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# INVESTIGATION OF ACQUISITION OF TRIPLE SULFURS FROM $Pb(CH_3COO)_2$-$Na_3AsO_4$-$H_2S$-$H_2O$ SYSTEM BY HYDROCHEMICAL METHOD

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**Abstract:** Acquisition conditions by hydrothermal method of triple sulfides from $Pb(CH_3COO)_2$-$Na_3AsO_4$-$H_2S$-$H_2O$ system were investigated using X-ray phase (X-ray), Differential Thermal (DTA) and Scanning Electron Microscopy (SEM) analysis, TG analysis methods. It was determined that sediments were obtained containing $Pb_{26+x}As_{12}S_{44+x}$ content in pH=1-6 range and $Pb_{28-x}As_{12}S_{46-x}$ content (0,6 < x < 1,5) in pH=6-14 range. The durability limits of PbS, $As_2S_5$, $As_2S_3$, $Pb(OH)_2$, and $Na_3AsO_4$ were determined, and pCb-pH (pCb- difference between initial and final concentrations of metal) diagram was formed. The results of the X-ray phase analysis methods indicate that when the precipitates having a Pb:As:S=1:2:4; 2:2:5 and 9:4:15 molar ratio (pH=1-6) are thermally processed in vacuum at 400 °C (~$10^{-2}$ Pa) in a dual-zone regime, phases containing $PbAs_2S_4$, $Pb_2As_2S_5$ and $Pb_9As_4S_{15}$ are conveniently formed. All three compounds are composed of nanoparticles, and high adhesion between particles is observed. Depending on the pH, concentration, and temperature of the condition, a large number of different precipitates and layers are obtained in the $Pb(CH_3COO)_2$-$Na_3AsO_4$-$H_2S$-$H_2O$ system. Based on TG analysis, the stoichiometric composition of $PbAs_2S_4$, $Pb_9As_4S_{15}$, and $Pb_2As_2S_5$ compounds was determined.

**Keywords:** Triple sulfur, hydrochemical sedimentation, semiconductor, concentration, phase, micromorphology.

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## INTRODUCTION

Thio-salts formed by lead with arsenic are glass semiconductors and are widely used in the radio-electronics industry, such as perspectively materials, or are considered necessary for application. It is known from the literature that there are intermediate phases with the composition $PbAs_2S_4$, $Pb_3As_4S_9$, $Pb_4As_6S_{13}$, $Pb_{13}As_{18}S_{40}$, $Pb_{19}As_{26}S_{58}$, $Pb_2As_2S_5$, $Pb_{27}As_{14}S_{48}$, $Pb_9As_4S_{15}$ etc. in the Pb-As-S system (3). Many of these intermediate phases have been found in minerals found in nature (7, 8). The compounds present in the Pb-As-S system were obtained by vacuum (~900 °C) synthesis, and glasses were prepared by rapidly cooling the alloys. It was found that in the PbS-$As_2S_3$ system, glasses were obtained in 0-50 mol% PbS concentration areas (3).

Recently, interest in the acquisition of thioarsenides and thioarsenates in different solvent environments has increased (5). There is little information in the literature on the acquisition of thioarsenides and thioarsenates in water and organic solvent conditions. Only (1,2) studies arsenic(V) sulfide was affected with the copper(II) sulfate in aqueous condition, $Cu(AsS_3)_2$ - containing compound (copper(II) metathioarsenate) was obtained and the

effect of the pH and temperature of the condition on its' yield was studied.

With this in mind, we aim to investigate the acquisition condition and properties of thin layers from the $Pb(CH_3COO)_2$-$Na_3AsO_4$-$H_2S$-$H_2O$ system.

In this article, the synthesis of some triple sulfides from $Pb(CH_3COO)_2$-$Na_3AsO_4$-$H_2S$-$H_2O$ system by X-ray phase, Differential Thermal (DTA) and Scanning Electron Microscopy (SEM), TG analysis methods by the hydrochemical method, micromorphology and depending on conditions (concentration, temperature, and pH of the condition) the results of the composition of phases are given.

