Raman spectroscopy characterisation of synthetic platinum-group minerals (PGM) in the Pd–Sn–Te and Pd–Pb–Te ternary systems

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Abstract: The identification of minerals that occur as tiny and rare phases such as most of the natural platinum-group minerals (PGM) is a challenging target. The main reason for that resides in their size (generally less than 10 micrometres) and mode of occurrence (*i.e.* polyphasic aggregates) that make problematic the identification by standard X-ray diffraction methods. In this contribution we have applied the Raman spectroscopy to synthetic PGM in the ternary systems Pd–Sn–Te and Pd–Pb–Te. Some of the analyzed PGM show characteristic Raman bands and the following PGM can be distinguished using the Raman spectroscopy: merenskyite, kotulskite, kojonenite, pašavaite and Pd_3Te_2. Other PGM in the ternary Pd–Sn–Te and Pd–Pb–Te systems cannot be identified using this technique. These results demonstrate that Raman spectroscopy can be considered as an innovative and complementary methodology with a potential to identify and to better characterize the PGM.

Key-words: platinum group minerals (PGM); tellurides; Pd–Sn–Te system; Pd–Pb–Te system; Raman spectra.

1. Introduction

The platinum-group elements (Os, Ir, Ru, Rh, Pt and Pd) are internationally known with the acronym PGE. They are considered exceptionally rare elements, due to their low amount in the Earth crust. As a result, data available are very scarce due to the difficulty to obtain reliable whole-rock analyses for elements that occur as ultra-trace. However, according to Park *et al.* (2012), the average concentrations of PGE, except Os, in the upper continental crust (in ppb) are the following: Ir = 0.023, Ru = 0.03, Rh = 0.018, Pt = 0.751, Pd = 0.546. The PGE are also considered strategic metals because they have gained tremendous economic importance due to their application in many modern and advanced technologies. The PGE are carried by the so called platinum-group minerals (PGM). They are rare in nature, and up to now, only 128 PGM have been officially approved as new mineral species. However, Daltry & Wilson (1997) have shown that more than 500 PGM are still waiting for a clear identification, in particular for crystallographic characterization to the degree required for acceptance as new mineral species. The main reason for the significant lack of sufficient identification of PGM is their mode of occurrence, *i.e.* as minute phases, often less than 10 μm in size (Fig. 1), and frequently characterized by complex intergrowths. Optical and electron microscopy, and electron-microprobe analyses are the

most used techniques for chemical and physical identification of PGM. However, PGM are difficult to identify during petrographic investigation owing to their small sizes and the similarity of the optical properties of many minerals. Furthermore, where the PGM are only a few micrometres in size, the electron microprobe generally provides only semi-quantitative analyses due interferences from surrounding minerals. The small size of natural PGM grains does also not allow identification with standard X-ray diffraction (XRD) methods. Identification of mineral micrograins requires rather complex techniques such as X-ray microdiffraction, SEM-based electron back-scatter diffraction (EBSD), or TEM-based electron diffraction. We propose here Raman spectroscopy as a convenient alternative/complementary method. Raman spectroscopy is a non destructive and structurally sensitive technique that can be easily used to identify small mineral phases less than 10 μm in size, such as the PGM. However, after the pioneer work of Mernagh & Hoatson (1995), few data have been published on the application of Raman technique to recognize the natural PGM (Zaccarini *et al.*, 2009, 2010; McDonald *et al.*, 2010; Grammatikopoulos *et al.*, 2011; Vymazalová *et al.*, 2012) as well as to investigate synthetic PGM (*e.g.* Weber *et al.*, 1988; Graham *et al.*, 1991; Merkle *et al.*, 1997; Pikl *et al.*, 1999; Vermaak *et al.*, 2007). Therefore, the Raman spectra available on PGM are still scarce. The aim of this study is to provide, for the first time,
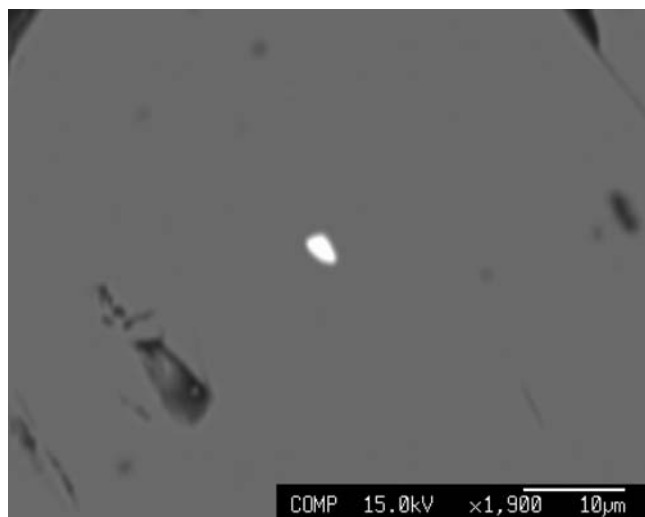
Fig. 1. Backscattered-electron image showing a natural merenskyite crystal included in pyrrhotite.

