Synthesis and Characterization of New Bismuth Lead Vanadate Pb$_2$BiV$_3$O$_{11}$

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It has been shown that BiVO$_4$ and Pb$_2$V$_2$O$_7$ react with each other, forming a new compound of the formula Pb$_2$BiV$_3$O$_{11}$ at molar ratio equal to 1:1. This compound has also been obtained from PbO, Bi$_2$O$_3$, and V$_2$O$_5$, mixed at a molar ratio of 4:1:3. It melts congruently at a temperature of 725 ± 5 °C and crystallizes in the triclinic system with unit-cell parameters: $a = 0.710076$ nm, $b = 1.41975$ nm, $c = 1.42972$ nm, $\alpha = 134.552°$, $\beta = 97.2875°$, $\gamma = 89.6083°$, and $Z = 4$.

1. Introduction

Literature information implies that there exists a series of new compounds of the general formula $M_2^{II}M^{III}V_3O_{11}$ in the ternary system of metal oxides $M^{II}O$-V_2O_5- $M_2^{III}O_3$, where M^{II} = Co, Mg, Ni, and Zn, and M^{III} = Fe, Cr, In.[1-4] Also, compounds of $M_3^{II}Fe_4V_6O_{24}$ type are formed in the $M^{II}O$-V_2O_5-Fe_2O_3 systems.[5,6] In the structure of these compounds, VO$_4$ tetrahedra as well as VO$_5$ bipyramids can be distinguished.[5,6] The compounds have good catalytic properties.[7]

Literature search showed that in the systems Bi$_2$O$_3$-V$_2$O$_5$-MO, where M = Sr, Ba compounds are formed with general formula Bi $M_2^{II}V_3O_{11}$.[8,9] Those compounds for Sr and Ba are not isostructural. BiSr$_2$V$_3$O$_{11}$ crystallizes in the triclinic system with the space group $P\bar{1}$, its cell parameters are: $a = 7.0332(6)$ Å, $b = 10.213(2)$ Å, $c = 6.982(2)$ Å, $\alpha = 96.01(2)°$, $\beta = 92.87(2)°$, $\gamma = 99.16(2)°$, $V = 491.3(1)$ Å^3, and $Z = 2$.[8] Both the pyrovanadate groups $(V_2O_7)^{4-}$ and the orthovanadates groups $(VO_4)^{3-}$ are isolated in the structure of that compound. As a result of the substitution of Sr for Ba, a compound crystallizing in the monoclinic system is formed, despite the fact that it contains the same coordinated polyhedra as BiSr$_2$V$_3$O$_{11}$. The cell parameters of BiBa$_2$V$_3$O$_{11}$ are: $a = 12.332(4)$ Å, $b = 7.750(4)$ Å, $c = 11.279(4)$ Å, $\beta = 103.22(3)°$, and $V = 1049(1)$ Å^3, with the space group $P2_1/c$, $Z = 4$.[9]

The aim of this work was determining the phase relations in the system Pb$_2$V$_2$O$_7$-BiVO$_4$ and checking whether a compound belonging to the family Bi $M_2^{III}V_3O_{11}$ is formed in the investigated system. Research on the PbO-Bi$_2$O$_3$-V$_2$O$_5$ system is motivated by the fact that many of these tetrahedral anion compounds display interesting properties due to the presence of Bi and Pb lone-pair electrons.[10] It is particularly interesting that these compounds exhibit transport behavior typical of anions.[10]

The components of the system Pb$_2$V$_2$O$_7$-BiVO$_4$ are well known. Pb$_2$V$_2$O$_7$ is one of the five compounds belonging to the system PbO-V$_2$O$_5$. This compound does not have polymorphic forms. Pb$_2$V$_2$O$_7$ melts congruently at 740 °C.[11] This lead(II) pyrovanadate(V) crystallizes in the monoclinic system with the space group $P2_1/c$, $Z = 4$, and its unit-cell parameters are: $a = 7.1027$ Å, $b = 7.1607$ Å, $c = 13.368$ Å, and $\beta = 105.935°$.[11]

