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Short communication

Phase equilibria in the subsolidus area in the $ZnO–Cr_2O_3–V_2O_5$ system

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ABSTRACT

The phase diagram of the $ZnO–Cr_2O_3–V_2O_5$ system in subsolidus area has been elaborated by DTA and XRD methods. It has been shown that the system consists of eight subsidiary subsystems in which there coexist in equilibrium three solid phases in each case. The melting temperatures of these subsystems have also been determined.

1. Introduction

A phase diagram is a characteristic feature of a given system, and it is also an ample source of information about the kind of the occurring phases as well as about the ranges of the component concentrations and of temperatures within which these phases coexist in thermodynamic equilibrium. An experimental determination of phase diagrams generally includes two stages, namely a preparation of samples followed by appropriate measurements of phase relation parameters under conditions as close as possible to the equilibrium state [1].

Application of phase diagrams enables the relationship between the crystal growth conditions and the crystal composition to be better understood. For this reason the diagrams are very useful not only in research but also in industry.

In recent years, more and more interest has been attracted by double vanadates(V) of divalent and trivalent metals, mainly because of their interesting catalytic properties [2]. The high selectivity and activity of such double vanadates is closely associated with the structure of these compounds, *i.e.* with the presence of isolated VO_4 tetrahedras in their crystal lattices [2].

Our literature review has shown that in the systems $AO–M_2O_3–V_2O_5$ (A = Zn, Ni, Mg; M = Cr, Fe) some double vanadates are formed with their formula $A_2MV_3O_{11}$ [3–9]. These compounds crystallize in the triclinic system and are isostructural with $GaMg_xZn_{2-x}V_3O_{11}$ [10]. Phase relations occurring in some of the above-mentioned ternary systems are also known [4,8,9].

$Zn_2CrV_3O_{11}$ has been obtained as a result of a reaction between $CrVO_4$ and zinc divanadate(V) [3]. This compound crystallizes in the triclinic system. Its unit cell parameters are: $a = 0.6277$ nm, $b = 0.7038$ nm, $c = 1.1006$ nm, $\alpha = 114.17^\circ$, $\beta = 101.27^\circ$, $\gamma = 101.89^\circ$ [3]. Literature information implies that the compound $Zn_2CrV_3O_{11}$ is isostructural with $Zn_2FeV_3O_{11}$ [11]. In available literature no information has been found about other compounds to be formed in the ternary system $ZnO–Cr_2O_3–V_2O_5$. The present work was intended to check whether in the system $ZnO–Cr_2O_3–V_2O_5$ there exist any other compounds, beside $Zn_2CrV_3O_{11}$, involving in their formation all the components of this system. The aim of this work was also a determination of phase relations in the above system.

2. Experimental

The reagents used for research were:

- V_2O_5, a.p., a product of Riedel-de Haën, Germany.
- Cr_2O_3, a.p., a product of Aldrich, Germany.
- ZnO, a.p., a product of Aldrich, Germany.

Moreover, the phases used for research were also: $CrVO_4$, $Cr_2V_4O_{13}$, $ZnCr_2O_4$, and $Zn_2CrV_3O_{11}$. The syntheses of these compounds have been described in the works [3,12,13].

Adequate weighed amount were homogenized by grinding, pelletized and heated under air in several stages until an equilibrium state had been attained. After each heating cycle, the phase composition of the samples was established by using the XRD method and they were subjected to DTA investigations. The synthesis conditions of individual samples differed, depending on the composition of their initial mixtures, both as to the heating temperature and as to the time of heating at a given temperature.

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Table 1
The composition, the heating conditions, and the kind of phases detected after the last heating stage in the samples from the system ZnO–$CrVO_4$.

No	Contents [mol%]		The heating temperature and time	The composition of the sample in an equilibrium state
	ZnO	$CrVO_4$		
1	20.00	80.00	600 °C(2× 24 h) + 610 °C(4× 24 h)	V_2O_5, $CrVO_4$, $ZnCr_2O_4$
2	30.00	70.00		
3	40.00	60.00		V_2O_5, $ZnCr_2O_4$, $Zn_2CrV_3O_{11}$
4	50.00	50.00		$ZnCr_2O_4$, $Zn_2CrV_3O_{11}$
5	60.00	40.00	700 °C(2× 24 h)	$ZnCr_2O_4$, $Zn_2V_2O_7$
6	66.67	33.33	700 °C(2×24 h)	$ZnCr_2O_4$, $Zn_3V_2O_8$
7	71.43	28.57	+ 740 °C(6 h) + 820 °C(6 h)	$ZnCr_2O_4$, $Zn_3V_2O_8$, ZnO
8	80.00	20.00		
9	90.00	10.00		

