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High-temperature Behavior of $PtBi_2$ and Possibility of Using the Mineral Insizwaite as a Geothermometer

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Abstract—The article presents investigation of polymorphic transformations of the $PtBi_2$ phases that occur during heating in inert atmosphere and in vacuum. A synthetic medium-temperature β-$PtBi_2$ modification corresponding to the mineral insizwaite was studied by high-temperature X-ray diffraction and differential thermal analysis in the temperature range of 20–640°C. Two phase transitions are established by in situ X-ray powder diffraction: from β into γ-$PtBi_2$, and then into δ-$PtBi_2$. Two endothermic peaks are recorded on the DTA curve, which correspond to the phase transitions. High-temperature X-ray powder diffraction data determined γ- and δ-$PtBi_2$ formation at high temperature in inert atmosphere and in vacuum. Reverse polymorphic transformation were not observed by X-ray powder diffraction during cooling. It is suggested that insizwaite is a mineral geothermometer and its presence in the geological system implies certain temperature ranges of mineral formation environments.

Keywords: insizwaite, platinum bismuthide, polymorphic transformations, differential thermal analysis, high-temperature X-ray powder diffraction, geothermometer

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INTRODUCTION

The phase relations in the binary diagram Pt–Bi were reviewed by H. Okamoto (1991). The Pt–Bi system contains six binary compounds: PtBi, α-$PtBi_2$, β-$PtBi_2$, γ-$PtBi_2$, δ-$PtBi_2$ and Pt_2Bi_3. The crystallographic data for the phases are shown in Table 1. The phase with the composition $PtBi_2$ forms different structural modifications depending on the crystallization temperature (Okamoto, 1991; Zhuravlev and Stepanov, 1962).

The low-temperature modification α-$PtBi_2$ was synthesized by T. Biswas and K. Schubert in 1969. Its structure was solved later (Bhatt and Schubert, 1980b). It is orthorhombic, sp. gr. *Pbca*; the structure type is $AuSn_2$.

The β-$PtBi_2$ modification has a cubic crystal structure, sp. gr. $Pa\bar{3}$, unit cell parameters: $a = 6.625$(A), $V = 290.775$ (A3), $Z = 4$ with a pyrite structure type (Zhuravlev et al., 1962, Furuseth et al., 1965, Brese and Schnering, 1994). This synthetic phase corresponds to the mineral insizwaite, which was found and described by L. Cabri and D. Harris (1972).

The crystal structure and properties of γ-$PtBi_2$ modification have been studied several times. The first structural model for the γ-$PtBi_2$ in trigonal sp. gr. $P\bar{3}$ was obtained by Schubert et al. (1968). The same model was used in structure refinement by Xu et al. (2016). Synthesis of γ-$PtBi_2$ was performed using a melt-growth method in both cases. M. Kaizer et al. (2014) discovered that γ-$PtBi_2$ can also be obtained at 70°C by reductive decomposition of layered $Bi_{13}Pt_3I_7$. Using this unconventional growth method, the γ-$PtBi_2$ single crystals were synthesized, and structure was solved in another sp. gr. $P31m$.

Recently in 2020, one more structural study of γ-$PtBi_2$ published (Shipunov et.al., 2020). Both structural models were considered: in sp. gr. $P\bar{3}$ and $P31m$. The structure refinement in the group $P31m$ gave the lowest *R*-factor: 5.2% against 11.8%. Selected area

Table 1. Crystallographic data for Pt–Bi system

Phase	Crystal system	Sp. gr.	Unit cell parameters, volumes, Z					Reference
			a, Å	b, Å	c, Å	V, Å^3	Z	
PtBi	Hexagonal	$P6_3/mmc$	4.315	4.315	5.49	88.52	2	(Zhuravlev et al., 1962)
α-$PtBi_2$	Orthorhombic	$Pbca$	6.732	6.794	13.346	610.41	8	(Bhatt, Schubert, 1980b)
β-$PtBi_2$	Cubic	$Pa\bar{3}$	6.7014	6.7014	6.7014	300.95	4	(Brese, Schnering, 1994)
γ-$PtBi_2$	Trigonal	$P31m$	6.5730	6.5730	6.1665	266.42	3	(Kaiser et al., 2014), (Shipunov et al., 2020)
		$P\bar{3}$	6.553	6.553	6.165	264.74	3	(Xu et al., 2016) (Schubert et al., 1968), (Biswas, Schubert, 1969)
δ-$PtBi_2$	Orthorhombic	$Pnnm$	?	?	?			(Bhatt, Schubert, 1980b)
	Hexagonal	$P6_3/mmc$	4.391	4.391	5.552		1	This work
Pt_2Bi_3	Hexagonal	$P6_3/mmc$	4.13	4.13	5.58	82.43	1	(Schubert et. al., 1968)

electron diffraction (SAED) also confirmed the group $P31m$.

