ISSN : 0974 - 7540 Volume 4 Issue 4

Trade Science Inc.

Research & Reviews In Electrochemistry

Full Paper

RREC, 4(4), 2013 [130-135]

Electrochemical oxidation of phenol on thick films of the doped tin oxide

Dionisiy Kolomytsev

Institute of general and inorganic chemistry, 03142, Ukraine, Kyiv, Akademik's Palladin ave., 32/34, (UKRAINE)

E–mail : dolopichtis@gmail.com

ABSTRACT

It was proposed to create a thick film from nanosized powder of the doped tin oxide. Synthesized tin oxide was successfully used for electrochemical analysis of phenol oxidation. It is found that metal-oxide formation on powders surface influences oxidation potential; change of the amount of the doping component leads to the change of the oxidation reaction rate.

KEYWORDS

Doped tin oxide;
Electrochemical oxidation;
Phenol;
Quinone/hydroquinone.

INTRODUCTION

It's widely known that electro-oxidation of phenol on the doped tin oxide electrodes is more effective (90% COD removes) than on Pt (38%) or then with Fenton reactive (only 30%)[1,2]. Widely used methods of doped tin oxide synthesis such as CVD and spray-pyrolysis can provide only thin films, that have low mechanical and electrochemical stability[3-6]. We proposed to create a thick film from nano- sized powder of doped tin oxide, which was synthesized in molten salts. This can give the following results: more variables of simpler reactants for tin oxide doping[7] and higher films stability, than the above described method. Electrochemical properties of the material are mainly influenced by the method of it's syntheses, here the necessity of the new material's research appears.

EXPERIMENTAL

In this work nano-sized powders of doped tin oxide were synthesized in molten salt (described in[7]). To form the metal-oxides on powders' surface ($Sn_{0.93}Sb_{0.07}O_2$ powders covered by CuO and V_2O_5) thermal hydrolysis method was applied. Electrode paste was prepared by mixing of doped tin oxide powders with ethylene-glycol. Thick films were prepared by covering of the Ti base (previously polished, etched in HCl and rinsed with distillate) with the electrode paste using the stencil-plate and finally fixed by thermal treatment at 450°C.

The electrolyte solution was 0,5M KNO_3 containing with different concentration of phenol and quinone/hydroquinone redox couple.

Electrochemical characterization of the produced tin oxide electrodes was performed by cyclic voltamperometry at different conditions (i.e. scan rate, concentration of electrochemically active species, etc.)

Electrochemical investigations were carried out with potentiostate PI-50-1.1 in thermostatic three electrodes cell with dispersed cathodic and anodic space. The working electrode was a thick film of doped SnO_2, the reference electrode was Ag/AgCl, and the counter electrode was flat Pt sheet that has 1cm^2 area.

Prior to any electrochemical experiment a standard voltammogram was recorded to check purity of the system.

RESULTS AND DISCUSSION

Typical examples of CV's for freshly prepared film of $Sb_{0,05}Sn_{0,95}O_2$ electrode in 0,5M KNO_3 with 10^{-2}M Q/HQ at different scan rate are shown in Figure 1. It was found, that quasi-reversible electron transfer with diffusion control took place in this redox couple.

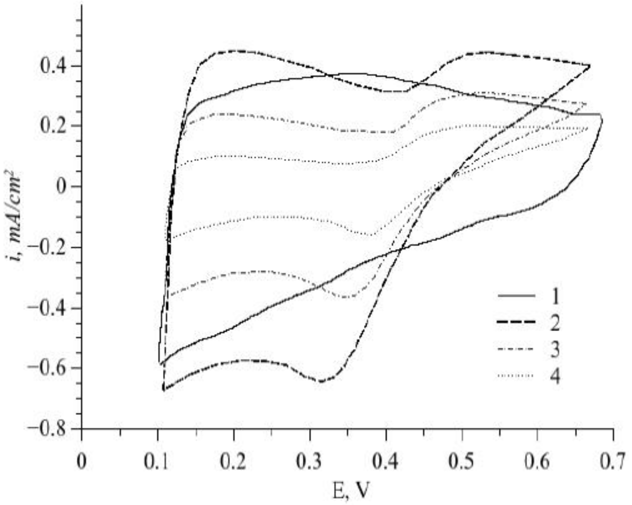


Figure 1 : CV's of $Sb_{0,05}Sn_{0,95}O_2$ electrode in 0,5M KNO_3: ν = 10V/s (1), with 10^{-2}M Q/HQ: ν = 0,01 (2); 0,005 (3); 0,002 V/s (4).

