

Zn(Ta_{1-x}Nb_x)₂O₆ nanomaterials. Synthesis, characterization and corrosion behaviour

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Abstract: Zn(Ta_{1-x}Nb_x)₂O₆ pseudo-binary oxide nanocrystalline materials (where x = 1; 0.5; 0.1; 0.05 and 0) were obtained through the solid-state method and characterized by X-ray diffraction, Fourier Transform Infrared Spectroscopy and Ultraviolet-visible spectroscopy. In addition, their morphology and topography have been determined by field emission-scanning electron microscopy (SEM) and atomic force microscopy (AFM). There is a significant dependence between the rugosity and the uniformity of crystals. The evenly crystals organized in multilayers have the lowest value of rugosity and the non uniform fractal type architectures have the highest value of rugosity. The compounds' anti-corrosion features were evaluated after deposition on carbon steel (OL) in 0.1 M Na₂SO₄ media by open circuit potential measurement and potentiodynamic polarization technique with Tafel representation. The inhibition efficiency of pseudo-binary oxides deposited on carbon steel electrode was in the range 42.3-52.7 % promising for their further multiple layer deposition with porphyrins in order to improve anticorrosion properties. Due to the high band gap (3.80 - 4.30 eV) provided by increasing the

31 tantalum content, four of these pseudo-binary oxides might find applications in photovoltaic
32 cells.

33

34 *Keywords:* nanomaterials, solid-state method, pseudo-binary oxides, corrosion inhibition, Tafel
35 curves

36

37 **RUNNING TITLE: PSEUDO-BINARY OXIDES NANOMATERIALS**

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INTRODUCTION

40

41 A widely used material in many industries, the steel¹ is prone to corrosion as a result of
42 reactions with the environment. This spontaneous process can compromise the material integrity
43 and might bring serious impact to the environment and that is why measures to prevent and
44 control it are required.

45 Zinc is the most widely used material for protection of steel against corrosion²⁻⁴. Its
46 corrosion resistance, however, is limited. Zinc alloys can create improved corrosion resistance
47 compared to pure zinc in the protection of ferrous-based metals⁵⁻⁹. The efforts to improve the
48 corrosion stability of pure zinc coatings have been directed toward alloying with more noble
49 metal or adding surface inhibitors¹⁰. Recently, niobium and tantalate oxides were applied in
50 chemical processing applications due to their outstanding corrosion resistance¹¹⁻¹³.

51 The binary niobate and tantalate compounds with general formula $Zn(Ta_{1-x}Nb_x)_2O_6$
52 were found to be promising candidates for application in microwave devices based on the
53 improved dielectric properties of these compounds revealing both high quality factor ($Q \times f$) and
54 dielectric constant (ϵ_r)¹⁴⁻¹⁸.

55 $ZnTa_2O_6$ have been obtained based on several modern chemistry preparation routes, e.g.
56 citrate sol-gel¹⁹, but the most used method is the conventional solid-state reaction of mixed
57 oxides¹⁷⁻²¹. $Zn(Nb_{1-x}Ta_x)_2O_6$ (where $x = 0; 0.2; 0.4; 0.6; 0.8; 0.9; 1$) novel derivatives exhibiting
58 remarkable dielectric properties were usually prepared by the conventional mixed oxide route²².

59 The $ZnNb_2O_6$ material is also used as a dielectric^{23, 24} and was obtained using the
60 molten salt synthesis^{25, 26}, sol-gel method²⁷, solid-state reaction^{23, 24, 28} and optical floating zone

61 method²⁹. These materials are used in photocatalysis³⁰⁻³⁵, for electrochemical gas sensors³⁶, in
62 energy storage field³⁷ and in solar cell formulations³⁸.

63 The present study was focused on obtaining of three novel pseudo-binary compounds,
64 namely: $Zn(Ta_{1-x}Nb_x)_2O_6$, (where $x = 0.5; 0.1; \text{ and } 0.05$) and on their investigation regarding
65 structural, morphological and optical properties in comparison with the already known $ZnNb_2O_6$
66 and $ZnTa_2O_6$. The effects produced by the increased content of tantalum on the properties of
67 these novel pseudo-binary oxides are discussed. Based on our successful experience in corrosion
68 protection (inhibition efficiency up to 96 %) by bilayer depositions of $Zn_3Ta_2O_8$ or $Zn_3Nb_2O_8$
69 and 5 - (4 - pyridyl) - 10, 15, 20 - tris (phenoxy - phenyl) porphyrin or 5 - (4 - pyridyl) - 10, 15,
70 20 - tris(3, 4 - dimethoxy - phenyl) porphyrin³⁹ on carbon steel electrodes, another important
71 purpose was to evaluate the anticorrosion activity exhibited by thin films of these compounds on
72 carbon steel in acid environment.

73

74

EXPERIMENTAL

75

76 *Apparatus:* The structural information of the nanomaterials was obtained by X-ray diffraction on
77 a XRD, X'pert Pro MPD X-ray diffractometer using Cu K α radiation, at room temperature. FT-
78 IR measurements have been performed on JASCO 430 FT-IR spectrometer (KBr pellets). The
79 morphology and the particle dimension of the samples were investigated by SEM / EDAX
80 (Model INSPECT S) and AFM (Model Nanosurf® EasyScan 2 Advanced Research). The band
81 gap of the nanomaterials was estimated from the diffuse reflectance spectrum, at room
82 temperature, recorded on an UV-VIS-NIR spectrometer Lambda 950. Electrochemical
83 measurements were made using a Voltalab potentiostat, Model PGZ 402. The degree of
84 inhibition efficiency *IE* (%) has been calculated on the basis of the equation⁴⁰. For method for
85 corrosion testing and cell description see Supplementary Materials.