the Raman spectra obtained on synthetic PGE phases described in the ternary systems Pd–Sn–Te (Vymazalová *et al*., 2010a and b) and Pd–Pb–Te (Vymazalová & Drábek, 2011) (Fig. 2). Some of the studied synthetic PGM correspond to the minerals zvyagintsevite (Pd_3Pb), pašavaite ($Pd_3Pb_2Te_2$), kojonenite ($Pd_{7-x}SnTe_2$), telluro-palladinite (Pd_9Te_4), kotulskite (PdTe), merenskyite ($PdTe_2$), atokite (Pd_3Sn) and paolovite (Pd_2Sn).

2. Materials and methods

The studied PGE phases were synthesized in the Experimental Laboratory of the Czech Geological Survey (Prague). The evacuated silica-glass tube technique was used for the synthesis. Charges were weighed out from native elements. Experimental charges were first melted at 1200°C for 3 days, afterwards ground in an agate mortar under acetone, and reheated to 400°C for several weeks to months (Vymazalová *et al*., 2010a and b, 2011).

Phases investigated in this contribution are illustrated in the ternary diagrams of Fig. 2. The homogeneity of the grains selected for the Raman investigation was checked using a Jeol JXA 8200 Superprobe installed at the Eugen F. Stumpfl laboratory at the Montanuniversity Leoben (Austria). The Raman spectra were conducted on the same area analyzed by electron microprobe. The same instrument was used to obtain electronic image of the PGM as illustrated in Fig. 1. Raman spectra were collected using a LABRAM (ISA Jobin Yvon) instrument at the Montanuniversity Leoben. A frequency-doubled 100 mW Nd-YAG laser with an excitation wavelength of $\lambda = 532.068$ nm was used. The laser power at the sample surface is about 1 to 2 mW. Both notch-filter (532 nm, blocking relative wavenumbers below 170 cm^{-1}) and edge-filter (532 nm, blocking relative wavenumbers below 80 cm^{-1}) were used to suppress Rayleigh scattering and anti-Stokes scattering. Measurements were carried out with an LMPlanFI 100x/0.8 (Olympus) objective lens and they have a spectral resolution of 1.62 cm^{-1} at low Δv (about 0 cm^{-1}) and of 1.1 cm^{-1} at high Δv (about 3000 cm^{-1}). Additional neutral filters with variable optical densities were used to decrease the laser power to prevent damage or transformation of the samples. Simultaneously measured neon emission lines were used for calibration. The investigated crystals were embedded in round epoxy plugs that were highly polished to obtain a flat surface without any traces of oxidation. The size of the crystals varies between 50 and 200 μm in length.
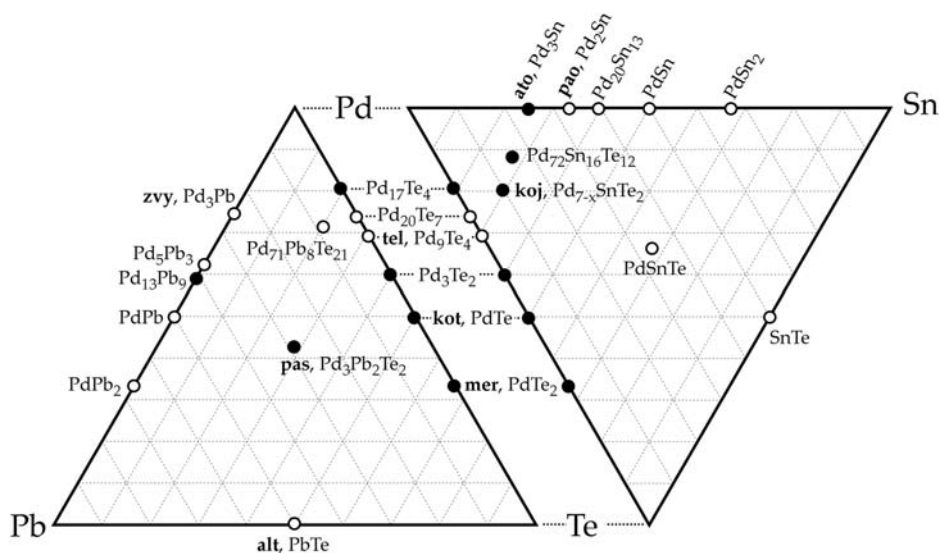