The only information about the highest modification contains in the paper (Bhatt and Shubert, 1980b). Authors found that δ-$PtBi_2$ forms solid solution with a compound Pt_4Bi_7Pb.

Zhuravlev et al. (1962a, 1962b) provides first high-temperature X-ray diffraction study of the $PtBi_2$ phase. Three modifications were obtained, and thermal expansion coefficients were calculated. The crystallographic data were obtained for cubic $PtBi_2$. Polymorphic transitions under cooling were not studied. It needs to be mentioned that names of the $PtBi_2$ polymorphs in the Zhuravlev's works do not correspond to modern nomenclature.

We report the results of $PtBi_2$ polymorphic transitions temperature dependence study using several methods: thermal analysis coupled with thermogravimetric analysis (DTA+TG); high-temperature X-ray powder diffraction and electron microprobe analysis. Experiments were performed under inert atmosphere and in vacuum. Reversibility of transitions was addressed. The authors suggest that mineral insizwaite, β-$PtBi_2$, can be used as a geothermometer for estimating temperature of crystallization in a geological system.

EXPERIMENTAL

Synthesis

The β-$PtBi_2$ polymorph was obtained via solid phase synthesis in vacuum-sealed silica-glass tubes. Mixture of pure metals Pt and Bi in molar proportion Pt : Bi = 1 : 2 was placed in a silica tube, evacuated and sealed. To obtain the precursor compound the tube with the charge was placed in a furnace and heated at 850°C for a week, then quenched by dropping in cold water. The precursor material was grounded and divided in to several portions. Each portion was placed in the tube, evacuated, and sealed again. One tube was heated at the temperature 350°C during a week leading to the β-$PtBi_2$ polymorph formation. Another tube heated at the temperature 250°C during four months with a purpose to obtain the α-$PtBi_2$ polymorph.

X-ray Powder Diffraction

The synthesis products were ground in an agate mortar and analyzed by X-ray diffraction method on the Rigaku DMAX 2200/PC diffractometer at the Institute of Geology of Ore Deposits RAS (IGEM RAS, Moscow, Russia). X-ray diffraction data were acquired at room temperature using Cu-λK_α radiation, time-counting scanning mode, step size 0.05°θ, exposure 1.5 sec, in the 2θ range from 3° to 80°. Phase analysis was performed with the Jade 6.5 program (Materials Data Incorporation LTD).

Electron Microprobe Analysis

The chemical composition and homogeneity of the grains were determined using a Microanalyzer Cameca SX100 with five wavelength spectrometers and a Bruker Xflash6 energy dispersive spectrometer at the Common User Center Geoanalyst of the Zavaritzkiy Institute of Geology and Geochemistry UB RAS (IGG UB RAS, Ekaterinburg, Russia).

Differential Thermal Analysis

Thermal effects were studied via differential thermal analysis (DTA+TG) using an STA 449F5 Jupiter analyzer, NETZSCH (Germany) at Zavaritskiy Insti-

