



Sulfur–selenium isomorphous substitution in the AgAu(S,Se) series

Galina A. Palyanova^{a, b}, Yurii V. Seryotkin^{a, b}, Vladimir V. Bakakin^c,
Konstantin A. Kokh^{a, b, *}^a Sobolev Institute of Geology and Mineralogy, Novosibirsk, Russia^b Novosibirsk State University, Russia^c Nikolaev Institute of Inorganic Chemistry, Novosibirsk, Russia

ARTICLE INFO

Article history:

Received 20 October 2015

Received in revised form

23 December 2015

Accepted 24 December 2015

Available online 29 December 2015

Keywords:

AgAuS–AgAuSe system

Petrovskaites-like solid solution

ABSTRACT

Our experimental study of the system AgAuS–AgAuSe was urged by the misfit in literature data on the isomorphism of sulfur and selenium in this series and on the existence of AgAuSe phase. Scanning electron microscopy, optical microscopy methods, electron microprobe analysis and X-ray powder diffraction method have been applied to study samples synthesized by heating stoichiometric mixtures of initial compositions AgAuS_{1-x}Se_x ($x = 0; 0.25; 0.5; 0.75; 0.875; 1$).

Results of the studies evidence the existence of continuous solid solution of the AgAuS–AgAuSe series. As a result of the partial isomorphous replacement Se → S, the unit cell parameters of petrovskaites-like type ($R\bar{3}m$) phases are slightly increased compared to AgAuS. The phases AgAuS_{1-x}Se_x at $0.5 < x \leq 1$ are, most likely, metastable, their instability drastically increasing with the growing content of selenium. The phases partly decompose to form a fischesserite-like phase Au₃Au(Se,S)₂ or fischesserite (Au₃AuSe₂) (at $x = 1$), high-fineness Au–Ag alloy, S,Se phase or Se (at $x = 1$) and β -(Au,Ag)(Se,S) (at $x = 0.875$ and 1). Gold selenide AuSe showed isomorphism Se → S to 0.17 mol fraction of sulfur and Au → Ag – to 0.1 mol fraction of silver. The content of AgAuSe phase, synthesized under different heating, annealing and cooling conditions, was the highest in the experiment with rapid cooling from 1050 °C without annealing. The existence of phase AgAuSe in natural systems is likely to be very problematic.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The main parageneses of epithermal gold–silver deposits are characterized by the system Ag–Au–chalcogene (S, Se, Te) in which anionic solid solutions play the most important part [1]. The data on the isomorphism of sulfur and selenium of the AgAuS–AgAuSe series in literature are conflicting. Trace selenium contents frequently occur in natural petrovskaites, but their concentrations do not exceed 2 wt.% [2–5]. Studies of synthetic AgAuS_{1-x}Se_x phases [6] supported the discontinuity of the isomorphous range AgAuS–AgAuSe. The AgAuSe and AgAuS_{1-x}Se_x phases were determined in the electrolytic slimes after electrorefining process [7]. The experimental works studying phase relationships in the Ag–Au–Se system [8,9] evidence the absence of the ternary compound AgAuSe. The ternary phase diagrams of Ag–Au–chalcogene were studied in Refs. [8–12] but no data are available on the

quaternary system Ag–Au–S–Se.

The aim of the work is to synthesize and study sulfoselenides AgAuS_{1-x}Se_x ($0 \leq x \leq 1$) and to reveal the specific features of isomorphous sulfur–selenium replacement in the AgAuS – AgAuSe series. One of the main tasks of the research is to establish the relationships between gold and silver sulfoselenides and other phases in the Ag–Au–S–Se system.

2. Experiment and analytical methods

2.1. Starting compositions

We have synthesized phases of the AgAuS_{1-x}Se_x ($x = 0; 0.25; 0.5; 0.75; 1$) series by the procedure used for the pseudobinary systems Ag₃AuS₂–Au₃AuSe₂ and Ag₂S–Ag₂Se [13–15]. The starting materials for the synthesis were elemental silver, gold (99.99%), selenium and sulfur (99.9%); the total weight of the charges was 250–500 mg. The accuracy of weighing was ± 0.05 mg (“Mettler Instrument Ag CH-8606 Greifensee–Zurich”). Ampoules were heated during 3 days at a rate of 0.2–0.5 °C/min to 1050 °C, kept for

* Corresponding author. IGM SB RAS, Koptyuga Ave., 3, Novosibirsk 630090, Russia.

E-mail address: k.a.kokh@gmail.com (K.A. Kokh).

12 h at this temperatures and then cooled to 150 (N^o1–5, Table 1) or 500°C (N^o6–10, Table 1) at a rate of 0.2°/min with following annealing during 3 or 30 days, respectively. After annealing, the ampoules were cooled to room temperature in the switched off furnace. For the starting mixtures of AgAuSe compositions, synthesis with cooling from 1050°C to room temperatures in cold water (N^o11), and in the switched off furnace (N^o12) was performed. For two selenium-rich compositions at $x = 0.875$ and 1 (N^o13, 14, Table 1) synthesis was also carried out by the Nekrasov's method (1990) with heating to 750°C for 4 days, annealing at 300°C during a month and quenching in cold water.

2.2. Analytical techniques

Optical microscopy, scanning electron microscopy with energy-dispersive and wavelength-dispersive spectrometers, X-ray powder diffraction method were applied to study synthesized samples. A polished section was prepared from synthesized phases for microscopy analyses. Studies on the chemical composition were carried out using MIRA 3 LMU SEM (TESCAN Ltd.) combined with microanalysis system INCA Energy 450 + on the basis of the high sensitive silicon drift detector XMax-80, and WDS INCA Wave 500 (Oxford Instruments Ltd.). Operation conditions: accelerating voltage, 20 kV; probe current, 1.5 nA; spectrum recording, 15 s; and spot size, 7 nm. In all measurements the electron beam was slightly defocused for reducing the effect of a sample microrelief and decreasing the destructive influence of the electron beam on unstable silver-gold sulfoselenides. Pure silver, gold, CuFeS₂, and PbSe were used as standards for Ag, Au, S, and Se, respectively. The analysis accuracy was 1–1.5 relative %.

