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The binary system PbO – $BiVO_4$

Research Article

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Abstract: Phase equilibria established in the PbO – $BiVO_4$ system over the whole component concentration range up to 1000°C have been investigated. A phase diagram has been constructed using DTA and XRD.

Keywords: *Phase diagram • Bismuth(III) vanadate(V) • Bismuth(III) lead(II) vanadates(V) • Thermal analysis • X-ray diffraction*

1. Introduction

The knowledge of phase diagrams is essential to understand, control and improve the stability of materials [1]. Phase diagrams also provide basic information with regard to the preparation of new types of materials [1]. The experimental determination of phase diagrams generally includes two stages: the preparation of samples and the measurement of phase relation parameters under conditions as close to the equilibrium state as possible. The phase diagrams show the phase relations against the temperature – composition coordinates. Phase diagrams supply information without which it would be difficult to understand relations between properties, composition and structure. This is why phase diagrams are needed not only for research but also for industrial purposes.

The metal oxide systems which consist of bismuth(III) oxide have received a considerable amount of attention over the past decade [2-4]. The ternary system PbO – Bi_2O_3 – V_2O_5 has been under intensive study due to the fact that phases which exist in this system display good transport properties, which are better than some of the more traditional phases used in these applications [4]. In solid state reactions between PbO and $BiVO_4$ three compounds are formed: $PbBiVO_5$, Pb_2BiVO_6 and Pb_4BiVO_8 [5,6]. The phase relations in the system PbO – $BiVO_4$, over the whole components concentration range up to 1000°C, have not been fully characterized in the past.

Previous studies imply that $PbBiVO_5$ exists in two polymorphic forms where the phase transition occurs at 480°C [7,8]. A low-temperature polymorph $PbBiVO_5$ crystallizes in triclinic system [7]. Its unit cell parameters are: a = 7.1082(5) Å, b = 7.2802(6) Å, c = 5.6203(1) Å, α = 111.788°, β = 95.207°, γ = 108.717(5)°, Z = 2. A high-temperature polymorph $PbBiVO_5$ crystallizes in monoclinic system with cell parameters: a = 13.635 Å, b = 5.657 Å, c = 7.202 Å, β = 113.82°, Z = 4 [7]. $PbBiVO_5$ melts congruently at 855°C [7].

Pb_2BiVO_6 has four polymorphic modifications labeled α to δ [7,9]. The temperatures at which the phase changes occur are: 415°C for α → β, 475°C for β → δ [7]. The phase transition δ–Pb_2BiVO_6 → α–Pb_2BiVO_6 is observed on cooling at 460°C [7]. The existence of the γ–Pb_2BiVO_6 form was observed in a small amount as a mixture of Pb_4BiVO_8 and the high-temperature form of $PbBiVO_5$ [7]. The transformation γ-Pb_2BiVO_6 → δ–Pb_2BiVO_6 occurs at 635°C and it is relatively slow and it is not observed at a fast heating rate [7].

The α-Pb_2BiVO_6 polymorph crystallizes in the monoclinic system with the space group P2N1 [5,6,10]. Its cell parameters are: a = 7.642(6) Å, b = 5.812(5) Å, c = 28.85(2) Å, β = 100.3(1)° and Z = 8 [10]. δ-Pb_2BiVO_6

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crystallizes in tetragonal system [3,4,7] with cell parameters a = 12.110(2) Å, c = 9.472(8) Å and Z = 8 [7,10]. The literature does not provide any information about cell parameters of β- and γ-Pb_2BiVO_6 forms. Pb_2BiVO_6 melts congruently at 780°C [7].

Pb_4BiVO_8, which is also formed in the system PbO – $BiVO_4$, occurs only in one polymorphic modification [6]. Pb_4BiVO_8 crystallizes in the triclinic system with cell parameters: a = 6.221(2) Å, b = 7.603(5) Å, c = 10.457(4) Å, α = 100.40(3)°, β = 102.18(2)°, γ = 90.03(3)° and Z = 2 [4]. It melts congruently at 780°C [6].

The aim of this work was to determine the phase relations in the system PbO – $BiVO_4$ over the whole concentration range of the components.

2. Experimental Procedures

The reagents used in this research were: PbO (a.p., Merck), Bi_2O_3 (a.p., POCh, Gliwice, Poland), V_2O_5 (a.p., Riedel-de Haën, Germany), as well as $BiVO_4$ obtained as a result of heating an equimolar mixture of Bi_2O_3 and V_2O_5 in the stages: 600ºC (24 h) + 650ºC (24 h).