## EXPERIMENTAL SECTION

Aqueous solutions of $Pb(CH_3COO)_2$ and $Na_3AsO_4$ were used as primary components to obtain triple sulfides by the hydrochemical method. 0.1 M solutions of the primary substances were mixed at different molar ratios, and $H_2S$ gas was introduced into the solution. Experiments were performed in the range of pH 0-14 to determine the conditions of the formation of the phases. Triple sulfur precipitates were obtained in a chemical cup made of molybdenum glass containing a volume of 100 mL. Sedimentation was completed in 60 minutes at 70 °C. The thermal process of the sediments was carried out under vacuum (~$10^{-2}$ Pa) at 100-400 °C.

Thin layers were obtained to investigate the micromorphology of the phases formed in the $Pb(CH_3COO)_2$-$Na_3AsO_4$-$H_2S$-$H_2O$ system. Chemical sedimentation was performed on the glass substrate (Microscope Slides, Cat. No.7101, 25.4x76.2 mm) cleaned with a mixture of $NaHCO_3$, HF, and chrome to obtain thin layers. The substrate was placed in $SnCl_2$ -in hydrochloric acid solution and after 2-3 minutes, washed with boiling distilled water to ensure homogeneous sedimentation on the substrate. Then, 1 M sulfurizing reagent ($(NH_4)_2S$) was added to the solution and left to stand for 2-3 minutes, then washed with hot distilled water. Following these processes, the substrate was placed in a chemical cup, and a reaction mixture was added to it.

### Effect of pH of the Solution

The mass of sediments formed at pH=0-14 and the concentration of ions into the solution were determined to determine the acquisition conditions of binary and triple compounds by hydrochemical method from $Pb(CH_3COO)_2$-$Na_3AsO_4$-$H_2S$-$H_2O$ system. The durability limits of PbS, $As_2S_5$, $As_2S_3$, $Pb(OH)_2$, and $Na_3AsO_4$ were determined, and $pC_b$-pH ($pC_b$- difference between initial and final concentrations of metal) diagram was formed based on the results obtained (Figure 1). The solubility values of the related compounds (PbS, $As_2S_5$, $As_2S_3$, $Pb(OH)_2$) mentioned in the literature were used in the calculations (4). 0.5 M $HNO_3$ and NaOH solutions were used to change the pH of the condition.

Figure 1 shows the common precipitation areas of PbS, $As_2S_3$, and $As_2S_5$ in the $Pb(CH_3COO)_2$-$Na_3AsO_4$-$H_2S$-$H_2O$ system are observed in the range of pH=0-6. These results have been widely used in the planning of experimental studies.

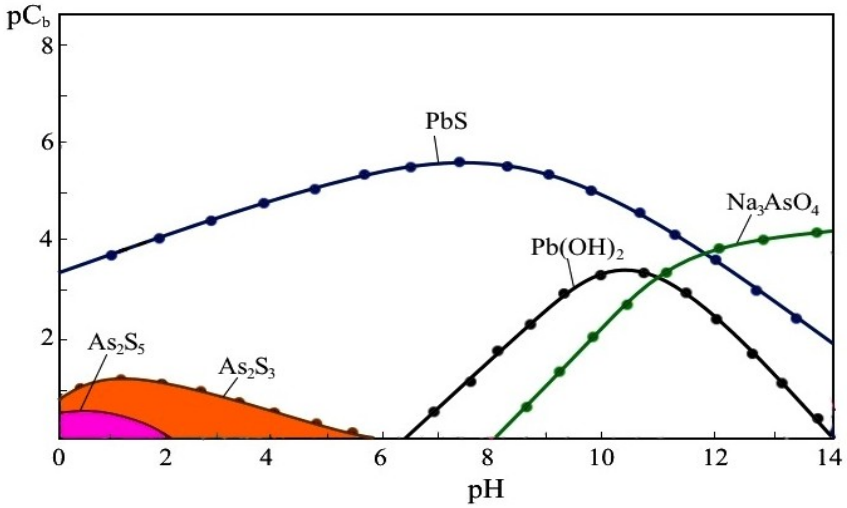


**Figure 1:** Common deposition areas of PbS, $As_2S_3$, and $As_2S_5$ compounds in the $Pb(CH_3COO)_2$-$Na_3AsO_4$-$H_2S$-$H_2O$ system: colored areas.

