

## MS41-O3 Proving relaxor-type ferroelectricity in Pr-doped SrTiO<sub>3</sub> by XRPD

Stefano Checchia<sup>1</sup>, Mauro Coduri<sup>2</sup>, Marco Scavini<sup>1</sup>, Michela Brunelli<sup>3</sup>, Claudio Ferrero<sup>3</sup>, Mattia Allietta<sup>1</sup>

1. Università Degli Studi di Milano - Dipartimento di Chimica, via C. Golgi 19, 20133 Milano (Italy)
2. IENI-CNR, corso Promessi Sposi 29, 23900 Lecco (Italy)
3. ESRF - The European Synchrotron, 6 rue Jules Horowitz B.P 220 F, 38043 Grenoble (France)

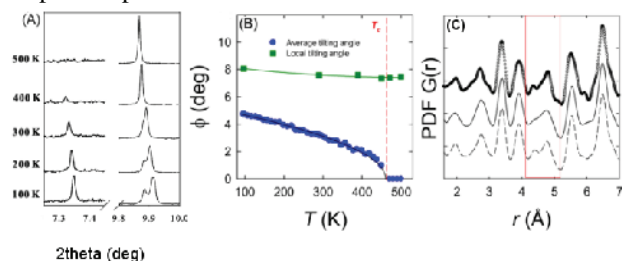
email: stefano.checchia@unimi.it

Chemical doping at both the Sr and Ti sites is a feasible way to break the quantum paraelectric state of SrTiO<sub>3</sub>. Room temperature ferroelectricity has been detected in Pr-doped SrTiO<sub>3</sub>, but the mechanism leading to ferroelectric response is controversial. Recently, the dielectric permittivity behavior of doped SrTiO<sub>3</sub> was attributed to relaxor-type ferroelectricity, generally associated with the formation of Polar Nanoregions (PNRs). From a structural point of view, PNRs are the outcome of a nanoscale phase separation of regions in which cations are off-centered with respect to the long-range phase.

We present a thorough x-ray powder diffraction study performed at ID22 (ESRF) on Sr<sub>1-x</sub>Pr<sub>x</sub>TiO<sub>3</sub> (SPTO) samples with 1% to 15% Pr in a wide range of T. In view of the smaller ionic radius of Pr<sup>3+</sup> (0.99 Å) and Pr<sup>4+</sup> (0.85 Å) with respect to Sr<sup>2+</sup> (1.44 Å), the relaxor FE state could be supported by an off-centred position of Pr ions in their oxygen cage, that would give rise to dielectric dipoles around which PNRs can form.

Rietveld analysis evidenced a second-order structural phase transition from *Pm-3m* to *I4/mcm* with a critical temperature T<sub>c</sub> strongly dependent on Pr doping. Temperature dependence of the superstructure reflections, of the FWHM of cubic reflections, and of the *a<sup>0</sup>a<sup>0</sup>c<sup>-</sup>* type tilting of TiO<sub>6</sub> octahedra were sensible parameters of the transition (Figure 1-A,B).

PDF analysis of XRPD data for x=0.150 showed that the local structure of SPTO is consistent with *I4/mcm* even at T > T<sub>c</sub> (Figure 1-B,C), suggesting tetragonal domains of 30 Å size within a cubic long range structure. The evidence of centrosymmetry is not consistent at any T with a BaTiO<sub>3</sub>-like FE state in SPTO, thus, a displacive phase transition can be ruled out.



**Figure 1.** For the x=0.150 sample: (A) T-evolution of 211 superstructure reflection and of a structure peak. (B) Tilting angle vs T (blue), tilting angle from local PDF refinement (green). (C) PDF at T=500 K. Observed (circles) and calculated PDF (lines) obtained from cubic and tetragonal structural models.

**Keywords:** ferroelectrics, total scattering, strontium titanate, polar nanoregions

## MS41-O4 Clean and energy-efficient syntheses of M-MOF-74 materials by mechanochemistry and accelerated ageing, monitored through *in-situ* powder x-ray diffraction

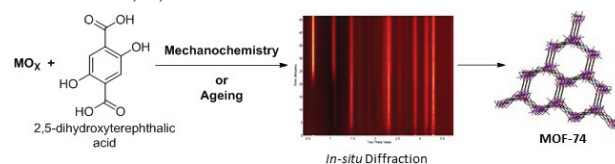
Patrick A. Julien<sup>1</sup>, Krunoslav Užarević<sup>2</sup>, Athanassios Katsenis<sup>1</sup>, Ivan Halasz<sup>2</sup>, Tomislav Friščić<sup>1</sup>

1. McGill University, Montreal, Qc, Canada
2. Institut Ruder Bošković, Zagreb, Croatia

email: patrick.julien@mail.mcgill.ca

Microporous metal organic frameworks (MOFs) based on 2,5-dihydroxyterephthalic acid, generally known as M-MOF-74 have emerged as promising class of materials for a wide variety of applications including gas storage and separation<sup>1</sup>, catalysis<sup>2</sup>, and sensors<sup>3</sup>. “Accelerated ageing” and mechanochemical syntheses are environmentally friendly and economical techniques which allow the reaction of abundant, stable, and inexpensive metal oxides with MOF linker precursors to provide synthesis which avoids the use of bulk solvents and reduce the energy cost when compared to traditional solvothermal synthesis<sup>4</sup>. This work discusses how mechanistic insights from *in-situ* synchrotron powder X-ray diffraction of these milling reactions<sup>5</sup> were used to optimize the synthesis of various M-MOF-74 analogues in very high yields, using both accelerated ageing and milling techniques.

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**Figure 1.** Monitoring the synthesis of M-MOF-74 by milling or “accelerated ageing” through *In-situ* Synchrotron Powder X-Ray Diffraction

**Keywords:** Metal Organic Frameworks, Powder X-ray Diffraction, Synchrotron, Mechanochemistry