Table 2. X-ray diffraction data for β-$PtBi_2$

Synthetic β-$PtBi_2$, (annealing at 250°C)		Synthetic β-$PtBi_2$, (annealing at 350°C)		Insizwaite (Cabri, Harris, 1972)		Synthetic β-$PtBi_2$, (PDF no. 26-0221)		
d_{exp} (Å)	I_{exp} (%)	d_{exp} (Å)	I_{exp} (%)	d (Å)	I	d (Å)	I (%)	hkl
3.889	5	3.873	5	3.79	0.5	3.860	30	1 1 1
3.368	25	3.348	21	3.31	2	3.340	50	2 0 0
3.011	**98**	**2.994**	**82**	**2.96**	**8**	**2.996**	**100**	2 1 0
2.748	**78**	**2.733**	**70**	**2.70**	**8**	**2.732**	**80**	2 1 1
2.378	28	2.368	24	2.34	5	2.365	50	2 2 0
2.026	**100**	**2.021**	**100**	**1.998**	**10**	**2.017**	**90**	3 1 1
1.938	9	1.935	11	1.915	2	1.932	30	2 2 2
1.863	25	1.858	28	1.836	4	1.854	40	2 3 0
1.794	**55**	**1.791**	**64**	**1.774**	**7**	**1.788**	**60**	3 2 1
1.678	8	1.675	10	1.655	1	1.672	30	4 0 0
1.500	15	1.498	22	1.484	4	1.494	40	4 2 0
1.464	33	1.462	39	1.443	5	1.459	50	4 2 1
1.432	12	1.429	20	1.414	3	1.426	40	3 3 2
1.369	12	1.368	19	1.354	3	1.366	30	4 2 2
1.291	40	1.290	44	1.277	6	1.288	50	5 1 1
1.246	31	1.244	37	1.231	4	1.242	40	2 5 0
1.225	18	1.224	24	1.210	3	1.221	30	5 2 1

tute of Geology and Geochemistry UB RAS (Ekaterіburg). DTA experiments were conducted in α-Al_2O_3 crucible in argon flow 50 mL/min with ramp rate 10°/min in the temperature range 30–800°C. Prior to the heating two corundum crucibles with the same mass were annealing up to 1100°C on air and were subsequently used for crucib the background line ("blank line") measurement. Inert α-Al_2O_3 used as standard. The work chamber was evacuated then filled with argon.

High-temperature Powder X-ray Diffraction

High-temperature powder X-ray diffraction (HTXRD) experiments of $PtBi_2$ phase were done using an Empyrean Panalytical BV diffractometer with Anton Paar HTK-1200N high-temperature attachment at the Frumkin Institute of Physical chemistry and Electrochemistry RAS (IPCE RAS, Moscow, Russia). β-$PtBi_2$ powder were deposited on a Al_2O_3 sample holder. HTXRD experiments were performed in vacuum in a temperature cycle 50–640–50°C (heating and cooling) using Cu-λK_α radiation in 2θ range from 10° to 80°. Temperature steps were 10/20/50°C, average heating rate was about 5°/min, collecting time at each temperature step was about 30 min. The total time of the experiments, including heating, cooling, and diffraction data collection, was about 17.5 h.

RESULTS AND DISCUSSION

X-ray powder diffraction data of the samples synthesized at temperature 250 and 350°C, correspond to benchmark diffraction patterns of the β-$PtBi_2$ modification (PDF card no. 26-0221) and insizwaite (Cabri and Harris, 1972) (Table 2). The low temperature α-modification of $PtBi_2$ was not obtained despite the long time of the synthesis experiment.

Homogeneity of the samples was confirmed by electron microprobe analysis. The composition was obtained at 16 points on three grains (Table 3). The average element contents (in wt %) are Pt 32.82, Bi 67.59. The empirical formula for synthetic insizwaite is $Pt_{1.03}Bi_{1.97}$, calculated based on atoms per formula unit.

The DTA curve of the $PtBi_2$ sample contains two endothermic peaks at the temperatures 421.0 and 639.4°C, respectively (Fig. 1, Table 4). These data are in agreement with the temperature of polymorphic transformations (Okamoto, 1991). The thermal effect

Table 3. Microprobe analysis of β-$PtBi_2$

Grain	Point	Content (wt %)		
		Pt	Bi	Total
9308-1	9308-1-1	32.9	67.74	100.64
	9308-1-2	32.7	67.53	100.22
	9308-1-3	33.44	67.65	101.09
	9308-1-4	32.9	67.61	100.51
	9308-1-5	32.71	67.85	100.55
	9308-1-6	32.77	67.5	100.27
9308-2	9308-2-1	32.56	67.67	100.23
	9308-2-2	32.87	67.4	100.27
	9308-2-3	32.76	67.53	100.29
	9308-2-4	32.99	67.39	100.38
	9308-2-5	33.07	67.8	100.87
9308-3	9308-3-1	32.5	67.73	100.23
	9308-3-2	32.93	67.66	100.59
	9308-3-3	32.87	67.37	100.23
	9308-3-4	32.74	67.59	100.33
	9308-3-5	32.42	67.45	99.87
Average content (minimum–maximum)		32.82 (32.42–33.44)	67.59 (67.37–67.85)	100.41
Empirical formula		$Pt_{1.03}Bi_{1.97}$		

