Synthesis of nanocomposites based on strontium stannate

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Abstract. The process of thermolysis of double strontium-tin(IV) hydroxide obtained by precipitation from hydrochloric acid solutions by adding ammonia to pH=10 and the phase composition of its degradation products were studied by differential thermal analysis, X-ray phase analysis and scanning electron microscopy. It was shown that the main stages of dehydration are completed at about 350°C and as a result of thermolysis an X-ray amorphous product is formed, which at temperatures above 700°C transitions to the strontium stannate crystalline phase.

1 Introduction

Lately, materials based on tin dioxide SnO_2 doped with various transition and alkaline earth metals have attracted increased interest of researchers associated with many promising areas of their application [1-3]. Thus, stannates of alkaline earth metals are used as components of ceramic dielectric materials, heat-resistant capacitors and semiconductor sensors of various gases [4-8]. $SrSnO_3$ nanorods obtained by thermolysis and hydrothermal treatment of $SrSn(OH)_6$ nanowires are used as anode material in lithium-ion batteries, since they have a discharge capacity of up to 200 mA h/g and improved cyclability [8, 9]. Materials based on $SrSnO_3$ exhibit luminescent and photocatalytic properties, and ceramic pigments are synthesized on its basis [10-13]. One of the most promising methods for obtaining strontium stannate is the process of thermal decomposition of the precursor, mixed strontium and tin (IV) hydroxide, with the composition $SrSn(OH)_6$. In this work data on the preparation and study of the compositions and properties of the products of its thermal decomposition are considered.

2 Experimental

Mixed tin-strontium hydroxide of the composition $SrSn(OH)_6$ was synthesized by precipitation from a mixture of 1 M hydrochloric acid solutions of $SrCl_2$ and $SnCl_4$ by adding 1M ammonia solution to pH ~ 10.5. Ammonia solution was added at a constant rate of 2.5 ml/min (the reagent was dosed with a LAB-NP-1 peristaltic pump). The reaction mixture was stirred intensively for 4 h at room temperature. The resulting precipitates were separated by

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centrifugation, washed with distilled water and dried at 100°C for 6 h. The dried precipitates were calcined at 300, 500 and 700°C for 4 h.

The phase composition of the powders were analyzed using X-ray diffraction technique (XRD) on diffractometers Bruker D8 Advance and DRON-3M using Cu-Kα radiation. Identification of the phases formed in the system was carried out using the program Crystallographica Search-Match, Version 2.1 and the database PDF2. The average grain size of the crystal phases was estimated by the broadening of the reflexes on the diffractograms using the Scherrer formula. The thermal analysis of the dried powders was carried out on a synchronous thermal analyzer NETZSCH Jupiter 449C STA coupled with a QMS 403C Aëolos mass spectrometer (TG-QMS) in an argon stream at temperatures of 25-1000 °C with a heating rate of 10 deg·min^{-1}. Microstructure of the powders was studied by scanning electron microscopy (SEM) using Hitachi TM 1000 Scanning Electron Microscope. In parallel, the elemental composition of the samples was studied using energy dispersive analyzer TM-1000 Oxsford Instrument. The ionic conductivity was measured on tableted samples with silver electrodes using a two-electrode circuit in a vacuum (5·10^{-2} Torr) in the temperature range from 40 to 200°C at alternating current using a Hewlett Packard HP 4284A precision electrical parameter meter in the frequency range of 20 Hz-1 MHz.

3 Results and discussion

According to the data of X-ray phase analysis (XRD) the diffractogram of freshly-precipitated sample is a mixed strontium and tin(IV) hydroxide of the composition $SrSn(OH)_6$ (**Fig**. **1**, *curve 1*) and well agrees with the literature data (file 9-86 PDF 2).
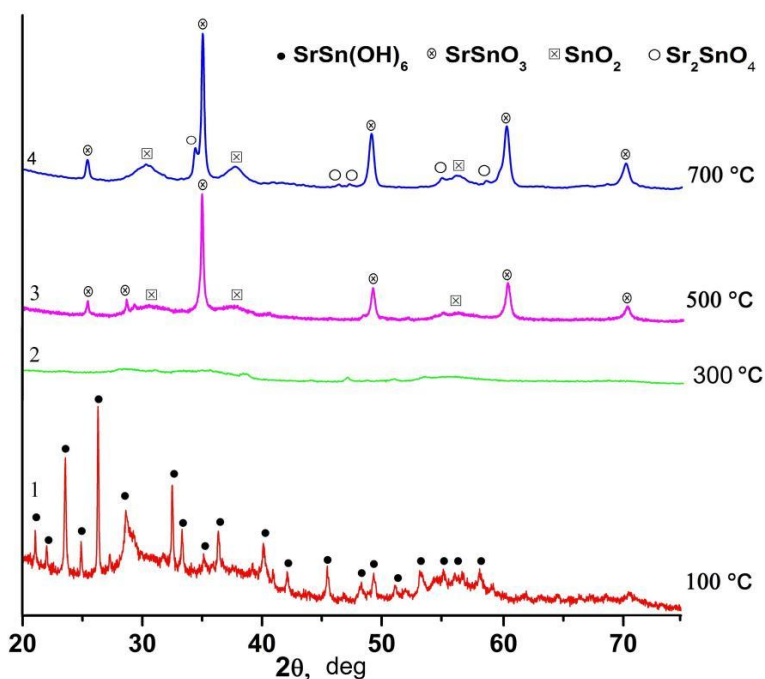

Fig. 1. X-ray diffraction patterns of $SrSn(OH)_6$ (*curve 1*) and products of its thermolysis (*curves 2,3,4*).