Bismuth(III) orthovanadate(V) occurs in nature as a mineral named pucherite, crystallizing in the orthorhombic system.[12] This polymorph has never been obtained in laboratory conditions. As a result of the synthesis of this compound, at low temperature a tetragonal polymorph of BiVO$_4$ is obtained, possessing a zircon-type structure. A monoclinic phase forms at high temperatures. At a temperature of 255 °C, monoclinic BiVO$_4$ undergoes a reversible second-order phase transition to the tetragonal scheelite-type structure. Above 255 °C, BiVO$_4$ has an ideal scheelite structure. At temperatures higher than 400 °C, the zircon form of BiVO$_4$ transforms irreversibly into the monoclinic form.[12-14] Bismuth(III) orthovanadate(V) melts congruently at 940 °C.[15] The high-temperature modification of BiVO$_4$ (scheelite) crystallizes in the tetragonal system with the space group $I4_1/a$; its cell parameters are: $a = 7.307(0)$ A and $c = 6.466(3)$ Å.[14]

The phase relations in the Bi$_2$O$_3$-V$_2$O$_5$-PbO system were studied.[16,17] Only one work[17] on the reactivity between lead(II) pyrovanadate(V) and bismuth(III) orthovanadate(V) has been found in literature. In that paper, it was shown that a compound with the formula Pb$_6$Bi$_2$V$_8$O$_{29}$ was obtained as a result of a reaction between Pb$_2$V$_2$O$_7$ and BiVO$_4$ at the molar ratio 3:2. That compound melts at 710 °C;[17] whether the melting was congruent or peritectic was not specified.

2. Experimental Procedure

The reagents used in this research were: PbO (Merck, Darmstadt, Germany), Bi$_2$O$_3$ (POCh, Gliwice, Poland), and

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V_2O_5 (Riedel-de Haën, Steinheim, Germany). The high-temperature modification of $BiVO_4$ was obtained as a result of heating an equimolar mixture of Bi_2O_3 and V_2O_5 in the cycles: 600 °C (24 h) + 650 °C (24 h). $Pb_2V_2O_7$ was obtained as a result of heating the mixture of PbO and V_2O_5 at a molar ratio 2:1 in three cycles: 500 °C (2 h) + 600 °C (24 h) + 650 °C (24 h).

For the research, 16 samples were prepared from the investigated system $Pb_2V_2O_7$-$BiVO_4$, belonging to the ternary system PbO-V_2O_5-Bi_2O_3. The reagents were weighed in appropriate portions, homogenized by grinding, and next pressed into pellets and heated in an air atmosphere in a furnace. All samples were heated in two cycles: 600 °C (24 h) + 650 °C (24 h). After each heating cycle, the pellets were ground and subjected to x-ray diffraction (XRD) and differential thermal analysis (DTA) investigations.

The equilibrium phases were determined by XRD analysis of samples heated additionally for 2 to 4 h in selected temperatures and then rapidly cooled to ambient temperature.

The XRD examinations were performed using a diffractometer DRON-3 (Bourevestnik, St. Petersburg, Russia) Co Kα radiation and an Fe filter. The identification of individual phases was based on the accordance of obtained diffraction patterns with the data contained in the PDF cards.[18]

The DTA investigations were conducted by using a derivatograph of F.Paulik-J.Paulik-L.Erdey type (MOM, Budapest, Hungary). The measurements were performed in an air atmosphere, in quartz crucibles at a heating rate of 10 °C/min in the temperature range 20 to 1000 °C. The weight of the investigated samples always amounted to 500 mg.

The density of the compound was determined by the method described in an earlier work.[19] The unit-cell parameters of the resultant compound were calculated by using the program POWDER.[20] Exact positions of the diffraction lines were determined by the internal standard method. The internal standard used was KCl (space group $Fm\overline{3}m$, a = 0.6293 nm).

3. Results and Discussion

The first stage of this work was an attempt to synthesize the compound $Pb_2BiV_3O_{11}$. For this purpose, a sample of the composition 50 mol% $Pb_2V_2O_7$ and 50 mol% $BiVO_4$ was weighed and prepared by conventional methods in two cycles: 600 °C (24 h) + 650 °C (24 h).

