Bendadaite from Krásno near Horní Slavkov (Czech Republic), description and Raman spectroscopy

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Abstract

A rare Fe\textsuperscript{2+}-Fe\textsuperscript{3+} dominant arsenate of the arthurite group, bendadaite, was determined at two samples from an abandoned Huber open pit in the Krásno ore district near Horní Slavkov, Slavkovský les area (Czech Republic). Bendadaite occurs there as brownish to olive green crystalline aggregates up to 2 - 6 mm in size in cavities of quartz gangue. The aggregates are composed by elongate prismatic crystals up to 100 - 200 μm in length, partly in radial arrangement. It is opaque to semi-translucent (aggregates) to translucent (thin fragments). It has vitreous to subadamantine (crystals) or greasy to dull (aggregates) lustre. Bendadaite is monoclinic, space group P2\textsubscript{1}/c, with the unit-cell parameters refined from X-ray powder diffraction data: a = 10.183(2), b = 9.672(2), c = 5.536(1) Å, β = 94.15(2)°, V = 543.6(1) Å\textsuperscript{3} (sample NM) and a = 10.175(2), b = 9.682(2), c = 5.532(1) Å, β = 94.13(2)°, V = 543.6(1) Å\textsuperscript{3} (sample JT). The chemical composition of bendadaite agrees with general stoichiometry of the arthurite group minerals and corresponds to the following empirical formulae: \((\text{Fe}_{0.25}\text{Zn}_{0.26}\text{Cu}_{0.02}\text{Mg}_{0.01})\text{Al}_{0.16}\text{Fe}_{0.38}\text{Zn}_{0.13}\text{Al}_{0.63}\text{Zn}_{0.28}\text{O} \cdot 4\text{H}_2\text{O} \) (sample JT). The Raman spectra of both studied bendadaite samples as well as tentative assignment of observed bands are given in this paper. Origin of bendadaite from Krásno is connected to in-situ supergene weathering of primary arsenopyrite, sphalerite and phosphates and high activity of arsenate and Fe\textsuperscript{3+}, Fe\textsuperscript{3+} ions in acidic supergene fluids.

Key words: bendadaite, arthurite, supergene weathering, Raman spectroscopy, Krásno near Horní Slavkov, Czech Republic

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Introduction

Arthurite group minerals comprise monoclinic arsenates and phosphates with general formula \(\text{AB}_2(\text{TO}_4)(\text{OH},\text{O}_2) \cdot 4\text{H}_2\text{O} \) (Table 1). The structural position A is occupied mainly by M\textsuperscript{2+} elements, such as Cu\textsuperscript{2+}, Fe\textsuperscript{3+}, Mn\textsuperscript{2+}, Zn\textsuperscript{2+}, Co\textsuperscript{2+}, Mg\textsuperscript{2+} and Ca\textsuperscript{2+} (Peacor et al. 1984; Jambor et al. 2002; Mills et al. 2008). According to Moore et al. (1974) and Kolitsch et al. (2010), also Fe\textsuperscript{3+} and vacancy may occur in this site. The results of crystal structure study (Keller, Hess 1978; Hughes et al. 1996; Kampf 2005; Kolitsch et al. 2010) indicate that Zn, Cu and Co enter exclusively the A-site. The B-site is occupied predominantly by Fe\textsuperscript{3+} and some Al\textsuperscript{3+} (Peacor et al. 1984; Staněk 1988; Kolitsch et al. 2010) and probably minor Ti\textsuperscript{4+} (Staněk 1988). The tetrahedral T-position may contain minor S and Si, in addition to dominating As and P (Davis, Hey 1969; Jambor et al. 2002; Sejkora et al. 2006c).