86 *Reagents:* The starting materials used during the synthesis of $Zn(Ta_{1-x}Nb_x)_2O_6$ (where $x =$
87 $1; 0.5; 0.1; 0.05$ and 0) pseudo-binary oxides were: tantalum (V) oxide - Ta_2O_5 (99.99 %, Sigma),
88 niobium (V) oxide - Nb_2O_5 (99.99 %, Merck) and zinc oxide – ZnO (99.99 %, Merck).

89 *General method for obtaining $Zn(Ta_{1-x}Nb_x)_2O_6$ (where $x = 1; 0.5; 0.1; 0.05$ and 0)*
90 *nanomaterials:* $Zn(Ta_{1-x}Nb_x)_2O_6$ (where $x = 1; 0.5; 0.1; 0.05$ and 0) nanomaterials were obtained
91 by solid-state method varying the molar ratios (Table 1). The mixtures were afterwards heated at

92 1200 °C for 3 h soaking time. A rate of 5°C/min of the heating and cooling was set up for the
93 heated furnace.

94

95 Table 1. The Zn(Ta_{1-x}Nb_x)₂O₆ nanomaterials obtained by solid-state method

The Obtaine naomaterials	x	Molar Ratios
ZnTa ₂ O ₆	0	ZnO / Ta ₂ O ₅ = 1 / 1
ZnNb ₂ O ₆	1	ZnO / Nb ₂ O ₅ = 1 / 1
Zn(Ta _{0.95} Nb _{0.05}) ₂ O ₆	0.05	ZnO / Ta ₂ O ₅ / Nb ₂ O ₅ = 1 / 0.95 / 0.05
Zn(Ta _{0.9} Nb _{0.1}) ₂ O ₆	0.1	ZnO / Ta ₂ O ₅ / Nb ₂ O ₅ = 1 / 0.9 / 0.1
Zn(Ta _{0.5} Nb _{0.5}) ₂ O ₆	0.5	ZnO / Ta ₂ O ₅ / Nb ₂ O ₅ = 1 / 0.5 / 0.5

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RESULTS AND DISCUSSION

98

99 *Structural characterization*

100 Figure 1 presents the X-ray diffraction patterns for: a) ZnTa₂O₆, b) Zn(Ta_{0.95}Nb_{0.05})₂O₆,
101 c) Zn(Ta_{0.9}Nb_{0.1})₂O₆, d) Zn(Ta_{0.5}Nb_{0.5})₂O₆ and e) ZnNb₂O₆ and it can be observed that besides
102 the main peaks associated with the ZnTa₂O₆ and ZnNb₂O₆ pure nanomaterials, some associated
103 peaks did appear (indexed with JCPDS, card No. 01-076-1827 and 01-076-1826), belonging to
104 the *Pbcn* space group.

105 The intensity of the peaks, relative to the background signal, demonstrates high purity
106 and good quality of the samples. The highest intensity peak is located at $2\theta = 30.4769^\circ$ for
107 ZnTa₂O₆ and $2\theta = 30.3424^\circ$ for ZnNb₂O₆ and they belong to the 131 for ZnTa₂O₆ and 311 for
108 ZnNb₂O₆ plane⁴¹. The novel structures have the highest intensity peaks located at $2\theta = 30.4569^\circ$
109 for Zn(Ta_{0.95}Nb_{0.05})₂O₆, $2\theta = 30.4273^\circ$ for Zn(Ta_{0.9}Nb_{0.1})₂O₆ and $2\theta = 30.3964^\circ$ for
110 Zn(Ta_{0.5}Nb_{0.5})₂O₆, the values belonging to the interval limited by ZnTa₂O₆ and ZnNb₂O₆.

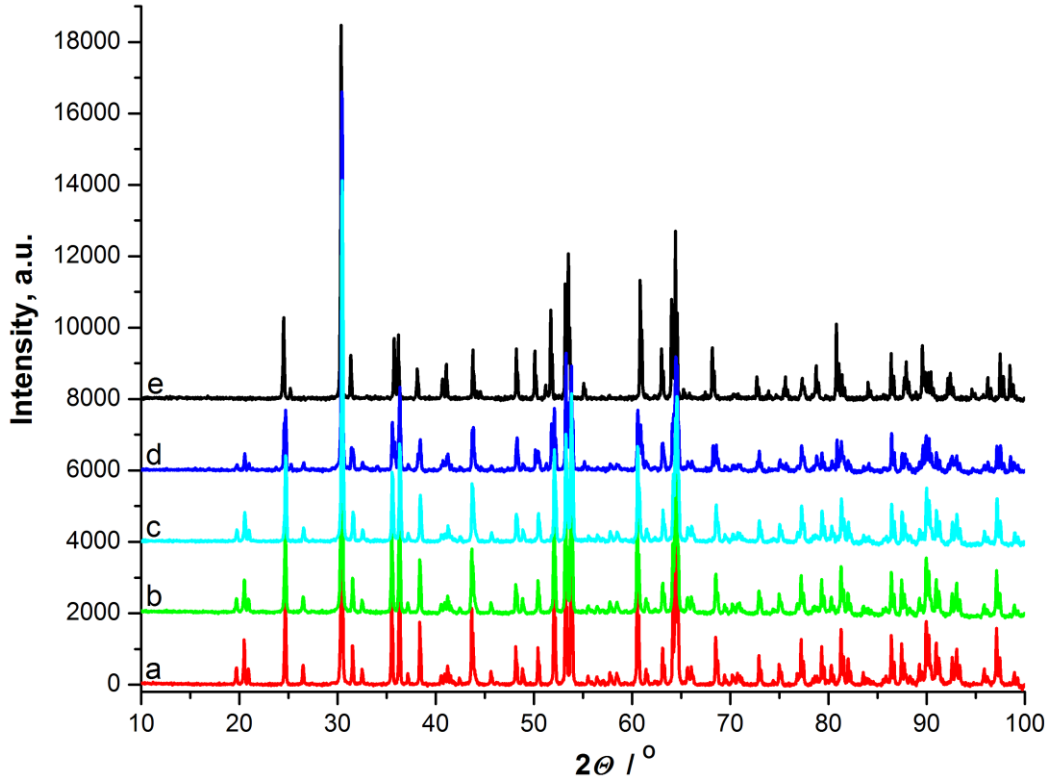


Fig. 1. The XRD patterns of (a) ZnTa_2O_6 , (b) $\text{Zn}(\text{Ta}_{0.95}\text{Nb}_{0.05})_2\text{O}_6$, (c) $\text{Zn}(\text{Ta}_{0.9}\text{Nb}_{0.1})_2\text{O}_6$, (d) $\text{Zn}(\text{Ta}_{0.5}\text{Nb}_{0.5})_2\text{O}_6$ and (e) ZnNb_2O_6

