	<b>Experiment title:</b> Structural characterization of bidimensional charge ordered compounds with high dielectric constant	<b>Experiment number:</b> <b>HE-2641</b>
<b>Beamline:</b> BM25A	<b>Date of experiment:</b> from: <b>10/09/07</b>	

## Report:

This experiment deals with studies on transition metal oxides  $\text{Ca}_{2-x}\text{Pr}_x\text{MnO}_4$  ( $x=0.25$  and  $0.50$ ) with interesting dielectric properties arising from charge ordering (CO) and orbital ordering (OO) that take place in these compounds at  $T_{\text{CO}}$  ( $x=0.25$ )  $\approx 270$  K and  $T_{\text{CO}}$  ( $x=0.50$ )  $\approx 315$  K. The aim of this study was to structurally characterize these compounds above and below their  $T_{\text{CO}}$  and obtain more information about the CO/OO patterns then present. This would help clarifying the origin of their high dielectric intrinsic constant.

**Experimental details:** The compounds were prepared as polycrystalline powders. Each sample was introduced in a capillary of 0.3 mm of diameter to perform high resolution powder diffraction studies in the Spanish BM25A beamline. The wavelength used was  $\lambda=0.826096$  Å and the range of scan was  $5-60^\circ$  ( $2\theta$ ) with a step of  $0.02^\circ$  ( $2\theta$ ). The HRPD patterns were recorded at different temperatures from 400 K to 150 K and were refined by the Rietveld method with the Rietan software.

**$\text{Ca}_{1.75}\text{Pr}_{0.25}\text{MnO}_4$ :** This compound presents the  $\text{K}_2\text{NiF}_4$  structure, which is the two-dimensional analogue of the 3D perovskite, consists of perovskite layers of corner-sharing  $[\text{MnO}_6]$  octahedra that are separated from one another by the presence of rock-salt type (Ca/Pr-O) layers along the larger axis.

The here obtained synchrotron diffraction patterns showed a structural transition around  $T_{CO}$ . Figure 1 shows a detail of the obtained diffraction patterns at 400 K ( $T > T_{CO}$ ) and 200 K ( $T < T_{CO}$ ). In this figure, the broadening and splitting of several peaks indicate a decrease of symmetry in the CO state.

By Rietveld refinement of the diffraction pattern, we have estimated that above  $T_{CO}$  this compound presents an orthorhombic symmetry (S.G.: Cmca) and cell parameters values of:  $a = 5.3047(10)$  Å,  $b = 11.8953(3)$  Å and  $c = 5.3048(11)$  Å at 400 K. The Mn-ions are in a tetragonally-distorted octahedral site and there are two different Mn-O bond lengths: a shorter Mn-O distances in the a-c plane and a longer Mn-O distances along the b axis.

Figure 2 shows the obtained refinement pattern at 400 K, and Table I summarizes the obtained atomic coordinates and agreement factors.

**Table I**

S.G.: Cmca				
a= 5.3047(10) Å b=11.8953(3) Å c= 5.3048 (11) Å				
	x	y	z	B (Å <sup>2</sup> )
<b>Ca/Pr</b>	0	0.3541(1)	-0.001(1)	1.83(3)
<b>Mn</b>	0	0	0	1.25(4)
<b>O1</b>	0	0.1646(3)	0.016(3)	2.4(1)
<b>O2</b>	0.25	0.001(1)	0.25	2.9(1)
$R_{wp} = 8.21$ $R_p = 5.95$ G.O.F= 3.18				

On the other hand, this compound presents a monoclinic symmetry (S.G.: C2/c) below  $T_{CO}$  and cell parameters values of  $a = 5.2942(3)$  Å,  $b = 11.9047(5)$  Å,  $c = 5.3048(11)$  Å and  $\beta = 90.130(2)$  at 150 K. The Mn-ions are in a tetragonally-distorted octahedral site and there are three different Mn-O bond lengths: two shorter Mn-O distances in the a-c plane and a longer Mn-O distances along the b axis. Figure 3 shows the obtained refinement pattern at 200 K, and Table II summarizes the obtained atomic coordinates and agreement factors.

