

VALENCE OF VANADIUM IN HYDRATED COMPOUNDS*

V. Bondarenka^a, S. Grebinskij^a, S. Mickevičius^a, H. Tvardauskas^a, S. Kačiulis^b,
V. Volkov^c, G. Zakharova^c, and A. Pašiškevičius^a

^a Semiconductor Physics Institute, A. Goštauto 11, LT-01108 Vilnius, Lithuania

E-mail: bond@pfi.lt

^b Institute for the Study of Nanostructured Materials (ISMN-CNR), P.O. Box 10, I-00016 Monterotondo Scalo (RM), Italy

E-mail: saulius.kaciulis@mliib.cnr.it

^c Institute of Solid State Chemistry, Pervomaiskaya 91, 620219, Yekaterinburg, Russia

E-mail: volkov@ihim.uran.ru

Received 14 June 2007; revised 2 July 2007

Problems of the definition of vanadium chemical states in the mixed valency compounds are examined. The statistical analysis of the literature data on the values of binding energy and full width at half maximum (FWHM) of V $2p_{3/2}$ peaks in different vanadium oxides is carried out.

X-ray photoelectron spectroscopy was used to determine the chemical shift and FWHM of V $2p$ peaks of V⁴⁺ and V⁵⁺ cations in the vanadium pentoxide matrix of hydrated vanadium compounds HV₁₂O₃₁·*n*H₂O and (VO)V₁₂O₃₁·*n*H₂O, prepared by using sol–gel technology. It was found that the binding energy of V⁴⁺ ions shifts to the lower energy side of about 1.3 eV as compared to the main V⁵⁺ ions in the matrix. The V $2p_{3/2}$ line width for tetra-valent vanadium ions in xerogels is actually the same as for penta-valent ions.

Keywords: sol–gel method, XPS, vanadium oxides

PACS: 81.20.FW, 79.60.-i, 82.80.Pv

1. Introduction

The identification of mixed valence metal species in solid oxides is not a trivial task. In fact, chemical analytical methods often fail owing to the relative instability of the various oxidation states of metals in common dissolution media.

Even when they are applicable, long and multi-step procedures have to be scheduled. Moreover, only the bulk concentration of the various species may be extracted, while the investigation of surface chemistry of these compounds is usually required and the surface electronic structure of oxide is also of interest in its own right.

X-ray photoemission spectroscopy (XPS) is a very useful technique for determining such important parameters as the chemical state of different metal species and their relative concentration [1]. By using XPS analysis, species of elements at the surface are identified from XPS spectra, and the oxidation states of the elements are determined from the chemical shift (CS)

defined as the binding energy (BE) difference $CS_{ij} = BE_i - BE_j$ of the electron concerned (*i* and *j* denote the different valence states). The accurate BE has to be measured in order to determine the chemical state from the CS. Quantitative information on the relative surface amount of element species then may be obtained from the relative areas of the peaks corresponding to the single components of the envelope spectra. This may be easily done, if the individual peaks are well resolved, i. e. FWHM intensity of the peak is less than the CS for the corresponding species.

1.1. XPS study of integer valence vanadium oxides

Vanadium oxides have been intensively studied lately, and the relatively full collection of V $2p_{3/2}$ line BE and FWHM data for the main valence oxides (V₂O₅, VO₂, and V₂O₃) may be obtained from the literature analysis.

Unfortunately, the BE values for the various valence vanadium oxides are in a relatively low energy range of about 515.5–517.5 eV [2], while FWHM of the corresponding peaks varies from 1.2 eV (V₂O₅ [3]) to 3.0 eV

* The report presented at the 37th Lithuanian National Physics Conference, 11–13 June 2007, Vilnius, Lithuania.

(NaV_2O_5 [4]). Moreover, the CS of V $2p$ peaks for V^{3+} and V^{4+} ions from the main valence V^{5+} is lower than the FWHM of corresponding peaks [5] and the resulting spectra cannot be straightforwardly separated into individual components.

The attempts to fit the V $2p_{3/2}$ peak (well resolved from the V $2p_{1/2}$ counterpart) in mixed valence vanadium compounds were done with an initially estimated BE separation and the FWHM corresponding to the literature data [6] or directly obtained from the analysis of reference samples XPS spectra [7]. It should be noted, however, that a comparison between BE and FWHM data, presented in literature for V_2O_3 , VO_2 , and V_2O_5 , shows large discrepancies that may be associated either with the equipment calibration or with inaccuracy in the correction for sample charging. Thus, the quantitative estimation of vanadium oxidation states is quite complicated, and the suitable standards for the calibration of BE and FWHM values for V^{5+} , V^{4+} , and V^{3+} species in oxides are required. The discrepancies of the reference samples' surface composition from the bulk one may also have influence on the measured values of BE and FWHM. Thus, a statistical review of the data presented in literature is desirable.

1.2. Literature analysis

The analysis of literature data on BE and FWHM values of the V $2p_{3/2}$ line for the main valence oxides (V_2O_5 , VO_2 , and V_2O_3) is presented in Table 1. The statistical methods then may be applied to obtain the mean values of BE for the corresponding valence vanadium species and to estimate the inaccuracy of the data presented in literature.

The probability that a reported in literature value of parameter X (X is BE_i or CS_{ij}) within $X \pm dX$ interval is given by $2f_X \Delta X$, where f_X is the distribution function. The data listed in Table 1 were used to construct the approximate distribution function f_X defined as

$$f_X = \frac{\Delta N}{2N_t \cdot \Delta X}, \quad (1)$$

where ΔN is the number of references in Table 1 for which X is within $X - \Delta X < X \leq X + \Delta X$ interval (we use $\Delta X = 0.2$ eV for the convolution of the literature data) and N_t is the total number of corresponding references.

Figure 1 presents the BE distribution function f_{BE} for the main valence vanadium oxides. Three fairly well resolved peaks might be seen in Fig. 1, indicating that three different data sets (corresponding to V_2O_5 ,

Table 1. The literature data of FWHM and BE values for V $2p_{3/2}$ peak of main valence vanadium oxides.

