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Synthesis and selected properties of $CrSbVO_6$ and phase relations in the V_2O_5–Cr_2O_3–α-Sb_2O_4 system in the solid state

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Abstract Phase relations in the ternary oxide system V_2O_5–Cr_2O_3–α-Sb_2O_4 in the solid state in the atmosphere of air have been investigated by using the XRD, DTA/TG and IRS methods. Obtained results have shown that in the system the compound $CrSbVO_6$ is formed. This compound has been obtained both from oxides and from a mixture comprising $CrSbO_4$, $CrVO_4$ and $SbVO_5$ as well as from mixtures: $CrSbO_4/V_2O_5$, $CrVO_4/\alpha$-Sb_2O_4 and $SbVO_5/Cr_2O_3$. A Solid product of incongruent melting of $CrSbVO_6$ at ~1300°C is Cr_2O_3. $CrSbVO_6$ crystallizes in the tetragonal system and its calculated unit cell parameters amount to: $a = b = 0.45719(12)$ nm, $c = 0.30282(8)$ nm, $Z = 2$. The obtained results have allowed us also to divide the investigated system V_2O_5–Cr_2O_3–α-Sb_2O_4 into seven subsidiary subsystems and to determine temperatures and components concentration range in which $CrSbVO_6$ remains at equilibrium in the solid state with other phases formed in corresponding binary systems.

Introduction

In recent years intensive investigations have been performed aimed—first of all—at obtaining new, active, highly selective catalysts for the reaction of obtaining acrylonitrile (ACN) by direct amooxidation of propane [1–3]. Among various investigated catalysts of this reaction the most promising ones for technological applications appear to be those comprising V_2O_5, α-Sb_2O_4 and Cr_2O_3 as well as compounds formed in respective systems built from these oxides [4–6]. While studying the composition and phases formed in the system formulating a catalyst as well as the structure, the thermal and spectroscopic properties of these phases, profound knowledge is gained about the solid on the surface of which an elementary catalytic process takes place.

The literature review has shown that the three component oxide system V_2O_5-Cr_2O_3–α-Sb_2O_4, and reactions taking place in this system in the solid state in air have not been subject of research before our preliminary investigations [7, 8]. On the other hand, the binary oxide systems V_2O_5–Cr_2O_3; V_2O_5–α-Sb_2O_4 and Cr_2O_3–α-Sb_2O_4 have been investigated both as to the kind of phases formed in these systems, their properties and as to the phase equilibria being established in these systems in the solid state in the atmosphere of air [9–26]. It is known, among others, that in the system V_2O_5–Cr_2O_3 two compounds $CrVO_4$ and $Cr_2V_4O_{13}$ are formed [9–14]. The compound $CrVO_4$ crystallizes in the orthorhombic system [12] and melts incongruently at 860 °C with a deposition of solid Cr_2O_3 [12]. The other compound formed in this system, i.e. $Cr_2V_4O_{13}$, crystallizes in the monoclinic system and is stable up to ~640 °C, a temperature at which it starts irreversibly decomposing in the solid state to $CrVO_4$ and V_2O_5 [13, 14].

In the second binary system, i.e. Cr_2O_3–α-Sb_2O_4, there exists the compound $CrSbO_4$, the synthesis of which involves atmospheric oxygen [15–19]. $CrSbO_4$ possesses a rutile-type structure and is stable up to

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~1380 °C, a temperature at which it decomposes and a solid product of this decomposition is Cr_2O_3 [15].

On the other hand, the kind of phases formed in the system V_2O_5–α-Sb_2O_4 in the atmosphere of air depends among others on the temperature at which the synthesis is conducted [20–26]. Accordingly, if an equimolar oxide mixture of V_2O_5/α-Sb_2O_4 or V_2O_5/Sb_2O_3 was heated in the atmosphere of air at ~800 °C then the formula $Sb_{0.92}V_{0.92}O_4$ (~$SbVO_4$) was ascribed to the formed compound [20–22]. This is a non-stoichiometric compound $Sb^{5+}_{0.92}V^{3+}_{0.28}V^{4+}_{0.64}\square_{0.16}O_4$ with cationic vacancies, possessing a rutile-type structure similarly to $CrSbO_4$ [20]. $Sb_{0.92}V_{0.92}O_4$ melts in the atmosphere of air at ~820 °C with a formation of a low-concentration solid solution of V_2O_5 in α-Sb_2O_4 [21, 22]. The literature data imply also that a heating of the equimolar oxide mixture V_2O_5/α-Sb_2O_4 in the atmosphere of air at temperatures up to 650 °C leads to a formation of the compound $SbVO_5$ known for not long. This compound is stable in air up to ~720 °C and afterwards it decomposes to $Sb_{0.92}V_{0.92}O_4$ and oxygen [23].

Results of our earlier investigations of the ternary system V_2O_5–Cr_2O_3–α-Sb_2O_4, presented only during the 8th European Conference on Solid State Chemistry in Oslo and the 9th Conference on Calorimetry and Thermal Analysis in Zakopane, have shown that the components of the system enter into a solid-state reaction in the atmosphere of air with a formation of the compound $CrSbVO_6$ [7, 8].

The research of other authors indicated that $CrSbVO_6$ can be obtained by heating a mixture (in evacuated silica glass tubes) of V_2O_4, Cr_2O_3 and Sb_2O_5, at 890 °C for 24 h as well as by the method of co-precipitation and calcination of the obtained precipitate in air at 700 °C [27, 28]. Results of the research conducted by Balarini et al. in 2003 allowed moreover a statement that in the system labelled by the elements Cr–Sb–V–O some phases are formed being solid solutions with the formulas: $Cr_1V_xSb_1O_{4+2x}$ and $CrV_xSb_{1+x+2z}O_{4+4x+4z}$, where $0 < x < 1$ [28]. These phases were obtained by the authors using the co-precipitation method from alcohol solutions containing $SbCl_5$, VO_2 and $Cr(NO_3)_3 \cdot 6H_2O$ [28]. The literature information implies also that, when the (Cr + V)/Sb ratio in the oxide catalyst was lower than ~0.5 i.e. in systems having excessive Sb, the selectivity to acrylonitrile was higher than 30%, with a low formation of carbon oxides and of propylene [6].

