Effect of preparation conditions on the polymorphism and transport properties of lanthanum molybdates

J.M. Porras-Vázquez[1,*], A. López-Vergara[1], A. Infantes-Molina[1], J. Canales-Vázquez[2], A. Cabeza[1], E.R. Losilla[1], D. Marrero-López[3]

[1] Departamento. de Química Inorgánica, Universidad de Málaga, Málaga, 29071, Spain
[2] Inst. Energías Renovables. Univ. Castilla La Mancha, Albacete, 02071, Spain
[3] Departamento de Física Aplicada, Universidad de Málaga, Málaga, 29071, Spain

In this work, La_6MoO_{12}-based compounds were investigated as part of a new family of materials very competitive as hydrogen separation membranes [1,2].

$La_{5.4}MoO_{11.1}$ was synthesized by the freeze-drying precursor method and the calcination conditions were optimized in order to obtain single phases. Several cooling rates were applied and different polymorphs were obtained: a simple cubic fluorite symmetry (Fm-3m) for the sample cooled by quenching, and two different rhombohedral (R-3) space groups for the samples cooled at 50 ºC·min^{-1} and 0.5 ºC·min^{-1} (see Figure below). For the quenched sample, the Rietveld refinement was satisfactory in a Fm-3m space group. For the other two compositions no structural model was available and were indexed in a R-3 space group, however some small reflections were not given any intensity by the model used. Transmission electron microscopy confirmed the presence of superstructures for those samples. All ceramic materials were obtained with relative densities close to 100% after sintering at 1500 ºC. Stability studies demonstrated that all three polymorphs were stable in oxidizing and reducing conditions at 800 ºC for 48 hours.

The three samples present a significant proton contribution to the conductivity at temperatures lower than 800 ºC. These results were confirmed by thermogravimetric analysis. The highest conductivity values were observed for the samples prepared by quenching. The three polymorphs display a small p-type electronic contribution to the overall conductivity in oxidizing conditions and n-type electronic one in very reducing conditions, much more significant for the samples cooled by quenching and at 50 ºC·min^{-1}.

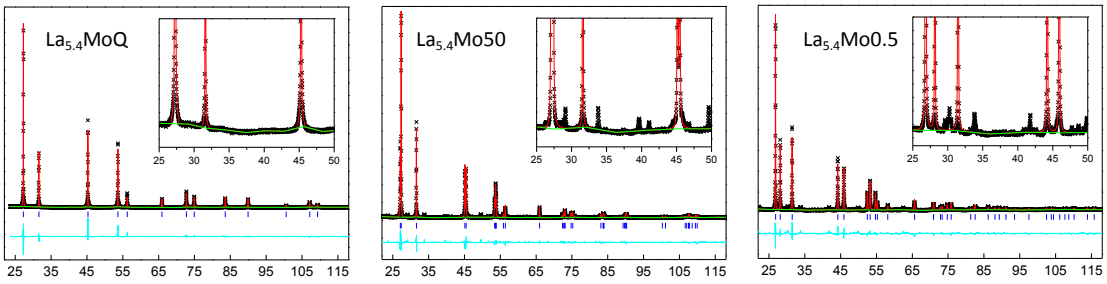

Figure 1. Rietveld plot for (a) cubic $La_{5.4}Mo\_Q$ and Le Bail plots for rhombohedral (b) $La_{5.4}Mo\_50$ and (c) $La_{5.4}Mo\_0.5$. [Observed data (open circles), calculated pattern (continuous line), and difference curve (bottom)

[1] Amsif M, Magraso A, Marrero-Lopez D, Ruiz-Morales J C, Canales-Vazquez J and Núñez P, Chemistry of Materials, 2012, 24, 3868−3877.

[2] Magraso A, Journal of Power Sources, 2013, 240, 583−588.