and Φ^2 in the two ceramics. The inset shows the [222] Bragg peaks at 10K, emphasizing the splitting in STOμm(ZrO).

This assumption is further supported by the splitting of the [hhh] Bragg peak at 10 K (Fig.2 inset) and by the strong broadening of the superstructure peak on cooling (not shown). It is worth noting that c/a-1 measured by X-ray diffraction matches with the soft TO-mode splitting, ω^2_{A2u} -ω^2_{Eu}, measured using hyper-Raman scattering [Ref 2]. For that sample the results of the profile matching and Reitveld refinement of the full diffraction pattern reveal that the structure is likely *orthorhombic* at 10 K with four competing possibility for the space group, three of them being polar and the other one not [Ref 3].

Diffraction patterns of the nanograin ceramic were also recorded. In that case the Bragg peaks are much too broad to observe any splitting limiting therefore a detailed analysis.

This experimental campaign has fully satisfied our expectations insofar it has been possible to measure simultaneously c/a-1 and Φ. It was a challenging experiment since the former deserves high resolution and the latter (very) high luminosity. Our analysis highlights pronounced differences in the structural properties of ceramics having the same grain size but synthesized by slightly different routes. In particular, it confirms the anomalous behavior of STOμm(ZrO) at low-T pointed-out previously by hyper-Raman scattering [Ref 2]. The refinement revealed that this sample exhibits an *orthorhombic* structure at low-T instead of the usual tetragonal one (I4/mcm). We believe this effect could be due to the strain field the shell imposes on the core grain. $SrTiO_3$ is a textbook example for phase transitions and the origin of these unexpected properties strongly motivates further investigations.

[1] J.-M. Kiat, C. Bogicevic, P. Geimener, A. Al-Zein, F. Karolak, N. Guiblin, F. Porcher, B. Hehlen, and R. Haumont, Phys. Rev. B **87**, 024106 (2013).

[2] B. Hehlen, A. Al-Zein, C. Bogicevic, P. Gemeiner, and J.-M. Kiat, Phys. Rev. B **87**, 014303 (2013).

[3] J.-M. Kiat *et al.* (in preparation).