

Vanadium valency and hybridization in V-doped hafnia investigated by electron energy loss spectroscopy

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Abstract. The valency of vanadium, and thus indirectly the oxygen stoichiometry, of V-doped hafnia synthesized under different atmospheres have been investigated on a nanometer scale by means of electron energy loss spectroscopy (EELS). The EELS V $L_{2,3}$ spectra are compared with the results of crystal field multiplet calculations and experiments on reference vanadium oxides. The EELS spectra indicate that V-doped hafnia prepared under reducing (H_2) and neutral (Ar) atmosphere are unambiguously substituted with trivalent vanadium atoms leading to the creation of oxygen vacancies in the structure. On the contrary, stoichiometric (Hf, V)O₂ compound (*i.e.* V⁴⁺) is more likely to be stabilized under oxidative (air) atmospheres. We also show that the amount of hybridization alters for the different compounds studied but may in part be analyzed by high spatially resolved EELS. The crystal field multiplet calculations particularly indicate that a simple reduction of the Slater integrals gives a good account of the spectral modification induced by hybridization for the case of tetravalent vanadium atoms.

PACS. 61.50.Nw Crystal stoichiometry – 71.28.+d Narrow-band systems; intermediate-valence solids – 78.70.Dm X-ray absorption spectra

1 Introduction

Electron energy loss spectroscopy (EELS), which permits the electronic density of states to be probed at a nanometer scale, is a powerful tool to study the chemical state of doping elements in nano-powders or inhomogeneous materials [1–3]. Furthermore, the EELS of transition metal (TM) oxides, on which this study will be focused, can, in a first approximation, be successfully described within a nearly atomic picture as far as TM $3d$ states are involved [4,5]. So, EELS experiments combined with atomic multiplet calculations may be an efficient method to study the ground state symmetry of TM substituted into an oxide, and so indirectly deduce the oxygen stoichiometry of the compound as will be demonstrated in this paper. On the other hand, one has to note that the oxygen stoichiometry cannot be accurately quantified on the nanometer scale with conventional techniques, such as energy dispersive X-ray spectroscopy (EDS), which involves low energy X-ray and strong absorption phenomena within the analysis volume.

In this paper we investigate on a nanometer scale the valency of vanadium, *i.e.* the oxygen stoichiometry, in V-doped hafnia synthesized under different atmospheres by mean of electron energy loss spectroscopy. The nanometre size of the powders [6,7], the questionable heterogeneity, as well as the need to examine crystallographic structure and cation compositions prior to spectroscopic experiments governs the choice of the EELS in the context of a transmission electron microscope (TEM).

Hafnia HfO₂, like zirconia ZrO₂, exists in three different polymorphs, depending on temperature. From room temperature up to 1700 °C, the structure is monoclinic. Above 2600 °C, hafnia adopts a cubic fluorite type structure. Between 1700 °C and 2600 °C, hafnia has a tetragonal structure, which corresponds to a small displacement of the oxygen positions, compared to the cubic structure [8]. The high temperature cubic phase can be stabilized at room temperature by doping with a trivalent ion, usually Y³⁺ leading, in the case of ZrO₂, to the well known YSZ or Yttrium Stabilized Zirconia. The main applications for YSZ are mechanically stable refractory ceramics, and high temperature oxygen sensors. The latter application is related to the alio-valent substitutions and to the existence of oxygen vacancies in the YSZ [9–11]. The close structural analogy between ZrO₂ and HfO₂, as

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well as the fact that vanadium atom may adopt different valencies, has motivated the EELS study of the V 3d ground state for various vanadium-doped hafnia powders.

We first present an EELS study of the V L_{2,3} edges from a set of reference vanadium oxides: VO₂ (rutile structure isostructural to TiO₂ [12]), V₂O₃ (corundum structure isostructural to Al₂O₃ [13]), V₂O₅ (orthorhombic structure, space group Pmmm [14]) and HfV₂O₇ [15]. For the binary oxides, the V atoms are 6-fold coordinated with the oxygen ligands and are located in nearly octahedral sites. Nevertheless, the effect of the metal-metal interaction may easily distort the crystal structure of binary oxides and complicated temperature-dependent structural changes occur. In HfV₂O₇, the V ions are located in tetrahedral sites [15]. The EELS V L_{2,3} features of these references are discussed in relation to the results of multiplet calculations taking into account effects of local symmetry as well as finite covalency effects. Indeed, variation of the covalency has already been shown to alter the TM L_{2,3} and O-K features for other transition metal oxides (Fe [16], Ni [17]). For instance, analysis of the O-K edges fines structures achieved by Hu *et al.* [17] suggest that cation ordering between Li and Ni into Nd₂Li_{0.5}Ni_{0.5}O₄ results in isolated NiO₆ clusters and to a more localized ground state compared to the (La, Sr)₂NiO₄ structure where NiO₆ polyhedra are interconnected. As similar non-local effect might be expected with the dilution of vanadium atoms inserted as impurity in the different structures, the preliminary study of binary oxides is required to afford reliable support for the EELS interpretation for the V-doped hafnia.