In the Czech Republic, the P-dominant members of arthurite group are known from the Krásno ore district - earlshannonite, whitmoreite (Sejkora et al. 2006d), kunatite (Mills et al. 2008) and two unnamed phases UNK7 and UNK8 (Sejkora et al. 2006c). Earlshannonite and whitmoreite were also described from pegmatite near Dolní Bory, western Moravia (Staněk 1988, 1997) and whitmoreite from the Sn-Li deposit Verněřov near Aš (Breiter et al. 2009). The occurrences of As-dominant members of arthurite group are very rare, they were found only at the Krásno ore district - arthurite (Vrtiška et al. 2018) and bendadaite, which is subject of this study. Bendadaite, the Fe-Fe-As dominant member of arthurite group, was described by Kolitsch et al. (2010) as a

<table>
<thead>
<tr>
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</tr>
<tr>
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<td>Fe</td>
</tr>
<tr>
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<td>Co</td>
<td>Fe</td>
</tr>
<tr>
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<td>Fe</td>
</tr>
<tr>
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<td>Mn</td>
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<td>Whitmoreite</td>
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<td>UNK8</td>
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</table>

A, B and T - sites of general formula \(\text{AB}_2(\text{TO}_4)(\text{OH},\text{O}_2) \cdot 4\text{H}_2\text{O} \)
The Krásno ore district belongs to one of the most important areas of tin and tungsten mining in Central Europe (Beran, Sejkora 2006). The district is represented by greisen mineralization in several granite cupolas of the large Krušně hory (Erzgebirge) granite batholith, which is underlying metamorphic rock (mainly gneisses). The largest Sn-W deposit in this district is the Huber stock. In the past, it was mined via the Huber open pit and Huber (Stannum) shaft down to 200 m under the surface (5th level at 425 m a.s.l.). The stock is bell-shaped in section, similar to a blunt cone. At 100 m beneath the present surface, the stock is 200 x 100 m in cross-section, while at a depth of 150 m, the stock extends NE-SW and is about 400 x 250 m in cross section. The Huber stock consists basically of autometamorphosed Li-mica-topaz granite. It is assumed that entire apical part of this cupola was formed by greisen and quartz veins with rich ore mineralization (Beran, Sejkora 2006). Detailed descriptions of the mineralogy (more than 230 mineral species) of the Krásno ore district were published by Beran, Sejkora (2006) and Sejkora et al. (2006a-d). More recently, the new minerals tvrdýite (Sejkora et al. 2016), krásnoite (Mills et al. 2012), and iangreyite (Mills et al. 2011) were described from this locality, which also hosts the second world occurrence of kunatite (Mills et al. 2008) and plimerite (Sejkora et al. 2011).

**Occurrence**

Bendadaite was found at the Huber open pit in the Krásno ore district near Horní Slavkov, Slavkovský les area, Czech Republic. It was identified at two samples of coarse-grained quartz gangue labelled „berauinite“ from collection of the National Museum, Prague (catalogue number P1N 95.003 - sample NM) and private collection of Jaromír Tvrdý (Liberec - sample JT). The both samples come from the same find at 1986 (JT).

**Morphology and physical properties**

Bendadaite was identified at two samples of coarse-grained quartz gangue with abundant cavities, 8 x 8 x 7 cm (sample NM) and 8 x 6 x 2 cm (sample JT) in size. At both samples, bendadaite forms brownish to olive green crystalline aggregates up to 2 - 6 mm in size in cavities of quartz (Figs. 1 and 2). These aggregates are composed of elongated prismatic crystals up to 100 - 200 μm in length, partly in radial arrangement. Bendadaite is opaque to semi-translucent (aggregates) to translucent (thin fragments). It has vitreous to subadamantine (crystals) or greasy to dull (aggregates) lustre and greenish yellow streak. Bendadaite is brittle with irregular fracture, the good cleavage in one direction was observed. The calculated density (based on combination of empirical formula and refined unit-cell parameters) is 3.312 g/cm$^3$ for NM sample and 3.238 g/cm$^3$ for JT sample, respectively.

**X-ray powder diffraction**

Powder X-ray diffraction data were collected on a Bruker D8 Advance diffractometer (National Museum, Prague) with a solid-state 1D LynxEye detector using CuK$_\alpha$ radiation.
and operating at 40 kV and 40 mA. The powder patterns were collected using Bragg–Brentano geometry in the range 3 - 60° 2θ, in 0.01° steps with a counting time of 30 s per step. Positions and intensities of reflections were found and refined using the PearsonVII profile-shape function with the ZDS program package (Ondruš 1993) and the unit-cell parameters were refined by the least-squares algorithm implemented by Burnham (1962). The experimental powder pattern was indexed in line with the calculated values of intensities obtained from the crystal structure of bendadaite (Kolitsch et al. 2010), based on Lazy Pulverix program (Yvon et al. 1977). The experimental powder data sets given in Table 2 agree well with the pattern calculated from the single-crystal data for bendadaite; experimental intensities are partly affected by preferred orientation as well as by the small amount of material available for the study. The refined unit-cell parameters of bendadaite are compared in Table 3 with published data for As-dominant members of arthritic group.

