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Polymorphism of the $Ag_8S_4O_4$ and $Ag_6S_3O_4$ compounds

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Experimental results of the reaction occurring between aqueous solutions of $AgNO_3$ and $Na_2S_2O_3$ were presented in this work. It has been demonstrated that these reagents form two phases to which the summary formulas: α-$Ag_8S_4O_4$ and α-$Ag_6S_3O_4$ were ascribed. The α-$Ag_8S_4O_4$ phase crystallizes in a tetragonal system and has the following parameters of the unit cell: $a = b = 0.72052$ nm, $c = 0.51140$ nm, $V = 0.26550$ nm^3, $Z = 1$, $d_x = 6.60$ g/cm^3. At 223°C α-$Ag_8S_4O_4$ undergoes an irreversible, endothermic polymorphic transition. The heat of this transition amounts 8.03×10^{-3} J/mol. A high-temperature polymorphic form β-$Ag_8S_4O_4$ melts at 400°C. The α-$Ag_6S_3O_4$ phase crystallizes in a monoclinic system and has the following parameters of the unit cell: $a = 2.09616$ nm, $b = 0.53118$ nm, $c = 1.49885$ nm, $\beta = 102.78°$, $V = 1.62753$ nm^3, $Z = 8$, $d_x = 6.59$ g/cm^3. α-$Ag_6S_3O_4$ also undergoes an irreversible, endothermic polymorphic transition at 221 °C. The heat of this transition amounts 7.65×10^{-3} J/mol. A high-temperature form, β-$Ag_6S_3O_4$, melts at 390°C.

1. Introduction

Potographic techniques have been widely used in human everyday life for a long time and therefore other applications of photography become imperceptible on that background. The most important applications include: aerophotography and infrared photography as well as photography used as non-destructive method of material investigations i.e. scanning and transmission electron microscopy (SEM and TEM). Nuclear magnetic resonanse photography (NMR photography) finding application in medicine, significantly widens the perceptional possibilities of the human body, therefore this is one of the most modern diagnostic methods.

Among the photographic processes taking place in the photographic emulsion development of a film, followed by its fixation are the most important. Film development is based on the reduction of sensitive (as a result of exposure) grains of silver halides to metallic silver. Unexposed and nondestroyed silver salts in a developer are removed from an emulsion by their dissolution in a fixing agent (sodium thiosulfate(VI)) followed by washing with water. Knowledge on the reaction mechanism which may take place during the development and fixation of the film as well as on the reaction products affect the quality of obtained negative and the photography afterwards.

Hirsch [1] found, during the studies carried out in Research Division Kodak Limited, that the reaction carried out in an aqueous solution between the silver salts (nitrate(V) or sulfate(VI)) and sodium thiosulfate(VI)—a component of a developer, led to a new phase, to which he attributed the formula $Ag_8S_3SO_4$. According to Hirsch, this phase crystallizes in a tetragonal system and its unit cell has the following parameters: $a = b = 0.7201$ nm, $c = 1.0200$ nm, $Z = 2$, $d_{exp} = 6.67$ g/cm^3. Hirsch [1] has also demonstrated that at 246°C $Ag_8S_3SO_4$ undergoes an irreversible, endothermic transition and melts at 405°C. The $Ag_8S_3SO_4$ phase conduct the electric current in the solid state [1].

Our studies were aimed at stating whether the phases obtained previously by us i.e. $Ag_6S_3O_4$ [2] and $Ag_8S_4O_4$ [3], arising from a reaction carried out in the solid state between Ag_2SO_4 and Ag_2S, can be obtained from the reaction performed in an aqueous solution between the Ag^+ and $S_2O_3{}^{2-}$ ions.

2. Experimental

$AgNO_3$ p.a. and pure $Na_2S_2O_3 \cdot 5H_2O$, both reagents of POCh production (Gliwice, Poland), were used for the experiments. The reagents weighed in suitable amounts were dissolved in double-distilled water. Such obtained solutions were transferred to a beaker. When the solution were combined, the formation of precipitate was observed, the colour of which turned within five minutes from bright yellow to brown. The precipitates obtained were stirred magnetically for two days in a dark room. Subsequently, the precipitates were filtrated, rinsed with double-distilled water and dried at 110°C until a constatnt weight was attained.