For the research, 19 samples were prepared. The reagents were weighed in appropriate portions, homogenized by grinding and next pressed into pellets and heated in an air atmosphere in a furnace. After each heating stage the pellets were cooled rapidly to room temperature, ground and subjected to XRD and DTA investigations.

To verify the thermal properties of $PbBiVO_5$, Pb_2BiVO_6 and Pb_4BiVO_8 the measurements were carried out using a high-temperature chamber UVD-2000 (Bourevestnik, Saint-Petersburg, Russia) with an HZG4/A2 XRD diffractometer (Carl Zeiss, Jena, Germany).

The XRD examinations were performed by using the diffractometer DRON-3 (Bourevestnik, Saint-Petersburg, Russia) applying the radiation CuK_α and Ni filter. The identification of individual phases was based on the accordance of the obtained diffraction patterns with the data contained in the PDF cards [11] and literature [5-7,9].

The DTA measurements were performed in an atmosphere of air, in quartz crucibles at a heating rate of 10 °C min^{-1} in the range of 20 - 1000ºC. The weight of investigated samples always amounted to 500 mg. The accuracy of reading the temperature of thermal effects on the DTA curves, as evaluated on the base of repetitions, amounted to ±5°C. The DTA investigations were conducted by using a derivatograph of F. Paulik-J. Paulik-L. Erdey type (MOM, Budapest, Hungary).

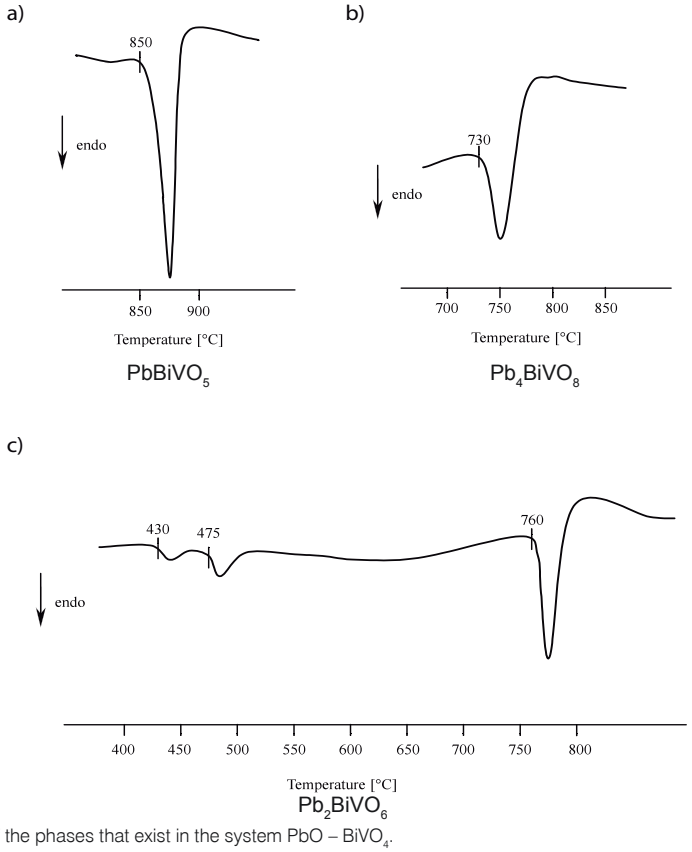

Figure 1. DTA curves of the phases that exist in the system PbO – $BiVO_4$.

3. Results and discussion

The work was begun with the aim to verify the literature information [3-6] concerning thermal properties of the compounds which are formed in the system PbO – $BiVO_4$: $PbBiVO_5$, Pb_2BiVO_6 and Pb_4BiVO_8. Fig. 1 presents DTA curves of well known bismuth(III) lead(II) vanadates(V). In DTA curves of $PbBiVO_5$ and Pb_4BiVO_8 one endothermic effect was recorded (Figs. 1a and 1b). The measurement was repeated with slower heating rates of 5 and 2.5°C min^{-1}, however, still only one endothermic effect was observed. To confirm that $PbBiVO_5$ and Pb_4BiVO_8 do not have polymorphic modifications the measurements were carried out using a high-temperature chamber equipped with an XRD diffractometer. The experiments confirmed that under normal pressure Pb_4BiVO_8 exists only in one polymorphic modification. The results of the measurements in the high-temperature chamber for $PbBiVO_5$ show that at 480 ± 5°C one polymorphic modification occurs, which is not observed in the DTA curve (Fig. 2). The temperature of the phase transition is in agreement with literature information [6].

