

# Lukkulaisvaaraite, Pd<sub>14</sub>Ag<sub>2</sub>Te<sub>9</sub>, a new mineral from Lukkulaisvaara intrusion, northern Russian Karelia, Russia

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## ABSTRACT

Lukkulaisvaaraite, Pd<sub>14</sub>Ag<sub>2</sub>Te<sub>9</sub>, is a new platinum-group mineral discovered in the Lukkulaisvaara intrusion, northern Russian Karelia, Russia. In polished section crystals are ~40 µm across, rimmed by tulameenite and accompanied to varying degrees by telargpalite and Bi-rich kotulskite. Lukkulaisvaaraite is brittle, has a metallic lustre and a grey streak. Values of VHN<sub>20</sub> fall between 339 and 371 kg mm<sup>-2</sup>, with a mean value of 355 kg mm<sup>-2</sup>, corresponding to a Mohs hardness of ~4. In plane-polarized light, lukkulaisvaaraite is light grey with a brownish tinge, has strong birefractance, light brownish-grey to greyish-brown pleochroism and distinct to strong anisotropy; it exhibits no internal reflections. Reflectance values of lukkulaisvaaraite in air (*R*<sub>1</sub>, *R*<sub>2</sub>, in %) are: 40.9, 48.3 at 470 nm, 47.6, 56.4 at 546 nm, 52.1, 61.0 at 589 nm and 57.5, 65.2 at 650 nm. Five electron microprobe analyses of natural lukkulaisvaaraite gave the average composition Pd 52.17, Ag 7.03 and Te 40.36, total 99.61 wt.%, corresponding to the empirical formula Pd<sub>14.05</sub>Ag<sub>1.88</sub>Te<sub>9.06</sub> based on 25 atoms; the average of nine analyses on synthetic lukkulaisvaaraite is Pd 52.13, Ag 7.31 and Te 40.58, total 100.02 wt.%, corresponding to Pd<sub>13.99</sub>Ag<sub>1.93</sub>Te<sub>9.08</sub>. The mineral is tetragonal, space group *I4/m*, with *a* = 8.9599(6), *c* = 11.822(1) Å, *V* = 949.1(1) Å<sup>3</sup> and *Z* = 2. The crystal structure was solved and refined from the powder X-ray diffraction (XRD) data of synthetic Pd<sub>14</sub>Ag<sub>2</sub>Te<sub>9</sub>. Lukkulaisvaaraite has a unique structure type and shows similarities to that of sopcheite (Ag<sub>4</sub>Pd<sub>3</sub>Te<sub>4</sub>) and palladseite (Pd<sub>17</sub>Se<sub>15</sub>). The strongest lines in the powder XRD pattern of synthetic lukkulaisvaaraite [*d*(Å), *I*, *hkl*] are: 2.8323(58)(130,310), 2.8088(92),(213), 2.5542(66)(312), 2.4312(41)(321,231), 2.1367(57)(411,141), 2.1015(52)(233,323), 2.0449(100)(314), 2.0031(63)(420,240), 1.9700(30)(006), 1.4049(30)(246,426), 1.3187(36)(543,453). The mineral is named for the type locality, the Lukkulaisvaara intrusion in Russian Karelia.

**KEYWORDS:** lukkulaisvaaraite, platinum-group mineral, Pd-Ag telluride, Pd<sub>14</sub>Ag<sub>2</sub>Te<sub>9</sub> phase, electron microprobe data, reflectance data, X-ray diffraction data, crystal structure, Lukkulaisvaara intrusion, Russian Karelia, Russia.

## Introduction

THE holotype specimen (polished section), that contains lukkulaisvaaraite, ideally Pd<sub>14</sub>Ag<sub>2</sub>Te<sub>9</sub>, comes from platinum group element (PGE)

mineralization in gabbronorite from the Early Proterozoic Lukkulaisvaara layered intrusion, northern Russian Karelia, Russia. Another sample of lukkulaisvaaraite from the same locality was used as a comparative sample.

The phase was described as unnamed Pd<sub>6</sub>AgTe<sub>4</sub> from the Lukkulaisvaara layered intrusion by Yakovlev *et al.* (1991),

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Grokhovskaya *et al.* (1992) and Barkov *et al.* (2001). Consequently, it was listed as a valid unnamed mineral (UM1991-25-Te:AgPd, UM1992-Te:AgPd, UM2001/Te:AgPd; Smith and Nickel, 2007). The same phase was also observed, as an unnamed phase, from the South Sopcha massif (Grokhovskaya *et al.*, 2003) and from the Monchetundra deposit (Grokhovskaya *et al.*, 2009) of the Monchegorsk Complex, Kola Peninsula, Russia.

The mineral is named for the type locality, the Lukkulaisvaara intrusion in Russian Karelia. The mineral and the mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA No. 2013-115, Vymazalová *et al.* 2014b). The holotype is deposited in the collections of the Department of Mineralogy of the National Museum, Prague, Czech Republic, catalogue number P1P 15/2013.

### Occurrence and association

The Lukkulaisvaara intrusion is part of the Paleoproterozoic Oulanka Group of intrusions situated along the eastern edge of the Paanajarvi–Kuolajarvi rift system (northern Russian Karelia). The Lukkulaisvaara massif was intruded into Archaean gneisses  $2442 \pm 1$  Ma ago (according to U–Pb zircon data; Amelin *et al.*, 1995) and then overlain by Palaeoproterozoic metavolcanic and clastic beds. At the present erosion level the size of the intrusion is  $\sim 8$  km  $\times$  5.5 km, with a maximum thickness of 4.6 km.

