Supporting Information for

Tungsten-Niobium Oxide Bronzes: A Bulk and Surface Structural Study

by

Daniel Delgado [a,b,*], Patricia Concepción [a], Annette Trunschke [b], Jose M. López Nieto [a,*]

[a)] Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas, Avenida de los Naranjos s/n, 46022 Valencia, Spain. E-mail: jmlopez@itq.upv.es ; dadelmuo@gmail.com

[b)] Department of Inorganic Chemistry, Fritz-Haber-Institute der Max-Planck-Gesellschaft e.V., Faradayweg 4-6, 14195 Berlin, Germany.

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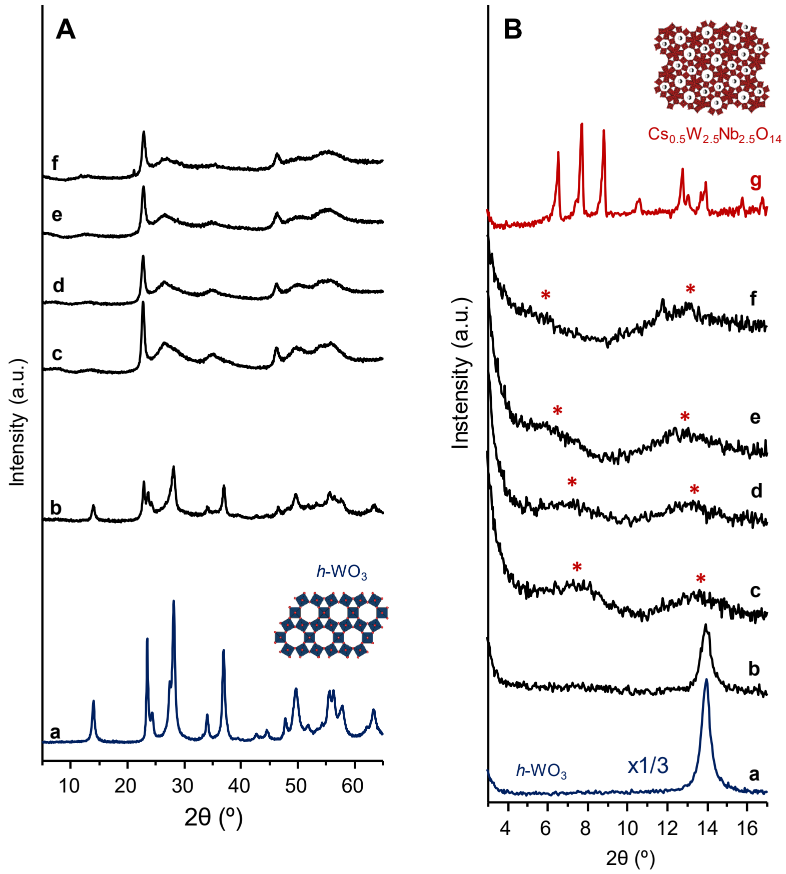

Figure S1. A) XRD patterns in the 2θ region 5-65º of as-prepared W-Nb-O oxides. a) WOx; b) WNb29; c) WNb62; d) WNb80; e) WNb95; f) Nb100. B) XRD patterns in the 2θ region 3-17º W-Nb-O oxides. For comparison, the pattern of a $Cs_{0.5}W_{2.5}Nb_{2.5}O_{14}$-type phase is included (g).