### Chemical composition

Samples of bendadaite were analysed with a Cameca SX-100 electron microprobe (National Museum, Prague) operating in the wave-length-dispersive mode with an accelerating voltage of 15 kV, a specimen current of 10 nA, and a beam diameter of 10 μm. The following lines and standards were used: Kα: hematite (Fe), ZnO (Zn), diopside (Mg), rhodonite (Mn), chalcopyrite (Cu), sanidine (Al), fluorapatite (P); Lα: clinoclase (As). Peak counting times (CT) were 20 s for main elements and 60 s for minor elements; CT for each background was one-half of the peak time. The raw intensities were converted to the concentrations automatically using PAP (Pouchou, Pichoir 1985) matrix-correction software. The elements Ba, Bi, Cl, Co, Cr, F, In, K, N, Na, Ni, Pb, S, Si, Sr, Th, U, V and Y were sought, but found to be below the detection limit (about 0.05-0.20 wt. %). Water content could not be analysed directly because of the minute amount of material available. The H2O content was confirmed by Raman spectroscopy and calculated by stoichiometry of ideal formula.

### Table 2 X-ray powder diffraction data of bendadaite from Krásno

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...
The empirical formulae calculated on the basis of \(\text{As}^+\text{P}^- = 2\) are following: NM sample (mean of 23 analyses): \([\text{Fe}_{0.66}\text{Zn}_{0.26}\text{Cu}_{0.05}\text{Mg}_{0.02}]_{0.66}\text{P}_{0.34}\text{O}_{1.66}\text{(OH)}_{2.00}\text{H}_4\text{O}, and for JT sample (mean of 29 analyses): \([\text{Fe}_{0.66}\text{Zn}_{0.26}]_{0.65}\text{Mg}_{0.02}\text{Al}_{1.80}]_{2.00}\text{P}_{0.35}\text{O}_{1.65}\text{H}_2\text{O}, \text{respectively.}

### Table 3
Unit-cell parameters for As-dominant members of arthurite group (for monoclinic space group \(P2_1/c\))

<table>
<thead>
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<th>(a) [Å]</th>
<th>(b) [Å]</th>
<th>(c) [Å]</th>
<th>(\beta) [°]</th>
<th>(V) [Å³]</th>
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<td>10.183(2)</td>
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<td>5.536(1)</td>
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<td>543.8(1)</td>
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<tr>
<td>bendadaite JT</td>
<td>10.175(2)</td>
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<td>94.13(2)</td>
<td>543.6(1)</td>
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<td>548.1(1)</td>
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<td>5.598(1)</td>
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<td>549.9(2)</td>
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<td>92.2(1)</td>
<td>539.1(6)</td>
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<td>94.277(2)</td>
<td>552.33(3)</td>
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*1 - type locality, PXRD; *2 - cotype locality SXRD

### Table 4
Chemical composition of bendadaite (sample NM) from Krásno (wt. %)

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### Raman spectroscopy

The Raman spectra (Fig. 6, Table 6) were collected in the range 4000–45 cm⁻¹ using a DXR dispersive Raman Spectrometer (Thermo Scientific) mounted on a confocal Olympus microscope. The Raman signal was excited by an unpolarised red 633 nm He-Ne gas laser and detected by a CCD detector. The experimental parameters were: 100x objective, 60 s exposure time, 100 exposu-

\[\text{Mean of 23 point analyses; 1-13 selected representative analyses; apfu on the base As+P = 2; H}_2\text{O and FeO/Fe}_2\text{O}_3\text{ contents were calculated on the basis of ideal formula.}\]
res, 50 μm pinhole spectrograph aperture and 8 mW laser power level. The spectra were repeatedly acquired from different grains in order to obtain a representative spectrum with the best signal-to-noise ratio. The eventual thermal damage of the measured point was excluded by visual inspection of excited surface after measurement, by observation of possible decay of spectral features in the start of excitation and checking for thermal downshift of Raman lines. The instrument was set up by a software-controlled calibration procedure using multiple neon emission lines (wavelength calibration), multiple polystyrene Raman bands (laser frequency calibration) and standardized white-light interferometry (intensity calibration). Spectral manipulations were performed using the Omnicon 9 software (Thermo Scientific).

