



Article Synthesis of BaSnO₃ as a Highly Dispersed Additive for the Preparation of Proton-Conducting Composites

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Abstract: The process of thermolysis of barium hydroxostannate $BaSn(OH)_6$ as a precursor for preparing barium stannate $BaSnO_3$ has been investigated using the method of differential thermal analysis. Thermal decomposition products of the precursor were characterized using X-ray diffraction, IR spectroscopy, low-temperature nitrogen adsorption, and scanning electron microscopy. It was shown that dehydration at nearly 270 °C resulted in the formation of an X-ray amorphous multiphase product, from which single-phase barium stannate crystallized at temperatures above 600 °C. The synthesized barium stannate was used as a functional additive to prepare composite proton electrolytes in the CsHSO₄-BaSnO₃ system. The structural and transport properties of the obtained system were investigated. It is shown that the highly conductive state of the salt is stabilized in a wide range of temperatures. High conductivity values of composite solid electrolytes in the medium temperature range create the possibility of their use as solid electrolyte membrane materials.

Keywords: barium hexahydroxostannate; barium stannate; composite proton solid electrolytes; thermolysis of precursors

1. Introduction

Recently, materials based on tin dioxide SnO_2 doped with various transition and alkaline–earth metals have attracted increased interest and great attention from researchers, which is associated with many promising areas of their application. Among the promising materials based on tin dioxide and stannates are composites and nanocomposites such as $MSnO_3-SnO_2$ and $M_2SnO_4-SnO_2$ (M = Mg, Ca, Ba, Sr, Zn, Cd, Cu, Mn, Co, and Ni). The latter are widely used as components for electronics, optoelectronics, gas sensors, and various catalysts [1–27], as well as anode materials for Li-ion batteries and various autonomous devices for energy storage and conversion [28–40].

Nanomaterials are known to have properties different from those of individual compounds. In particular, nanocomposite solid electrolytes based on acidic salts have enhanced proton conductivity. Among such salts, cesium hydrosulfate exhibits one of the highest conductivity values in the high-temperature phase $(10^{-2} \text{ S} \cdot \text{cm}^{-1})$. Cesium hydrosulphate belongs to the solid acids $M_mH_n(XO_4)_p$ family (where X = S, Se, P, As; M = Li, Na, K, Rb, Cs, NH₄; and n = 1.5, m = 1.5, p = 1.5). These salts undergo a "superprotonic" phase transition at temperatures 50–230 °C accompanied by a sharp increase in the conductivity up to 10^{-3} – 10^{-2} S·cm⁻¹. CsHSO₄ in the superprotonic phase is the most conductive salt in this family. However, at the phase transition (414 K), it decreases by four orders of magnitude to $\sigma = 10^{-6}$ – 10^{-8} S·cm⁻¹. Therefore, it would be desirable to find methods to stabilize the highly conductive state of this compound in the low-temperature region. For this purpose, proton conducting composites based on alkali metal hydrosulfates with



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). various dispersed oxides $(1 - x)MHSO_4$ -xA, $(M = Cs, Rb, K; A = SiO_2, TiO_2, Al_2O_3)$ were synthesized and studied [41–43]. In addition, comprehensive studies of composite systems based on a number of acidic salts of Me_xH_y(AO₄)z: MeHSO₄ (Me = Cs, Rb, K), Cs₅H₃(SO₄)₄, (NH₄)₃H(SO₄)₂, CsH₂PO₄, and silicon dioxide with a different specific surface area (10...580 m²/g) were carried out [44–48].

A number of interesting correlations were found between the concentration of the components, nature, and morphology of the heterogeneous additive and physicochemical properties of the ionic salt in the composite. It was shown that heterogeneous doping of salts with highly dispersed oxide leads to a significant increase in low-temperature conductivity (by orders of magnitude), a decrease in the superionic phase transition temperature, an increase in mechanical strength, and in some cases, the thermal stability of composites. High values of conductivity of composites based on acidic salts and increased mechanical strength give reason to believe that these materials can be promising for use in various kinds of electrochemical devices.