The preparations obtained in this way were object of a chemical analysis for the content of silver and total amount of sulfur. Silver was determined by titrating weighed samples, dissolved in a dilute HNO_3 solution, with a NH_4SCN standard solution in the presence of $NH_4Fe(SO_4)_2$ solution. The total amount of sulfur was determined gravimetrically, in the form of $BaSO_4$, after sulfur has been oxidized to SO_4^{2-} by a mixture of Br_2 and concentrated HNO_3 solution.

The solubility of obtained preparations in a 6-molar aqueous ammonia solution was also examined. For this purpose the weighed samples were shaken with the ammonia solution for 24 hours and then filtered using Schott's funnels. The filtrate was object of a chemical analysis for the content of Ag^+ and SO_4^{2-} ions. The Ag^+ ions were determined by titration, whereas the SO_4^{2-} ions gravimetrically, in the form of $BaSO_4$, after previous precipitation of AgCl precipitate in a strongly acidic medium. A weight of precipitate insoluble in an aqueous ammonia solution was also determined. The precipitates dried to a constant weight were examined by XRD method.

The DTA examinations of the phases were preformed using a TA Instruments STD 2960 apparatus. These measurements were carried out in an atmosphere of helium, using corundum crucibles at a heating rate of 10 deg/min.

The DSC measurements of formed preparations were performed using a TA Instruments DSC 2010 apparatus. The measurements were carried out in aluminium crucibles using helium as the carrier gas and at a heating rate of 5 deg/min.

X-ray diffraction phase analysis of the samples was performed by a diffractometer DRON-3 using Co K_α radiation, $\lambda = 0.179021$ nm.

The microscopic examinations were made using a JOEL JSM-5400 scanning electron microscope.

3. Results and discussion

Investigations were started with trials of synthesis of $Ag_8S_3SO_4$ phase, previously obtained by Hirsch. For this purpose, there were made several experiments consisting in mixing together aqueous solutions of $AgNO_3$ and $Na_2S_2O_3$. The precipitates, obtained as a result of the reaction, were filtered and then dried until a constant weight was attained. The phase composition of the obtained preparations was determined by XRD method. The diffraction pattern of a sample obtained from a reaction mixture in which the initial concentrations of Ag^+ and $S_2O_3^{2-}$ ions were ca. 0.156 and ca. 0.017 mol/dm^3, respectively (sample No. 1), showed diffraction lines characterizing the $Ag_8S_3SO_4$ phase. On the other hand, the diffraction pattern of a sample obtained from a reaction mixture in which the initial concentrations of the Ag^+ and $S_2O_3^{2-}$ were ca. 0.617 and ca. 0.020 mol/dm^3, respectively (sample No. 2), contained a set of diffraction lines which could not be attributed neither to the initial reagents nor to any of the known phases occuring in the silver-oxygen-sulfur system. The obtained samples were object of a chemical analysis for a total amount of silver and sulfur (oxygen content was determined from the difference). The obtained results are presented in Table I. The experimental results concerning the solubility of the prepared samples in the aqueous ammonia solution were also presented in this Table.

The data collected in Table 1 unequivocally imply that:

—the percentage of silver, sulfur and oxygen in sample 1 corresponds to the percentage of these elements in the $Ag_8S_4O_4$ phase, which we have earlier prepared by a reaction taking place in the solid state between Ag_2SO_4 and Ag_2S, at the molar ratio of initial reagents — 1 : 3 [2],

—the percentage of silver, sulfur and oxygen in sample 2 corresponds to the precentage of these elements in the $Ag_6S_3O_4$ phase, also prepared by a reaction taking plase in the solid state between Ag_2SO_4 and Ag_2S at the molar ratio — 1 : 2 [3].

The XRD investigations have shown that the dry residue, obtained by an action of ammonia aqueous solution on the sample 1 and 2, is Ag_2S in both cases. The mass balance calculated for the weight portions of samples 1 and 2 treated with an ammonia solution has shown that the contents of Ag^+ and SO_4^{2-} ions correspond to the composition of Ag_2SO_4, owing to the selective solubility of both samples in an aqueous

