

Attikaite, $\text{Ca}_3\text{Cu}_2\text{Al}_2(\text{AsO}_4)_4(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, a New Mineral Species¹

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Abstract—Attikaite, a new mineral species, has been found together with arsenocrandalite, arsenogoyazite, conichalcite, olivenite, philipsbornite, azurite, malachite, carminite, beudantite, goethite, quartz, and allophane at the Christina Mine No. 132, Kamareza, Lavrion District, Attiki Prefecture (Attika), Greece. The mineral is named after the type locality. It forms spheroidal segregations (up to 0.3 mm in diameter) consisting of thin flexible crystals up to $3 \times 20 \times 80 \mu\text{m}$ in size. Its color is light blue to greenish blue, with a pale blue streak. The Mohs' hardness is 2 to 2.5. The cleavage is eminent mica-like parallel to {001}. The density is 3.2(2) g/cm³ (measured in heavy liquids) and 3.356 g/cm³ (calculated). The wave numbers of the absorption bands in the infrared spectrum of attikaite are (cm⁻¹; *sh* is shoulder; *w* is a weak band): 3525*sh*, 3425, 3180, 1642, 1120*w*, 1070*w*, 1035*w*, 900*sh*, 874, 833, 820, 690*w*, 645*w*, 600*sh*, 555, 486, 458, and 397. Attikaite is optically biaxial, negative, $\alpha = 1.642(2)$, $\beta = \gamma = 1.644(2)$ ($X = c$), $2V_{\text{meas}} = 10(8)^\circ$, and $2V_{\text{calc}} = 0^\circ$. The new mineral is microscopically colorless and nonpleochroic. The chemical composition (electron microprobe, average over 4 point analyses, wt %) is: 0.17 MgO, 17.48 CaO, 0.12 FeO, 16.28 CuO, 10.61 Al₂O₃, 0.89 P₂O₅, 45.45 As₂O₅, 1.39 SO₃, and H₂O (by difference) 7.61, where the total is 100.00. The empirical formula calculated on the basis of (O,OH,H₂O)₂₂ is: Ca_{2.94}Cu_{1.93}Al_{1.97}Mg_{0.04}Fe_{0.02}²⁺[(As_{3.74}S_{0.16}P_{0.12})_{Σ4.02}O_{16.08}](OH)_{3.87} · 2.05H₂O. The simplified formula is Ca₃Cu₂Al₂(AsO₄)₄(OH)₄ · 2H₂O. Attikaite is orthorhombic, space group *Pban*, *Pbam* or *Pba2*; the unit-cell dimensions are $a = 10.01(1)$, $b = 8.199(5)$, $c = 22.78(1)$ Å, $V = 1870(3)$ Å³, and $Z = 4$. In the result of the ignition of attikaite for 30 to 35 min at 128–140°, the H₂O bands in the IR spectrum disappear, while the OH-group band is not modified; the weight loss is 4.3%, which approximately corresponds to two H₂O molecules per formula; and parameter c decreases from 22.78 to 18.77 Å. The strongest reflections in the X-ray powder diffraction pattern [d , Å (I , %)(hkl)] are: 22.8(100)(001), 11.36(60)(002), 5.01(90)(200), 3.38(5)(123, 205), 2.780(70)(026), 2.682(30)(126), 2.503(50)(400), 2.292(20)(404). The type material of attikaite is deposited in the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow. The registration number is 3435/1.

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Recent studies resulted in revealing natural copper arsenates with structures that contain clusters composed of four or five edge-shared polyhedrons CuO₅ as distorted square pyramids in shape (Cooper et al., 1999; Cooper and Hawthorne, 2000; Zubkova et al., 2003, 2004, 2005; Pushcharovsky et al., 2004; Sarp and Černý, 2004). We have studied a new mineral *attikaite* that is close to members of this family in physical properties, IR spectrum, and X-ray parameters and which was found by Harry Sniasehek at the Christina Mine No. 132, Kamareza, Lavrion District, Attiki Prefecture (Attika), Greece. The mineral is named after the type

locality (prefecture, peninsula and well-known historical region of Attika; the Greek transcription is Αττική).