As highly dispersed additives for obtaining proton composite solid electrolytes, it is possible to use stannates of alkali and transition metals $MSnO_3$ (M = Mg, Ca, Sr, Ba, Zn, Ni, etc.), which can be obtained via thermolysis of precursors, -hydroxostannates of the $MSn(OH)_6$ type. It should be noted that stannates obtained via thermolysis are characterized by a relatively high specific surface area (within 10...100 m²/g) and can be used as functional additives for obtaining composite materials [49].

One of the most reliable methods for obtaining compounds of the $MSn(OH)_6$ type (M = Mg, Ca, Sr, Ba, Zn, Ni, etc.) in the form of uniformly mixed powder compositions is the method of co-precipitation of salts. It is based on the precipitation of poorly soluble compounds in the form of hydroxides or metal salts from aqueous solutions of precursor salts by a precipitant solution [50]. The precipitant reacts chemically with the salt solutions, leading to the precipitation of new poorly soluble compounds. If the experiment is set up correctly, a homogeneous mixture of salts with a given ratio of cations can be reproducibly obtained. In the ideal case, the cations from the solution are precipitated simultaneously and at the same rate. The advantages of the chemical precipitation method should be attributed to the granulometric homogeneity of the resulting powders and the high rate of the process. This method avoids the disadvantages inherent in powder technology. For example, it eliminates the need to use the grinding procedure. As a result, the obtained powders are not contaminated by the abrasion products. $MSn(OH)_6$ compounds obtained via precipitation under different conditions [51–58], and consequently their thermal decomposition products, are characterized by a high homogeneity of chemical composition, which is important for their application as functional additives in nanocomposite materials.

Previously, we have shown that the addition of $MSn(OH)_6$ thermolysis products, -nanocomposites based on $MSnO_3$ (M = Mg, Ca, and Sr) with a small admixture of SnO_2 , leads to an increase in the ionic conductivity of cesium nitrite by more than an order of magnitude [53,59]. Recently, it was found that the addition of zinc stannate to cesium dihydrophosphate leads to an increase in the proton conductivity of the salt in the lowtemperature region and an improvement in the stability of the proton electrolyte in the high-temperature region [49]. It is also known that the introduction of oxides with proton conductivity into acidic salts leads to an increase in their proton conductivity [48,60]. Unlike zinc stannate, systems based on barium stannate BaSnO₃ are high-temperature proton electrolytes [61–63]. Consequently, it can be expected that composites based on acidic salts with the addition of nanocrystalline barium stannate will have increased proton conductivity.

Barium stannate can be obtained via thermolysis of the precursor $BaSn(OH)_6$. It has been found earlier [64,65] that $BaSn(OH)_6$ crystallizes during precipitation as an array of nanorods with a diameter of 20–50 nm and a length up to several micrometers, and the microstructure of its thermolysis products remains unchanged. This makes it possible to use barium stannate as an additive for the creation of composite proton solid electrolytes, for example, on the basis of acidic hydrosulfates. The works on synthesis and investigation of transport properties of proton nanocomposite electrolytes based on acidic salts with the addition of nanocrystalline $BaSnO_3$ have not been carried out before. The aim of the present work is to optimize the conditions for the synthesis of nanocrystalline barium stannate from the $BaSn(OH)_6$ precursor and to study the transport and structural properties of proton composite solid electrolytes $CsHSO_4$ - $BaSnO_3$.

2. Materials and Methods

2.1. Materials

The following reagents were used: $BaCl_2 \times 2H_2O$ (GOST 4108-72 "Barium chloride 2-water", chemical pure, JSC "Reahim", Donetsk), $Na_2SnO_3 \times 3H_2O$ (metastannate 3-water, TU 6-09-1506-76, pure, LLC "Spektr-chem SPb", St. Petersburg, Russia), and NaOH (GOST 4328-77 "Sodium hydroxide", chemical pure, LLC "Khimprom, Perm Region, Russia,). CsHSO₄ crystals were grown via isothermal evaporation from an aqueous solution of cesium carbonate (99% purity, Rare Metals Plant, Novosibirsk, Russia) and sulfuric acid (pure "ReaKhimLab", Moscow, Russia) in a stoichiometric ratio. All chemicals were used as received without additional purification. For the preparation of 1M solutions of salts and sodium hydroxide, deionized water obtained using the purification system of the laboratory deionizer BE-2 was used.