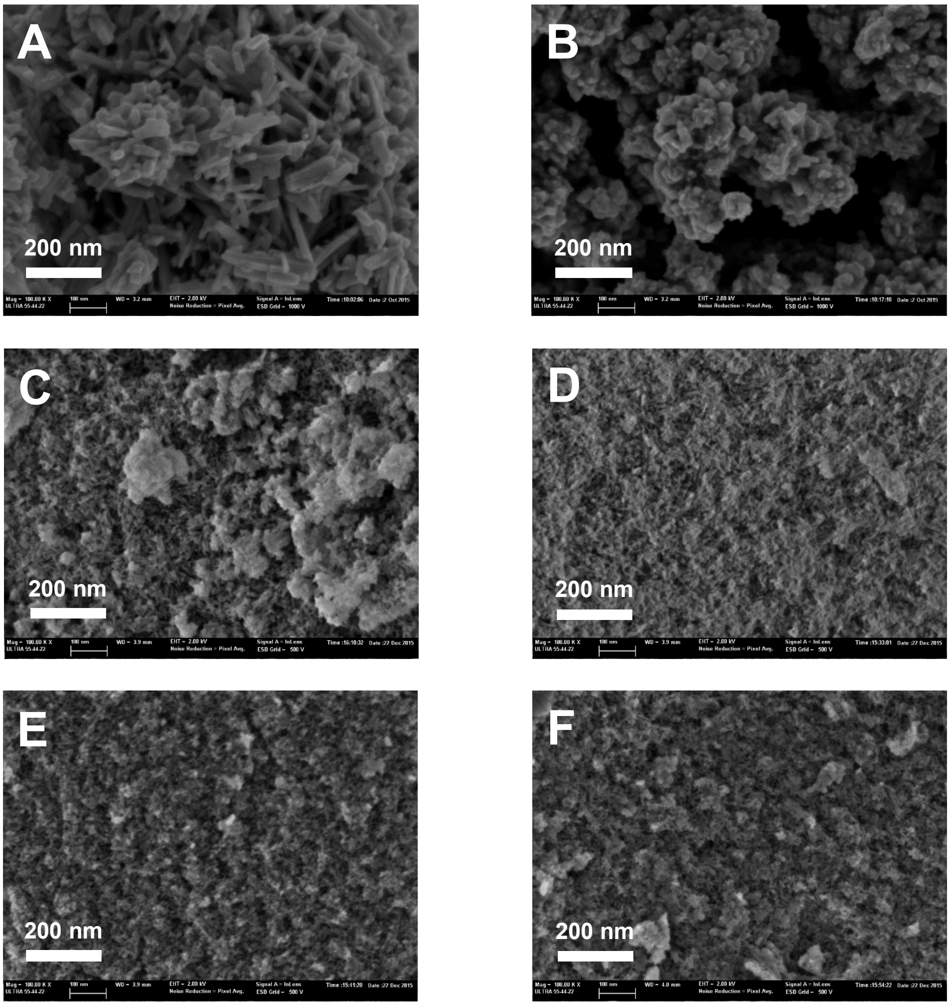

Figure S2. Scanning Electron Microscopy images of W-Nb-O oxides heat-treated at 550 ºC in N_2 flow. A) WOx; B) WNb29; C) WNb62; D) WNb80; E) WNb95; F) Nb100.