X-ray phase (2D PHASER "Bruker", CuK↙, 2 ⁻ , 10-80 deg.) and chemical analysis methods (gravimetric and volume) revealed that sediments were obtained containing $Pb_{26+x}As_{12}S_{44+x}$ content in pH=1-6 range and $Pb_{28-x}As_{12}S_{46-x}$ content (0.6 < x < 1.5) in pH=6-14 range (Table 1).

**Table 1:** Composition of sediments obtained from $Pb(CH_3COO)_2$-$Na_3AsO_4$-$H_2S$-$H_2O$ system at 70 °C.

| The composition of the sediment | pH value |
|---|---|
| $Pb_{25.6}As_{12}S_{44.9}$ | 1 |
| $Pb_{25.7}As_{12}S_{44.8}$ | 2 |
| $Pb_{25.9}As_{12}S_{44.6}$ | 3 |
| $Pb_{26.2}As_{12}S_{44.6}$ | 4 |
| $Pb_{26.5}As_{12}S_{44.4}$ | 5 |
| $Pb_{26.8}As_{12}S_{44.1}$ | 6 |
| $Pb_{27.2}As_{12}S_{43.3}$ | 7 |
| $Pb_{27.3}As_{12}S_{42.7}$ | 8 |
| $Pb_{27.6}As_{12}S_{40.7}$ | 9 |
| $Pb_{27.8}As_{12}S_{40.2}$ | 10 |
| $Pb_{27.9}As_{12}S_{40.1}$ | 11 |
| $Pb_{28.3}As_{12}S_{39.4}$ | 12 |
| $Pb_{28.5}As_{12}S_{39.0}$ | 13 |
| $Pb_{28.7}As_{12}S_{34.9}$ | 14 |

**XRD Analysis**

The results of the X-ray phase (2D PHASER "Bruker", $CuK_\alpha$, 2θ, 10-80 deg.) analysis methods indicate that when the precipitates having a Pb:As:S=1:2:4; 2:2:5 and 9:4:15 molar ratio (pH=1-6) are thermally processed in vacuum at 400 °C (~$10^{-2}$ Pa) in a dual-zone regime, phases containing $PbAs_2S_4$, $Pb_2As_2S_5$ and $Pb_9As_4S_{15}$ are conveniently formed (Figure 2). When the other composition sediments are thermally processed, the mixtures of $PbAs_2S_4$, $Pb_3As_4S_9$, $Pb_4As_6S_{13}$, $Pb_{13}As_{18}S_{40}$, $Pb_{19}As_{26}S_{58}$, $Pb_2As_2S_5$, $Pb_{27}As_{14}S_{48}$, $Pb_9As_4S_{15}$, PbS, $As_2S_3$ and S phases are obtained. It was determined that the amount of oxygen was range of 7-14.8 mol% in the precipitates obtained in the range of pH = 8-14. It is because the hydrolysis products obtained under the same conditions remain in the precipitates.

