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SYNTHESIS AND THERMAL STABILITY OF $Zn_4V_2O_9$

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Abstract

A study of synthesis and thermal decomposition of the $Zn_4V_2O_9$ have been conducted by XRD method using a high-temperature X-ray attachment. A melting temperature and the way of melting that compound have been established.

Keywords: DTA, $Zn_4V_2O_9$, XRD

Introduction

It is known from the literature scan that a number of compounds arise from the reaction of ZnO with V_2O_5, that is, ZnV_2O_6, $Zn_2V_2O_7$, and $Zn_3(VO_4)_2$ [1–3], and also $Zn_4V_2O_9$ [3–6]. The last compound was identified as one of the products of $Zn_3(VO_4)_2$ thermal decomposition [3, 5, 6]. Makarov *et al.* [3] have stated existence of $Zn_4V_2O_9$ as a compound that belongs to the V_2O_5–ZnO system. They also have found that the compound is stable to ambient temperature and melts at 1183 K. Authors of work [4] admit that to carry out the synthesis of $Zn_4V_2O_9$ from oxides below 1073 K is difficult and its heating takes a long time. Clark and Pick [5] have confirmed the formation of $Zn_4V_2O_9$ from a suitable oxide mixture heated at 1100 K. Waburg and Müller-Buschbaum have obtained the monocrystals of $Zn_4V_2O_9$ between a CO_2-laser generated flux and the solid ZnO/V_2O_5 material [7]. The compound crystallises in a monoclinic system, space group $P2_1$, the parameters a=1.0488(5) nm, b=0.8198(6) nm, c=0.9682(5) nm, β=118.66(4)°; the number of molecules in the elementary cell Z=4 [7]. According to the workers [7], $Zn_4V_2O_9$ heated below melting temperature of V_2O_5 suffers decomposition.

Due to the divergence in information about thermal properties of $Zn_4V_2O_9$ it seemed advisable to carry out investigations aiming at stating the thermal stability range for the compound precisely, and conduct the synthesis of $Zn_4V_2O_9$ from reactants that would enable the reaction to run in the solid state at a temperature higher than that used in synthesis from V_2O_5/ZnO mixture.

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Experimental

For the experiments ZnO, (p.a., Ubichem Ltd, England) and $Zn_3(VO_4)_2$ prepared by the method described in work [8] were used. $Zn_3(VO_4)_2$/ZnO mixture with a 50/50 mol% content of the reactants was prepared for the investigations. One-gram samples of the mixture were placed in a high-temperature X-ray attachment of a UVD-2000 type (Bourevestnik, Sankt Petersburg, Russia) linked to an X-ray diffractometer of an HZG4/A2 type (Carl Zeiss, Jena, Germany). The samples were heated to the given temperature at a rate of 20 K min^{-1}, kept in a thermostat for 2 h and a powder diffraction pattern was taken at a suitable temperature – raised by 10 K afterwards. That procedure was repeated until the temperature was achieved at which diffraction lines characteristic of $Zn_4V_2O_9$ were noticed in a powder diffraction pattern. The further stage of investigation consisted in decreasing the temperature by 10 K followed by keeping the sample in a thermostat for 2 h and finally taking its powder diffraction pattern. That procedure was repeated until the temperature was reached at which an X-ray powder diffraction pattern of the sample showed an evidently decreased intensity in diffraction lines characteristic of the $Zn_4V_2O_9$ compound and presence of lines brought about by products of breaking down the phase. A number of examinations were made at 973–1033 K.

A set of selected samples was examined by using a scanning electron microscope (JSM-1600, Jeol, Japan) linked to an X-ray microanalyser (ISIS 300, Oxford).

Measurements by DTA method were made by using an apparatus of an SDT 2960 type (TA Instruments, USA). The measurements were carried out in air with samples of 5 mg, placed in platinum crucibles and heated at a rate of 10 K min^{-1}.

The identification of the compounds was made depending on the X-ray characteristics of PDF charts [9], and on an X-ray diffraction pattern generated on the grounds of data pertaining to the $Zn_4V_2O_9$ structure [7].