Attikaite was formed in the supergene zone of base-metal sulfide–quartz veins. Arsenocrandalite, arsenogoyazite, conichalcite, olivenite, philipsbornite, azurite, malachite, carminite, beudantite, goethite, quartz, and allophane are associated minerals. Attikaite forms commonly distorted flakes up to $3 \times 30 \times 60 \mu\text{m}$ in size, strongly flattened in the [001] direction and combined into spheroidal segregations up to 0.3 mm in diameter (Figs. 1 and 2) coating the walls of small slit cavities in oxidized ore. The flakes are flexible; the Mohs' hardness is 2 to 2.5 (for segregations). The cleavage is perfect mica-like parallel to {001}. The color is light blue to greenish blue, with a pale blue streak.

The density of the new mineral measured with equilibration in heavy liquids is 3.2(2) g/cm³ and $D_{\text{calc}} =$

¹ A new mineral attikaite and its name were accepted by the Commission on New Minerals and Mineral Names, Russian Mineralogical Society, March 30, 2006. Approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association, July 1, 2006. IMA no 2006-017.

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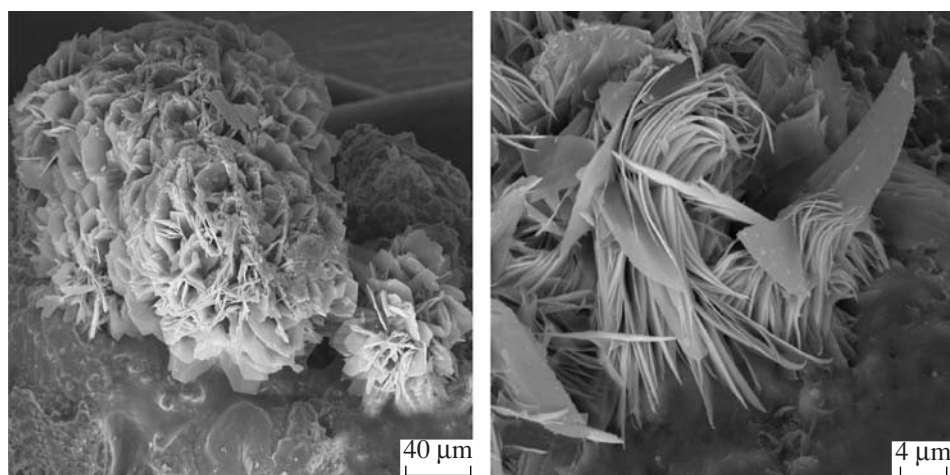


Fig. 1. SEM images of attikaite aggregates.

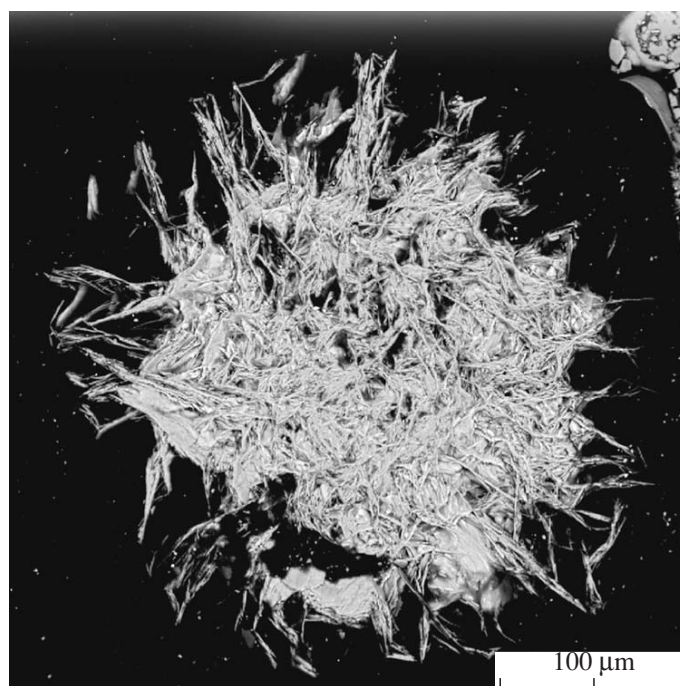


Fig. 2. BSE image of an attikaite aggregate, polished section.

