New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. V. Katiarsite, KTiO(AsO₄)

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ABSTRACT

A new mineral katiarsite, ideally $KTiO(AsO_4)$, occurs in sublimates of the Arsenatnaya fumarole at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. It is associated with hatertite, bradaczekite, johillerite, yurmarinite, tilasite, arsmirandite, hematite, tenorite, As-bearing orthoclase, fluorophlogopite and aphthitalite. Katiarsite occurs as long prismatic to acicular, typically sword-like, crystals up to $3 \,\mu\text{m} \times 10 \,\mu\text{m} \times 50 \,\mu\text{m}$ in size, and rarely up to 0.15 mm long. Crystal forms are {011}, {201}, {100} and {001}. Katiarsite is transparent, colourless, with a vitreous lustre. The mineral is brittle. Cleavage was not observed, the fracture is uneven. D_{calc} is 3.49 g cm⁻³. Katiarsite is optically biaxial (+), $\alpha = 1.784(3)$, $\beta = 1.792(3)$, $\gamma = 1.870(5)$; $2V_{obs}$ is small. Orientation is X = b, Y = a, Z = c. The Raman spectrum is reported. The chemical composition (wt.%, electron-microprobe data) is K₂O 18.98, Fe₂O₃ 5.07, TiO₂ 27.49, As₂O₅ 47.48, total 99.02. The empirical formula, calculated based on 5 O apfu, is $K_{1,00}(Ti_{0.85}Fe_{0.16}^{3+})_{\Sigma_{1,01}}As_{1,02}O_5$. The strongest reflections of the powder X-ray diffraction pattern [d,Å(I)(hkl)] are 5.91(17)(110), 5.62(74)(011), 4.18(19)(202), 3.157(66) (013), 2.826(100)(221), 2.809(96)(022) and 2.704(19)(004). Katiarsite is orthorhombic, a = 13.174(4), b = 13.174(6.5635(10), c = 10.805(2) Å, V = 934.3(3) Å³, Z = 8, space group $Pna2_1$, by analogy with KTA, synthetic KTiO(AsO₄), a notable non-linear optical crystalline material. The name of the mineral reflects its chemical composition, kalium titanyl arsenate.

Keywords: katiarsite, new mineral, potassium titanium arsenate, non-linear optical material KTA, fumarole sublimate, Tolbachik volcano, Kamchatka.

Introduction

THIS article is the fifth in a series of papers devoted to new arsenate species from the Arsenatnaya fumarole located at the top of the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano,

*E-mail: igorpekov@mail.ru DOI: 10.1180/minmag.2016.080.007 Kamchatka Peninsula, Far-Eastern Region, Russia (55°41′N 160°14′E, 1200 m asl). A general characterization of this fumarole, discovered by us in July 2012, is given in the first paper of the series describing yurmarinite Na₇(Fe³⁺,Mg,Cu)₄(AsO₄)₆ (Pekov *et al.*, 2014*a*). A second article was devoted to two polymorphous modifications of Cu₄O (AsO₄)₂, ericlaxmanite and kozyrevskite (Pekov *et al.*, 2014*b*), a third to popovite Cu₅O₂(AsO₄)₂ (Pekov *et al.*, 2015*b*) and a fourth to the structurally related minerals shchurovskyite K₂CaCu₆O₂

 $(AsO_4)_4$ and dmisokolovite $K_3Cu_5AlO_2(AsO_4)_4$ (Pekov *et al.*, 2015*c*).

In this paper we describe the new mineral species (Russian katiarsite. KTiO(AsO₄) Cyrillic: катиарсит). The name reflects its chemical composition, kalium titanyl arsenate. An additional reason for this name is its agreement with the abbreviation KTA in wide use for the synthetic analogue of the mineral [derived from its main chemical constituents, $KTiO(AsO_4)$], a very important non-linear optical crystalline material (see below). Both the new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2014-025). The type specimen is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, registration number 4540/1.

