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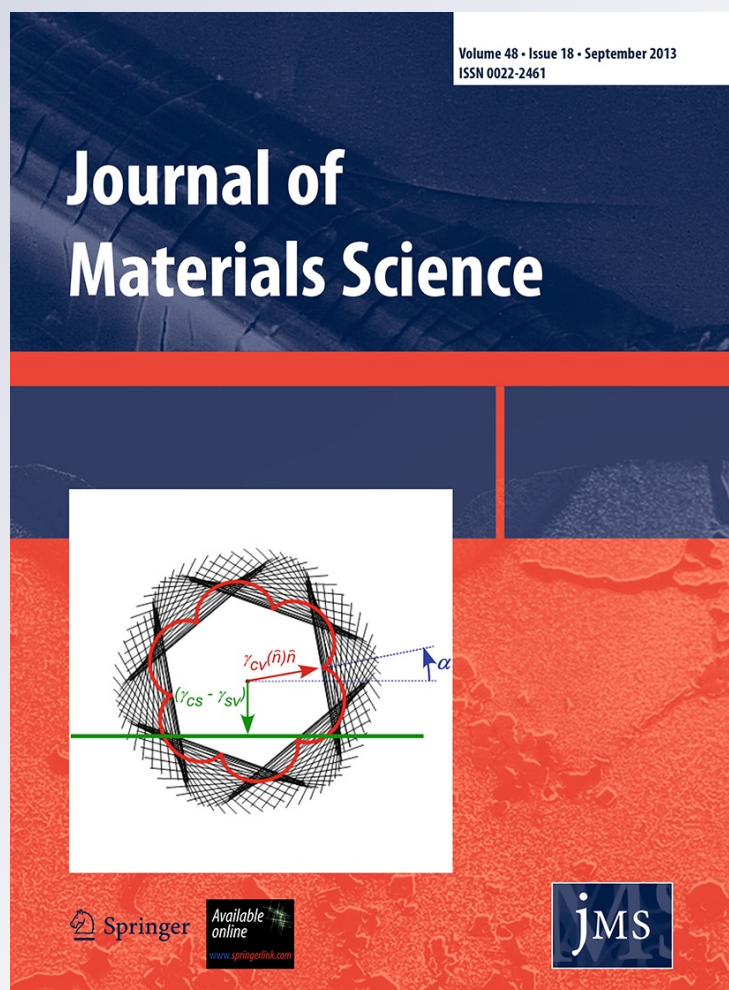
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Excited states in yttrium orthovanadate YVO_4 measured by soft X-ray absorption spectroscopy

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Abstract We present the electronic structure of vanadium in YVO_4 compound obtained by X-ray absorption (XAS) at the $\text{L}_{2,3}$ edge. We also performed a charge transfer multiplet calculation (CTM) to analyze the experimental results. YVO_4 compound was synthesized by the polyacrylamide sol–gel method. For a comparative evaluation, YVO_4 compound was prepared by solid-state reaction. XAS results show that the increase of heat treatment favored the presence of one oxidation state V^{5+} . We observed a distinctive broadening at L_2 edge of vanadium due to the L_2L_{3v} Coster–Kronig process. We identify the excitations of $3d$ bonding orbitals by CTM on the XAS

results. Tetragonal parameters (D_s and D_t) in D_{4h} symmetry reveal a compression of the $3d$ orbitals in the z direction.

Introduction

It is well known that the crystalline form of yttrium vanadate (YVO_4) compound is tetragonal, with space group of D_{19}^{4h} I_{41}/amd , which is related to tetragonal zircon (ZrSiO_4 -type) [1–3]. The crystal structure of YVO_4 compound is shown in Fig. 1 in a polyhedral representation. The YVO_4 compound crystal includes two kinds of polyhedral: VO_4 tetrahedron and YO_8 triangular dodecahedron. Each V^{5+} site is surrounded by four oxygen atoms ($4c\text{-V}$, T_{2d}) with a separation of 1.71 Å between V and O, and each Y is surrounded by eight O atoms ($8c\text{-Y}$) with a Y–O distance of either 2.29 Å (for four of the eight Y–O bonds) or 2.44 Å (for the remaining four Y–O bonds), the point symmetry of Y^{3+} is D_{2d} without an inversion center. The shortest V–V, Y–Y, O–O, and V–Y distances are about 3.9, 3.9, 2.6, and 3.1 Å, respectively. The space between the isolated VO_4 tetrahedral units is occupied by Y^{3+} ions. Along the z -axis, alternating tetrahedral and dodecahedra share edges.