On the base of literature data concerning the system Cr–Sb–V–O it can thus be stated that this system has been investigated so far only to a very limited extent, i.e. first of all within the formation range of the compound $CrSbVO_6$ [27,28].

Present state of research on a three-component oxide system: V_2O_5–Cr_2O_3–α-Sb_2O_4 indicates that there is some need to investigate the phase equilibria established in this system in the solid state in the atmosphere of air. We have conducted within this work also some investigations aimed at obtaining the compound $CrSbVO_6$, establishing its basic properties (first of all thermal properties) and determining the components concentration range of the system V_2O_5–Cr_2O_3–α-Sb_2O_4 within which this compound remains at equilibrium with other phases formed in corresponding lateral binary systems.

Experimental

The following reagents were used in experiments:

- V_2O_5 a.p. (POCh, Poland),
- Cr_2O_3 a.p. (Aldrich, USA),
- α-Sb_2O_4 obtained by heating in air the commercial Sb_2O_3 p. (Merck, Germany) under the following conditions: 400 °C (2 h) → 500 °C (24 h) → 600 °C (48 h).
- $CrVO_4$, $Cr_2V_4O_{13}$, $CrSbO_4$ and $SbVO_5$–compounds specially prepared from oxides by the methods described in the works [13–16, 23].

The research presented in this work was started with attempts to synthesize the compound $CrSbVO_6$ both from the oxides being components of the investigated system, i.e. V_2O_5, Cr_2O_3 and α-Sb_2O_4, and from reacting mixtures that contained the compound or the compounds existing in binary systems of these oxides together with the necessary additional oxide. For this purpose, mixtures were prepared comprising:

$$-33.33\,\mathrm{mol\%}\ V_2O_5; 33.33\,\mathrm{mol\%}\ Cr_2O_3\ \text{and}\ 33.34\,\mathrm{mol\%}\ \alpha\text{-}Sb_2O_4 \quad \text{(sample labeled as S-1)}$$

$$-33.33\,\mathrm{mol\%}\ V_2O_5\ \text{and}\ 66.67\,\mathrm{mol\%}\ CrSbO_4 \quad \text{(S-2)}$$

$$-33.33\mathrm{mol\%}\ \alpha\text{-}Sb_2O_4\ \text{and}\ 66.67\,\mathrm{mol\%}\ CrVO_4 \quad \text{(S-3)}$$

$$-33.33\,\mathrm{mol\%}\ \mathrm{mol}\ Cr_2O_3\ \text{and}\ 66.67\,\mathrm{mol\%}\ SbVO_5 \quad \text{(S-4)}$$

$$-33.33\,\text{mol\%}\ \text{mol}\ CrVO_4;\ 33.33\,\text{mol\%}\ CrSbO_4\ \text{and}\ 33.34\,\text{mol\%}\ SbVO_5 \qquad \text{(S-5)}$$

The mixtures of reacting substances (S-1 ÷ S-5) after homogenizing mechanically by triturating in a agate mortar and shaping them into pellets were heated in the atmosphere of air in the following cycles: I: 600 °C (24 h); II: 700 °C (24 h); III: 800 °C (24 h).

After each heating cycle the samples were gradually cooled to room temperature, weighed, homogenized by triturating and shaped again into pellets before the subsequent heating cycle. In order to obtain monophase preparations, i.e. containing only the compound $CrSbVO_6$, the mixtures S-1 and S-5 were additionally heated at 1000 °C for 24 h.

In order to complete the study of phase equilibria being established in the three–component V_2O_5–Cr_2O_3–α-Sb_2O_4 system in the solid state, 24 samples were prepared from the oxides Cr_2O_3, V_2O_5 and α-Sb_2O_4. The composition of these samples was selected in such a way that they represented the whole components concentration range of the investigated system (Table 1). The reacting substances were weighed in appropriate portions, homogenized by grinding in the mortar, shaped into pellets and heated, depending on the composition, under conditions showed in Table 1. These conditions were determined in preliminary investigations the results of which were presented on conferences [7, 8]. The phase composition of all samples after subsequent stages of their heating was determined on the base of XRD analysis results. All samples after the final heating stage were additionally subjected to DTA/TG investigations. After each heating stage the mass changes of the samples as well as their color were recorded.

Attaining of the equilibrium state was verified by XRD and DTA measurements, made for selected samples after two successive calcination cycles. Two identical results were taken as an indication of the established equilibrium state. Moreover, for investigations verifying the division of the system V_2O_5–Cr_2O_3–α-Sb_2O_4 into subsidiary subsystems a series of mixtures were prepared from the compounds: $CrVO_4$, $Cr_2V_4O_{13}$, $SbVO_5$, $CrSbO_4$ and $CrSbVO_6$ and from appropriate oxides Cr_2O_3, V_2O_5 and α-Sb_2O_4 that according to the preliminary division of the investigated system ought to be mixtures of phases remaining at equilibrium with each other in the solid state (Table 3).

The DTA/TG investigations were performed by means of an F. Paulik–L. Paulik–L. Erdey derivatograph, product of MOM Budapest. The measurements

Table 1 Composition of initial mixtures, their preparation conditions and XRD analysis results for samples after final heating cycle

