

UNKNOWN THERMAL PROPERTIES OF ZnSb_2O_6 AND $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ COMPOUNDS

Reactivity of $\alpha\text{-Sb}_2\text{O}_4$ with ZnO on heating in air

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The investigations by XRD, DTA/TG and IR methods show that two compounds: ZnSb_2O_6 and $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ are formed in the $\text{ZnO}\text{-}\alpha\text{-Sb}_2\text{O}_4$ system in air. Oxygen contained in the air participates in the synthesis of these compounds. ZnSb_2O_6 was observed as an intermediate phase, during the $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ synthesis. The temperature of the $\beta\rightarrow\alpha\text{-Zn}_7\text{Sb}_2\text{O}_{12}$ transition was fixed at $1225\pm 10^\circ\text{C}$. The mechanisms of the reactions of ZnSb_2O_6 and $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ thermal decomposition have been proposed. The IR studies of α and $\beta\text{-Zn}_7\text{Sb}_2\text{O}_{12}$ have initially indicated that the structures of both polymorphous forms differ in the reciprocal connection of the SbO_6 and ZnO_6 octahedra and the ZnO_4 tetrahedra.

Keywords: antimony-zinc oxide, DTA/TG, IR, reactivity of oxides, XRD

Introduction

Basic physico-chemical properties as well as the structure of ZnO and $\alpha\text{-Sb}_2\text{O}_4$ are well-known [1–9]. According to literature findings regarding the binary system of $\alpha\text{-Sb}_2\text{O}_4\text{-ZnO}$ oxides, this system has not been studied in reference to the component's reactivity in the solid state in air, yet. It follows from the scanty literature data that two compounds: ZnSb_2O_6 and $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ are formed in the Sb-Zn-O system. The data concerning the thermal properties of this phase are fragmentary and frequently contradictory. Thermal stability of the ZnSb_2O_6 and $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ is very important when considering their practical applications. It is well known that ZnSb_2O_6 represents good potential as a new sensing material for a conductivity-type sensor to dilute hydrogen sulphide [10]. At the same time varistors based on $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ are also intensely investigated [11].

So far the ZnSb_2O_6 and $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ compounds have been prepared by means of precipitation from the solution containing zinc sulfate(VI) and potassium metaantimonate(V) [12] as well as by means of the reaction taking place in air between $\text{Zn}(\text{NO}_3)_2$ and Sb_2O_3 [13] or between ZnO and Sb_2O_3 [14–18].

The researchers agree that ZnSb_2O_6 crystallizes in the tetragonal system and belongs to the P4/mnm space group [13, 14, 19] and demonstrates the tri-rutile structure [19–21].

ZnSb_2O_6 was subjected to research by means of IR spectroscopy [19–21] and the Raman spectroscopy [19, 21].

The other compound, that is $\text{Zn}_7\text{Sb}_2\text{O}_{12}$, appears in two polymorphous forms, the cubic and the orthorhombic [16–18, 22–24]. The cubic form of $\alpha\text{-Zn}_7\text{Sb}_2\text{O}_{12}$ exhibits the structure of the inverse spinel [16–18, 22], whereas the structure of the $\beta\text{-Zn}_7\text{Sb}_2\text{O}_{12}$ form has not been finally determined [18, 23].

The literature data regarding the polymorphous transformation of $\alpha\text{-Zn}_7\text{Sb}_2\text{O}_{12}\rightarrow\beta\text{-Zn}_7\text{Sb}_2\text{O}_{12}$ are inconsistent. Kim *et al.* claim that the orthorhombic form of $\beta\text{-Zn}_7\text{Sb}_2\text{O}_{12}$ is present only in the narrow range of temperatures, namely from 1200 to 1300°C [15]. Miles *et al.* [17] report that the orthorhombic form, that is $\beta\text{-Zn}_7\text{Sb}_2\text{O}_{12}$ undergoes transition into a high-temperature cubic form of $\alpha\text{-Zn}_7\text{Sb}_2\text{O}_{12}$ at the temperature of $1225\pm 25^\circ\text{C}$. According to this research this transformation is thoroughly reversible, however it is slower in the $\alpha\rightarrow\beta$ direction, thus the high-temperature α form can be obtained easier at lower temperatures.

$\text{Zn}_7\text{Sb}_2\text{O}_{12}$ has been neither investigated by means of IR spectroscopy, nor examinations have been conducted with the view to determining its thermal properties.