Furthermore, the possibility of using EELS to quantify accurately the transition metal (TM) valency is still a matter of debate due to the limited energy resolution of high spatially resolved EELS experiments and to the wide spread application of phenomenological rules which may fail for specific systems (white line ratio methods, for example, [18]). In particular, we will show that multiplet features are visible on V L_{2,3} edges with the energy resolution of a conventional TEM-EELS system (*i.e.* around 0.5–1 eV, which is 2–6 times larger than the lifetime broadening of a TM multiplet).

In the second part we present the EELS V L_{2,3} spectra of V-doped hafnia. These are examined in terms of valency, hybridization and oxygen stoichiometry, which are deduced and analyzed together with considerations about the nature of processing atmosphere.

2 Experimental procedure

2.1 Materials processing

The detailed preparation processes of the V-doped hafnia and of the reference oxides (VO₂, V₂O₃, V₂O₅, HfV₂O₇) are described in a previous article [6]. The V-doped HfO₂ powders were labeled R, N or O, depending on the preparation atmosphere, either reducing (H₂), neutral (Ar) or oxidising (air), followed by the indication of the percentage of vanadium inserted. For instance, compound named R30

corresponds to a cationic composition of 30% of vanadium atoms and of 70% of hafnium atoms as determined by EDS measurements [6]. Turquat *et al.* [6] have already showed that the cubic fluorite phase was stabilized for R10, R20 and R30 as well as for N20 and N30. The solubility limit of vanadium in the cubic phase is not reached until 30% of inserted vanadium. The powders prepared under air always exhibit the monoclinic structure, and the solubility limit of vanadium was found to be 7%. The excess of vanadium in O10, O20, and O30 leads to the formation of HfV₂O₇ nano-crystals [6].

2.2 EELS measurements

For the EELS investigation, thin areas of samples were obtained by crushing small crystals and suspending powders on a holey carbon grid. The electron energy-loss spectra were recorded using a Philips CM20 (LaB₆ gun) transmission electron microscope operating at 100 keV and fitted with a Gatan PEELS 666 parallel electron spectrometer. The energy resolution estimated at the full width at half maximum of the zero-loss peak was $\Delta E = 0.7$ eV. The following conditions were chosen to acquire the EELS spectra: an illumination semi-angle $\alpha = 2.5$ mrad, a collection semi-angle $\beta = 3$ mrad and an energy dispersion of 0.1 eV/ch. The spatial resolution, governed by the probe size, was between 10 to 50 nm. A STEM VG HB501 field emission gun fitted with a modified Gatan 666 parallel-EELS spectrometer equipped with a CCD detector has also been used to get higher spatially resolved information. Series of spectra were then acquired by scanning the 1 nm probe across a chosen line on the sample.

In order to calibrate the energy positions of the V L_{2,3} edges accurately, the compounds studied as well as a V₂O₃ reference oxide were deposited on the same carbon grids. The EELS measurements may thus be achieved rapidly for the two phases, avoiding any energy drifts. The chemical energy shift measured on the V L₃ maximum is thus determined with 0.1 eV accuracy. Finally the V L₃ maximum for V₂O₃ was measured using the coarse internal calibration system based on the electrostatic drift tube of the EELS spectrometer and set at 517.6 eV.

The EELS spectra were obtained in the CM20 transmission electron microscope, using an under-heated filament in order to improve the energy resolution of the EELS system. Under these conditions, the incident intensity was very low and vanadium oxides were found to be stable (neither amorphisation nor fine structure alterations were observed) during long beam exposure (several minutes). When performing STEM-VG microscope measurements, the use of a CCD detector and the line spectrum technique permit rapid acquisition of the EELS spectra (< 1 s), thus avoiding beam damage. We are confident in this procedure since the shape of the V L_{2,3} spectra for the beam-sensitive HfV₂O₇ samples collected in the STEM-VG and the CM20 microscope are similar. Furthermore, reference HfV₂O₇ oxide and crystals, obtained when the solubility limit of vanadium in monoclinic HfO₂ is reached, have been observed.

