Sol-gel Synthesis of Materials in the System $ZnO - SnO_2$

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Abstract. The effect of the anionic composition on the preparation of powder material in the $ZnO - SnO_2$ system by the sol-gel method has been investigated. It was found that the best composition of zinc orthostannate is obtained using zinc sulfate and tin (IV) chloride. According to the data of X-ray phase analysis, the optimum temperature for the synthesis of the material is 1050 °C.

1 Introduction

Binary system $ZnO - SnO_2$, depending on the ratio of the initial components, can represent two compounds: $ZnSnO_3$ – zinc metastannate with a perovskite structure and Zn_2SnO_4 – zinc orthostannate with a reverse spinel structure [1, 2]. Zinc orthostannate is an electron semiconductor due to its low toxicity, high temperature stability and high electron mobility. Zinc orthostannate material (Zn_2SnO_4) can be used as lithium batteries [3], photocatalysts [4] and gas sensors [5].

The most promising methods for preparing zinc orthostannate are the sol-gel method, solid-phase synthesis from oxides [6], and co-precipitation of salts [7]. The sol-gel method is a well-controlled, low-temperature, and high-performance method for obtaining homogeneous ultradispersed nanostructures.

The sol-gel process is the best chemical route used for the low-temperature synthesis of one- and multicomponent ceramic systems in the form of ultradisperse powders, thin-films, and dense abrasive materials.

The study is a comparison of the results of the interaction of various zinc salts with tin (IV) chloride and the further preparation of zinc orthostannate by sol-gel synthesis.

2 Experimental procedure

The synthesis of the sol-gel method of $ZnO - SnO_2$ powder was carried out using tin (IV) chloride and zinc salts of different anionic compositions: $(CH_3COO)_2Zn \times 2H_2O$, $Zn(NO_3)_2$, $ZnSO_4 \times 7H_2O$ и $ZnCl_2$. The ratio of the starting salts was $2Zn : Sn$. Dissolution of salts was carried out with isobutanol at low-temperature. The main goal at this stage was to obtain 2 zinc and tin salts dissolved in isobutanol.

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Then the solutions of 2 salts were mixed using a magnetic stirrer. Next, an aqueous solution of ammonia was poured in a deficiency, until a curdled precipitate appeared and from the environment to the alkaline side (Equation 1, 2).

The resulting precipitate was placed in an oven at 80 ° C for a day. The synthesis of powders was carried out in a furnace in an air atmosphere at temperatures of 800, 850, 900, 950, 1000, 1050, 1100, 1150, 1200, 1250, 1300 ° C, heating rate 2 ° C / min, exposure at final temperatures was 2 hours (Equation 3, 4, 5).

The phase composition of the obtained powders was investigated using X-ray phase analysis.

2.1 X-ray diffraction analysis (XRD)

The phase composition of the obtained powders was investigated using X-ray diffraction analysis. When zinc and tin (IV) chloride are used as starting components (Fig. 1), no product of the co-reaction is formed (Equation 6.). This may be due to the reactivity of zinc chloride, which forms a complex compound tetraamminezinc (II) chloride [8], which further decomposes into zinc chloride, which does not interact with tin (IV) oxide (Equation 7).

Fig. 1. Comparison of XRD analysis of powders obtained using tin (IV) chloride and zinc chloride at 900 - 1200 °C

In fig. 2 and 3, nitrate and acetate are used as starting zinc salts. In fig. 3, the formation of a product is observed at 1000 °C. The presence of a nitrate and acetate group in the zinc compound promotes the formation of a complex compound tetraamminezinc hydroxide (II), which upon heating forms zinc oxide and then reacts with tin oxide (IV) to form zinc orthostannate.

Fig. 2. Comparison of XRD analysis of powders obtained using tin (IV) chloride and zinc nitrate at 1000 - 1300 °C

Fig. 3. Comparison of XRD analysis of powders obtained using tin (IV) chloride and zinc acetate at 1100 - 1200 °C

Based on the results obtained, the synthesis of orthostannate from zinc and tin oxides occurs at 1050 °C using zinc sulfate and tin chloride as starting salts. In fig. 4, the best crystallization of the orthostannate phase is observed. Zinc sulfate is more reactive compound than other salts.

