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Cadmium Stannates Synthesis via Thermal Treatment of Coprecipitated Salts

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ABSTRACT

Cadmium meta- and orthostannate were synthesized by thermal treatment using the coprecipitation method. Tin (*IV*) *chloride*, *cadmium acetate were used as the initial components*, *the ammonium carbonate was a precipitant. The coprecipitated compounds and the thermolysis products were analyzed by TGA/DSC methods*, *the thermal treatment samples were studied by XRD and SEM. The formation of proper products in soft thermal treatment conditions was confirmed. The stannates formation in terms of submicron sized particles was observed by microscopial investigation.*

Keywords: *Cadmium Metastannate*, *Cadmium Orthostannate*, *Chemical Precipitation*, *Powders*, *Thermolysis*, *Synthesis*

1. Introduction

$CdSnO_3$ и Cd_2SnO_4 cadmium stannates are interesting due to their optical and electrical properties. These compounds, related to so-called optically limpid conductive oxides, are used as thin films which are transparent in visible spectrum part [1], in semiconductor technology [2], as sensitive elements of chemical sensors [3-5] etc.

Different ways of stannates obtaining are used depending on a purpose. Thin films are prepared by means of aerosol of cadmium and tin compounds solutions composition pyrolysis [6], substrate covering with metalorganic compounds followed their thermolysis [7], sodium stannate and water-soluble cadmium salt ion-exchanging reaction [8], etc. For stoichiometric products powders obtaining the conventional method of solid-phase synthesis from prepared powder oxides [5,9,10] is used. The method is simple but rather time-consumimg because of the necessity to perform some intermediate mechanical grinds and also requires high temperatures and long time of synthesis. Such product is not optimal e.g. for electroconductive composite materials technologies because they require high dispersibility and statisticcally homogeneous stannate phase distribution [11]. Stannate synthesis of fine-grained form with soft temperature conditions and of short duration is desirable for electroconductive composite materials technologies.

Evidently there is no data for kinetics of cadmium stannates synthesis. We can meet with some descriptions of syntheses e.g. in [9,12,13]: they are carried out in the open air under 1073 - 1273 K temperature range using long stepped anneals for volatile cadmium oxide loss reduction. On the other hand it is well known that high dispersibility of initial powder components substantially accelerates kinetics and decreases the temperature of efficient solid-phase synthesis. It also concerns the examined compounds [14].

Thus, the work is devoted to study the potential of cadmium meta- and orthostannate powder forms synthesis under low temperatures by means of thermal treatment of tin and cadmium thermally unstable salts coprecipitated composition.

2. Experimental Part

The decomposition of thermally unstable salts-precursors to obtain $CdSnO_3$ and Cd_2SnO_4 was used. The powder precursors with Cd:Sn molar ratios 1:1 and 1:2 were prepared by a chemical coprecipitation. Analytically pure reagents of $SnCl_4 \cdot 5H_2O$, $Cd(CH_3COO)_2 \cdot 2H_2O$ and $(NH_4)_2CO_3$ were used as starting materials. Solutions with 0.1 mol/L tin and cadmium salts, in stoichiometric ratios 1:1 and 2:1, for $CdSnO_3$ and Cd_2SnO_4, accordingly, were mixed and then a 0.2 mol/L solution $(NH_4)_2CO_3$ was added. White fine-grained precipitates, dried for 10 h at temperature 383 K. Further products were calcinated in the open air at 783, 873, 973, 1073, 1173, 1223 K for an hour.

Thermal, XRD, elemental and microscopic analyses of obtained samples were carried out at different stages.

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Elemental analysis was performed by means of XRF using the ARL Advant`X (Thermo) spectrometer (Joint Use Center SFU) with an Rh anode X-ray tube. Quantitative elements content was evaluated by fundamental parameter method using the UniQuant 5. Thermal decomposition processes of precipitates were studied by thermogravimetry (TG) and differential scanning calorimetry (DSC) methods using the synchronous thermal analysis STA Jupiter 449C (Netzsch) device (heating rate 10 K/min in flowing Ar atmosphere and a corundum crucible).

Thermal treatment products were studied by an X'Pert-Pro (PANalytical) X-ray diffractometer (XRD) with monochromatized Cu Kα radiation ($\lambda_1 = 0.15406$). The angular 2θ range of registration was from 5˚ to 80˚ with the step of 0.026˚. Micrographs were obtained using a JEOL JSM-7001F scanning electron microscope (Joint Use Center SFU).

