

## PHASE RELATIONS IN THE SYSTEM Pt-Sb-Te

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### ABSTRACT

The phase relations of the system Pt-Sb-Te have been investigated at 1000°, 800°, and 600°C using the conventional sealed-capsule technique. The identification of phases present in the products was made by reflected light microscopy, X-ray diffraction, and electron-probe microanalysis. At 1000°C, platinum, PtSb (stumpflite), PtSb<sub>2</sub> (geversite), Pt<sub>3</sub>Te<sub>4</sub>, and PtTe<sub>2</sub> (moncheite) coexist with a large field of liquid. PtTe and Pt<sub>2</sub>Te<sub>3</sub> appear as additional stable solid phases at 800°C, and Pt<sub>5</sub>Sb, Pt<sub>3</sub>Sb, Pt<sub>3</sub>Sb<sub>2</sub>, Sb<sub>2</sub>Te<sub>3</sub> (tellurantimony) and antimony at 600°C. No ternary Pt-Sb-Te phases were found. Pt<sub>5</sub>Sb or Pt<sub>83</sub>Sb<sub>17</sub>, whose X-ray powder data are indexable on a tetragonal cell with *a* 3.948(3), *c* 16.85(1) Å, is presumably the same phase as previously reported to be Pt<sub>4</sub>Sb and Pt<sub>4+</sub>Sb. Some physical properties and limits of solid solution for the constituent phases are reported.

**Keywords:** phase relations, phase diagram, system Pt-Sb-Te, platinum-group minerals, synthetic phases.

### SOMMAIRE

Nous avons établi les relations de phases dans le système Pt-Sb-Te à 1000°, 800° et 600°C au moyen de la technique conventionnelle des tubes scellés. Les phases ainsi synthétisées ont été identifiées par microscopie en lumière réfléchie, par diffraction X, et par microsonde électronique. A 1000°C, platine, PtSb (stumpflite), PtSb<sub>2</sub> (geversite), Pt<sub>3</sub>Te<sub>4</sub> et PtTe<sub>2</sub> (moncheite) coexistent avec une phase liquide répandue. Les phases PtTe et Pt<sub>2</sub>Te<sub>3</sub> ont un champ de stabilité à 800°C, et Pt<sub>5</sub>Sb, Pt<sub>3</sub>Sb, Pt<sub>3</sub>Sb<sub>2</sub>, Sb<sub>2</sub>Te<sub>3</sub> (tellurantimoine) et antimoine sont présents à 600°C. Il n'y a aucune phase ternaire. La phase Pt<sub>5</sub>Sb ou Pt<sub>83</sub>Sb<sub>17</sub>, dont le spectre de diffraction X est indexable sur une maille tétragonale, *a* 3.948(3), *c* 16.85(1) Å, serait la même que Pt<sub>4</sub>Sb ou Pt<sub>4+</sub>Sb des études antérieures. Nous présentons des mesures de certaines propriétés physiques et des limites de solution solide pour les phases synthétisées.

(Traduit par la Rédaction)

**Mots-clés:** relations de phases, diagramme de phase, système Pt-Sb-Te, minéraux du groupe du platine, phases synthétiques.

### INTRODUCTION

Platinum commonly occurs in nature as com-

pounds with antimony and tellurium, which form important platinum-group minerals. In spite of this association, the only reference on phase relations in the system Pt-Sb-Te appears to be that of El-Boragy & Schubert (1971), who investigated the system at 650°C. Because platinum-bearing antimonides and tellurides tend to form early in a mineralized sequence, phase relations at temperatures higher than 650°C also are of interest. Optical and micro-indentation hardness data for the ten synthetic phases that occur in the system, Pt<sub>4</sub>Sb, Pt<sub>3</sub>Sb, Pt<sub>3</sub>Sb<sub>2</sub>, PtSb (stumpflite), PtSb<sub>2</sub> (geversite), PtTe, Pt<sub>3</sub>Te<sub>4</sub>, Pt<sub>2</sub>Te<sub>3</sub>, PtTe<sub>2</sub> (moncheite), and Sb<sub>2</sub>Te<sub>3</sub> (tellurantimony), are very sparse or nonexistent, because their characterization was largely based on crystallographic work.

The purpose of this study is to investigate the phase relations of the system Pt-Sb-Te at 1000°, 800° and 600°C and to better document physical properties for the phases encountered in the system. We reviewed the constituent Pt-Sb, Pt-Te, and Sb-Te binary diagrams before investigating the ternary system. The first two binary phase diagrams were studied between 600° and 1000°C, and the last between 400° and 800°C.

### EXPERIMENTAL DETAILS

Mixtures were prepared from platinum wire (99.999% purity) and spectrographically pure antimony and tellurium ingots. Materials were weighed accurately into silica glass tubes, which were subsequently evacuated and sealed. The capsules were then placed in horizontal muffle furnaces and heated at selected temperatures. Temperatures were checked frequently and found to be constant within ± 2°C. To ensure homogeneity, most samples were opened after initial heating, ground under acetone, pelletized and reloaded in the furnaces for a further period of heating, after sealing in evacuated silica tubes. The total heating period ranges from a few days to three months. Experimental runs were quenched by dropping the charges in ice water.

Run products were identified by reflected light microscopy, X-ray diffraction and electron-probe microanalysis. X-ray powder-diffraction patterns were obtained with 114.6-mm Gandolfi cameras using Ni-filtered CuK $\alpha$  radiation. A Philips automated X-ray diffractometer was employed using monochromatic CuK $\alpha$  radiation for the determination of cell dimensions. Cell parameters were calcu-

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lated by a least-squares method. Compositions of individual phases in each run product were determined with a Cambridge MK5 electron-microprobe analyzer. All analyses were carried out at an accelerating voltage of 25 kV and a specimen current of 50 nA measured on a synthetic PtSb<sub>2</sub> standard. Errors associated with the microprobe analyses are approximately  $\pm 1\%$  of major elements present. Differential thermal analyses were carried out for samples of the system Sb-Te using a Fisher Series 100A DTA-TGA system. All analyses were made in a nitrogen atmosphere to avoid oxidation of samples on heating, and the specimen thermocouples were shielded within very fine silica glass tubing (3 mm ID, 4 mm OD) to prevent reaction between the thermocouples and samples. Micro-indentation hardness was measured for the synthetic phases using a Leitz DURIMET small hardness-tester. Experimental data for the runs (starting compositions, temperatures, duration, reaction products, and their microprobe analyses) are shown in Table 1, which has been placed in the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

