Study of the Influence of Anionic Composition of Salts on Synthesis of Zinc Orthostannate by the Sol-Gel Method

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Abstract. The effect of anionic composition of zinc salts upon interaction with tin (IV) chloride on preparation of zinc orthostannate by the sol-gel method was studied. It was determined that the minimum temperature for the synthesis of zinc orthostannate was 800 °C. It was revealed that when zinc chloride was used, tetraaminezinc chloride was formed, which decomposed during firing. When zinc acetate or zinc sulfate was used, the synthesis of zinc orthostannate was not fully completed up to 1100 °C.

1 Introduction

Depending on the ratio of elements in ZnO-SnO₂ system, there are two compounds: zinc metastannate ZnSnO₃ with a perovskite structure and zinc orthostannate Zn₂SnO₄ with a reverse spinel structure [1-3]. Zinc orthostannate, which is an n-type semiconductor, due to its low toxicity, high electron mobility, resistance to high temperatures and thermodynamic stability is used in gas analyzers, photocatalysts, photovoltaic devices, transparent electrodes and lithium batteries [4-6]. Recently, zinc orthostannate has been used as a buffer layer in solar cells due to its high optical transparency and significant resistivity, which makes it a promising material for new highly efficient solar cells [7, 8].

Zinc orthostannate is obtained by various methods: solid-phase synthesis from oxides [9], electrochemically [10], by co-precipitation of salts [11, 12]. The sol-gel method is promising for the synthesis of ultradispersed zinc orthostannate powder that is active for sintering. A feature of the sol-gel method is the possibility of obtaining fragments of oxides of complex composition in a gel, which minimizes diffusion obstacles during synthesis, shortens the time of its implementation, and promotes a uniform distribution of components at the molecular level [13, 14]. In addition, the use of the sol-gel method makes it possible to reduce production costs by reducing the synthesis temperature, as well as to obtain materials with desired properties, such as phase composition, structure, specific surface area, etc.

Modification of the sol-gel technology based on the synthesis of a gel of a high molecular weight polymer and distribution of a homogeneous true solution of one or several components in it, followed by drying and calcination, enables one to obtain monodisperse powders of metal oxides of simple or complex composition [15, 16].

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The study is an observation of the effect of anionic composition of zinc salts on the synthesis of zinc orthostannate by the sol-gel method when interacting with tin (IV) chloride.

2 Experimental part

For the study, we used the following salts: $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, ZnCl_2 , $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, as well as NH_4OH and $(\text{NH}_4)_2\text{CO}_3$ as precipitants. The taken substances had a level of purity 'Purified' and higher.

For preparation of gels of a mixture of tin (IV) and zinc salts $\text{SnCl}_4 + \text{Zn}(\text{NO}_3)_2$; $\text{SnCl}_4 + \text{Zn}(\text{CH}_3\text{COO})_2$; $\text{SnCl}_4 + \text{ZnSO}_4$, taken in the stoichiometric ratio $\text{ZnO} : \text{SnO}_2 = 2 : 1$, taking into account losses on ignition, were dissolved in a previously prepared 8%* solution of polyvinyl alcohol upon heating (40 - 50 °C) and stirring. To obtain hydroxides, an aqueous solution of ammonia or a saturated aqueous solution of ammonium carbonate was poured into the resulting mixture to a value of $\text{pH} = 7 - 8$, while precipitation and intense gas evolution were observed. The resulting gels were kept for 24 h at room temperature to complete gelation process, after which they were dried to constant weight using microwave radiation (at a power of 800 W). Xerogels were fired in a furnace in the temperature range from 700 to 1100 °C with a holding time of 2 h. The phase composition of the samples was studied using a DRON-3M X-ray unit. Radiation - $\text{CuK}\alpha$, detector - scintillation counter. To identify crystalline phases, the Joint Committee on Powder Diffraction Standards international card index was used.

3 Discussion of the results

Based on the literature data [9], the synthesis of zinc orthostannate from tin (IV) and zinc oxides occurs at a temperature of 1300 °C. When using chemical methods, for example, coprecipitation of salts, due to formation of small defective particles, the synthesis temperature of zinc orthostannate decreases to 950 °C [12]. To study the possibility of obtaining orthostannate by the sol-gel method, the temperature range of 800-1100 °C was chosen, which was explained by the expectation of a decrease in the temperature of the beginning of synthesis due to the formation of ultradispersed particles active during sintering. Since the use of alkalis to obtain hydroxides from initial salts in the case of the sol-gel technology will be unjustified due to the further need to purify the powder from alkali metal cations and their negative impact on the electro-physical properties of the resulting gels and final powders, an aqueous solution of ammonia was initially chosen as a precipitant, which is associated with its availability, as well as the ease of removal of by-products formed during hydrolysis of salts with the formation of α -stannic acid and zinc hydroxide (Schemes 1-4).

During subsequent firing, α -stannic acid decomposes to tin (IV) oxide, and zinc hydroxide to zinc oxide, after which zinc orthostannate is formed (Schemes 5-7). The onset of formation of zinc orthostannate is observed at 1000 °C, which follows from the results of XRF (Fig. 1).

