Comparative studies in subsolidus areas of ternary oxide systems PbO–V₂O₅–In₂O₃ and PbO–V₂O₅–Fe₂O₃

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Abstract Thermal stability of PbO was studied. Reactivity of oxides in the systems PbO–M₂O₃ (*M* = In, Fe) was investigated up to 650 °C. Using the DTA and XRD methods, parts of investigated ternary oxide systems, labelled by compounds: V₂O₅, Pb₈V₂O₁₃ and M₂O₃ (*M* = In, Fe), have been divided into partial ternary systems. IR spectra of compounds Pb₂MV₃O₁₁ (*M* = In, Fe) have been compared.

Keywords Lead(II) oxide · Lead(II) vanadate(V) · System PbO–In₂O₃ · System PbO–Fe₂O₃ · System PbO–V₂O₅–In₂O₃ · System PbO–V₂O₅–Fe₂O₃ · DTA · XRD

Introduction

The ternary oxide systems PbO–V₂O₅–M₂O₃ (where *M* = In, Fe) are worthy of study because their components as well as compounds forming in their side systems have found a lot of applications, e.g. as catalysts in different processes [1–4], as electrode materials [5] or as glasses with relatively high electrical conductivity and high thermal stability [6, 7]. It can be expected that also new phases forming with an involvement of all components of these ternary systems will have interesting properties, too.

Recently, the reactivity of vanadates in two of the cross-sections of the systems PbO–V₂O₅–M₂O₃, have been investigated. As a result of the conducted reactions three new compounds were obtained [8–10], namely Pb₂InV₃O₁₁

in the system InVO₄–Pb₂V₂O₇ [8], whereas Pb₂FeV₃O₁₁ [9] and Pb₂Fe₂V₄O₁₅ [10] in the system FeVO₄–Pb₂V₂O₇. Basic physicochemical properties and crystallographic data of these new phases are known [8–10]. Both Pb₂InV₃O₁₁ and Pb₂FeV₃O₁₁ crystallize in the monoclinic system, but, based on XRD investigations, it was stated that they are not isostructural [8, 9]. In Fig. 1 the X-ray diffraction patterns of both compounds [8, 9] are shown for comparison. Pb₂InV₃O₁₁ and Pb₂FeV₃O₁₁ melt incongruently, at 800 ± 5 °C [8] and 650 ± 5 °C [9], respectively. Pb₂Fe₂V₄O₁₅ melts also incongruently at 640 ± 5 °C, but it crystallizes in the triclinic system [10].

The presented study was focused on determining the range of co-existence of these new phases with other compounds occurring in the systems PbO–V₂O₅–M₂O₃ (*M* = In, Fe) and on checking whether any other phases, unknown hitherto, are formed in these systems, involving all their components. The aim of the research has been realized by studies on the phase equilibria in the subsolidus areas of the ternary oxide systems in the whole concentration range of their components. These results are very important to study both possibility and limitation of the practical application of the obtained new multicomponent vanadates.

Experimental

The following reagents were used in the study:

- PbO (p.a., Aldrich), V₂O₅ (p.a., Aldrich), In₂O₃ (p.a., Aldrich), α-Fe₂O₃ (p.a., POCh)
- vanadates: FeVO₄, Fe₂V₄O₁₃, Pb₂V₂O₇, Pb₂FeV₃O₁₁, Pb₂Fe₂V₄O₁₅, InVO₄, Pb₂InV₃O₁₁ obtained by the procedures described in the papers [8–11]

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Fig. 1 X-ray diffraction patterns of: $\text{Pb}_2\text{FeV}_3\text{O}_{11}$ (a) and $\text{Pb}_2\text{InV}_3\text{O}_{11}$ (b)

- vanadate PbV_2O_6 , obtained as a result of heating the equimolar mixture of PbO and V_2O_5 in three 20-h stages at 440 °C.

