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THE SYNTHESIS AND SELECTED PROPERTIES OF $Co_2InV_3O_{11}$

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It has been demonstrated that $Co_2V_2O_7$ and $InVO_4$ react with each other forming a new compound of the $Co_2InV_3O_{11}$ formula, when their molar ratio is equal to 1:1, or among $CoCO_3$, In_2O_3 and V_2O_5, mixed at a molar ratio of 4:1:3. This compound melts incongruently at the temperature of 960±5°C, depositing crystals of $InVO_4$. It crystallizes in the triclinic system and the unit cell parameters amount to: a=0.6524(6) nm, b=0.6885(5) nm, c=1.0290(4) nm, α=96.5°, β=104.1°, γ=100.9°, Z=2. The phase equilibria being established in the $Co_2V_2O_7$–$InVO_4$ system over the whole components concentration range up to the solidus line were described.

Keywords: *cobalt(II) divanadate(V), double vanadate, DTA, indium(III) orthovanadate(V), XRD*

Introduction

Photocatalytic decomposition of water with the use of solar energy and semiconductors to generate clean energy hydrogen has attracted growing attention [1]. Only few semiconductors find application in the photocatalytic water decomposition processes. The fact whether a given semiconductor can be used in this type processes is dependent on both the narrow energetic gap between the conduction and the fundamental bands as well as the crystal structure of the compound [2]. As a result of the conducted investigations it was found that the best results in the processes of photocatalytic decomposition of water can be obtained when compounds such as WO_3 [3, 4], $RbPb_2Nb_3O_{10}$ and its modifications exhibiting the Perovskite type structure [4], $In_2O_3(ZnO)_m$ [3], $BiVO_4$ [5] and $InMO_4$ (M=V, Nb, Ta) are used [6–8]. A research on applying complex compounds with the structure containing the VO_4 tetrahedra has recently been started [2].

Literature data report that in the MO–Fe_2O_3/Cr_2O_3–V_2O_5 systems, where M=Mg, Zn, Co, Ni, binary vanadates with the $M_2FeV_3O_{11}$ (M=Mg, Zn, Co, Ni) and $M_2CrV_3O_{11}$ (M=Mg, Zn, Ni) formulas are formed [9–12]. These compounds undergo crystallization in the triclinic system and are isostructural with $GaMg_xZn_{2-x}V_3O_{11}$ [11]. The VO_4 tetrahedra as well as the VO_5 bipyramids can be distinguished in the structure of these compounds [11]. In the MO–Bi_2O_3–V_2O_5 systems where M=Ba, Sr compounds with the $Ba_2BiV_3O_{11}$ and $Sr_2BiV_3O_{11}$ formulas are generated [13, 14]. Despite the fact that these compounds are not isostructural and do not belong to the same family, the structural analyses of both compounds demonstrated that both the orthovanadate and the pyrovanadate groups can be distinguished in their structure [14]. There is a large group of compounds which are isostructural with $Ba_2BiV_3O_{11}$ where indium ions or rare-earth elements were introduced for the Bi^{3+} ion [14]. $Ba_2InV_3O_{11}$ crystallizes in a monoclinic system, the space group is $P2_1/c$, Z=4 [14]. The parameters of the unit cell are as follows: a=1.2077(6) nm, b=0.7528(9) nm, c= 1.0985(8) nm, β=104.1(5) [14]. According to literature data, during the reaction between $M_2V_2O_7$ and $InVO_4$, where M=Mg, Zn, compounds of a general $M_2InV_3O_{11}$ formula, being isostructural with $Mg_2FeV_3O_{11}$ are formed [15]. They crystallize in the triclinic system [15]. The aim of this work was to establish whether a compound of the $Co_2InV_3O_{11}$ formula can be formed in the $Co_2V_2O_7$–$InVO_4$ system, and also to investigate the phase relations in this system in the whole components concentration range up to the solidus line.

Experimental

In order to conduct the studies adequate mixtures such as: V_2O_5 (analytically pure, Aldrich, Germany), In_2O_3 (analytically pure, Aldrich, Germany), $CoCO_3$ (analytically pure, Fluka, Germany) were used. Samples were also made with $InVO_4$ and $Co_2V_2O_7$ which were obtained by heating the stoichiometric mixtures of appropriate compounds in the following cycles:

- $InVO_4$: 550°C (12 h)+650°C (12 h)+750°C (12 h)
- $Co_2V_2O_7$: 550°C (12 h)+650°C (12 h)+700°C (12 h)+750°C (12 h)

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The reacting substances were weighed in adequate proportions, then thoroughly homogenized by powdering, forming into pellets and then heated in cycles in the sylit furnace in air atmosphere. After each heating cycle the samples and the furnace were cooled down to ambient temperature, next ground and subjected to the DTA tests and their content was established with the XRD method. After another pelletizing they underwent further heating. These activities were repeated until the state of equilibrium for the samples was obtained [16, 17].

