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Synthesis and some properties of $\text{Ag}_8\text{S}_4\text{O}_4$

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(Refereed)

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Abstract

It has been found that in addition to the $\text{Ag}_6\text{S}_3\text{O}_4$ phase discovered earlier, the reaction between Ag_2SO_4 and Ag_2S in the solid state leads to a phase having the formula $\text{Ag}_8\text{S}_4\text{O}_4$. This phase can be obtained by heating in air a mixture comprised initially of Ag_2SO_4 (25.0 mol%) and Ag_2S (75.0 mol%). $\text{Ag}_8\text{S}_4\text{O}_4$ melts at 400°C. In air, the melt starts decomposing immediately. The final solid product of $\text{Ag}_8\text{S}_4\text{O}_4$ decomposition is metallic silver. In inert atmosphere, thermal decomposition of the melt starts at 445°C and the final solid products of the decomposition are silver sulfide and metallic silver. $\text{Ag}_8\text{S}_4\text{O}_4$ phase crystallizes in a monoclinic system and has the following unit-cell parameters: $a = 1.42669$ nm, $b = 0.65824$ nm, $c = 1.05039$ nm, $\beta = 91.32^\circ$, $Z = 4$, $V = 0.98617$ nm³, and $d_x = 7.10$ g/cm³. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Current literature not only gives information on the well-known compounds existing in the three-component system silver–sulfur–oxygen, i.e., Ag_2O , Ag_2S , Ag_2SO_3 , Ag_2SO_4 [1–12], and others, but also contains a brief reference to a phase with the formula $\text{Ag}_8\text{S}_3\text{SO}_4$ [13]. According to Hirsch [13], this phase can be prepared by the coprecipitation method in which

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a reaction takes place in an aqueous solution between AgNO_3 and $\text{Na}_2\text{S}_2\text{O}_3$, or between Ag_2SO_4 and $\text{Na}_2\text{S}_2\text{O}_3$.

Our earlier work [14] has shown that another phase, $\text{Ag}_6\text{S}_3\text{O}_4$, was formed in that system. This phase resulted from a solid-state reaction according to the equation



In order to synthesize $\text{Ag}_6\text{S}_3\text{O}_4$, a mixture of Ag_2S and Ag_2SO_4 with the molar ratio 2:1 was heated in air until the reaction was complete [14]. Only one report on the $\text{Ag}_8\text{S}_3\text{SO}_4$ phase was found, but it seems reasonable that this phase can be obtained by the solid-state reaction:



2. Experimental

Ag_2S pure and Ag_2SO_4 analar (both of POCh, Gliwice production) were used. The reagents, weighed in suitable molar proportions, were ground and heated in air for several cycles. After each heating cycle, the samples were cooled to ambient temperature, weighed, ground, analyzed by X-ray diffraction (XRD) method, then heated again. After the final heating cycle, the samples were examined by differential thermal analysis (DTA) using a TA Instruments SDT 2960 apparatus linked to a Balzers QMS 300 ThermoStar quadrupole mass spectrometer. The DTA examinations were carried out in a helium atmosphere using platinum crucibles and a heating rate of 10 K/min. Microscopic examinations were performed using a JEOL JSM-5400 scanning electron microscope linked to an X-ray microprobe. XRD measurements of the obtained samples were performed using a DRON-3 diffractometer and $\text{Co K}\alpha$ radiation ($\lambda = 0.179021 \text{ nm}$).

Chemical analysis of the samples was done after the final heating cycle. Silver concentration was determined by titration of weighed amounts of the sample dissolved in HNO_3 with a NH_4SCN standard solution, in the presence of a $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ solution. The total amount of sulfur was determined gravimetrically, after the element had been oxidized to SO_4^{2-} by a Br_2/HNO_3 mixture and then precipitated as BaSO_4 .