An attainment of the equilibrium state was ascertained by making a collation of the XRD results and of the DTA results obtained after two successive heating stages. When the obtained results were identical, it was concluded that the equilibrium state had been attained and the heating was then finished. When the XRD or DTA results (taken after two successive heating cycles) differed, then the samples were pelletized again and subjected to a further heating at the last stage temperature.

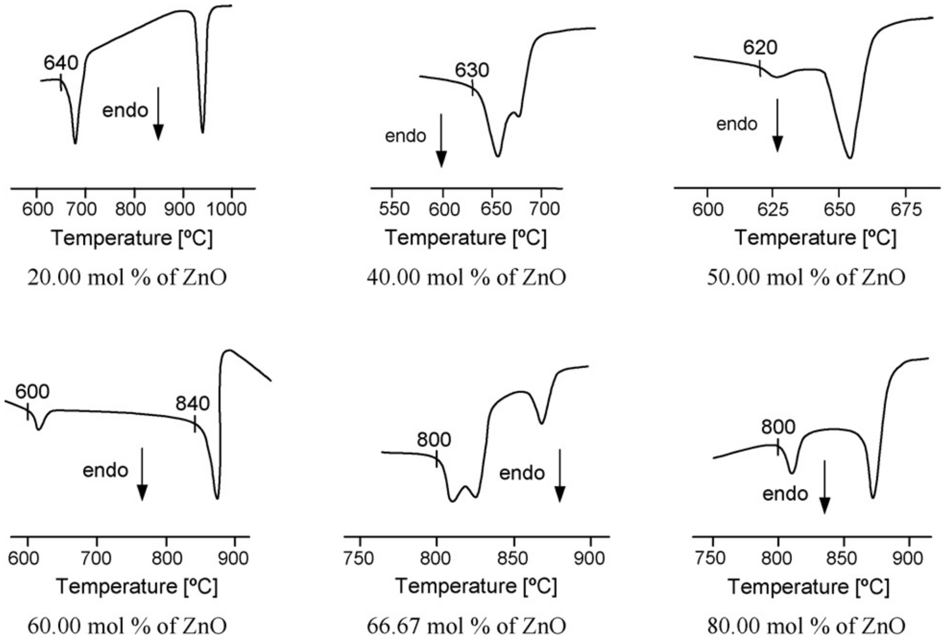
The phase composition of the samples was determined on the base of the XRD investigations (a DRON – 3 diffractometer, the radiation Co Kα, an Fe filter) as well as the data contained by the PDF files [14] or presented in the work [3]. While elaborating the diffractograms, we availed ourselves of the computer program package DHN/PDS (Program Packing for Powder Diffraction).

The DTA investigations were carried out with the aid of an F. Paulik–L. Paulik–L. Erdey derivatograph (MOM, Budapest). The samples to be examined by this method, in portions of 500 mg, were placed in quartz crucibles. All the measurements were performed under air, within the temperature range 20–1000 °C, at a heating rate of 10°/min. The temperature precision was ±5 °C.

3. Results

The investigations, intended to work out a phase equilibrium diagram of the oxide system ZnO–Cr_2O_3–V_2O_5, were begun with a preparation of 9 samples whose composition corresponded to one of the intersections, *i.e.* to the system ZnO–$CrVO_4$. The compositions of these samples are listed in Table 1.

