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Melting and thermal decomposition of β-$Ag_6S_3O_4$

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Abstract

It was found that, in air as well as in an inert atmosphere, β-$Ag_6S_3O_4$ melts incongruently at 390°C. Solid product of the incogruent melting of β-$Ag_6S_3O_4$ is β-$Ag_8S_4O_4$, the second phase existing in the Ag_2SO_4-Ag_2S system. β-$Ag_8S_4O_4$ melts at 400°C. At this temperature and in air the liquid obtained after melting starts decomposing to give metallic silver. In an inert atmosphere or at reduced pressure the liquid starts decomposing at 530°C and the final solid products of this decomposition are silver sulfide and metallic silver, gaseous product is SO_2. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: β-$Ag_6S_3O_4$; Ag_2SO_4-Ag_2S system; DTA-TG; SEM; MS

1. Introduction

Our earlier studies on the reactivity in the solid state between Ag_2SO_4 and Ag_2S showed that both reagents are not mutually inert and react to give two compounds: β-$Ag_6S_3O_4$ and β-$Ag_8S_4O_4$ [1,2]. As was found, β-$Ag_8S_4O_4$ is formed by heating in air an initial mixture: 25.00 mol% of Ag_2SO_4 and 75.00 mol% of Ag_2S according to the following reaction:

$$Ag_2SO_{4(s)} + 3Ag_2S_{(s)} \rightarrow \beta\text{-}Ag_8S_4O_{4(s)} \qquad (1)$$

β-$Ag_8S_4O_4$ crystallizes in a monoclinic system and has the following parameters of the unit cell: $a = 1.426(7)$ nm, $b = 0.658(2)$ nm, $c = 1.050(4)$ nm, $\beta = 91.3(2)^\circ$, $Z = 4$ [2]. Thermal properties of β-$Ag_8S_4O_4$ were determined in detail in air and inert atmosphere [2].

β-$Ag_6S_3O_4$, the second phase in the Ag_2SO_4-Ag_2S system, can be obtained by heating in air an initial mixture: 33.33 mol% of Ag_2SO_4 and 66.67 mol% of Ag_2S according to Eq. (2):

$$Ag_2SO_{4(s)} + 2Ag_2S_{(s)} \rightarrow \beta\text{-}Ag_6S_3O_{4(s)} \qquad (2)$$

or by heating in air β-$Ag_8S_4O_4$ and Ag_2SO_4 mixed at the molar ratio of 2 : 1 according to following reaction:

$$2\beta\text{-}Ag_8S_4O_{4(s)} + Ag_2SO_{4(s)} \rightarrow 3\beta\text{-}Ag_6S_3O_{4(s)} \qquad (3)$$

β-$Ag_6S_3O_4$ is also monoclinic with lattice constants of $a = 1.778(2)$ nm, $b = 0.698(2)$ nm, $c = 1.343(2)$, $\beta = 105.60^\circ$, $Z = 8$ [1]. In the earlier [1] work it was found that β-$Ag_6S_3O_4$ melts at 390 ± 5°C.

Hirsch [3] found, that a reaction carried out in an aqueous solution between silver salts (nitrate(V) or sulfate(VI)) and sodium thiosulfate(VI) led to a phase, to which he attributed the formula $Ag_8S_3SO_4$. Accord-

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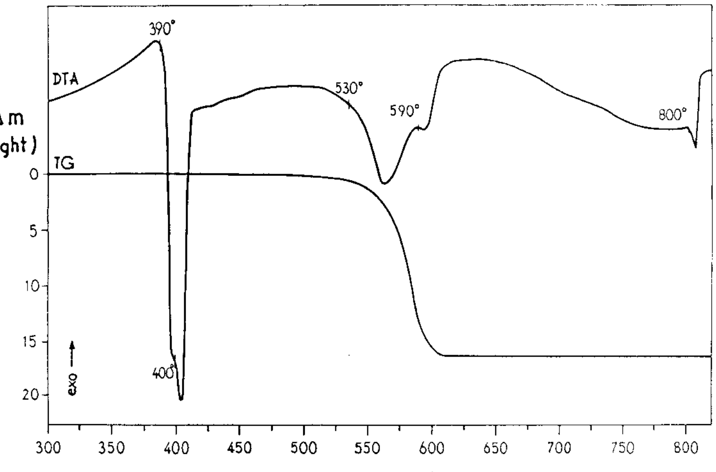

Fig. 1. DTA and TG curves of β-$Ag_6S_3O_4$ (helium, heating rate 10 K/min).

ing to Hirsch, this phase crystallizes in a tetragonal system with lattice constants: $a=b=0.7201$ nm, $c=1.0200$ nm, $Z=2$.

