

REACTIVITY IN THE SOLID STATE BETWEEN Ag_2S AND Ag_2CrO_4

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Abstract

Reactivity, in the solid state between Ag_2S and Ag_2CrO_4 , was investigated by DTA, XRD and IR methods. It was found that, according to a composition of an initial $\text{Ag}_2\text{S}/\text{Ag}_2\text{CrO}_4$ mixture, the products of a reaction of Ag_2S with Ag_2CrO_4 can be: solid solution with Ag_2CrO_4 structure ($\text{Ag}_2\text{Cr}_{1-x}\text{S}_x\text{O}_4$) and AgCrO_2 ; or solid solution $\text{Ag}_2\text{Cr}_{1-x}\text{S}_x\text{O}_4$, Ag_2SO_4 , AgCrO_2 and metallic silver; or Ag_2S , $\beta\text{-Ag}_8\text{S}_4\text{O}_4$, Ag , AgCrO_2 , Ag_2SO_4 and $\text{Ag}_2\text{Cr}_{1-x}\text{S}_x\text{O}_4$ solid solution.

Keywords: DTA, IR, silver chromate(VI), silver sulfide, XRD

Introduction

Our earlier studies on the reactivity in the solid state between Ag_2S and Ag_2SO_4 showed that both reagents enter into reaction to give two phases: $\beta\text{-Ag}_6\text{S}_3\text{O}_4$ and $\beta\text{-Ag}_8\text{S}_4\text{O}_4$ [1–4]. These compounds had not been known in the literature before. $\beta\text{-Ag}_6\text{S}_3\text{O}_4$ is formed by heating in air atmosphere Ag_2S and Ag_2SO_4 mixed at the molar ratio 2:1 according to the following reaction [1, 2, 4]:



$\beta\text{-Ag}_8\text{S}_4\text{O}_4$, the second phase occurring in the $\text{Ag}_2\text{S}-\text{Ag}_2\text{SO}_4$ system, is formed as a result of the reaction between Ag_2S and Ag_2SO_4 , at the molar ratio of the reagents – 3:1 [3, 4]:



In the light of above information it deemed advisable to ascertain whether silver chromate(VI), the phase crystallizes just the same as silver sulfate(VI) in orthorhombic system (space group – Pnma , $a=1.0063(11)$ nm; $b=0.7029(4)$ nm; $c=0.5540(2)$ nm; $Z=4$ [5]), could form similar compounds.

Experimental

The following reagents were used for experiments: pure Ag_2S (POCh, Gliwice, Poland) and Ag_2CrO_4 (a precipitate obtained as a result of the reaction between Ag^+ and CrO_4^{2-} , filtered, washed and dried at 110°C for 24 h). The mixtures of Ag_2S with Ag_2CrO_4 were prepared with a range of silver sulfide from 10.00 to 90.00 mol%. These mixtures were heated in air, in the following cycles: 250 (8 h); 300 (8 h); 350 (8 h); 400 (8 h); 450 (8 h); 475 (8 h); 525 (2×8 h); 550°C (13 h). After each heating cycle the samples were gradually cooled to ambient temperature, weighed, ground and examined for their contents by XRD method and then heated again. After the final heating cycle, the samples were examined by DTA and IR methods. The DTA examinations were made by using a TA Instruments SDT 2960 apparatus. These measurements were carried out in air, at the heating rate of 10 K min^{-1} . X-ray diffraction phase analysis of the samples was performed by a diffractometer DRON-3 using CoK_α radiation ($\lambda=0.179021 \text{ nm}$). The IR spectra were recorded on a Specord M-80 spectrometer (Carl Zeiss Jena).

Results and discussion

Table 1 shows the contents of the initial mixtures of Ag_2S with Ag_2CrO_4 and results of XRD analysis of samples obtained after the final heating cycle. Mass change investigations show mass increases for the samples obtained by heating initial mixtures comprising initially to 70.00 mol% of Ag_2S and mass decreases of the samples, the initial mixtures of which contained over 70 mol% of Ag_2S .