3. Results and discussion

In order to obtain the $\text{Ag}_8\text{S}_3\text{SO}_4$ phase [13] by reaction of Ag_2SO_4 with Ag_2S in the solid state, several mixtures of the reagents were prepared with a range of silver sulfate concentration from 16.67 to 30.0 mol%. The mixtures were heated in air at the following cycles: 270°C (24 h), 290°C (24 h), 310°C (24 h), and 340°C (24 h). No mass changes of these mixtures were observed after each heating cycle. The diffraction pattern of a sample initially containing 25.0 mol% Ag_2SO_4 , heated as above, contains diffraction lines that cannot be considered characteristic for any of the reagents used or $\text{Ag}_6\text{S}_3\text{O}_4$ [14]. Nor does it contain any of the diffraction lines attributed by Hirsch [13] to the $\text{Ag}_8\text{S}_3\text{SO}_4$ phase. On the ground

Table 1
Chemical analysis of $\text{Ag}_8\text{S}_4\text{O}_4$ phase

Component	Results of chemical analysis (average % by weight)	Calculated content of $\text{Ag}_8\text{S}_4\text{O}_4$ components (% by weight)
Ag	81.71	81.78
S	11.84	12.16
O	6.45	6.06

of this investigation, one can infer that Ag_2S and Ag_2SO_4 in a molar ratio 3:1 react to form a new compound. This new phase is characterized by the new set of diffraction lines observed in the diffraction pattern. The formula $3\text{Ag}_2\text{S} \cdot \text{Ag}_2\text{SO}_4$ ($\text{Ag}_8\text{S}_4\text{O}_4$) has been ascribed to the new phase. $\text{Ag}_8\text{S}_4\text{O}_4$ is formed in the solid state according to the following equation:



$\text{Ag}_8\text{S}_4\text{O}_4$ has also been obtained by heating a mixture comprised of 50.0 mol% $\text{Ag}_6\text{S}_3\text{O}_4$ and 50.0 mol% Ag_2S under conditions identical to those used for the synthesis of $\text{Ag}_8\text{S}_4\text{O}_4$

Table 2
Results of indexing $\text{Ag}_8\text{S}_4\text{O}_4$ powder diffraction pattern

Line	d_{obs} (nm)	d_{calc} (nm)	h	k	l	I/I_0	Figure of merit
1	0.65829	0.65824	0	1	0	14	1049.11
2	0.59756	0.59767	1	1	0	26	377.91
3	0.59550	0.59636	2	0	3	21	60.50
4	0.52509	0.52505	0	0	2	15	61.50
5	0.48367	0.48370	2	1	0	19	63.18
6	0.33526	0.33531	4	0	1	30	45.93
7	0.31712	0.31712	2	0	3	38	46.90
8	0.31140	0.31141	2	0	3	23	49.05
9	0.30712	0.30715	1	2	1	10	49.29
10	0.29883	0.29883	2	2	0	48	50.46
11	0.28812	0.28815	2	2	1	100	48.19
12	0.27890	0.27886	0	2	2	80	46.40
13	0.27690	0.27690	5	0	1	55	47.94
14	0.26291	0.26288	3	2	1	20	44.85
15	0.25673	0.25675	3	1	3	31	43.97
16	0.25276	0.25273	5	1	1	13	41.14
17	0.24385	0.24385	0	1	4	15	40.89
18	0.24124	0.24122	1	1	4	66	40.14
19	0.23771	0.23772	6	0	0	14	40.52
20	0.23302	0.23301	6	0	1	88	40.34
21	0.22918	0.22924	2	1	4	26	31.12
22	0.21380	0.21376	4	0	4	24	26.94
23	0.21176	0.21177	5	1	3	40	27.15
24	0.20412	0.20413	6	1	2	11	26.34
25	0.19019	0.19017	6	2	1	11	23.72
26	0.18893	0.18892	6	2	1	21	23.87
27	0.18299	0.18299	3	1	5	9	23.53