Occurrence and general appearance

Katiarsite was found in a single specimen collected in July 2012. The new mineral is a minor constituent of arsenate incrustations mainly consisting of three chemically different members of the alluaudite group, green hatertite $Na_2(Ca,Na)$ (Fe³⁺,Cu)₂(AsO₄)₃, blue bradaczekite $NaCu_4(AsO_4)_3$ and lilac johillerite $NaMg_3Cu$ (AsO₄)₃, with subordinate amounts of yurmarinite $Na_7(Fe^{3+},Mg_2Cu)_4$ (AsO₄)₆, tilasite CaMg(AsO₄)F and arsmirandite $Na_{18}Cu_{12}Fe^{3+}O_8(AsO_4)_8Cl_5$ (IMA2014–081, Pekov *et al.*, 2015*a*). Other closely associated minerals are As-bearing



FIG. 1. Colourless acicular crystals of katiarsite (marked with arrows) closely associated with green hatertite and blue bradaczekite in cavities of basalt scoria (redbrownish) partially altered by fumarolic gas to massive aggregates of As-bearing orthoclase (colourless). FOV 2.15 mm, Photo: I.V. Pekov and A.V. Kasatkin.



FIG. 2. SEM secondary electron images of katiarsite: (a) typical sword-like crystal and (b) long prismatic crystals on a crust consisting mainly of small crystals of arsmirandite, $Na_{18}Cu_{12}Fe^{3+}$ O₈(AsO₄)₈Cl₅ (IMA2014–081).

orthoclase, hematite, tenorite, fluorophlogopite and late aphthitalite. Arsenic-bearing orthoclase occurs as crusts on basalt scoria and replaces it as a



FIG. 3. Elongated crystals of katiarsite (grey) included in massive hatertite (light grey) and overgrowing hatertite in a cavity. White grains are hematite. Polished section; SEM backscatter electron image.



FIG. 4. Idealized crystals of katiarsite; most complex (a) and typical (b, c).

result of the influence of fumarolic gases. The arsenates overgrow the orthoclase crusts. Katiarsite is one of the last minerals in this assemblage. It overgrows other arsenates in cavities (Figs 1–3) or is included in hatertite (Fig. 3). The temperature in this area of the fumarole measured using a chromel-alumel thermocouple was 360–380°C.

Katiarsite occurs as long prismatic to acicular, typically well-terminated, sword-like crystals elongated along [010] and usually flattened on [100] (Figs 1, 2 and 4). They are up to $3 \,\mu\text{m} \times 10 \,\mu\text{m} \times 50 \,\mu\text{m}$ in size, and rarely up to 0.15 mm long. Based on morphology of katiarsite crystals observed under the scanning electron microscope (SEM) (Fig. 2), we conclude that crystal forms of the mineral are {011} (terminations), {201}, {100} and {001} (prismatic zone) in different combinations (Fig. 4); these forms were also reported as major crystal forms of KTA, the synthetic analogue of the mineral, and of the isostructural phosphate KTP, KTiO(PO₄) (Novikova *et al.*, 2010). Taking into account crystal class *mm*2, we consider that faces {011}, {201} and {001} are also present on katiarsite crystals; for simplicity, only forms with positive *l* are marked in Fig. 4. Crystals of the mineral are either isolated or form sprays or chaotic groups (Figs 2 and 3).

Physical properties and optical data

Katiarsite is transparent and colourless, with a vitreous lustre. It is non-fluorescent under ultraviolet rays or an electron beam. The mineral is brittle. Cleavage or parting are not observed (for the synthetic analogue, cleavage is absent). The fracture is uneven (observed under the electron microscope). Hardness and density were not measured for katiarsite because of the tiny size of its crystals. For KTA, Mohs hardness is 3 (Weber, 2003). Density calculated for the mineral using its empirical formula is 3.488 g cm⁻³. Katiarsite is optically biaxial (+), $\alpha = 1.784(3)$, $\beta = 1.792(3)$, $\gamma = 1.870(5)$ (589 nm); $2V_{obs}$ is small, $2V_{calc} = 37^{\circ}$. Dispersion was not observed. Extinction is straight and elongation is negative. Orientation is X = b, Y = a, Z = c. Under the microscope, the mineral is colourless and non-pleochroic.



FIG. 5. The Raman spectrum of katiarsite. Bands due to admixed fluorophlogopite are marked with an asterisk.