In the light of the literature data provided it seemed purposeful to examine in the first place the reactivity of $\alpha\text{-Sb}_2\text{O}_4$ with ZnO in the solid state in air. It also involved determining the physicochemical properties (first of all the thermal properties) of the phases formed in air in the $\alpha\text{-Sb}_2\text{O}_4\text{-ZnO}$ system.

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Experimental

The following oxides were used for the examination: analytically pure ZnO (Aldrich, USA) and α -Sb₂O₄ which has not been used so far by other researchers. The low-temperature polymorphous form of the diantimony tetraoxide was obtained by heating in air pure Sb₂O₃ (Merck, Germany) [25]. 12 samples from the α -Sb₂O₄ and ZnO oxides were prepared for the examinations. The samples' compositions were selected in such a way that they would represent the whole components' concentration range of the α -Sb₂O₄-ZnO system (Table 1). The reacting substances were weighed in appropriate quantities, homogenized by grinding, shaped into pastilles and heated in air. The method of heating and cooling the samples was the same as it was applied in papers [26, 27]. The conditions of heating the samples were established on the basis of the literature available, regarding the synthesis of the ZnSb₂O₆ and Zn₇Sb₂O₁₂ compounds, the compounds which were expected to be obtained in the studied system [14–16, 23, 24]. The samples of 5.00–50.00 mol% ZnO were heated over the following cycles: I 700°C (24 h), II 800°C (24 h), III 850°C (24 h), IV 900°C (24 h), V 950°C (24 h); the samples of 50.00–100.00 mol% ZnO were heated: I 700°C (24 h), II 800°C (24 h), III 850°C (24 h), IV 900°C (24 h), V 950°C (24 h), VI 1000°C (24 h), VII 1100°C (24 h).

The phase compositions of the samples, following the successive stages of their heating, were determined on the basis of the results arrived by means of the XRD method. After the last stage of heating all the samples were subjected to additional examination by the DTA/TG method up to 1000°C.

The studies performed with the use of the DTA/TG method were conducted with the Paulik–Paulik–Erdelyi derivatograph (MOM, Hungary). The measurements were taken in air atmosphere, within the temperature range of 20–1000°C and at the heating rate of 10 K min⁻¹. All the measurements were taken in corundum crucibles. The mass of the examined samples was always 500 mg.

The selected samples were subjected to examinations conducted by means of the DTA/TG method with the use of the SDT 2960 apparatus, made by the TA Instruments Company or the TGA/SDTA 851 produced by the Mettler Toledo Company. The measurements were taken in nitrogen atmosphere, within the temperature range 20–1500°C, at the heating rate of 10 K min⁻¹. The tests were conducted in corundum crucibles. The mass of the examined samples comprised ~50 mg. The tests were not conducted in air atmosphere for technical reasons (the heating element's rapid wearing off during the experiments conducted in air and at the temperatures above 1000°C).

The type of the phases contained in the samples was identified on the basis of the results of the X-ray phase analysis (the DRON-3 diffractometer, of Russian production, CoK_α radiation, Fe filter) and the data included in the PDF cards [28].

The experiments conducted by means of the IR method were run with the help of the IR SPECORD M 80 spectrometer, produced by Carl Zeiss Jena, East Germany, using the technique of pressing pellets with KBr in 1:300 mass ratio. The measurements were taken within the wavenumbers range 1200–250 cm⁻¹.

The density of the ZnSb₂O₆ and Zn₇Sb₂O₁₂ compounds was determined by means of the method presented in the work [29].

Table 1 The composition of the initial mixtures, the conditions of preparation and the XRD phase analysis results after the final heating stage of the samples

No.	Samples composition in terms of oxides percentage/mol%		Phase composition of samples after		
	α -Sb ₂ O ₄	ZnO	heating stage at 850°C	heating stage at 950°C	final heating stage
1	95.00	5.00			
2	85.00	15.00			
3	75.00	25.00	α -Sb ₂ O ₄ , ZnO, ZnSb ₂ O ₆	α -Sb ₂ O ₄ , ZnSb ₂ O ₆	α -Sb ₂ O ₄ , ZnSb ₂ O ₆
4	66.67	33.33			
5	60.00	40.00			
6	50.00	50.00	α -Sb ₂ O ₄ , ZnO, ZnSb ₂ O ₆	ZnSb ₂ O ₆	ZnSb ₂ O ₆
7	40.00	60.00			
8	33.33	66.67			
9	25.00	75.00	ZnO, α -Sb ₂ O ₄ , ZnSb ₂ O ₆ , α -Zn ₇ Sb ₂ O ₁₂	ZnSb ₂ O ₆ , α -Zn ₇ Sb ₂ O ₁₂	ZnSb ₂ O ₆ , β -Zn ₇ Sb ₂ O ₁₂
10	20.00	80.00			
11	12.50	87.50		α -Zn ₇ Sb ₂ O ₁₂ , β -Zn ₇ Sb ₂ O ₁₂	β -Zn ₇ Sb ₂ O ₁₂
12	5.00	95.00		ZnO, ZnSb ₂ O ₆ , α -Zn ₇ Sb ₂ O ₁₂	β -Zn ₇ Sb ₂ O ₁₂ , ZnO

