

PHOTOCATALYTIC INDIUM-TANTALUM-OXIDE AND ITS PHOTOLUMINESCENCE

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ABSTRACT

Both bulk ceramic and powder like samples $\text{In}_{0,9}\text{Ni}_{0,1}\text{TaO}_4$ photocatalytic semiconductor oxides have been obtained by the method of solid phase reactions. The photocatalytic activity on water splitting has been investigated using for identification of hydrogen yield a chemoresistive gas sensor ROGS-3. For the first time the material photoluminescence (PL) properties have been studied in the wide - 350-850 nm and narrow - 360-410 nm ranges of the light spectrum and some spectrum peculiarities at $T=10$ and 300 K are observed. The correlation between photocatalytic action of $\text{In}_{0,9}\text{Ni}_{0,1}\text{TaO}_4$ on water splitting processes and its photoluminescence peculiarities has been established. The materials with high photocatalytic activity are characterized by PL peak increase at 450 nm and the maximum attenuation at 660 nm.

1. INTRODUCTION

A significant direction in the development of a technology for the direct production of hydrogen is connected to using a renewable source of energy in the direct photoelectrolysis of the water. The main components in doing direct photoelectrolysis of the water by incident light are well known. Under illumination the light is absorbed in materials and the electrons (or holes), which are generated on the surface, lead to the water splitting. The challenges for the material properties are: 1) efficient solar light absorption (the bandgap must be less than 2.0 eV); 2) corrosion stability of the semiconductor in the water; 3) water-semiconductor energetics (the matching of the semiconductor band edge energies with the hydrogen and oxygen evolution reactions).

The most stable materials in water solution are semiconductor oxides, and last years important attention is given to the problem of obtaining and investigation of materials with reasonable solar efficiencies and appropriate interface energetics for the direct photoelectrolysis of water [1-6]. Among the most important photocatalytic materials there are considered the ones working under visible light irradiation because it makes up approximately 43% used solar energy. Recently it was shown [6] that the oxide material $\text{In}_{1-x}\text{Ni}_x\text{TaO}_4$ at $x=0,1$ provides the above mentioned conditions for the efficient process of water splitting and hydrogen production.

The present paper includes some preliminary results concerning the powder synthesis of $\text{In}_{1-x}\text{Ni}_x\text{TaO}_4$ semiconductor, some of its optical properties and its action on water photocatalytic splitting. In particular, the photoluminescence (PL) properties of $\text{In}_{0,9}\text{Ni}_{0,1}\text{TaO}_4$ compound in the wide - 350-850 nm and narrow - 360-410 nm ranges of the spectrum are studied for the first time.

2. SAMPLES AND METHODS OF EXPERIMENT

The $\text{In}_{1-x}\text{Ni}_x\text{TaO}_4$ phase ($x=0,1$) was synthesized by the method of solid phase reactions at the temperature 1370 K in the air, using high purity binary compounds In_2O_3 ,

Ta₂O₅ and NiO as initial oxide components. The obtained material was of white-yellow color, it was subjected to the X-ray investigation. In case of need an additional annealing at the same temperature was performed, it removed a small amount of impurity of the initial substances. The diffractograms of the finite products contained lines of spectra of In_{0,9}Ni_{0,1}TaO₄ belonging to the monoclinic crystal structure with space group P2/a. Thus, the diffractograms served indicators of formation of the phase sought for. Further it was tested for investigation of physical properties or was prepared for the process of the photocatalysis of water. For intensification of photocatalytic activity of the material it was additionally impregnated with aqueous Ni(NO₃)₂ solution to load the phase surface with 1,0wt% partly oxidized nickel. These impregnated alloys act as electron traps and H₂ evolution sites. This photocatalyst was calcined at the temperature 620 K for 1 hour. Decomposition of water and evolution of H₂ took place while changing of intensity and length of wave by optic filters from xenon lamp ДКСН-600. For indication of hydrogen evolution we used chemoresistive gas sensor ROGS-3 fabricated on the basis of lead dioxide by the thick film technology [7]. The main characteristics of the sensor are the following:

Range of measurements by H ₂ , %	0,1...2
Actuation time, s	3
Restoring time, s	10
Power consumption, wt	0,85

The installation for photoluminescence measurement allowed property investigation with high optic resolution in a wide spectral and temperature (10-300 K) ranges. The excitation was performed by a monochromatic beam of Ar⁺ laser Spectra physics ($\lambda=334$ nm). The given methods are described in detail in [8].