The lattice constant was calculated from XRD analysis data, using FullProf Suite computer package⁴²: $a = 4.80 \text{ \AA}$, $b = 18.09 \text{ \AA}$, $c = 5.13 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$; elementary cell's volume ($V / 10^6 / \text{pm}^3$) is 409.71 for ZnTa_2O_6 and $a = 15.30 \text{ \AA}$, $b = 5.96 \text{ \AA}$, $c = 5.14 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$; elementary cell's volume ($V / 10^6 / \text{pm}^3$) is 413.07 for ZnNb_2O_6 .

The mean crystallite size (d) of the powder samples was calculated using Scherrer's equation⁴³. The average crystallite size determined from XRD line broadening for each of the samples, was: 58 nm for ZnTa_2O_6 , 47 nm for $\text{Zn}(\text{Ta}_{0.95}\text{Nb}_{0.05})_2\text{O}_6$, 42 nm for $\text{Zn}(\text{Ta}_{0.9}\text{Nb}_{0.1})_2\text{O}_6$, 39 nm for $\text{Zn}(\text{Ta}_{0.5}\text{Nb}_{0.5})_2\text{O}_6$ and 34 nm for ZnNb_2O_6 , respectively. The values are increasing with the increase of the Ta content in the nanomaterial.

The FT-IR spectra of the obtained pseudo-binary oxides and the precursor oxides: a) ZnNb_2O_6 , b) ZnTa_2O_6 , c) Nb_2O_5 , d) Ta_2O_5 , e) ZnO , f) $\text{Zn}(\text{Ta}_{0.95}\text{Nb}_{0.05})_2\text{O}_6$, g) $\text{Zn}(\text{Ta}_{0.9}\text{Nb}_{0.1})_2\text{O}_6$ and h) $\text{Zn}(\text{Ta}_{0.5}\text{Nb}_{0.5})_2\text{O}_6$ are comparatively presented in Figure 2. The spectrum of ZnO presents a single broad and intense IR band located at wavenumber $\nu = 430 \text{ cm}^{-1}$; the spectrum of Ta_2O_5

oxide shows four broad weak absorption bands located around 900 cm^{-1} , 840 cm^{-1} , 755 cm^{-1} and 530 cm^{-1} ; the Nb_2O_5 oxide reveals two intense not clearly separated bands at 685 cm^{-1} and 800 cm^{-1} .

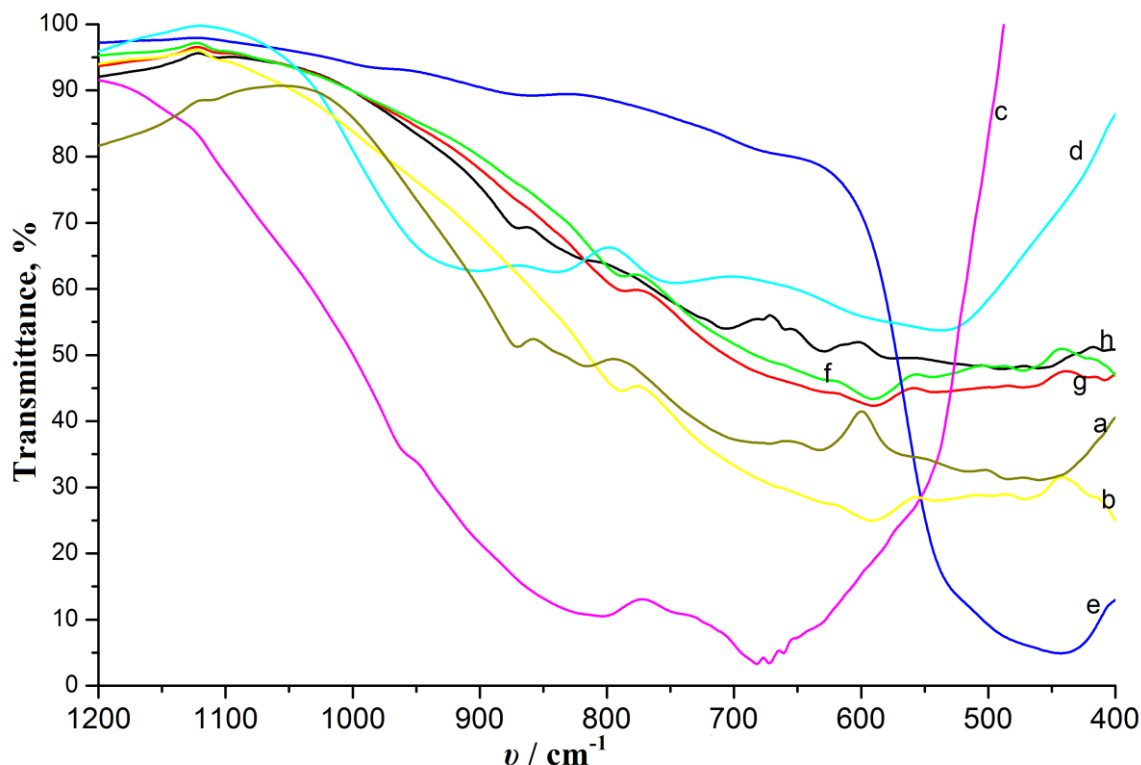


Fig. 2. FT-IR spectra of the obtained (a) ZnNb_2O_6 , (b) ZnTa_2O_6 , (c) Nb_2O_5 , (d) Ta_2O_5 , (e) ZnO , (f) $\text{Zn}(\text{Ta}_{0.95}\text{Nb}_{0.05})_2\text{O}_6$, (g) $\text{Zn}(\text{Ta}_{0.9}\text{Nb}_{0.1})_2\text{O}_6$ and (h) $\text{Zn}(\text{Ta}_{0.5}\text{Nb}_{0.5})_2\text{O}_6$

