Structural and vibrational properties of WO_3-based materials

As previously indicated in Chapter 1, tungsten trioxide does not only exhibit different phases depending on the temperature, but it is also likely to host several kind of defects and specially oxygen vacancies. The crystalline structure of some of these phases has been a matter of discussion in Chapter 3, so in this appendix some structural parameters are provided. Table 1 is a summary of the different phases, PDF Card numbers and Space groups (adapted from Depero et al.[*])

	Card number	*Spce group*	*a (Å)*	*b (Å)*	*c (Å)*	*α (º)*	*β (º)*	*γ (º)*
WO_3	20-1323	P*	7.30	7.52	7.69	88.83	90.91	90.93
WO_3	32-1395	P1	7.309	7.522	7.678	88.81	90.92	90.93
WO_3	43-1035	P21/n	7.297	7.539	7.688	90	90.91	90
WO_3	20-1324	-	7.384	7.512	3.846	90	90	90
WO_3	5-388	P4/nmm	5.25	5.25	3.91	90	90	90
WO_3	33-1387	P6/mmm	7.298	7.298	3.899	90	90	120
$W_{25}O_{73}$	30-1387	P2/c	11.93	3.82	59.72	90	98.30	90
$W_{20}O_{58}$	5-386	P2/m	12.05	3.767	23.59	90	94.72	90
$WO_{2.9}$	18-1417	P4/nmm	5.30	5.30	3.83	90	90	90
$WO_{2.9}$	36-102	-	12.1	3.78	23.6	90	94.6	90
$W_{24}O_{68}$	36-106	-	19.31	3.781	17.07	90	104.4	90
W_5O_{14}	41-745	P-421m	23.33	23.33	3.797	90	90	90
$W_{17}O_{47}$	44-396	P2/m	18.84	3.787	12.326	90	102.67	90
$W_{18}O_{49}$	5-392	P2/m	18.28	33.775	13.98	90	115.2	90
$W_{18}O_{49}$	36-101	P2/m	18.32	3.784	14.035	90	115.20	90

Table 1: *Structural parameters of the WO_3 and WO_{3-x} phases found in the PDF database*

Appart from these oxygen-deficient structures, another important point discussed in this work are the Raman and Infrared vibrations for tungsten trioxide and the $WO_3 \cdot xH_2O$ compounds. A summary of the characteristic frequencies, according to Daniel et al.[**] is provided in Table 2.

[*] *L.E. Depero, S. Groppelli, I. Natali-Soria, L. Sangaletti, G. Sberveglieri, E. Tondello, Structural studies of tungsten-titanium oxide thin films, J. Sol. State Chem 121 (1996) 379-387.*

[**] *M.F. Daniel, B. Desbat, J.C. Lassegues, B. Gerand and M. Figlarz, Infrared and Raman study of WO_3 tungsten trioxides and WO_3,xH_2O tungsten trioxides hydrates, J. Solid State Chem. 67 (1987) 235-247.*

	m-WO₃		***WO₃·1/3H₂O***		***WO₃·H₂O***	
	IR	R	IR	R	IR	R
ν***(OH)***			3390		3550	
					3495	
			3170			
δ***(OH)***			1620		1609	
					1410	
ν***(W=O)***			1000	945		
			950		948	948
ν***(O-W-O)***	870		820			
	815	807	740			
	755	715	710	680	730	
	665		660		680	
Water					420	
Librations					370	
					330	
ν***(W-OH₂)***				320	370	377
	380	434	420			
	330	327			330	
δ***(O-W-O)***	280	273			270	
ν***(W-O-W)***	225	218	360			253
				320		235
						192
			270	255		
Lattice		187				
modes		134		190		150
		93		155		90
		71				50
		61				36
		44				
		34				

Table 2: *Characteristic frequencies (cm^{-1}) of the WO_3 and $WO_3 \cdot xH_2O$ compounds.*