Results and discussion

The compositions of the initial mixtures of α -Sb₂O₄ oxides with ZnO as well as the XRD phase analysis results of all the samples after the selected and final heating stage, were demonstrated in Table 1.

X-ray analysis of all the samples processed showed after the first and second heating stages that they contained only the initial substances, i.e. α -Sb₂O₄ and ZnO.

Phase analysis of the samples containing in the initial mixtures up to 50.00 mol% ZnO after the third heating cycle (850°C) has demonstrated that they were triphase and apart from α -Sb₂O₄ and ZnO, they also contained the ZnSb₂O₆ compound. Phase analysis of these samples after the subsequent heating cycles (up to 950°C) has demonstrated that they were biphasic and contained α -Sb₂O₄ and ZnSb₂O₆. The samples, additionally heated at 1000°C apart from α -Sb₂O₄ with ZnSb₂O₆ have produced the minor quantities β -Sb₂O₄. The temperature of polymorphous transformation $\alpha \rightarrow \beta$ -Sb₂O₄ according to [5] is 960°C, by [9] is 935°C, whereas according to [6] is 1130°C and is dependent on the conditions under which it is conducted, among others the gas atmosphere. Moreover, it follows from literature data that the transformation is preceded by the thermal decomposition of α -Sb₂O₄ to the gaseous products of Sb₄O₆ and O₂ [6, 9]. The results of our studies pointed out that the polymorphous transformation of α -Sb₂O₄ \rightarrow β -Sb₂O₄ in air atmosphere begins at 1080°C [7]. Only a few researchers think that α -Sb₂O₄ undergoes sublimation [5, 8]. The results obtained in this work show, that the polymorphous transformation of α -Sb₂O₄ into β -Sb₂O₄ in the presence of ZnSb₂O₆ is performed at the temperature of 1000°C, namely at the temperature of about 80°C lower than that of the $\alpha \rightarrow \beta$ -Sb₂O₄ polymorphous transition. At this stage of research has not been established why the temperature of the polymorphous transformation of $\alpha \rightarrow \beta$ -Sb₂O₄ in the examined system is lower. The investigations will be continued.

Within the range of the concentrations of the components of the studied system from 50.00 to 80.00 mol% ZnO, the samples after the final heating cycle, i.e. at 1100°C, were diphasic and besides the ZnSb₂O₆ compound, they contained another compound, that is β -Zn₇Sb₂O₁₂.

The sample representing the remaining range of the concentrations of the examined system's components, i.e. over 87.50 mol% ZnO after the IV and V heating stages was triphase and contained apart from ZnO and ZnSb₂O₆ also α -Zn₇Sb₂O₁₂. Further stage of heating, i.e. at 1000 and 1100°C, resulted in the sample becoming diphasic and containing ZnO, besides β -Zn₇Sb₂O₁₂.

Among the examined samples only the ones containing in the initial mixtures of oxides, 50.00 or

87.50 mol% ZnO, were monophasic after the last stage of heating and contained ZnSb₂O₆ or β -Zn₇Sb₂O₁₂, respectively.

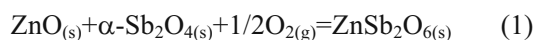
The inspection of the change of the samples' mass, carried out after successive stages of their heating, allowed to draw conclusions that the synthesis of all the preparations was accompanied by the mass gain. The complete mass gain of the samples was dependent on their composition and following all the heating stages, fluctuated from 0.40 to 3.15 mass%. The greatest mass gain accompanied the heating of the equimolar mixture of ZnO with α -Sb₂O₄ which was monophasic after the last heating stage and contained only the ZnSb₂O₆ compound. The samples' mass gain recorded during their heating proved that the oxygen, present in the air, participates in the synthesis of the preparations.

