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Kinetics and mechanism of Sb_2S_3 oxidation process

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Abstract

This paper presents the results of experimental investigations of Sb_2S_3 oxidation process in an air atmosphere. Methods of investigation, including DTA–TG–DTG and DSC analysis, enabled the determination of heat effects, kinetic parameters and mechanism of the investigated process.

Keywords: Kinetics; Oxidation process; Sb_2S_3; DTA–TG–DTG; DSC

1. Introduction

Antimony and sulfur form Sb_2S_3 and Sb_2S_5 sulfide [1]. Antimony trisulfide can be found as a stable, black modification, stibnite. If deposited from solution, either cold or on heating, it is orange-red and amorphous. After heating in the absence of air, it transforms into a crystalline gray-black modification. The melting temperature for Sb_2S_3 is 546 °C [2], while its density is 4.562 g cm^{-3} [3]. Antimony trisulfide is usually used as a pigment in making matches and in pyrotechnics [1].

Crystal structure of stibnite has been investigated by Hofmann [4], Scavnicar [5], Bayliss and Nowacki [6]. It has rhombic structure with parallel chains $(Sb_4S_6)_n$ [3], and lattice parameters are $a = 1.122$, $b = 1.130$ and $c = 0.384$ nm.

Phase diagram Sb–S, constructed according to thermal analysis results [2] is shown in Fig. 1.

Due to lack of literature data for antimony sulfides behavior during oxidation, results of DTA–TG–DTG, DSC and X-ray analysis for the Sb_2S_3 oxidation process are presented in this paper in order to determine the mechanism and kinetic parameters.

2. Experimental

A Sb_2S_3 sample was synthesized and prepared in the Department of Inorganic Chemistry, University "Paisiy Hilendarski".

Non-isothermal investigations were performed using simultaneous DTA–TG–DTG and DSC analysis, on Derivatograph 1500 (MOM Budapest) and DSC-404 (NETZSCH, Germany). Roentgen Siemens, with Cu–anticatode and Ni–filters, current intensity of 18 mA and voltage 40 kV was used for characterization of initial sample and oxidation products.

3. Results and discussion

X-ray analysis of the initial sample, which confirmed the presence of Sb_2S_3 is presented in Fig. 2. The obtained results show that the sample was pure and

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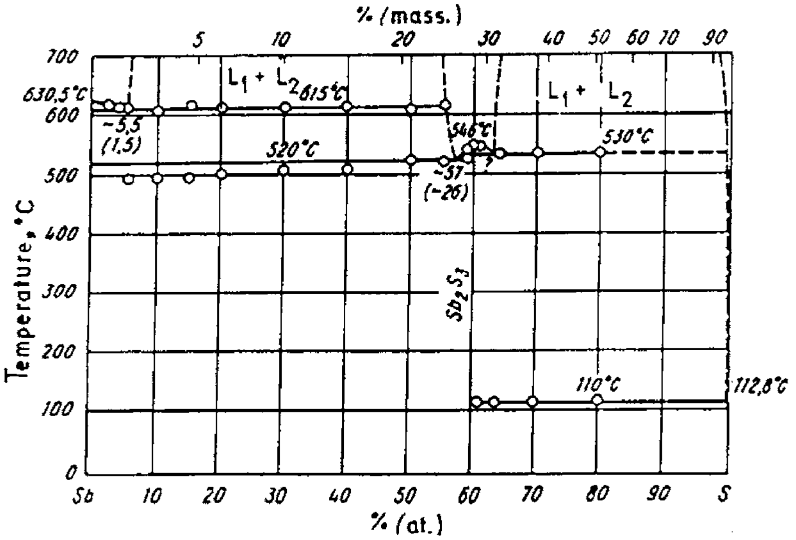

Fig. 1. Phase diagram of Sb–S [2].