Fig. 2. Compositional diagrams of the ternary systems Pd–Pb–Te and Pd–Sn–Te, with synthetic and natural PGM phases. Mineral names are only available for part of these phases: **zvy** = zvyagintsevite; **pas** = pašavaite; **tel** = telluropalladinite; **kot** = kotulskite; **mer** = merenskyite; **ato** = atokite; **pao** = paolovite; **koj** = kojonenite. This study contains Raman spectra of the phases shown with a solid symbol.

3. Results

The minerals synthesized in the Pd–Pb–Te and Pd–Sn–Te ternary systems have relatively weak Raman signals. Most of them have a broad band between 400 and 1100 cm^{-1}, which can be assigned to various deconvolved Gaussian-Lorentzian distribution curves (Fig. 3). Deconvolution with six distribution curves is determined by the minimum number of best-fit curves that describe accurately the obtained spectrum. The best-fit curves are not associated with specific theoretical vibration and rotation modes of the material, or interference patterns. These curves are centred at about 380, 465, 570, 792, 984, and 1091 cm^{-1}, with relatively large full width at half maximum (*FWHM*) varying between 25 and 180 cm^{-1} (Fig. 3). The uncertainty in the centre positions is about 20 cm^{-1}. This value was automatically calculated by the PeakFitTM 4.11 software. The Raman spectra in the binary Pd–Te sub-system (PdTe, Pd_3Te_2, $PdTe_2$, $Pd_{17}Te_4$), the binary Pd–Sn sub-system (Pd_3Sn, $Pd_{20}Sn_{13}$), and the binary Pd–Pb sub-system (Pd_5Pb_3 and $Pd_{13}Pb_9$) reveal the same pattern in the range of 400 to 1100 cm^{-1} (Fig. 3 and 4). Therefore, the characteristics of these Raman spectra cannot be used to identify specific phases within these systems (*cf*. Figs. 3 and 4). However, at lower relative wavenumbers, the

spectra of PdTe (kotulskite), $PdTe_2$ (merenskyite) and Pd_3Te_2 are significantly different, and consist of relatively narrow bands at about 97, 132, and 124 cm^{-1}, respectively (Fig. 5, Table 1). The phase PbTe (altaite) is Raman inactive, and does not reveal a spectrum in the range of 80 to 1600 cm^{-1} (Fig. 6).

Phases consisting of three components in both ternary systems reveal a larger variability in Raman spectra. Pašavaite ($Pd_3Pb_2Te_2$) does not reveal any broad Raman bands in the range of 400 to 1100 cm^{-1}, but its spectrum contains two relatively narrow peaks at 119 and 159 cm^{-1} (Fig. 6, Table 1). The Raman spectrum of kojonenite ($Pd_{7-x}SnTe_2$) consists of a band at 197 cm^{-1}, with a *FWHM* of about 10 cm^{-1} (Fig. 7a, Table 1). In contrast, $Pd_{72}Sn_{16}Te_{12}$ only reveals the broad bands between 400 and 1100 cm^{-1} (Fig. 7b), similar to spectra illustrated in Figs. 3 and 4. Therefore, this spectrum cannot be used to identify $Pd_{72}Sn_{16}Te_{12}$ with Raman spectroscopy.