X-ray powder diffraction patterns were collected on a Stoe STADI MP diffractometer (CuK α 1 radiation, Ge (111) monochromator, 40 kV, 40 mA). Powdered silicon was used as the external standard ($a = 5.4309$ Å). The diffraction data were collected from 5 to 60° 2 θ angular range. For the phase analysis, the database of PDF-4 Minerals (The Powder Diffraction File PDF-4+, 2006) was used. The refinement of the unit cell parameters was carried out by Rietveld method using GSAS program [16].

3. Results and discussions

Results of studies of solid phase synthesis products of 14 experiments with the starting compositions of AgAuS_{1-x}Se_x mixtures are given in Table 1. Each of the synthesized samples was found to contain petrovskaitite-like phase with the chemical composition identical or close to that of the initial stoichiometric mixture AgAuS_{1-x}Se_x. However, single phase ingots were synthesized only in two experiments with annealing temperature of 500°C and $x = 0$ and 0.25 (N^o6, 7, Table 1). SEM and EPMA showed that the ingots are heterogeneous. In the experiments with $x = 0$ (N^o1) we synthesized petrovskaitite AgAuS with scarce microinclusions of uytenbogaardtite (Ag₃AuS₂). The detailed results of this experiment and interpretation of petrovskaitite structure were reported in Refs. [15,17–19]. The SEM photo of polished sections of synthesized samples from experiments N^o2–4 (Table 1) are shown in Fig. 1a–d. At $x = 0.25, 0.5,$ and 0.75 in addition to petrovskaitite-like phase AgAuS_{1-x}Se_x ($0 < x \leq 1$), products of synthesis contained fischerite-like phase Ag₃AuSe_{2-y}S_y ($0 < y < 2$). In the sample with $x = 0.25$ (N^o2, Table 1) fischerite-like phase forms thin veinlets and microinclusions in petrovskaitite-like phase (Fig. 1a), in the sample with $x = 0.5$ (N^o3, Table 1) the interaction of petrovskaitite- and fischerite-like phases are similar to eutectoid intergrowth (Fig. 1b). At higher selenium concentrations $x = 0.75$ (N^o4, Table 1), in addition to two Au–Ag sulfoselenides, the samples contained xenomorphic grains of high-fineness Au–Ag alloy and S₂Se-phase (Fig. 1c,d).

In the samples with annealing temperature of 500°C (N^o8,9, Table 1) and selenium concentrations $x = 0.5$ and 0.75 , the same as in the experiments annealed at 150°C (N^o3,4, Table 1), we determined petrovskaitite- and fischerite-like, S₂Se-phases and high-fineness Au–Ag alloy. For the experiment with $x = 0.875$ and annealed at 300°C (N^o13), four similar phases were found to coexist with one more phase of Au_{0.89}Ag_{0.09}Se_{0.83}S_{0.21} composition (Table 1). A similar, but sulfur-free, phase of Au_{0.9–0.96}Ag_{0.1–0.04}Se compositions was detected in the AgAuSe samples prepared by different techniques (N^o5,10–12, 14, Table 1). It is present as crystals measuring to 200 microns. Fig. 2a shows inclusions of gold selenide and high-fineness Au–Ag alloy in the petrovskaitite-fischerite matrix (N^o14, Table 1), and in Fig. 2b one can see a

Table 1
Results of study of solid phase products of synthesis in experiments with different initial compositions of AgAuS_{1-x}Se_x mixtures ($x = 0; 0.25; 0.5; 0.75; 0.875; 1$) and different modes of heating, annealing and cooling.

N ^o	Initial composition	Phase assemblages				
		AgAu(S,Se)	Ag ₃ Au(Se,S) ₂	Ag ₂ Au	S ₂ Se	(Au,Ag)Se
T of heating 1050 °C, T of annealing 150°C						
1	AgAuS	Ag _{0.94} Au _{0.85} S	Ag _{2.6} Au _{0.9} S ₂	–	*	–
2	AgAuS _{0.75} Se _{0.25}	Ag _{0.97} Au _{1.03} S _{0.77} Se _{0.23}	Ag _{3.01} Au _{0.99} Se _{1.18} S _{0.82}	–	*	–
3	AgAuS _{0.5} Se _{0.5}	Ag _{1.02} Au _{0.98} S _{0.54} Se _{0.46}	Ag _{3.01} Au _{0.99} Se _{1.84} S _{0.16}	–	*	–
4	AgAuS _{0.25} Se _{0.75}	Ag _{0.99} Au _{1.01} S _{0.35} Se _{0.65}	Ag _{3.01} Au _{0.99} Se _{1.91} S _{0.09}	Au _{0.97} Ag _{0.03}	S _{0.51} Se _{0.49}	–
5	AgAuSe	Ag _{1.05} Au _{0.97} Se _{0.98}	Ag _{3.03} Au _{1.01} Se _{1.95}	Au _{0.96} Ag _{0.04}	Se*	Au _{0.92} Ag _{0.10} Se _{0.98}
T of heating 1050 °C, T of annealing 500°C						
6	AgAuS	Ag _{0.97} Au _{0.98} S _{1.05}	–	–	*	–
7	AgAuS _{0.75} Se _{0.25}	AgAuS _{0.74} Se _{0.26}	–	–	S _{0.95} Se _{0.05} *	–
8	AgAuS _{0.5} Se _{0.5}	Ag _{0.99} Au _{0.92} S _{0.59} Se _{0.49}	Ag _{2.99} Au _{0.98} Se _{1.64} S _{0.36}	Au _{0.95} Ag _{0.05}	S _{0.82} Se _{0.18} *	–
9	AgAuS _{0.25} Se _{0.75}	Ag _{1.01} Au _{0.99} S _{0.33} Se _{0.67}	Ag _{3.03} Au _{1.08} Se _{1.72} S _{0.17}	Au	S _{0.48} Se _{0.52} *	–
10	AgAuSe	Ag _{0.99} Au _{1.00} Se _{1.01}	Ag _{3.01} Au _{1.02} Se _{1.97}	Au _{0.97} Ag _{0.03}	Se	Au _{0.94} Ag _{0.05} Se _{1.01}
T of heating 1050 °C, no annealing						
11**	AgAuSe	Ag _{0.97} Au _{1.02} Se _{1.01}	Ag _{3.03} Au _{0.99} Se _{1.97}	Au _{0.97} Ag _{0.03}	Se*	Au _{0.90} Ag _{0.10} Se _{1.00}
12***	AgAuSe	AgAuSe****	Ag _{3.00} Au _{1.03} Se _{1.97}	Au _{0.95} Ag _{0.05}	Se*	Au _{0.90} Ag _{0.10} Se _{1.00}
T of heating 750 °C, T of annealing 300°C						
13	AgAuS _{0.125} Se _{0.875}	Ag _{0.99} Au _{0.98} S _{0.21} Se _{0.82}	Ag _{2.85} Au _{1.09} Se _{1.88} S _{0.19}	Au _{0.97} Ag _{0.03}	Se*	Au _{0.89} Ag _{0.09} Se _{0.83} S _{0.21}
14	AgAuSe	Ag _{0.97} Au _{1.02} Se _{1.01}	Ag _{2.99} Au _{1.01} Se _{2.01}	Au _{0.94} Ag _{0.06}	Se	Au _{0.92} Ag _{0.04} Se _{1.02}