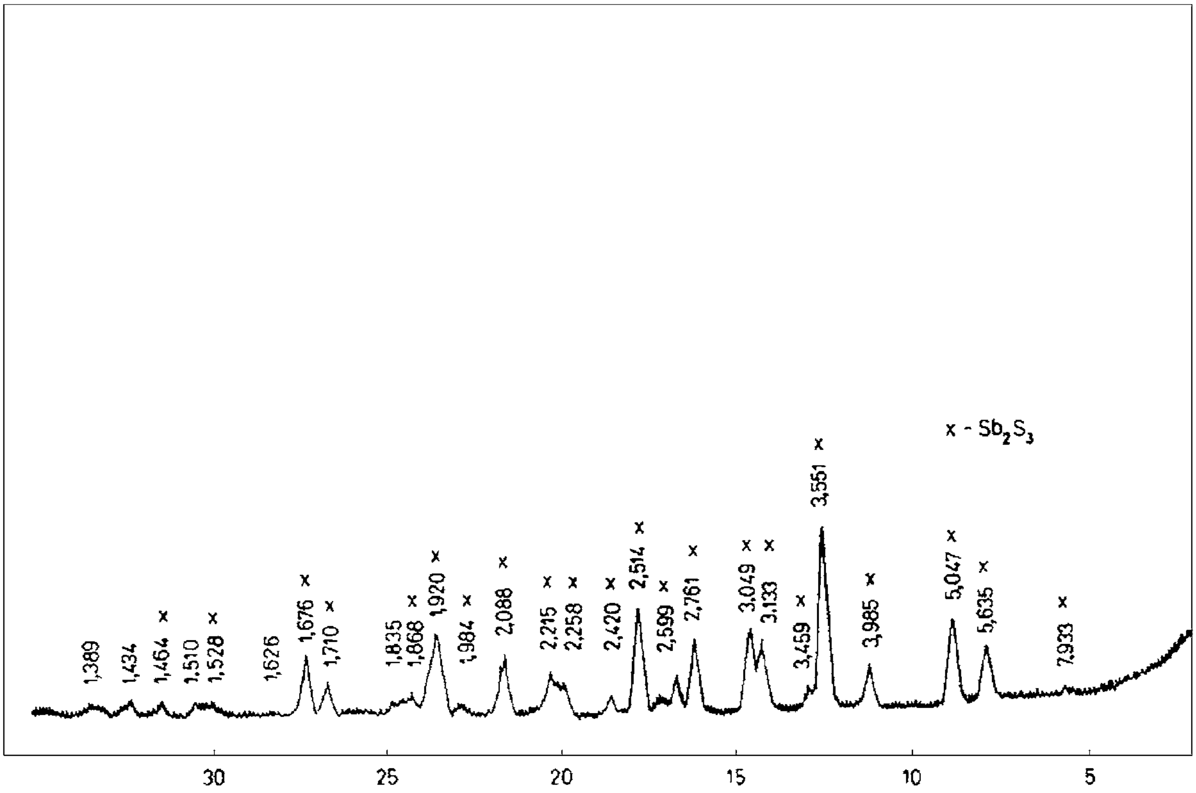

Fig. 2. Results of X-ray analysis for the initial sample.

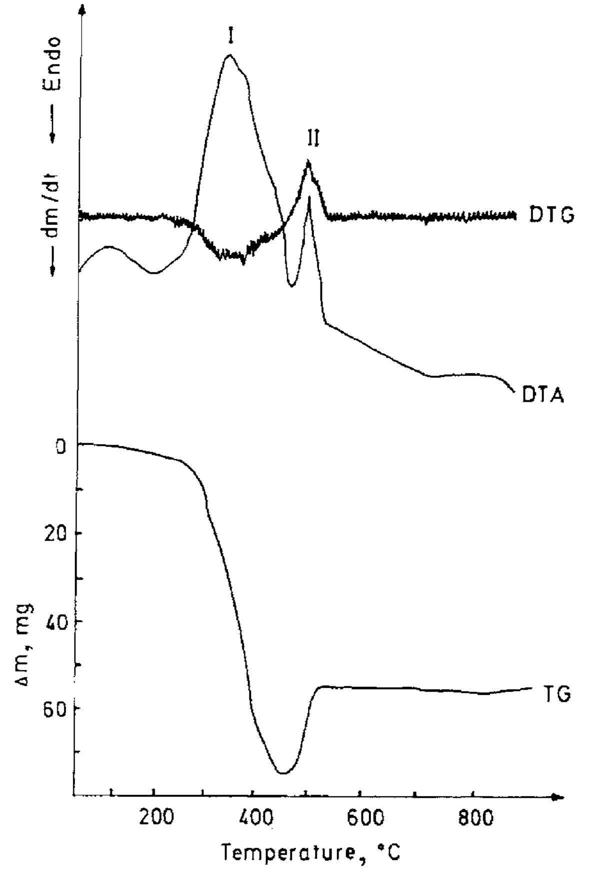

Fig. 3. Results of DTA–TG–DTG analysis.