2.2. Synthesis of the Precursor $BaSn(OH)_6$

Barium hexahydroxostannate BaSn(OH)₆ was synthesized via hydrolytic co-precipitation as follows: First, 0.1 mol of BaCl₂ × 2H₂O was dissolved in 100 mL of 1M hydrochloric acid solution. To the resulting solution, a 26.67 g (0.1 mol) Na₂SnO₃ × 3H₂O suspension was added, which corresponds to the atomic ratio of Ba:Sn = 1:1. Then, a 1M NaOH solution was gradually added, maintaining the pH of the medium within 8.9...9.4. The pH value was monitored using a laboratory pH meter HI 2221. For complete quantitative co-precipitation of barium and tin (IV), the mixture was stirred continuously for 12 h. The resulting white precipitate was filtered from the mother liquor and washed with distilled water until a negative qualitative reaction to the presence of Cl⁻ ions in the solution was achieved and dried in a desiccator at 110 °C for 4 h. The synthesis reaction of BaSn(OH)₆ can be written as:

$$BaCl_{2} + Na_{2}Sn(OH)_{6} + 2NaOH = BaSn(OH)_{6} \downarrow + 2NaCl$$
(1)



The scheme of $BaSn(OH)_6$ precursor preparation is presented in Figure 1.

Figure 1. Synthesis scheme of the precursor.

2.3. Characterization

The microstructure and phase composition of the samples were determined using X-ray diffraction (XRD). X-ray diffraction patterns were recorded at room temperature using a Bruker D8 Advance diffractometer with $CuK\alpha$ radiation in the 20 range from

10 to 70°. The phases formed in the system were identified using the Crystallographica Search-Match, Version 2.1 program, and the PDF4 database. The average crystallite size was estimated from the diffraction line broadening in X-ray diffraction patterns using the Scherer formula.

$$d = \frac{k\lambda}{\beta cos\theta},\tag{2}$$

where *d* is the average crystallite size, λ is the X-ray wavelength (1.54051 Å), β is the full width at half maximum of the diffraction peak, θ is the diffraction angle, and k = 0.9. Thermal analysis of the dried powders was performed on a NETZSCH Jupiter 449C STA synchronous thermal analyzer coupled to a QMS 403C Aëolos (TG-QMS, Netzsch—Geratebau GmbH, Berlin, Germany) mass spectrometer in an argon flow at temperatures in the range of 20–700 °C at a heating rate of 10 K·min⁻¹. Thermal treatment of the powder was carried out in a SNOL 6.7/1300 muffle furnace at temperatures of 110, 270, 600, and 700 °C for 4 h at each temperature. The microstructure of the samples was studied via field emission scanning electron microscopy (SEM) on a Hitachi SU8000 electron microscope (Hitachi, Tokyo, Japan). The images were taken in the secondary electron mode at an accelerating voltage of 2–30 kV and a working distance of 8–10 mm. The sample's electron dispersion spectra (EDS) were analyzed using an Oxford Instruments X-max energy dispersive spectrometer. Analytical measurements of the EDS were optimized using a previously established method, as outlined in the references [66]. Prior to the measurements, the samples were affixed to an aluminum mount with a 25 mm diameter and secured firmly with conductive graphite adhesive tape. Additionally, the morphology of the unmodified samples was studied to preclude any surface effects due to the application of the conductive layer, as noted in [67]. The specific surface area values and the average pore size were calculated using the Brunauer-Emmett-Teller (BET) method described in detail in papers [68,69]. Infrared spectra were recorded on a Carry 660 FTIR (Fourier transform infrared) spectrometer (Agilent Technologies, Santa Clara, CA, USA) with a PIKE Technologies Gladi ATR (diamond crystal) broken total internal reflection attachment in the range of $500-4000 \text{ cm}^{-1}$. The samples were prepared as vacuum-pressed KBr pellets with an admixture of the compound under study. The composites in the system $(1 - x)C_{s}HSO_{4}-xBaSnO_{3}$ (where x = 0.2, 0.4-mol fraction of barium stannate) were synthesized by thoroughly mixing the components in an agate mortar and heating the granulated samples for 10–20 min at a temperature of 200–210 °C, close to the melting point of CsHSO₄. The proton conductivity of the composites was measured using a two-electrode scheme on an alternating current using an Instek LCR-821 Impedance Meter (frequency range 12 Hz–200 kHz) and a precision electrochemical meter IPU-1RLK-1/2008 (CIT LLC, Moscow, Russia) (frequency range 1 Hz–3.3 MHz). To measure the electrical conductivity, pellets with a diameter of 6 mm and a thickness of 1–1.5 mm were pressed from the samples under a pressure of 30-50 MPa. The electrical conductivity of the samples with silver or platinum electrodes was measured under cooling at a rate of 1-2 °C/min in an air atmosphere at a relative humidity of RH = 30%.

