

Effect of the modification of the cationic and anionic framework on the structural and electrical properties of lanthanum molybdates

A. López-Vergara¹, M. Bergillos-Ruiz¹, J.M. Porras-Vázquez^{1,*}, D. Marrero-López², E.R. Losilla¹

¹ Universidad de Málaga, Dpto. de Química Inorgánica, Cristalografía y Mineralogía, 29071-Málaga, Spain.

² Universidad de Málaga, Dpto. de Física Aplicada I, 29071-Málaga, Spain.

(*) Corresponding author: josema@uma.es

Keywords: Lanthanum molybdate, cation and anion doping, fluorination, polymorphism, mixed ionic-electronic conductor, proton conductivity

1. Introduction

Nowadays, lanthanide molybdates ($\text{Ln}_{6-x}\text{MoO}_{12-\delta}$, Ln = La-Lu) are attracting attention as candidates for hydrogen separation membranes due to its high ambipolar proton-electron conductivity.

In these compounds, a very high degree of polymorphism is detected depending on the composition and synthesis-sintering conditions. Very recently, we carried out a comprehensive study of $\text{La}_{5.4}\text{MoO}_{11.1}$ and the effect of the synthesis temperature and cooling rate on the symmetry of the samples [1]. We found out that those samples suddenly cooled from 1500 °C present a simple cubic fluorite structure, whereas those cooled at slower rates, such as 50 and 0.5 °C min⁻¹, present complex rhombohedral polymorphs with superstructures, denominated in that work as R1 and R2, respectively. In addition, in our research group we also proceed to the modification of the cationic framework of these materials through metal-doping [2], a strategy already proved successful for related materials such as lanthanum tungstates [3]. The best results were obtained for Nb-doping, observing a stabilization of a different rhombohedral polymorph and an improvement of the densification and electrical properties.

Usually, cation doping is the most common strategy to modify/enhance the structural, microstructural and electrical properties of advance materials for energy applications, however, another possible approach is the modification of the anionic framework by substituting O^{2-} by other anions such as F^- or Cl^- [4]. Related materials to lanthanum molybdates, such as $\text{La}_{5.5}\text{W}_{0.6}\text{Mo}_{0.4}\text{O}_{11.25-\delta}$, have been fluorinated, resulting in an improvement of the hydrogen permeability [5].

The aim of this work is to study the synergic effect of the modification of the cationic (Ti^{4+} , Zr^{4+} and Nb^{5+} doping) and anionic (F^- doping) framework on the structural and electrical properties of $\text{La}_{5.4}\text{MoO}_{11.1}$ -based materials. The structural and microstructural aspects of these materials were studied by X-ray powder diffraction (XRPD), neutron powder diffraction (NPD), and scanning and transmission electron microscopy (SEM and TEM). The electrical characterization in reducing atmospheres was carried out by impedance spectroscopy.

2. Experimental

2.1 Synthesis

Materials with composition $\text{La}_{5.4}\text{Mo}_{1-x}\text{A}_x\text{O}_{12-\delta}$ ($x = 0$ and 0.1 ; A = Ti, Zr and Nb) were prepared by the freeze-drying precursor method, following the synthetic procedure detailed in a previous work for similar materials [3]. The dried precursor powders were firstly calcined at 300 °C for combustion and then at 800 °C for 1 h to remove the carbon species.

In order to prepared the fluorinated compositions, $\text{La}_{5.4}\text{Mo}_{1-x}\text{A}_x\text{O}_{12-y-\delta}\text{F}_{2y}$, the powders calcined at 800 °C were mixed with a stoichiometric amount of PVDF ($-\text{CH}_2-\text{CF}_2-$), $2y = 3$. The corresponding amount of PVDF and powder calcined were ground for 15 min in an agate mortar and then calcined at 360 °C for 12 h with heating and cooling rates of 1 and 10 °C min⁻¹, respectively.

Finally, the resulting powders, fluorinated and non-fluorinated, were calcined from 1200 to 1500 °C for 1h with heating and cooling rates of 10 and 5 °C min⁻¹, respectively.

2.2 Structural characterization

All samples were analyzed by laboratory X-ray powder diffraction (XRPD) by using a PANalytical Empyrean diffractometer with CuK α 1,2 radiation. The phase identification and structural analysis were performed using the X'Pert HighScore Plus and GSAS software.

2.3 Electrical characterization

Impedance spectra were acquired using a frequency response analyzer (Solartron 1260 FRA) in wet (2 vol.% H₂O) 5% H₂-Ar. The data were collected in the 0.01 Hz to 1 MHz frequency range with an ac perturbation of 100 mV on cooling from 800 to 200 °C.