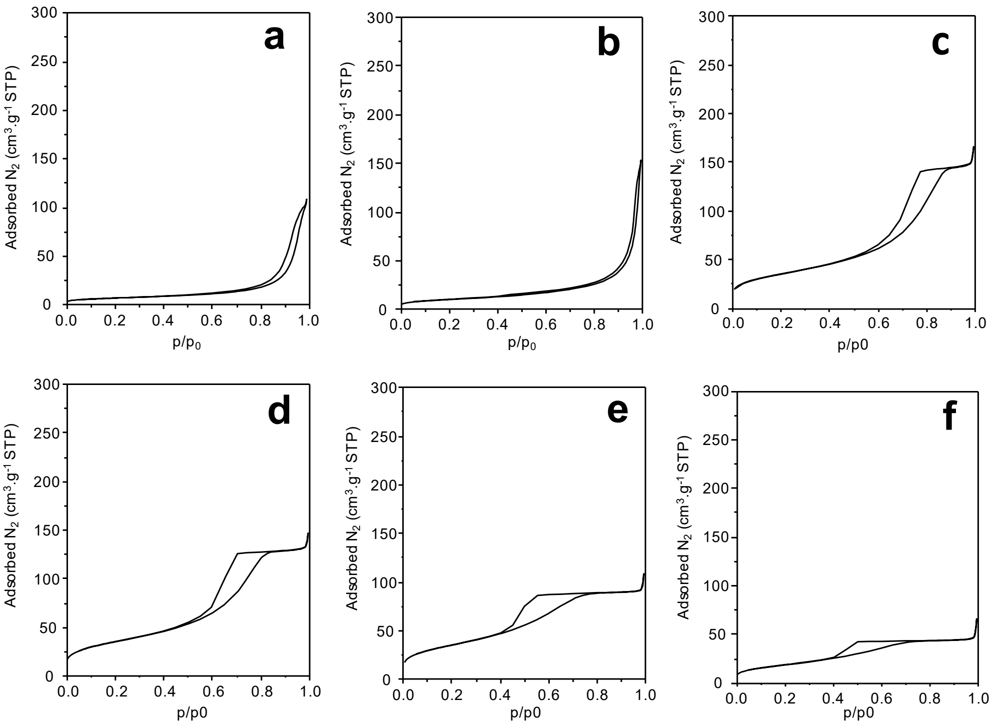

Figure S3. N_2-adsorption-desorption isotherms of W-Nb-O oxide bronzes: a) WOx, b) WNb29, c) WNb62, d) WNb80, e) WNb95, f) WNb-1

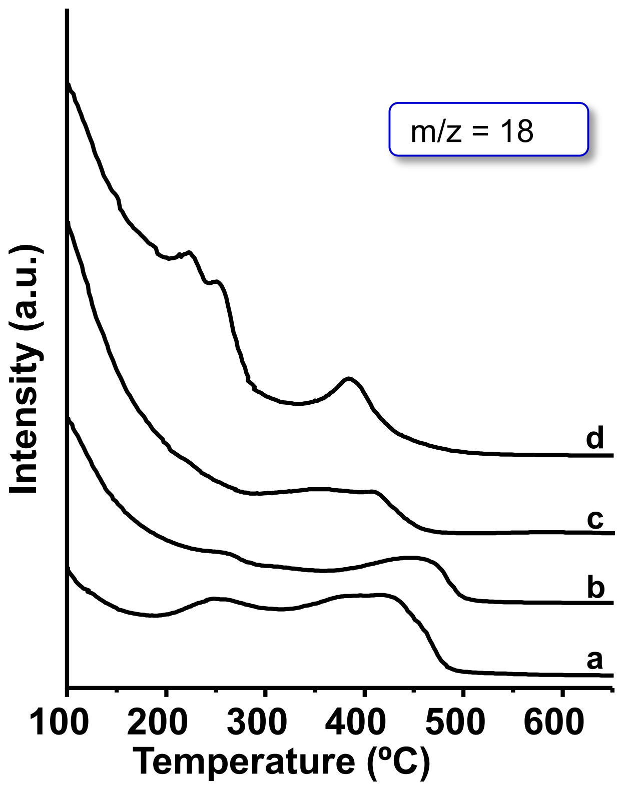

Figure S4. Temperature-programmed oxidation (TPO) profiles of selected as-prepared W-Nb-O samples, followed by mass spectrometry (characteristic mass of water, m/z=18). Samples: a) WOx; b) WNb29; c) WNb62; d) Nb100.