In the asymmetric part of the monoclinic space group P2₁/c, Z=2), bendadaite unit-cell (Kolitsch et al. 2010), there are two symmetrically distinct Fe, one (AsO₃)³⁻ (partly with P substitution), two H₂O molecules and one (OH)⁻ unit. The crystal structure of arthurite group minerals (Kampf 2005) is based upon a unique corrugated sheet of Fe³⁺-O octahedra.

**Table 5** Chemical composition of bendadaite (sample JT) from Krásno (wt. %)

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Mean of 29 point analyses; 1-13 selected representative analyses; apfu on the base As+P = 2; H₂O and FeO/Fe₂O₅ contents were calculated on the basis of ideal formula.
Each octahedron shares an edge (O1-O1) and two vertices (OH) with equivalent octahedra; two remaining vertices (O2 and O4) are shared with AsO$_4$ tetrahedras. Three of the four tetrahedrons vertices link to octahedron vertices in the same sheet of Fe$^{3+}$-O octahedra, the remaining corner links to a Fe$^{2+}$-O octahedron. Two trans vertices of the Fe$^{2+}$-O octahedron link to AsO$_4$ tetrahedra attached to different sheets, thereby forming bridges between the sheets.

In the case of free tetrahedra (AsO$_4$)$_2^-$ and (PO$_4$)$_3^-$ (Td symmetry), there are nine normal vibrations, characterized by four fundamental modes of vibrations - $\nu_1$ (A$_1$g) symmetric stretching vibration, Raman active, $\nu_2$ (E$_g$) doubly degenerate bending vibration, Raman active, $\nu_3$ (Z$_2$g) triply degenerate antisymmetric stretching vibration, Raman and infrared active, and $\nu_4$ (E$_g$) triply degenerate bending vibration, Raman and infrared active (Nakamoto 2009). Symmetry lowering Td $\rightarrow$ C$_{3v}$, C$_{2v}$, C$_i$ may be connected with infrared activation of infrared inactive vibrations and splitting of degenerate vibrations. For the classification of molecular vibrations, the total reducible representations decompose into $\Gamma = A_1 + E + 2F_2$ (Mielke, Ratajczak 1972; Vansant et al. 1973) vibrations. The FeO$_6$ octahedra XY$_6$ are characterized by six normal modes of vibration. The $\nu_1$ (v XY, A$_1$g), $\nu_2$ (v XY, E$_g$), and $\nu_4$ (v XY, F$_2$) are Raman active, whereas only $\nu_3$ (v XY, F$_2$) and $\nu_4$ (v XY, F$_2$) are infrared active. The $\nu_4$ (v XY, F$_2$) is inactive in infrared and Raman spectrum (Nakamoto 2009).

