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Raman spectra of synthetic 'braggite', (Pd,Pt,Ni)S

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ABSTRACT

Raman spectra of synthetic 'braggite' ((Pd,Pt,Ni)S) vary systematically with changes in Pt/Pd ratios, but this change is less pronounced than in 'cooperite' ((Pt,Pd,Ni)S). Compared to 'vysotskite' (ideally PdS), the incorporation of Pt leads to broadening of bands but the spectra of 'vysotskite' and 'braggite' are similar, and spectra of 'cooperite' and the 'braggite/vysotskite' solid-solution series are sufficiently different to facilitate distinction of these platinum group minerals by Raman spectroscopy.

Keywords: Raman spectroscopy, braggite, mineral chemistry, platinum group minerals.

Introduction

The Laser-Raman microprobe technique is an emerging tool in the identification of small platinum-group minerals (PGM) (Mernagh and Hoatson, 1995; Merkle *et al.*, 1997), especially in cases where the notoriously small PGM grains are difficult to identify during petrographic studies. Even micro-analytical techniques do not always allow a positive identification due to structural differences of minerals with very similar, or overlapping, compositions. In addition, solid solution ranges are temperature dependent and can overlap, as is the case with the Pt-Pd±Ni-S minerals cooperite and braggite (Skinner *et al.*, 1976; Cabri *et al.*, 1978). Synthetic 'cooperite' was shown to display systematic changes in the Raman spectra as a function of composition (Merkle *et al.*, 1997) and a similar effect was expected for synthetic 'braggite'; braggite displays a much wider range of compositional variation in nature than cooperite (Merkle and Verryn, 1991; Verryn and Merkle, 1994).

Compositional variation and source of material

The material used for this investigation is synthetic 'braggite' with variable Pt/Pd ratios (atomic ratios between 0.31 and 1.37) and saturated in Ni (up to 1.99 at.%) under the experimental conditions described below. A comparison is made with pure synthetic PdS, which can be seen as the extreme Pd-rich end of the solid-solution range.

Experimental procedures

The synthetic 'braggite' was obtained following standard procedures under dry conditions in evacuated quartz-glass capsules (Kullerud, 1971; Moh and Taylor, 1971). Charges of 200–300 mg each were prepared and sealed under a pressure of ~8×10^{-5} bar. All charges contained 47.99–51.94 at.% S, 0–9.54 at.% Ni, and Pt/Pd atomic ratios from 0.14–1.82. These charges were pre-reacted at 800°C for 24 days, melted for 8 h at 1200°C and tempered at 1000°C for 38 days before being quenched in ice-water (Verryn and Merkle, 1996). Crystals of synthetic 'braggite' in excess of 500 μm in size were in equilibrium with quenched sulphide melt or with synthetic 'cooperite' + quenched sulphide melt. Pure PdS was prepared from charges with stoichiometric proportions of metal and S by pre-reacting them at 800°C for 50 days, tempering them at 1200°C for 5 days, and quenching in ice-water.

The composition and homogeneity of the synthetic 'braggite' was established by wavelength-dispersive electron microprobe analysis at 20 kV accelerating potential and a beam current of 2×10^{-8} A with synthetic PdS, $Pt_{0.7}Pd_{0.3}S$, and NiS as standards.

Raman spectra were obtained by exciting the samples with the 514.5 nm line of an argon ion laser (Coherent model Innova 300) in polished sections of the experimental charges. The scattered light was dispersed by means of a Dilor XY multichannel spectrometer. The spectral resolution was 3 cm^{-1}, the laser output power was 120 mW, and the integration time was 300 s. The spectra were evaluated and fitted utilizing standard software. To examine the influence of the orientation of the 'braggite' crystals, Raman spectra of up to 5 grains, representing different orientations in one sample, were recorded. Although the crystal shapes and optical properties implied different orientation of the crystals in the polished sections, no effect on the Raman spectra was noticeable.

