	Experiment title: Microstructural and phase separation study of B-substituted manganites ($Pr_{0.5}Ca_{0.5}Mn_{1-y}M_yO_3$ and $Bi_{1-x}Sr_xMn_{0.95}M_{0.05}O_3$; M = Ti, Cr, Co)	**Experiment number:** he1629
ESRF		
Beamline: ID31	**Date of experiment:** from: 14-11-2003 to: 18-11-2003	**Date of report:** 24-02-2004
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Report:

During the last years the substitution of manganese by a series of other transition metals, and by other atoms, in manganites ($Ln_{1-x}A'_xMnO_3$ Ln≡ Rare earth, $A' \equiv$Ca, Sr) has revealed surprising behavior. One of the most amazing is the quick loose of charge order (CO) in Cr, Co or Ni substituted Pr-Ca manganites. At very low levels of substitution (about 3%) the CO-AFM insulator $Pr_{0.5}Ca_{0.5}MnO_3$ becomes the FM metallic $Pr_{0.5}Ca_{0.5}Mn_{0.97}M_{0.03}O_3$ (M=Cr, Co, Ni) [1]. The concentration of Cr needed to break CO is smaller if its stability is weaker (for instance it is a 2% in $Nd_{0.5}Sr_{0.5}Mn_{0.98}Cr_{0.02}O_3$ [2]). Initially this was interpreted as an effect of the randomness introduced by the "impurity" in the B sublattice of the perovskite, but it is doubtful that this local effect is enough to produce the breakdown of the CO in the whole sample. In some cases (Ga-5%, Co-5%), the substitution drives to the apparition of sharp steps in the low temperature $M(H)$ and $\rho(H)$ curves [3]. It is believed that the ground state of these compounds corresponds to an inhomogeneous phase separated state.

We have found that all $Pr_{0.5}Ca_{0.5}Mn_{1-y}M_yO_3$ studied samples are very well crystallized and single phased (with exception of small impurities detected in some cases) at RT. However, most of the samples present a phase separation on cooling. This can be clearly seen in Figs. 1(a) and (b) for Co-5% compounds. In Tab. I we list the cell parameters found at RT and at $T = 15\,\mathrm{K}$ (for the two $Pnma$ phases found) for M = Cr and Co and y = 2% and 5%. It can be seen that ϵ_c is small at RT, signaling that cell parameters are not distorted as expected. At low temperature, in most of the cases one of the phases is not distorted but the second one (as reflected in values of ϵ_c around or above 20) is distorted. This distortion is also present (at low T) in

the parent compound and is attributed to the anisotropic charge reallocation concomitant with CO. It can be guessed from Tab. I that at 2% of substitution level the distorted phase (labeled as phase-1) is majority and the undistorted one is the minority phase. The contrary happens in the 5% doping level. (At this level the distorted phase has almost disappeared -only a 2.5% remains- in the Cr case). It is also worth to mention that the distortion of the "undistorted" phase decreases with doping. In fact phase 2 in the Co-2% case is very distorted ($\epsilon_c = 22$). This indicates that the microstructure is very important in these phases. To illustrate this Fig. 1(c) shows the Williamson-Hall plot corresponding to Co-5% compound. From the extrapolation, one can infer that the peak broadening is mainly due to strain effects. In addition, the strain is more important (and more anisotropic) in the undistorted phase than in the distorted one. The same result is found in the other cases with exception on the Cr-5% where the distorted phase has almost disappeared. This stress must be attributed to the presence of the substituting cations. These results highlight the importance of the stress in inducing the ferromagnetic phase in these compounds.

Table I Refined cell parameters at RT (single phase) and at 15 K where two phases are encountered. The fraction of each phase and the apical distortion of the lattice $\epsilon_c \equiv \left(\frac{a+c}{\sqrt{2}b} - 1\right) \times 10^3$ are also given.

	Cr-2%	Cr-5%	Co-2%	Co-5%
	Room Temperature			
a(Å)	5.40275	5.40104	5.40228	5.40311
b(Å)	7.61397	7.61452	7.61264	7.61439
c(Å)	5.39327	5.39191	5.39294	5.39354
ϵ_c	2.6	2.3	2.7	2.6
	$T = 15$ K Phase 1			
a(Å)	5.43231	5.41812	5.43201	5.42690
b(Å)	7.49263	7.50551	7.49145	7.52058
c(Å)	5.42812	5.4195	5.42817	5.41648
ϵ_c	24.9	21.0	25.1	19.5
Fraction	89.5%	2.5%	69.2%	18.4%
	$T = 15$ K Phase 2			
a(Å)	5.40832	5.39541	5.42817	5.41019
b(Å)	7.58918	7.6003	7.50392	7.57449
c(Å)	5.37078	5.38136	5.42088	5.39572
ϵ_c	4.3	2.6	22.3	8.8
Fraction	9.2%	96.2%	30.8%	81.6%

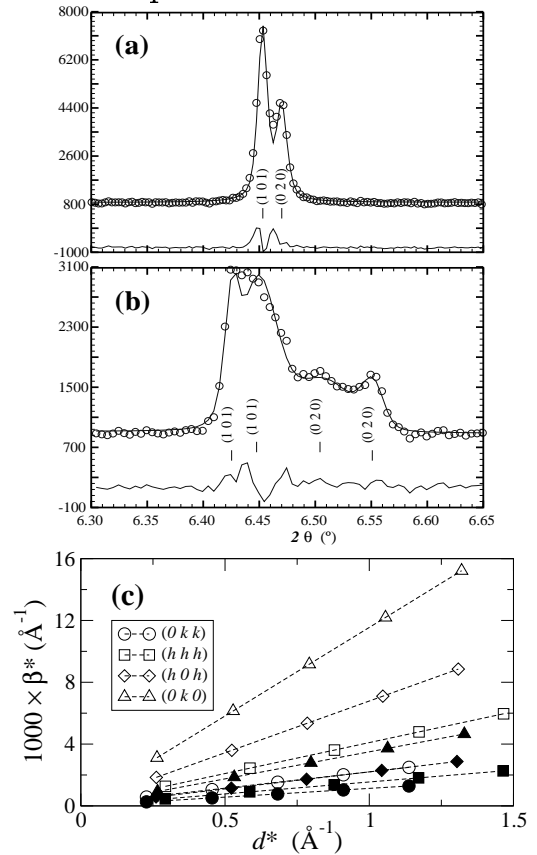**FIG. 1** (a) and (b) detail of the refined patterns of $Pr_{0.5}Ca_{0.5}Mn_{0.95}Co_{0.05}O_3$ (Co-5%) at RT and $T = 15$ K respectively. (c) Williamson-Hall plot of some families of peaks of the same compound at 15 K. Open (filled) symbols correspond to the majority (minority) phase.

References:

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[2]. K. Takenaka *et al.*, J. Appl. Phys. **91**, 294 (2002).

[3]. R. Mahediran *et al.*, Phys. Rev. Lett. **89**, 286602 (2002); S. Hérbert *et al.*, J. Solid State Chem. **165**, 6 (2002).