ESRF	**Experiment title:** XRPD STUDY OF LOCAL ORDER EFFECTS IN AL DOPED REBCO	**Experiment number**: HS-2168
Beamline: ID31	**Date of experiment**: from: 13/03/2003 to: 17/03/2003	**Date of report**: 07/04/04
Shifts: 12	**Local contact(s)**: Dr. Andy Fitch	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Marco Scavini*, Matteo Daldosso*

Department of Physical Chemistry and Electrochemistry, University of Milan, Italy.

Paolo Arosio*

Dep. of Chemistry, Materials and Chemical Engineering "G.Natta", Politecnico di Milano, I.

Claudio Ferrero*,

ESRF, Grenoble, France.

Report:

Short and medium range order induced by Al doping in $SmBa_2Al_xCu_{3-x}O_{6+\delta}$ ($0< \delta < 1$, x = 0, 0.15, 0.33) superconductor was studied as a function of aluminium concentration x and oxygen non-stoichiometry δ. For each aluminium concentration a "reduced sample", annealed at 800 °C and $P(O_2)=10^{-4}$ atm, and an "oxidised sample" annealed at 400 °C and $P(O_2)$=1 atm have been produced. For x = 0.15 a "clusterised" oxidised sample has been produced by inducing Al clustering through an appropriate annealing procedure.

The diffraction patterns were collected at 80, 100, 120 and 250 K with a cold N_2 cryostream at λ = 0.33483(1) Å, in a large 2θ range ($0< 2\theta < 60$ °). This correspond to $Q_{max} \sim 18$ Å^{-1}. Data have been refined both in the reciprocal space, using GSAS programs package and in real space (PDF method), using the PDFgetX-PDFFIT package.

All our data were affected by an aberration, that is the systematic presence of a shoulder under the most intense Bragg peaks independently from the nature of the samples (Sm-123 or GeO_2 which was also measured). These "shoulder" have an unknown origin and affected negatively the Rietveld analysis, while modelling the peak's tails.

In $SmBa_2Cu_3O_{6+\delta}$ a long range tetragonal to orthorhombic phase transition occur $\delta \sim 0.5$; the phase transition is driven by Cu-O ordering along b axis in the xy, z=0 plane. In doped samples the same is inhibited. In figure 1 is shown a structural model for the same plane in a doped (reduced) samples, which can explain the role of aluminium. The local tetrahedric environment for Aluminium inhibit the formation of long Cu-O chains while oxidising. The length of the Cu-O chains is a function of aluminium concentration and clustering. In fact it is possible to fit the pattern of the cluserised oxidised sample (x=0.15) only with a biphasic model: a Sm-123 aluminium free orthorombic phase and a Sm-123 doped tetragonal one (see Figure 2).

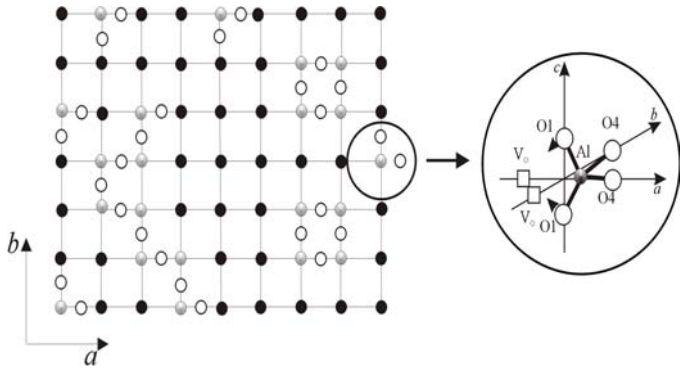

Figure 1 Model for the xy, z=0 plane in reduced doped samples. Cu (black circles), Al (grey circles) and oxygen (hollow circles) are shown. Insert: local environment for Aluminium

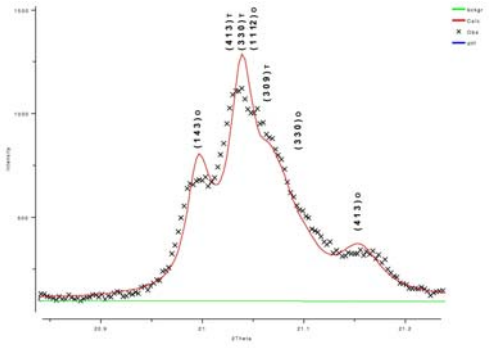

Figure 2 Detail of the pattern relative to the "cluserised" oxidised sample (x=0.15). T and O beside the (hkl) symbols are relative to Tetragonal and Orthorombic phase, respectively.