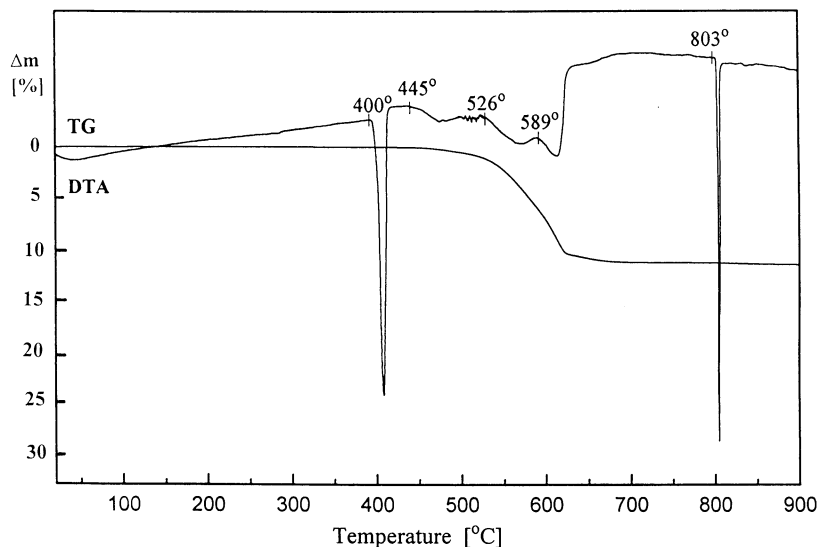
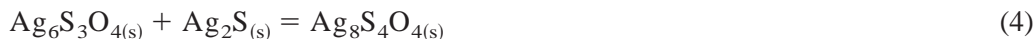


Fig. 1. DTA and TG curves of $\text{Ag}_8\text{S}_4\text{O}_4$ phase (under helium atmosphere).

from Ag_2S and Ag_2SO_4 . Thus, the compound can be formed from the $\text{Ag}_6\text{S}_3\text{O}_4/\text{Ag}_2\text{S}$ mixture according to the equation:



To determine the molar ratio Ag:S:O proposed for the new phase, elementary analysis was carried out on a sample obtained using Eq. (4). In this analysis, concentration of silver and total sulfur was determined (oxygen was determined from the difference). The results are tabulated in Table 1. Column 3 shows the calculated percentage of components in the $\text{Ag}_8\text{S}_4\text{O}_4$ phase.

Table 1 shows that the molar ratio of Ag:S:O for the new phase is 2:1:1, which is identical to that reported by Hirsch for $\text{Ag}_8\text{S}_3\text{SO}_4$ [13]. Thus, the simplest stoichiometric unit is Ag_2SO . However, the formula of the new compound was proposed on the grounds of the simplest molar proportion of the $\text{Ag}_2\text{S}:\text{Ag}_2\text{SO}_4$ reagents: 3:1. This ratio was obtained by analogy to the formula of another compound existing in the system: $\text{Ag}_2\text{SO}_4\text{--Ag}_2\text{S}$, i.e., $\text{Ag}_6\text{S}_3\text{O}_4$; the $\text{Ag}_2\text{S}:\text{Ag}_2\text{SO}_4$ molar ratio is 2:1.

The density of the $\text{Ag}_8\text{S}_4\text{O}_4$ phase was determined by the method given in ref. 15 to be $d(\text{in CCl}_4) = 6.86 \pm 0.05 \text{ g/cm}^3$. In order to determine the crystal system and parameters of the unit cell, the $\text{Ag}_8\text{S}_4\text{O}_4$ powder diffraction pattern was indexed using the program POWDER [16,17]. Table 2 shows the results of indexing. The positions of diffraction lines characteristic of $\text{Ag}_8\text{S}_4\text{O}_4$ were precisely determined using calcite as an internal standard. For indexing purposes, 27 successive reflections (2θ 12–60° region) were taken. The calculated cell parameters for $\text{Ag}_8\text{S}_4\text{O}_4$ are $a = 1.42669 \text{ nm}$, $b = 0.65824 \text{ nm}$, $c = 1.05039 \text{ nm}$, $\beta = 91.32^\circ$, $Z = 4$, $V = 0.98617 \text{ nm}^3$, the unit cell is of type P, and $d_x = 7.10 \text{ g/cm}^3$. The value of figure-of-merit (FM) for each diffraction line is defined as a reciprocal of a probability of randomly ascribing the Miller indices to a given diffraction line [18]. Accord-