YVO_4 compound has sparked a great interest in the fields of solid-state chemistry, material science, and technology. YVO_4 compound has good thermal stability, large birefringence, and a very wide transparency range from the visible to the infrared. Compared with the other well-known birefringent crystals such as calcite (CaCO_3) or rutile (TiO_2), YVO_4 compound has larger hardness and better fabrication properties. In addition, it is water insoluble and easier to obtain in large, high-quality crystals at lower cost. Owing to its outstanding physical properties, it is an excellent synthetic substitute for conventional crystals in many applications for optical polarizing components including fiber-optic isolators, circulators, and beam

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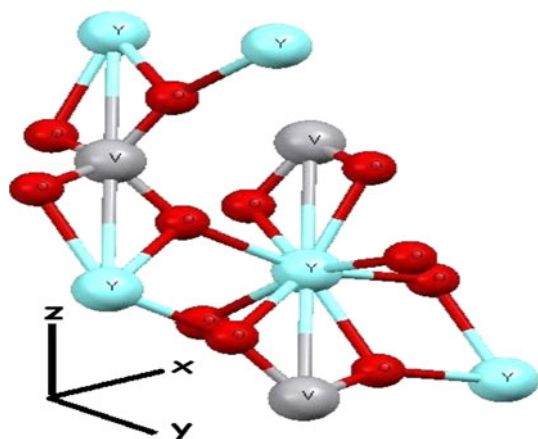


Fig. 1 A Schematic representation of zircon-type crystal structure of YVO_4 at ambient conditions, space group 141, $I4_1/amd$ $Z = 4$. This one was obtained by CIF file of Fullprof and plotted by Mercury 3.0 software. For positional parameters see Table 2. The V ions are in distorted tetrahedral coordinated. The Y ions are in dodecahedral coordination

displacers. As for the hosts, YVO_4 compound has been shown to be a useful host lattice for rare earth ions (Re^{3+}) to produce phosphors emitting a variety of colors in color television, fluorescent lamps, X-ray detectors, cathode ray tubes (CRTs), and field emission displays. Recent studies show that nanosized doped YVO_4 compound has significant promise in plasma display panels (PDP).

This compound thus shows a great potential both as incoherent as well as coherent light emitter, and certainly has a wide range of applications in the photo electronic industry and in opto-communication devices operating at room temperature such as optical data storage and processing, quantum information and computing, and frequency standards. Perhaps YVO_4 compound single crystal has the most important application as diode-pumped solid state lasers where it serves as a host material for the rare earth ions.

It is known that different material preparation methods have some important effects on material microstructure and physical properties. Goldschmidt and Haraldsen fabricated YVO_4 compound first in 1928. The higher temperature solid state reaction (SSR) produces relatively large grain size materials in addition to the oxygen defects [4], evaporation of vanadium (V_2O_5 with melting point $\sim 690^\circ\text{C}$), and introduction of contamination from crucibles. The reduction of particle size by mechanical grinding results in crystal particle damage and lower luminescent efficiency in the YVO_4 compound. The wet techniques are strongly recommended for the improvement of phosphors in high-resolution displays and miniature CRTs. During the 1960s, the first works reporting the production of YVO_4 compound in aqueous solution appeared. Other aqueous solution synthesis was reported during the next decades. Since then, YVO_4 compound has been prepared by hydrolysis,

hydrolyzed colloid reaction (HCR) technique [5], solution combustion process, colloidal routes [6, 7], urea precipitation [8], microemulsion mediated synthetic process [9], hydrothermal method [10–18], microwave irradiation method [19], direct precipitation reaction, spray pyrolysis [20], and sonochemical route [21]. Low-temperature ($<400^\circ\text{C}$) sol–gel method [22] and sol–gel acrylamide polymerization (SGAP) have been successful for producing nanometer size particulate powders with phase and morphology (size and shape distribution) homogeneity [23–27]. This method is based on forming an auxiliary three-dimension (3D) tangled network, in which a solution of the respective chelated cations is soaked [28–30]. A steric entrapment of stoichiometric cation solution occurs in nanocavities formed inside the gel, that is, a homogeneous microsolution with cations in the desired stoichiometry. It was known that transition elements (V and Ti) and rare earth elements (La and Y) impede the formation of the polyacrylamide gel because they react with the acrylamide monomers to form complexes in which the element is bonded to their amino group [31]. Therefore, to avoid this side reaction, a chelating agent (i.e., citric acid, ethylenediaminetetraacetic) must be used to isolate the cations from the monomers.