**Table II**

S.G.: C2/c				
a= 5.2942(3) Å b= 11.9047(5) Å c= 5.3048(11) Å				
$\beta = 90.130(2)$				
	x	y	z	B (Å <sup>2</sup> )
<b>Ca/Pr</b>	0.25	0.6039 (1)	-0.0010 (9)	1.85(3)
<b>Mn</b>	0.25	0.25	0	1.40(4)
<b>O1</b>	0.25	0.4151 (4)	0.021 (2)	2.1(1)
<b>O2</b>	0.5	0.253(7)	0.25	2.2(4)
<b>O3</b>	0.5	0.751(8)	0.25	1.7(3)
$R_{wp} = 7.97$ $R_p = 5.74$ G.O.F= 2.60				

Moreover, by Rietveld refinement we have found that there is a small amount (~3.5%) of perovskite  $Ca_{1-x}Pr_xMnO_3$  phase as impurity in the material. We have note that it is not possible to observe this impurity by conventional X-ray diffraction, because of the overlapping between the  $K_2NiF_4$  and perovskite peaks.

**Ca<sub>1.5</sub>Pr<sub>0.5</sub>MnO<sub>4</sub>**: As in the previous case, this material is not single phase, as the synchrotron diffraction patterns show the additional presence of a minor impurity perovskite phase (about 4.5%). For this material, we have not observed a structural modification above and below  $T_{CO}$ . In the whole temperature range studied, this material presents a tetragonal symmetry (S.G.: I4/mmm) and cell parameters  $a = 3.7810(1) \text{ \AA}$  and  $c = 11.8782(2)$  at 400 K, that structure corresponds to the conventional symmetry of the K<sub>2</sub>NiF<sub>4</sub> structure. Figure 4 shows an example of the Rietveld refinement at 400 K and Table III summarizes the obtained atomic coordinates and agreement factors.

**Table III**

S.G.: I4/mmm				
$a = 3.7810(1) \text{ \AA}$		$c = 11.8782(2) \text{ \AA}$		
	<b>x</b>	<b>y</b>	<b>z</b>	<b>B (<math>\text{\AA}^2</math>)</b>
<b>Ca/Pr</b>	0	0	0.3560 (1)	3.01 (3)
<b>Mn</b>	0	0	0	1.94 (4)
<b>O1</b>	0	0.5	0	2.82 (8)
<b>O2</b>	0	0	0.1653(3)	3.41 (8)
$R_{wp} = 5.87 \quad R_p = 4.22 \quad G.O.F = 2.27$				

Interestingly, in both materials, the cell parameters show an anomalous thermal expansion from 150 K to 400 K, as we can see in Figure 5 for Ca<sub>1.5</sub>Pr<sub>0.5</sub>MnO<sub>4</sub>: instead an expected regular expansion, we have observed that the cell parameters and volume keep almost temperature independent below  $T_{CO}$ , being much smaller than above  $T_{CO}$ .

In this context, we have to indicate that Ca<sub>2-x</sub>Pr<sub>x</sub>MnO<sub>4</sub> (x=0.25 and 0.50) compounds present a complex magnetic behaviour: around 200 K it shows a short-range spin order (intra-perovskite blocks), and around 120 K it shows a long-range spin order (inter-perovskite blocks). We suspect that the anomalous thermal expansion calculated from the present experiment would be related to a coupling between the lattice and the magnetic arrangements in the studied Ca<sub>2-x</sub>Pr<sub>x</sub>MnO<sub>4</sub> materials. These lattice and magnetic arrangements would be the origin of their large dielectric constants.

Finally, we have to indicate that the Ca<sub>2-x</sub>Pr<sub>x</sub>MnO<sub>4</sub> structure deduced from Synchrotron X-Ray Powder Diffraction data is an average structure of multiple domains with different charge arrangements. In the case of those very complex materials this fact is a drawback to obtain a complete and detailed structural characterization. X-Ray Single Crystal Diffraction should be more useful to determinate the charge and orbital arrangement of these materials.