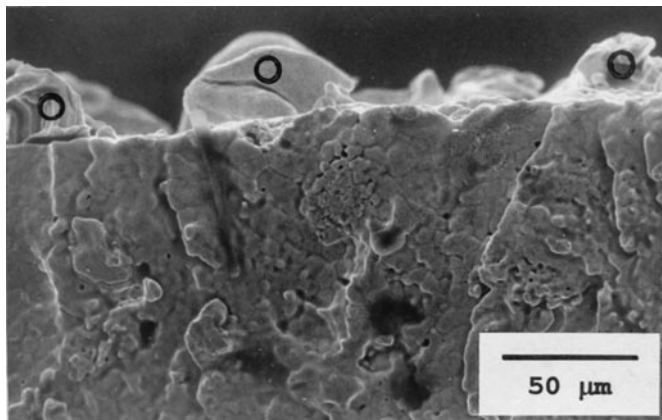


Fig. 2. Scanning electron micrograph of a sample obtained by heating $\text{Ag}_8\text{S}_4\text{O}_4$ in air at 401°C , then quenching the product in liquid nitrogen (○ metallic silver).

ing to de Wolff [18], Table 2 values of FM (all greater than or equal to 10) guarantee the correctness of indexing.

To specify thermal properties of the $\text{Ag}_8\text{S}_4\text{O}_4$ phase, DTA, TG, and microscopic investigations were carried out in helium. For microscopic measurements, samples of $\text{Ag}_8\text{S}_4\text{O}_4$ were used. They were preheated in air and at a reduced pressure for 15 min at 401 or 670°C , then quenched in liquid nitrogen.

Fig. 1 shows the DTA and TG curves for $\text{Ag}_8\text{S}_4\text{O}_4$. The first endothermic effect, observed on the DTA curve at 400°C , is characterized by melting of the phase. This fact may be confirmed by the disappearance of $\text{Ag}_8\text{S}_4\text{O}_4$ crystallites (Figs. 2 and 3) when the phase is heated in air at 401°C and reduced pressure. For comparative purposes, a scanning electron micrograph of $\text{Ag}_8\text{S}_4\text{O}_4$ polycrystallites is shown in Fig. 4.

When heated in air at 401°C , an $\text{Ag}_8\text{S}_4\text{O}_4$ sample becomes nonhomogeneous, that is, some

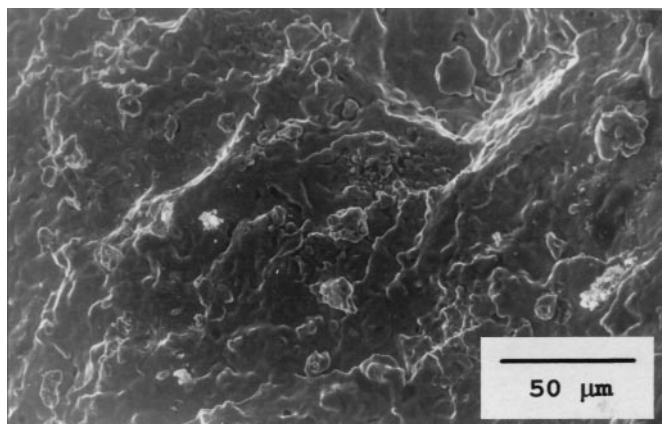


Fig. 3. Scanning electron micrograph of a sample obtained by heating $\text{Ag}_8\text{S}_4\text{O}_4$ under reduced pressure at 401°C , after quenching in liquid nitrogen.