For the tests on phase relations being formed in the $Co_2V_2O_7$–$InVO_4$ system, 10 samples were prepared for which the components of the studied system were taken as the initial substances. The components of the initial mixtures were weighed in appropriate proportions, homogenized by grinding, moulded into pellets and heated in the resistance furnace. After each heating cycle the pellets were ground and tested with the XRD and DTA methods. All the samples were heated in the 12 h cycles.

The types of the phases occurring in particular samples were determined with the XRD method. The diffraction patterns were obtained with the use of the Philips X-ray instrument, (the X” Pert PRO type), applying the CoK_α radiation and the Fe filter. The identification of particular phases was carried out on the basis of the X-ray characteristics included in the PDF cards [18] and literature data [11].

The DTA investigations were carried out by means of the apparatus Metler Toledo TGA/SDTA 851. All measurements were conducted in the atmosphere of nitrogen. The samples subjected to the measurements weighed as little as ca. 10 mg and were placed in quartz crucibles. The heating rate amounted to 10° min^{-1}.

The unit cells’ parameters were calculated with the help of the POWDER program belonging to the crystallographic program library X Ray System 70. The exact position of diffraction lines was determined with the internal standard method. KCl was applied as the internal standard (space group Fm3m, a=0.6293 nm) [19].

The compound’s density was determined with the method described in the [20] work.

Results and discussion

The works were started by trying to obtain the $Co_2InV_3O_{11}$ compound, analogous to the compounds presented in literature of the $M_2InV_3O_{11}$ formula, where M=Ba, Mg, Zn [14, 15]. In order to achieve that a mixture of 12.50 mol% In_2O_3, 37.50 mol% V_2O_5 and 50.00 mol% $CoCO_3$ was prepared, it was then heated in the following cycles: 500→600°C (12 h)+650°C (12 h)+700°C (12 h)+750°C (12 h·2). The diffraction pattern of this sample, made after the last cycle of heating did not record any lines characterizing oxides or any known phase belonging to the In_2O_3–V_2O_5 or CoO–V_2O_5 systems. The diffraction pattern of the sample was similar to the diffraction patterns of the phases described in literature [15]. It was understood that the obtained compound of the $Co_2InV_3O_{11}$ formula, is formed according to the following reaction:

$$4CoCO_{3(s)}+3V_2O_{5(s)}+In_2O_{3(s)}=2Co_2InV_3O_{11(s)} \quad (1)$$

This compound was also procured in the reaction where $InVO_4$ and $Co_2V_2O_7$ mixed in the mol ratio 1:1, were its substrates. This mixture was heated in a similar way as in the case of the mixture made of vanadate(V) oxide, indium(III) oxide and cobalt(II) carbonate. The diffraction pattern which was noted after the last cycle of heating the mixture, exhibited a set of diffraction lines whose location and intensity were identical with those on the diffraction pattern of $Co_2InV_3O_{11}$ obtained according to Eq. (1). It was assumed that $Co_2InV_3O_{11}$ was also obtained in the reaction occurring according to the following equation:

$$InVO_{4(s)}+Co_2V_2O_{7(s)}=Co_2InV_3O_{11(s)} \quad (2)$$

$Co_2InV_3O_{11}$ is of dark green colour. It melts incongruently releasing $InVO_4$ at the temperature of 970°C. The DTA curve of Co_2InVO_{11} is presented in Fig. 1.

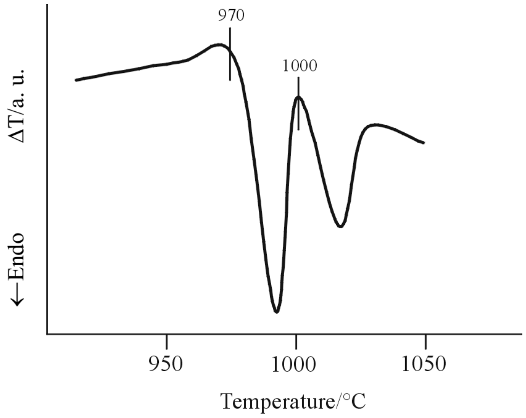

Fig. 1 DTA curves of $Co_2InV_3O_{11}$

The diffraction powder of $Co_2InV_3O_{11}$ was subjected to indexing and the obtained results are presented in Table 1. The parameters of the triclinic unit cell are as follows: a=0.65224(6) nm, b= 0.6885(5) nm, c=1.0290 nm, α=96.5°C, β=104.1°C, γ=100.9°C, Z=2. The X-ray density is d_{rtg}= 4.30 g cm^{-3}, whereas the pictometric one is d= 4.35±0.05 g cm^{-3}.