3. Results and Discussion

3.1. Synthesis of Precursor BaSn(OH)₆

The X-ray diffraction patterns of the sample obtained as a result of co-deposition and drying at 110 °C in air (Figure 2) show reflexes characteristic of barium hexahydroxostannate BaSn(OH)₆, which has a crystal structure with a monoclinic unit cell (space group symmetry P21/n, PDF4, card no. 09-0053). Along with the BaSn(OH)₆ phase, the diffractogram of the sample shows reflexes related to the barium carbonate BaCO₃ phase with an orthorhombic unit cell of the witherite type (symmetry space group Pmcn, PDF4, card no. 05-00378).



Figure 2. Experimental X-ray diffractogram of the sample (black points) in comparison with the diffractogram calculated using the Rietveld method (red line). The green line is a difference between the experimental data and the calculated curve. Theoretical diffractograms of BaSn(OH)₆ and BaCO₃ are also presented for comparison.

The processing of diffractograms using the Rietveld method in the Topas v. 4.2 program allowed us to determine the unit cell parameters of BaSn(OH)₆ and BaCO₃ phases in the initial sample. The unit cell parameters of BaSn(OH)₆ (a = 9.3892 ± 0.0004 Å, b = 6.3400 ± 0.0003 Å, c = 10.5649 ± 0.0005 Å, β = 113.211 ± 0.003°, $\alpha = \gamma = 90°$, Z = 4, V_{cell} = 577.96 Å³, and ρ = 4.115 g/cm³) are close to the corresponding values for this compound reported earlier [64]. A small difference in the values of the parameter a and the angle β is observed. The best-fitting parameters are obtained under the assumption that BaSn(OH)₆ crystallites have a size of about 175 nm and a preferred (200) orientation. The BaCO₃ unit cell parameters (a = 5.205 ± 0.002 Å, b = 9.120 ± 0.004 Å, c = 6.430 ± 0.002 Å, V_{cell} = 305.22 Å³, and ρ = 4.294 g/cm³) are consistent with the data presented in the PDF database (PDF4, card no. 05-00378), and the particle size of the witherite phase is 28 nm. Analysis of diffraction data using the Rietveld method shows that the synthesized BaSn(OH)₆ sample contains 33 weight % BaCO₃. The presence of witherite impurity can be explained by the reaction of BaSn(OH)₆ with carbon dioxide contained in the air:

$$BaSn(OH)_{6} + CO_{2} = BaCO_{3} + SnO_{2} \cdot xH_{2}O + (3 - x)H_{2}O$$
(3)