Reactions were carried out by the standard method of sintering samples described *inter alia* in the works [12–14]. The mixtures, containing reagents weighed in appropriate proportions, were homogenized by grinding in a mechanical agate mortar and then they were heated in the atmosphere of air for several stages, with intermediate grinding. The phase composition of the samples was checked on the base of their XRD patterns, recorded after each heating stage. The phase equilibrium was stated when the composition of given samples did not change after two consecutive heating stages at temperatures several dozen of degrees lower than their melting temperatures. Melting temperatures of the samples were read in each case from their DTA curves as the onset temperature of the first recorded endothermic effect (in this study effects due to polymorphic transitions were not registered on DTA curves). Accuracy of reading the temperatures of thermal effects on DTA curves, as determined by repetitions, amounted to ± 5 °C. The results of the DTA investigations enabled to conduct reactions in the solid-state. The exact conditions of calcining samples are given in Tables 1, 2, 3, 4.

The DTA investigations were conducted in static air atmosphere using the Paulik–Paulik–Erdey type derivatograph (MOM, Hungary). Samples of 500 mg were heated in quartz or in alumina crucibles in the temperature range 20–1,000 °C with a constant heating rate of 10 °C min^{-1} .

The XRD patterns of the samples were recorded with the aid of the diffractometer HZG4/A2 (Carl Zeiss, Germany) with the radiation $\text{CuK}_\alpha/\text{Ni}$. The identification of phases,

present in the samples, was conducted based on their XRD characteristics contained in the PDF cards and on the data presented in the papers [8–10].

The IR spectra of the $\text{Pb}_2\text{InV}_3\text{O}_{11}$ and $\text{Pb}_2\text{FeV}_3\text{O}_{11}$ compounds were obtained with the use of the spectrometer Specord M 80 (Carl Zeiss, Germany), applying the technique of pressing pastilles of the investigated sample with KBr in a ratio 1:300 by mass.

Results and discussion

Thermal stability of lead(II) oxide

It is known from the literature that PbO forms two stable modifications: low-temperature tetragonal PbO-L (litharge) and high temperature orthorhombic PbO-M (massicot) [15, 16]. The temperature of the transformation $\text{PbO-L} \leftrightarrow \text{PbO-M}$, assessed in the study [15], is equal to 489 °C. The rate of reverse transition $\text{PbO-M} \leftrightarrow \text{PbO-L}$ is very low at room temperature, thus, PbO-M can exist in metastable state over prolonged period [16]. Under heating in air, lead(II) oxide oxidizes to Pb_3O_4 which heated at higher temperatures decomposes back to PbO [15]. The temperature of the reversible reaction $\text{Pb}_3\text{O}_4 \leftrightarrow \text{PbO-M}$, assessed in the study [15], amounts to 535 °C. From the literature data it follows that the value of the melting temperature of lead(II) oxide lies between 830 and 897 °C [15], depending on the source. It is also known that lead(II) oxide sublimes before melting. This process, according to the data given in [17], was observed in temperature range 627–877 °C.

The research in the present study was begun with the verification of thermal stability of lead(II) oxide. The results of the XRD investigations have been shown that commercial PbO , used in the presented study, is the mixture of its two polymorphic modifications. DTA measurements for this oxide were conducted in alumina crucible to avoid the reaction of PbO with crucible material. On DTA curve of PbO studied only one endothermic effect was recorded (Fig. 2). Melting temperature of lead(II) oxide, read as the onset temperature of this effect, is equal to 890 ± 5 °C. The aim of the next stage of the research was to determine the maximum temperature of heating of some samples containing PbO at which sublimation of PbO is yet negligible. The samples of PbO were heated in alumina crucibles in 20-h stages at 600, 650, 700, 750 and 800 °C. The mass losses, stated after these heating stages, were: 0.21, 0.22, 0.33, 0.36 and 0.65 %, respectively. Based on the obtained results it was decided that ‘safe’ maximum temperature of heating of some samples containing PbO is about 650 °C. Such temperature enables to conduct reaction with PbO without the deviation from stoichiometry.

Table 1 Composition of initial mixtures of PbO, V₂O₅ and In₂O₃ (in terms of PbO and InVO₄), their heating conditions and their phase composition after last heating stage