In the powder diffraction pattern of this sample, recorded after the last heating stage, no lines were registered characteristic for any known phases belonging to the ternary system PbO-V_2O_5-Bi_2O_3. Figure 1 presents the powder diffraction pattern of the investigated sample and of the initial mixture. The results of the XRD examinations allow us to conclude that a compound with the formula $Pb_2BiV_3O_{11}$ was obtained as a result of the reaction between $Pb_2V_2O_7$ and $BiVO_4$ at the molar ratio 1:1 according to the reaction:
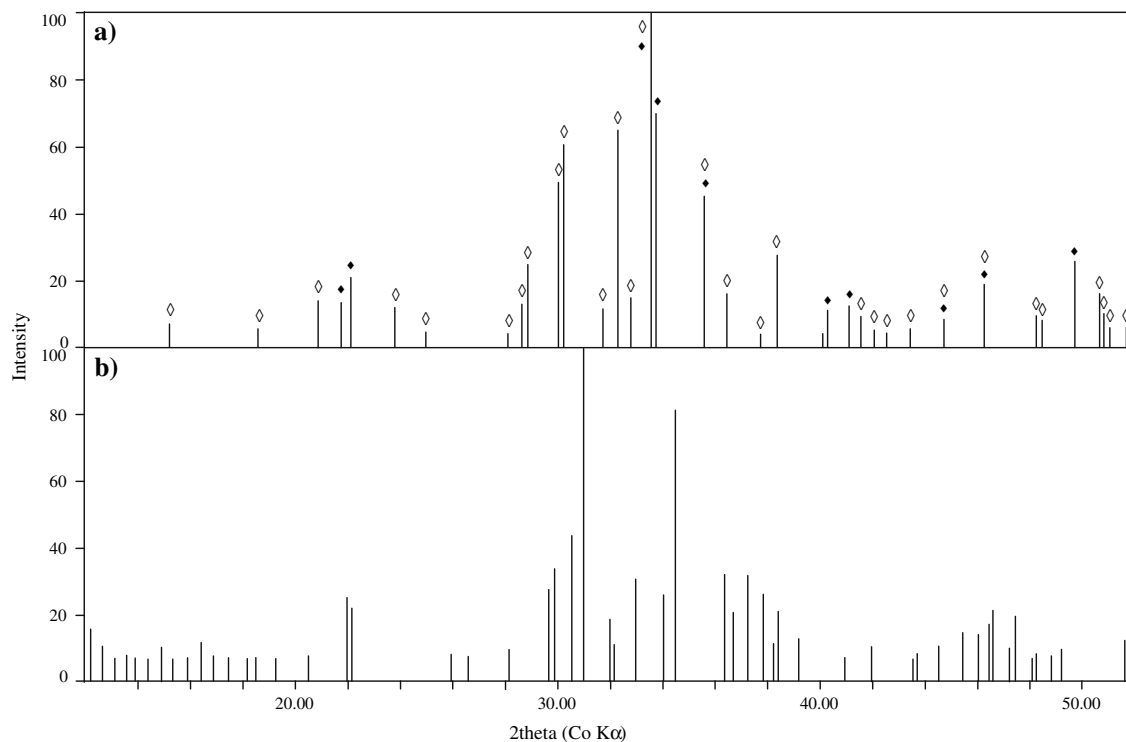

Fig. 1 Powder diffraction patterns. (a) $Pb_2V_2O_7$ + $BiVO_4$ mixture and (b) $Pb_2BiV_3O_{11}$. ◇, $Pb_2V_2O_7$ (PDF: 73-0150); ◆, $BiVO_4$ (PDF: 14-688)

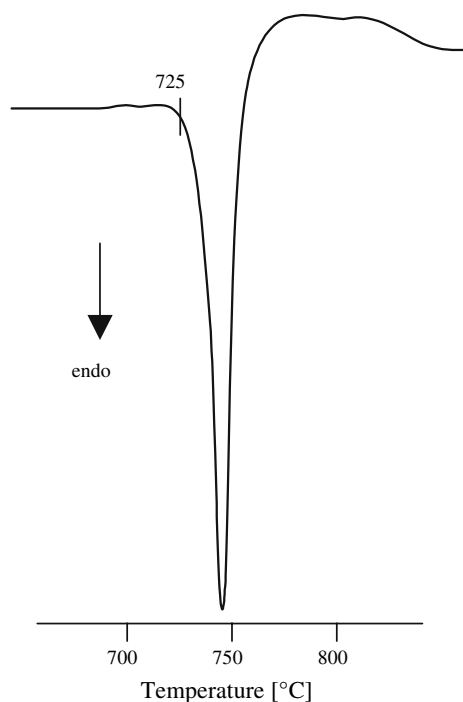**Fig. 2** Differential thermal analysis curve of $Pb_2BiV_3O_{11}$

$$Pb_2V_2O_{7(s)} + BiVO_{4(s)} = Pb_2BiV_3O_{11(s)} \qquad (Eq\ 1)$$

This compound was also obtained by heating a mixture of the oxides: PbO, Bi_2O_3, and V_2O_5 at the molar ratio 4:1:3 in the cycles: 500 °C (24 h) + 600 °C (24 h). After the first cycle of heating, the diffractogram of this mixture revealed a set of diffraction lines characteristic of the reagents and a set of lines identical with those recorded in the diffractogram of $Pb_2BiV_3O_{11}$ obtained from $BiVO_4$ and $Pb_2V_2O_7$ (reaction shown in Eq 1). It was concluded that $Pb_2BiV_3O_{11}$ can be also obtained as a result of a reaction:

$$4PbO_{(s)} + Bi_2O_{3(s)} + 3V_2O_{5(s)} = 2Pb_2BiV_3O_{11(s)} \qquad (Eq\ 2)$$
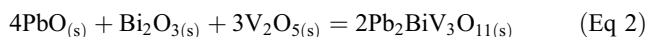
$Pb_2BiV_3O_{11}$ is yellow and melts congruently at 725 °C. The DTA curve of $Pb_2BiV_3O_{11}$ is presented in Fig. 2.

The powder diffraction pattern of $Pb_2BiV_3O_{11}$ was indexed, and the results are presented in Table 1. The triclinic unit-cell parameters of $Pb_2BiV_3O_{11}$ are: $a = 0.710076$ nm, $b = 1.41975$ nm, $c = 1.42972$ nm, $\alpha = 134.552°$, $\beta = 97.2875°$, $\gamma = 89.6083°$, and $Z = 4$. The calculated x-ray density amounts to $d_{rtg} = 6.25$ g/cm^3, and the pycnometric density $d = 6.27 \pm 0.05$ g/cm^3.

Further investigation was aimed to check whether only one compound can be obtained in the reaction between $BiVO_4$ and $Pb_2V_2O_7$. For that purpose, 15 extra samples were prepared. Table 2 presents the initial composition of the samples and the phases detected after the last stage of heating. Table 2 shows that only one compound is formed, and that was in accord with the reaction shown in (Eq 1).

Sample 12 in Table 2 has the composition of the compound $Pb_6Bi_2V_8O_{29}$. In the diffraction pattern of that

Table 1 Results of indexing the powder diffraction pattern of $Pb_2BiV_3O_{11}$

No.	d_{exp}, nm	d_{cal}, nm	hkl	I/I_0, %
1	1.0048	1.0038	001	1.3
2	0.7003	0.6996	100	1.7
3	0.6268	0.6265	10 $\bar{1}$	4.3
4	0.6051	0.6082	1 $\bar{1}$0	1.7
5	0.5448	0.5452	110	1.5
6	0.5347	0.5327	101	2.8
7	0.5028	0.5024	020	2.6
8	0.4730	0.4725	03 $\bar{2}$	7.3
9	0.4681	0.4658	1 $\bar{1}\bar{1}$	11.5
10	0.4627	0.4619	1 $\bar{2}$2	6.3
11	0.4455	0.4455	10 $\bar{2}$	3.5
12	0.4385	0.4369	03 $\bar{3}$	3.4
13	0.4311	0.4326	1 $\bar{2}$0	1.2
14	0.3999	0.4001	111	3.3
15	0.3875	0.3873	120	3.0
16	0.3826	0.3832	13 $\bar{3}$	1.4
17	0.3685	0.3692	1 $\bar{2}$3	2.8
18	0.3537	0.3539	03 $\bar{4}$	8.3
19	0.3500	0.3498	200	10.0
20	0.3480	0.3481	13 $\bar{1}$	9.2
21	0.3405	0.3400	1 $\bar{2}\bar{1}$	14.1
22	0.3353	0.3346	003	100.0
23	0.3251	0.3242	10 $\bar{3}$	5.1
24	0.3180	0.3175	2 $\bar{1}\bar{1}$	6.3
25	0.3157	0.3165	2 $\bar{2}$1	16.1
26	0.3132	0.3132	20 $\bar{2}$	9.8
27	0.3100	0.3115	1 $\bar{4}$2	4.5

sample, we observed only lines characteristic for $Pb_2V_2O_7$ and $Pb_2BiV_3O_{11}$.