Fig. 4. Comparison of XRD analysis of powders obtained using tin (IV) chloride and zinc sulfate at 950 - 1250 °C

The best crystallization of the product is observed at 1050 °C and using zinc sulfate and tin (IV) chloride as starting salts. This may be due to the activity of the anionic composition of the zinc salt. It is assumed that the more active the acid forming the acidic residue of the salt, the better the reaction of interaction between SnO_2 и ZnO в Zn_2SnO_4 .

2.2 Scanning Electron Microscopy (SEM)

In fig. 5 (a), noticeable recrystallization of grains is observed. When the temperature of the material rises to 1200 °C, the grains in the polycrystalline structure begin to coalescence of particles. Good crystal growth steps are also noticeable. The structure of the polycrystal is represented by intergrown cubic crystals with a size of 2 to 5 μm, which form screw dislocations (Fig. 5 (b)). In some crystals, the distribution of cracks between crystals and along the grain structure is noticeable (Fig. 5 (b)). As the temperature rises, the crystals grow very actively.

Fig. 5 (a, b) Photographs of the microstructure of the Zn_2SnO_4 material synthesized from $ZnSO_4$ and $SnCl_4$. Firing temperature 1200 °C. Magnifications 3000× and 8000×.

A photograph of the microstructure of a material synthesized from zinc chloride and tin (IV) chloride is shown in Fig. 6. The structure is presented in the form of unbound grains of

crystals of zinc and tin oxide, cylindrical, with an average size of 0.5 - 1 μm . This material is less reactive than others.

Fig. 6. Photograph of the microstructure of the Zn_2SnO_4 material synthesized from ZnCl_2 and SnCl_4 . Firing temperature 1200 $^\circ\text{C}$. Magnification 8000 $\times$.

In fig. 7. shows the material synthesized from zinc acetate and tin (IV) chloride. Significant crystal growth is observed. The polycrystalline structure is composed of spherical grains with an average size of 0.5 to 1.5 μm .

Fig. 7. Photograph of the microstructure of the Zn_2SnO_4 material synthesized from $(\text{CH}_3\text{COO})_2\text{Zn}$ and SnCl_4 . Firing temperature 1200 $^\circ\text{C}$. Magnification 8000 $\times$.

In fig. 8. shows the material synthesized from zinc nitrate and tin (IV) chloride. Good crystallization of the material is observed. A stepwise growth of crystals is observed. The polycrystalline structure of the material is presented in the form of prismatic and tetrahedral crystals with an average size of 0.5 to 1.5 μm , which are added together to form screw dislocations.

Fig. 8. Photograph of the microstructure of the Zn_2SnO_4 material synthesized from $Zn(NO_3)_2$ and $SnCl_4$. Firing temperature 1200 °C. Magnification 8000×.

3 Conclusions

When zinc and tin (IV) chloride is used as starting components, the product of the joint reaction is not formed. This may be due to the reactivity of zinc chloride, which forms a complex compound tetraamminezinc (II) chloride.

Materials synthesized from zinc nitrate and zinc acetate form reaction products at 1000 °C. The presence of a nitrate, sulfate and acetate group in the zinc compound promotes the formation of a complex compound tetraamminezinc (II) hydroxide, which in turn, upon heating, forms zinc oxide and then reacts with tin (IV) oxide to form zinc orthostannate.

The microstructure of the material, synthesized from sulfate, nitrate, zinc acetate and tin (IV) chloride, is represented by well-defined crystals. The polycrystalline structure consists of bound grains of various shapes, depending on the anionic composition of the initial components. A clear recrystallization is noticeable after a temperature of 1200 °C.

When using zinc chloride and tin (IV) chloride as starting components, poor crystal growth is observed. The structure is represented by unbound grains consisting of zinc oxide and tin (IV). Zinc chloride is less reactive than other salts.

The best crystallization of the product is observed at 1050 °C and the use of sulfatac and tin (IV) chloride as starting salts.

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