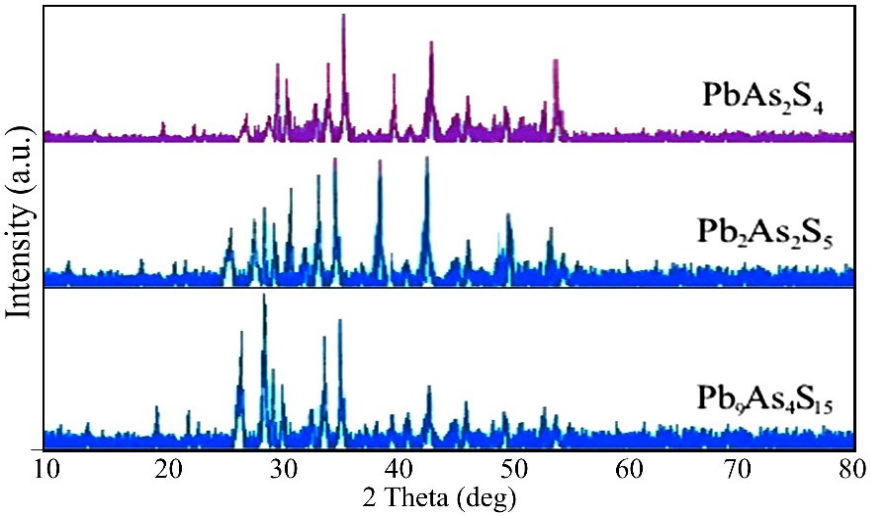


**Figure 2:** Diffractogram of $PbAs_2S_4$, $Pb_2As_2S_5$ and $Pb_9As_4S_{15}$.

**Scanning Electron Microscopy (SEM)**

Micromorphology of newly deposited and thermally processed $PbAs_2S_4$, $Pb_2As_2S_5$ and $Pb_9As_4S_{15}$ layers was studied on a HITACHI TM 3000 brand scanning electron microscope (Figure 3).

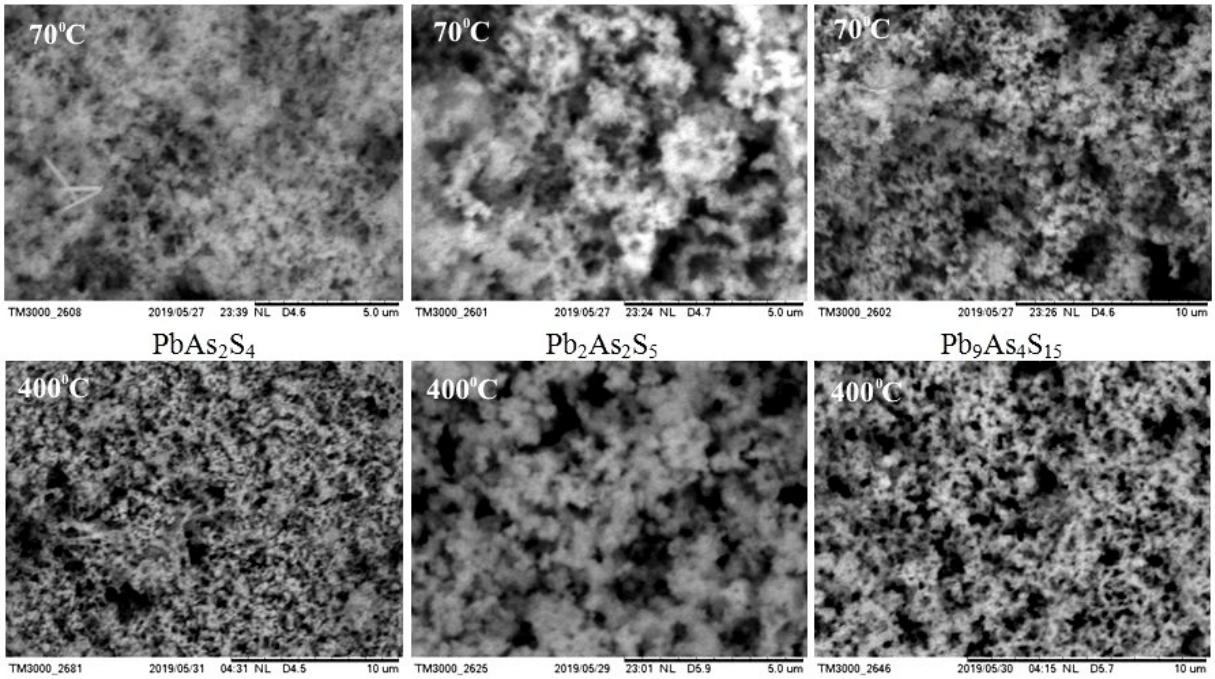


**Figure 3:** SEM images of $PbAs_2S_4$, $Pb_2As_2S_5$ and $Pb_9As_4S_{15}$ compounds.

As seen from SEM images of the compounds $PbAs_2S_4$, $Pb_2As_2S_5$ and $Pb_9As_4S_{15}$, all three compounds were composed of nanoparticles. High adhesion is observed among the nanoparticles. At 400 °C, the mesh-shaped structure is formed in the thermally processed layers, which increases the size of the particles.