## RESULTS AND DISCUSSION

### Pt<sub>5</sub>Sb

Instead of stoichiometric Pt<sub>4</sub>Sb (Friedrich & Leroux 1909, Nemilow & Woronow 1936, Bhan *et al.* 1969) or Pt<sub>4+</sub>Sb (Bhan & Schubert 1969) of composition 81–82 at. % Sb, a phase having the composition of Pt<sub>83</sub>Sb<sub>17</sub> was found in run products from 600°C and 650°C. The formula Pt<sub>5</sub>Sb is tentatively assigned to it. Under reflected light, it is pale brownish grey or yellowish grey in air and in oil, and shows no birefractance. Micro-indentation hardness

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR SYNTHETIC Pt<sub>5</sub>Sb

h	k	l	d (calc)	d (obs)	I/I <sub>0</sub>
1	1	4	2.327	2.318	100
1	0	6	2.288	2.293	100
0	0	8	2.106	2.110	30
2	0	8	1.440	1.440	50
2	2	1	1.391	1.390	15
2	0	10	1.281	1.283	5
0	0	14	1.203	1.203	70
3	0	6	1.191	1.192	40

X-ray powder pattern was obtained from a mixture of Pt<sub>5</sub>Sb + Pt<sub>3</sub>Sb + PtTe, quenched from 600°C. X-ray lines indexed on a tetragonal cell with  $a = 3.948(3)$ ,  $c = 16.85(1)$  Å. CuK $\alpha$  radiation ( $\lambda = 1.5418$  Å) and 114.6-mm Gandolfi camera used.

measurements gave a VHN<sub>100</sub> of 225 (206–243) for four indentations. Attempts to synthesize single-phase Pt<sub>5</sub>Sb directly from a mix of the same bulk composition were unsuccessful, and the X-ray powder pattern (Table 2), obtained from a mixture of Pt<sub>5</sub>Sb, PtTe and Pt<sub>3</sub>Sb (run 631), cannot be indexed with the cubic cell ( $a$  3.99 Å) given by Bhan & Schubert (1969) for the Pt<sub>4+</sub>Sb phase. However, the X-ray powder data of Pt<sub>5</sub>Sb are indexable on a tetragonal cell with  $a$  3.948(3) and  $c$  16.85(1) Å. The Pt<sub>5</sub>Sb phase is presumably equivalent to Pt<sub>4+</sub>Sb and Pt<sub>4</sub>Sb, but this cannot be confirmed, because of the lack of X-ray data for the phases reported earlier in the literature.

### Pt<sub>3</sub>Sb

The existence of Pt<sub>3</sub>Sb of Bhan *et al.* (1969) is confirmed. It is pale greyish yellow in air, with very weak birefractance and anisotropism. Micro-indentation hardness tests gave a VHN<sub>25</sub> of 216 (183–240) for four measurements. The X-ray powder pattern (Table 3) was obtained from Pt<sub>3</sub>Sb coexisting with Pt<sub>3</sub>Sb<sub>2</sub> and indexed on the basis of a tetragonal cell with  $a$  3.9455(7),  $c$  16.959(5) Å, in good agreement with  $a$  3.94,  $c$  16.96 Å given by Bhan *et al.* (1969). Two unindexable weak reflections (2.482 and 2.450 Å) apparently do not belong to Pt<sub>3</sub>Sb<sub>2</sub>, which coexists with Pt<sub>3</sub>Sb. Bhan & Schubert (1969) also noted a few weak X-ray lines ( $d$  values not specified) in their Guinier film that do not fit

TABLE 3. X-RAY POWDER-DIFFRACTION DATA FOR SYNTHETIC Pt<sub>3</sub>Sb

h	k	l	d (calc)	d (obs)	I/I <sub>0</sub>
1	0	5	2.572	2.570	35
				2.482*	5
				2.450*	5
1	1	4	2.330	2.328	100
0	0	8	2.119	2.115	45
2	0	0	1.972	1.970	50
2	1	1	1.755	1.753	20
2	0	6	1.617	1.616	2
2	0	8	1.444	1.444	65
2	2	0	1.394	1.394	30
2	1	9	1.288	1.287	10
1	1	12	1.260	1.261	45
3	1	4	1.196	1.197	50
2	2	8	1.165	1.165	15
3	1	6	1.141	1.141	5

X-ray powder pattern was obtained from a mixture of Pt<sub>3</sub>Sb and Pt<sub>3</sub>Sb<sub>2</sub>, quenched from 600°C. X-ray lines indexed on a tetragonal cell with  $a = 3.9455(7)$ ,  $c = 16.959(5)$  Å. CuK $\alpha$  radiation ( $\lambda = 1.5418$  Å) and 114.6-mm Gandolfi camera used. \* not indexable on the tetragonal cell.

well the  $ZrAl_3$  structure proposed for the  $Pt_3Sb$  phase. Bhan *et al.* (1969) also reported that  $Pt_3Sb$  has a very weak X-ray line indexable on the tetragonal cell with the  $a$  dimension doubled. They suggested that this small discrepancy from the  $ZrAl_3$  structure might have resulted from a slight distortion of the structure. However, it is not certain whether the problematic weak X-ray line(s) mentioned by Bhan & Schubert (1969) and Bhan *et al.* (1969) are identical to those found in the present study.

### $Pt_3Sb_2$

$Pt_3Sb_2$  reported by Bhan *et al.* (1969) was synthesized at 600°C. It is creamy yellow in reflected light, with a weak bireflectance from cream to pale greenish yellow. Anisotropism is moderate to strong, and  $VHN_{100}$  is equal to 275 (240–306), based on five indentations. As shown in Table 4, the X-ray powder-diffraction data for  $Pt_3Sb_2$  synthesized at 600°C in this study do not fully agree with those of Bhan *et al.* (1969), for material prepared at an unspecified temperature. The difference in the X-ray patterns cannot be explained at present. The cell parameters, refined on the basis of an orthorhombic cell, are  $a$  6.414(7),  $b$  10.941(6),  $c$  5.28(1) Å. No natural analogue of the  $Pt_3Sb_2$  phase is known. However, an unnamed mineral ( $Pt_{1.76-1.78}Pd_{1.24-1.22}Sb_{2.05-2.09}$  or  $Pt_{1.69}Pd_{1.18}Sb_{1.96}Bi_{0.06}Sn_{0.09}As_{0.01}$ ) (Tarkian & Stumpfl 1975) from the Driekop mine, South Africa, suggested by Cabri *et al.* (1977) to be a possible Sn-bearing, Rh-free variety of genkinite  $[(Pt,Pd)_4Sb_3]$ , may rather be the natural analogue of the synthetic  $Pt_3Sb_2$  phase.