Table 1 presents also the conditions of heating the samples as well as the formulae of the compounds identified in the samples that had attained the equilibrium state. The obtained results imply that the system ZnO–$CrVO_4$ is not a real binary system but only an intersection of the ternary oxide system ZnO–V_2O_5–Cr_2O_3. It results from literature data that at 800 °C zinc orthovanadate(V) decomposes in solid state, and the products of this decomposition are: β-$Zn_2V_2O_7$ and $Zn_4V_2O_9$ that is synthesized only at temperatures above 740 °C [15]. Likewise, the compound $Cr_2V_4O_{13}$ undergoes a solid-state decomposition at 640 °C [12]. In order to determine a full division of the investigated ternary system into partial subsystems, 19 samples were prepared with their compositions chosen in such a way that they represented the pseudobinary systems: ZnV_2O_6–$CrVO_4$, $Zn_2V_2O_7$–$Zn_2CrV_3O_{11}$, $ZnCr_2O_4$–$CrVO_4$, $Zn_2CrV_3O_{11}$–V_2O_5 as well as some selected hypothetical subsystems into which the investigated system could be divided. The compositions of initial mixtures for this second series of samples, their heating stages, and the kind of phases detected in the equilibrium state are compiled in Table 2. Considering the thermal properties of $Zn_3V_2O_8$ and $Zn_4V_2O_9$ (*i.e.* the solid-state thermal decomposition of $Zn_3V_2O_8$ and the thermal stability range of $Zn_4V_2O_9$ from the melting temperature 900 °C to 740 °C), it has been concluded that the compound $Zn_4V_2O_9$ is a metastable phase,



20.00 mol % of ZnO
40.00 mol % of ZnO
50.00 mol % of ZnO
60.00 mol % of ZnO
66.67 mol % of ZnO
80.00 mol % of ZnO

Fig. 1. DTA curves of some investigated samples lying on the intersection ZnO–$CrVO_4$.

Table 2
The composition, the heating stages, and the kind of phases identified after the final heating stage of selected samples lying within the binary or ternary subsystems.

No	Contents [mol%]			The heating temperature and time	The phase composition of the sample in an equilibrium state
	ZnO	V_2O_5	Cr_2O_3		
1	45.00	50.00	5.00	500 °C(12 h) + 580 °C(12 h) + 590 °C(12 h) + 600 °C(12 h)	$Zn_2CrV_3O_{11}$, ZnV_2O_6, V_2O_5
2	45.00	52.00	3.00		
3	40.00	53.50	6.50		
4	40.00	50.00	10.00	500 °C(12 h) + 580 °C(12 h) + 590 °C(12 h) + 600 °C(2× 12 h)	$Zn_2CrV_3O_{11}$, V_2O_5
5	36.00	55.00	9.00		
6	35.00	50.00	15.00	500 °C(12 h) + 580 °C(12 h) + 590 °C(12 h) + 600 °C(12 h) + 620 °C(3× 12 h)	$Zn_2CrV_3O_{11}$, V_2O_5, $ZnCr_2O_4$
7	30.00	50.00	20.00		
8	25.00	50.00	25.00		V_2O_5, $ZnCr_2O_4$
9	20.00	60.00	20.00		
10	20.00	50.00	30.00		V_2O_5, $ZnCr_2O_4$, $CrVO_4$
11	15.00	50.00	35.00		
12	53.35	38.09	8.56	500 °C(12 h) + 560 °C(24 h) + 580 °(3×24 h)	$Zn_2V_2O_7$, $Zn_2CrV_3O_{11}$
13	60.00	35.00	5.00		
14	55.00	40.00	5.00		ZnV_2O_6, $Zn_2CrV_3O_{11}$, $Zn_2V_2O_7$
15	50.00	45.00	5.00		$Zn_2CrV_3O_{11}$, ZnV_2O_6
16	20.00	15.00	65.00	500 °C(12 h) + 580 °C(12 h) + 590 °C(12 h) + 600 °C(2× 12 h)	$ZnCr_2O_4$, Cr_2O_3, $CrVO_4$
17	10.00	10.00	80.00		
18	20.00	30.00	50.00		$ZnCr_2O_4$, $CrVO_4$
19	10.00	40.00	50.00		

and therefore in the phase diagram of the system no line is drawn linking the compounds $Zn_4V_2O_9$ and $ZnCr_2O_4$.

Owing to the fact that $Cr_2V_4O_{13}$ was not identified in any sample, in order to check the way in which the division of an area circumscribed by the compounds V_2O_5–$Zn_2CrV_3O_{11}$–$ZnCr_2O_4$–$CrVO_4$–$Cr_2V_4O_{13}$ occurs, two mixtures were additionally prepared, *i.e.* an equimolar mixture of $Cr_2V_4O_{13}$ with $ZnCr_2O_4$ and a mixture of $Zn_2CrV_3O_{11}$ with $Cr_2V_4O_{13}$ at a molar ratio of 2:1. Both mixtures were heated under air at 550 °C for 24 h, and this heating temperature amounted to 6/7 of the melting temperature of the component exhibiting a lower melting temperature. In a diffractogram of these samples, three compounds were identified: V_2O_5, $CrVO_4$, and $ZnCr_2O_4$. This result indicates that under the conditions of the experiment the compound $Cr_2V_4O_{13}$ decomposes in solid state into $CrVO_4$ and V_2O_5 at a temperature of 550 °C already.