FWMH, eV	BE, eV	Oxide		
		V_2O_3	V_2O_4	V_2O_5
4.8	515.15	[8]		
	515.2	[9]		
	515.3	[10]		
4.5	515.4	[11]		
	515.5		[12]	
4.5	515.6	[13]	[10, 11]	
			[11]	
4.0	515.65		[8]	
4.2	515.7	[5, 14]	[15, 16]	
		[5]		
	515.8	[15]		
	515.85	[3]		
1.95	516		[3]	
3.2	516.2		[5]	
	516.3		[14, 17]	
	516.4		[18]	
	516.45		[19]	
	516.5		[20]	
2.2	516.55		[13, 21]	
			[21]	
2.2	516.6		[22]	[11, 23]
1.6			[22]	[23]
	516.8			[16]
	516.9			[5, 10]
1.6				[5]
	517			[8, 24]
1.4				[8]
	517.1			[25]
	517.2			[3, 14, 18, 21, 22, 26, 27]
1.2				[3]
1.7				[21]
2.0				[22]
	517.3			[28]
	517.4			[20, 29–31]
	517.45			[19]
	517.6			[13]
	517.65			[32]
	517.7			[32–34]

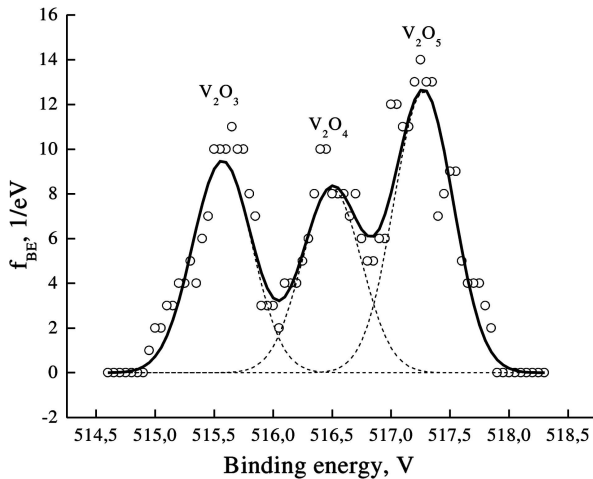


Fig. 1. Distribution function of the V $2p_{3/2}$ binding energy values found in the literature for the main valence vanadium oxides. The points correspond to the reference data. The dashed lines present the Gaussian distribution for different oxides, and the solid line is the distribution envelope. Total number of the references $N_t = 50$.

VO_2 , and V_2O_3 reference samples) are involved in the distribution function. Further analysis was done assuming that the reference data for individual oxides are distributed according to the Gaussian law:

$$G_X = \frac{\exp\left(-\frac{X - X_m}{2W_X}\right)}{W_X(2\pi)^{1/2}}, \quad (2)$$

where X_m is an average value of X and W_X is the standard deviation of X .

The analysis of f_{BE} spectrum (Fig. 1) has been performed by using a curve-fitting procedure in order to distinguish vanadium species in different oxidation states and to obtain the corresponding values of BE_m and W_{BE} .

It is clear from Fig. 1 that V $2p_{3/2}$ line BE distribution function may be deconvoluted into three Gaussian peaks centred at 517.3, 516.5, and 515.6 eV with the statistical deviation $W_{\text{BE}} = 0.25$ eV. These peaks may be attributed to V^{5+} , V^{4+} , and V^{3+} species in V_2O_5 , VO_2 , and V_2O_3 oxides respectively. Therefore, it may be concluded that the use of the data reported in literature for the main valence vanadium oxides permits separation of vanadium species in different oxidation states. On the other hand, the statistical error δ_{BE} of BE determination obtained from the literature analysis ($\delta_{\text{BE}} = W_{\text{BE}} = 0.25$ eV and $\delta_{\text{BE}} = 2W_{\text{BE}} = 0.5$ eV for the 70% and 95% probability levels respectively) may be compared with the estimated values of CS for the adjacent valence vanadium oxides ($\text{CS}_{34} = -0.9$ eV and $\text{CS}_{54} = 0.8$ eV). Thus, the accuracy in CS determination from BE analysis ($\delta_{\text{CS}} = 2W_{\text{BE}} = 0.5$ eV and

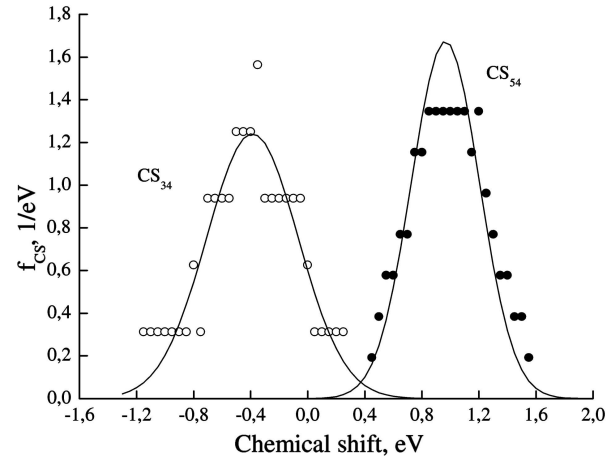


Fig. 2. Distribution function of the V $2p_{3/2}$ chemical shift CS_{ij} values found in the literature for the main valence vanadium oxides. Open circles correspond to the V^{3+} and V^{4+} ions. Bold circles correspond to the V^{5+} and V^{4+} ions. Total number of the references for CS_{34} $N_t = 8$ and for CS_{54} $N_t = 13$.

$\delta_{\text{CS}} = 4W_{\text{BE}} = 1.0$ eV for the 70% and 95% probability levels respectively) is insufficient to use these data for the accurate deconvolution of the multicomponent V $2p_{3/2}$ XPS peak envelope. It should be noted that the error in the V $2p_{3/2}$ line position determination in vanadium oxides may be compared with the uncertainty (of about 0.3 eV) of presented in the literature BE values for the main peaks of Cu, Ag, and Au, normally used for the equipment calibration [1]. The wide use of C 1s level, associated with adventitious carbon as an energy reference in XPS studies, may also contribute to the scattering of the BE values in vanadium oxides [8, 35]. On the basis of this background, only the BE data obtained by means of the same equipment employed under the same conditions were used for further statistical analysis of CS in order to minimize the uncertainty related with the equipment calibration and the charge correction procedure. In spite of the relatively low statistics ($N_t = 8$ for V_2O_3 – VO_2 and $N_t = 13$ for V_2O_5 – VO_2 reference oxides), the CS analysis is still useful, since not the absolute values but only the BE difference in various valence vanadium oxides with a similar structure and measured at the same conditions is considered.

The results of statistical analysis are presented in Fig. 2. It is evident that either CS_{45} and CS_{43} may be approximated by the individual Gaussian distribution (X in (2) denote CS) with the centres located at -0.4 and 1.0 eV for CS_{34} and CS_{54} , respectively. These values are in good agreement with the previously obtained results (Fig. 2). However, the uncertainty in the CS determination is relatively high, indicating that the main error in BE determination may be attributed to the

inaccuracy of the charge correction procedure and to the deviation of the surface composition from the bulk one, rather than to the equipment calibration.

