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Determination of Cobalt Concentration in Nanostructured Powders Obtained by Means of Hydrothermal Treatment of the Aqueous Solutions of Sn (II) and Co (II) Chlorides

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Abstract

The cobalt content of nanostructured powders obtained by means of the hydrothermal treatment of the aqueous solutions of Sn (II) and Co (II) chlorides is studied using two spectral methods – energy-dispersive (EDS) and atomic absorption (AAS). Liquid samples for atomic absorption analysis were prepared along two routes: by boiling the products of hydrothermal synthesis in concentrated acids and by fusing the products of hydrothermal synthesis with a mixture of sodium peroxide and borax, followed by diluting the liquid alloy. It is shown that low-temperature alloying of samples is most preferable to determine cobalt concentration in ferromagnetic $Sn_{1-x}Co_xO_{2-\delta}$ nanostructures. Results obtained in the present work allow us to better understand the process of the formation of Co-doped SnO₂ nanostructures and use these structures to develop new functional materials.

Keywords: $Sn_{1-x}Co_xO_{2-\delta}$, nanostructured powders, atomic absorption analysis, hydrothermal synthesis, diluted magnetic semiconductors

INTRODUCTION

Special attention is paid to the determination of cobalt concentration in $\operatorname{Sn}_{1-x}\operatorname{Co}_x\operatorname{O}_{2-\delta}$ powders because these powders are used for the development of new highly sensitive gas sensors [1], light-sensitive detectors [2], supercapacitors [3], optoelectronic and magnetoelectronic devices [4], including the development of a principally different kind of electronic devices based on spin-dependent magnetic transport of charge carriers. The development of the latter devices implies true changes in information technologies due to a substantial increase in the rate of information transfer. The introduction of cobalt into the matrix of tin (IV) oxide causes changes in the lattice parameters of SnO_2 , faceting, packing and grain size. Due to these changes, the material may exhibit new properties and unexpected effects. Because of this, the revelation of the factors having a substantial effect on electrophysical, ferromagnetic and structural properties of the formed material is of fundamental importance for the understanding of the processes of formation of $\text{Sn}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ systems and the possibility of their use in the development of new devices with improved performance characteristics.

It is known [5-7] that Co^{2+} ions (radius 0.72 Å) are able to replace Sn^{4+} ions (radium 0.69 Å) in the lattice of SnO_{2} when the fine powders of $\operatorname{Sn}_{1-x}\operatorname{Co}_{x}\operatorname{O}_{2-\delta}$ are obtained by the joint precipitation of the components from the aqueous solutions of inorganic salts, which leads to the formation of solid solutions. According to the data reported in [8, 9], the solubility of cobalt in the matrix of SnO, does not exceed 0.5-1.0 mass %. In addition to stable solid solutions $Sn_{1-x}Co_xO_{2-\delta}$ with the low content of the transition metal, the formation of metastable solutions with cobalt content much higher than the equilibrium is also possible. Cobalt concentration in fine powders is usually determined by means of elemental energy-dispersive analysis [10, 11]. Only a few works [12] report the data on the concentration of the doping element in the oxide matrix, obtained with the help of other spectral methods. The difficulties in carrying out these analyses are connected first of all with the low solubility of these systems and insufficient knowledge on the behaviour of their solid solutions in acid and basic media.

In the present work, we made an attempt to determine the concentration of cobalt in nanostructured $\operatorname{Sn}_{1-x}\operatorname{Co}_x\operatorname{O}_{2-\delta}$ powders prepared by means of hydrothermal treatment of the aqueous solutions of tin (II) and cobalt (II) chlorides. For the purpose of revealing the most reliable method of determining the concentration of the doping element in highly crystallized structures formed through the spontaneous growth of crystals at increased temperatures and pressures, two analysis methods were used: atomic absorption spectroscopy (AAS) and energy-dispersive spectroscopy (EDS).

EXPERIMENTAL

Synthesis procedure

Initial reagents for the analyzed samples were sodium hydroxide NaOH, tin (II) chloride dihydrate $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and cobalt (II) chloride hexa-hydrate $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. Hydrothermal treatment of the components was carried out in steel autoclaves with teflon cells at 160 °C for 24 h. For this purpose, the $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ powder was mixed with the aqueous solution of NaOH until slightly opalescent suspension was prepared. Then $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was added to the resulting mixture in the amount corresponding to 2–10 mass % of

cobalt with respect to the mass of SnO_2 . The mixture was transferred into a steel autoclave with teflon cells, after which the autoclave was heated to the necessary temperature. After the completion of the hydrothermal reaction, the precipitate was washed many times with distilled water to achieve pH 6–7 and dried in the air at 80 °C for 10–12 h. This process may be described by the following reactions. During reagent mixing at room temperature:

 $SnCl_2 + 4NaOH = Na_2[Sn(OH)_4] + 2NaCl$ $CoCl_2 + NaOH = Co(OH)Cl\downarrow + NaCl$

During hydrothermal treatment of the aqueous solution of a mixture of components:

 $\begin{aligned} \text{Na}_{2}[\text{Sn(OH)}_{4}] \xrightarrow{T = 160 \text{ °C}} \text{SnO} \downarrow + 2\text{NaOH} + \text{H}_{2}\text{O} \\ 2\text{SnO} + \text{O}_{2} &= 2\text{SnO}_{2} \downarrow \\ \text{Co(OH)Cl} + \text{H}_{2}\text{O} \xrightarrow{T = 160 \text{ °C}} \text{Co(OH)}_{2} \downarrow + \text{HCl} \end{aligned}$

 $Co(OH)Cl + H_2O \xrightarrow{1-100} C \to Co(OH)_2 \downarrow + HCl$ Under increased pressure and temperature, the possibility of the oxidation-reduction process cannot be excluded:

 $\begin{array}{l} \operatorname{Na}_{2}[\operatorname{Sn}(\operatorname{OH})_{4}] + \operatorname{Co}(\operatorname{OH})\operatorname{Cl} \xrightarrow{T = 160 \, ^{\circ}\operatorname{C}} & \operatorname{SnO}_{2} \downarrow \\ + \operatorname{Co} \downarrow + \operatorname{Na}\operatorname{Cl} + \operatorname{Na}\operatorname{OH} + 2\operatorname{H}_{2}\operatorname{O} \end{array}$

Investigation procedures

To carry out the analyses for the determination of cobalt concentration in the products of hydrothermal synthesis by means of AAS and EDS, we used a Varian AA280FS atomic absorption spectrometer (the USA) and a Swift-TM device of the Hitachi TM1000 scanning electron microscope (Japan), respectively.

Solutions for the AAS analysis were prepared using two procedures. According to one of them, the preparation of liquid samples was carried out by acid treatment through boiling the samples under analysis in a mixture of concentrated acids $HCl/HNO_{2} = 3 : 1$, followed by multiple washing of the precipitate with distilled water. According to another procedure, the synthesized powders were fused with a mixture of sodium peroxide and sodium tetraborate at the mass ratio of 2:1:1 in glass carbon crucibles at 450 °C for 20 min to form a liquid alloy, which was then cooled to the room temperature, then diluted with distilled water to the necessary concentration, and then analyzed. Cobalt concentration was determined using a standard sample GSO 7268-96 of cobalt ions with mass concentration 0.95- 1.05 mg/cm^3 at the background of mol/dm³ HNO₃ using a deuterium background corrector under the conditions for the relative standard deviation of cobalt determination results to be not higher than 0.01.

The phase composition of the products of hydrothermal synthesis was studied by means of X-ray phase analysis (XPA) with a DRON-4 diffractometer (Russia) using monochromatic CuK_{α} radiation. The morphology and texture of the samples were studied by means of scanning electron microscopy (SEM) with the help of a Hitachi TM1000 microscope.

RESULTS AND DISCUSSION

Typical SEM images and EDS spectra of the samples obtained by the hydrothermal synthesis in the presence of different amounts of cobalt are shown in Fig. 1. One can see that the morphology and texture of the formed product change noticeably with an increase in the concentration of the doping element in the initial reaction mixture. However, the objects of another nature or morphology are not detected by means of detailed SEM analysis, including increased magnification. The elemental EDS analysis (see Fig. 1) confirms the presence of cobalt in the formed structures. The values of averaged cobalt concentrations over 5-7 samples for each of the compositions under analysis are shown in Fig. 2. According to the data of EDS analysis (see Fig. 2), the concentration of the doping element (C_{C_0}) in the formed structures is recorded above the calculated one, introduced into the initial reaction mixture. In



Fig. 2. Relations between the averaged cobalt concentrations introduced into the initial reaction mixture (load) and cobalt content determined by means of EDS in the product of hydro-thermal synthesis.

our opinion, the reason may be in the effects connected with secondary fluorescence of nanostructured products exhibiting pronounced ferromagnetic properties. However, along with similar effects, absorption of cobalt fluorescence by the matrix components is possible.

According to the data of magnetic analysis obtained by us previously [13], saturation magnetization in the formed nanostructured samples is



Fig. 1. SEM images and EDS spectra of products of the ghydrothermal synthesis obtained at different cobalt content in the reaction mixture, mass %: 2 (a), 6 (b), 10 (c).