No.	Composition of initial mixtures/mol%		Heating conditions	Phase composition after last heating stage
	PbO	InVO ₄		
1	90.00	10.00	440 °C(20 h) + 570 °C(20 h) +	PbO, Pb ₈ V ₂ O ₁₃ , In ₂ O ₃
2	80.00	20.00	600 °C(20 h) + 635 °C(20 h)	Pb ₈ V ₂ O ₁₃ , In ₂ O ₃
3	70.00	30.00	440 °C(20 h) + 500 °C(12 h) +	Pb ₈ V ₂ O ₁₃ , Pb ₄ V ₂ O ₉ , In ₂ O ₃
4	66.67	33.33	600 °C(12 h) + 650 °C(12 h) + 700 °C(2 × 12 h)	Pb ₄ V ₂ O ₉ , In ₂ O ₃
5	65.00	35.00		Pb ₄ V ₂ O ₉ , Pb ₃ V ₂ O ₈ , In ₂ O ₃
6	60.00	40.00	440 °C(20 h) + 500 °C(12 h) + 600 °C(12 h) + 700 °C(12 h) + 750 °C(12 h) + 800 °C(2 × 12 h)	Pb ₃ V ₂ O ₈ , In ₂ O ₃
7	55.00	45.00	440 °C(20 h) + 500 °C(12 h) + 600 °C(12 h) +	Pb ₃ V ₂ O ₈ , Pb ₂ V ₂ O ₇ , In ₂ O ₃
8	50.00	50.00	650 °C(2 × 12 h)	Pb ₂ V ₂ O ₇ , In ₂ O ₃
9	45.00	55.00		Pb ₂ V ₂ O ₇ , Pb ₂ InV ₃ O ₁₁ , In ₂ O ₃
10	40.00	60.00		Pb ₂ InV ₃ O ₁₁ , In ₂ O ₃
11	35.00	65.00	440 °C(20 h) + 500 °C(12 h) + 600 °C(12 h) +	Pb ₂ InV ₃ O ₁₁ , InVO ₄ , In ₂ O ₃
12	33.33	66.67	700 °C(2 × 12 h)	
13	25.00	75.00		
14	15.00	85.00		
15	5.00	95.00		

Phases in the side system PbO–V₂O₅

In the binary oxide system PbO–V₂O₅ five compounds, i.e. PbV₂O₆, Pb₂V₂O₇, Pb₃V₂O₈, Pb₄V₂O₉ and Pb₈V₂O₁₃ [18, 19] were reported. In order to verify the literature data, eleven mixtures of the oxides were prepared with their composition covering the whole component concentration range of the system PbO–V₂O₅. These samples were heated in several stages at the temperatures from the range 430–750 °C, depending on their composition. Five lead(II) vanadates(V), reported by authors [18, 19], were confirmed to form by solid-state reaction.

Study of the side systems PbO–M₂O₃,
where $M = \text{In, Fe}$

In the available literature no phase diagram of PbO–In₂O₃ system and no information about phases forming in the reaction between the oxides PbO and In₂O₃ have been found. To check the reactivity of oxides in the PbO–In₂O₃ system five mixtures were prepared of the compositions corresponding to the PbO:In₂O₃ molar ratio of 3:1, 2:1, 1:1, 1:2 and 1:3. These samples were heated in the following stages: 500 °C(12 h), 600 °C(12 h), 650 °C(2 × 12 h). After the last stage of heating the diffractograms of the samples did not reveal any new diffraction lines besides those characteristic for the oxides PbO and In₂O₃. From the conducted experiments it can be concluded that in the system PbO–In₂O₃, studied only up to 650 °C, no phases are formed.

The system PbO–Fe₂O₃, contrary to the PbO–In₂O₃ system, was the object of numerous investigations. Nevertheless, there are still some disagreements about the kind of phases forming in this system. From the literature it is known that formation of the phases in the PbO–Fe₂O₃ system presents some problems due to a low-mutual reactivity of the oxides as well as due to PbO evaporation during thermal treatment [20, 21]. Some authors [21–23] use another methods of synthesis instead of solid-state reactions between PbO and Fe₂O₃. According to the latest informations [20, 24] three phases, with their compositions corresponding to: Pb₂Fe₂O₅, Pb₂Fe₁₀O₁₇ and PbFe₁₂O₁₉, are formed in the investigated system. In the presented study attempts to verify the kind of phases formed in the PbO–Fe₂O₃ system were undertaken. Nine mixtures were prepared of the compositions corresponding to the PbO:Fe₂O₃ molar ratio of 3:1, 2:1, 1:1, 1:2, 2:5, 1:3, 1:4, 1:6, 1:9. Probably, the divergences concerning the kind of phases existing in the PbO–Fe₂O₃ system, are caused by evaporation of PbO and as a consequence by deviation from stoichiometry. Therefore, prepared mixtures were heated in seven 20-h stages at the ‘safe’ temperature 650 °C, at which evaporation of PbO is negligible. However, XRD analysis results of these samples after their last heating stage testified that equilibrium state was not attained in this reasonable time.