Nanocrystalline BaCO₃ and an equivalent amount of amorphous tin dioxide hydrate $SnO_2 \times xH_2O$, which does not give reflexes on X-ray diffractograms, are formed. According to the data of scanning electron microscopy (Figure 3a), a freshly deposited mixed hydroxide BaSn(OH)₆ sample consists of clearly visible rod-shaped particles 10–50 microns in size, the surface of which is covered with a loose layer, apparently consisting of a mixture of nanosized particles of barium carbonate and hydrated tin dioxide. According to the results of chemical microanalysis carried out using energy dispersive spectroscopy, the atomic ratio Ba:Sn:O lies in the range (10 ± 1) : (12 ± 2) : (65 ± 3) , which is close to the stoichiometric ratio for both BaSn(OH)₆ and the mixture BaCO₃–SnO₂ × xH₂O (at a molar ratio of components 1:1). It was found that the amount of barium carbonate in the sample increases when the freshly deposited BaSn(OH)₆ precursor is stored in air (Figure 3b).



Figure 3. (a) Scanning electron microscopy images of freshly deposited $BaSn(OH)_6$ and (b) after storage in air for one month.

3.2. Characteristics of Intermediate Products of Thermolysis and Final Sample of Barium Stannate

The processes occurring during the heating of the freshly deposited $BaSn(OH)_6$ sample were studied using the method of synchronous thermal analysis; the results obtained are presented in Figure 4. The process of $BaSn(OH)_6$ thermolysis includes two stages of dehydration, which correspond to endothermic effects: a weak one with a maximum at 160 °C and a strong effect at $T_{max} = 270$ °C. The dehydration reaction is indicated by a change in the ionic current of the mass spectrometric sensor corresponding to the release of water molecules with an atomic mass of 18 amu. The dehydration process is fully completed at a temperature of nearly 500 °C and can be described by the equations:

$$BaSn(OH)_6 \rightarrow BaSnO_3 + SnO_2 + 3H_2O \tag{4}$$

$$SnO_2 \times xH_2O = SnO_2 + xH_2O$$
(5)



Figure 4. The change in mass (TG) and thermal effects (DSC) observed when the initial BaSn(OH)₆ sample is heated at a rate of 10 K·min⁻¹. The ion current values of the mass spectrometric sensor corresponding to the concentration of released water and CO₂ molecules are shown by blue and light green curves, respectively.

Taking into account that the initial sample contains $BaSn(OH)_6$, $BaCO_3$ (being in weight ratio 0.67:0.33), and amorphous phase $SnO_2 \times xH_2O$, the molar fraction of which is equal to the molar fraction of $BaCO_3$, it is possible to calculate the residual value of relative mass after full dehydration. These values are 86.9 wt.% and 89.8 wt.% for the limiting

values of the degree of hydration of tin dioxide x = 2 (tin acid) and x = 0 (anhydrous tin dioxide), respectively. The experimentally found value of the residual mass fraction is 88 wt.%, which corresponds to the value x = 1.24 or the calculated formula of hydrated tin dioxide SnO₂ × 1.24H₂O.

Upon further heating of the sample in the temperature range of 500–650 °C, an exothermic peak is observed. The thermal effect is accompanied by a symbatic release of carbon dioxide molecules with m/z of 44 amu, which is recorded using a mass spectrometric sensor (Figure 4), which suggests that the thermal effect is caused by the occurrence of the chemical reaction

$$BaCO_3 + SnO_2 \rightarrow BaSnO_3 + CO_2, \tag{6}$$

in which barium carbonate, formed as a result of reaction (3), reacts with tin dioxide as the product of the amorphous $SnO_2 \times xH_2O$ dehydration. Taking into account the weight fraction of barium carbonate in the initial mixture (33 wt.%) and the equality of molar fractions of BaCO₃ and SnO₂, it is possible to calculate the limiting value of the relative mass of the product after the dehydration reactions (4) and (5) and CO₂ elimination (6). The calculated value, 84.9 wt.%, is close to the experimental value of 85.3 wt.%, which indicates the adequacy of the interpretation of the thermogravimetric analysis data.

