The Canadian Mineralogist
Vol. 47, pp. 53-62 (2009)
DOI: 10.3749/canmin.47.1.53

PAŠAVAITE, $Pd_3Pb_2Te_2$, A NEW PLATINUM-GROUP MINERAL SPECIES FROM THE NORIL'SK–TALNAKH Ni–Cu CAMP, RUSSIA

Anna VYMAZALOVÁ[§], František LAUFEK, Milan DRÁBEK,
Jakub HALODA and Tamara SIDORINOVÁ

Czech Geological Survey, Geologická 6, 152 00 Prague 5, Czech Republic

Jakub PLÁŠIL

Faculty of Science, Charles University, Albertov 6, 128 43, Prague 2, Czech Republic

Abstract

Pašavaite, $Pd_3Pb_2Te_2$, is a new palladium-bearing mineral species discovered at the Talnakh deposit, Noril'sk–Talnakh Ni–Cu camp, Taimyr Autonomous District, Russia. It was observed in two polished sections, where it occurs as subhedral grains not exceeding 20 μm in diameter embedded in polarite, and accompanied by unknown Pd–Pb–Bi–Te phases and sperrylite or intergrown with Au–Ag phases. The other associated minerals are: taimyrite, froodite, galena, and the chalcopyrite + pentlandite matrix. Synthetic pašavaite is megascopically grey in color, has a metallic luster and a grey streak. The mineral is brittle, with a weak {001} cleavage. Values of VHN_{25} (15 indentations on five grains of synthetic $Pd_3Pb_2Te_2$) range between 173 and 281, for a mean value of 233 kg/mm^2, which corresponds to a Mohs hardness of approximately 2. In plane-polarized light, pašavaite is pale pink with brownish tinge, has strong bireflectance, pleochroic from brownish to light pink, distinctly to strongly anisotropic, and exhibits no internal reflections. Reflectance values of synthetic pašavaite in air (R_{max}, R_{min}) are: 49.9, 42.4 at 470 nm, 51.8, 44.6 at 546 nm, 52.2, 45.7 at 589 nm, and 52.8, 46.9 at 650 nm. The average result of four electron-microprobe analyses of pašavaite is: Pd 31.51, Pb 41.54, Bi 0.19, and Te 25.75, total 98.99 wt.%, corresponding to an empirical formula (based on 7 atoms) $Pd_{2.96}(Pb_{2.01}Bi_{0.01})Te_{2.02}$; synthetic pašavaite (average of seven analyses) gave: Pd 32.17, Pb 41.78, and Te 25.93, total 99.88 wt.%, corresponding to $Pd_{2.99}Pb_{2.00}Te_{2.01}$. The mineral is orthorhombic, space group *Pmmn*, with *a* 8.599(1), *b* 5.9381(6), *c* 6.3173(8) Å, *V* 322.6(1) Å^3, and Z = 2. The crystal structure was solved and refined from the powder X-ray-diffraction data of synthetic $Pd_3Pb_2Te_2$. Pašavaite is structurally related to shandite and parkerite. The strongest lines in the X-ray powder-diffraction pattern of synthetic pašavaite [*d* in Å(I)(*hkl*)] are: 6.3152(34)(001), 3.1572(33)(002), 3.0495(100)(211), 2.5456(63)(202), 2.4424(34)(220), 2.2786(42)(221), 2.1637(71)(022), 2.1496(30)(400), 1.8906(42)(203), and 1.5248(31)(422). The mineral is named after Jan Pašava, in recognition of his important contributions to the geochemistry of platinum-group elements in anoxic environments and related ore deposits.

Keywords: pašavaite, new mineral species, platinum-group mineral, Pd–Pb telluride, electron-microprobe data, reflectance data, synthetic $Pd_3Pb_2Te_2$, X-ray-diffraction data, crystal structure, Noril'sk–Talnakh, Russia.

Sommaire

La pašavaite, $Pd_3Pb_2Te_2$, est une nouvelle espèce minérale palladifère découverte dans un minerai du gisement de Talnakh, camp minier à Ni–Cu de Noril'sk–Talnakh, district autonome de Taimyr, en Russie. Nous l'avons observée dans deux sections polies, où elle forme des grains sub-idiomorphes ne dépassant pas 20 μm englobés dans la polarite; elle est accompagnée de phases Pd–Pb–Bi–Te et de sperrylite ou bien se trouve en intercroissance avec des phases contenant Au–Ag. Lui sont aussi associées taimyrite, froodite, galène, et la matrice de chalcopyrite + pentlandite. La pašavaite synthétique est mégascopiquement grise, et possède un éclat métallique et une rayure grise. C'est un minéral cassant, avec un faible clivage {001}. Les valeurs de dureté VHN_{25} (15 indentations sur cinq grains de $Pd_3Pb_2Te_2$ synthétique) s'étalent entre 173 et 281, pour une moyenne de 233 kg/mm^2, ce qui correspond à une dureté de Mohs d'environ 2. En lumière polarisée, la pašavaite est rose pâle avec une teinte brunâtre; elle montre une forte biréflectance, est pléochroïque du rose brunâtre à rose pâle, distinctement ou fortement anisotrope, et semble sans réflections internes. Les valeurs de réflectance de la pašavaite synthétique dans l'air (R_{max}, R_{min}) sont: 49.9, 42.4 à 470 nm, 51.8, 44.6 à 546 nm, 52.2, 45.7 à 589 nm, et 52.8, 46.9 à 650 nm. La composition chimique, résultat moyen de quatre analyses de la pašavaite avec une microsonde électronique, est: Pd 31.51, Pb 41.54, Bi 0.19, et Te 25.75, pour un total de 98.99% (poids), ce qui correspond à la formule empirique (fondée sur sept atomes) $Pd_{2.96}(Pb_{2.01}Bi_{0.01})Te_{2.02}$; la pašavaite

---

[§] *E-mail address*: anna.vymazalova@geology.cz

synthétique (moyenne de sept analyses) a donné: Pd 32.17, Pb 41.78, et Te 25.93, pour un total de 99.88%, ce qui correspond à $Pd_{2.99}Pb_{2.00}Te_{2.01}$. Le minéral est orthorhombique, groupe spatial *Pmmn*, avec *a* 8.599(1), *b* 5.9381(6), *c* 6.3173(8) Å, *V* 322.6(1) Å^3, et Z = 2. Nous avons résolu la structure cristalline et nous l'avons affiné à partir de données en diffraction X sur $Pd_3Pb_2Te_2$ synthétique en poudre. La pašavaite est structuralement semblable à la shandite et à la parkerite. Les raies les plus intenses du spectre de diffraction X sur poudre de pašavaite synthétique [*d* en Å(I)(*hkl*)] sont: 6.3152(34)(001), 3.1572(33)(002), 3.0495(100)(211), 2.5456(63)(202), 2.4424(34)(220), 2.2786(42)(221), 2.1637(71)(022), 2.1496(30)(400), 1.8906(42)(203), et 1.5248(31)(422). Le minéral honore Jan Pašava, en reconnaissance de ses contributions importantes à la géochimie des éléments du groupe du platine en milieux anoxyques et à l'étude des gîtes minéraux associés.