From the literature analysis it may be concluded that:

- the XPS technique permits separation of vanadium species in the adjacent oxidation states;
- the accuracy of BE determination is insufficient for precise deconvolution of the XPS spectra of mixed valence vanadium oxides into individual components;
- the XPS data for the reference samples of vanadium oxides must be interpreted carefully, when they are used for the analysis of mixed valence vanadium compounds.

Moreover, the parameters deduced from the XPS analysis of reference samples may be used only as a rough approximation for those of mixed valence compounds because:

- CS_{ij} in mixed valence vanadium oxides depends not only on the vanadium ion charge V^{+i} and V^{+j} , but also on the value of crystal field long-range potential [1]. The last correction may be of the same order of magnitude as the first one;
- in the compounds of transition metal oxides, the FWHM depends on the degree of population of the narrow d -band [5], thus the $V\ 2p_{3/2}$ line width of V^{4+} species may differ significantly in VO_2 crystals and in V_2O_5 -based xerogels containing V^{4+} ions [5, 3].

1.3. The aim of work

The aim of this work was to determine the chemical shift and FWHM of admixture V^{4+} ions in the V_2O_5 -based compounds. It seems that a better way is to compare the samples with the same host matrix, but with different concentrations of reduced valence vanadium ions. In this case, the crystal field is the same for various valence ions, and only the vanadium ions charge affects the CS. The best materials, in our opinion, are the vanadium pentoxide-based hydrated compounds allowing easy intercalation of alkali metal and substitution of vanadium by other transition metals [36, 37]. This may be done in two different ways:

- (1) by a partial substitution of vanadium in V_2O_5 -based compounds with the transition metal ions of higher or lower valence [38–40] or by using alkali metals (Na, K, Rb, Cs) [41, 42] or vanadyl $(VO)^{2+}$

intercalates [43]. In the last case the additional increase of the reduction ratio $RR = C_4/(C_4 + C_5)$ (C_i is the atomic concentration of the i -valence ion) may be roughly estimated from the nominal chemical formulae, assuming that RR is the same for the basic V_2O_5 layers and additional V^{4+} ions from $(VO)^{2+}$ species;

- (2) by varying the concentration of V^{4+} ions by some external treatment (thermal [44], UV irradiation [45], ion or electron bombardment [39, 46]) and comparing photoelectron spectra before and after the treatment. The advantage of this technique is that the same sample is used to study the comparison spectra; therefore the structure-related effects may be neglected.

In the present paper we tried to apply these approaches in order to determine the parameters of the $V\ 2p_{3/2}$ line in V_2O_5 -based xerogels. First of all, the reference V_2O_5 and VO_2 powder oxides were used to determine the CS_{54} and FWHM in pure oxides. The thin films of $H_2V_{12}O_{31} \cdot nH_2O$ and $(VO)V_{12}O_{31} \cdot nH_2O$ xerogels were used for comparison of the materials with a similar structure. Finally, a thin film of $(VO)V_{12}O_{31} \cdot nH_2O$ xerogel before and after the heat treatment was used to separate the additional influence of V^{4+} ions on photoelectron spectra.

2. Experimental

A polyvanadic acid $H_2V_{12}O_{31} \cdot nH_2O$ was produced by using the sol–gel technology. The vanadium pentoxide powder was dissolved in hydrogen peroxide at 270 K, because this reaction is exothermic. Then the solution was heated at 350 K for one hour for the dissociation of the peroxide complexes of vanadium [47].

$(VO)V_{12}O_{31} \cdot nH_2O$ samples were prepared from $H_2V_{12}O_{31} \cdot nH_2O$ by using an ionic exchange method. Polyvanadic acid (0.5 g) was placed in a solution of the vanadyl sulfate $VOSO_4 \cdot 3H_2O$ (1 M, 100 mg) and maintained at constant hashing up to balance during 5 days. Then a deposit was filtered, washed out with water, and dried in air at 330 K [48].

The chemical composition of obtained gels was analysed by IR spectroscopy, chemical, and gravimetric analysis methods, which showed that the investigated compounds can be described by the formulae $HV_{12}O_{31} \cdot nH_2O$ and $(VO)V_{12}O_{31} \cdot nH_2O$ (more details of the composition determination are described in [49]). The obtained gels were deposited on the Ni substrates and annealed in air at 330 K.

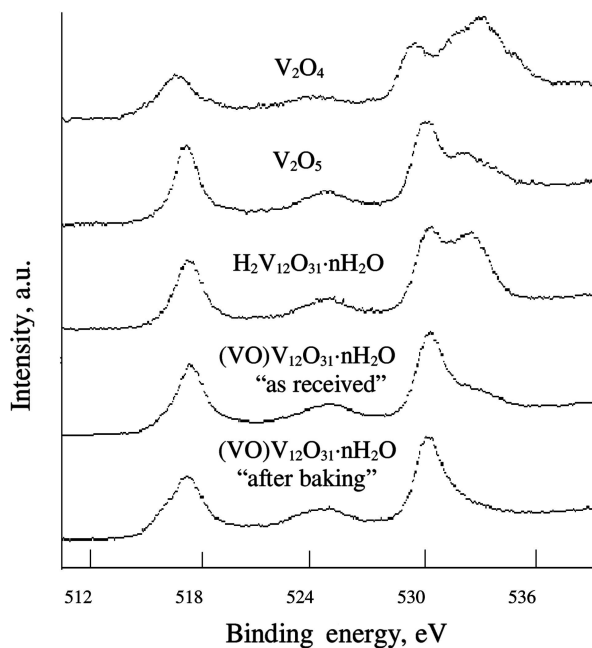


Fig. 3. XPS core-level spectra of V $2p$ and O $1s$ region for different samples.

The XPS experiments were carried out in an Escalab MkII (VG Scientific) spectrometer, equipped with an Al K_{α} (1486.6 eV) excitation source, a five-channeltron detection system, and a hemispherical analyzer, which was set to 20 eV pass energy. The binding energy scale was corrected for the charging effect by assigning a value of 284.6 eV to the C $1s$ peak. Photoemission data have been collected and processed by using a VGX-900 data system. After Shirley background subtraction, a nonlinear least square curve-fitting routine has been used for the analysis of XPS spectra.

3. Results and discussion

Figure 3 presents the original XPS core-level spectra of the V $2p$ and O $1s$ region for all treated samples. All the spectra have been corrected by removal of X-ray source satellites.