### $PtSb$

$PtSb$  was synthesized at 1000°, 800° and 600°C. Under reflected light,  $PtSb$  is creamy yellow. It is weakly bireflectant and strongly anisotropic;  $VHN_{50}$  is equal to 417 (296–473).  $PtSb$  was reported to be hexagonal, space group  $P6_3/mmc$ , with  $a$  4.130(4),  $c$  5.472(5) Å (Thomassen 1929). The cell parameters of pure  $PtSb$  vary slightly, depending on temperatures from which the phase was quenched:  $a$  4.1318(6),  $c$  5.483(1) Å at 800°C, and  $a$  4.1420(5),  $c$  5.486(1) Å at 1000°C. The physical properties of the synthetic  $PtSb$  phase are virtually identical to those of stumpflite, first established as a new species by Johan & Picot (1972).

### $PtSb_2$

$PtSb_2$  was synthesized at 1000°, 800° and 600°C. Under reflected light,  $PtSb_2$  is white with a yellowish tinge in air. Micro-indentation hardness values

TABLE 4. X-RAY POWDER-DIFFRACTION DATA FOR SYNTHETIC  $Pt_3Sb_2$

			1		2		
h	k	l	d (obs)	$I_0$	d (calc)	d (obs)	$I/I_0$
1	0	0	5.447	m-			
0	2	0	5.447	m-	5.471	5.470	89
1	2	1	3.282	vw			
2	0	0	3.221	vw			
1	3	0	3.173	m	3.169	3.172	87
2	2	0	2.778	m			
0	4	0	2.735	w	2.734	2.731	85
2	1	1	2.675	m+	2.659	2.658	15
0	0	2	2.661	m-			
1	1	2	2.400	st			
0	2	2	2.400	st			
1	4	1	2.277	m	2.272	2.276	30
2	3	1	2.200	m			
3	1	0	2.109	m-			
2	4	0	2.086	w+			
1	5	0	2.073	m-	2.070	2.070	100
2	0	2	2.053	m			
0	4	2	1.907	st	1.907	1.907	30
3	2	1	1.874	m			
0	6	0	1.826	vw-			
2	5	1	1.715	vw			
1	6	1	1.669	vw			
1	2	3	1.632	vw			
2	1	3	1.539	w			
3	3	2	1.520	w			
1	7	0	1.520	w	1.518	1.519	7
0	6	2			1.501	1.501	8
1	4	3			1.444	1.444	4
0	8	0			1.367	1.364	21
2	7	1			1.357	1.358	15
1	8	1			1.2966	1.2979	24
5	3	2			1.1000	1.1002	6
3	6	3			1.0904	1.0898	10

- Bhan *et al.* (1969). Guinier camera using  $CuK\alpha$  radiation. w: weak, m: medium, st: strong. d-values converted from  $\sin^2\theta$ . Orthorhombic system,  $a$  6.446,  $b$  10.939,  $c$  5.391 Å.
- This study. Run 109, quenched from 600°C.  $CuK\alpha$  radiation ( $\lambda = 1.54059\text{Å}$ ), automated diffractometer. Indexed on an orthorhombic cell with  $a$  6.410(8),  $b$  10.939(7),  $c$  5.29(1) Å.

for the  $PtSb_2$  phase are  $VHN_{50}$  664 (566–766) and  $VHN_{100}$  701 (681–724). Pure  $PtSb_2$  has a cubic structure, and the cell dimension of the phase, synthesized at 1000°C, is  $a$  6.4373(2) Å. The cell parameter increases significantly with increasing amount of Te in substitution for Sb, e.g.,  $a$  6.4844(9) Å for  $Pt_{1.00}Sb_{1.49}Te_{0.51}$  (run 452). Geversite, the natural analogue of synthetic  $PtSb_2$ , first found from the Driekop mine, South Africa, was characterized as a new mineral by Johan & Picot (1972). The physical properties of geversite reported by Tarkian & Stumpfl (1975) are in excellent agreement with those of  $PtSb_2$ .

### $PtTe$

$PtTe$ , first reported by Roessler (1897), was synthesized at 650°C. Under reflected light, it is yellowish grey in air and pale brownish grey in oil. The bireflectance varies from nil to very weak. It is moderately anisotropic, from brownish grey to bluish grey;  $VHN_{15}$  is equal to 63.1 (50.4–85.9) for four indentations. The X-ray powder pattern of the  $PtTe$

phase is comparable to that given by Bhan *et al.* (1969), and the cell parameters determined are  $a$  6.857(3),  $b$  3.952(4),  $c$  6.988(3) Å,  $\beta$  108.99(8)°.

### $Pt_3Te_4$

The presence of  $Pt_3Te_4$ , reported by Bhan *et al.* (1969), is confirmed. Microprobe analyses of  $Pt_3Te_4$  gave  $57.1 \pm 0.4$  at. % Te; it is considered to have a fixed composition. Under reflected light, it is pale yellow and moderately anisotropic.  $VHN_{15}$  is equal to 73.2 (68.2–80.4) for four measurements. Because the  $Pt_3Te_4$  phase was found to be stable at 1000°C in this study, the melting point of the phase must be higher than 985°C (Bhan *et al.* 1969). The X-ray powder pattern of  $Pt_3Te_4$  quenched from 800°C is comparable to that of Bhan *et al.* (1969); the refined cell-parameters are  $a$  6.942(4),  $b$  3.980(2),  $c$  12.00(1) Å,  $\beta$  100.4(1)°.

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

h	k	l	d (calc)	d (obs)	I/I <sub>0</sub>
1	0	2	3.659	3.624	7
1	0	6	3.116	3.111	100
1	0	12	2.254	2.268	45
1	1	2	2.146	2.141	28
1	1	6	2.018		
0	0	17	1.979	1.998	2
1	1	8	1.923	1.909	14
2	0	0	1.873		
2	0	3	1.847	1.844	2
1	1	11	1.766	1.765	17
2	0	12	1.557	1.558	9
0	0	22	1.529	1.527	1
1	0	21	1.473	1.471	5
2	0	15	1.438		
1	0	22	1.416	1.427	9
1	0	23	1.363	1.363	10
2	1	8	1.342		
1	1	20	1.328	1.338	3
2	1	12	1.264	1.262	7
2	0	20	1.251	1.253	1
3	0	3	1.241		
3	0	4	1.235	1.238	3
1	1	23	1.212	1.213	1
2	0	22	1.185	1.186	1
3	0	12	1.140		
2	1	18	1.128	1.136	2
2	1	20	1.083		
2	2	0	1.081	1.082	2
2	2	4	1.072	1.072	2
3	0	17	1.056	1.056	1
2	0	27	1.037	1.037	3
2	0	28	1.011	1.011	3

X-ray powder pattern was obtained from a mixture of antimony and phase X, quenched from 510°C, using an automated diffractometer. Indices are based on a hexagonal cell with  $a$  4.328(2),  $c$  33.65(2) Å.  $CuK\alpha_1$  radiation ( $\lambda = 1.54059$  Å).