The Lukkulaisvaara intrusion is composed of rhythmically layered rocks aggregated from the bottom to the top in the sequence peridotite, norite, gabbro and gabbro series. PGE mineralization is associated with late magmatic complexes disrupting the layering of the intrusion. Major zones of PGE mineralization are associated with microgabbro bodies hosted by mafic rocks (e.g. Begizov and Batashov, 1978; Grokhovskaya *et al.*, 1992; Barkov *et al.*, 1995; Semenov *et al.*, 2008). Maximum PGE concentrations of up to 20 ppm Pt and Pd were found in the Nadezhda microgabbro body in the upper part of the norite series. This body is sill-like, extending for  $\sim 700$  m along strike, and is nearly conformable to modal layering in the norite series. PGE mineralization occurs as veins, veinlets and pods of sulfide-bearing pegmatoid pyroxenites within the microgabbro.

Lukkulaisvaaraite was found in this body, at coordinates  $66^{\circ}19'20''$  N and  $30^{\circ}49'50''$  E.

Lukkulaisvaaraite occurs as anhedral grains  $\sim 40$   $\mu$ m in diameter rimmed by tulameenite and accompanied randomly by telargpalite and Bi-rich kotulskite, enclosed within chalcopyrite in association with millerite, bornite and hematite. A backscatter electron image is shown in Fig. 1a. The mineral also occurs as 5–10  $\mu$ m crystals in intergrowths with telargpalite and Bi-rich kotulskite in association with moncheite, tulameenite, hongshiite and telluropalladinite as shown in Fig. 1b.

In the South Sopcha locality lukkulaisvaaraite was observed in association with kotulskite, sperrylite and palarstanide (Grokhovskaya *et al.*, 2003) and from the Monchetundra deposit in polyminerally platinum-group mineral grains, replacing kotulskite, intergrown with an unnamed Pd<sub>2</sub>NiTe<sub>2</sub> phase, at the contact between pentlandite and secondary silicates (Grokhovskaya *et al.*, 2009).

The mineral formed under post-magmatic conditions below 600°C (Grokhovskaya *et al.*, 1992; Barkov *et al.*, 2001).

### Synthetic analogue

The small grain size of lukkulaisvaaraite, embedded in chalcopyrite, prevented the extraction and isolation of the mineral in sufficient amounts for crystallographic and structural investigations. Therefore, the X-ray study and crystal structure determination were performed on synthetic Pd<sub>14</sub>Ag<sub>2</sub>Te<sub>9</sub>.

The synthetic phase was prepared in an evacuated and sealed silica glass tube in a horizontal furnace in the Laboratory of Experimental Mineralogy of the Czech Geological Survey in Prague. To prevent loss of material to the vapour phase during the experiment, the free space in the tube was reduced by placing a closely fitting glass rod against the charge. The temperature was measured with Pt–PtRh thermocouples and is accurate to within  $\pm 3^{\circ}$ C. A charge of  $\sim 200$  mg was weighed out carefully from the native elements. The starting chemicals were: silver powder (Aldrich Chem. Co., 99.999% purity), tellurium ingot (Aldrich Chem. Co., 99.999% purity) and palladium powder (Aldrich Chem. Co., 99.95% purity). The starting mixture was first melted at 1000°C for two days. The product was then ground in an agate mortar under acetone and reheated to 350°C

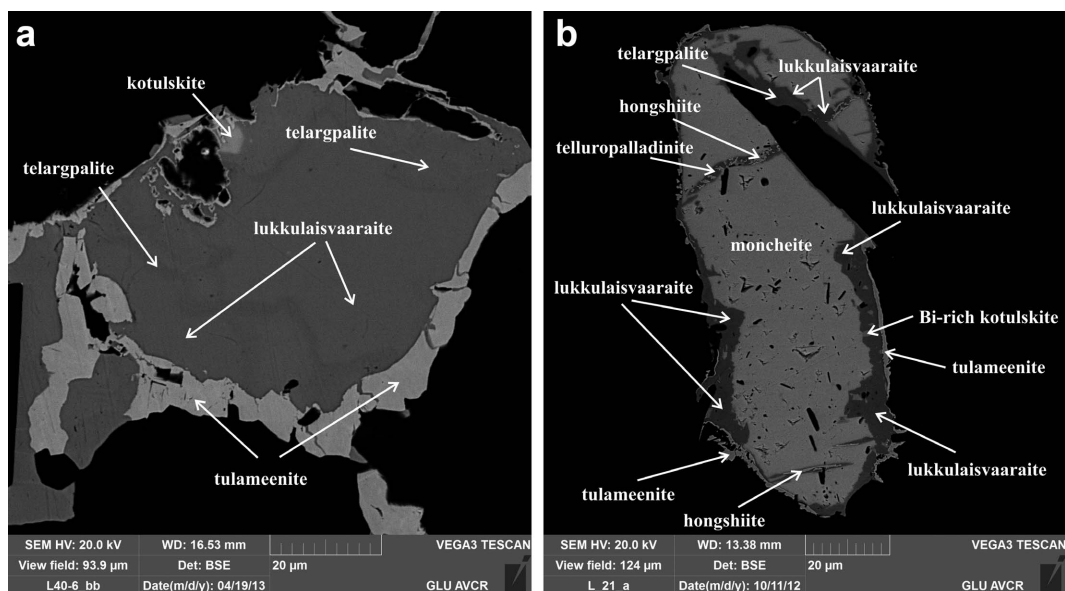


FIG. 1. Backscatter electron images of lukkulaisvaaraite and associated minerals; (a) lukkulaisvaaraite in intergrowths with telargpalite and kotulskite rimmed by tulameenite, holotype specimen; (b) moncheite surrounded by lukkulaisvaaraite, telargpalite, Bi-rich kotulskite and tulameenite, with veinlets of hongshiite and telluropalladinite.