Figure 3 shows a phase diagram of the system $Pb_2V_2O_7$-$BiVO_4$. The diagram implies that $Pb_2V_2O_7$-$BiVO_4$ is a real quasi-binary system with one compound melting congruently. A eutectic composition of 25 mol% $BiVO_4$ and 75 mol% $Pb_2V_2O_7$ was found to melt at 700 °C. Another eutectic composition near 56 mol% $BiVO_4$ and 44 mol% $Pb_2V_2O_7$ melts at 710 °C.
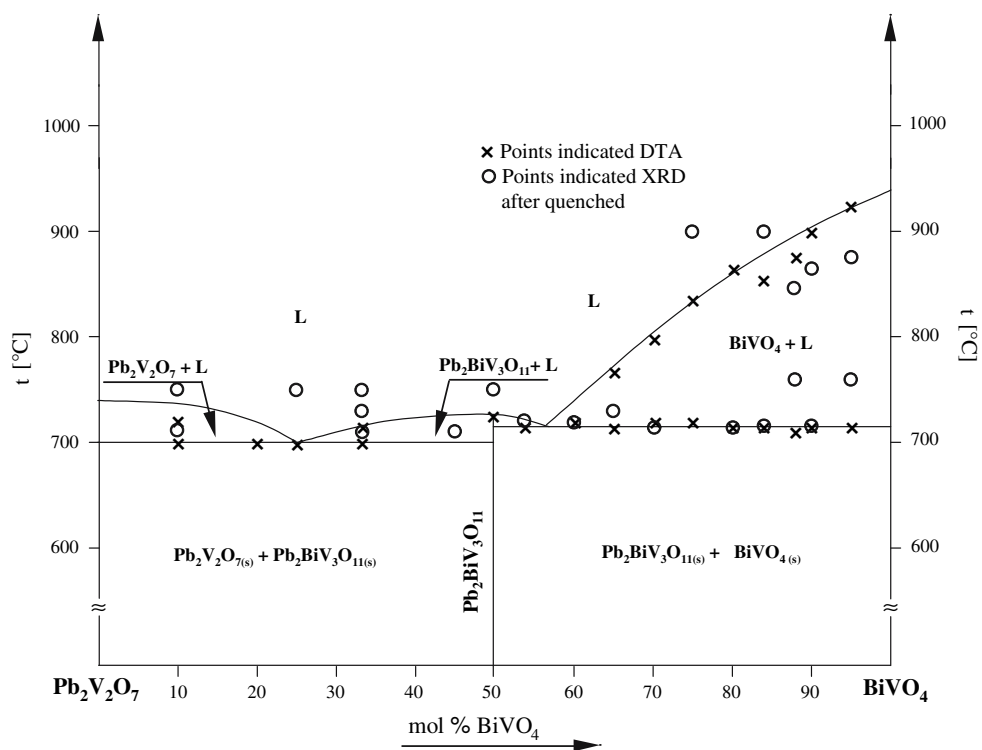
X-ray diffraction analyses of the samples containing initial mixtures of less than 50 mol% $Pb_2V_2O_7$ after the last heating step shows that the phases in equilibrium are $Pb_2BiV_3O_{11}$ and $BiVO_4$. The analysis of samples in the concentration range above 50 mol% $Pb_2V_2O_7$, indicated equilibrium phases $Pb_2V_2O_7$ and $Pb_2BiV_3O_{11}$.

4. Summary

- It is demonstrated that $Pb_2V_2O_7$ and $BiVO_4$ react in solid state, forming a new compound of $Pb_2BiV_3O_{11}$.
- $Pb_2BiV_3O_{11}$ melts congruently at the temperature 725 ± 5 °C.
- $Pb_2BiV_3O_{11}$ crystallizes in the triclinic system; its unit-cell parameters are: $a = 0.710076$ nm, $b = 1.41975$ nm,

Table 2 Composition of samples prepared for research and phases detected in equilibrium samples

No.	Composition of initial mixtures in terms of the system components, mol%		Heating conditions	Composition of equilibrium samples
	$Pb_2V_2O_7$	$BiVO_4$		
1	5.00	95.00	600 °C (24 h) + 650 °C (24 h)	$Pb_2BiV_3O_{11}$ + $BiVO_4$
2	10.00	90.00		
3	12.00	88.00		
4	16.00	84.00		
5	20.00	80.00		
6	25.00	75.00		
7	30.00	70.00		
8	35.00	65.00		
9	40.00	60.00		
10	46.00	54.00		
11	50.00	50.00		$Pb_2BiV_3O_{11}$
12	60.00	40.00		$Pb_2V_2O_7$ + $Pb_2BiV_3O_{11}$
13	66.67	33.33		
14	75.00	25.00		
15	80.00	20.00		
16	90.00	10.00		

Fig. 3 Diagram of phase equilibria of the system $Pb_2V_2O_7$-$BiVO_4$

c =1.42972 nm, α =134.552°, β = 97.2875°, γ =89.6083°, Z = 4. $Pb_2BiV_3O_{11}$ is not isostructural with the compounds of the general formula $M_2^{II}BiV_3O_{11}$.

• A diagram of phase relations has been constructed for the system $Pb_2V_2O_7$-$BiVO_4$ over the entire component concentration range at temperatures up to 1000 °C.

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