Raman spectroscopy

The Raman spectrum of katiarsite (Fig. 5) was obtained for a randomly oriented crystal using an

EnSpectr R532 instrument (Dept. of Mineralogy, Moscow State University) with a green laser (532 nm) at room temperature. The output power of the laser beam was \sim 30 mW. The spectrum was

TABLE 1. Powder X-ray diffraction data of katiarsite and its synthetic analogue KTA.

Katiarsite			KTA, synthetic KTiO(AsO ₄)*		
I _{meas}	d _{meas} , Å	d _{calc} **, Å	Icalc	$d_{\text{calc}}, \dot{\text{A}}$	hkl
17	5.91	5.875	12	5.871	110
74	5.62	5.610	100	5.607	011
19	4.18	4.177	11	4.164	202
15	3.633	3.650	16	3.639	310
11	3.529	3.524	14	3.517	212
13	3.454	3.458	12	3.448	311
66	3.157	3.157	54	3.152	013
15	3.058	3.071, 3.055	5, 10	3.065, 3.054	113, 121
12	2.915	2.937	6	2.936	220
100	2.826	2.834	61	2.831	221
96	2.809	2.805	50	2.804	022
19	2.704	2.701	14	2.695	004
9	2.581	2.581	4	2.578	222
8	2.547	2.554	4	2.551	321
6	2.420	2.430	2	2.422	403
10	2.223	2.228	11	2.220	512
7	2.169	2.171	4	2.166	314
7	2.154	2.158	2	2.159	130
6	2.127	2.123	4	2.120	323
7	2.075	2.076	4	2.076	230
6	2.048	2.053, 2.053	4, 4	2.048, 2.048	205,015
7	2.012	2.018	4	2.013	521
7	1.997	2.004, 1.988	3, 1	2.004, 1.985	132, 224
4	1.956	1.958	1	1.957	330
4	1.879	1.870	4	1.869	033
5	1.834	1.841	4	1.840	332
5	1.807	1.813	3	1.807	514
6	1.753	1.762	10	1.758	424
5	1.737	1.741	8	1.737	225
6	1.681	1.683	6	1.681	530
5	1.671	1.679, 1.669	3, 1	1.676, 1.666	216, 325
5	1.591	1.592	1	1.592	240
10	1.574	1.579, 1.575	9,9	1.576, 1.576	026, 241
5	1.565	1.567	2	1.565	126
4	1.529	1.532, 1.527	1, 1	1.526, 1.526	812, 135
7	1.504	1.503, 1.503	6, 6	1.499, 1.499	714,017
6	1.494	1.497	4	1.495	235
6	1.451	1.460, 1.455	4, 4	1.455, 1.455	813, 441
6	1.442	1.450	3	1.446	516
7	1.432	1.429	8	1.426	534
6	1.412	1.414, 1.414	2, 2	1.413, 1.411	343, 731
4	1.391	1.394, 1.393, 1.392	2, 2, 1	1.391, 1.391, 1.388	625, 435, 606
4	1.351	1.351	2	1.348	008

*Calculated from the structure data reported by Northrup *et al.* (1994); only reflections with $I_{calc} \ge 1$ are given. **For the unit-cell parameters calculated from single-crystal data. The strongest reflections are given in bold.

processed using the EnSpectr expert mode program in the range from 100 to 4000 cm⁻¹ with the use of a holographic diffraction grating with 1800 lines cm⁻¹ and a resolution of 5–8 cm⁻¹. The diameter of the focal spot on the sample was ~25 μ m. The backscattered Raman signal was collected with a 40 × objective; signal acquisition time for a single scan was 1500 ms and the signal was averaged over ten scans.

