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Pt- and Pd-bismuthotellurides: phase relations in the Pt-Bi-Te and Pd-Bi-Te systems

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Abstract. The phase relations in the Pt-Bi-Te and the Pd-Bi-Te systems have been studied in the temperature range of 350–550°C. In the case of the Pt-Bi-Te system, neither the mineral maslovite (PtBiTe), nor ternary phases were detected. In addition, maslovite was not obtained, even if Pd was involved in the system. Five solid solutions: ss-$PtTe_2$, ss-PtTe, ss-Pt_3Te_4, ss-Pt_2Te_3, ss-$PtBi_2$ forming all phase relations in the system have been found. The Pd-Bi-Te system has been studied in the PdBi – PdTe – Te – Bi region. Three solid solutions were found on the $PdTe_2$-$PdBi_2$ line: ss-$PdTe_2$, ss-PdBiTe and ss-$PdBi_2$. Besides, in the Pd-Bi-Te system, ss-PdTe – ss-PdBi equilibrium was detected; ss-PdTe has a wide range of homogeneity across all components.

1 Introduction

The tellurides of palladium, platinum and bismuth occur commonly in Cu-Ni-PGE mineral deposits associated with mafic and ultramafic igneous rocks but also can be found in less traditional environments e.g. porphyry copper deposits.

Platinum and palladium often accompany each other. In particular, there are close associations between Pt- and Pd-bismuthotellurides in nature (e.g. Viljoen et al. 2015). There are a number of natural phases that fall into the compositional fields of kotulskite (PdTe) – sobolevskite (PdBi), merenskyite ($PdTe_2$) – moncheite ($PtTe_2$), moncheite ($PtTe_2$) – maslovite (PtBiTe) series.

The kotulskite – sobolevskite series was reported by e.g. Evstigneeva et al. (1975), Cook et al. (2002) from Noril'sk; Kingston (1966) from Merensky Reef; Viljoen (2015) from Akanany project in northern Bushveld complex, among many other deposits.

Merenskyite – moncheite series are described by Zhu et al. (2010) in Xinjie layered intrusion in the Pan-Xi area of the Sichuan Province (SW China).

The moncheite – maslovite series was reported Viljoen et al. (2015) in Akanany project in northern Bushveld complex.

The study of phase relations in the Pt-Bi-Te and Pd-Bi-Te systems is a crucial task. Information about phase relations in these systems will help to understand the conditions of their formation, as well as to predict stable mineral complexes in natural conditions.

The data on phase relations in the Pt-Bi-Te and Pd-Bi-Te systems are not complete (Vymazalová and Chareev 2018). The Pt-Bi-Te system has not been studied experimentally yet, only the phase relations in binary systems and a ternary mineral maslovite (PtBiTe, cubic, a = 6.689 Å; Kovalenker et al. 1979) are known.

The Pd-Bi-Te system is better studied compared to the Pt-Bi-Te system. The system has been studied by El-Boragy and Shubert (1970) in the Pd-rich corner at 480°C and by Hoffman and MacLean (1976) in the region Te-Bi_4Te_3-$Bi_{60}Pd_{40}$-PdTe at 480°C. In this system is the ternary mineral michenerite (PdBiTe, cubic, a = 6.65 Å).

In this study were present the phase relations in the Pt-Bi-Te and Pd-Bi-Te systems in the temperature range of 350–550°C at their own vapor pressure (nearly atmospheric pressure).

2 Materials and methods

The investigation of phase equilibria was carried out by analysis of quenched products obtained by the solid synthesis method. The synthesis was conducted from the pure elements in silica-glass evacuated ampoules (~10^{-4} bar). The mass of each sample was averaged ~400 mg. The ampoules with charges were heated in horizontal tube furnaces for 30–120 days, with one re-grinding during the experiment. The experimental run products were rapidly quenched in cold water.

Examination of run products was carried out using electron microscope with EDX system (TESCAN VEGA II XMU electron microscope) in polished sections and using powder X-Ray diffractometry (XRD, Cu*K*α, Fe filter).

3 Results and discussion

3.1 The Pt-Bi-Te system

Based on the literature data on binary systems (Table 1) (Babanly et al. 2017; Okamoto 1991; 1994) and our experimental data three isothermal sections were assessed: at 350, 450 and 550°C. It was found that in the entire temperature range (and even at 200°C) there is no maslovite (PtBiTe) synthetic analogue or any ternary phases. Five solid solutions were observed: ss-$PtTe_2$ (with moncheite structure), ss-$PtBi_2$ (with insizwaite structure), ss-Pt_3Te_4 (analogue of the mitrofanovite), ss-PtTe and ss-Pt_2Te_3.