3.356 g/cm^3 . The underestimated value of the measured density is caused by the looseness of the attikaite segregations that contain microcavities (Fig. 2).

The wave numbers of the absorption bands in the infrared spectrum of attikaite and their attribution are (cm^{-1} ; *sh* is shoulder; *w* is the weak band; the wave numbers of the strongest bands (Fig. 3) are underlined): 3525_{sh} , 3425 (O–H stretching vibrations of H_2O molecules), 3180 (O–H stretching vibrations of OH-groups), 1642 (bending vibrations of the H_2O molecules),

1120_w , 1070_w (SO_4^{2-} (?) stretching vibrations), 1035_w (PO_4^{3-} (?) stretching vibrations), 900_{sh} , 874 , 833 , 820 (AsO_4^{3-} stretching vibrations), 690_w , 645_w (bending vibrations of the SO_4^{2-} (?) ions), 600_{sh} (bending vibrations of the PO_4^{3-} (?) ions), 555 (Al–O stretching vibrations), 486 , 458 , and 397 (combination of the Cu–O and Ca–O stretching vibrations and bending vibrations of the AsO_4^{3-} ions). The IR spectrum of attikaite is the

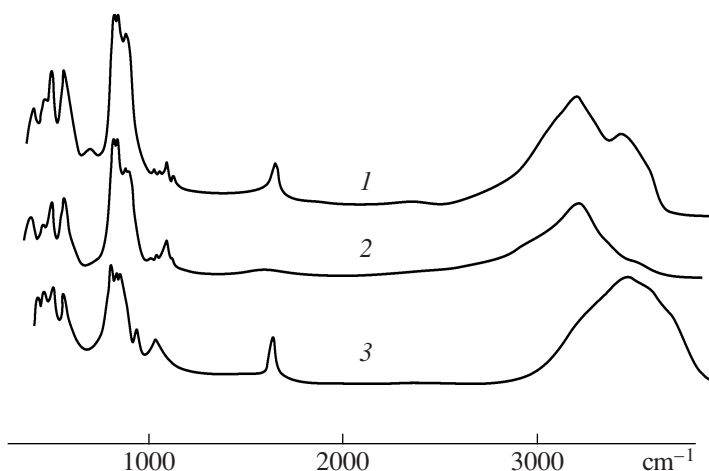


Fig. 3. Infrared spectra of (1) initial attikaite, (2) attikaite heated at 140°C for 35 min, and (3) lavendulan.

closest to that of lavendulan and zdenekite, differing from them by the presence of strong bands in the vibration range of the OH-groups, which form stable hydrogen bonds (region 3000–3300 cm^{-1}). After the ignition of the attikaite sample at 140°C for 35 min, the bands attributing to the H_2O molecules (at 3425 and 1642 cm^{-1}) disappear, but the band of the OH-stretching vibrations at 3180 cm^{-1} are retained (Fig. 3).

The new mineral is biaxial, optically negative; with $\alpha = 1.642(2)$, $\beta = \gamma = 1.644(2)$, and $2V_{\text{meas}} = 10(8)^\circ$; $2V_{\text{calc}} = 0^\circ$. Optical orientation is $X = c$. No dispersion is observed. Attikaite is microscopically colorless and is not pleochroic.

The chemical composition (electron microprobe, average over 4 point analyses) is presented in Table 1. The Na, K, Sr, Ba, Zn, Ni, Pb, Di, Sb, Si, V, Cl, and F contents are below detection limits for these elements. The empirical formula calculated on the basis of $(\text{O,OH,H}_2\text{O})_{22}$ ($Z = 4$) with allowance for