No.	Sample composition [mol%]			Preparation conditions	Kind of phases contained in samples after final heating cycle	
	Cr_2O_3	Sb_2O_4	V_2O_5			
1	10.00	25.00	65.00	I 600 °C (24 h)	~$SbVO_4$, $SbVO_5$, Cr_2O_3, V_2O_5	*
2	10.00	45.00	45.00	II 640 °C (24 h)	V_2O_5, ~$SbVO_4$, $SbVO_5$, $CrSbVO_6$	*
3	20.00	40.00	40.00	III 640 °C (24 h)	$SbVO_5$, $CrSbVO_6$,	E
4	25.00	25.00	50.00	IV 640 °C (96 h)	V_2O_5, $CrSbVO_6$,	E
5	30.00	15.00	55.00		$CrSbVO_6$, V_2O_5, $Cr_2V_4O_{13}$, $CrVO_4$	*
6	33.33	16.67	50.00		$CrSbVO_6$, $Cr_2V_4O_{13}$	E
7	40.00	15.00	45.00		$CrSbVO_6$, $CrVO_4$, V_2O_5, $Cr_2V_4O_{13}$ v.l.	*
8	40.00	20.00	40.00	I 600 °C (24 h)	$CrVO_4$, $CrSbVO_6$,	E
9	50.00	16.66	33.34	II 700 °C (48 h)	$CrVO_4$, $CrSbVO_6$, Cr_2O_3	E
10	65.00	10.00	25.00	III 800 °C (24 h)		
11	80.00	5.00	15.00	IV 825 °C (24 h)		
12	42.86	28.57	28.57	I 600 °C (24 h)	$CrSbVO_6$, Cr_2O_3	E
13	50.00	25.00	25.00	II 700 °C (48 h)		
14	66.66	16.67	16.67	III 800 °C (24 h)		
15	75.00	12.50	12.50	IV 900 °C (24 h)		
16	22.23	44.44	33.33		$CrSbVO_6$, Cr_2O_3, $CrSbO_4$	E
17	65.00	25.00	10.00			
18	33.33	33.34	33.33		$CrSbVO_6$	E
19	40.00	40.00	20.00		$CrSbVO_6$, $CrSbO_4$	E
20	45.00	45.00	10.00			
21	27.50	45.00	27.50	I 600 °C (24 h)	~$SbVO_4$, α-Sb_2O_4, Cr_2O_3, $SbVO_5$—v.l.	*
22	17.00	50.00	33.00	II 640 °C (24 h)	$SbVO_5$, $CrSbO_4$	E
23	25.00	50.00	25.00	III 640 °C (24 h)	~$SbVO_4$, α-Sb_2O_4, Cr_2O_3, $CrSbO_4$—v.l. $SbVO_5$—v.l.	*
24	15.00	70.00	15.00	IV 640 °C (96 h)	~$SbVO_4$, Cr_2O_3, α-Sb_2O_4, $SbVO_5$—v.l.	*

E—phase composition of samples in equilibrium state; *—phase composition of non-equilibrium samples; v.l.—very little, but detected by XRD method; ~$SbVO_4$ = $Sb_{0.92}V_{0.92}O_4$

were conducted both in the atmosphere of air and of argon, in the temperature range 20–1000 °C, at the DTA galvanometer sensitivity of 1/5 and a constant heating rate of 10°/min. All investigations were performed in quartz crucibles. The mass of investigated samples amounted always to 500 mg. The accuracy of temperature reading determined on the base of repetitions was established as ±5 °C. Some selected samples were subjected to DTA/TG investigations by using the apparatus SDT 2960 of TA Instruments. The measurements were conducted in the atmosphere of air, in the temperature range 20–1500 °C, at a heating rate of 10°/min. They were performed in corundum crucibles. For collecting the data and running the apparatus the program Thermal Solution of WINDOWS NT was applied [29]. The investigation results were worked up with the use of the program ORIGIN 5.0 [30]. The kind of phases contained in the samples was identified on the base of X-ray phase analysis results (diffractometer DRON–3 made in USSR, radiation CoK_{α}, filter Fe) and the data found in the PDF cards [31] as well as in the works [13, 18, 23, 27]. The IRS investigations of $CrSbVO_6$ were performed by means of the IR spectrometer SPECORD M 80, product of Carl Zeiss Jena, GDR, applying the technique of pressing pellets with KBr at a weight ratio of 1:300. The measurements were conducted within the wave-number range of 1500 ÷ 200 cm^{-1}.

Experimental densities of monophase preparations were determined by degassing the samples and hydrostatic weighing in a pycnometric liquid—CCl_4 by the method described in [32].

Results and discussion

Synthesis of $CrSbVO_6$

The results of X-ray phase analysis and DTA for all samples (S-1 ÷ S-5) after their final heating cycle allowed a statement that independently of the kind of reactants contained in the reacting mixtures the solid-state reaction leads always to a formation of the same phase, graphite-black in color, to which the formula $CrSbVO_6$ has been ascribed on the base of literature data [27, 28]. Hence it was concluded that the reactions in the mixtures S-1 ÷ S-5 occurred according to the equations:

$$V_2O_{5(s)} + Cr_2O_{3(s)} + Sb_2O_{4(s)} = 2CrSbVO_{6(s)} \quad (1)$$

$$V_2O_{5(s)} + 2\ CrSbO_{4(s)} = 2\ CrSbVO_{6(s)} + 1/2O_{2(g)} \quad (2)$$

$$Sb_2O_{4(s)} + 2\ CrVO_{4(s)} = 2\ CrSbVO_{6(s)} \quad (3)$$

$$Cr_2O_{3(s)} + 2\ SbVO_{5(s)} = 2\ CrSbVO_{6(s)} + 1/2O_{2(g)} \quad (4)$$

$$\begin{aligned} &CrVO_{4(s)} + CrSbO_{4(s)} + SbVO_{5(s)} \\ &\quad = 2\ CrSbVO_{6(s)} + 1/2O_{2(g)} \end{aligned} \quad (5)$$

Such course of the reactions (2), (4) and (5) was additionally corroborated by the total values of sample mass losses resulting from the heating and amounting to ~2.1 ± 0.2 wt.%.

In order to additionally corroborate the course of the reaction (1), i.e. the synthesis of $CrSbVO_6$ from an equimolar mixture of the oxides V_2O_5, Cr_2O_3 and α-Sb_2O_4, and first of all to prove that this synthesis does not involve atmospheric oxygen, an oxides mixture (S-1) was heated in the same cycles, but in the atmosphere of spectrally pure argon (content of oxygen below 2 ppm) flowing at a rate of 10 dm^3/h. The diffraction pattern of such obtained sample was identical with the diffractogram of the sample obtained in air, which finally confirms the course of the reaction (1).

Figure 1 presents besides fragments of diffractograms given by the equimolar mixture of the oxides V_2O_5, Cr_2O_3 with α-Sb_2O_4 and the mixture of $SbVO_5$ with Cr_2O_3 containing 33.33 mol% Cr_2O_3, a fragment of a diffractogram given by the compound ($CrSbVO_6$) obtained from these mixtures. Figure 1 indicates that the shown diffraction patterns differ significantly both as to the number of registered diffraction lines, their location and as to their mutual intensity relations.