TABLE I Results of chemical analysis of prepared samples

	Determined values for sample No. 1 [% by weight]	Theoretical content for $Ag_8S_4O_4$ [% by weight]	Theoretical content for a mixture comprising 25.00 mol % of Ag_2SO_4 and 75.00 mol % of Ag_2S [% by weight]	Determined values for sample No. 2 [% by weight]	Theoretical content for $Ag_6S_3O_4$ [% by weight]	Theoretical content for a mixture comprising 33.33 mol % of Ag_2SO_4 and 66.67 mol % of Ag_2S [% by weight]
Ag_{total}	81.701	81.780	81.780	80.124	80.159	80.159
S_{total}	12.092	12.156	12.156	11.867	11.915	11.915
O	6.207	6.064	6.064	8.009	7.926	7.926
Dry residue from interaction with aqueous NH_3 (Ag_2S)	70.502	——	70.451	61.408	——	61.382
Ag^+ (in aq. NH_3)	19.867	——	20.445	26.662	——	26.720
SO_4^{2-} (in aq. NH_3)	9.077	——	9.104	11.891	——	11.898

ammonia solution. It also results from the mass balance that the molar ratio of Ag_2SO_4, contained in an aqueous ammonia solution, to Ag_2S, which is the dry residue after dissolution of sample 1, amounts 1 : 3, whereas for the sample 2 amounts 1 : 2. On the basis of data contained in Table I, the summary formula $Ag_8S_4O_4$ has been attributed to sample 1, whereas $Ag_6S_3O_4$ to sample 2.

The $Ag_8S_4O_4$ is dark-brown in colour. Its density measured by the method according to [4] amounts $d(CCl_4) = 6.54 \pm 0.05$ g/cm^3. The $Ag_6S_3O_4$ phase is chocolate-brown in colour, its density amounts $d(CCl_4) = 6.58 \pm 0.05$ g/cm^3. As was confirmed by XRD method, both phases, exposed to the light, undergo a slow decomposition to metallic silver.

Figs. 1 and 2 show the DTA curves of the phases recorded in the temperature range: 20–420°C. The endothermic effect recorded on the DTA curve for $Ag_8S_4O_4$ and starting at 400°C is associated with melting of this phase. The onset temperature of this effect exactly corresponds to the melting temperature of the phase previously obtained by us as a result of a reaction taking place in the solid state between Ag_2SO_4 and Ag_2S, at the molar ratio of these reagents—1 : 3 [2]. Similarly, the effect recorded on the DTA curve of $Ag_6S_3O_4$, starting at 390°C, is also associated with the melting of this compound. The onset temperature of this effect strictly corresponds to the melting temperature of the phase which is formed by the reaction in the solid state between Ag_2SO_4 and Ag_2S at the molar ratio of these reagents—1 : 2 [3]. The consistency of both the melting temperatures and the quantitative compositions, determined for phases obtained by the co-precipitation method with those determined for the phases obtained as a result of reactions taking place in the solid state suggests that the first endothermic effects observed on the DTA curves of "wet" prepared phases are associated with polymorphic transition. These effects start at 223°C in a case of $Ag_8S_4O_4$ and at 221°C for $Ag_6S_3O_4$.

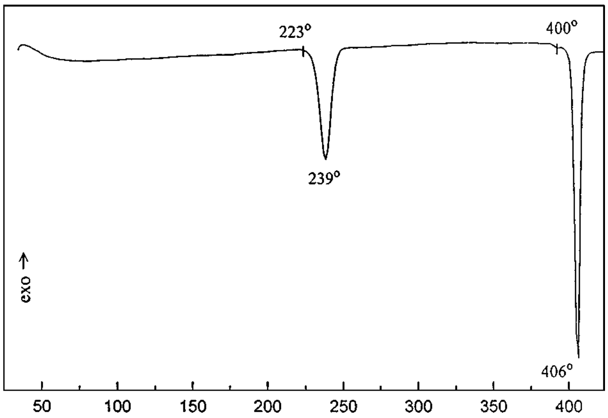

Figure 1 DTA curve of α-$Ag_8S_4O_4$ phase.

