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A NEW PHASE IN THE Ag–O–S SYSTEM

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Abstract

The investigations of reaction between Ag_2SO_4 and Ag_2S in air atmosphere have been carried. Results of DTA and X-ray phase powder diffraction of a reaction mixture have confirmed that in the Ag–O–S system exists a new phase. A formula of the phase is Ag_2SO_2.

Keywords: Ag–O–S system, DTA, X-ray

Introduction

Our studies made so far on the mechanism and kinetics of the reaction running between Cu_2S and $CuSO_4$ have shown that one of the reaction products is Cu_2SO_2. That phase had not been known before our investigations [1–5]. Therefore it seemed reasonable to establish whether the other member of the copper group – silver forms an analogical phase.

Literature survey previous to the studies presented herein has permitted to state that it is three compounds: Ag_2O, Ag_2S and Ag_2SO_4 that are formed in the Ag–O–S system. The properties and the structure of Ag_2S and Ag_2SO_4 are known well [6–9].

Experimental

For experiments were used Ag_2SO_4, p.a. and Ag_2S, p.a., both reagents being of POCh production (Gliwice, Poland). Weighed in equimolar amounts the substrates were mixed by prolonged grinding, then shaped into pastilles and heated in air in the following cycles:

395°C (6 h), 300°C (66 h), 350°C (48 h), 300°C (19 h),

370°C (24 h), 300°C (48 h)

After each heating cycle the preparations were allowed to cool to ambient temperature, ground down and examined by DTA and X-ray phase analysis, once

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Table 1 Interplanar distances in the reaction product: $Ag_2S + Ag_2SO_4 \rightarrow 2Ag_2SO_2$ and relative intensities of corresponding reflexions

d/ Å	*I*/ %	*d*/ Å	*I*/ %	*d*/ Å	*I*/ %	*d*/ Å	*I*/ %
4.82	13	2.75	14	2.32	8	1.98	10*
3.99	27*	2.73	8	2.29	78*	1.96	10*
3.79	14	2.69	95	2.27	11	1.93	34*
3.17	90*	2.64	70*	2.24	8	1.92	16*
3.11	12	2.63	13	2.21	18	1.91	9
3.07	56	2.57	11	2.19	31	1.90	13
2.99	67	2.53	21	2.15	10	1.88	7
2.93	9	2.42	69*	2.14	9	1.83	11
2.90	31	2.38	5	2.05	22		
2.87	100*	2.36	22	2.04	17		
2.78	5	2.33	3	2.00	7		

* reflexions common to the new phase and Ag_2SO_4

again shaped in pastilles and heated. Before the last heating cycle the preparations were not shaped into pastilles. DTA was also made for a physical mixture comprising 50% mol of Ag_2SO_4 and 50% mol of Ag_2S.

DTA was performed using a derivatograph (MOM, Budapest) in quartz crucibles at a heating rate of 10 deg·min^{-1}. The mass of the samples under investigation was 1000 mg in each case. X-ray phase powder diffraction was made using a diffractometer DRON-3 (USSR) with CoK_α radiation.

Results and discussion

Screening tests accomplished by DTA in air have shown that a physical mixture of Ag_2S and Ag_2SO_4 with a molar ratio of 1:1 melts at 400°C without change in mass. The melt cooled to ambient temperature where X-rayed showed a number of unidentified lines which could not be ascribed either to the substrates or to Ag_2O. The fact has given rise to the thought that the process of melting taking place without any variation in mass is not a result of formation of a eutectic mixture in the Ag–O–S system. Thus the results of preliminary investigations imply that there take place a reaction in the system, leading to a phase not described so far:

$$Ag_2S + Ag_2SO_4 \rightarrow 2\ Ag_2SO_2 \qquad (1)$$

The essential difference between formation of Ag_2SO_2 and Cu_2SO_2 lies in that it is Cu_2SO_2 which is the product of the following reaction:

$$2\ Cu_2S + 2CuSO_4 \rightarrow 3\ Cu_2SO_2 + SO_2 \qquad (2)$$

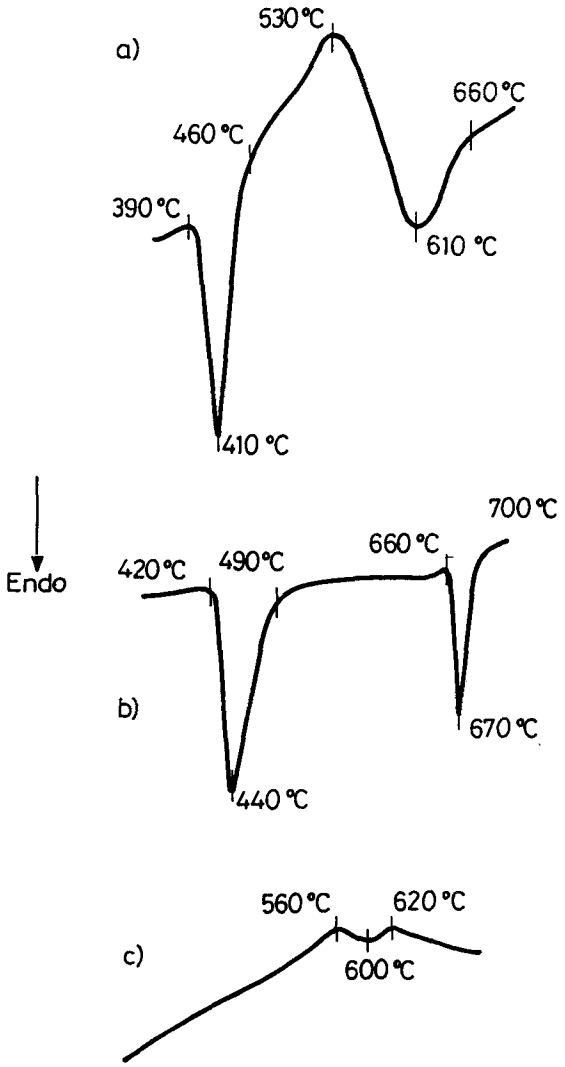

Fig. 1 DTA curves of the Ag_2SO_2 phase (a), non-admixed Ag_2SO_4 (b) and Ag_2S (c)

The reaction runs in the atmosphere of SO_2, involving a mass loss caused by concurrent formation of SO_2 – a gaseous product of the reaction.

The results of preliminary investigations considered, the further works on the synthesis of Ag_2SO_2 were carried out in atmospheric pressure when the mix-

ture of Ag_2S and Ag_2SO_4 was heated at the conditions given in the experimental part. The results of preliminary study have been confirmed by X-ray phase analysis of the preparation obtained after the last cycle of heating. The diffraction pattern of that preparation showed reflexions considered to be characteristic for Ag_2SO_2. The set of reflexions has been given in Table 1. The set consists of reflexions that can not be attributed to any of the known phases occurring in the Ag–O–S system. The set consists as well of reflexions that belong to the set characteristic of Ag_2SO_4. It seems that the later reflexions can be considered as joint reflexions, that is, typical of both Ag_2SO_2 and Ag_2SO_4. The reason for such opinion is the change in intensities of the reflexions, observed after the successive heating cycles – the reflexions are being decreased with the process of synthesis.

Figure 1 shows the DTA curves of the Ag_2SO_2 phase (a), non-admixed Ag_2SO_4 (b) and Ag_2S (c). The first endothermic effect, recorded on a DTA curve of the new phase, started at 390±10°C and was bound with congruent melting of Ag_2SO_2. This effect does not occur on the DTA curve of Ag_2SO_4 the melting temperature of which is 652°C [7], although by our findings it makes up 660±10°C (curve b). The effect has not been found on the DTA curve of Ag_2S, either (curve c). The second endothermic effect occurring on the DTA curve of Ag_2SO_2 (a) starting at 530±10°C has been bound with the decomposition at onset of liquid Ag_2SO_2, which is evidenced by loss in mass starting at this temperature. The fact is proved by records on the TG and DTG curves – not shown in the Fig. 1.

The results presented show that apart from copper, silver is another element to form a new phase for which a formula Ag_2SO_2 has been ascribed. The fact of formation of such a phase in the Ag–O–S system calls for further studies, especially in respect of X-ray characteristics and other properties.

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Zusammenfassung — Es wurden Untersuchungen der Reaktion zwischen Ag_2SO_4 und Ag_2S an Luft angestellt. Ergebnisse einer DTA- und Röntgen-Pulveruntersuchung des Reaktionsgemisches bestätigten, daß im Ag-O-S System eine neue Phase existiert. Eine Formel der Phase ist Ag_2SO_2.