Our earlier studies on the reaction occurring between aqueous solutions of $AgNO_3$ and $Na_2S_2O_3$ showed that these reagents form two phases to which the summary formulas: α-$Ag_8S_4O_4$ and α-$Ag_6S_3O_4$ were ascribed [4]. It was found that quantitative contents of elements as well as a diffraction pattern and lattice constants ($a=b=0.720(5)$ nm, $c=0.511(4)$ nm, $Z=1$ [4]) for α-$Ag_8S_4O_4$ were very similar to these obtained by Hirsch for $Ag_8S_3SO_4$. On the ground of the chemical analysis it was also found that quantitative contents of elements in α-$Ag_6S_3O_4$ were the same as in β-$Ag_6S_3O_4$ phase obtained by a reaction in the solid state [4]. The α-$Ag_6S_3O_4$ phase crystallizes in a monoclinic system and has the following lattice constants: $a=2.096(2)$ nm, $b=0.531(2)$ nm, $c=1.498(8)$ nm, $\beta=102.7(8)^\circ$, $Z=8$ [4]. Our DTA and X-ray studies [4] showed that α-$Ag_8S_4O_4$ and α-$Ag_6S_3O_4$ phases were low-temperature polymorphic modifications of β-$Ag_8S_4O_4$ or β-$Ag_6S_3O_4$, respectively [4]. The α-$Ag_8S_4O_4$ and α-$Ag_6S_3O_4$ undergo irreversible, endothermic polymorphic transitions to high-temperature polymorphic forms at 223 and 221°C, respectively [4].

This work presents the results of investigations carried out in order to study the thermal properties of β-$Ag_6S_3O_4$ in air or inert atmosphere.

2. Experimental

β-$Ag_6S_3O_4$ was prepared by heating a Ag_2SO_4 and Ag_2S mixture as described previously [1].

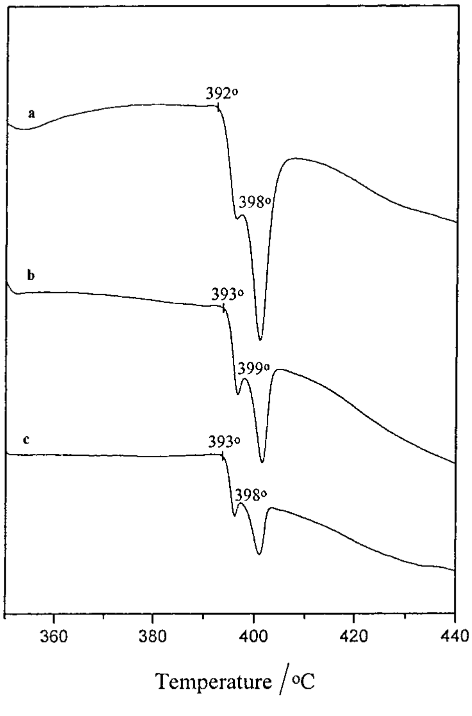

Fig. 2. DTA curve of β-$Ag_6S_3O_4$ (helium, heating rate (a) 5 K/min; (b) 2 K/min; (c) 1 K/min).