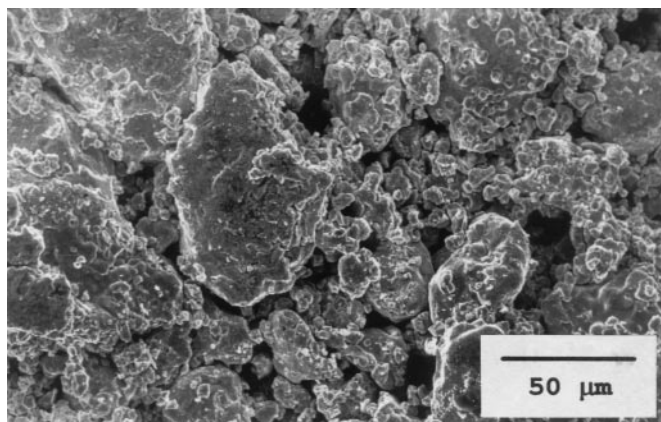


Fig. 4. Scanning electron micrograph of $\text{Ag}_8\text{S}_4\text{O}_4$ polycrystallites.

microareas solely comprised of metallic silver can be detected by X-ray microprobe (Fig. 2). By contrast, an $\text{Ag}_8\text{S}_4\text{O}_4$ sample heated under the same conditions, but at a reduced pressure, was homogeneous; the occurrence of silver, sulfur, and oxygen in the whole mass was observed (Fig. 3). The observations indicate that the liquid resulting from the melting of $\text{Ag}_8\text{S}_4\text{O}_4$ decomposes immediately in air.

At a reduced pressure, the liquid starts to decompose at 445°C . This is evident from the fact that the endothermic effect and the mass loss start at the same temperature (Fig. 1). Another endothermic effect, recorded on the DTA curve, started at 526°C and was caused by decomposition of the liquid.

An $\text{Ag}_8\text{S}_4\text{O}_4$ sample heated in air at 670°C and then quenched is homogeneous in its whole mass and contained only metallic silver (Fig. 5). On the other hand, when the same temperature was applied, but at reduced pressure, the sample was nonhomogeneous; there were some microareas of only metallic silver, and some microareas where silver and sulfur occurred together (Fig. 6).

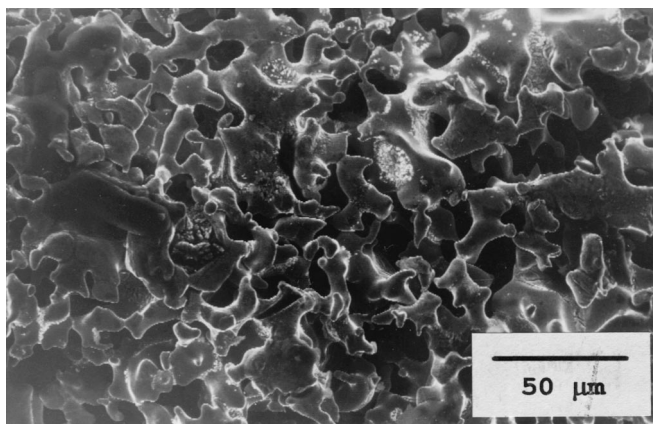


Fig. 5. Scanning electron micrograph of sample obtained by heating $\text{Ag}_8\text{S}_4\text{O}_4$ in air at 670°C , after quenching in liquid nitrogen.

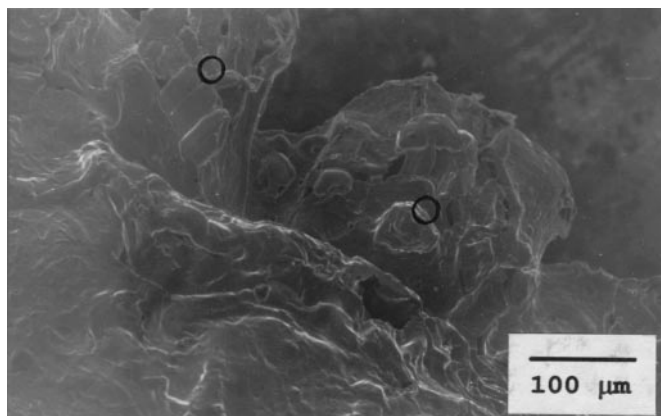


Fig. 6. Scanning electron micrograph of a sample obtained by heating $\text{Ag}_8\text{S}_4\text{O}_4$ under reduced pressure at 670°C , after quenching in liquid nitrogen (O: metallic silver).