Then, at this stage of research phase equilibria up to the solidus line of the systems PbO–M₂O₃ ($M = \text{In, Fe}$) have not been determined.

Table 2 Composition, heating conditions and XRD phase analysis results after final heating stage of samples prepared for verifying investigations in area surrounded by $\text{Pb}_2\text{V}_2\text{O}_7$ – V_2O_5 – InVO_4

No	Kind of components	mol%	Sample composition in terms of oxides percentage/mol%			Heating conditions	Phase composition of samples in equilibrium state
			PbO	V_2O_5	In_2O_3		
1	PbV_2O_6	62.50	52.38	42.86	4.76	460 °C(20 h × 2)	PbV_2O_6 , $\text{Pb}_2\text{V}_2\text{O}_7$, $\text{Pb}_2\text{InV}_3\text{O}_{11}$
	$\text{Pb}_2\text{V}_2\text{O}_7$	12.50					
	$\text{Pb}_2\text{InV}_3\text{O}_{11}$	25.00					
2	PbV_2O_6	50.00	50.00	41.70	8.30		PbV_2O_6 , $\text{Pb}_2\text{InV}_3\text{O}_{11}$
	$\text{Pb}_2\text{InV}_3\text{O}_{11}$	50.00					
3	PbV_2O_6	80.00	44.44	44.44	11.12	400 °C(20 h) + 450 °C(20 h) + 460 °C(20 h × 4)	PbV_2O_6 , $\text{Pb}_2\text{InV}_3\text{O}_{11}$, InVO_4
	In_2O_3	20.00					
4	PbV_2O_6	3.28	35.00	45.00	20.00	460 °C(20 h × 2)	
	$\text{Pb}_2\text{InV}_3\text{O}_{11}$	40.58					
	InVO_4	56.04					
5	PbV_2O_6	35.80	26.36	50.00	23.64		PbV_2O_6 , InVO_4
	InVO_4	64.20					
6	$\text{Pb}_2\text{InV}_3\text{O}_{11}$	50.00	40.00	50.00	10.00	400 °C(20 h) + 450 °C(20 h) + 460 °C(20 h × 4)	PbV_2O_6 , InVO_4
	V_2O_5	50.00					
7	PbV_2O_6	42.86	30.00	55.00	15.00	450 °C(20 h × 2)	PbV_2O_6 , InVO_4 , V_2O_5
	InVO_4	42.86					
	V_2O_5	14.28					
8	PbV_2O_6	25.00	20.00	65.00	15.00		
	InVO_4	37.50					
	V_2O_5	37.50					

Table 3 Composition of initial mixtures of PbO, V_2O_5 and Fe_2O_3 (in terms of PbO and FeVO_4), their heating conditions and their phase composition at equilibrium state

No.	Composition of initial mixtures/mol%		Heating conditions	Phases at equilibrium state
	PbO	FeVO_4		
1	20.00	80.00	440 °C(20 h) + 570 °C(3 × 20 h)	$\text{Pb}_2\text{Fe}_2\text{V}_4\text{O}_{15}$, FeVO_4 , Fe_2O_3
2	33.33	66.67		$\text{Pb}_2\text{Fe}_2\text{V}_4\text{O}_{15}$, Fe_2O_3
3	36.00	64.00		$\text{Pb}_2\text{Fe}_2\text{V}_4\text{O}_{15}$, Fe_2O_3 , $\text{Pb}_2\text{FeV}_3\text{O}_{11}$
4	40.00	60.00		Fe_2O_3 , $\text{Pb}_2\text{FeV}_3\text{O}_{11}$
5	45.00	55.00		Fe_2O_3 , $\text{Pb}_2\text{FeV}_3\text{O}_{11}$, $\text{Pb}_2\text{V}_2\text{O}_7$
6	50.00	50.00	440 °C(20 h) + 570 °C(20 h) + 650 °C(2 × 20 h)	Fe_2O_3 , $\text{Pb}_2\text{V}_2\text{O}_7$
7	55.00	45.00		Fe_2O_3 , $\text{Pb}_2\text{V}_2\text{O}_7$, $\text{Pb}_3\text{V}_2\text{O}_8$
8	60.00	40.00	440 °C(20 h) + 570 °C(20 h) + 860 °C(2 × 20 h)	Fe_2O_3 , $\text{Pb}_3\text{V}_2\text{O}_8$
9	63.00	37.00	440 °C(20 h) + 570 °C(20 h) + 740 °C(2 × 20 h)	Fe_2O_3 , $\text{Pb}_3\text{V}_2\text{O}_8$, $\text{Pb}_4\text{V}_2\text{O}_9$
10	66.67	33.33		Fe_2O_3 , $\text{Pb}_4\text{V}_2\text{O}_9$
11	73.00	27.00	440 °C(20 h) + 570 °C(20 h) + 680 °C(2 × 20 h)	Fe_2O_3 , $\text{Pb}_4\text{V}_2\text{O}_9$, $\text{Pb}_8\text{V}_2\text{O}_{13}$
12	80.00	20.00		Fe_2O_3 , $\text{Pb}_8\text{V}_2\text{O}_{13}$