for 124 days. The sample was quenched by dropping the capsule into cold water.

### Physical and optical properties

Lukkulaisvaaraite is opaque with a metallic lustre and grey streak. The powder of synthetic lukkulaisvaaraite is grey in colour. The mineral is brittle. Values of  $VHN_{20}$  measured from seven indentations is in the range from 339 to 371  $\text{kg mm}^{-2}$ , with a mean value of 355  $\text{kg mm}^{-2}$ , which corresponds to a Mohs hardness of  $\sim 4$ . The density calculated on the basis of the empirical formula is 9.993  $\text{g cm}^{-3}$ . The density measured for the synthetic sample by weighing in toluene is 9.9  $\text{g cm}^{-3}$ . The hand specimen was polished using standard diamond polishing procedures. In plane-polarized reflected light, lukkulaisvaaraite is light grey with a brownish tinge, has strong bireflectance, light brownish-grey to greyish-brown pleochroism and distinct to strong anisotropy. It exhibits no internal reflections.

Reflectance values of lukkulaisvaaraite were measured in air using an MSFU-312 microspectrophotometer (LOMO, Russia) with a WTiC standard ( $R_{589}$  in air = 48.7%).

Reflectance data are given in Table 1 and plotted in Fig. 2 and are in agreement with data presented by Barkov *et al.* (2001).

### Chemical composition

Chemical analyses were performed with a CAMECA SX-100 electron probe microanalyser (EPMA) in wavelength dispersive mode using an electron beam focused to 1–2  $\mu\text{m}$ . Pure elements were used as standards. Concentrations were quantified on the Pd $L\alpha$ , Ag $L\alpha$  and Te $L\alpha$  lines (overlap correction on Pd $L\beta$ ) with an accelerating voltage of 15 keV and a beam current of 10 nA on the Faraday cup. Other elements were below detection limits.

The electron microprobe results are given in Table 2. The empirical formula (based on 25 atoms) for natural lukkulaisvaaraite (average of five analyses) is  $\text{Pd}_{14.05}\text{Ag}_{1.88}\text{Te}_{9.06}$ , and for synthetic lukkulaisvaaraite (average of nine analyses), is  $\text{Pd}_{13.99}\text{Ag}_{1.93}\text{Te}_{9.08}$ , ideally  $\text{Pd}_{14}\text{Ag}_2\text{Te}_9$ . Chemical composition data of other studied grains of lukkulaisvaaraite (Fig. 1b) are given in Table 3, together with data reported in the literature on the phase. Barkov *et al.* (2001), according to the chemical composition data,

TABLE I. Reflectance data for lukkulaisvaaraite.

$\lambda$ (nm)	$R_1$ (%)	$R_2$ (%)
400	34.6	40.7
420	36.8	43.0
440	38.6	45.2
460	40.2	47.2
<b>470</b>	<b>40.9</b>	<b>48.3</b>
480	41.7	49.3
500	43.4	51.4
520	45.1	53.6
540	47.0	55.8
<b>546</b>	<b>47.6</b>	<b>56.4</b>
560	49.0	58.0
580	51.1	60.1
<b>589</b>	<b>52.1</b>	<b>61.0</b>
600	53.3	62.0
620	55.2	63.7
640	56.9	64.8
<b>650</b>	<b>57.5</b>	<b>65.2</b>
660	58.0	65.4
680	58.4	65.1
700	57.7	63.7

Note: The values for wavelengths ( $\lambda$ ) recommended by the IMA Commission on Ore Microscopy (COM) were interpolated and are given in bold.

suggested the alternative ideal formula  $\text{Pd}_{13}\text{Ag}_2\text{Te}_9$  to that originally assumed ( $\text{Pd}_6\text{AgTe}_4$ ) by Yakovlev *et al.* (1991) and Grokhovskaya *et al.* (1992).

### X-ray crystallography

Crystallographic and structural investigations were performed on synthetic  $\text{Pd}_{14}\text{Ag}_2\text{Te}_9$ .

Attempts to prepare a synthetic single crystal suitable for single-crystal XRD were unsuccessful. Thus, the crystal structure of  $\text{Pd}_{14}\text{Ag}_2\text{Te}_9$  was determined from the powder XRD data, *ab initio*. The proof of structural identity between natural and synthetic materials was performed using electron backscatter diffraction (EBSD, see below).

The XRD pattern used for structure determination was collected in Bragg-Brentano geometry on an X'Pert Pro PANalytical diffractometer, equipped with an X'Celerator detector and a  $\text{CoK}\alpha$  radiation source. Data were collected between 10 and  $120^\circ 2\theta$ ; a full width at half maximum of  $0.097^\circ$  in  $2\theta$  was obtained at  $37.12^\circ 2\theta$ , indicating good crystallinity of the sample. Details of data collection and basic crystallographic data are given in Table 4.