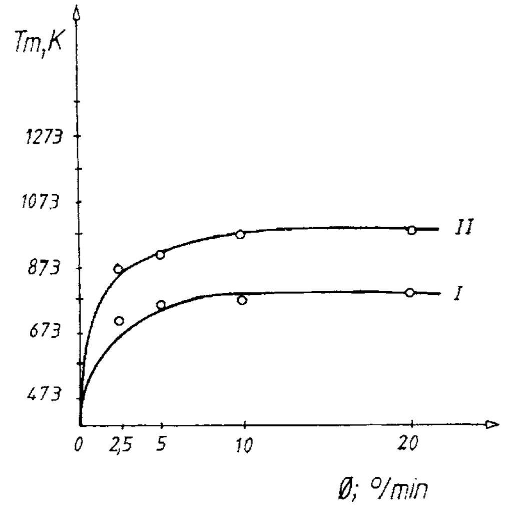

Fig. 4. Dependence of T_m on heating rate for DTA results.

well crystallized, because there are no other peaks in difractogram except for Sb_2S_3.

Plots of DTA–TG–DTG curves versus temperature for the process of Sb_2S_3 oxidation, obtained on heating at 2.5 °C min^{-1}, are presented in Fig. 3.

There are two exotherms in Fig. 3 (temperature interval 210–450 and 460–530 °C). As seen in the TG curve, there is a significant decrease of sample mass at the first exotherm, while the mass increased after the second exotherm. Further increase in temperature above 530 °C did not change the sample mass.

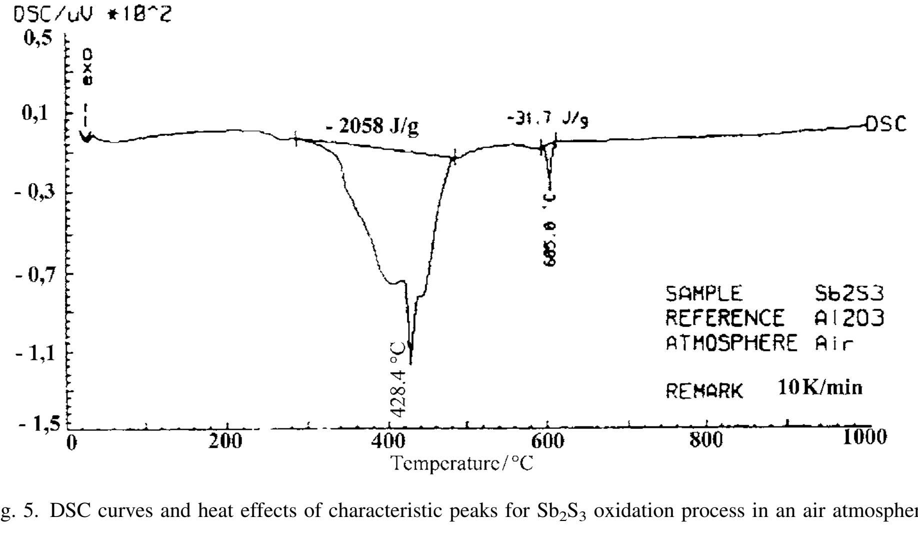

Fig. 5. DSC curves and heat effects of characteristic peaks for Sb_2S_3 oxidation process in an air atmosphere.