The results of diffraction studies, shown in Figure 5, agree well with the data of thermal analysis. On the diffractogram obtained after heating the sample at 500 °C, i.e., after complete dehydration of the sample, there are only reflections related to the BaCO₃ witherite phase, which was initially contained in the sample (Figure 5, curve 2). Consequently, the dehydration products, BaSnO₃ and SnO₂, formed as a result of reactions (4) and (5) at this temperature are X-ray amorphous.



Figure 5. X-ray diffraction patterns of the initial sample (curve 1) and thermolysis products obtained at temperatures of 500 (curve 2), 600 (curve 3), and 700 $^{\circ}$ C (curve 4).

After heating the sample at 600 °C, the reflections related to the crystalline BaSnO₃ phase appear on the diffractogram, and the intensity of the diffraction peaks of the witherite BaCO₃ phase decreases significantly. According to the data of thermal analysis at this temperature, the exothermic effect and chemical reaction (5) with the formation of CO₂ are observed. These processes are associated with the crystallization process, the transition of the amorphous phase of barium stannate into the crystalline phase, and the formation of a nanocomposite, which is a mixture of BaSnO₃ with residual unreacted nanocrystalline BaCO₃ (Figure 5, curve 3). At further increase of the heating temperature up to 700 °C, the reaction (6) comes to an end, and the diffractogram of the sample (Figure 5, curve

4) corresponds to monophasic barium stannate with the structure of perovskite with a cubic unit cell (symmetry space group Pm3m). The lattice parameter of the obtained sample a = 4.1139 ± 0.0002 Å agrees with the literature data (PDF4, card no. 015-00780 and 03-00675) [64,70,71].

A comparison of electron microscopic images of the sample heated at 700 °C (Figure 6) and the original sample (Figure 3) shows that heating the sample leads to an unusual change in its morphology. Initially, aggregated particles covered with a rough film turn into an array of nanorods with a thickness of 10–50 nm and a length of a few microns after heating. This change in morphology can be explained by two processes: the formation of pseudomorphosis with a preferred orientation of particles during the dehydration of the initial BaSn(OH)₆ crystallites and the subsequent selective crystallization of the amorphous phases on the end surfaces of the pseudomorphosis. As a result, the impurity phases BaCO₃ and SnO₂·xH₂O localized on the surface of crystallites are removed from most of the surface and recrystallize in the end region of the pseudomorphosis. Finally, the particles of the pseudomorphosis become thinner and longer, forming nanorods.



Figure 6. (**a**,**b**) Scanning electron microscopy images of the BaSnO₃ sample obtained after heating BaSn(OH)₆ at 700 °C at various magnifications.

The analysis of FT spectra of the synthesized compounds allows us to confirm their composition and some features of their structure. The characteristic bands in the spectra were identified based on the literature data [72,73]. The FTIR spectra of the obtained samples of barium hydroxanthanate BaSn(OH)₆ (Figure 7, curve 1) and barium stannate BaSnO₃ (Figure 7, curve 2) agree with those obtained earlier [74]. The spectrum of $BaSn(OH)_6$ clearly shows a broad band in the region of \sim 562 cm⁻¹ corresponding to the vibrations of Sn-O bonds. The absorption band in the frequency region of ~750 cm⁻¹ is characteristic of bonds of more than one type of Ba-O and Sn-O-Ba groups. A series of bands in the 875–980 cm⁻¹ region corresponds to deformation vibrations of Sn-OH groups having partially ionic character [73,75]. The appearance of bands at ~1475 and 1254 cm⁻¹ indicates the presence of carbonate impurities in the sample, and the presence of these peaks at different frequencies can be explained by the conjugate motion of C-O and C=O bonds. Carbonates, mainly $BaCO_3$, can also be formed as a result of the absorption of carbon dioxide from the atmosphere directly during FTIR spectra [76]. The broad absorption of medium intensity at 1630–1750 cm⁻¹ definitely indicates the presence of water, while the broad band of valence vibrations v(OH) in the region at ~3410 cm⁻¹ shows the presence of hydroxyl groups in the composition of the obtained $BaSn(OH)_6$ precursor (Figure 7, curve 1).