The powder diffraction patterns of the obtained $CrSbVO_6$ differed slightly by the location of diffraction reflections from the diffractogram of this compound presented in the work [27]. Therefore the diffractogram of the compound obtained within this work i.e. $CrSbVO_6$, was subjected to indexing. Indexing the diffractogram of $CrSbVO_6$ was performed by using the program POWDER [33, 34]. The diffraction lines subjected to indexing were the subsequent 9 lines recorded within the angular range 10–80° 2θ (CoK_{α}/Fe). An exact position of diffraction lines that belong to the set characteristic of $CrSbVO_6$ was established by comparison with internal standards such as: SiO_2 and $CaCO_3$. The results of indexing are presented in Table 2. The parameters of the tetragonal unit cell amount to: a = b = 0.45719(12) nm, c = 0.30282(8) nm. The volume of such selected unit cell is V = 0.0632987 nm^3, and the number of stoichiometric units per unit cell

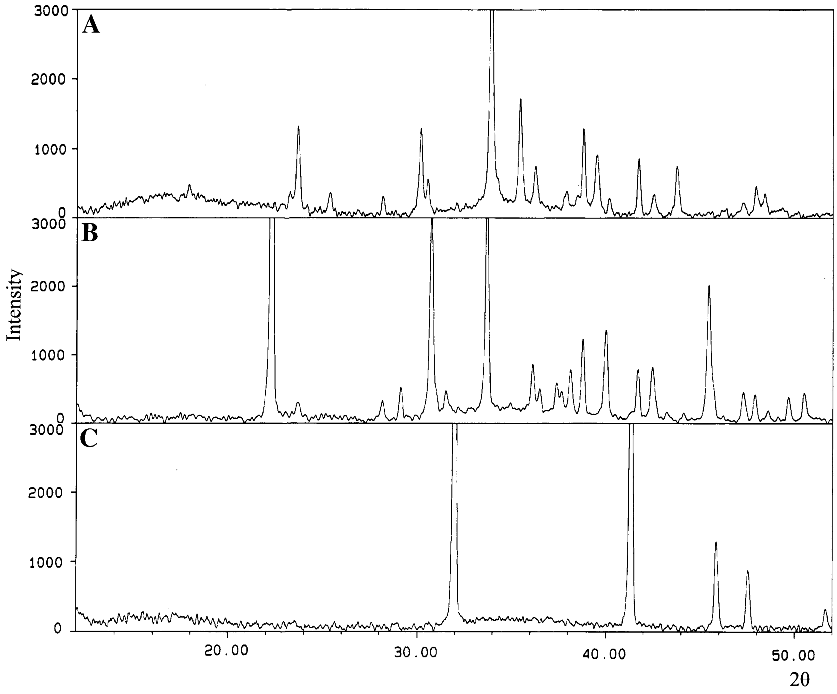


Fig. 1 X-ray diffraction patterns of: A—mixture of oxides (33.34 mol% V_2O_5; 33.33 mol% Cr_2O_3; 33.33 mol% α-Sb_2O_4) B—mixture of 66.67 mol% $SbVO_5$ + 33.33 mol% Cr_2O_3 C—$CrSbVO_6$

Z = 2. When choosing this outcome we have taken into consideration high values of the "figure of merit" as well as a consistency between the X-ray calculated density (d_{rtg} = 5.61 g/cm^3) and the experimentally measured density (d = 5.55 g/cm^3). The obtained unit cell parameters of $CrSbVO_6$ differ very little from the parameters determined by Isasi et al. [27] that are the following: a = b = 0.45708(4) nm, c = 0.30281(3) nm, Z = 2.

On a DTA curve of the compound $CrSbVO_6$ up to 1000 °C any distinct thermal effects were not recorded, which indicates that this compound is stable up to at least 1000 °C. In order to establish the temperature and the way of melting of $CrSbVO_6$, samples containing only this compound were heated for 3 h at 1100, 1200 and 1300 °C, next rapidly cooled to ambient temperature, ground and investigated by the XRD method. After these investigations it was found that only the sample of $CrSbVO_6$ heated at 1300 °C underwent evidently a partial melting. The XRD analysis showed that after this heating temperature the phases present in the sample were, beside the still not molten compound $CrSbVO_6$, the oxides Cr_2O_3, α- and β-Sb_2O_4 as well as V_2O_5. The oxides α- and β-Sb_2O_4 and V_2O_5 do not exist at 1300 °C any longer as solid phases, thus they seem to be phases crystallizing from the liquid. An additional proof of this fact is that the diffraction lines characteristic for these oxides were shifted towards lower angles and their mutual intensity relations differed much from the data given in literature [35–37]. This experiment shows that $CrSbVO_6$ melts incongruently with a deposition of Cr_2O_3 as a solid product of a meritectic reaction. Differential thermal analysis of a monophase sample containing $CrSbVO_6$ conducted up to 1500 °C has confirmed that this compound melts at 1300 °C.

Figure 2 presents an IR spectrum of a mixture of oxides comprising 33.34 mol% V_2O_5, 33.33 mol% Cr_2O_3 and 33.33 mol% α-Sb_2O_4 (A) next to an IR spectrum of the compound obtained from this mixture, i.e. $CrSbVO_6$ (B). Figure 2 indicates that the IR spectrum of the compound differs from the spectrum

Table 2 Indexing results for powder diffraction pattern of $CrSbVO_6$

No	Miller indices			$d_{exp.}$[Å]	$d_{calc.}$ [Å]
	h	*k*	*l*		
1	1	1	0	3.2330	3.23284
2	1	0	1	2.5260	2.52469
3	2	0	0	2.2850	2.28596
4	1	1	0	2.2100	2.21010
5	2	1	0	2.0440	2.04463
6	2	1	1	1.6940	1.69455
7	2	2	0	1.6170	1.61642
8	0	0	2	1.5140	1.51414
9	3	0	0	–	1.52397
10	1	0	2	1.4460	1.43737
11	2	2	1	–	1.42599
12	3	1	0	–	1.44577