Table 1 Contents of initial mixtures and results of XRD analysis of samples obtained after the final heating cycle

No.	Ag_2S content in initial mixtures/mol%	Phase identified
1	10.00; 20.00; 30.00; 40.00	$\text{Ag}_2\text{Cr}_{1-x}\text{S}_x\text{O}_4$; AgCrO_2
2	50.00; 60.00; 66.67; 70.00; 75.00; 80.00	$\text{Ag}_2\text{Cr}_{1-x}\text{S}_x\text{O}_4$; Ag_2SO_4 ; AgCrO_2 ; Ag
3	90.00	Ag_2S ; $\beta\text{-Ag}_8\text{S}_4\text{O}_4$; Ag; AgCrO_2 (traces)

The data of Table 1 and the results of mass change studies point out that Ag_2S and Ag_2CrO_4 are not mutually inert in air. It was found that, at the concentration range to 40.00 mol% of Ag_2S , the products of reaction between Ag_2S and Ag_2CrO_4 are solid solution with Ag_2CrO_4 structure ($\text{Ag}_2\text{Cr}_{1-x}\text{S}_x\text{O}_4$) and AgCrO_2 . The result of solid solution formation is moving the position of diffraction lines, recorded on diffraction patterns of the samples obtained by heating the $\text{Ag}_2\text{S}/\text{Ag}_2\text{CrO}_4$ mixtures, in comparison with the position of diffraction lines for pure Ag_2CrO_4 (Fig. 1).

At the concentration range from 40.00 to 90.00 mol% of Ag_2S it was found that three solid phases, i.e. $\text{Ag}_2\text{Cr}_{1-x}\text{S}_x\text{O}_4$ solid solution, AgCrO_2 and metallic silver (Table 1), occurred in the samples on treatment.

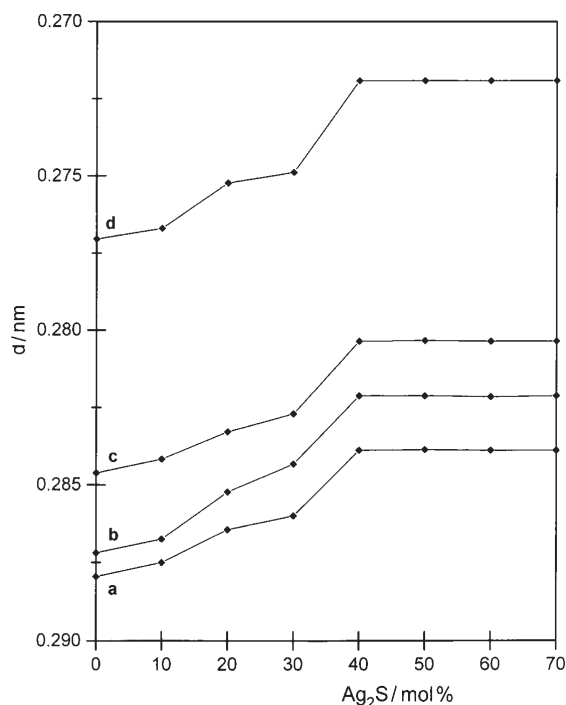


Fig. 1 Dependence of interplanar distances on Ag_2S concentration in initial $\text{Ag}_2\text{S}/\text{Ag}_2\text{CrO}_4$ mixtures for four diffraction lines: $d=0.2879$ nm – pure Ag_2CrO_4 ($hkl\ 2\ 2\ 0$) (a); $d=0.2870$ nm – pure Ag_2CrO_4 ($hkl\ 2\ 1\ 1$) (b); $d=0.2844$ nm – pure Ag_2CrO_4 ($hkl\ 2\ 1\ 1$) (c); $d=0.2769$ nm – pure Ag_2CrO_4 ($hkl\ 0\ 0\ 2$) (d)

XRD measurements of the sample, obtained by heating the mixture comprising initially 90.00 mol% of Ag_2S , showed the presence of four solid phases, i.e. Ag_2S , metallic silver, $\beta\text{-Ag}_8\text{S}_4\text{O}_4$ and traces of AgCrO_2 .