Table 1 The results of indexing the powder diffraction pattern of $Co_2InV_3O_{11}$

No.	d_{exp}(nm)	d_{cal}(nm)	$h\ k\ l$	I/I_0(%)
1	0.6662	0.6666	$0\ 1\ 0$	6.1
2	0.6146	0.6167	$1\ 0\ 0$	9.7
3	0.5961	0.6005	$0\ 1\ \bar{1}$	19.2
4	0.5143	0.5140	$1\ \bar{1}\ 0$	3.0
		0.5135	$0\ 1\ 1$	
5	0.4928	0.4921	$0\ 0\ 2$	10.3
6	0.4760	0.4748	$1\ \bar{1}\ \bar{1}$	3.6
7	0.4688	0.4686	$1\ 0\ 1$	3.7
8	0.4383	0.4385	$1\ \bar{1}\ 1$	5.4
9	0.4324	0.4319	$0\ 1\ \bar{2}$	4.4
10	0.3334	0.3333	$0\ 2\ 0$	28.6
11	0.3284	0.3281	$0\ 0\ 3$	100
12	0.3250	0.3254	$1\ \bar{2}\ 0$	14.6
13	0.3072	0.3074	$2\ \bar{1}\ 0$	93.0
14	0.3005	0.3008	$0\ 2\ 1$	7.7
		0.3003	$0\ 2\ \bar{2}$	
15	0.2890	0.2895	$1\ \bar{1}\ \bar{3}$	3.5
16	0.2704	0.2702	$2\ 1\ \bar{1}$	4.3
17	0.2691	0.2690	$1\ 2\ 0$	4.4
		0.2689	$1\ \bar{2}\ \bar{2}$	
18	0.2614	0.2617	$1\ 0\ 3$	10.4
19	0.2573	0.2570	$2\ \bar{2}\ 0$	6.1
20	0.2466	0.2461	$0\ 0\ 4$	19.6

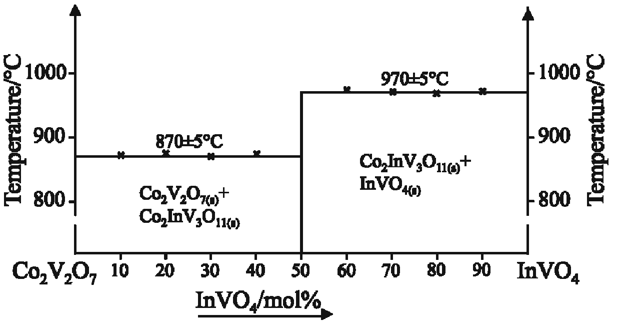

Fig. 2 Phase diagram of $Co_2V_2O_7$–$InVO_4$ system

The aim of further investigation was to determine phase equilibria being established in the whole range of components concentrations of the $Co_2V_2O_7$–$InVO_4$ system up to solidus line. Table 2 demonstrates the compositions of the samples prepared for the tests as well as the phases detected in particular samples after the last cycle of heating. The data presented in the table imply that in the solid state of concentration, the components of the tested system are not at equilibrium one with another. The XRD of the samples containing in their initial mixtures up to 50.00 mol% $Co_2V_2O_7$ per the system's components, proved the presence of two phases, the $InVO_4$ and the $Co_2InV_3O_{11}$ one, in them. The sample containing 50.00 mol% $Co_2V_2O_7$ and 50.00 mol% $InVO_4$ in the initial mixture includes only one phase, i.e. $Co_2InV_3O_{11}$. In the remaining samples $Co_2InV_3O_{11}$ and $Co_2V_2O_7$ were identified. Thus, the content of samples in the state of equilibrium proves that in the studied system, in the solid state, a reaction according to Eq. (2) resulting in the formation of the $Co_2InV_3O_{11}$ compound, takes place.

Figure 2 presents a phase diagram of the $Co_2V_2O_7$–$InVO_4$ system built on the basis of the DTA curves and the results of the XRD analysis of the samples belonging to the studied system (Table 2). The temperatures of the solidus line were determined on the basis of the onset temperatures of the initial endothermic effects recorded on the DTA curves of the examined samples.

Conclusions

- The research results prove that $Co_2V_2O_7$ and $InVO_4$ are not inert towards each other in the solid state, but they react forming a new compound of $Co_2InV_3O_{11}$.
- $Co_2InV_3O_{11}$ melts incongruently at the temperature 970±5°C to deposit a solid $InVO_4$.
- $Co_2InV_3O_{11}$ crystallizes in the triclinic system, its unit cell parameters are: a=0.65224(6) nm, b=0.6885(5) nm, c=1.0290 nm, α=96.5°C, β=104.1°C, γ=100.9°C, Z=2.

Table 2 The composition of initial mixtures, conditions of preparation (heating temperature and time) and the XRD results for all samples

Samples composition over the whole system (mol% $Co_2V_2O_7$)	Conditions of preparation	Phases detected after the last heating cycle
10.00; 20.00; 30.00; 40.00	550°C (12 h) + 600°C (12 h) + 650°C (12 h) + 700°C (12 h) + 750°C (12 h·2)	$InVO_4$, $Co_2InV_3O_{11}$
50.00		$Co_2InV_3O_{11}$
60.00; 70.00; 80.00; 90.00		$Co_2V_2O_7$, $Co_2InV_3O_{11}$

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