3 Results and discussions

3.1 Reference oxides

Figure 1 shows the V $L_{2,3}$ spectra and the first ten eV of the O-K spectra of binary oxides V_2O_3 , VO_2 and V_2O_5 , which can be taken as reference spectra of V^{3+} , V^{4+} and V^{5+} respectively. The spectrum of HfV_2O_7 compound which corresponds to vanadium in formal valence 5, is also shown for comparison. Since intra-atomic correlations are preeminent, EELS V $L_{2,3}$ edges correspond to excitations from the $2p^63d^n$ V ground state towards the $2p^53d^{n+1}$ V states [19]. The two major features of these edges are the strong white-lines L_3 and L_2 due to the spin orbit splitting of the $2p$ core hole and separated by about 6.5 eV. Additional fine structures appearing as shoulders on the sides of the two main L_3 , L_2 peaks or as pre-peaks have been marked by arrows. Meanwhile, chemical shifts of 1.2 eV and 1.3–1.4 eV have been respectively measured, at the maximum of the V L_3 line, between the two higher oxidation states (V^{4+} and V^{5+}) and the trivalent compound (V^{3+}).

3.1.1 V $L_{2,3}$ electron energy loss spectrum of V_2O_3

The EELS spectrum recorded for V_2O_3 (Fig. 1) closely resembles those previously obtained by X-ray absorption spectroscopy (XAS) [20–22] and by EELS equipped with a monochromator filter [23]. In particular, the small bump-in between the L_3 and L_2 edge can be seen in spite of our poor energy resolution of about 0.7 eV (compared to an energy resolution of about 0.1–0.2 eV for the previously cited work). In order to assess how characteristic of the V d^2 high spin ground state these particular fine structures are, crystal field multiplet calculations of the V $L_{2,3}$ spectra using TT-MULTIPLETS programs have been performed. We have in particular investigated if the spectral shapes are highly sensitive to the environment of the V atom, since in V-doped hafnia the local surroundings of the vanadium atoms may change from a perfect cubic symmetry in the fluorite type structure to a lower symmetry for monoclinic, tetragonal, or non stoichiometric hafnia. The code used consists of a package of Cowan's atomic multiplet program [24] and Butler's group-theory program [25]. Detailed descriptions of these techniques may be found in the review article by De Groot [5]. The fitting parameters of the multiplet model are the crystal field parameters (Dq , Ds , Dt defined in [26] and Δ_t equal to $E(e_g^\pi) - E(a_{1g})$), which take into account the local symmetry of the ion. Reduction factors for the atomic Hartree-Fock values of the Slater integrals (r_{pd} and r_{dd} for the p - d and d - d Slater integrals respectively) may also be introduced to account for intra-atomic configuration interaction and to mimic part of the hybridization effects.

Figure 2a displays the calculated spectra of a $3d^2$ ground state, which correspond to V^{3+} ground state, in octahedral symmetry O_h . Calculations have been performed for different values of the crystal field splitting parameter $10Dq$ between the t_{2g} and e_g orbitals. The Slater

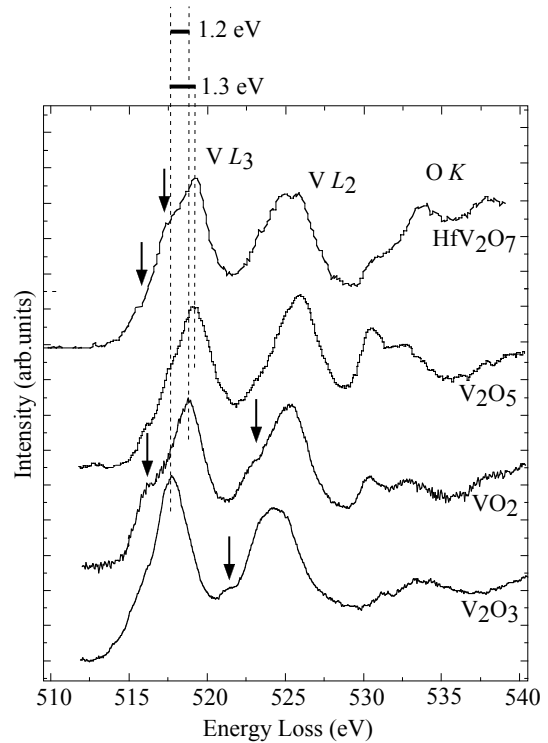


Fig. 1. Comparison between the V $L_{2,3}$ EELS spectrum of reference oxides.

integrals have been reduced to the typical 70% of their atomic values in order to take into account intra-atomic configuration interaction. The calculated lines arising from the atomic transitions between the $2p^63d^2$ V ground state and the $2p^53d^3$ configuration have been broadened by a Lorentzian function of 0.2 eV (full width at half maximum) to take into account the finite core hole life time. Furthermore, all the spectra showed in Figure 2 have been broadened by a Gaussian function of 0.3 eV (full width at half maximum), which is around two times better than our experimental resolution and enable a clearer picture of the evolution of the fine structures. Except for the splitting of the L_2 edge the calculated spectra are close to the experimental spectra of the V_2O_3 . In particular the small peak in-between the two white lines is well reproduced (see also the calculated spectra from De Groot [27] and Van der Laan [19] in cubic symmetry). Figure 2a also shows that this small bump is still clearly visible for a small crystal field splitting (for an oxide) of 1 eV and is maintained for a crystal field value of 2 eV (and also in fact for unrealistic values up to 3–4 eV). The energy position of this remarkable bump is linearly related to the crystal field parameter and the fine structures of V_2O_3 are better modelled for a value of $10Dq$ equal to 1.7 eV. Spectra of V^{3+} for lower symmetry of the vanadium site have also been calculated. Figure 2b displays two spectra calculated in the D_{4h} symmetry (typical of a uniaxial distorted octahedron) with $10Dq = 1.5$ eV, $Dt = 0$ eV, and $Ds = 0.1$ and 0.2 eV [26]. When the Dt parameter is set to zero, the degenerate yx and yz orbitals are both occupied and the