3. RESULTS AND DISCUSSION

In the pyrex cell a suspension consisting of 250 ml of pure water and 0,5 g of powder of In_{1-x}Ni_xTaO₄ (x=0,1) photocatalyst with intensified activity was prepared. Under the suspension irradiation with the xenon lamp light there took place decomposition of water into H₂ and O₂. This was testified by a response of a special hydrogen detector. The amount of H₂ depended on the intensity of irradiation and wavelength λ . The largest amount of H₂ evolved at $\lambda \approx 395-425$ nm (Fig.1). All the above-mentioned confirmed experiments of [6] and is a very important result, because we practically possess a generator of H₂, i.e. a renewable source of fuel. Evolution of H₂ takes place also under the cell irradiation by the 580 Wt filament lamp. Amount of H₂ depends also on sizes of the powder grains, the finer the material the higher evolution per

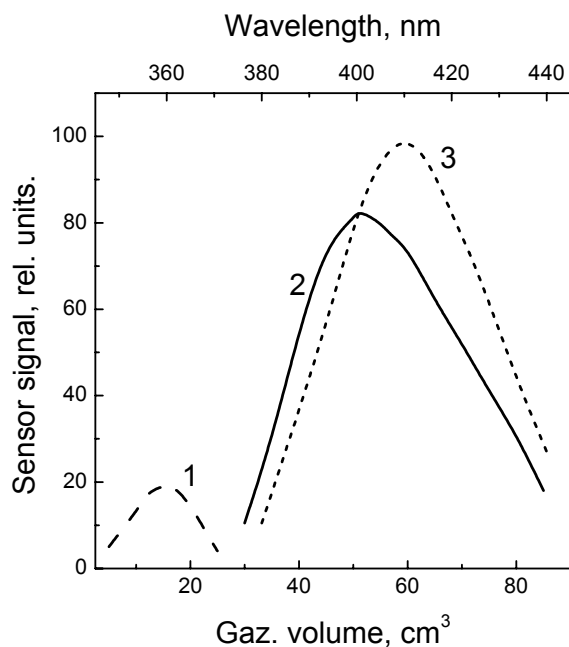


Fig.1. Hydrogen evolution in the case of tantalum oxide (1), activated compound In_{0,9}Ni_{0,1}TaO₄ (2) and its spectral dependence (3)

minute. Searches for an optimal variant continue [10-13]. There are different suggestions. For example, the authors of [9] are prone to find a suitable alloy in different combinations of InTaO_4 and InNbO_4 , i.e. new combinations including mixtures. The idea is this: one material is a wide-range (E_g) effective photocatalyst, the other - with smaller E_g with the purpose to intensify evolution of H_2 under irradiation closer to the middle of the visible light spectrum. Proceeding from the spectrum of diffuse reflection the authors of [6] for $\text{In}_{0,9}\text{Ni}_{0,1}\text{TaO}_4$ phase indicate the maximal light absorption in ultraviolet at ~ 250 nm and visible light of 420-520 nm.

Fig.2 shows the spectral distribution of photoluminescence (PL) of $\text{In}_{0,9}\text{Ni}_{0,1}\text{TaO}_4$ compound in the wide - 350-850 nm and narrow - 360-410 nm (inserted) ranges of the spectrum at the temperature of 300 and 10 K. As it is seen, in the first case at $T=10$ K a wide intensive band with the maximum at 660 nm and the half-width $\Delta h\nu=0,32$ eV is clearly shown. Other peculiarities are not clear, so they are shown also in narrower spectral range. At $T=300$ K a band with the maximum at 380 nm and $\Delta h\nu=0,12$ eV is obviously found. The temperature decrease down to 10 K leads to the spectrum shift into the short-wave range to 367 nm and $\Delta h\nu=0,004$ eV. Narrow bands with maxima at $\lambda=374$ nm, $\lambda=382$ nm and an arm at $\lambda=391$ nm are also observed.

The material activation intensifies the process of water photocatalysis, but sharply changes the PL spectrum. Fig.3 shows the spectral distribution of the PL of this compound at $T=10$ K. At $T=300$ K the luminescence is weak, even its registration failed. At low temperature weak peaks in the vicinity of 450 nm (curve 2) and 660 nm are shown. The increase of the photocatalytic activation degree of the materials are accompanied by the PL

