Journal of Thermal Analysis and Calorimetry, Vol. 64 (2001) 1081–1085

STUDY ON PHASE RELATIONS IN $Zn_3V_2O_8$–$ZnMoO_4$ SYSTEM

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Abstract

The phase equlibria established in the $Zn_3V_2O_8$–$ZnMoO_4$ system over the whole component concentration range up to 1000°C have been investigated. A phase diagram has been constructed using the results of DTA and XRD methods.

Keywords: DTA, phase equilibria, thermal properties, XRD, $Zn_3V_2O_8$–$ZnMoO_4$ system

Introduction

It has been known for a long time that $ZnMoO_4$ is one of two compounds existing in the two-component ZnO–MoO_3 system [1, 2]. Zinc molybdate(VI) crystallises in the triclinic system, a space group P1 with 6 molecules in its unite cell that has the following parameters: a=9.625(15) Å, b=6.965(10) Å, c=8.373(25) Å, α=103.28(15)°, β=96.30(15)°, γ=106.72(15)° [1]. Zinc molybdate(VI) does not display polymorphism under atmospheric pressure. On the other hand, high-pressure modification of zinc molybdate with a $NiWO_4$ structure is sure to be known [1, 3]. That polymorph crystallises in the monoclinic system, belongs to a space group and parameters of its unit cell are as follows: a=4.695 Å, b=5.729 Å, c=4.894 Å, β=90.32° [1]. At 580°C, the high-pressure modification undergoes an irreversible conversion into a modification stable at atmospheric pressure [3]. According to the current information available, $ZnMoO_4$ melts incongruently at 1007±2°C [1]. The published data concerning polymorphism and thermal properties of $Zn_3V_2O_8$ are controversial. Authors of some works [4–6] inform that the zinc orthovanadate(V) displays tri-morphism. On the other hand, Clark and Pick maintain that $Zn_3V_2O_8$ yields two polymorphic forms: low-temperature α-form and a high-temperature β-form [7]. The reversible $\alpha\Leftrightarrow\beta$ conversion takes place at 792°C [7]. At 815°C, β-$Zn_3V_2O_8$ breaks down into two solid phases: β-$Zn_2V_2O_7$ and $Zn_4V_2O_9$ [7]. Makarov *et al.* and Chang and Wang [8, 9] confirm the thermal decomposition of $Zn_3V_2O_8$. The authors of the works point at the fact that zinc orthovanadate(V) does not possess any polymorphic modifications at all.

Zinc orthovanadate is isotypical with $Mg_3V_2O_8$, $Co_3V_2O_8$ and $Ni_3V_2O_8$, it crystallises in the orthorhombic space group Cmca (a=6.1009(1) Å, b=11.522(2) Å,

1418–2874/2001/ $ 5.00

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c=8.295(2) Å, Z=4) [10, 11]. Furthermore, according to the results of our investigations concerning thermal properties of $Zn_3V_2O_8$, the compound does not display polymorphism within a temperature range 20–800°C, but breaks down into β-$Zn_2V_2O_7$ and $Zn_4V_2O_9$ [12]. Phase relations in the $Zn_3V_2O_8$–$ZnMoO_4$ system in the whole component concentration range up to 1000°C have not been an objective of the research work so far. It is only known that $Zn_{2.5}VMoO_8$ results from the reaction of $Zn_3V_2O_8$ with $ZnMoO_4$ in the solid state [13]. The compound melts incongruently at 845°C depositing crystal $ZnMoO_4$, and crystallises in orthorhombic system (a=5.064 Å, b=10.420 Å, c=17.586 Å, Z=6) [13, 14]. By the current information, a full crystal structure of $Zn_{2.5}VMoO_8$ has been established, too [14].

Experimental

For the experimentals there were prepared 17 samples from ZnO, V_2O_5 and MoO_3 – commercial analytically pure products (POCH, Gliwice, Poland). The oxides weighed in suitable proportions, after thorough homogenisations were shaped into pastilles to be heated in a resistance furnace. After each heating stage the pastilles were triturated and then examined for their composition by using the XRD method. The samples examined were again shaped into pastilles and heated further. This procedure was repeated until the samples had achieved a state of equilibrium. This was regarded as established when two consecutive heating stages did not cause any changes in the composition of the samples.