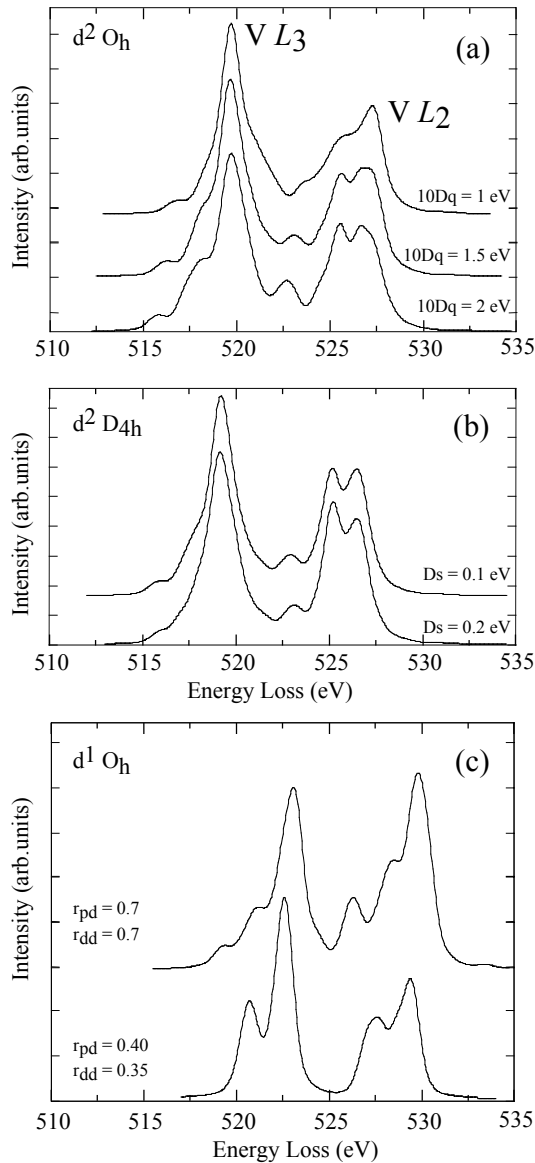


Fig. 2. (a) V $L_{2,3}$ EELS calculated spectrum of $3d^2$ ground state for various octahedral crystal field strength $1 \text{ eV} < 10Dq < 2 \text{ eV}$. (b) V $L_{2,3}$ EELS calculated spectra of $3d^2$ ground state for various D_{4h} crystal field splitting ($10Dq = 1.5 \text{ eV}$, $Dt = 0 \text{ eV}$ and $Ds = 0.1$ and 0.2 eV). (c) V $L_{2,3}$ EELS calculated spectra of d^1 ground state for “usual” (top) and larger (bottom) reduction of the Slater integrals. Crystal field multiplet calculations are not suitable for the calculation of absolute energy and the spectra have to be shifted for comparison to experiments.

V $3d^2$ ion may not suffer any high spin to low spin transition whatever the value of the Ds distortion parameter. Thus, one can calculate the spectra for large values of the Ds distortion parameter keeping a high-spin ground state: we found that spectra hardly ever alter with the distortion parameter and the small bump is visible until a Ds value of 0.45 eV , which we believe to be an unrealistically large value [28]. More generally, changes in the tetragonal

component of the crystal field (varying Ds but also Dt) are evidence of the presence of a small peak between the two white lines, provided that the high-spin ground state is maintained. Calculations in T_d symmetry, and lower C_{4h} , C_{3v} symmetry confirmed the permanency of these remarkable features. One can also find in the literature simulations for a trigonal distortion (C_{3v} symmetry) [29]. For this symmetry, the occupied t_{2g} orbital splits into a non degenerate a_{1g} and a doubly degenerate e_g^π orbital. The calculations of Park *et al.* [22] thus show that the spectrum, for a trigonal component Δ_t of the crystal field as strong as $\Delta_t = E(e_g^\pi) - E(a_{1g}) = 1.7 \text{ eV}$, still resembles to that for an undistorted O_h situation (*i.e.* $\Delta_t = 0 \text{ eV}$).