the charge balance is $\text{Ca}_{2.94}\text{Cu}_{1.93}^{2+}\text{Al}_{1.97}\text{Mg}_{0.04}\text{Fe}_{0.02}^{2+}[(\text{As}_{3.74}\text{S}_{0.16}\text{P}_{0.12})_{\Sigma 4.02}\text{O}_{16.08}](\text{OH})_{3.87} \cdot 2.05\text{H}_2\text{O}$. The simplified formula is $\text{Ca}_3\text{Cu}_2\text{Al}_2(\text{AsO}_4)_4(\text{OH})_4 \cdot 2\text{H}_2\text{O}$. The theoretical chemical composition calculated from this formula is (wt %): 17.51 CaO, 16.55 CuO; 10.61 Al_2O_3 , 47.83 As_2O_5 , 7.50 H_2O , where the total is 100.00. The amount of H_2O attributing to OH-groups is 3.75 wt % and that of molecular water, 3.75 wt %. The latter is close to the weight loss of 4.3% derived from the heating of attikaite from room temperature to 140°C (see below).

Attempts at the X-ray single-crystal study of attikaite failed due to distortion and the small sizes of its individual crystals. However, the affinity of the new mineral to the arsenates from the lavendulan family in X-ray parameters and physical properties (Table 2) allowed the attikaite unit cell to establish on the basis of X-ray powder data. Experiments on the mineral dehydration (see below) indicated its unambiguously layered structure and allowed precise identification of the 00 l reflection set (accepted as the direction normal to sheets). According to the results of these experiments and by analogy with allied arsenates (Table 2), one of the unit-cell parameters normal to [001] was established (it was accepted as a). Using these data, we could adequately index the powder pattern of attikaite (Table 3) obtained with an RKG-86 camera constructed for the observation of the reflections within a small angle region (FeK_α radiation, the diameter of the camera is 86 mm, and Si is the inner standard).

According to the powder data, the new mineral is orthorhombic; the unit-cell dimensions are $a = 10.01(1)$, $b = 8.199(5)$, $c = 22.78(1)$ Å, $V = 1870(3)$ Å³, and $Z = 4$. Special extinctions indicate the probable space groups $Pban$, $Pbam$ and $Pba2$.

The attikaite X-ray powder pattern could be formally indexed on the basis of the small unit cell with

Table 1. Chemical composition of attikaite

| Component | Content, wt % | Range | Standard |
|-------------------------|---------------|-------------|-------------------------|
| MgO | 0.17 | 0–0.33 | MgO |
| CaO | 17.48 | 16.19–18.43 | Wollastonite |
| FeO | 0.12 | 0–0.22 | Fe |
| CuO | 16.28 | 15.48–17.94 | Cu |
| Al_2O_3 | 10.61 | 9.46–11.43 | Al_2O_3 |
| P_2O_5 | 0.89 | 0.59–1.10 | LaPO_4 |
| As_2O_5 | 45.45 | 44.02–47.53 | As |
| SO_3 | 1.39 | 1.15–1.72 | FeS_2 |
| H_2O^* | (7.61) | | |
| Total | (100.00) | | |

* Water content is estimated from the difference.