Weak bands or shoulders at 3564 cm$^{-1}$ (NM) and 3533 cm$^{-1}$ (JT) are assigned to the $\nu$ OH stretching vibrations of weakly hydrogen-bonded hydroxyls, OH, while bands at 3349, 3252 and 3051 cm$^{-1}$ (NM), and 3366, 3269 and 3136 cm$^{-1}$ (JT) are connected with $\nu$ OH stretching vibrations of hydrogen-bonded water molecules. According to Libowitzky (1999), approximate O-H×××O hydrogen bond lengths vary in the range from 3.06 to 2.69 Å. Bands at 1654 cm$^{-1}$ (NM) and 1676 cm$^{-1}$ (JT) are attributed to the $\nu_2$ (E$_g$) hydrogen-bonded water molecules. Bands at 1097, 1038 and 995 cm$^{-1}$ (NM) and 1096, 1035 and 995 cm$^{-1}$ (JT) are related to the split triply degenerate $\nu_3$ (PO$_4$)$_3^-$ antisymmetric stretching vibrations and bands at 970 cm$^{-1}$ (NM) and 967 cm$^{-1}$ (JT) to the $\nu_1$ (PO$_4$)$_3^-$ symmetric stretching vibrations. Any tentative assignment...
of bands to the triply degenerate $\nu_3$ (AsO$_4$)$^{3-}$ antisymmetric stretching vibrations makes problems. Because of the Td symmetry lowering, these degenerate $\nu_3$ (AsO$_4$)$^{3-}$ vibrations split, the number of the observed bands may depend on the number of molecules in the unit cell ($Z = 2$), and the $\nu_3$ and $\nu_{1}$ (AsO$_4$)$^{3-}$ may coincide (Nakamoto 2009). Bands at 929, 892, 869, 810 and 782 cm$^{-1}$ (NM) and 924, 893, 870, 807, 779 and 696 cm$^{-1}$ (JT) may be attributed to the split $\nu_3$ (AsO$_4$)$^{3-}$; however, some coincidence with libration modes of water molecules is possible. The very strong bands at 844 cm$^{-1}$ (NM) and 841 cm$^{-1}$ (JT) are assigned to the $\nu_1$ (AsO$_4$)$^{3-}$ symmetric stretching vibrations. Bands at 552 and 499 cm$^{-1}$ (NM) and 547 and 499 cm$^{-1}$ (JT) are assigned to the split triply degenerate $\nu_2$ (PO$_4$)$^{3-}$ out-of-plane bend. A coincidence with the $\delta$ Fe-(O,OH) bend is supposed. Bands at 447 and 402 cm$^{-1}$ (NM) and 445, 413 and 396 cm$^{-1}$ (JT) relates to the split triply degenerate $\nu_4$ (AsO$_4$)$^{3-}$ out-of-plane bend. A probable coincidence of the bands at 447 and 445 cm$^{-1}$, respectively, with one of the bands assigned to the doubly degenerate $\nu_6$ (PO$_4$)$^{3-}$ out-of-plane bend and $\delta$ Fe-(O,OH) bend may be also possible. Bands at 340 and 310 cm$^{-1}$ (NM) and 344 and 311 cm$^{-1}$ (JT) are attributed to the split doubly degenerate $\nu_3$ (AsO$_4$)$^{3-}$ in-plane bend. Bands at 258, 235 and 204 cm$^{-1}$ (NM) and 296, 279, 233 and 202 cm$^{-1}$ (JT) are connected with $\nu$ Fe-(O,OH) stretch in Fe-(O,OH)$_2$ octahedra. Bands at 184, 149, 131, 95 and 63 cm$^{-1}$ (NM) and 182, 147, 128, 92 and 62 cm$^{-1}$ (JT) are attributed to lattice modes. Infrared spectrum of bendadaite was published by Kollitsch et al. (2010), infrared and Raman spectra of arthurite and cobaltarthurite by Jambor et al. (2002). All these spectra are comparable with

<table>
<thead>
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<th>Table 6</th>
<th>Tentative assignment of Raman spectra for bendadaite</th>
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$I_{\text{int}}$ calculated from the band area.
Raman spectrum of bendadaite, presented in this paper. Kolitsch et al. (2010) observed bands and shoulders in the infrared spectrum of bendadaite: 3220, 3250, 3085 and 1643 cm⁻¹ (v OH stretch), 1092, 1045, 1033, 955 and 969 cm⁻¹ (PO₄²⁻ stretch), 925, 881, 854, 811 and 768 cm⁻¹ (AsO₄³⁻ stretch), 650 and 620 cm⁻¹ (PO₄³⁻ bend), and 490, 467 and 431 cm⁻¹ (mixed modes involving O-As-O angles and Fe-O bands. Frost et al. (2003), on the contrary, incorrectly assigned in the Raman spectra of unsatisfactory determined arthurite and whitmoreite a band at 1044 cm⁻¹ and to (CO₃)²⁻ stretch. Palmer, Frost (2011) described infrared and Raman spectra of arthurite containing SO₄²⁻ ions (?) with proposed chemical formula CuFe³⁺[AsO₄PO₄][OH]₄·4H₂O.

Condition of formation

The conditions of formation of bendadaite and its thermodynamic stability field appear to be restricted, with an equilibrium between Fe²⁺ and Fe³⁺ oxidation states being necessary (Kolitsch et al. 2010). At Krásno, bendadaite is formed under conditions of in-situ supergene zone from acidic fluids with high activity of arsenate and Fe³⁺, Fe²⁺ ions, derived from weathering of primary arsenopyrite. The determined Zn and phosphate contents in studied ions, derived from weathering of primary arsenopyrite.

Acknowledgements

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