Figure 2 shows the results of differential thermal (DTA) and thermogravimetric (TG) analyzes of the initial sample $SrSn(OH)_6$. When it is heated in air between 100 and 350°C two endothermic effects are observed on the DTA curve which are accompanied by a weight loss

on the TG curve associated with dehydration of the sample proceeding in accordance with the reaction equation:
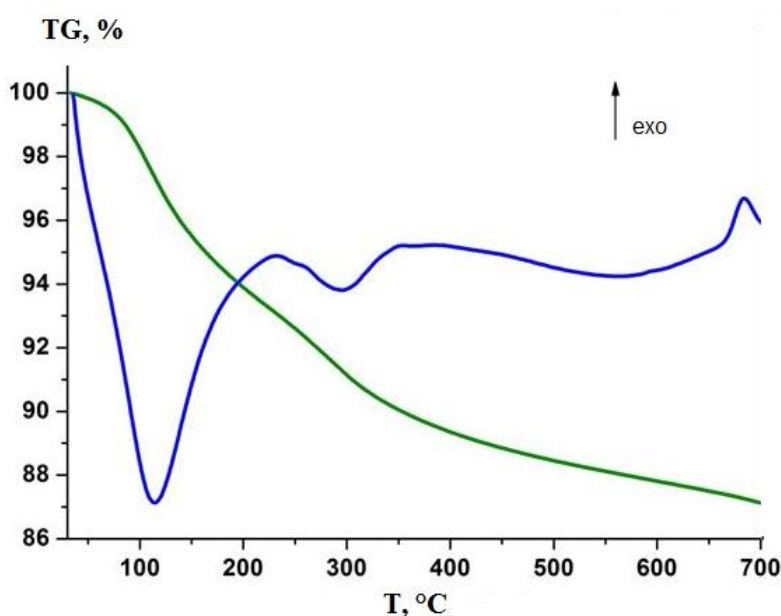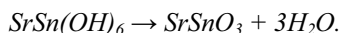
$$SrSn(OH)_6 \rightarrow SrSnO_3 + 3H_2O.$$

Fig. 2. Curves of differential thermal analysis of freshly deposited $SrSn(OH)_6$.

XRD data indicate that the sample obtained by heating the mixed hydroxide at 300°C for 4 hours is an X-ray amorphous product with no characteristic diffraction peaks in the diffractogram (**Fig. 1**, *curve 2*). Further heating of the sample at 500°C leads to the transition of amorphous phase into crystalline with formation of a two-phase $SnO_2/SrSnO_3$ composite consisting of nanocrystalline particles of strontium stannate $SrSnO_3$ and tin dioxide SnO_2 (**Fig. 1**, *curve 3*) that indicates the complicated mechanism of amorphous product crystallization. The obtained strontium stannate has a perovskite structure and its lattice parameters are consistent with the literature data (file 3-715 PDF2). Exothermic effect observed on the DTA curve after sample calcination at 680-700°C and not accompanied by weight loss (**Fig. 2**), according to XRD data (**Fig. 1.**, *curve 4*), is associated with the decomposition of $SrSnO_3$ and the formation of SnO_2 phase and weakly crystallized Sr_2SnO_4 phase with the spinel structure which is consistent with the literature data (file 24-1241 PDF2).

The results of studying the microstructure of samples by the SEM method are shown in Figure 3. Mixed hydroxide $SrSn(OH)_6$ consists of aggregated rod-shaped particles up to 3 microns in size with a high degree of agglomeration (**Fig. 3.** a). The particles retained a rod-like shape after calcination at a temperature of 700°C (**Fig. 3.** b, c.). The size of the rods reaches 6-7 microns, but their diameter is smaller than that of the precursor and particles are less aggregated. The elemental analysis of samples composition has shown that the tin content on the surface of $SrSnO_3$ sample obtained as a result of heat treatment significantly exceeds its calculated amount (in wt. %): Sn - 72 (calculated 46.7); Sr - 28 (34.5). It can be connected both with surface segregation of tin atoms in the crystal lattice of strontium stannate, and with the possibility of formation of tin dioxide particles on the surface of $SrSnO_3$ crystals.