**TG analysis**

From the DTA (pyrometer HTP-70, device Термоскан -2) results, it is understood that $PbAs_2S_4$ compound melts congruently at 454 °C, $Pb_9As_4S_{15}$ compound is durable to the temperatures of 549 °C, and $Pb_2As_2S_5$ compound melts incongruently at 508 °C. TG analysis (NETZSCH STA 449F3) was performed to determine the stoichiometric composition of $PbAs_2S_4$, $Pb_9As_4S_{15,}$ and $Pb_2As_2S_5$ compounds. Samples were heated under nitrogen-oxygen at 700-800 °C for 1 hour. As seen from the TG curves, the maximum mass loss in $Pb_2As_2S_5$ compound was observed at 340 °C, 690 °C in $PbAs_2S_4$ compound and 660 °C in $Pb_9As_4S_{15}$ compound (Figure 4). The compositions of the compounds were determined based on the maximum mass loss. It has been found that the compounds correspond to formulas $PbAs_2S_4$, $Pb_9As_4S_{15}$ and $Pb_2As_2S_5$ as appropriate.

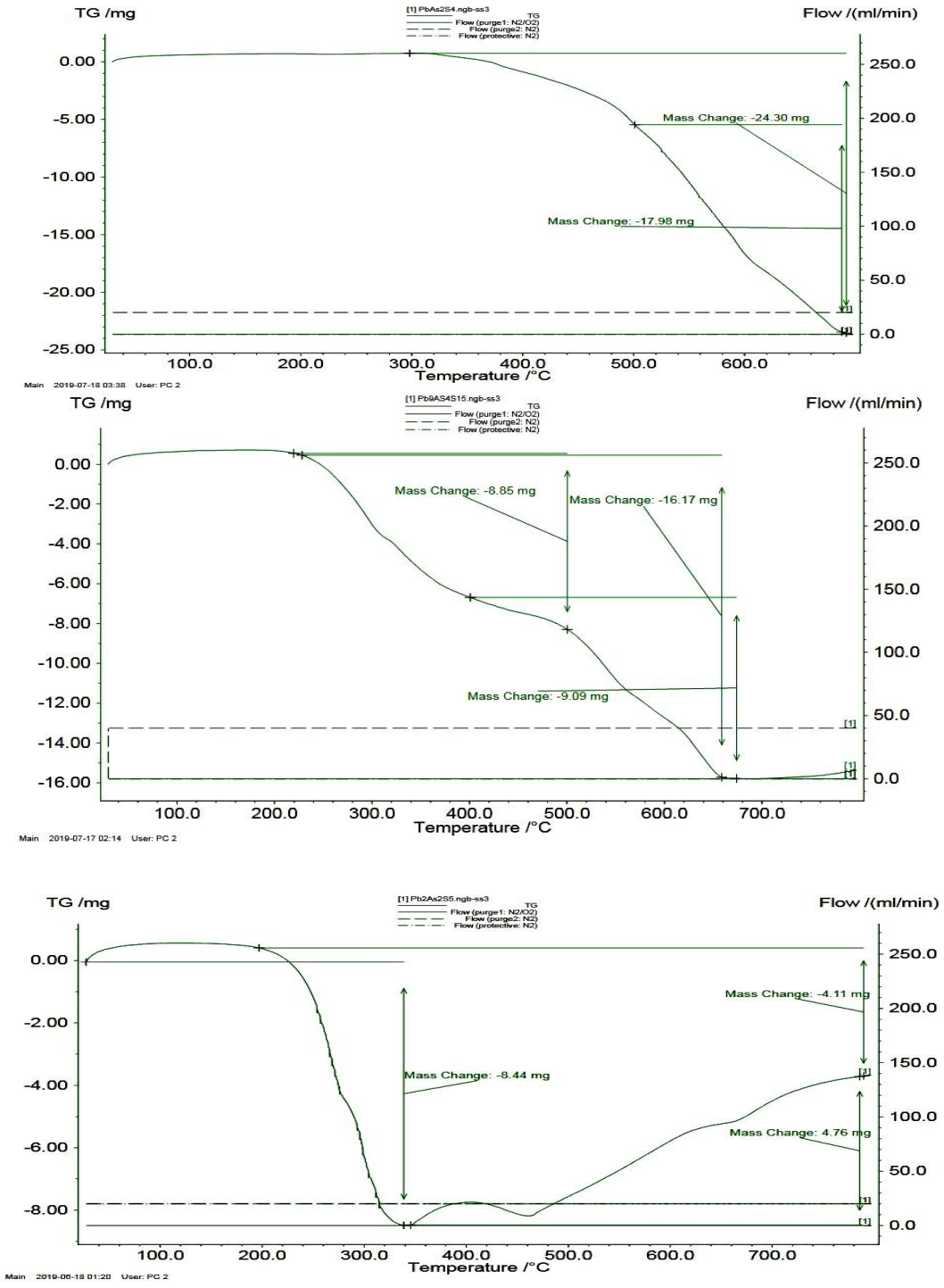


**Figure 4:** TG curves of $PbAs_2S_4$, $Pb_9As_4S_{15}$ and $Pb_2As_2S_5$.

## RESULTS

In general, it is understood from the experimental results that, depending on the conditions, it is possible to obtain a large number of different composition precipitates and layers from the $Pb(CH_3COO)_2$-$Na_3AsO_4$-$H_2S$-$H_2O$ system. Arsenic is generally trivalent in the composition of the phases formed when these deposits and layers are thermally processed. It is indicative of the observation that