Core-level spectroscopies, such as X-ray photoemission spectroscopy (XPS) and soft X-ray absorption spectroscopy (XAS), are powerful tools in the study of d electron systems [32]. XAS is a first-order optical process where a single photon participates in the process [33]. XAS penetrates the solids a few micrometers, but the main detection technique is total electron yield (TEY), where the electrons have an escape depth of only a few nanometers [34]. XAS in the vicinity of the $L_{2,3}$ edge of the transition metal oxides and related compounds gives information about the unoccupied states of $3d$ symmetry which is of predominantly metal $3d$ character hybridized with a significant amount of O $2p$ character [35]. In recent years, it has also become apparent that the analysis of the intensity distribution and energy can allow the determination of the valency of the atom undergoing excitation. Thus, for the $L_{2,3}$ edges, the two components observed arise from transitions from the $2p_{3/2}$ (L_3 edge) and $2p_{1/2}$ (L_2 edge). These two features are separated by the spin–orbit splitting of the inner $2p$ shell, with the L_2 edge sitting on the high-energy background of the L_3 edge [36]. By analyzing the core level spectroscopic data of transition metal compounds with the atomic multiplet calculation, important information on the electronic states of these materials has been obtained systematically. In some analyses of these spectroscopic data, the interplay between intra-atomic multiplet coupling and inter-atomic hybridization plays an essential role [37]. In the case of oxyanions, XAS–TEY data showed that the intrinsic width of the L_2 edge is considerably broader than that of the L_3 owing to the existence of an extra Coster–Kronig Auger decay channel

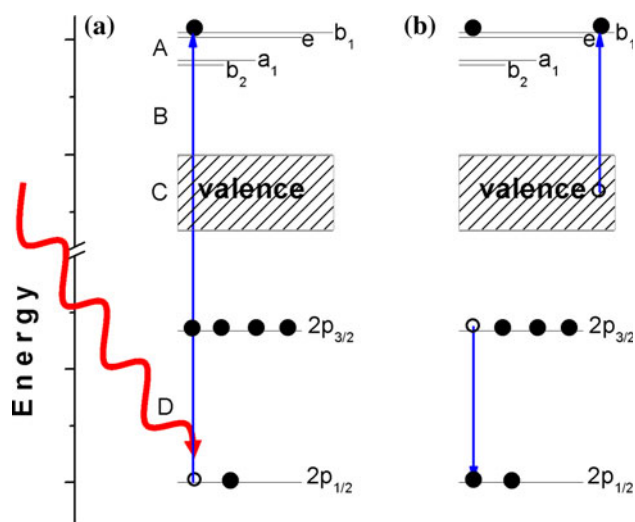


Fig. 2 A schematic picture of the Coster–Kronig decay of a $2p_{1/2}$ core hole. **a** An X-ray photon produces a $2p_{1/2}$ hole. **b** An electron in the $2p_{3/2}$ subshell fills the $2p_{1/2}$ hole and the remaining energy produces the excitation of a valence electron. The $2p_{3/2}$ hole then decays by Auger processes or X-ray emission

in which the $2p_{1/2}$ core–hole state decays via production of a $2p_{3/2}$ core hole, and the simultaneous ejection of a d electron [36], a process schematically depicted in Fig. 2. The figure presents at the top label A: where it represents the energy level for 3d orbitals in D_{4h} symmetry, see XAS section for more details; label B is the gap for YVO_4 compound approximately 3.8 eV [38–40]; label C is the valence band approximately 2.7 eV, and label D represents the energy difference between V $2p_{3/2}$ and V $2p_{1/2}$ equal to 6.7 eV.

The motivation of the present work is to study the local environment of vanadium in the zircon-type crystal structure of YVO_4 compound prepared by sol–gel acrylamide polymerization (SGAP) and SSR. In the first part, we study the crystallographic and morphological aspects of this compound by the conventional techniques XRD and SEM. In the second part, we want to elucidate the electronic structure of vanadium $L_{2,3}$ edge by XAS. We have also performed Rietveld refinement in order to follow the evolution of lattice. Respect to the ligand, field parameters $10Dq$, D_s , and D_t [2] are then varied until the best agreement between experiment and theory for the X-ray absorption spectra is found. This study constitutes an extension of previous studies [41–43] with the purpose to correlate the local crystal structure of vanadium with their local electronic structure.