Powders of the composition SnO_2–$SrSnO_3$ were tested as oxide heterogeneous additives for the obtaining of composite solid electrolytes based on ionic salts. **Fig. 4.** shows the concentration dependence of the conductivity of composites $(1-x)CsNO_2-xSrSnO_3$, from

which it follows that the conductivity increases and reaches a maximum when the composite is doped with
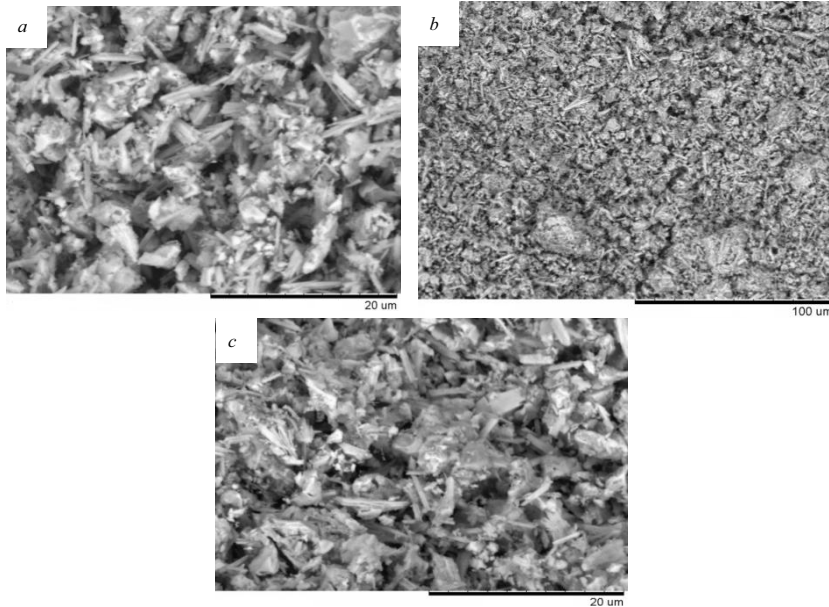

Fig. 3. SEM image of freshly deposited $SrSn(OH)_6$ (a), after calcination at 700°C of aggregates (b) and particles (c)

strontium stannate by 60%. A further increase in the amount of added $SrSnO_3$ leads to a decrease in the ionic conductivity of the studied composite. The character of the conductivity change is typical for composite solid electrolytes, the ionic conductivity of which is carried out due to the ionic salt/oxide interfaces.
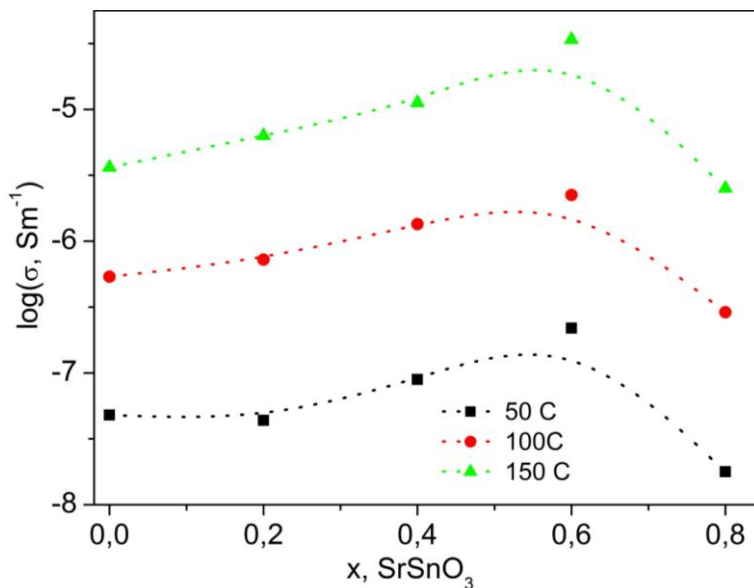

Fig. 4. Dependence of the conductivity of composites $(1-x)CsNO_2-xSrSnO_3$ from the concentration of the $SrSnO_3$ additive.

4. Conclusion

It was shown that strontium hexahydroxostannate $SrSn(OH)_6$ was obtained by precipitation of tin(IV) and strontium hydroxides from hydrochloric acid solutions.

Aggregated particles with rod morphology up to 7 μm in size and with perovskite structure of $SrSnO_3$ composition are formed during thermolysis of mixed tin-strontium hydroxides $SrSn(OH)_6$.

It was found that mixed $SrSn(OH)_6$ hydroxides are stable at normal temperatures, and calcination at 300°C leads to the formation of amorphous phases. At temperatures > 500°C amorphous phases recrystallize to form SnO_2-$SrSnO_3$ nanocomposites and at 680-700°C to form SnO_2-Sr_2SnO_4 nanocomposites.

The ionic conductivity of composite solid electrolytes based on cesium nitrite with the addition of $SrSnO_3$ obtained by thermal decomposition of $SrSn(OH)_6$ was studied. It is shown that composites $CsNO_2$-$SrSnO_3$ have an increased ionic conductivity exceeding the conductivity of pure cesium nitrite at 200°C and may be promising for use as heterogeneous additives in composite solid electrolytes.

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