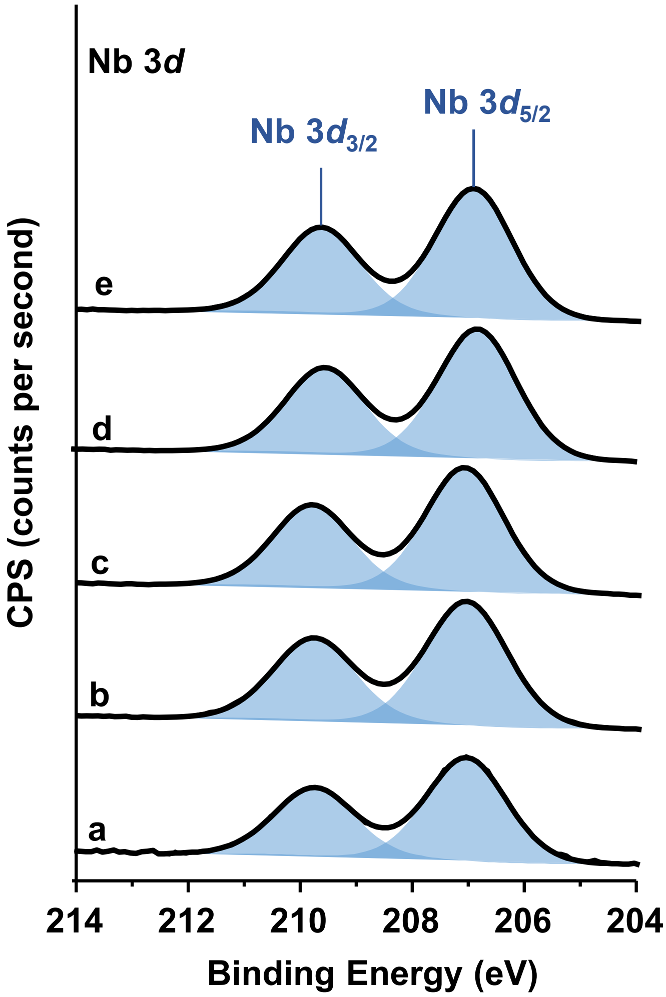

Figure S5. Nb 3d core-level XPS spectra of W-Nb-O oxides heat-treated at 550 ºC in N_2 flow. Samples: a) WNb29; b) WNb62; c) WNb80; d) WNb95; e) Nb100.