Experimental procedure

Synthesis I (polyacrylamide gel method, SGAP)

High-purity Y_2O_3 (ALDRICH, 99.99 %) and V_2O_5 (CE-RAC, 99.9 %) were taken as the starting chemicals.

Ethylenediaminetetraacetic acid (EDTA, Fluka 99 %) was used as chelating agent. Acrylamide ($CH_2=CHCONH_2$, 99 %), N,N -methylenebisacrylamide ($CH_2=CHCONHCH_2NHCOCH=CH_2$, 99 %) and α, α' azoisobutyronitrile (AIBN, $C_8H_{12}N_4$, 98 %) were used as polymerization agents for polymerization process.

The polyacrylamide sol–gel process used to prepare nanosized YVO_4 compound is as follows. First, 50 wt% stoichiometric proportion of Y_2O_3 was dissolved in aqueous solution of HNO_3 , to obtain a solution of $2Y(NO_3)_3$. Also, 50 wt% of V_2O_5 was dissolved in H_2O_2 and in 40 mL of dilute HNO_3 to prepare the solution and to obtain 2 g of the sample. After their dissolution, the cations of transition (V) and rare earth (Y) elements were complexed by the addition of EDTA, in the ratio of 1:1 and the pH was adjusted to 3.8, to ensure the cations complex completely and stirred continuously to convert them to stable V- and Y, complexes. Subsequently, the monomers of acrylamide (2 g) and the cross-linker N,N -methylenebisacrylamide (0.4 g) were added into the clear solution, in proportions indicated in Ref. 25. The resulting solution was heated in a water bath and during the whole process, the system was continuously stirred. The solution became gradually transparent with the rising temperature. When the temperature reached about 80 °C, a small amount of compound initiator, AIBN, was added to the solution and polymerization occurred quickly and a transparent polymeric resin was obtained without any precipitation. At last, the gel was dried at 100 °C for 24 h to yield a xerogel. The xerogel was heated in a laboratory microwave furnace at 300 °C in Ar atmosphere to burn out the organic residues. This xerogel was grinded in an agate RM 100 mortar grinder (Retsch). The powders were heated at higher temperature (600–1200 °C) to obtain different samples.

Synthesis II (solid-state reaction, SSR)

The stoichiometric amounts of Y_2O_3 and V_2O_5 were mixed with ethanol in an agate mortar. The mixture was heated at 800 °C for 12 h in air. After grinding, the powders were pressed into pellets and heated at 1000, 1100 and 1200 °C for 12 h in air, respectively.

Characterization techniques

X-ray diffraction powders, XRD and scanning electron microscopy, SEM

Crystalline phases were identified by X-ray powder diffraction (XRD), using a Bruker–AXS D8–Advance diffractometer with λ (CuK_{α}) = 1.54 Å radiation. The diffractograms were recorded with a $2\theta^\circ$ step size of 0.02° and a counting time of 10 s. Lattice constants and other structural parameters of

YVO_4 –zircon phase were determined by refinement with the Rietveld technique using Fullprof98 [44, 45] available in the software package Winplotr [46]. The refinement involved the following parameters: scale factor; zero displacement correction; unit cell parameters; peak profile parameters using a pseudo-Voigt function, and overall temperature factor. The starting structural parameters and atomic positions of zircon-type crystal structure, YVO_4 compound [47] were taken from the literature. They were also refined and plotted with Mercury 3.0 [48] as shown in Fig. 1. The morphology of the YVO_4 compound was investigated by scanning electron microscopy, SEM, on a Cambridge-Leica Stereoscan 400. The micrographs were taken at $5.00 \text{ k}\times$ and $10.0 \text{ k}\times$ with a voltage of 20 kV, current intensity of 1000 pA, and work distance of 25 mm.

Soft X-ray absorption spectroscopy, XAS

The experiments took place at beam line 8.0.1 of The Advanced Light Source in Berkeley. Details of the beam line can be found elsewhere [49]. The radiation is produced in a 5.0 period undulator. It is monochromatized by one of the three gold-coated spherical gratings and then it is focused onto the sample. The X-ray absorption signal is monitored by the total sample current. This results in TEY spectra. The monochromator energy is calibrated by comparing our V_2O_5 TEY spectrum with those reported in the literature [50].

