Lanthanide molybdates, $Ln_{5.4}MoO_{11.1}$ (Ln = Nd, Sm and Gd), for hydrogen separation membranes

José M. Porras-Vázquez[1,*], Javier. Zamudio-García[1], David Marrero-López[2], Enrique R. Losilla[1]
[1]Universidad de Málaga, Dpto. de Química Inorgánica, Cristalografía y Mineralogía, Málaga, Spain
[2]Universidad de Málaga, Dpto. de Física Aplicada I, Málaga, Spain
Corresponding author*: josema@uma.es

INTRODUCTION

Nowadays, lanthanide molybdates ($Ln_{6-x}MoO_{12-\delta}$, 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 $La_{5.4}MoO_{11.1}$ 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 ºC present a simple cubic fluorite structure, whereas those cooled at slower rates, such as 50 and 0.5 ºC min-1, present complex rhombohedral polymorphs with superstructures, denominated in that work as R1 and R2, respectively. Here, we extend this study to lanthanides smaller than lanthanum and evaluate the influence of composition and synthesis-sintering conditions on the structural and electrical properties.

EXPERIMENTAL

Samples with composition $Ln_{5.4}MoO_{11.1}$ (Ln = Nd, Sm and Gd) were prepared by a freeze-drying precursor method. The resulting powders were compacted into pellets and sintered at 1500 ºC for 1 h with a heating rate of 10 ºC min^{-1} and cooled down at three different rates: quenching (rapid cooling), 5 and 0.5 ºC min^{-1}. The samples were characterized by different techniques: X-ray diffraction, scanning and transmission electron microscopy and X-ray photoelectron and impedance spectroscopies.

RESULTS AND DISCUSSION

It was determined by X-ray diffraction that the materials are single phase after heating at 1500 ºC and cooling at different rates. Those cooled by quenching present a simple cubic fluorite structure. At lower rates, 5 and 0.5 ºC min^{-1}, the cubic symmetry is stabilized as the size of the lanthanide decreases, as can be seen in Figure 1.

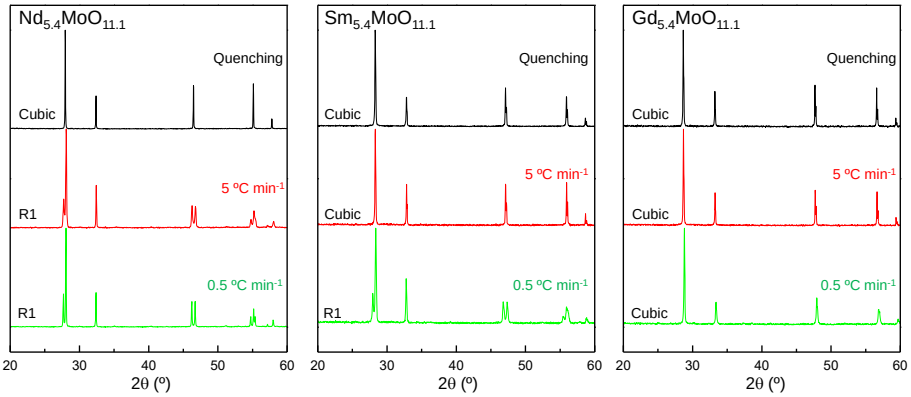

Figure 1: XRPD patterns for $Ln_{5.4}MoO_{11.1}$ heated for 1h at 1500 ºC and cooled down at different rates.

XPS analysis showed the presence of Mo^{6+} and Mo^{5+} for all samples. The reduction of the cooling rate for the same composition leads to an increase of the average grain size. For a same cooling rate, the decrease of the size of the lanthanide leads to a lower average grain size. The materials are stable in very reducing conditions and the electronic conductivity increases as the size of the lanthanide becomes smaller.

CONCLUSION

By selecting the composition and synthesis-sintering conditions is possible to fine-tune the structural and electrical properties of $Ln_{5.4}MoO_{11.1}$ (Ln = Nd, Sm and Gd).

REFERENCES

1. A. López-Vergara *et al*. Chem. Mater. 2017, 29, 6966−6975

ACKNOWLEDGMENTS

This work was supported by Min. Cienc. Inno. Univ. through the RTI2018-093735-B-I00 grant.

(HE) Hydrogen Energy