Results and discussion

Table 1 shows X-ray phase analysis of samples heated according to the procedure described. Samples heated up to 1003 K contained only original substances (Fig. 1a). X-ray diffraction pattern of a sample heated at 1013 K showed, apart from diffraction lines characteristic of the output products, lines of a low intensity brought about by $Zn_4V_2O_9$ (Fig. 1b). Therefore, temperature 1013 K was taken as an onset temperature of $Zn_4V_2O_9$ synthesis - running in accordance with the equation:

$$Zn_3(VO_4)_2+ZnO=Zn_4V_2O_9 \quad (1)$$

Samples heated at 1023 and 1033 K comprised compounds that had been identified at 1013 K, the amount of $Zn_4V_2O_9$ being considerably larger. However, an extra 6 hour's keeping a sample in thermostat at 1033 K failed to bring the reaction of reagents to completion. That sample was then heated for 1 h at 1108 K, that is, above the breakdown temperature of $Zn_3(VO_4)_2$, although below melting temperature of β-$Zn_2V_2O_7$ [3, 5, 6]. An X-ray diffraction pattern showed only lines characteristic of $Zn_4V_2O_9$ (Fig. 1c).

Table 1 Temperatures of heating and X-ray phase analysis of samples examined with the aid of high-temperature X-ray attachment

Temperatures of heating/K	Phases detected
Initial reagents: $Zn_3(VO_4)_2$ + ZnO	
973, 983, 993, 1003	$Zn_3(VO_4)_2$, ZnO
1013	$Zn_3(VO_4)_2$, ZnO, $Zn_4V_2O_9$ – traces
1023, 1033	$Zn_3(VO_4)_2$, ZnO, $Zn_4V_2O_9$
1108	$Zn_4V_2O_9$
Initial reagent: $Zn_4V_2O_9$	
1033, 1023, 1013, 1003	$Zn_4V_2O_9$
993	$Zn_4V_2O_9$, $Zn_3(VO_4)_2$, ZnO

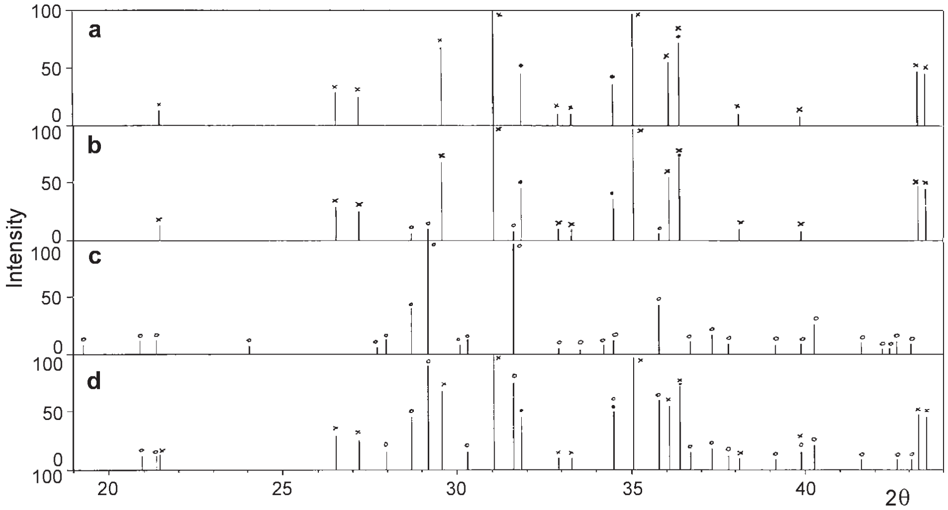

Fig. 1 X-ray diffraction patterns of the mixture comprising 50.00% mol $Zn_3(VO_4)_2$ and 50.00% mol ZnO heated at: a – 973 K, b – 1013 K, c – 1108 K and d) $Zn_4V_2O_9$ cooled to 993 K. × – $Zn_3(VO_4)_2$, • – ZnO, ◦ – $Zn_4V_2O_9$