Compositions are given in mole fractions with the values exceeding the significant digits by one unit.

*Minor amounts of S₂Se-phases are present on the walls of ampoules in the form of semispheres.

Rapid cooling (in cold water); * slow cooling (in the switched-off furnace); **** – accurate determination of the composition was impossible owing to small sizes of grains.

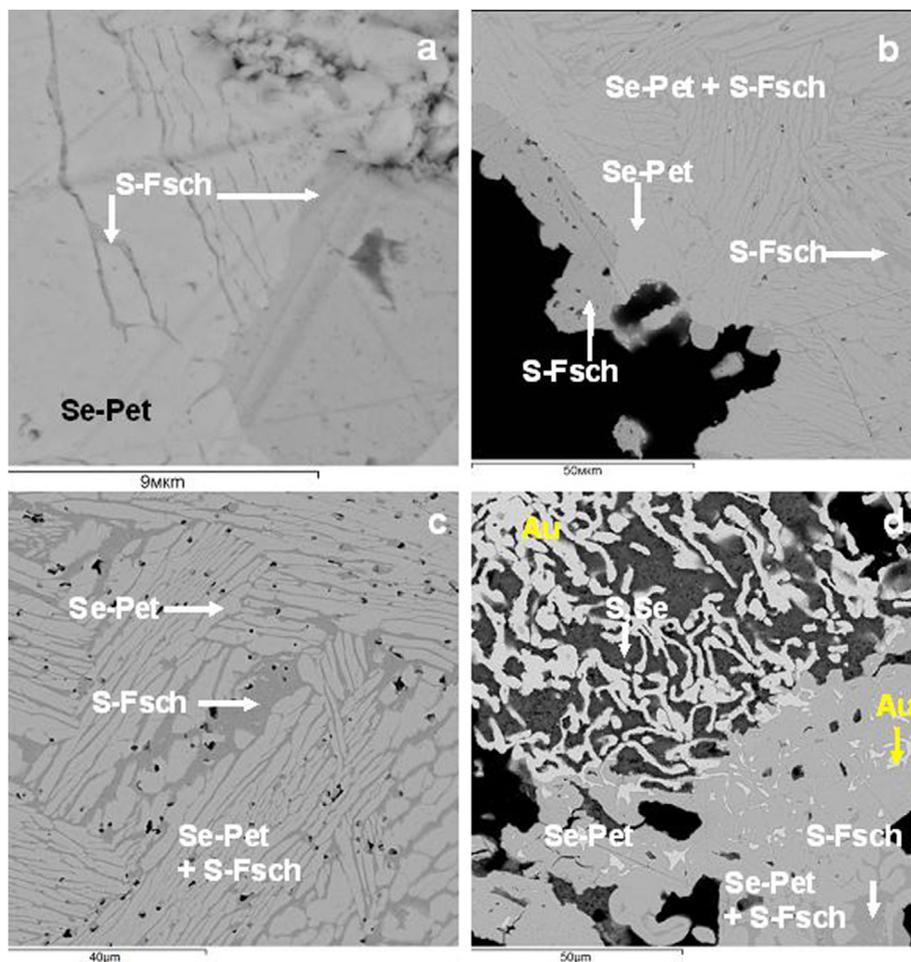


Fig. 1. SEM photo of synthesis products of experiments with annealing $T = 150\text{ }^{\circ}\text{C}$ (a–d) and initial compositions: a – $\text{AgAu}_{0.75}\text{Se}_{0.25}$ (N²); b – $\text{AgAu}_{0.5}\text{Se}_{0.5}$ (N³), c,d – $\text{AgAu}_{0.25}\text{Se}_{0.75}$ (N⁴). Legend: Se-Pet – petrovskaita-like phase, S-Fsch – fischerite-like phase, Au – high fineness Au–Ag alloy, S,Se – sulfur-selenium phase.

fragment of gold selenide crystal.

In the experiment with rapid cooling (N¹¹), the content of petrovskaita-like phase AgAuSe is considerably higher than both in the experiment with slow cooling (N¹²) (Fig. 3) and in those with annealing (N^{5,10,14}, Table 1; Fig. 4). In all the experiments with the initial composition AgAuSe , the quantity of fischerite predominates over the petrovskaita-like phase. Au–Ag alloy in the ingot grown by the method described in Ref. [6] (N¹⁴, Table 1) occurs as skeleton crystals (Fig. 4b).

It is worth noting that on the walls of all ampoules after synthesis we observed minor semispheres $<0.5\text{ mm}$ in size. Their composition was similar to S,Se-compounds and changed with increasing selenium content in the initial mixture from pure sulfur (yellow, N^{1,6}) to intermediate compositions (orange, red and wine red) (N^{2–4}, 7–9, 13) and to pure selenium (black) (N^{5,10–14}) (Table 1). They seem to be the condensation products of gas phase. The exception is experiments N⁴, 10, 14 (Table 1), the synthesis products of which showed a higher amount of Se and this phase was detected not only on the walls of ampoules but inside the ingot as well (Figs. 1d; 4b,c).

