Study of the dielectric properties of $La_{0.67}Ca_{0.33}MnO_3$ nanoparticles and $La_{0.67}Ca_{0.33}MnO_3@SiO_2$ nanocomposites

S. Yáñez-Vilar[1], *M. Sánchez-Andújar*[1], *S. Castro-García*[1], *J. Mira*[2], *J. Rivas*[2], *M. A. Señarís-Rodríguez*[1]

[1]*Dept. Química Fundamental, Univ. da Coruña, A Zapateira s/n, 15071 A Coruña, España*
[2]*Dept. Física Aplicada, Univ. Santiago de Compostela, 15781 Santiago de Compostela, España*
syanez@udc.es

The search of materials with high dielectric constant has been a field of interest due to the important applications of this property in many electronic devices, like high-performance capacitors [1]. In this materials group, oxides with the perovskite structure are well known for their ability to produce high dielectric constants.

In this context, in a previous work, our investigation group have studied the dielectric properties of a polycrystalline sample of the manganese perovskite $La_{0.67}Ca_{0.33}MnO_3$ with particle size ~ 10 μm [2]. We have found that, at room temperature, it shows, high values of dielectric constant ($\varepsilon_r' > 10^4$) in a wide frecuency range ($10^2 < \nu < 10^5$ Hz). Nevertheless, despite this attracting high ε_r', it also shows high dielectric losses, associated to a relatively high conductivity of the sample, a serious drawback for potential technological applications.

In this work, and with the aim to reduce the dielectric losses, we have reduced the particle size of the polycrystalline material to the nanometric scale, and have prepared core-shell composites growing nanolayers of an insulating material (SiO_2) over the obtained $La_{0.67}Ca_{0.33}MnO_3$ nanoparticles.

For this purpose, nanometric particles of $La_{0.67}Ca_{0.33}MnO_3$, with $\phi \sim 100$ nm, were synthesized by the sol-gel method described in [3] with a final heat treatment at 700 ºC/3 hours. $La_{0.67}Ca_{0.33}MnO_3@SiO_2$ core-shell nanocomposites with different thickness of SiO_2 shell (Figure 1) were prepared using the Stöber method [4]. The obtained samples were morphologically and structurally characterized by means of X-ray powder diffraction and transmission electron microscopy. Its complex dielectric permittivity, $\varepsilon_r = \varepsilon_r' - i\varepsilon_r''$, was measured as a function of frequency ($20 \leq \nu$ (Hz) $\leq 10^6$) and temperature ($200 \leq T$ (K) ≤ 300).

The room temperature frequency dependent dielectric behavior of the so obtained materials is compared in Figure 2. As it can be seen, the dielectric constant of the $La_{0.67}Ca_{0.33}MnO_3$ nanoparticles is higher than in the case of the nanocomposites (Figure 2a). Nevertheless and most interestingly, in the coated samples the loss tangent has decreased by a factor of ~ 10, as compared to the uncoated sample (Figure 2b). From the practical point of view, the best dielectric behaviour is found in the $La_{0.67}Ca_{0.33}MnO_3@SiO_2$ ($\phi_{SiO2} \sim 3$ nm) nanocomposite: it still shows a rather high dielectric constant ($\varepsilon_r' > 10^2$), while its dielectric losses have decreased ($\tan\delta < 10$ for $\nu > 10^4$ Hz).

Acknowledgments:

The authors are grateful for financial support from Xunta de Galicia under project PGIDIT06PXB103298PR. S. Yáñez-Vilar want to thank to MEC of Spain for her FPI fellowship.

References:

[1] R. J. Cava, J. Mater. Chem., **11** (2001) 54-62.
[2] B. Rivas-Murias, Tesis Doctoral, Universidade da Coruña **2006**.
[3] C. Vázquez-Vázquez, M. C. Blanco, M. A. López-Quintela, R. D. Sánchez, J. Rivas, S. B. Oseroff, J. Mater. Chem., **8** (1998) 991-1000.
[4] W. Stöber, A.Fink, E. Bohn, J. Colloid Interface Sci., **26** (1968) 62.

Figures:

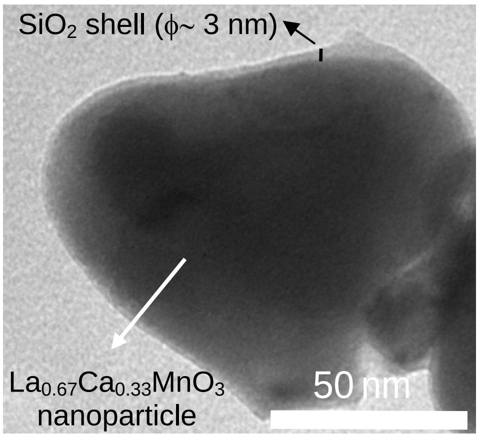

Figure 1. TEM micrograph of $La_{0.67}Ca_{0.33}MnO_3@SiO_2$ core-shell composite. The thickness of the SiO_2 nanocoating is ~ 3 nm.

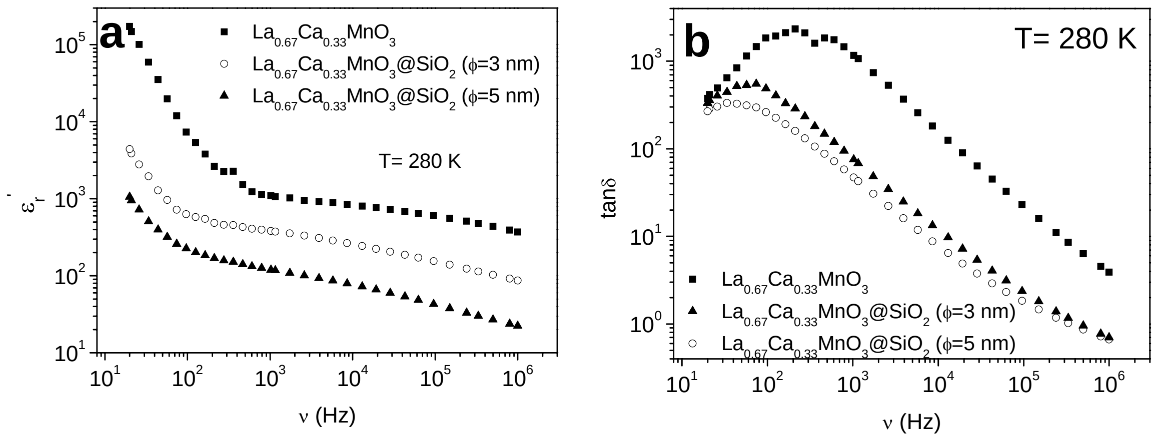

Figure 2. Frequency (ν) dependence of a) the dielectric constant (ε'_r) and b) the loss tangent (tanδ) for the $La_{0.67}Ca_{0.33}MnO_3$ nanoparticles and the $La_{0.67}Ca_{0.33}MnO_3@SiO_2$ nanocomposites measured at T= 280 K.