Table 1. Phases, their mineral analogues and temperature stability in the Pt-Te, Pt-Bi, Bi-Te and Pt-Bi-Te systems.

Phase	Mineral	Temperature stability, °C	Reference
		Pt-Te system	
PtTe	–	<957	Okamoto 1994
$PtTe_2$	Moncheite	<1147	
Pt_2Te_3	–	<737	
Pt_3Te_4	Mitrofanovite	<1017	
		Pt-Bi system	
PtBi	–	<765	Okamoto 1991
α-$PtBi_2$	–	<269	
β-$PtBi_2$	Insizwaite	269–420	
γ-$PtBi_2$	–	420–640	
δ-$PtBi_2$	–	640–660	
Pt_2Bi_3	–	570–685	
		Bi-Te system	
$Bi_{14}Te_6$ (Bi_7Te_3)	Hedleyite	<312	Babanly et al. 2017
Bi_2Te	–	<375	
Bi_4Te_3	–	<450	
BiTe	Tsumoite	<520	
Bi_8Te_9	–		
Bi_6Te_7	–	<540	
Bi_4Te_5	Pilsenite	<562	
Bi_2Te_3	Tellurobismuthite	<586	
		Pt-Bi-Te system	
PtBiTe	Maslovite	–	Kovalenker et al. 1979

Three phase associations, that have been experimentally confirmed are: ss-$PtTe_2$ – Te(L)-Bi_xTe_{1-x}; ss-$PtTe_2$ – Bi_xTe_{1-x} – Bi(L); ss-$PtTe_2$ – Bi(L) – ss-$PtBi_2$; ss-$PtTe_2$ – ss-$PtBi_2$ – PtBi and ss-$PtTe_2$ – PtBi – Pt.

Three phase associations that have not been experimentally confirmed are ss-$PtTe_2$ – Pt – ss-Pt_2Te_3 and ss-PtTe – Pt – ss-Pt_3Te_4.

It is important that the determination of phase relations in the Pt-rich corner was complicated by the low kinetics associated with the metallic platinum presence and an absence of the liquid phases. On the contrary, the Bi-rich corner is characterized by high kinetics. In a number of experiments Bi-Te phases released during cooling of the Te-rich bismuth melt (Fig. 1).

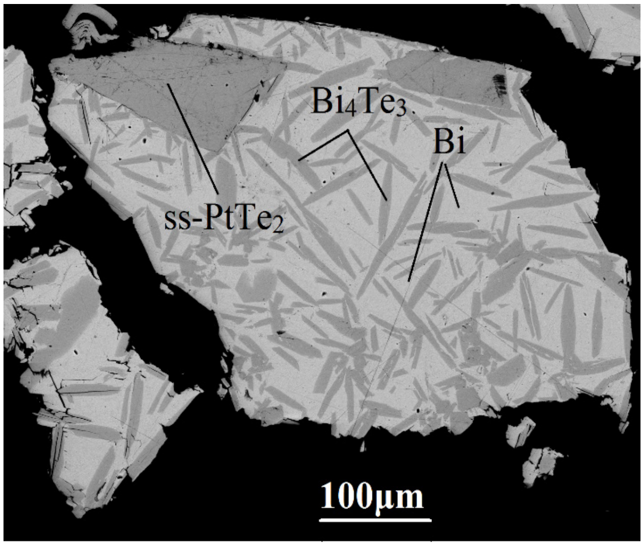

Figure 1. Back-scattered electron image of ss-$PtTe_2$ – Bi(L) phase association and Bi_4Te_3 released during bismuth melt cooling.

The phase relations in the system do not change significantly with a temperature decrease. Only the composition of the equilibrium phases change.

3.2 The Pd-Bi-Te system

In the case of the Pd-Bi-Te system, the PdBi – PdTe – Te – Bi part of phase diagram was studied. The binary phases were studied prior the ternary system (Table 2) based on Babanly et al. (2017), Okamoto (1992; 1994) and on our experiments series.