Diffraction analyses showed that the ingots of experiments with AgAuS and $\text{AgAu}_{0.75}\text{Se}_{0.25}$ starting compositions (N^{1,2}, Table 1) consist of petrovskaita [15] and petrovskaita-like phase, correspondingly. As a result of partial isomorphous replacement $\text{Se} \rightarrow \text{S}$, the unit cell parameters of $\text{AgAu}_{0.75}\text{Se}_{0.25}$ are slightly increased compared to AgAuS (Table 2). In samples $\text{AgAu}_{1-x}\text{Se}_x$, $x \geq 0.5$,

petrovskaita coexists with fischerite-like phase $\text{Ag}_3\text{AuSe}_{2-y}\text{S}_y$, in the structure of which up to half of selenium atoms can be isomorphously replaced by sulfur atoms [13,14]. In the presence of fischerite-like phase in the synthesized samples the $V_{\text{u.c.}}(\text{Se}/(\text{S} + \text{Se}))$ dependence for petrovskaita deviates from linear one (Fig. 5a). This can be due to the enrichment of fischerite with selenium relative to the sample bulk composition and, hence, the higher content of sulfur in petrovskaita-like phase (Tables 1 and 2). With the assumption of linear dependence $V_{\text{u.c.}}(\text{Se}/(\text{S} + \text{Se}))$ for petrovskaita-like phase, estimation of selenium fraction in its structure for sample 4 (Table 1) yields $\text{Se}/(\text{S} + \text{Se}) = 0.65$ (Table 2). From the results of refinement of petrovskaita-like phase structure by the Rietveld method, a refined formula unit of petrovskaita-like phase is $\text{AgAu}_{0.30}\text{Se}_{0.70}$. For sample 3 (Table 1) the calculated value $\text{Se}/(\text{S} + \text{Se})$ was 0.45 (Table 2). In both cases selenium fraction in $\text{AgAu}(\text{S,Se})$ is less compared to the bulk composition of sample (N^{3,4}, Table 1). The obtained value of the composition of phases is in good agreement with the results of EPMA. The unit cell metrics of fischerite-like phase is close to that of fischerite Ag_3AuSe_2 (Table 2), which suggests similarity of their compositions. Results of X-ray diffraction study of a series of samples annealed at $500\text{ }^{\circ}\text{C}$ are identical to those annealed at $150\text{ }^{\circ}\text{C}$.

The sample of bulk composition $\text{AgAu}_{0.125}\text{Se}_{0.875}$ (Fig. 6) along with the petrovskaita- and fischerite-like phases (N¹³, Table 1) also contains about 5% of $\beta\text{-AuSe}$ phase [20]. The estimated composition of petrovskaita-like phase is similar to $\text{AgAu}_{0.3}\text{Se}_{0.7}$,

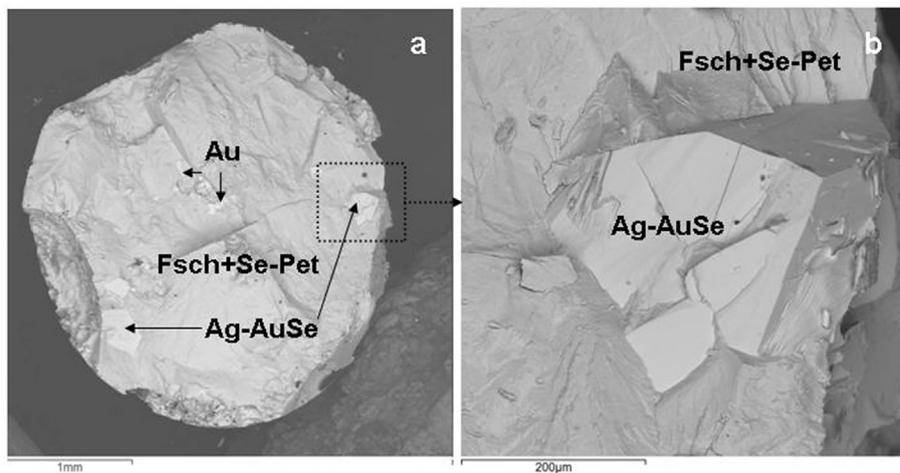


Fig. 2. SEM photo of ingot fragment (a), synthesized by the procedure (Nekrasov et al., 1990) with the initial composition AgAuSe (N^o14, Table 1), b – increased segment on (a) with gold selenide crystal.

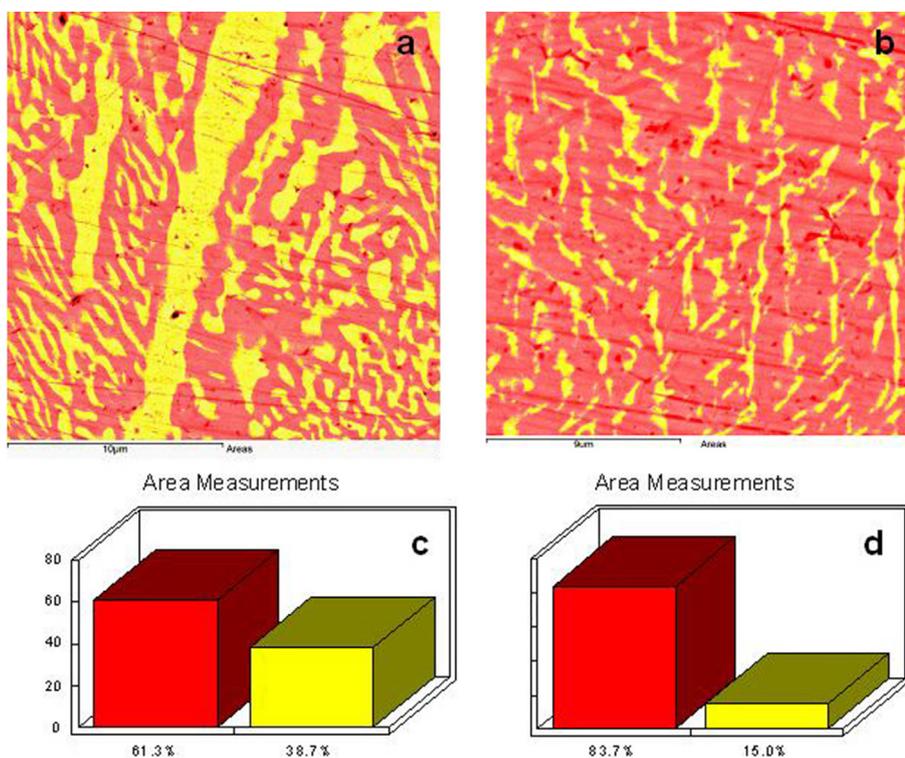


Fig. 3. Ratio of fischerite and petrovskaita-like phase in solid phase products of experiments with the initial composition AgAuSe - rapid (N^o11, Table 1) (a,c) and slow cooling (N^o12, Table 1) (b,d).