For a determination of the melting temperatures of two-component and three-component mixtures formed in the ternary system ZnO–Cr_2O_3–V_2O_5, all the samples were subjected to DTA investigations. Fig. 1 presents selected DTA curves of samples representing the system ZnO–$CrVO_4$. The melting temperatures of the mixtures of phases were established in such a way that they were based on the onset temperatures of first endothermic effects being not due to polymorphic transformations and recorded in the DTA curves.

On the ground of the obtained results and of the literature data [3], we constructed a phase diagram of the ternary system ZnO–Cr_2O_3–V_2O_5 in the subsolidus area (Fig. 2). Fig. 2 is additionally supplied with the melting temperatures of those mixtures of phases remaining in thermodynamic equilibrium that represent the partial subsystems or the intersections being conjugation lines (in other words, being real binary intersections).

It can be concluded from the phase diagram presented in Fig. 2 that the system ZnO–Cr_2O_3–V_2O_5 can be divided into 8 partial subsystems in which there coexist in equilibrium three solid phases in each case. These are the following partial subsystems:

I	$ZnO–ZnCr_2O_4–Zn_3V_2O_8$	$t_m = 800 \pm 5\,°C$
II	$Zn_3V_2O_8–ZnCr_2O_4–Zn_2V_2O_7$	$t_m = 800 \pm 5\,°C$
III	$Zn_2V_2O_7–Zn_2CrV_3O_{11}–ZnV_2O_6$	$t_m = 620 \pm 5\,°C$
IV	$Zn_2V_2O_7–ZnCr_2O_4–Zn_2CrV_3O_{11}$	$t_m = 620 \pm 5\,°C$
V	$ZnV_2O_6–Zn_2CrV_3O_{11}–V_2O_5$	$t_m = 630 \pm 5\,°C$
VI	$V_2O_5–Zn_2CrV_3O_{11}–ZnCr_2O_4$	$t_m = 630 \pm 5\,°C$
VII	$V_2O_5–ZnCr_2O_4–CrVO_4$	$t_m = 640 \pm 5\,°C$
VIII	$CrVO_4–ZnCr_2O_4–Cr_2O_3$	$t_m = 840 \pm 5\,°C$

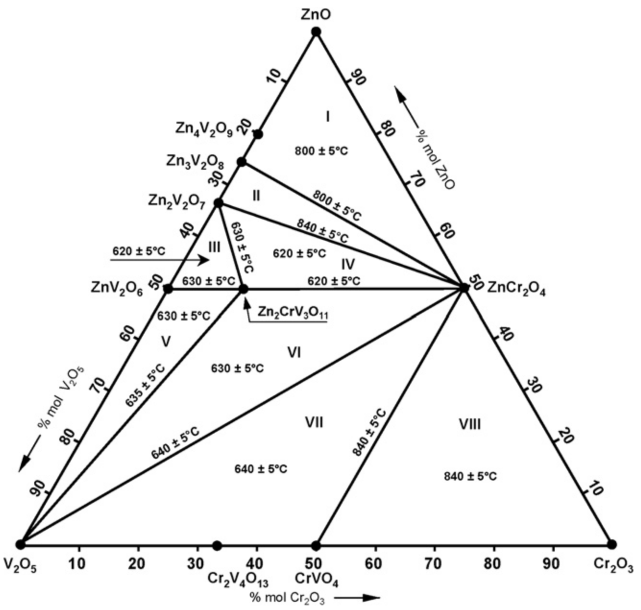


Fig. 2. A division of the component concentration triangle of the system ZnO–Cr_2O_3–V_2O_5 into partial subsystems.

4. Conclusion

In the ternary system ZnO–Cr_2O_3–V_2O_5, only one compound is formed involving all the three oxides in its formation; its formula is $Zn_2CrV_3O_{11}$ [3]. As a result of the conducted research, a phase equilibrium diagram for the subsolidus area of the ternary system ZnO–Cr_2O_3–V_2O_5 has been worked out. It has been found that the investigated system can be divided into 8 partial subsystems.

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