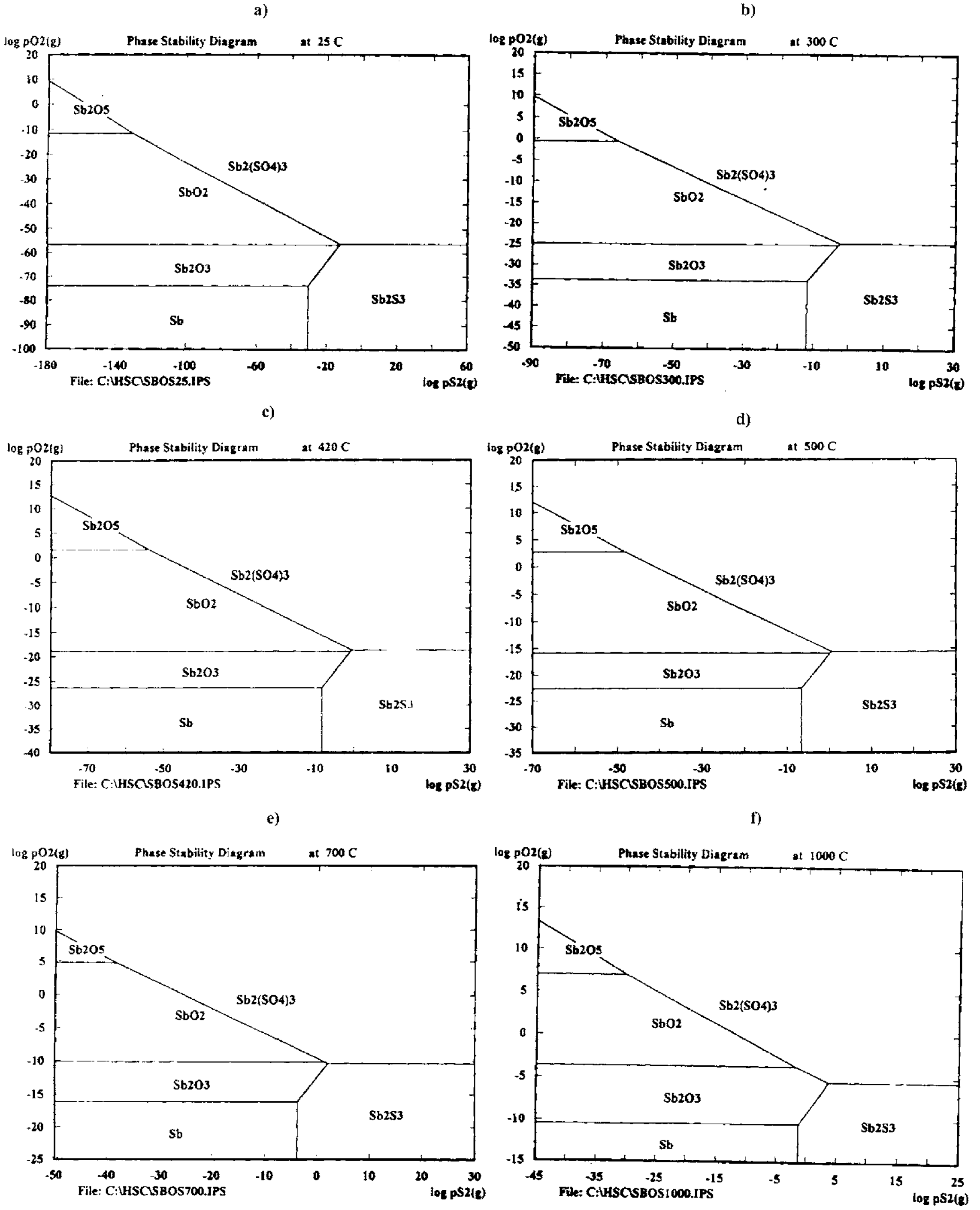

Fig. 6. Phase stability diagrams of $\log p_{S2}$–$\log p_{O2}$ as a function of T for system Sb–S–O.

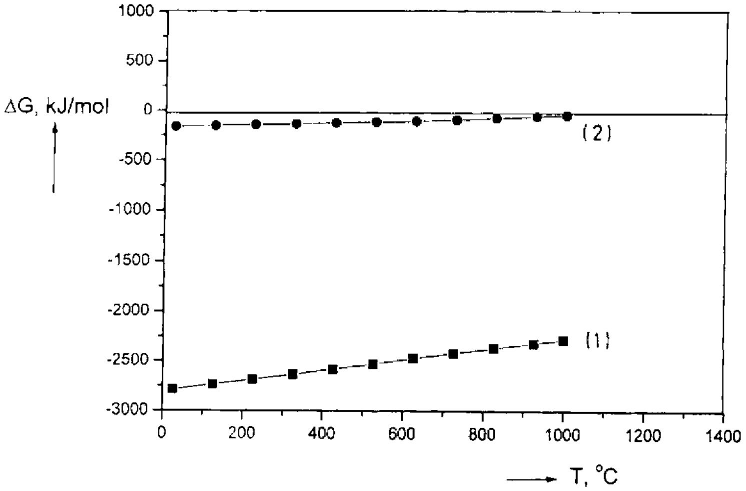

Fig. 7. Graphic presentation of ΔG° vs. T for reactions (1) and (2).