3. Results and Discussion

3.1 Optimisation of the synthesis temperature

The fluorinated and non-fluorinated powders of La_{5.4}MoO_{11.1} were calcined from 1200 to 1500 °C for 1h with heating and cooling rates of 10 and 5 °C min⁻¹, respectively. At 1500 °C the fluorinated sample is a single phase, with a R1 rhombohedral symmetry, whereas the non-fluorinated equivalent in the same conditions is a mixture of R1 and R2. At 1400 and 1300 °C is not possible to stabilize any polymorph, being the samples a mixture of R1 and R2. However, it is worth mentioning the evolution from the non-fluorinated samples, a mixture of different polymorphs with the presence of La₂O₃. The most significant result is obtained at 1200 °C, where a single polymorph with cubic symmetry and a fluorite-type structure is detected, without the presence of secondary phases. This polymorph has been only obtained previously by the sudden cooling of the non-fluorinated samples from 1500 °C. Therefore, through fluorination is possible to obtain high symmetry polymorphs at lower temperatures, less expensive methods and procedures feasible at a laboratory scale.

3.2 Fluorination of La_{5.4}Mo_{0.9}A_{0.1}O_{12- δ} (A = Ti, Zr and Nb)

Bearing in mind the excellent results obtained for La_{5.4}MoO_{11.1}, it was carried out the simultaneous modification of the cationic and anionic frameworks of these compounds, La_{5.4}Mo_{0.9}A_{0.1}O_{12-y- δ} F_{2y} (A = Ti, Zr and Nb, 2y=3). Firstly, the non-fluorinated samples were calcined at 1200 °C for 1h with heating and cooling rates of 10 and 5 °C min⁻¹, respectively. As can be seen in Figure 1, Ti and Zr does not possess any stabilization effect on these materials, being detected the presence of the R2 polymorph and La₂O₃. On the other hand, for Nb doping, in addition to R2 and La₂O₃, it is also detected the presence of R1, highlighting the beneficial effect of niobium on the polymorphism of these materials. This behaviour was already detected in a previous work of our research group, where Nb doping led to stabilization of the R1 polymorph at 1500 °C with a cooling rate of 0.5 °C min⁻¹ [2].

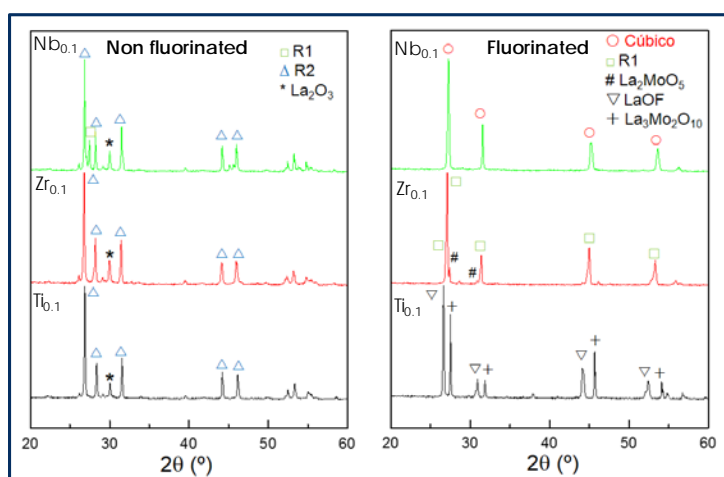


Figure 1. XRD patterns for La_{5.4}A_{0.9}M_{0.1}O_{12- δ} (A = Ti, Zr y Nb) non fluorinated (left) and fluorinated (right), sintered at 1200 °C for 1h and cooled down at 5 °C min⁻¹

Afterwards, it was carried out the fluorination of the metal doped samples, with the same sintering conditions described previously. As can be seen in Figure 1, for Ti and Zr doping is observed a clear evolution respect to the non-fluorinated ones, however, the samples are not single phase. However, excellent results were obtained for Nb and F doping, where the cubic polymorph is obtained. This polymorph has been only obtained previously by the sudden cooling of the non-fluorinated samples from 1500 °C.

Therefore, after these studies the only samples that were single phase and further characterised are: $\text{La}_{5.4}\text{MoO}_{12-\delta-y}\text{F}_{2y}$, sintered at 1500 (R1) y 1200 °C (cubic) for 1h; and $\text{La}_{5.4}\text{Mo}_{0.9}\text{Nb}_{0.1}\text{O}_{12-\delta-y}\text{F}_y$ (cubic) sintered at 1200 °C for 1h, all of them cooled down at 5 °C min⁻¹. The samples will be named hereafter as Undoped_1500, Undoped_1200 and Nb_{0.1}_1200, respectively.