lead thioarsenates are present only at low temperatures (T < 100 °C). When the temperature rises, they decompose into the corresponding thioarsenites ($PbAs_2S_4$, $Pb_3As_4S_9$, $Pb_4As_6S_{13}$, $Pb_{13}As_{18}S_{40}$, $Pb_{19}As_{26}S_{58}$, $Pb_2As_2S_5$, $Pb_{27}As_{14}S_{48}$, $Pb_9As_4S_{15}$).

## CONCLUSIONS

The durability limits of PbS, $As_2S_5$, $As_2S_3$, $Pb(OH)_2$ and $Na_3AsO_4$ were determined by hydrochemical method and $pC_b$-pH ($pC_b$- the difference between initial and final concentrations of metal). Depending on the molar ratio of the primary components, it was determined that variable content phases were obtained from $Pb(CH_3COO)_2$-$Na_3AsO_4$-$H_2S$-$H_2O$ system at 70 °C. When these phases are thermally processed, mixtures of $PbAs_2S_4$, $Pb_3As_4S_9$, $Pb_4As_6S_{13}$, $Pb_{13}As_{18}S_{40}$, $Pb_{19}As_{26}S_{58}$, $Pb_2As_2S_5$, $Pb_{27}As_{14}S_{48}$, $Pb_9As_4S_{15}$, PbS, $As_2S_3$ and S phases are formed. The results of the X-ray phase analysis methods indicate that when the precipitates having a Pb:As:S=1:2:4; 2:2:5 and 9:4:15 molar ratio (pH=1-6) are thermally processed in vacuum at 400 °C ($\sim 10^{-2}$ Pa), phases containing $PbAs_2S_4$, $Pb_2As_2S_5$ and $Pb_9As_4S_{15}$ are conveniently formed. All three compounds were composed of nanoparticles and high adhesion is observed among the particles. Based on TG analysis, stoichiometric composition of $PbAs_2S_4$, $Pb_9As_4S_{15}$ and $Pb_2As_2S_5$ compounds were determined.

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