The results and discussion are split into three corresponding regions: core lines of V $2p_{3/2}$, V $2p_{1/2}$, and O $1s$.

The preliminary information may be obtained directly from the visual view of the presented spectra. First of all, note, that the spectral lines of the corresponding regions overlap, hence the attempt to analyse each region independently may cause a significant error in the estimations of the areas of related peaks. So, it is necessary to study the whole V $2p$ and O $1s$ region in order to obtain reliable results. On the other hand, V $2p_{3/2}$ and O $1s$ lines are considerably separated in

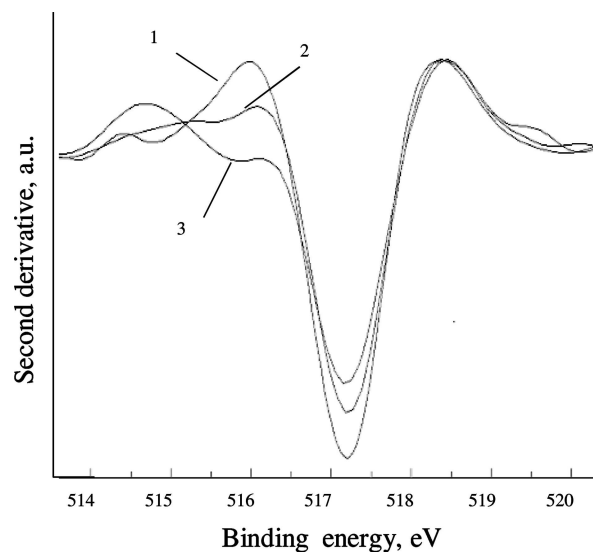


Fig. 4. The second derivatives of XPS spectra for V_2O_5 -based xerogels: 1 for $H_2V_{12}O_{31} \cdot nH_2O$ xerogel, 2 for $(VO)V_{12}O_{31} \cdot nH_2O$ xerogel “as received”, 3 for $(VO)V_{12}O_{31} \cdot nH_2O$ xerogel “after annealing” at 510 K.

BE scale and the main particularities of corresponding peaks may be revealed by applying the usual methods of the spectra analysis [1].

It is clear that O $1s$ line exhibit a complex structure, indicating that various oxide species are present in the samples. At least three peaks should be introduced to simulate the shape of this line for the studied samples. According to [50], this line may be decomposed into three well-distinguished components: the basic ‘oxide’ peak, corresponding to vanadium oxide lattice matrix (BE \approx 530 eV), and two additional peaks arising from H_2O (BE \approx 533 eV) and hydrogen or carbon-bonded oxygen ‘hydro’ species (BE \approx 532 eV) (see Table 2).

Considering the vanadium lines, it may be stated that V $2p_{3/2}$ is actually symmetric for V_2O_5 and V_2O_4 samples, while the obvious widening at the lower BE shoulder of this spectra may be seen on going from the sample of $H_2V_{12}O_{31} \cdot nH_2O$ to $(VO)V_{12}O_{31} \cdot nH_2O$ “as received” and to $(VO)V_{12}O_{31} \cdot nH_2O$ annealed at 510 K.

This dependence becomes more evident in the plots of the second derivative (see Fig. 4). For the $H_2V_{12}O_{31} \cdot nH_2O$ sample, the derivation spectrum is actually symmetric, indicating that V^{5+} (BE \approx 517.2 eV) ions dominate in this xerogel. The evident shoulder is, however, seen at BE \approx 515.8 eV for the $(VO)V_{12}O_{31} \cdot nH_2O$ “as received” and “after baking” samples. The appearance of this feature may be attributed to the significant increase of V^{4+} ions in xerogels after the substitution of $(H_2)^{2+}$ ions by $(VO)^{2+}$ and the following annealing.

The spectra comparison technique was used for further examination of the core-level states of V^{4+} ions.

Table 2. Peak fitting parameters for O 1s line.

Sample	Species	BE, eV	FWHM, eV	RA*
$\text{H}_2\text{V}_{12}\text{O}_{31}\cdot n\text{H}_2\text{O}$	oxide	530.1	1.7	0.47
	“hydro”	531.9	1.7	0.32
	H_2O	533.0	1.7	0.21
$(\text{VO})\text{V}_{12}\text{O}_{31}\cdot n\text{H}_2\text{O}$ “as received”	oxide	530.1	1.7	0.73
	“hydro”	531.9	1.7	0.17
	H_2O	533.3	1.7	0.10
$(\text{VO})\text{V}_{12}\text{O}_{31}\cdot n\text{H}_2\text{O}$ “after baking”	oxide	530.1	1.6	0.81
	“hydro”	531.7	1.6	0.13
	H_2O	533.0	1.9	0.06
V_2O_5	oxide	530.1	1.8	0.49
	“hydro”	532.2	1.8	0.26
	H_2O	533.9	2.4	0.26
V_2O_4	oxide	529.3	1.7	0.25
	“hydro”	531.8	1.7	0.08
	H_2O	533.8	3.4	0.68

* RA is relative area of corresponding peaks.