Method developed by Nicholson[8,9] was applied for Q/HQ system (Figure 1) for calculating of the standard reaction rate constant. In this method one needs to measure only one experimental parameter – difference between potentials of cathodic and anodic peaks of current (ΔE_p) – this is function of kinetic parameter ψ:

$$\psi = (D_O/D_R)^{\alpha/2} k_0 / (\pi D_O \nu F/(RT))^{1/2} \tag{1}$$

were D – diffusion coefficient, ñm^2/s; α – cathodic transfer coefficient; k_0 – standard reaction rate constant, ñm/s; ν – scan rate, V/s; F – Faraday constant; R – universal gas constant; T – temperature, K.

Obtained value of k_o was presented in TABLE 1.

It can be seen, that speed of intra-sphere reaction (with formation or destruction of molecular boundaries in quinon/hydroquinone redox system) on doped tin oxide reaches value obtained on Hg, and much more higher value than obtained on doped diamond (see TABLE 1).

Addition of phenol (Figure 2) in base solution leads to increasing of the current in potential region from E_{st} to 0,7V that was early proved[12] as hydrogen desorption process, standard potential shift in anodic region by 100mV, that is explained by adsorption activity of phenol on electrode surface.

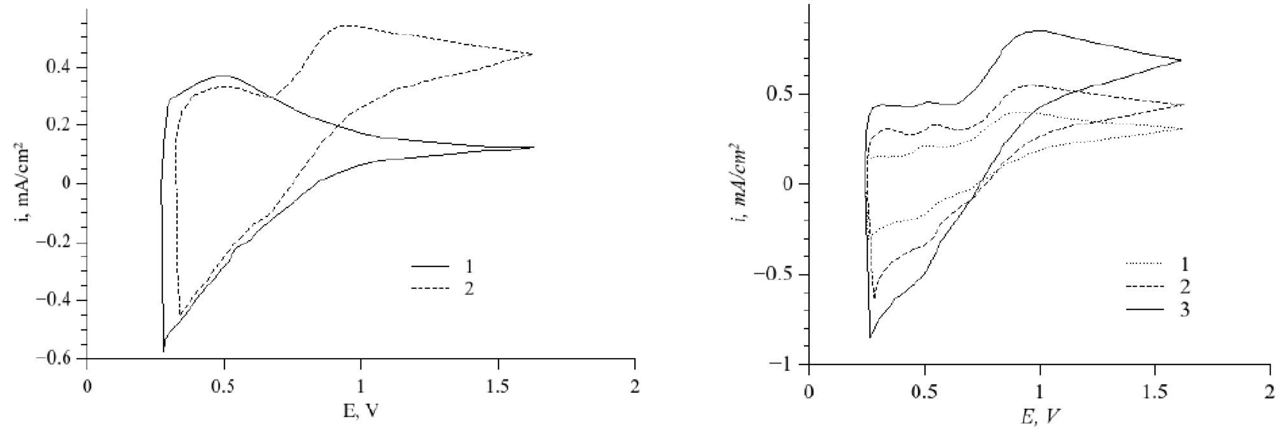
Starting from 700mV the increase of anodic current with peak – irreversible oxidation of phenol can be seen. Increasing of the current in region of potentials more than 1,2V in contrast to the base electrolyte is explained by the organic hydroxy- radical indirect oxidation, that was proved for SnO_2 by Comnenellis[13]. Starting from second scan there appear two peaks of current – anodic and cathodic between 0,480 and 0,376 V. It can be seen (Figure 1) that these peaks correspond to redox couple Q/HQ. So it can be proposed reaction pathways for direct phenol electro-oxidation which include the following: adsorption of phenol on surface of electrode; it's oxidizing to hydroquinone, which accumulates on electrode's surface and oxidizes into quinone – forming redox couple that appears on CV's.

