$BiSbO_4$ PHASE AND ITS BEHAVIOR UNDER THE ACTION OF LIGHT

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Abstract

$BiSbO_4$ phase was prepared using a method similar to that used for making ceramics. Its properties (photoluminescence and water photocatalysis) were studied. The main parameters of the material were studied and their interpretation was proposed.

In recent years, a new scientific direction appeared: the growth and characterization of semiconductors that can decompose water into hydrogen and oxygen under illumination. When the first successful experiments in this field were fulfilled, this became promising to obtain a clean and renewable source of hydrogen fuel that is in great demand nowadays. First of all, among these semiconductors, oxide materials $BiTaO_4$, $InNbO_4$, $InTaO_4$, Bi_2RNbO_7 (R = Y, Ce, … La), etc., dominate that can be doped or their composition can be varied to increase the H_2 yield [1-4]. Investigation of this problem is very attractive. In the given paper, we report the results related to the preparation of $BiSbO_4$ semiconductor oxide similar to $InNbO_4$ and its characterization under the action of light.

1. Experimental

We paid the greatest attention to investigation of $BiTaO_4$ (similar to $InTaO_4$ semiconductor with a simple composition and monoclinic structure of the wolframite type).

With the aim to obtain a similar oxide, a fine compressed material with a stoichiometric composition was annealed in air at 800°C for 20 h. Oxides Bi_2O_3 and Sb_2O_3 (1 : 1) were used as initial materials. The structure of the samples was investigated using a DRON-3 diffractometer (Co Kα radiation, Fe filter, Θ/2Θ method).

The photoluminescence (PL) was measured using a standard method [5] by a multichannel optical analyzer OVA-284 at 20°C. The spectral resolution of the registration system was not worse than 2 nm. The photoluminescence was excited by monochromatic LGI-21 laser beam (λ = 337.1 nm). The photocatalysis set up was described earlier in [2, 3]. In these papers the UV illumination was used, but we observed the hydrogen elimination under the illumination with visible light.

2. Results and discussion

$BiSbO_4$ phase was prepared using a method similar to that used for making ceramics. The obtained samples were of light grey color. A typical diffraction pattern is presented in Fig. 1. The diffraction spectrum corresponds to $BiSbO_4$ compound according to ASTM(7-191) data. The weak lines denoted by *x* and *o* correspond to an insignificant impurity of antimony oxides Sb_2O_3 and Sb_2O_5, respectively.

The radiation spectra of $BiSbO_4$ sample at 20°C are shown in Fig. 2. The photoluminescence spectrum (curve 1) involves the bands with their maxima at λ = 581 and 656 nm. Extrapolating the long-wave wing of the first maximum we obtained λ = 683 nm and calculated the forbidden gap (according to the Moss principle) that amounts to E_g^{opt} = 2.1 eV, and it is a reasonable value. This is a rather wide band, its half-width amounts to $\Delta h\nu$ = 1.7 eV. The maximum at 656 nm is evidently caused by the radiative recombination involving an impurity level near the bottom of the conduction band.