To sum up, despite the apparent small differences in these spectra, most of the peaks and shoulders of the pure octahedral site could be recognized in spectra for lower symmetry. Thus the small bump may be confidently regarded as a fingerprint of the presence of a trivalent vanadium (high spin) in an oxide, whatever the structure of this compound. Experimentally, this is confirmed by the weak changes of the isotropic V $L_{2,3}$ spectra during the metal-insulator transition of V_2O_3 despite the fact that this transition is accompanied by a strong distortion of the VO_6 octahedra, as evidenced by Abe *et al.* [23] and Park *et al.* [22]. The similarity between the XAS V $L_{2,3}$ spectra of various compounds such as $Z_2V_2O_4$ [30], $LiVO_2$ [29], YVO_3 [31] and V_2O_3 [22] strengthen this assumption.

3.1.2 V $L_{2,3}$ electron energy loss spectrum of VO_2

For the case of VO_2 oxide, the maximum of the V L_3 line in the EELS (Fig. 1) occurs at about 1.2 eV higher in energy relative to V_2O_3 , in agreement with previous XAS experiments on this binary oxide [21]. The main features of the EELS VO_2 spectrum are the strong shoulders on the lower energy side of the L_3 and L_2 lines, also reported in the works from Abe *et al.* [32].

Figure 2c shows in its upper part the spectrum calculated for a V d^1 ground state in an octahedral symmetry, with $10Dq = 1.5 \text{ eV}$ and a scaling factor of the Slater integrals of 70%. The spectrum is in clear disagreement with the experimental one from the VO_2 compound, showing a small peak in-between the two white lines and a much higher $I(L_2)/I(L_3)$ (note that the calculated spectra do not contain transitions to the continuum which tends to increase the $I(L_2)/I(L_3)$ ratio in the case of experimental data shown in Fig. 1). However the calculated spectrum is identical to the experimental results of Pen *et al.* [31], who identified their calculation with the XAS V $L_{2,3}$ spectrum of the V^{4+} created in $Y_{1-x}Ca_xVO_3$ by hole doping, for low x values.

The discrepancy between the experimental and calculated spectra may be reduced by scaling to lower values the Slater integrals. Figure 3c displays (lower part of the figure) multiplets calculation of $3d^1$ ($10Dq = 1.7 \text{ eV}$) using a reduction factor of 40% for pd integrals and 35% for dd integrals. The calculated spectrum more accurately reproduced the main fine structures of the EELS V $L_{2,3}$ edges for VO_2 , demonstrating that strong Slater integral

reductions give a good account of the spectral modification induced by the increased hybridization of tetravalent vanadium atoms. However, one has to keep in mind that, for vanadium oxides, the crystal field multiplet description is at the limit of its domain of applicability since, unlike the case of the later transition metals, correlation effects do not entirely dominate the electronic behavior (the band description approach being however less suitable). Indeed, the $3d^1$ and $3d^2$ configurations have a partially t_{2g} band behaving in a more extended character. One of the consequences for these binary oxides is a larger metal-metal interaction, made possible because the vanadium-oxygen polyhedra are connected. This, for instance, results in the formation of dimers below 350 K in VO_2 .

To summarize, significant changes both in the white line ratio and in the different fine structures may allow us to detect, using our EELS equipment, the presence of V^{4+} at a nanometer scale. On the other hand, the change of the white lines ratio with the hybridization clearly shows that the unique use of the L_3/L_2 white lines intensity ratio [18] is not reliable to determine the oxidation state of V cations in solids by EELS.

3.1.3 V $L_{2,3}$ electron energy loss spectra of V_2O_5 and HfV_2O_7

Spectra of V_2O_5 and HfV_2O_7 , the vanadium being in formal valency 5, are presented in Figure 1. They exhibit similar fine structures in spite of the different local symmetry of the vanadium atoms (distorted octahedra and tetrahedra), suggesting that valency strongly dominates these features. Our EELS V_2O_5 spectrum is close to the XAS spectra of Abbate *et al.* [21], and in particular the two weak shoulders on L_3 may be detected. The shape of the $L_{2,3}$ edges does not show well resolved multiplet structures, in contrast to other $3d^0$ configuration such as TiO_2 , which have been successfully simulated using a multiplet calculation with a $3d^0$ ground state in O_h symmetry [19]. On the contrary, for these systems, no clear agreement with multiplet calculations can be achieved by using O_h , D_{4h} , or T_d symmetries. This is not surprising given the experimental similarities observed between the spectra of the two compounds despite the different local environment of the vanadium atoms. A large Slater integral reduction, or the use of a ground state consisting of a mixture of an ionic $3d^0$ configuration and of a $3d^1\bar{L}$ ligand hole configuration (where \bar{L} denotes a hole in $2p$ oxygen orbital) does not lead to a better simulation of the main fine structure of the EELS spectra. No significant chemical shift has been measured compared to the VO_2 spectrum in agreement with previous XAS data [21].