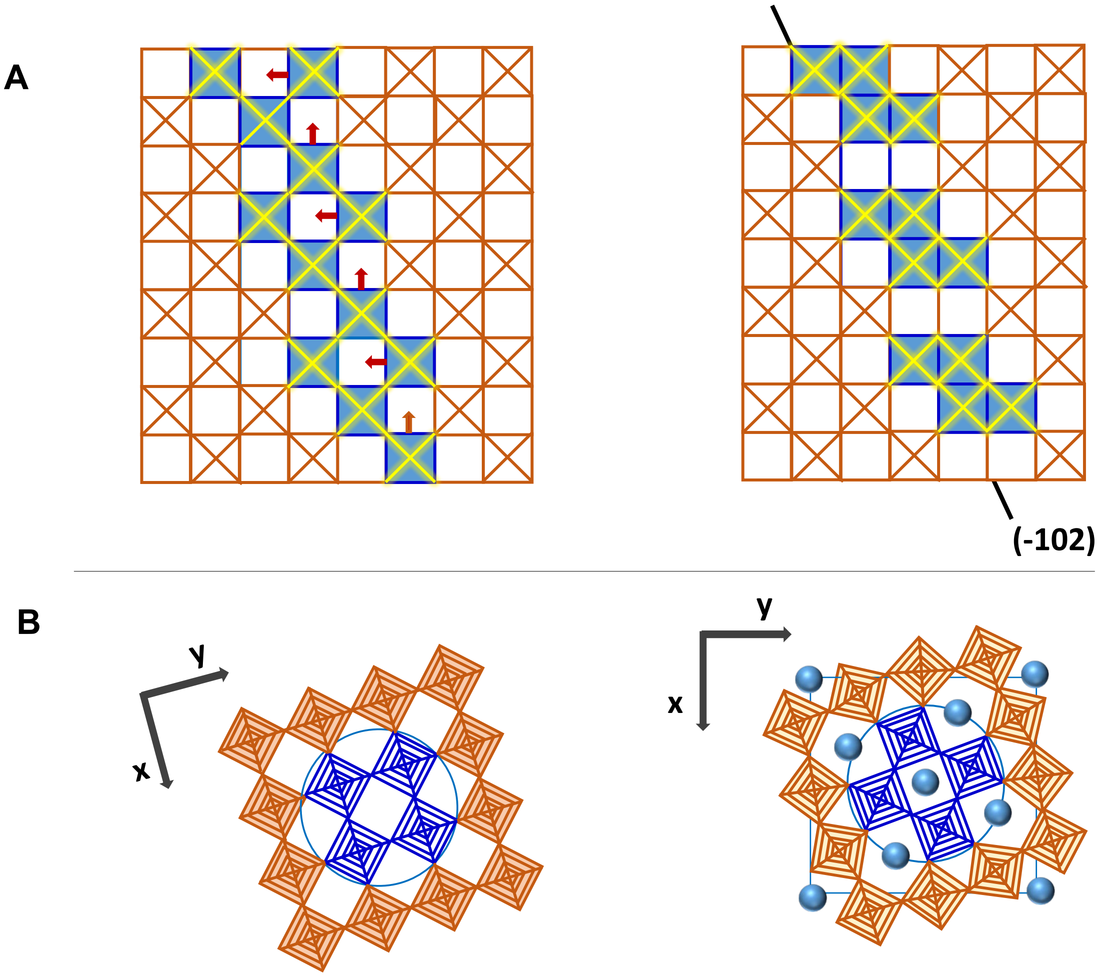

Figure S6. Schemes of the formation of the so-called Magneli phases (A) and tetragonal tungsten bronze (TTB) (B) from a ReO_3-type structure. Adapted from references [1] and [2].

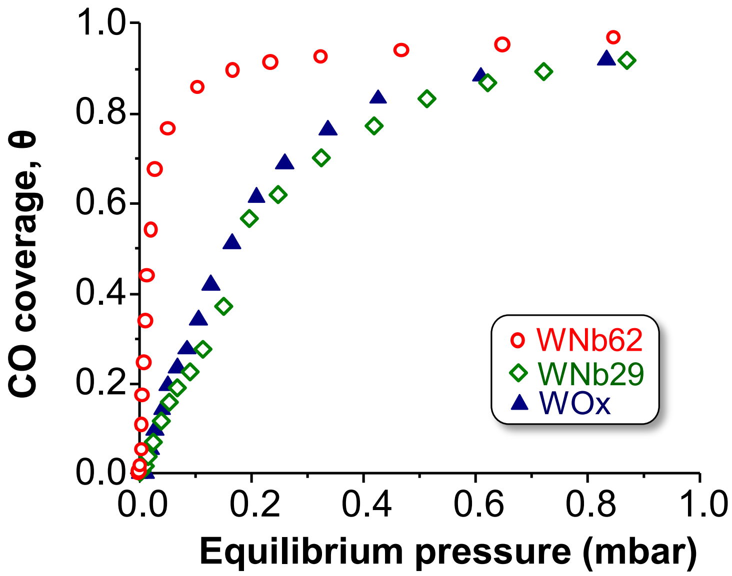

Figure S7. Variation of CO-coverage as a function of equilibrium pressure for selected W-Nb-O oxides, heat-treated at 550 ºC.