Figure 7. FTIR absorption spectra of $BaSn(OH)_6$ (1) and $BaSnO_3$ (2).

In the FTIR spectrum of BaSnO₃ (Figure 7, curve 2), a strong band at 715 cm⁻¹ is observed, related to the symmetric valence vibrations of Sn-O bonds. The presence of physically adsorbed moisture (δ (OH) strain vibrations) is also recorded above 1630 cm⁻¹. These bands decrease their intensity as a result of the dehydration of the sample during heat treatment at 600 °C, as evidenced by the mass loss from thermogravimetry results. It was found that as a result of exposure of the BaSnO₃ sample to air, a broad diffuse absorption band in the region of ~3410 cm⁻¹ corresponding to the valence vibrations of ν (H₂O) is again recorded in the IR spectrum.

Table 1 shows the results of studies of the textural properties of the obtained samples calcined at different temperatures for 4 h. It can be seen that the pseudomorphosis formed during the thermolysis of BaSn(OH)₆ is characterized by high values of specific surface area and the presence of mesopores with sizes in the range of 2–6 nm. With increasing heating temperature, the values of specific surface area monotonically decrease.

Heating Temperature, °C	110	500	600	700
Phase composition	$BaSn(OH)_6$, $BaCO_3$, amorphous phase $SnO_2 \times xH_2O$	BaCO ₃ , amorphous phases BaSnO ₃ and SnO ₂	BaSnO ₃ , BaCO ₃ (traces)	BaSnO ₃
Specific surface area, m ² ·g ⁻¹	59	43	23	15
Pore size, nm	4.4	5.8	3.3	2.6

Table 1. Values of specific surface area and pore size of samples as a function of heating temperature.

The decrease in the specific surface area of composites during calcination is associated with the growth of the grain size. The crystallite size L can be estimated from the known values of specific surface area S' using a simplified expression obtained for spherical or cubic particles:

$$L=\frac{6}{\rho\times S},$$

where ρ is the density of the substance (for BaSnO₃ the value of $\rho = 7.236 \text{ g} \cdot \text{cm}^{-3}$). The evaluation shows that by increasing the heating temperature from 600 °C to 700 °C, the size of BaSnO₃ particles increases from 36 to 55 nm, which is close to the corresponding values estimated from the broadening of diffraction peaks on diffractograms. Further, the sample of barium stannate obtained by heating the initial sample at 700 °C was used as an oxide additive for the preparation of proton composite solid electrolytes.

3.3. Study of Transport Properties of Composites

Cesium hydrosulphate exists in a low-temperature (LT) monoclinic phase (spacegroup P2₁/m) at room temperature, which contains statistically symmetric hydrogen bonds organized in infinite (HSO₄–)_n chains. At 141 °C, CsHSO₄ transforms to the high-temperature superprononic tetragonal phase (I4₁/amd) with a conductivity change from 10^{-6} up to 3×10^{-2} S·cm⁻¹ and proton transfer numbers equal to one [77]. Figure 8 shows temperature dependences of the conductivity of pure CsHSO₄ and composites (1 – x)CsHSO₄-xBaSnO₃ of different compositions (where x-mole fraction). As seen, at low temperatures, the introduction of a heterogeneous additive leads to a significant (up to 2.5 orders of magnitude) conductivity rise with an increase in the BaSnO₃ mole fraction up to x = 0.2 (13.2 vol.%). The conductivity enhancement depends markedly on the BaSnO₃ additive concentration.



Figure 8. Temperature dependence of the conductivity of pure CsHSO₄ and composite systems (1 - x)CsHSO₄-xBaSnO₃.