The initial sample examined was subjected to oxidation in an air atmosphere at different heating rates from 2.5 to 20 °C min^{-1} under the same conditions, and the results obtained for the maximum dependence on the heating rate in the DTA curve are shown in Fig. 4.

DSC response on heating Sb_2S_3 up to 1000 °C given in Fig. 5, is in agreement with DTA results. Certain

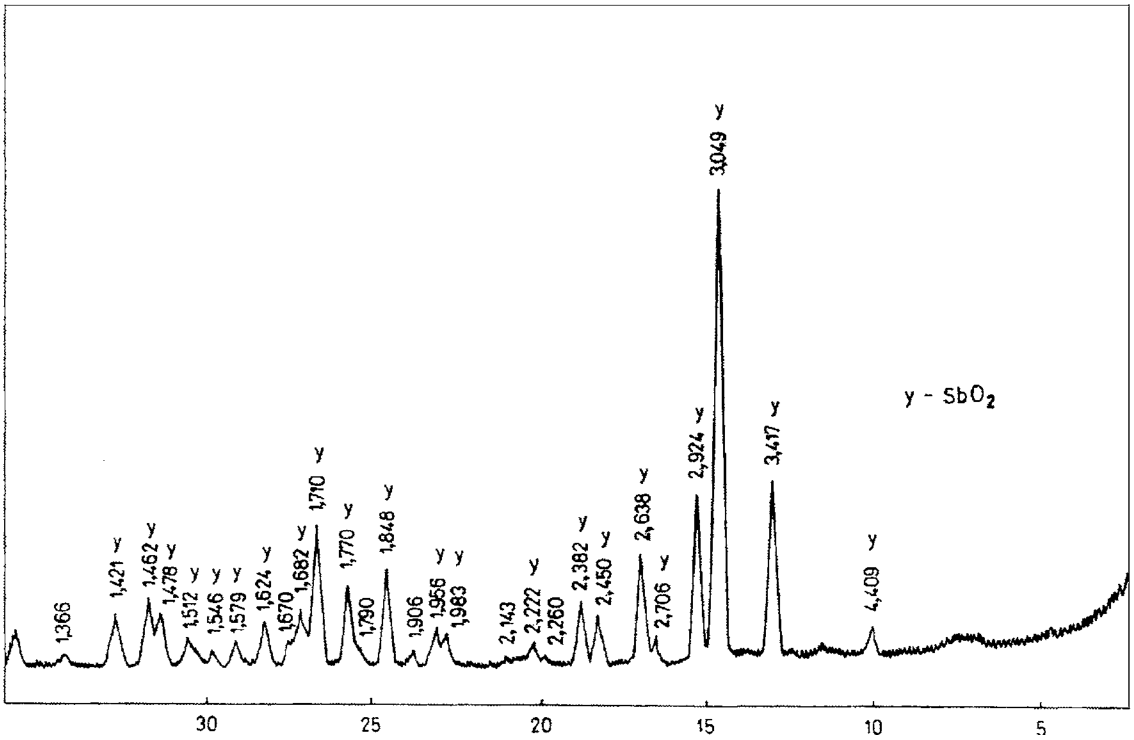

Fig. 8. X-ray diagram of the Sb_2S_3 sample, heated at 1000 °C in an air atmosphere.