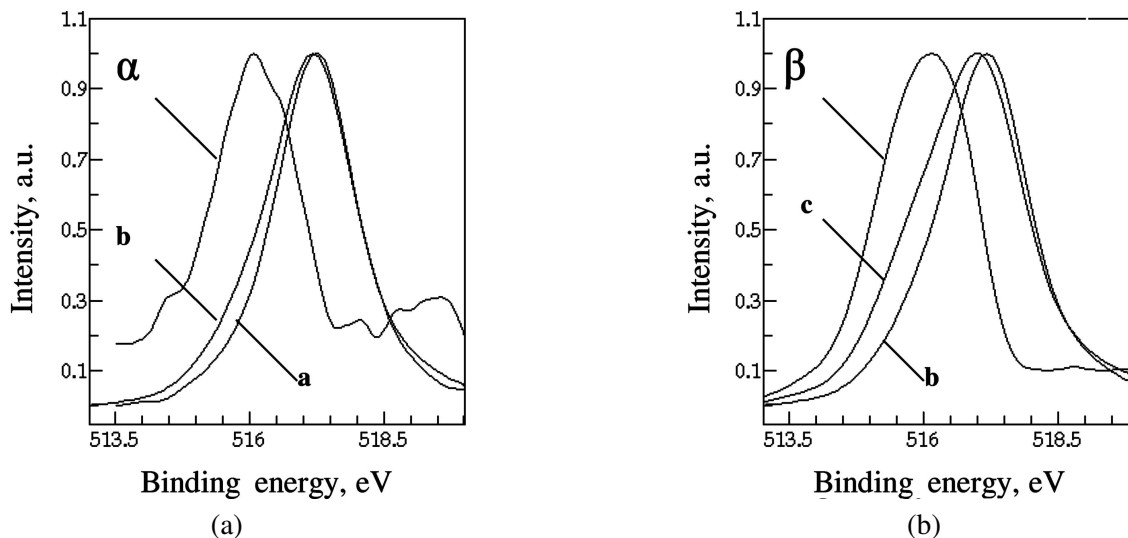


Fig. 5. The comparison and the difference spectra for V $2p_{3/2}$ line in V_2O_5 -based xerogels: *a* for $\text{H}_2\text{V}_{12}\text{O}_{31}\cdot n\text{H}_2\text{O}$, *b* for $(\text{VO})\text{V}_{12}\text{O}_{31}\cdot n\text{H}_2\text{O}$ “as received”, *c* for $(\text{VO})\text{V}_{12}\text{O}_{31}\cdot n\text{H}_2\text{O}$ “after annealing” at 510 K; $\alpha = b - a \cdot 0.93$; $\beta = c - b \cdot 0.85$.

Figure 5 presents the comparison and the difference spectra for $\text{H}_2\text{V}_{12}\text{O}_{31}\cdot n\text{H}_2\text{O}$ and $(\text{VO})\text{V}_{12}\text{O}_{31}\cdot n\text{H}_2\text{O}$ samples, as well as for $(\text{VO})\text{V}_{12}\text{O}_{31}\cdot n\text{H}_2\text{O}$ sample before and after annealing at 510 K.

The optimal weighting procedure was used to extract the low intensity $\text{V}^{4+} 2p_{3/2}$ peak from the high background of the main peak of $\text{V}^{5+} 2p_{3/2}$ [1].

It is clear from Fig. 5(a,b) that the replacement of $(\text{H}_2)^{2+}$ by $(\text{VO})^{2+}$ ions, like the annealing of $(\text{VO})\text{V}_{12}\text{O}_{31}\cdot n\text{H}_2\text{O}$ sample, leads to the appearance of an additional peak shifted by 1.1–1.2 eV to the lower energy side. This peak may be attributed to V^{4+} species and the CS of about 1.2 eV may be expected for V^{4+} ions in V_2O_5 -based xerogels that is in

a good agreement with a value estimated from the second derivative plots (Fig. 4). Note that this value also agrees with an average CS = 1.1 eV, obtained from the literature analysis.

There are no problems related with the presence of the mixed valence vanadium species in the reference powders of V_2O_5 and V_2O_4 , where the corresponding peak positions and FWHM of V $2p$ and O $1s$ lines can be obtained without any trouble. The peak fitting parameters are given in Tables 2 and 3. The obtained results are in a good agreement with the values reported in Ref. [5].

It should be mentioned that the doublet splitting of V $2p$ line, obtained from a fitting procedure, is actually

Table 3. Peak fitting parameters for V $2p_{3/2}$ line.

Sample	Valence of vanadium	BE, eV	FWHM, eV	Reduction ratio	Chemical shift
$\text{H}_2\text{V}_{12}\text{O}_{31} \cdot n\text{H}_2\text{O}$	5+	517.2	1.7	0.04	1.3
	4+	515.9			
(VO) $\text{V}_{12}\text{O}_{31} \cdot n\text{H}_2\text{O}$ “as received“	5+	517.3	1.6	0.13	1.3
	4+	516.0			
(VO) $\text{V}_{12}\text{O}_{31} \cdot n\text{H}_2\text{O}$ “after baking“	5+	517.3	1.6	0.26	1.3
	4+	516.0			
V_2O_5	5+	517.2	1.7	0	0.6
V_2O_4	4+	516.6	2.2	1	0.6

the same for all samples (about 7.4 eV). Also the V $2p_{1/2}$ and V $2p_{3/2}$ peak intensity ratio of 0.5 is in a good agreement with the theoretical value. The peaks of V $2p_{3/2}$ are positioned at BE = 517.2 and 516.6 eV for V_2O_5 and V_2O_4 powders, respectively (Table 3). Therefore, the $\text{CS}_{54} \approx 0.6$ eV, i. e. more than two times lower than the corresponding value for xerogels. This difference may be attributed to the diverse field potential of the surrounding crystal. Moreover, the V $2p_{3/2}$ and V $2p_{1/2}$ line widths for V_2O_4 powder are significantly higher than for V_2O_5 reference sample, indicating that the broadening related to the d -band population is taking place [5]. So, it may be concluded that the parameters of V $2p$ peaks, deduced from the examination of reference samples, can not be directly used as the initial approximation for the peak-fitting procedure to obtain the accurate value of the reduction ratio of vanadium ions in the xerogels.

The more important conclusion, which may be derived from the comparison plots (Fig. 5), is that the line width of V $2p_{3/2}$ peak for tetra-valent vanadium ions in xerogels is actually the same as for penta-valent ions. It seems that this result contradicts the results obtained from the comparison of the photoelectron spectra of reference oxides V_2O_5 and V_2O_4 (Fig. 3) [5]. Nevertheless, this contradiction may be easily explained, taking into account that the FWHM of the V $2p$ line in vanadium oxides depends on the degree of completion of the narrow d -band [5]. So, in contrast to vanadium tetra- and penta-oxides, with a significantly different concentration of electrons in d -band, it is possible to expect the same additional broadening of V $2p$ lines of V^{5+} and V^{4+} species, simultaneously present in xerogels with a common d -band.

For the further quantitative analysis of the various valence vanadium species in the V_2O_5 -based xerogels, the peak-fitting procedure has been used. To obtain the position, width, and intensity of spectral components

for various vanadium and oxygen species, the photoelectron spectra have been fitted in the whole V $2p$ and O $1s$ region. According to the previously obtained results, the following initial assumptions about the corresponding peak parameters were done:

- FWHM of V $2p_{3/2}$ and V $2p_{1/2}$ peaks is the same for both V^{5+} and V^{4+} ions;
- the doublet splitting of V $2p$ line is the same for V^{5+} and V^{4+} ions;
- the V $2p_{1/2}$ and V $2p_{3/2}$ peak intensity ratio is equal to 0.5 for V^{5+} and V^{4+} ions.

The fixed value of $\text{CS} = 1.3$ eV and the above-mentioned parameters were used as a starting approximation for the fitting procedure. The O $1s$ peaks corresponding to “oxide”, “hydro”, and “ H_2O ” species position were selected at 530, 532, and 533 eV, respectively. After that, these parameters were unfixed, and the fitting procedure was repeated.