It was found that there are three solid solutions on the $PdTe_2$ – $PdBi_2$ line: ss-$PdTe_2$ (merenskyite structure), ss-PdBiTe (michenerite structure) and ss-$PdBi_2$. In addition, the ss-PdTe – ss-PdBi (kotulskite – sobolevskite) association was detected; ss-PdTe has a wide homogeneity range across all components.

As in the case of Pt-Bi-Te system the Bi-rich corner is characterized by high kinetics. However, in this case not just various bismuth tellurides are released during the cooling of the bismuth melt, but also other phases like ss-PdBiTe and ss-$PdBi_2$ (Fig. 2-3).

Table 2. Phases, their mineral analogues and temperature stability in the Pd-Te, Pd-Bi, Bi-Te and Pd-Bi-Te systems.

Phase	Mineral	Temperature stability, °C	Reference
		Pd-Te system	
$Pd_{13}Te_3$	–	<770	
Pd_3Te	–	727–785	
$Pd_{20}Te_7$	Keithconnite	<750	
Pd_8Te_3	–	563–905	
Pd_7Te_3	–	<495	
Pd_9Te_4	Telluropalladinite	<472	
Pd_3Te_2	–	<507	
PdTe	Kotullskite	<746	
$PdTe_2$	Merenskyite	<752	
		Pt-Bi system	
α-$BiPd_3$	–	<800	
β-$BiPd_3$	–	800–935	
$Bi_{12}Pd_{31}$	–	550–605	
Bi_2Pd_5	–	<550	
γ (Bi_3Pd_5)	–	400–683	Okamoto 1994
α-BiPd	–	<210	
β-BiPd	Sobolevskite	210–618	
α-Bi_2Pd	Froodite	<380	
β-Bi_2Pd	–	380(?)–485	
		Bi-Te system	
		See Table 1	
		Pd-Bi-Te system	
PdBiTe	Michenerite	<480?	El-Boragy and Shubert 1970; Hoffman and MacLean 1976

Three phase associations, that have been experimentally confirmed are: ss-PdBiTe – Bi_xTe_{1-x} – Bi(L); ss-$PdTe_2$ – Te(L) – Bi_xTe_{1-x}; ss-PdTe – Bi(L) – ss-$PdBi_2$.

Two phase associations, that have been experimentally confirmed are: ss-PdBiTe – Bi_xTe_{1-x}, Bi(L) – Bi_xTe_{1-x}, ss-PdTe – Bi(L), ss-PdTe – $PtBi_2$ and ss-PtTe – PdBi.

3.3 The Pt-Pd-Bi-Te system

As noted above, in the Pt-Bi-Te system, a maslovite synthetic analogue was not obtained. This fact can probably be associated with a lower temperature of its formation (below 200°C) or with its stabilization by impurity components.

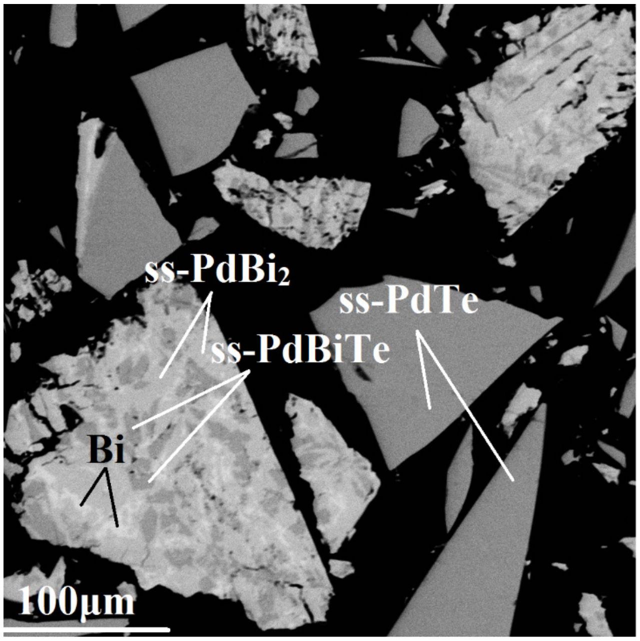

Figure 2. Back-scattered image of Bi(L) – ss-PdTe phase association and ss-$PdBi_2$ and ss-PdBiTe released during bismuth melt cooling.