Table 4. Temperature of polymorphic transformations, solidus (t_s) and liquidus temperature (t_l) for $PtBi_2$

Polymorphic transformation	Temperature of polymorphic transformations by (Okamoto, 1991); t, °C	Temperature of polymorphic transformations in argon atmosphere estimated via DTA method (this work); t, °C
α→β	270	–
β→γ	420	421
γ→δ	640	639.4
t_s	660	653.2
t_l	~710	717.3
TG		0.05%

at the temperature of 653.2°C corresponds to incongruent melting of the $PtBi_2$ and to solidus temperature (t_s), above which the two-component field exists. The melting ends at the temperature 717.3°C—the liquidus (t_l), at which the small endothermic peak on the DTA curve appears. The sample weight change was 0.05% in the temperature range 30–775°C, this value is within the measurement error of. The endothermic peak at 639.4°C temperature just before melting indicates the formation of the δ-$PtBi_2$ phase, which exists in a narrow temperature range.

Table 5 presents the diffraction data of the γ-$PtBi_2$, obtained by high-temperature X-ray diffraction at 500°C, in comparison with the theoretical data. Card

Table 5. X-ray diffraction data for γ-$PtBi_2$

Experimental diffcartion pattern for γ-$PtBi_2$, collected at 500°C			Theoretical diffcartion pattern for γ-$PtBi_2$ (Kaiser et. al., 2014)			
d_{exp}, Å	I_{exp}, %	*hkl*	$2\theta_{calc}$	d_{calc}, Å	I_{calc}, %	*hkl*
			14.35	6.167	19	001
			15.55	5.693	1	010
4.236	2	011	21.23	4.183	1	011
			27.11	3.287	1	−120
3.113	6	002	28.94	3.083	4	002
2.933	**100**	**−121, 111**	**30.80**	**2.900**	**100**	**−121, 111**
2.737	22	012	33.01	2.711	18	012
2.612	15	021	34.69	2.584	16	021
2.270	**34**	**−122, 112**	**40.07**	**2.249**	**27**	**−122, 112**
2.174	13	−130	41.96	2.152	15	−130
2.072	12	003	43.23	2.091	6	022
			44.02	2.056	4	003
2.042	16	−131, 121	44.57	2.031	14	−131, 121
1.948	6	013	46.96	1.933	6	013
1.916	**17**	**030**	**47.90**	**1.900**	**24**	**030**
			50.27	1.814	2	031
1.780	3	122, −132	51.77	1.764	3	−132, 122
1.759	10	113, −123	52.46	1.743	13	−123, 113
1.682	2	023	55.07	1.666	5	023
			55.91	1.643	1	−240
1.632	4	032	56.94	1.616	5	032
1.603	7	−241, 221	58.04	1.588	8	−241, 221
			58.41	1.579	3	−140
1.552	3	004	59.96	1.542	4	004
			60.48	1.530	4	−141, 131
1.500	7	014, 123, −133	62.35	1.488	2	014, −133
1.463	3	−242, 222	64.17	1.450	4	−242, 222
			65.54	1.423	1	040
1.420	2	−142, −134	66.48	1.405	7	−142, 132
1.408	2	114, −124	67.00	1.396	2	−124, 114
1.408	1	033	67.08	1.394	2	033
1.390	1	041	67.49	1.387	2	041
			69.26	1.356	1	024
1.319	3	−250	72.29	1.306	2	−250
			73.19	1.292	7	042
1.289	4	−243, 223	73.76	1.284	2	−243
			74.16	1.278	6	223, −251
1.265	6	124, −134	75.86	1.253	6	−134, 124
1.264	2	−143, 133	75.94	1.252	5	−143, 133
1.256	2	−150	76.65	1.242	2	−150
1.244	1	−129, 005	77.30	1.233	1	005
1.231	3	141, −151	78.48	1.218	5	−151, 141
1.216	1	015				
1.215	2	232, −252	79.67	1.203	3	−252, 232
1.208		034	80.15	1.197	5	034

