Among strongly correlated electron systems, La_{1-x}Ca_{x}MnO_3 is probably one of the most studied due to the peculiar relationship between magnetic and electric properties in addition to the presence of colossal magnetoresistance. The competence between local phenomena as lattice, spin, charge and orbital ordering is on the basis of this complex behaviour. The phase segregation model proposes the coexistence of two types of nanometer-size clusters corresponding to a FM-M phase and a correlated AFM-I one involving a charge ordering state. Actually, hole doping is induced by the substitution of La by Ca. Although this model is in reasonable agreement with numerous experimental results, it has also been proposed that in addition to providing holes to the band, the divalent substituting cation acts as effective attractor for these holes. This effect influences the magnetic response as the Mn^{4+} location around Ca creates nanoclusters which affects the total magnetic moment. A complete understanding of these phenomena would require an atomically resolved characterization in order to identify the La and Ca positions as well as the Mn^{3+} and Mn^{4+} distribution. Nowadays, this is possible as a consequence of the integration of spherical aberration correctors in the TEM. In this context, the aim of this work is to study the Mn^{4+} location in the La_{0.9}Ca_{0.1}MnO_3, according to the hole-attractor model.

La_{0.9}Ca_{0.1}MnO_3, prepared by ceramic method, shows an orthorhombic perovskite cell. The average cation ratio was determined by means of EPMA. The oxygen content was determined by thermogravimetric methods. To determine the local cation distribution the aberration corrected JEOL JEMARM200cFEG electron microscope was used. Fig. 1 shows a characteristic HAADF image of La_{0.9}Ca_{0.1}MnO_3 along [10-1], in which apparently ordered perovskite areas are evident. Nevertheless, it should be noticed the different contrast at the dots corresponding to the A sites of the perovskite (ABO_3) lattice. According to the HAADF contrast, it could be proposed that the brightest contrast corresponds to La and the less one to Ca. For further compositional information an atomically resolved EELS study was performed. The HAADF image recorded simultaneously to EELS acquisition and the sum spectra obtained over the area marked in figure 1a are depicted on fig. 1a and b, respectively. The chemical maps (fig. 1d-f) suggest a heterogeneous arrangement of the La and Ca cations. A more detailed study of individual atomic positions has led to the detection of Ca free A positions, according to spectra shown in fig. 2a and b. This allows us to localize Ca. Atomically resolved EELS mapping for the Mn oxidation states is in due course.
Fig. 1: (a) HAADF image of La$_{0.9}$Ca$_{0.1}$MnO$_3$. Schematic model for the cationic position has been inserted; (b) EELS spectra sum, acquired over the area marked in (a); (c) HAADF image simultaneously recorded to EELS; (d) mapping obtained for the La-L$_{2,3}$; (e) Ca-M$_{4,5}$ and (f) Mn-L$_{2,3}$ signals.

Fig. 2: Figure 2. HAADF images simultaneously recorded to EELS acquisition and resultant EELS spectra sum corresponding to two different marked cell evidencing the presence of different cation occupation at the A site (a) La and (b) La and Ca.