It was also noticed that during the heating of the samples, the change in their colour took place as well. All the initial mixtures of the oxides were white, whereas the samples in the state of equilibrium, depending on their composition demonstrated different shades of light gray and light yellow.

The phase composition of all the examined samples after the last stage of their heating pointed out that in the studied α -Sb₂O₄-ZnO system, in air two compounds, namely ZnSb₂O₆ and β -Zn₇Sb₂O₁₂ are formed. So far these compounds, according to the literature data, have not been received from such substrates [12–18].

Synthesis and the thermal properties of the ZnSb₂O₆ compound

The results of the conducted research allow us to state that the ZnSb₂O₆ compound can be received through the heating of the equimolar mixture of α -Sb₂O₄ oxides with ZnO in air atmosphere in the following stages: I: 700°C (24 h), II: 800°C (24 h); III: 850°C (24 h); IV: 950°C (24 h). The (XRD) phase analysis conducted after particular heating stages of this mixture made it possible to establish that the ZnSb₂O₆ synthesis runs in agreement with the reaction equation:



Oxygen presence in reaction (1) was confirmed by the mass gain of this sample, which was ~3.15 mass% after all the heating stages. This result is compatible with the mass gain of the sample calculated from reaction (1), constituting 4.11 mass%. The difference between the theoretical and the recorded mass gain of this sample, might be caused by the fact that the complete mass gains are influenced by its simultaneous loss. The loss of the mass is the result, first of all, of removing all sorts of impurities adsorbed on the surface of the reacting substance during

their lasting many hours heating. It can also be connected with an insignificant thermal dissociation of antimony oxide [5, 8].

The obtained ZnSb_2O_6 compound exhibits gray colour and the density of $6.7 \pm 0.05 \text{ g cm}^{-3}$.

Indexing the diffractogram of ZnSb_2O_6 was performed by employing the Powder program [30, 31]. 23 successive diffraction lines recorded within the $10\text{--}100^\circ 2\theta$ ($\text{CoK}_\alpha/\text{Fe}$) angular range were subjected to indexing. The parameters of the tetragonal unit cell ZnSb_2O_6 calculated for the selected solution are: $a=0.4665 \text{ nm}$, $b=0.92697 \text{ nm}$ and differ only insignificantly from the parameters determined in 1941 by Byström *et al.* [14].

During the next stage of the research, the investigations aimed at establishing the thermal properties of the ZnSb_2O_6 compound were conducted. No thermal effects were noted on the DTA curves of the ZnSb_2O_6 to 1000°C . Two endothermal effects were recorded on the DTA curve of the ZnSb_2O_6 compound up to 1500°C (Fig. 1a). The first of them started at the temperature of $1250 \pm 10^\circ\text{C}$ and was accompanied by the loss in mass comprising $\sim 68 \text{ mass}\%$. The other effect, the end of which was not recorded on the DTA curve up to 1500°C , was commenced at the temperature of $1350 \pm 10^\circ\text{C}$ and reached its maximum at $\sim 1495^\circ\text{C}$. The other endothermal effect ($\sim 1350^\circ\text{C}$) was connected with the loss of mass recorded on the TG curve, and comprising $\sim 10.5 \text{ mass}\%$.

With the view to establishing the nature of the effects recorded on the DTA/TG curves of the investigated ZnSb_2O_6 compound, the samples containing only this compound were heated in air for 4 h at the following temperatures: 1250 , 1300 and 1500°C and next cooled intensely to room temperature. The samples prepared in this way were examined by the XRD method after their homogenizing by grinding. It was found that the sample of the ZnSb_2O_6 compound heated at 1250 and 1300°C did not undergo melting and its color changed from gray to yellow-gray. The phase analysis performed after heating at 1250°C demonstrated that the sample contained mainly $\alpha\text{-Zn}_7\text{Sb}_2\text{O}_{12}$, besides an insignificant amount of ZnSb_2O_6 , however after 1300°C it was only $\alpha\text{-Zn}_7\text{Sb}_2\text{O}_{12}$ that was found in the sample. The phase analysis of the preparation heated at the temperature of 1500°C demonstrated that it contained mainly ZnO and only the trace quantities of $\beta\text{-Sb}_2\text{O}_3$. Moreover, it was found that the sample of the ZnSb_2O_6 compound, heated at 1500°C also did not melt.