The DTA curve of Pb_2BiVO_6 contains three endothermic effects with their onset temperatures 430, 475 and 760°C, respectively (Fig. 1c). The onset temperatures of the two first effects are similar to the temperatures at which polymorphic modifications occur [7]. It suggests that Pb_2BiVO_6 has three polymorphic forms. The existence of the polymorphic forms of Pb_2BiVO_6 was confirmed by heating the samples above the modification temperatures for three hours followed by rapid cooling to ambient temperature. The temperatures at which the phase changes of Pb_2BiVO_6 occur were confirmed using high- temperature chamber equipped with an XRD diffractometer.

Table 1 presents the contents of initial mixtures, the conditions of preparation and the results of XRD analysis of all samples in equilibrium, detected after the last stage of heating.

Fig. 3 presents the DTA curves of selected samples belonging to the investigated system at equilibrium state.

In the DTA curve of the sample containing in the initial mixture 30.00 mol% PbO, one endothermic effect was recorded at 775 ± 5°C (Fig. 3a). A similar effect, in addition to other peaks, was observed in DTA curves of the samples with PbO concentration from 10.00 to 50.00 mol%. This effect occurred as the only one in the DTA curve of the sample containing 30.00 mol% PbO and its intensity was the biggest, hence the composition of the eutectic mixture (E_1) was determined to be: ~30.00 mol% PbO and 70.00 mol% $BiVO_4$.

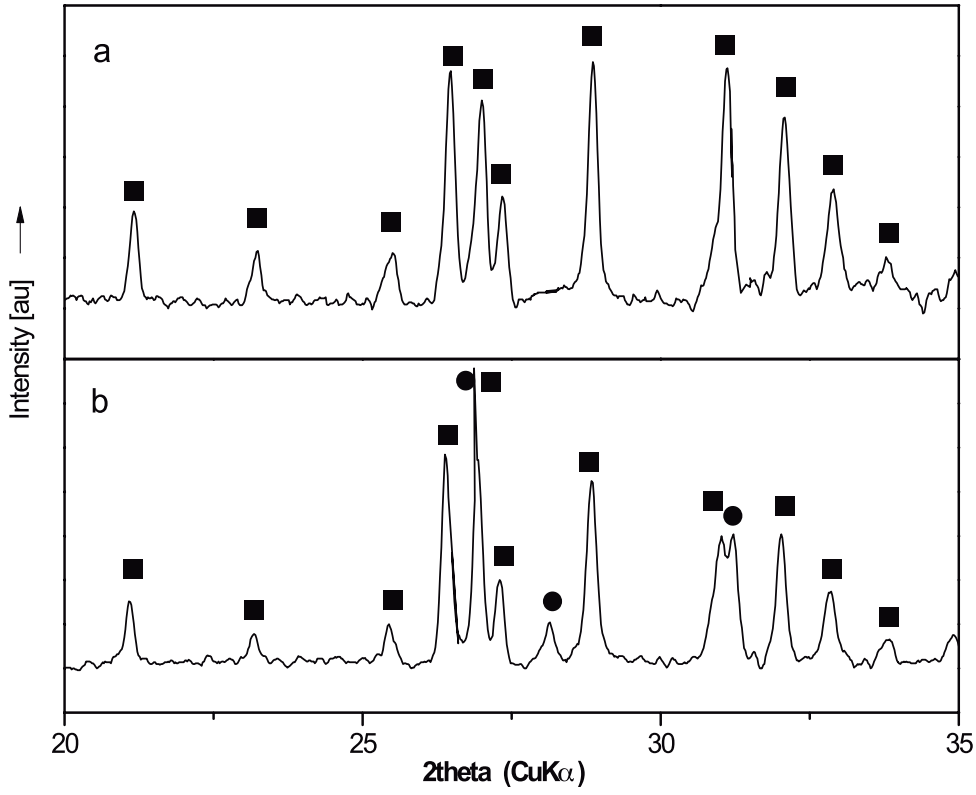

Figure 2. Powder diffraction patterns: a) $PbBiVO_5$; b) $PbBiVO_t$ after heating at 490°C for 3.5 h; ■ - low-temperature $PbBiVO_5$ (PDF: 26-830), ● - high-temperature $PbBiVO_5$ [7].

Table 1. Composition of initial mixtures, conditions of preparation and XRD results for samples after last heating stage.