Multiplet charge transfer calculations

The interpretation of the X-ray absorption of transition metal compounds is aided by calculations that have been very successful in reproducing the experimental results. The calculations must take into account the major interactions in the system [51]. The first one is the structure of the 3d n atomic multiplet that results from the intra-atomic electron–electron Coulomb repulsion. The agreement with experiment is further improved once ligand field effects are included. Charge transfer effects may also be added to the calculation [52–55].

Results and discussion

XRD and SEM

In order to investigate the thermodynamically stable products for the samples prepared by SGAP, reactions were carried out at different temperatures up to 800°C . At 100°C , the reaction is incomplete after 12 h and V_2O_5 remains as an impurity in the product, indicating that the dissolution of V_2O_5 and subsequent nucleation of YVO_4

compound in an acidic solution takes time. At a temperature of 250°C or lower for 12 h, no YVO_4 could be detected by XRD. The only product from the acidic system detected by XRD was V_2O_5 . These results demonstrate that a longer reaction time at a higher temperature favors the formation of the so-called thermodynamically stable YVO_4 compound. When the reaction was carried out at 400°C for 12 h or more, V_2O_5 was not detected by XRD, indicating that V_2O_5 had been transformed completely into phase-pure YVO_4 JCPDS 17-0341 database (Fig. 3a). The indexed powder XRD in Fig. 3b, c indicates that this “thermodynamically stable” product is phase-pure YVO_4 compound, ($I4_1/amd$) whose refined lattice parameters, R_p , R_{wp} , and R_{exp} data related to the Rietveld fitting are summarized in Table 1. The sample prepared by SSR and heated at 1200°C during 12 h showed a pure zircon-type crystal structure [25].

One can observe that the VO_4 tetrahedron is slightly compressed respect to the values reported by Chakoumakos et al. [47] (Table 2). This could be attributed to the compensation of larger distances of O–O edges shared with the bisphenoids.

Figure 4 shows the morphology evolution of SGAP powders treated at 800°C during 12 h. Those powders were analyzed by XAS results. One can observe that these YVO_4 crystals are bipyramid-capped and truncated square plate in the shape with (111) and (100) type faces, expressing an ideal growth of tetragonal YVO_4 compound in aqueous solution. In addition, pores and voids can also

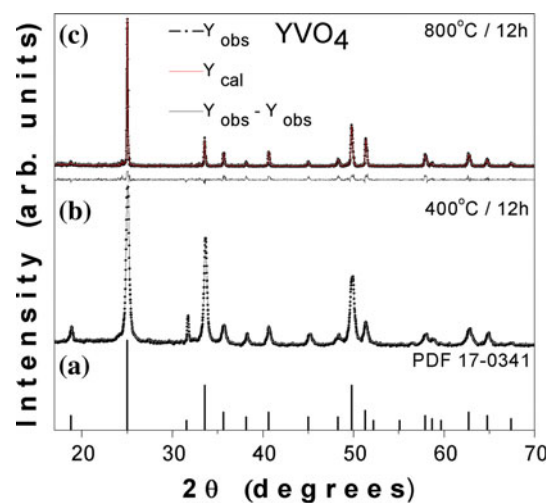


Fig. 3 X-ray powder diffraction data for the two samples annealed at 400 and 800°C for 12 h prepared by SGAP. **a** Peak positions of powder diffraction File No. 17-0341. **b** YVO_4 (zircon) pure structure without impurities. It shows the effect of the size of the nanoparticles. **c** Rietveld refined X-ray diffraction pattern of YVO_4 , figure shows the observed intensity (Y_{obs}), the calculated intensity (Y_{calc}) and the difference between observed and calculated intensities ($Y_{obs} - Y_{calc}$)

Table 1 Crystallographic data and results of Rietveld refinement of X-ray diffraction patterns of YVO_4 annealed at 400 and 800 °C for 12 h, in which zircon is detected as single crystalline phase