(Traduit par la Rédaction)

Mots-clés: pašavaite, nouvelle espèce minérale, minéral du groupe du platine, tellurure de Pd–Pb, données de microsonde électronique, données de réflectance, $Pd_3Pb_2Te_2$ synthétique, données de diffraction X, structure cristalline, Noril'sk–Talnakh, Russie.

INTRODUCTION

In the course of a re-investigation of platinum-group minerals in polished sections from the Noril'sk–Talnakh deposits, we observed a yet unknown Pd–Pb telluride of ideal composition $Pd_3Pb_2Te_2$. The holotype specimen measures 0.6 × 1.1 × 0.4 cm and was obtained from a Czech mineral collector. Two polished sections were made, and both contain the new mineral species. We have named it *pašavaite* in honor of Jan Pašava (b. 1957), geologist with the Czech Geological Survey, in recognition of his important contributions to the mineralogy and geochemistry of platinum-group elements in anoxic environments and other geological settings, and in the field of related ore deposits. The mineral and the mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification of the IMA (CNMNC 2007–059). The holotype material, a polished section, is deposited at the Department of Mineralogy in the National Museum, Prague, Czech Republic, under the catalogue number P1p 15/2007. Our aim here is to describe the properties of the new species, pašavaite, and its crystal structure.

OCCURRENCE AND ASSOCIATED MINERALS

The Ni–Cu deposits of the Noril'sk–Talnakh region are the second largest economic concentration of PGE in the world after the Bushveld Complex in South Africa. A large number of platinum-group minerals, mainly of palladium and platinum, occur in the ore of Noril'sk–Talnakh deposits. Extensive studies have been dedicated to these deposits (*e.g.,* Genkin *et al.* 1981, Genkin & Evstigneeva 1986, Czamanske *et al.* 1992, Naldrett *et al.* 1992, among others).

The associations of platinum-group minerals in the Noril'sk deposits vary according to the types of Cu–Ni ores. The main minerals in disseminated ores in intrusive gabbrodolerites are isoferroplatinum and cooperite. These are lacking in massive ores, where the intermetallic compounds of Pd and tetraferroplatinum commonly occur. The Pd and Pt sulfides, tellurides, and bismuthotellurides are specific to veinlet-disseminated and brecciated ores (Genkin & Evstigneeva 1986).

Pašavaite was found in massive Ni–Cu ore, embedded in polarite, in association with Au–Ag phases, unknown Pd–Pb–Bi–Te phases and sperrylite; the specimens are from Talnakh deposit, Noril'sk–Talnakh Ni–Cu mining camp, Taimyr Autonomous District, Russia. Pašavaite, embedded in polarite, was observed in both polished sections. Grains of polarite (about 200 μm long) are rimmed by Au–Ag phases and galena, enclosed in a chalcopyrite–pentlandite matrix. Together with pašavaite, an inclusion of an unknown Pd–Pb–Bi–Te phase, of variable proportion of Pb–Bi–Te, and sperrylite were observed in polarite. A phase of similar chemical composition (Pd 36.2, Pb 31.2, Bi 12.2, and Te 17.6, total 97.2 wt.%) as our inclusion (not exceeding 30 μm) in polarite, found in cubanite–talnakhite ores of the Talnakh deposit, has been described by Kovalenker *et al.* (1972). It corresponds to four inclusions (average value: Pd 36.90, Pb 30.99, Bi 11.66, and Te 19.26, total 98.81 wt.%) observed in polarite in our sample. Roundish grains of taimyrite with sperrylite, sobolevskite and froodite inclusions were identified also.

The ore deposits of Noril'sk–Talnakh district are associated with hypabyssal intrusions related to the Siberian flood basalt province. According to Genkin & Evstigneeva (1986), during the formation of massive ores of the Noril'sk deposits, differentiation of the sulfide melt led to separation of large volumes of a copper-rich melt in which platinum, palladium, and other elements such as Sn, Pb, As, Sb, Te and Bi were concentrated. The residual liquid evolved from the copper-rich melt. We believe that the proposed new mineral most likely originated from a Pd–Pb–Te residual liquid at temperatures of about 400–500°C, as the last phase of liquid segregation of the Ni–Cu ores.

EXPERIMENTAL PROCEDURES

The small grains of pašavaite embedded intimately in polarite prevented its extraction and isolation in an amount required for the relevant crystallographic and structural investigations, measurements of reflectance and density, and determination of physical properties. Therefore, these measurements were performed on synthetic $Pd_3Pb_2Te_2$. A similar approach had also been used in case of milotaite (Paar *et al*. 2005) and vavřínite (Laufek *et al*. 2007).

The synthetic $Pd_3Pb_2Te_2$ phase was prepared using Kullerud's evacuated silica glass tube method (Kullerud 1971) in the experimental laboratory of the Czech Geological Survey in Prague. Palladium (99.95%), lead (99.999%) and tellurium (99.999%) supplied by Johnson Matthey Co. Ltd. were used as starting materials for synthesis. A carefully weighed sample was loaded into the high-purity silica tube and a tightly fitting silica glass rod was placed on top of the reagents in order to keep the charge in place and also to reduce the volume of vapor on heating. The evacuated tube was sealed with its charge and then annealed at 1200°C for three days. After cooling in a cold-water bath, the charge was carefully taken out of the tube so as not to lose any of the products, which were ground into powder in acetone using an agate mortar, and thoroughly mixed so as to become homogeneous. The pulverized charge was sealed in an evacuated silica-glass tube again, and reheated at 400°C for five months. The temperature was controlled electronically (±4°C). The experimental product was rapidly quenched in a cold-water bath.