Subsolidus area of the system PbO – V_2O_5 – In_2O_3

The investigations, intended to determine phase equilibria in the subsolidus area of the oxide system PbO – V_2O_5 –

In_2O_3 , were begun with the study of phase equilibria in one of cross-sections of this system, i.e. PbO – InVO_4 . 15 mixtures of oxides were prepared for the research. The compositions of these samples, in terms of PbO and InVO_4 , are

Table 4 Composition, heating conditions and XRD phase analysis results after final heating stage of samples prepared for verifying investigations in the $\text{PbO-V}_2\text{O}_5\text{-Fe}_2\text{O}_3$ system

No.	Composition of initial mixtures	mol%	Composition of initial mixtures in terms of oxides percentage/mol%			Heating conditions	Phase composition of samples at equilibrium state
			PbO	V_2O_5	Fe_2O_3		
1	$\text{Pb}_2\text{FeV}_3\text{O}_{11}$	28.57	55.00	40.00	5.00	440 °C (20 h × 2)	$\text{Pb}_2\text{FeV}_3\text{O}_{11}$
	PbV_2O_6	42.86					PbV_2O_6
	$\text{Pb}_2\text{V}_2\text{O}_7$	28.57					$\text{Pb}_2\text{V}_2\text{O}_7$
2	$\text{Pb}_2\text{FeV}_3\text{O}_{11}$	66.67	50.00	40.00	10.00		$\text{Pb}_2\text{FeV}_3\text{O}_{11}$
	PbV_2O_6	33.33					PbV_2O_6
3	$\text{Pb}_2\text{FeV}_3\text{O}_{11}$	25.00	46.15	42.31	11.54		$\text{Pb}_2\text{FeV}_3\text{O}_{11}$
	PbV_2O_6	50.00					PbV_2O_6
	$\text{Pb}_2\text{Fe}_2\text{V}_4\text{O}_{15}$	25.00					$\text{Pb}_2\text{Fe}_2\text{V}_4\text{O}_{15}$
4	$\text{Pb}_2\text{Fe}_2\text{V}_4\text{O}_{15}$	33.33	44.44	44.44	11.12		$\text{Pb}_2\text{Fe}_2\text{V}_4\text{O}_{15}$
	PbV_2O_6	66.67					PbV_2O_6
5	$\text{Pb}_2\text{Fe}_2\text{V}_4\text{O}_{15}$	22.22	35.00	55.00	10.00		$\text{Pb}_2\text{Fe}_2\text{V}_4\text{O}_{15}$
	PbV_2O_6	33.33					PbV_2O_6
	V_2O_5	44.45					V_2O_5
6	$\text{Pb}_2\text{Fe}_2\text{V}_4\text{O}_{15}$	50.00	33.33	50.00	16.67	470 °C (20 h × 2)	$\text{Pb}_2\text{Fe}_2\text{V}_4\text{O}_{15}$
	V_2O_5	50.00					V_2O_5
7	$\text{Pb}_2\text{Fe}_2\text{V}_4\text{O}_{15}$	16.67	15.00	65.00	20.00	440 °C (20 h × 2)	$\text{Pb}_2\text{Fe}_2\text{V}_4\text{O}_{15}$
	V_2O_5	55.55					V_2O_5
	$\text{Fe}_2\text{V}_4\text{O}_{13}$	27.78					$\text{Fe}_2\text{V}_4\text{O}_{13}$
8	$\text{Pb}_2\text{Fe}_2\text{V}_4\text{O}_{15}$	40.00	21.05	52.63	26.32	490 °C (20 h × 2)	$\text{Pb}_2\text{Fe}_2\text{V}_4\text{O}_{15}$
	$\text{Fe}_2\text{V}_4\text{O}_{13}$	60.00					$\text{Fe}_2\text{V}_4\text{O}_{13}$
9	$\text{Pb}_2\text{Fe}_2\text{V}_4\text{O}_{15}$	13.64	15.00	50.00	35.00	440 °C (20 h × 2)	$\text{Pb}_2\text{Fe}_2\text{V}_4\text{O}_{15}$
	$\text{Fe}_2\text{V}_4\text{O}_{13}$	13.64					$\text{Fe}_2\text{V}_4\text{O}_{13}$
	FeVO_4	72.72					FeVO_4