Figure 2 shows DTA curves for the samples obtained after the last heating cycle of $\text{Ag}_2\text{S}/\text{Ag}_2\text{CrO}_4$ mixtures comprising initially 10.00, 20.00, 30.00 and 40.00 mol% of Ag_2S as well as, for comparison purposes, DTA curves for pure Ag_2CrO_4 and an equimolar $\text{Ag}_2\text{CrO}_4/\text{Ag}_2\text{SO}_4$ mixture. DTA curves of the samples obtained after heating the mixtures comprising initially 50.00 and 90.00 mol% of Ag_2S are shown in Fig. 3.

The endothermic effect recorded on the DTA curve of the equimolar $\text{Ag}_2\text{CrO}_4/\text{Ag}_2\text{SO}_4$ mixture at 426°C (Fig. 2b) is characterised by polymorphic transition of Ag_2SO_4 [6, 7]. The second endothermic effect, with its onset at 480°C , is due to polymorphic transition of Ag_2CrO_4 [8, 9]. The last endothermic effect starting at 665°C is associated with the melting of the $\text{Ag}_2\text{CrO}_4/\text{Ag}_2\text{SO}_4$ mixture. On each DTA curve of the samples obtained after heating $\text{Ag}_2\text{S}/\text{Ag}_2\text{CrO}_4$ mixtures (Figs 2c–2f) two endothermic effects were recorded. The first effects starting at: 445°C (curve c), 405°C (curve d), 367°C (curve e) and 326°C (curve f), are associated with polymorphic transition of $\text{Ag}_2\text{Cr}_{1-x}\text{S}_x\text{O}_4$ solid solution. The second effects with their onset at: 662°C (curve c), 659°C (curve d), 658°C

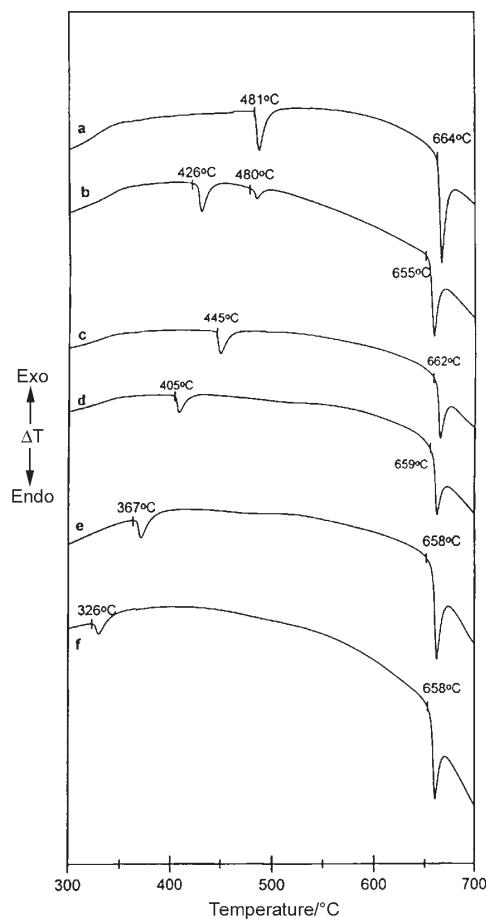


Fig. 2 DTA curves for Ag_2CrO_4 (a), an equimolar $\text{Ag}_2\text{CrO}_4/\text{Ag}_2\text{SO}_4$ mixture (b) and the samples obtained after the final heating cycle of $\text{Ag}_2\text{S}/\text{Ag}_2\text{SO}_4$ mixtures comprising initially 10.00 (c), 20.00 (d), 30.00 (e) and 40.00 mol% of Ag_2S (f)

(curves e and f) correspond to melting $\text{Ag}_2\text{Cr}_{1-x}\text{S}_x\text{O}_4$ solid solution. The appearance of solid solution (Ag_2SO_4 in Ag_2CrO_4) resulted in reducing temperature of polymorphic transition ($\Delta t_{\text{max}}=155^\circ\text{C}$) and melting point ($\Delta t_{\text{max}}=8^\circ\text{C}$) of $\text{Ag}_2\text{Cr}_{1-x}\text{S}_x\text{O}_4$ in comparison with the temperature of polymorphic transition and melting point of pure Ag_2CrO_4 , respectively.