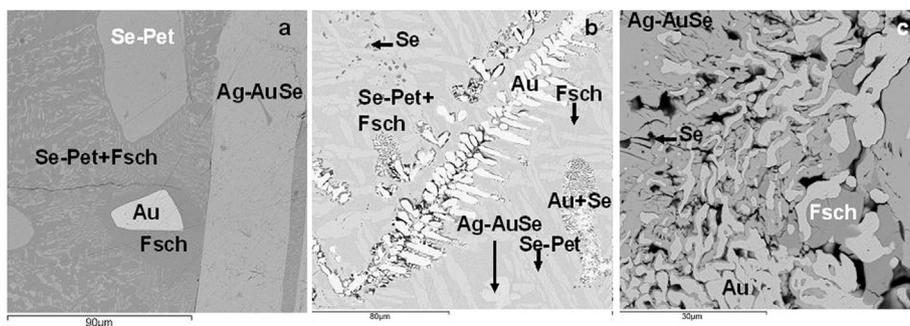


Fig. 4. SEM photos of petrovskaita-like, fischerite-like and other phases in the experiments (N^o5, 14, 10, Table 1) with initial composition AgAuSe and annealing T at 500 (a), 300 (b) and 150°C (c).

Table 2
Unit-cell parameters and concentration of synthesized phases of $\text{AgAuS}_{1-x}\text{Se}_x$ compounds.

Sample*	Phase composition**	Space group	Type***	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	Phase concentration, %
1	AgAuS	$R\bar{3}m$	1	13.4235	9.0873	1418.07	100
2	$\text{AgAuS}_{0.75}\text{Se}_{0.25}$	$R\bar{3}m$	1	13.5434(6)	9.1331(9)	1450.80(12)	100
3	$\text{AgAuS}_{0.55}\text{Se}_{0.45}$	$R\bar{3}m$	1	13.6484(5)	9.1544(7)	1476.80(11)	90
3	$\text{Ag}_3\text{AuS}_{0.60}\text{Se}_{1.40}$	$I4_132$	2	9.915(3)	974.8(8)	974.8(8)	10
4	$\text{AgAuS}_{0.35}\text{Se}_{0.65}$	$R\bar{3}m$	1	13.7447(6)	9.1845(8)	1502.65(14)	65
4	$\text{Ag}_3\text{AuS}_{0.15}\text{Se}_{1.85}$	$I4_132$	2	9.9672(8)	990.2(2)	990.2(2)	35
13	$\text{AgAuS}_{0.30}\text{Se}_{0.70}$	$R\bar{3}m$	1	13.7724(6)	9.1953(10)	1510.49(16)	65
13	$\text{Ag}_3\text{AuS}_{0.15}\text{Se}_{1.85}$	$I4_132$	2	9.9670(9)	990.1(2)	990.1(2)	30
10	AgAuSe	$R\bar{3}m$	1	13.813(3)	9.281(4)	1533.6(6)	<5
10	Ag_3AuSe_2	$I4_132$	2	9.9863(3)	995.89(9)	995.89(9)	20
11	AgAuSe	$R\bar{3}m$	1	13.8260(9)	9.2277(12)	1527.6(2)	25
11	Ag_3AuSe_2	$I4_132$	2	9.9865(4)	995.94(11)	995.94(11)	40

*Numbering is according to Table 1.

**The S:Se value was calculated from linear dependences $V_{\text{uc}}(\text{S/Se})$ for petrovskaitite (this work) and for fischesserite (Seryotkin et al., 2013).

***1 – petrovskaitite type, 2 – petzite type.

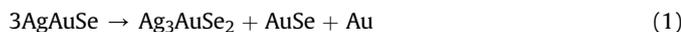
and the fischesserite-like phase is, respectively, enriched in selenium (Table 2).

The phase composition of synthesized samples from the experiments with the initial composition AgAuSe depends on their thermal history and, first of all, on cooling conditions. Thus, samples N^o5, 10 (Table 1) consist mainly of fischesserite, β -AuSe phase and metal phase. The unit cell volume of fischesserite (Table 2) is somewhat larger compared to 989.5 Å³ [21], which may be due to the isomorphous Au → Ag substitution in Ag-positions. This is, however, not supported by the refinement of their occupancies. The diffraction profile of AgAuSe sample annealed at 500°C (N^o10, Table 1) displays weak peaks which can be referred to a petrovskaitite-like phase (Fig. 6). Estimation of its concentration by the Rietveld method yielded the value of about 3%, i.e., only a minor amount if any of this phase is present in the sample. The diffraction profile of AgAuSe sample annealed at 150°C (N^o5) demonstrates no peaks of petrovskaitite-like phase (Fig. 6). The refinement of its concentration by the Rietveld method yielded a value close to zero.

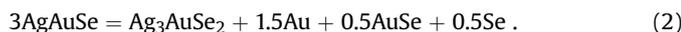
The quenched sample (N^o11, Table 1), on the contrary, along with fischesserite contains a considerable quantity of AgAuSe phase ($\approx 25\%$). The content of β -AuSe phase in this sample is lower than 10%, whereas in the sample annealed at 500°C (N^o10, Table 1) its concentration is higher than 20%. The phase composition of sample N^o 12 annealed in the conditions of a switched-off furnace is close to that of sample N^o 5: presence of abundant Ag_3AuSe_2 and AuSe phases and absence of petrovskaitite-like phase (Fig. 6).