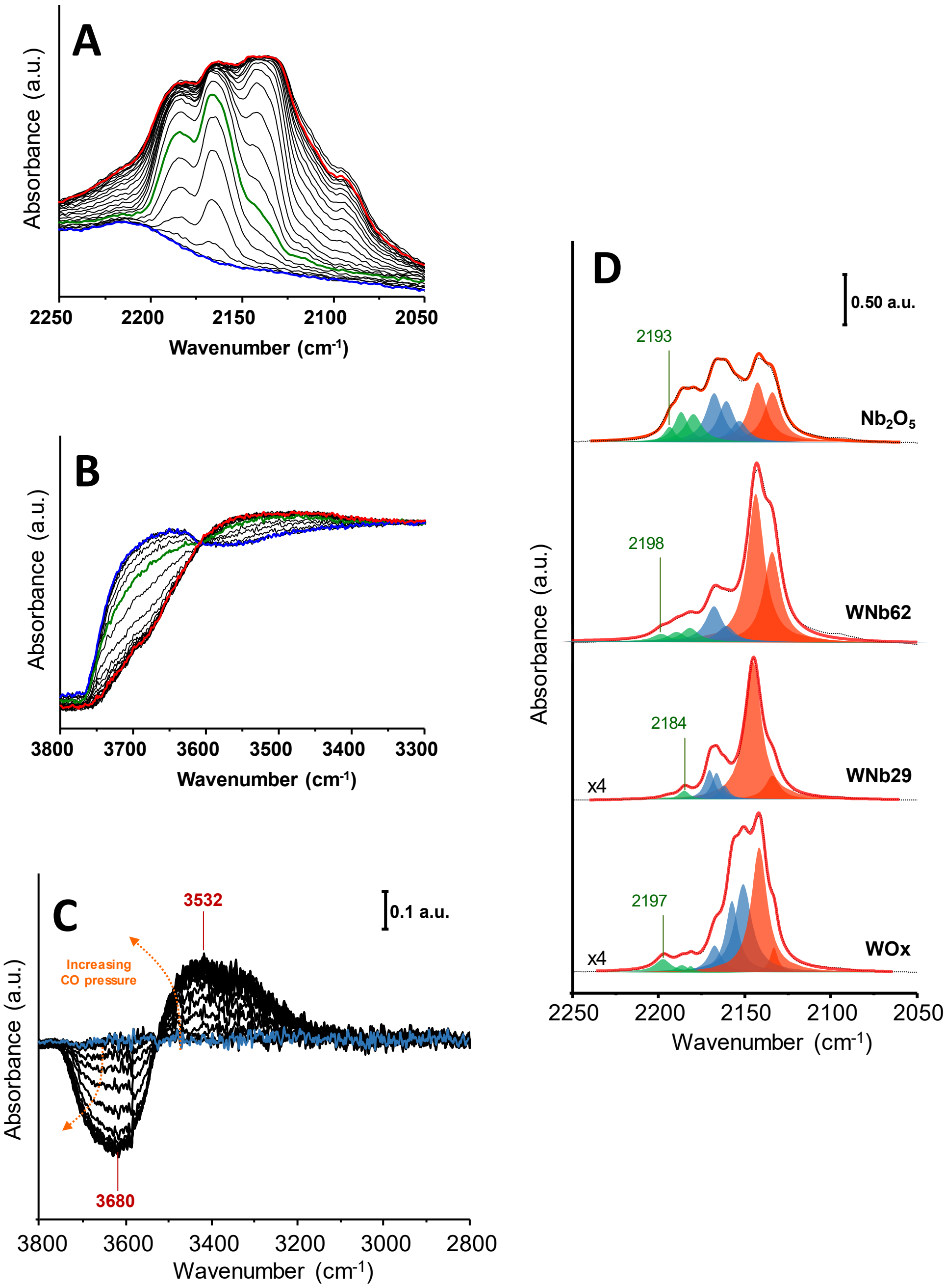

Figure S8. Low temperature (77K) FTIR spectra of adsorbed CO in the C-O (A) and O-H (B) stretching regions for hydrothermally synthesized Nb_2O_5 heat-treated at 400 ºC in N_2. C) Background-subtracted FTIR spectra of adsorbed CO in the OH/NH stretching region for hydrothermally synthesized Nb_2O_5 heat-treated at 400 ºC in N_2. D) CO-adsorption FTIR spectra (background-subtracted) and the corresponding deconvoluted spectra recorded at low temperature (77 K) at a CO-coverage of θ=0.65.

Table S1. Textural properties of W-Nb-O oxide bronzes

Sample	S_{BET} ($m^2\ g^{-1}$)[a]	Mesopore Volume ($cm^{-3}\ g^{-1}$)[b]
WOx	28	0.045
WNb29	38	0.050
WNb62	124	0.216
WNb80	129	0.192
WNb95	129	0.130
Nb100	70	0.061

[a] Calculated from N2 adsorption isotherms.
[b] Calculated by BJH method.

Table S2. Binding energies for main surface species in W-Nb-O oxides

Sample	C 1*s* (eV)	W $4f_{7/2}$ (eV)[a]		Nb 3*d* (eV)[a]	O 1*s* (lattice) (eV)[a]
		W^{6+}	W^{5+}		
WOx	285.7	35.4	34.6	---	530.1
WNb29	287.2	35.7	34.1	207.0	530.1
WNb62	286.4	35.7	34.7	207.0	530.2
WNb80	286.4	35.7	34.7	207.1	530.2
WNb95	286.3	35.4	34.4	206.8	529.9
Nb100	286.3	---	---	206.9	529.9

a. Corrected to C1s= 284.5 eV

References:

[1] C. N. R. Rao, J. Gopalakrishnan, New directions in Solid State Chemistry, Second Edition, Cambridge University Press, 1997, pp. 258.[2] L. A. Bursill, B. G. Hyde, Nature Physical Science 240 (1972) 122-124