### $Pt_2Te_3$

The existence of  $Pt_2Te_3$ , claimed by Bhan *et al.* (1969), is confirmed. It has a compositional range of  $60.8 \pm 0.8$  at. % Te at 650°C. It is white with a yellow tint under reflected light. It is weakly anisotropic, from greenish grey to reddish grey;  $VHN_{10}$  is equal to 627. The X-ray powder data, indexed according to the monoclinic cell given by Bhan *et al.* (1969), gave the cell parameters  $a$  6.910(1),  $b$  3.985(1),  $c$  17.115(3) Å,  $\beta$  97.82(4)°.

### $PtTe_2$

$PtTe_2$  was synthesized over the complete range of temperature, 1000° – 600°C. Under reflected light, it is white with a yellowish tinge and very weakly birefractant. The polished surface of the synthetic phase is either unpitted or pitted, probably depending on the orientation of the grains. Micro-indentation hardness tests gave poor diamond imprints, accompanied by sets of parallel fractures, similar to those described for moncheite by Cabri & Laflamme (1976). Micro-indentation hardness values for  $PtTe_2$  differ with the texture of the polished surface:  $VHN_{10}$  is equal to 84.2 (76.2–90.7), and  $VHN_{100}$ , 50.7 (44.7–54.9) for unpitted surfaces; the pitted surfaces give a  $VHN_{10}$  of 83.2 (70.7–92.0) and a  $VHN_{100}$  of 66.8. The cell parameters of the phase, quenched from 1000° and 800°C, are  $a$  4.025(1),  $c$  5.222(1) Å and  $a$  4.0242(4),  $c$  5.2207(4) Å, respectively, in good agreement with those given by Grønvold *et al.* (1960). Moncheite,  $(Pt,Pd)(Te,Bi)_2$ , first described by Genkin *et al.* (1963) from the Monchegorsk deposits, U.S.S.R., is the natural equivalent of  $PtTe_2$ . The physical properties of synthetic  $PtTe_2$  are in good agreement with those of moncheite (Kingston 1966, Cabri & Laflamme 1976).

### $Sb_2Te_3$

$Sb_2Te_3$  was synthesized between 400° and 600°C.  $Sb_2Te_3$  is creamy yellow under reflected light, with a very weak birefractance. It is moderately anisotropic, from brownish grey to light grey. Microprobe analyses indicate that  $Sb_2Te_3$  has a fixed composition of  $60.0 \pm 0.4$  at. % Te at 430°C, contrary to the result of Poretskaya *et al.* (1963), who reported deficiencies in Te in the phase as temperature decreases. The X-ray powder pattern for material synthesized at 500°C and the refined cell-parameters,  $a$  4.262(1),  $c$  30.435(2) Å, are in good agreement with the data reported by Brown & Lewis (1962) and Kuznetsov & Palkina (1963).

Synthetic crystals of  $Sb_2Te_3$  are hexagonal and tabular, and most crystals in polished sections seem lath-shaped. The compound is very brittle and frac-

tures easily during micro-indentation testing under heavy loads (e.g., 100 g). The Vickers micro-indentation hardness of the compound was, therefore, determined using a 15-g load to be 33.4 (28.6–41.8) for four indentations. The mineral tellurantimony,  $\text{Sb}_{1.91}\text{Te}_3$  or, ideally,  $\text{Sb}_2\text{Te}_3$ , described by Thorpe & Harris (1973) from the Mattagami Lake mine, Quebec, is the natural analogue of  $\text{Sb}_2\text{Te}_3$ . The X-ray powder-diffraction data and physical properties of tellurantimony compare well with those of the synthetic phase.

### Phase X

A phase with a composition  $12.5 \pm 0.5$  at.% Te on the Sb side, and an unknown boundary on the Te side, was encountered in the binary system. It occurs as discrete grains having a maximum grain-size of 0.05 mm, with antimony. This phase, tentatively referred to as "phase X", was synthesized at 420°, 510° and 520°C. Phase X may be identical to the Sb-rich  $\delta$  phase of Brown & Lewis (1962), which has a composition extending from 11 to 60 at.% Te, or it may be an independent phase for which the

uncertain compositional boundary may be due to failure in attaining equilibrium in the region 20–60 at.% Te. The X-ray powder data of phase X ( $\text{Sb}_{87.8}\text{Te}_{12.2}$ ) coexisting with almost pure antimony (run 22), indexed on hexagonal axes, are given in Table 5. The refined  $c$  parameter of the phase is approximately 3 times that of antimony. Under reflected light, phase X is pale brownish yellow in air, and shows a weak birefractance. It is weakly anisotropic from brownish yellow to yellowish brown.

### PHASE RELATIONS

#### Pt-Sb system

Phase relations in this system were previously investigated by Friedrich & Leroux (1909), Nemilov & Woronow (1936), and Bhan *et al.* (1969). There is a substantial agreement from 50 to 100 at.% Sb, as indicated by the existence of PtSb and PtSb<sub>2</sub>, and a liquidus between them. However, there is a considerable difference in the 10–50 at.% Sb region. Friedrich & Leroux (1909) reported a eutectic