Fig. 2 DTA curve of PbO

listed in Table 1. Table 1 presents also conditions of heating of these samples as well as the formulae of the compounds identified in the samples after their last heating stage. The obtained results imply that PbO and InVO_4 do not form a real binary system, PbO-InVO_4 is only an

intersection of the ternary oxide system $\text{PbO-In}_2\text{O}_3\text{-V}_2\text{O}_5$, which crosses its (at least) six partial ternary systems. In the concentration range above 80.00 mol% of PbO (i.e. in the polygon labelled by the compounds: $\text{Pb}_8\text{V}_2\text{O}_{13}$, PbO, In_2O_3) phase equilibria have been not determined.

It has been earlier established that the intersection $\text{Pb}_2\text{V}_2\text{O}_7\text{-InVO}_4$ of the ternary system is in the subsolidus area a real binary system in the whole concentration range of its components, in which $\text{Pb}_2\text{InV}_3\text{O}_{11}$ undergoes crystallization [8]. On the basis of the data taken from Table 1, from the phase equilibrium diagram of the system $\text{Pb}_2\text{V}_2\text{O}_7\text{-InVO}_4$ [8] and from the phase diagrams of $\text{PbO-V}_2\text{O}_5$ [19] and $\text{In}_2\text{O}_3\text{-V}_2\text{O}_5$ [25, 26] it was possible to propose a preliminary division of the part of the subsolidus area of $\text{PbO-V}_2\text{O}_5\text{-In}_2\text{O}_3$ system into the regions corresponding to partial ternary systems. The division proposed did not include the polygon whose apices corresponded to the compounds: V_2O_5 , PbV_2O_6 , $\text{Pb}_2\text{V}_2\text{O}_7$, $\text{Pb}_2\text{InV}_3\text{O}_{11}$ and InVO_4 . In order to establish the phase relations in this polygon and to verify the predicted partial systems in the other area of the system $\text{PbO-V}_2\text{O}_5\text{-In}_2\text{O}_3$, the mixtures of

oxides were prepared of the compositions chosen to represent the ranges hitherto not studied and some hypothetical partial systems comprised in the oxide systems studied. The composition of initial mixtures from which the second series samples were obtained are given in Table 2. Due to the thermal properties of PbO–V₂O₅ system, especially relatively low-melting temperature of PbV₂O₆ (about 500 °C) forming in this area, samples were heated at about 400 °C in very long cycles (over 100 h). The resulting samples were not at equilibrium state. In order to corroborate such a division of the subsolidus area of the system PbO–V₂O₅–In₂O₃, eight various mixtures were prepared from separately obtained PbV₂O₆, Pb₂V₂O₇, Pb₂InV₃O₁₁, InVO₄ and oxides: V₂O₅ and In₂O₃. The composition of these mixtures, the stages of heating and phases detected in the equilibrium state are presented in Table 2.

On the ground of the obtained results and of the literature data [8], the part of the ternary oxide system PbO–V₂O₅–In₂O₃, labelled by compounds: V₂O₅, Pb₈V₂O₁₃ and In₂O₃, has been divided into eight partial ternary systems (Fig. 3), in which there coexist in equilibrium three solid phases in each case. The same figure also shows the melting points of the mixtures of phases coexisting at equilibrium in given partial ternary system. These temperatures were read as the onset temperature of the first endothermic effect recorded in the DTA curve of given mixture. The melting points of the compounds existing in the side systems are also presented.