PHYSICAL AND OPTICAL PROPERTIES

Pašavaite occurs as subhedral grains (Fig. 1) not exceeding 20 μm in diameter embedded in polarite, and randomly accompanied by unknown Pd–Pb–Bi–Te phases and sperrylite or intergrown with Au–Ag phases. Synthetic pašavaite is megascopically grey in color, opaque, and has a metallic luster, and a grey streak. The mineral is brittle, with a weak {001} cleavage.

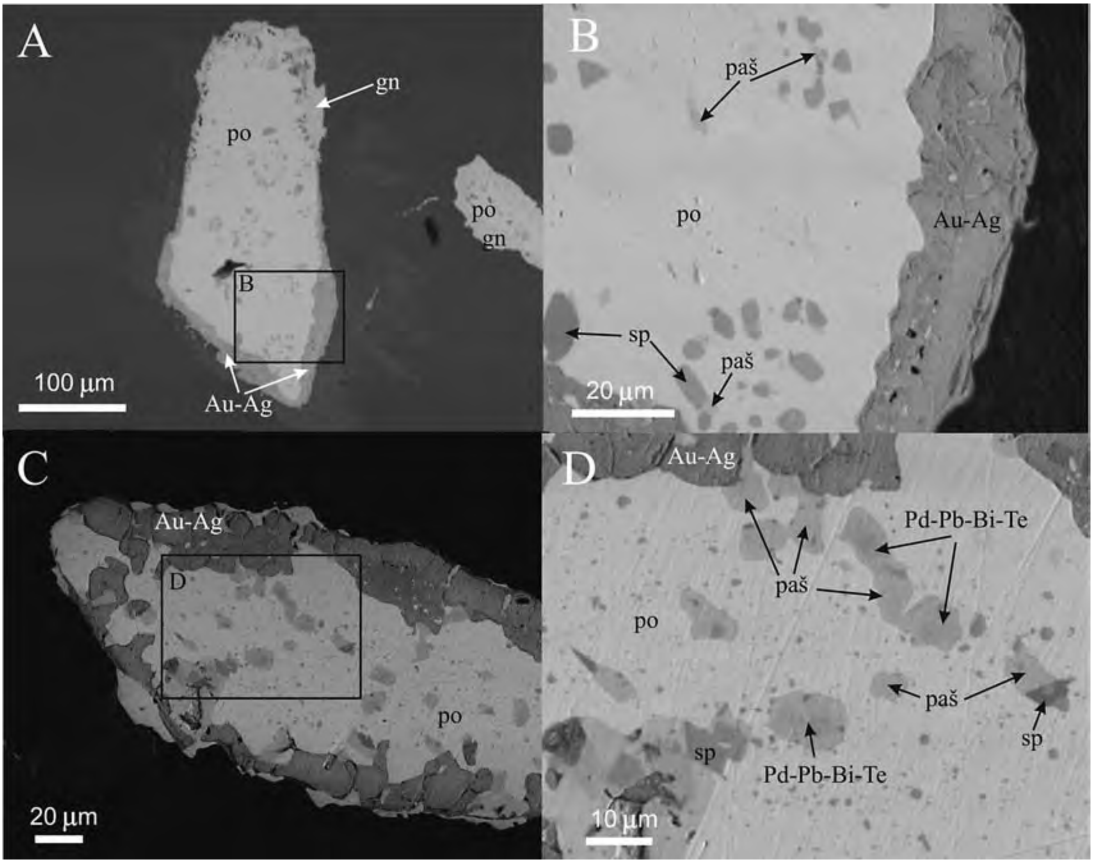

FIG. 1. Back-scattered electron image of pašavaite and associated minerals. A, C. Polarite (po) grains rimmed by Au–Ag phases and galena (gn). B, D. Pašavaite (paš) embedded in polarite (po) in association with sperrylite (sp), Pd–Pb–Bi–Te and Au–Ag phases.

The VHN_{25} (15 indentations on five grains) was determined on synthetic $Pd_3Pb_2Te_2$ and ranges between 173 and 281 (mean 233) kg/mm^2. The Mohs hardness is approximately 2. The density, calculated on the basis of the empirical formula, is 10.18 g/cm^3. The density, measured by weighing in toluene, is 9.9 g/cm^3. In plane-polarized light, pašavaite and synthetic $Pd_3Pb_2Te_2$ are pale pink with a brownish tinge, have a strong bireflectance, are pleochroic from brownish to light pink, distinctly to strongly anisotropic, and exhibit no internal reflections. Reflectance values of synthetic pašavaite were measured in air using an Ortholux Pol I (Leitz) equipped with a photomultiplier MPV–1 (Leitz) and a Veril S–200 transmission-interference filter (Leitz). A WTiC standard was used as a reference material. The reflectance data are given in Table 1. Figure 2 shows the reflectance curves of synthetic pašavaite compared to those of parkerite, $Ni_3(Bi,Pb)_2S_2$ (data from Criddle & Stanley 1993).

CHEMICAL DATA

Chemical analyses were performed on Cameca SX–100 electron microprobe using the wavelength-dispersion mode. The accelerating voltage was set to 15 keV, and the beam current was 10 nA. The samples were analyzed using Pd$L\alpha$, Pb$M\alpha$, and Te$L\alpha$. Pure metals (Pd, Te) and PbSe were used as primary standards. The spectra collected were processed by dedicated software using a ZAF type correction procedure. The results of analyses are given in Table 2. The empirical formula of pašavaite (based on seven atoms) is $Pd_{2.96}(Pb_{2.01}Bi_{0.01})Te_{2.02}$, and for synthetic pašavaite, $Pd_{2.99}Pb_{2.00}Te_{2.01}$.

CRYSTALLOGRAPHIC DATA

The small grain-size of natural material embedded in polarite prevented its extraction and investigations by means of X-ray diffraction. Therefore, the relevant crystallographic and structural investigations were performed on synthetic $Pd_3Pb_2Te_2$. Preliminary scanning-electron observations showed that the crystals of synthetic $Pd_3Pb_2Te_2$ are subhedral grains, with a typical size of grains up to 20 μm, rarely up to 40 μm. Our attempts (*e.g.*, long-term annealing in silica glass tube in the presence of KI flux, vapor transport using iodine as a transport agent) to prepare single crystals suitable for single-crystal X-ray-diffraction examinations failed. Thus, the crystal structure of $Pd_3Pb_2Te_2$ was solved and refined from the powder X-ray diffraction data *ab initio*.