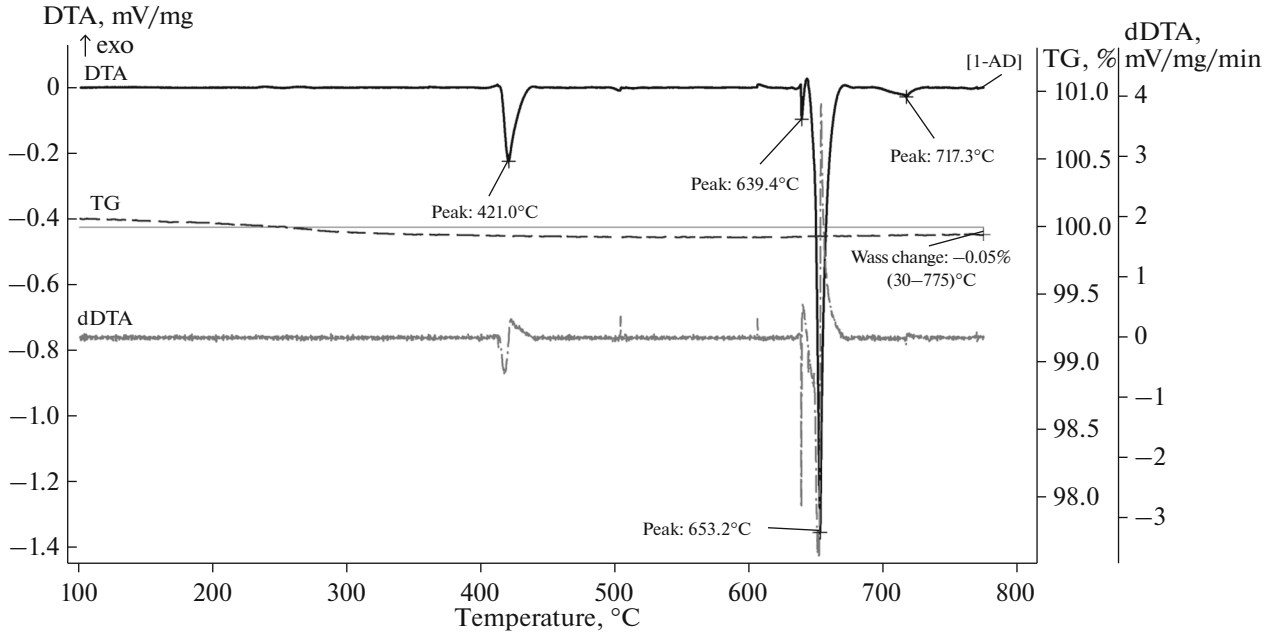

Fig. 1. Temperature dependence of DTA signal for $PtBi_2$ in argon atmosphere with ramp rate of 10°C/min.

no. 9-269 of the International Powder Diffraction Database Powder Diffraction File (PDF) is considered the γ-$PtBi_2$ standard. However, our experimental data and structural studies by other authors (Schubert et al., 1968; Biswas & Schubert, 1969; Xu et al., 2016) indicate that this card for γ-$PtBi_2$ is apparently erroneous.

Table 6. X-ray Diffraction data for δ-$PtBi_2$ collected at 620°C

2θ	*d*, Å	*I*, %	*hkl*
23.361	3.805	19.3	100
28.417	3.138	100.0	101
40.240	2.239	81.7	102
41.211	2.189	58.5	2–10
47.798	1.895	2.3	200
50.901	1.793	21.1	201
55.250	1.661	17.2	103
59.027	1.564	32.6	202
64.814	1.432	1.6	3–10
67.482	1.387	25	004, 3–11
71.288	1.322	4.1	203
72.624	1.301	1.9	104
74.452	1.271	23.3	3–12
75.063	1.262	8.1	300
77.177	1.2489	1.9	301

The X-ray diffraction pattern of the high-temperature δ-$PtBi_2$ modification obtained at 620°C (Table 6). It was indexed in hexagonal crystal system, possible space groups are—$P6_3/mmc$, $P6_3/m$, $P6_122$. The unit cell parameters were calculated: a = 4.391 Å, c = 5.552 Å. The hypothesis (Bhatt and Schubert, 1980b) of the isostructural nature of the δ-$PtBi_2$ and Pt_4Bi_7Pb phases is not confirmed.