YVO_4	400 °C	800 °C	1200 °C
a (Å)	7.1161(2)	7.1014(2)	7.1105(2)
c (Å)	6.2875(3)	6.2898(4)	6.2885(4)
V (Å ³)	318.392(1)	317.200(1)	317.941(5)
R_p (%)	11.21	9.90	14.4
R_{wp} (%)	16.59	12.48	12.8
R_{exp} (expected)(%)	17.04	10.55	11.73
χ^2	1.33	1.30	1.28

Table 2 Interatomic distances for YVO_4 and comparison with Chakoumakos et al. [47]

Bond type	Num. Bonds	Distance (Å)	Chakoumakos et al. (Å)
Y–V	2	3.1441	
Y–O	4	2.2922	
	4	2.4306	
V–Y	2	3.1441	
V–O	4	1.7059	1.7088
O–Y	1	2.2922	
	1	2.4306	
O–O	1	2.6156	
	1	2.6927	
	2	2.8671	2.623
	4	3.0346	2.870



Fig. 4 SEM micrograph of surface of YVO_4 compound at the end of synthesis at 800 °C during 12 h in air prepared by SGAP

be seen, which result probably from the escaping gases during calcinations. The fine grains which consist of the homogeneous aggregates which are composed of a large number of small grains. The grain size is nearly $1.02 \pm 0.12 \mu\text{m}$.

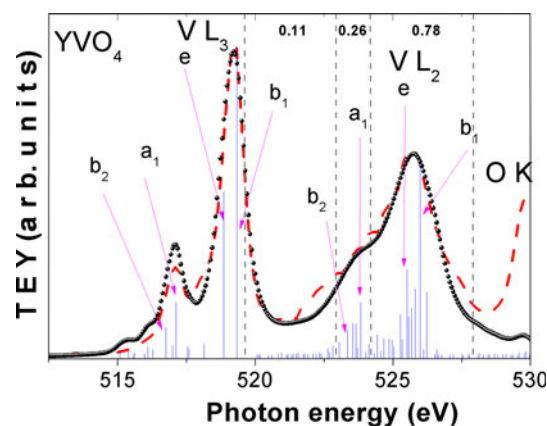


Fig. 5 Comparison between the experimental TEY spectrum (dots) and the result of the charge transfer multiplet calculation (solid line) for YVO_4 . The vertical lines give the position of the transitions in the multiplet calculation, which are then convoluted with broadening functions. The values for the core-hole widths (HWHM) used in the calculations are at the top of spectrum. The symmetry species (and the 3d-orbitals) a_1 ($3d_{z^2}$), b_1 ($3d_{x^2-y^2}$), b_2 ($3d_{xy}$), and e ($3d_{xz}$, $3d_{yz}$) are located on $L_{2,3}$ edge of V

XAS

The soft X-ray absorption at the V $2p$ and O $1s$ edges, measured in TEY mode, is shown in Fig. 5. Both spectra are normalized and calibrated. The X-ray absorption spectrum at the V $2p$ edge shows two small pre-edge features that arise at photon energies of 515.39 and 516.10 eV. The spin orbit interaction splits the spectrum into the L_3 and L_2 components, as indicated in the figure. In the L_3 component of the spectrum, two peaks can be identified. The first one arises at 517.12 eV, reflecting the empty V $3d$ states with a t_{2g} symmetry. The width of this peak is around 0.18 eV. The following peak is located at 519.29 eV. These transitions show the properties of the $3d$ states with e_g symmetry. The distortion of the VO_4 from perfect O_h symmetry to D_{4h} symmetry, causes the splitting of the e_g transition into two components. In the L_2 region, two lines can be identified, being located at 525.53 and 525.99 eV. In comparison to the features in the L_3 region, the features are significantly broadened and the t_{2g} and e_g components exhibit stronger overlap.

Multiplet charge transfer calculations, CTM4XAS

X-ray absorption calculations were performed for YVO_4 compound prepared by SGAP, SSR and also for the reference compound V_2O_5 using charge-transfer atomic multiplet codes [52–54]. The calculation was performed in D_{4h} symmetry with $10D_q$, D_s , and D_t as the ligand field parameters. The relation between the three parameters and the energy positions of the d -orbitals is shown in Table 3.