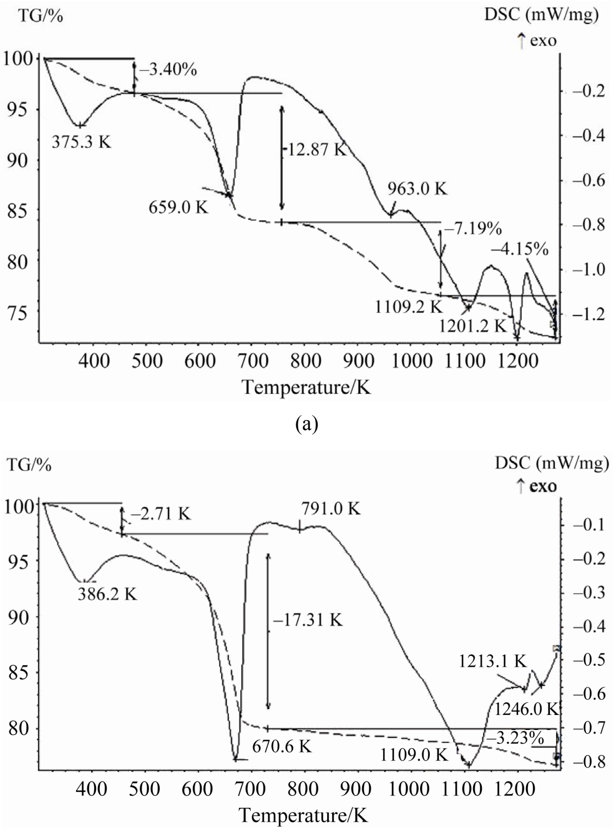
3. Results and Discussion

3.1. Thermal Analysis of Precipitated Salt Mixtures

The thermal behavior of Precipitated salts was investigated to obtain typical temperature intervals of the thermolysis. The TG and DSC curves for mixtures of $CdSnO_3$ and Cd_2SnO_4 proper compositions are presented in **Figure 1**. TG-curves are substantially different: $CdSnO_3$ mixture has two defined stages of weight loss and Cd_2SnO_4 mixture has only one. The first stage begins at the temperature of about 375 K and finishes at ~650 K for both systems. We can notice the overlapping of some thermal effects within this temperature range. First of all the crystal water loss and cadmium carbonate decomposition are possible during the process:

$$CdCO_3 = CdO + CO_2 \qquad (1)$$

The authors [15] recorded the intensive peak of precipitated cadmium carbonate decomposition at the temperature of 623 K. Our data are in accordance with their values.



(a)

(b)

Figure 1. TG (dotted line) and DSC (solid line) curves of precipitated salt mixtures for $CdSnO_3$ (a) and Cd_2SnO_4 (b) compositions.

For $CdSnO_3$ precursors the second stage of weight loss is observed in the range 780 K to 950 K. It is probably caused by tin (IV) compounds decomposition. It is well known that during the tin (IV) precipitation from water solutions the α-stannic acid $SnO_2·nH_2O$ is formed (n is closed to 1.8) [16]. Makeup precipitated α-$SnO_2·nH_2O$ is an X-ray amorphous phase but ageing and heating lead to water loss. Thus α-$SnO_2·nH_2O$ turns into β-$SnO_2·nH_2O$ ($n < 0.4$), which then detaches the rest of water step-by-step and crystallizes in SnO_2 form. This process finishes at 870 K [17]. Our results of weight loss value and temperature range correlate to the mentioned above. The absence of significant weight loss for Cd_2SnO_4 precursors in the range of 780 - 950 K (**Figure 1(b)**) is con- nected with powder sample keeping for a week before the experiment. It led to natural ageing of α-$SnO_2·nH_2O$ in the sample and its turning into β-$SnO_2·nH_2O$. Gradual weight decrease at the temperature above 1150 K in both cases is caused by cadmium oxide sublimation. And also crystallization thermal effects can be observed under the same conditions.

The results of X-ray fluorescence analysis for samples at different stages treatment are presented in **Table 1**. As you can see, low-temperature samples correspond to the specific composition. Thermal treatment temperatures higher than ~1000 K lead to substantial cadmium oxide evaporation and Cd: Sn molar ratio decreasing.