Indexing of the X-ray powder pattern was performed using the DICVOL06 program (Boultif and Louër, 2004). The first 20 lines, with the exception of a few diffraction peaks attributable to  $\text{PdTe}$  (4 wt.%) and  $\text{Ag}_4\text{Pd}_3\text{Te}_4$  (2 wt.%), were indexed on the basis of the tetragonal cell (Table 4). The figures of merit for assessing the quality of the solution were  $M_{20} = 58.3$  (de Wolff, 1968) and  $F_{20} = 47.6$  (0.0079;53) (Smith and Snyder, 1976).

The powder diffraction pattern was fitted using the LeBail algorithm implemented in the *JANA2006* program (Petříček *et al.*, 2011). The structure solution was performed using the *Superflip* program (Palatinus and Chapuis, 2007), which uses the charge-flipping method (Ozslanyi and Suto, 2004) for structure solution. *Superflip* suggested the  $I4/m$  space group. This is consistent with systematic absences observed in the powder diffraction data. Other space groups

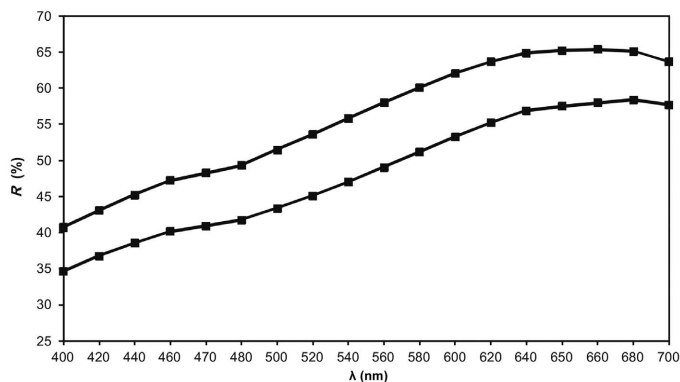


FIG. 2. Reflectance data for lukkulaisvaaraite.

TABLE 2. Electron microprobe analyses of natural (holotype specimen, Fig. 1a) and synthetic lukkulaisvaaraite.

Wt.%	Pd	Ag	Te	Bi	Total
Natural sample ( $n = 5$ )					
Mean	52.17	7.03	40.36	0.05	99.64
Range	51.06–53.27	6.26–7.69	39.77–41.23	0.03–0.09	
Std. dev.	0.66	0.4	0.5	0.05	
Synthetic sample ( $n = 9$ )					
Mean	52.13	7.31	40.58		100.02
Range	51.60–52.90	6.65–7.94	40.16–41.25		
Std. dev.	0.45	0.48	0.3		

were also tested, but no sensible solutions were obtained.

The structural model found by *Superflip* was introduced subsequently into the *FullProf* program (Rodríguez-Carvajal, 2006) for Rietveld refinement. A pseudo-Voigt function was used to generate the shape of the diffraction peaks; the background was determined by linear interpolation between consecutive points in the pattern. Refined parameters include those describing the peak shape and width, peak asymmetry, unit-cell parameters and isotropic displacement parameters. In total, 26 parameters were refined (including nine coordinates and six isotropic displacement parameters). The final cycles of refinement converged to the agreement factors  $R_{\text{Bragg}} = 0.065$ ,  $R_{\text{wp}} = 0.036$  and  $R_p = 0.065$ . The final Rietveld plot is shown in Fig. 3.

Crystal structure data are presented in Table 5. As it is nearly impossible to distinguish between

the Ag and Pd atoms in the conventional powder diffraction experiments ( $\text{CoK}\alpha$  radiation), all metal positions labelled M1 to M4 were refined as mixed sites (Ag/Pd) with occupancies based upon the empirical chemical composition. Possible coordination preferences of Ag and Pd in the lukkulaisvaaraite crystal structure are discussed below. Table 6 summarizes selected bond distances and Table 7 presents powder diffraction data for lukkulaisvaaraite.

### Crystal structure

#### *Coordination of cations and occupancies of metallic positions*

The asymmetric unit of lukkulaisvaaraite contains four independent metal (M1–M4) and two Te sites. Figure 4 shows the crystal structure.

The coordination geometry of the M(1) site can be viewed as a transition between tetrahedral and

TABLE 3. Electron microprobe analyses of lukkulaisvaaraite reported in the literature and for the comparative samples studied (Fig. 1b).

Wt.%	Pd	Ag	Te	Cu	Total	Reference
Lukkulaisvaara intrusion						
$n = 4$	52.15	7.34	39.98		99.47	This study
$n = 17$	52.28	7.54	40.65		100.47	Barkov <i>et al.</i> (2001)
$n = 9$	51.49	7.68	41.03		100.20	Barkov <i>et al.</i> (2001)
	52.12	7.89	40.39		100.37	Grokhovskaya <i>et al.</i> (1992)
Monchetundra deposit						
	47.87	7.18	43.97	3.88	102.9	Grokhovskaya <i>et al.</i> (2009)
South Sopcha						
	50.99	7.19	42.06	0.69	100.93	Grokhovskaya <i>et al.</i> (2003)

TABLE 4. Data collection and Rietveld analysis for lukkulaisvaaraite.