4. Discussion

To the best of our knowledge, the Raman spectra available for PGM are very limited. In particular, the following Os, Ir, Ru, Rh and Pt bearing minerals have been previously
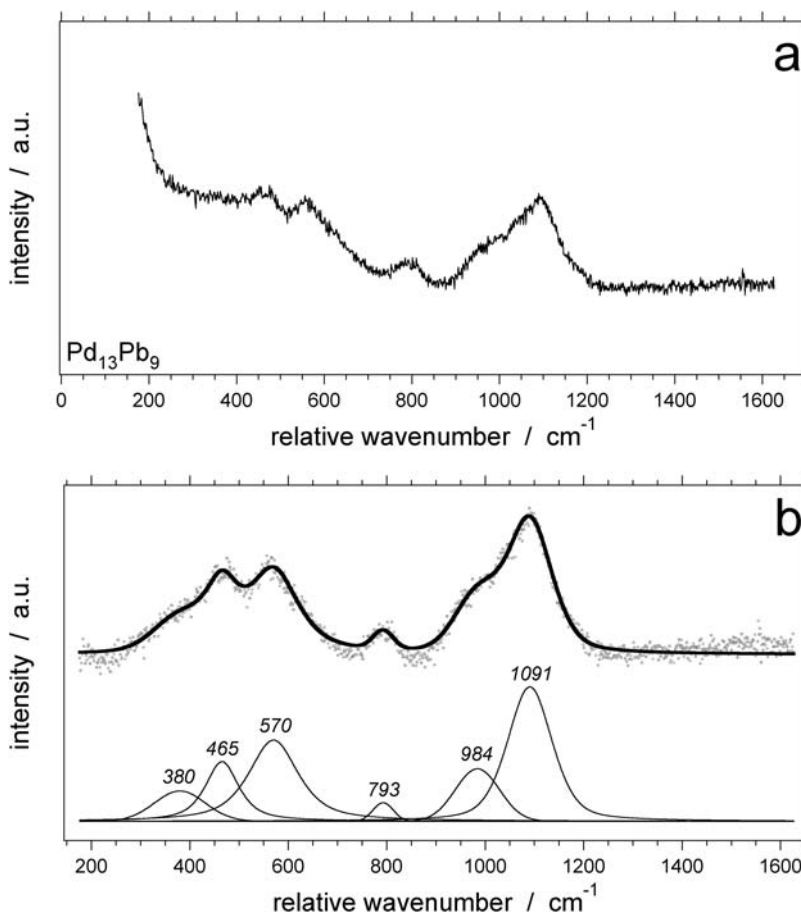

Fig. 3. (a) Raman spectrum of $Pd_{13}Pb_9$; (b) deconvolution of this Raman spectrum after background subtraction with six best-fit Gaussian-Lorentzian distribution curves; numbers in diagram indicate the centre position of distribution curves. The software Peakfit (2002, version 4.11) was used to deconvolve this spectrum.
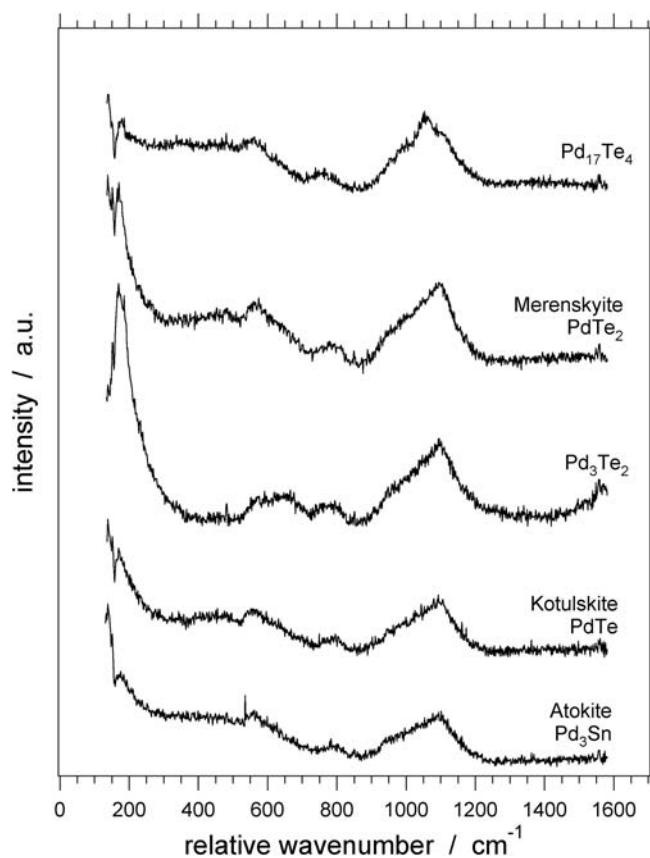
Fig. 4. Comparison of Raman spectra in the Pd–Te and Pd–Sn binary systems.
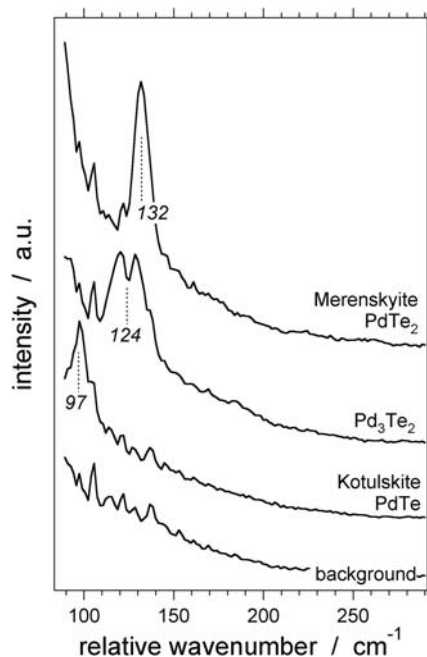

