



	<b>Experiment title:</b> GAS ADSORPTION PROCESS OF $\text{Ca}_{0.83}\text{CuO}_2$ COMPOSITE CRYSTAL: A STRUCTURAL STUDY BY TIME RESOLVED DIFFRACTION EXPERIMENT	<b>Experiment number:</b> 08-02-623
<b>Beamline:</b> BM08	<b>Date of experiment:</b> from: 15-05-2005 to: 20-05-2005	<b>Date of report:</b> 28/02/2007
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**Report:**

Calcium cuprates with general formula  $\text{Ca}_x\text{CuO}_2$  with  $0.82 < x < 0.85$  are characterized by a structure consisting of layers of alkaline earth atoms interpenetrated by edge-sharing  $\text{CuO}_4$  ribbons. The spatial distribution of  $\text{CuO}_2$  chains forms channels with octahedral cavities and only a fraction of these sites is occupied by the alkaline earth. This kind of compound can be regarded as a composite crystal formed by two independent sub-lattices (see Table1), one related to  $\text{CuO}_2$  chains, the other related to  $\text{Ca}^{2+}$  ions. The different symmetry and periodicity of the two sub-systems gives rise to incommensurate displacive modulation.

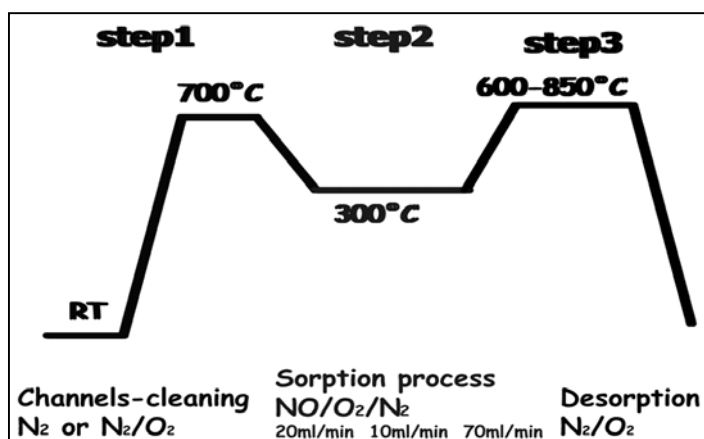
**Table1.** Unit cell parameters and q vector for the two Ca and  $\text{CuO}_2$  sublattices

	$\text{CuO}_2$	Ca
Unit Cell ( $\text{\AA}$ , °)	a= 2.8032(5)	a= 3.3686(5)
	b=6.3209(1)	b=6.3209(1)
	c=10.5788(2)	c=10.5932(2)
	$\eta=90^\circ$	$\eta=92.99^\circ$
<b>q= <math>\mathbf{a}^* + \mathbf{c}^*</math></b>	0.83215(7) $\mathbf{a}^*$ + 0.1593(3) $\mathbf{c}^*$	1.20163(7) $\mathbf{a}^*$ - 0.1971(3) $\mathbf{c}^*$

The crystal structure of  $\text{Ca}_{0.83}\text{CuO}_2$  has been solved within superspace approach by powder neutron diffraction [1]. Moreover, the  $\text{Ca}_x\text{CuO}_2$  system shows an unusual ability to adsorb small molecules such as  $\text{NO}_x$ , CO,  $\text{CO}_2$ , with strong selectivity toward  $\text{NO}_x$ . The high efficiency in storing huge amounts of gas (with respect the

mass of the ceramic material) and the reversibility of the sorption phenomenon, induced by thermal treatments, make  $\text{Ca}_x\text{CuO}_2$  a suitable material for de- $\text{NO}_x$  applications.

In order to study the mechanism at the base of this important chemical property, we have monitored the absorption process in-situ by time resolved powder diffraction technique. The experiment has been performed on the BM08 (GILDA) diffraction line at ESRF with the radiation  $\lambda = 0.6853 \text{ \AA}$ , by using a  $\text{N}_2/\text{O}_2/\text{NO}$  gas flux at different relative concentrations. The main purpose was the study of the structural evolution of the composite crystal during the absorption process and the subsequent re-conversion to the starting structure. In Fig.1 it is



summarized the experimental conditions regarding the three fundamental steps studied. A translating imaging plate (IP) has been used to record the evolution of the involved chemical processes. The preliminary results of the diffraction study carried out in this experimental session have been reported at XXXV congress of AIC (Ferrara 18- 21/09/2006) [2].

**Figure 1.** Experimental details: temperature and chemical conditions.

The analysis, by Rietveld method, of the dynamic collection of PXRD patterns evidenced the following aspects:

- 1) During the first heat treatment (step 1), the composite crystal shows a structural deformation (at about 550°C) related to the contraction of the only Ca sublattice (negative expansion coefficient).
- 2) During the adsorption process with the mixture of  $\text{N}_2/\text{NO}/\text{O}_2$  (step 2), it is observed the formation of  $\text{Ca}(\text{NO}_3)_2$ . After 30 min of NO flux the 27% wt. of  $\text{Ca}(\text{NO}_3)_2$  with respect to  $\text{Ca}_{0.83}\text{CuO}_2$  is formed. During the calcium nitrate formation the composite crystal rearrange the two sublattices in order to compensate the lack of Ca atoms. The growth of  $\text{Ca}(\text{NO}_3)_2$  is preceded by an intermediate state where the Ca sublattice shows a triclinic distortion. This stage could be related to the sorption process of  $\text{NO}_2$  molecules through the channels present in  $\text{Ca}_{0.83}\text{CuO}_2$  structure.
- 3) The re-conversion of the material to the original conditions ( $\text{Ca}_{0.83}\text{CuO}_2$  as unique phase) is obtained after several hours of heat treatment beyond 700°C. The calcium nitrate decomposes to give CaO which is slowly absorbed by the composite crystal.

The present results indicate that the absorption process exploits the particular elasticity of the composite crystal, connected to the presence of two almost independent sub-lattices, in accommodating the gas molecules.

## References

- [1] Y. Miyazaki, M. Onoda, P.P. Edwards, S. Shamoto and T. Kajitani *J. of Solid State Chem.* **163** 540(2002)
- [2] Gas adsorption process of the composite crystal  $\text{Ca}_{0.83}\text{CuO}_2$ : a structural study by time resolved powder diffraction experiment. L. Righi, M. Merlini, P. Nozar, C. Dionigi, M. Gemmi and G. Calestani. (Oral contribution) XXXV Congresso Associazione Italiana Cristallografia (AIC) Ferrara 18-21/09/2006