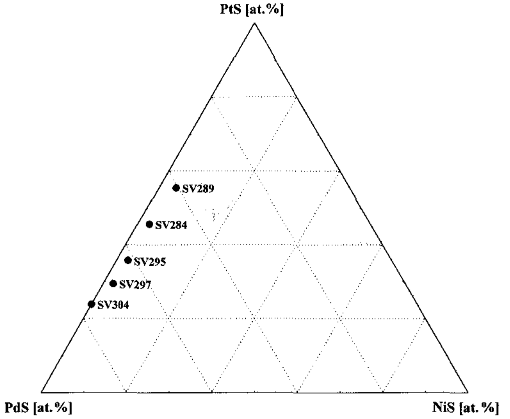

FIG. 1. Projection points of synthetic PdS and 'braggite' used in this study (in atomic proportions).

Results

Five samples of 'braggite' from the system Pt-Pd-Ni-S (Table 1) fall on a chemical trend where Pd substitutes for Pt (with only small changes in the Ni content) (Fig. 1). It therefore stands to reason to expect Raman spectra between those of the two extremes of $(Pt_{0.55}Pd_{0.40}Ni_{0.04})S_{1.01}$ (i.e. coexisting with 'cooperite' and therefore having the highest possible Pt content under the experimental conditions; Sample SV289) and PdS ('vysotskite') (Fig. 2).

Factor group analysis (De Angelis *et al.*, 1972) performed by means of the correlation method (Fateley *et al.*, 1971) resulted for 'vysotskite' as ideal PdS with space group $P4_2/m$ and $Z = 8$ (Childs and Hall, 1973) in 14 modes (2 A_{2g}, 3 B_{1g}, 2 B_{2g}, 7 E_g). With the incorporation of Pt into the crystalline unit, the environment and interaction of the ions can be expected to change. Therefore the Raman bands are broadenend and the relative intensities will vary. In this way the separate signals in the Raman spectrum of 'vysotskite' between 350 and 400 cm^{-1} appear in 'braggite' as one broad band (Fig. 3) and cannot be resolved any further or deconvoluted by means of curve-fitting procedures to determine the wave numbers and intensity of the components. The intensity of the signal/band at ~330 cm^{-1} decreases in comparison to this broad band with increasing Pt content and is not present in the Raman spectra of synthetic 'cooperite' with a Pt content of at least 34.45 at.% (Merkle *et al.*, 1997). In addition, this band shifts slightly to higher wave numbers with increasing Pt content from 326 cm^{-1} (PtS) to 329 cm^{-1} (SV304), 331 cm^{-1} (SV297), 332 cm^{-1} (SV295), 333 cm^{-1} (SV284) and 334 cm^{-1} (SV289).

Nickel in vysotskite is not considered an essential constituent (Cabri *et al.*, 1978) and compositional changes of braggite/vysotskite are not associated with structural changes (Childs and

TABLE 1. Mean compositions of 'braggite' used for the Raman spectroscopy in at.%. Values in parentheses show the standard deviation at the 1 σ level. N = number of analyses

Sample No	Pt (at.%)	Pd (at.%)	Ni (at.%)	S (at.%)	N
SV284	22.63 (0.39)	25.60 (0.40)	1.37 (0.04)	50.39 (0.22)	123
SV289	27.44 (0.41)	20.04 (0.41)	1.99 (0.17)	50.53 (0.14)	31
SV295	17.94 (0.28)	31.02 (0.33)	1.37 (0.03)	49.68 (0.22)	11
SV297	14.52 (0.20)	33.79 (0.19)	1.18 (0.06)	50.51 (0.13)	50
SV304	11.92 (0.22)	38.08 (0.30)	0	50.00 (0.37)	62