Fig. 5. Details of the Raman spectra of PdTe$_2$ (merenskyite), Pd$_3$Te$_2$, and PdTe (kotulskite) in the range of 90 to 290 cm^{-1}.

Table 1. Raman peak positions (in relative wavenumber, Δv) of the PGM in the ternary systems Pd–Pb–Te and Pd–Sn–Te that are significantly Raman active and reveal a peak signal with relatively narrow *FWHM*.

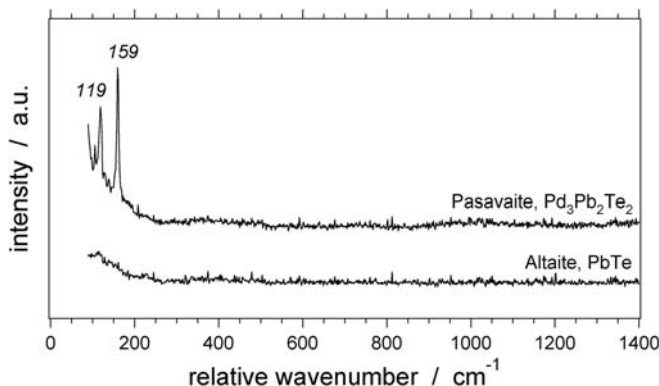| PGM	Δv
PdTe (kotulskite)	97
Pd$_3$Te$_2$	124
PdTe$_2$ (merenskyite)	132
Pd$_{7-x}$SnTe$_2$ (kojonenite)	197
Pd$_3$Pb$_2$Te$_2$ (pašavaite)	119
	159

Fig. 6. Raman spectra of Pd$_3$Pb$_2$Te$_2$ (pašavaite) and PdPb (altaite).

sperrylite (PtAs$_2$), platarsite (PtAsS), moncheite ((Pt,Pd)(Te,Bi)$_2$) and braggite (Pt,Pd,Ni)S (Mernagh & Hoatson, 1995; Merkle *et al.*, 1997; Pikl *et al.*, 1999; Zaccarini *et al.*, 2009, 2010; Vymazalová *et al.*, 2012). Despite of the fact that the majority of PGM are Pd-dominant, only Raman spectra of vysotskite (PdS) and potarite (PdHg) have been provided (Mernagh & Hoatson, 1995; Merkle *et al.*, 1999). However, the data of potarite are controversial. According to Mernagh & Hoatson (1995) potarite displays a distinctive band; however, repeated (unpublished) analyses by the authors on potarite from different natural occurrences had shown that it is not Raman sensitive.