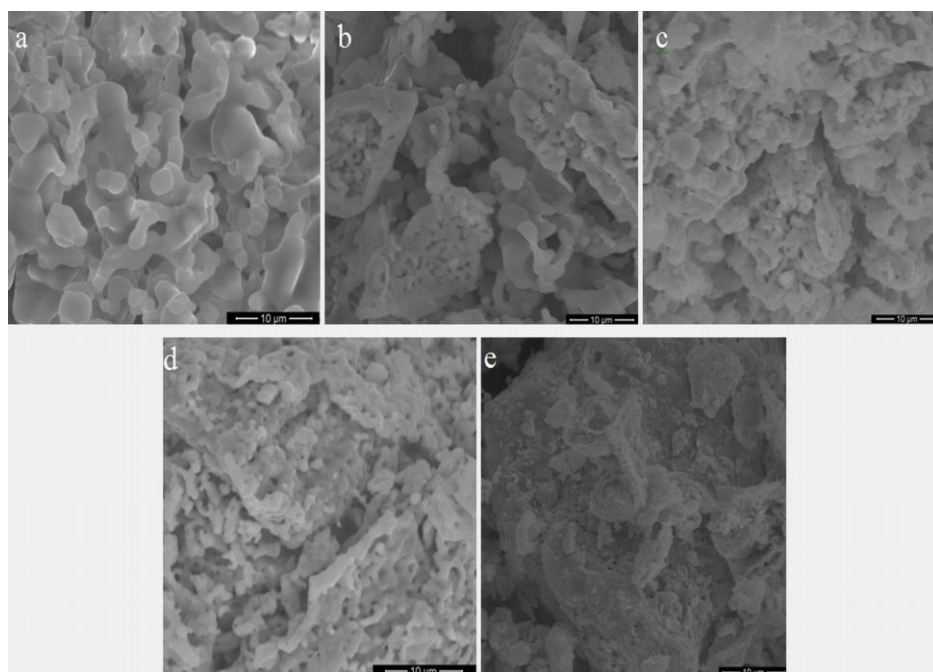
The FT-IR spectra of the newly obtained nanomaterials $(\text{Zn}(\text{Ta}_{1-x}\text{Nb}_x)_2\text{O}_6$ ($x = 0.5; 0.1; 0.05$)) displayed some distinctive bands, located at 600 cm^{-1} [$\text{Zn}(\text{Ta}_{0.5}\text{Nb}_{0.5})_2\text{O}_6$], 620 cm^{-1} [$\text{Zn}(\text{Ta}_{0.9}\text{Nb}_{0.1})_2\text{O}_6$, $\text{Zn}(\text{Ta}_{0.95}\text{Nb}_{0.05})_2\text{O}_6$], and 640 cm^{-1} [$\text{Zn}(\text{Ta}_{0.5}\text{Nb}_{0.5})_2\text{O}_6$], respectively. Analyzing the structure of the novel nanomaterials and the presence of the known bands from the precursor oxides, these new displayed bands at 640 cm^{-1} and at 620 cm^{-1} can be assigned to Zn-O-Nb and to Zn-O-Ta novel generated bonds. As expected, these new bands are strongly associated with the increased presence of each element in the structure of the nanomaterials. Thus, the intensity of the peaks at 600 cm^{-1} increase with increasing of Ta content, and the position of the peaks tend to be shifted towards lower wave numbers with increasing of ZnO content, in agreement with reported data^{21, 44}. Besides, equal molar ratios of Ta and Nb will

145 generally favor large non resolved bands. Another aspect is that the very weak bands with peaks
146 around $540\text{-}560\text{ cm}^{-1}$ can be attributed to symmetrical stretching vibration modes $\nu_s(\text{O-Metal-}$
147 $\text{O})$, where the metal is Ta or Nb.

148

149 *Morphological characterization*

150 The morphological aspect of the resulting powders was examined by SEM, as shown in
151 Figure 3. The micrographs for ZnNb_2O_6 , $\text{Zn}(\text{Ta}_{0.5}\text{Nb}_{0.5})_2\text{O}_6$, $\text{Zn}(\text{Ta}_{0.9}\text{Nb}_{0.1})_2\text{O}_6$,
152 $\text{Zn}(\text{Ta}_{0.95}\text{Nb}_{0.05})_2\text{O}_6$ and ZnTa_2O_6 nanomaterials reveal the formation of soft spherical
153 agglomerates (a- ZnNb_2O_6) which display an irregular morphology or fractal-like (e- ZnTa_2O_6)
154 crystal structures.