High-temperature powder X-ray diffraction data confirm the stability of the β-$PtBi_2$ polymorph in the temperature range 30–420°C. Additional peaks appear in the diffraction patterns starting from 420°C. The intensity of the β-$PtBi_2$ peaks becomes smaller at the same time (Fig. 2). Process of transformation from the cubic β-polymorph to the trigonal γ-polymorph is going on. At 500°C the peaks of the β-$PtBi_2$ disappear completely: the first polymorphic transformation ends. Only intensity of diffraction peaks varies at the temperature range 500–600°C. Diffraction pattern is changing again at New peaks appear at 600°C corresponding to polymorphic transformation from γ-$PtBi_2$ to δ-$PtBi_2$. Decomposition process is beginning at 630°C. At this point diffraction peaks of metallic platinum appear. Peaks of the δ-$PtBi_2$ polymorph persist up to 640°C. Heating above 640°C was not carried out to avoid melting of the sample. After that the sample was cooled to the room temperature. During the cooling process X-ray diffraction patterns did not change.

The stability field of the β-$PtBi_2$ polymorph extends from 20 to 420°C, the γ-$PtBi_2$ polymorph forms and exists in the temperature range 450–600°C, δ-$PtBi_2$ polymorph crystalizes and exists from 600 to

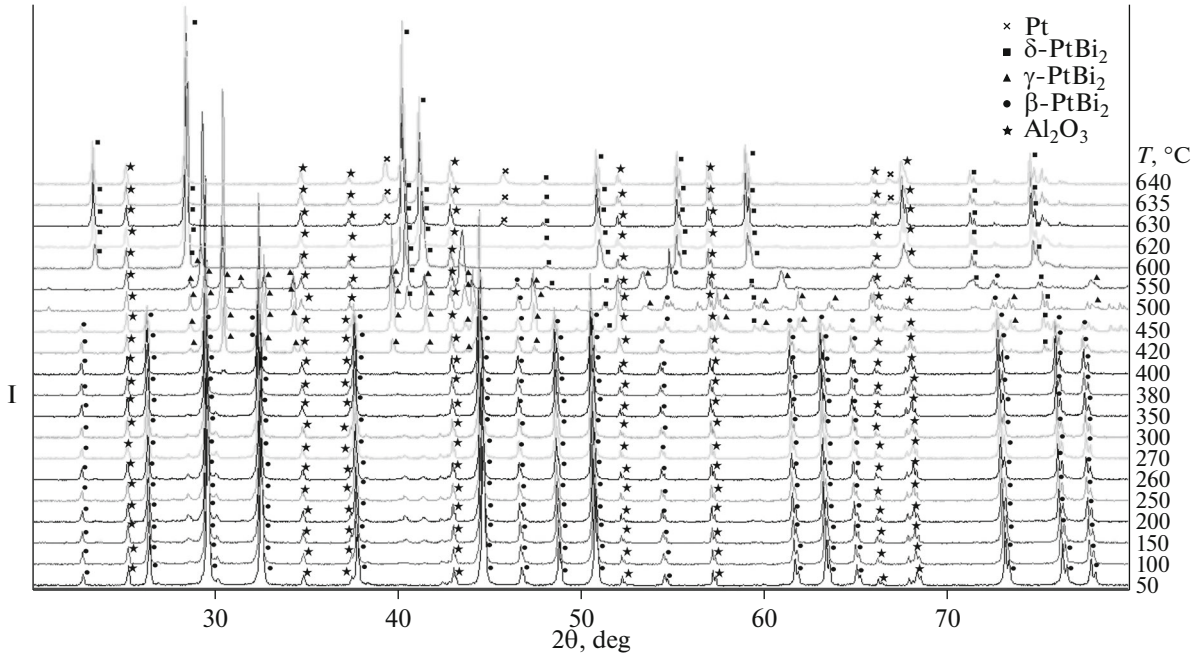

Fig. 2. High-temperature X-ray diffraction experiments for $PtBi_2$ in temperature range from 30 to 640°C in vacuum.