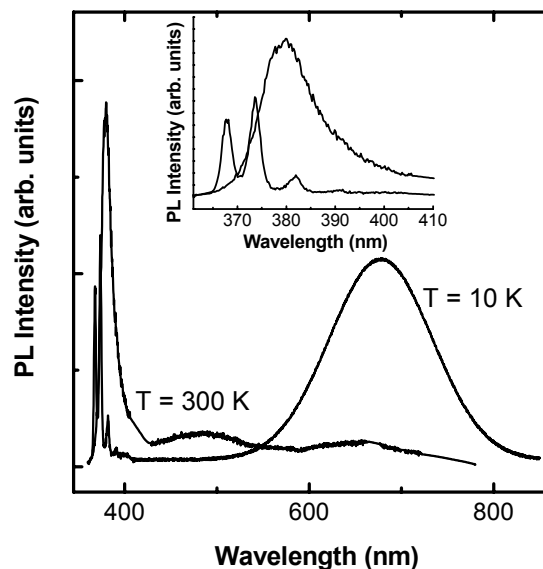


Fig.2. Spectra of photoluminescence of $\text{In}_{0,9}\text{Ni}_{0,1}\text{TaO}_4$ phase in the regions of 350-850 nm and 360-410 nm.

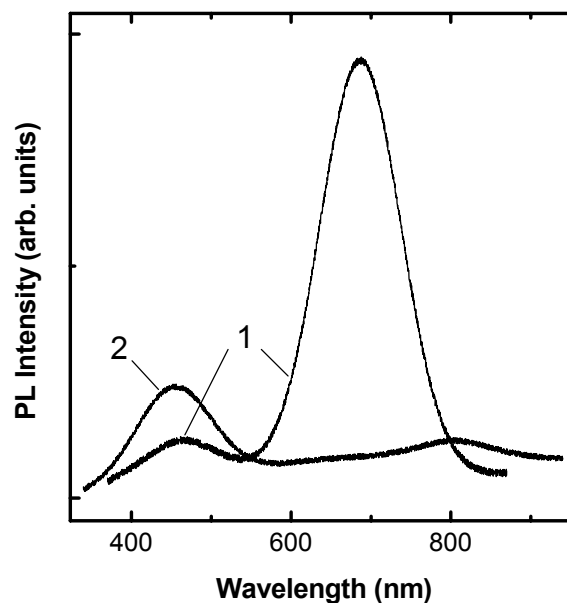


Fig.3. PL spectra of $\text{In}_{0,9}\text{Ni}_{0,1}\text{TaO}_4$ alloy with low photocatalytic activation degree (1) and high photocatalytic activation degree (2) measured at $T=10$ K.

peak increase at 450 nm (curve 2) and the maximum attenuation at 660 nm. In fact there takes place the effect of concentration attenuation of the PL peculiarities. In [6] an intensive absorption in the vicinity of 450 nm is noted. In the sample under study a weak band of the recombination radiation is shown.

According to the data of [6] for $\text{In}_0\text{In}_{0,9}\text{Ni}_{0,1}\text{TaO}_4$ $E_g=2,3$ eV and only the band with the maximum of 660 nm can be related to recombination within the limits of the band gap with participation of a concrete impurity level. The energy E of the other peculiarities exceeds the band gap E_g . It is appropriate to emphasize here remarkable properties of Ni additions. In particular, under ZnIn_2S_4 doping ($E_g=2,86\text{eV}$) [14] depending on the impurity concentration the curves of the spectra of absorption, photoconductivity and excitation of the PL can be set in a certain range, i.e. we obviously picture desirable properties of the compound. In [6] the decrease of E_g from 2,9 eV for InTaO_x down to 2,3 eV for $\text{In}_{0,9}\text{Ni}_{0,1}\text{TaO}_4$ and activation of the water photocatalysis process are noted because d-orbitals play an important role here.

An unambiguous interpretation of the revealed peculiarities of the PL at $\lambda < 539$ nm is impeded at the present stage of investigation. In the master phase there probably are signs of wider band compound causing the given PL. This could be expected, since the principle of the photocatalyst search was larger yield of H_2 of water. For explanation of high-energy peaks of the diffuse reflection in [6] the optic transitions in the energy diagram of the Ni 3d levels were used. In [15] the compound of the given group AlV_2O_4 obtained at the temperature 1370 K for 150 hours is described. It has anomalous transport and magnetic properties. The alloy of $\text{In}_{0,9}\text{Ni}_{0,1}\text{TaO}_4$ compound studied by us is anomalous in its way, it has intensified photocatalytic properties. There is a number of patents on the theme discussed [16, 17]. Mainly photocatalytic materials being semiconductor oxides of titanium, zirconium, tantalum, zinc and niobium are patent protected. In [17] it is indicated on the primary oxide of titanium and secondary one which can be oxide of niobium, tantalum, vanadium, etc. The search for variants of intensification of the water splitting reaction continues. In particular, Z.Zou [18] uses an impregnated powder photocatalyst $\text{In}_{0,9}\text{Ni}_{0,1}\text{TaO}_4$ and a co-catalyst NiOx. The quantum yield of the process achieves 0,66%.

