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Ag—bearing mica: synthesis and crystal chemistry

V.G. THOMAS*, S.Z. SMIRNOV, O.A. KOZMENKO, YU. V. SERYOTKIN
Institute of Mineralogy and Petrography, Siberian Branch of the Russian Academy of Science, Novosibirsk 630090, Russia
E-mail: thomas@uiggm.nsc.ru

D. A. FURSENKO
JV Tairus, Institute of Mineralogy and Petrography, Novosibirsk 630090, Russia

V.S. PAVLYUCHENKO, L. N. POSPELOVA
Institute of Mineralogy and Petrography, Siberian Branch of the Russian Academy of Science, Novosibirsk 630090, Russia

A pioneer hydrothermal synthesis of a silver aluminosilicate has been performed at 600°C and 1.3 kbar in Physical and Chemical Modeling Laboratory of the Institute of Mineralogy and Petrography SB RAS, Novosibirsk, Russia. The synthesized Ag-bearing aluminum silicate has the $Ag(LiAl)[AlSi_3(O_8(OH)_2)]F_2$ chemical furmula. Its X-ray study showed that it could be regarded a dioctahedral mica. Argentum ions enter interlayer sites in the mica crystal structure. The unit-cell parameters are as follows: $a = 5.205(4)$, $b = 9.013(8)$, $c = 19.361(18)$ Å, $\beta = 97.78(13)^\circ$, $V = 900(1)$Å^3. The synthesized Ag-bearing mica can be regarded an experimental proof for a possibility of existence of Li-bearing dioctahedral micas.

1. Introduction

Silver has been regarded as typical chalcophile element since Goldschmidt's times. In nature silver mainly occurs as compounds with chalcogens and halogens. Oxygen-bearing compounds of Ag are mainly the salts of strong acids, e.g. nitric and sulphuric. Salts of Ag and weak oxygen-bearing acids, for example, carbonic acid, are unstable and decompose at a heating up to 200–300°C and easily hydrolyze in the presence of water [1].

That is why the hydrothermal synthesis of silver aluminosilicate, particularly Ag-bearing mica at 600°C is of special interest. Although Ag-bearing analcite and Ag-bearing fluorphlogopite have been already reported in literature [2, 3], these substances were not directly synthesized but produced through a cationic exchange between respective aluminosilicates exposed in $AgNO_3$ melt, i.e. in a water-free medium at a relatively low temperature of 250°C.

The paper presents the results of the pioneer synthesis of an Ag-bearing mica and its X-ray and chemical studies. The obtained experimental results are an important step in understanding of Ag geochemistry and mica crystal chemistry.

2. Experimental details

Ag-bearing mica was synthesized during the experimental study of beryl stability in fluorine-bearing hydrothermal media. The experiments were performed in 200 ml stainless steel autoclaves. An initial 100 × 20 × 5 mm rectangular block was cut from a natural beryl crystal so that its large planes were oriented parallel to an much easily dissolved $\{55.\overline{10}.6\}$ plane and long flanks were parallel to the $\{10\bar{1}0\}$ prism. The block was hung on a frame approximately in the middle of the autoclave work space. Five grams of Li_3AlF_6—a source of fluorine—was placed on the bottom of the autoclave [4]. Silver was introduced into the system as 0.75M $AgNO_3$ aqueous solution, which volume was equal to a half of the autoclave work volume. The autoclave was heated up to 600°C and held at that temperature during one month. We estimated the experimental pressure to be 1.3 kbar based on the ischores of pure water [5].

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*Author to whom all correspondence should be addressed.

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The phase composition of the crystalline products, which were formed during the experiment, was determined by an DRON-3 X-ray diffractometer ($Cu_{K\alpha}$ radiation). Besides, the X-ray examination of Ag-bearing mica was performed with a photo technique in a Ø57.3 mm Gondolfi chamber. The chemical composition of the mica was studied with microprobe analysis (EMPA), secondary ionic mass spectrometry (SIMS) and wet chemistry analysis. EMPA was performed on a "Camebax-Micro" electron microprobe analyzer. Nine intergrowths and single crystals of mica were mounted in an epoxy resin so that the analyzed section was perpendicular to the flattening of platelet crystals. The analyses were performed at 20 kV accelerating voltage, sample current of 20 nA and a beam diameter of 3–5 μm. Natural quartz, hematite, albite, orthoclase and synthetic fluorphlogopite were used as calibration standards. Synthetic proustite Ag_3AsS_3 was used as a standard for Ag. The measurement error was about 10 rel.%, in average.