<b>Data collection</b>	
Radiation type, source	X-ray, CoK $\alpha$
Generator settings	40 kV, 30 mA
Range in 2 $\theta$ (°)	10–120
Step size (°)	0.02
<b>Crystal data</b>	
Space group	<i>I4/m</i> (No. 87)
Unit-cell content	Pd <sub>14</sub> Ag <sub>2</sub> Te <sub>9</sub> , <i>Z</i> = 2
Unit-cell parameters (Å)	<i>a</i> = 8.9599(6) <i>c</i> = 11.822(1)
Unit-cell volume (Å <sup>3</sup> )	941.1(1)
<b>Rietveld analysis</b>	
No. of reflections	248
No. of structural parameters	15
No. of profile parameters	4
<i>R</i> <sub>Bragg</sub>	0.065
<i>R</i> <sub>p</sub>	0.026
<i>R</i> <sub>wp</sub>	0.036
Weighting scheme	1/ <i>y</i> <sub>o</sub>

The *R* agreement factors defined according to McCusker *et al.* (1999).

square planar. It can be described as a strongly deformed tetrahedron, flattened along one of its four axes. As a consequence, Te–M(1)–Te angles have the values 148° and 155°, which differ significantly from that of an ideal tetra-

hedron. M(1)–Te distances range from 2.648(2) to 2.724(3) Å. The M(1) position also interacts with one M(4) and three M(1) and M(2) positions at distances from 2.891(4) to 3.056(4) Å. While Ag has a linear coordination preference (CuAgS; Baker *et al.*, 1991), a trigonal one (low temperature form of Ag<sub>2</sub>S; Frueh, 1958), a tetrahedral one (AgTe; Bindi *et al.*, 2004) or an octahedral one (AuAgTe<sub>2</sub>; Bindi and Cipriani, 2004) for Ag-bearing chalcogenides, similar Pd-occupied, flattened tetrahedra were observed in the crystal structure of Pd<sub>17</sub>Se<sub>15</sub> (Geller, 1962). Therefore, the M(1) position is most likely to be occupied predominantly by Pd atoms.

M(2) and M(3) positions are at the centres of rectangles formed by Te atoms. While the M(3)Te<sub>4</sub> polyhedron is perfectly planar with four equal M(3)–Te distances of 2.679(2) Å, the M(2)Te<sub>4</sub> polyhedron is more distorted. The M(2) position is shifted out of the plane of the four Te atoms towards the adjacent M(4) position by 0.12 Å; M(2)–Te distances are 2.721(3) Å and 2.801(3) Å. As is indicated in Table 6, both positions are involved in numerous metal–metal interactions up to 3.073(4) Å. The crystal structure of chrisstanleyite (Ag<sub>2</sub>Pd<sub>3</sub>Se<sub>4</sub>; Topa *et al.*, 2006) demonstrates the differences in coordination preference of Ag and Pd in chalcogenides; Pd atoms assume square planar coordination whereas Ag atoms show tetrahedral coordination. Considering these coordination preferences, the M(2) and M(3) sites in lukkulaisvaaraite are probably occupied mainly by the Pd atoms.

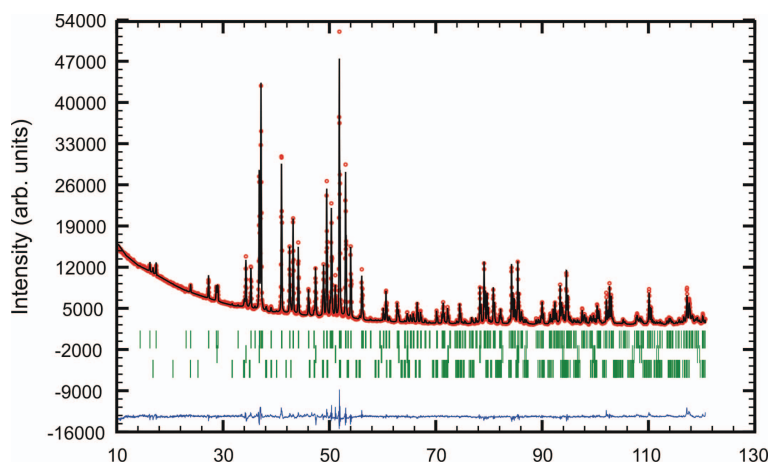


FIG. 3. Observed (red circles), calculated (solid line) and difference Rietveld profiles for lukkulaisvaaraite. The upper reflection markers correspond to lukkulaisvaaraite; the middle and the lower markers to PdTe (4 wt.%) and Ag<sub>4</sub>Pd<sub>3</sub>Te<sub>4</sub> (2 wt.%) impurities, respectively.



TABLE 5. Atom positions and isotropic displacement parameters ( $\text{\AA}^2$ ; M(1–4) represent Pd and/or Ag atoms).