3.2 EELS study of the vanadium valence and hybridization in V-doped hafnia

The V $L_{2,3}$ spectra of the vanadium-richer hafnia, synthesized under both reducing and neutral conditions are

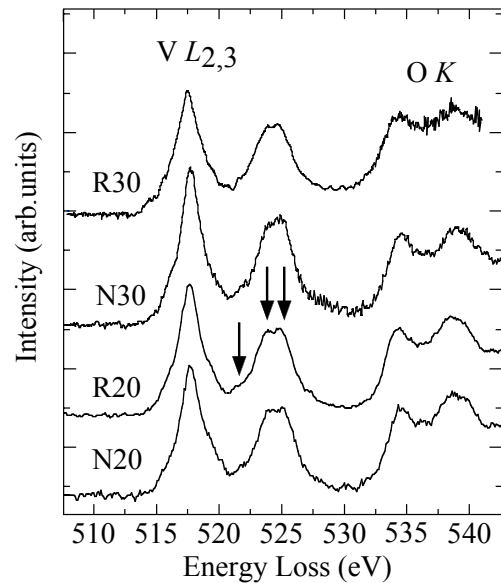


Fig. 3. Comparison between the V $L_{2,3}$ EELS spectra of R30, R20, N30 and N20.

gathered in Figure 3. For both types of samples, the absolute energy and the main structures (the small bump between L_3 and L_2 , the splitting of L_2) clearly indicate that the vanadium atoms are trivalent whatever the exact substitution site, the vanadium content (20 to 30%) and the conditions of preparation (neutral or reductive). One may remark that if V substitutes for Hf in the perfect cubic HfO_2 structure (as expected from selected area electron diffraction patterns and EDS measurements), it will be located at the center of an oxygen cube with a large V-O bond length of around 0.22 nm. This assumption is strengthened by the fact that a crystal field splitting of $10Dq = 1.1-1.2$ eV is required in the multiplet calculation for V^{3+} in perfect cubic symmetry to simulate the experimental spectra. This low value of the crystal field may be ascribed to the large distance bond. However, the presence of oxygen vacancies, as well as small structural distortions or even monoclinic hafnia may decrease the local symmetry and the coordination number without invalidating the measurement of nearly pure V^{3+} $L_{2,3}$ edges shape in these compounds as discussed in previous section. Furthermore, compared to the V_2O_3 spectrum, the white lines of the V- HfO_2 are much narrower, and we measure a L_3 line width (FWHM) of about 3.1 eV and 2.05 eV respectively. We believe that this spectrum narrowing is mainly the result of the presence of isolated vanadium ions in HfO_2 : (i) This results in a band narrowing (in the initial state) compared to the binary oxide, (ii) The coupling of the final state $\text{V } 2p^5 3d^{n+1}$ with vibrational modes is suggested from the Frank-Condon principle to severely broadens the EELS spectra of the V_2O_3 compound [20]. In the case of structures in which VO_n polyhedra are interconnected, leading to a V-O-V percolated network and thus to a V-V hybridization, the V $L_{2,3}$ excitation that promotes an electron into an antibonding d orbital, strongly affects

the V-V potential. The resulting difference in the equilibrium position between ground state and final state allows vibronic excitations to occur in a wide energy range, leading to a spectral broadening of the V $L_{2,3}$ edges [20]. On the contrary, isolated vanadium ions as found in V-doped hafnia, will experience less Frank-Condon broadening.

The samples prepared under oxidizing conditions appear as V-doped HfO_2 crystals of 10–30 nanometers size in contact with discrete HfV_2O_7 crystals. Spatial resolution of the order of ten nanometers was not sufficient to study the individual crystallites. Thus in order to get information at the sub-nanometer scale, we used the line spectrum approach available in dedicated STEM-EELS equipment [33, 34]. In this technique, a series of spectra are acquired at regular increments along a line by scanning the probe over the area of interest. Simultaneous EELS acquisition and probe progression are produced by computer control. One can visualize the line spectrum as 3D plots of intensities measured as a function of both the probe position along one axis and the energy loss along the other axis. This technique is particularly well suited to measure chemical shift or evolution of fine structures, since all spectra are acquired under the same experimental conditions. Such a line spectrum containing 128 spectra and acquired along an analysis line of 100 nm across a HfV_2O_7 /monoclinic $(\text{Hf}_{0.93}\text{V}_{0.07})\text{O}_2$ (*i.e.* O7)/ HfV_2O_7 region at the specimen is presented in Figure 4a. Because of the short acquisition time necessary to avoid beam damage, each spectrum from the line has a low signal to noise ratio and fine structures are barely perceivable. We have improved their quality (Fig. 4b) by simply adding the spectra of the same phase along a line. Boundaries between the different phases are determined by intensity profile (Fig. 4c). Spectra of HfV_2O_7 and O7 phases hence extracted from these line spectra are shown in Figure 4b, and compared to the V $L_{2,3}$ spectrum from R20 sample.

