Solid-Phase Synthesis of Indium and Tin Oxide Materials

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Abstract

Comparative investigations of phase formation processes and electronic properties of indium and tin oxide materials obtained under different conditions of solid-phase synthesis are presented. Substantial influence of synthesis conditions and temperature of hydrolysis product annealing on phase composition and size of crystallites of the synthesized indium and tin oxide materials is demonstrated. It is stated that the best optimal method to obtain materials with high concentration of free charge carriers is hydrolytic procedure with the use of hydrochloric acid solutions.

INTRODUCTION

Polycrystalline indium oxide doped with tin (ITO) is widely used as a gas-sensitive material for sensor electronics, catalyst of organic synthesis, conducting material in the form of ceramics of thick-film electrodes. Solid-phase synthesis at increased temperature from reaction mixtures obtained either by mechanical mixing of components or hydrolytically is used to obtain this material [1]. However, the effect of synthesis conditions and of the nature of initial reagents on physicochemical properties of polycrystalline indium and tin oxide materials has been insufficiently investigated for reliable predicting their functional characteristics.

In the present work, we describe the results of investigation of phase formation and changes in the concentration of free electrons (N_e) in indium and tin oxide system during thermal treatment of indium and tin hydroxides coprecipitated with an alkaline reagent from nitric and hydrochloric solutions, as well as a mixture of indium and tin nitrates.

EXPERIMENTAL

Hydrolytic synthesis of indium and tin oxide materials was performed as follows. Nitric solutions were obtained by dissolving indium oxide in 7M HNO_3 of specially pure grade (os. ch. 27–4), followed by adding $Sn(NO_3)_2 \cdot 20H_2O$ salt; hydrochloric solutions were obtained by dissolving indium oxide in 7M HCl (os.ch. 20–4), followed by adding $SnCl_4 \cdot 5H_2O$ of pure grade (ch.). The amount of initial substances corresponded to the atomic fraction of tin in final products from 1 to 14 %. Indium and tin hydroxides were precipitated with aqueous solution of alkaline reagent (6M NH_4OH) at 25 °C till the establishment of the necessary pH. The direct hydrolytic method (neutralization of acid solutions by an alkaline reagent) (I) and inverse one (neutralization of alkaline reagent by acidic solutions) were used.

The X-ray phase analysis (XPA) was used to analyze the initial samples, intermediate and final products. The XPA was performed with DRON-3M diffractometer using CuK_α radiation. The size of crystallites was estimated using the broadening of diffraction peaks and applying Sherer equation [2]. The error of crystallite size determination was not more than 10 nm. Thermal analysis (TA) was performed with MOM derivatograph (Hungary) in the air with the heating rate of 10 °C/min (weighed portion 0.1–0.5 g, platinum crucibles, accuracy of temperature measurement ±5 °C). IR absorption spectra were recorded with Specord 75 IR spectrophotometer in the region of 400–

4000 cm^{-1}. Samples for IR analysis were prepared by pressing tablets with the calcined KBr.

Concentration of free electrons in ITO materials was determined using the wavelength of plasma resonance in the IR spectra of diffuse reflection [3].

RESULTS AND DISCUSSION

It is stated on the basis of X-ray structural investigations that a defect-bearing In$_2$O$_3$ structure of cubic modification with increased interplane distances, compared to the standard values, or a two-phase mixture of this phase and tin oxide of tetragonal modification is formed in ITO materials obtained by thermal treatment (above 240 °C) of indium and tin hydroxides (Figs. 1 and 2). In the case when nitric solutions are used, In$_2$O$_3$ of hexagonal modification can appear (see Fig. 1, *b*, *c*); in the case of thermolysis of nitrates, In$_4$Sn$_3$O$_{12}$ compound can appear (see Fig. 1, *d*).

The degree of changes of lattice parameters of indium oxide obtained from different initial products differs (see Fig. 1). This can be due to different amount of tin built into the crystallites of In$_2$O$_3$ powder, because of segregation of SnO$_x$ on the surface of crystallites [1]. The XPA shows that finer products are precipitated from nitric solutions; hence, smaller extent of changes in the lattice parameter of the materials obtained in this case can be connected with smaller amount of tin introduced into In$_2$O$_3$ crystallite powder as a result of increased segregation of SnO$_x$. A decrease in the degree of In$_2$O$_3$ doping with tin in the materials obtained from nitric solutions leads to the decrease in the concentration of free electrons in them, which is most clearly

observed in the case of small initial concentration of tin (Table 1).