TABLE 1 : Values of k_o for Q/HQ system on different electrodes

	$Sn_{0.95}Sb_{0.05}O_2$	$Sn_{0.93}Sb_{0.07}O_2/CuO$	$Sn_{0.93}Sb_{0.07}O_2/V_2O_5$	Doped diamond[10]	Hg[11]
k_o, cm/s	$0,5\cdot10^{-3}$	$0.74\cdot10^{-4}$	$0.6\cdot10^{-3}$	$2\cdot10^{-7}$	$1,5\cdot10^{-3}$

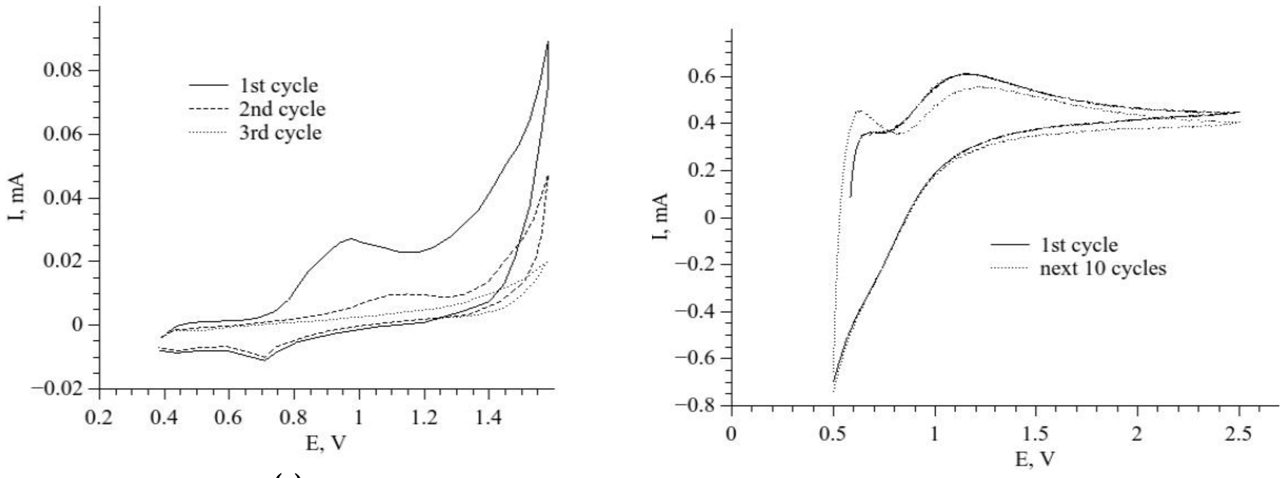
Because of the passivation (Figure 3), that took place on SnO_2 it can be suggested, that oxidation of phenol to hydroquinone passed stage of phenoxy radical formation. As widely known, phenoxy radical formation is primary reason of passivation on metallic electrodes (including Pt) through polymerization processes[14]. But it can be seen, that passivation of the doped tin oxide was incomparably lower than on Pt.

This can be explained by destruction of polymeric compounds by electrochemically generated hydroxy radicals which clean a surface of electrode and decrease passivation effect of phenoxy radicals.



(a) (b)

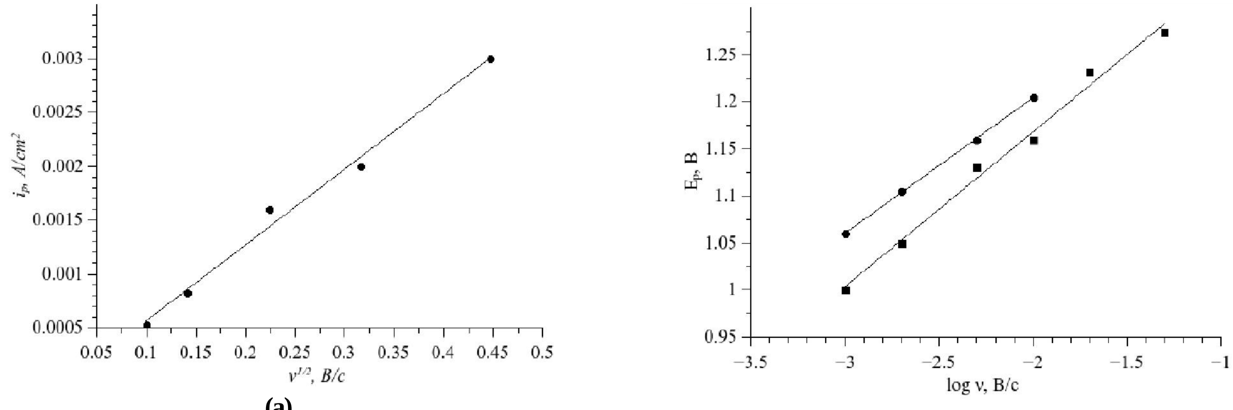
Figure 2 : CV's curves of $Sn_{0.95}Sb_{0.05}O_2$ electrode in 0,5M KNO_3 with 10^{-2} M of phenol a) in background electrolyte (1) and 1st cycle with phenol (2), ν = 0,01V/s; b) 2nd cycle with phenol ν = 0,005 V/s (1), ν = 0,01 V/s (2), ν = 0,02 V/s (3)