First, two aspects are noted from this analysis: the white line ratio varies only slightly along the line scan (Fig. 4c) and no significant chemical shift of the V L_3 maximum between the HfV_2O_7 (V^{5+}) and the O7 hafnia is measured. This excludes the presence of trivalent vanadium in the V-doped hafnia phase prepared under an oxidizing atmosphere. Furthermore, since the spectroscopic signatures of the V d band roughly correspond to the EELS signature of a VO_2 sample with a strong multiplet density on the lower energy side of the two white lines, we will assume that V^{4+} may be predominant in the V-doped HfO_2 oxidized samples. On the other hand, the spectrum does not resemble one from a more ionic V^{4+} ground state, which has been simulated by scaling the Slaters integral at 70% of their atomic values (Fig. 2c). These differences reveal a more significant amount of delocalization of the d band in $(\text{Hf}, \text{V}^{4+})\text{O}_2$, than we might have expected for dilute vanadium doping based on the previous XAS investigation on hole-doped $\text{Y}_{1-x}\text{Ca}_x\text{VO}_3$ [31].

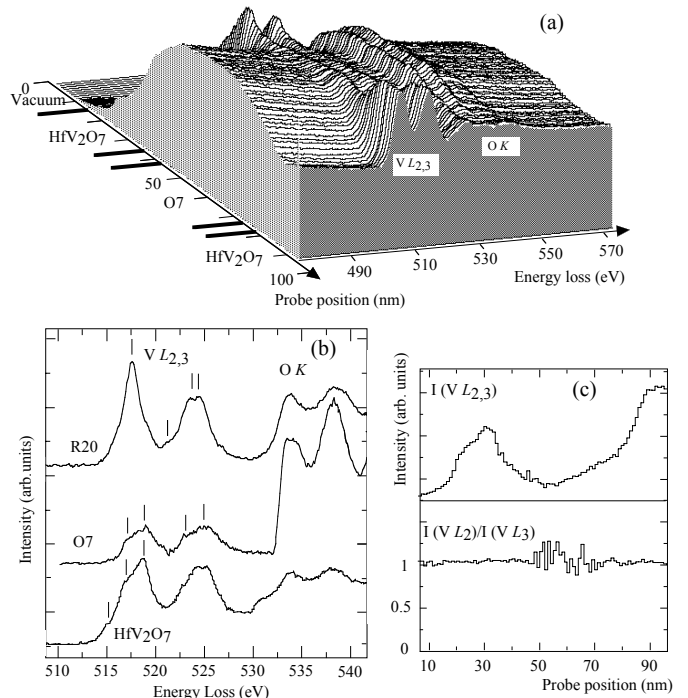


Fig. 4. (a) Variation of the EELS O K and V $L_{2,3}$ edges across a HfV_2O_7 /monoclinic $(\text{Hf}_{0.93}\text{V}_{0.07})\text{O}_2$ (*i.e.* O7)/ HfV_2O_7 sequence measured during a line-spectrum acquisition. (b) Comparison between the V $L_{2,3}$ EELS spectrum of R20, O7 and HfV_2O_7 . (c) Intensity profiles calculated by integrating the signal over EELS V $L_{2,3}$ edges (top), intensity profiles of the $I(L_2)/I(L_3)$ estimated by integrating the signal over a 2 eV wide energy-window centered on the two white lines maxima (bottom).

3.3 Stoichiometry considerations concerning V-doped hafnia

We now address the following question about the comparison between the R-N samples (assuming to be V^{3+}) prepared under reducing or neutral conditions and those prepared under oxidizing conditions (O samples considered more likely as predominantly V^{4+}): are these presumed differences in the formal number of d holes compensated by vacancies in the oxygen sub-lattice?

Primarily, one has to note that previous XAS results indicate that the general trend for extra holes or electrons in vanadium oxide is to reside in the V $3d$ band [30, 31, 35, 36] and so to classify vanadium oxides, primarily as Mott Hubbard insulators [37]. Thus, contrary to insulators with strong charge transfer character, if oxygen vacancies in $(\text{Hf}, \text{V})\text{O}_{2-y}$ induced change in valency, this may confidently be detected and quantified by probing the TM $L_{2,3}$ edges.