An increase in temperature of solid-phase synthesis leads to an increase in crystallite size (Fig. 3), however, the particles of SnO$_2$ phase remain smaller than In$_2$O$_3$ particles (see Figs. 1 and 2). For example, the size of In$_2$O$_3$ crystallites after thermal treatment at 1000 °C of products obtained from hydrochloric solutions by the direct method at pH 10 is ~220 nm, while the size of SnO$_2$ is not more than 100 nm. In X-ray diffraction patterns of these products, weakly expressed reflections of the crystal SnO$_2$ phase appear only at 1000 °C (see Fig. 2, *c*, curve *3*). When the inverse hydrolytic method is used, the traces of crystal SnO$_2$ phase are observed at 600 °C (see Fig. 2, *d*, curve *2*). Hence, in the case when the temperature of treatment of the products obtained by the inverse hydrolytic precipitation is above 600 °C, larger crystallites are formed than in the case of direct precipitation (see Fig. 3).

The formation of smaller crystallites during thermal treatment of the products of direct hydrolytic synthesis can be explained by the features of gel formation. Coprecipitated hydrogels are composed mainly of mixed aggregates of primary hydroxide particles and the products of incomplete hydrolysis, formed in larger amount in the direct synthesis. The intercalation of the latter into hydrogels decelerates their crystallization thus causing a decrease in the size of the formed particles. The DTA (Fig. 4) and IR spectroscopic (Fig. 5) data of the coprecipitated gels confirm the presence of the products of incomplete hydrolysis in them. Exo- and endothermic peaks at the temperature above 600 °C are present in derivatograms of the samples obtained by the direct method from both hydrochloric and

TABLE 1

Free electron concentration (N_e, 10^{-20} cm^{-3}) in polycrystalline indium oxide doped with tin, under different obtaining conditions (T = 900 °C, pH 7)

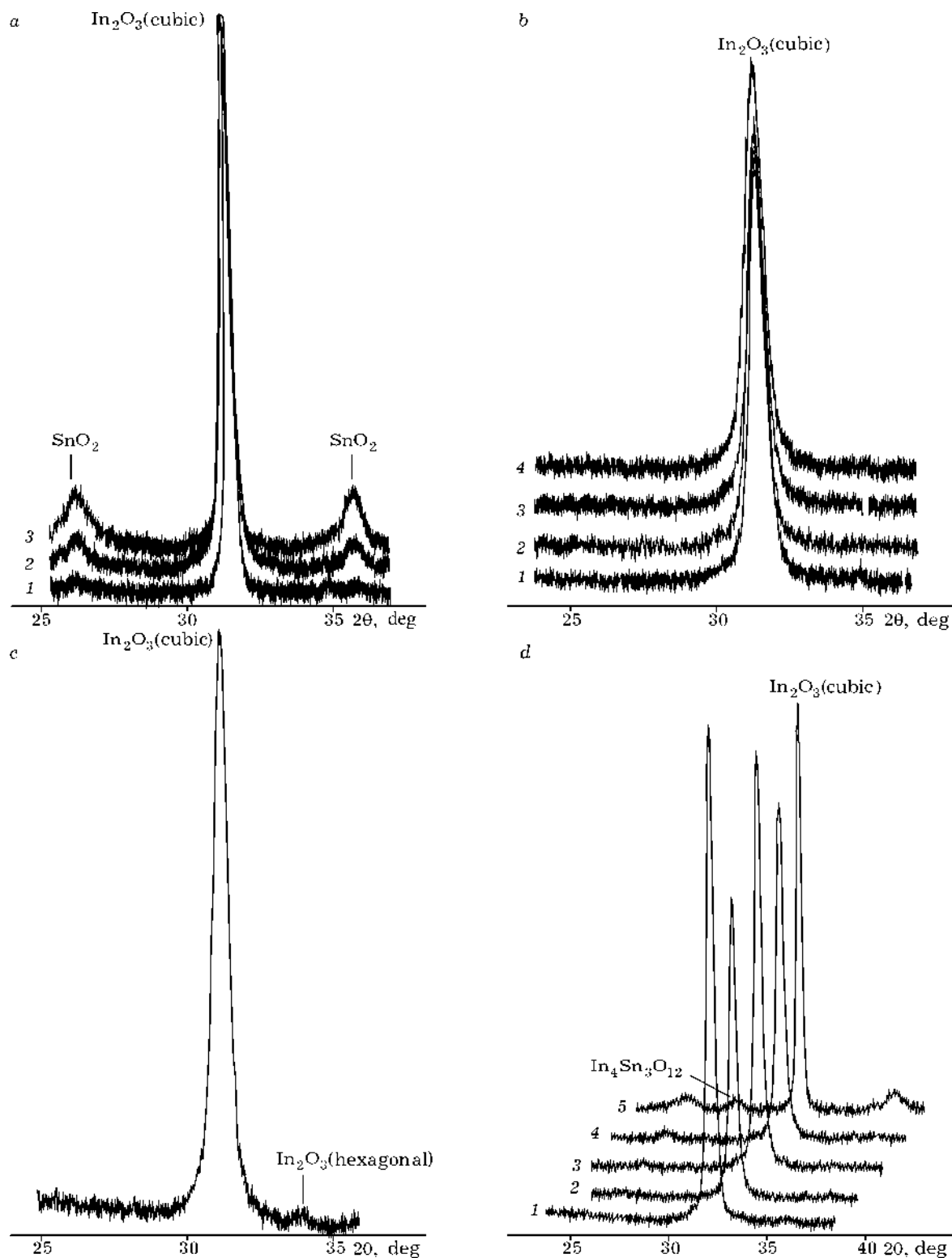| Reagents	Tin content, % at.							
	0.1	0.5	1	2	4	6	10	14
InCl$_3$, SnCl$_4$, NH$_4$OH	2.6	2.6	2.3	2.2	2.1	2.1	2.1	2.0
In(NO$_3$)$_3$, Sn(NO$_3$)$_2$, NH$_4$OH	1.5	1.7	2.0	2.1	2.1	2.1	2.1	2.1
In(NO$_3$)$_3$, Sn(NO$_3$)$_2$	0.5	0.9	1.1	1.2	1.2	1.3	1.3	1.4