All the samples were heated for 24 h at temperatures: 550, 600, 700 and 750°C. Next the samples still kept in the furnace were being slowly cooled down during 12 h to ambient temperature. Each of the samples, the initial mixture of which comprised over 33.33 mol% of $Zn_3V_2O_8$, was divided into two portions. One portion was examined by using the DTA and XRD methods, the other reshaped into pastilles was extra heated for 5 h at 805°C, that is, at the temperature higher by 5°C of the temperature of thermal decomposition of $Zn_3V_2O_8$ in the solid state; the samples were quenched to ambient temperature afterwards. All the samples, viz. both the samples cooled slowly and those cooled rapidly to ambient temperature, were examined by means of DTA and XRD after the pastilles had been triturated. That procedure permitted to determine the types of phases originated in the system under study and to investigate their co-existence in the solid state. On the other hand, the types of solid phases being at equilibrium with liquid in the high-temperature area of the phase diagram were established depending on the XRD analysis of selected samples heated for 2–3 h at given temperature of the 830–950°C range and quenched to ambient temperature afterwards.

The phases occurring in samples were identified by means of the XRD analysis (a diffractometer of DRON-3 type, CoK_α radiation, Fe filter) and characteristics included in PDF charts [15] or given in works [13, 14, 16]. X-ray diffraction patterns were worked out by using a DHN/PDS software package (Program Package for Powder Diffraction).

Examinations by means of DTA method were made with the aid of a derivatograph (MOM, Hungary). All the measurements were carried out in air within, at the temperature range of 20–1000°C and at a heating rate of 10 K min^{-1}. The mass of the samples investigated was 1000 mg in each case. The measurements were made in quartz crucibles. Some selected samples were examined by means of the DTA by using instruments of SDT 2960 type (TA Instruments, USA). The measurements of samples weighing 5 mg each were carried out in air, at a heating rate of 10 K min^{-1}. The containers used for measurements were platinum crucibles.

Results and discussion

Table 1 presents the compositions of initial mixtures, heating conditions and result XRD analysis of samples, both those cooled slowly, and the other ones cooled rapidly, to ambient temperature. A diagram of phase equlibria in the $Zn_3V_2O_8$–$ZnMoO_4$ system was worked out within the whole component concentration range up to 1000°C (Fig. 1) by using the data shown in Table 1 and depending on the DTA curves of the samples examined. Solidus line temperatures were determined on the basis of onset temperatures of the first endothermic effects recorded on the DTA curves. Because of the thermal decomposition of $Zn_3V_2O_8$ taking place at 800°C in the solid state, the solidus line in the $Zn_3V_2O_8$–$Zn_{2.5}VMoO_8$ region of the X-ray phase pattern was determined depending on the DTA curves of samples quenched from 805°C to ambient temperature. For the other component concentration range of the $Zn_{2.5}VMoO_8$–$ZnMoO_4$ system, the determination of solidus line temperatures was performed by using DTA curves of the samples slowly cooled to ambient temperature. The liquidus curves were determined by reading the onset temperatures of effects recorded as the finalones in the DTA curves. The types of phases being at equi-

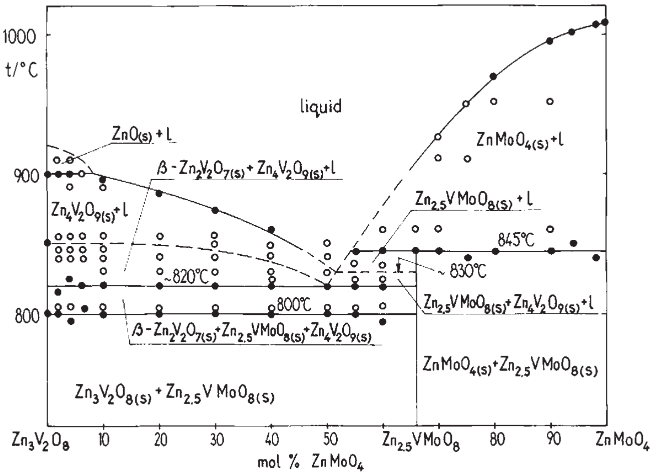

Fig. 1 Phase diagram of the $Zn_3V_2O_8$ – $ZnMoO_4$ system; ● – points indicate DTA, o – XRD investigation after air 'quenching'

librium with liquid in relevant ranges of the temperature and component concentration of the system under study were established on the basis of result of XRD analysis of samples ‘frozen’ at temperatures selected from the temperature range of 830–950°C. The compositions of samples and temperatures of the ‘freezing’ have been marked in the figure.