Table 2. Comparative characteristics of attikaite and allied arsenate minerals*

| Mineral | Attikaite | Lavendulan | Zdenekite | Mahnerite | Andyrobertsite | Calico-andyrobertsite** |
|--|--|---|---|---|---|---|
| Formula | Ca ₃ Cu ₂ Al ₂ (AsO ₄) ₄ (OH) ₄ · 2H ₂ O | NaCaCu ₅ (AsO ₄) ₄ Cl · 5H ₂ O | NaPbCu ₅ (AsO ₄) ₄ Cl · 5H ₂ O | (Na, Ca)Cu _{2.75} (AsO ₄) ₂ Cl _{0.62} · 3.62H ₂ O | KCdCu ₅ (AsO ₄) ₄ [AsO ₂ (OH) ₂] · 2H ₂ O | KCaCu ₅ (AsO ₄) ₄ [AsO ₂ (OH) ₂] · 2H ₂ O |
| Symmetry | Orthorhombic | Monoclinic | Monoclinic, pseudotetragonal | Tetragonal | Monoclinic | Space group |
| Space group | <i>Pban</i> , <i>Pbam</i> or <i>Pba2</i> | <i>P12₁/n1</i> | <i>P2₁/n</i> | <i>I4/mmm</i> | <i>P2₁/m</i> | <i>Pnmma</i> |
| <i>a</i> , Å | 10.01 | 10.011 | 10.023 | 10.037 | 9.810 | 19.647 |
| <i>b</i> , Å | 8.199 | 19.478 | 19.55 | 10.037 | 10.034 | 10.087 |
| <i>c</i> , Å | 22.78 | 10.056 | 10.023 | 23.797 | 9.975 | 9.963 |
| β, ° | 90 | 90.39 | 90.02 | 90 | 101.84 | 90 |
| <i>V</i> , Å ³ | 1870 | 1960.8 | 1964.6 | 2397.3 | 961.0 | 1974.4 |
| <i>Z</i> | 4 | 4 | 4 | 8 | 2 | 4 |
| Strong reflections in X-ray powder pattern | 22.8 (100) | 9.77 (100) | 9.83 (100) | 11.90 (100) | 9.64 (100) | 9.80 (50) |
| <i>d</i> , Å (<i>I</i> , %) | 11.36 (60) | 7.01 (40) | 4. (60) | 9.29 (60) | 4.46 (40) | 7.084 (70) |
| | 5.01 (90) | 4.87 (50) | 4.4 (50) | 7.132 (50) | 3.145 (50) | 6.665 (60) |
| | 3.38 (50) | 4.41 (40) | 3.132 (90) | 5.046 (60) | 3.048 (40) | 4.830 (70) |
| | 2.780 (70) | 3.11 (70) | 2.772 (40) | 3.098 (80) | 2.698 (40) | 4.487 (90) |
| | 2.503 (50) | 2.90 (20) | 2.515(50) | 3.061 (70) | | 3.965 (60) |
| | | 2.76 (20) | | | | 3.116 (100) |
| | | | | | | 2.760 (90) |
| Optical parameters: | | | | | | |
| α | 1.642 | 1.645 | 1.710 | 1.635 | 1.720 | 1.715 |
| β | 1.644 | 1.748 | 1.770 | 1.686 | 1.749 | 1.730 |
| γ | 1.644 | 1.748 | 1.770 | 1.686 | 1.757 | 1.735 |
| 2 <i>V</i> , optical sign | -10° | -0° | -0° | -0° | -50° | -55° |
| Density, g/cm ³ | 3.355 (calc) | 3.59 (calc) | 4.16 (calc) | 3.14 (calc) | 4.01 (calc) | 3.80 (calc) |
| | 3.2 (meas) | 3.54 (meas) | 4.08 (meas) | 3.33 (meas) | | 3.9 (meas) |
| Source | This study | Guillemin, 1956; Sarp, Černý, 2004 | Chiappero, Sarp, 1995; Zubkova et al., 2003 | Sarp, 1996; Pushcharovský et al., 2004 | Cooper et al., 1999 | Sarp, Černý, 2004 |

Notes: * Sampleite NaCaCu₅(PO₄)₄Cl · 5H₂O is allied phosphate.*** Polytype 2*O*; for polytype 1*M*, see Cooper et al. (1999). Unit-cell parameters are given after the authors' data. Sheets are arranged normally to axis *c* for mahnerite and attikaite, normally to *b* for lavendulan and zdenekite, and normally to *a* for andyrobertsite and calico-andyrobertsite.