The disorder induced by aluminium doping can be evaluated comparing the atomic thermal factors (U_{iso}) of doped and undoped samples. As an exemplum in figure 3 are shown the barium U_{iso} for undoped (circles) and x=0.33 (squares) oxidised (full symbols) and reduced (hollow symbols) samples, as a function of temperature.

The slopes of the $U_{iso}(T)$ fitting straight lines relative to doped and undoped samples are similar, while the intercepts are quite different. This suggests that doping introduces a large extent of disorder in Ba position.

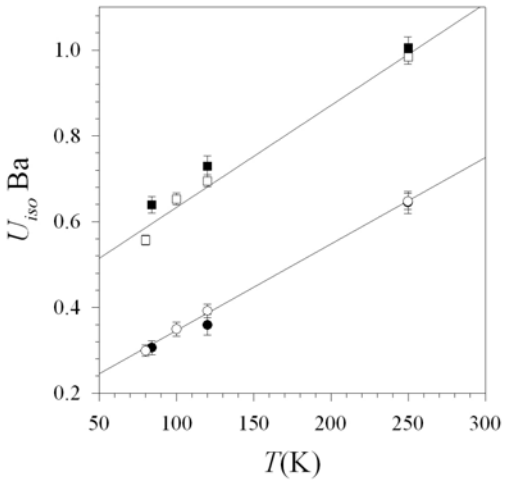

Figure 3 Barium thermal factors (*Uiso*) as a function of temperature. See text for details.

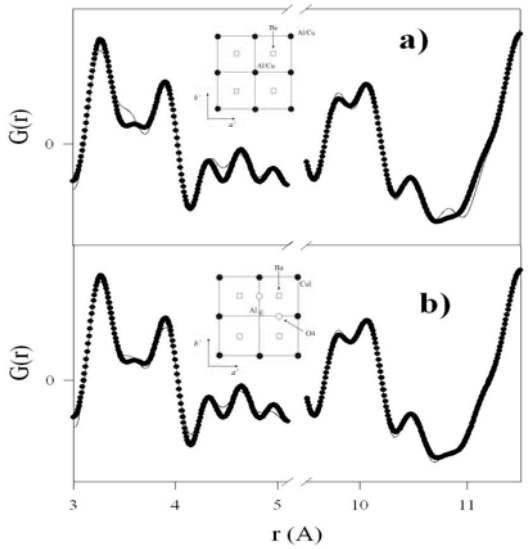

Figure 4 G(r) for reduced x=0.33 sample. Circles: experimental data; line: calculated G(r). a) Pure model; b) supercell. The symbols of the insert are the same of figure 1.

Disorder can be suitably modelled by Real space analysis (PDF). In figure 4 are shown two details of the PDF function [G(r)] relative to reduced x=0.33 sample. In Fig. 4a the experimental data (full circles) are fitted with a "pure" model (full line): all the symmetry constrains of the long range structure are retained and the proper Cu/Al occupational factor is fixed. In the same figure also the xy, z=0 section of the structure [more the Ba position, which is at (½ ½ ~0.19)] is shown. In figure 4b the same data are fitted with a supercell (2x2x1) which takes into account the local structural fluctuations. All the Cu positions are occupied by copper but the central one (see the insert), where Al is positioned. Oxygen atoms are added to the structure in order to guarantee the Al tetrahedric coordination. Moreover zBa can vary in each cell. The agreement factors better significantly for this new model (wR=0.138 instead of 0.156). In respect to the mean value determined by Rietveld analysis the z level of the barium ion nearest to the two oxygen ions decreases while all the other ones increases. Thus the real space analysis can properly describe differences in the barium thermal parameters determined for doped and undoped samples as positional disorder.