The X-ray-diffraction pattern used for the structure determination was collected in Bragg–Brentano

TABLE 1. REFLECTANCE VALUES FOR SYNTHETIC PAŠAVAITE

λ	R_{max}	R_{min}	λ	R_{max}	R_{min}	λ	R_{max}	R_{min}
420	46.8	38.9	520	51.3	43.8	600	52.2	46.0
440	48.3	40.2	540	51.7	44.5	620	52.6	46.4
460	49.6	41.6	**546**	**51.8**	**44.6**	640	52.7	46.6
470	**49.9**	**42.4**	560	52.0	45.0	**650**	**52.8**	**46.9**
480	50.2	42.7	580	52.2	45.4	660	52.9	47.1
500	50.6	43.3	**589**	**52.2**	**45.7**	680	53.4	47.2
						700	53.7	47.4

The standard wavelengths (COM) are in bold. Values of λ are expressed in nm, whereas values of R_{max} and R_{min} are expressed in %.

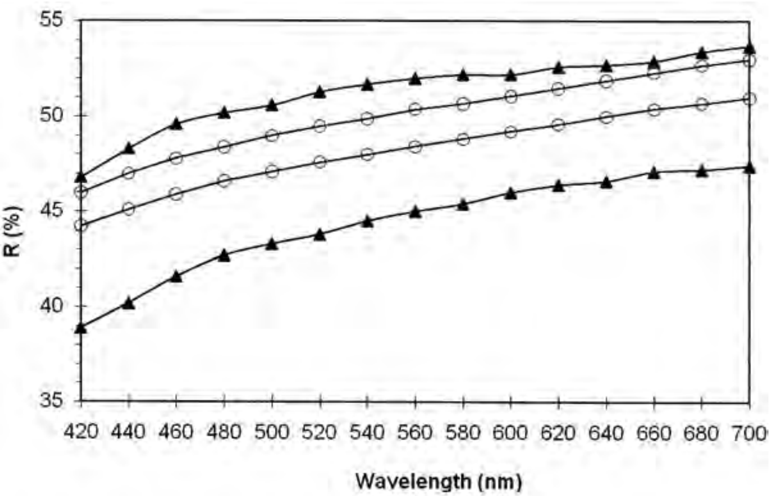

FIG. 2. Reflectance data for synthetic pašavaite (triangles) compared to parkerite (circles) in air (Criddle & Stanley 1993). The reflectance values (R %) are plotted *versus* wavelength λ in nm.

geometry on X’Pert Pro PANanalytical diffractometer, equipped with X’Celerator detector using Cu*K*α radiation. The data were collected in the range between 10 and 109° 2θ, a full width at half maximum of 0.078° in 2θ was obtained at 14.00° 2θ, indicating good crystallinity of the sample studied. The details of data collection and basic crystallographic data are given in Table 3.

The indexing of the X-ray powder pattern was performed using the DICVOL04 program (Boultif & Louër 2004). The first 20 lines, with the exception of two weak diffraction peaks attributable to PdTe as an impurity phase (*ca.* 3 wt.%, from results of the Rietveld analysis), were indexed on the basis of the orthorhombic cell with lattice parameters listed in Table 3. The figures of merit for assessing the quality of the solution were M_{20} = 95 (de Wolff 1968) and F_{20} = 125 (0.0043;68) (Smith & Snyder 1976). The systematic absences were found to be consistent with space groups *Pmmn* (No. 59) and $Pm2_1n$ (No. 31). The extraction of the integral intensities as well as the structure solution by direct methods were accomplished using the program EXPO04 (Altomare *et al.* 2004) for the two possible space-groups. After the background subtraction, the integral intensities were extracted with the Pearson VII profile function using the modified LeBail method.

TABLE 2. ELECTRON-MICROPROBE DATA FOR PAŠAVAITE AND SYNTHETIC $Pd_3Pb_2Te_2$

		Range		Std. dev.	standard
		Min	Max	σ	
		Natural material (*n* = 4)			
Pd wt.%	31.51	31.31	31.68	0.14	Pd metal
Pb	41.54	40.76	42.16	0.53	Pb metal
Bi	0.19	0.06	0.42	0.14	Bi_2Se_2
Te	25.75	25.61	26.10	0.20	Te metal
Total	98.99			0.46	
		Synthetic material (*n* = 7)			
Pd	32.17	31.77	32.42	0.24	Pd metal
Pb	41.78	41.40	42.16	0.24	Pb metal
Te	25.93	25.68	26.30	0.19	Te metal
Total	99.88			0.46	

TABLE 3. DATA COLLECTION AND RIETVELD ANALYSIS OF PAŠAVAITE

Data collection	
Radiation type, source	X radiation, Cu*K*α
Generator settings	40 kV, 30 mA
Range in 2θ (°)	10 - 109
Step size (°)	0.02
Crystal data	
Space group	*Pmmn* (No. 59)
Unit-cell content	$Pd_3Pb_2Te_2$, *Z* = 2
Unit-cell parameters (Å)	*a* 8.599(1), *b* 5.9381(6), *c* 6.3173(8)
Unit-cell volume (Å^3)	322.6(1)
Rietveld analysis	
No. of reflections	537
No. of structural parameters	10
No of. profile parameters	4
R_F	0.032
R_{Bragg}	0.037
R_p	0.055
R_{wp}	0.072
Weighting scheme	$1/y_o$

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

Two structural models found by EXPO04 in space groups *Pmmn* and $Pm2_1n$ were introduced into the FullProf program (Rodríguez-Carvajal 2006) for a Rietveld refinement. Although the refinement in the noncentrosymmetric space-group $Pm2_1n$ resulted in an acceptable agreement between observed and calculated intensities, it failed to reach convergence. Moreover, applying of PLATON ADDSYM program (Spek 1988, 2003) to identify missing elements of symmetry to this structure model (space group $Pm2_1n$) indicated that there is a center of inversion missing, and therefore the structure of this mineral should be better described in the centrosymmetric space-group *Pmmn*. Consequently, the Rietveld refinement was performed in the space group *Pmmn* with the pseudo-Voigt function; the background was determined by the linear interpolation between consecutive breakpoints in the pattern. The refined parameters include those describing the peak shape and width, peak asymmetry, unit-cell parameters, fractional coordinates preferred orientation along [001] and isotropic displacement parameters. Finally, 20 parameters were refined. The final cycles of refinement converged to the residual factors: $R_{Bragg} = 0.037$, $R_{wp} = 0.072$ and $R_p = 0.055$. The crystal-structure data are presented in Table 4, and the X-ray powder-diffraction data are listed in Table 5. The final Rietveld plot and the crystal structure are shown in Figures 3 and 4, respectively.