(a) (b)

Figure 3 : CV's curves of $Sn_{0.95}Sb_{0.05}O_2$ (a) and Pt (b) electrodes in 0,5M KNO_3 with $1{\cdot}10^{-2}$ M of phenol; ν= 10 mV/s; area of electrodes was 1cm² (SnO_2) and 0,1 cm² (Pt).

Fast passivation of Pt electrodes leads to impossibility of diffusion coefficient determination (it has shown incredibly low value: $8{\cdot}10^{-9}$ ρm²/s[15]) with help of CV analysis.



(a) (B)

Figure 4 : Dependence of a) oxidation current of 10^{-2} mol/l phenol in 0,5M KNO_3 by square root of scan rate on $Sn_{0.95}Sb_{0.05}O_2$ electrode; b) oxidation potentials of phenol (• 1-10^{-3} and ■ 4-10^{-3} mol/l) in 0,5M KNO_3 on $Sn_{0.95}Sb_{0.05}O_2$ electrode by log ν.

In contrast, diffusion coefficient of phenol in 0,5M KNO_3 solution (D = $1 \cdot 10^{-5}$ ρm²/s) was successively determined with SnO_2 electrodes from dependence of current's peaks by square root of scan rate (Figure 4) with following equation[16]:

$$I_p = (2,99 \cdot 10^5) n (\alpha n)^{1/2} A C D^{1/2} \nu^{1/2}, \qquad (2)$$

were $^{2}_{P}$__ peak of current, A; β – anodic transfer coefficient; n – number of electrons; A - electrode area, ñm²; C – phenol concentration, mol/sm³.

Value of βn was calculated from dependence E_p by scan rate (Figure 4 b) at 25°C:

$$dE_p/d\log\nu = 0,0296/\beta nF, \qquad (3)$$

More over, $Sn_{0.95}Sb_{0.05}O_2$ electrode has more linear dependence of density of current's peaks by bulk phenol concentration (see Figure 5) than Pt electrode[15,17], so can be used as phenol sensor.

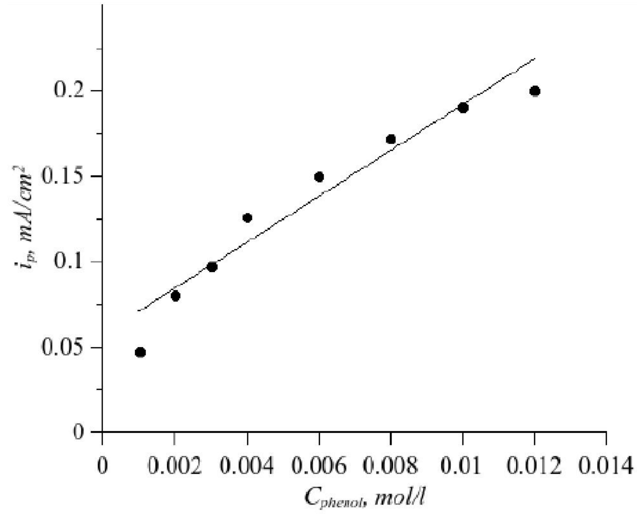


Figure 5 : Dependence peak of phenol oxidation current by phenol concentration in 0,5M KNO_3; ν= 2mV/s; A= 1cm²; electrode material: $Sn_{0.95}Sb_{0.05}O_2$.