No.	Composition of initial mixtures [%mol] PbO	$BiVO_4$	Conditions of preparation	Phases detected
1.	2.50	97.50	600°C (24 h) + 650°C (24 h) + 700°C (24 h)	$PbBiVO_5 + BiVO_4$
2.	5.00	95.00		
3.	10.00	90.00		
4.	15.00	85.00		
5.	17.50	82.50		
6.	20.00	80.00		
7.	30.00	70.00		
8.	40.00	60.00		
9.	50.00	50.00		$PbBiVO_5$
10.	60.00	40.00		$Pb_2BiVO_6 + PbBiVO_5$
11.	65.00	35.00		
12.	64.00	36.00		
13.	66.67	33.33		Pb_2BiVO_6
14.	70.00	30.00		$Pb_4BiVO_8 + Pb_2BiVO_6$
15.	75.00	25.00		
16.	80.00	20.00		Pb_4BiVO_8
17.	82.50	17.50	600°C (24 h) + 650°C (24 h)	$PbO + Pb_4BiVO_8$
18.	90.00	10.00		
19.	95.00	5.00		

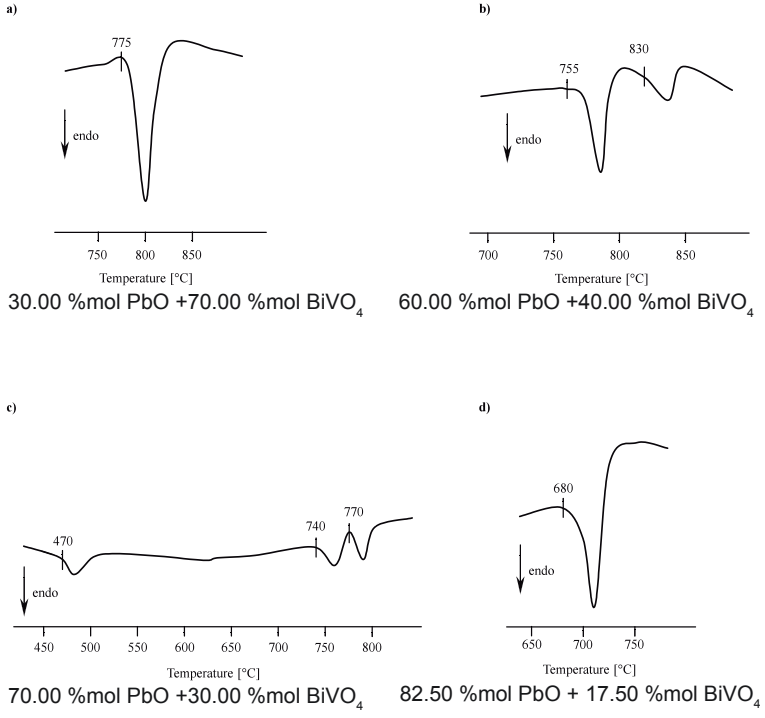

Figure 3. DTA curves of selected samples of the investigated system.