According to chemical composition of the starting charge the resulted mica should contain BeO, Li_2O and H_2O which can not be analyzed with EMPA. Their concentrations were determined by SIMS on a Cameca IMS-4f ion microprobe at Institute of Microelectronics and Informatics RAS, Yaroslavl', Russia in two crystal samples previously studied by EMPA. The ionic microprobe was used with a 25 μm beam of O^- oxygen ions. H_2O was determined according to the technique reported in [6] implying that during oxygen ion bombardment all the sample water passes into protons and hydroxyl-ions. Well characterized synthetic glasses were used as calibration standards. The concentrations were calculated as an average of 5 analyses made in one point and the analytical error was below 15 rel.%. The applied SIMS technique was the same as reported in [6, 7].

The concentrations of Li_2O, Ag_2O, SiO_2 and F^- in mica were determined by the wet chemistry method. F^- was determined like described in [8, p. 225], SiO_2 like in [8, pp. 377–378], and Li_2O and Ag_2O were analyzed by flame atomic absorption method on a 400 Perkin-Elmer instrument. The measurement errors for F^-, SiO_2, Li_2O and Ag_2O were rather high— 10, 1.5, 5.5 and 7.5 rel.%, respectively due to a small weight of the specimen (5–18 micrograms).

3. Results and discussion

3.1. Newly formed phases

The experiments performed in the Li_3AlF_6-$AgNO_3$-H_2O system at 600°C and 1.3 kbar showed that beryl was unstable and broke down into fluortopaz $Al_2SiO_4(F,OH)_2$, phenakite Be_2SiO_4 and a nearly transparent platelet phase, which was under investigation. Below we will show that that phase was an Ag-bearing mica. F^-topaz crystallized on the autoclave bottom as a typical (for given conditions—[9]) aggregate of up to 0.5 mm long colorless needle-like crystals. Phenakite occurred as 1 mm isometric crystals (Fig. 1).

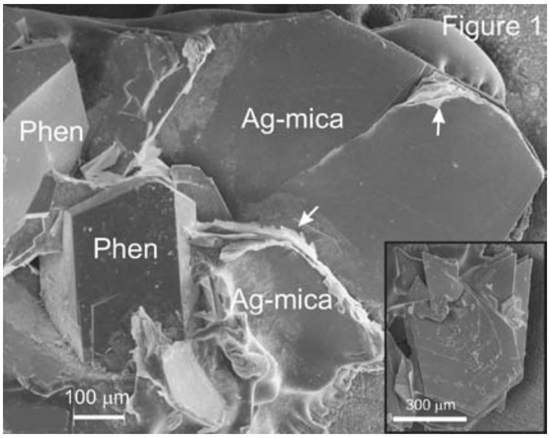

Figure 1 Platelet crystals of Ag-bearing mica (Ag-mica) intergrown with phenakite crystals (Phen). Arrows indicate the corners of mica crystals possessing eminent cleavage and high elasticity. Frame: rhomboid and pseudohexagonal mica crystals with growth steps on the $\{001\}$ pinacoid.

The mica crystallized as light yellow transparent platelet crystals of pseudohexagonal, rhomboid or irregularly round shape. Sometimes the mica crystals reached 2 mm across. The mica plates are elastic: they are easily folded at loading and are restored to their original form when unloaded. Large mica crystals display eminent cleavage developed parallel to the flattening. As far as the mica reveals no expansion on heating, we believe that it is not a hydromica.