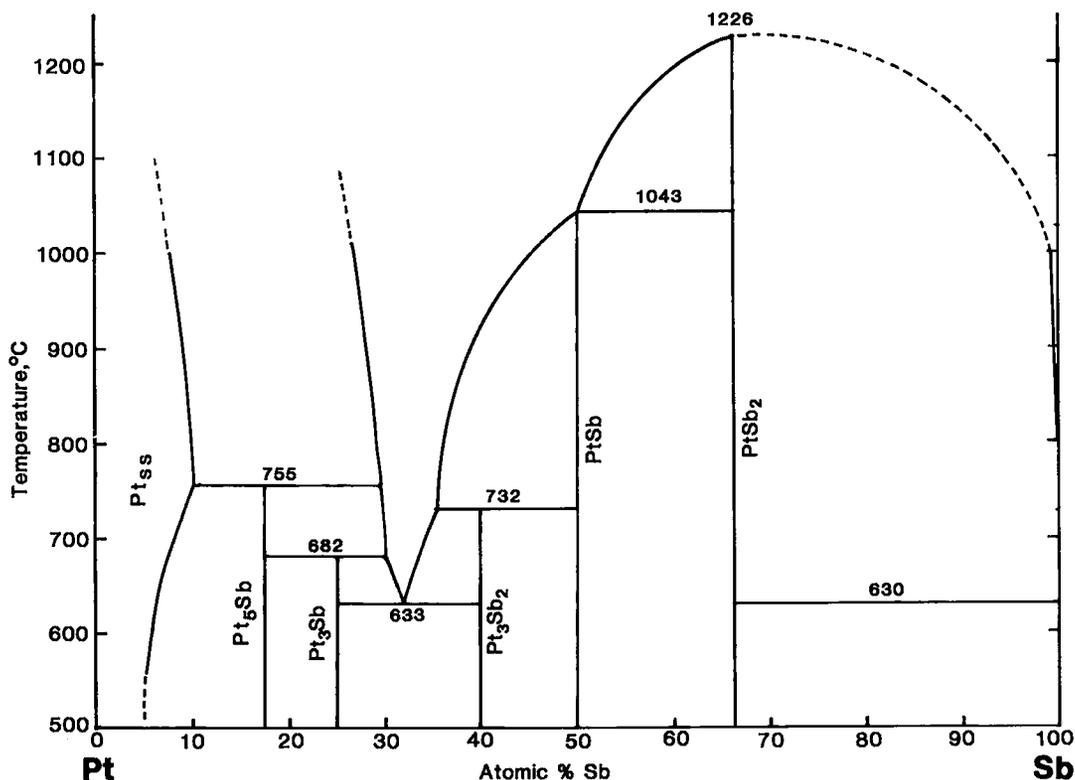


FIG. 1. Revised phase diagram of the system Pt-Sb. Temperatures are taken from Bhan *et al.* (1969) and Hansen & Anderko (1958).

between  $Pt_4Sb$  and  $PtSb$  at  $690 \pm 8^\circ C$ , 33.6 at. % Sb, and found  $Pt_5Sb_2$  formed peritectoidally at  $637 \pm 8^\circ C$ . Nemilow & Woronow (1936) also reported the same eutectic at  $633 \pm 8^\circ C$ , but did not find  $Pt_5Sb_2$ . Bhan *et al.* (1969) found two previously unreported phases,  $Pt_3Sb$  and  $Pt_3Sb_2$ , and incorporated these in their phase diagram. The formula of the  $Pt_4Sb$  phase was revised by Bhan & Schubert (1969) to  $Pt_{4+}Sb$ , as the Pt content of the phase was found to be about  $81.5 \pm 0.5$  at. %.

The experimental results from the present study confirm that the phases and the phase diagram given by Bhan *et al.* (1969) are essentially correct, with only minor revisions necessary. The earlier reported  $Pt_4Sb$  (or  $Pt_{4+}Sb$ ) phase was not found. Instead, a phase having a composition of  $Pt_{83}Sb_{17}$ , or more simply  $Pt_5Sb$ , was found in this study. The solid solution of Sb in Pt was determined to vary with temperature: 7.5 at. % Sb at  $1000^\circ C$ , 10 at. % Sb at  $800^\circ C$ , and 6.1 at. % Sb at  $600^\circ C$ . These values are in good agreement with those of Friedrich & Leroux (1909) and Nemilow & Woronow (1936): 8 at. % Sb

at  $1000^\circ C$ , 10 at. % Sb at  $800^\circ C$ . But they are much greater than the values given by Bhan *et al.* (1969): 3 at. % Sb at  $1000^\circ C$  and 4 at. % Sb at  $800^\circ C$ , as deduced from their phase diagram. The liquidus curve determined by earlier investigators also needs revision. The liquid phase coexisting with  $PtSb_2$  at  $1000^\circ$  and  $800^\circ C$  is nearly pure Sb in composition, which suggests that the liquidus curve over much of the range between  $PtSb_2$  and Sb must be somewhere above  $1000^\circ C$  and dip steeply near the 100 at. % Sb line. The revised phase diagram is shown in Figure 1.

#### Pt-Te system

Phase relations in the system Pt-Te were first investigated by Gimpl *et al.* (1963), and later by Bhan *et al.* (1969). Two main differences exist between their findings. Firstly, Gimpl *et al.* reported only two intermediate phases,  $PtTe$  and  $PtTe_2$ , whereas Bhan *et al.* added two more phases,  $Pt_3Te_4$  and  $Pt_2Te_3$ .  $Pt_3Te_4$  has a compositional range of about 2 at. % and melts incongruently at  $985^\circ C$  to form  $PtTe_2$

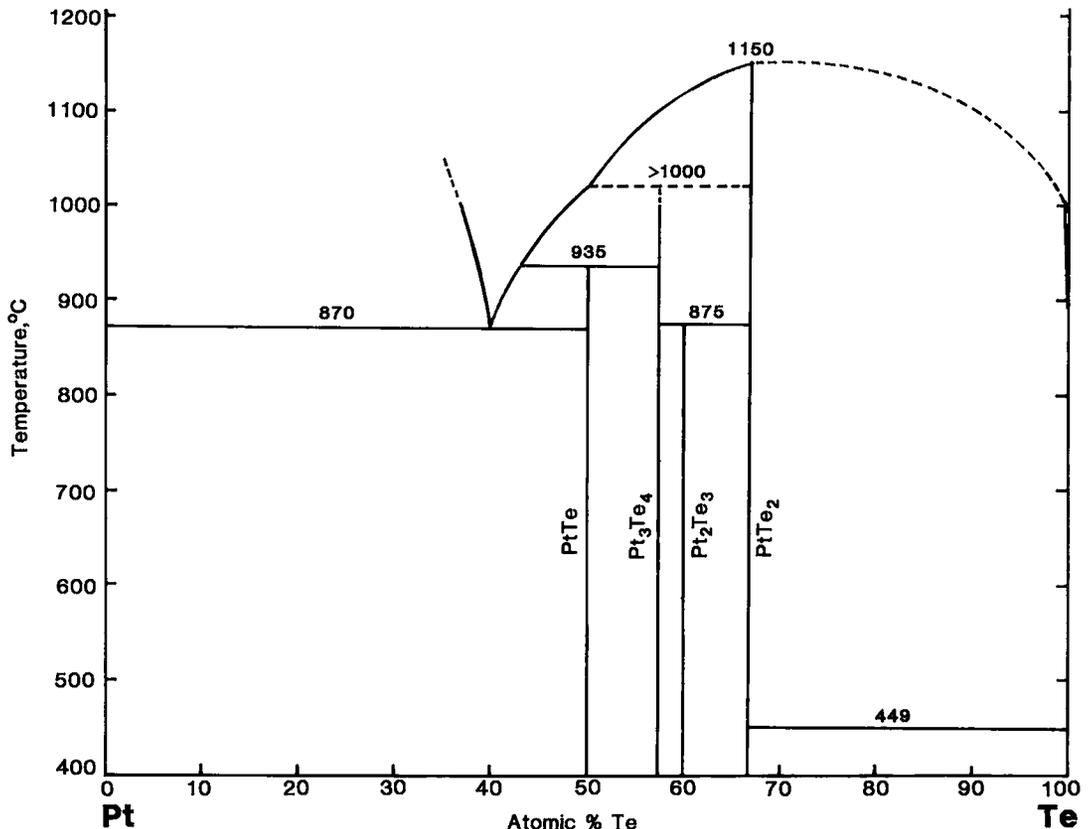


FIG. 2. Revised phase diagram of the system Pt-Te. Temperatures are taken from Bhan *et al.* (1969) and Gimpl *et al.* (1963).

and liquid. Secondly, Gimpl *et al.* did not report a liquidus curve between the PtTe<sub>2</sub> and Te phases, whereas Bhan *et al.* assumed a liquidus curve by joining the melting points of PtTe<sub>2</sub> and Te.