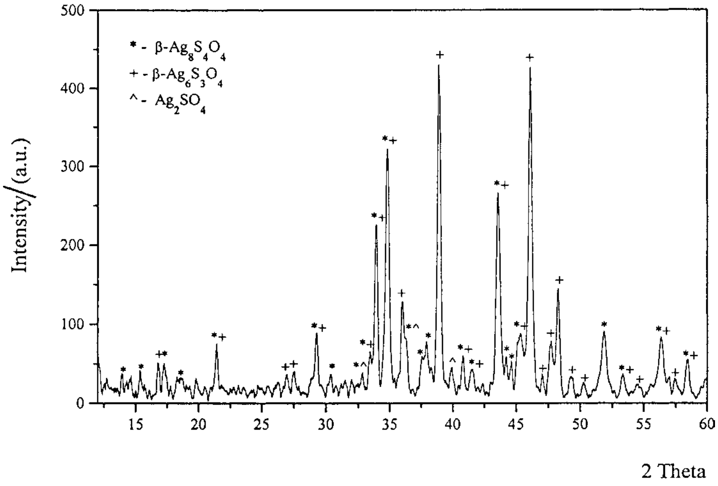

Fig. 3. Diffraction pattern for a sample obtained by heating, in air, β-$Ag_6S_3O_4$ at 395°C and then quenched.

DTA-TG examinations of β-$Ag_6S_3O_4$ were made using a TA Instruments SDT 2960 apparatus. These investigations were accomplished in different atmospheres (helium, air) using corundum crucibles and heating rate of 1, 2, 5 or 10 K/min. X-ray diffraction (XRD) measurements were performed using a DRON-3 diffractometer and CoKα radiation ($\lambda = 0.179021$ nm). Mass spectroscopic analysis of gaseous products of β-$Ag_6S_3O_4$ decomposition was made in a helium atmosphere using a Balzers QMS 300 ThermoStar quadrupole mass spectrometer.

For microscopic and XRD studies samples of β-$Ag_6S_3O_4$ were heated in air or at reduced pressure for 15 min. at 395, 401 or 670°C and then rapidly quenched. Microscopic observations were made using a JOEL JSM-5400 scanning electron microscope linked to a X-ray microprobe.

3. Results and discussion

3.1. Thermal properties in an inert atmosphere or at reduced pressure

Fig. 1 shows DTA and TG curves of β-$Ag_6S_3O_4$ for temperature range 300–820°C, recorded in the helium atmosphere with a heating rate of 10 K/min. For

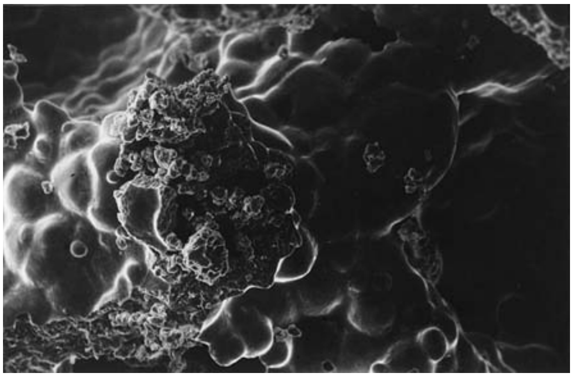

Fig. 4. Scanning electron micrograph of a sample obtained by heating, at reduced pressure, β-$Ag_6S_3O_4$ at 395°C and then quenched, magnification 1000×.

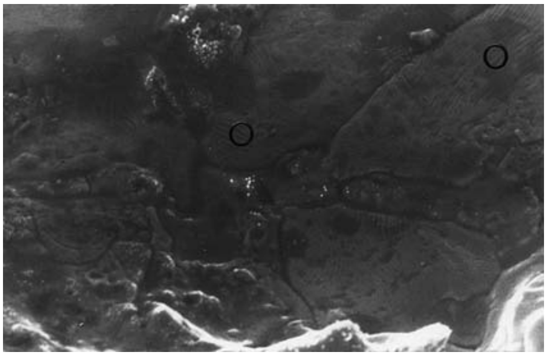

Fig. 5. Scanning electron micrograph of a sample obtained by heating, at a reduced pressure, at 670°C and then quenched, magnification 2000× (o-metallic silver).