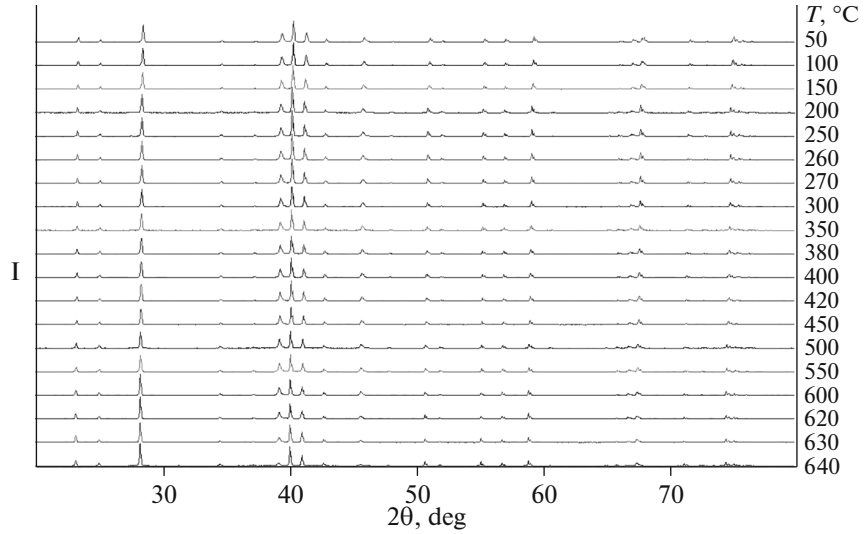

Fig. 3. X-ray diffraction experiments collected during cooling $PtBi_2$ in temperature range from 640 to 50°C in vacuum.

640°C (Kaizer et. al., 2014). The high-temperature X-ray diffraction experiment is an in situ method, and it dynamically shows the transformation process. That is why the peaks of two polymorphs coexist in some X-ray patterns collected near the transformation temperatures. The peak intensities of the polymorphs and their ratio change gradually in such diffraction patterns. The main diffraction peaks of the β-$PtBi_2$ polymorph appear together with γ-polymorph peaks in the X-ray diffraction patterns taken in the temperature range 450–550°C. The diffraction pattern acquired at 600°C contains the highest-intensity peak of the γ-$PtBi_2$ together with the peaks of δ-$PtBi_2$ polymorph. Also, all collected diffraction patterns contain the peaks of Al_2O_3 phase, which is the sample holder and internal standard.

Upon successive cooling of the sample from 640 to 50°C, the diffraction pattern did not shown significant changes (Fig. 3).

CONCLUSIONS

High-temperature transformations of the $PtBi_2$ phase were studied by a set of methods. It is shown that

the transformation from the δ-$PtBi_2$ polymorph in to the γ-$PtBi_2$ and then in to the β-$PtBi_2$ one did not occur during cooling in HTXRD experiments. The results of the DTA and HTXRD analyzes agree well and correlate with the temperatures of polymorphic transformations. The β-$PtBi_2$ polymorph is stable under an inert atmosphere at temperatures up to 450°C, γ-$PtBi_2$ is stable in the temperature rangs from 450 to 620°C, and δ-$PtBi_2$, from 620°C to 640°C. The existence of the high-temperature polymorph is confirmed.

The low temperature polymorph α-$PtBi_2$ was not obtained. Instead, the β-$PtBi_2$ (insizwaite) crystallized during annealing at 250°C. That is why, the α-$PtBi_2$ polymorph behaviour at high temperatures and its transformation in to β-form are not studied.

The experimental results indicate that insizwaite, β-$PtBi_2$, can be used as a mineral geothermometer. Insizwaite crystallizes at up to 450°C under inert atmosphere and in vacuum. The γ- and δ-polymorphs form at temperatures higher than 450°C. That is true only for processes under inert atmosphere and vacuum conditions. Other transformations occur during heating of insizwaite in air (Mezhueva et al., in press). The possibility of using insizwaite as geothermometer requires further study. It is necessary to estimate the influence of different factors, such as pressure, annealing time, and the presence of additional phases in the system on crystallization of high-temperature polymorphs.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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