Both, phenakite and mica were formed over the whole volume of the autoclave and their crystals precipitated over the autoclave internal walls and bottom and on the slowly dissolving flank surfaces of the beryl block parallel to the $\{10\bar{1}0\}$ prism faces. Several experimental runs resulted in complete decomposition of beryl and formation of a flank-face frame "jacket" composed of an aggregate dominated by mica with subordinate phenakite crystals. The presence of such a "jacket" suggests that the mica was formed directly during the experiment and it is not a quench phase.

The other newly formed phases are elementary silver, hematite Fe_2O_3 and silver chromate Ag_2CrO_4 resulted from the $AgNO_3$ interaction with autoclave's steel.

3.2. Diffractometry of Ag-bearing mica

The first powder diffraction patterns of the synthesized mica showed a high degree of sample texturing. The patterns displayed basal reflections at 9.61_3, 4.80_3, 3.49_1, 3.20_{10}, 1.92_6 Å (the subscript index shows a relative intensity of reflection) whereas other reflections were depressed and low intensive. All this allowed us to suggest that our samples could be regarded phyllosilicates.

The first diffraction maximum at 9.61Å is within the 9.5–10.5Å interval that is typical of micas [10]. The first maximums of other phyllosilicates and aluminosilicates, which displayed no expansion upon heating and formed macrocrystals, were significantly shifted. For example, the first maximums of pyrophyllite and chlorite were at 9.3Å and 14–15Å, respectively [11]. Thus, we attribute our synthesized aluminosilicate to the mica group based on the position of its basal reflections, its layered structure and physical properties (see Section 3.1).

Later on we added about 30 vol.% of amorphous silica to the diffracted mica sample before it was powdered in order to avoid preferential orientation. The use of such a technique allowed us to reveal non-basal reflections as well. Table II shows the diffractometry data on those samples.

Simultaneously, we performed X-ray examination of two mica samples in the Gondolfi chamber. The diffraction pattern and both X-ray patterns were completely identical suggesting the absence of significant amounts of alien phases in the mica samples under investigation. Unfortunately, we have failed to find single crystals of a quality sufficient for X-ray single crystal experiment.

3.3. Composition of Ag-bearing mica

Table I shows the chemical analyses of the Ag-bearing mica performed by three methods. The column "Integrated results" of Table I includes the three-method average results, which were used to calculate the crystal chemical formula. The first attempts to calculate atomic amounts of Ag-bearing mica components showed that the mica contained an excess of OH+F. Therefore the crystal chemical formula was calculated based on the number of cations.

We have tried two models for the calculation of formula coefficients:

a) dioctahedral mica model $XY_2[Z_4O_{10}](OH,F)_2$ (7 cations per formula) and

b) trioctahedral mica model $XY_3[Z_4O_{10}](OH,F)_2$ (8 cations per formula).

The atoms are distributed as follows. Whole Si^{4+} and Be^{2+} (by analogy with Be-margarite, [11]) enter the Z tetrahedral position and Al^{3+} fills the deficiency in the Z site up to 4 apfu. Mn^{2+}, Fe^{3+}, Ti^{4+} and the remained Al^{3+} enter the Y octahedral site of gibbsite layers. Besides, Li^{+} also enters the Y site by analogy with lepidolite. The remained monovalent cations enter the interlayer X sites. F^{-} enters the $(OH,F)^{-}$ site which, if necessary, is filled up to 2 apfu. We suggest that the excess of OH^{-} and F^{-} replaces a part of 10 apfu O^{2-}. The resulted empirical structural formulas were calculated on the basis of dioctahedral and trioctahedral mica models, are presented as follows.

TABLE I Chemical analyses of Ag-bearing mica (wt%).