DESCRIPTION OF THE STRUCTURE

The unit cell of pašavaite contents two Pb positions (four atoms), one Te position (four atoms) and two Pd positions (six atoms). The crystal structure can be described as a layered structure formed by face-sharing $[PdPb_4Te_2]$ octahedra running parallel to the *b* axis. Two independent Pd atoms are surrounded by four Pb and two Te atoms showing distorted octahedral coordinations, with the Te atoms in *trans* positions with respect to one another. The Pd–Te and Pd–Pb

TABLE 4. POSITIONS AND ISOTROPIC DISPLACEMENT PARAMETERS OF ATOMS IN SYNTHETIC PAŠAVAITE

Atom	Wyckoff symbol	*x*	*y*	*z*	B_{iso} (Å^2)
Pb(1)	2*b*	¼	¾	0.8069(3)	0.64(3)
Pb(2)	2*a*	¼	¼	0.2571(3)	0.70(3)
Te(1)	4*f*	0.9558(3)	¼	0.6656(3)	0.49(4)
Pd(1)	2*a*	¼	¼	0.7826(4)	0.78(4)
Pd(2)	4*c*	0	0	0	0.65(4)

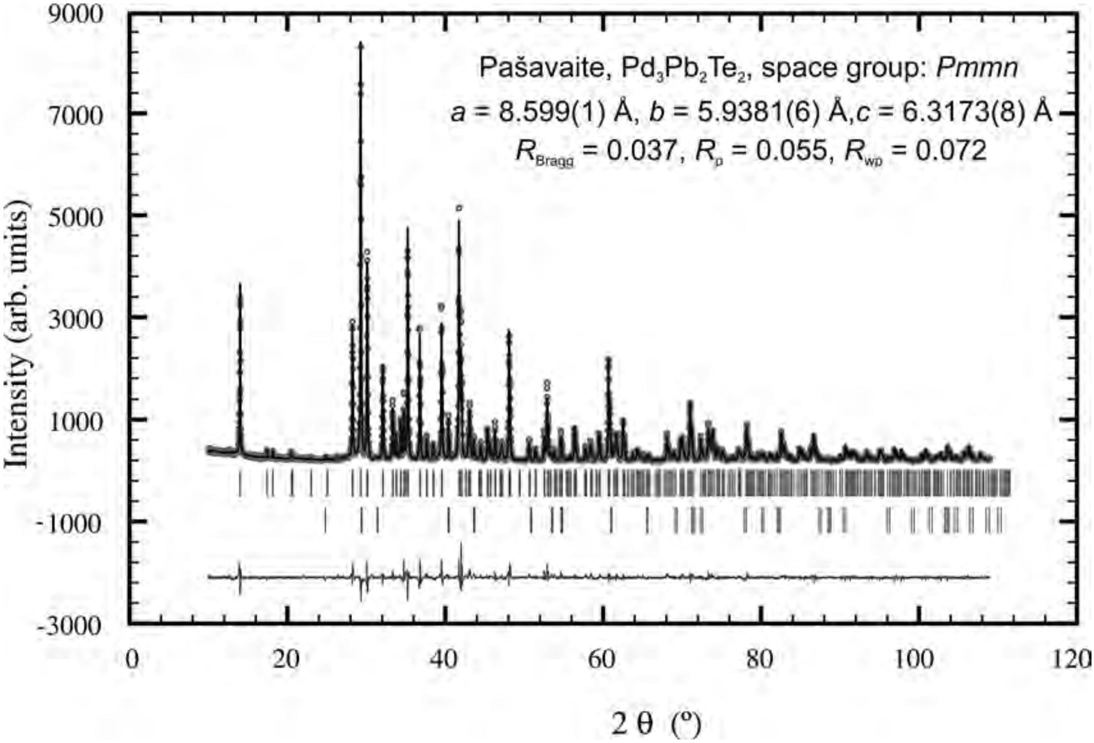

FIG. 3. The observed (circles), calculated (solid line) and difference Rietveld profiles for pašavaite. The upper reflections markers correspond to pašavaite, and the lower markers to a 3 mass percent PdTe impurity.

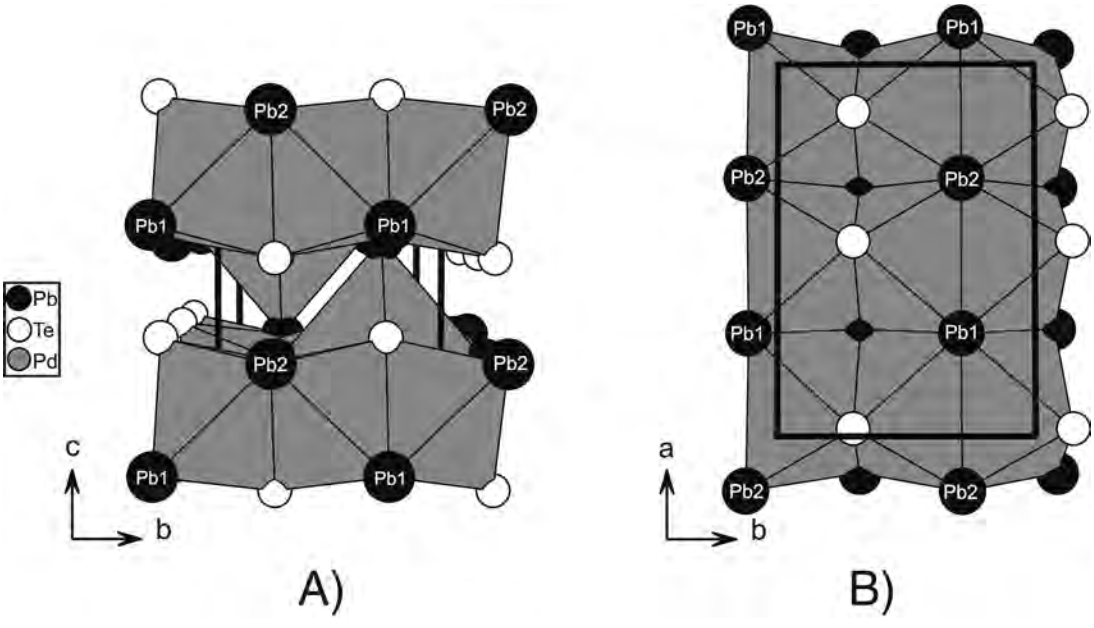

FIG. 4. Polyhedral representation of the pašavaite structure showing edge- and face-sharing octahedra [$PdPb_4Te_2$]. Projections onto (A) *c–b* and (B) *a–b* planes.