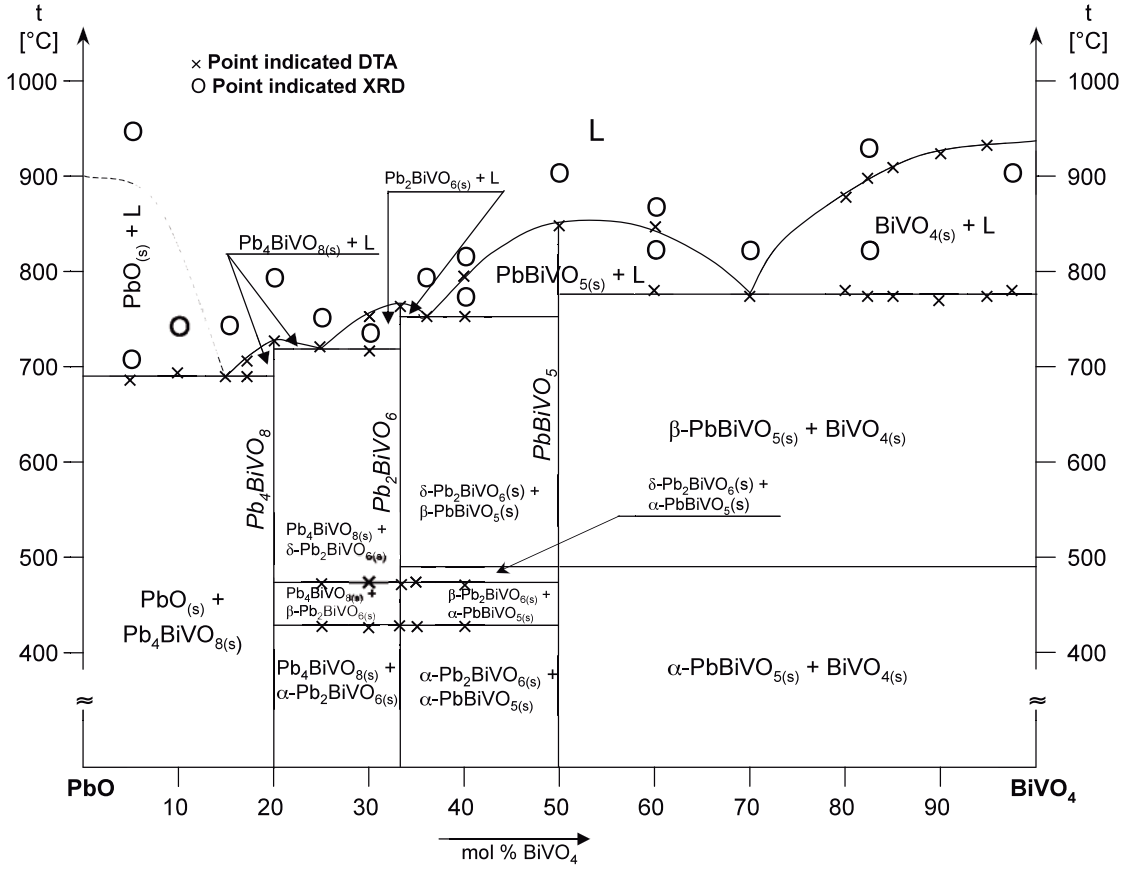

Figure 4. Phase diagram of PbO – $BiVO_4$ system.

The composition of other eutectic mixtures: 64.00 mol% (E_2), 75.00 mol% (E_3) and 82.50 mol% PbO (E_4) were determined in the same way. The DTA curves of the samples with PbO concentration from 50.00 to 64.00 mol% PbO contained two endothermic effects (Fig. 3b), with the first one exhibiting an onset temperature at 755 ± 5°C; this effect was assumed to be associated with melting of the eutectic mixture of 65.00 mol% PbO and 35.00 mol% $BiVO_4$. In DTA curves of the samples containing in their initial mixtures from 75.00 to 80.00 mol% PbO, with constant heating rate 10 °C min^{-1}, three endothermic effects were detected (Fig. 3c). The first of these effects, quite wide, with the onset temperature between 450 and 475°C, was considered to be due to polymorphic modification of Pb_2BiVO_6. This effect was split into two small endothermic effects after decreasing the heating rate to 2.5 °C min^{-1}. The DTA curves of the samples with PbO concentration from 80.00 to 82.50 mol% and above 82.50 mol% show two endothermic effects, the first of them exhibiting an onset temperature at 680 ± 5°C, which was assumed to be due to melting of the eutectic mixture: 82.50 mol% PbO and 17.50 mol% $BiVO_4$ (Fig. 3d).

Fig. 4 presents a diagram of phase equilibria of the system PbO – $BiVO_4$ over the whole components concentration range up to 1000°C. This diagram has been established on the basis of the results of XRD analysis (Table 1) and the DTA curves of equilibrium samples. The temperatures of the solidus line were determined on the basis of the onset temperatures of first endothermic effects, which were not due to the polymorphic modifications, recorded in DTA curves of the investigated samples. The liquidus curves were determined by reading the temperatures of the endothermic effects recorded as the last ones in the DTA curves.

The ranges where solid state phases co-exist with liquid were determined on the basis of DTA curves of the samples at equilibrium but the type of phases were determined on the basis of XRD analysis of samples heated additionally for two hours and then rapidly cooled to ambient temperature. The composition of the sample and the temperature at which some samples were “frozen” are marked in the phase diagram.