	EMPA	SIMS	Wet chemical analysis	Integrated results
SiO_2	40.52	na	41.42	40.52
Al_2O_3	18.21	na	na	18.21
TiO_2	0.05	na	na	0.05
Fe_2O_3	1.34	na	na	1.34
BeO	na	0.14	na	0.14
MnO	0.08	na	na	0.08
Li_2O	na	3.36	3.55	3.46
Na_2O	0.63	na	na	0.63
K_2O	0.07	na	na	0.07
Rb_2O	0.04	na	na	0.04
Cs_2O	0.08	na	na	0.08
Ag_2O	22.29	na	27.49	24.89
F	8.76	na	7.00	8.19
H_2O	na	2.88	na	2.88
Total	92.08			100.58

Note: the contents of K_2O, Rb_2O and Cs_2O are close to the detection limit (∼0.03 wt%), ≪na≫ – the element was not analyzed.

a) Dioctahedral mica model:

$(Ag_{0.986}Na_{0.096}K_{0.007}Cs0.003Rb_{0.002})$

$(Li_{1.062}Al_{0.762}Fe_{0.077}Mn_{0.005}Ti_{0.003})$

$[Be_{0.06}Al_{0.878}Si_{3.096}(O_{8.554}(OH)_{1.446})]$

$(F_{1.978}(OH)_{0.022})$;

amounts of units per site: X = 1.092, Y = 1.91, Z = 4, (OH,F) = 2; charge misfit: −0.79.

b) Trioctahedral mica model:
$(Ag_{1.127}Na_{0.107}K_{0.008}Cs_{0.003}Rb_{0.002})$
$(Li_{1.213}Al_{1.441}Fe_{0.088}Mn_{0.006}Ti_{0.003})$
$[Be_{0.029}Al_{0.433}Si_{3.538}(O_{8.062}\quad(OH)_{1.677}\quad F_{0.260})]$

F_2; amounts of units per site: X = 1.247, Y = 2.75, Z = 4, (OH,F) = 2; charge misfit: +2.78.

TABLE II X-ray powder diffraction data for Ag-bearing mica.

h k l	d_{exp}, Å	d_{calc}, Å	I/I_0
002	9.61	9.59	3
004	4.80	4.80	3
$\bar{1}11$; 110	4.44	4.47	1
022	4.11	4.08	2
112; $\bar{1}13$	3.88	3.89	3
$\bar{1}14$	3.49	3.48	5
006	3.20	3.20	10
114	3.08	3.10	2
025	2.86	2.92	1
$\bar{1}16$; 115	2.76	2.75	2
$\bar{2}02$; 200; 131	2.58	2.59	9*
$\bar{2}21$	2.24	2.25	3
$\bar{2}06$	2.14	2.15	3
00.10	1.92	1.92	6
060	1.50	1.50	4

d_{exp}— experimentally measured interplanar spacing, d_{calc}— calculated interplanar spacing, I/I_0— relative intensities of reflexes in the experimentally measured XRD pattern. *— line is thickened.

We can see that the dioctahedral model (a) satisfactory describes the composition of the Ag-bearing mica because the amount of cations in the interlayer and octahedral sites is close to the theoretical one, the deviations are within the analytical errors and the charge misfit is small.

The trioctahedral model presents a worse chemical formula of the mica, which displays a greater deviation of the amount of interlayer and octahedral positive charges from the theoretical one and does not balance electrostatically.

Thus, the chemical formula based on the dioctahedral model, neglecting minor isomorphic impurities and implying the change of the O/OH ratio from $O_{8.5}(OH)_{1.5}$ to $O_8(OH)_2$ to provide the electric neutrality will be as follows:

$$Ag\ (LiAl)\ [AlSi_3(O_8(OH)_2)]\ F_2 \qquad (1)$$

The formula (1) shows that the +5 total positive charge of interlayer and octahedral ions of the Ag-bearing mica is notably lower than that of other micas $(+6 \div +8)$ [10], and the composition of its tetrahedral sheet is analogous to that of muscovite. The difference in charges is compensated by a partial $OH^- > O^{2-}$ replacement, which can be regarded an entrance of additional H^+ in the Ag-bearing mica crystal structure.

Our synthesized mica is of special interest because (1) it contains Ag and (2) it represents an exotic Li-bearing mica. All known natural Li-micas have either trioctahedral (e.g. polylithionite, protolithionite) or di-trioctahedral (lepidolite) crystal structure. No dioctahedral Li-bearing micas have ever been reported before. Our experiments supported a possibility for the existence of such dioctahedral Li-bearing micas.