The O-K edges are also expected to be sensitive to the formal valency of the TM and to the degree of covalency since in an ionic picture the O $2p$ shell would be completely filled. For instance, Pen *et al.* show that for large doping ($x > 0.4$) in $\text{Y}_{1-x}\text{Ca}_x\text{VO}_3$, the V^{4+} ions tend to become a stronger mixing of $3d^1$ and $3d^2\bar{L}$ configurations, leading to an increase in the intensity near the O-K edges

attributed to the states with mixed $O2p$ - $V3d$ character. From this point of view, one might expect the O-K edges of the V doped hafnia to be sensitive, at least partially, to the V ground state. Nevertheless, the O-K edges do not change dramatically with the vanadium content and with the different processing atmospheres. In fact, no clear pre-peaks, which could be attributed to $O2p$ - $V3d$ hybridization, are observed for any of the hafnia samples. Although this $O2p$ - $V3d$ hybridization states should be present at around 533–534 eV, it may be masked by the dominant Hf and O interactions (this assumption is strengthened by close O-K edge features even in V-free hafnia such as R0 and N0 compounds). This may also arise when analyzing certain aspects previously reported. (i) For R-N samples, as discussed previously, V^{3+} bearing hafnia has a strongly localized character leading to a weak contribution of the $3d^3\bar{L}$ configuration in the ground state and then to a presumably weak contribution of the V $3d$ states in the O-K edge. (ii) Conversely, for oxidized V-doped hafnia (V^{4+}) and as inferred from its V $L_{2,3}$ edge analysis, the vanadium ground state is more delocalized but the V $3d$ contribution in the O-K edges may remain weak because the amount of vanadium inserted under these conditions is very limited. However, as stated before, the V $L_{2,3}$ edge is expected to be highly sensitive to the presence of oxygen vacancies in hafnia.

Structural investigations have also been performed on the same samples and may help to answer the present question. For R-N samples, vanadium doping leads to solely stabilized cubic hafnia. If one keeps in mind that the iso-structural zirconia is also stabilized in its cubic structure by Y^{3+} doping accompanied with the creation of vacancies, structural investigation strengthens the assumption of presence of oxygen vacancies in R-N hafnia. Local compositional measurements of $[Hf]/[V]$ [6] confirm that at least 30% of vanadium may be inserted in place of Hf, which in the rudimentary scheme where two trivalent vanadium atoms create one oxygen vacancy, leads to about 3/40 of the oxygen sites vacant. Such a small number of oxygen vacancies cannot be directly determined by routine EELS quantitative analysis, because of the sensitive background removal for the superposed V $L_{2,3}$ and O K edges and of the inadequate cross-section models available. Using reference spectra to fit the R-N EELS spectra would however increase the accuracy of EELS quantitative analysis despite the difficult choice in the reference spectra but may still not be accurate enough to achieve the desired precision (close to one percent in the determination of the $[O]/[V]$ ratio). No attempt of such accurate EELS quantitative analysis has been made in this paper.

For the series of O samples, the lack of structural rearrangement of the monoclinic hafnia while vanadium impurities are inserted and the much lower solubility limits (a distinct HfV_2O_7 structure is formed) suggest the absence of oxygen vacancies.

It can thus be reasonably deduced that presumed differences in the formal number of d holes for R-N and O samples should be compensated by vacancies in the oxygen sub-lattice.

4 Conclusions

In summary, we have demonstrated that EELS combined with multiplet calculation is a powerful tool to study the local stoichiometry in vanadium oxides and we have observed that vanadium-doped hafnia may be synthesized with different oxygen stoichiometries.

Hafnia prepared under reducing (H_2) and neutral (Ar) atmosphere are unambiguously substituted with trivalent vanadium atoms as demonstrated by V $L_{2,3}$ EELS fine structures, leading to the creation of oxygen vacancies in the structure and to a believed general formula close to $(Hf_{1-x},V_x)O_{2-x/2}$. An absolute classification of the vanadium $3d$ electrons as being “localized” or “delocalized”, if *meaningful*, is not possible from solely these EELS measurements. Nevertheless vanadium $3d$ electronic waves are closer to a “localized” limit in the V-doped hafnia compared to the case of the binary trivalent oxide. This large decrease of the d - d hybridization may be related to a non-percolated V-O-V network, even in the case of the compounds richer in vanadium.

On the contrary, the stoichiometric compound $(Hf,V)O_2$ (*i.e.* V^{4+}) is stabilized under oxidative (air) atmospheres with a solubility limit of the V atomic concentration of about 2.3%. Surprisingly, spectroscopic signatures of the V d band do not correspond to the XAS signal obtained from V^{4+} atoms occurring in hole-doped $Y_{1-x}Ca_xVO_3$ but closely resemble those from the more “delocalized” picture of the binary VO_2 oxide. Our crystal field multiplet calculations also reveal that simple reductions of the Slater integrals still give a good account of the spectral modification for the change in hybridization in these systems.

In addition, we want to point out that EELS techniques enable us to rule out any compositional, valence and hybridization heterogeneity of these powders at a nanometer scale.

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