Table 1 Composition of initial mixtures, conditions of preparation (heating temperature and time) and XRD results for all samples

Composition of samples in terms of components of the system (mol% $ZnMoO_4$)	Conditions of preparation	Phases detected
2.0; 4.0; 6.0; 10.0; 20.0; 30.0;	550°C(24 h)+600°C(24 h)+ 700°C(24 h)+750°C(24 h) gradually cooling	$Zn_3V_2O_8$, $Zn_{2.5}VMoO_8$
40.0; 50.0; 55.0; 60.0;	550°C(24 h)+600°C(24 h)+ 700°C(24 h)+750°C(24 h)+ 805°C(24 h) rapidly cooling	β-$Zn_2V_2O_7$, $Zn_4V_2O_9$, $Zn_{2.5}VMoO_8$
66.67	550°C(24 h)+600°C(24 h)+ 700°C(24 h)+750°C(24 h) gradually cooling	$Zn_{2.5}VMoO_8$
70.0; 75.0; 80.0; 90.0; 94.0; 98.0		$ZnMoO_4$, $Zn_{2.5}VMoO_8$

It follows from the phase diagram shown in Fig. 1 that only one compound – $Zn_{2.5}VMoO_8$ – occurs inside the $Zn_3V_2O_8$–$ZnMoO_4$ system. The compound melts incongruently at 845°C, depositing a crystal $ZnMoO_4$, which was confirmed by XRD analysis of $Zn_{2.5}VMoO_8$ additionally heated at 860°C for 3 h and then quenched to ambient temperature. In the component concentration range of over 66.67 mol% of $ZnMoO_4$, $Zn_{2.5}VMoO_8$ and zinc molybdate(VI) coexist at equilibrium up to the solidus line temperature, which is determined by the temperature of the $Zn_{2.5}VMoO_8$ incongruent melting. Above that temperature, it is $ZnMoO_4$ that remains in equilibrium with liquid. At the left component concentration range and up to 800°C, it is $Zn_3V_2O_8$ that is at equilibrium with $Zn_{2.5}VMoO_8$. At 800°C, $Zn_3V_2O_8$ decomposes into two solid phases: β-$Zn_2V_2O_7$ and $Zn_4V_2O_9$. The temperature of the thermal decomposition was determined by using the DTA curves of the samples slowly cooled to ambient temperature. It was also inferred from X-ray phase diagram (Fig. 1) that the title system within the $Zn_3V_2O_8$–$Zn_{2.5}VMoO_8$ region, at 800°C and upwards, ceases to be a two-component system. The proof for this fact is the co-existence at equilibrium within this component concentration range of three solid phases: $Zn_{2.5}VMoO_8$, $Zn_4V_2O_9$ and β-$Zn_2V_2O_7$. The fact has also provided a supporting evidence that in the component concentration range at 800°C and upwards, the $Zn_3V_2O_8$–$Zn_{2.5}VMoO_8$ system is a vertical section of the three-component ZnO–V_2O_5–MoO_3 system. The above-mentioned two-component system crosses the subsidiary ternary system, $Zn_{2.5}VMoO_8$–$Zn_4V_2O_9$–β-$Zn_2V_2O_7$. The phase diagram of the $Zn_3V_2O_8$–$ZnMoO_4$ system shows that the subsidiary $Zn_{2.5}VMoO_8$–$Zn_4V_2O_9$–β-$Zn_2V_2O_7$ system is an eutectic system, and melting temperature of the ternary eutectic is 825°C. Above the solidus line temperature, that is, above 825°C, the phase relations in the

$Zn_2V_2O_8$–$Zn_{2.5}VMoO_8$ region of the title system are a consequence of melting the ternary eutectic, $Zn_{2.5}VMoO_8$–$Zn_4V_2O_9$–β-$Zn_2V_2O_7$.

The experimental results have not always made it possible to delimit the areas of the existing fields where the solid phases should be at equilibrium with liquid. The maximum temperature range of the existing fields of $Zn_4V_2O_{9(s)}$+$Zn_{2.5}VMoO_{8(s)}$+liquid and β-$Zn_2V_2O_{7(s)}$+$Zn_4V_2O_{9(s)}$+liquid was determined by using XRD analysis of samples ‘frozen’ at suitable temperature.

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