Why then the Ag-bearing micas have never been found in natural mineral assemblages hitherto? We suggest two natural factors preventing crystallization of micas which X site is almost completely occupied by Ag: 1) in natural mineral forming media Ag competes in entering the X site with K and Na, which amounts are much higher than that of Ag; 2) natural media are usually characterized by a high activity of sulfur and therefore Ag which is a chalcophile element would rather occur as Ag-sulfides. On the other hand Ag-bearing micas with minor Ag entering the X site instead of K and Na can be synthesized without significant problems. Such Ag-bearing micas could be primary concentrators of Ag under high-temperature hydrothermal conditions. As far as micas possess strong ion-exchange properties further $Ag^+ \Rightarrow K^+, Na^+$ replacements are quite possible under an increasing sulfur activity.

3.4. Ag-bearing mica crystal structure

Based on the calculated formula we performed the indexing of the reflections of the Ag-bearing mica diffraction pattern and defined more exactly the unit-cell dimensions. The structure of phengite [12]—a high-Si analogue of muscovite, C2/c space group—was used as a basic model. Li^+ and excessive Al^{3+} enter the octahedral site in 1:1 proportion of site occupancies. The interlayer Ag^+ takes a special position on the two-fold axis. The reflection intensities were calculated using the XPOW program of the SHELXTL Crystallographic Software Package (Siemens Analytical X-ray Inst. Inc., 1989). The obtained results showed that Ag was a main contributor to the intensity of basal reflections. According to the base-model calculation the intensity of the (004) reflection must be close to zero however it can be clearly seen in the diffraction pattern (Table II). To adjust the calculations and the experimental data the Ag ions were displaced from special to general position with a shift of ∼0.5Åalong *z* in order to weaken the affect of the interlayer Ag on the intensity of basal reflections. This resulted in better proportions of the calculated reflections intensities. Table II shows the experimental and calculated values of interlayer distances and the indices of reflections.

The unit-cell dimensions more exactly defined with the CELL software [13] are as follows: $a = 5.205(4)$, $b = 9.013(8)$, $c = 19.361(18)$Å, $\beta = 97.78(13)^\circ$, $V = 900(1)$Å^3. Compared to phengite [12] the Ag-bearing mica has a smaller unit cell volume due to smaller *b* and *c* (which appeared 3–4% less), although *a* remained practically unchanged.

The reduction of *c* is explained by a smaller ionic radius of Ag^+ compared to that of K^+, which is a major interlayer ion in the phengite crystal structure. The smaller *b* parameter agrees with the suggested shift of Ag^+ along *z*, because such a shift requires crimping of tetrahedral layers in order to maintain an acceptable coordination environment of interlayer cations.

The displacement of the interlayer cation (Ag^+ in our case) from special to general position is uncommon for micas. However, such displacement is quite explicable if we suggest that the above mentioned deficiency in the interlayer and octahedral sites positive charges (+ 5 in the Ag-bearing mica compared to + 6 x÷ + 8 in other micas) is compensated by the partial replacement $OH \Rightarrow O^{2-}$. If H^+ ions of hydroxyl groups enter the interlayer site, two similarly charged ions – Ag^+ and H^+ – will start to repel from each other resulting in the Ag^+ displacement from special to general position.

4. Conclusions

1. The authors performed the pioneer direct synthesis of the Ag–bearing mica and proposed the formula $Ag(LiAl)[AlSi_3(O_8(OH)_2)]F_2$.

2. The comparison of the X-ray powder diffraction data for the Ag-bearing mica with different models showed that its crystal structure can be represented as muscovite structure where Ag^+ substitutes for K^+ and a half of octahedral Al^{3+} is replaced by Li^+. Therein appeared

deficiency of the positive charge is compensated by the $2OH \Rightarrow O^{2-}$ replacement.

3. The unit-cell dimensions of the Ag-bearing mica are as follows: $a = 5.205(4)$, $b = 9.013(8)$, $c = 19.361(18)$Å, $\beta = 97.78(13)^\circ$, $V = 900(1)$Å^3.

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