The unit cell volume of petrovskaitite-like phase AgAuSe (Table 2) is reliably expanded compared to the isostructural sulfur-bearing phases and falls out of the general relationship $V_{\text{uc}}(\text{Se}/(\text{S} + \text{Se}))$ for the series $\text{AgAuS}_x\text{Se}_{1-x}$ (Fig. 5a). This supports our assumption about the sulfur enrichment of petrovskaitite-like phases relative to the bulk composition of samples in the presence of fischesserite.

The decay of metastable phase AgAuSe on cooling is quite simple:



or



Reaction 1 evidences that the concentration of three phases resulting from phase decomposition is the same. This conclusion cannot be inferred from X-ray diffractometry data. The most striking differences are seen between the phase compositions of quenched sample (N^o11) and those annealed at different temperatures (N^o5,10,14). In the quenched sample, as it was mentioned

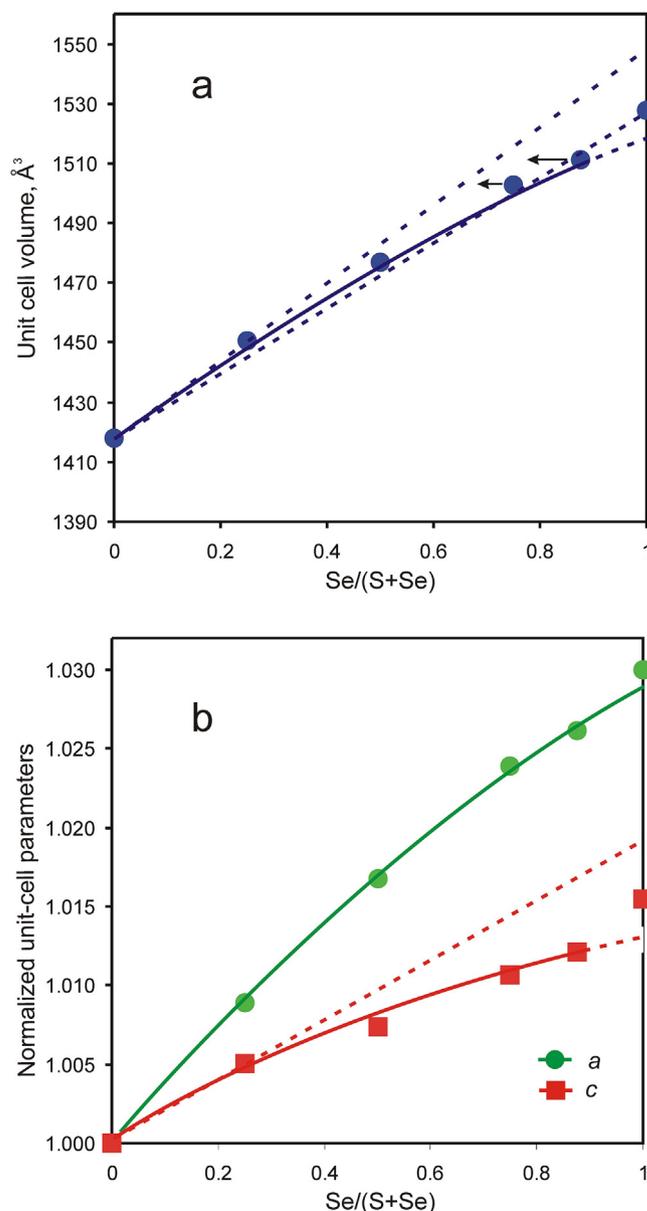


Fig. 5. Variations of unit-cell volume (a) and normalized unit-cell parameters (b) of petrovskaitite-like phases $\text{AgAuS}_{1-x}\text{Se}_x$.

above, AuSe phase is present in a rather minor amount, which can be due to the occurrence of **reaction 2** and decomposition of AuSe into Au and Se.

In **Fig. 1d** petrovskaite-like phase contains grains of high-fineness Au–Ag alloys of xenomorphic form and contacts with fischerite and S–Se phases. According to this data, the decomposition reaction of sulfoselenides $\text{AgAuS}_{1-x}\text{Se}_x$ ($0.5 < x < 1$) on the example of composition $x = 0.75$ can be presented without formation of AuSe:



Data from **Table 1** demonstrate that fischerite-like phase in the experiments with annealing at 500°C (N \circ 4) has a higher sulfur content than in the experiment with annealing at 150°C (N \circ 9) but lower than the theoretical value (**Table 1**). At $x = 1$, when the system lacks sulfur, AgAuSe phase decomposes to form fischerite Ag_3AuSe_2 , high-fineness Au–Ag alloys, gold selenide and (or) selenium (**reaction 1 and (or) 2**).

The structure of AgAuS [15] has a rigid porous framework of trigonal-prismatic columns along the three-fold symmetry axis containing edge-connected tetrahedra AgS_4 . The columns are reinforced on each edge by cations $(\text{Au,Ag})^+$ in a strictly linear coordination. The presence of linear triads $\text{S}-(\text{Au,Ag})-\text{S}$ in the structure is responsible for the increase of c parameter and deformation of AgS_4 tetrahedra. To compare, pyrrargyrite Ag_3SbS_3 [22] has a

topologically similar framework composed of $[\text{Ag}_3\text{S}_3]$ columns but without additional $(\text{Au,Ag})^+$ on their edges. The edges of AgS_4 -tetrahedron in Ag_3SbS_3 range within 4.0–4.8 Å. Whereas in AgAuS, these variations are extended to 3.4–5.1 Å which in turn results in the increment of column “height” (parameter c) by 0.4 Å. Thus, AgS_4 -tetrahedra in AgAuS have a configuration that is strongly elongated in c direction. Therefore, when S is replaced by Se, the tetrahedron expands irregularly, with a major contribution rather to thickening of the column than to its elongation. As a result, during the process of S–Se isomorphism the growth of c parameter is slower than the growth of horizontal parameter a (**Fig. 5b**).