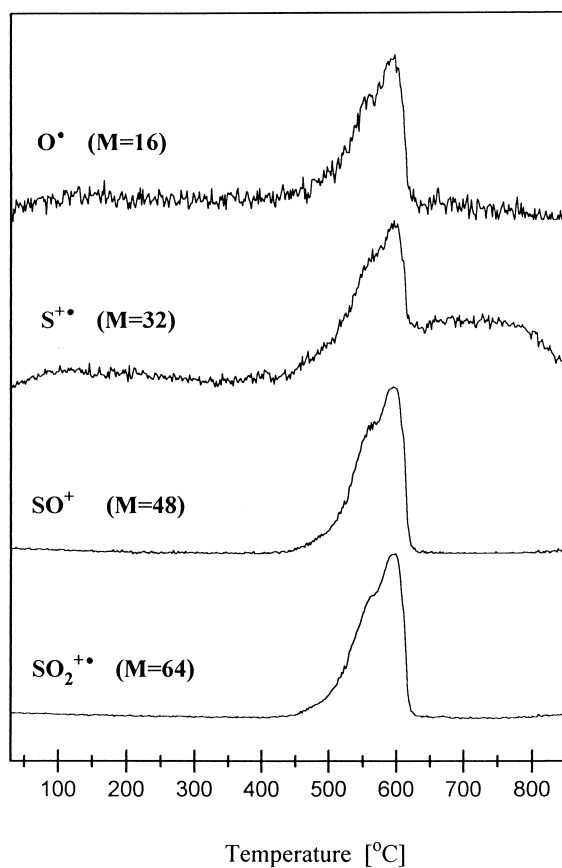


Fig. 7. MS profiles of gaseous products of $\text{Ag}_8\text{S}_4\text{O}_4$ decomposition.

In summary, decomposition of the liquid in air gives metallic silver. This fact is confirmed by the total mass loss recorded on a TG curve, which equaled 18.220% by weight. Decomposition at a reduced pressure gives a mixture of silver sulfide and metallic silver.

Endothermic effects at 589 and 803°C, observed on the $\text{Ag}_8\text{S}_4\text{O}_4$ DTA curve, were due, respectively, to a polymorphic transition of $\beta\text{-Ag}_2\text{S}$ to $\gamma\text{-Ag}_2\text{S}$ and to the melting of Ag_2S . For technical reasons, the DTA measurements of $\text{Ag}_8\text{S}_4\text{O}_4$ carried out in helium were terminated before the melting point of metallic silver was reached.

Analysis of the mass loss recorded on the TG curve of $\text{Ag}_8\text{S}_4\text{O}_4$ (Fig. 1) showed that the gaseous product of decomposition of the liquid in inert atmosphere is SO_2 . Its percentage was 11.909% by weight, which corresponds to 2 moles of SO_2 for 1 mole of $\text{Ag}_8\text{S}_4\text{O}_4$.

Additional proof of such a course of decomposition was the liberation of gases during decomposition, shown by the ionic current corresponding to the mass of the molecular SO_2^{++} ion ($M = 64$) (Fig. 7). The presence of ionic currents corresponding to the mass $M = 16$, 32, and 48 is thought to be a result of advanced fragmentation of the molecular SO_2^{++} ion, leading to radical O^{\bullet} ($M = 16$), fragmentary radical cation $\text{S}^{+\bullet}$ ($M = 32$), and fragmentary cation SO^+ ($M = 48$). Hence, the inert-medium decomposition of the liquid, arising from melting $\text{Ag}_8\text{S}_4\text{O}_4$, can be presented as follows:



4. Conclusions

From the experiments conducted, we draw the following conclusions:

- The reaction taking place in the solid state between Ag_2S and Ag_2SO_4 mixed in the molar ratio 3:1 leads to a new phase, with a molecular formula $\text{Ag}_8\text{S}_4\text{O}_4$.
- $\text{Ag}_8\text{S}_4\text{O}_4$ melts at 400°C.
- In air, the melt decomposes immediately to give metallic silver.
- In inert atmosphere and reduced pressure, the melt starts to decompose at 445°C, to give silver sulfide and metallic silver.
- $\text{Ag}_8\text{S}_4\text{O}_4$ crystallizes in a monoclinic system.

Acknowledgments

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