Table 3. X-ray powder diffraction data for attikaite

| $I_{\text{meas}}, \%$ | $d_{\text{meas}}, \text{\AA}$ | $d_{\text{calc}}, \text{\AA}$ | hkl |
|-----------------------|-------------------------------|-----------------------------------|-------------------------|
| 100 | 22.8 | 22.78 | 001 |
| 60 | 11.36 | 11.39 | 002 |
| 10 | 7.61 | 7.593 | 003 |
| 90 | 5.01 | 5.005 | 200 |
| 10 | 4.55 | 4.582, 4.556 | 202, 005 |
| 10 | 4.09 | 4.099 | 020 |
| 50 | 3.38 | 3.394, 3.369 | 123, 205 |
| 10 | 3.12 | 3.141, 3.116 | 221, 215 |
| 10 | 3.06 | 3.063, 3.055 | 311, 222 |
| 10 | 2.906 | 2.915, 2.895 | 125, 117 |
| 70 | 2.780 | 2.786 | 026 |
| 30 | 2.682 | 2.684 | 126 |
| 50 | 2.503 | 2.503 | 400 |
| 20 | 2.292 | 2.291 | 404 |
| 10b | 2.25 | 2.259, 2.250, 2.241 | 209, 325, 317 |
| 10b | 2.08 | 2.089, 2.079, 2.073 | 406, 332, 2.0.10 |
| 10b | 1.98 | 1.984, 1.982, 1.979, 1.978, 1.978 | 407, 334, 043, 229, 142 |
| 10b | 1.93 | 1.934, 1.934, 1.931, 1.929, 1.928 | 138, 425, 237, 044, 417 |
| 10 | 1.738 | 1.741, 1.741, 1.739 | 341, 239, 419 |
| 20 | 1.666 | 1.670, 1.669, 1.668, 1.664, 1.664 | 344, 517, 600, 601, 048 |
| 15 | 1.570 | 1.573, 1.571, 1.571, 1.568 | 149, 614, 442, 2.3.11 |
| 15 | 1.511 | 1.512, 1.512 | 4.0.12, 0.2.14 |

the dimensions $a = 5.004$, $b = 4.097$, $c = 22.76 \text{ \AA}$, and $Z = 1$ (probable space groups $Pmmm$, $Pmm2$, and $P222$). However, a comparison with allied minerals (Table 2) shows that such an unit cell is unlikely. Really, the crystal structures of the detailed studied minerals allied to attikaite (namely, zdenekite, andyrobertsite, calico-andyrobertsite, and mahnerite) (Cooper et al., 1999; Cooper and Hawthorne, 2000; Zubkova et al., 2003, 2004, 2005; Pushcharovsky et al., 2004; Sarp and Černý, 2004) are based on heteropolyhedral sheets consisting of the AsO_4 tetrahedrons and clusters of four or five CuO_5 polyhedrons. Large structural units of the $\text{Cu}_5(\text{AsO}_4)_4[\text{As}(\text{O},\text{OH})_4]\text{O}_9$ type clusters described for andyrobertsite and calico-andyrobertsite (Sarp and Černý, 2004) or $\text{Cu}_5(\text{AsO}_4)_4\text{ClO}_n$ clusters being presented in mahnerite and zdenekite (Zubkova et al., 2003; Pushcharovsky et al., 2004) are incompatible with a small unit cell with $a = 5.004 \text{ \AA}$ and $c = 4.097 \text{ \AA}$.

One of the five polyhedrons CuO_5 is characterized by increased Cu–O distances in comparison with the four other polyhedrons of this type. By analogy with the structurally studied minerals of the lavendulan family, attikaite may be considered to contain cluster $\text{Cu}_2\text{Al}_2\text{Ca}(\text{AsO}_4)_4(\text{OH})\text{O}_n$, where a Ca atom occupies a site with an increased cation–anion distance. In this

case, the other two Ca atoms (from the three presented in the simplified formula of the new mineral) occupy interlayer sites like K, Na, Ca, Cd, and Pb in other members of this family (Table 2). A lower value of the unit-cell parameter b of attikaite in comparison with allied arsenates appears to be the result of the substitution of two Cu^{2+} ions with Al^{3+} ions characterized by a much smaller radius. Despite these differences, the unit-cell volumes of the minerals listed in Table 3 are practically commensurable: for all minerals except for the mahnerite unit-cell volume is a multiple of $960 \pm 30 \text{ \AA}^3$, whereas the doubled unit-cell volume is a multiple of 959 \AA^3 for mahnerite.

Taking into account the loosely bonded interlayer water molecules in zdenekite, lavendulan, and mahnerite, which are allied with attikaite and have layered structures, a number of heating experiments were carried out for the new mineral. These experiments were based on the techniques of thermal dehydration, which have been well developed for aqueous phyllosilicates (smectites, mixed-layer minerals, etc.) and allow for the estimation of a decrease in the degree of the basal unit-cell parameter caused by the loss of interlayer water.