In the light of the results received, it can be stated that the ZnSb_2O_6 compound does not melt but decomposes in the solid state, at the temperature of $\sim 1250^\circ\text{C}$ with the solid $\alpha\text{-Zn}_7\text{Sb}_2\text{O}_{12}$ being released. The mass loss, related to the thermal decomposition of ZnSb_2O_6 ,

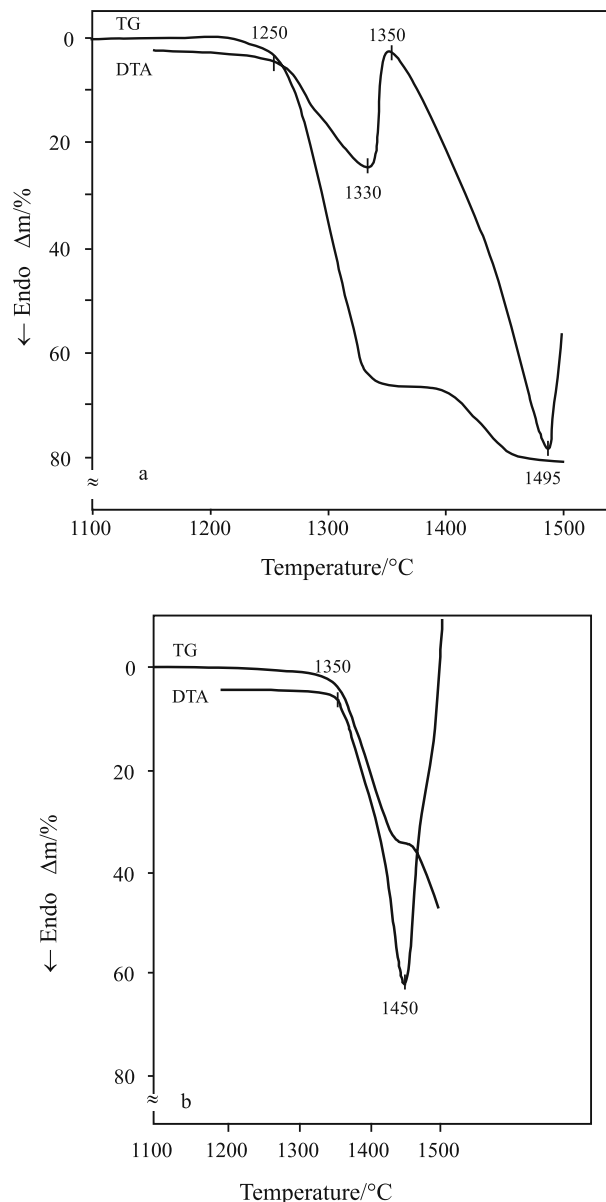
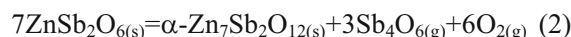


Fig. 1 DTA/TG curves of a – ZnSb_2O_6 , b – $\alpha\text{-Zn}_7\text{Sb}_2\text{O}_{12}$

indicated additionally that the content of the decomposition products may reveal the compound which undergoes decomposition to gaseous products at $\sim 1250^\circ\text{C}$. Therefore, it can be noted that the first endothermal effect, recorded on the DTA curve of the ZnSb_2O_6 compound, is connected with its decomposition, which starts at 1250°C .

On the basis of the received results we suggest that the products of the thermal decomposition of ZnSb_2O_6 , initially show the presence of Sb_2O_4 , among others, which decomposes to $\text{Sb}_4\text{O}_{6(g)}$ and oxygen at the temperature of the decomposition of the examined compound, that is at 1250°C [5, 6]. In such case the decomposition of ZnSb_2O_6 can be demonstrated by means of the following equation:



The mass loss calculated on the basis of the reaction (2) is equal to 68.48 mass% and is compatible with the changes of the mass recorded on the TG curve of the ZnSb₂O₆ compound, which additionally confirms the recommended mechanism of its decomposition. Based on this part of the research, it was also found that the other effect recorded on the DTA curve of the ZnSb₂O₆ compound, is linked with the thermal properties of the solid product of its decomposition, namely that of the Zn₇Sb₂O₁₂ compound.