Values of a standard phenol electrochemical oxidation potential (E_0)[18] and a phenol oxidation rate constant (k_0)[16] on created SnO_2 electrodes can be calculated from dependence of E_p by scan rate (Figure 6 a,b) by equations:

$$E_p = E_0 - RT/\beta nF[0,78 - \ln (D^{1/2}/k_0) + 0,5\ln (\alpha nF\nu/RT)], \qquad (4)$$

$$E_p = E_0 + (nFpK/M)^{1/2} [(\delta/\kappa) + R_0 A (1 - \theta_p)\nu^{1/2}], \qquad (5)$$

were, for equation (5): A is the electrode area, m²; M – molecular weight, kg/mol; n – number of electrons; θ – surface coverage; R – surface resistance of electrode, Ohm; ν – scan rate, V/s; p – film density, kg/m³; δ – film thickness; κ – specific conductivity of solution, Sm/m.

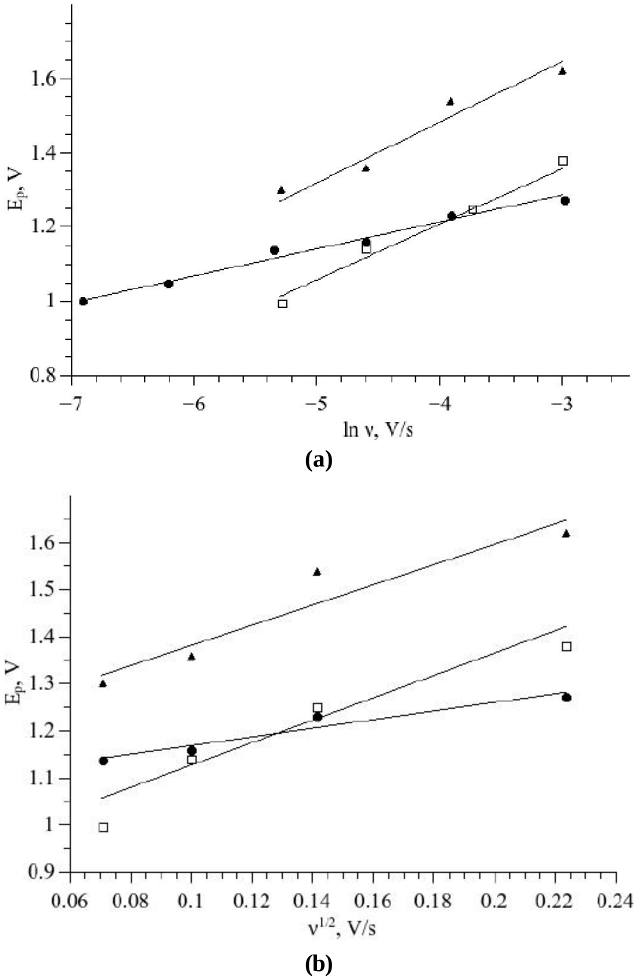


Figure 6 : a) Dependence of E_p of electrochemical oxidation $4 \cdot 10^{-3}$ mol/l of phenol in 0,5M KNO_3 by scan rate (V/s): a) ln ν; b) $\nu^{1/2}$. Electrodes: • $Sn_{0.95}Sb_{0.05}O_2$; □ $Sn_{0.93}Sb_{0.07}O_2/CuO_2$; ▲ $Sn_{0.93}Sb_{0.07}O_2/V_2O_5$

According to the received data (see TABLE 2) we can suppose that change of the amount of doping component (Sb) in SnO_2 leads to the change of the rate of oxidation reaction; and modification of surface of SnO_2 by metal-oxides influences mainly the oxidation potential.

Dependence of the potential and peak current of phenol oxidation in 0,5M KNO_3 on $Sn_{0.95}Sb_{0.05}O_2$ electrode by temperature are shown in Figure 7. The activation energy values are calculated from Arhenius equation:

