

Characterization of molybdenum substituted lanthanum tungstate: a Transmission Electron Microscopy study

Mayer, J.^{1,2}, Ran, K.³, Deibert, W.⁴, Ivanova, M.⁴ and Meulenberg, W.⁴

¹ Central Facility for Electron Microscopy, RWTH Aachen University, Germany, ² Ernst Ruska-Centre (ER-C) for Microscopy and Spectroscopy with Electrons, Forschungszentrum Jülich GmbH, Germany, ³ Central Facility for Electron Microscopy (GFE) RWTH Aachen University, Germany, ⁴ Institute of Energy and Climate Research IEK-1, Forschungszentrum Jülich GmbH, Germany

As an outstanding candidate for gas separation membranes, much attention has been recently received by lanthanum tungstate (LWO).^[1,2] LWO holds appreciable mixed protonic and electronic conductivity, thermal and hydrothermal stability as well as chemical stability in reducing and water-containing atmospheres at elevated temperatures. At low and intermediate temperatures, LWO is a relatively pure protonic conductor by hydration of intrinsic oxygen vacancies. In order to optimize its gas separation performance, enhancing its electronic conductivity while retaining a similar protonic conductivity would be desired. Among many studies, partial substitution of tungsten by a more reducible cation such as molybdenum or rhenium was reported to serve this purpose.^[3] However, in spite of extensive studies on the conducting properties of LWO or Mo/Re-substituted LWO and several reports determining their structures by neutron and X-ray diffraction,^[4] only a few attempts were made to characterize the mixed conductors using transmission electron microscopy (TEM) with atomic resolution.

Pure LWO and LWO with 20 at.% and 35 at.% molybdenum substitution (LWO-Mo₀₀, LWO-Mo₂₀ and LWO-Mo₃₅) were prepared by Pechini method. Scanning electron microscopy (SEM) and electron probe micro-analyzer (EPMA) results confirmed a single phase and a successful Mo substitution into these dense LWO membranes. Comprehensive TEM techniques, including high angle annular dark field (HAADF) imaging, electron diffraction and energy dispersive X-ray (EDX) chemical mapping were utilized to investigate the crystal structure of the Mo-substituted LWO. Consistent with HAADF image simulation, the experimental HAADF images from LWO-Mo₀₀, LWO-Mo₂₀ and LWO-Mo₃₅ show no significant difference from each other. Fig. 1a compares the experimental image from LWO-Mo₃₅ along [101] direction and a simulated one from LWO-Mo₀₀. In contrast, extra reflections were observed in diffraction patterns from the Mo-substituted LWOs, Fig.1b. Similar extra reflections show up in the simulations, when a W atom at the W₁ site is replaced by a Mo atom, Fig. 1c-d. Meanwhile, EDX chemical mapping allowed direct visualization of individual La, W and Mo atoms, and demonstrated the Mo replacing W atoms at the W₁ sites, in Fig. 2. Further analysis determined, that these extra reflections are originally forbidden scattering in the non-substituted LWO, and the accommodation of Mo set them free to appear. Moreover, diffuse scattering was detected in the diffraction patterns as well, which is a direct sign of clustering of oxygen vacancies in short range order and could be further related to the conducting performance of the LWO membranes.

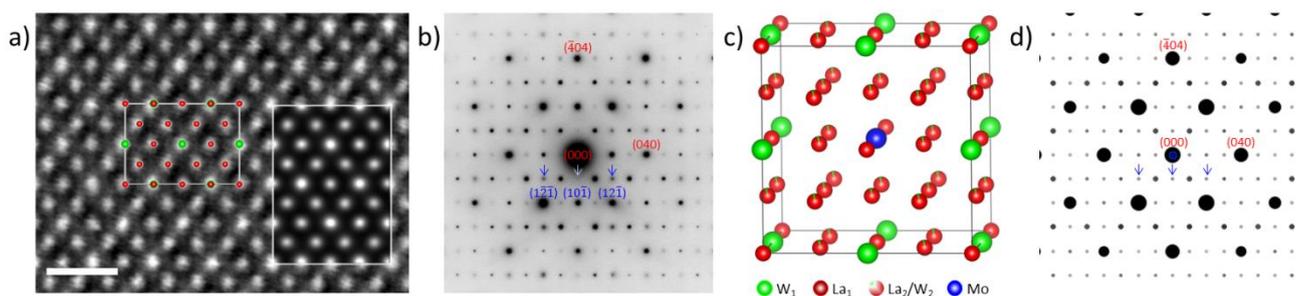


Fig. 1 (a) HAADF image from LWO-Mo₃₅ along [101] direction. Scale bar is 1 nm. Insets are the LWO structural model and a simulated HAADF image based on the LWO model along [101]. (b) Diffraction pattern from LWO-Mo₃₅ along [101]. (c) LWO model with the central W atom replaced by a Mo atom. (d) Simulated diffraction pattern based on the model in (c) along [101].

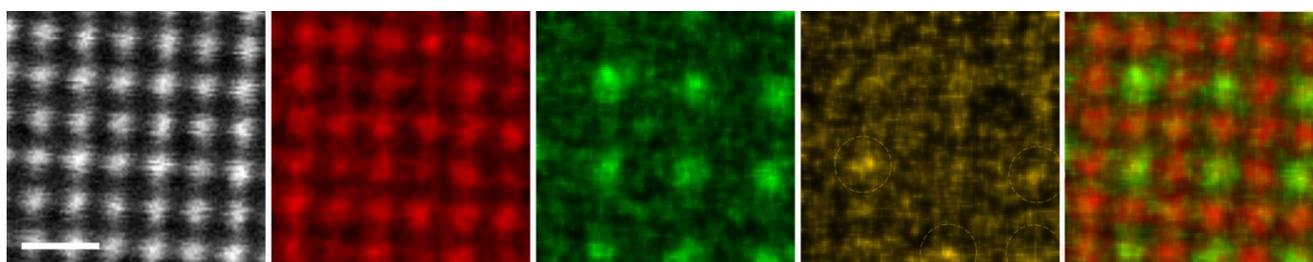


Fig. 2 (left to right) HAADF image, La, W, Mo and the mixed La/W map from LWO-Mo₂₀ along [001] direction. Scale bar is 5 Å.

Acknowledgement

We acknowledge support from the Bundesministerium für Bildung und Forschung (BMBF) under the Grant ProtOMem (FK 03SF0537A).

Reference

- [1] Seeger, J. *et al.*, Inorg Chem **2013**, 52, (18), 10375-10386.
- [2] Escolastico, S. *et al.*, Solid State Ionics **2012**, 216, 31-35.
- [3] Amsif, M. *et al.*, Chem Mater **2012**, 24, (20), 3868-3877.
- [4] Fantin, A. *et al.* J Appl Crystallogr **2016**, 49, 1544-1560.