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Experiment Report Form

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Reports on experiments relating to long term projects

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Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
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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:** Investigating the structure of polar nanoregions in relaxor ferroelectric $Sr_{1-x}Pr_xTiO_3$ using Pr-K edge differential PDF	**Experiment number**: CH4024
Beamline: ID22	**Date of experiment**: from: 27 giu 2014 to: 01 lug 2014	**Date of report**: 01 sept 2014
Shifts: 12	**Local contact(s)**: **Christina Drathen**	*Received at ESRF:*

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Report:

Ferroelectric (FE) perovskitic $ATiO_3$ oxides hold great scientific interests as well as potential for industrial applications in integrated microelectronics and memory storage due to their high dielectric constant and switchable electric polarization **[1].**

A new class of FE materials called Relaxor ferroelectrics has attracted a lot of interest. In Relaxor ferroelectric materials the disorder produced by chemical doping at both the A and B sites of ABO_3 lead to the formation of dipolar entities which can induced polar properties in the pristine paraelectric material. These dipolar entities can form polar nanoregions (PNRs) that exhibit dielectric relaxation in an applied *ac* field.

FE ordering in relaxor ferroelectric system occurs below room temperature **[2]** but in $Sr_xPr_{1-x}TiO_3$ the existence of FE phase was reported at room temperature **[3]**,**[4]**. The evolution of the $Sr_xPr_{1-x}TiO_3$ stucture and dieletric properties upon doping has been reported by some authors but a direct structural evidence of PNRs in the system was not reported to date.

We performed XRPD measurements for pair distribution function (PDF) analysis by considering different data collection strategies.

In the first part of the experiment, the aim was to determine the local and medium range structure of $Sr_{1-x}Pr_xTiO_3$ sample by using the differential PDF approach **[5]**. We focused our attention on the x=0.15 composition and we collected diffraction data at two different wavelength λ_1, λ_2 just below and below the Pr absorption edge. Differential PDF measurements were repeated at three different temperatures to follow the temperature evolution of the Pr-sensitive PDF. Data are still under analysis to extract properly the differential structure factor **[5]** at each temperature.

In the second part of the experiment, we performed total PDF measurements at six temperatures between 100K<T<500K for x=0 and x=0.15 (SPTO15) covering a Q range with Qmax~28Å^{-1} (λ=0.35422(1) Å). Shorter XRPD patterns for Rietveld refinements have been collected at every 10K in the same T range.

At room temperature we confirm the tetragonal structure (s.g. I4/mcm) for SPTO15. With increasing temperature, we found a structural transition from I4/mcm to Pm-3m space group occurring at T_C~450K.

The tilting angle (ϕ) between TiO_6 units is the main order parameter of this structural phase transition. The temperature evolution of the refined ϕ are shown in Fig.1(a).

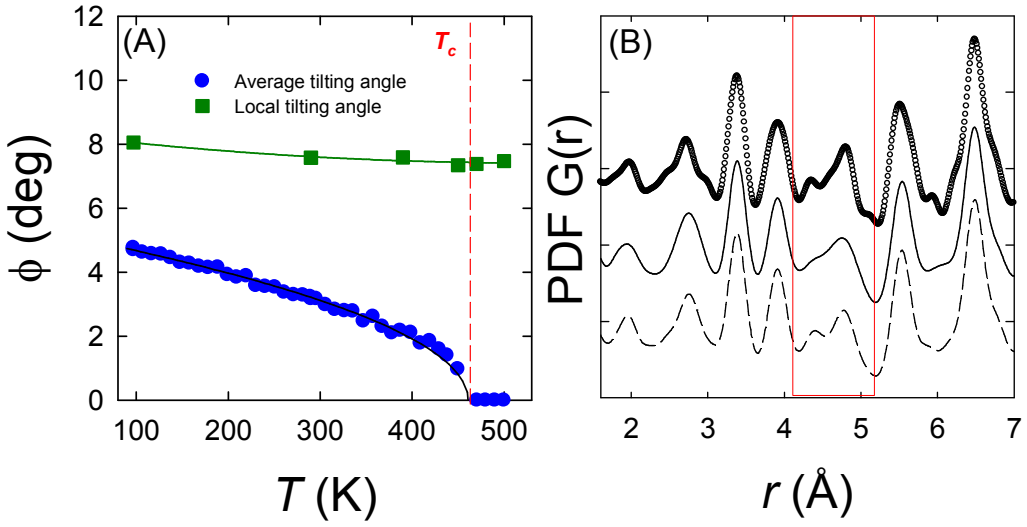

FIG 1. *(a) Temperature evolution of tilting angle for x=0.15. Continuous lines are mean field equation with critical exponent β=0.5. In the same plot the tilting angle obtained from local PDF refinement are also reported. (b) PDF obtained from x=0.15 sample at T=500K. Empty circles are observed data, continuous and dashed lines are calculated PDF obtained from cubic and tetragonal structural models.*

By fitting these data with mean field equation $\phi=\phi_0(1-T/T_C)^{\beta}$, we found that the best agreement is obtained with β=0.5 indicating a second order character for the transition. Observed T_C agrees with the anomaly temperature reported by Durán et al. **[3]** by using differential thermal analysis**.** As pointed out by Grag et al.**[4]**, the T_C is ~ 50K lower than T_m~500K and the symmetry breaking cannot be associated to a paraelectric to ferroelectric $BaTiO_3$-like transition **[4]**. In addition, the centrosymmetrical I4/mcm space group excludes *a priori* long range polar correlations.

We explored the structural coherence of I4/mcm model at different length scales by using Pair distribution function (PDF) method. By performing real space refinements from the local (10 Å) to the long range scales (200 Å), we found that below T_C the long range I4/mcm model seems to agree well with the observed PDF.

At $T_m > T_C$, the long range model Pm-3m provides a satisfactory agreement only at $r > 20$ Å providing evidence of a mismatch between average and local structures. In particular, as shown in Fig.1(b), the short range PDF at T=500 K is poorly described by the cubic model and the I4/mcm model provides a better agreement with the observed data. By refining the short range PDF data at each temperature against the I4/mcm model, we obtained the values corresponding to local tilting angle.

These local tilting angle values are compared with the average values obtained by Rietveld in Fig.1(a). Two main considerations can be drawn: (1) At each temperature the magnitude of the local tilting angle is greater than the average magnitude; (2) the local tilting angle has a weak temperature dependence.

Our preliminary results provide evidence of a second order structural transition at T_C~450K in SPTO15. However, the mismatch between the temperature evolution of the average and local order parameters suggest an unusual nature of the transition which has to be unveiled by extending the temperature range of PDF investigation.

References

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[4] R. Garg *et al.*, *Phys. Rev.* **B79** (2009) 144122.
[5] M. Allieta *et al.*, *Z. Kristallogr.* **1** (2011) 15.