Table 3 Comparison between energy of the d-levels in D_{4h} symmetry for YVO_4 compound for SSR and SGAP

Level	Energy in D terms	SSR	SGAP	Orbital
b_1	$6Dq + 2D_s - 1Dt$	0.66	0.60	$3d_{x^2-y^2}$
e	$-4Dq - 1D_s + 4Dt$	0.36	0.40	$3d_{xz}, 3d_{yz}$
a_1	$6Dq - 2D_s - 6Dt$	-0.54	-0.60	$3d_{z^2}$
b_2	$-4Dq + 2D_s - 1Dt$	-0.84	-0.80	$3d_{xy}$

We assumed that the ground state is an admixture of d^0 and d^1L electronic configurations, where L represents a hole in the ligand. The Slater integrals were reduced to 70 % of the Hartree–Fock values in order to take into account some degree of electron–electron correlation. The ligand field parameters and the configuration mixing strength were varied until the best agreement with experiment was found. The final values of the ligand field parameters were respectively $10Dq = 1.4$ eV, $D_s = 0.0$ eV, and $D_t = 0.24$ eV for YVO_4 compound. Similar values were founded for the sample prepared by SSR. One can observe that our results presented in Table 3 suggest an axial compression, in which the order of these orbital energies is reversed i.e., orbitals with z-components have increased energies while the orbitals with only x- and y-components have lower energy. As it is shown in the previous XRD section, the local structure of the (MO_4) tetrahedron in the introduced transition metal oxides (M) is more complex, i.e., additional distortions occur.

In order to do a comparison respect to the standard compound, we obtained $10Dq = 1.0$ eV, $D_s = 0.0$ eV, and $D_t = 0.5$ eV for V_2O_5 . These calculations take into account the charge transfer parameters, leads to a weight of the d^0 and d^1L configurations in these spectra with 75 and 25 % for YVO_4 compound and 50 and 50 % for V_2O_5 , respectively. These results indicate a more hybridized nature for the valence and conduction orbitals in V_2O_5 . One consequence of including the charge transfer into the calculations is an adjustment of the ligand field parameters. In addition to the charge transfer parameter, the core hole potential U_{pd} and the d – d repulsion U_{dd} have to be included, but the influence of these parameters is mainly limited to the position of the spectrum rather than the shape.

The main features of the experimental spectrum are already well reproduced, as one can observe in Fig. 5. This figure also presents the energy positions of the d -orbitals. One can observe that the $L_{2,3}$ edge in YVO_4 -TEY is split into two major peaks separated by the $2p$ fine structure. The calculation indicates that each of these peaks is split further in D_{4h} symmetry. Between 520 and 530 eV, one finds a very broad L_2 edge with no apparent structure. In the calculated absorption spectra, we indicate by a vertical line the position and relative intensity of each transition from the ground

state. There are as much as 346 lines. We then perform the convolution of these lines with Lorentzian functions to simulate the broadening due to the $2p$ core hole lifetime. This is the first indication of a fast CK decay [36] in YVO_4 compound because we had to increase this Lorentzian broadening from the expected 0.26 eV (HWHM) for L_3 [56] to 0.78 eV for L_2 . YVO_4 compound is not the only case, this broadening has also been observed in vanadium $L_{2,3}$ edge by XAS for $LaVO_4$ compound [57]. The resulting spectrum is then convoluted with a Gaussian function of constant width (0.18 eV HWHM) to take into account the contribution of the monochromator finite resolution.

Conclusions

Zircon-type crystal structure for YVO_4 compound was prepared by SGAP route. The mechanism of formation and the structural characteristics of YVO_4 zircon were studied by XRD and SEM.

The results indicated that the first stage of the formation and stabilization of nanoparticulated YVO_4 compound occurred at 400 °C during 12 h. Bipyramid-capped morphology of YVO_4 compound was fully developed after annealing at 800 °C during 12 h. The grain size distribution is center at 1.02 ± 0.12 μm .

XAS results presented the V $L_{2,3}$ and O K edge spectra for YVO_4 compound obtained at 800 °C. The theoretical spectra obtained by the atomic multiplet calculation show a remarkable similarity with the TEY spectra. The Vanadium $L_{2,3}$ edge determined by the atomic multiplet picture is more accurately described using a V^{5+} oxidation state. The Coster–Kronig process was observed due to the broadening of vanadium L_2 edge. On the other hand, the energy level determined for the $3d$ orbitals reveals the compression of z-axes orbitals in comparison with xy -orbitals. This slight distortion could be associated with the VO_4 tetrahedron distortion determined by the Rietveld refinements. The multiplet calculations also allow confirming the ionic character of YVO_4 compound respect to the covalent character observed in V_2O_5 .

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