On the DTA curve of the sample obtained after heating the mixture composed of 50.00 mol% of Ag_2S and 50.00 mol% of Ag_2CrO_4 (Fig. 3) three effects were recorded. The endothermic effects with their onset at 367 and 653°C, are associated with polymorphic transition and melting solid solution $\text{Ag}_2\text{Cr}_{1-x}\text{S}_x\text{O}_4$, respectively. Additional studies are necessary for determining a reason for the appearance of the exothermic effect starting at 324°C (Fig. 3).

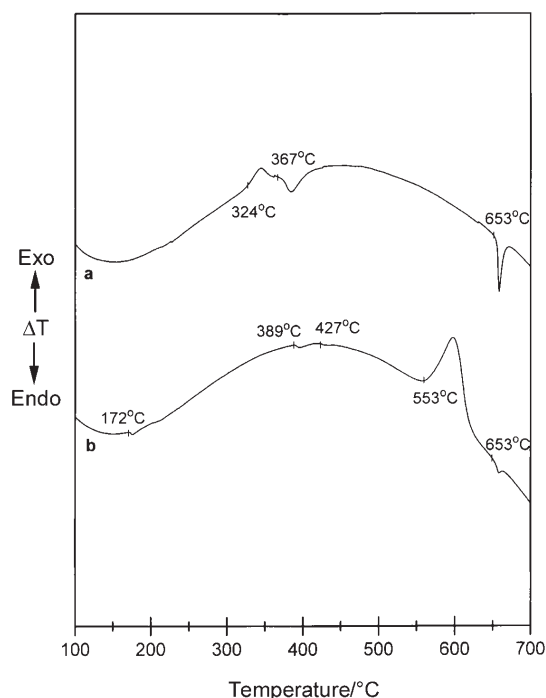


Fig. 3 DTA curves of the sample obtained after the last heating cycle of the mixtures comprising initially 50.00 mol% of Ag_2S (a) and 90.00 mol% of Ag_2S (b)

The endothermic effects recorded on the DTA curve (Fig. 3, sample comprising initially 90.00 mol% of Ag_2S) starting at 172 and at 389°C, correspond to the polymorphic transition of $\alpha\text{-Ag}_2\text{S}$ to $\beta\text{-Ag}_2\text{S}$ [10] and melting $\beta\text{-Ag}_8\text{S}_4\text{O}_4$ [3, 4], respectively. The endothermic effect recorded at 427°C is associated with the polymorphic transition of Ag_2SO_4 [6,7]. This effect shows the presence of Ag_2SO_4 traces in the products of reaction. The presence of Ag_2SO_4 was not proved by XRD method. Ag_2SO_4 can appear, during DTA measurement, as a result of incongruent melting $\beta\text{-Ag}_8\text{S}_4\text{O}_4$. The exothermic effect starting at 553°C corresponds to the crystallization of metallic silver [4]. Metallic silver is a product of the thermal decomposition of a liquid obtained after melting $\beta\text{-Ag}_8\text{S}_4\text{O}_4$ [3, 4]. In air decomposition of $\beta\text{-Ag}_8\text{S}_4\text{O}_4$ starts at the melting point of this phase [3, 4]. The endothermic effect with its onset at 653°C is probably due to the melting traces of $\text{Ag}_2\text{Cr}_{1-x}\text{S}_x\text{O}_4$ solid solution. The presence of $\text{Ag}_2\text{Cr}_{1-x}\text{S}_x\text{O}_4$ solid solution was not confirmed by XRD method.