3.2. X-Ray Phase Analysis of the Products

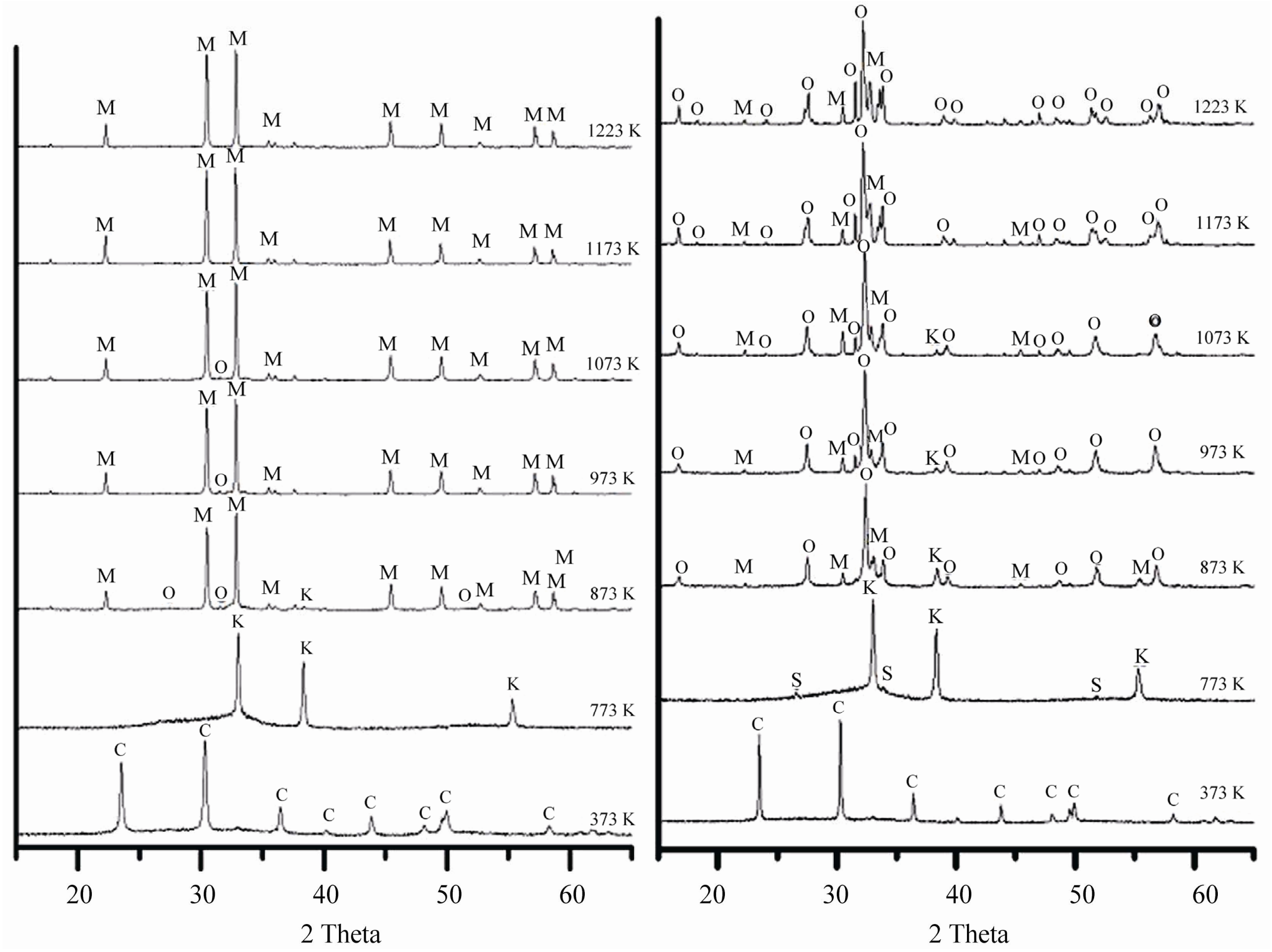
Both **Figure 2** and **Table 2** show the XRD results for powder mixtures with a specific compositions which were annealed at different temperatures. The initial dried mixture consists of only crystal phase of cadmium carbonate. X-ray amorphous phase corresponding to tin (IV) oxide is present at the sample which was annealed at

Table 1. Elemental composition (XRFA) of thermally treated powder mixtures.