As an example, a typical deconvolution spectra for “as received” sample of (VO) $\text{V}_{12}\text{O}_{31} \cdot n\text{H}_2\text{O}$, exhibiting the main features related to the simultaneous presence of the V^{5+} , V^{4+} , “oxide”, “hydro”, and “ H_2O ” species is presented in Fig. 6. The fitting results for all studied samples are listed in Tables 2 and 3.

It should be noted that for V^{5+} and V^{4+} ions the V $2p_{1/2}$ and V $2p_{3/2}$ peak intensity ratio for all investigated samples is in the range of 0.50–0.53, i. e. it is in a good agreement with the value of 0.52 from Scofield’s calculations [51]. For a further check, the chemical composition (x in the chemical formulae V_2O_x) of the tested samples was derived:

- from the reduction ratio (RR), assuming that only tetra- and penta-valent vanadium is present in the all tested samples. Then $x = 5 - \text{RR}$;

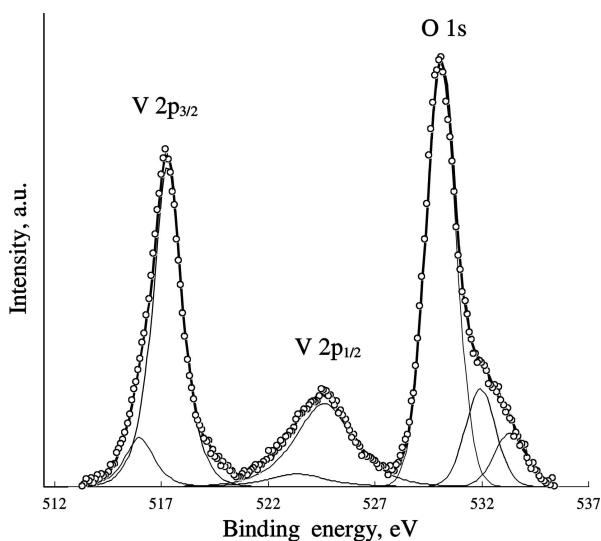


Fig. 6. Fitted X-ray photoelectron spectrum of V $2p$ and O $1s$ region for the “as received” sample of $(VO)V_{12}O_{31} \cdot nH_2O$ xerogel. Assignment of the spectral components is discussed in the text.

Table 4. Comparison of the chemical compositions of the reference oxides and V_2O_5 -based xerogels obtained by different methods.

Sample	x in V_2O_x estimated from:	
	reduction ratio	peak intensity
$H_2V_{12}O_{31} \cdot nH_2O$	4.96	5.00
$(VO)V_{12}O_{31} \cdot nH_2O$ “as received”	4.87	4.73
$(VO)V_{12}O_{31} \cdot nH_2O$ “after baking”	4.74	4.64
V_2O_5	5.00	4.91
V_2O_4	4.00	4.15

– from the relative intensities of vanadium and oxygen peaks, assuming that the O_{ox} peak corresponds to the basic oxide matrix.

These results are presented in Table 4.

4. Conclusions

The BE of V $2p_{3/2}$ line of V^{4+} ions in V_2O_5 -based xerogels is shifted by about 1.3 eV to the lower energy side compared to the basic V^{5+} line. The chemical shift for pure V_2O_5 and V_2O_4 oxides is about 0.6 eV, i. e. more than two times lower than that obtained for xerogels. This difference may be attributed to the diverse field potential of the surrounding matrix. The peak parameters of the vanadium ions, deduced from the examination of main valence oxides, cannot be directly

used for the determination of vanadium valence states in mixed valence compounds.

The V $2p_{3/2}$ line width for tetra-valent vanadium ions in xerogels is the same as for penta-valent ions. It contradicts to the results obtained for the pure V_2O_5 and V_2O_4 oxides where the line widths are different. It may be attributed to the different occupation of the d -bands in the mixed valence and stoichiometric vanadium oxides. In contrast to vanadium tetra- and penta-oxides with significantly different concentration of electrons in d -band, it is possible to expect the same additional broadening of V $2p$ lines of V^{5+} and V^{4+} species present in xerogels with a common d -band.

The substitution of the hydrogen ions by the vanadyl (VO) groups in the V_2O_5 -based xerogels leads to the significant increase of the V^{4+} ions concentration in these compounds. A similar increase was observed when the samples were annealed in vacuum, where it may be related to the preferential removal of oxygen from the host layers of the vanadium oxide.

Acknowledgement

This work was partly supported by Agency for International Science and Technology Development in Lithuania, Grant No. 10V-125 within the frame of COST D35.

References

- [1] S. Briggs and M.P. Seah, *Practical Surface Analysis*, Vol. 1 (Wiley, New York, 1990).
- [2] J.F. Moulder, W.F. Strickle, P.E. Sobol, and K.D. Bomben, *Handbook of X-Ray Photoelectron Spectroscopy* (Perkin-Elmer Corporation, Physical Electronics Division, 1995).
- [3] M. Demeter, M. Neumann, and W. Reichelt, Mixed-valence vanadium oxides studied by XPS, *Surf. Sci.* **454–456**(18), 41–44 (2000).
- [4] V. Bondarenka, Z. Martunas, S. Kaciulis, and L. Pandolfi, Sol-gel synthesis and XPS characterization of sodium-vanadium oxide bronze thin films, *J. Electron Spectrosc. Related Phenom.* **131–132**(1), 99–103 (2003).
- [5] G.A. Sawatzky and D. Post, X-ray photoelectron and Auger spectroscopy study of some vanadium oxides, *Phys. Rev. B* **20**(4), 1546–1555 (1979).
- [6] C. Malitesta, L. Sabbatini, L. Torsi, P.G. Zamboni, D. Ballivet-Tkatchenko, J. Galy, J.-L. Parize, and J.M. Savariault, Copper speciation by analytical electron spectroscopies: Case of the intercalation phase $Cu_{0.5}V_2O_5 \cdot 0.5H_2O$, *Surf. Interf. Analysis* **19**(1–12), 513–518 (1992).