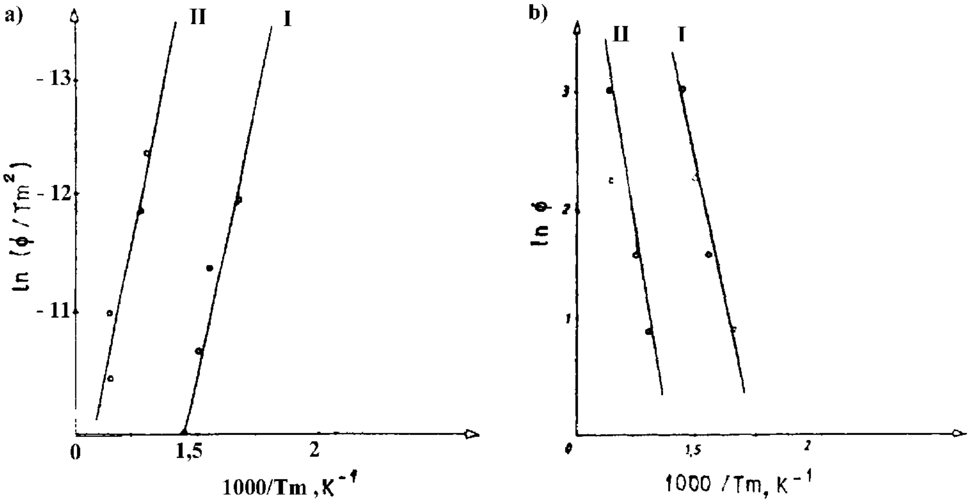

Fig. 9. (a) Dependencies of $\ln(\phi/T_m^2)$ vs. $1/T$ and (b) $\ln\phi$ vs. $1/T$ for the Sb_2S_3 oxidation process.

deviation could be explained by the use of smaller sample mass in the DSC analysis, and the use of different heating rates.

As can be seen, the first exotherm occurs in the temperature interval 283–478 °C, with enthalpy of -2050 J/g, while second exotherm occurs in the temperature interval 595–610 °C, with enthalpy of -31.7 J/g.

According to the DTA and DSC results, and constructed phase stability diagrams of $\log p_{S2}$–$\log p_{O2}$ at different temperatures (25, 300, 420, 500, 700, 1000 °C) for the system Sb–S–O are shown in Fig. 6. The mechanism of the Sb_2S_3 oxidation process is defined as follows:

$$2Sb_2S_3 + 9O_{2\,(g)} = 2Sb_2O_3 + 6SO_{2\,(g)} \qquad (1)$$

$$Sb_2O_3 + 0.5O_{2\,(g)} = 2SbO_2 \qquad (2)$$

In order to prove this mechanism of Sb_2S_3 oxidation, values for the Gibbs energy change for the proposed reactions (1) and (2) versus temperature were calculated. This is presented in Fig. 7.

X-ray analysis of the products of Sb_2S_3 oxidation was carried out to confirm the mechanism. The results are given in Fig. 8.

While the results from Fig. 8 confirm the suggested mechanism, one should keep in mind that antimony dioxide decomposes at much higher temperatures [7].

Kinetic analysis of the investigated oxidation process of Sb_2S_3 was carried out according to methods developed by Kissinger [8] and Ozawa [9]. Fig. 9 shows the dependencies of $\ln(\phi/T_m^2)$ and $\ln\phi$ as a function of $1/T_m$, where ϕ is the heating rate and T_m is the temperature of the maximum in weight loss as shown by the DTA curve.

Table 1
Calculated values for activation energy and integration constants for the oxidation process of Sb_2S_3

Process	Method			
	Kissinger		Ozawa	
	E (kJ/mol)	C	E (kJ/mol)	C_1
I	80	45.94	90	1.39×10^8
II	84	2.24	97	1.09×10^7

Based on these results, the corresponding values for activation energy E and the integration constants C and C_1 have been calculated for the process and these are presented in Table 1.

These values are consistent with oxidation of Sb_2S_3 taking place in kinetic region, which implies that reaction surface and temperature have the limiting influence on reaction rate.

4. Conclusions

Sb_2S_3 oxidation process has been experimentally investigated by DTA–TG–DTG, DSC and X-ray analysis. The results including heat effects, kinetic parameters and mechanism of the investigated process have been determined and presented in the paper.

Two exotherms were noticed, with enthalpy of −2050 and −31.7 J/g, respectively. They respond to the two stadiums in oxidation process: $Sb_2S_3 \rightarrow Sb_2O_3$ and $Sb_2O_3 \rightarrow SbO_2$, which was confirmed by constructed Sb–S–O phase stability diagram, calculated Gibbs energy change versus temperature, and literature data [7]. Kinetic analysis, carried out according to Kissinger [8] and Ozawa [9], showed that the values of activation energy are consistent with oxidation of Sb_2S_3 taking place in kinetic region, which implies that reaction surface and temperature have the limiting influence on reaction rate.

As the next step in further investigation of antimony sulfides, research of Sb_2S_5 oxidation process could be done, since there is a lack in references dealing with the mentioned process.

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