ESRF	**Experiment title:** PDF investigation of relaxor ferroelectric Sr1-xPrxTiO3 at high temperature	**Experiment number**: CH-4324
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Names and affiliations of applicants (* indicates experimentalists):

Mattia Allieta, Marco Scavini*, Stefano Checchia*, Serena Cappelli*
Università di Milano, Dipartimento di Chimica, I-20133 Milano, Italy

Michela Brunelli*, Claudio Ferrero*
European Synchrotron Radiation Facility, av. J. Horowitz, BP 220, 38043 Grenoble Cedex, France

Report:

Summary:
Aim of the experiment was to determine systematically the temperature evolution of the structure of $Sr_{1-x}Pr_xTiO_3$ (SPTO) in a range of compositions. We planned the XRPD data collection strategy so as to encompass all the long-range phase changes in SPTO as well as possible structural distortions in the high-temperature cubic phase while getting very high quality data (i.e. wide *Q* range and high counting statistics).
The results allowed us to assess the antiferrodistortive soft-mode character of the long-range phase transition in SPTO. We also found a few robust order parameters of the structural evolution as a function of temperature; some of the samples exhibited high-temperature distortion that fits into a relaxor ferroelectric model for SPTO.

Experimental:
The powdered $Sr_{1-x}Pr_xTiO_3$ samples ($0 \leq x \leq 0.15$) were prepared by standard ceramic method at the University of Milan. SPTO powders were packed into 1 mm quartz capillaries and spun at 700 rpm during data collection. XRPD patterns were collected while ramp-heating the samples between 85 K and 300-400 K (depending on sample composition) using the cryostream. In addition, we collected fixed-*T* scans at temperatures up to 650 K using the hot-air blower. Ramp data were binned every 8 K and a 0.002° binsize was used.

Results:
We collected a number of temperature-resolved datasets in a range of momentum transfer *Q* up to ~14 $Å^{-1}$, excellent for both direct profile analysis and Rietveld fitting. All the SPTO samples are tetragonal at 85 K: the best-fitting tetragonal unit cell is a centrosymmetric *I*4/m*cm* supercell of the cubic perovskite, with $\sqrt{2}a \times \sqrt{2}a \times 2a$ cell parameters [2].
Figure 1 shows the temperature of the tetragonal-cubic structural phase transition increasing from just above 100 K to almost 500 K depending on Pr concentration (*x*). The T/*x* range corrsponding to the tetragonal phase is shaded in blue.
Intensity of superlattice reflections, magnitude of the TiO_6 octahedra rotation, and the tetragonal elongation of the cell were all reliable indicators of the evolution from the tetragonal *I*4/*mcm* to the cubic *Pm*3*m* structure on heating. In particular, the temperature-dependence of tilt angle accounts for a second-order transition when fitted using a mean-field equation. As shown in Figure 2, the magnitude of the tetragonal

distortion as indicated by all of the above parameters dramatically increases on increasing the Pr concentration in SPTO. Overall, the SPTO phase transition well agrees with the change in the perovskite tolerance factor effected by increasing *x*, delineating a soft-mode transition to a tetragonal phase.

Pr doped samples with x≤0.05 show a dilatational lattice strain in respect to to thermal linear expansion. (3.5% doped sample is shown in Figure 3), which suggested the onset of spontaneous polarization below a T* temperature according to the classical electrostriction argument by Cross [3]. With the T* point lying ~50 K above the maximum in dielectric permittivity, the behavior of the SPTO samples with 2% and 3.5% Pr closely resemble model relaxor ferroelectrics such as PLZT.[3] The composition dependence of the cubic-tetragonal phase transition and of the electrostrictive strain evidences a crossover point around 7.5% Pr. An evolution between two different AFD-FE regimes is thus anticipated on moving along the compositional axis. We can propose a provisional phase diagram for the SPTO system based on the cubic-tetragonal phase transition temperature, and the onset temperature of electrostriction.

References:

[1] a) R Ranjan, Physical Review B 79 (2009); A Duran, b) J. Phys.: Condens. Matter 20, 085219 (2008)

[2] S Checchia et al, article in preparation.

[3] LE Cross, Ferroelectrics 76 (1987); G. Burns and B. Scott, Solid State Comm. 13 (1973) 423

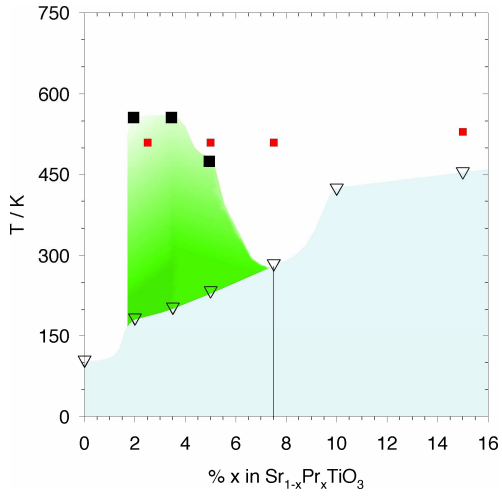

Figure 1. Proposed phase diagram. Triangles: temperature of the cubic-tetragonl phase transition (Tc); Large squares: onset temperature of the electrostrictive strain (Ts); Small squares: temperature of the dielectric permittivity peak from ref.[1b].

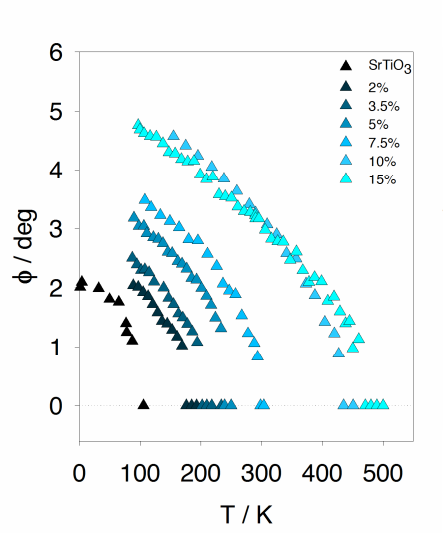

Figure 2. TiO6 tilt angles as a function of T for the studied compositions.

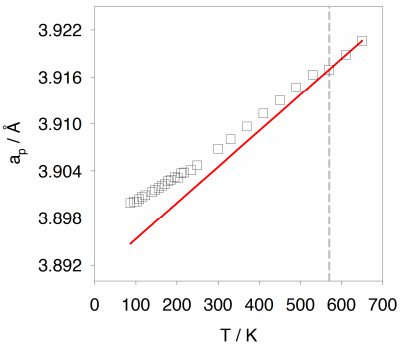

Figure 3. T-dependence of the a cell parameter. For temperatures below Tc, the tetragonal a was reduced to the cubic perovskite equivalent.