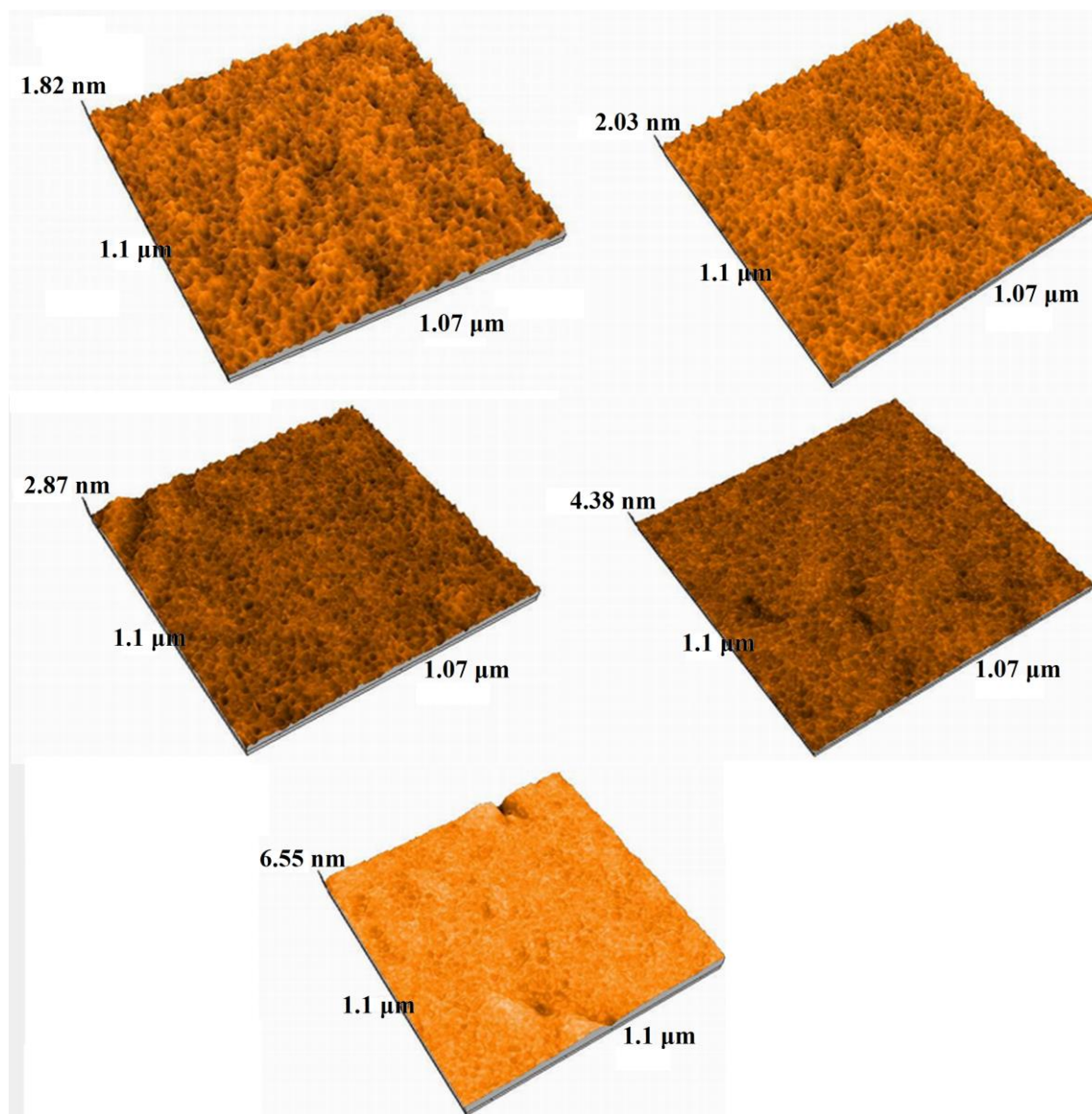
155
156 Fig. 3. The SEM images of: (a) ZnNb_2O_6 , (b) $\text{Zn}(\text{Ta}_{0.5}\text{Nb}_{0.5})_2\text{O}_6$, (c) $\text{Zn}(\text{Ta}_{0.9}\text{Nb}_{0.1})_2\text{O}_6$, (d)
157 $\text{Zn}(\text{Ta}_{0.95}\text{Nb}_{0.05})_2\text{O}_6$ and (e) ZnTa_2O_6

158

159 Depending on the nature and chemical composition of the nanomaterials the
160 morphology is different: crystals organized in multilayer as in case of ZnNb_2O_6 , with uniform
161 covering aspect or various size distributed crystals with porous aspect (both mesopores and
162 macropores are present) or even sponge like shape in case of [b- $\text{Zn}(\text{Ta}_{0.5}\text{Nb}_{0.5})_2\text{O}_6$, c-
163 $\text{Zn}(\text{Ta}_{0.9}\text{Nb}_{0.1})_2\text{O}_6$, d- $\text{Zn}(\text{Ta}_{0.95}\text{Nb}_{0.05})_2\text{O}_6$] and going to fractal kind aspect in case of e- ZnTa_2O_6

164 (and a touch of amorphous aspect). The EDAX analysis certified initial molar ratios between Zn,
165 Nb and Ta see Supplementary Materials for detailed information.

166 In Figure 4 are shown the AFM images of the surface for each of the studied materials
167 deposited on OL electrodes, using a scan size of $1\mu\text{m} \times 1\mu\text{m}$. The contact mode cantilever was
168 used to measure the samples.



169
170 Fig. 4. AFM images of: a) ZnNb_2O_6 , b) $\text{Zn}(\text{Ta}_{0.5}\text{Nb}_{0.5})_2\text{O}_6$, c) $\text{Zn}(\text{Ta}_{0.9}\text{Nb}_{0.1})_2\text{O}_6$, d)
171 $\text{Zn}(\text{Ta}_{0.95}\text{Nb}_{0.05})_2\text{O}_6$ and e) ZnTa_2O_6

172
173 The particle size analysis for ZnNb_2O_6 , $\text{Zn}(\text{Ta}_{0.5}\text{Nb}_{0.5})_2\text{O}_6$, $\text{Zn}(\text{Ta}_{0.9}\text{Nb}_{0.1})_2\text{O}_6$,
174 $\text{Zn}(\text{Ta}_{0.95}\text{Nb}_{0.05})_2\text{O}_6$ and ZnTa_2O_6 deposited on OL electrodes was performed from the AFM

175 measurements data (Nanosurf EasyScan 2 AFM software). The average grain sizes was
176 determined, as follows: about 30 nm for ZnNb_2O_6 , around 38 nm for $\text{Zn}(\text{Ta}_{0.5}\text{Nb}_{0.5})_2\text{O}_6$, about 45
177 nm for $\text{Zn}(\text{Ta}_{0.9}\text{Nb}_{0.1})_2\text{O}_6$, about 50 nm for $\text{Zn}(\text{Ta}_{0.95}\text{Nb}_{0.05})_2\text{O}_6$ and about 70 nm for ZnTa_2O_6 in
178 very good agreement with RDX measurements results. The particle size is increasing in
179 accordance with the increase of tantalum content. The surface roughness was calculated using
180 equations from⁴⁵.