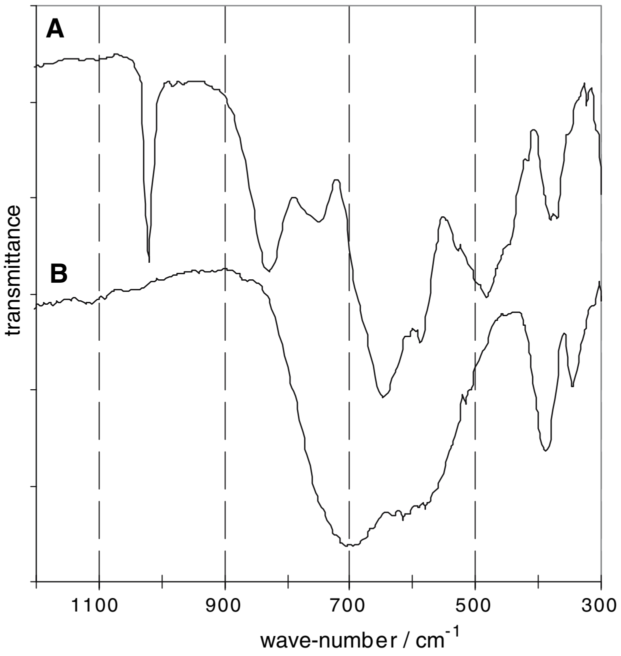


Fig. 2 IR spectra of: A—mixture of oxides (33.34 mol% V_2O_5 + 33.33 mol% Cr_2O_3 + 33.33 mol% α-Sb_2O_4), B—$CrSbVO_6$

of the oxides mixture both as to the number of the registered bands, their location and as to their intensities. Absorption bands characteristic for the phase $CrSbVO_6$ were recorded within the wave-number range 1200–300 cm^{-1}. Unlike the IR spectrum of the oxides mixture, the spectrum of $CrSbVO_6$ possesses one broad absorption band with its maximum at 708 cm^{-1}. This band exhibits three evident shoulders from the lower wave-numbers side, recorded at 628, 604 and 516 cm^{-1}. This band can be ascribed to stretching vibrations of the bonds Sb–O in SbO_6 octahedra [38, 39] as well as to stretching vibrations of the bonds Cr–O in CrO_6 octahedra [40–43]. Analogous bands occur similarly in the IR spectrum of chromium(III) oxide [40] and in the spectra of chromium(III) meta-, pyro-, and ortho-vanadates(V) prepared by the co-precipitation method [41–43]. The absorption bands with their maxima at 388 i 344 cm^{-1}, that means those recorded within the wave-number range 400–300 cm^{-1} of the $CrSbVO_6$ spectrum, could not be unambiguously interpreted on the base of the available literature data. Some authors consider the bands registered in this range to be due to bending vibrations both of the bonds V–O and O–V–O [44, 45]. According to other papers, these bands are due to bending vibrations of the bonds Cr–O [43] and to bending vibrations of the bonds O–Sb–O [38, 39].

Subsolidus phase equilibria in the V_2O_5–Cr_2O_3–α-Sb_2O_4 system

In a further part of the present work investigations were conducted on the phase equilibria being established in the atmosphere of air in the ternary oxide system V_2O_5–Cr_2O_3–α-Sb_2O_4. They were started with a preparation, from oxides, of 24 samples the composition of which was selected in such a way that the samples covered the whole components concentration range of the investigated system. Some samples for the investigations represented some selected intersections of the ternary oxide system, *i.e.*: $SbVO_5$–Cr_2O_3, $SbVO_5$–$CrVO_4$, $CrVO_4$–$CrSbVO_6$, $CrVO_4$–$CrSbO_4$, $CrSbO_4$–$SbVO_5$, $CrSbVO_6$–α-Sb_2O_4, $CrSbVO_6$–$CrSbO_4$, $CrSbVO_6$–V_2O_5, $CrSbVO_6$–$Cr_2V_4O_{13}$, $Cr_2V_4O_{13}$–α-Sb_2O_4, $Cr_2V_4O_{13}$–$CrSbO_4$. The composition of the remaining samples corresponded to subsidiary subsystems into which we divided the investigated system preliminarily [7, 8]. Table 1 presents the composition of the investigated samples, their preparation conditions as well as the XRD analysis results for all the preparations from the oxides after the final heating cycle.

By analyzing the phase composition of all samples after their last heating cycle, it was found that the samples 1, 2, 5, 7, 21,23 and 24 were not in an equilibrium state. This is evidenced, among others, by the kind and first of all the number of phases identified in these samples.

Non–equilibrium samples did not change their phase composition despite their additional heating at the temperature of the IV cycle (Table 1) and for a period of time longer by 24 h. A small change occurred only as to the relative amounts of the identified compounds. This means that attaining an equilibrium state by these samples would require a very long time of calcination, which is due to kinetic reasons. On the other hand, any increasing in the calcination temperature of these samples was not possible because of the thermal stability of the compounds that finally ought to remain at equilibrium with one another, e.g. $Cr_2V_4O_{13}$, $SbVO_5$ and V_2O_5 [13, 14, 23].

The kind of compounds in an equilibrium state in the samples 1, 2, 5, 7, 21, 23 and 24 was clearly indicated by the phase composition of the remaining investigated samples.

The phase composition of the samples at equilibrium (Table 1, samples labeled as E) allowed a preliminary dividing of the investigated system into seven subsidiary subsystems, i.e.: I: $CrSbVO_6$–$SbVO_5$–V_2O_5; II: $CrSbVO_6$–V_2O_5–$Cr_2V_4O_{13}$; III: $CrSbVO_6$–$Cr_2V_4O_{13}$–$CrVO_4$; IV: $CrSbVO_6$–$CrVO_4$–Cr_2O_3; V: $CrSbVO_6$–Cr_2O_3–$CrSbO_4$; VI: $CrSbVO_6$–$CrSbO_4$–$SbVO_5$; VII: $CrSbO_4$–α-Sb_2O_4–$SbVO_5$.