distances, 2.605(2)–2.635(1) Å and 2.883(1)–3.319(3) Å (Table 6), respectively, are comparable to those observed in $PdTe_2$ (Furuseth *et al.* 1965) and $Pd_{13}Pb_9$ (Mayer *et al.* 1980). Two independent Pb atoms are coordinated by six Pd atoms in two different ways (Fig. 5). In addition, these Pb atoms are surrounded by eight Te atoms at distances larger than 3.469(2) Å, showing distorted cubic coordination. A similar observation has been also made for $Ni_3Bi_2S_2$ by Baranov *et al.* (2001). An important feature found in the structure of pašavaite is the presence of *zig-zag* chains of palladium atoms running along the *a* axis, with a Pd–Pd distance of 2.951(1) Å. This distance is somewhat longer than the corresponding value observed in elemental palladium, 2.749 Å (King & Manchester 1978); however, it is short enough to indicate a certain degree of *d*-orbital interaction. In contrast, the shortest Te–Te and Pb–Pb distances in pašavaite, 3.539(1) and 4.111(2) Å, respectively, are fairly large, and these atoms therefore can be considered as nonbonded to each other. The crystal structure of pašavaite shows many structural similarities to the structure of shandite ($Ni_3Pb_2S_2$, $R\overline{3}m$) (Fleet 1973, Brower *et al.* 1974) and parkerite ($Ni_3Bi_2S_2$, $C2/m$) (Brower *et al.* 1974, Baranov *et al.* 2001). As has been mentioned by Natarajan *et al.* (1988, and references therein) for parkerite and shandite, all three structures show same basic structural unit: a pseudocubic subcell of the CsCl type (Cs = Pb or Bi, Cl = S or Te). The Ni (Pd) atoms occupy octahedral holes (face centers of ideal cube) in the cube of Pb (Bi) atoms centered by S (Te) atoms (Fig. 6). The nearest environment of Ni or Pd atoms is essentially equivalent in all structures. The major structural difference displayed by these three structures lies in the coordination of Ni (Pd) atoms around Pb (Bi) atoms. In all structures, Pb (Bi) atoms are surrounded by six Ni (Pd) atoms; in shandite, the Ni atoms form a distorted octahedron about the Pb(1) site and a planar hexagonal ring about Pb(2) site (Fleet 1973), whereas in parkerite and pašavaite, the corresponding coordination polyhedra are quite a bit more distorted, and thus non-planar.

TABLE 5. X-RAY POWDER-DIFFRACTION DATA FOR SYNTHETIC PAŠAVAITE

I_{calc}	I_{obs}	d_{calc}	d_{obs}	h	k	l	I_{calc}	I_{obs}	d_{calc}	d_{obs}	h	k	l
33	34	6.3173	6.3152	0	0	1	9	10	1.9988	1.9986	3	1	2
2	2	5.0911	5.0919	1	0	1	5	5	1.9847	1.9844	0	1	3
1	1	4.8863	4.8831	1	1	0	9	9	1.9604	1.9604	3	2	1
1	1	4.3267	4.3240	0	1	1	4	4	1.9252	1.9256	4	1	1
32	**33**	**3.1587**	**3.1572**	**0**	**0**	**2**	**39**	**42**	**1.8911**	**1.8906**	**2**	**0**	**3**
100	**100**	**3.0498**	**3.0495**	**2**	**1**	**1**	6	7	1.8020	1.8018	2	1	3
24	24	2.9650	2.9683	1	0	2	7	7	1.7413	1.7411	4	2	0
24	24	2.7887	2.7875	0	1	2	19	21	1.7293	1.7292	2	3	1
13	14	2.6871	2.6868	0	2	1	10	10	1.6317	1.6318	3	1	3
6	7	2.6527	2.6518	1	1	2	4	4	1.5951	1.5953	2	2	3
10	10	2.6102	2.6106	3	0	1	5	5	1.5793	1.5792	0	0	4
13	14	2.5814	2.5812	3	1	0	8	8	1.5533	1.5532	1	0	4
61	63	2.5456	2.5456	2	0	2	**30**	**31**	**1.5249**	**1.5248**	**4**	**2**	**2**
34	**34**	**2.4431**	**2.4424**	**2**	**2**	**0**	13	13	1.4845	1.4843	0	4	0
5	6	2.3896	2.3892	3	1	1	8	10	1.3764	1.3763	1	2	4
4	4	2.3396	2.3391	2	1	2	6	6	1.3462	1.3461	5	2	2
37	**42**	**2.2787**	**2.2786**	**2**	**2**	**1**	19	20	1.3263	1.3263	2	2	4
67	**71**	**2.1634**	**2.1637**	**0**	**2**	**2**	10	11	1.2824	1.2823	2	4	2
28	**30**	**2.1498**	**2.1496**	**4**	**0**	**0**	9	10	1.2216	1.2214	4	4	0
6	7	2.1058	2.1056	0	0	3	10	8	1.1677	1.7673	2	4	3
12	14	2.0980	2.0979	1	2	2	5	4	1.1264	1.1262	2	5	1
4	5	2.0352	2.0349	4	0	1	7	6	0.9802	0.9798	6	4	2

PROOF OF STRUCTURAL IDENTITY OF NATURAL AND SYNTHETIC PAŠAVAITE

The structural identity of synthetic $Pd_3Pb_2Te_2$ and natural material was confirmed by results of the electron back-scattering diffraction (EBSD) study. The CamScan CS 3200 scanning electron microscope combined with EBSD system NORDLYS II by HKL Technology, Denmark, was used for the purpose of this study. The natural sample was prepared for investigation by etching the mechanically polished surface with colloidal silica (OP–U) for 30 minutes to reduce the

TABLE 6. SELECTED BOND-LENGTHS (Å) IN SYNTHETIC PAŠAVAITE

Pb(1) –	Pd(2)	× 4	2.883(1)	Pb(2) –	Pd(1)		2.997(2)
	Pd(1)	× 2	2.9728(2)		Pd(2)	× 4	3.075(1)
					Pd(1)		3.319(2)
Pd(1) –	Te(1)	× 2	2.635(1)	Pd(2) –	Te(1)	× 2	2.605(2)
	Pd(2)	× 4	2.951(1)		Pb(1)	× 2	2.883(1)
	Pb(1)	× 2	2.9728(2)		Pd(1)	× 2	2.951(1)
	Pb(2)		2.997(2)		Pd(2)	× 2	2.9688(3)
	Pb(2)		3.319(3)		Pb(2)	× 2	3.075(1)