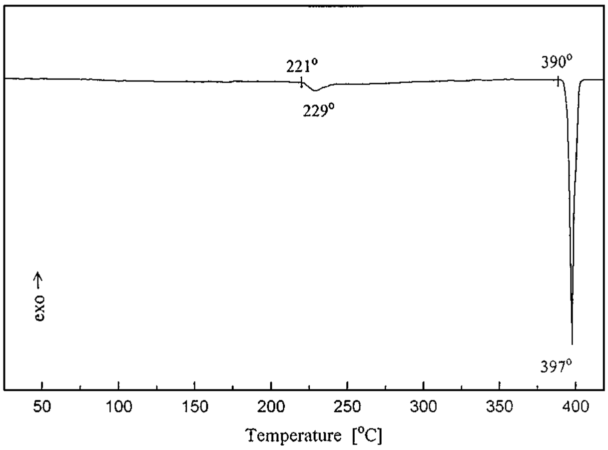

Figure 2 DTA curve of α-$Ag_6S_3O_4$ phase.

In order to confirm this assumption, the phases obtained by the precipitation method were heated at 260°C, i.e. above the temperature of the polymorphic transition, and then quenched to ambient temperature. Such prepared samples were examined by XRD metod. Based on the experimental results it was concluded that:

- —the diffraction pattern of a sample obtained by heating of the $Ag_8S_4O_4$ phase contains only a set of diffraction lines characterizing a phase of the same molecular formula, prepared as a result of the reaction in the solid state between Ag_2SO_4 and Ag_2S at the molar ratio 1 : 3 [2],
- —the diffraction pattern of the sample obtained by heating the $Ag_6S_3O_4$ phase contains only a set of diffraction lines characterizing a phase of the same molecular formula, previously obtained by a reaction taking place in the solid state between Ag_2SO_4 and Ag_2S, at the molar ratio of the reagents 1 : 2 [3].

Microscopic examinations of the phases prepared by the "wet" method (Figs. 3 and 4) and of samples obtained by heating these phases above their polimorphic transition temperatures (Figs. 5 and 6) have shown morphological differences of polycrystallites.

The XRD examinations have shown that heating of the phases prepared by the reaction taking place in the solid state between Ag_2SO_4 and Ag_2S over long periods of time (even one week) at 200°C, i.e. below the temperature of the polymorphic transition does not lead to the formation of the phases obtained from an aqueous solution by the precipitation method. This entitles us to the conclusion that the polymorphic transition of the phases obtained by "wet" method, is a monotropic transition. For the sake of distinction, the low-temperature polymorphic forms of the $Ag_8S_4O_4$ and $Ag_6S_3O_4$ compounds, obtained as a result of precipitation from an aqueous solution, were designated as α-modifications, whereas the high-temperature forms, obtained by the reaction taking place in the solid state, as β-modifications.

Heats of the endothermic, polymorphic transitions, determined by DSC method, amount: for α-$Ag_8S_4O_4$ – 8.03×10^{-3} J/mol, whereas for α-$Ag_6S_3O_4$ – 7.65×10^{-3} J/mol.

In order to specify the crystal systems and parameters of the unit cells, an indexing of α-$Ag_8S_4O_4$ and α-$Ag_6S_3O_4$ powder diffraction patterns has been made using the programme POWDER [5, 6]. The positions of diffraction lines characteristic of α-$Ag_8S_4O_4$

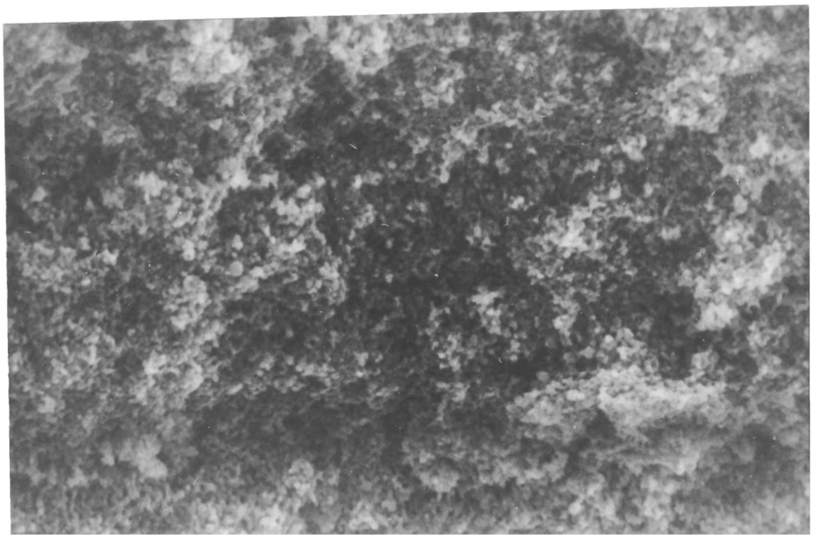

Figure 3 Scanning electron micrograph of α-$Ag_8S_4O_4$, magnification 5000×.