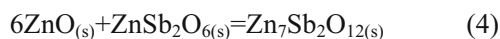
Synthesis and thermal properties of the Zn₇Sb₂O₁₂ compound

The Zn₇Sb₂O₁₂ compound was obtained as a result of a reaction conducted in the solid phase from the mixture of oxides containing 87.5 mol% of ZnO and 12.5 mol% of α -Sb₂O₄ under conditions presented in experimental part, according to the reaction:



The received compound exhibits the light yellow colour and the density of $6.17 \pm 0.05 \text{ g cm}^{-3}$.

On the basis of the X-ray phase analysis and the control of the mass gain of the samples, conducted after each heating stage it was additionally found that reaction (3) goes through the direct stage, where the ZnSb₂O₆ compound is created, according to reaction (1). Furthermore, the received ZnSb₂O₆ compound reacts with ZnO following this reaction:



The analysis of the sample's phase composition after successive stages of the Zn₇Sb₂O₁₂ synthesis enabled establishing that its synthesis begins at a considerable rate only at the temperature of 850°C. Moreover, it was found that after this heating stage, the diffraction lines characterizing this compound, corresponds to the α -Zn₇Sb₂O₁₂ forms only [16]. The next two heating stages of this sample, that is 900 and 950°C, resulted in a change of its phase composition, namely apart from the α -Zn₇Sb₂O₁₂ form, minute quantities of the β -Zn₇Sb₂O₁₂ form occurred. It was only after heating at 1100°C that the sample contained β -Zn₇Sb₂O₁₂ solely. Figure 2 presents besides fragments of diffractograms given by the mixture of the oxides ZnO with α -Sb₂O₄ (87.5 mol% ZnO, 12.5 mol% α -Sb₂O₄) and the mixture of ZnSb₂O₆ with ZnO, as well as a fragment of diffractogram given by the Zn₇Sb₂O₁₂ compound obtained from these mixtures.

In order to establish the thermal properties of the β -Zn₇Sb₂O₁₂ phase, the sample which was monophasic and contained this phase only, was heated additionally at the 1150, 1225 and 1300°C temperatures for a few hours and cooled down rapidly to room temperature.

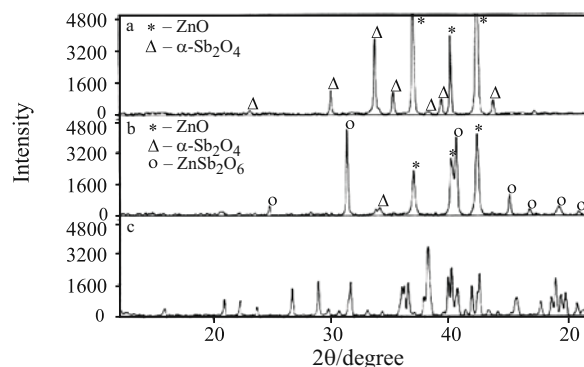


Fig. 2 X-ray diffraction patterns of a – mixture of oxides (87.5 mol% ZnO+12.5 mol% α -Sb₂O₄, b – after heating of mixture a – at 800°C (24 h), c – β -Zn₇Sb₂O₁₂

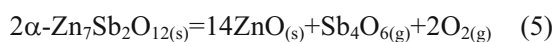
Heating β -Zn₇Sb₂O₁₂ at the temperature of 1150°C (4 h) failed to result in the change of the phase composition of the sample. After the heating at 1225°C for 4 h, the sample contained β -Zn₇Sb₂O₁₂ and small quantities of α -Zn₇Sb₂O₁₂, which means that the polymorphous transformation of β -Zn₇Sb₂O₁₂ to α -Zn₇Sb₂O₁₂ commenced at this temperature. It was also found that heating β -Zn₇Sb₂O₁₂ at the temperature of 1300°C led to a complete polymorphous transformation of this phase to α -Zn₇Sb₂O₁₂, already within 2 h.

With the view to establishing whether the polymorphous transformation of $\beta \rightarrow \alpha$ -Zn₇Sb₂O₁₂ is reversible, the sample containing α -Zn₇Sb₂O₁₂ only, was additionally heated at 1150°C for 8 h, and next subjected to the XRD examinations. It was found that the sample contained only the β -Zn₇Sb₂O₁₂ form. On this basis it was assumed that the examined transformation is reversible. The conducted experiments confirmed the literature data [17].