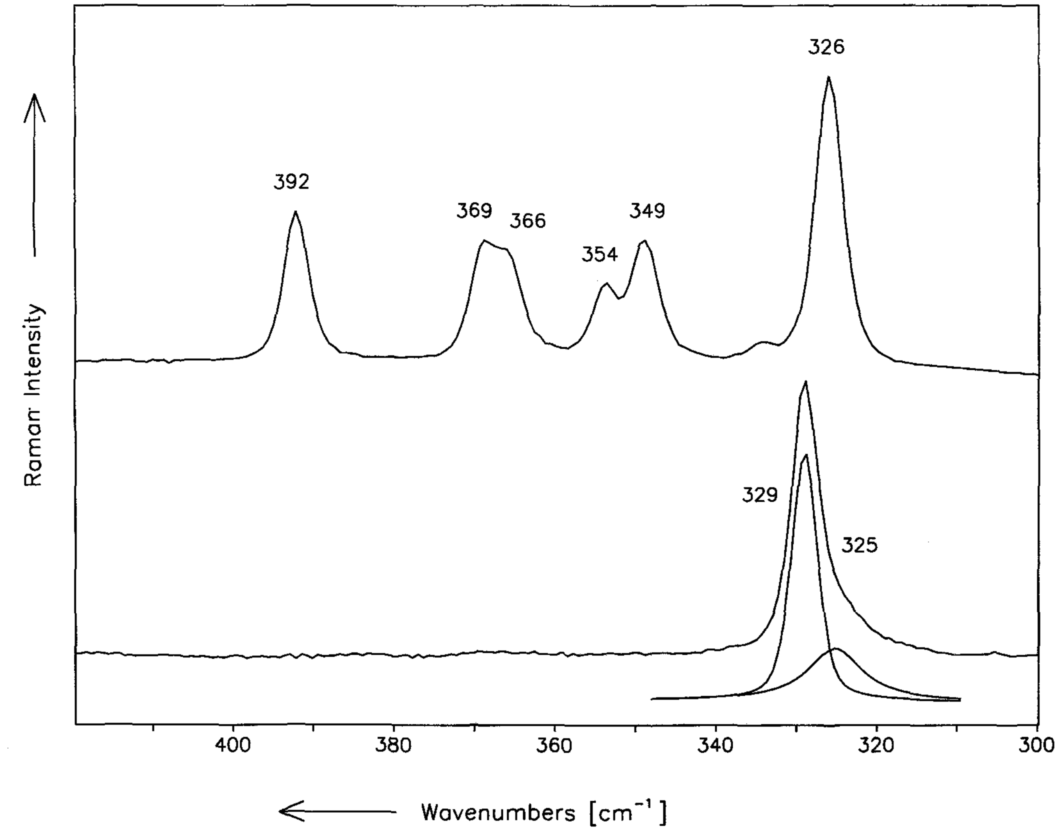

FIG. 2. Raman spectra of synthetic PdS (upper spectrum) and PtS (lower spectrum) in the range of 300 to 420 cm^{-1}; laser power P = 120 mW, slit width s = 3 cm^{-1}, temperature T = 300 K; CCD-detection.

Hall, 1973). The variation of Ni in our samples, therefore, does not seem to have an influence and the spectrum of sample SV304 (with no Ni) does not show any obvious difference from those of the other samples.

Application to natural braggite

The compositional variation of this synthetic 'braggite' does not follow the systematic relationships discussed by Merkle and Verryn (1991), and Verryn and Merkle (1994), where it was tentatively suggested that in natural braggite, Pd + Ni substitute in an atomic ratio of ~2:1 for Pt (in association with pentlandite) or 3:1 (if coexisting with millerite). However, current research on braggite from the Sompujärvi mineralization in the Penikat Intrusion in Finland (unpublished results) has identified a similar trend of substitution, although at slightly higher Ni-contents (Verryn and Merkle, 1996). Rare examples of braggites from placer deposits (Cabri *et al.*, 1996) also span a similar compositional range. Although an understanding for the reasons for such a substitution trend is only emerging, this implies that the Raman spectra from this investigation of synthetic material is most likely applicable to natural minerals as well.