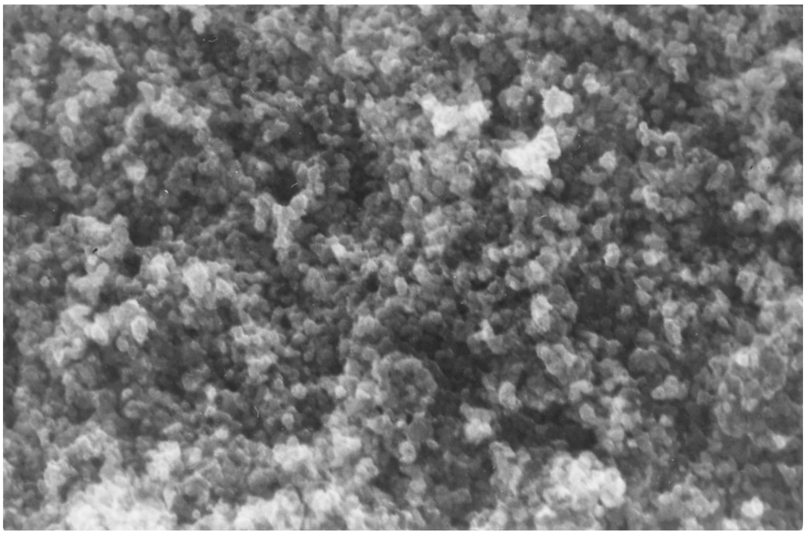

Figure 4 Scanning electron micrograph of α-$Ag_6S_3O_4$, magnification 5000×.

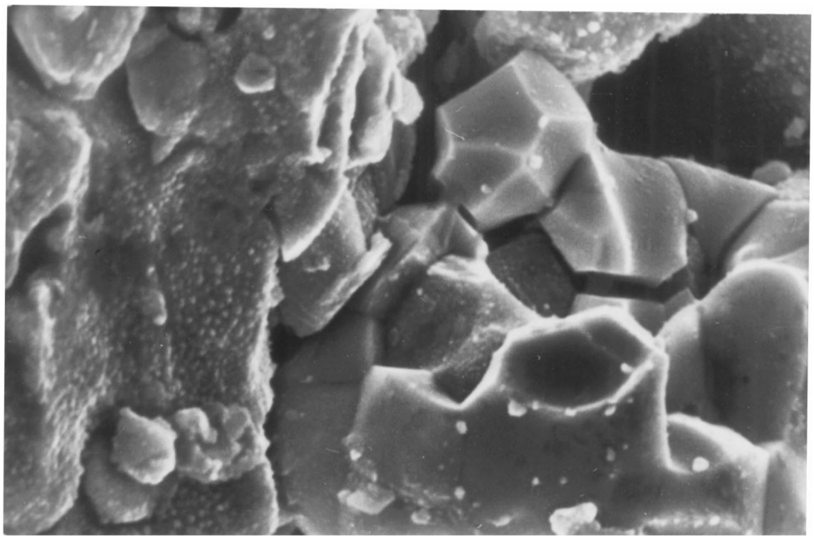

Figure 5 Scanning electron micrograph of sample obtained after heating α-$Ag_8S_4O_4$, magnification 2000×.

and α-$Ag_6S_3O_4$ have been precisely determined using calcite as an internal reference standard. For the indexing purposes 35 successive reflexions (for α-$Ag_8S_4O_4$, 2Θ 12–110° region) and 38 (for α-$Ag_6S_3O_4$, 2Θ 12–47° region) have been taken. Tables II and III show the results of indexing powder diffraction patterns of α-$Ag_8S_4O_4$ and α-$Ag_6S_3O_4$. The calculated parameters of the unit cell for α-$Ag_8S_4O_4$ amount:

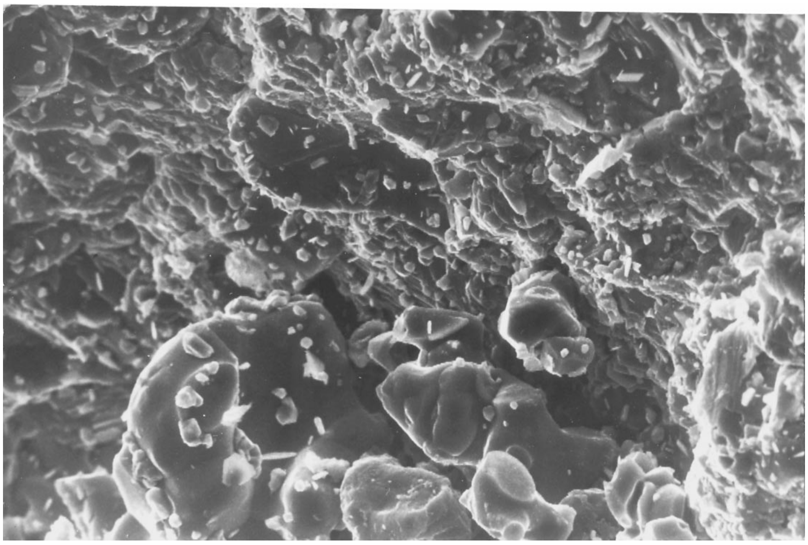

Figure 6 Scanning electron micrograph of sample obtained after heating α-$Ag_6S_3O_4$, magnification 5000×.

TABLE II Results of indexing α-$Ag_8S_4O_4$ diffraction pattern

No.	$d_{obs.}$ (nm)	$d_{cal.}$ (nm)	*hkl*	I/I_0 (%)	Figure of merit
1	0.72116	0.72052	1 0 0	5	1542.83
2	0.51344	0.51140	0 0 1	4	171.12
3	0.41834	0.41703	1 0 1	10	110.85
4	0.36042	0.36026	2 0 0	18	109.19
5	0.32200	0.32223	2 1 0	19	104.70
6	0.29433	0.29452	2 0 1	66	100.43
7	0.27286	0.27262	2 1 1	44	91.46
8	0.25565	0.25570	0 0 2	32	91.19
9	0.24014	0.24018	3 0 0	20	90.47
10	0.22791	0.22785	3 1 0	100	88.95
11	0.21726	0.21739	3 0 1	8	81.48
12	0.20826	0.20813	3 1 1	19	74.03
13	0.20040	0.20030	2 1 2	11	69.93
14	0.18607	0.18613	3 2 1	2	65.09
15	0.18011	0.18013	4 0 0	22	64.96
16	0.17514	0.17506	3 0 2	7	60.48
17	0.16989	0.16990	4 0 1	5	60.36
18	0.16578	0.16589	1 0 3	2	52.52
19	0.16107	0.16111	4 2 0	7	51.33
20	0.15749	0.15746	3 2 2	2	50.53
21	0.15375	0.15367	4 2 1	8	46.43
22	0.15075	0.15068	2 1 3	4	43.66
23	0.14722	0.14726	4 0 2	10	42.70
24	0.14406	0.14410	5 0 0	3	41.23
25	0.14158	0.14167	2 2 3	7	36.44
26	0.13889	0.13901	3 0 3	2	30.86
27	0.13626	0.13631	4 2 2	7	29.91
28	0.12936	0.12944	5 2 1	7	26.41
29	0.12732	0.12737	4 4 0	7	25.62
30	0.12552	0.12554	5 0 2	7	25.51
31	0.12361	0.12360	4 4 1	3	25.41
32	0.11846	0.11845	6 1 0	2	24.73
33	0.11685	0.11691	6 0 1	3	23.12
34	0.11390	0.11392	6 2 0	4	22.62
35	0.11116	0.11120	6 2 1	4	21.54

$a = b = 0.72052$ nm, $c = 0.51140$ nm, the volume of the unit cell $V = 0.26550$ nm^3, the unit cell of type P, the number of molecules in the unit cell $Z = 1$, $d_x = 6.60$ g/cm^3, $\Delta d = 0.06$ g/cm^3. The values of parameters a and b are very close to these parameters obtained by Hirsch. According to Hirsch, the c parameter value is twofold larger, therefore the differences result in the value Z (according to Hirsch $Z = 2$).