Atom	Wyckoff letter	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>iso</sub> ( $\text{\AA}^2$ )
M(1)	16 <i>i</i>	0.5718(3)	0.2790(2)	0.3616(2)	0.65(5)
M(2)	8 <i>h</i>	0.7051(4)	0.4068(3)	0	0.60(7)
M(3)	4 <i>c</i>	½	0	0	0.8(1)
M(4)	4 <i>e</i>	½	½	0.1919(4)	0.8(1)
Te(1)	2 <i>a</i>	½	½	½	0.8(1)
Te(2)	16 <i>i</i>	0.6262(2)	0.1880(3)	0.1480(2)	0.70(5)

The M(4) site is surrounded by four M(1) and four M(2) sites showing a distorted square antiprismatic coordination. M(4)–M(1) and M(4)–M(2) distances are 2.891(4) and 3.037(4) Å, respectively. M(4) coordination is completed by four Te atoms at 3.060(2) Å lying in the equatorial plane of the antiprism. Considering the multiplicity of this position (4*e*) and the Ag content (4 Ag atoms per unit cell), this position appears to be occupied by Ag atoms.

#### Polyhedral description

The crystal structure of lulkulaisvaaraitte can be viewed as a three-dimensional framework composed of two types of blocks of polyhedra (Fig. 4). These are interconnected by common Te atoms.

The first type consists of edge-sharing, flattened M(1)Te<sub>4</sub> tetrahedra. Four of these are linked into a tetramer by sharing common Te–Te edges. As a consequence, the M(1) position has two short contacts at 2.944(3) Å across the shared Te–Te edge with two adjacent M(1) positions. The

tetramers show convex and concave sides; the concave side faces the M(4) position. The convex side faces a symmetry-related tetramer; both tetramers share a common Te atom (Fig. 5). Moreover, each tetramer shares four Te–Te edges with the adjacent four tetramers forming slabs parallel to (001). In these slabs the tetramers are arranged in a chessboard fashion.

The second type of coordination polyhedra is composed of M(2)Te<sub>4</sub> and M(3)Te<sub>4</sub> rectangles. Each rectangle shares two opposite Te–Te edges with adjacent rectangles forming layers parallel to (001). Their topology is shown in Fig. 6*a*. The layers contain large and small tetragonal gaps, both of which are defined by faces of M(2)Te<sub>4</sub> and M(3)Te<sub>4</sub> rectangles. Whereas the smaller gaps are crossed by a number of metal–metal bonds (Fig. 6*a*), the larger gaps are filled by pairs of symmetry-related (M(1)Te<sub>4</sub>)<sub>4</sub> tetramers (Fig. 6*b*). The layers lie at *c* ~0 and ½ and show AB stacking along the *c* axis. The M(4) position is inserted between the concave site of the (M(1)Te<sub>4</sub>)<sub>4</sub> tetramer and the smaller gaps of the M(2)Te<sub>4</sub> rectangles.

TABLE 6. Selected bond distances in the lulkulaisvaaraitte crystal structure.

M(1)	1 × Te(1)	2.648(2)	M(2)	2 × Te(2)	2.721(3)
	1 × Te(2)	2.698(3)		1 × M(3)	2.771(4)
	1 × Te(2)	2.703(3)		2 × Te(2)	2.801(3)
	1 × Te(2)	2.724(3)		2 × M(2)	2.855(5)
	1 × M(4)	2.891(4)		2 × M(4)	3.037(4)
	2 × M(1)	2.944(4)		2 × M(1)	3.073(4)
	1 × M(3)	3.056(2)			
	1 × M(2)	3.073(4)			
M(3)	4 × Te2	2.679(2)	M(4)	4 × M(1)	2.891(4)
	2 × M2	2.771(3)		4 × M(2)	3.037(4)
	4 × M1	3.056(3)		4 × Te(2)	3.060(3)

TABLE 7. Powder XRD data for synthetic lukkulaivaraite (CoK $\alpha$  radiation).