Conclusions

In synthetic 'braggite', Ni and the Pt/Pd ratio can be shown to have a much less pronounced effect on the Raman spectra than for synthetic 'cooperite'. The spectra show distinct differences from those of synthetic 'cooperite' (Merkle *et al.*, 1997), but clear similarities exist between synthetic 'braggite' and pure PdS. The structure

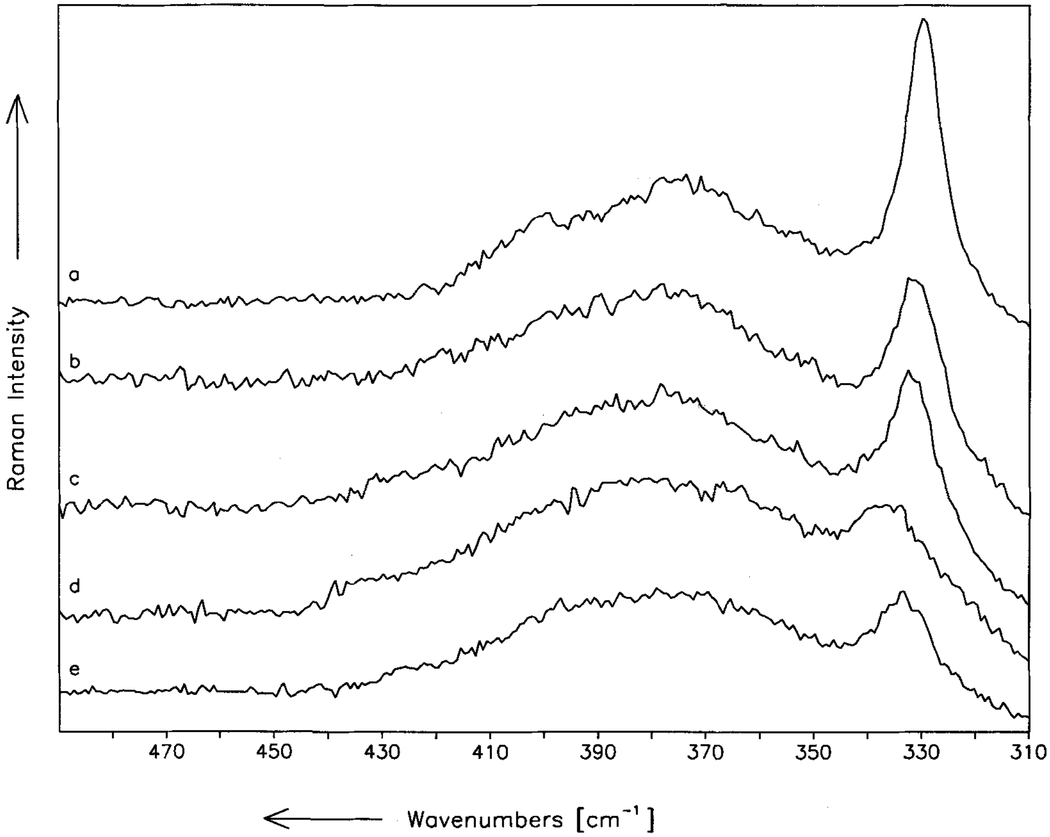

FIG. 3. Raman spectra of synthetic 'braggite' from samples SV304 (*a*), SV297 (*b*), SV295 (*c*), SV284 (*d*) and SV289 (*e*) in the range from 300 to 470 cm^{-1}; laser power P = 120 mW, slit width s = 3 cm^{-1}, temperature T = 300 K; CCD-detection.

of these phases is not changed distinctly by compositonal variations and it is, therefore, concluded that compositional variation in the braggite/vysotskite solid solution series will not cause difficulties in identifying this group of minerals by Raman spectroscopy as a fast and cost-efficient technique.

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