$$\ln i = \ln A + \ln E_a/RT, \qquad (6)$$

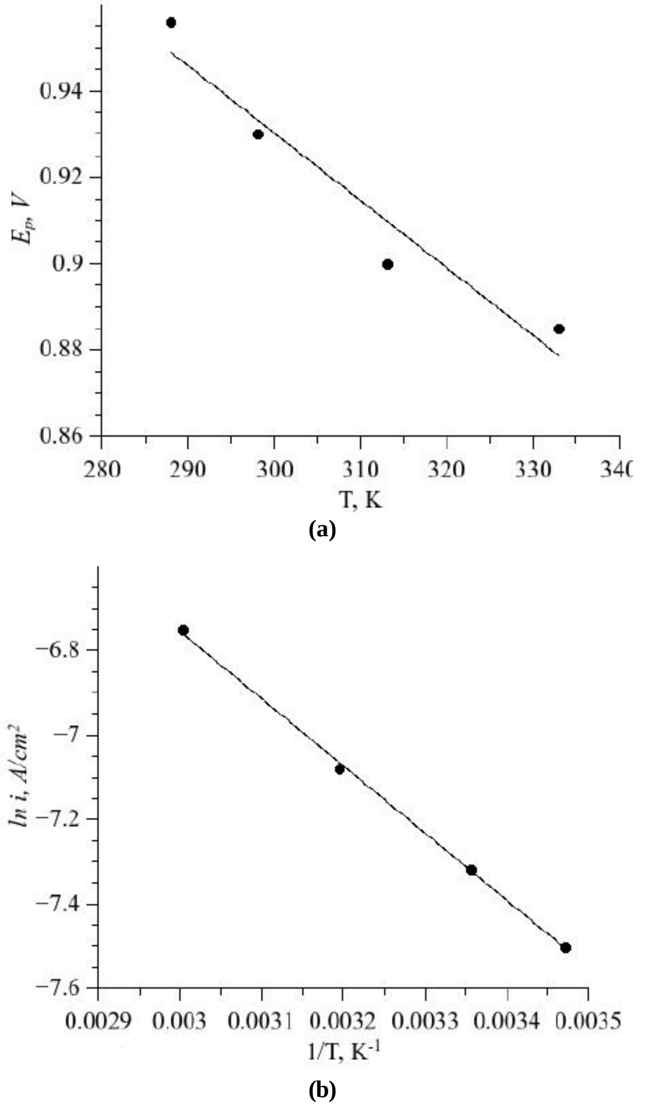
were A — constant, E_a – activation energy.

It was found that in 0,5M KNO_3 activation energy of phenol oxidation on $Sn_{0.95}Sb_{0.05}O_2$ electrode are

13,23 kJ/mol (3,05 kcal/mol), that proves the diffusion control of the oxidation. More over, increasing of the temperature moves shifts potential to lover value (dE/dT= -1,5mV/K). This proves the simplification of oxidation reaction by increasing amount of active cites on electrode surface.

TABLE 2 : Value of the standart potencials and the rate constants of electrochemical oxidation of phenol on SnO_2 electrodes in 0,5M KNO_3

Electrode material's	$Sn_{0.95}Sb_{0.05}O_2$	$Sn_{0.93}Sb_{0.07}O_2$/CuO	$Sn_{0.93}Sb_{0.07}O_2/V_2O_5$
k_0, cm/s	$1{,}5\cdot10^{-7}$	$0{,}97\cdot10^{-7}$	$0{,}75\cdot10^{-7}$
E^0, V	1,07	0,9	1,17



(b)

Figure 7 : The potential (a) and the peak current (b) of $8\cdot10^{-3}$ M phenol oxidation in 0,5M KNO_3 on $Sn_{0.95}Sb_{0.05}O_2$ electrode at different temperatures.

LIST OF ABBREVIATIONS

COD - chemical oxygen demount;
CVD - chemical vapor deposition;
CV - cyclic voltammogram;
Q/HQ - quinone/hydroquinone.

CONCLUSIONS

Electrochemical properties of developed thick films of the doped tin oxides were investigated. It was found that activity of the synthesized tin oxide in Q/HQ redox couple reaches value obtained on metallic electrodes.

Reaction pathways for direct phenol electro-oxidation were proposed. They include: adsorption of phenol on surface of electrode; it's oxidizing to hydroquinone, which accumulates on electrode's surface and oxidizes to quinone and forms the redox couple. Oxidation of phenol to hydroquinone passes stage of the phenoxy radical formation that leads to passivation. It was found that passivation of tin oxide is incomparably lower than Pt.

It is shown, that thick films of synthesized in molten salts doped tin oxide can be successfully used as a stable indicator electrodes for electrochemical analysis needs.

It was found that metal-oxide formation on doped tin oxide surface influences oxidation potential; and change of the doping component (Sb) amount in SnO_2 leads to the change of the rate of oxidation reaction.

ACKNOWLEDGEMENTS

I frankly thank to Panov E.V. (full phd, professor, Institute of general and inorganic chemistry NAS of Ukraine) for help in experimental data interpretation, also thank to Mal'ovany S.M. (phd, senior research assistant, Institute of general and inorganic chemistry NAS of Ukraine) for synthesized doped tin oxide materials.

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