In order to establish the thermal properties of α -Zn₇Sb₂O₁₂, particularly the fact whether this compound melts or decomposes, it was subjected to the DTA/TG investigations (Fig. 1b). On the DTA/TG curves of the α -Zn₇Sb₂O₁₂ compound no thermal effects were noted up to 1000°C. Therefore, the preparation underwent the DTA/TG analysis up to 1500°C. On the DTA curve of the sample up to 1500°C, containing the α -Zn₇Sb₂O₁₂ compound only, one distinct endothermic effect was recorded. It began at the 1350°C temperature and reached its maximum at 1450°C. The end of this effect was not recorded on the DTA curve to 1500°C. This effect was accompanied by the change of the sample's mass, recorded on the TG curve, and amounting to ~35 mass%. Moreover, it was found that the sample, containing α -Zn₇Sb₂O₁₂ did not undergo melting.

The phase analysis of Zn₇Sb₂O₁₂ after its heating at 1500°C demonstrated the presence of ZnO and only the trace quantities of β -Sb₂O₃. Under the conditions of the conducted experiment, that is at 1500°C,

only ZnO is the solid phase which makes it possible to assume that the β - Sb_2O_3 identified in the sample, is a phase formed as a result of vapor condensation of Sb_2O_4 decomposing under these conditions [7, 10]. Taking into consideration the size of the mass loss accompanying the thermal decomposition of α - $\text{Zn}_7\text{Sb}_2\text{O}_{12}$, it can be assumed in all likelihood that this decomposition, which begins at 1350°C , runs according to the following reaction equation:



In the next part of the work, the examinations of two polymorphous forms of $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ were conducted by means of the IR spectroscopy, as no IR spectra corresponding to them, have been found in literature available. In Fig. 3 the IR spectrum of the mixture of oxides containing 87.5 mol% of ZnO and 12.5 mol% of α - Sb_2O_4 besides the spectra of two polymorphous forms of $\text{Zn}_7\text{Sb}_2\text{O}_{12}$, received from this mixture, were presented. From the demonstrated figure it follows that these spectra differ one from another, both in relation to the number of recorded bands, as well as their position and intensity. In accordance with the literature data, absorption bands comprising the IR spectrum of the oxides mixture (Fig. 3a) correspond to the stretching or deformation vibrations of the bonds in the coordinating polyhedra in the structure of these oxides [4, 8, 32, 33].

The IR spectrum of the α - $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ form (Fig. 3b) has two wide and one narrow absorption bands. The first wide absorption band is recorded within the range of wave numbers $750\text{--}550\text{ cm}^{-1}$, with the maximum at 630 cm^{-1} . The other wide absorption band is recorded in the range of the $550\text{--}350\text{ cm}^{-1}$ wave numbers, reaching its maximum with 420 cm^{-1} . The maximum of the sharp absorption band is recorded with 280 cm^{-1} .

The vibrational spectrum of the β - $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ form (Fig. 3c) as opposed to the IR spectrum of α - $\text{Zn}_7\text{Sb}_2\text{O}_{12}$, is composed of seven intense absorption bands demonstrating the distinctly developed maxima at $720, 640, 600, 560, 510, 480, 390\text{ cm}^{-1}$ as well as a wide absorption band with the maximum at 435 cm^{-1} and the shoulder at 450 cm^{-1} . The number of these bands suggests that the structure of β - $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ is of a much more complicated nature than that of α - $\text{Zn}_7\text{Sb}_2\text{O}_{12}$.

Based on the literature data, the absorption bands registered in the range of wave numbers from $720\text{--}550\text{ cm}^{-1}$ can be attributed to the stretching vibrations of the Sb–O bonds in the SbO_6 octahedra [4, 20, 21], as well as the stretching vibrations of Zn–O bonds in the ZnO_6 octahedra [34–36]. Whereas, the bands located within the range of the lower wave numbers, which is $550\text{--}350\text{ cm}^{-1}$, according to litera-