- [7] M.P. Casaletto, L. Lisi, G. Mattogno, P. Patrono, G. Ruoppolo, and G. Russo, Oxidative dehydrogenation of ethane on γ -Al₂O₃ supported vanadyl and iron vanadyl phosphates: Physico-chemical characterisation and catalytic activity, *Appl. Catalysis A* **226**(1–2), 41–48 (2002).
- [8] J. Medialdua, R. Casanova, and Y. Barbaux, XPS studies of V₂O₅, V₆O₁₃, VO₂ and V₂O₃, *J. Electron Spectrosc. Related Phenom.* **71**(3), 249–261 (1995).
- [9] Z. Zhang and V.E. Henrich, Electronic interactions in the vanadium/TiO₂(110) and vanadia/TiO₂(110) model catalyst systems, *Surf. Sci.* **277**(3), 263–272 (1992).
- [10] G. Hopfengartner, D. Borgmann, I. Rademacher, G. Wedler, E. Hums, and G.W. Spitznagel, XPS studies of oxidic model catalysts: Internal standards and oxidation numbers, *J. Electron Spectrosc. Related Phenom.* **63**(2), 91–116 (1993).
- [11] S.L.T. Andersson, ESCA investigation of V₂O₅+TiO₂ catalysts for the vapour phase oxidation of alkylpyridines, *J. Chem. Soc. Faraday Trans. I* **75**, 1356–1370 (1979).
- [12] J. Cui, D. Da, and W. Jiang, Structure characterization of vanadium oxide thin films prepared by magnetron sputtering methods, *Appl. Surf. Sci.* **133**(3), 225–229 (1998).
- [13] R. Holm and S. Storp, ESCA studies of chemical shifts for metal oxides, *Appl. Phys. A* **9**(3), 217–222 (1976).
- [14] R.J. Colton, A.M. Guzman, and J.W. Rabalais, Electrochromism in some thin-film transition-metal oxides characterized by x-ray electron spectroscopy, *J. Appl. Phys.* **49**(1), 409–416 (1978).
- [15] B. Horvath, J. Strutz, J. Geyer-Lippmann, and E.G. Horvath, Preparation, properties, and ESCA characterization of vanadium surface compounds on silicagel. II, *Z. Anorg. Allg. Chem.* **483**(12), 193–204 (1981).
- [16] G. Blaauw, F. Leenhouts, F. van der Woude, and G.A. Sawatsky, The metal–non-metal transition in VO₂: X-ray photoemission and resistivity measurements, *J. Phys. C* **8**(4), 459–468 (1975).
- [17] J. Kasperkiewicz, J.A. Kovacich, and D. Lichtman, XPS studies of vanadium and vanadium oxides, *J. Electron Spectrosc. Related Phenom.* **32**(2), 123–132 (1983).
- [18] V. Bondarenka, S. Grebinskij, S. Kačiulis, G. Mattogno, and S. Mickevičius, Surface chemical composition of MV₁₀Mo₂O₃₁·nH₂O (M = Na₂, K₂, Ca, Sr, Cu) xerogels, *J. Electron Spectrosc. Related Phenom.* **107**(3), 253–259 (2000).
- [19] S. Lu, L. Hou, and F. Gan, Preparation and optical properties of phase-change VO[2] thin films, *J. Mater. Sci.* **28**(8), 2169–2177 (1993).
- [20] A.I. Minyaev, I.A. Denisov, V.E. Soroko, and V.A. Konovalov, Study of solid phase transformation of vanadium based systems, *Zh. Prikl. Khim. [Russ. J. Appl. Chem.]* **59**(2), 339–343 (1986).
- [21] Present paper.
- [22] M.P. Casaletto, S. Kaciulis, L. Lisi, G. Mattogno, A. Mezzi, P. Patrono, and G. Ruoppolo, XPS characterisation of iron-modified vanadyl phosphate catalysts, *Appl. Catalysis A* **218**(1–2), 129–137 (2001).
- [23] R. Larsson, B. Folkesson, and G. Schoen, X-ray photoelectron spectroscopy and homogenous catalysis. 1. Investigations on some vanadium compounds, *Chem. Scr.* **3**(2), 88–90 (1973).
- [24] B. Barbaray, J.P. Contour, and G. Mouvier, Effects of nitrogen dioxide and water vapour on oxidation of sulphur dioxide over vanadium pentoxide particles, *Env. Sci. Technol.* **12**(12), 1294–1297 (1978).
- [25] M. Takagi-Kawai, M. Soma, T. Onishi, and K. Tamaru, The adsorption and the reaction of NH₃ and NO_x on supported V₂O₅ catalysts: Effect of supporting materials, *Canadian J. Chem.* **58**(20), 2132–2137 (1980).
- [26] W.E. Slinkard and P.B. Degroot, Vanadium–titanium oxide catalysts for oxidation of butene to acetic acid, *J. Catalysis* **68**(2), 423–432 (1981).
- [27] Z. Zhang and V.E. Henrich, Surface electronic structure of V₂O₅(001): Defect states and chemisorption, *Surf. Sci.* **321**(1–2), 133–144 (1994).
- [28] J.L.G. Fierro, L.A. Arrua, J.M.L. Nieto, and G. Kremenec, Surface properties of co-precipitated V–Ti–O catalysts and their relation to the selective oxidation of isobutene, *Appl. Catalysis* **37**(1–2), 323–338 (1988).
- [29] A. Meisel, K.H. Hallmeier, R. Szargan, J. Muller, and W. Schneider, Investigation of soft X-ray emission and K-edge absorption spectra of V₂O₅ and Li_xV₂O₅ electrodes, *Phys. Scripta* **41**(4), 513–516 (1990).
- [30] V.I. Nefedov, Y.V. Salyn, G. Leonhardt, and R. Scheibe, A comparison of different spectrometers and charge corrections used in X-ray photoelectron spectroscopy, *J. Electron Spectrosc. Related Phenom.* **10**(2), 121–124 (1977).
- [31] Y. Schuhl, H. Baussart, R. Delobel, M. Le Bras, J. Leroy, L.G. Gengembre, and J. Rimblot, Study of mixed-oxide catalysts containing bismuth, vanadium and antimony. Preparation, phase composition, spectroscopic characterization and catalytic oxidation of propene, *J. Chem. Soc. Faraday Trans. I* **79**(9), 2055–2069 (1983).
- [32] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder, and G.E. Muilenberg, *Handbook of X-Ray Photoelectron Spectroscopy* (Perkin–Elmer Corporation, Physical Electronics Division, 1979).
- [33] F.J. Berry, M.E. Brett, R.A. Marbrow, and W.R. Patterson, An X-ray photoelectron spectroscopic study of the surface properties of vanadium antimonate and β -antimony tetroxide, *J. Chem. Soc. Dalton Trans.*, No. 5, 985–987 (1984).
- [34] V.I. Nefedov, M.N. Firsov, and I.S. Shaplygin, Electronic structures of MRhO₂, MRh₂O₄, RhMO₄ and