Figure 4 shows the infrared absorption spectra for an equimolar mixture of Ag_2CrO_4 with Ag_2SO_4 , initial $\text{Ag}_2\text{S}/\text{Ag}_2\text{CrO}_4$ mixtures contained 20.00, 50.00 and 90.00 mol% of Ag_2S as well as the samples obtained after the last heating cycle of the $\text{Ag}_2\text{S}/\text{Ag}_2\text{CrO}_4$ mixtures mentioned above. As it is seen the spectra of the samples, obtained after heating $\text{Ag}_2\text{S}/\text{Ag}_2\text{SO}_4$ mixtures, show a general similarity with the spectrum of $\text{Ag}_2\text{CrO}_4/\text{Ag}_2\text{SO}_4$ mixture. Only absorption bands, recorded in the spectrum

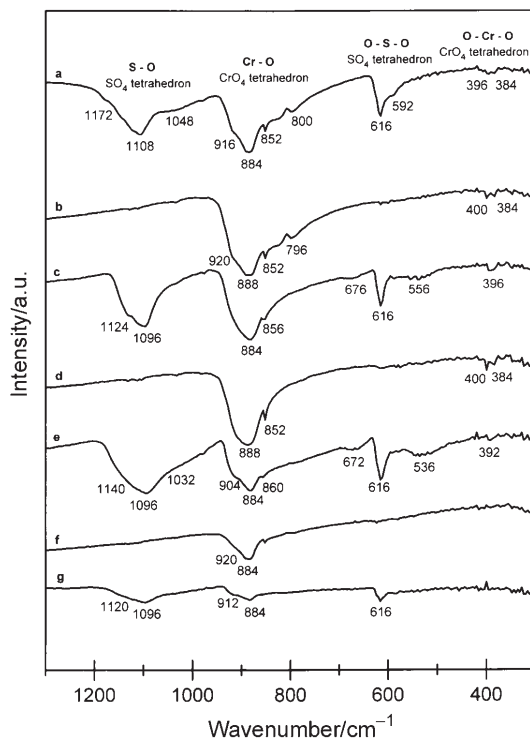


Fig. 4 IR absorption spectra for: an equimolar mixture of Ag_2CrO_4 with Ag_2SO_4 (a); initial $\text{Ag}_2\text{S}/\text{Ag}_2\text{CrO}_4$ mixtures contained 20.00 (b), 50.00 (d) and 90.00 mol% of Ag_2S (f); the samples obtained after the final heating cycle of mixtures comprising initially 20.00 (c), 50.00 (e) and 90.00 mol% of Ag_2S (g)

of the sample obtained after heating the mixture comprising initially 90.00 mol% of Ag_2S , are very weak in comparison with the absorption bands for the remaining samples. The broad absorption bands, with the maximum at $\sim 1100\text{ cm}^{-1}$, can be assigned to the stretching mode of S–O bonds in isolated SO_4 tetrahedra [10–13]. The bands occurring at 616 cm^{-1} are related to the stretching modes of O–S–O bonds in SO_4 tetrahedra [10–13]. In the light of literature information [14] the broad bands with maximum at 884 cm^{-1} correspond to the stretching vibrations of Cr–O bonds in CrO_4 tetrahedra. Then the absorption bands occurring at $\sim 400\text{ cm}^{-1}$ can be due to the stretching modes of O–Cr–O in CrO_4 tetrahedra [14]. The simultaneous presence of absorption bands, which are related to the stretching modes S–O and O–S–O bonds in SO_4 tetrahedra as well as to the stretching vibrations of Cr–O and O–Cr–O bonds in CrO_4 tetrahedra, is due to a big difference between ion radii of S^{6+} and Cr^{6+} (ion radius of tetrahedrally coordinated S^{6+} – 12 pm; ion radius of tetrahedrally coordinated Cr^{6+} – 26 pm [15]).

Additionally, very weak bands at ~ 670 and at $\sim 540\text{ cm}^{-1}$ were recorded in the spectra of samples obtained after heating the mixtures comprising initially 20.00 and

50.00 mol% of Ag₂S. These bands can be assigned to the stretching mode of Cr–O bonds in CrO₆ octahedra, which form anion lattice of AgCrO₂ [16].

Conclusions

The experimental results obtained have led to the following conclusions:

- redox reaction of Ag₂S with Ag₂CrO₄ runs with an involvement of oxygen from air,
- at the concentration range from 10.00 to 90.00 mol% of Ag₂S in initial Ag₂S/Ag₂CrO₄ mixtures a presence of the solid solution with Ag₂CrO₄ structure (Ag₂Cr_{1-x}S_xO₄) was found.

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