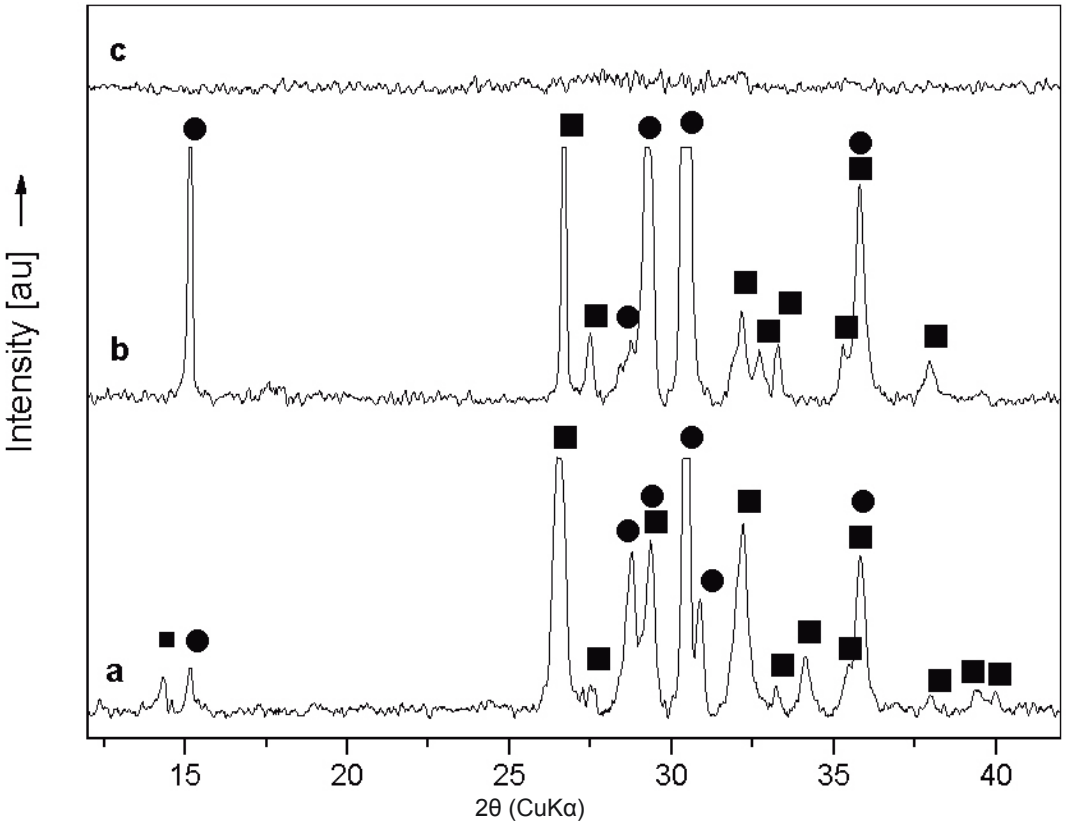

Figure 5. Powder diffraction patterns. a) sample containing in the initial mixture 95.00 mol% PbO, before melting; (b) after melting at 715°C and (c) after melting at 950°C. ■ - Pb_4BiVO_8 (PDF: 50-0493), ● - PbO (PDF: 88-1589)

The phase diagram (Fig. 4) shows that in the system PbO – $BiVO_4$ three compounds exist: $PbBiVO_5$, Pb_2BiVO_6 and Pb_4BiVO_8. They melt congruently.

Reading the temperature of the maximum of the second endothermic effect in DTA curves of the samples containing in the initial mixture above 90 mol% PbO was impossible. The liquidus curve in Fig. 4 for the concentration of PbO above 82.50 mol% is marked as dashed line. The compositions of the samples above the solidus curve were determined on the basis of the samples melted above this curve. The point where the liquidus curve crosses the temperature axis was determined on the basis of the melting temperature of PbO [12]. Fig. 5 presents the powder X-ray diffraction patterns of the sample containing in the initial mixture 95.00 mol% PbO, before melting, after melting at 715°C (above solidus curve) and at 950°C (above liquidus curve). Powder X-ray diffraction pattern of the sample containing in the initial mixture 95 mol% PbO, melted at 715°C (Fig. 5b) consists of line characteristic for the Pb_4BiVO_8 compound. This compound crystallized from the liquid (Pb_4BiVO_8 melts congruently).

4. Conclusion

The phase relationships in the PbO – $BiVO_4$ system were studied in air up to 1000°C using XRD and DTA methods. The following conclusions were drawn from these studies:

- Three bismuth(III) lead(II) vanadates(V): $PbBiVO_5$, Pb_2BiVO_6 and Pb_4BiVO_8 are formed in the PbO – $BiVO_4$ system according to the authors [5,6].
- $PbBiVO_5$, Pb_2BiVO_6 and Pb_4BiVO_8 melt congruently.
- In the system PbO – $BiVO_4$ four eutectic mixtures exist: 30.00 mol% (E_1), 64.00 mol% (E_2), 75.00 mol% (E_3), 82.50 mol% PbO (E_4).

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