Fig. 3. Diffraction patterns of the product of hydrothermal synthesis depending on cobalt content in the reaction mixture, mass %: 0 (1), 2 (2), 6 (3), 10 (4).

almost two orders of magnitude higher than in the fine powders of the same composition prepared by means of chemical precipitation [5-7].

The diffraction reflections from the products obtained in the presence of different amounts of cobalt correspond to tetragonal SnO₂ (card JCPDS No. 41-1445) of rutile type (Fig. 3). The absence of additional reflections in the diffraction patterns may mean that cobalt-containing components of the structures are X-ray amorphous, they are present in the form of nanocrystalline particles less than 2-3 nm in size, or the result of the hydrothermal reaction is the solid solutions $Sn_{1-x}Co_{x}O_{2-\delta}$ (where x = 0.02, 0.06, 0.10). After annealing at $T \leq 700$ °C, additional weak reflections are observed in the diffraction patterns of hydrothermal products formed in the presence of 10 mass % Co (Fig. 4). These weak reflections may be the evidence of the formation of $Co_{3}SnO_{4}$ (card JCPDS No. 11-1137). With an increase in annealing temperature from 450 to 700 °C, the intensity of the reflections of $Co_{2}SnO_{4}$ phase increases slightly.

Cobalt concentration in the formed structures may be determined more reliably and accurately by means of AAS. However, to carry out the elemental analysis using this method, the substance under analysis should be dissolved preliminarily. Liquid samples may be prepared by the dissolution of the SnO_2 matrix in acids or by alloying the products of hydrothermal synthesis with a mix-

Fig. 4. Diffraction patterns of the product of hydrothermal synthesis depending on the temperature of sample annealing, °C: 80 (1), 450 (2), 600 (3), 700 (4). Co content in reaction mixture: 10 mass %.

ture of sodium peroxide and sodium tetraborate. However, as the results of our studies showed, the powders obtained by means of hydrothermal synthesis do not dissolve completely even in a mixture of concentrated acids $HCl/HNO_3 = 3:1$ during boiling for 2 h. The reason of this behaviour of the analyzed samples, on the one hand, may be the high degree of the crystallization of SnO₂ formed under hydrothermal conditions; on the other hand, the formation of $Sn_{1-x}Co_xO_{2-\delta}$ solid solutions, their solubility in concentrated acids is only poorly studied and insufficiently described in the literature at present. As a result of low-temperature alloying of the synthesis products with a mixture of sodium peroxide and sodium tetraborate, a liquid alloy is formed; its dilution with distilled water leads to the required solutions.

The data of AAS for cobalt determination in solutions obtained during acid treatment of the structured material and alloying the synthesized samples are presented in Table 1. It may be stressed that cobalt, as a chemical element, only partially passes into solution as a result of boiling the synthesis products in a mixture of concentrated acids.

In the case of liquid samples prepared by alloying, analysis results are in complete agreement with the amount of doping element introduced into the reaction mixture. On the basis of the data obtained, it may be concluded that the doping

TABLE 1

Cobalt content in the initial reaction mixture and in the products of hydrothermal synthesis

The amount of introduced cobalt, mass %	Cobalt concentration in synthesis products according to AAS data, mass $\%$	
	Acid treatment	Alloying
1.85	1.43 ± 0.02	1.85 ± 0.04
5.56	4.64 ± 0.50	5.53 ± 0.06
10.11	8.80 ± 0.09	9.24 ± 0.12

element completely passes from the mixture of initial solutions to the crystallizing nanostructured solution during the hydrothermal treatment of the aqueous solutions of the inorganic salts of tin (II) and cobalt (II). The results obtained are in good agreement with the previously published data on the solubility of cobalt in the lattice of SnO_2 , leading to the formation of solid solutions $\text{Sn}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ [8, 9].

CONCLUSION

Cobalt concentration in highly crystallized ferromagnetic structures Sn_{1-x}Co_xO₂₋₈ formed during the spontaneous growth of crystals under the conditions of the hydrothermal treatment of the aqueous solutions of Sn (II) and Co (II) chlorides was studied using two spectral methods: elemental energy-dispersive and atomic absorption. According to the data of elemental EDS analysis, the concentration of the doping element in the formed products is recorded to be higher than the calculated value, which may be connected with the manifestation of the effects of secondary fluorescence of nanostructured materials themselves, exhibiting clearly pronounced ferromagnetic properties. A comparative analysis of cobalt in liquid samples prepared by the acid treatment and low-temperature alloying allows one to determine the content of the doping element in the SnO_2 matrix and gives a valuable information for the understanding of the processes of the formation of nanostructured SnO_2 doped with cobalt, and the possibility of its application in the development of new devices with improved performance characteristics.

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