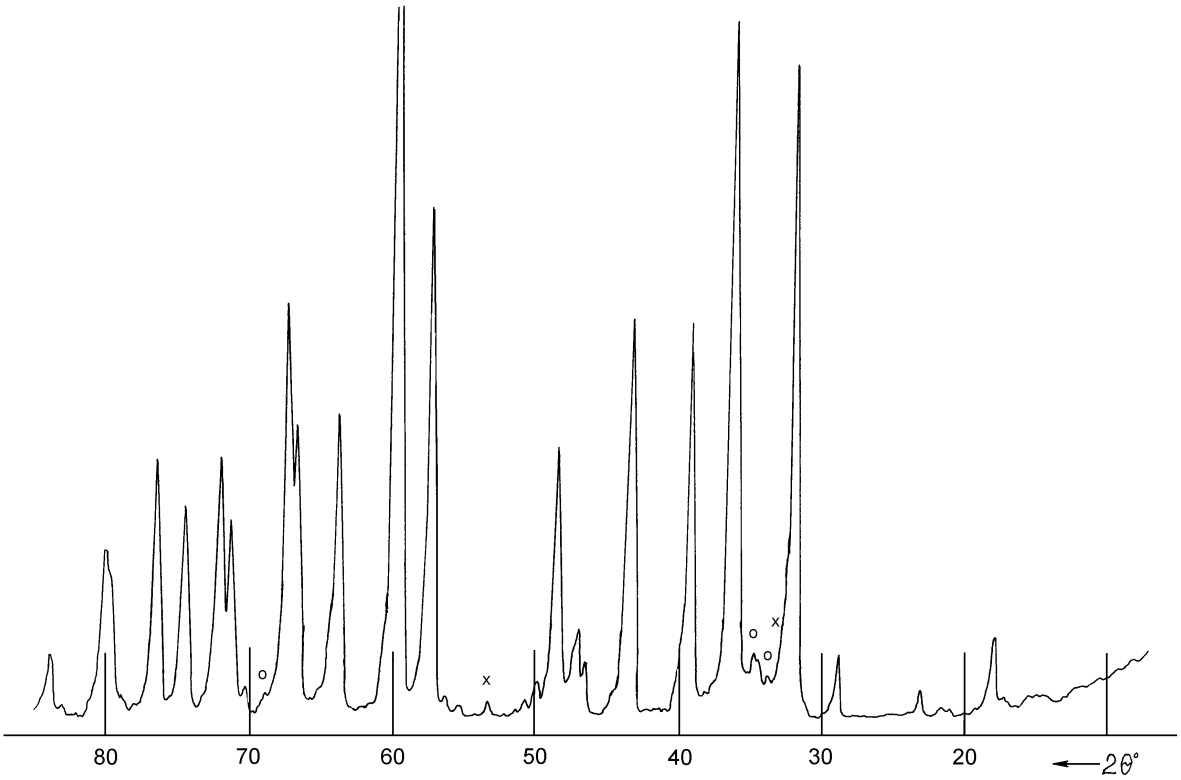

Fig. 1. Diffraction pattern of $BiSbO_4$ powder.

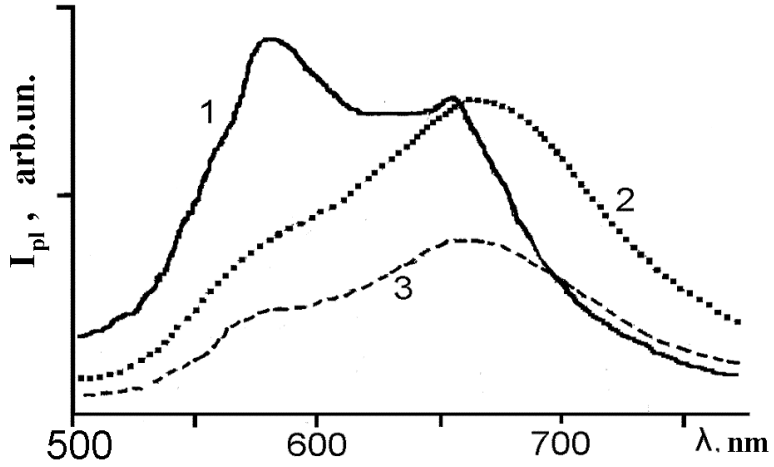

Fig. 2. Photoluminescence spectra of $BiSbO_4$ at 20°C. Curves 1-3 were measured for the samples with various preparation conditions.

For a slightly less annealing temperature, the short-wave maximum (curve 2) smears, and the long-wave peak corresponds to λ = 663 nm. Annealing of the second sample at T = 800°C (as for the first sample) with subsequent compression at the less pressure (by 10 atm) leads to obtaining of the material with less density. Its radiation spectrum slightly changes (curve 3); the long-wave maximum at λ = 663 nm was observed. This is the dynamics of the PL spectra that was observed. For comparison, the main parameters of two similar phases are given in the table.

Main parameters of photoluminescence

Phase	E_g, eV	PL maximum, nm		Half-width of the intensive peak (581 nm), eV	Reference
$BiSbO_4$	2.1	581	656	1.7	our data
- " -	2.1	580	665	1.0	- " -
- " -	2.1	580	663	1.0	- " -
$In_{0.9}Nb_{0.1}TaO_4$	2.3	450	660	0.32	[3]

As reported in [1], $InTaO_4$ changes its parameters, including the crystalline structure, at doping. In our opinion, $In_{1-x}Nb_xTaO_4$, where x = 0.1, is a solid solution. In curves 2 and 3, the short-wave peak appears, because it is distorted by the strong edge absorption as was observed in other materials ($CdGa_2S_4$, for example) [6]. The large width of the bands (see the table) is probably determined by the fact that the systems of levels near the conduction and valence bands (E_c and E_v) are involved in the radiation recombination, similar to the exponential distribution of traps near the E_c in $ZnIn_2S_4$ single crystals [7], which act as donors and stipulate the wide radiation band.