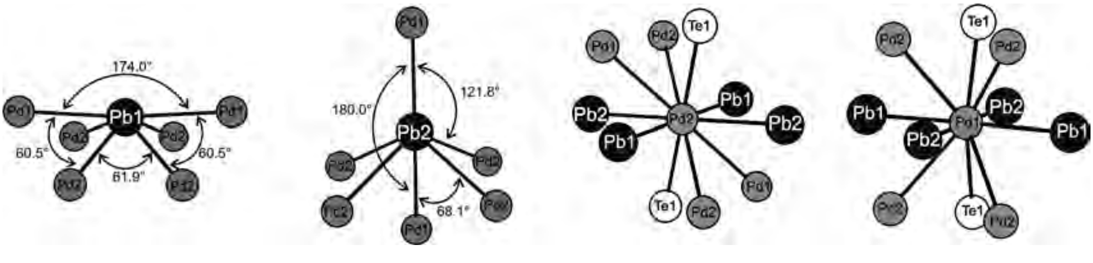

FIG. 5. Coordination of Pb and Pd atoms in the structure of pašavaite.

extent of surface damage. The EBSD patterns were collected and processed using the software CHANNEL 5 provided by HKL Technology (2004). The center of six Kikuchi bands was automatically detected using the Hough transform routine (Schmidt *et al.* 1991) with a resolution of 100 (internal Hough resolution parameter in the HKL software). The solid angles calculated from the patterns were compared with a synthetic $Pd_3Pb_2Te_2$ match containing 80 reflections to index the patterns. The EBSD patterns (also known as Kikuchi patterns) obtained from the natural material (eight measurements from different natural grains of pašavaite) were found to match the patterns generated from the structure of synthetic $Pd_3Pd_2Te_2$ (Fig. 7). The values of the mean angular deviation (MAD, *i.e.*, goodness of fit of the solution) between the calculated and measured Kikuchi bands range between 0.269° and 0.808°. These values reveal a very good match; as long as values of the mean angular deviation are less than 1%, they are considered as indicators of an acceptable fit (HKL Technology, 2004).

The EBSD study and chemical identity support the identity of the natural and synthetic materials, and consequently render legitimate the use of the synthetic phase for the complete characterization of pašavaite. However, it should be noted that in general, the positive match obtained with EBSD is not a conclusive proof of structural identity, since EBSD cannot necessarily

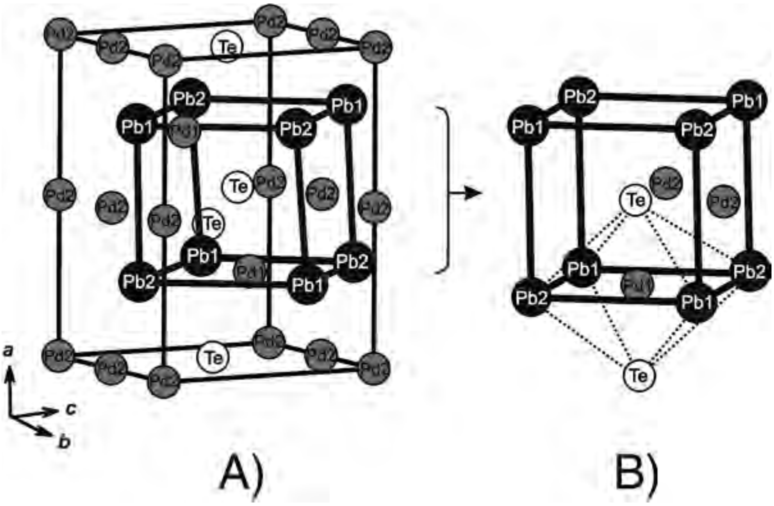

FIG. 6. Two views of basic structural unit of pašavaite structure showing the CsCl type of sublattice formed by Pb and Te atoms and the octahedral coordination of Pd atoms: (A) position in pašavaite unit cell, (B) idealized drawing.

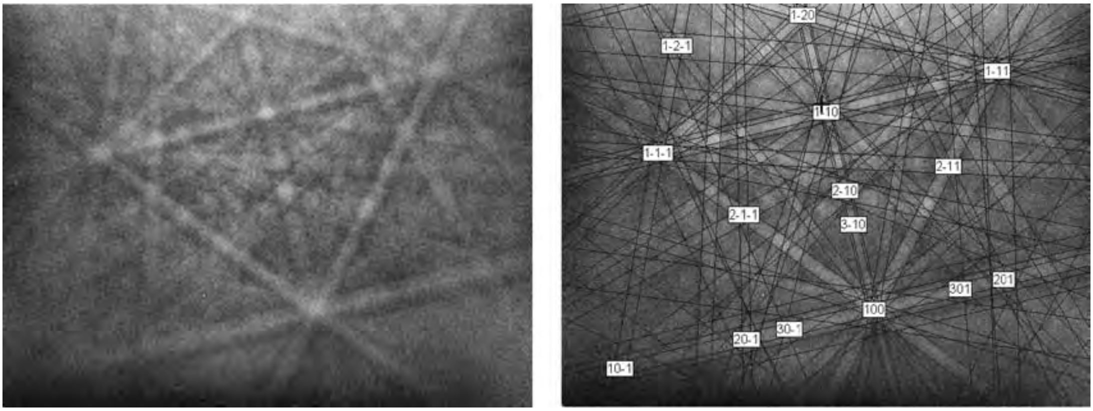

FIG. 7. EBSD image of natural pašavaite; in the right pane, the Kikuchi bands are indexed.

distinguish between closely similar structures that differ in a few reflectors observable in specific orientations only. Nevertheless, the positive match between eight calculated and measured patterns collected on different natural grains in mutually different orientations seems to provide a solid base for identification in this case.

ACKNOWLEDGEMENTS

The authors are most grateful to Luděk Kráčmar for providing the material, to Ivan Vavřín for his constructive comments, and to František Veselovký for density measurement. This work was supported by internal projects of the Czech Geological Survey (3240, 3230 and 3323), and by a grant from the Ministry of Culture of the Czech Republic (MK00002327201). The comments of Emil Makovicky, Louis J. Cabri and Associate Editor Werner H. Paar are appreciated. They helped to improve the manuscript. The editorial care of Robert F. Martin is especially acknowledged.