<i>h</i>	<i>k</i>	<i>l</i>	<i>I</i> <sub>(obs)</sub>	<i>I</i> <sub>(calc)</sub>	<i>d</i> <sub>(obs)</sub>	<i>d</i> <sub>(calc)</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>I</i> <sub>(obs)</sub>	<i>I</i> <sub>(calc)</sub>	<i>d</i> <sub>(obs)</sub>	<i>d</i> <sub>(calc)</sub>
1	1	0	5	3	6.3494	6.3358	2	3	7	12	11	1.3968	1.3969
0	0	2	4	5	5.9161	5.9113	3	2	7				
1	1	2	6	3	4.3235	4.3222	1	6	3	17	18	1.3798	1.3798
1	2	1	8	9	3.7941	3.7950	6	1	3				
0	1	3	6	6	3.6031	3.6073	5	3	4	4	1	1.3632	1.3634
0	2	2	8	6	3.5710	3.5705	3	5	4				
0	0	4	21	17	2.9548	2.9556	5	2	5	5	2	1.3607	1.3607
1	3	0	58	12	2.8323	2.8334	2	5	5				
3	1	0		44			4	1	7	29	25	8	1.3336
2	1	3	92	93	2.8088	2.8097	1	4	7				
3	1	2	66	70	2.5542	2.5551	3	6	1	12	10	1.3273	1.3272
0	2	4	28	31	2.4662	2.4671	6	3	1				
3	2	1	41	36	2.4312	2.4319	5	4	3	36	18	1.3187	1.3187
2	3	1		7			4	5	3				
0	3	3	28	29	2.3796	2.3803	2	6	4	2	2	1.2776	1.2775
0	1	5	20	13	2.2857	2.2862	3	6	3				
2	2	4	32	22	2.1610	2.1611	6	3	3	11	9	1.2650	1.2650
4	1	1	57	36	2.1367	2.1373	1	2	9				
1	4	1		23			2	1	9	5	1	4	1.2483
2	3	3	36	6	4	0							
3	2	3	52	14	2.1015	2.1020	4	6	0	7	6	1.2426	1.2425
3	1	4		100			100	2.0449	2.0454				
4	2	0	63	17	2.0031	2.0035	1	7	2	10	5	1.2392	1.2390
2	4	0		55			3	4	7				
0	0	6	30	36	1.9700	1.9704	4	3	7	20	11	1.2291	1.2291
1	4	3	23	19	1.9026	1.9030	0	5	7				
4	1	3		3			0	7	3	31	33	2	1.2174
0	4	4	6	6	1.7850	1.7852	4	2	8				
0	5	1	15	8	1.7715	1.7718	2	4	8	8	6	1.1894	1.1893
4	3	1		8			2	7	3				
3	3	4	10	10	1.7181	1.7183	7	2	3	4	1	1.1747	1.1748
4	2	4	3	2	1.6587	1.6584	1	7	4				
2	4	4		1			7	1	4	13	7	3	1.1646
2	5	1	2	5	5	4							
5	2	1	5	3	1.6475	1.6476	6	2	6	17	16	1.1503	1.1503
0	5	3		5			6	4	4				
3	4	3	8	1	1.6312	1.6313	0	2	10	6	25	1.1454	1.1454
4	3	3		5			0	2	10				
1	3	6	5	1	1.6177	1.6177	4	7	1	7	1	1.1066	1.1065
3	1	6		1			7	4	1				
1	2	7	6	7	1.5563	1.5563	8	1	1	3	5	1.0911	1.0911
5	3	0	0	1	3	10							
3	5	0	7	5	1.5363	1.5366	3	1	10	24	16	1.0560	1.0559
5	2	3		2			6	6	0				
2	5	3	11	6	1.5329	1.5328	6	3	7	3	3	1.0477	1.0476
0	0	8		10			11	1.4778	1.4778				
6	2	0	17	19	1.4167	1.4167	3	3	10	6	6	1.0317	1.0316
2	4	6	30	29	1.4049	1.4048	4	4					



## LUKKULAISVAARAITE, A NEW Ag-Pd TELLURIDE

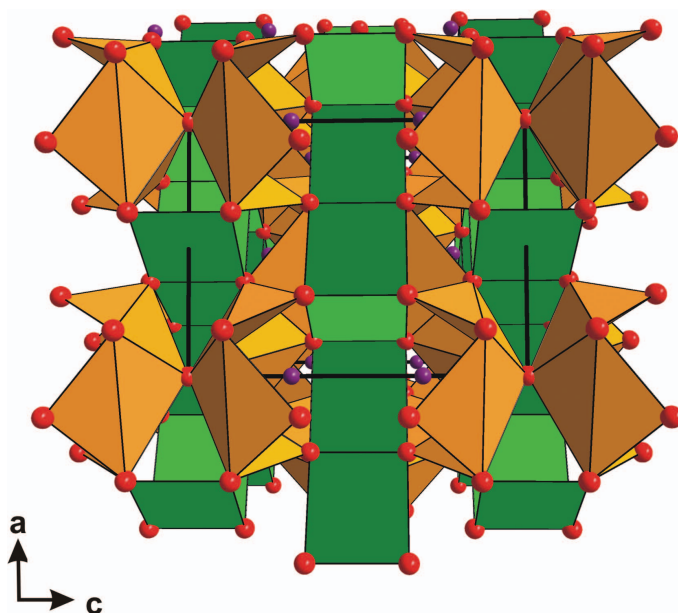


FIG. 4. The crystal structure of lulkulaisvaaraite.  $M(2)Te_4$  and  $M(3)Te_4$  coordination polyhedra are in green and the flattened  $M(1)Te_4$  tetrahedra are in light orange.  $M(4)$  positions are in violet. Parallel projection onto the  $ac$  plane; unit-cell edges are highlighted.

### Relation to other structures

The crystal structure of lulkulaisvaaraite represents a unique structure type; no exact structural analogue is known. Lulkulaisvaaraite shows some structural similarities with sopcheite ( $Ag_4Pd_3Te_4$ ), but the structures differ substantially. On the one hand, edge-sharing layers of  $PdTe_4$  coordination squares or rectangles are present in both structures. On the other hand,

the three-dimensional framework observed in the lulkulaisvaaraite structure contrasts with the layered structure of sopcheite (Laufek *et al.*, 2013).

The crystal structure of another Ag-Pd-telluride, telargpalite,  $(Ag,Pd)_{3+x}Te$ , has not been determined precisely. Flattened tetrahedra, characteristic of the lulkulaisvaaraite structure, were also observed in palladseite,  $Pd_{17}Se_{15}$  (Geller, 1962) and in the synthetic compound  $Ni_{9.54}Pd_{7.46}S_{15}$  (Dubost *et al.*, 2007). In all structures, the flattened tetrahedra are linked into tetramers by sharing edges. Another observation is worth mentioning. The experimental study of Vymazalová *et al.* (2014a) showed that lulkulaisvaaraite does not have an Se analogue.