TABLE III Results of indexing α-$Ag_6S_3O_4$ diffraction pattern

No.	d_{exp} [nm]	d_{cal} [nm]	*hkl*	I/I_0 [%]	Figure of merit
1	0.76155	0.76220	2 0 1	4	75.52
2	0.74239	0.74221	$\bar{1}$ 0 2	6	99.56
3	0.57156	0.57112	3 0 1	16	51.09
4	0.54064	0.54062	2 0 2	13	55.76
5	0.48751	0.48724	0 0 3	3	43.75
6	0.47682	0.47675	1 1 1	2	46.22
7	0.46247	0.46258	$\bar{2}$ 1 1	3	46.38
8	0.43571	0.43579	2 1 1	3	45.32
9	0.41585	0.41590	$\bar{2}$ 1 2	4	45.29
10	0.40889	0.40885	5 0 0	3	46.33
11	0.37143	0.37142	$\bar{4}$ 1 1	12	44.12
12	0.36030	0.36041	3 0 3	7	37.98
13	0.34926	0.34933	$\bar{6}$ 0 1	7	35.82
14	0.34674	0.34669	1 0 4	10	35.75
15	0.34074	0.34071	6 0 0	4	35.91
16	0.32884	0.32872	$\bar{5}$ 1 1	4	29.85
17	0.32219	0.32225	2 0 4	11	29.22
18	0.31750	0.31753	$\bar{5}$ 1 2	7	29.38
19	0.30844	0.30846	$\bar{5}$ 0 4	9	29.19
20	0.30109	0.30106	0 1 4	13	29.04
21	0.29473	0.29465	$\bar{5}$ 1 3	100	26.38
22	0.29044	0.29032	1 1 4	13	22.37
23	0.28674	0.28678	6 1 0	80	22.08
24	0.28202	0.28207	$\bar{4}$ 0 5	9	21.57
25	0.27362	0.27357	4 1 3	46	20.68
26	0.27008	0.27011	$\bar{6}$ 1 3	60	20.60
27	0.26743	0.26744	$\bar{5}$ 0 5	50	20.76
28	0.26077	0.26081	$\bar{7}$ 1 1	9	20.25
29	0.25788	0.25792	1 2 1	18	19.86
30	0.25553	0.25553	8 0 0	25	20.01
31	0.24831	0.24826	1 1 5	20	19.15
32	0.24554	0.24556	1 2 2	21	19.09
33	0.24364	0.24362	0 0 6	46	19.15
34	0.24030	0.24032	$\bar{3}$ 2 2	27	18.85
35	0.23833	0.23838	2 2 2	53	18.02
36	0.23634	0.23648	$\bar{4}$ 2 1	12	13.44
37	0.23127	0.23129	$\bar{4}$ 2 2	27	13.29
38	0.22801	0.22813	7 1 2	51	11.01

The calculated parameters of the unit cell for α-$Ag_6S_3O_4$ have the following values: $a = 2.09616$ nm, $b = 0.53118$ nm, $c = 1.49885$ nm, $\beta = 102.78^\circ$, the volume of the unit cell $V = 1.62753$ nm^3, the unit cell of type P, the number of molecules in the unit cell $Z = 8$, $d_x = 6.59$ g/cm^3, $\Delta d = 0.01$ g/cm^3.

4. Summary

On the basis of preformed studies it has been concluded that:

—in the reaction taking place between the Ag^+ and $S_2O_3{}^{2-}$ ions at the initial concentrations of ions equal ca. 0.156 mol/dm^3 and ca. 0.017 mol/dm^3, respectively, a phase is formed to which the molecular formula α-$Ag_8S_4O_4$ has been attributed, whereas at the initial concentrations of ca. 0.617 mol/dm^3 and ca. 0.020 mol/dm^3, respectively, a phase with the molecular formula α-$Ag_6S_3O_4$,

—α-$Ag_8S_4O_4$ at 223°C undergoes a monotropic polymorphic transition to β-$Ag_8S_4O_4$ of a high-temperature form, which is formed by reaction taking place in the solid state between Ag_2SO_4 and Ag_2S mixed at the molar ratio—1 : 3,

—α-$Ag_8S_4O_4$ crystallizes in a tetragonal system,

—α-$Ag_6S_3O_4$ at 221 °C also undergoes an irreversible polymorphic transition to the high-temperature form, β-$Ag_6S_3O_4$, which is formed by reaction taking place in the solid state between Ag_2SO_4 and Ag_2S, at the molar ratio of the reagents—1 : 2,

—α-$Ag_6S_3O_4$ crystallizes in a monoclinic system.

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