Accordingly, the magnitude of the conductivity jump at the phase transition decreases with increasing x; the conductivity jump due to the phase transition becomes much smoother and shifts to the temperature region of ~85 °C. The shift of the phase transition temperature indicates the stabilization of the high-temperature phase in the low-temperature region. The proton conductivity of the composite $0.8CsHSO_4-0.2BaSnO_3$ is 3×10^{-3} S/cm⁻¹ at 160 °C. With further growth of the additive fraction up to x = 0.4 (28.3 vol.% of BaSnO_3), the conductivity decreases both in the high-temperature and low-temperature regions. The activation energy of conductivity decreases to 0.47 eV. The superionic phase transition completely disappears, and there is only a slight change in the slope at 85 °C on the temperature dependence. The conductivity of the high-temperature

phase decreases with increasing additive fraction by an order of magnitude at x = 0.2 and by about 1.5 orders of magnitude at x = 0.4 (see Figure 8). The observed composite effect is similar to $(1 - x)CsHSO_4-xSiO_2$ (or TiO₂) systems; however, the conductivity enhancement is somewhat different [41–43].

X-ray diffraction data (Figure 9) show that the diffraction pattern of the composite may be represented as a sum of contributions of individual phases. The structure of the CsHSO₄ salt is preserved in the composite systems with a significant decrease in the intensity of reflections and their significant broadening, which may be caused by the dispersion and partial amorphization of the salt in (1 - x)CsHSO₄-xBaSnO₃ composites due to the surface interaction between acid salt and the additive. With the increase in the additive fraction in the composites, the X-ray diffraction contribution of BaSnO₃ (marked with an asterisk) becomes more pronounced.



Figure 9. X-ray diffraction patterns of composites $(1 - x)CsHSO_4$ -xBaSnO₃ of different compositions in comparison with the parent compounds.

4. Conclusions

In this work, we have demonstrated the possibility of the preparation of nanocrystalline barium stannate BaSnO₃ via the thermal decomposition of barium hexahydroxostannate precursor BaSn(OH)₆. The latter, characterized by rod morphology up to 10–50 µm in size, was synthesized via hydrolytic precipitation from solutions of barium chloride BaCl₂ and sodium stannate Na₂SnO₃. It was shown that thermolysis at a temperature of about 270 °C resulted in the formation of an X-ray amorphous multiphase product consisting of amorphous phases of hydrated tin dioxide and barium stannate, as well as an impurity of crystalline barium carbonate BaCO₃. During thermal treatment of the sample at 600 °C, barium stannate (with a specific surface area of 23 m²/g) with traces of barium carbonate is formed. At temperatures of 600–700 °C, the BaSnO₃ phase crystallizes with a particle size of 36–55 nm. As a result of the study, it is shown that heating at temperatures of 600–700 °C is the optimal condition for obtaining single phase and highly dispersed barium stannate.

The proton conductivity of composite systems of composition $(1 - x)CsHSO_4$ -xBaSnO₃ (x = 0.2–0.4) has been investigated. The crystal structure of CsHSO₄ is preserved in the composite systems with a significant decrease in the intensity of reflexes and their significant broadening due to dispersion and partial amorphization of the salt in $(1 - x)CsHSO_4$ -xBaSnO₃. As a result of the conductivity study, it is shown that the introduction of the heterophase BaSnO₃ additive leads to a significant (up to 2.5 orders of magnitude) increase in conductivity in the low-temperature region with an increasing mole fraction

of BaSnO₃ up to x = 0.2. An increase in the conductivity is accompanied by the shift of the superionic phase transition to a lower temperature region and its practical disappearance at x = 0.4. The proton conductivity of the composite 0.8CsHSO₄-0.2BaSnO₃ reaches 3×10^{-3} S·cm⁻¹ at 160 °C. This will allow the use of this material in electrochemical applications. Thus, it is demonstrated that highly dispersed barium stannate BaSnO₃ is a suitable heterogeneous additive in composite solid electrolytes. CsHSO₄-BaSnO₃ composite solid electrolytes can be used as solid electrolyte membrane materials for hydrogen production in the medium-temperature region. This approach may prove to be competitive with alternative technologies.

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