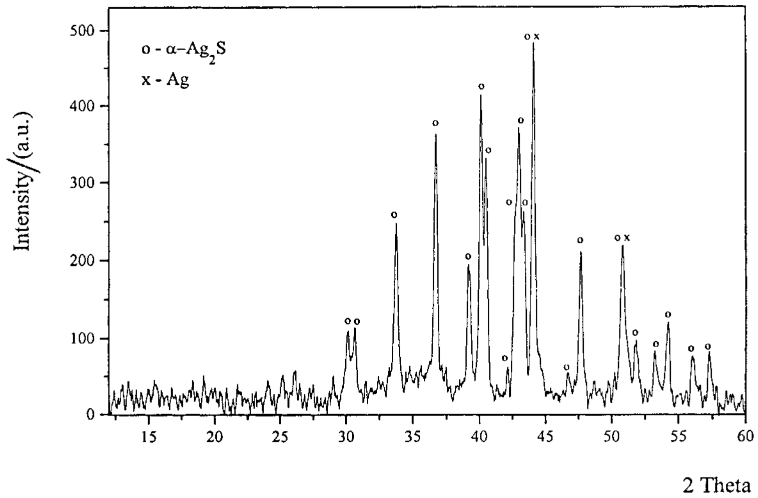

Fig. 6. Diffraction pattern for a sample obtained by heating β-$Ag_6S_3O_4$, at reduced pressure, at 670°C and then quenched.

comparison Fig. 2 shows DTA curves of β-$Ag_6S_3O_4$ for temperature range 350–440°C recorded in helium with heating rates: 1, 2 or 5 K/min. The first endothermic effect, observed on DTA curve (Figs. 1 and 2) at about 390°C, is characterized by incongruent melting β-$Ag_6S_3O_4$. The second effect with its onset at about 400°C, is associated with melting β-$Ag_8S_4O_4$, phase deposited during the incongruent melting β-$Ag_6S_3O_4$. Thus, the melting β-$Ag_6S_3O_4$ can be described by the following equation:

$$\beta\text{-}Ag_6S_3O_{4(s)} \rightarrow \beta\text{-}Ag_8S_4O_{4(s)} + \text{liquid} \qquad (4)$$

The liquid resulting from melting β-$Ag_6S_3O_4$ and then β-$Ag_8S_4O_4$ starts decomposing at 530°C. This fact can

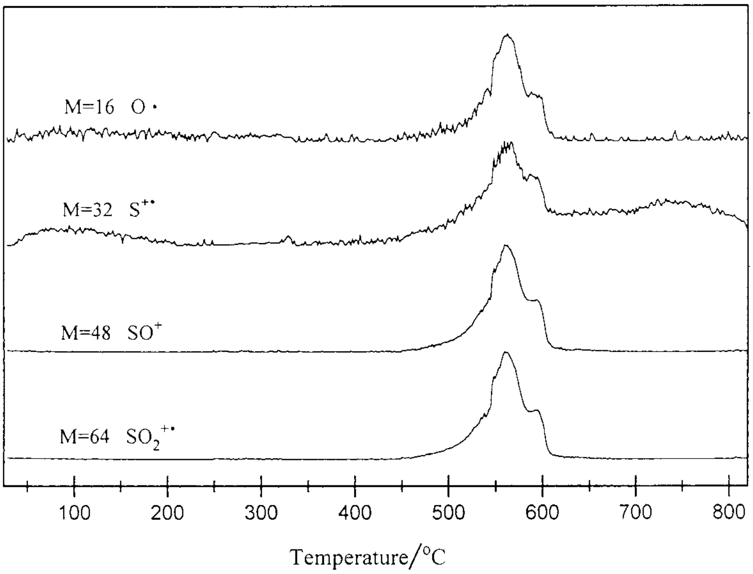

Fig. 7. MS profiles of gaseous products of the decomposition of β-$Ag_6S_3O_4$.