Ignition of attikaite at moderate temperatures (128–140°C) for 30–35 min results in a decreasing weight of solid residue by 4.3% that corresponds approximately

Table 4. X-ray powder diffraction data for attikaite heated at 128°C for 30 min

| $I_{\text{meas}}, \%$ | $d_{\text{meas}}, \text{\AA}$ | $d_{\text{calc}}, \text{\AA}$ | hkl |
|-----------------------|-------------------------------|--|---------------------------------|
| 80 | 19.1 | 18.77 | 001 |
| 90 | 9.32 | 9.385 | 002 |
| 100 | 5.01 | 5.008 | 200 |
| 40 | 4.39 | 4.418 | 202 |
| 30 | 4.10 | 4.106 | 020 |
| 70 | 3.75 | 3.762, 3.754 | 022, 005 |
| 20 | 3.57 | 3.530 | 213 |
| 80 | 3.43 | 3.433, 3.424 | 023, 204 |
| 40 | 3.14 | 3.131 | 221 |
| 40 | 2.970 | 3.008, 3.004, 2.953 | 222, 205, 124 |
| 30 | 2.841 | 2.832 | 223 |
| 70 | 2.788 | 2.806, 2.773, 2.771 | 116, 313, 025 |
| 70 | 2.675 | 2.681, 2.670 | 007, 125 |
| 10 | 2.563 | 2.566 | 321 |
| 50 | 2.503 | 2.504 | 400 |
| 40 | 2.375 | 2.383, 2.376, 2.364 | 231, 411, 207 |
| 10 | 2.161 | 2.160 | 135 |
| 20 | 2.083 | 2.086, 2.084, 2.083 | 009, 422, 405 |
| 30 | 1.895 | 1.902, 1.900, 1.890 | 416, 240, 241 |
| 40 | 1.783 | 1.789, 1.786, 1.773 | 237, 417, 145 |
| 30 | 1.720 | 1.719, 1.719, 1.719 | 342, 434, 2.1.10 |
| 40 | 1.670 | 1.672, 1.669 | 427, 600 |
| 10 | 1.614 | 1.617, 1.616, 1.615, 1.615, 1.613 | 530, 2.2.10, 2.0.11, 151, 603 |
| 60 | 1.574 | 1.576, 1.575, 1.575, 1.573, 1.573, 1.572 | 0.2.11, 517, 239, 419, 604, 338 |

to the loss of two water molecules per formula. The IR spectrum of the ignited sample demonstrates the absence of H₂O molecules with the retention of OH-groups (Fig. 3). The powder X-ray pattern of the ignited attikaite sample obtained with an RKG-86 camera (Table 3) is characterized by the same reflection set as that of the initial sample (Table 4), but the d -spacings for most of the reflections with nonzero l values are reduced. The greatest shifts after ignition are characteristic of the $00l$ reflection series; moderate shifts are observed for $h0l$, $0kl$, and hkl , whereas the location of the $h00$ and $0k0$ reflections remains unchanged. The calculated unit-cell dimensions of attikaite are as follows: $a = 10.016(5)$, $b = 8.212(5)$, $c = 18.77(1)$ Å, $V = 1544$ Å³, and $Z = 4$. The “basal” parameter c decreases after heating approximately by 4 Å, whereas two other parameters were not modified.

Thus, the thermogravimetric, infrared, and X-ray data derived from the experiments on thermal dehydration of attikaite indicates unambiguously the layered structure of the mineral and the presence of loosely bonded molecular water in the interlayer, emphasizing that the new mineral pertains to arsenates of the laven-dulan family, which are given in Table 3.

The compatibility index of the chemical composition, optical parameters, and density calculated from the Gladstone–Dale equation is good: $1 - (K_p/K_C) = -0.006$ for the measured density and $1 - (K_p/K_C) = -0.055$ for the calculated density.

The type material of attikaite is deposited in the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow. Registration number is 3435/1.

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