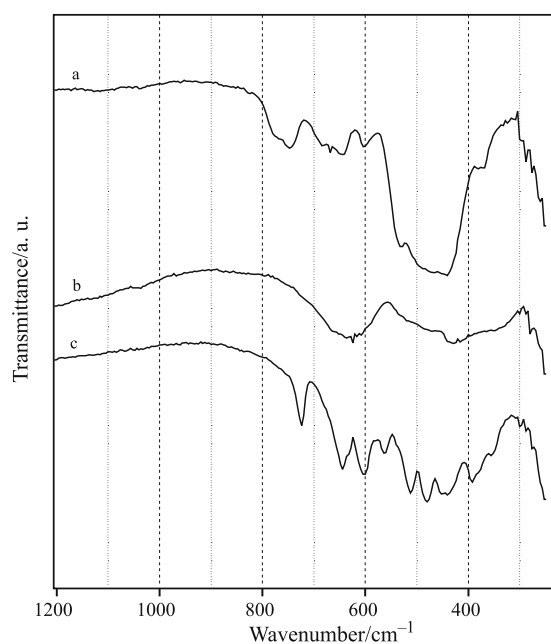


Fig. 3 IR spectra of a – the mixture of oxides containing 87.5 mol% α - Sb_2O_4 and 12.5 mol% ZnO, b – α - $\text{Zn}_7\text{Sb}_2\text{O}_{12}$, c – β - $\text{Zn}_7\text{Sb}_2\text{O}_{12}$

ture data are caused by the deformation vibrations of the Zn–O bonds in the ZnO_4 tetrahedra [33, 36]. Next, the bands registered in the range of wave numbers $350\text{--}280\text{ cm}^{-1}$ correspond to the stretching vibrations of the Zn–O bonds in the ZnO_6 octahedra [34–36], as well as the deformation vibrations of the O–Sb–O bonds in the SbO_6 polyhedra [4, 20, 21].

Despite the fact that the performed investigations demonstrate the qualitative character only, it can be concluded on their basis that the structure of both forms of the polymorphous $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ compound is made up of SbO_6 and ZnO_6 octahedra and ZnO_4 tetrahedra. From the presented IR spectra it follows that the polyhedra symmetry comprising the structure of β - $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ is much lower than that of α - $\text{Zn}_7\text{Sb}_2\text{O}_{12}$. It can be assumed then that these structures differ one from another by means of bonding adjacent polyhedra (with their corners or edges). In order to confirm this assumption a full knowledge of the structures of both polymorphous forms of the studied compound is necessary. The IR studies provide only the preliminary information regarding their structure. These findings correspond with the literature data, according to which α - $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ has the structure of an inverse spinel, where $2/3$ of the cations of Zn^{2+} occupy the tetrahedra positions, whereas the remaining cations of Zn^{2+} ($1/3$) and all the other cations of Sb^{5+} take up the octahedra positions [37, 38].

The powder diffraction patterns of both polymorphous forms of $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ underwent indexing with the help of the Powder program [31, 32]. The unit

cell's parameters for α -Zn₇Sb₂O₁₂ are as follows: $a=0.86027$ nm in relation to $a=0.8585$ nm according to Bayer [16]. The number of molecules in the unit cell is $Z=8$. The calculated X-ray density is $d_{\text{rtg}}=6.25$ g cm⁻³. The unit cell's parameters for β -Zn₇Sb₂O₁₂ are as follows: $a=1.20982$ nm, $b=1.85888$ nm, $c=0.85148$ nm in comparison with $a=1.2103$ nm, $b=1.8559$ nm, $c=0.8518$ nm according to Russwurm [23]. The number of molecules in the unit cell is $Z=8$. The calculated X-ray density is $d_{\text{rtg}}=6.19$ g cm⁻³.

Conclusions

The results obtained in this work entitle to draw the following conclusions:

- Zinc oxide and diantimony tetraoxide react one with another in the solid phase in air, as a result of which two compounds, i.e. ZnSb₂O₆ and Zn₇Sb₂O₁₂, are formed.
- The ZnSb₂O₆ compound is stable up to 1250°C, after that undergoes decomposition to α -Zn₇Sb₂O₁₂, with a deposition of Sb₄O_{6(g)} and O_{2(g)}.
- The orthorhombic form, i.e. β -Zn₇Sb₂O₁₂ which undergoes a reversible polymorphous transition into a high-temperature cubic form of α -Zn₇Sb₂O₁₂ at 1225°C, is a thermodynamically stable form of Zn₇Sb₂O₁₂ at low temperatures.
- The α -Zn₇Sb₂O₁₂ is stable up to 1350°C, above which its decomposition to ZnO, followed by the release of Sb₄O_{6(g)} and O_{2(g)}, begins.
- The IR investigations of α -Zn₇Sb₂O₁₂ and β -Zn₇Sb₂O₁₂ permitted a conclusion that the structure of both polymorphous forms of the compound is made up of the octahedra of SbO₆ and ZnO₆, as well as the ZnO₄ tetrahedra. The symmetry of polyhedra comprising the structure of β -Zn₇Sb₂O₁₂ is much lower than in the case of the α -Zn₇Sb₂O₁₂ structure.

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