181 The measured surface has an area of 1.243 pm^2 . Using the Nanosurf EasyScan 2
182 computer software the values of S_a and S_q for the nanomaterials were calculated as follows: $S_a =$
183 0.21 nm and $S_q = 0.38 \text{ nm}$ for ZnNb_2O_6 , $S_a = 0.26 \text{ nm}$ and $S_q = 0.43 \text{ nm}$ for $\text{Zn}(\text{Ta}_{0.5}\text{Nb}_{0.5})_2\text{O}_6$, $S_a =$
184 0.42 nm and $S_q = 0.53 \text{ nm}$ for $\text{Zn}(\text{Ta}_{0.9}\text{Nb}_{0.1})_2\text{O}_6$, $S_a = 0.53 \text{ nm}$ and $S_q = 0.89 \text{ nm}$ for
185 $\text{Zn}(\text{Ta}_{0.95}\text{Nb}_{0.05})_2\text{O}_6$ and $S_a = 0.73 \text{ nm}$ and $S_q = 1 \text{ nm}$ for ZnTa_2O_6 .

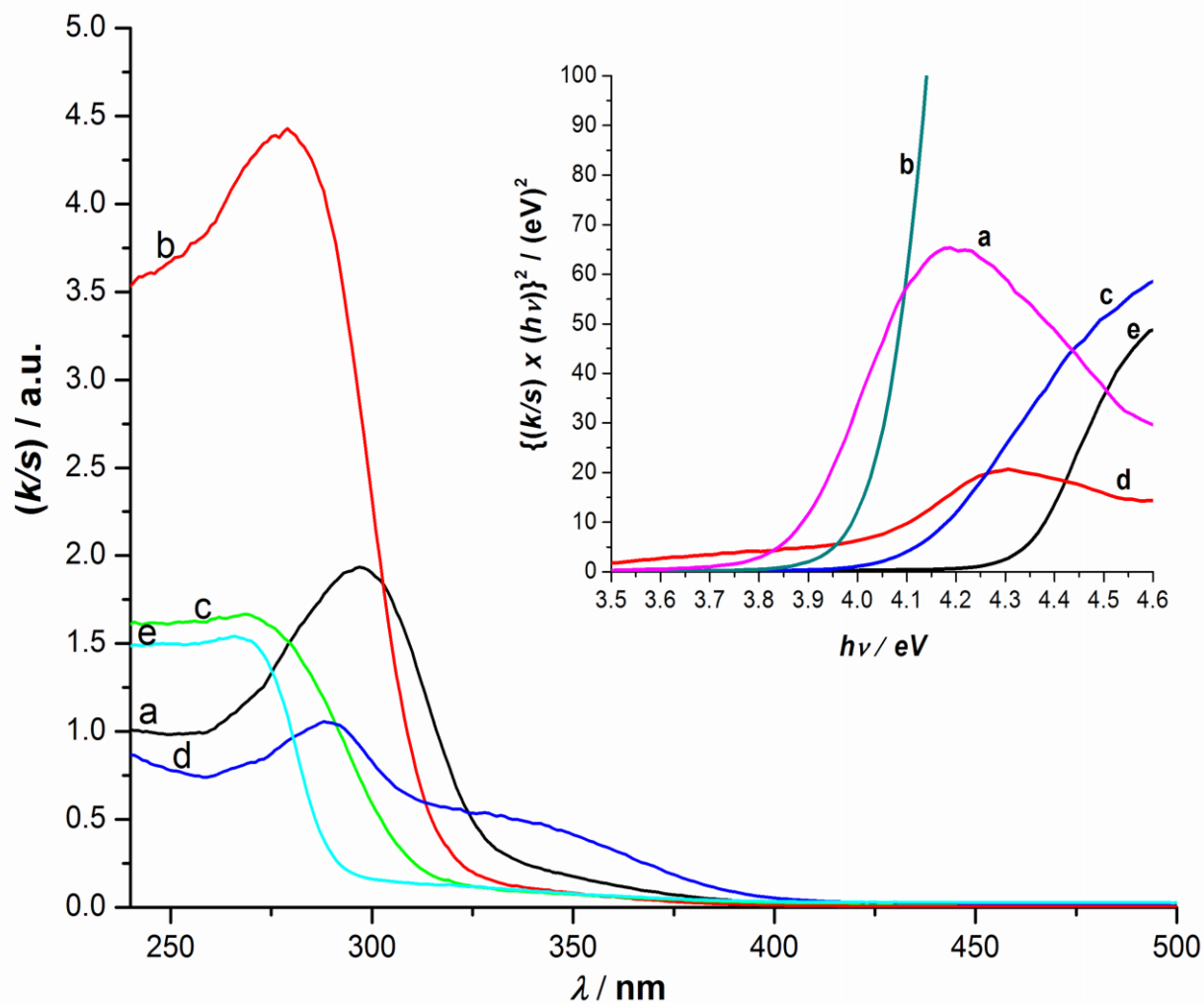
186 There is a strong correlation between the aspect of the samples (SEM images) and the
187 rugosity. The more uniform crystals, displayed in multilayers reflect in the lowest value of
188 rugosity and the non uniform fractal type architectures present the highest value of rugosity.
189 Some failure of the surfaces producing deep pores and channels can be noticed (Figures 5c, 5d,
190 5e).