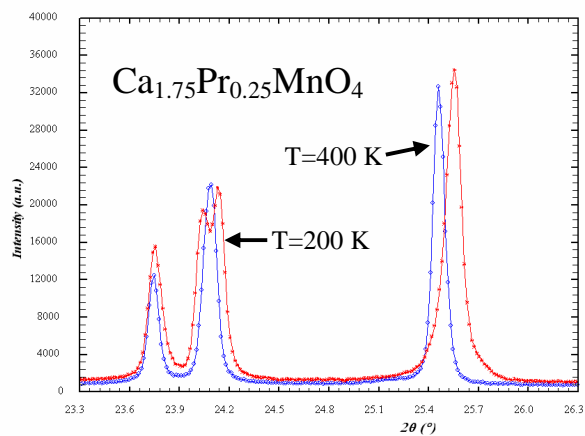


Figure 1

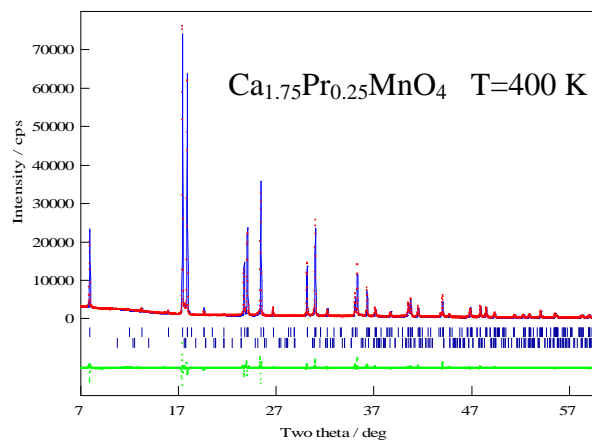


Figure 2

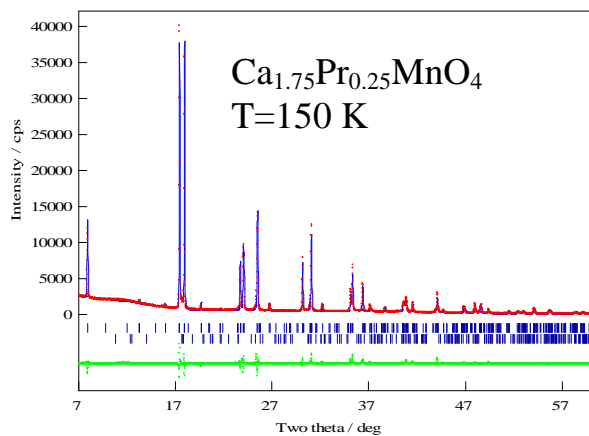


Figure 3

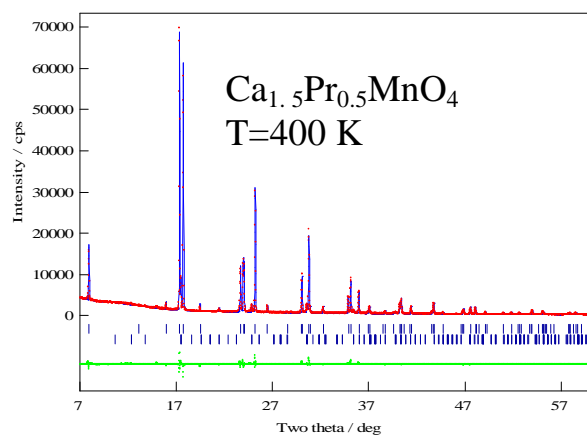


Figure 4

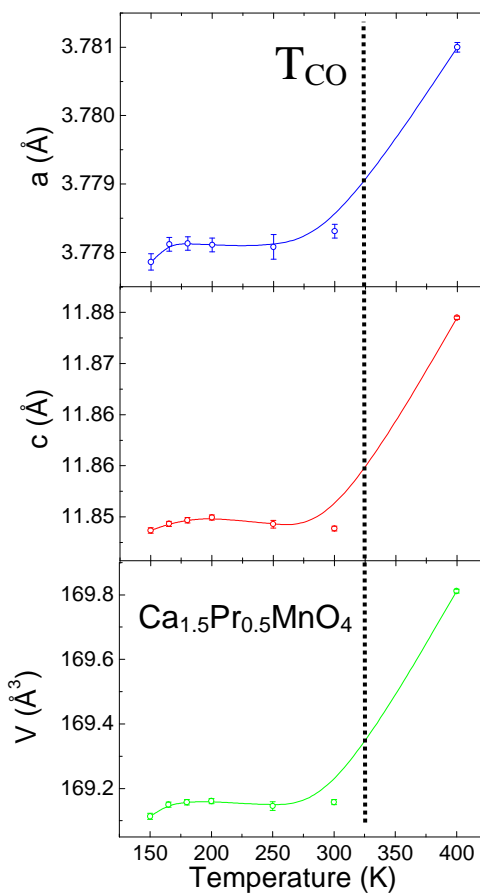


Figure 5