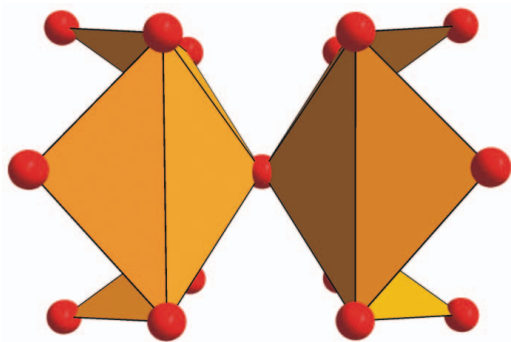


FIG. 5. Two symmetry-related tetramers composed of four edge-sharing, flattened  $M(1)Te_4$  tetrahedra.

### Proof of identity of natural and synthetic lulkulaisvaaraite

The structural identity of synthetic  $Pd_{14}Ag_2Te_9$  and the natural material was confirmed by electron backscatter diffraction (EBSD). This was performed using a TESCAN Vega scanning electron microscope combined with an EBSD system developed by HKL Technology, Denmark. The natural sample was prepared for

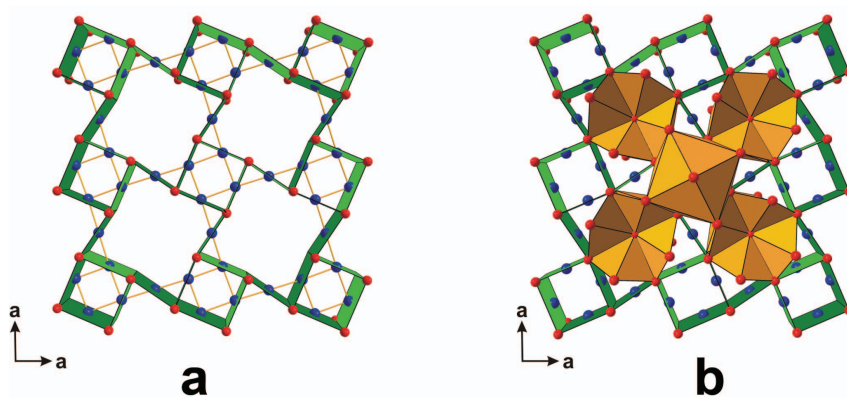


FIG. 6. (a) Detailed view showing the connectivity of  $M(2)Te_4$  and  $M(3)Te_4$  rectangles and metal–metal bonds within one layer. Note the alternation of small and large tetragonal gaps; (b) interconnection of  $(M(1)Te_4)_4$  tetramers and layers composed of  $M(2)Te_4$  and  $M(3)Te_4$  rectangles.

investigation by etching the mechanically polished surface with colloidal silica (OP-U) for 20 min to reduce surface damage. EBSD patterns were collected and processed using a proprietary computer program, *Channel 5*, provided by HKL Technology (2004). The centre of six Kikuchi bands was detected automatically using the Hough transform routine (Schmidt *et al.*, 1991) with a resolution of 50 (internal Hough resolution parameter in the HKL software). The solid angles calculated from the patterns were compared with a synthetic  $Pd_{14}Ag_2Te_9$  match containing 95 reflectors to index the patterns. EBSD patterns (also known as Kikuchi patterns) obtained from the natural material (nine measurements on different spots

on natural lukkulaisvaaraitte) were found to match the patterns generated from the structure of synthetic  $Pd_{14}Ag_2Te_9$  provided by our crystal structure determination (Fig. 7). The values of the mean angular deviation (MAD goodness-of-fit in the solution) between the calculated and measured Kikuchi bands range between  $0.46^\circ$  and  $0.17^\circ$ . These values reveal a very good match; mean angular deviations  $<1^\circ$  are considered as indicators of an acceptable fit (HKL Technology, 2004).

The EBSD study, chemical identity and optical properties confirmed the correspondence between natural and synthetic materials and thereby legitimize the use of the synthetic phase for the complete characterization of lukkulaisvaaraitte.

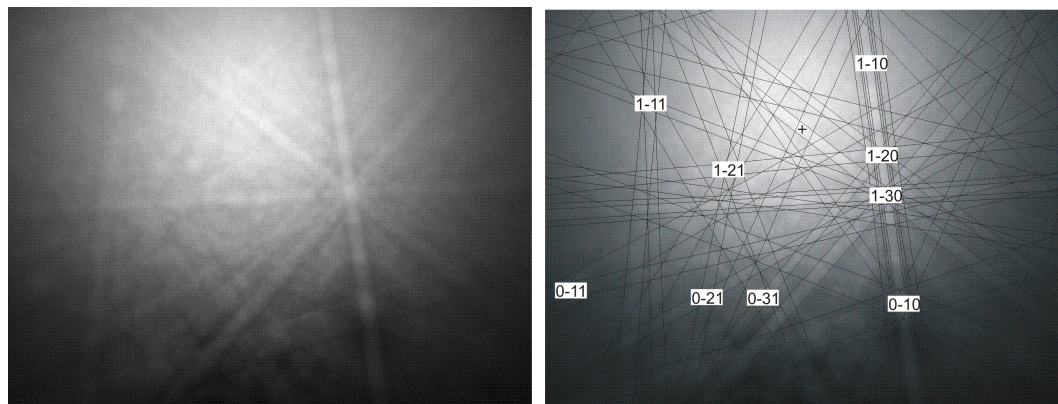


FIG. 7. EBSD image of natural lukkulaisvaaraitte; in the right pane, the Kikuchi bands are indexed.

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