Fig. 3 Division of the part of the system PbO–V₂O₅–In₂O₃ into partial ternary systems

Subsolidus area of the system PbO–V₂O₅–Fe₂O₃

As in the case of the system PbO–V₂O₅–In₂O₃, studies on subsolidus area of the PbO–V₂O₅–Fe₂O₃ system were begun with the investigation of phase equilibria establishing in one of its cross-sections, i.e. PbO–FeVO₄. 12 mixtures of oxides were prepared for the study. Table 3 presents composition of these samples in terms of PbO and FeVO₄, their heating conditions and phase composition of the samples being at equilibrium state. Presented data shows that phase equilibria in the cross-section PbO–FeVO₄ have been investigated only up to 80.00 mol% PbO in the initial mixtures (sample 12). On the base of the obtained results it has been stated that the cross-section PbO–FeVO₄, as the cross-section PbO–InVO₄, is an intersection of the ternary system of oxides, crossing its (at least) seven partial ternary systems. In the samples with PbO content above 80.00 mol% in the initial mixture, the presence of Pb₂Fe₂O₅ was noted. Therefore, in this concentration range, the phase existing in the PbO–Fe₂O₃ system, is formed. Thus, in this concentration range the phase equilibria were not determined.

The presented results as well as the results of the earlier studies on the system Pb₂V₂O₇–FeVO₄ [9, 10] and literature data according to the system Fe₂O₃–V₂O₅ [11, 27], allowed a preliminary dividing of the part of the subsolidus area of the system PbO–V₂O₅–Fe₂O₃ into partial ternary systems. The proposed division did not embrace the

Fig. 4 Division of the part of the system $\text{PbO}-\text{V}_2\text{O}_5-\text{Fe}_2\text{O}_3$ into partial ternary systems

polygon labelled by the compounds: V_2O_5 , PbV_2O_6 , $\text{Pb}_2\text{V}_2\text{O}_7$, $\text{Pb}_2\text{FeV}_3\text{O}_{11}$, $\text{Pb}_2\text{Fe}_2\text{V}_4\text{O}_{15}$ and FeVO_4 . In this area the presence of $\text{Fe}_2\text{V}_4\text{O}_{13}$ can be expected. However, the synthesis of pure $\text{Fe}_2\text{V}_4\text{O}_{13}$ by solid-state reaction is difficult and requires very long time of heating [11]. On the other hand, the presence of lead(II) metavanadate(V) ($t_m = 500 \pm 5^\circ\text{C}$), forming in this area, can hinder attainment of equilibrium state (as in the case of the system $\text{PbO}-\text{V}_2\text{O}_5-\text{In}_2\text{O}_3$, mentioned above). Owing to these facts, it was decided that to establish which compounds coexist at equilibrium in this polygon, ready-made phases will be used. Nine mixtures were prepared with their compositions corresponding to partial ternary systems, that can be expected based on the previous results of investigations and on the law of neighbouring phase regions. The composition of these samples (also in terms of components of the $\text{PbO}-\text{V}_2\text{O}_5-\text{Fe}_2\text{O}_3$ system) are given in Table 4. These samples were heated in two 20-h stages at temperatures several dozen of degrees lower than their melting temperatures. The contents of all samples did not change after these heating stages. This proves that the phases contained in the mixtures do not react with each other, but they coexist at equilibrium state.

Figure 4 presents a division of the part of the ternary oxide system $\text{PbO}-\text{V}_2\text{O}_5-\text{Fe}_2\text{O}_3$, labelled by compounds: V_2O_5 , $\text{Pb}_8\text{V}_2\text{O}_{13}$ and Fe_2O_3 , into eleven partial ternary systems, in which there coexist in equilibrium three solid phases in each case. The melting temperatures of the

Fig. 5 IR spectra of: $\text{Pb}_2\text{FeV}_3\text{O}_{11}$ (a) and $\text{Pb}_2\text{InV}_3\text{O}_{11}$ (b)

mixtures of phases being at equilibrium, representing given partial ternary systems, are also shown in the Fig. 4. These temperatures were read as the onset temperature of the first endothermic effect recorded in the DTA curve of given mixture. The melting temperatures of the compounds existing in the side systems are also shown.