- Rh_2MO_6 on the basis of X-ray spectroscopy and ESCA data, *J. Electron Spectrosc. Related Phenom.* **26**(1), 65–78 (1982).
- [35] S. Hashimoto, K. Hirokawa, Y. Fukuda, K. Suzuki, T. Suzuki, N. Usuki, N. Gennai, S. Yoshida, M. Koda, H. Sezaki, H. Horie, A. Tanaka, and T. Ohtsubo, Correction of peak shift and classification of change of X-ray photoelectron spectra of oxides as a result of ion sputtering, *Surf. Interf. Analysis* **18**(12), 799–806 (1992).
- [36] J. Bullot, P. Cordier, O. Gallais, M. Gauthier, and J. Livage, Thin layers deposited from V_2O_5 gels: I. A conductivity study, *J. Non-Cryst. Solids* **68**(1), 123–134 (1984).
- [37] J. Livage, Synthesis of polyoxovanadates via “chimie douce”, *Coordination Chem. Rev.* **178–180**(2), 999–1018 (1998).
- [38] V. Bondarenko, S. Kaciulis, A. Plesanovas, V. Volkov, and G. Zacharova, Photoelectron spectroscopy of the poly-vanadium transition metal acids, *Appl. Surf. Sci.* **78**(1), 107–112 (1994).
- [39] V. Bondarenka, H. Tvardauskas, S. Grebinskij, S. Mickevicius, Z. Martunas, V. Volkov, and G. Zakharova, Ion beam induced preferential removal of oxygen from vanadium hydrates, *Nucl. Instrum. Methods B* **178**(1–4), 323–326 (2001).
- [40] V. Bondarenka, S. Grebinskij, S. Mickevicius, H. Tvardauskas, Z. Martūnas, V. Volkov, and G. Zakharova, Humidity sensors based on $\text{H}_2\text{V}_{11}\text{TiO}_{30.3}\cdot n\text{H}_2\text{O}$ xerogels, *Sensors Actuators B* **55**(1), 60–64 (1999).
- [41] T. Yao, Y. Oka, and N. Yamamoto, Layered structures of hydrated vanadium oxides. Part 1. – Alkali-metal intercalates $\text{A}_{0.3}\text{V}_2\text{O}_5\cdot n\text{H}_2\text{O}$ ($\text{A} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ and NH_4), *J. Mater. Chem.* **2**(3), 331–336 (1992).
- [42] V. Bondarenka, S. Mickevicius, H. Tvardauskas, S. Grebinskij, S. Kačiulis, G. Mattogno, V. Volkov, and G. Zakharova, X-ray photoelectron spectroscopy of $\text{Na}_x\text{V}_2\text{O}_5$ (β) bronze, *Lithuanian J. Phys.* **40**(5), 353–355 (2000).
- [43] T. Yao, Y. Oka, and N. Yamamoto, Layered structures of hydrated vanadium oxides. Part 2. – Vanadyl intercalates $(\text{VO})_x\text{V}_2\text{O}_5\cdot n\text{H}_2\text{O}$, *J. Mater. Chem.* **2**(3), 337–340 (1992).
- [44] S. Mickevicius, V. Bondarenka, S. Grebinskij, S. Kačiulis, H. Tvardauskas, and Z. Martūnas, The study of dehydration of $\text{H}_2\text{V}_{11.5}\text{Cr}_{0.5}\text{O}_{31}\cdot n\text{H}_2\text{O}$ xerogel by XPS and TDS, *Lithuanian J. Phys.* **42**(2), 127–130 (2002).
- [45] V. Bondarenka, Z. Martūnas, S. Kačiulis, L. Pandolfi, S. Grebinskij, and S. Mickevicius, Influence of UV radiation on the vanadium ions in vanadium hydrates, *Lithuanian J. Phys.* **42**(4), 281–284 (2002).
- [46] V. Bondarenka, Sol–gel technology: Vanadium compounds, in: *Proceedings of Conference ‘Lithuanian Science and Industry; Applied Physics’* (Kaunas, Lithuania, 2004) pp. 29–30.
- [47] V.L. Volkov, G.S. Zakharova, and A.A. Ivakin, Synthesis and properties of hydrated polyvanadomolybdic acid, *Zh. Neorg. Khim. [Russian J. Inorg. Chem.]* **30**(3), 642–645 (1985).
- [48] G.S. Zakharova and V.L. Volkov, Intercalation compounds based on vanadium oxide (V) xerogel, *Usp. Khim. [Russ. Adv. Chem.]* **72**(4), 346–362 (2003).
- [49] V.L. Volkov, G.S. Zakharova, and V. Bondarenka, *Xerogels of Simple and Modified Polyvanadates* (Ural Branch of the Russian Academy of Sciences, Yekaterinburg, 2001) [in Russian].
- [50] N. Soga and M. Senna, Change in the dehydration and crystallization processes of V_2O_5 xerogel due to mechanical pretreatment, *J. Solid State Chem.* **107**(1), 159–165 (1993).
- [51] J.H. Scofield, Hartree–Slater subshell photoionization cross-sections at 1254 and 1487 eV, *J. Electron Spectrosc. Related Phenom.* **8**(2), 129–137 (1976).

VANADŽIO VALENTINGUMAS HIDRATUOTUOSE JUNGINIULOSE

V. Bondarenka^a, S. Grebinskij^a, S. Mickevicius^a, H. Tvardauskas^a, S. Kačiulis^b, V. Volkov^c, G. Zakharova^c,
A. Pašiškevičius^a

^a Pusuaidininkų fizikos institutas, Vilnius, Lietuva

^b Nanostruktūrinių medžiagų tyrimo institutas, Roma, Italija

^c Kietojo kūno chemijos institutas, Jekaterinburgas, Rusija

Santrauka

Analizuojama cheminė daugiavalenčių vanadžio junginių sandara. Atlikta $V 2p_{3/2}$ smailių ryšio energijos ir jų pusplėčio įvairiuose vanadžio oksiduose literatūrinių duomenų statistinė analizė.

Rentgeno fotoelektronų spektroskopijos (RFS) metodu buvo tirti hidratuoti vanadžio pentoksido $\text{HV}_{12}\text{O}_{31}\cdot n\text{H}_2\text{O}$ ir $(\text{VO})\text{V}_{12}\text{O}_{31}$

$\cdot n\text{H}_2\text{O}$ bandiniai, pagaminti taikant standartinę zolio ir gelio technologiją. Nustatyta, kad V^{4+} jonų ryšio energija (RE), lyginant su pagrindinių matricos V^{5+} jonų RE, pasislinkusi į mažesnių energijos verčių pusę maždaug per 1,3 eV, o abiejų jonų smailių pusplėčiai yra vienodi.