191

192 *Optical properties*

193 Using Kubelka-Munk equation^{46, 47} the absorbance was calculated from the reflectance
194 spectra (Figure 5). The diffuse reflectance spectra was also recorded (see Supplementary
195 Materials). In Figure 5 were plotted the $\{(k/s) / hv\}^2$ versus hv , where k denotes absorption
196 coefficient, s is the scattering coefficient and hv is the photon energy. The band gap was
197 calculated and its value was: 3.20 eV for ZnNb_2O_6 , 3.80 eV for $\text{Zn}(\text{Ta}_{0.5}\text{Nb}_{0.5})_2\text{O}_6$, 4.00 eV for
198 $\text{Zn}(\text{Ta}_{0.9}\text{Nb}_{0.1})_2\text{O}_6$, 4.10 eV for $\text{Zn}(\text{Ta}_{0.95}\text{Nb}_{0.05})_2\text{O}_6$ and 4.30 eV for ZnTa_2O_6 . The values of band
199 gap are increasing in the same way as the increasing of inhibition of corrosion, proving the
200 differentiated chemical stability of the tested nanomaterials.

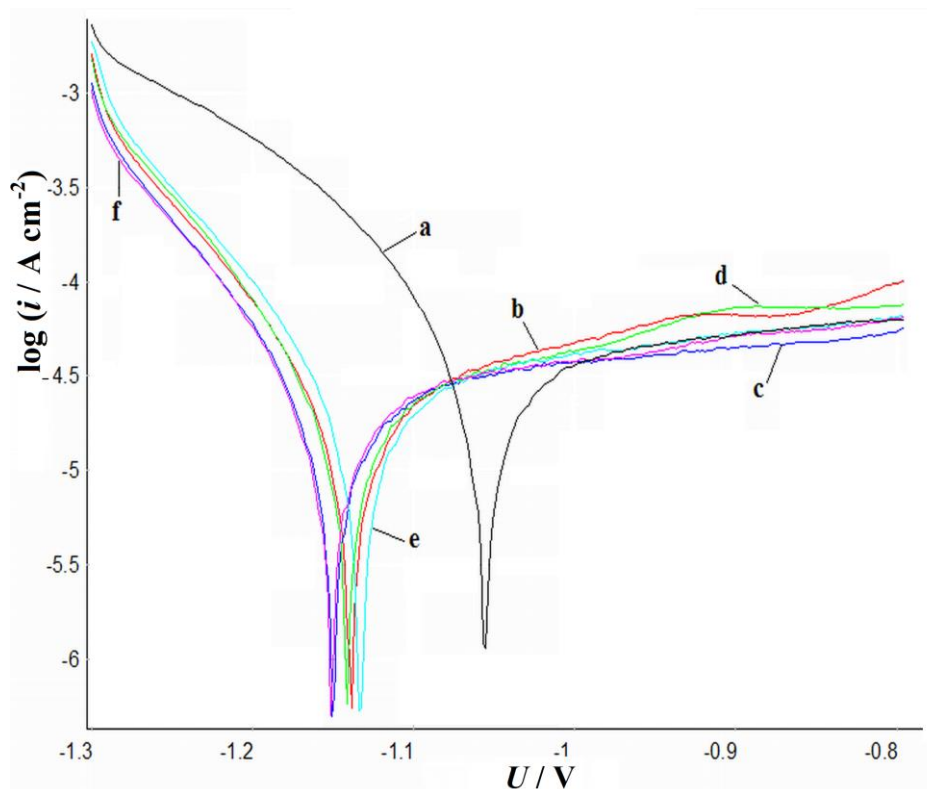
201



202
 203 Fig. 5. Absorption spectra of: (a) $\text{Zn}(\text{Ta}_{0.5}\text{Nb}_{0.5})_2\text{O}_6$, (b) $\text{Zn}(\text{Ta}_{0.9}\text{Nb}_{0.1})_2\text{O}_6$, (c)
 204 $\text{Zn}(\text{Ta}_{0.95}\text{Nb}_{0.05})_2\text{O}_6$, (d) ZnNb_2O_6 and (e) ZnTa_2O_6 . Plot of $\{(k/s)h\nu\}^2$ vs. $h\nu$ (energy) of: (a)
 205 $\text{Zn}(\text{Ta}_{0.5}\text{Nb}_{0.5})_2\text{O}_6$, (b) $\text{Zn}(\text{Ta}_{0.9}\text{Nb}_{0.1})_2\text{O}_6$, (c) $\text{Zn}(\text{Ta}_{0.95}\text{Nb}_{0.05})_2\text{O}_6$, (d) ZnNb_2O_6 and (e) ZnTa_2O_6
 206

207 *Tafel polarization plots*

208 Tafel plots of the investigated OL electrodes, recorded after 30 minutes OCP (see
 209 Supplementary Materials) in 0.1 M Na_2SO_4 solution, are shown in Figure 6. The parameters
 210 calculated from these plots are summarized in Table 2.



211
 212 Fig. 6. Tafel representation of polarization curves recorded in 0.1 M Na₂SO₄ for the studied
 213 electrodes. (a) OL, (b) ZnTa₂O₆, (c) ZnNb₂O₆, (d) Zn(Ta_{0.95}Nb_{0.05})₂O₆, (e) Zn(Ta_{0.9}Nb_{0.1})₂O₆
 214 (f) Zn(Ta_{0.5}Nb_{0.5})₂O₆

215
 216 The slopes were determined in the Tafel region of the anodic and cathodic curves for
 217 segments of approximately 50 mV, before and after the corrosion potential (U).