Bands in the region between 740 and 900 cm^{-1} correspond to As⁵⁺–O antisymmetric stretching vibrations of AsO₄ groups. A strong band at 701 cm⁻¹ can be assigned to a combination of symmetric stretching vibrations of AsO₄ groups and asymmetric stretching vibrations of Ti-O-Ti bridges in chains formed by corner-connected TiO₆ octahedra. A strong band at 492 cm⁻¹ corresponds to stretching vibrations of non-bridging Ti-O bonds and antisymmetric vibrations of Ti-O-Ti bridges. Bands with frequencies lower than 400 cm^{-1} correspond to lattice modes involving As-O and Ti-O bending and K-O stretching vibrations. Two weak bands with maxima at 912 and 996 cm⁻¹ marked with asterisk in Fig. 5 are due to admixture (micro-inclusions) of fluorophlogopite. The Raman spectroscopy data for katiarsite are in good agreement with those obtained by Watson (1991) for synthetic $KTiO(AsO_4)$. The absence of bands with frequencies higher than 1000 cm⁻¹ indicates the absence of groups with O-H, C-H, C-O, N-H, N-O and B-O bonds in katiarsite.

Chemical composition

The chemical composition of katiarsite was studied using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength dispersive spectrometer (Laboratory of local methods of matter investigation, Faculty of Geology, Moscow State University), with an acceleration voltage of 20 kV, a beam current of 20 nA and a 3 µm beam diameter. The following standards were used: orthoclase (K), CuFeS₂ (Fe), ilmenite (Ti) and FeAsS (As). The average (four spot analyses) chemical composition of katiarsite (wt.%, ranges in parentheses) is K₂O 18.98 (18.51-19.94), Fe₂O₃ 5.07 (4.93-5.36), TiO₂ 27.49 (26.97-28.01), As₂O₅ 47.48 (46.05-48.60), total 99.02. Contents of other elements with atomic numbers higher than carbon are below detection limits. Iron is considered as Fe³⁺ taking into account the extremely oxidizing conditions of mineral deposition in the Arsenatnava fumarole: all other known Fe minerals from the locality contain only Fe³⁺(Pekov *et al.*, 2014*a*, 2015*c*). The empirical formula of katiarsite, calculated based on 5 O atoms per formula unit, is $K_{1.00}(Ti_{0.85} \ Fe_{0.16}^{3.1})_{\Sigma 1.01}As_{1.02}O_5$. The simplified, end-member formula is KTiO(AsO₄), which requires K₂O 19.47, TiO₂ 33.03, As₂O₅ 47.50, total 100.00 wt.%. The Gladstone-Dale compatibility index 1 – (K_p/K_c) (Mandarino, 1981) is 0.028 (excellent).

X-ray crystallography

A single-crystal X-ray study of katiarsite was carried out using an Xcalibur S diffractometer equipped with a CCD detector and gave an orthorhombic unit cell with a = 13.174(4), b = 6.5635(10), c = 10.805(2) Å, V = 934.3(3) Å³ and Z = 8. Powder X-ray diffraction (XRD) data (Table 1) were collected with a STOE IPDS II single-crystal diffractometer using the Gandolfi method; MoK α -radiation; detector-tosample distance 160 mm. Unit-cell parameters

TABLE 2. Comparative data for katiarsite and its synthetic analogue KTA.

Mineral / Compound Idealized formula Crystal system Space group a, Å b, Å c, Å $V, Å^3$ Z $D, g cm^{-3}$ Refractive indices α β	Katiarsite* KTiO(AsO ₄) Orthorhombic <i>Pna2</i> ₁ ** 13.174 6.5635 10.805 934.3 8 3.49 (calc.) 1.784 1.792	KTA KTiO(AsO ₄) Orthorhombic <i>Pna2</i> ₁ 13.10–13.24 6.55–6.64 10.72–10.78 923–942 8 3.45–3.48 1.783 1.789
γ References	1.870 this work	1.868 El Brahimi and Durand (1986); Mayo <i>et al.</i> (1994); Northrup <i>et al.</i> (1994); Weber (2003); Novikova <i>et al.</i> (2010)

*Slightly higher values of density and refractive indices of katiarsite in comparison with synthetic KTA are probably caused by the substitution of \sim 15% of Ti for Fe in the mineral. **By analogy with KTA. For comparison of the powder XRD patterns see Table 1.

calculated from the powder data are a = 13.15(2), b = 6.556(4), c = 10.793(7) Å, V = 930(2) Å³.