REFERENCES

ALTOMARE, A., CALIANDRO, R., CAMALLI, M., CUOCCI, C., GIACOVAZZO, C., MOLITERNI, A.G.G. & RIZZI, R. (2004): Automatic structure determination from powder data with EXPO2004. *J. Appl. Crystallogr.* **37**, 1025-1028.

BARANOV, A.I., OLENEV, A.V. & POPOVKIN, B.A. (2001): Crystal and electronic structure of $Ni_3Bi_2S_2$ (parkerite). *Russ. Chem. Bull.* **50**, 353-358.

BOULTIF, A. & LOUËR, D. (2004): Powder pattern indexing with the dichotomy method. *J. Appl. Crystallogr.* **37**, 724-731.

BROWER, W.S., PARKER, H.S. & ROTH, R.S. (1974): Reexamination of synthetic parkerite and shandite. *Am. Mineral.* **59**, 296-301.

CRIDDLE, A.J. & STANLEY, C.J. (1993): *Quantitative Data File for Ore Minerals* (3rd ed.). Chapman & Hall, London, U.K.

CZAMANSKE, G.K ., KUNILOV, V.Y., ZIENTEK, M.L., CABRI, L.J., LIKHACHEV, A.P., CALK, L.C. & OSCARSON, R.L. (1992): A proton-microproprobe study of magmatic sulfide ores from the Noril'sk–Talnakh district, Siberia. *Can. Mineral.* **30**, 249-287.

DE WOLFF, P.M. (1968): A simplified criterion for reliability of a powder pattern indexing. *J. Appl. Crystallogr.* **1**, 108-113.

FLEET, M.E. (1973): The crystal structure of parkerite ($Ni_3Bi_2S_2$). *Am. Mineral.* **58**, 435-439.

FURUSETH, S., SELTE, K. & KJEKSHUS, A. (1965): Redetermined crystal structures of $NiTe_2$, $PdTe_2$, PtS_2, $PtSe_2$. *Acta Chem. Scand.* **19**, 257-258.

GENKIN, A.D., DISTLER, V.V., GLADYSHEV, G.D., FILIMONOVA, A.A., EVSTIGNEEVA, T.L., KOVALENKER, V.A., LAPUTINA, I.P., SMIRNOV, A.B. & GROKHOVSKAYA, T.L. (1981): *Sulphide nickel–copper ores of the Norilsk deposits*. Nauka, Moscow, Russia (in Russ.).

GENKIN, A.D. & EVSTIGNEEVA, T.L. (1986): Associations of platinum-group minerals of the Norilsk copper–nickel sulfide ores. *Econ. Geol.* **81**, 1203-1212.

HKL TECHNOLOGY (2004): CHANNEL 5. HKL Technology A/S, Hobro, Denmark.

KING, H.W. & MANCHESTER, F.D. (1978): Low-temperature X-ray diffraction study of Pd and some Pd–H alloys. *J. Phys. F - Metal Physics* **8**, 15-26.

KOVALENKER V.A., LAPUTINA I.P., VYAL'SOV, L.N., GENKIN, A.D. & ESVTIGNEEVA T.L. (1972): Tellurium minerals in copper–nickel sulfide ores at Talnakh and Oktyabr` (Noril'sk district). *Int. Geol. Rev.* **15**, 1284-1294.

KULLERUD, G. (1971): Experimental techniques in dry sulfide research. *In* Research Techniques for High Pressure and High Temperature (G.C. Ulmer, ed.). Springer-Verlag, New York, N.Y. (288-315).

LAUFEK, F., DRÁBEK, M., SKÁLA, R., HALODA, J., TÁBORSKÝ, Z. & CÍSAŘOVÁ, I. (2007): Vavřínite, Ni_2SbTe_2, a new mineral species from Kunratice Cu–Ni sulfide deposit, Czech Republic. *Can. Mineral.* **45**, 1213-1219.

MAYER, H.W., ELLNER, M. & SCHUBERT, K. (1980): Crystal structure of $Pd_{13}Pb_9$. *J. Less-Common Metals* **71**, P29-P38.

MCCUSKER, L.B., VON DREELE, R.B., COX, D.E., LOUËR, D. & SCARDI, P. (1999): Rietveld refinement guidelines. *J. Appl. Crystallogr.* **32**, 36-50.

NALDRETT, A.J., LIGHTFOOT, P.C., FEDORENKO, V., DOHERTY, W. & GORBACHEV, N.S. (1992): Geology and geochemistry of intrusions and flood basalts of the Noril'sk region, USSR, with implications for the origin of the Ni–Cu ores. *Econ. Geol.* **87**, 975-1004.

NATARAJAN, S., SUBBA RAO, G.V., BASKARAN, R. & RADHAKRISHNAN, T.S. (1988): Synthesis and electrical properties of shandite–parkerite phases, $A_3M_2Ch_2$. *J. Less-Common Metals* **138**, 215-224.

PAAR, W.H., TOPA, D., MAKOVICKY, E. & CULETTO, F.J. (2005): Milotaite, PdSbSe, a new palladium mineral species from Předbořice, Czech Republic. *Can. Mineral.* **43**, 689-694.

RODRÍGUEZ-CARVAJAL, J. (2006): FULLPROF.2K Rietveld profile matching & integrated intensities refinement of X-ray and/or neutron data (powder and/or single-crystal). Laboratoire Léon Brillouin, Centre d'Etudes de Saclay, Gif-sur-Yvette Cedex, France.

SCHMIDT, N.H., BILDESORENSEN, J.B. & JENSEN, D.J. (1991): Band positions used for online crystallographic orientation determination from electron back scattering patterns. *Scanning Microsc.* **5**, 637-643.

SMITH, G.S. & SNYDER, R.L. (1976): F_N: a criterion for rating powder diffraction patterns and evaluating the reliability of powder-pattern indexing. *J. Appl. Crystallogr.* **12**, 60-65.

SPEK, A.L. (1988): LEPAGE – an MS–DOS program for the determination of the metrical symmetry of a translation lattice. *J. Appl. Crystallogr.* **21**, 578-579.

SPEK, A.L. (2003): Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.* **36**, 7-13.

Received April 16, 2008, revised manuscript accepted January 12, 2009.