Moreover, it was found that the set of diffraction lines recorded in the diffractograms of the equilibrium samples, i.e. 16, 17 and 19, could be ascribed either to the compound $CrSbO_4$ or to $CrSbVO_6$ or to both these compounds at the same time. This results from the fact that both these compounds are phases with a rutile-type structure and possess very similar unit cell parameters. In the light of recent reports [28] it cannot be excluded that these compounds form solid solutions which can also be considered as a solid solution of V_2O_5 in $CrSbO_4$ with the general formula $CrSbV_xO_{4+2x}$, where $1 \geq x > 0$, because for x = 1 at the maximum solubility of V_2O_5 we would obtain the compound $CrSbVO_6$.

In order to corroborate such a division of the subsolidus area of the system V_2O_5–Cr_2O_3–α-Sb_2O_4, nine various mixtures were prepared from separately obtained $SbVO_5$, $Cr_2V_4O_{13}$, $CrVO_4$, $CrSbO_4$, $CrSbVO_6$ and appropriate oxides. The composition of these mixtures is presented in Table 3 (samples No. 25 to No. 33).

Excepting the sample No. 26, all these mixtures contained compounds that ought to remain with one another at equilibrium, as it was preliminarily established in our investigations. This means that their calcination at temperatures close to the temperatures of the solidus line should not cause any change of their phase composition. The composition of the samples was selected in such a way that in terms of the content of the oxides V_2O_5, Cr_2O_3 and α-Sb_2O_4 they corresponded to samples previously synthesized just from these oxides.

Seven samples among the additional ones, i.e. 25, 28–33, contained compounds that ought to be at equilibrium with one another and the composition of these samples corresponded to those synthesized from the oxides that had not attained an equilibrium state because of the reasons explained above.

These mixtures of compounds (samples 25–33) were subjected to a prolonged heating at temperatures slightly lower than the temperatures of corresponding solidus planes and next they were cooled to room temperature. The heating temperatures of these samples were determined on the base of the onset temperatures of the first endothermic effects recorded on the DTA curves of prepared mixtures (No. 25 to No. 33). XRD analysis of these preparations showed that despite the many hours' heating at temperatures close to the beginning of melting - the composition of the samples, except the sample 26, did not undergo any change. This proves that the initial mixtures corresponded, as to their composition, to the earlier determined phases coexisting at equilibrium in individual subareas of the subsolidus area.

Table 3 Composition of initial mixtures and XRD phase analysis results after final heating cycle of samples prepared for verifying investigations

No	Kind of components	mol%	Sample composition in terms of oxides percentage [mol%]			Phase composition of samples in equilibrium state
			V_2O_5	Cr_2O_3	α-Sb_2O_4	
25	$SbVO_5$ $CrSbVO_6$	77.78 22.22	45.00	10.00	45.00	$SbVO_5$, $CrSbVO_6$
26	$CrSbO_4$ $CrVO_4$	50.00 50.00	25.00	50.00	25.00	$CrSbVO_6$, Cr_2O_3
27	$CrSbO_4$ $CrSbVO_6$	50.00 50.00	20.00	40.00	40.00	$CrSbO_4$, $CrSbVO_6$
28	$SbVO_5$ $CrSbO_4$	50.00 50.00	25.00	25.00	50.00	$SbVO_5$, $CrSbO_4$
29	V_2O_5 $SbVO_5$ $CrSbVO_6$	44.44 33.34 22.22	65.00	10.00	25.00	V_2O_5, $SbVO_5$, $CrSbVO_6$
30	V_2O_5 $Cr_2V_4O_{13}$ $CrSbVO_6$	18.18 27.28 54.54	55.00	30.00	15.00	V_2O_5, $Cr_2V_4O_{13}$, $CrSbVO_6$
31	$CrVO_4$ $Cr_2V_4O_{13}$ $CrSbVO_6$	53.33 6.67 40.00	45.00	40.00	15.00	$CrVO_4$, $Cr_2V_4O_{13}$, $CrSbVO_6$
32	$SbVO_5$ $CrSbO_4$ $CrSbVO_6$	38.89 38.88 22.22	27.50	27.50	45.00	$SbVO_5$, $CrSbO_4$, $CrSbVO_6$
33	α-Sb_2O_4 $SbVO_5$ $CrSbO_4$	40.00 30.00 30.00	15.00	15.00	70.00	α -Sb_2O_4, $SbVO_5$, $CrSbO_4$

The sample 26, being initially an equimolar mixture of the compounds $CrSbO_4$ and $CrVO_4$, changed its phase composition after two identical heating cycles, i.e. at 800 °C for 24 h, and it was finally a mixture of $CrSbVO_6$ and Cr_2O_3. Figure 3 presents, besides a fragment of a diffractogram given by the equimolar mixture of $CrSbO_4$ with $CrVO_4$ (A), a fragment of a diffractogram obtained from this mixture after the last heating cycle, i.e. a mixture of $CrSbVO_6$ with Cr_2O_3 (B). This proves that just these two are the phases remaining finally at equilibrium in this concentration range of the investigated system in the solid state. Thus it can be concluded that the following reaction occurred:

$$CrSbO_{4(s)} + CrVO_{4(s)} = CrSbVO_{6(s)} + 1/2\ Cr_2O_{3(s)} + 1/4\ O_{2(g)} \qquad (6)$$

Such course of this reaction is additionally corroborated by a change in color of the sample as well as by the mass loss recorded during its heating and amounting to ~1.8 wt.%, while the theoretical mass loss calculated for this reaction is equal to 1.98 wt.%.

The results of all conducted investigations allowed a determination of a phase diagram of the subsolidus area of the system V_2O_5–Cr_2O_3–α-Sb_2O_4 over the whole components concentration range (Fig. 4). The diagram presented in Fig. 4 implies that the solidus surface of the system V_2O_5–Cr_2O_3–α-Sb_2O_4 consists of seven subsidiary subsystems. In this diagram we have put down the onset temperatures of melting for all mixtures of phases coexisting in given subsidiary subsystem. These temperatures were assumed to be the onset temperatures of first endothermic effects recorded in DTA curves of equilibrium preparations corresponding to the given subsidiary subsystem (Fig. 5).