Annealing temperature, K	molar fraction of the element		Cd:Sn ratio
	Cd	Sn	
$CdSnO_3$ proper composition			
Initial mixture	0.49	0.51	0.97
783 K	0.49	0.51	0.97
873 K	0.49	0.51	0.97
973 K	0.48	0.52	0.94
1073 K	0.47	0.53	0.88
1173 K	0.46	0.54	0.86
1223 K	0.46	0.54	0.86
Cd_2SnO_4 proper composition			
Initial mixture	0.66	0.34	1.96
783 K	0.66	0.34	1.96
873 K	0.66	0.34	1.96
973 K	0.66	0.34	1.96
1073 K	0.65	0.35	1.87
1173 K	0.64	0.36	1.77
1223 K	0.65	0.35	1.87

873 K. These results confirm the data of thermal analysis. The CdO phase formation comes to an end up to 670 K according to TGA data. It is also confirmed by XRF analysis. The Quantitative phase contribution is conditional with the X-ray amorphous phase presence in the sample. Such values are marked with "*" in **Table 2**.

XRF analysis results of specific composition Cd_2SnO_4 mixtures are presented in both **Figure 2(b)** and **Table 2**. The phase of tin dioxide is possible to be registered in Cd_2SnO_4 system in contrast to $CdSnO_3$ system. Starting from 873 K the samples contain both $CdSnO_3$ and Cd_2SnO_4 cadmium stannates. As the temperature increases the comparative amount of metastannate slightly increases too. It seems to be connected with the increasing of volatile CdO velocity elimination. Orthostannate is presented by two modifications: they are cubic modification and orthorhombic one. However the content of orthorhombic modification exceeds 5% at the temperature over 973 K only.



(a) (b)

Figure 2. X-ray diffraction patterns of $CdSnO_3$ (a) and Cd_2SnO_4 (b) proper composition powder mixtures annealed at given temperatures: O – Cd_2SnO_4 (cubic), O_1 – Cd_2SnO_4 (orthorhombic), M – $CdSnO_3$, K – CdO, C – $CdCO_3$, S – SnO_2.

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Table 2.Thermally treated powder mixtures composition (XRD).

Annealing temperature	mass fraction					
	$CdCO_3$	CdO	SnO_2	$CdSnO_3$	Cd_2SnO_4 (cubic)	Cd_2SnO_4 (orthorhombic)
			$CdSnO_3$ proper system			
without annealing	1*	-	-	-	-	-
773 K	-	1*	-	-	-	-
873 K	-	0.15	-	0.77	-	0.08
973 K	-	-	-	0.91	-	0.09
1073 K	-	-	-	0.99	-	0.01
1173 K	-	-	0.06	0.94	-	-
1223 K	-	-	0.05	0.91	0.04	-
			Cd_2SnO_4 proper system			
without annealing	1*	-	-	-	-	-
773 K	-	0.76*	0.24*	-	-	-
873 K	-	0.19	-	0.11	0.65	0.05
973 K	-	0.07	-	0.11	0.73	0.09
1073 K	-	0.08	-	0.13	0.71	0.08
1173 K	-	-	-	0.17	0.66	0.17
1223 K	-	-	-	0.16	0.66	0.18

Shortage of cadmium oxide, comparatively to assigned stoichiometry of $CdSnO_3$ and Cd_2SnO_4 compositions, is recorded in both involved systems in the samples at 1073 K and above what is caused by CdO sublimation. CdO loss in Cd_2SnO_4 system leads to phase composition change (**Table 2**) at the expense of $CdSnO_3$ metastannate formation.

Thus specific compositions synthesis completes during an hour at 873 K. In both cases the samples of the mixture contain some amount of CdO and improper stannate (**Table 2**).

The authors [9] studied of a cadmium stannates synthesis from prefabricated powders had evaluated phase ratios of CdO-SnO_2 and 2CdO-SnO_2 mixtures after six-hours-long annealing at the range 970 to 1420 K above. Cd_2SnO_4 appears in an equimolar mixture at about 970 K. At 1170 K orthostannate is absolutely synthesized and CdO is used up. Metastannate forms at 1170 K above:

$$Cd_2SnO_4 + SnO_2 = 2CdSnO_3 \qquad (2)$$

This process finishes at about 1340K and then $CdSnO_3$ decomposes into CdO and SnO_2. Cd_2SnO_4 synthesis in 2CdO-SnO_2 mixture comes to an end at about 1320 K. At 1320 K above Cd_2SnO_4 decomposes into $CdSnO_3$ and CdO.