IR spectra of the compounds $\text{Pb}_2\text{MV}_3\text{O}_{11}$ ($M = \text{In, Fe}$)

Figure 5 shows the IR spectrum of $\text{Pb}_2\text{FeV}_3\text{O}_{11}$ (curve a) in comparison with the IR spectrum of $\text{Pb}_2\text{InV}_3\text{O}_{11}$ (curve b). (The IR spectrum, recorded for $\text{Pb}_2\text{FeV}_3\text{O}_{11}$, is the same as presented in the earlier work [9]). The differences in positions and intensities of absorption bands recorded in these spectra confirm the earlier assumption [8, 9] that the compounds $\text{Pb}_2\text{MV}_3\text{O}_{11}$ ($M = \text{In, Fe}$), forming in analogous ternary oxide systems and having the same general formula, are not isostructural. The absorption bands recorded in the higher wave number range are sharp and intense. It suggests a deformation of the polyhedra building the structure of both compounds. Considering the fact, that the full structures of both compounds are unknown, univocal attribution of the recorded absorption bands to the concrete vibrations is not possible. However, in the light of the literature data [28–34], probable attribution can be made. The intensive absorption bands recorded in the wave number range about $1,050\text{--}630\text{ cm}^{-1}$, with a big probability, can be ascribed to stretching vibrations of V–O bonds in VO_4 or/and in VO_5 polyhedra, first maximum of this band being due to stretching vibrations of the shortest V–O bond. The band with its maximum recorded at $1,010\text{ cm}^{-1}$, characteristic for $\text{Pb}_2\text{FeV}_3\text{O}_{11}$ (curve a), is shifted much more towards higher wave number than analogous band in IR spectrum of $\text{Pb}_2\text{InV}_3\text{O}_{11}$ (curve b), which suggests higher degree of distortion of VO_x polyhedra building $\text{Pb}_2\text{FeV}_3\text{O}_{11}$ structure. In this wave number range some absorption bands connected with stretching vibrations of Fe–O bonds in FeO_5 polyhedra as well as of the bridging bonds V–O–V, V–O–Fe and V–O–In cannot be excluded. In the remaining wave number range, i.e. $630\text{--}300\text{ cm}^{-1}$, much less intense absorption bands were recorded. Based on the literature data, these bands are most probably due to stretching vibrations within the MO_6 ($M = \text{Fe, In}$) octahedra and/or the PbO_x polyhedra. They may be caused by deformation vibrations of O–V–O and V–O–V bonds or they can have a mixed character.

Conclusions

PbO and MVO_4 ($M = \text{In, Fe}$) do not form real binary systems up to the solidus line. In the ternary oxide system $\text{PbO}\text{--}\text{V}_2\text{O}_5\text{--}\text{In}_2\text{O}_3$ one compound, involving all its components, is formed, i.e. $\text{Pb}_2\text{InV}_3\text{O}_{11}$. In the analogous ternary oxide system $\text{PbO}\text{--}\text{V}_2\text{O}_5\text{--}\text{Fe}_2\text{O}_3$ two compounds, involving all its components, are formed, i.e. $\text{Pb}_2\text{FeV}_3\text{O}_{11}$ and $\text{Pb}_2\text{Fe}_2\text{V}_4\text{O}_{15}$. The IR spectrum of $\text{Pb}_2\text{InV}_3\text{O}_{11}$ confirms the earlier statement that compounds $\text{Pb}_2\text{MV}_3\text{O}_{11}$ ($M = \text{In, Fe}$) are not isostructural. In the parts of the ternary oxide systems: $\text{PbO}\text{--}\text{V}_2\text{O}_5\text{--}\text{In}_2\text{O}_3$ and

$\text{PbO}\text{--}\text{V}_2\text{O}_5\text{--}\text{Fe}_2\text{O}_3$, labelled by compounds: V_2O_5 , $\text{Pb}_8\text{V}_2\text{O}_{13}$ and M_2O_3 ($M = \text{In, Fe}$), eight and eleven partial ternary systems can be distinguished, respectively. In all of them three compounds coexist at equilibrium state. In no ternary system formation of new phase, other than the known, is found.

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