Fig. 1. Fragments of X-ray diffraction patterns of ITO materials with different tin content, obtained by direct hydrolytic method at 900 °C from hydrochloric (a) and nitric (b, c (curve 4, recorded with magnification)) of the solutions, and obtained by thermolysis of indium and tin nitrates at 1100 °C (d). Tin content, % at.: 1 (1), 2 (2), 6 (3), 10 (4), 14 (5).
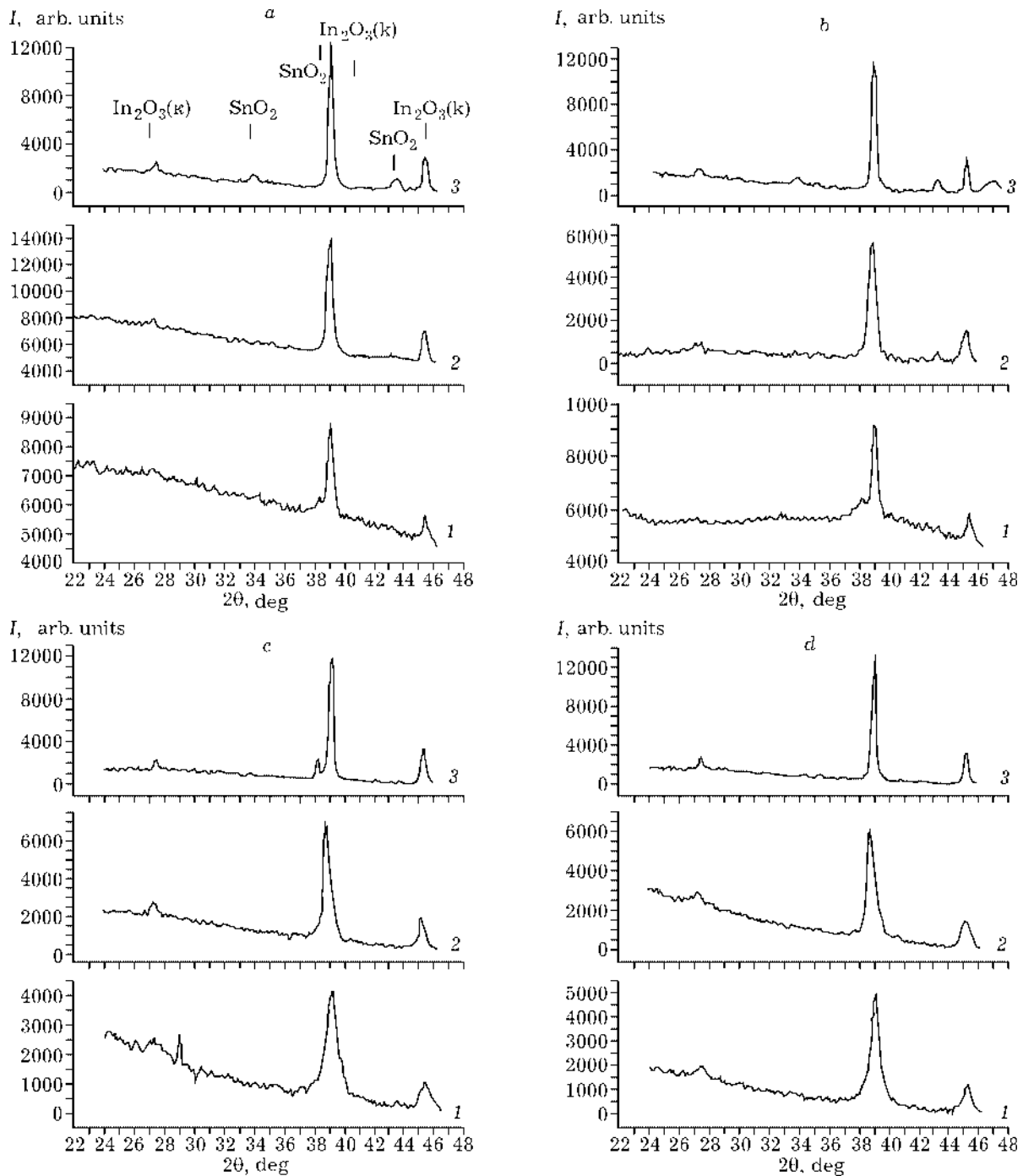
Fig. 2. Fragments of X-ray diffraction patterns of the products of direct (*a*, *c*) and inverse (*b*, *d*) hydrolytic precipitation from hydrochloric (*a*, *b*) and nitric (*c*, *d*) solutions with tin content 10 % at. Temperature, °C: 240 (*1*), 600 (*2*).