DTA measurements of all the thermally-induced samples being in an equilibrium state, obtained in this work, imply that the $CrSbVO_6$ compound, when in the solid state and in air, coexists with $SbVO_5$ and V_2O_5 up to ~640 °C, whereas, it occurs beside $Cr_2V_4O_{13}$ and V_2O_5 up to 610 °C. The experiments and measurements have also shown that the melting temperature of a mixture comprising $CrSbVO_6$ together with $Cr_2V_4O_{13}$ and $CrVO_4$ is ~630°C, while mixtures of $CrSbVO_6$ with $CrVO_4$ and Cr_2O_3 melt at 840 °C. Furthermore, it has been found that $CrSbVO_6$ coexists, in the solid state, with $CrSbO_4$ and $SbVO_5$ up to ~710 °C. The phase $CrSbO_4$ coexists with $SbVO_5$ and α-Sb_2O_4 also up to ~710 °C.

In order to corroborate the temperatures of melting in the subsidiary subsystems of interest, the samples at equilibrium were heated for 3 h at a temperature higher than the onset of the first effect recorded on the DTA curves of all these preparations. Next the samples were rapidly cooled to room temperature and it was found that the samples representing the subsidiary subsystems I–IV underwent a distinct beginning of melting. On the other hand, the samples representing the subsystems VI and VII did not melt at all, but changed their phase composition as it was evidenced

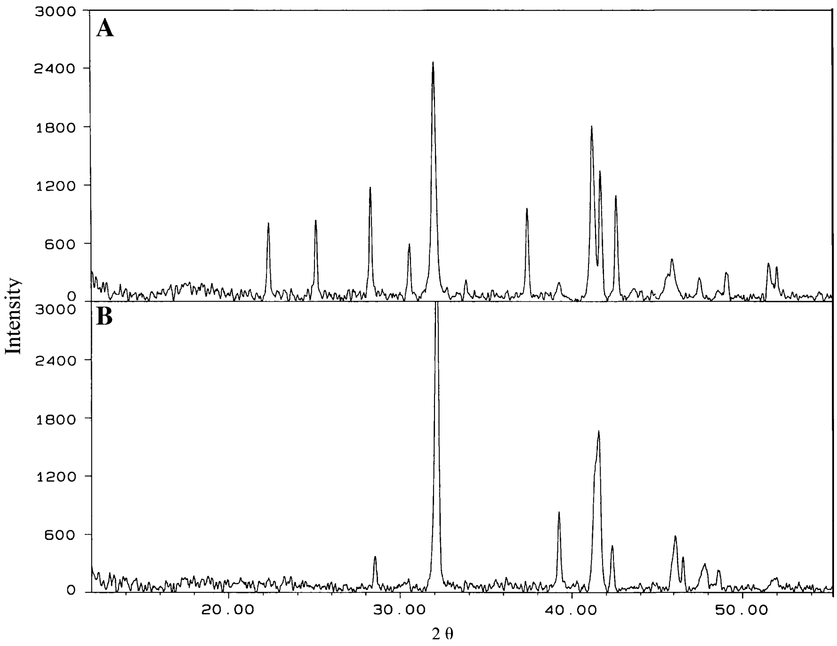


Fig. 3 X-ray diffraction patterns of: A—mixture of 50.0 mol% $CrSbO_4$ + 50.0 mol% $CrVO_4$, B—mixture of 66.67 mol% $CrSbVO_6$ + 33.33 mol% Cr_2O_3

Fig. 4 Division of the investigated system into subsidiary subsystems, *i.e.*: I: $CrSbVO_6$–$SbVO_5$–V_2O_5 (t_m = 640 °C); II: $CrSbVO_6$–V_2O_5–$Cr_2V_4O_{13}$(t_m = 610 °C); III: $CrSbVO_6$–$Cr_2V_4O_{13}$–$CrVO_4$(t_m = 630 °C); IV: $CrSbVO_6$–$CrVO_4$–Cr_2O_3 (t_m = 840 °C); V: $CrSbVO_6$–Cr_2O_3–$CrSbO_4$ (t_m > 1000 °C); VI: $CrSbVO_6$–$CrSbO_4$–$SbVO_5$(t = 710 °C); VII: $CrSbO_4$–α-Sb_2O_4–$SbVO_5$(t = 710 °C)