Follow-up investigations depended on cooling $Zn_4V_2O_9$ to 1033, 1023, 1013 and 1003 K. Analysis of X-ray diffraction patterns taken after each cooling stage showed that keeping $Zn_4V_2O_9$ in thermostat at these temperatures did not lead to any changes in contents of the sample. It was not until the sample was cooled to 993 K, *viz* X-ray diffraction pattern contained lines characteristic of $Zn_3(VO_4)_2$ and ZnO beside those indicative of $Zn_4V_2O_9$ (Fig. 1d). Therefore it was possible to assume that the decomposition of $Zn_4V_2O_9$ started at 993 K and the decomposition process run according to the equation:

$$Zn_4V_2O_9=Zn_3(VO_4)_2+ZnO \qquad (2)$$

Indicated by the experiments difference in the onset temperature of the $Zn_4V_2O_9$ synthesis and that in the temperature of decomposition of the compound is most likely related to different reaction rate both of synthesis and decomposition of $Zn_4V_2O_9$. The research on kinetics of both processes will be carried out.

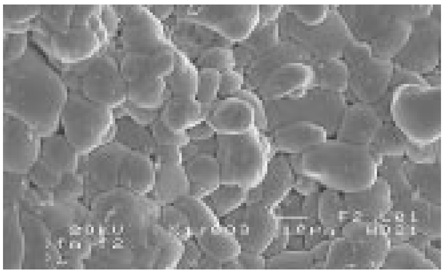

Fig. 2 SEM image of $Zn_4V_2O_9$

The synthesis of $Zn_4V_2O_9$ was also carried out by heating an equimolar $Zn_3(VO_4)_2$/ZnO mixture in a sylite furnace at 1108 K for 20 h followed by rapid quenching (freezing) of the reaction product. The pure $Zn_4V_2O_9$ obtained was examined using a scanning electron microscope (Fig. 2). Analytical results obtained by using X-ray microanalyser proved consistent with the composition of $Zn_4V_2O_9$. Next a sample of pure $Zn_4V_2O_9$ was kept in a sylite furnace at 993 K for 20 h, to be then rapidly quenched to ambient temperature. The sample was also examined by scanning electron microscope (Fig. 3). In the figure there can be seen two types of crystals noticeably different in morphology. Analytical results obtained by X-ray microanalyser give indication that some of them match $Zn_3(VO_4)_2$ in their composition, and the other – ZnO.

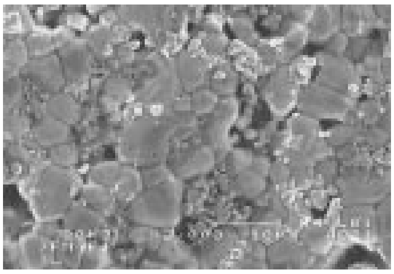

Fig. 3 SEM image of $Zn_4V_2O_9$ cooled to 993 K

Figure 4 shows a DTA curve of $Zn_4V_2O_9$. The endothermic peak with an onset temperature 1173±5 K is related with melting of the compound. It follows from X-ray analysis of the molten products that the compound melts incongruently, and the solid product is ZnO.

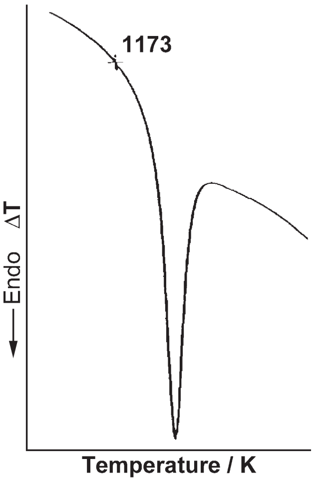

Fig. 4 DTA curve of $Zn_4V_2O_9$

Conclusions

1. Synthesis of the $Zn_4V_2O_9$ compound carried out from a $Zn_3(VO_4)_2$/ZnO mixture starts at 1013 K.
2. A pure $Zn_4V_2O_9$ can be obtained from the reaction running in a solid state at 1108 K, in accordance with Eq. (1).
3. $Zn_4V_2O_9$ melts incongruently at 1173±5 K, and the solid product is ZnO.
4. The thermal decomposition of $Zn_4V_2O_9$ starts at 993 K to give $Zn_3(VO_4)_2$ and ZnO as products of the decomposition.

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