218 The current density corresponds to the rate of electrochemical reactions associated with
 219 corrosion processes taking place on OL surface, under polarization in 0.1 M Na₂SO₄ media.

220 Table 2. Tafel parameters of investigated electrodes after 30 minutes immersion in 0.1 M
 221 Na₂SO₄ solution.

Electrod	$E_{corr} /$ V	$i_{corr} /$ $\mu\text{A}/\text{cm}^2$	$R_p /$ kohm x cm^2	$v_{cor} /$ $\mu\text{m}/\text{Y}$	$IE /$ %
Bare OL	-1.05	40.36	0.90	469.1	-
ZnTa ₂ O ₆	-1.14	20.74	1.40	241.1	48.61
ZnNb ₂ O ₆	-1.15	19.09	1.41	221.9	52.70
Zn(Ta _{0.95} Nb _{0.05}) ₂ O ₆	-1.14	23.25	1.34	270.2	42.39

Zn(Ta _{0.9} Nb _{0.1}) ₂ O ₆	-1.13	22.51	1.27	261.7	44.22
Zn(Ta _{0.5} Nb _{0.5}) ₂ O ₆	-1.15	21.23	1.43	246.8	47.40

222

223 The corrosion potential (E_{corr}) of the bare OL electrode is -1.05 V and the
 224 corresponding corrosion current density (i_{corr}) is 40.36 $\mu\text{A}/\text{cm}^2$. In all cases the presence of
 225 Zn(Ta_{1-x}Nb_x)₂O₆ shifted the polarization curves towards the region of lower corrosion current
 226 densities because of the better stability of the covering metal oxides. For all studied covering
 227 materials a similar corrosion inhibiting activity is observed, as presented in Table 2. The
 228 differences in the inhibition efficiencies (IE) are probably generated by the differences in the
 229 stability of these materials, the roughness and the porosity of the protective coatings. Comparing,
 230 for instance, ZnNb₂O₆ and ZnTa₂O₆, the average roughness is rising from $S_a = 0.21\text{nm}$ to $S_a =$
 231 0.73nm and the IE decrease from 52.7% to 48.61% respectively. Furthermore, ZnNb₂O₆ has a
 232 uniform covering aspect being less porous than ZnTa₂O₆. This study clearly showed that the
 233 decrease of the niobium content in the pseudo-binary oxides accompanied by the increasing of
 234 average roughness values has the effect of decreasing the inhibition efficiency.

235 The shift of E_{corr} toward negative values in the presence of Zn(Ta_{1-x}Nb_x)₂O₆ is caused
 236 by the different nature of the electrochemically active species from the metal surface (Zn, Ta,
 237 Nb) beside Fe. The presence of solely niobium ions next to the zinc ones (the case of ZnNb₂O₆)
 238 shifted the corrosion potential towards more negative values (-1.15 V), the corrosion current
 239 density being decreased from 40.36 (OL) to 19.09 $\mu\text{A}/\text{cm}^2$ that means a decrease of the corrosion
 240 rate (v_{cor}) and a better inhibition efficiency.

241 The polarization resistance (R_p) increases slightly from 0.9 kohm x cm² for bare OL to
 242 1.43 kohm x cm² for the Zn(Ta_{0.5}Nb_{0.5})₂O₆ covered electrode, also indicating an inhibition of the
 243 corrosion in the presence of Zn(Ta_{1-x}Nb_x)₂O₆ nanomaterials.

244

245

CONCLUSIONS

246

247 Three novel pseudo-binary oxides, namely: Zn(Ta_{0.5}Nb_{0.5})₂O₆, Zn(Ta_{0.9}Nb_{0.1})₂O₆ and
 248 Zn(Ta_{0.95}Nb_{0.05})₂O₆ were obtained by solid-state method and comparatively characterized by
 249 XRD, FT-IR, SEM/EDAX, AFM and UV-VIS investigations with already known ZnNb₂O₆ and
 250 ZnTa₂O₆ compounds.

251 The existence of a single crystalline phase and the average crystallite size were
252 evidenced from the XRD diagrams and confirmed by the AFM measurements. A strong
253 correlation between the aspect of the samples (SEM images) and the rugosity properties was
254 found. The nanomaterial capacity to agglomerate might justify the continuously and uniform
255 covering of the OL materials.

256 The structure of the studied materials was confirmed by FT-IR spectra and EDAX
257 analysis. The values of the band gap increased in the order: ZnNb_2O_6 , $\text{Zn}(\text{Ta}_{0.5}\text{Nb}_{0.5})_2\text{O}_6$,
258 $\text{Zn}(\text{Ta}_{0.9}\text{Nb}_{0.1})_2\text{O}_6$, $\text{Zn}(\text{Ta}_{0.95}\text{Nb}_{0.05})_2\text{O}_6$ and ZnTa_2O_6 according to the chemical stability of the
259 tested material and with the increase in tantalum content, recommending these materials for
260 application in photovoltaic cells.

261 The electrochemical parameters of the Tafel plots illustrate corrosion inhibition in the
262 presence of the all new synthesized $\text{Zn}(\text{Ta}_{1-x}\text{Nb}_x)_2\text{O}_6$ compounds deposited on OL surface. Zn
263 oxide combinations with Ta and Nb oxides evidently show that the inhibition efficiency increase
264 with the niobium content of the material. The best results reveal that ZnNb_2O_6 treated electrode
265 exhibits an inhibition efficiency of 52.7 %.

266 Due to the inhibition efficiency of pseudo-binary oxides deposited on carbon steel
267 electrode the nanomaterials with increased niobium content will be used in multiple layer
268 deposition with porphyrins in order to improve anticorrosion properties. Due to the high band
269 gap (3.80-4.30 eV) provided by increasing the tantalum content, four of these pseudo-binary
270 oxides might find applications in photovoltaic cells.

271
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