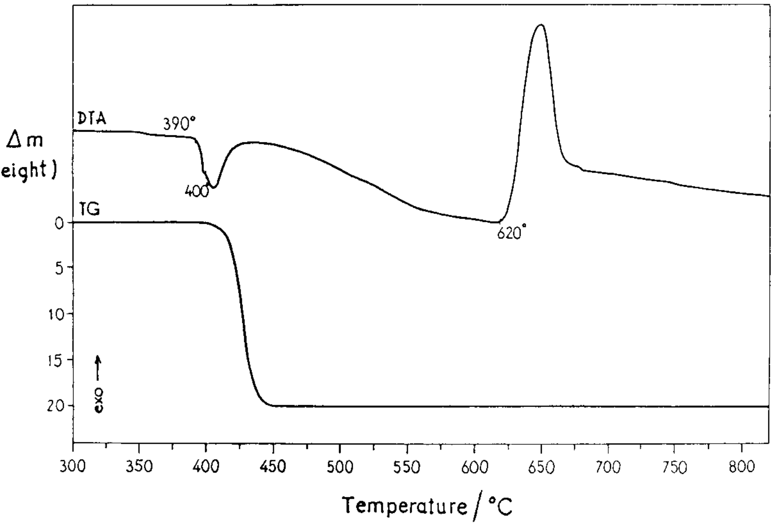

Fig. 8. DTA and TG curves of β-$Ag_6S_3O_4$ (air, heating rate 10 K/min).

be confirmed by the endothermic effect, recorded on the DTA curve (Fig. 1), and starting at the same temperature a mass loss recorded on the TG curve (Fig. 1). The endothermic effect with its onset at 590°C is also associated with the decomposition of the liquid. The endothermic effect with its onset at 800°C is due to melting Ag_2S. For technical reasons the DTA measurements of β-$Ag_6S_3O_4$ carried out in helium were terminated before the melting point of metallic silver.

The melting behaviour of β-$Ag_6S_3O_4$ was also confirmed by XRD method and microscopic observations. On the ground of XRD method it was found that β-$Ag_6S_3O_4$ sample, heated at a reduced pressure at 395°C and then quickly quenched contained β-$Ag_8S_4O_4$, β-$Ag_6S_3O_4$ and Ag_2SO_4 (Fig. 3). It was also found that, this sample contained liquid and polycrystallites (Fig. 4). The occurrence of silver, sulfur and oxygen in the crystallites as well as in the liquid can be detected using a X-ray microprobe.

It was also found that the sample of β-$Ag_6S_3O_4$, heated at a reduced pressure and the temperature a little higher than the β-$Ag_8S_4O_4$ melting point, i.e. at 401°C, and then rapidly quenched, did not contain any crystallites. The presence of silver, sulfur and oxygen in its whole mass can be observed using the same instrument.

The sample obtained by heating β-$Ag_6S_3O_4$ at 670°C at a reduced pressure and then quenched, is non-homogeneous. Many microareas containing sole metallic silver and those where silver and sulfur were occurring together were detected (Fig. 5). Diffraction patterns of considered sample (Fig. 6) and solid residue obtained after DTA measurements contain the set of diffraction lines characteristic for Ag_2S and the set of reflections attributed to silver.

Analysis of the total mass loss recorded on the TG curve of β-$Ag_6S_3O_4$ (Fig. 1) gives an indication that

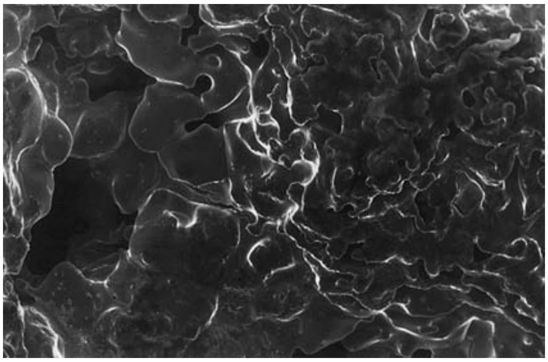

Fig. 9. Scanning electron micrograph of β-$Ag_6S_3O_4$ sample heated, in air, at 670°C and then quenched, magnification 500×.