The experimental data obtained in this investigation confirm the phase diagram of Bhan *et al.* (1969) and the existence of four binary phases, namely, Pt<sub>3</sub>Te<sub>4</sub>, PtTe, Pt<sub>2</sub>Te<sub>3</sub> and PtTe<sub>2</sub>. Minor revisions made are: (1) the Pt<sub>3</sub>Te<sub>4</sub> phase is a stoichiometric compound within the error range of the electron-microprobe data, and stable at 1000°C, and (2) the liquid phase in equilibrium with PtTe<sub>2</sub> at 1000° and 800°C is nearly pure Te in composition, which suggests that below 1000°C, a liquidus curve, if present, is located very close to the 100 at.% Te line. The slightly modified phase diagram is presented as Figure 2.

*Sb-Te system*

Considerable uncertainty exists in the 0 - 60 at.% Te area of the Sb-Te phase diagram. According to Hansen & Anderko (1958), no intermediate phase exists between the Sb and Sb<sub>2</sub>Te<sub>3</sub>. However, Abrikosov *et al.* (1959) reported two intermediate phases, β and λ, with the relevant single-phase fields

TABLE 6. DIFFERENTIAL THERMAL ANALYSIS DATA FOR THE Sb-Te SYSTEM

Run no.	Composition (at.%)		Peaks* T (°C)
	Sb	Te	
3	94.82	5.18	549 616
2	85.09	14.91	547 583
1	79.92	20.08	544 549
8	74.97	25.03	544.8
7	65.03	34.97	545
4	59.75	40.25	544
5	55.08	44.92	544 567
9	50.10	49.90	544 585
6	43.14	56.86	539 618.5

\* Endothermic reactions measured on heating.

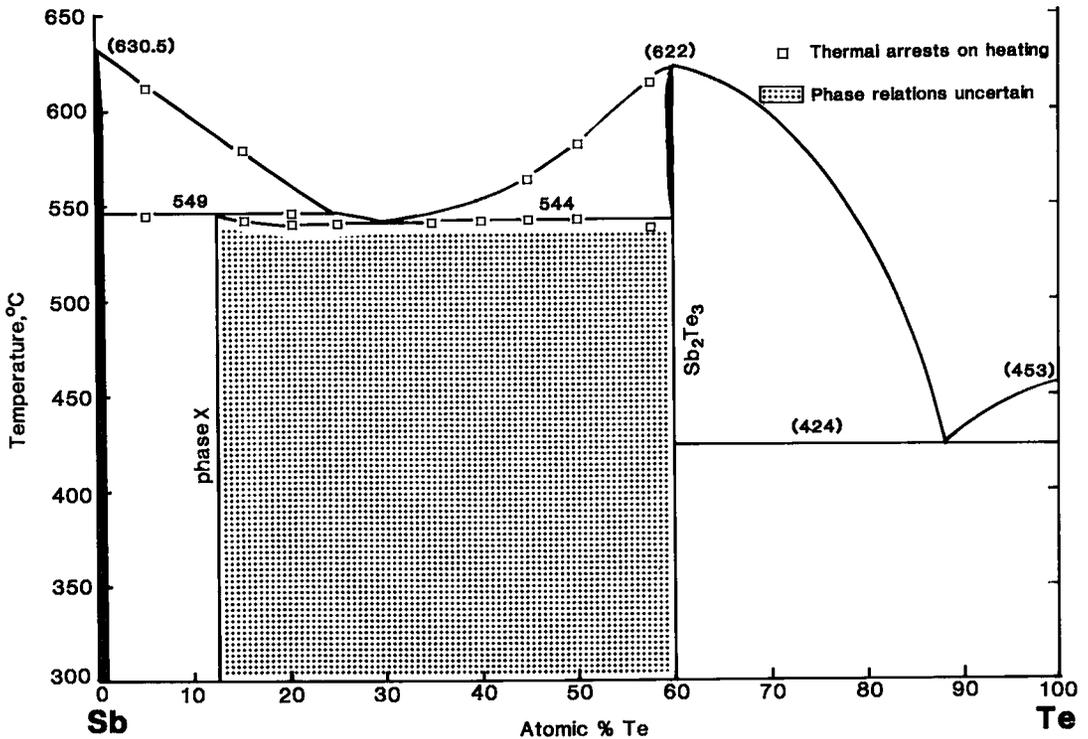


FIG. 3. Revised phase diagram of the system Sb-Te. Temperatures in parentheses are taken from Hansen & Anderko (1958).

covering 17.3–36.9 at. % Te and 40.9–53.8 at. % Te. They were unable to synthesize single-phase stoichiometric  $\text{Sb}_2\text{Te}_3$ . Brown & Lewis (1962) re-investigated the system and reported a single phase ( $\delta$ ) over the compositional range 11–60 at. % Te. They suggested that the  $\beta$  and  $\gamma$  phases of Abrikosov *et al.* could be metastable products. In addition, there is no unanimity concerning the shape and position of the liquidus and solidus in the region 0–60 at. % Te.

In this study, differential thermal analyses were carried out for samples in the Sb –  $\text{Sb}_2\text{Te}_3$  region in order to bracket the solidus and liquidus. The DTA data (Table 6) show that the liquidus and solidus curves present between Sb and  $\text{Sb}_2\text{Te}_3$  are comparable in shape to those given by Hansen & Anderko (1958) and Brown & Lewis (1962), respectively, with only small differences in absolute temperatures.  $\text{Sb}_2\text{Te}_3$ , however, was successfully synthesized at 500°C in this study from a mix of stoichiometric  $\text{Sb}_2\text{Te}_3$  composition. The compound has a composition range of 58.7–60.0 at. % Te at 600°C. Experiments performed on bulk compositions in the 3–10 at. % Te region and quenched from 420° – 520°C invariably yielded products consisting of Sb and phase X; the composition limit of the latter on the Te-rich side is uncertain. Electron-

microprobe analyses revealed wide compositional variations in every experiment in the 20–60 at. % Te region, which leaves no doubt concerning the disequilibrium nature of the assemblages. We thus conclude that the phase relations in the area involving phase X and  $\text{Sb}_2\text{Te}_3$ , below the solidus temperature (about 550°C), are uncertain, and the phase diagrams reported by earlier workers cannot be confirmed. The revised Sb–Te phase diagram is shown in Figure 3.