The reason of the increase in instability of AgAu(S,Se) with growing fraction of selenium is the specific features of coordination of two subsystems – framework of trigonal-prismatic columns and the out-of-framework component of three-dimensional nets from linearly coordinated cations $(\text{Au,Ag})^+$. Its fragments on triple axes have non-bonding contacts (S,Se): $(\text{Se,S})-\text{Ag}-(\text{S,Se})\cdots(\text{Se,S})-\text{Ag}-(\text{S,Se})$. In petrovskaite AgAuS the distance $\text{S}\cdots\text{S} \approx 4.3$ Å. When $\text{Se} \rightarrow \text{S}$ replacement takes place, with the increase in $\text{Ag}-(\text{S,Se})$ distances and limited growth of c parameter, these non-bonding distances decrease and the $\text{Se}\cdots\text{Se}$ contact might become shorter than the $\text{S}\cdots\text{S}$, which is responsible for in the instability of the system. The increased metrics of the structure at high temperatures avoids this problem, which most likely explains the stability of AgAuSe phase close to the melting point.

It is worth noting that gold selenide with silver concentration to

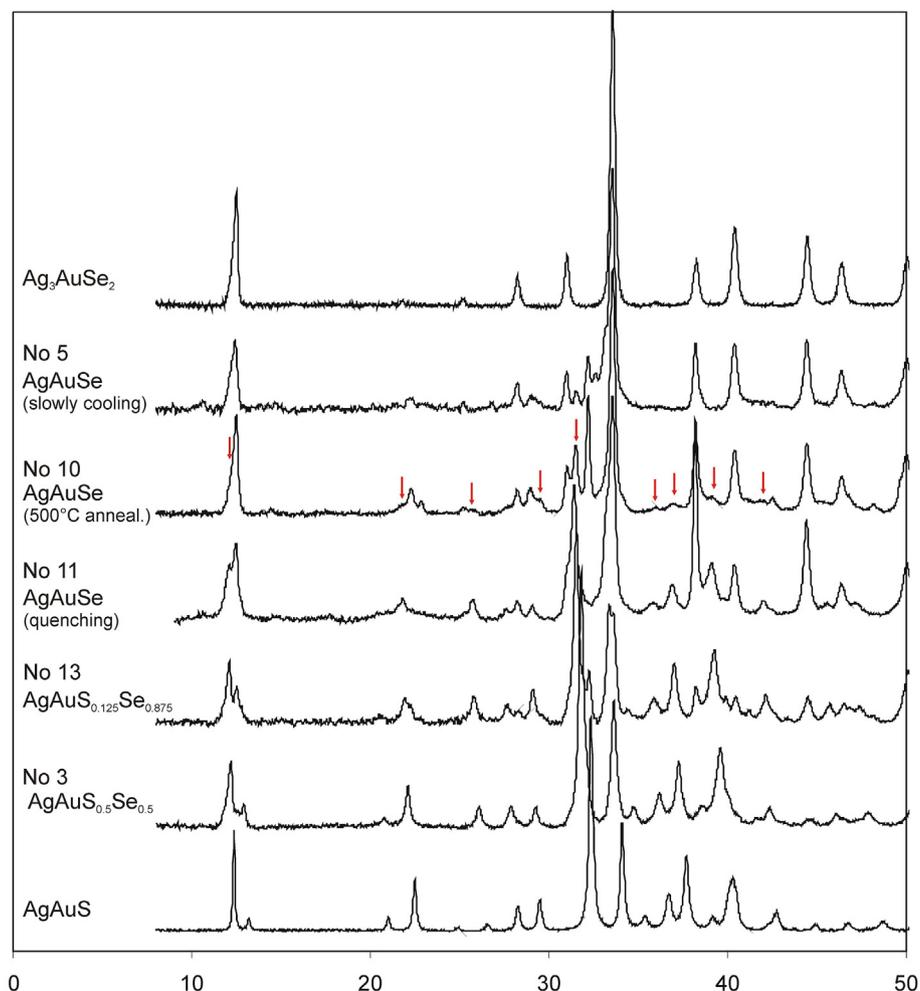


Fig. 6. The comparison of powder XRD patterns of synthesized samples 3,5,10,11,13 (see **Table 1**) with diffraction profiles for trigonal petrovskaite AgAuS (Seryotkin et al., 2014) (bottom) and cubic fischerite Ag_3AuSe_2 (top). Arrows in the profile of sample N \circ 10 show weak diffraction lines of petrovskaite-like phase.

0.1 mol fraction was detected only in the synthesis products of experiments with starting composition AgAuSe under all conditions of synthesis ($N_{\text{S}}^{\text{O}}5$, 10–12, 14). At $x = 0.875$ gold selenide along with silver contains sulfur, which suggests isomorphism S–Se to 0.17 mol fraction of sulfur and Au–Ag to 0.1 mol fraction of silver. It is known that gold selenide α -AuSe is stable at temperatures up to 425 °C [23]. The metastable β -AuSe decomposes at about 376 °C into solid gold and liquid selenium on heating [24]. Feng and Taskinen [25] report the decomposition temperature of AuSe to be 349 °C. Presence of this phase in synthesized samples annealed at 500 °C suggests that gold selenide may be stable at higher temperatures in the presence of silver.

4. Conclusions

Results of our studies prove the existence of continuous solid solution of the series AgAuS – AgAuSe. They have the same structural type as AgAuS (petrovskaita, space group $R\bar{3}m$). Owing to the partial isomorphous replacement $\text{Se} \rightarrow \text{S}$, unit cell parameters of petrovskaita-like phase $\text{AgAuSe}_{1-x}\text{S}_x$ are higher compared to AgAuS.

Petrovskaita-like phase $\text{AgAuS}_{1-x}\text{Se}_x$ is stable at $0 \leq x < 0.5$, and in the range of $0.5 \leq x < 1$ the phase is metastable and partly decomposes to form stable fischesserite-like phase $\text{Ag}_3\text{Au}(\text{Se},\text{S})_2$, high-fineness Au–Ag alloy, S, Se phase (at $0.5 \leq x \leq 0.75$) or selenium ($x = 1$) and phase β -AuSe (at $0.875 \leq x \leq 1$). Gold selenide AuSe revealed isomorphism S–Se to 0.17 mol fraction of sulfur and Au–Ag – to 0.1 mol fraction of silver. Phase AgAuSe is better preserved on rapid cooling from extremely high temperature (~1050 °C). In nature, conditions providing such quenching can hardly be realized and, therefore, the existence of phase AgAuSe in natural systems is very problematic. More real findings are fischesserite, high-fineness gold, selenium or AuSe at Au–Ag epithermal deposits with elevated concentrations of gold and selenium in ores.