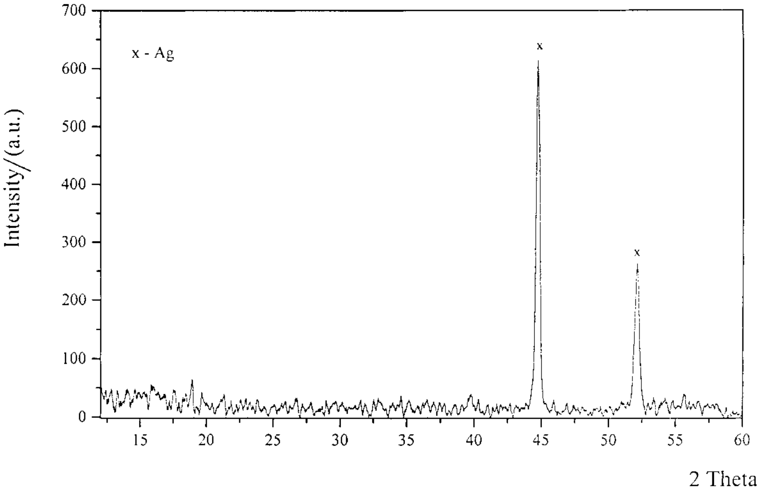

Fig. 10. Diffraction pattern for a sample obtained by heating β-$Ag_6S_3O_4$, in air, at 670°C and then quenched.

the gaseous product of decomposition of the liquid resulting from melting β-$Ag_6S_3O_4$ in an inert atmosphere is SO_2. The value of the mass loss equals 15.791% by weight (theoretical value–15.869% by weight), which corresponds to 2 moles of SO_2 falling to 1 mole of β-$Ag_6S_3O_4$.

An additional proof of this fact can be presence of ionic current corresponding to the mass of molecular $SO_2^{+\bullet}$ ion ($M = 64$) in the MS profiles of gaseous products of β-$Ag_6S_3O_4$ decomposition (Fig. 7). The presence of ionic currents corresponding to the mass $M = 16$, 32 and 48 is due to an advanced fragmentation of the molecular $SO_2^{+\bullet}$ ion leading to radical $O^\bullet$ ($M = 16$), fragmentary radical cation $S^{+\bullet}$ ($M = 32$) and fragmentary cation SO^+ ($M = 48$).

The total mass loss recorded on the TG curve (Fig. 1), microscopic observations and X-ray measurements of a sample obtained by heating β-$Ag_6S_3O_4$ at 670°C and at a reduced pressure and then quenched indicate that final solid products of decomposition of liquid resulting from melting β-$Ag_6S_3O_4$ are silver sulfide and metallic silver.

Hence, in an inert atmosphere and at reduced pressure, the decomposition of the liquid arising from melting β-$Ag_6S_3O_4$ can be described as the following process:

$$\text{liquid} \rightarrow 4Ag_{(s)} + Ag_2S_{(s)} + 2SO_{2(g)} \quad (5)$$

3.2. Thermal properties in air

Fig. 8 shows DTA and TG curves of β-$Ag_6S_3O_4$ recorded in air with heating rate of 10 K/min. The endothermic effects at about 390 and 400°C are associated with incongruent melting β-$Ag_6S_3O_4$ and melting β-$Ag_8S_4O_4$, respectively. The exothermic effect, recorded on the DTA curve (Fig. 8) with its onset at 620°C is probably due to oxidation of SO_2 to SO_3. It is suggested that sulfur dioxide is liberated during the β-$Ag_6S_3O_4$ decomposition in air.

Microscopic observations of a sample obtained after heating, in air, at 401°C and then quenched indicate that this sample did not contain any crystallites. Some microareas composed of sole metallic silver can be detected. Therefore, the liquid resulting from melting β-$Ag_6S_3O_4$ in air decomposes immediately.

It was also found, on the ground of microscopic examinations, that a sample of β-$Ag_6S_3O_4$ heated in air at 670°C and then quickly quenched, contained only metallic silver in its whole mass (Fig. 9). This fact is also confirmed by X-ray measurements. The diffraction patterns of the considered sample and a solid residue after DTA measurements contain only reflections characteristic for silver (Fig. 10).

Therefore, decomposition of the liquid, obtained after melting β-$Ag_6S_3O_4$ in air, gives finally metallic silver. Additional proof of this fact can be the total mass loss–19.930% by weight (theoretical value–

19.841% by weight) recorded on the TG curve (Fig. 8).

Acknowledgements

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