#### Pt–Sb–Te system

The phase diagram at 1000°C (Fig. 4) shows five solid phases: Pt (platinum), PtSb (stumpflite),  $\text{PtSb}_2$  (geversite),  $\text{PtTe}_2$  (moncheite) and  $\text{Pt}_3\text{Te}_4$ . In addition, two fields of liquid exist: a large field extends across the ternary system from the Pt–Sb join to the Pt–Te join [referred to as liquid (1)], and a second liquid is restricted to a thin strip near the Sb–Te join [referred to as liquid (2)]. Electron-microprobe analyses show that the Pt content of liquid (2) is less than 1 at. %. All the solid phases present are solid solutions. Platinum in equilibrium with liquid (1) contains up to about 7 at. % Sb in solid solution, but negligible amounts of Te (less than 0.5 at. %), corresponding well to our results in the Pt–Sb and Pt–Te systems. PtSb becomes Pt-poor as sub-

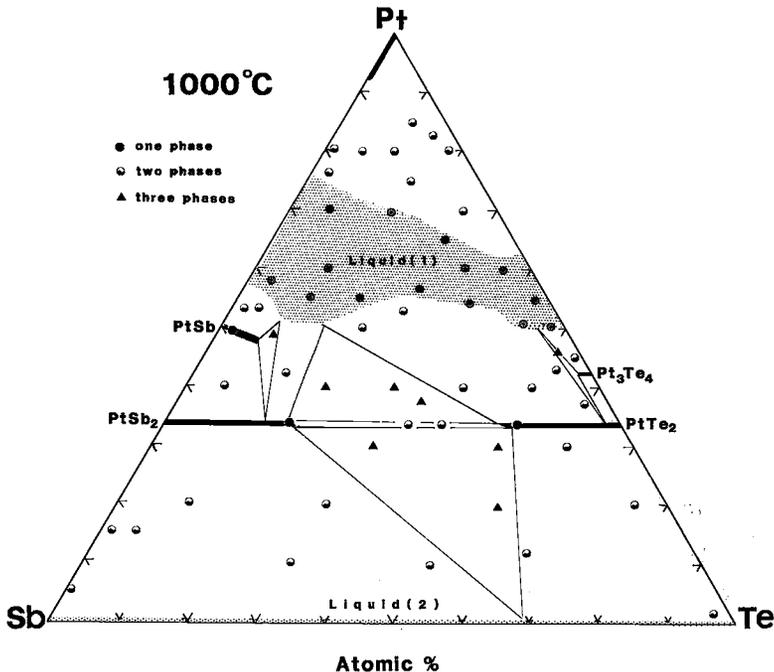


FIG. 4. Phase relations in the system Pt–Sb–Te at 1000°C. Minerals with known synthetic equivalents are platinum (Pt), stumpflite (PtSb), geversite ( $\text{PtSb}_2$ ), and moncheite ( $\text{PtTe}_2$ ).

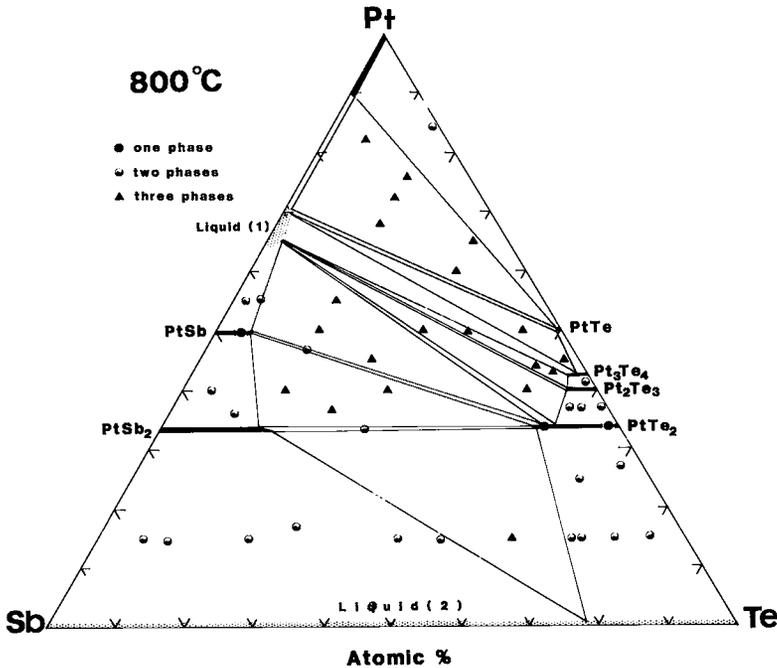


FIG. 5. Phase relations in the system Pt-Sb-Te at 800°C. Minerals with known synthetic equivalents are platinum (Pt), stumpflite (PtSb), geversite (PtSb<sub>2</sub>), and moncheite (PtTe<sub>2</sub>).

stitution of Te for Sb increases, and the composition of the phase coexisting with liquid (1) and PtSb<sub>2</sub> is Pt<sub>47</sub>Sb<sub>47</sub>Te<sub>6</sub>, which corresponds to its largest departure (3 at.% Pt) from stoichiometry. PtSb<sub>2</sub> and PtTe<sub>2</sub> exhibit the largest ranges in solid solution among the solid phases present, but the solid solution is not complete between them; approximately 28.5 at.% Te substitutes for Sb in PtSb<sub>2</sub>, and the same amount of Sb substitutes for Te in PtTe<sub>2</sub>. PtSb<sub>2</sub> and PtTe<sub>2</sub> in equilibrium with liquid (1) are richer in Sb by 3 and 6 at.%, respectively, than those in equilibrium with liquid (2). The Pt<sub>3</sub>Te<sub>4</sub> phase shows solid solution of only 2 at.% by substitution of Sb for Te.

At 800°C, Pt<sub>2</sub>Te<sub>3</sub> and PtTe appear as stable phases in addition to the solid phases existing at 1000°C (Fig. 5). The liquid (1) field has retreated markedly toward the Pt-Sb join, occupying an area between 29 and 35 at.% Sb on the Pt-Sb join to 3 at.% toward Te. Liquid (2) remains as a thin strip along the Sb-Te join. The extent of solid solution of Sb in Pt increases to 10 at.%. PtSb does not show any apparent deviation from its ideal Pt-content at this temperature. PtSb<sub>2</sub> in equilibrium with PtTe<sub>2</sub> and liquid (2) contains as much as 28.5 at.% Te in substitution for Sb, whereas that coexisting with PtSb and PtTe<sub>2</sub> contains less Te (24.8–25.5 at.%

Te). The limit for PtTe<sub>2</sub> solid solution is close to Pt<sub>33.3</sub>Te<sub>54.2</sub>Sb<sub>12.5</sub>. The substitution of Sb for Te in the Pt<sub>2</sub>Te<sub>3</sub>, Pt<sub>3</sub>Te<sub>4</sub>, and PtTe phases is 6.7, 5.2, and 2.0 at.%, respectively.