Discussion

The crystal structure of katiarsite was not studied because of the imperfection of single crystals (even the best crystals tested that gave the unit-cell data reported above) and scarcity of material for a Rietveld refinement. However, the stoichiometry, single-crystal and powder XRD data undoubtedly show that katiarsite (or, more correctly, its end-member) is the natural analogue of the well-known synthetic compound KTA, KTiO(AsO₄); Tables 1 and 2.

The crystal structure of KTA (Fig. 6) is based on undulating chains of corner-connected Ti-centred octahedra. These chains are cross-linked via isolated AsO₄ tetrahedra, forming a threedimensional framework. Potassium cations are located in channels of the framework (Mayo *et al.*, 1994; Northrup *et al.*, 1994). KTA belongs to the KTP [KTiO(PO₄)] structure type. The KTP family contains more than forty isostructural (*Pna*2₁) synthetic phosphates and arsenates with the general formulae $A^+M^{4+}O(T^{5+}O_4)$ [$T^{5+}=P$, As; $M^{4+}=Ti$, Ge, V, Sn, Zr, (Ga³₅Nb⁵₅), (Fe³₅Nb⁵₅), $(Mn_{0.5}^{3+}Nb_{0.5}^{5+}), (Mg_{0.33}^{2+}Nb_{0.67}^{5+}); A^+ = K, Na, Rb, Cs,$ Ag, NH₄, Tl] and $KM^{3+}(F,OH)(T^{5+}O_4)$ [$T^{5+} = P$, As; $M^{3+} =$ Ga, Fe]. Some representatives of this family are important optical crystalline materials. They are unique second-order non-linear and electrooptic compounds with large hyperpolarizability, excellent temperature windows, wide wavelength ranges for phase matching, and outstanding crystal stabilities (Stucky et al., 1989; Phillips et al., 1992). In particular, KTA, synthesized using different methods in a wide temperature range, has commercial applications for second-harmonic generation owing to its superior non-linear character compared to KTP and other representatives of the family, and its mechanical stability is notable (Mayo et al., 1994; Weber, 2003). Katiarsite is the first natural representative of the KTP structural family. No mineral related to it in terms of chemistry and structure is known. In addition, katiarsite is the first arsenate mineral with species-defining titanium. In braithwaiteite with idealized formula NaCu₅ $(TiSb)_{\Sigma 2}(AsO_4)_4(AsO_3OH)_2O_2 \cdot 8H_2O, Ti^{4+}$ and Sb^{5+} are disordered (Paar *et al.*, 2009) and Sb > Ti.

Titanium-bearing minerals are typically minor constituents of sublimates in fumaroles located at the Second scoria cone of the Northern Breakthrough of



FIG. 6. The crystal structure of KTA, the synthetic analogue of end-member katiarsite (Northrup et al., 1994).

the Great Tolbachik Fissure Eruption, including the Arsenatnava fumarole. The most common mineral with species-defining Ti is pseudobrookite Fe³₂ ⁺TiO₅; the Fe- and Sb-enriched variety of rutile (Ti,Fe³⁺,Sb⁵⁺)O₂ is also not rare. The exhalation Asbearing titanite was found by us in Arsenatnaya, as well as Ti-bearing varieties of cassiterite, gahnite and fluorophlogopite containing up to 12.6, 3.5 and 1.4 wt.% TiO₂, respectively. Titanium significantly substitutes Fe³⁺ in two vanadates formed in fumaroles at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, lyonsite $Cu_{3+x}(Fe_{4-2x}^{3+}Cu_{2x})(VO_4)_6$ with $0 \le x \le 1$ (up to 2.2 wt.% TiO₂; Pekov *et al.*, 2013) and grigorievite $Cu_3Fe_2^{3+}Al_2(VO_4)_6$ (1.1–1.7 wt.% TiO2; Pekov et al., 2014c). Titanium has low volatility in volcanic gases, as both thermodynamic calculations (Churakov et al., 2000) and direct measurements carried out for gases of Tolbachik (Zelenski et al., 2014) show. We believe that katiarsite (as well as other Ti-bearing minerals in these fumaroles) was formed as a result of the interaction between volcanic gases (a source of As and K) and basalt scoria (a source of Ti) at temperatures not lower than 360°C, rather than deposited directly from the gas phase.

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