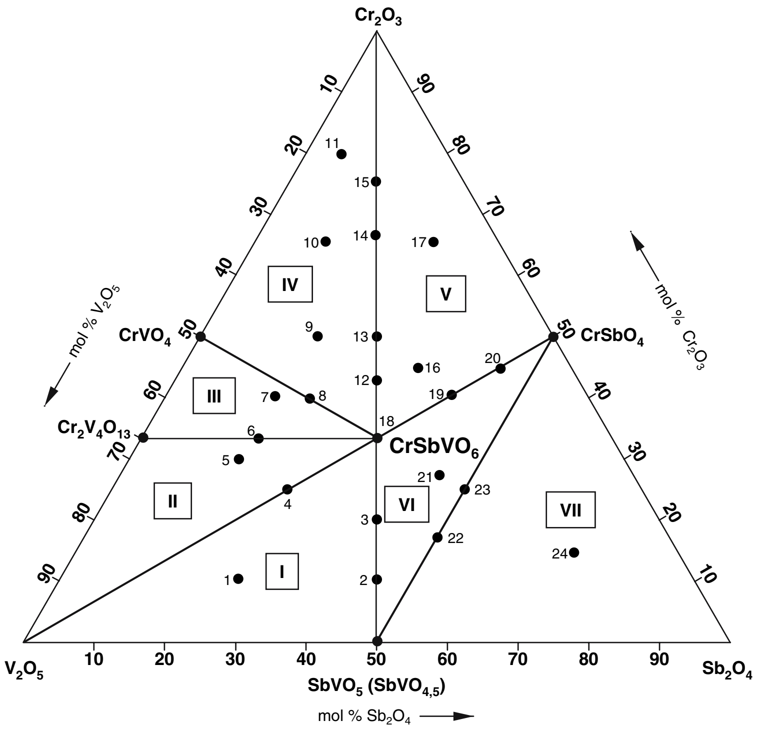
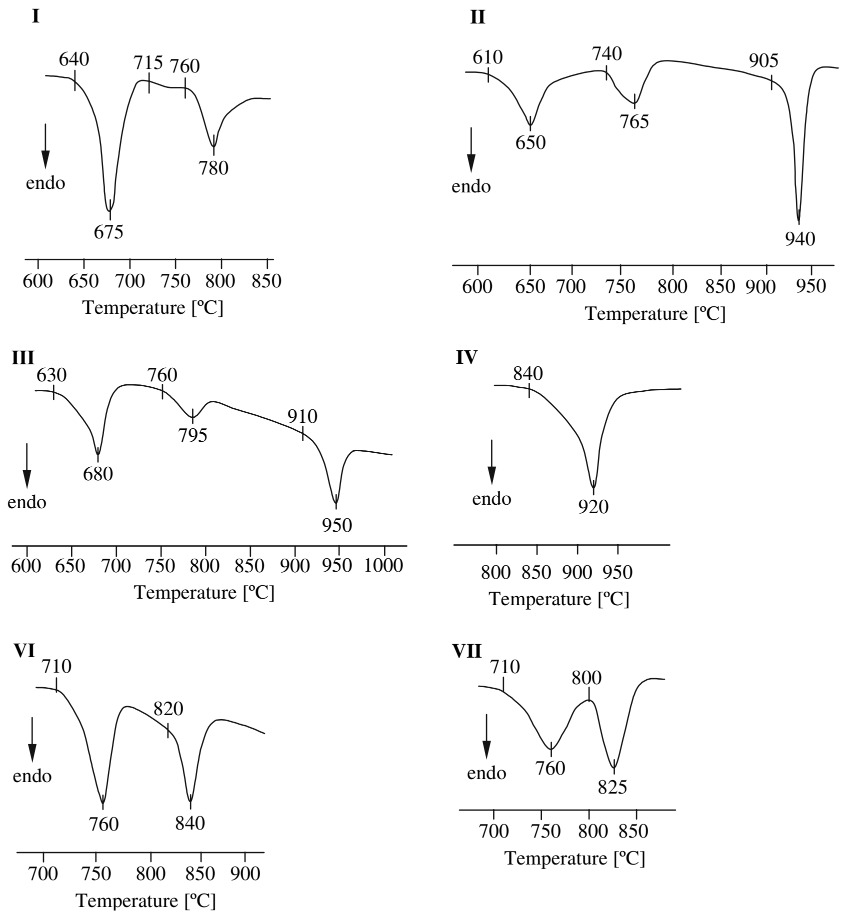


Fig. 5 DTA curves of samples at equilibrium and representing selected subsidiary subsystems of ternary system V_2O_5–Cr_2O_3–α-Sb_2O_4, i.e.: I: $CrSbVO_6$–$SbVO_5$–V_2O_5; II: $CrSbVO_6$–V_2O_5–$Cr_2V_4O_{13}$; III: $CrSbVO_6$–$Cr_2V_4O_{13}$–$CrVO_4$; IV: $CrSbVO_6$–$CrVO_4$–Cr_2O_3; VI: $CrSbVO_6$–$CrSbO_4$–$SbVO_5$; VII: $CrSbO_4$–α-Sb_2O_4–$SbVO_5$



by XRD. This was associated with a thermal decomposition of the compound $SbVO_5$ [23] contained by these samples. These experiments finally proved that the onset temperature of the first effect recorded on the DTA curves of the equilibrium samples determines the temperature range of coexistence of respective phases in the solid state.

On the DTA curve of a mixture comprising the $CrSbVO_6$ together with $CrSbO_4$ and Cr_2O_3 up to 1000 °C thermal effects were not recorded, which indicates that these compounds coexist in the solid state up to at least 1000 °C.

Summary

The results obtained within this work allow the following conclusions to be drawn:

1. In the ternary system V_2O_5–Cr_2O_3–α-Sb_2O_4 the compound $CrSbVO_6$ is formed, known for not long. This compound has been obtained by solid-state reactions occurring in air among various reactants according to Eqs. 1–5.

The XRD characteristics of this compound is identical with the characteristics of a compound that was obtained prior to our investigations in an inert atmosphere from an equimolar mixture of the oxides: V_2O_4/Sb_2O_5/Cr_2O_3 [28] as well as by the co-precipitation method from solutions containing $Cr(NO_3)_3 \cdot 6H_2O$, VO_2 and $SbCl_5$ [27].

2. $CrSbVO_6$ has a graphite-black color and melts incongruently at 1300 °C with a deposition of solid Cr_2O_3.
3. Indexing the powder diffractogram of $CrSbVO_6$ has confirmed that it crystallizes in the tetragonal system and possesses a rutile-type structure. The calculated unit cell parameters: $a = b = 0.45719(12)$ nm, $c = 0.30282(8)$ nm, $V = 0.0632987$ nm^3, $Z = 2$ differ a little from the parameters given in literature [27].
4. On the base of the investigations on phase equilibria being established up to the solidus surface in the system V_2O_5–Cr_2O_3–α-Sb_2O_4 we have determined the components concentration ranges in which the compound $CrSbVO_6$ coexists with other phases.
5. The ternary metal-oxide system V_2O_5–Cr_2O_3–α-Sb_2O_4 has been divided into seven subsidiary subsystems:

I: $CrSbVO_6$–$SbVO_5$–V_2O_5;
II: $CrSbVO_6$–V_2O_5–$Cr_2V_4O_{13}$;
III: $CrSbVO_6$–$Cr_2V_4O_{13}$–$CrVO_4$;
IV: $CrSbVO_6$–$CrVO_4$–Cr_2O_3;
V: $CrSbVO_6$–Cr_2O_3–$CrSbO_4$;
VI: $CrSbVO_6$–$CrSbO_4$–$SbVO_5$ and
VII: $CrSbO_4$–α-Sb_2O_4–$SbVO_5$.

Investigations aimed at establishing the phase equilibria in the V_2O_5–Cr_2O_3–α-Sb_2O_4 system above the solidus surface and interpreting the next DTA effects will be continued.

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