At 600°C (Fig. 6), five additional compounds appear as stable phases: Pt<sub>3</sub>Sb, Pt<sub>3</sub>Sb<sub>2</sub>, Sb<sub>2</sub>Te<sub>3</sub> and Sb. Liquid (1) disappears completely, whereas the field of liquid (2) splits into two fields of liquid, along the Sb-Te binary join between 7 and 50 at.% Te [liquid (2a)] and between 66.6 and 100 at.% Te [liquid (2b)]. The quenched liquid (2b) coexisting with PtSb<sub>2</sub> and PtTe<sub>2</sub> contains a metastable phase of Sb<sub>2</sub>Te<sub>3</sub> composition and an amorphous phase of 90 at.% Te composition. The compositional range of this liquid (2b) was thus assumed to be somewhere between 68 and 76 at.% Te, estimated indirectly from the tie lines PtSb<sub>2</sub> - liquid (2b) and PtTe<sub>2</sub> - liquid (2b).

Platinum contains Sb up to 9 at.% in solid solution, which is higher than that (6.1 at.%) found in the binary system. PtSb<sub>2</sub> in equilibrium with PtTe<sub>2</sub> and liquid (2b) has an almost identical composition (27.0–28.5 at.% Te) to that in the same assemblage at 800°C. However, PtSb<sub>2</sub> in equilibrium with PtSb and PtTe<sub>2</sub> is close to its ideal composition, as it contains less than 1 at.% Te in substitution for Sb. Pt<sub>3</sub>Sb<sub>2</sub> contains up to 5 at.% Te. The limits of sub-

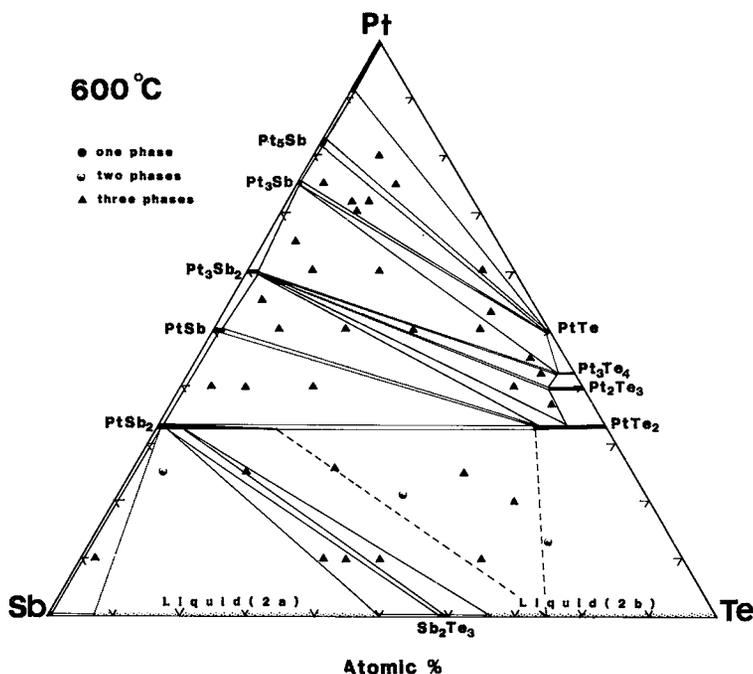


FIG. 6. Phase relations in the system Pt-Sb-Te at 600°C. Minerals with known synthetic equivalents are platinum (Pt), stumpflite (PtSb), gerversite (PtSb<sub>2</sub>), moncheite (PtTe<sub>2</sub>), tellurantimony (Sb<sub>2</sub>Te<sub>3</sub>), and antimony (Sb).

stitution of Sb for Te in the Pt<sub>2</sub>Te<sub>3</sub> and Pt<sub>3</sub>Te<sub>4</sub> phases are 8.3 and 3.5 at.%, respectively.

A comparison between the isothermal section at 650°C of El-Boragy & Schubert (1971) and that in Figure 6 shows substantial agreement in the region 33.3–100 at.% Pt, except that the phase Pt<sub>4</sub>Sb of El-Boragy & Schubert has now been replaced by Pt<sub>5</sub>Sb. However, there is considerable disagreement in phase relations for the 0–33.3 at.% Pt portion. Besides the Sb and Sb<sub>2</sub>Te<sub>3</sub> phases, El-Boragy & Schubert (1971) showed the presence of four additional solid phases having the compositions of 19–21, 25–37, 40–52, and 100 at.% Te on the Sb–Te join. Similar metastable phases formed during quenching were frequently encountered in this study. However, all versions of the Sb–Te phase diagram (Hansen & Anderko 1958, Abrikosov *et al.* 1959, Brown & Lewis 1962) illustrate that liquid is the only stable phase at 650°C, which is supported by the well-established melting points of the stable phases in the system: Sb (630.5°C: Hansen & Anderko 1958), Sb<sub>2</sub>Te<sub>3</sub> (621–622°C: Hansen & Anderko (1958) and Te (450°C: Kracek 1941). It is possible that all the solid phases on the Sb–Te join observed by El-Boragy & Schubert (1971) are metastable. A more reasonable phase diagram for the region at 650°C is perhaps similar to that for 800°C for this study (Fig.

2), where liquid is the only stable phase within the entire range of the Sb–Te binary join.

According to the experimental data obtained in this study, platinum cannot coprecipitate with stumpflite (PtSb), gerversite (PtSb<sub>2</sub>), and moncheite (PtTe<sub>2</sub>) from Pt-rich basic magma over the temperature range of 1000°–600°C. Thus, a mineral assemblage consisting of Pt-Fe alloy, gerversite and stumpflite, reported by Stumpfl (1961) from the Driekop mine, Transvaal, South Africa, may be interpreted to have been formed under disequilibrium conditions or at subliquidus temperatures in the presence of Fe. If the mineral assemblage stumpflite + gerversite + moncheite exists in nature, it must have formed below 1000°C. The composition of gerversite for this case, however, may be an important clue in deducing the temperature of formation, because gerversite in that assemblage at 800°C differs in composition significantly from that at 600°C. Common intergrowths of stumpflite and gerversite, reported by Stumpfl (1961), may not yield any specific temperature of formation because such an assemblage persists over the temperature range 1000°–600°C.

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