The data presented in this contribution obtained on synthetic palladium (tin/lead) tellurides indicate that some of these phases are Raman sensitive and their spectra are different from those previously reported for other PGM. In particular, the following PGM show characteristic absorption bands that can be used to distinguish them: merenskyite (PdTe$_2$), kotulskite (PdTe), pašavaite (Pd$_3$Pb$_2$Te$_2$), kojonenite (Pd$_{7-x}$SnTe$_2$), and the phase Pd$_3$Te$_2$ (Table 1). However, Figure 4 shows a close similarity of the spectra obtained on different phases such as the synthetic equivalent of kotulskite (PdTe), merenskyite (PdTe$_2$) and atokite (Pd$_3$Sn). Since the homogeneity of the studied grains was carefully investigated by electron-microprobe analyses, we are sure that no more than one phase was analyzed simultaneously. Therefore we can argue that the Raman spectra of these PGM are not controlled by their structure,
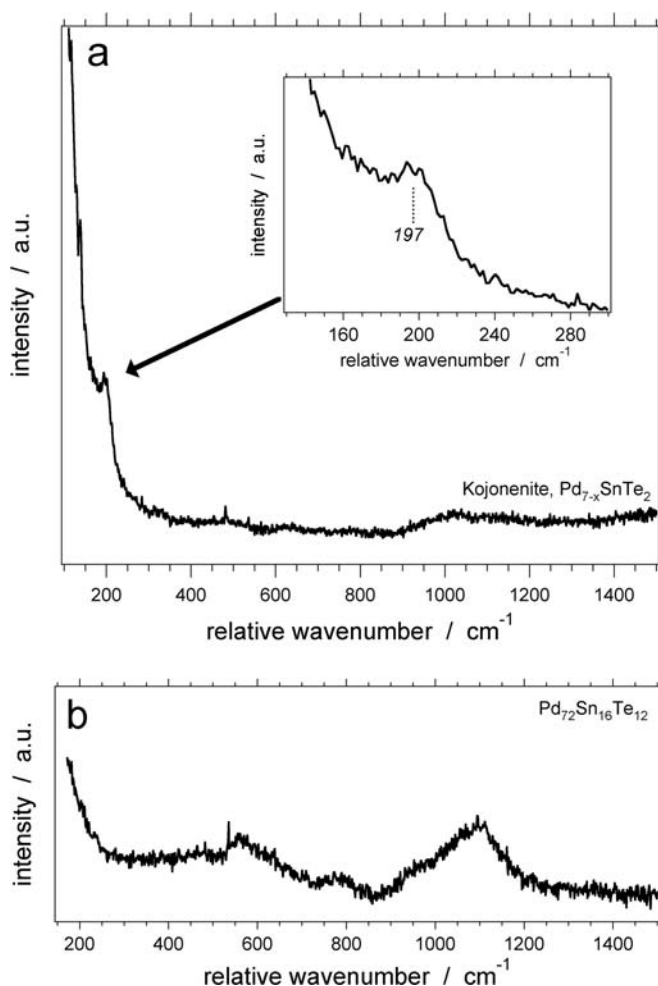
investigated by Raman and proved to be sensitive to this technique: erlichmanite (OsS$_2$), irarsite (IrAsS), laurite (RuS$_2$), zaccariniite (RhNiAs), cooperite ((Pt,Pd,Ni)S),

Fig. 7. (a) Raman spectrum of $Pd_{7-x}SnTe_2$ (kojonenite), with detail in the range 130 to 300 cm^{-1}; (b) Raman spectrum of $Pd_{72}Sn_{16}Te_{12}$ with a similar pattern in the range 400 to 1100 cm^{-1} as illustrated in Figures 3 and 4.

since kotulskite (PdTe) is hexagonal, merenskyite ($PdTe_2$) is trigonal, and atokite (Pd_3Sn) is cubic. This observation may suggest that, in the PGM studied in this work, the chemical bonds are responsible for the observed Raman spectra, as already observed for other PGM. In particular, Zaccarini *et al.* (2010, 2011) have shown that some natural PGM such as sulphides, arsenides and sulpharsenides display a very well defined and characteristic Raman spectrum, as typical for the compounds characterized by the presence of covalent bonding. On the contrary, the Raman spectra of a number of natural PGE alloys and native elements show no discernible scattering bands, suggesting that the bonds present in these PGM have a dominant metallic nature.

5. Concluding remarks

The results presented in this contribution confirm that Raman spectroscopy can be considered as an innovative technique with a potential to better characterize and identify rare and tiny phases such as PGM that occur in natural rocks.

The Raman spectra obtained on synthetic PGM such as merenskyite ($PdTe_2$), kotulskite (PdTe), pašavaite ($Pd_3Pb_2Te_2$), phase Pd_3Te_2 and kojonenite ($Pd_{7-x}SnTe_2$) can be used as standards for the identification of the natural equivalent.

Caution is warranted in using the Raman spectra of merenskyite ($PdTe_2$), kotulskite (PdTe) and phase Pd_3Te_2 because of their similarity in the pattern region comprised between 400 and 1100 cm^{-1}. However, at lower relative wavenumbers, the spectra of PdTe (kotulskite) and $PdTe_2$ (merenskyite) differ, showing narrow bands at about 97 and 132 cm^{-1}, respectively.

Other PGM in the ternary Pd–Sn–Te and Pd–Pb–Te systems cannot be identified by Raman spectroscopy. In particular the synthetic PGM corresponding to the natural minerals zvyagintsevite (Pd_3Pb), telluropalladinite (Pd_9Te_4) and paolovite (Pd_2Sn) proved to be Raman inactive.

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