Fig. 1. XRD results for powders obtained using tin (IV) chloride, zinc nitrate, and aqueous ammonia as a precipitant

When tin (IV) chloride and zinc chloride are used as starting components, the target product is not formed during precipitation with an aqueous solution of ammonia. Obviously, this is due to peculiarities of the chemistry of zinc, which is an amphoteric metal and, when interacting with ammonia, forms a hydroxide (Scheme 8), which subsequently dissolves in an excess of ammonia with the formation of tetraminezinc chloride (Scheme 9). The resulting complex salt decomposes during firing to zinc chloride ($T_b = 732^\circ\text{C}$) and ammonia (Scheme 10).

Thus, the further use of ammonia as a precipitant for tin (IV) and zinc chlorides is impractical.

Subsequent studies were carried out using a saturated aqueous solution of ammonium carbonate, which underwent hydrolysis to form ammonium bicarbonate (Scheme 11). During thermolysis, ammonium bicarbonate completely decomposes with formation of ammonia, carbon dioxide and water, which eliminates the influence of foreign ions on gelation process and the properties of powders. The reactions of ammonium bicarbonate with tin (IV) chloride, zinc nitrate, zinc chloride, zinc acetate and zinc sulfate are shown in Schemes 12-16, respectively.

As with the use of ammonia as a precipitant of tin (IV) chloride and zinc nitrate, formation of zinc orthostannate when using ammonium bicarbonate is observed at temperatures of 1000 °C and above (Fig. 2).

Fig. 2. XRF results for powders obtained using tin (IV) chloride, zinc nitrate, and an aqueous solution of ammonium bicarbonate as a precipitant

The yield of zinc orthostannate when using ammonium bicarbonate is lower than when using ammonia, which is associated with a higher pH value of the latter and, therefore, a deeper course of precipitation reactions.

The use of ammonium bicarbonate for the precipitation of tin (IV) chloride and zinc chloride made it possible to obtain zinc orthostannate, in contrast to experiments with ammonia (Fig. 3).

Fig. 3. XRF results for powders obtained using tin (IV) chloride, zinc chloride, and an aqueous solution of ammonium bicarbonate as a precipitant

It follows from the radiographs that formation of the zinc orthostannate phase is completed at 1100 °C. The yield of the target zinc orthostannate was 20%. Apparently, this is due to the fact that when zinc chloride interacts with ammonium bicarbonate, zinc

hydroxide is formed, which, in an excess of the precipitant, does not completely transform into a complex compound (Schemes 14, 17), but remains in the system, and decomposes to zinc oxide, which, in turn, reacts with tin (IV) oxide to form zinc orthostannate.

Further studies were carried out using tin (IV) chloride and zinc acetate. The obtained X-ray diffraction patterns (Fig. 4) show that the phase of zinc orthostannate is formed already at 800 °C, but the synthesis does not proceed to the end: up to a temperature of 1100 °C, zinc and tin oxides are present.

Fig. 4. XRF results for powders obtained using tin (IV) chloride, zinc acetate, and an aqueous solution of ammonium bicarbonate as a precipitant

As in the case of zinc acetate, when zinc sulfate is used as the initial salt upon interaction with tin (IV) chloride, the formation of zinc orthostannate phase is observed at 800 °C, but the reaction does not proceed completely, which follows from the XRF results, in which at all temperatures tin and zinc oxides are present (Fig. 5).

Fig. 5. XRF results for powders obtained using tin (IV) chloride, zinc sulfate, and an aqueous solution of ammonium bicarbonate as a precipitant

It is obvious that for the reaction of zinc orthostannate formation when using tin (IV) chloride, as well as zinc acetate or sulfate, it is necessary to select the heat treatment mode and use a longer holding time at the studied synthesis temperatures.

In the synthesis of zinc orthostannate from tin (IV) chloride and zinc nitrate in the temperature range 1000-1100 °C, in addition to the target product, tin (IV) oxide is present, while zinc oxide is consumed completely (Fig. 1, 2). This may be due to the fact that zinc metastannate preliminarily formed in the system at 750 °C transforms into zinc orthostannate with the formation of tin (IV) oxide (Scheme 18) [17].

On the other hand, the literature describes the possibility of influence of the difference in the diffusion coefficients of cations on the stoichiometry of complex oxides. During the synthesis of complex oxides from a mixture of oxides taken in a stoichiometric ratio and the vacancy diffusion mechanism, due to the difference in the diffusion coefficients of the metals forming the oxides, a solid oxide solution containing a more slowly diffusing cation is initially formed in the complex oxide. The second cation forms a separate or enriched phase with it. The appearance of a solid solution (deviation from stoichiometry) causes formation of oxygen and cation vacancies, the diffusion rate of which in the complex oxide is higher [18]. Consequently, to obtain a complex oxide with a composition close to stoichiometric, it is necessary to select a heat treatment mode, which is the subject of separate studies.

4 Conclusions

Thus, as a result of the study, it was found that:

1. The use of tin (IV) chloride and zinc chloride as starting components for obtaining zinc orthostannate by the sol-gel method is impractical;
2. When tin (IV) chloride interacts with zinc acetate or zinc sulfate, the phase of zinc orthostannate is formed at relatively lower temperatures, but the reaction does not proceed completely up to 1100 °C, and therefore their use is irrational;
3. When using tin (IV) chloride and zinc nitrate, the target zinc orthostannate is formed at 1000 °C, which is confirmed by XRF data;
4. It is preferable to use an aqueous solution of ammonium bicarbonate as a precipitant.

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