Acknowledgments

This work is supported by RFFR grant N^o 11-05-00504a. Authors are grateful to Dr. N.S. Karmanov and M.V. Khlestov (Institute of Geology and Mineralogy SB RAS) for electron microprobe data.

References

- [1] E. Spiridonov, D. Yanakieva, Modern mineralogy of gold: overview and new data, *Archeosciences* 33 (2009) 67–73.
- [2] I.Ya Nekrasov, V.P. Samusikov, N.V. Leskova, A first finding of the sulfide AgAuS—an analog of petrovskaita, *Dokl. Akad. Nauk. SSSR+* 303 (1988)

- 944–947.
- [3] G.V. Nesterenko, A.P. Kuznetsova, N.A. Pal'chik, Yu.G. Lavrent'ev, Petrovskaita AuAg(S,Se), a new Se-containing Au–Ag sulfide, *Zap. VMO* 5 (1984) 602–607 (in Russian).
- [4] V.P. Samusikov, I.Ya. Nekrasov, N.V. Leskova, Gold–Silver Sulfoselenide (AgAu)₂(S,Se) from the Yuakutskoe Deposit, *Zap. VMO* 6 (2002) 61–64 (in Russian).
- [5] N.E. Savva, G.A. Palyanova, E.E. Kolova, Gold and silver minerals and conditions of their formation at the Dorozhnoye deposit (Magadan region, Russia), *Nat. Resour.* 5 (2014) 478–495.
- [6] I.Ya Nekrasov, S.E. Lunin, L.N. Egorova, X-ray study of the compounds of the system Au–Ag–S–Se, *Dokl. Akad. Nauk.* 311 (1990) 943–946.
- [7] K. Soldenhoff, Selective gold extraction from copper anode slime with an alcohol. Patent US 20110083531 A1, 20.04.2011.
- [8] E.G. Osadchii, E.A. Echmaeva, The system Ag–Au–Se: phase relations below 405 K and determination of standard thermodynamic properties of selenides by solid-state galvanic cell technique, *Am. Mineral.* 92 (2007) 640–647.
- [9] E.A. Echmaeva, E.G. Osadchii, Determination of the thermodynamic properties of compounds in the Ag–Au–Se and Ag–Au–Te systems by the EMF method, *Geol. Ore Deposits* 51 (2009) 247–258.
- [10] B.H. Tavernier, J. Verweken, P. Messien, M. Baiwir, Über das thermische Verhalten von Silber- und Silber-gold(I)-chalkogeniden, *Z. Anorg. Allg. Chem.* 356 (1967) 77–88.
- [11] M.D. Barton, The Ag–Au–S system, *Econ. Geol.* 75 (1980) 303–316.
- [12] H. Sakai, M. Ando, S. Ichiba, Yu Maeda, Au-197 Mossbauer spectroscopic study of the ternary-systems (Ag, Au)₂X (X = S and Se), *Chin. Chem. Lett.* 20 (1991) 223–226.
- [13] Yu.V. Seryotkin, G.A. Pal'yanova, V.V. Bakakin, K.A. Kokh, Synthesis and crystal structure of gold–silver sulfoselenides: morphotropy in the Ag₃Au(Se,S)₂ series, *Phys. Chem. Min.* 40 (2013) 229–237.
- [14] Yu.V. Seryotkin, G.A. Pal'yanova, N.E. Savva, Sulfur–selenium isomorphous substitution and morphotropic transition in the Ag₃Au(Se,S)₂ series, *Russ. Geol. Geophys.* 54 (2013) 646–651.
- [15] Yu.V. Seryotkin, V.V. Bakakin, G.A. Pal'yanova, K.A. Kokh, Synthesis and crystal structure of silver–gold sulfide AgAuS. Four-fold interpenetrated three-dimensional {(Au,Ag)₁₀S₈}-networks, *CrystEngComm* 16 (2014) 1675–1680.
- [16] A.C. Larson, R.B. Von Dreele, General Structure Analysis System (GSAS), Los Alamos National Laboratory Report LAUR, 2000, pp. 86–748.
- [17] G.A. Pal'yanova, K.A. Kokh, Yu.V. Seryotkin, Formation of gold and silver sulfides in the system Ag–Au–S, *Russ. Geol. Geophys.* 52 (2011) 443–449.
- [18] Yu. L. Mikhlin, V.A. Nasluzov, A.S. Romanchenko, A.M. Shor, G.A. Pal'yanova, XPS and DFT studies of the electronic structures of AgAuS and Ag₃AuS₂, *J. Alloys Compd.* 617 (2014) 314–321.
- [19] Yu.V. Seryotkin, V.V. Bakakin, G.A. Pal'yanova, K.A. Kokh, Synthesis and Crystal Structure of the Trigonal Silver(I) Dithioaurate(I), Ag₃AuS₂, *Cryst. Growth Des.* 11 (2011) 1062–1066.
- [20] A. Rabenau, H. Schulz, The crystal structures of α -AuSe and β -AuSe, *J. Less-Common Met.* 48 (1976) 89–101.
- [21] L. Bindl, C. Cipriani, Structural and physical properties of fischesserite, a rare Gold–silver selenide from the de Lanar Mine, Owyhee County, Idaho, USA, *Can. Mineral.* 42 (2004) 1733–1737.
- [22] P. Engel, W. Nowacki, Die Verfeinerung der Kristallstruktur von Proustit, Ag₃AsS₃ und Pyrargyrit, Ag₃SbS₃, *Neues Jahrb. Mineral. Monatsh.* 1966, pp. 181–184.
- [23] G.E. Cranton, R.D. Heyding, The gold/selenium system and some gold selenotellurides, *Can. J. Chem.* 46 (1968) 2637–2640.
- [24] A. Rabenau, H. Rau, G. Rosenstein, Phase relations in the gold – selenium system, *J. Less-Common Met.* 24 (1971) 291–299.
- [25] D. Feng, P. Taskinen, Thermodynamic stability of AuSe at temperature from (400 to 700) K by a solid state galvanic cell, *J. Chem. Thermodyn.* 71 (2014) 98–102.