The process of water photocatalysis was arranged and performed according to a standard method. When the cell with water suspension of $BiSbO_4$ powder is illuminated with visible light, a direct decomposition of water accompanied by hydrogen liberation occurs. This was the first qualitative observation of the catalytic action of this material. Nowadays this effect is widely studied. Recently it has been shown that the photocatalytic activity depends on the growth temperature of the material (in ZnO, for example) [8]. It was stated that the main factor, which determines the effect, is the value of specific area of the powder. The majority of publications on photocatalytic activity were performed in multinary compounds, in particular, in $AgInW_2O_8$, $CaIn_2O_4$, $MCrO_4$ (M = Sr and Ba), $BaCr_2O_4$ as well as in Zn doped composites Lu_2O_3/Ga_2O_3 [9-13]. Materials with composition $In_{1-x}Ni_xTaO_4$ (x = 0 ÷ 0.2) were studied in [1-3], and it was shown that for x = 0.1 and E_g = 2.3 eV the greatest yield of hydrogen was observed. This gives evidence that this direction of research is urgent and important.

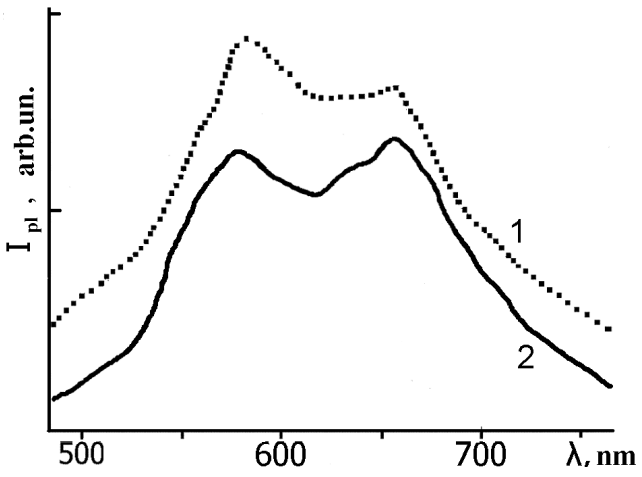

Fig. 3. Photoluminescence spectra of $BiSbO_4$ at 20°C before (1) and after (2) a long photocatalysis process.

After the water photocatalysis process has been continuously performed for 3 months, $BiSbO_4$ powder was separated,

dried, compressed, and annealed at 800°C for 10 h. Then its PL spectra were measured at 20°C (Fig. 3). They are principally similar to the initial spectra. The right-hand part is slightly shifted to the long-wave range owing to the influence of impurities. The intensity of the spectra is less, and they contain peaks at $\lambda = 578$ nm and $\lambda = 656$ nm.

The spectra before and after the photocatalysis process nearly coincide; this confirms the published data that it is possible to perform the process for a long time using the same material [1-3, 9-13]. The weak shift of the first peak by 3 nm to the short-wave side occurs probably owing to the strong edge absorption.

3. Conclusions

$BiSbO_4$ phase was prepared using a method similar to that used for making ceramics. Its photoluminescence and photocatalytic activity of the powder were studied for the first time. The main parameters of the material were studied and their interpretation was proposed.

References

[1] Z. Zou, J. Je, K. Sagama, and H. Arakawa, Nature, 414, 625, (2001).
[2] Z. Zou, J. Je, K. Sagama, and H. Arakawa, J. Phys. Chem. B, 106, 517, (2002).
[3] V.G. Kantser, V.F. Zhitar, S.P. Muntean, V.V. Ursaki, and V.I. Kaplin, Mold. J. Phys. Sci., 2, 3-4, 286, (2003).
[4] H. Arakawa, Z. Zou, J. Je, K. Sagama, and R. Abe, Abstracts of MRS Conf., 117, (2003).
[5] V.S. Dneprovskii, I.I. Dobynda, E.A. Zhukov, and A.N. Santalov, FTT, 49, 741, (2007).
[6] A.I. Machuga, V.F. Zhitar, and E.D. Arama, FTP, 34, 652, (2000).
[7] A.N. Georgobiani, V.F. Zhitar, A.I. Machuga et al., Kratkie soobshcheniya po fizike FIAN SSSR, 4, 34, (1984).
[8] A.S. Shaporev, V.K. Ivanov, A.E. Baranchikov, and Yu.D. Tretyakov, Neorganicheskiye materialy, 43, 38, (2007).
[9] D. Wang, Z. Zou, and J. Je, Chem. Phys. Letters, 384, 139, (2004).
[10] J. Tang, Z. Zou, and J. Je, J. Phys. Chem., B107, 142, (2003).
[11] J. Tang, Z. Zou, J. Jin, and J. Je, Chem. Phys. Letters, 382, 175, (2003).
[12] J. Jin, Z. Zou, and J. Je, Chem. Phys. Letters, 378, 24, (2003).
[13] D. Wang, Z. Zou, and J. Je, Chem. Phys. Letters, 373, 191, (2003).