3.3 Stability in reducing conditions

In order to evaluate the stability of these materials in reducing conditions and their possible use as hydrogen separation membranes, they were heated at 800 °C under a flux of 5% H₂-Ar. Undoped_1500 and Nb_{0.1}_1200 are stable after the thermal treatment, maintaining their original symmetry. However, Undoped_1200 is not stable under reducing conditions, being observed the segregation of La₂MoO₅ as secondary phase. These results highlight the stabilizing effect of Nb doping in lanthanum molybdates. Therefore, hereafter the only samples under study will be Undoped_1500 and Nb_{0.1}_1200.

3.4 Electrical characterisation

In Table 1 it can be seen the conductivity values in 5% H₂-Ar for the fluorinated Undoped_1500 and Nb_{0.1}_1200; and the non-fluorinated $\text{La}_{5.4}\text{MoO}_{12-\delta}$ and $\text{La}_{5.4}\text{Mo}_{0.9}\text{Nb}_{0.1}\text{O}_{12-\delta}$, prepared at 1500 °C for 1h and cooled down at 50 °C min⁻¹ (R1) and by quenching (cubic), respectively, in order to compare the results of the fluorinated samples with similar compositions but non-fluorinated.

Undoped_1500 present higher conductivity values that the non-fluorinated sample with the same symmetry, and very similar to the quenched cubic $\text{La}_{5.4}\text{Mo}_{0.9}\text{Nb}_{0.1}\text{O}_{12-\delta}$, highlighting the beneficial effect of the fluorination. Finally, Nb_{0.1}_1200, despite its cubic symmetry, present lower conductivity values, due to its low sintering temperature.

Table 1. Conductivity values (mS·cm⁻¹) at 400 y 800 °C for fluorinated and non-fluorinated samples.

Sample	Symmetry	$\sigma_{800\text{ °C}}$	$\sigma_{400\text{ °C}}$
$\text{La}_{5.4}\text{MoO}_{12-\delta}$ (1500 °C, 50°C min ⁻¹)	R1	7.33	2.6 10 ⁻¹
$\text{La}_{5.4}\text{MoO}_{12-y-\delta}\text{F}_{2y}$ (1500 °C, 5°C min ⁻¹)	R1	11.6	2.8 10 ⁻¹
$\text{La}_{5.4}\text{Mo}_{0.9}\text{Nb}_{0.1}\text{O}_{12-\delta}$ (1500 °C, quenching)	Cubic	11.9	2.7 10 ⁻¹
$\text{La}_{5.4}\text{Mo}_{0.9}\text{Nb}_{0.1}\text{O}_{12-y-\delta}\text{F}_{2y}$ (1200 °C, 5°C min ⁻¹)	Cubic	6.0	7.0 10 ⁻²

4. Conclusions

Fluorinated lanthanum molybdates have been prepared at 1500 and 1200 °C for 1 h and cooled down at 5 °C min⁻¹. The combination of anionic (F⁻) and cationic (Nb⁵⁺) doping stabilizes the cubic polymorph without needing a sudden cooling of the samples, increases the stability in reducing conditions and enhances the electrical properties.

Acknowledgements

This work has been supported by MINECO (Ministerio de Economía y Competitividad) through the MAT2016-77648-R research grant. J.M. Porrás-Vázquez thanks to the University of Malaga for the funding.

References

- [1] A. López-Vergara, J.M. Porrás-Vázquez, A. Infantes-Molina, J. Canales-Vázquez, A. Cabeza, E. R. Losilla, D. Marrero-López, *Chem. Mater.* 29 (2017) 6966–6975.
- [2] A. López-Vergara, J.M. Porrás-Vázquez, E. Vøllestad, J. Canales-Vázquez, E. R. Losilla, D. Marrero-López, *Inorg. Chem.* 57 (2018) 12811–12819.
- [3] M.J. Zayas-Rey, L. dos Santos-Gómez, D. Marrero-López, L. León-Reina, J. Canales-Vázquez, M.A.G. Aranda, E. R. Losilla, *Chem. Mater.* 25 (2013) 448–456.
- [4] H. X. Dai, C. F. Ng, C. T. Au, *Journal of Catalysis* 189 (2000) 52–62.
- [5] L. Chen, L. Zhuang, J. Xue, Y. Wei, H. Wang, *J. Mater. Chem. A*, 5 (2017) 20482-20490.