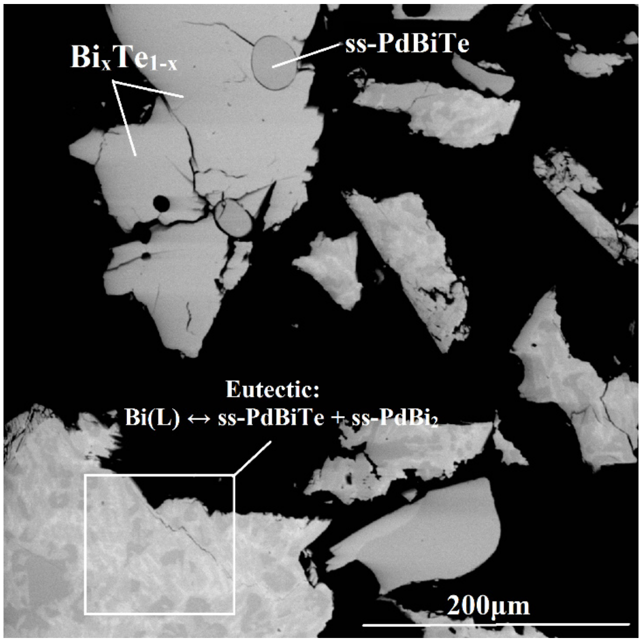

Figure 3. Back-scattered image of Bi(L) – ss-PdBiTe – Bi_xTe_{1-x} phase association and ss-$PdBi_2$ and ss-PdBiTe released during bismuth melt cooling.

Palladium-rich maslovite is common in nature. In connection with this fact, two experiments were carried out to obtain synthetic analogue of maslovite in the palladium bearing system, i.e. in the Pt-Pd-Bi-Te system.

Both samples were annealed for 30 days at 450°C with one re-grinding. The initial charges and the results of EPMA and XRD are presented in Table 3.

However, in both cases we did not obtain maslovite synthetic analogue (Table 3), which means an absence of the palladium effect on the stabilization of maslovite.

Table 3. Information about the initial charges and EPMA and XRD

results of the experiments in the Pt-Pd-Bi-Te system.

Run No	Starting material, at.%	EPMA results, at.%	XRD results
1	Pt 22.6 Pd 9.0 Bi 45.1 Te 22.3	$Pt_{5.7\pm1.6}Pd_{29.4\pm1.7}Bi_{62.9\pm1.1}Te_{2.0\pm0.3}$ $Pt_{34.0\pm1.2}Pd_{0.7\pm1.0}Bi_{35.3\pm1.3}Te_{30.0\pm0.9}$ $Pt_{9.6}Pd_{0.6}Bi_{82.6}Te_{7.3}$	α-$PdBi_2$ $PtTe_2$ Bi
2	Pt 17.6 Pd 16.3 Bi 39.6 Te 26.6	$Pt_{32.5\pm0.2}Pd_{2.3\pm0.2}Bi_{29.3\pm1.4}Te_{35.9\pm1.3}$ $Pt_{3.0\pm1.5}Pd_{42.4\pm0.6}Bi_{38.2\pm1.3}Te_{16.4\pm0.7}$ $Pt_{12.6\pm1.6}Pd_{20.0\pm2.5}Bi_{40.2\pm3.4}Te_{27.2\pm2.3}$ $Pt_{2.7\pm1.6}Pd_{31.8\pm0.5}Bi_{61.8\pm1.7}Te_{3.7\pm0.5}$	α-$PdBi_2$ $PtTe_2$ PdBiTe

4 Conclusions

Based on experimental data, phase relations in the Pt-Bi-Te and Pd-Bi-Te systems were established in the temperature range of 350–550°C.

The synthetic analogue of maslovite (PtBiTe) is unstable in the studied temperature range. In addition, Palladium admixture does not affect stability of the maslovite. There are five solid solutions in the system: ss-$PtTe_2$, ss-$PtBi_2$, ss-Pt_3Te_4, ss-PtTe and ss-Pt_2Te_3. The solid solution $PtTe_2$ has the widest homogeneity range.

In the Pd-Bi-Te system there are three solid solutions on the $PdTe_2$ – $PdBi_2$ line: ss-$PdTe_2$, ss-PdBiTe and ss-$PdBi_2$. In addition, the ss-PdTe – ss-PdBi association was detected. The solid solution PdTe has a wide homogeneity range across all components.

We have proved a range of solid solutions in the systems Pd/Pt-Bi-Te, that have been often misinterpreted in natural samples and in some cases interpreted as a new unnamed phase. The associations observed are widely spread in Cu-Ni-PGE mineral deposits associated with mafic and ultramafic igneous rocks.

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