Thus long time and temperature of about 1300 K is necessary to synthesize both stannates from prefabricated powder components. Though the processes laws of stannates synthesis from coprecipitated salts confirm the observations given in the work [9], they require lower temperatures and shorter time for thermal treatment.

Cd_2SnO_4 and $CdSnO_3$ obtaining in terms of individual phases requires the adjustment of firing regimes and formation of conditions preventing cadmium oxide volatilization. However practical application of such process of synthesis that gives the powder mixture with predominant content of proper cadmium stannates is possible e.g. in metalloxide electrocontact composites production when silver(copper)/oxide powder pressings sintering is combined with oxide phase synthesis. It provides high dispersion ability and statistical homogeneity of phase inclusions and also it does the production less power-consuming.

3.3. Microscopy of Powder Products

SEM-micropictures of $CdSnO_3$ and Cd_2SnO_4 powders thermally treated at 1223 K are presented in **Figure 3**. We can see the likeness of microstructure and the morphology of particles when comparing. The powders are rather massive, loose, weakly bonded agglomerates, formed from crystal particles in the submicron range of dispersibility (from ~50 - 100 nm to 1 μm).

4. Conclusions

The synthesis of $CdSnO_3$ and Cd_2SnO_4 by thermal treatment of thermally unstable tin and cadmium compositions were carried out. It allows to obtain fine-grained products in the form of submicron sized powders with predominant content of proper stannates for short period of time under soft temperature conditions. Decomposition of salt mixture components carries in wide temperature range but cadmium meta- and orthostannates formation generally completes at 873 K already. In spite of powder products complicated structure which includes both of stannates and tin and cadmium oxides, the given powder synthesis method can be used for metalloxide composite materials "*in-situ*" synthesis in practice. With

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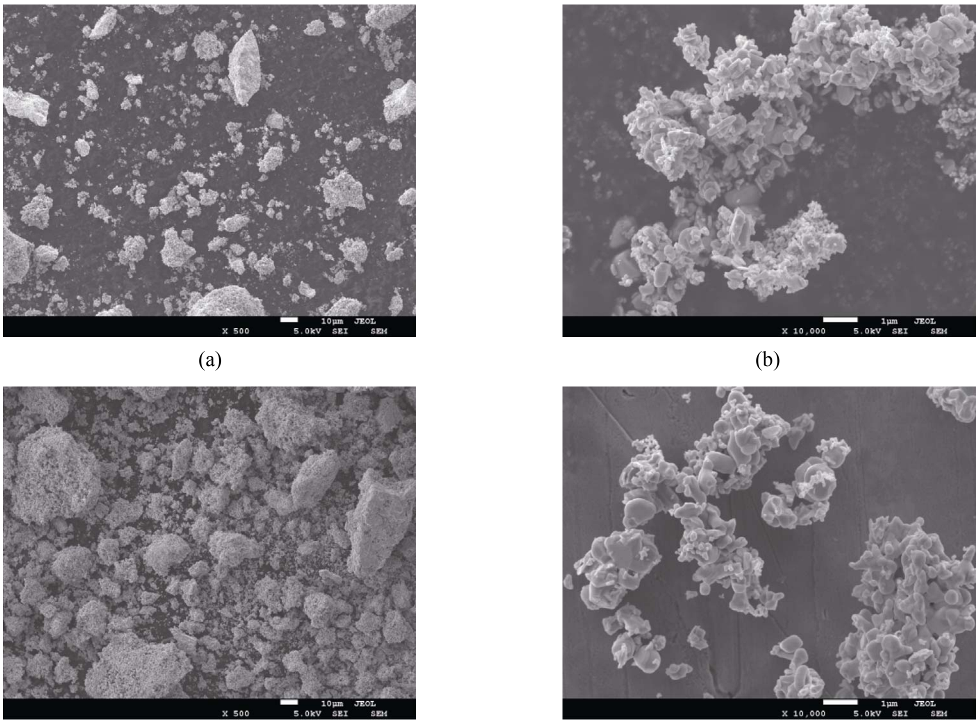

(a) (b)

(c) (d)

Figure 3. SEM-micropictures of $CdSnO_3$ (a, b) and Cd_2SnO_4 (c, d) proper composition powders (zoomed ×500 and ×10000).

all this the technology is simplified substantially and time and energy charges for the production are reduced.

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