For the sake of correctness for $\text{In}_{0,9}\text{Ni}_{0,1}\text{TaO}_4$ in [6, 11] they used the term "semiconductor" and it is studied up to $x=0,2$ inclusive. In this case the word "doping" may be used up to $x \leq 0,05$. At $x > 0,05$ "solid solution", "phase", "compound material" are recommended.

4. SUMMARY

The $\text{In}_{0,9}\text{Ni}_{0,1}\text{TaO}_4$ oxide materials both in the bulk and powder phases have been obtained by the method of solid phase reactions. Technological conditions for the growth process are established. It is shown that the obtained compounds have good photocatalytic properties and under visible light irradiation lead to the water splitting. i.e. it is a renewable source of hydrogen. It is found that the photocatalysis is long-term stable process and it can be used for hydrogen yield.

For the first time the oxide photoluminescence properties have been studied and some spectrum peculiarities at $T=10$ and 300 K are revealed. At $T=10$ K a wide intensive band with the maximum at 660 nm and the half-width $\Delta h\nu=0,32$ eV is clearly observed. The energy value of long-wave (660 nm) recombination with participation of impurity is determined. Narrow bands with maxima at $\lambda=374$ nm, $\lambda=382$ nm and an arm at $\lambda=391$ nm are also revealed. At $T=300$ K a band with the maximum at 380 nm and $\Delta h\nu=0,12$ eV is obviously found. The temperature decrease down to 10 K leads to the spectrum shift into the short-wave range to 367 nm and $\Delta h\nu=0,004$ eV. A possible explanation of this short-wave PL is given on

the basis the optic transitions of the energy diagram of the Ni 3d levels, which has been early proposed for analyzing of the high-energy of the diffuse reflection.

An important correlation between material photocatalytic activity, which is measured by the hydrogen yield, and the oxide photoluminescence properties has been identified. The increase of the photocatalytic activity of the materials is accompanied by the PL peak increase at 450 nm and the maximum attenuation at 660 nm.

REFERENCES

- [1]. Zhang G.. *Electrochemistry of Silicon and Its Oxide*. Canada (2002).
- [2]. Volodina G., Muntean S., Zhitar V., Arama E., Machuga A., Shemyakova T.. *Moldavian Journal of the Physical Sciences*, 1, 73 (2002).
- [3]. Kudo A., Mikami I.. *Chem.Lett.*, 1027 (1998).
- [4]. Zou Z., Arakawa H.. *Chem. Phys. Lett.*, 332, 271 (2000).
- [5]. Zou Z., Arakawa H.. *Chem. Matt.*, 13, 1765 (2001).
- [6]. Zou Z., Jinhua F., Kazuhiro S., Hironori A.. *Nature*, 414, 625 (2001).
- [7]. Ionescu R., Vasilescu V. and Vancu Ana. *Sensors and actuators. B.*, 8, 151 (1992).
- [8]. Ursaki V., Ricci P., Tiginyanu I., Anedda A., Syrbu N., Tezlevan V.. *J. Phys. Chem. Solids.*, 63, 1823 (2002).
- [9]. Arakawa H., Zou Z., Sayama K., Abe R.. *Abstract, Conf. MRS (2003) (in press)*.
- [10]. Zou Z. et al. *J. Phys. Chem. B.*, 106, 517 (2002).
- [11]. Zou Z. et al. *J. Mater. Res.*, 17, 1446 (2002).
- [12]. Zou Z. et al. *J. Photochem. Photobiol. A.*, 148, 65 (2002).
- [13]. Sayama K. et al. *J. Photochem. Photobiol. A.*, 148, 71 (2002).
- [14]. Житарь В., Мачуга А., Арама Е.. *Изв. РАН, Неорганические материалы*, 38, 6, 662 (2002).
- [15]. Matsuno K., Katsufuji T. et al. *J. of the Physical Soc. Jap.*, 70, 6, 1456 (2001).
- [16]. Kazuhiro S. et al. *Catalyst for photoreaction. Patent JP 000869 (2001)*.
- [17]. Ogino E. et al. *Photocatalysis. Patent JP 025666 (2001)*.
- [18]. Zou Z.. *AIST Today*, 2, 2, 21 (2002).