nitric solutions (see Fig. 4). These peaks are likely to be connected with the decomposition of these products [4]. For the inverse co-precipitation method, the mentioned peaks are absent from derivatograms. Endoeffects observed at 150 and ~260 °C are conditioned by the removal of the adsorbed water and by the transformation of $In(OH)_3$ into In_2O_3, respectively [5].

In the IR absorption spectra of the products obtained by the joint direct precipitation of indium and tin from hydrochloric and nitric solutions, a broad absorption band is observed in the region of 2500–3600 cm^{-1}, which is assigned to the stretching vibrations of hydroxyl groups and water molecules, and a band of bending vibrations of water molecules with
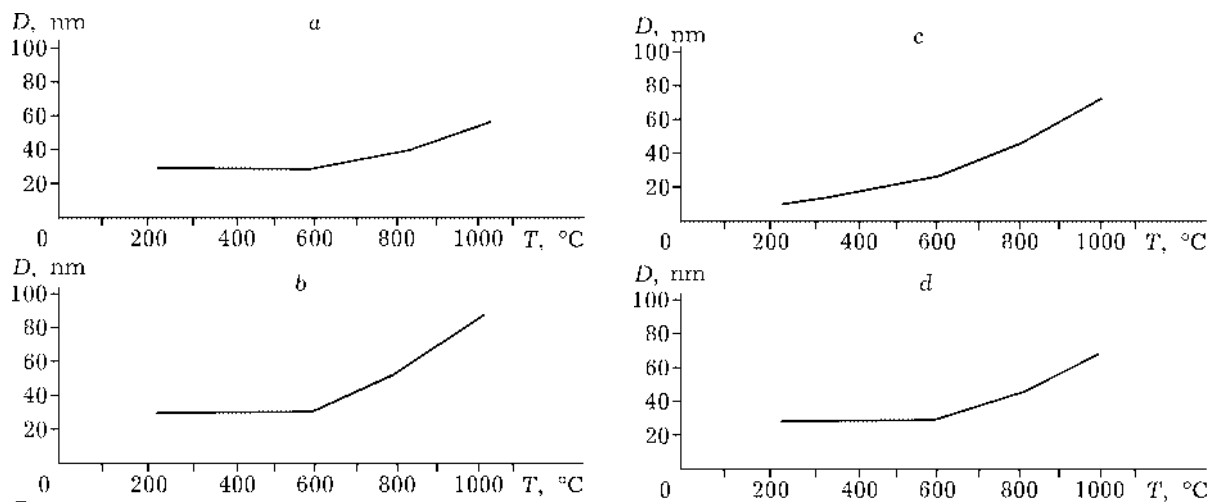
Fig. 3. Dependence of the apparent size of crystallites in the products of direct (a, c) and inverse (b, d) hydrolytic precipitation from hydrochloric (a, b) and nitric (c, d) solutions on annealing temperature.
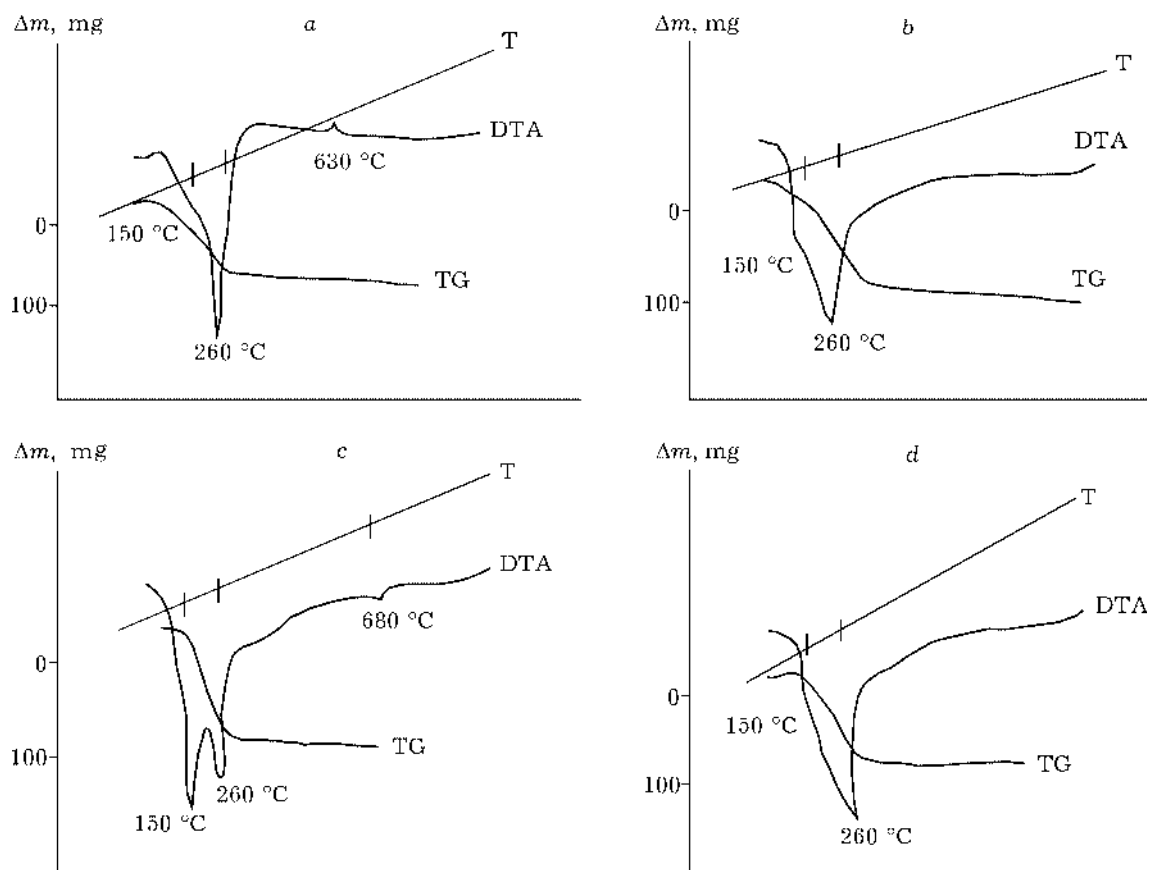
Fig. 4. Thermograms of samples obtained by the direct (a, c) and inverse (b, d) co-precipitation of indium and tin from hydrochloric (a, c) and nitric (b, d) solutions at pH 10. Tin content: 10 % at.
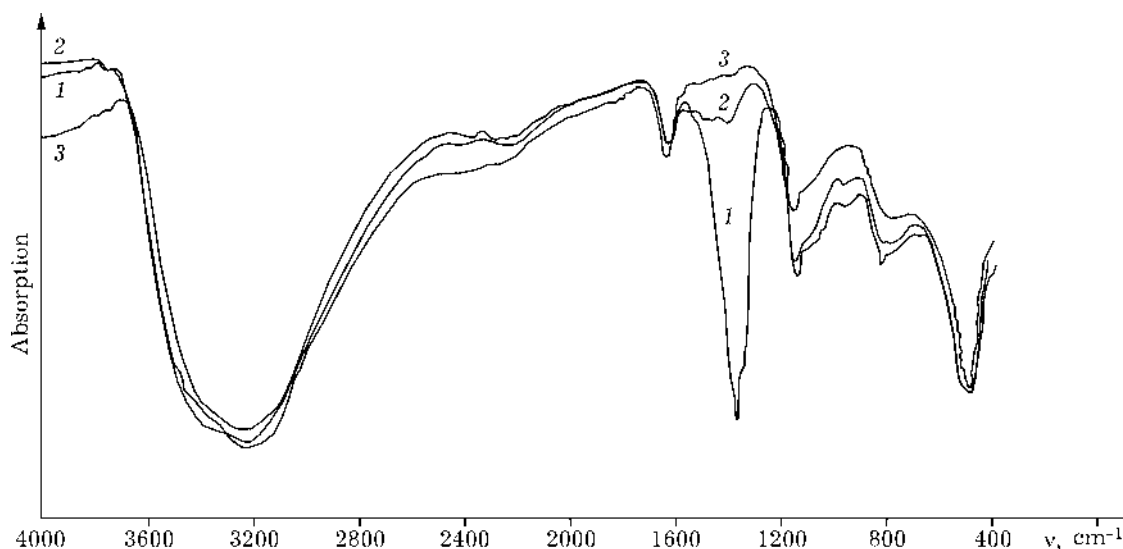
Fig. 5. IR absorption spectra of the products of direct co-precipitation of indium and tin from nitric (*1*) and hydrochloric (*2, 3*) solutions at pH 7. Tin content, %: 2 (*1, 2*) and 50 (*3*).

maximum at 1630 cm^{-1} (see Fig. 5) [6]. The bands of 1150, 857, and 780 cm^{-1} are assigned to the bending vibrations of OH groups in In(OH)$_3$; the bands of 3300, 2600 and 500 cm^{-1} are attributed to water which is present in In(OH)$_3$ [7]. In addition, absorption bands of NH$_4^+$ ion (1400 cm^{-1}) and NO$_3^-$ ion (1380 cm^{-1}) are observed in the spectra of the product with the atomic fraction of tin 50 % (see Fig. 5, curve *3*).

An increase in nitrate ion content of indium and tin oxide materials, for example in those obtained by thermolysis of nitrate salts of indium and tin, leads to the appearance of nonconducting phase In$_4$Sn$_3$O$_{12}$ which helps decreasing free electron concentration (see Table 1).

CONCLUSIONS

Investigation of the physicochemical properties of polycrystalline indium oxide doped with tin shows that, depending on obtaining conditions and on chemical composition of the initial products, as well as on tin content in them, we observe the formation of SnO$_2$ of tetragonal modification, hexagonal In$_2$O$_3$ phase, and In$_4$Sn$_3$O$_{12}$ phase along with solid solutions of tin in indium oxide of cubic modification in the indium and tin oxide system. It is demonstrated that during the direct hydrolytic synthesis the products of incomplete hydrolysis from the mother solution get built into the gel structure. At the inverse hydrolytic precipitation, the products are formed which are free from any admixtures. These features of the synthesis lead to the formation of smaller crystallites in the products of direct co-precipitation treated at the temperature above 600 °C than those formed in the products of inverse co-precipitation. These features also cause differences in the size of crystallites of indium and tin oxide materials obtained from hydrochloric and nitric solutions.

The application of hydrolytic method and the use of hydrochloric solutions as initial ones allow us to achieve the highest electron concentration in the final products of synthesis when the initial atomic fraction of tin is less than 2 %. A decrease in the concentration of free electrons on introducing nitrate ion into the system is explained by at least two reasons: 1) finer state of materials obtained from the products containing nitrate ion and, as a consequence, more substantial segregation of SnO$_x$ on the surface of In$_2$O$_3$ crystallites and lower level of tin-doping in the final products; 2) the presence of non-conducting phases In$_2$O$_3$ (hexagonal) and In$_4$Sn$_3$O$_{12}$ in the materials obtained from the products with nitrate ions.

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